

Interstate Technology & Regulatory Council (ITRC)

LNAPL Site Management: LCSM Evolution, Decision Process, and Remedial Technologies

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1. How to Use the Document

In 2009, ITRC published [LNAPL-1: Evaluating Natural Source Zone Depletion at Sites with LNAPL \(ITRC 2009b\)](#) and [LNAPL-2: Evaluating LNAPL Remedial Technologies for Achieving Project Goals \(ITRC 2009a\)](#) to aid in the understanding, cleanup, and management of LNAPL at thousands of sites with varied uses and complexities. These documents have been effective in assisting implementing agencies, responsible parties, and other practitioners to identify concerns, discriminate between LNAPL composition and saturation-based goals, to screen remedial technologies efficiently, to better define metrics and endpoints for removal of LNAPL to the “maximum extent practicable,” and to move sites toward an acceptable resolution and eventual case closure.

This guidance, [LNAPL-3: LNAPL Site Management: LCSM Evolution, Decision Process, and Remedial Technologies](#), builds upon and supersedes both previous ITRC LNAPL guidance documents in an updated, web-based format. LNAPL-1 and LNAPL-2 are still available for review; however, LNAPL-3 is inclusive of those materials with new topics presented and previous topics elaborated upon and further clarified.

Light Non-Aqueous Phase Liquid (LNAPL) Management is the process of LNAPL site assessment, monitoring, LNAPL Conceptual Site Model development, identification and validation of relevant LNAPL concerns, and the possible application of remediation technologies. The presence of LNAPL can create challenges at any site. In the subsurface, LNAPL can be difficult to assess or recover accurately and can lead to:

- human health, ecological risk, and exposure concerns (e.g., vapor, groundwater, and soil contamination)
- acute-risk concerns (e.g., explosive conditions)
- migration or occurrence concerns (e.g., regulations that require recovery of “free-product” regardless of thickness, recovery to prevent potential LNAPL migration, or recovery for aesthetic or non-technical reasons).

This guidance can be used for any LNAPL site regardless of size and site use and provides a systematic framework to:

- develop a comprehensive LNAPL Conceptual Site Model (LCSM) for the purpose of identifying specific LNAPL concerns;
- establish appropriate LNAPL remedial goals and specific, measurable, attainable, relevant, and timely (SMART) objectives for identified LNAPL concerns that may warrant remedial consideration;
- inform stakeholders of the applicability and capability of various LNAPL remedial technologies
- select remedial technologies that will best achieve the LNAPL remedial goals for a site, in the context of the identified LNAPL concerns and conditions;
- describe the process for transitioning between LNAPL strategies or technologies as the site moves through investigation, cleanup, and beyond; and
- evaluate the implemented remedial technologies to measure progress toward an identified technology specific endpoint.

Initial development and continued refinement of the LCSM is important to the identification and ultimate abatement of site-specific LNAPL concerns. Figure 1-1 identifies the stepwise evolution of the LCSM, the specific purpose of each LCSM phase, and the tools presented within this guidance to aid in the development of the LCSM. As depicted, the LCSM is the driving force for identifying actions to bring an LNAPL site to regulatory closure.

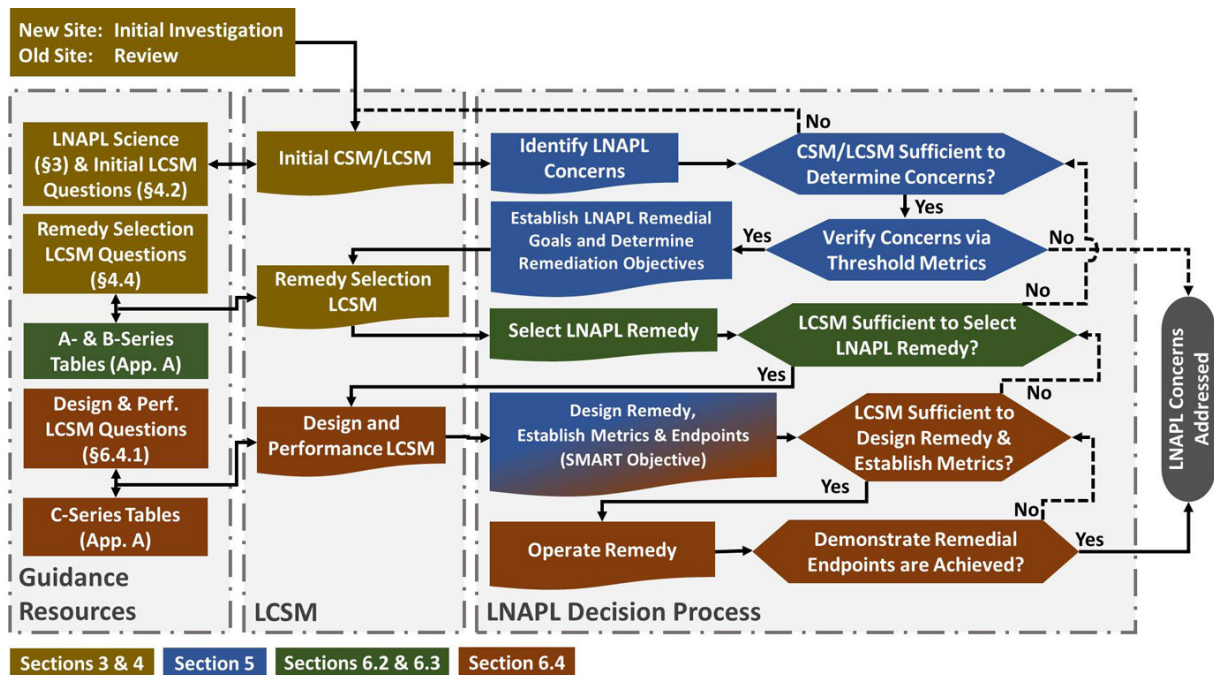


Figure 1-1. LNAPL remediation process and evolution of the LNAPL conceptual site model (LCSM).

This guidance document is organized into sections that lead you through the LNAPL site management process:

- **Section 2 - LNAPL Regulatory Context, Challenges, and Outreach**

Section 2 identifies some of the challenges implementing agencies face when investigating, evaluating, or remediating LNAPL sites. These challenges include regulatory or guidance constraints, a lack of familiarity or understanding of LNAPL issues, and poorly or undefined objectives and strategies. This section also stresses the importance of identifying and communicating with stakeholders early in the process in order to address issues or concerns that can lead to delays or changes in strategy. Understanding and recognizing these challenges and concerns during development of a comprehensive LCSM can help reduce costs and lead to a more effective and efficient resolution at an LNAPL site.

- **Section 3 - Key LNAPL Concepts**

Section 3 provides an overview of key LNAPL terminology and concepts including LNAPL behavior following a release to the subsurface (i.e., how LNAPL spreads away from the primary release point, its behavior above and below the water table, and how its migration eventually stops and naturally depletes). An understanding of these basic terms and concepts is crucial for developing a comprehensive LCSM and an effective LNAPL management plan.

- **Section 4 - LNAPL Conceptual Site Model (LCSM)**

The LCSM is a component of the overall conceptual site model (CSM), and emphasizes the concern source (i.e., the LNAPL) of the CSM. The presence of LNAPL necessitates an additional level of site understanding. The unique elements of the LCSM are presented as a series of questions for the user to answer to help build their site-specific LCSM. Ultimately, a thoroughly-developed, initial LCSM provides the basis for identifying the LNAPL concerns associated with an LNAPL release.

- **Section 5 - LNAPL Concerns, Remedial Goals, Remediation Objectives, and Remedial Technology Groups**

Section 5 describes the decision process for identifying LNAPL concerns, verifying concerns through the application of threshold metrics, establishing LNAPL remedial goals, and determining LNAPL remediation objectives. This section also introduces remedial technology groups, the concept of a treatment train approach, and how to transition between technologies to address the identified LNAPL concern(s) systematically and effectively. It is important to understand the content of this section prior to selecting and implementing an LNAPL remedial strategy.

- **Section 6 - LNAPL Remedial Technology Selection**

Section 6 describes the remedial technology screening, selection, and performance monitoring process. This section begins by identifying technologies recognized as effective for mitigating specific LNAPL concerns and achieving site-specific LNAPL remediation objectives based on the collective experience of the LNAPL Update Team. The [LNAPL Technologies Appendix](#) summarizes each of the technologies in detail and presents a systematic framework to aid the user in screening out technologies that are unlikely to be effective, ultimately leading to selection of the most appropriate technology(ies) to address the specific LNAPL concerns.

This guidance also includes relevant, state-of-the-science appendices for more detailed information on LNAPL specific topics:

- [LNAPL Technologies Appendix](#)

This appendix describes in more detail each of the 21 LNAPL technologies introduced in the main document. The A-series tables describe information to evaluate the potential effectiveness of each technology for achieving LNAPL goals under site-specific conditions. Information includes the basic remediation process of each technology, the applicability of each technology to specific remedial goals, and technology-specific geologic screening factors. The B-series tables describe information to evaluate the potential implementability of each technology considering the most common site-specific factors. The C-series tables describe the minimum data requirements to make a final technology selection through bench-scale, pilot, and/or full-scale testing; they also describe metrics for tracking remedial technology performance and progress.

- [Natural Source Zone Depletion \(NSZD\) Appendix](#)

This appendix provides a technical overview of NSZD for LNAPL and the methods by which rates can be estimated and measured. It also provides a discussion of long-term LNAPL site management and how NSZD can be applied as a remedy including decision charts to support integration of NSZD and case studies demonstrating its use. For this document, the original ITRC NSZD document (ITRC LNAPL-1) was updated and incorporated into the main body and appendix.

- [Transmissivity \(\$T_v\$ \) Appendix](#)

LNAPL transmissivity has application throughout the life cycle of a LNAPL project. This appendix provides an understanding of how transmissivity connects to the broader framework for LNAPL management including LNAPL recovery and mobility, and the potential for NSZD to decrease LNAPL transmissivity and mobility over time.

- [Fractured Rock Appendix](#)

This appendix describes the behavior and differences of how LNAPL behaves in fractured bedrock formations. While some of the same physical principles apply for multiphase flow in fractured aquifers as in porous aquifers, unique characteristics of finite and restricted fluid flow paths can lead to unexpected results in fractured settings.

- [LNAPL Sheens Appendix](#)

This appendix details how LNAPL sheens form, the concerns and challenges of sheens, and potential sheen mitigation technologies.

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2. LNAPL Regulatory Context, Challenges, and Outreach

The [2009 ITRC LNAPL guidance](#) noted that implementing agencies have historically required removal of LNAPL (“free product” as used in the Code of Federal Regulations (CFR)) to the “maximum extent practicable” (MEP) at underground storage tank (UST) sites. This was largely due to a provision in the Code of Federal Regulations (40 CFR §280.64) pertaining to USTs, with the specific definition of MEP left to the “implementing agency.” At a minimum, LNAPL removal was intended to minimize the spread of contamination into previously uncontaminated zones. This regulation was intended to protect human health and the environment while giving program flexibility to the implementing agencies. Since MEP was not defined in the regulation, agency interpretations could range from no formal meaning to a specific maximum allowable LNAPL thickness in a monitoring well (e.g., sheen or 1/8-inch thickness). If these thickness interpretations were then incorporated into a state statute, LNAPL monitoring or recovery activities might continue long after the LNAPL body had stabilized.

In contrast, the Resource Conservation and Recovery Act (RCRA) Corrective Action regulations or guidance do not discuss removal of LNAPL to MEP, even though numerous RCRA Corrective Action sites (e.g., petroleum refineries and chemical plants) have LNAPL in monitoring wells. In RCRA Corrective Action, EPA guidance discusses “returning usable groundwater to its maximum beneficial use, where appropriate, within a timeframe that is reasonable given the particular circumstances of the facility” ([EPA 1996](#)). When restoration of groundwater is not practicable, EPA expects to prevent or minimize further migration of the plume, prevent exposure to contamination and evaluate further risk reduction ([EPA 1996](#)). The April 2004 guidance, “[Handbook of Groundwater Protection and Cleanup Policies for RCRA Corrective Action for Facilities Subject to Corrective Action Under Subtitle C of the Resource Conservation and Recovery Act](#)” indicates that “The term ‘restore’ or ‘restoration’ used in this context refers to achieving a certain cleanup level(s) developed to ensure protection based on maximum beneficial use of the groundwater at a particular facility. Restoring contaminated groundwater does not necessarily imply cleanup to pristine conditions” ([EPA 2004](#)).

LNAPL removal to MEP may leave LNAPL in the subsurface. As noted in the [2009 guidance](#), the EPA recognized that “...only a portion of the total volume of the LNAPL release will be recoverable. Even under ideal conditions a significant proportion of the free product will remain in the subsurface as immobile residue” ([EPA 1996](#)). Likewise with RCRA Corrective Action sites, since a significant proportion of immobile free product will remain in place, returning groundwater to its maximum beneficial use may simply not be feasible or realistic.

One of the goals of the original LNAPL guidance was to provide a framework for implementing agencies and stakeholders to evaluate and approve appropriate LNAPL remedial technologies within the confines of guidance interpretations or regulatory requirements (such as MEP). As with the original guidance, the ITRC LNAPL Team sent an updated survey in 2017 to implementing agencies in all 50 U.S. states, the District of Columbia, and Puerto Rico. The purpose was to gauge any change in how an implementing agency addresses LNAPL management issues, remedy selection, and site closures since the issuance of the 2009 ITRC LNAPL guidance. Multiple implementing agencies from 48 states responded, with the majority of responses from the programs directly involved with underground and aboveground petroleum storage tanks. Other responses were provided by the brownfields/voluntary remediation or waste programs. The recent survey indicated that 20 states had updated or changed their LNAPL management approach since the issuance of the original guidance.

2.1 Regulatory Challenges

Both the 2008 and 2017 surveys indicated that implementing agencies face regulatory challenges when managing, evaluating, or remediating LNAPL sites. If a requirement exists to remove LNAPL to a specified thickness, the implementing agency may assume that any selected removal strategy will be long and costly. This assumption could have a detrimental impact on the assessment and remediation decision. However, a more cost-effective or risk-appropriate decision, consistent within the regulatory constraints of the implementing agency, may be made if there is sufficient or increased understanding of the site and LNAPL concerns.

For RCRA Corrective Action sites, EPA outlines Technical Impracticability (TI), and believes that it is appropriate to recognize the limitations of current technologies to clean up groundwater to its maximum beneficial use. When discussing a TI, the

presence of LNAPL is one of the factors to consider. Examples of a TI for LNAPL sites may be LNAPL distribution within low-permeability or highly heterogeneous soils, or complex fractures in bedrock. EPA guidance states a TI evaluation should be based on a comprehensive understanding of hydrogeological factors, chemical characteristics, as well as limitations of conventional and innovative technologies ([EPA 2004](#)). [Section 6](#) of this guidance discusses these factors and characteristics as well as various conventional and innovative remedial technologies. Additional relevant discussion on TI can also be found in the ITRC Guidance Document “Remediation Management of Complex Sites” ([ITRC 2017b](#)).

The following subsections summarize six primary themes encountered in the 2017 regulator survey.

2.1.1 Lack of Familiarity and Understanding of LNAPL Subsurface Behavior

Sufficient understanding of LNAPL behavior in the subsurface is important in making appropriate site management decisions. Without a sufficient LCSM, the most appropriate remedies or endpoints may not be selected. This lack of understanding or familiarity of the site may be due to multiple reasons. Case managers may have minimal experience with LNAPL sites or funding for LNAPL site work may be limited or constrained. Additionally, site owners or consultants may not propose technologies or strategies outside of their experience or abilities. The 2017 updated LNAPL survey responses indicated that:

- Over half of the regulatory staff had less than 10 years of experience dealing with LNAPL sites.
- The majority of the responses indicated formal internal LNAPL training is not required.

Since issuance of the original guidance, over 2,000 participants have attended the multi-day LNAPL classroom training. These participants represented local/state/federal agencies, environmental consultants, site owners, academia, and other interested parties. Additionally, over 17,000 have participated in the three-part ITRC internet-based training (IBT). This suggests a real and tangible interest in understanding the complexities and issues associated with management and remedy selection of LNAPL sites. The 2017 regulator survey is a telling indicator that formal LNAPL training is useful. Seventy-seven percent of respondents indicated that their program uses the 2009 LNAPL guidance and 20 respondents indicated that there have been changes or updates in their program since the issuance of the 2009 ITRC guidance.

2.1.2 Undefined Strategies or Objective-Based LNAPL Characterization

Standard practice in many petroleum release investigations has been to include general remediation objectives in the CSM. These objectives, or the strategies to achieve them, may be defined by regulatory or guidance procedures utilized by the implementing agencies. However, as noted in the 2008 survey, risk-based approaches to define LNAPL remediation objectives were not considered within many regulatory agencies. The 2017 survey indicated that although 31 programs define when active recovery of LNAPL is no longer required, only half of the respondents indicated that their specific programs define when a site with remaining LNAPL can be issued a no further action/case closure/site completion letter. Many respondents commented that the site remedial goals and objectives were selected on a case-by-case basis. While this approach may promote flexibility, it can lead to cases being unresolved or inadequately defined.

It is important to develop and select realistic and SMART remediation objectives. [Section 4](#) and [Section 5](#) of this guidance describe the development of an LCSM and the factors affecting SMART remedial strategies and objectives. Additional discussion on the development and selection of SMART objectives can be found in the November 2011 [ITRC Integrated DNAPL Site Strategy guidance](#) ([ITRC 2011](#)).

2.1.3 Lack of Familiarity with Nontraditional LNAPL Characterization Methods

Many regulators are accustomed to traditional investigative methods such as borings to collect soil and soil gas samples and monitoring wells to collect groundwater. These traditional methods are sometimes incorporated into state regulations or reimbursement criteria for petroleum trust funds. Both the 2008 and 2017 regulator surveys indicated that some non-traditional methods, such as Laser Induced Fluorescence (LIF), coupled with Cone Penetrometer Testing (CPT), are utilized for investigative work. However, the recent survey did not indicate a clear increase or decrease in use of these methods over the years. Some of the comments indicated that non-traditional methods were used, but they were not “successful,” or that new methods were not proposed by the consultant/owner. This may simply be a function of inexperience with the case managers within the implementing agency, or an insufficient LCSM.

As discussed in this guidance, the use of non-traditional methods can provide useful, higher resolution information that provides an improved understanding of LNAPL distribution. Although not included in this guidance, a discussion of non-traditional methods or tools can be found in [Section 4](#) of the April 2015 [ITRC Integrated DNAPL Site Characterization and Tools Selection guidance](#) ([ASTM 2015](#)). Additionally, in 2017, ITRC approved the development of new guidance to address

the selection, application, and integration of Advanced Site Characterization Tools (i.e., non-traditional methods) into the project life cycle of site characterization, remediation, monitoring, and closure. This guidance will be available in 2020.

2.1.4 Establishing Appropriate Remedial Goals and Determining Remediation Objectives

Establishing appropriate cleanup goals promotes consistency within the program and allows the regulated community to understand what is expected or required for LNAPL investigations. Most decisions regarding remedial goals and remediation objectives at LNAPL UST sites are driven by thickness and contaminant concentrations. The 2017 regulator survey responses indicated that:

- Twenty-four state programs define MEP.
- Nineteen programs use total petroleum hydrocarbon (TPH) toxicity or screening values as an indicator if LNAPL is not readily apparent in soil or groundwater.
- Twenty-three programs evaluate individual constituents for analytical compliance.

Thickness or concentration data alone may not provide a sound basis for defining the point at which a cleanup objective is achieved. These decisions can be improved by also considering contaminant mass discharge and mass flux. Mass discharge and flux estimates can help the implementing agency or regulated community understand the role or influence of natural attenuation and the risks to downgradient receptors. The estimates can also help prioritize which sites need further characterization and remediation, identify stratified aquifers, and evaluate performance data, all of which can promote more cost-effective cleanups. A discussion of mass discharge and flux can be found in the April 2010 [ITRC Use and Measurement of Mass Flux and Mass Discharge guidance \(ITRC 2010\)](#).

2.1.5 Differentiating Between Residual, Mobile, and Migrating LNAPL

In choosing an effective source remedy, it is important to differentiate between residual, mobile, and migrating LNAPL. The 2017 survey indicated that only 13 programs have defined these terms. In order for the implementing agencies to establish appropriate cleanup objectives, it is important to understand the differences between residual, mobile, and migrating LNAPL. [Section 3](#) of this guidance discusses the differences and provides tools (e.g., LNAPL transmissivity) and suggestions in understanding the importance of establishing realistic and achievable objectives.

2.1.6 Transitioning between Technologies

One of the principal components of this guidance is to identify and select appropriate remediation strategies and technologies for LNAPL sites. Multiple technologies or “treatment trains” may be necessary in order to effectively control, recover, or conduct a phase change of the LNAPL mass. It is important to recognize and address this “transition” from one technology or strategy to the next in order to address the LNAPL and the identified risks and concerns effectively. Just as important, this should include the transition from an active technology driven strategy to the next, and perhaps final, less active strategy. The latter may include identification and measurement of NSZD rates, moving the site into Monitored Natural Attenuation (MNA), establishing institutional controls, or even approving case closure.

Describing the process and metrics for transitioning between LNAPL strategies or technologies can promote consistent remedial progress and navigation through the regulatory process as the site moves through investigation, cleanup, and beyond. This can allow the regulatory program to identify relevant permits, technical reviews, and approvals that may be required as the site transitions from one technology to the next. Describing the transition process and metrics can also provide financial efficiencies and assist with the budgeting process. Identifying relevant objectives and concerns during the transitions is just as important and can promote understanding and support from stakeholders that may be impacted or involved with the LNAPL case. A more detailed discussion of treatment trains and transitioning is located in [Section 5](#) of this guidance.

2.2 Weather Vulnerabilities

In recent years, the EPA has identified possible additional LNAPL concerns associated with extreme weather events. There may be a need to increase engineering controls for contaminant migration at sites where a remedy is constructed in areas that are vulnerable to a greater incidence of flooding, hurricanes, drought, wildfires, or other consequences of extreme weather. The EPA’s Office of Underground Storage Tanks published the [Underground Storage Tank Flood Guide \(EPA 2010\)](#) to provide information about preparing for a flood, important actions to take after the flood, and information on financial assistance. In addition, the Institute for Sustainable Communities (ISC), partnering with the EPA, provides states and tribes with an increased understanding of specific vulnerabilities for sites under extreme weather conditions ([EPA 2010](#)).

2.3 Stakeholder Concerns, Community Outreach and Engagement

As noted in the 2017 regulator survey, multiple implementing agencies have made changes and improvements to project decision-making practices regarding LNAPL. However, it should be expected that changes in any implementing agencies' past actions regarding site assessment, remediation, or closure strategies (e.g., "What does "clean" mean?") can be met with skepticism in the stakeholder community. Presenting and explaining both the technical information and regulatory requirements to those who may be unfamiliar with the process can create difficulties and challenges for any case manager and implementing agency.

Identifying and recognizing potential stakeholders is of primary importance. Stakeholder types are listed and defined in several ITRC publications [(ITRC 2014) and (ITRC 2017b)] and can be generally defined as any person, group of persons, or organizations with some interest in a specific site, area or project. Stakeholders may include: local residents, tenants, and other potentially-impacted local parties or groups; local and other government agencies (as implementing agencies, land use officials, and safety professionals); local landowners; and/or land operators or tenants and their representatives. Impairments or impacts to these persons or groups can be physical (community health), mental (stress-related), financial (property values, loss of business activity, loss of property rights, etc.) and/or cultural (loss of resources).

Stakeholder issues for LNAPL are not dissimilar from other types of contaminants. Petroleum and potential LNAPL issues can be present in any industrial, commercial, or residential setting regardless of size or location. Petroleum and LNAPL can be associated with releases of short or long duration, from emergency responses to long-term maintenance and monitoring. Stakeholder issues for each of these situations will be dealt with in different ways, in accordance with a well-informed plan for dissemination of information, public education, and stakeholder outreach.

Recommended resources for public education and outreach involving public and tribal stakeholder issues include:

- stakeholders and stakeholder concerns (ITRC 2014),
- communication methods (ITRC 2014),
- community engagement plans and planning (ITRC 2014) that also include existing federal and state resources,
- risk communication (ITRC 2014), and
- regulatory processes for stakeholder involvement (ITRC 2017b).

Presenting technical data to the stakeholder community can be challenging. Presentations may need to include the science supporting the technology as well as the science-based conclusions that can be drawn from the data. Statistical representation of the confidence associated with the data can also be part of the presentation. It is recommended that explanations of the technology and how it contributes to the LCSM be presented in a manner that is understood easily by the stakeholders. Public acceptance and understanding of the difficulties with the site can be enhanced if the information is presented and explained in a way that defines the technical and regulatory steps in a clear and understandable format.

2.4 Streamlining the Corrective Action Process by Increased Communication

Inadequate or limited communication between the implementing agencies, the responsible party, and identified stakeholders can increase the amount of time to move a site through the investigation and corrective action process. In some cases, performance of initial emergency actions and abatement may be needed prior to communication with stakeholders. However, it is recommended that outreach and communication occur before corrective action is performed. Identifying and discussing difficult issues before any field work or report writing is done can often mitigate interruption, delay, and additional expense. RCRA FIRST (EPA 2015) is a streamlined process promoted by EPA for investigation and remediation at RCRA Corrective Action sites. This process can be applied at LNAPL corrective action sites.

Not every LNAPL site will require outreach or significant communication with stakeholders. The implementing agencies will determine the amount and effort based on their specific requirements and guidance. When appropriate, increased communication between the groups can facilitate better agreements on major issues at the beginning of the process, thereby reducing the amount of time to project completion.



3. Key LNAPL Concepts

The concepts presented in this section are integrated into the framework and tools presented in this guidance. They are fundamental to understanding the logic used in the development of the tools and key to appropriate application of this guidance. The remainder of this guidance assumes the reader is familiar with these key concepts and has a level of knowledge commensurate with the content of the ITRC's LNAPL Internet-Based Training (IBT) courses. The training courses are available online (www.clu-in.org/live/archive) at no cost.

3.1 Common Misconceptions

Understanding of LNAPL releases, the behavior of LNAPL in the subsurface, and the methods used to evaluate LNAPL releases have evolved significantly in recent years. Unfortunately, misconceptions derived from our early, less-informed understanding of LNAPL releases are frequently encountered. Table 3-1 outlines common misconceptions relating to LNAPL releases and the associated current understanding and key concepts which are discussed in detail in referenced sections of the document. A glossary of familiar LNAPL related terms is presented at the end of this document (Glossary).

Table 3-1. Common LNAPL misconceptions

Common Misconceptions	Key Concepts
LNAPL Distribution	
LNAPL enters soil pores just as easily as groundwater (Section 3.2). LNAPL floats on the water table or capillary fringe like a pancake and does not penetrate below the water table (Section 3.2).	• Typically, water is the wetting fluid in the saturated zone, in direct contact with the soil, and occupies the smaller pores. LNAPL must displace the water (and gases) within a pore space before it can migrate. For this to occur, it must have a driving head and overcome the capillary pressure exerted by the water in the pore. • LNAPL does not float on the water table in a uniform, high-saturation, "pancake"-like layer. The LNAPL is distributed above, at, and below the water table at saturations that vary vertically depending on past conditions such as LNAPL driving head and water table fluctuations.
LNAPL Occurrence	
If there is no LNAPL visible in a well, then there is no LNAPL present (Section 3.4).	• If LNAPL in soil adjacent to the well is below residual saturation, then LNAPL will not appear in the well, although the presence of a sheen is possible. • Persistent measurable dissolved- and/or vapor-phase petroleum hydrocarbon concentrations are indicative of the presence of LNAPL at or below residual saturation in the saturated and/or vadose zone.
Risk Assessment	
Risk assessment should not be conducted if LNAPL is present in a well (Section 3.5).	• Risks posed by mobile or residual LNAPL can be assessed using generally-accepted risk characterization and assessment practices (including Risk-Based Corrective Action). A mobile LNAPL that is migrating laterally may pose different risks than the same LNAPL at residual saturation within the same plume.
In-Well LNAPL Thickness	

Common Misconceptions	Key Concepts
LNAPL thicknesses in monitoring wells are exaggerated (compared to the formation) by factors of 2, 4, 10, etc. (Section 3.4) LNAPL thicknesses in monitoring wells are equal to the LNAPL thicknesses in the formation (Section 3.4).	• For unconfined LNAPL in a uniform geology at a location not significantly affected by water-table fluctuation, the thickness of LNAPL in the well will be similar to the thickness of the mobile LNAPL interval in the adjacent formation. • For LNAPL under confined or perched conditions, the LNAPL thickness in the adjacent well will likely be exaggerated. • For the same LNAPL in-well thickness, the volume of LNAPL per unit footprint area of the formation (LNAPL specific volume) can be different for different wells. The LNAPL specific volume is generally higher in coarse-grained soils than in fine-grained soils. • Due to the dependence of in-well LNAPL thickness on geology and variable groundwater hydraulics, it should not generally be used as a sole metric for recoverability and indication of migration.
LNAPL Saturation	
All soil pores in an LNAPL body are completely filled with LNAPL (Section 3.2). You can hydraulically recover all of the LNAPL from the subsurface (Section 3.6).	• The presence of LNAPL in a monitoring well indicates proximal presence of LNAPL above residual saturation. Soil pores are never 100% filled with LNAPL due to the concurrent presence of other fluids such as water and gases. The LNAPL saturation depends on the geology, LNAPL fluid properties, and release dynamics. • LNAPL cannot be completely removed from soil by hydraulic recovery due to mechanical limitations in subsurface soils. The lowest saturation theoretically attainable by hydraulic recovery is residual saturation, and that is rarely achieved.
Migrating LNAPL	
If you see LNAPL in a monitoring well, then it is migrating (Sections 3.2 and 3.4). LNAPL bodies spread due to groundwater flow (Section 3.2). LNAPL bodies continue to move long after the release is stopped (Section 3.5).	• The presence of LNAPL in a well is an indication that the LNAPL adjacent to the well exceeds residual saturation and is mobile. The LNAPL has the ability to flow into the “large” pore which is the well. However, mobility of the LNAPL into the well does not imply migration of the LNAPL body within the (much smaller) pore space of the adjacent soil. • LNAPL is considered migrating when it is observed to expand into previously unimpacted locations over time (i.e., in-well LNAPL appears in a monitoring well that had an initially clean borehole). • Migration of LNAPL cannot occur unless LNAPL is present above residual and within the mobile range of LNAPL saturations. • LNAPL bodies associated with a terminated or finite source (i.e., UST removal or a pipeline leak repaired) eventually stop migrating within a relatively short timeframe as the driving head dissipates. • Not all mobile LNAPL migrates, but LNAPL must be mobile in order to migrate. • Multiple lines of evidence may be needed to make the distinction between mobile and migrating LNAPL. • Reduction of LNAPL saturation to the residual range is not necessary to arrest LNAPL migration.
Mobile LNAPL	

Common Misconceptions	Key Concepts
If you see LNAPL in a monitoring well, then it is mobile and migrating (Section 3.5).	• LNAPL is considered mobile when it accumulates in a well (assuming the well is properly constructed and screened across the LNAPL smear zone). • LNAPL is mobile when it is present at a saturation greater than residual. • Mobile LNAPL is potentially hydraulically recoverable, but recoverability depends on various physical factors. • LNAPL presence in a well does not necessarily mean that the LNAPL body is migrating.
Residual LNAPL Saturation	
Residual saturation is easily determined (Section 3.5).	• Residual LNAPL saturation is different for the saturated and unsaturated zones due to the variable presence of other fluids such as water and gases. Typically, unsaturated (vadose) zone residual saturation is generally lower. • Water table fluctuations (e.g., seasonal or tidal) result in a dynamic change in the extent of the unsaturated and saturated zones, causing the LNAPL to continuously redistribute vertically. Consequently the amount of mobile LNAPL changes with time, while the total LNAPL volume remains unchanged. • Residual LNAPL saturation is not a single number, rather a range of saturations.
Concentrations in Groundwater and Vapor	
Hydraulic recovery of LNAPL reduces associated dissolved phase plume concentrations (Section 3.6).	• Most types of petroleum hydrocarbon LNAPL are a multi-constituent mixture (e.g., gasoline, diesel), the exception being single-constituent LNAPL (e.g., benzene). • Constituent concentrations in groundwater and/or vapor depend primarily on LNAPL composition (i.e., mole fractions of the individual constituents in the LNAPL and their pure phase solubility). They have limited dependence on LNAPL saturation. Therefore, rarely does hydraulic recovery reduce dissolved phase concentrations.
LNAPL Transmissivity	
There is no definition of evaluating “LNAPL removal to the maximum extent practicable” or recoverability (Section 3.6).	• LNAPL transmissivity is a reliable indicator of the ability of the formation to transmit LNAPL to a well. LNAPL transmissivity depends on soil type, LNAPL type, LNAPL saturation, and thickness of mobile LNAPL. • Since LNAPL transmissivity is related to all key variables (see above) that can affect recoverability, it is a better metric than the conventionally used metric of in-well LNAPL thickness. • The higher the LNAPL transmissivity, the higher the LNAPL recoverability.
Saturation vs. Composition	

Common Misconceptions	Key Concepts
Any LNAPL remediation technology can address all remediation objectives (Sections 3.2 and 3.6).	• Saturation reduction technologies (e.g., mass recovery) are best suited to abating LNAPL body migration and can shorten dissolved plume longevity. • Composition change technologies (e.g., phase change) are best suited to address remediation objectives of reducing constituent concentrations in groundwater and vapor. • Where mobile LNAPL is present, but LNAPL migration is not a concern, evaluate LNAPL saturation reduction in terms of added net benefit.

3.2 Life Cycle and Anatomy of an LNAPL Body

The following subsections discuss the key concepts associated with the initial formation of the LNAPL body from a release, its subsurface distribution, and changes that it undergoes over time.

3.2.1 LNAPL Body Formation and Initial Distribution

When an LNAPL release occurs, the LNAPL will move vertically downward under the influence of gravity through the permeable pathways (e.g., unconsolidated soil, fractures, and macropores) and, if sufficient LNAPL volume and head is generated by the release, the LNAPL will eventually encounter the water table. During the downward movement of LNAPL through the soil, the presence of confining layers, subsurface heterogeneities, or other preferential pathways may result in irregular and complex lateral spreading and/or perching of LNAPL before the water table is encountered. Once at the water table, the LNAPL will spread laterally in a radial fashion as well as penetrate vertically downward into the saturated zone, displacing water to some depth proportional to the driving force of the vertical LNAPL column (or LNAPL head). The vertical penetration of LNAPL into the saturated zone will continue to occur as long as the downward force produced by the LNAPL head or pressure from the LNAPL release exceeds the counteracting forces produced by the resistance of the soil matrix and the buoyancy resulting from the density difference between LNAPL and groundwater. Once the release of LNAPL is terminated, the areal extent of the LNAPL body will continue to expand for a relatively short time, and eventually stop once the resistive forces in the soil balance the driving force of the diminishing LNAPL head. When the LNAPL body reaches this state, the LNAPL body has stabilized in extent, and will not typically expand further unless additional releases or significant subsurface hydraulic changes occur. Conceptual depictions of an LNAPL release and the initial stabilization of an LNAPL body are provided in Figure 3-1. [Section 4](#) of this document discusses the development of an LCSM that incorporates a release history and summary of processes that create the observed LNAPL distribution in the subsurface.

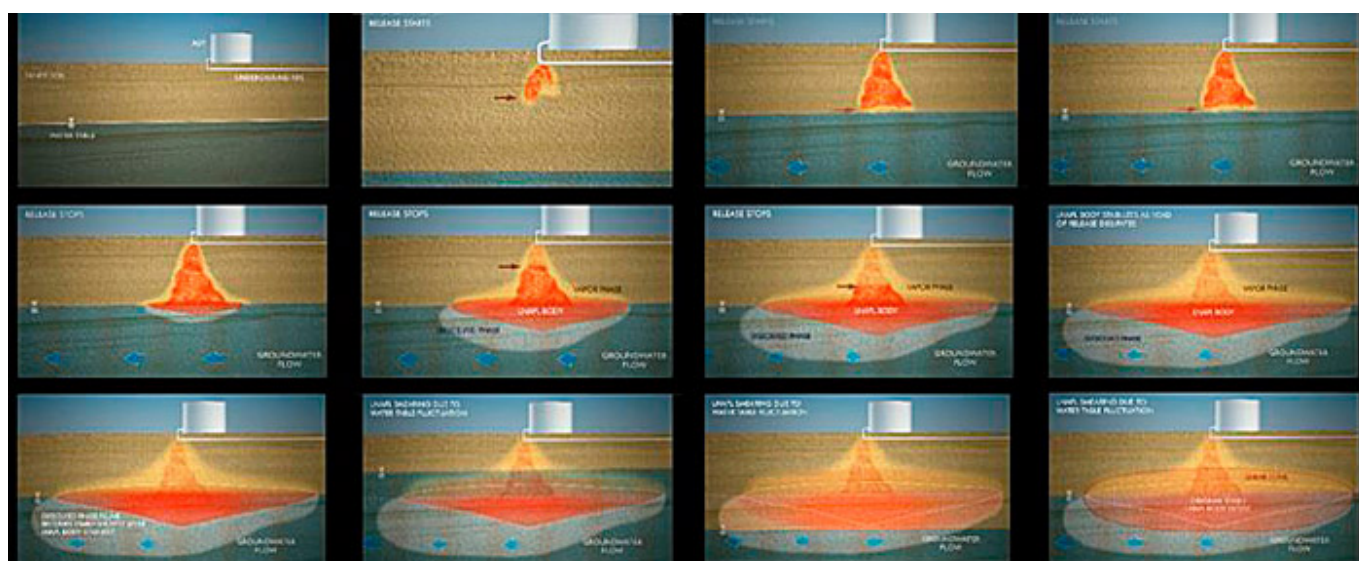


Figure 3-1. Time lapse conceptualization of LNAPL body formation (Courtesy of Matthew Rousseau/GHD).

A typical LNAPL body consists of LNAPL partially filling the soil pore space in a highly variable and often discontinuous distribution. The volume of aquifer occupied by an LNAPL body is not comprised of a single fluid phase, but rather of multiple

fluids and soil in proportions that will vary throughout. An LNAPL body is therefore a multiphase system where the pore space contains varying quantities of LNAPL, groundwater, and/or gases both above and below the static water table elevation. Generally speaking, the spatial extent occupied by an LNAPL body is predominantly comprised of water, followed by a lesser amount of LNAPL, with the smallest fraction of the pore space occupied by gas. As shown in Figure 3-2, LNAPL saturations within an LNAPL body will typically be much less than 100%.

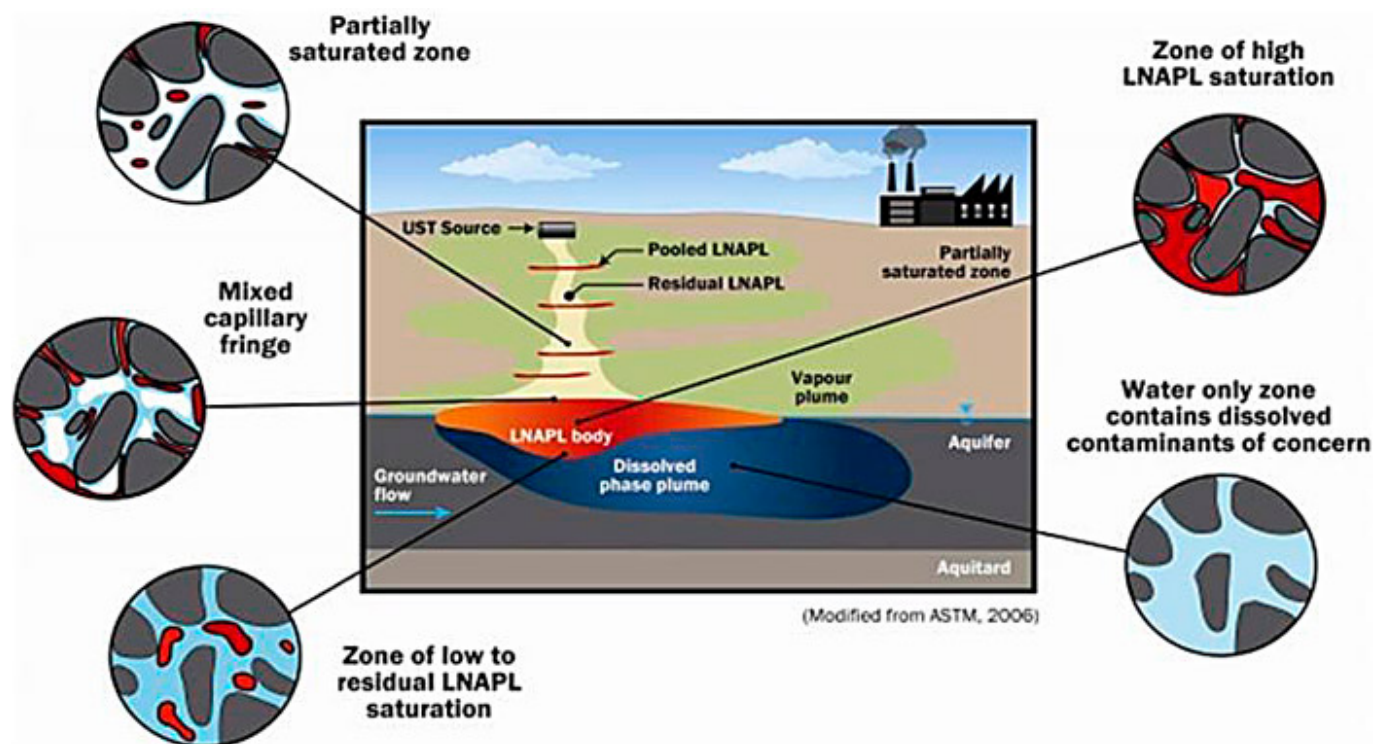


Figure 3-2. The multiphase system of a typical LNAPL body (CL:AIRE 2014).

In the simplest scenario of homogeneous sandy soil and unconfined conditions, the vertical distribution of LNAPL saturation will typically occur in a pattern commonly referred to as a 'shark fin' – visible on a plot of LNAPL saturation percent versus depth (Figure 3-3). The most highly saturated zone will generally be within the capillary fringe, coincident with and slightly above the water table, with diminishing saturations above and below. Considering this along with Figure 3-2, LNAPL saturations are continuously variable throughout an LNAPL body in three dimensions. Note that vertical equilibrium, a basis for the green lines on Figure 3-3, is a primary modeling assumption to satisfy the founding hydrostatic pressure equations.

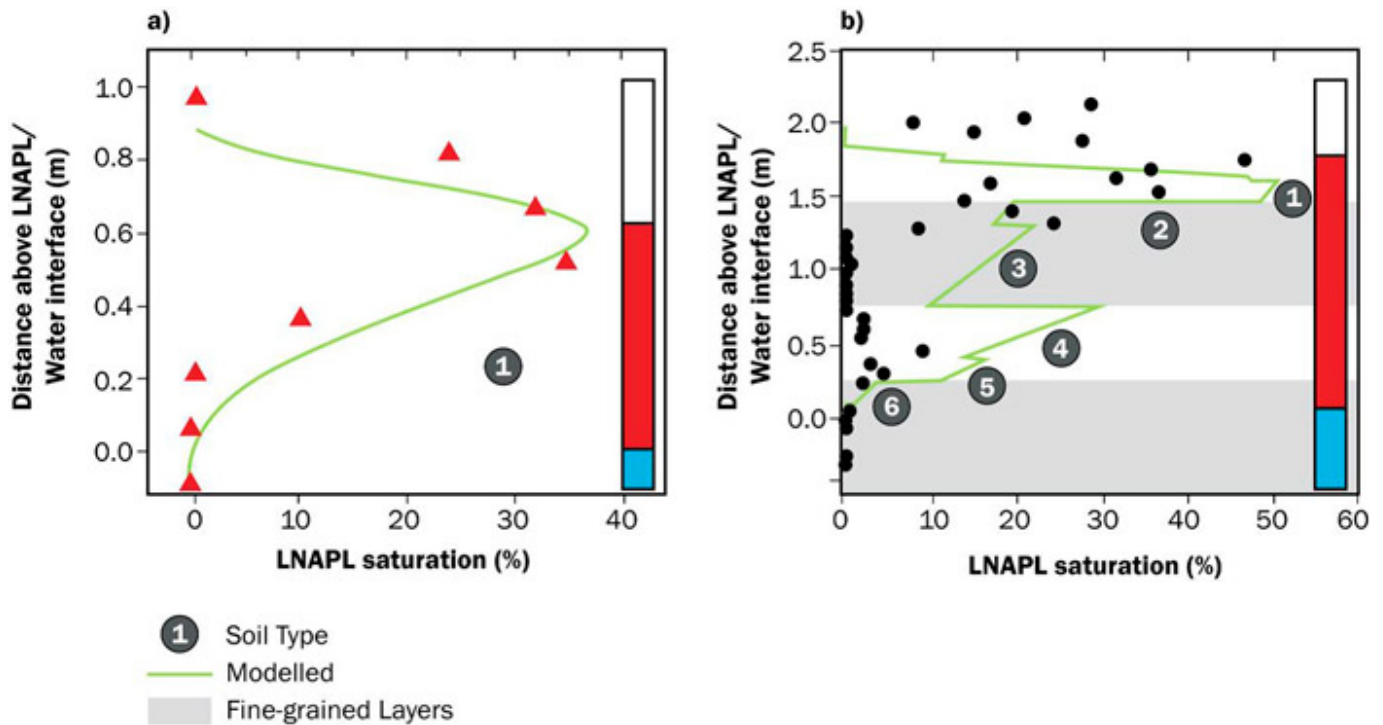


Figure 3-3. LNAPL saturation near the water table showing observed LNAPL saturation (a. red triangles; b. black dots) compared to vertical equilibrium model simulation predictions (green lines). The observed in-well LNAPL thickness is shown for: a) homogeneous soil (Beckett and Lundegard 1997); b) a heterogeneous case with finer grained layers (2, 3 and 6) and coarser grained layers (1, 4 and 5) (Huntley, Hawk, and Corley 1994) (Huntley, Wallace, and Hawk 1994).

On the pore-scale, LNAPL coexists with water and gases in different ways depending on where the LNAPL is located. LNAPL that occurs in the unsaturated zone will typically behave as a wetting phase with soil moisture. LNAPL becomes the non-wetting phase as moisture content increases toward the capillary fringe into the saturated zone (where water will be the wetting phase). This pore-scale distribution is illustrated in Figure 3-4.

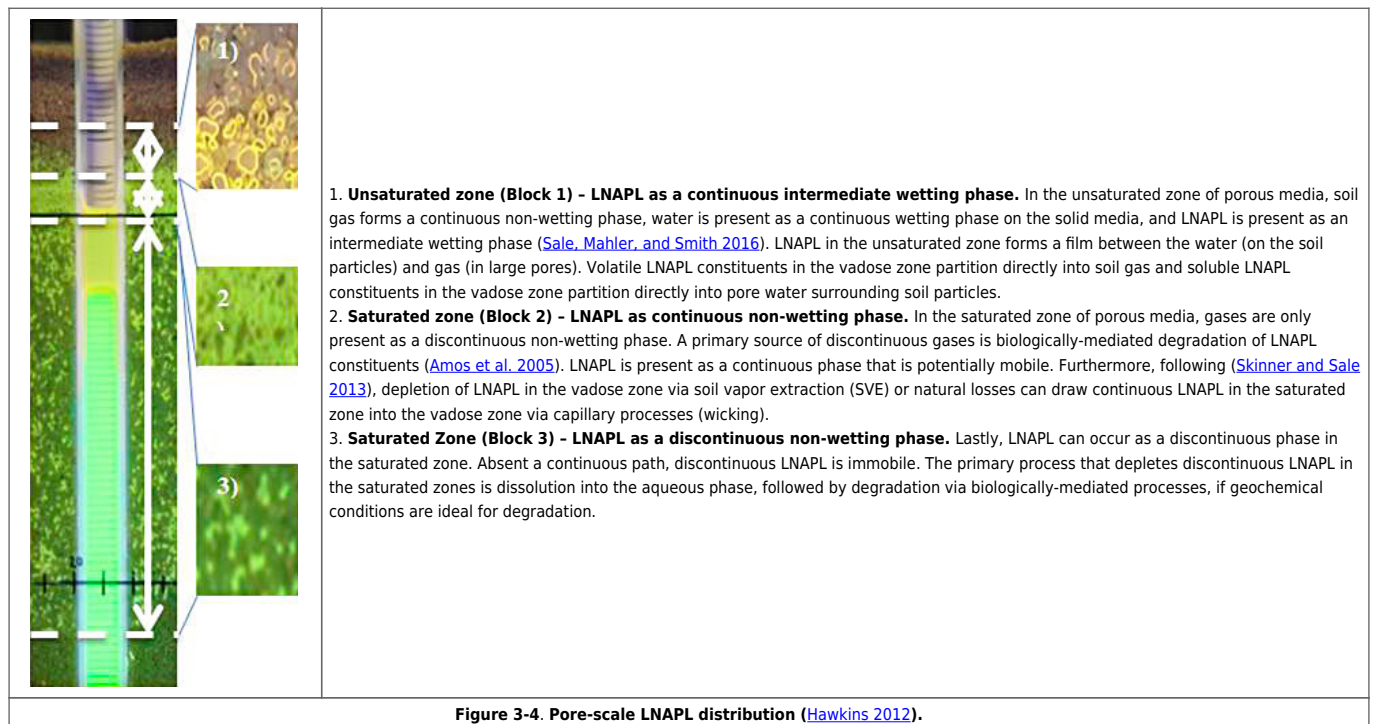


Figure 3-4. Pore-scale LNAPL distribution (Hawkins 2012).

As with any fluid, LNAPL will take the path of least resistance in the subsurface, with preferential pathways (both natural and man-made) often controlling the ultimate LNAPL body geometry. Similarly, LNAPL is typically the non-wetting or intermediate wetting phase and will preferentially occupy larger pore spaces in the subsurface or macropores such as

fractures in clays or bedrock. As a result, LNAPL may be found in all directions from a release point (i.e., not just downgradient) in highly irregular distributions. Conceptual distributions of LNAPL in different geologic settings are provided by Contaminated Land: Applications in Real Environments ([CL:AIRE 2014](#)).

3.2.2 Constituent Partitioning

Partitioning refers to the transfer of chemical mass from the LNAPL into other phases (gas, groundwater, and soil) adjacent to the LNAPL body. Partitioning results in LNAPL constituent presence in the vapor, dissolved, and/or adsorbed phases. Evaluation of the vapor phase is discussed in greater detail in the ITRC PVI document ([ITRC 2014](#)). Understanding constituent partitioning is important when investigating the occurrence of LNAPL, when evaluating the migration of LNAPL and its constituents, and when evaluating risk and safety concerns associated with LNAPL sites. Partitioning of petroleum constituents into other phases can result in additional risks (e.g., vapor intrusion into indoor air or migration of dissolved phase contaminants with groundwater). It is also important to account when appropriate remedial technologies are applied (e.g., soil vapor extraction [SVE] to remove vapors). Certain LNAPL remediation technologies rely upon constituent partitioning to remove mass (e.g., via a vapor phase using SVE) or to remove more volatile constituents and reduce risk (e.g., removal of benzene via air sparging). As such, a basic understanding of constituent partitioning is also important to develop and revise the conceptual site model, evaluate concerns, and select and implement a remedy.

As most commonly described, the tendency of a chemical constituent to partition from one phase to another is described by the following governing principles:

- Raoult's Law – relates LNAPL constituent concentrations and the associated dissolved and vapor phase constituent concentrations;
- Henry's Law – relates dissolved and vapor phase constituent concentrations; and
- Linear sorption isotherms – relate sorbed and dissolved phase constituent concentrations.

Data collected in the field (e.g., co-located LNAPL, soil, groundwater, and vapor samples) may also provide information relating to the partitioning of LNAPL constituents at a particular location. Further detail relating to chemical partitioning of LNAPL can be found in the ITRC TPH Risk document ([ITRC 2018](#)). Additional detail specifically with respect to partitioning within the vapor phase can be found in the January 2007 [ITRC Vapor Intrusion Pathway: Investigative Approaches for Typical Scenarios](#) ([ITRC 2007](#)).

One key phase partitioning relationship is LNAPL and groundwater. The dissolved concentration of an LNAPL constituent in groundwater, according to Raoult's Law, is the product of its concentration in the LNAPL (mole fraction) and the aqueous solubility of the pure constituent; it is not based on the saturation of LNAPL in the pore space. For example, if benzene is present in gasoline at 0.5% by weight (0.6 mole %), its effective solubility (equilibrium groundwater concentration) is approximately 11 milligrams per liter (mg/L) (Scenario A, Figure 3-5). If the benzene concentration in gasoline is reduced to 0.25% by weight without any measurable reduction in LNAPL saturation (e.g., using SVE), the corresponding effective solubility would also be halved to about 5.5 mg/L (Scenario C, Figure 3-5). On the other hand, if the LNAPL saturation were halved with no change in LNAPL composition (e.g., by hydraulic recovery of LNAPL), the dissolved benzene concentration in groundwater would not change. In this case, however, the longevity of groundwater impacts (Scenario B, Figure 3-5) would decrease, as the total mass of benzene would be halved. Similar relationships exist for other constituents in different pairs of phases—for example, LNAPL and soil gas (vapor pressure and mole fraction), groundwater and soil gas (Henry's Law). In summary, the composition of LNAPL and not its mass (or saturation level) is the primary control for concentrations in adjacent phases (groundwater and soil gas). It therefore follows that the effects of chemical weathering of LNAPL in the subsurface can have a significant effect on concentrations in adjacent phases.

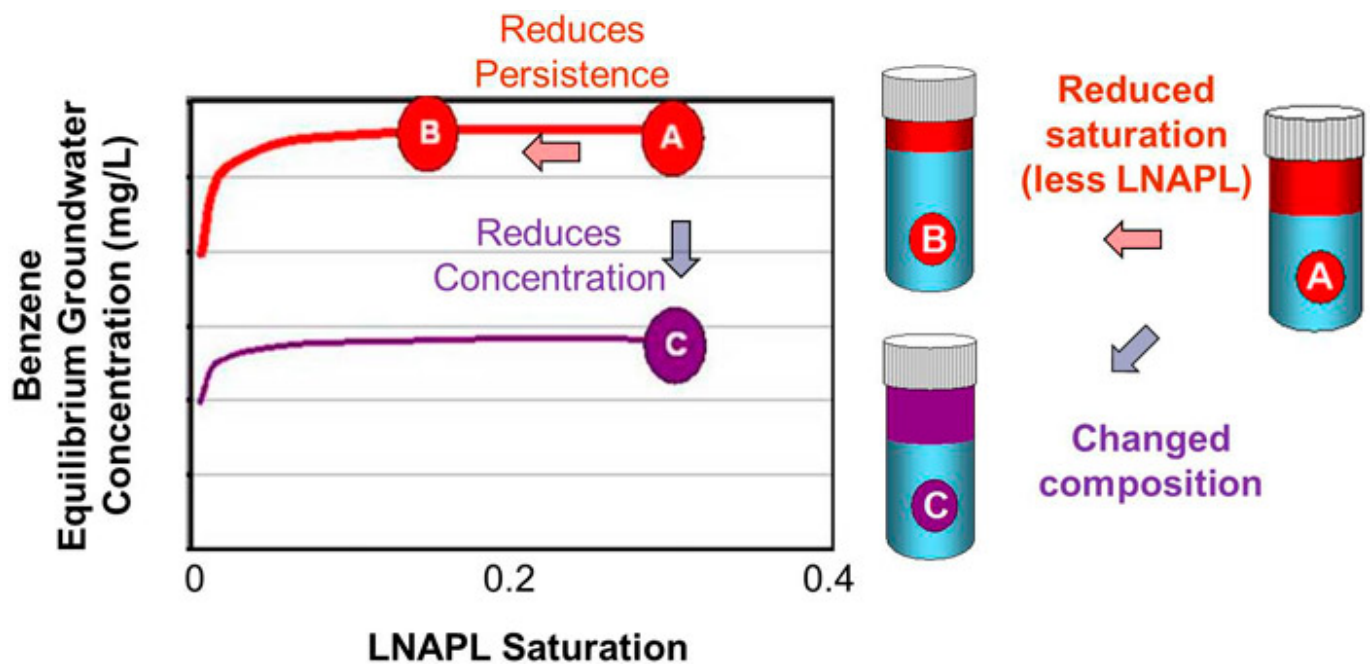


Figure 3-5. Comparison of LNAPL mass or saturation (S_o) reduction (A to B) and LNAPL composition reduction in constituent concentration in LNAPL (A to C) on dissolved phase benzene concentrations in groundwater
(Courtesy of S. Garg, Shell 2009).

3.2.3 Longer-Term Changes in the LNAPL Body

Once a release has terminated and the LNAPL body has initially stabilized, longer-term changes in the LNAPL body will be dominated by NSZD processes (including dissolution, volatilization, and biodegradation) and smearing due to water table fluctuations.

NSZD processes progressively reduce LNAPL mass over time via direct biodegradation of LNAPL by microbes and by physical partitioning processes, into other phases (e.g., soil gas and groundwater), where biodegradation also occurs. This results in the depletion of constituents from the LNAPL and reduction in mass, and eventually, diminishing amounts of constituent dissolution and volatilization. NSZD processes therefore play an important role in risk mitigation and the long-term stability of LNAPL bodies ([Mahler, Sale, and Lyverse 2012](#)). NSZD processes are discussed in more detail later in this section and in the [NSZD Appendix](#).

The smearing of LNAPL due to water table fluctuations will redistribute the LNAPL mass so that it becomes progressively less mobile and recoverable over time. For example, in a rising and subsequent falling water table in an unconfined condition: the mobile fraction of the LNAPL will move up with the water table during the rise (Figure 3-6), but some portion of this mobile fraction will become trapped in the pore space when the water table drops. Therefore, the vertical LNAPL distribution changes and the mobile fraction that remains afterwards are smaller. Seasonal fluctuations in the water table that redistribute the mobile LNAPL fraction, together with biodegradation, dissolution, and volatilization that deplete LNAPL mass, decrease the fraction of mobile LNAPL over time until all LNAPL exists as residual.

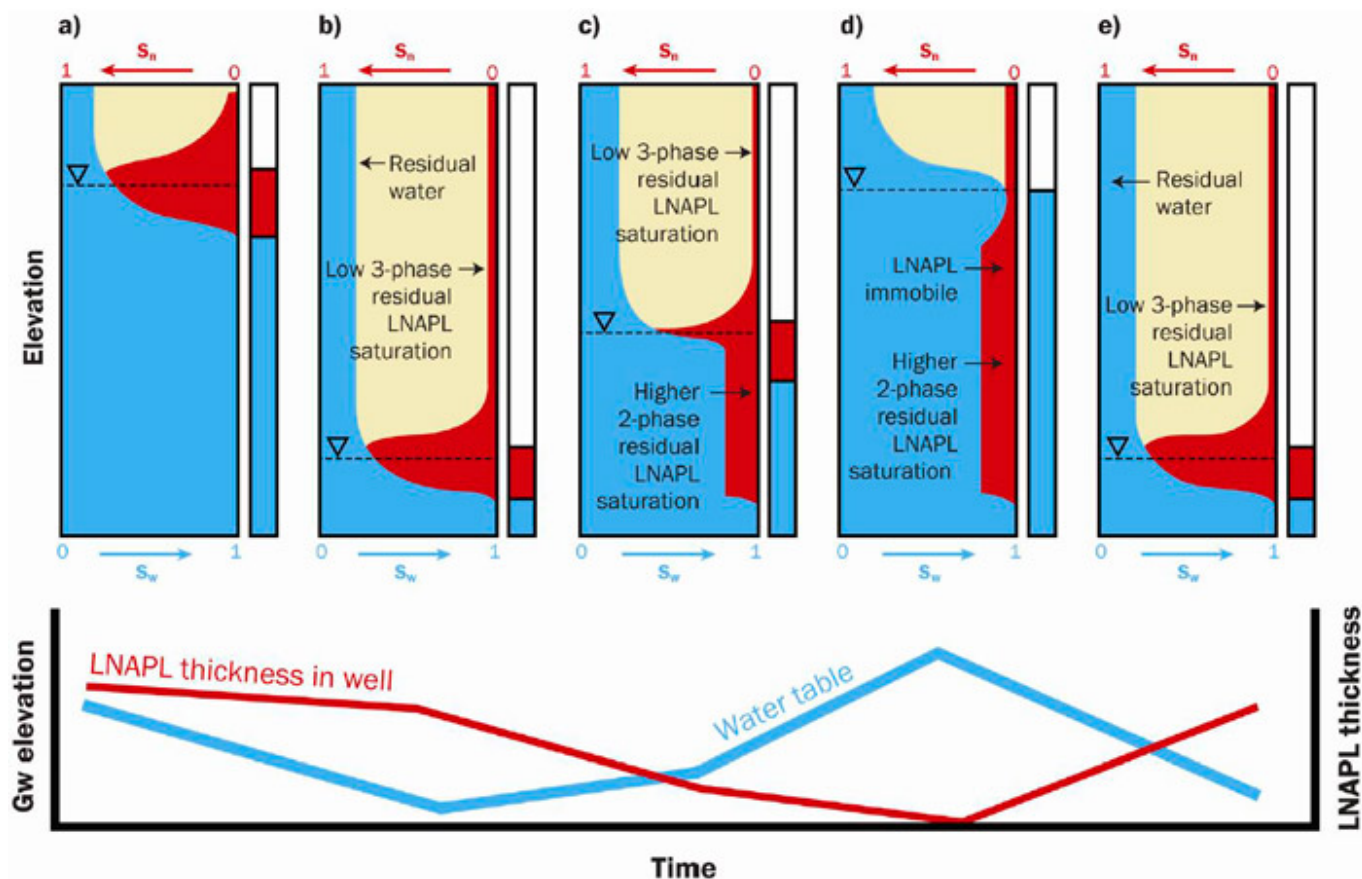


Figure 3-6. Conceptual depiction of LNAPL observed within the formation and within monitoring wells (a - e) during a variable water table and LNAPL thickness shown on the bottom graph (after (ITRC 2009a); (CL:AIRE 2014)). S_n is saturation of the pore space of NAPL, and S_w is saturation of water.

As described in [Section 3.2](#), concentrations of dissolved and vapor phase constituents may gradually decline, but will typically decrease by less than an order of magnitude. Risks associated with phase changes (e.g., vapor phase, dissolved phase) are discussed further in [Section 5](#) and [Section 6](#). Specific factors affecting the mobility of the LNAPL such as soil type and saturation levels are discussed later in this section.

Typically, LNAPL will remain the non-wetting (saturated zone) or intermediate wetting (unsaturated zone) fluid. These sites exhibited high fractions of silt and clay content and weathered diesel.

3.3 Overview of Natural Source Zone Depletion

LNAPL NSZD encompasses a variety of processes that act to biologically degrade and physically redistribute LNAPL constituents to the aqueous or gaseous phases where they are also subsequently broken down biologically ([ITRC 2009a](#)). NSZD occurs primarily through direct contact oil biodegradation, biodegradation of solubilized hydrocarbons at the oil/water interface, LNAPL volatilization and biodegradation in the vadose / smear zone, and less significantly through dissolution into groundwater and biodegradation in the saturated zone [([Ng et al. 2014](#)); ([Ng et al. 2015](#)); ([Johnson, Lundegard, and Liu 2006](#)); and ([Molins et al. 2010](#))].

NSZD begins as soon as LNAPL is released to the subsurface, typically via volatilization and dissolution, and eventually most prominently through biodegradation as intrinsic microorganisms acclimate to the presence of the petroleum hydrocarbons and use it as a growth substrate.

Direct-contact biodegradation occurs in the immediate proximity to the LNAPL, within pores with oil where air-phase porosity is present (e.g., top of LNAPL body). By-product gases from this reaction are directly outgassed to the vadose zone and do not enter aqueous phase. At the Bemidji crude oil research site, greater than 80% of the observed carbon efflux was attributed to direct-contact biodegradation and outgassing ([Ng et al. 2015](#)).

Biodegradation of LNAPL constituents occurs across the entire smear zone (from unsaturated, to partially, to fully saturated)

by naturally-occurring microorganisms. Biodegradation occurs via a multitude of mechanisms in both aerobic and anaerobic conditions. Aerobic biodegradation occurs where ample oxygen (O_2) is present. In a relatively short time (i.e., several months depending upon geochemistry), the often finite supply of electron acceptors within the LNAPL smear zone such as O_2 , nitrate (NO_3^-), ferric iron (Fe^{3+}), and sulfate (SO_4^{2-}) are consumed and conditions become increasingly more favorable to anaerobic biodegrading organisms that produce methane (CH_4). Gaseous by-products of biodegradation processes, carbon dioxide (CO_2) and CH_4 , are observable in the vadose zone soil gas above the LNAPL source zone. As the CH_4 diffuses upward, it encounters O_2 diffusing downward from the atmosphere which enables intrinsic methanotrophs and other microorganisms to consume the CH_4 and create CO_2 and water vapor. Vapor phase hydrocarbons (i.e., volatile organic compounds [VOCs]) are also degraded aerobically and anaerobically in the vadose zone, depending on the local (pore scale) conditions. CO_2 efflux, measurable at ground surface, provides evidence of these biodegradation processes.

In the saturated zone, dissolution losses are observed as dissolved phased hydrocarbons in analyzed groundwater samples collected from monitoring wells immediately adjacent to and downgradient from the LNAPL source. The effects of biodegradation of dissolved hydrocarbons can be observed in dissolved groundwater plumes by measuring changes in geochemical parameters: decreases in dissolved O_2 , NO_3^- , and SO_4^{2-} and increases in dissolved ferrous iron (Fe^{2+}), manganese (Mn^{+2}), CO_2 , and CH_4 ([NRC 2000](#)).

NSZD processes are observable at all LNAPL release sites. The rate that NSZD reduces the LNAPL mass (i.e., the bulk NSZD rate) can be estimated by measuring CO_2 efflux rates at the ground surface, CO_2 or O_2 gradients in vertically nested soil gas monitoring systems, and from temperature gradients measured with vertical thermocouple arrays placed in the ground ([API 2017](#)). The NSZD rates of individual compounds of interest (e.g., BTEX) are difficult to estimate with these approaches at this time, but can be assessed by observing the chemical changes in LNAPL composition over time.

NSZD rates at a given site are affected by a number of interrelated factors including: temperature, soil moisture, soil gas permeability, groundwater geochemistry, and microbiology. To date, most measurements have provided NSZD rates in a relatively narrow range. An analysis of rate information from 25 sites revealed the middle 50% of sites exhibited NSZD rates between 700 and 2,800 gallons/acre/year, with a median of approximately 1,700 gallons/acre/year ([Garg et al. 2017](#)).

The [NSZD Appendix](#) contains a more detailed discussion of NSZD processes.

3.4 LNAPL Thickness in Wells

Historically, thickness of LNAPL in a well was used to provide unit volume estimates of LNAPL, the mobile LNAPL interval, and as an indicator for the magnitude of recoverability. Today, it is better understood that higher resolution tools, such as LIF, provide a better resolution of LNAPL location, and in situ distribution and transmissivity provide a better indication of recoverability.

The apparent LNAPL thickness in a well relates to the hydrogeologic conditions and characteristics of the LNAPL and soil. Water table fluctuations can lead to the misconception that the LNAPL body is not stable. Water table fluctuations, due to seasonality or tidal fluctuations, influence the occurrence of LNAPL in the aquifer and wells [([ITRC 2009b](#)); ([Kemblowski and Chiang 1990](#))]. However, the changes in measurable thicknesses in a monitoring well are a result of changes in the vertical re-distribution of LNAPL saturation and do not typically indicate a change in the lateral extent of the LNAPL body.

The apparent thickness in the well is commonly exaggerated compared to the thickness of the mobile LNAPL interval in the formation as discussed below for unconfined, confined, perched, and fractured bedrock settings ([Marinelli and Durnford 1996](#)). For the reasons described below, assess the site-specific hydrogeologic conditions to interpret the data properly before using in-well LNAPL thickness in the LCSM.

3.4.1 Unconfined Conditions

Under unconfined conditions, LNAPL thickness in a monitoring well may increase as the water table falls and LNAPL flows into the well. As the water table rises, LNAPL becomes entrapped in the saturated soil and the apparent LNAPL thickness in the well decreases. When unconfined conditions are at equilibrium, the apparent LNAPL thickness in the well will closely match the equilibrium thickness of the mobile LNAPL interval intercepted by the well.

3.4.2 Confined Conditions

Under confined conditions, LNAPL thickness in a monitoring well typically increases as the potentiometric surface rises and decreases as the potentiometric surface falls. Often, the LNAPL thickness observed in the well may be exaggerated compared to the thickness of the mobile LNAPL interval within the formation.

Confined LNAPL is trapped in an aquifer beneath a layer that limits the upward movement of the LNAPL. The term 'confined LNAPL' is used because the mobile LNAPL is under pressure against the underside of a capillary confining layer (often fine-grained, lower permeability lithology). The LNAPL is under pressure within this zone, and a monitoring or recovery well screened across a mobile confined LNAPL interval acts as a "pressure release valve." After installation, the LNAPL enters the well screen and rises in the well to equalize with atmospheric pressure. LNAPL accumulates as an exaggerated in-well LNAPL thickness (see [Fractured Rock Appendix](#)).

Monitoring the in-well LNAPL thickness response to water table (potentiometric) elevation changes is one way to assess whether LNAPL is confined. For confined LNAPL, the variability of the water table elevation with in-well LNAPL thickness will be the opposite of that described for the unconfined condition. For confined systems, the in-well LNAPL thickness will increase with an increase in potentiometric surface elevation, as shown in Figure 3-7. For a given site, both unconfined and confined LNAPL may exist. Further, a given location or well may be initially unconfined but may become confined through a rise in elevation of the water table. Additional, more specific information relating to changes in LNAPL thickness in confined conditions is available in ([Kirkman 2013](#)) and ([ANSR 2012](#)).

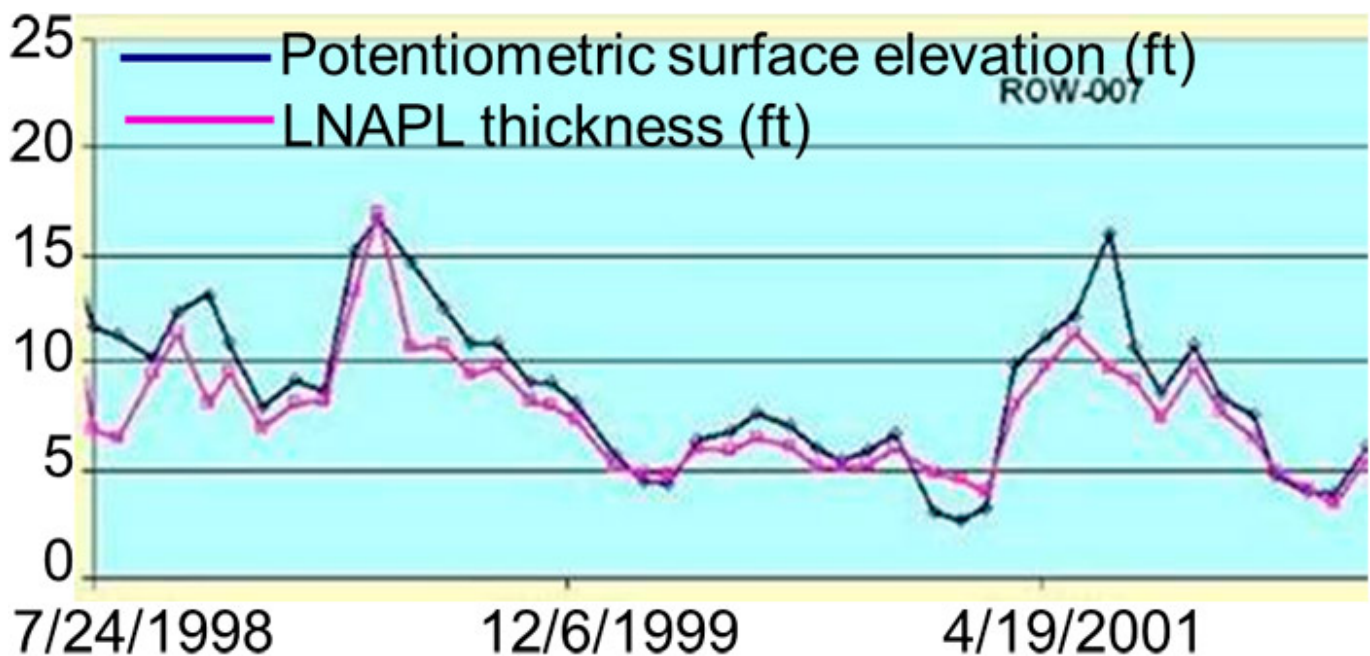


Figure 3-7. LNAPL thickness will mimic the potentiometric surface elevation for confined LNAPL conditions
(courtesy of BP).

3.4.3 Perched Conditions

Under perched conditions, LNAPL thickness in a monitoring well may be exaggerated compared to the adjacent mobile LNAPL interval. If the well extends into the underlying confining layer, LNAPL will flow into the "sump" or reservoir created by drilling into the underlying confining layer.

LNAPL may be perched due to the pooling of LNAPL on top of a lower permeability feature within the unsaturated zone, or at the interface of the overburden and bedrock. Perched LNAPL is mobile LNAPL that accumulates in the vadose zone above less permeable layers, which exhibit a pore entry pressure greater than the available LNAPL head, and thus impedes the downward migration of LNAPL. If a sufficient volume of LNAPL collects above a less permeable (perching) layer, the resulting LNAPL thickness within a monitoring well screened into the perched LNAPL layer and into the underlying lower-permeability formation will result in a measured thickness that is greater than that in the surrounding formation. This condition results, in part, because the portion of the well screened below the interface and into the less permeable perching layer acts as a sump and allows LNAPL to accumulate. When the water table on the perched layer rises, the thickness of LNAPL in a well screened

across the perching layer will decrease and again, will not be representative of the actual thickness of LNAPL within the formation at that location.

3.4.4 Fractured Preferential Pathway Conditions

In fractured and preferential pathway conditions (see the [Fractured Rock Appendix](#)), the relationship between the potentiometric surface and fractures intersected by the monitoring well may result in exaggerated LNAPL thickness compared to the mobile interval of LNAPL in the rock. Fractured and preferential pathway conditions represent LNAPL confined in a large pore network that is defined by capillary pressure contrasts, which may include open fractures in bedrock or desiccated soils, sand surrounded by clay, and macropores. For the same reasons as discussed for confined LNAPL above, the LNAPL thickness observed in a well is typically exaggerated compared to that within the formation. The LNAPL within the formation is limited to the secondary porosity features rather than being distributed within the primary porosity of the matrix. Indicators of LNAPL within a preferential pathway or fracture include:

- exaggerated LNAPL thicknesses in wells at equilibrium conditions;
- LNAPL observed at a considerable distance below the water table and laterally from the release location; and
- areas where the geology is known to have preferential pathways such as fractured clay and bedrock, or may have macropores or other secondary porosity features.

3.5 States of LNAPL Saturation

This section discusses the details of LNAPL occurrence in soil and how it relates to migrating, stable mobile, and residual LNAPL conditions. The terms migrating, mobile, and residual LNAPL saturation relate to LNAPL concerns, remedial technologies, and remedial metrics. This section explains the terminology and applies the understanding to LNAPL site management. For sites where LNAPL is not observed in-well, it also provides a summary of indicators in soil and groundwater that can be used to assess its presence.

Figure 3-8 illustrates the evolution of an LNAPL release. At the early stage of the release, the LNAPL head from the release develops a strong LNAPL gradient shown in the top figure; as the LNAPL continues to drain from the release—lowering the LNAPL head—the gradient dissipates and with time will mimic the water table gradient. The upper pane illustrates a situation before the LNAPL release is stopped. The LNAPL body is migrating due to the LNAPL head. LNAPL will continue to migrate laterally until the release is stopped and the LNAPL head dissipates. The middle pane illustrates a situation where the LNAPL release has been stopped and the LNAPL head had dissipated. LNAPL accumulates in a well installed in the LNAPL body, but the LNAPL is no longer migrating (spreading) laterally. The lower pane illustrates the situation where LNAPL is at residual saturation. LNAPL will not accumulate in a well installed in the LNAPL body unless the water table drops and LNAPL trapped below the water table can flow into the well.

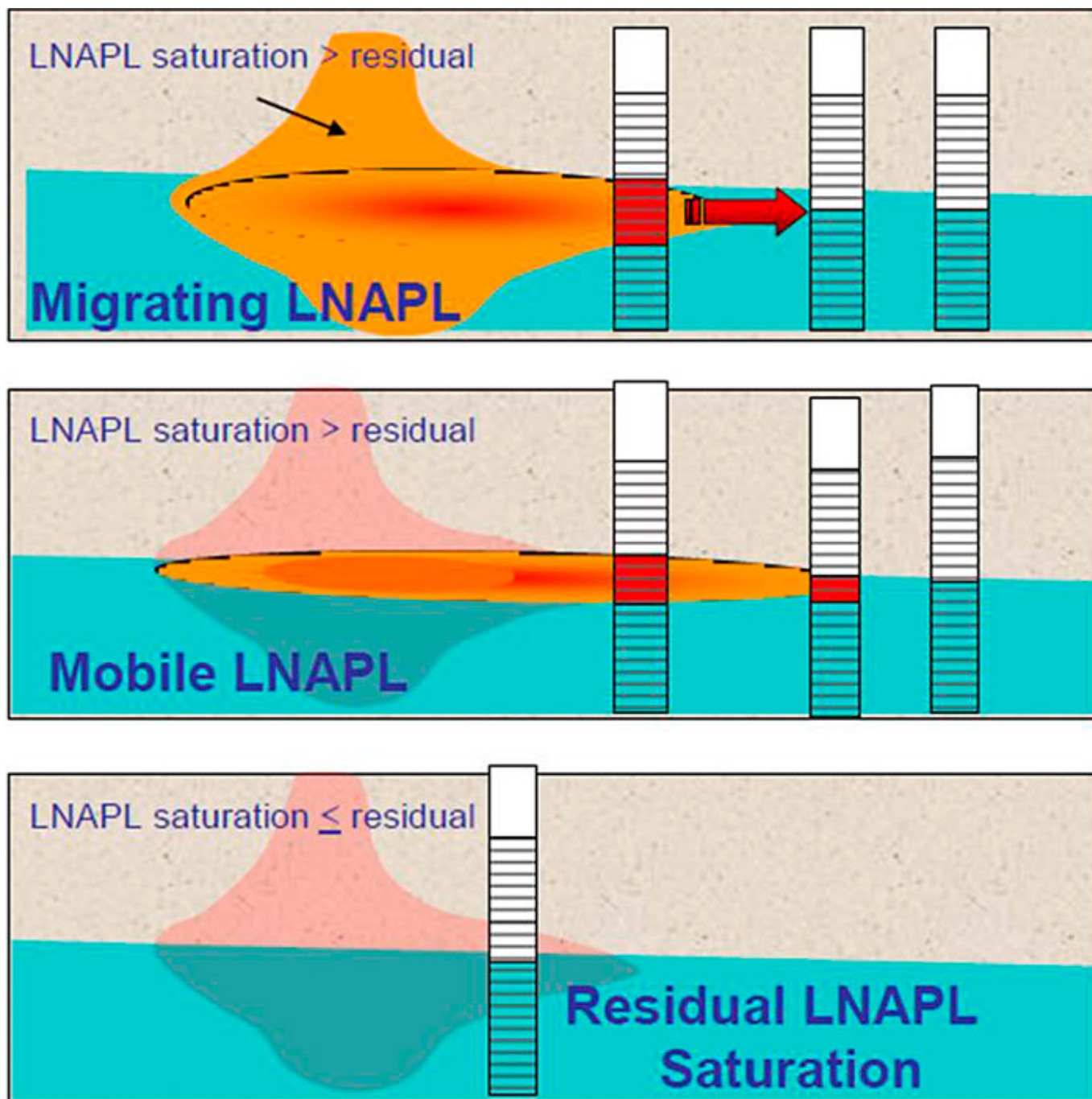


Figure 3-8. Three LNAPL conditions (ITRC 2009a).

LNAPL migration and mobility concerns have risk and non-risk implications at many LNAPL sites. It is important to understand the distinction between migrating LNAPL, mobile LNAPL, and residual LNAPL to establish appropriate remedial goals and determine remediation objectives. For each of these three conditions, physical properties of the LNAPL, aquifer properties, LNAPL saturation (including LNAPL relative permeability), LNAPL hydraulic conditions (e.g., LNAPL head) and NSZD affect the ability of an LNAPL body to expand or for LNAPL to flow into a well. [Section 5](#) of this document describes the decision process for identifying LNAPL concerns, verifying concerns through the application of threshold metrics, establishing LNAPL remedial goals, and determining LNAPL remediation objectives. An understanding of whether the LNAPL at your site is residual, mobile, or migrating is key to evaluating concerns, establishing remedial goals, and determining remediation objectives.

3.5.1 Migrating LNAPL

Migrating LNAPL refers to plume-scale behavior; the overall body or a portion of the LNAPL body is expanding. The mechanisms that drive LNAPL migration are sufficient to overcome resistive forces. Conversely, stable LNAPL represents an LNAPL body that does not change over time and does not contain the driving forces to exceed the resistive forces. A stable

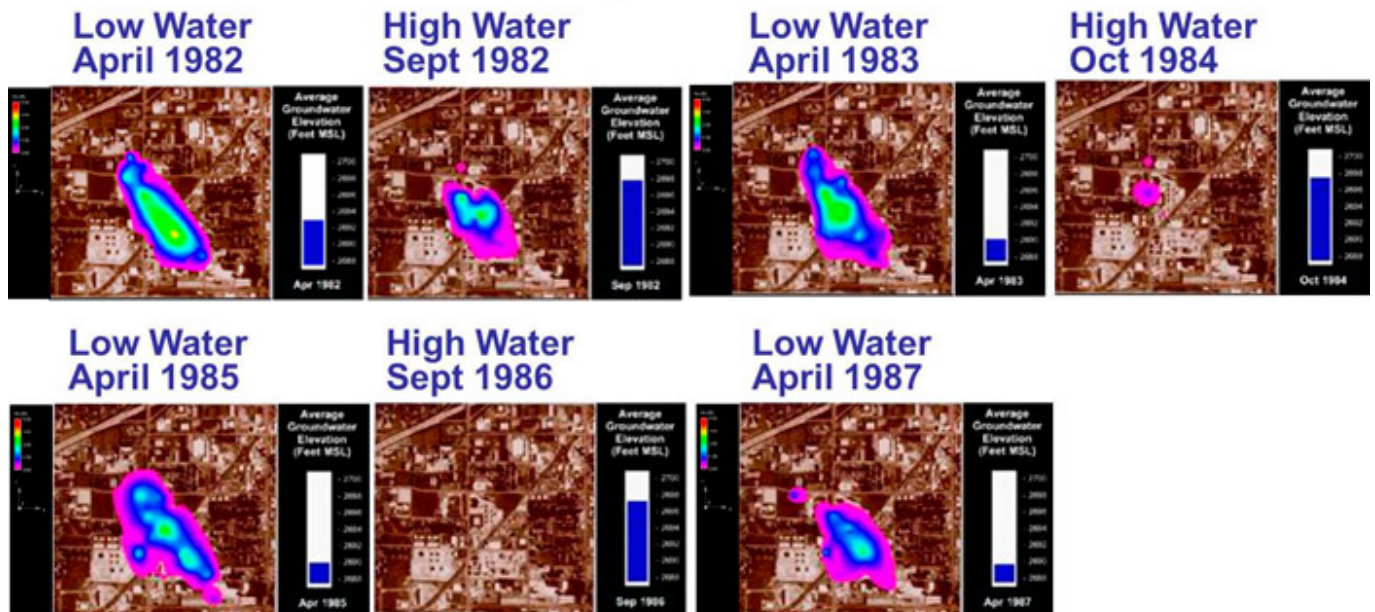
LNAPL body is comprised of residual LNAPL or a combination of mobile and residual LNAPL. LNAPL transmissivity is an indicator of the potential for migration, but by itself is insufficient to indicate the rate of migration. Assuming there are no resistive mechanisms, the rate of migration (or equivalently, the rate of LNAPL specific discharge) would be represented by LNAPL transmissivity times the LNAPL gradient. However, resistive mechanisms exist that render this calculation an overestimate of migration. These resistive mechanisms include water-table fluctuations, entry pressure head, and mass depletion via natural mechanisms (i.e., NSZD). Therefore, while mobile LNAPL and an LNAPL gradient may exist, migration may or may not occur because the resistive mechanisms may reduce the magnitude of migration, or counteract it completely.

LNAPL migration concern within an aquifer refers to lateral movement of the overall LNAPL body, whereby LNAPL enters aquifer pore spaces not previously containing LNAPL. This can occur only if the LNAPL possesses sufficient mobility potential (i.e., within the mobile range of LNAPL saturations) and sufficient LNAPL head (and capillary pressure) to drive the migration. Consequently, active LNAPL migration refers to spreading that occurs along the leading edge of the LNAPL body, where the LNAPL pressure head or driving force exceeds the capillary entry pressure (the resisting force) for the adjacent groundwater saturated aquifer. LNAPL migration tends to occur over the relatively early stages of a release, when the LNAPL head pressures and LNAPL saturations are greatest, except in the case of a change in hydraulic conditions (e.g., pumping on a nearby well). Following the termination of an active release, the LNAPL pressure head may decrease rapidly, which ultimately limits the overall volume of LNAPL available to migrate laterally. Afterwards, LNAPL typically is limited to vertical redistribution within the smear zone as new historical high or low water levels are attained. It is not necessary that the margin of the LNAPL body be at residual LNAPL saturation; equilibrium is typically established with the mobile (albeit diminished) LNAPL saturation still remaining. The water-filled pore spaces of the fully saturated aquifer simply act as a barrier to further LNAPL migration as capillary pressure decreases. Post release, as the plume spreads, the gradient decreases and the thickness decreases, which in turn decreases the transmissivity of the LNAPL, resulting in a self-limiting process.

Note that natural or manmade preferential pathways may exist at a given site that could allow migration to occur where it would not otherwise be expected. In such cases, the capillary entry pressure associated with the preferential pathway is less likely than that of the overall aquifer given the same LNAPL head pressure.

Care must be taken when using LNAPL thickness data from monitoring wells to assess LNAPL migration. Vertical redistribution of LNAPL with a rising or falling water table can result in the appearance of an increased (i.e., growing) or decreased (i.e., shrinking) footprint, or apparent lateral migration of LNAPL that is not representative of actual conditions. LNAPL that “disappears” from a well may not be related to LNAPL migration, but rather to drainage. Likewise, increasing LNAPL thickness or appearance within a well is not necessarily a sign of increased or renewed migration. Rather, LNAPL thickness within a well is continually affected by drainage and imbibition effects within the near well bore formation and sand pack environment as water levels change. Figure 3-9 shows the apparent horizontal redistribution of LNAPL at a refinery over time resulting from vertical changes in LNAPL distribution. In actuality, there was very little change in horizontal or lateral footprint over the five-year duration depicted.

LNAPL Monitoring Over Time - Refinery



- ▶ Measured LNAPL Depth in Monitoring Wells: 0 to 3 feet
- ▶ Seasonal Water Table Variation: 8 foot range

Figure 3-9. Examples of seasonal LNAPL redistribution ([API 2006](#)).

Multiple lines of evidence are recommended to fully assess the LNAPL migration for relatively recent releases (e.g., well gauging and dissolved phase plume behavior). LIF-based borings are a more technically sound means to define the leading edge of LNAPL accumulations, particularly in the early phases of an investigation. For late-stage release sites, it is often acceptable to assume lateral migration is at equilibrium, for the reasons discussed previously. Diagnostic gauge plots are a useful tool for evaluating whether or not the gauged thickness of LNAPL in a well is indicative of migration or rather more likely, the result of water table fluctuations.

Migration is also limited by NSZD processes (volatilization, dissolution, and biodegradation) resulting in mass loss and increased LNAPL viscosity ([Mahler, Sale, and Lyverse 2012](#)). NSZD losses can act to offset/balance the spreading effects caused by any local LNAPL pressure heads ([Mahler, Sale, and Lyverse 2012](#)). This is a dynamic relationship. When saturations are high, LNAPL mobility can cause LNAPL to migrate laterally toward the periphery of the body, while depletion processes act to remove LNAPL mass and diminish saturations, thereby balancing the movement. NSZD processes are discussed further in the [NSZD Appendix](#) of this document.

3.5.2 LNAPL Stability

Driving forces of a LNAPL release will penetrate below the water table. The LNAPL head gradient (i.e., the height of the LNAPL release above the water table) resulting from the LNAPL release principally determines the lateral spread of LNAPL near the water table, within the capillary fringe. Immediately following a release of sufficient volume, the LNAPL head is initially greater than the water table gradient. The LNAPL gradient will dissipate with time, eventually leading to LNAPL footprint stabilization (Figure 3-8). Stabilization depends on the type of LNAPL and the volume of the release. Commonly, low viscosity LNAPL (e.g., gasoline and diesel) takes weeks to months to stabilize, and high viscosity LNAPL (e.g., heating oil) requires months to years to eventually stabilize ([CL:AIRE 2014](#)). For distinct LNAPL releases, the LNAPL will eventually become stable and form a source of varying saturation levels within the pores of the formation. The LNAPL saturation at the leading edge will drop in saturation to below residual (i.e., fraction of the pore space occupied by LNAPL that cannot be mobilized under an applied gradient), and through balances of factors at the leading edge, will cease to migrate due to insufficient LNAPL head to exceed pore entry pressure, lower LNAPL saturations (i.e., residual), and NSZD processes ([Tomlinson et al. 2017](#)). Residual LNAPL is unlikely to become a problem if hydraulic conditions change, but mobile LNAPL may move with changes in hydraulic conditions (e.g., operation of a pumping well).

3.5.3 Mobile LNAPL

Mobile LNAPL represents a pore-scale concept. LNAPL occupies a sufficient fraction of the total porosity to form an interconnected network, but does not contain the driving forces on the LNAPL body to exceed the resistive forces. Mobile LNAPL can be detected via in-well fluid level gauging or through LNAPL transmissivity measurements. If an in-well thickness is measurable, then mobile LNAPL exists. The relative magnitude of LNAPL mobility can be assessed using LNAPL transmissivity.

Mobility refers to the ability of LNAPL to move or flow, vertically or horizontally, under a given gradient. LNAPL migration is the expansion of the LNAPL body footprint resulting from sufficient mobility and gradient, thus resulting in the expansion of the overall LNAPL body edge. LNAPL that accumulates in a well is considered mobile; however, its presence in a well is not a reliable indicator of potential recoverability nor the LNAPL body's migration potential.

The degree of mobility is dependent on both the proportion of movable LNAPL in the pore spaces (i.e., mobile LNAPL saturation) and the degree of interconnection between pore spaces (Figure 3-10). Residual LNAPL is not mobile. The proportion of the overall LNAPL body—associated with its residual LNAPL saturation—does not participate in its mobility (i.e., immobile fraction).

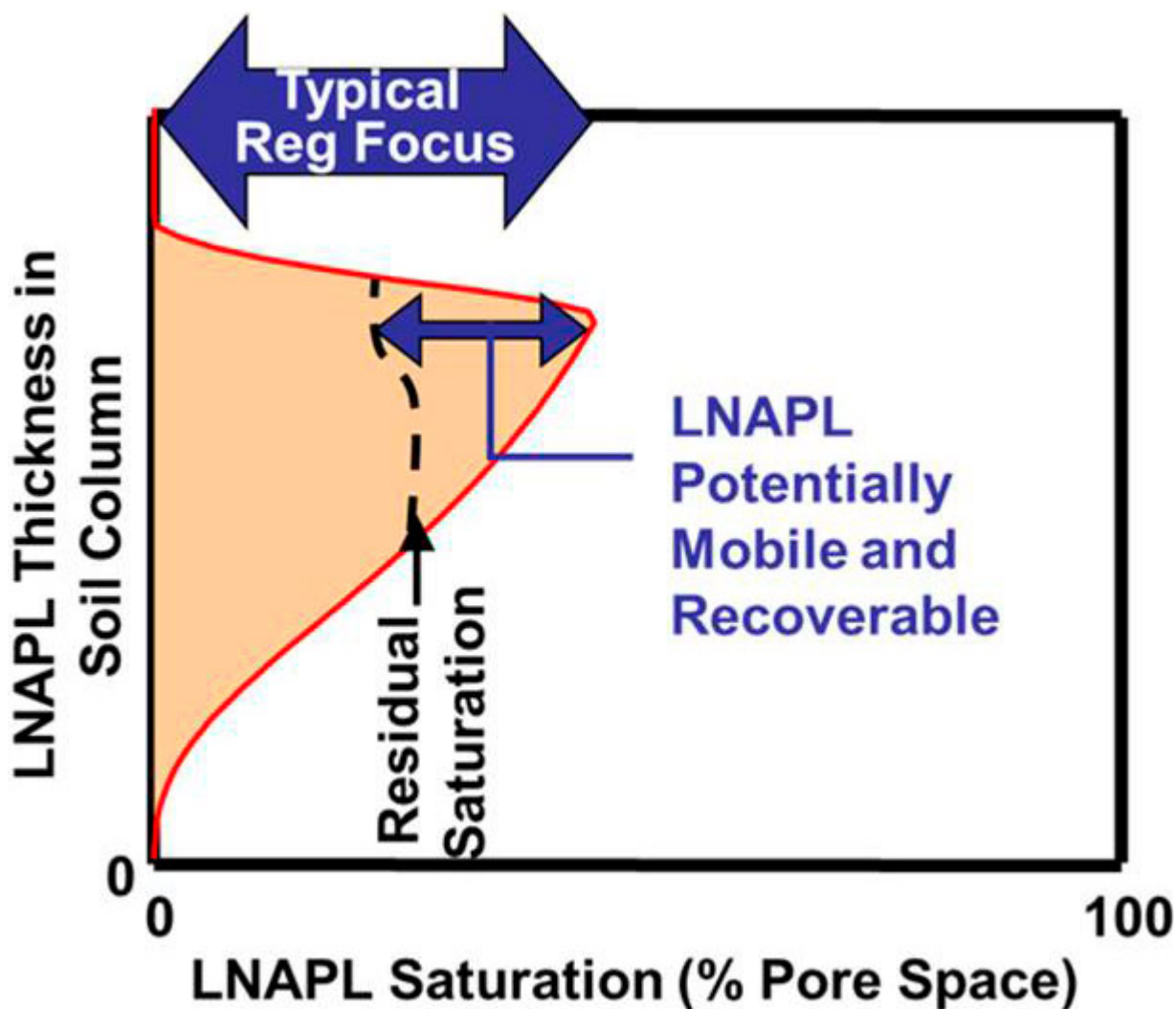


Figure 3-10. LNAPL mobility is the additional consideration due to exceeding residual saturation (courtesy of S. Garg 2017).

3.5.4 Residual LNAPL

Residual LNAPL represents a pore-scale concept whereby LNAPL occupies a fraction of pore space that is discontinuous and too small for LNAPL flow to occur. Residual LNAPL has an insignificant transmissivity. As discussed above, residual spans a range of LNAPL saturation levels for a given soil and LNAPL type. An additional and significant factor for determining the residual saturation of a given soil is the maximum historical saturation [([Johnston and Adamski 2005](#)); ([Lenhard, Rayner, and](#)

[Davis 2017](#)]]. Often the minimum and maximum historical saturation levels span a factor of 10 across a given LNAPL body.

Accepting residual saturation as a function of maximum saturation and applying it at plume scale can be useful to explain why quantifying residual saturation as a single value is not consistent with the current conceptual model of LNAPL occurrence and migration. The LNAPL head is greatest when a release occurs and LNAPL reaches the water table, resulting in the highest LNAPL saturations. After the release ceases and the LNAPL spreads out, LNAPL on the edges of the body is exposed to lower LNAPL heads resulting in lower LNAPL saturations. Thus, residual saturation is often higher in the center of the body than on the fringes. Similarly, the maximum historical LNAPL saturation will vary with depth at each location within the LNAPL footprint, resulting in vertically variable residual saturations. Water table fluctuations can help to reduce variability in residual saturation at some locations; however, variability still exists.

When considering site management options, determining whether LNAPL is mobile or residual is insufficient to identify the primary concerns (See [Section 5](#)). Most LNAPL concerns are driven by the migration of the LNAPL body, compositional risks, and abating LNAPL occurrence in wells to the maximum extent practicable. Migration can be evaluated using multiple lines of evidence.

If an LNAPL body is stable, then hydraulic recovery will have little impact on future management. Continued recovery will not reduce compositional-based risk, meaningfully reduce the source mass, nor significantly reduce source longevity. Conversely, if an LNAPL body is mobile, thus containing higher LNAPL transmissivity values, then hydraulic recovery may be beneficial to reduce LNAPL body mass. The efficacy of recovery indicated by LNAPL transmissivity is ultimately controlled by the ratio of residual to mobile LNAPL. High LNAPL transmissivity values with relatively thick smear zones will result in larger fractional source removal than thick residual smear zones exhibiting a similar LNAPL transmissivity value.

Residual saturation is discontinuous and immobile LNAPL under prevailing conditions and will not flow into a well ([ASTM 2014b](#)). The residual saturation within the unsaturated zone is the LNAPL saturation attained after an initially saturated soil is allowed to drain by gravity to equilibrium [([Hoag and Marley 1986](#)); ([Zytner, Biswas, and Bewtra 1993](#))], which is analogous to field moisture capacity as used in the agricultural engineering field. The residual LNAPL saturation in the saturated zone has been defined as the saturation at zero capillary pressure at the terminus of the spontaneous imbibition curve [([Pickell, Swanson, and Hickman 1966](#)); ([Bear 1972](#)); ([Dullien 1979](#)); ([Fetter Jr. 1992](#)); and ([Freeze and McWhorter 1997](#))]. Generally, the residual saturation will be lower within the unsaturated zone compared to the saturated zone. The unsaturated zone contains a more significant gas-filled porosity. Thus, the LNAPL becomes an intermediate wetting fluid which allows more of the fluid to drain from the soil as compared to the saturated zone where the gas phase is small and LNAPL is the non-wetting fluid.

It is notable that many literature values (particularly those developed based on petroleum exploration) of residual saturation typically overestimate residual saturation as they are frequently based on experimental data collected using sand or dry soils. This tends to result in a low threshold entry pressure and a higher initial LNAPL saturation resulting in a higher residual saturation. In all but well sorted sands, literature values of residual saturation are likely not applicable (becoming more so as soils get finer). Although some of the early references (e.g., ([Mercer and Cohen 1990](#)); ([EPA 1995](#))) were based on state of the art science, our current understanding indicates that sites do not reach initial saturations of 100% at environmental sites. The user of literature values needs to understand their limitations.

Residual saturation is a fraction of the total saturation and is proportional to the maximum LNAPL saturation occurring in a given soil. As soil is successively flooded with and drained of LNAPL, such as occurs with repeated water table fluctuations as shown in Figure 3-6, the residual saturation tends to increase. Residual saturation is also inversely related to the grain size; it is typically larger in finer-grained soils.

Prior guidance attempted to define remediation endpoints based on residual saturation. However, the current state of the science supports that residual saturation is a conceptual limit; residual saturation cannot be easily measured and is not a value that is currently used as a remediation endpoint metric. It is recognized that the practical limits of recoverability are above the conceptual residual saturation value; this is discussed further in the [Transmissivity Appendix](#).

Typically, a laboratory analysis can be performed to estimate the residual saturation. As discussed, these are estimates of the residual saturation for the given location and depth; residual saturation varies across any given site and typically, cannot be defined as a single number. To bind this range of variability, collect soil samples across a given boring and compare them to the mobile LNAPL interval. The samples outside of the mobile LNAPL interval represent residual LNAPL values.

3.5.5 LNAPL Indicators

At petroleum release sites where an LNAPL concern exists, but it has not been directly observed, a determination of LNAPL presence should rely on multiple lines of evidence to verify or eliminate the suspected LNAPL concern. Monitoring for the presence or absence of LNAPL in monitoring wells can be helpful; however, it should not be the only assessment tool. Where LNAPL is present in a properly constructed monitoring well, LNAPL can also be assumed present in the surrounding subsurface formation. However, it is a common misconception to assume that if no LNAPL is present in a monitoring well, then there is no LNAPL in the soil. Similarly, if in-well LNAPL thickness changes from measurable to not measurable following LNAPL remediation, it is a common misconception to assume that LNAPL is no longer present within the surrounding subsurface soil. In both of these scenarios, LNAPL may be present in discontinuous pores at saturations less than those needed to migrate laterally or to mobilize into a monitoring well.

Table 3-2 lists potential indicators of the presence of LNAPL in unconsolidated materials, and more importantly, also cautions the use of indicators that should be viewed as 'lines of evidence' rather than absolute indicators. Note also that Table 3-2 does not cover all situations (e.g., sediments nor fractured media). The use of soil or groundwater concentrations to assess whether LNAPL is present should be regarded as supporting evidence and not as absolute indicators. There is not a specific concentration in groundwater that indicates the presence of LNAPL, because varying product compositions and degrees of weathering affect concentrations of dissolved components. Similarly, the use of TPH concentrations in soil as an indicator of LNAPL presence should be exercised with caution as soil TPH concentrations may be affected by non-hydrocarbons (such as soil organic matter) and by the choice of analytical method. However, the closer a measured concentration in groundwater is to the effective solubility, the greater the likelihood that LNAPL is present. For more information, reference the ITRC TPH Risk Document ([ITRC 2018](#)).

A comparison of historic and current site-specific dissolved and vapor phase concentrations, and boring logs with notes about locations and depths of impacted soils, can provide additional lines of evidence pertaining to the presence or absence of an LNAPL body. For example, significant lateral migration and an increase in dissolved-phase concentrations, or the sudden appearance of vapor in buildings, may suggest that LNAPL is present.

Visual observations of the soil core combined with field screening tools such as a photoionization detector (PID) or flame ionization detector (FID) with CH₄ correction, or use of LIF tools as the boring is advanced, can confirm the presence or absence of LNAPL in the borings. Care should be taken to design a soil investigation that assesses the areas with the greatest potential for LNAPL. Inadequate distribution or placement of soil borings can lead to an incomplete investigation and the presumption of no LNAPL presence when it may indeed be present in the subsurface.

Table 3-2. Potential LNAPL indicators

Indicator ¹	Limitations
Groundwater	
• Effective solubility of a given constituent: Greater than 1% to 10% (e.g., for gasoline) • Benzene: > 1 - 5 mg/L^{2,3} • TPH_(gasoline): > 30 mg/L⁴ • BTEX: > 20 mg/L⁵ • Current or historical presence of LNAPL (including sheens) ^{2,3}	• There is not a specific petroleum hydrocarbon compound (PHC) concentration in groundwater that defines LNAPL because of varying product types and degrees of weathering.
Soil	

Indicator ¹	Limitations
• Current or historical presence of LNAPL (including sheens, staining)^{2,3} • Benzene > 10 mg/kg² • TPH_(gasoline) > 250 – 500 mg/kg^{2,5} • TPH_(diesel) > 10 – 30 mg/kg⁶ • Ultraviolet fluorescence (UV) or LIF response in LNAPL range⁷ • PID or FID readings for a recent release > 500 ppm⁸	• The use of TPH soil concentration data as LNAPL indicators should be exercised with caution. Note that the information in this table may not be applicable to media such as sediment or fractured media. • TPH soil concentrations can be affected by the presence of soil organic matter. • TPH soil concentrations are not well correlated with TPH or O₂ soil gas concentrations (Lahvis and Hers 2013). • Organic vapor readings are composition dependent. For older (weathered) releases, LNAPL may be present at much lower PID/FID readings.
Location Relative to Release Area	
• Adjacent to (e.g., within 20 feet of) a known or suspected LNAPL release area or petroleum equipment²	• The probability of encountering LNAPL increases closer to a known or suspected release.
Notes: Order of listing does not imply ranking. Indicators above are generalized and do not represent all possible situations. ¹ One or more of these indicators may be used to define LNAPL. ² Used in the derivation of PVI screening distances by (EPA 2013) and (Lahvis et al. 2013). ³ Used in the derivation of PVI screening distances by (Peargin and Kolhatkar 2011). ⁴ Used in the derivation of PVI screening distances by (EPA 2013). ⁵ Recommended by (Lahvis and Hers 2013). ⁶ From ITRC TPH Risk Document (ITRC 2018). ⁷ From ASTM E2531-06 (ASTM 2014b). ⁸ Recommended by (EPA 2013) and (Lahvis and Hers 2013).	

3.6 LNAPL Recoverability and Transmissivity

This section discusses the relation between mobile LNAPL and recoverability and introduces the key concept of LNAPL transmissivity.

3.6.1 LNAPL Recoverability

LNAPL recoverability refers to the ability to remove mobile LNAPL from the subsurface at a given location, as evaluated by comparing the measured LNAPL transmissivity to an agreed upon threshold. Understanding LNAPL recoverability is important, particularly for sites where one or more remediation endpoints are based on removal of LNAPL (e.g., to the maximum extent practicable). Although this discussion focuses on LNAPL recoverability under ambient site conditions, additional remedial technologies that rely on increasing the recoverability of LNAPL (e.g., water flooding, surfactant-enhanced remediation, and co-solvent flushing) are discussed in [Section 6](#) of this document.

Reaching a recoverability limit does not necessarily mean that LNAPL saturations are reduced to residual, but it does typically represent an endpoint where the majority of remaining LNAPL is of limited mobility and/or residual. It may continue to accumulate in a monitoring well, for example. A critical factor in LNAPL recoverability is the decrease in LNAPL relative permeability over the operating time of the remediation technology. As removal progresses over time, LNAPL saturations are reduced, which causes the relative permeability of LNAPL to decrease (red line on Figure 3-11), and also results in declining recovery rates.

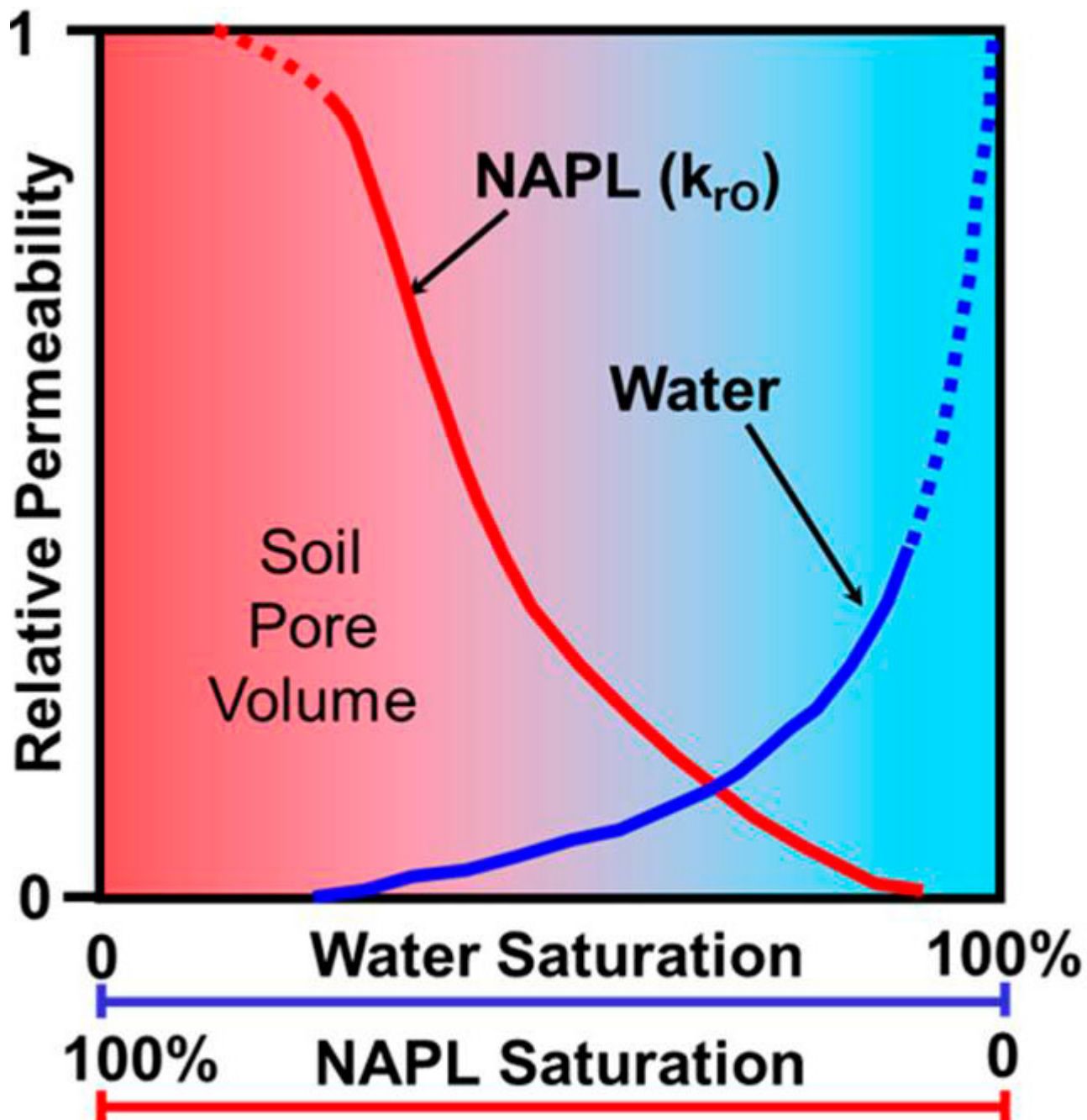


Figure 3-11. LNAPL relative permeability.

At the pore scale, LNAPL eventually becomes discontinuous by virtue of the decreasing saturations. While these isolated, discontinuous LNAPL occurrences may be above residual saturation locally, they are cut off from the overall, interconnected hydraulic flow field. Therefore, a practical limit for extraction (i.e., diminishing returns for LNAPL together with increasing groundwater extraction volumes and associated handling problems) typically is reached at a time when some proportion of mobile LNAPL remains within the zone of influence of the remedial system. LNAPL recovery is likely ineffective when the following conditions are reached:

- the plume is stable (not migrating, expanding, or inducing sheens), and
- recovery no longer reduces the source to the extent that conditions with respect to risk-based dissolved phase and/or vapor phase goals improve.

Practical limits can also be prepared in terms of economic return (e.g., cost per gallon) of LNAPL recovery, including the lifting and treatment cost of the produced groundwater), and/or physical restraints (e.g., gallon of LNAPL recovery/unit of time relative to the overall volume of in-place LNAPL, including the residual volumes or reduced LNAPL transmissivity values as recovery progresses). Again, some mobile LNAPL will remain after hydraulic recovery has ceased (in addition to the

immobile, [residual] fraction of LNAPL that is unrecoverable due to inherent extraction inefficiencies).

3.6.2 LNAPL Transmissivity

LNAPL transmissivity is analogous to groundwater transmissivity; higher transmissivity values indicate higher production rates for a given drawdown induced. However, groundwater is typically expansive, and recharge by precipitation may sustain groundwater extraction for years at similar rates and drawdowns without exhibiting a decline in water production. In contrast, LNAPL bodies often have a limited extent of mobile LNAPL and transmissivity and recovery decline as LNAPL is removed.

LNAPL recovery is often termed “asymptotic” because the rate keeps decreasing, but never reaches zero. Decline curves have been used to illustrate this for optimized recovery systems with robust data sets. Figure 3-12 provides a chart of real site data where recovery started out at a high rate and declined over time.

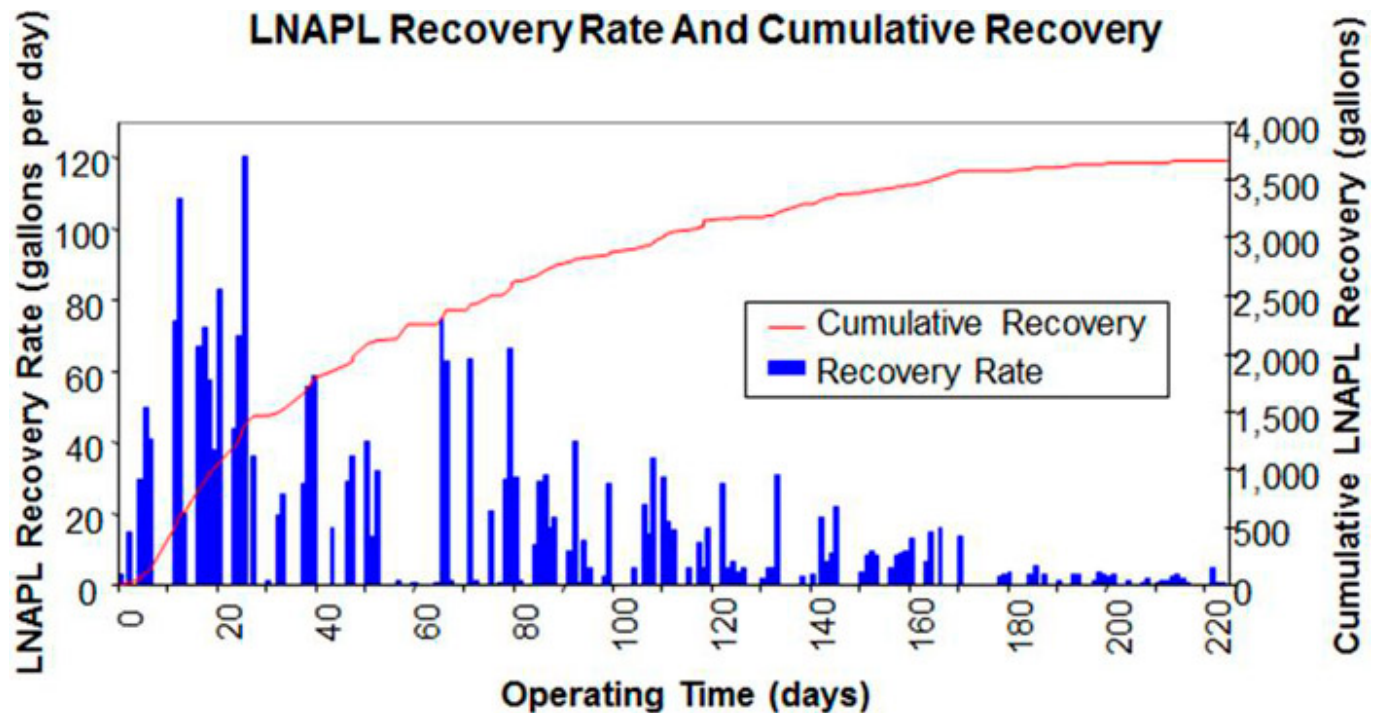


Figure 3-12. LNAPL recovery rate (blue columns) and recovered volume (red line) over time. (courtesy of AECOM)

The data in Figure 3-12 can also be plotted as recovery rate (y-axis) versus cumulative recovered volume (x-axis) to present a decline curve (Figure 3-13). The x-intercept of a best fit line through the data shows that the ultimate recovered volume is expected to be approximately 3,700 gallons. Although LNAPL may still occur in wells, it is understood from this analysis that continued LNAPL recovery will not perform as well as it had in the past. If additional remediation is warranted, this line of evidence indicates an alternative technology may be required, as the practicable limit of hydraulic recovery has been achieved.

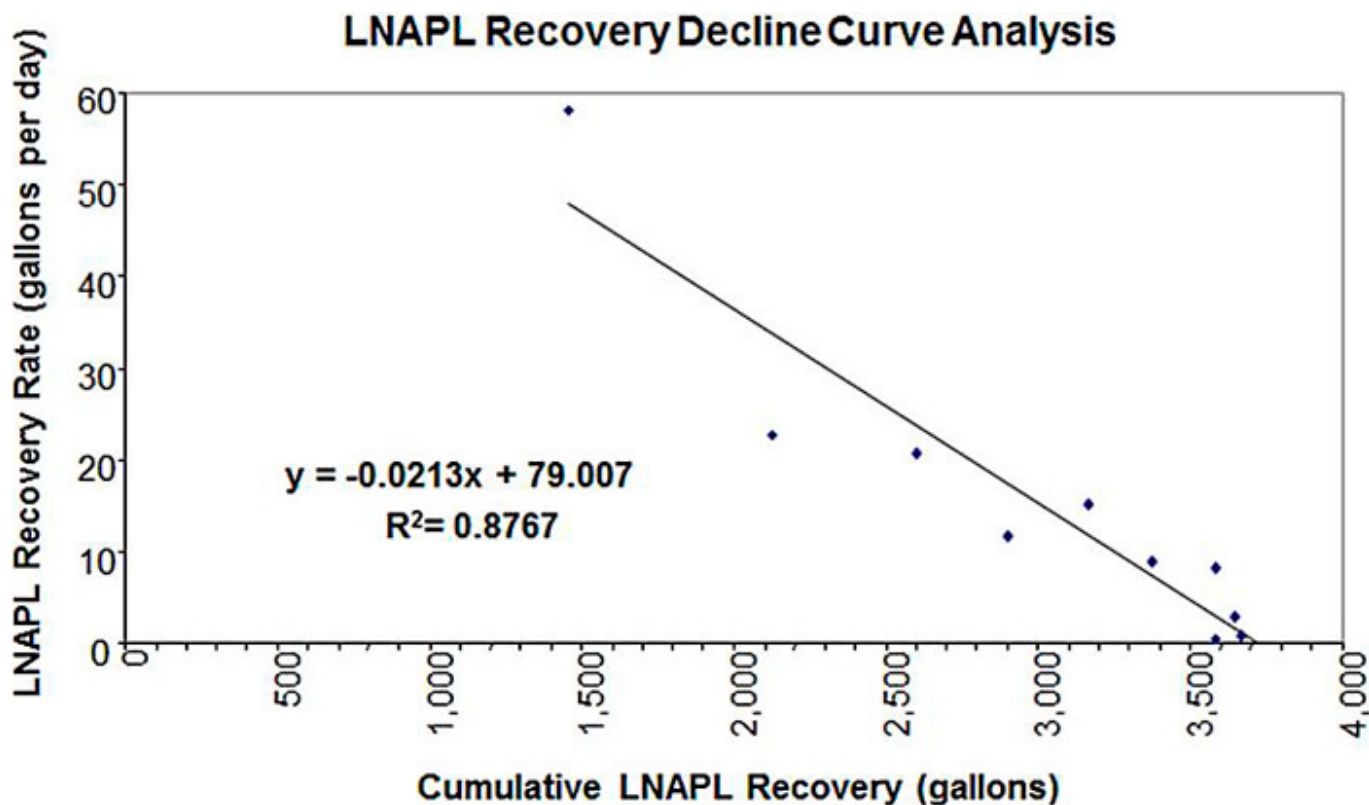


Figure 3-13. LNAPL recovery rate vs. cumulative volume recovered. (courtesy of AECOM)

Knowing of this practicable limit, LNAPL transmissivity can be used as a leading metric, in advance of system installation, to evaluate whether LNAPL recovery will be effective. Measurements of baseline LNAPL transmissivity, before system installation, can help provide a line of evidence to indicate if a site is already near its practicable limits for recovery.

Empirical data suggests that LNAPL transmissivity values below 0.1 to 0.8 ft²/day indicate low recoverability and therefore, the majority of the LNAPL at a site is in a state of lesser mobile and residual saturation. ITRC ([ITRC 2009a](#)) proposed this empirical limit based on five sites in California, Kentucky, and Florida. The sites were closed or granted no further action after developing comprehensive LCSMs and operating LNAPL recovery systems. All sites demonstrated achievement of the impracticable limit (i.e., the lack of LNAPL recoverability) irrespective of in-well LNAPL thickness remaining. Since that time, data from four additional sites, with comprehensive LCSMs based on high-resolution data, were analyzed and affirmed the proposed limits. Refer to the [LNAPL Transmissivity Appendix](#) for additional discussion on the basis for the proposed range of recoverability limits.

3.7 Relation of LNAPL Saturation and Composition to Technology Selection

This section describes subsurface chemical partitioning processes and introduces the key concept of saturation- and composition-based remedial goals as they relate to technology selection.

Figure 3-14 provides a graphical representation of mobile, migrating, and residual LNAPL and illustrates where compositional, hydraulic recovery, and saturation reduction technologies are applicable within the spectrum. For example, a site with migration concerns and high LNAPL transmissivity, can be addressed with LNAPL recovery, where the remediation endpoint is 0.1 to 0.8 ft²/day. However, if the remedial goal is to remove all LNAPL, then alternate technologies will be needed in addition to (or in lieu of) LNAPL recovery. Since the practicable limits of LNAPL recovery is represented by an LNAPL transmissivity of 0.1 to 0.8 ft²/day, LNAPL recovery cannot meet a remedial goal of removing all LNAPL.

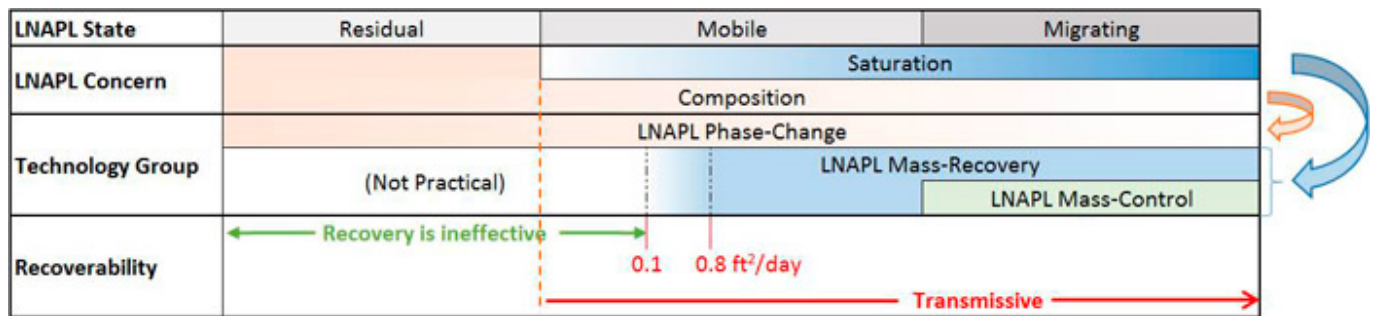


Figure 3-14. Relationship between LNAPL concern, LNAPL state, technology group and recoverability.

Where a compositional risk exists, consider phase-change technologies either in tandem with or in lieu of LNAPL recovery. While multi-phase extraction (MPE) would be worthwhile in a coarse sand with a dissolved phase concern and high transmissivity (e.g., mobile LNAPL) this technology may be less effective with a weathered diesel fuel and residual LNAPL. The weathered diesel fuel is unlikely to have a dissolved phase BTEX plume and will likely exhibit low or negligible LNAPL transmissivity. While excavation may target the total mass, depth limitations and cost may indicate that a bioremediation or NSZD alternative is more appropriate, as the majority of constituents within diesel are biodegradable.

4. LNAPL Conceptual Site Model (LCSM)

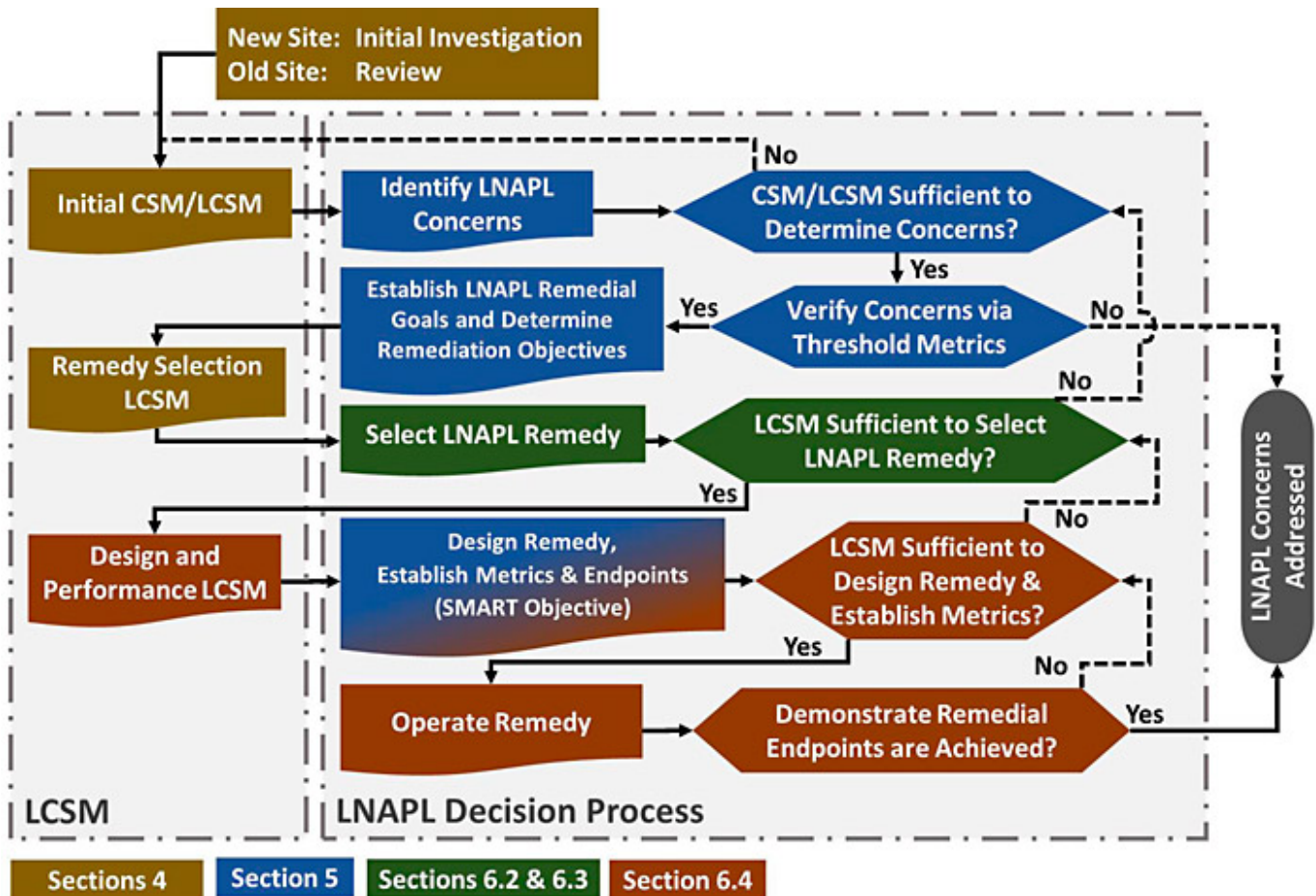


Figure 4-1. LNAPL conceptual site model (LCSM) stages and integration with LNAPL alternative evaluation.

The LCSM is the collection of information that incorporates key attributes of the LNAPL body with site setting and hydrogeology to support site assessment and corrective action decision-making. As with a conceptual site model for a non-LNAPL contaminated site, the LCSM integrates information and considerations specific to the LNAPL body relating to the risks of the contaminant source, exposure pathways, and receptors (for examples, see [ASTM 2014a](#)). The content of the LCSM will typically evolve over time as different phases of the corrective action process require different information. What remains consistent is the emphasis in the LCSM on characterizing and understanding the source component, the LNAPL (see [ASTM 2014b](#)).

From the moment of release and as a site matures, ongoing NSZD processes can affect significant changes to the LNAPL body such as stability, mobility, and recoverability and associated dissolved- and vapor-phase plumes. Ongoing remediation can also contribute to continuing changes or be ineffective. A complete and up-to-date LCSM allows the best possible management decisions about application and operation of remedial technologies (see [ASTM 2014b](#)). Further, remedial action data provides important feedback on the LCSM; for example, effective attainment of objectives provides validation, while non-attainment of objectives is often rooted in an incomplete LCSM and misdirected use of a given technology. The LCSM may comprise some or all of the following scientific and technological information (hereinafter referred to as the “science”):

- site setting (historical and current)—includes land use (as it informs potential sources), groundwater classification, presence and proximity of receptors, etc.
- geological and hydrogeological information/setting

- LNAPL physical properties (density, viscosity, interfacial tension, vapor pressure) and chemical properties (constituent solubilities and mole fractions)
- LNAPL body spatial distribution (vertical and horizontal delineation)
- LNAPL mobility and body stability information
- LNAPL recoverability information
- associated dissolved-phase and vapor-phase plume information (as it informs LNAPL distribution and pathways to receptor)
- LNAPL natural depletion processes (including rate measurements or estimates, if available)

These elements were introduced in ITRC's initial LNAPL guidance (LNAPL-1 and -2 documents), and for this update they have been grouped by the decisions that they support and transformed into the key questions in [Section 4.2](#) and [Section 4.4](#) that will help the investigator characterize, monitor, and understand LNAPL sources at their site. In answering the questions, the investigator will seek out the appropriate lines of evidence that bring the LNAPL concerns into sharper focus. This section is focused on what information is needed at what point for a given site. [Section 3](#) provides insight to detailed LNAPL science. In addition, [Section 4.3](#) includes a table summarizing LCSM data collection parameters, applicable tools, and educational references for investigation that may be useful in answering the key questions.

LNAPL source zones require utilizing lines of evidence which encompass microbiology, hydrogeology, petroleum chemistry, geochemistry, vapor transport. The reader must recognize the multifaceted aspects and utilize additional references provided throughout this document for detailed understanding of the LNAPL science.

The evolution of the LCSM during the corrective action is driven by the answers to questions shown in Figure 4-1 and by the three stages identified below:

1. The **Initial LCSM** identifies concerns by defining the nature and extent of LNAPL and how it relates to receptors and pathways. (see [Section 4.2](#))
2. The **Remedy Selection LCSM** provides for **remedy evaluation** and selection of the most efficacious remedial technology or controls by characterizing aspects of the LNAPL and site subsurface relative to the potentially employed remedial mechanisms. (see [Section 4.4](#))
3. The **Design and Performance LCSM** provides **remedy implementation** support and guides termination, remedy transition, or optimization through monitoring remedy performance metrics relative to the remediation objective. (see [Section 6.4.1](#))

Over the life cycle of a typical LNAPL site investigation and remediation, the LCSM may include, but does not necessarily require, the three stages of evolution, each with a specific focus and a specific set of outcomes.

At the first stage, the focus of the Initial LCSM is the identification of one or more *LNAPL concerns*. An *LNAPL concern* is an LNAPL condition or potential condition that could:

- pose a risk to health or safety;
- result in additional LNAPL migration;
- address an LNAPL-specific regulatory requirement; or
- create some other physical or aesthetic impact or other specific regulatory or stakeholder requirement.

A well-developed Initial LCSM summarizes LNAPL and site conditions sufficiently to guide the identification and refinement of LNAPL concerns. Some LNAPL concerns may be readily identified in the early stages of site characterization, and others may be identified or further refined. It is recommended that the Initial LCSM includes sufficient information to *verify* LNAPL concerns using *threshold metrics* where available, and to establish *Remedial/Control Goals*. [Section 5](#) provides further information on verifying initial LNAPL concerns, and translating verified LNAPL concerns into an LNAPL remedial strategy. This process is illustrated in Figure 4-1 in the blue steps and the initial green step.

At the second stage, the focus of the LCSM shifts to selecting potential remedial options. The outcome of the Remedy Selection LCSM is the identification of one or more *LNAPL remedies or controls* that address the verified LNAPL concerns. The Remedy Selection LCSM should include sufficient information to *select* appropriate remedies or control measures that are capable of abating the verified LNAPL concerns. These steps are illustrated by the green steps in Figure 4-1. [Section 5](#) and [Section 6](#) provide further information on selecting an LNAPL remedy/control strategy.

As illustrated by the red steps in Figure 4-1, in the third stage, the focus of the LCSM shifts to designing and implementing the selected remedial measures or controls, establishing technology-specific *remediation objectives*, and assessing progress

and performance toward identified technology-specific *remediation endpoints*. The outcome of the Design and Performance LCSM is the implementation of one or more *LNAPL remedies or controls* that can achieve the established remediation objectives. The Design and Performance LCSM should include sufficient information to establish remediation objectives, design and implement remedies or control measures, and track progress toward defined remediation endpoints. [Section 5](#) and [Section 6](#) provide further information on establishing remediation objectives, implementing remedies, and identifying and tracking progress toward remediation endpoints.

The level of detail required in an LCSM for a specific site is a function of the complexity of environmental conditions, potential risk considerations, the regulatory framework, and overall LNAPL site management and remediation objectives ([ASTM 2014b](#)).

4.1 How Much Data is Enough?

ASTM International ([ASTM 2014b](#)) advocates development of an LCSM to evaluate LNAPL sites in a manner consistent with the Risk-Based Corrective Action (RBCA) process (see ASTM E1739-95 ([ASTM 2015](#))) for more information about the 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 tier levels). Generally speaking, the LCSM for a given site is deemed adequate (in terms of level of detail) when the existing understanding is sufficient for the stakeholders to agree on a path forward. Ultimately, however, the judgment of the environmental professionals (e.g., environmental consultants, implementing agencies, responsible parties) is used to assess whether sufficient information has been gathered to make appropriate management decisions.

Figure 4-2 illustrates how as the level of risk or complexity of a site increases, a higher tier of LCSM is useful to provide sufficient information for decision making (after ([ASTM 2014a](#))). This higher tier of information could be higher data density (spatial or temporal), or additional tools for a given line of evidence (e.g., geology or LNAPL composition). For example, in certain situations, where the size of the LNAPL body is relatively small and soil excavation is adequate to satisfy remediation objectives, the LCSM may be limited to spatial distribution, and further evaluation of LNAPL degradation or mobility are unnecessary. In other situations, where excavation is not feasible, the LCSM requires this additional detail.

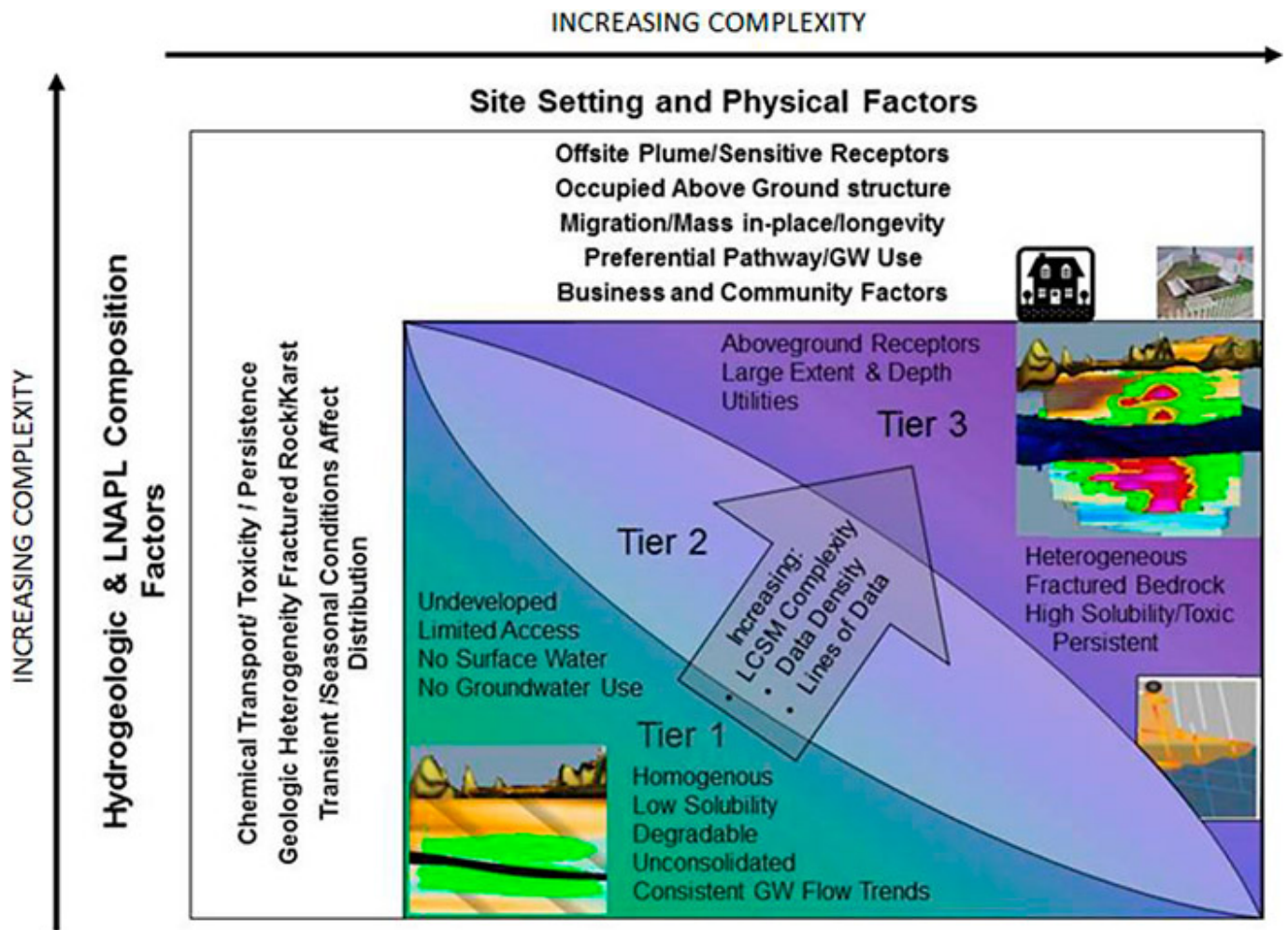


Figure 4-2. Factors governing 1) the potential to achieve a significant reduction in risk and 2) the cost of LNAPL depletion (arrows point in the direction of increase of the noted property). (adapted after (ASTM 2014a)).

It is important to note that a single factor may not increase the level of complexity by itself. Rather, if that factor results in challenges to remediation or confidence in the remedial decision, then the tier is increased. For example, a source zone in heterogeneous soil can either be a tier 3 or a tier 1. Where the source is shallow, the release history is known, and excavation can be performed, a tier 1 LCSM may be appropriate. In the event that excavation is not feasible or desirable due to cost, then additional information may be needed to characterize the distribution of impacts for alternate remedy evaluations. The additional data would identify cost and performance of alternate remedies for more informed decision making.

LNAPL sites are typically evaluated using various elements, including:

- historical data (e.g., LNAPL and dissolved phase footprint evolution, LNAPL occurrence versus potentiometric surface elevation, facility release record, and/or operational record);
- field data such as product recovery rates from interim measures, transmissivity values from baildown testing, and/or tracer dilution tests;
- site-specific laboratory data (e.g., TPH profiling and LNAPL saturations in soil cores);
- analytical and/or numerical modeling results;
- LNAPL risk assessment issues (including the consideration of both current and potential future site conditions);
- high resolution characterization data (e.g., DC resistivity, conductivity, LIF, and MIP); and
- combinations of the above.

The extent to which one particular line of evidence may be needed for the LCSM depends on other available lines of evidence. For example, at a site where there are little or no historical data or where the data sets are extremely sparse, there will be a stronger need for extensive sampling to obtain site-specific laboratory data, possibly supplemented with modeling that incorporates the new data to characterize LNAPL mobility and body stability issues. Conversely, at a site with

an abundance of historical data covering the range of water table fluctuations, there will likely be less need to engage in a comprehensive laboratory program or modeling to develop the LCSM. Utilizing this thinking with the tiered concept in Figure 4-2 will support the overall litmus test for an LCSM – is there agreement by all stakeholders that sufficient information is available to make decisions to advance the site forward?

4.2 Initial LCSM

The Initial LCSM is utilized to support identification of concerns, verifying those with the threshold metrics ([Section 5.1.1](#) and Table 5-1) and ultimately defining remedial goals ([Section 5.2](#)). Often data collected in the Initial LCSM will support additional portions of the LCSM and may be collected for efficiency of field mobilizations. However, it is not always plausible to understand the concerns, the remedial path forward, and the requirements for remedial design until an initial LCSM is created. A logical step is to collect sufficient information to understand the concerns and then verify them with threshold metrics. As discussed in [Section 5.1](#), the primary categories of concerns include Risk and Safety, Migration, LNAPL Occurrence, and Other Concerns.

The questions described in this section were designed to guide an investigator through the key components of developing the concerns portion of the Initial LCSM. This represents the first steps shown in Figure 4-1.

While there are many questions that can be answered for a site, not all are necessarily relevant or required depending on the level of detail required for the LCSM. The questions in this section are widely applicable to LNAPL sites as they generally have to be answered to develop the LCSM for understanding concerns, risks, and LNAPL source distribution—from the most general (green) to more LNAPL specific concepts (brown).



1. Is current and future land use known? [▼Read more](#)

The relevance of land use (both on-site and off-site) is of primary importance due to determination of exposure pathways (Question 8); the establishment of site cleanup goals; and any local, state, and federal requirements for institutional controls or other physical controls. Information regarding past and future land use and possible release(s) may dictate how aggressive a remedy needs to be to meet those cleanup goals, but may also limit the extent to which a remedy can be applied if the site is an active industrial facility or much of the site is covered by buildings or other structures that limit accessibility.

2. Does the potential for preferential pathways exist? [▼Read more](#)

What will this tell me about the LNAPL body? [Read More](#)

The potential for preferential pathways for flow and transport can be identified based on local and regional geology, geomorphology, and site setting. These preferential pathways can create conveyances for LNAPL to migrate at a rapid rate relative to the surrounding matrix, over longer distances, and in directions that might not otherwise be expected.

How is the answer informed by the below categories: [Read More](#)

• **Site setting, current and future land use, potential receptors**

Site setting can help identify the existence and location of anthropogenic preferential pathways. These features can provide conduits for exposure inconsistent with what is expected in a typical soil matrix and can convey LNAPL vapor ([ITRC 2011](#)), and/or dissolved impacts over longer distances.

• **Site geology and hydrogeology**

Understanding the distribution of preferential pathways in different geologic and hydrogeologic settings (e.g., heterogeneous unconsolidated soil, karst, and fractured rock) and the degree of anisotropy will better enable the investigator to understand the LNAPL migration potential relative to receptors. Preferential pathways should be evaluated and understood in both the vadose and saturated zones.

Varied stratigraphy can result in anisotropic LNAPL occurrences. Void spaces can also create collection points for LNAPL that can serve as persistent source areas for dissolution to groundwater and for LNAPL sources to the surrounding matrix. Characterization should account for soil variability influencing the anisotropy. This can be done with a simple increased boring and well density, but often improved approaches utilize the stratigraphy to strategically locate the same number of borings and wells and/or couple with tools such as geophysical or high resolution borings to provide an improved understanding with fewer wells for increased confidence in the LCSM. Preferential pathways for flow and transport may also exist in fractured rock, which is further discussed in the [Fractured Rock Appendix](#).

• **LNAPL body spatial distribution/extent**

Permeable soil layers may intersect a utility corridor or other preferential pathway, which results in anisotropic distribution and transport of LNAPL, vapor, and/or dissolved phase impacts. LNAPL can more easily flow through more permeable units as well as achieve a higher degree of impact within the matrix for a given release. Cross-sections and/or illustrations of the LNAPL body extent that include utilities and stratigraphic information are useful in illustrating the spatial relationship of the LNAPL impacts to site geology and anthropogenic subsurface features.

• **Dissolved and vapor phase plume characterization**

Dissolved and vapor impacts at greater distances or different locations than expected may be an indicator of an LNAPL intersecting a preferential pathway.

What information might already exist about a site that would help answer this question? [Read More](#)

Information included in the Phase I environmental site assessment (ESA), including local and regional geology, is often sufficient to provide a reasonable understanding of any anthropogenic preferential pathways. When combined with initial delineation activities (e.g., Phase II investigations or initial site characterization), Phase I ESA information can then be used to screen for the preferential pathways as a receptor or migration pathway.

What is the minimum information that might answer this question and what would that simple LCSM look like? [Read More](#)

Where no pathways exist, the pathways do not lead to receptors, or the LNAPL body does not intersect pathways, the information above is sufficient; where the potential exists, then additional investigation using a systematic elimination approach is often needed. This can include sampling alternate pathways to confirm they are not a complete pathway if a receptor is known to be impacted. Reporting includes a narrative, maps, cross-sections, site setting information, and soil borings.

What are more detailed data that might answer this question and what would that more complex LCSM look like? [Read More](#)

While the minimum consists of site setting review, LNAPL body, and dissolved and vapor phase extents, any remaining uncertainty related to risk and preferential pathways could be addressed with additional lines of evidence that provide confidence and utilize the existing sampling network (e.g., a period of resampling of wells and receptor points). Additional borings utilizing standard or high resolution tools, or a sampling frequency based on seasonal or other expected changes in transport potential, may be required.

What additional data is appropriate for the next steps in the evolution of the LCSM (i.e., remedy selection LCSM, remedy performance LCSM)? [Read More](#)

A higher density of data points that characterize the site's heterogeneity in addition to modeling, pilot studies, or bench scale studies may be required due to the added complexity of a site where preferential pathways dominate.

3. How does stratigraphy relate to affecting impacts and potential migration? [▼Read more](#)

What will this tell me about the LNAPL body? [Read More](#)

Soil type variations can influence the distribution of LNAPL as well as contaminant migration pathways. The depositional environment may result in natural anisotropy that can be inferred from existing geomorphology and regional geologic literature. Many physical soil properties can be estimated via visual logging, cone penetrometer, hydraulic profiling, and/or grain size analysis.

How is the answer informed by the below categories? [Read More](#)

• Site geology and hydrogeology

Site geology and hydrogeology provide a framework for understanding the preferred distribution of LNAPL upon being released to the subsurface. Typically, coarser materials are preferred over finer-grained. In addition, the confined/unconfined state of the impacted aquifer unit(s) stratigraphy should be understood. Areas of perched groundwater that are impacted with LNAPL can also serve as sources to underlying aquifer units.

• LNAPL body spatial distribution/extent

The extent of LNAPL compared to geology/hydrogeology and other site features will highlight the pathways of highest migration potential. Areas of higher permeability soils typically allow for a larger spatial extent of an LNAPL body than low permeability zones. In addition, the confined/unconfined state of the impacted aquifer unit(s) stratigraphy are important to understand as increases in gauged LNAPL thickness may be correlated to water table fluctuations rather than migration. Water table fluctuations can result in intermittent and non-uniform LNAPL occurrences for unconfined, perched, and confined conditions; in such instances, mobile LNAPL distribution will not be uniform and may be intermittent.

• LNAPL mobility

Evaluation of LNAPL mobility alone does not give a direct indication of LNAPL migration. Migration is the result of LNAPL being transmissive, exposed to a gradient such that the overall flux is greater than the total losses. The assessment of LNAPL mobility needs to be combined with other quantified factors.

Monitoring the magnitude of LNAPL mobility over time and accounting for seasonal water table fluctuations can be useful in monitoring plume stability. LNAPL mobility can be quantified using field transmissivity tests ([Transmissivity Appendix](#)). Quantification of mobility using gauged LNAPL thickness and soil capillary and permeability properties, combined with LNAPL physical fluid properties and LNAPL saturation soil samples, can support field transmissivity testing, but are difficult to utilize alone for quantifying LNAPL mobility.

Quantification of LNAPL mobility requires an understanding whether the LNAPL is confined, unconfined, or perched no matter the methodology.

What information might already exist about a site that would help answer this question? [Read More](#)

For a new release with no prior investigation, the only information that may be available is a regional geologic map, aerial photography, and possibly some state well reports for water wells located adjacent to the site. The EPA Hydrocarbon Spill Screening Model is also available to screen the vertical migration rates for a given spill ([EPA 1997](#)).

Existing boring logs, monitoring well logs, and fluid gauging measurements can be used to evaluate LNAPL body stability (see [Section 3.5.2](#)) for previously investigated sites. The boring logs should encompass the aerial and vertical extent of an LNAPL body and dissolved and vapor impacts.

What is the minimum information that might answer this question and what would that simple LCSM look like? [Read More](#)

Visual observations from soil borings delineating source areas and dissolved and/or vapor phase can be utilized to confirm and refine the depositional setting suggested from regional soil geology reports. This information would be sufficient to develop cross-sections and a general written description to support answering each of the other questions described in this document.

What are more detailed data that might answer this question and what would that more complex LCSM look like? [Read More](#)

As complexity increases or if the project requires a remedy, additional definition of the soil profile using high resolution tools or quantification of soil parameters such as hydraulic conductivity (see [Section 4.3](#) for additional parameters) would be expected.

What additional data is appropriate for the next steps in the evolution of the LCSM (i.e., remedy selection LCSM, remedy performance LCSM)? [Read More](#)

Collecting soil, groundwater, and vapor samples from fringes and within source plumes can support improved understanding of dissolved and vapor phase fate and transport and biodegradation processes. A variety of tools exist to develop proper characterization and are further described in [Section 4.3](#).

4. Is the source and extent of the LNAPL known? [▼Read more](#)

What will this tell me about the LNAPL body? [Read More](#)

Understanding the extent of LNAPL is required to understand the concerns posed by the LNAPL, including potential dissolved, vapor, and surface water concerns. The extent to which LNAPL delineation occurs (i.e., applicability of vertical, up-gradient, downgradient, and side-gradient directions) will be based upon the ultimate remedial endpoints and the scale and potential complexity of the site, subsurface, and LNAPL extent. The source can extend above and below the water table and occur as mobile or residual LNAPL. Residual LNAPL identification requires visual soil logging, shake tests, soil samples, LIF, or alternate forms of delineation.

How is the answer informed by the below categories? [Read More](#)

- **Site setting, current and future land use, potential receptors**

The locations of petroleum storage and processing can identify potential release source areas. Building foundations could be barriers to LNAPL migration, building drainage systems may provide preferential migration pathways, locations of operations or buildings can prevent or influence investigations in certain locations, and migration across property boundaries can either prevent investigations in certain locations or make access agreements necessary.

- **LNAPL release details (location, timing, volume)**

Potential release locations are useful starting points to understand where LNAPL could migrate and inform where to focus delineation activities. Where known, the volume and timing of a release can identify if the plume is expected to be stable or migrating. Experience by ITRC LNAPL Update team members indicates that the majority of plumes stabilize within six months to a few years post-release. Ultimately, the time for any release to stabilize is dependent on LNAPL type, loss rate, release rate, and subsurface characteristics.

- **Site geology and hydrogeology**

Site geology and hydrogeology provide clues on the lateral and vertical extent of the LNAPL body because they provide constraints on its migration. For example, fine-grained soil could constrain vertical extent causing perched or confined LNAPL conditions (reference basic concepts). Lateral extent is influenced by locations of more permeable soils and/or pathways.

The LNAPL extent should be considered in context with historical water table elevations, particularly where there have been extreme fluctuations in water level. Additionally, while LNAPL migration is influenced by the groundwater gradient, LNAPL heads during the early stages of release can be sufficient when combined with more permeable soils to allow up-gradient migration during the release.

- **Dissolved and vapor phase plume characterization**

Information on vapor phase characterization can be found in the ITRC PVI guidance document ([ITRC 2014](#)). Vapor phase concentrations represent indirect evidence of the presence of LNAPL. Decreasing dissolved phase concentrations or a consistent center of dissolved mass can indicate stability of an LNAPL source body. Increasing concentrations indicate the need to further evaluate stability of the LNAPL source body unless attributable to other factors such as seasonal changes in groundwater flow conditions.

What information might already exist about a site that would help answer this question? [Read More](#)

In addition to the LNAPL release details, there may be state records from drinking water well installation, previous environmental investigations, and previous geotechnical investigations at the site or neighboring sites that can be used to show presence or absence of LNAPL.

What is the minimum information that might answer this question and what would that simple LCSM look like? [Read More](#)

At a minimum, it is recommended that enough data be collected to understand the spatial extent and critical data gaps be filled. Field screening observations from a tank removal or soil borings are examples of information that could support a simple LCSM. It is suggested that a narrative with plan view and cross-sectional maps that depict the lateral and vertical extent of the LNAPL be developed.

What are more detailed data that might answer this question and what would that more complex LCSM look like? [Read More](#)

A more complex LCSM could include three-dimensional representation of the LNAPL body relative to heterogeneous subsurface, key site aspects such as utility corridors, surface water features, and other receptors. A variety of delineation tools and techniques are presented in the LCSM table in [Section 4.3](#).

Because several of these tools are indirect indicators, practical experience in their application may be helpful to properly apply and interpret them.

Are the detailed data more appropriate for the next steps in the evolution of the LCSM (i.e., remedy selection LCSM, remedy performance LCSM)?

[Read More](#)

Further delineation may include LNAPL body stability evaluations, identification of residual LNAPL areas, and internal delineation of LNAPL components, or potential exposure pathways.

5. Are dissolved or vapor issues expected based on LNAPL composition? [Read more](#)

What will this tell me about the LNAPL body? [Read More](#)

Understanding the LNAPL composition and chemical properties, and its effect on dissolved and vapor phase plume concentrations provides data to help interpret and support the assessment of the LNAPL body extent and related risks. When an LNAPL release potentially poses an unacceptable human health or ecological risk, it is often a result of specific components in the LNAPL rather than the magnitude of TPH in soil, the LNAPL saturation, or mobility of the LNAPL (see [\(ITRC 2018\)](#)). Understanding if the LNAPL composition has the potential to or is likely to cause dissolved or vapor issues, helps the practitioner plan site investigation work, collect data to document the dissolved and vapor phase concentrations, and/or collect data to assess remedial technologies that result in composition changes.

How is the answer informed by the below categories? [Read More](#)

• **Site setting, current and future land use, potential receptors**

Information on the current and future land use and receptors allows assessment of whether the dissolved and vapor plumes present potential current or future risks, which may influence the need for and prioritization of remedial actions.

• **LNAPL type, composition, physical properties**

Knowledge of the fuel type and composition can be used to estimate the constituents of concern and resulting vapor and dissolved phase concentrations in equilibrium with the LNAPL.

What information might already exist about a site that would help answer this question? [Read More](#)

Knowledge of the release details such as the LNAPL type (e.g., gasoline, diesel, heating oil, JP4, crude oil), age (recent release vs. decades-old release), release location, volume, and depth to groundwater can provide general information on the likelihood of dissolved phase and vapor phase issues.

What is the minimum information that might answer this question and what would that simple LCSM look like? [Read More](#)

The type and composition of the LNAPL is needed to understand the risk of dissolved and vapor phases that can be expected at a release site. Dissolved phase plumes emanating from LNAPL may be expected:

- in and downgradient from smear zone and saturated zone LNAPL bodies of lighter and more soluble hydrocarbons;
- below vadose zone LNAPL bodies of lighter and more soluble hydrocarbons; and
- in and immediately downgradient from smear zone and saturated zone LNAPL bodies of less soluble hydrocarbon mixtures.

Vapor phase plumes emanating from LNAPL that have the potential to cause issues if receptors are present may be expected:

- to overlie the LNAPL body where the LNAPL body is within approximately 15 feet of an occupied structure. If the LNAPL body is more than approximately 15 feet below grade then the vapors are likely mitigated ([ITRC 2014](#)).
- to overlie dissolved phase hydrocarbon plumes where the water table is within approximately 5 feet of the bottom of building. If the dissolved phase plume is more than approximately 5 feet below grade, then the vapors are likely attenuated.
- where basements or elevator shafts exist below grade; these features should be considered when comparing to the screening distances provided above.

What are more detailed data that might answer this question and what would that more complex LCSM look like? [Read More](#)

Detailed estimates of the dissolved phase and vapor phase concentrations can be made based on laboratory analysis of LNAPL samples or soil samples containing residual or mobile LNAPL. The laboratory analysis may characterize the VOC, PAH and bulk hydrocarbon concentrations in aromatic and aliphatic equivalent carbon groups (as recommended by [\(TPHCWG 1997\)](#) and [\(ITRC 2018\)](#)). The calculation of equilibrium LNAPL-water and equilibrium LNAPL-vapor concentrations is based on four-phase partitioning using Raoult's Law.

The results of the vapor phase concentration estimates can be used as input to vapor intrusion models such as BioVapor ([API 2010](#)). The results of the LNAPL-water dissolved phase calculations can be used:

- to help interpret groundwater sample data (e.g., assess whether groundwater samples contain LNAPL or polar biodegradation metabolites);
- along with dilution-attenuation factors to calculate groundwater concentrations at specific points of interest; and
- as input for dissolved phase transport models to assess the potential extent of and risk associated with the dissolved phase plumes.

The results of the dissolved and vapor phase concentration calculations can also be used to assess the degree of compositional change required for remedial options relying on compositional changes. In practice, it is likely that the dissolved phase plume delineation would be based on or supported by groundwater sampling.

What additional data are appropriate for the next steps in the evolution of the LCSM (i.e., remedy selection LCSM, remedy performance LCSM)? [Read More](#)

Tracking of LNAPL composition over time may assist remedy performance evaluation during the implementation phase.

6. Are dissolved or vapor plumes characterized? [Read more](#)

What will this tell me about the LNAPL body? [Read More](#)

The extent and nature of dissolved and vapor plumes may be required to assess the concerns related to the site, and can help inform the practitioner on the presence and location of LNAPL.

How is the answer informed by the below categories? [Read More](#)

- **Site setting, current and future land use, potential receptors**

Both current and future land use need to be considered in assessing the appropriate extent of dissolved or vapor plume characterization to identify current and future potential receptors.

- **Site geology and hydrogeology**

Geology and hydrogeology are critical considerations in exposure pathway assessment, particularly with respect to transport mechanisms from a contamination source to a receptor exposure point. Additional discussion is provided under the site geology/hydrogeology and preferential pathways discussion.

- **LNAPL mobility**

If LNAPL is migrating, then the delineation of ultimate dissolved and vapor phase plume extents will not be complete until LNAPL migration ceases or its ultimate extent can be confidently projected.

- **Natural degradation processes**

Natural degradation processes are important to understanding the transport of petroleum contaminants from the source to an exposure point for LNAPL, dissolved phase, and petroleum vapor impacts. Natural degradation is further discussed in the [NSZD Appendix](#).

What information might already exist about a site that would help answer this question? [Read More](#)

An existing monitoring well network and historical dissolved phase data can provide insights to dissolved delineation as well as LNAPL body delineation. Concentrations that approach the effective solubility or vapor pressure for a given constituent can be a screening level indicator of LNAPL being present near the sample location.

What is the minimum information that might answer this question and what would that simple LCSM look like? [Read More](#)

Delineation of affected groundwater to the specified or agreed-upon screening criteria is necessary to develop an LCSM. Screening assessment of potential vapor plumes can be based on depth to LNAPL and LNAPL composition, and depth to water and constituents of concern (COC) concentrations in groundwater.

What are more detailed data that might answer this question and what would that more complex LCSM look like? [Read More](#)

If distance-based screening of LNAPL and/or groundwater data indicates a potential vapor intrusion concern, the LCSM may require soil gas, sub-slab gas, or indoor air data to fully evaluate vapor intrusion potential. As site geology complexity increases, additional delineation points may be required (e.g., membrane interface probes, wells, etc.). Multiple sources could create the need for specialized sampling techniques such as forensic compositional analyses or compound specific isotope analyses.

What additional data is more appropriate for the next steps in the evolution of the LCSM (i.e., remedy selection LCSM, remedy performance LCSM)? [Read More](#)

Dissolved gases and higher vertical resolution COC sampling may be utilized for enhanced understanding of biodegradation mechanisms and remedy performance.

7. Do soil or groundwater concentrations exceed criteria? [▼Read more](#)

What will this tell me about the LNAPL body? [Read More](#)

The presence of COCs in soil, groundwater, or soil vapor at concentrations exceeding applicable criteria at compliance points identifies the need for remediation or alternate protection of receptors, in addition to remediation or control of the LNAPL source.

How is the answer informed by the below categories? [Read More](#)

- **Site setting, current and future land use, potential receptors**

Soil concerns apply primarily to the original LNAPL release point or when the LNAPL smear zone is shallow enough for potential receptor contact (e.g., future construction workers). Soil vapor should be assessed in consideration of existing or future planned buildings. Groundwater can be assessed in consideration of groundwater usage and ecological concerns.

- **LNAPL release details (location, timing, volume)**

Understanding the location, timing, and volume of an LNAPL release will help the investigator understand the potential for soil and dissolved phase impacts. If the release duration was short and/or volume was small, the extent of lateral and vertical delineation of soil or groundwater impact may be reduced. However, as the duration and size of the release grows, the extent of impact may increase. If the release is older than one year, then NSZD processes require consideration to assess plume stability ([NSZD Appendix](#)). Areas of perched LNAPL or groundwater may serve as sources to underlying aquifer units.

- **Natural degradation processes**

Understanding the occurrence and impact of natural degradation processes under site-specific circumstances is useful for assessing long-term plume behavior and risk. At any given location, natural degradation processes can result in significant reductions in dissolved or vapor phase COC concentrations over periods of time that are relevant to risk-based site management. While natural processes may effectively restore aquifer conditions, if receptors are currently exposed to unacceptable risks, it is not advised to solely rely on natural degradation processes for protection.

What information might already exist about a site that would help answer this question? [Read More](#)

Existing dissolved phase data provide direct evidence of groundwater concentrations. Depths to soil or groundwater impacts can be compared to screening distances for PVI. LNAPL compositional data can help estimate the likelihood of environmental media having COC concentrations above applicable criteria. For more information on this aspect, refer to Question 5: Are dissolved or vapor issues expected based on LNAPL composition?

What is the minimum information that might answer this question and what would that simple LCSM look like? [Read More](#)

Soil and groundwater concentrations require comparison to applicable screening criteria. The groundwater and LNAPL source depths relative to existing buildings are needed to screen PVI concerns. Note that some regulatory agencies may also require vapor assessment data.

What are more detailed data that might answer this question and what would that more complex LCSM look like? [Read More](#)

Exceeding applicable criteria may trigger the need for more refined delineation of the extent of impact. Quantification of remedy performance is beneficial when a remedy is implemented to address exceeded values at compliance points. The LCSM can be further developed to provide quantitative and qualitative indicators of the potential performance of various remedial mechanisms to support remedial selection. [Section 6](#) and the [LNAPL Technologies Appendix](#) can provide more information on data needs for a more complex LCSM as a site moves toward a remedy.

What additional data are appropriate for the next steps in the evolution of the LCSM (i.e., remedy selection LCSM, remedy performance LCSM)? [Read More](#)

Tracking changes in soil or groundwater concentrations over time can be useful for assessing remedy performance.

8. Are exposure pathways complete or incomplete? [Read more](#)

What will this tell me about the LNAPL body? [Read More](#)

Assessing the completeness of an exposure pathway will help the investigator prioritize actions related to LNAPL characterization and corrective action.

How is the answer informed by the below categories? [Read More](#)

• **Site setting, current and future land use, potential receptors**

Receptors may be broadly defined as persons, structures, utilities, surface waters, water supply wells, and sensitive environments that are adversely affected by a release under current conditions, or that could be adversely affected under future conditions ([ASTM 2015](#)). It is recommended that long-term land use within the area of actual or potential impact be considered in assessing exposure pathways under future conditions.

• **LNAPL release details (location, timing, volume)**

Details about the timing and extent of the LNAPL release can be useful for understanding the LNAPL body stability. [Read More](#)

• **Site geology and hydrogeology**

An understanding of the maximum extent of dissolved and vapor phase plumes is important for analyzing the exposure pathway. If LNAPL is present at mobile saturations, the potential exists for further LNAPL migration. If NSZD rates are not greater than the LNAPL mass flux from the source, then migration may occur.

• **Natural degradation processes**

Natural degradation processes are often central to understanding whether contaminants can migrate from the source to an exposure point. For example, sufficient dissolved phase plume characterization will often demonstrate the plumes are at a steady-state or declining status by virtue of natural attenuation processes, and therefore will not migrate to distal exposure points. Analysis of soil gas samples and/or comparison with screening distances can demonstrate whether bioattenuation will prevent sources of soil vapor from impacting overlying structures.

What information might already exist about a site that would help answer this question? [Read More](#)

Some LNAPL release sites come into the corrective action process because of concerns such as impacts to private water wells or sheen discharge to surface water. In these cases, it is important to focus the initial site assessment on the confirmation or refutation of complete exposure pathways because of specific LNAPL sources.

What is the minimum information that might answer this question and what would that simple LCSM look like? [Read More](#)

For an exposure pathway to be complete, the following five exposure elements must be in place: 1) contaminant source or release, 2) migration through an environmental medium, 3) contaminant presence at an exposure point, 4) route of receptor exposure, and 5) potentially exposed receptor population ([ATSDR 2005](#)). These are the minimum aspects of the LCSM that must be understood to identify concerns and develop corrective action objectives.

What are more detailed data that might answer this question and what would that more complex LCSM look like? [Read More](#)

The existence of a complete exposure pathway does not necessarily equate to an unacceptable risk that requires corrective action. In these cases, additional data may be required to understand the significance of the exposure and the resulting health risks.

What additional data is appropriate for the next steps in the evolution of the LCSM (i.e., remedy selection LCSM, remedy performance LCSM)?

[Read More](#)

If receptor assumptions should change during the course of the remedy or after remedy completion, the LCSM and remedy protectiveness may need reevaluation.

9. Is the LNAPL body stable? [▼Read more](#)

What will this tell me about the LNAPL body? [Read More](#)

An evaluation of LNAPL stability can provide key information for understanding potential risks and assessing LNAPL management alternatives. Demonstrating that an LNAPL body is stable and no longer expanding ensures that new risks will not occur in the future as the result of LNAPL migration into new areas. Determining whether there is potential for future expansion of the LNAPL body may be critical when assessing the need for a mass control remedy, or evaluating the potential effects of turning off an existing recovery or mass control system.

LNAPL stability is typically evaluated using multiple, complimentary lines of evidence, where agreement between multiple methods builds confidence in the conclusion. Examples of LNAPL stability lines of evidence highlighting key data requirements, relative weighting, and a brief summary of cautions for each line of evidence are presented in Table 4-1.

How is the answer informed by the below categories? [Read More](#)

• **Site setting, current and future land use, potential receptors**

Facility operational history can give an indication of stability. Sites that have been inactive for several years with complete petroleum storage removal are less likely to exhibit migration because any release would be historical in nature. Assessing LNAPL stability provides a basis for evaluating potential exposure pathways under current and future land use conditions. If LNAPL and associated vapor and/or dissolved phase plumes are stable and do not present unacceptable risks under current conditions, then unacceptable risks in the future are unlikely under current hydrogeologic conditions.

• **LNAPL release details (location, timing, volume)**

Knowledge of LNAPL release location, type, volume, age, and duration often provides useful information to support interpretation of LNAPL distribution and stability. The release point location relative to the position of the leading edge or the LNAPL body's center of mass, along with the release duration, can be utilized to place reasonable bounds on LNAPL migration history. Additionally, the time elapsed since the release provides a useful, qualitative line of evidence when assessing LNAPL stability, as LNAPL bodies originating from older releases are more likely to be stable than more recent releases because of dissipation of LNAPL head over time, smearing of LNAPL to residual levels, and mass depletion through remediation and/or NSZD processes.

• **Site geology and hydrogeology**

Site geology and hydrogeology influence how LNAPL and other fluids behave upon being released to the subsurface.

• **LNAPL body spatial distribution/extent**

Mapping of the current and historical distribution of LNAPL, permeable zones, and stratigraphy can provide direct evidence of recent and/or historical LNAPL body expansion. The distribution of LNAPL can be evaluated using multiple data types, including visual observations from current and historical soil borings, fluid level gauging data, laser-induced fluorescence results, and laboratory analytical soil data.

• **Dissolved phase plume characterization**

Temporal trends in dissolved phase concentrations of LNAPL constituents can be evaluated to infer LNAPL body extent over time when compared to effective solubility values. Additionally, dissolved phase trends can be evaluated statistically to infer LNAPL body stability. A stable or contracting dissolved phase plume suggests a stable or contracting LNAPL body. Table 4-1 provides additional detail on the use of dissolved phase plume stability data as a line of evidence for inferring LNAPL body stability.

• **LNAPL type, composition, physical properties**

LNAPL composition and weathering patterns over time can be used to verify release sources. LNAPL density and viscosity are fundamental to calculations involving LNAPL conductivity/velocity potential, while knowledge of fluid interfacial tensions provide data that can be used to evaluate LNAPL pore entry pressures.

• **LNAPL mobility**

The lack of mobile LNAPL (i.e., accumulations in wells) or LNAPL at low transmissivity values are indications that the majority of the LNAPL is at or close to residual saturation. This is a qualitative measure of plume stability. LNAPL transmissivity is best applied towards plume stability when combined with NSZD loss rates and gradient (see below).

• **Natural degradation processes**

LNAPL losses through NSZD processes act to limit LNAPL flux from the interior of an LNAPL body. At some threshold, NSZD rates will match or exceed rates of lateral expansion and the LNAPL body will stabilize and/or contract. Quantification of LNAPL loss rates through NSZD processes can be evaluated in conjunction with LNAPL flux toward the leading edge of the LNAPL body using a mass balance approach to evaluate LNAPL stability ([Mahler, Sale, and Lyverse 2012](#)). Table 4-1 provides additional detail on the use of NSZD results as a line of evidence for inferring LNAPL stability.

What information might already exist about a site that would help answer this question? [Read More](#)

Data collected during routine monitoring activities near the leading edge of an LNAPL body, (e.g., well gauging and dissolved phase concentration data) are often available at existing sites. These data, assuming adequate spatial coverage and sufficient temporal data density, provide direct field observations of LNAPL migration/stability. Table 4-1 provides examples of the use of temporal trends in well gauging and dissolved phase concentration data as lines of evidence for assessing LNAPL stability. Additionally, a boring log from an existing monitoring wells (MW) that indicates past LNAPL presence (e.g., soil staining), but currently contains no in-well LNAPL is useful evidence of NSZD.

What is the minimum information that might answer this question and what would that simple LCSM look like? [Read More](#)

Table 4-1 presents common lines of evidence used to assess LNAPL stability. Typically three or more of these lines provide sufficient evidence to demonstrate stability (or instability). A minimal LCSM may only include well gauging data, dissolved phase plume data, and age of release.

What are more detailed data that might answer this question and what would that more complex LCSM look like? [Read More](#)

A more detailed LCSM may include several of the lines of evidence presented in Table 4-1. Depending on the proximity of potential receptors and the significance or consequences of LNAPL migration, a more detailed assessment may include data collection at higher spatial and or temporal resolution to demonstrate stability at a scale that is commensurate with the level of detail required to support informed LNAPL management decisions.

Table 4-1. LNAPL migration lines of evidence.

[View Table 4-1 in Adobe PDF format.](#)

10. Is the mobile LNAPL hydrogeologic condition known? [▼Read more](#)

What will this tell me about the LNAPL body? [Read More](#)

Understanding hydrogeologic conditions that influence LNAPL mobility are important to developing a comprehensive LCSM. This includes determining whether the LNAPL is present under confined, unconfined, or perched condition as it affects the interpretation of site data (e.g., what does the in-well LNAPL thickness represent?), mobility/recoverability, and site management/remedial strategy.

How is the answer informed by the below categories? [Read More](#)

• Site setting, current and future land use, potential receptors

Certain site conditions may have impact on flow conditions and changes to these conditions may alter LNAPL mobility. These conditions include the presence of a surface impoundment or pond, climatic influences, or even the presence of treatment systems that can alter groundwater flow patterns.

• Site geology and hydrogeology

Question 3 discusses the importance of site geology and hydrogeology to LNAPL mobility.

What information might already exist about a site that would help answer this question? [Read More](#)

Soil boring data will provide initial information on the site lithology. If the site investigation is older, there may also be years of fluid level gauging data. In addition, release data, if available, can provide the LNAPL properties important to assessing the mobility.

What is the minimum information that might answer this question and what would that simple LCSM look like? [Read More](#)

Understanding hydrogeologic conditions that influence LNAPL mobility are important to developing an LCSM. At a minimum, this would include fluid levels over multiple years and/or seasons, lithology, and aquifer type (perched, confined, unconfined). Some basic estimated LNAPL properties may be known, either through direct measurement (e.g., viscosity and specific gravity), or based on composition of the release.

What are more detailed data that might answer this question and what would that more complex LCSM look like? [Read More](#)

More detailed data on the physical properties of the matrix such as hydraulic conductivity, grain size, residual water saturation, and capillary properties (i.e., van Genuchten, or Brooks-Corey models) representative of variations at the site may help refine understanding of the LNAPL saturation, transmissivity, velocity, and associated plume migration/dissolution. It may also be important to characterize LNAPL properties such as specific gravity, viscosity, and interfacial tension. Sufficient core and LNAPL samples may be collected and analyzed to characterize these physical properties. LNAPL baildown tests can also be a useful tool in determining matrix and LNAPL properties as well as LNAPL transmissivity ([Transmissivity Appendix](#)).

What additional data are more appropriate for the next steps in the evolution of the LCSM (i.e., remedy selection LCSM, remedy performance LCSM)? [Read More](#)

Over the course of remedy implementation, changes in groundwater elevations may impact plume migration by exposing mobile LNAPL to different stratigraphic units, and can impact groundwater flow and LNAPL flow patterns and directions. Seasonal impacts of rainfall and evaporation can induce these changes. Variations in groundwater elevations can change the extents of exposed and submerged LNAPL along the capillary fringe and impact NSZD processes. Variations in groundwater elevations may also impact groundwater velocities and LNAPL migration rates. Therefore, it is important to continue to collect and review seasonal/historical groundwater data and associated flow patterns. Time series plan view maps should be constructed to assist with this understanding.

It is also important to understand the presence of any groundwater sources and sinks. Areas of discharge to surface water bodies should be identified along with groundwater withdrawn from pumping for domestic and agricultural purposes. These features may influence LNAPL migration patterns and present receptor exposure pathways. If an area impacted by LNAPL fluctuates between unconfined, semi-confined, and/or confined, it may present unique challenges for LNAPL remediation. It is recommended that these situations be identified in the LCSM.

4.3 LNAPL Tools

Table 4.2 provides additional tools available to characterize a given component of the LCSM. Within the table, each tool typically includes a reference for the method and a brief description. The notes provide insights regarding recently improved best practices for tool selection at sites. It is the intent of this guide to identify available tools and provide an improved understanding of their use where existing standards or literature is not available or an update is needed.

Table 4-2. LNAPL tools for characterizing LCSM components.

[View Table 4-2 in Adobe PDF format.](#)

4.4 Remedy Selection LCSM

The Remedy Selection LCSM is utilized to support selection of a remedial technology(ies) and/or controls by characterizing aspects of the LNAPL and site subsurface relative to the potentially employed remedial mechanisms. Update the Initial LCSM (e.g., by pilot testing or detailed/spot assessment) to confirm the site is adequately characterized to screen technologies to address concerns.

The questions described in this section were designed to guide an investigator through the key components of developing the technology evaluation portion of the LCSM. This represents the middle steps shown in Figure 4-1 which seek to review the Initial LCSM and remediation objectives and select the most appropriate means for LNAPL remediation or control. While there are many questions that can be answered for a site, not all are necessarily relevant or required depending on the level

of detail required for the LCSM. The questions in this section are widely applicable to LNAPL sites as they generally have to be answered to develop the LCSM for understanding concerns, risks, and LNAPL source distribution—from the most general (green) to more LNAPL specific concepts (brown). Note that the discussion of the questions below are applicable to unconsolidated, bedrock and karst; however, further detail on LNAPL occurrence in fractured rock is provided in the [Fractured Rock Appendix](#).

1. Where is the source mass? [▼Read more](#)

The goal of this question is to understand how the water table, subsurface geology, preferential pathways, and the LNAPL distribution (mobile vs. residual) will affect the application of a technology.

A. Homogeneous Permeable Soil [▼Read more](#)

Multiple technologies are effective in homogeneous higher permeability soils. The primary improved LCSM would rely on further understanding the residual versus mobile fractions and distribution relative to the water table to ensure optimal remedial technology selection. The use of high resolution approaches—core photography, cone penetrometer tool, hydraulic profiling tool, or detailed visual soil boring logs—have revised several conceptual models where prior soil boring data did not give sufficient credit to variability that was significant for LNAPL source zone behavior. Thin seams of fine-grained layers that separate sand layers that can also behave as competent confining layers may be missed in less detailed visual soil boring logs and electrical conductivity logs.

B. Interbedded Soil [▼Read more](#)

In the event of concerns that require remediation and careful evaluation of the source distribution relative to the finer grained layers and more permeable layers, it is important to recognize that most technologies will be focused on the more permeable zones and have less influence on the finer grained layers. Note that sand layers and gravel layers can exhibit permeability values varying over three orders of magnitude. Understanding the distribution of more permeable layers relative to LNAPL impacts and connectivity will ensure that the remedial design will target the correct intervals. High-resolution approaches for both the LNAPL and soil profile are critical to identifying heterogeneity in the source area.

C. Within low permeability media, secondary porosity, fractures [▼Read more](#)

The lower the permeability, the more difficult it is to reduce the LNAPL source mass. LNAPL in fine-grained media often occurs in macro pores or secondary porosity when considering unconsolidated sites. The small pore spaces of the primary pore matrix, combined with sufficient moisture content, result in a large barrier to LNAPL migration; however, secondary porosity features can transport LNAPL vertically or horizontally more easily. The presence of confined or perched conditions should also be considered. High-resolution approaches may be worthwhile, but in many cases cannot substitute for detailed visual logging and core photography because secondary porosity in unconsolidated materials is not necessarily detectable by a cone penetrometer tool, a hydraulic profiling tool, or electrical conductivity.

D. Is the LNAPL source distributed above or below the water table? [▼Read more](#)

Characterizing the distribution of LNAPL sources relative to the water table ensures that the source of vapor and/or dissolved phase risks is properly identified.

Combining the hydraulic profiling tool or cone penetrometer tool with LIF can give a good overall picture of LNAPL distribution or a detailed look at a single boring with respect to the water table (see Figures 4-3 and 4-6). This is particularly important in confined LNAPL situations, where a remedy (e.g., SVE) may erroneously be applied opposite the confining layer (correlated to the top of the gauged thickness interval) instead of targeting the lower sand that is the actual source of LNAPL.

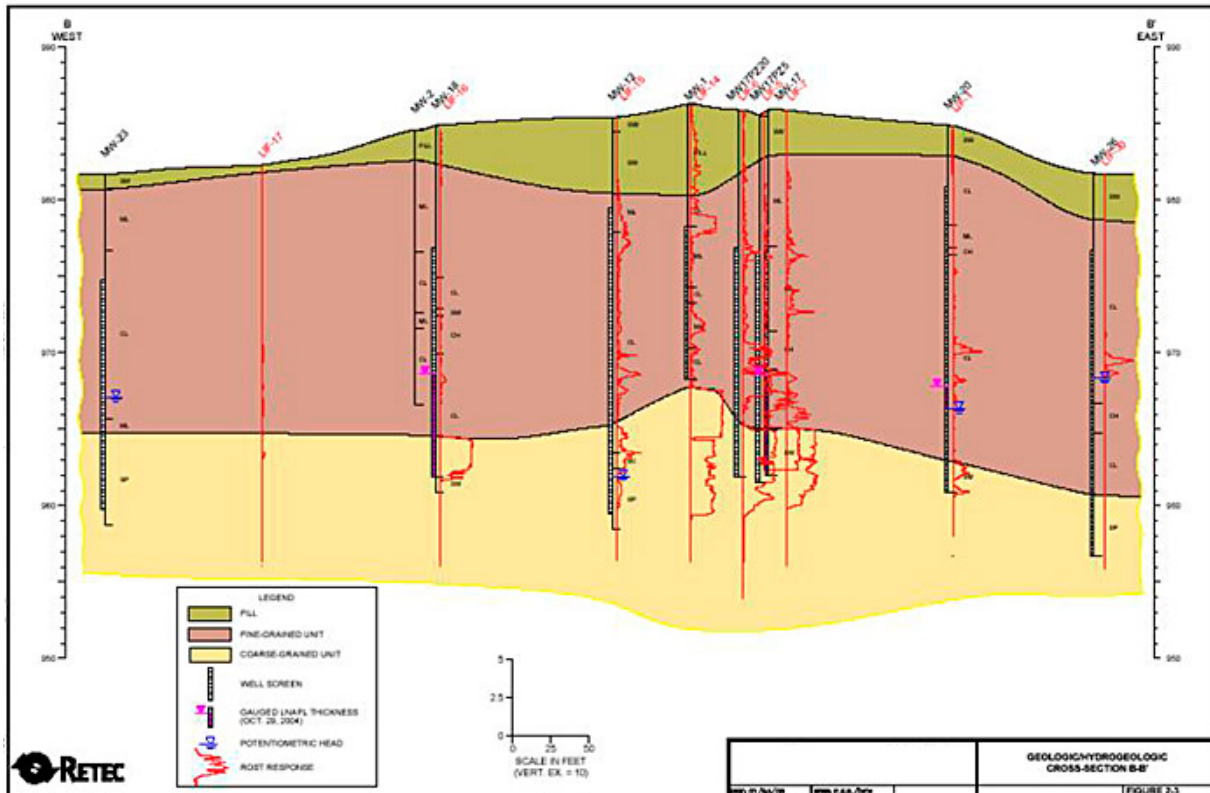


Figure 4-3. Cross-section using soil profiles with LIF.

The cross-section in Figure 4-3 illustrates that the gauged LNAPL thickness in MW-2 rises into the overlying clay is misleading due to confined conditions. The LIF more accurately identifies that the majority of impacts are in the sandy confined aquifer. Similarly, the LNAPL near well MW-1 in the center, while near a topographic high in the sand, is likely confined although shallow impacts within the finer grained layers will likely remain post-treatment of the sand. The data shown in Figure 4-3 identifies the distribution of LNAPL more accurately and demonstrates why gauged LNAPL thicknesses are misleading where confining conditions are present. Any required remediation at this site would need to consider multiple soil types and saturated zone treatment. This site was granted closure with no further action based on exhibited low LNAPL transmissivity values, gauged LNAPL thicknesses that were indicative of confining conditions, non-recoverability of LNAPL, and a stable dissolved phase plume with no receptors.

Evaluating LNAPL distribution goes beyond determining a bulk TPH concentration or LNAPL measurements since a historical release may have exhibited different natural weathering/biodegradation rates above and below the water table. More complex sites may benefit from more detailed soil analysis to identify specific zones that are higher in COC concern, such as BTEX.

Gauged LNAPL thickness in monitoring wells has often been a prioritized piece of data for LNAPL sources zone identification and remedial decision making. Gauged LNAPL thickness is easy to conceptualize and can be frequently monitored. As a result, technologies have often been focused on the mobile LNAPL via hydraulic recovery. Mobile LNAPL can generally be well characterized as utilizing gauging data representative of equilibrium conditions combined with subsurface geologic characterization. A comprehensive approach to identifying residual and mobile source areas allows a practitioner to better target remediation to achieve remedial goals and provide context on the effectiveness of LNAPL recovery. Characterization techniques for both the mobile and residual source zone have improved. Mobile LNAPL is now understood to exist in unconfined, confined, and perched states, as well as in secondary porosity. Residual smear zones are difficult or costly to routinely monitor over time although there are screening approaches (See Table 3-2, e.g., PID, visual observations, temporal evaluation, or vapor and/or dissolved phase indicators) as well as more definitive approaches (e.g., LIF, shake tests, TPH analysis) for soil borings that can be used for characterization and delineation.



2. What is the nature of the source? [▼Read more](#)

This question considers the chemical nature of the source LNAPL relative to the available remedial mechanism. The prior question primarily addressed the physical nature of the LNAPL and source removal via extraction. An alternate aspect of LNAPL remedial technologies relates to the chemical nature of the LNAPL and its mobility where the highest potential removal rates may be through a hydraulic gradient, a vapor removal mechanism, solubilization, or biodegradation, and taking into account the limits of these mechanisms. These questions may be too detailed if excavation is the presumptive remedy and alternate details may be required if surfactant flushing or steam is the recommended approach.

A. Volatile and/or Soluble [Read more](#)

Is the LNAPL source volatile and/or soluble?

Where a remedial technology encourages in situ destruction or removal of a hydrocarbon constituent via induced partitioning, the chemical nature of the LNAPL affects remedial performance. As discussed in [Section 3.2](#), the concentration of a constituent in LNAPL is directly related to its vapor or dissolved concentration as described by Raoult's Law. Therefore, if soil vapor extraction is being used, its efficacy can be forecasted using the LNAPL composition. Figure 4-4 provides an example composition of regular grade gasoline as it evaporates. The data illustrate that after 95% of the mass has evaporated, primarily 1,2,4 trimethylbenzene through naphthalene remain. The textbook vapor pressure of 1,2,4 trimethylbenzene and naphthalene at 37 degrees Celsius is near or less than 0.12 pounds per square inch (psi). In contrast, the vapor pressure of gasoline is typically 7.8 to 13.5 psi at similar temperature and pressure. Thus, the efficacy of volatilization to remove 1,2,4 trimethylbenzene and naphthalene is reduced by two orders of magnitude. Naphthalene and trimethylbenzene compounds are biodegradable, which may make it worthwhile to also evaluate the biodegradation potential in order to estimate a technology like biosparging or bioventing to achieve further degradation of the gasoline.

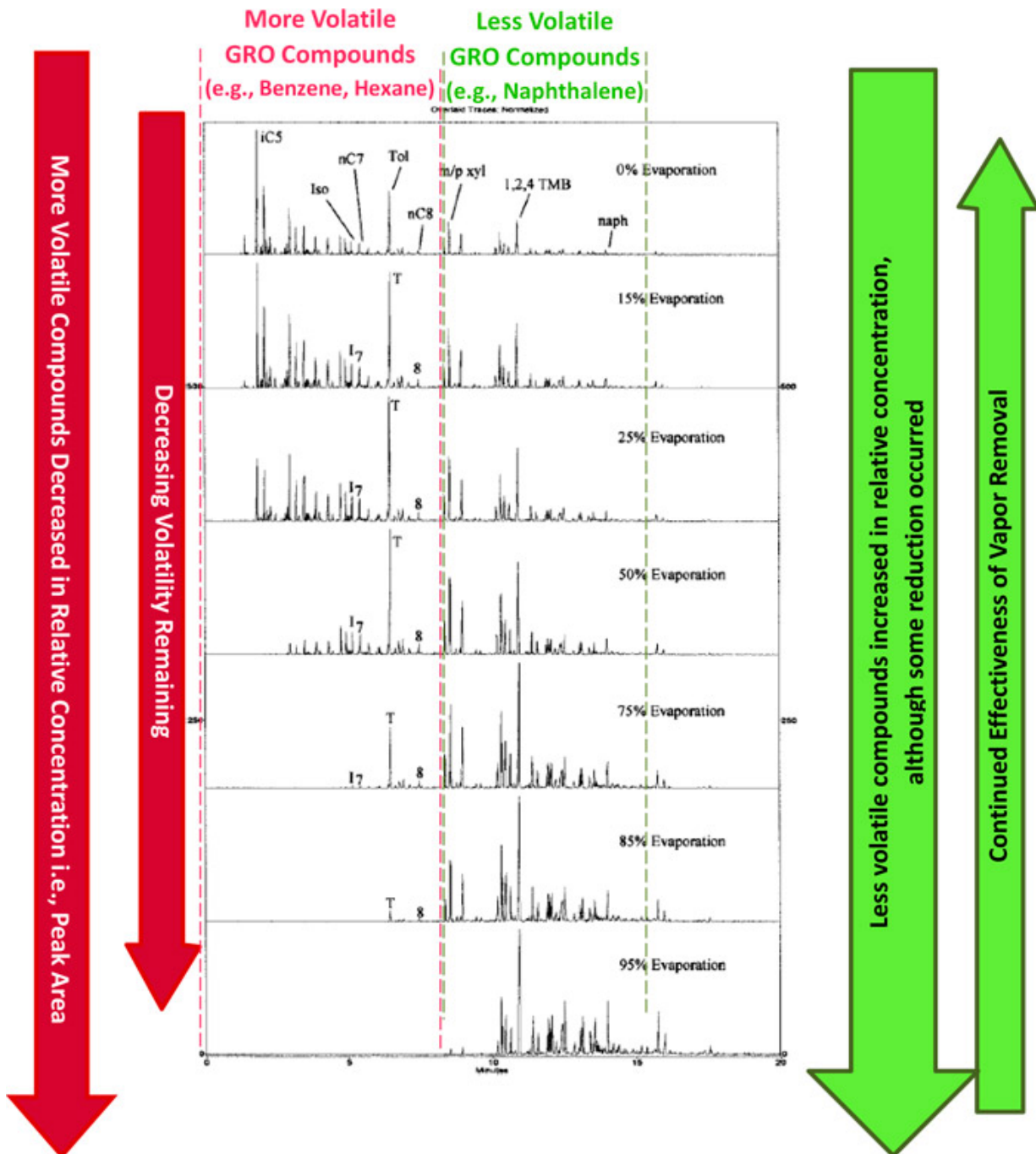


Figure 4-4. Gas chromatogram data chart (left) and simplified LNAPL composition bar chart (Right) illustrate change in LNAPL composition with increasing evaporation (Figure from (Schmidt, Beckmann, and Torkelson 2003)).

B. Biodegradable [Read more](#)

What is the efficacy of biodegradation?

Figure 4-5 represents the remedial performance of LNAPL recovery, vapor recovery, and biodegradation from a multi-phase extraction system. Overall biodegradation was the dominant component. LNAPL recovery was the least efficient, although initially LNAPL appeared to be the most promising.

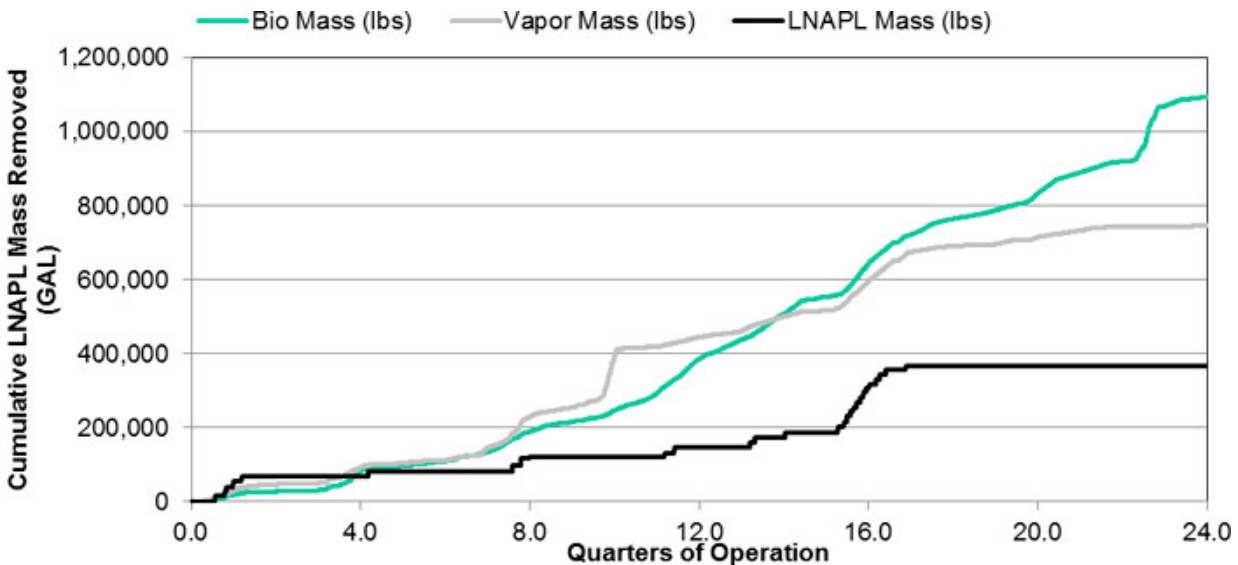


Figure 4-5. Remedial rate data from a multi-phase extraction system operating at a site with gasoline range LNAPL (unrefined product).

Characterizing the extent of LNAPL transmissivity, biodegradation rate, and vapor removal rates spatially, as well as at individual points, can help forecast longevity of a given mechanism. In this case, LNAPL recovery may not have been required and more resources could have been applied towards the biodegradation mechanism if additional up-gradient investigation had been performed. The LNAPL recovery decision here was based on mobile LNAPL in the recovery wells with no up-gradient testing of LNAPL transmissivity. For sites with LNAPL occurrence and risk-based concerns, there are technologies that can potentially address both types of concerns.

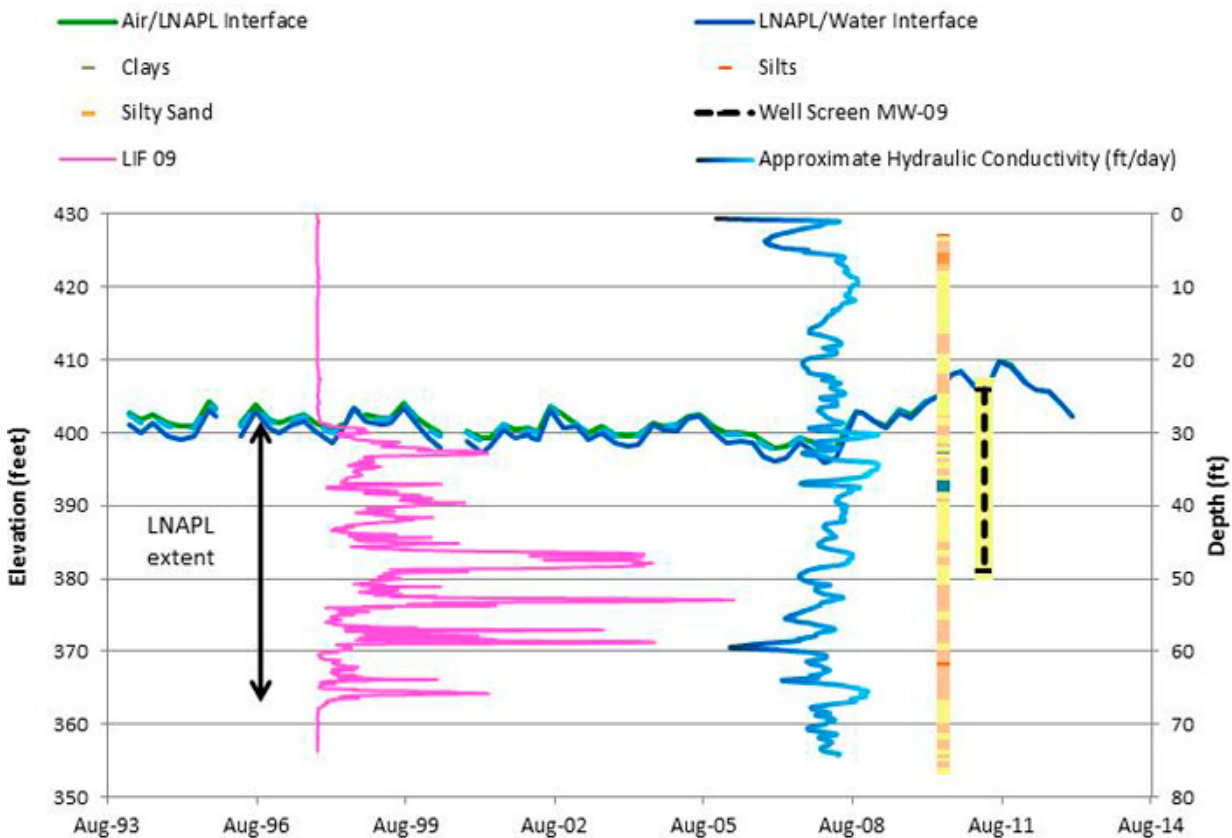


Figure 4-6. Hydrograph with well screen, LIF, hydraulic conductivity log, and soil profile (from cone penetrometer tool).

C. Mobile vs. Residual Fractions [▼Read more](#)

What are the fractions of mobile and residual LNAPL?

Due to heterogeneity in the subsurface, it can be difficult to quantify the residual and mobile fractions within 10 percent of the actual value. However, improved investigation tools do allow for more gross estimates, which are often sufficient to identify when residual dominates the source area, and when it is worthwhile to reduce the mobile fraction. Understanding these fractions improves the technology selection and allows the practitioner to evaluate the value of generating additional groundwater waste during mobile LNAPL recovery or if vapor enhanced recovery is preferred. Where residual LNAPL dominates, it may be preferable to focus resources towards the residual or both the mobile and residual fractions.

The data in Figure 4-6 illustrates that measurable LNAPL thickness can exist for potentiometric surface elevations below approximately 403 feet. If only this fact is considered for LNAPL source removal (i.e., skimming), the 35 feet of LNAPL identified below the water table by the LIF would be missed by the remedy, resulting in continued risk and an increased time to achieve remediation objectives.

When considering how to estimate the mobile and residual fractions shown in Figure 4-6, a variety of methods exist. While analytical soil TPH results above, at, and below the water table will give a good indication of relative fractions, this method can be costly.

Another line of evidence utilizes LNAPL transmissivity. LNAPL transmissivity values at this site are in the range of 0.1 to 0.8 ft²/day indicating that the majority of mass at the site is residual.

Seasonal fluctuations can affect the mobility of the LNAPL as well as distribution relative to the water table. Seasonal low water tables for unconfined sandy settings can result in submerged LNAPL becoming mobile. Quantification of this seasonality will help understand if recovering in low water level periods is beneficial to achieve remedial goals. Additionally, vapor removal and biodegradation rates for soil vapor extraction and bioventing have been observed to increase during seasonal water table lows. Understanding the period of improved availability and magnitude of improved LNAPL remediation rates is important to evaluating if a change in remedial approach due to seasonal differences is needed. The API NSZD Guidance ([API 2017](#)) encourages seasonal measurement of passive biodegradation mechanisms via NSZD rate measurement to understand this mechanism more fully and the benefits to site remedial goals.

3. What is achievable for a given technology? [▼Read more](#)

Knowing the limitations of a technology and what LNAPL fractions will remain when that limit is reached helps to set expectations for remedial outcomes and whether additional technologies are needed.

A. Mobility Based Limit [▼Read more](#)

What is the mobility based limit?

LNAPL recovery theoretically can remove the entire mobile fraction of LNAPL, which results in a limit at residual LNAPL saturation or zero LNAPL transmissivity. However, the asymptotic nature of LNAPL recovery results in a higher limit of LNAPL recovery, representing 0.1 to 0.8 ft²/day LNAPL transmissivity. At this point, the majority of LNAPL is residual and LNAPL recovery will not continue to meaningfully reduce the source mass.

B. Volatility Based Limit [▼Read more](#)

What is the volatilization based limit?

Volatilization remedial mechanisms typically address compounds with lower carbon numbers than C₁₀ (i.e., the gasoline range lighter than and including naphthalene). However, data in Figure 4-4, combined with vapor pressure data, indicate that a reduction in mass reduces the volatilization rate of the weathered fraction compared to fresh gasoline. Additional reductions through volatilization may require extended timeframes with little improvement. While volatilization does address both mobile and residual LNAPL above and below the water table, an alternate limit on the application may be the background biodegradation rate or other removal mechanisms.

C. Solubility Based Limit [▼Read more](#)

What is the solubilization based limit?

ISCO and co-solvent flushing would have limited effect when used alone on less soluble hydrocarbons. LNAPL analytical data, combined with the distribution of LNAPL, are often sufficient to illustrate that while these technologies may remove mass or further mobilize it for recovery, the costs limits and/or waste management for surfactants often result in these technologies not being selected.

D. Biodegradability Based Limit [▼Read more](#)

What is the biodegradation based limit?

Biodegradation is not limited to the light end of the carbon range like solubility or volatility. Biodegradation occurs regardless of carbon number and is more targeted towards molecular structure. Alkanes across a wide range of carbon numbers (i.e., light ends to longer chain alkanes in the C⁴⁰ range) are biodegradable. However, branched alkanes or isoprenoids, asphaltene, are less easily biodegraded. Variability also occurs due to aerobic and anaerobic degradation processes. Enhanced biodegradation limits are often defined by the magnitude of enhancement versus background degradation rates, as well as comparison to other remedial mechanisms.

Whether the technology focuses on liquid recovery, removal of volatiles, or biodegradation, there are limitations; performance will be dependent on the nature of the hydrocarbon and other physical site characteristics. Technology endpoints are often defined while considering site-specific physical obstructions, background degradation rates, and the nature of the LNAPL impacts. Qualitative methods available to help indicate relative performance rates are outlined in Table 4-3.

Table 4-3. Qualitative methods to indicate relative performance rates

Remedial Mechanism	Method
LNAPL Recovery	• 3D source and soil characterization • LNAPL transmissivity values as compared to 0.1 to 0.8 ft²/day range • Mobile vs. Residual fraction estimates
Vapor Removal Potential	• Site setting knowledge • 3D source and soil characterization • Field headspace screening • LNAPL analytical characterization • Pilot testing
Biodegradation	• NSZD rates represent lower bound for biodegradation • Single well in field respiration testing to represent aerobic potential • LNAPL analytical characterization
Thermal (resistive, radio wave, etc.)	• 3D source and soil characterization • LNAPL analytical characterization
ISCO, Surfactant	• 3D source and soil characterization • LNAPL analytical characterization

Quantified estimates of remedial performance can be completed via pilot testing, additional field characterization and/or modeling.

Table 4-4 provides a list of models or analytical methods for evaluating various technology aspects. The accuracy of these estimates is often dependent on the input accuracy and site variability.

Table 4-4. Analytical methods for evaluating technologies

Mechanism or Technology to Estimate	Applicable Technologies	Reference Document(s)
Diffusive vapor flux	NSZD, background rate for sparging or vapor extraction	• API 4784 (API 2017)
Advective vapor flux	SVE, Bioventing	• ASTM E2531 – Appendix X (ASTM 2014b) • USACE (USAEC 2002)
Respiration Rates	Bioventing, Soil Vapor Extraction, Air Sparging, NSZD	• AFCEE (AFCEE 2004) • USACE (USAEC 2002) • EPA (EPA 1995)
Natural Source Zone Depletion Rates	NSZD, potential lower bound for aerobic technologies (SVE, Air Sparging, Bioventing)	• API 4784 (API 2017) • Vadose Zone Biodegradation Loss model, VZBL (Wilson, Hers, and Jourabchi 2016)
LNAPL Transmissivity	LNAPL Recovery Technologies	• API 4729 (API 2003) • API 4762 (API 2016) • ASTM E2856-13 (ASTM 2013)
Hydraulic control and injection	Mass Control	• Modflow – USGS • Visual AEM University of Waterloo
Vapor Model	See ITRC PVI guidance	• (ITRC 2014)

5. LNAPL Concerns, Remedial Goals, Remediation Objectives, and Remedial Technology Groups

This section describes the decision process for identifying LNAPL concerns, verifying concerns through the application of threshold metrics, selecting LNAPL remedial goals, and determining LNAPL remediation objectives. These steps necessarily precede the selection of LNAPL remedial technologies, and the establishment of associated remedial performance metrics and remediation endpoints. This section also introduces remedial technology groups and the concept of a combined technologies approach.

Figure 5-1 shows the process of identification and verification of LNAPL concerns, and the subsequent selection of remedial goals, remediation objectives, remedial technologies, remediation performance metrics, and remediation endpoints. The following subsections describes each of these steps.

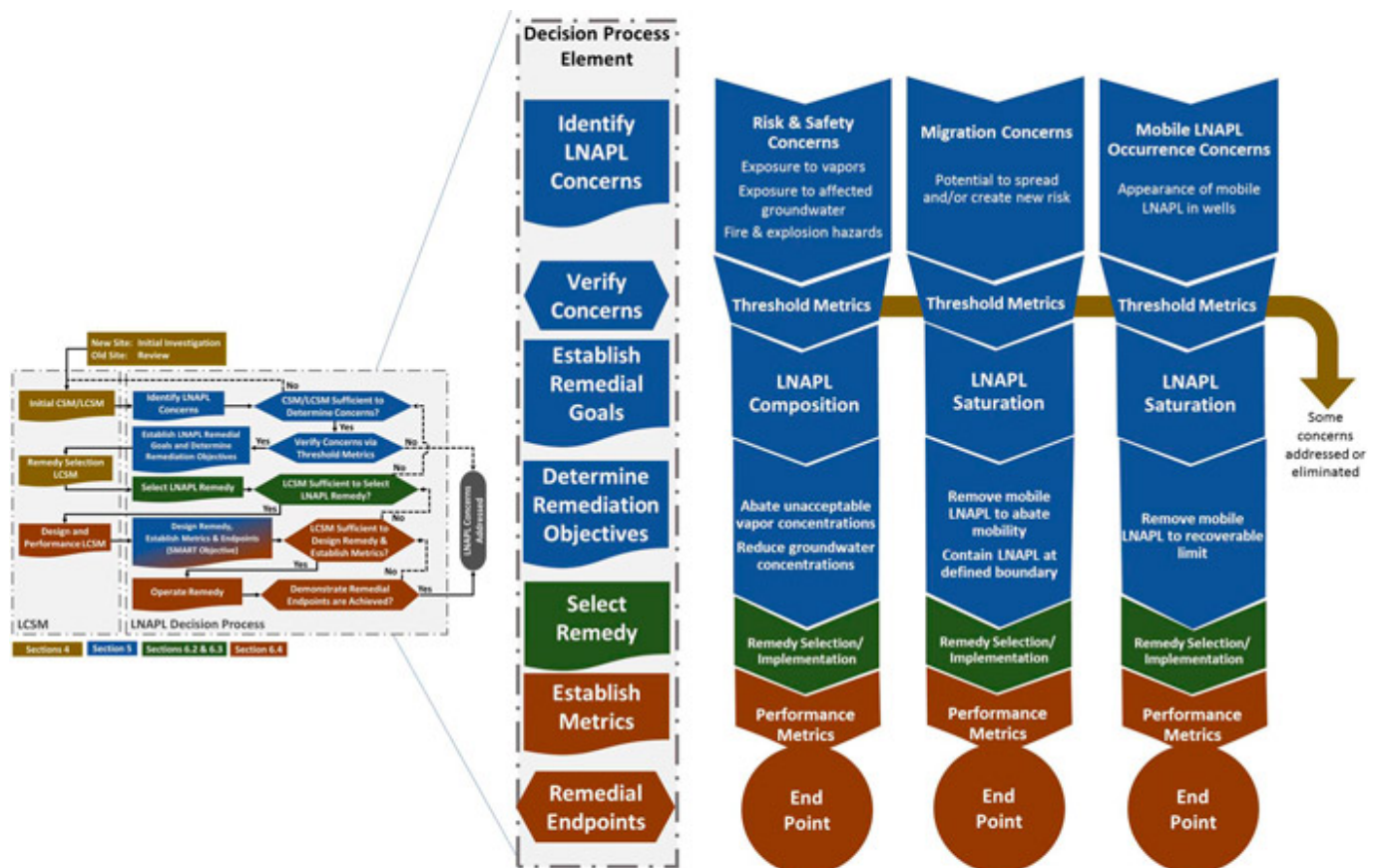


Figure 5-1. Decision process to identify/verify LNAPL concerns and establish remedial goals, objectives, technologies, performance metrics, and endpoints.

5.1 Identifying LNAPL Concerns

An LNAPL Concern is an LNAPL condition or potential condition that could:

- pose a risk to health or safety (composition-based),
- result in additional LNAPL migration (saturation-based),
- address an LNAPL-specific regulatory requirement (regulatory-based), or
- create some other physical or aesthetic impact or other specific regulatory or stakeholder requirements.

A well-developed Initial LCSM should summarize LNAPL conditions and guide the identification and refinement of LNAPL

concerns. Some LNAPL concerns may be readily identified in the early stages of site characterization, and others may be identified or further refined following further development of the LCSM.

When LNAPL is present at a site, potential LNAPL concerns tend to fall into four categories:

1. Risk and Safety Concerns –

- Are there human or ecological exposures and risk concerns arising from the presence of the LNAPL?
- Are there potential fire or explosivity concerns associated with the LNAPL?

2. Migration Concerns –

- Is there an ongoing LNAPL release?
- Is there potential for further LNAPL migration, which may create new exposures and risks?

3. Mobile LNAPL Occurrence Concerns –

- Are there LNAPL-specific regulatory requirements, such as removal of mobile LNAPL from existing wells to a defined threshold?

4. Other LNAPL Concerns –

- Are non-risk odors or surficial stains from the LNAPL a potential nuisance?
- Are there geotechnical concerns due to the presence of LNAPL in soil?
- Is stakeholder perception of the occurrence of LNAPL a concern?

The first three categories of concern are shown in Figure 5-1. “Other” LNAPL concerns are not explicitly shown in Figure 5-1, and are covered in less detail in the decision steps discussed below.

5.1.1 Using LNAPL Threshold Metrics to Verify LNAPL Concerns

Once identified, potential LNAPL concerns should be verified, because some concerns may be eliminated or managed without the need for remediation. As part of the verification process, LNAPL concerns may be compared to threshold metrics. A threshold metric can indicate whether an LNAPL concern may be eliminated, or whether it may be appropriate for carrying forward to establish remedial goals, complete a remedial technology selection process, establish remediation objectives, and lastly establish remedial performance metrics and remediation endpoints.

In contrast to performance metrics, which indicate whether a remediation technology is progressing toward its remediation endpoint, threshold metrics are used to indicate whether remediation is warranted or if it can be managed without remediation.

Not all LNAPL concerns will necessitate remediation; therefore, not all LNAPL concerns will generate LNAPL remedial goals and objectives. Verification of LNAPL concerns is a necessary step toward establishing LNAPL remedial goals and determining remediation objectives.

1. The appearance of measurable LNAPL in a monitoring well may be identified as a possible mobile LNAPL occurrence concern, potentially triggering a regulatory requirement to recover LNAPL to the extent practicable. An appropriate verification action would be to compare the measured LNAPL transmissivity in that well to a threshold metric, such as the ITRC-recommended LNAPL transmissivity endpoint range for LNAPL recoverability. If the measured LNAPL transmissivity exceeds the recommended endpoint range, the mobile LNAPL concern would be considered verified, and carried forward for remedial goal and objective development.
2. Buildings overlying an LNAPL body may be identified as a potential petroleum vapor intrusion (PVI) concern. This concern may be verified by comparing the vertical separation distance to the applicable risk-based screening distance (ITRC 2014) or other risk-based screening criterion¹. If the screening indicates that there is a potentially complete exposure pathway (current or future) that could result in an unacceptable risk, then the LNAPL PVI concern is verified, and the concern would be carried forward to select remedial goals.
3. A potential LNAPL migration concern has been identified at a large LNAPL body. One threshold metric that could be applied to verify this concern is an assessment of LNAPL body stability using existing site monitoring data. If the LNAPL body can be demonstrated to be stable or receding, the concern for LNAPL migration can be eliminated. Conversely, a site with a documented expanding LNAPL body and/or visible LNAPL seep(s) would be carried forward to remedial goal selection.

4. A potential concern about near-surface occurrence of LNAPL has been identified at a site with historical surface releases. The state has numerical limits for TPH in shallow soil based on a theoretical threshold for the occurrence of a separate phase (C_{sat}). Comparison of soil sampling data for TPH in soil to state numerical TPH standards can be used to validate or eliminate this concern.

Once LNAPL concerns have been evaluated, those that have not been eliminated or managed without remediation are considered in the selection of LNAPL remedial goals (Figure 5-1).

5.2 Establishing LNAPL Remedial Goals

Once LNAPL concerns have been verified, appropriate LNAPL remedial goals are established to address those concerns. LNAPL remedial goals are the desired LNAPL condition to be achieved by the remedial strategy or action that constitutes the end of LNAPL management for a specific LNAPL concern. The elimination of the LNAPL concern necessitating LNAPL management occurs when the goal is achieved.. Because more than one LNAPL concern may need to be addressed to render the site protected, multiple goals may be established so that the different concerns are eliminated. For example, if there are three LNAPL concerns at the site, then three LNAPL remedial goals may be selected – one to address each concern.

LNAPL remedial goals are generally expressed through three LNAPL conditions: LNAPL Composition, LNAPL Saturation, and LNAPL Aesthetics. Each LNAPL concern is linked closely to a corresponding LNAPL goal:

- LNAPL risk concerns typically generate LNAPL composition-based goals.
- LNAPL migration concerns typically generate LNAPL saturation-based goals.
- Mobile LNAPL occurrence concerns typically generate LNAPL saturation-based goals.
- “Other” LNAPL concerns typically generate LNAPL aesthetic goals.

A compilation of example concerns, potential threshold metrics, and remedial goals is shown in Table 5-1.

Table 5-1. Connecting LNAPL concerns and objectives with remedial goals and technology groups

LNAPL Concern	Potential Threshold Metrics	LNAPL Remediation Goal	LNAPL Remediation Objective	Technology Group	Performance Metrics	Remediation Technology Selection
<i>LNAPL saturation-based goals</i>						

LNAPL Concern	Potential Threshold Metrics	LNAPL Remediation Goal	LNAPL Remediation Objective	Technology Group	Performance Metrics	Remediation Technology Selection
<i>LNAPL occurrence in wells</i>	LNAPL transmissivity to assess recoverability	Reduce mobile LNAPL saturation	Recover LNAPL to a practicable limit	LNAPL mass recovery	See Tables 5-2 and 6-3	See Table 6-2
<i>LNAPL occurrence in soil</i>	Soil TPH regulatory standards	Abate unacceptable soil concentrations even if/when LNAPL is within residual saturation range	Reduce soil concentrations (e.g., TPH) to below soil regulatory limits	LNAPL mass recovery and LNAPL phase change		
<i>Potential LNAPL migration</i>	LNAPL body footprint stability	Terminate LNAPL body migration and reduce potential for LNAPL migration	Abate LNAPL body migration by sufficient physical removal of mobile LNAPL mass	LNAPL mass recovery		
			Stop LNAPL migration by physical barrier	LNAPL mass control		
LNAPL composition-based goals						
<i>Groundwater impacts from an LNAPL source</i>	Dissolved-phase regulatory standards	Abate unacceptable constituent concentrations in dissolved phase from an LNAPL source	Control or treat soluble plume to abate dissolved-phase concentrations. Contain LNAPL body and affected groundwater to prevent groundwater impacts at compliance point(s)	LNAPL mass control and LNAPL phase change		
	Dissolved-phase plume stability	Abate unacceptable constituent concentrations in dissolved phase from LNAPL source	Control or treat soluble plume to abate dissolved-phase concentrations	LNAPL mass control and LNAPL phase change		
<i>Petroleum vapor intrusion overlying dissolved plume aside from the LNAPL source</i>	Vapor intrusion screening distances	Abate unacceptable constituent concentrations in soil vapor from groundwater source	Reduction of groundwater and vapor concentrations beyond acceptable levels	LNAPL phase change and LNAPL mass control		
<i>Petroleum vapor intrusion overlying LNAPL source</i>	Vapor intrusion screening distances	Reduce constituent concentrations in soil vapor and/or LNAPL source	Abate unacceptable vapor accumulations by sufficient depletion of volatile constituents in LNAPL	LNAPL phase change and LNAPL mass control		
<i>LNAPL occurrence in soil</i>	Soil regulatory standards	Abate unacceptable soil concentrations even if/when LNAPL is within residual saturation range (e.g., TPH concentration)	Reduction of risk from specific components	LNAPL phase change		
LNAPL aesthetic-based goals						
<i>Geotechnical instability of LNAPL-affected soil</i>	Geotechnical structural tests	Restore soil stability (saturation-based goal)	Abate geotechnical soil instability	LNAPL mass recovery and LNAPL mass control		
<i>Stains and odors</i>	Field inspection	Remove aesthetic concerns (composition-based goal)	Abate offensive odors	LNAPL mass control and LNAPL phase change (vapor)		
	Odor-based screening levels					

5.3 Determining LNAPL Remediation Objectives

An LNAPL Remediation Objective describes how the remedial goal will be accomplished and must be linked to the

technology(ies) to be used. Combined with performance metrics and a remediation endpoint ([Section 5.5](#)), the LNAPL remediation objective becomes a “SMART” objective (Specific, Measurable, Attainable, Relevant and Timely).

LNAPL remedial goals are grouped in Table 5-1 by those that address LNAPL Saturation, LNAPL Composition, and LNAPL Aesthetics. LNAPL remediation objectives are closely linked to goals within those groups. Specifically, the remediation objective articulates the action required to address specific LNAPL remedial goals.

When stating an LNAPL remediation objective to accomplish a specific LNAPL remedial goal, the objective typically includes one of the phrases: “stop,” “abate,” “control,” “change,” “reduce,” “remove,” or “recover.” Articulating objectives with these words help connect the remedial goals to one of the technology groups described in [Section 5.4](#).

Therefore, for specific, agreed-upon LNAPL concerns and LNAPL remedial goals, remediation objectives can be defined. Example remediation objectives are included in Figure 5-1 in association with the concerns and goals to which they relate. Figure 5-2 illustrates the LNAPL decision process with specific examples.

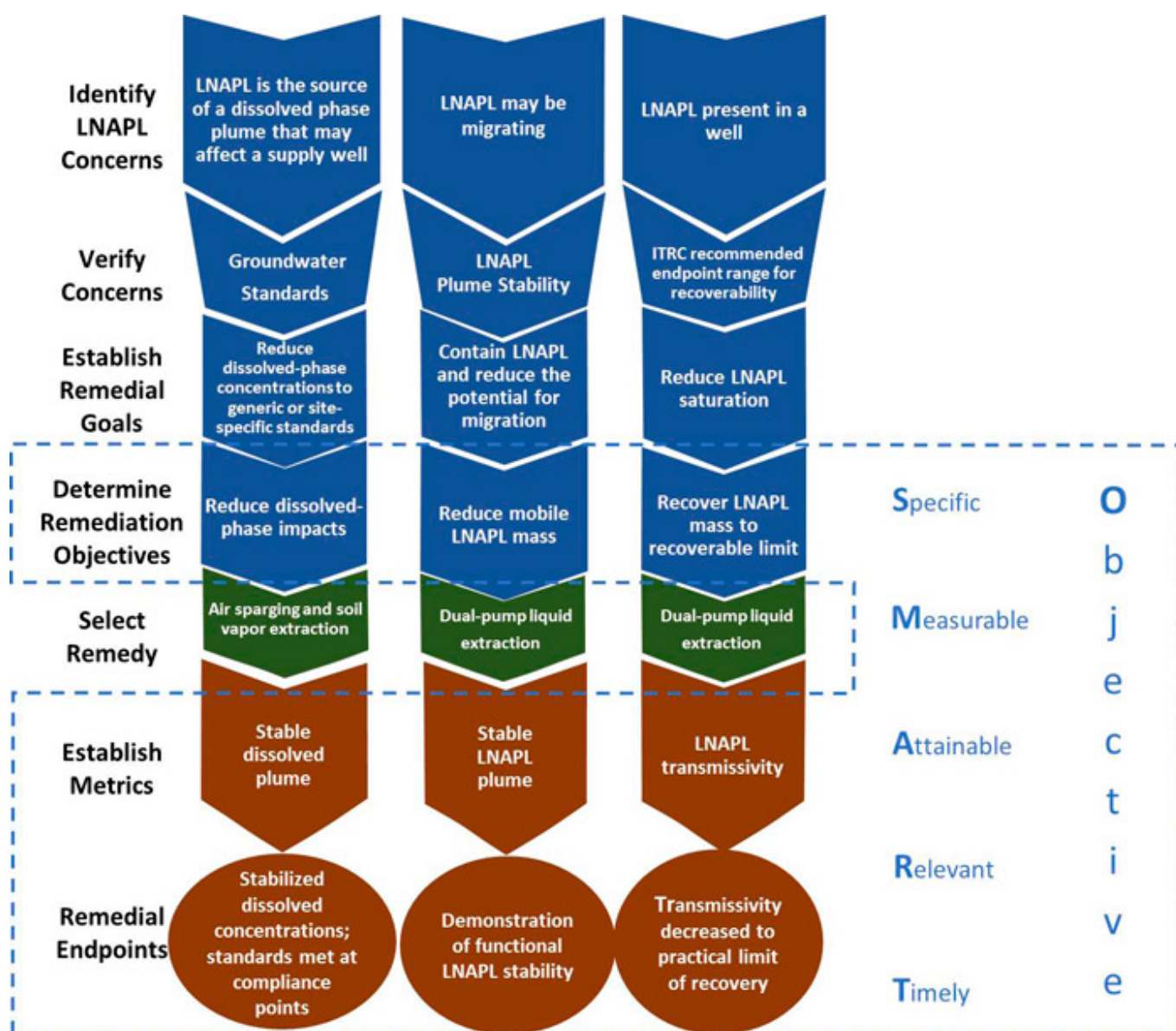


Figure 5-2. Example LNAPL decisions for verified LNAPL concerns.

Careful consideration and linkage of LNAPL concerns, goals, and remediation objectives is essential. For example, if the concern is “LNAPL is the source of the dissolved plume” and the goal is “to reduce the dissolved phase COCs from the LNAPL source” (a composition goal), then an objective of “removal of LNAPL with hydraulic recovery” would not address the concern or meet the goal, because LNAPL mass recovery addresses saturation, and not composition (see Figure 5-3).

5.4 LNAPL Remedial Technology Groups

[Section 6.1](#) describes the LNAPL remedial technology selection process with technology specific descriptions and information presented in [Table 6-1](#) and [Table 6-2](#), respectively. Each technology identified has unique applicability and capability, particularly with consideration to the LNAPL concerns, goals, and objectives. A selected LNAPL remedial technology should align with the particular LNAPL concern, remedial goal, and remediation objective. To aid in this alignment, this guidance identifies three basic groups to associate a technology with the primary mechanism by which it manages the LNAPL:

- Mass-recovery
- Phase-change
- Mass-control

LNAPL concerns can also be mitigated by implementing institutional controls (ICs) or engineering controls (ECs). It is a site-specific decision to choose between IC, EC, or remediation technologies. This guidance focuses on remediation technologies.

A specific technology may not necessarily be a pure end member of any particular technology group. For this reason, a ternary graph is included in [Table 6-1](#) for each technology to represent visually how the technology associates with the technology groups, which are described below.

5.4.1 LNAPL Mass-Recovery Technology

LNAPL mass-recovery technologies address saturation-based LNAPL remedial goals and are the technologies most frequently used exclusively for LNAPL remediation. These technologies recover LNAPL via physical removal, such as with excavation of LNAPL-saturated soil or hydraulic recovery (e.g., LNAPL pumping or skimming). Hydraulic recovery may be pursued with or without flow augmentation using remedial techniques that reduce LNAPL viscosity or interfacial tension (e.g., surfactants or solvents), thereby enhancing LNAPL mobility flow characteristics. Subject to logistical and practical limits, LNAPL mass recovery using pumping or skimming technologies is limited to reducing LNAPL saturation to residual saturation. One exception is excavation, which can achieve complete LNAPL removal. At residual saturation, LNAPL will not flow and, therefore, hydraulic recovery is no longer possible (see [Section 3.6](#) for more details on the limit of hydraulic recovery).

5.4.2 LNAPL Phase-Change Technology

LNAPL phase-change technologies do not directly remove LNAPL from the environment as is the case for LNAPL mass-recovery technologies. Instead, LNAPL phase-change technologies rely on the physical properties (e.g., vapor pressures, Henry's Constant, solubility) of LNAPL to partition from a multi-constituent liquid to other phases by increasing the rates of volatilization, dissolution, or degradation of the LNAPL constituents. Those LNAPL constituents are either degraded in situ or captured and treated in the vapor or dissolved phases as they are removed from the subsurface. The composition of LNAPL changes through the removal of LNAPL constituents that readily degrade, volatilize, or dissolve. LNAPL phase-change technologies are thus primarily applicable to composition-based LNAPL remedial goals. LNAPL phase change results in some saturation reduction (e.g., SVE for gasoline LNAPL can reduce overall LNAPL saturation), therefore these technologies may have some secondary application for saturation-based LNAPL remedial goals.

LNAPL phase-change technologies are not limited by residual LNAPL saturation because they do not depend on the presence of mobile LNAPL. Some LNAPL phase-change technologies are more elaborate to design and implement than LNAPL mass-recovery technologies, and their practicable limits may not be as well established as those of LNAPL mass-recovery technologies. Thus, LNAPL phase-change technologies may be costlier to design and/or deploy, but use of strategic/targeted applications may minimize such limitations and possibly shorten the LNAPL phase-change remediation life cycle. For example, to achieve a remedial goal of LNAPL recovery to saturations less than residual, it might be more appropriate to hold off deployment of the LNAPL phase-change remedial technology until after an LNAPL mass-recovery technology has reached its recovery limit, or an LNAPL remediation objective is reached that is set to transition between the two technologies.

5.4.3 LNAPL Mass-Control Technology

LNAPL mass-control technologies are primarily suited for saturation-based LNAPL remedial goals because they limit mobility or eliminate migration. LNAPL mass-control technologies may stabilize a migrating LNAPL by reducing the LNAPL saturation via blending a binding agent with the LNAPL zone (mixing technologies) or by physically blocking LNAPL migration (containment technologies). Such technologies alone may satisfactorily meet the remedial goal or can be used in combination with LNAPL mass-recovery or LNAPL phase-change technologies. Additional long-term operation and

maintenance and stewardship requirements may also be warranted, depending on site conditions and property use. The containment technologies are limited in applicability to LNAPL saturations in excess of residual saturation, since at residual saturations the LNAPL body is, by definition, immobile. In some instances, mixing technologies may also reduce cross-media impacts (e.g., recharge infiltration and leaching through the LNAPL zone) since some binding agents (e.g., Portland cement, bentonite) can reduce the soil permeability of the LNAPL zone or degrade the volatile or soluble LNAPL constituents.

5.4.4 Combination of Technologies

An effective remedial strategy depends on the optimum use of technologies to maximize LNAPL removal at the lowest cost and effort while achieving remedial goals. Formerly, LNAPL remedial designs used a single technology to remediate an LNAPL source or plume or both, with the expectation that the technology would achieve the remedial goal over the course of the design life cycle. Experience has shown this has not always been the case as remedial systems were found to be ineffective and costly while regulatory closures were not achieved. Based on lessons learned from this practice, a single technology approach may not be the most practical or cost effective for LNAPL management and remediation. A more practical and cost-effective strategy may be to sequence and/or combine technologies at different stages of the remediation life cycle based on the specific LNAPL remedial goals and targeted areas. It is of critical note that careful planning should be employed with regard to use of multiple technologies. Technologies should be chosen with consideration to their ability to progress toward the remedial goals. The use of multiple technologies should be thoughtful and deliberate, rather than a reaction to a failed technology.

The selection, sequencing, or combining of technologies for LNAPL management should be determined after LNAPL concerns have been verified, remedial goals have been stated, and a Remedy Selection LCSM has been developed and understood by all stakeholders (see [Section 4.4](#)). The sequencing or synergy of combining technologies may be either temporal, where the technologies are applied one after the other as treatment trains, or spatially at the same time in different parts of the source area and plume. Typically, the more aggressive technology is applied first to remove or contain LNAPL above residual saturation, followed by phase-change technologies. Examples of remediation technology combinations include:

- Targeted use of dual-pump liquid extraction (mass recovery technology) to reduce LNAPL saturation, followed by air sparging and soil vapor extraction (phase change and mass recovery technology) to change LNAPL composition (thus addressing risk concerns) and further reduce LNAPL mass. A final remedy might include natural source zone depletion, with adequate data collection to assess its efficacy and progress.
- Utilization of a barrier wall (mass control technology) to halt migration toward a receptor, followed by in situ smoldering (mass removal technology) to reduce LNAPL mass.

Figure 5-3 summarizes a sequenced technology deployment treatment train that shows remedial actions from aggressive controls or removals to passive technologies (e.g., NSZD).

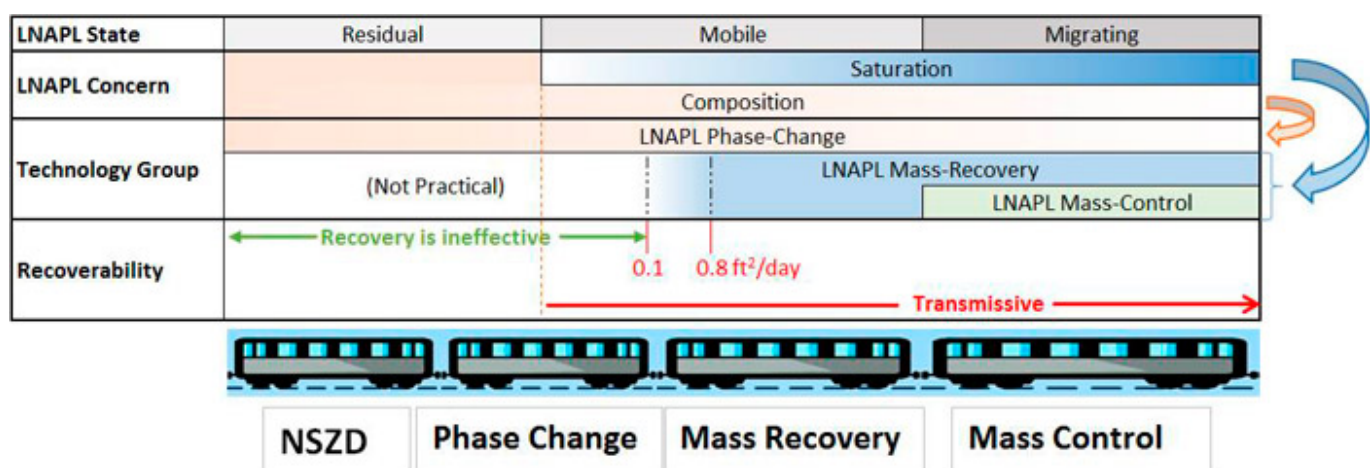


Figure 5-3. Relationship between LNAPL State, LNAPL Concern, Technology Group, and Recoverability.

5.4.5 Transitioning Remedial Technologies

As described in Section 5.4.4, the implementation of one sole remedial technology is often not practical for a timely cleanup, nor feasible for situations where there is more than one LNAPL concern. LNAPL bodies with both migration and risk concerns are common, and those differing concerns often lead to different technology selections. Many sites will require an adaptive

remedial strategy that includes deliberate and timely transitioning of technologies spatially or temporally to make satisfactory progress toward, or to achieve, the remedial goals. Technology transitions are intended to compliment remedial actions that have already taken place, and should be in consideration of changing site conditions. Transitioning from one technology to another (or a combination of technologies) should not be a reaction to a failed technology. “Failed technologies” are more typically ‘failed technology selections’ due to a gap in the site understanding or a lack of complete understanding of the LNAPL concerns and the types of technologies appropriate for those concerns. To prevent failed technology selections and assess the timing for a technology transition, the LSCM should be updated regularly to improve site understanding as active and/or natural processes affect site conditions. An updated Design and Performance LCSM may be utilized to identify successes and support system shutdown, and where applicable, identify areas where there has been a shift in concern, supporting technology transition.

Remedial technologies should be selected only after considering the technologies appropriate to the identified LNAPL concerns. After careful pairing of LNAPL concerns and remedial goals with appropriate technologies, the selected technology is implemented. Performance metrics for the implemented technology are evaluated during operations, which is critical to making a technology transition. The performance metrics may indicate the need for system optimization, or indicate that further progress toward achieving remedial goals is likely to be limited through continued use of the current technology. If the performance metrics indicate the practical endpoint for a technology has been met, then continued use of the technology is unlikely to move the site further toward achieving the remedial goals, and a technology transition is warranted.

5.5 Establishing Remedial Performance Metrics and Remediation Endpoints

For each LNAPL remediation objective, one or more “performance metrics” are defined. Performance metrics are measurable characteristics that relate to the remedial progress of a technology in abating the concern. LNAPL remediation technologies address LNAPL concerns differently (e.g., excavation vs. co-solvent flushing), and therefore, the performance metrics used to demonstrate progress toward the LNAPL remediation objective depend on the technology used. Table 5-2 lists example performance metrics and remediation objectives.

Table 5-2. Example performance metrics and remediation endpoints

Example performance metrics and remediation endpoints	Description
Asymptotic performance of optimized recovery system	Analysis of unit volume of LNAPL recovery or recovery rate per unit of time, after considering optimization. Endpoint reached when asymptotic curve indicates the limit of recovery effectiveness (e.g., analysis indicates that further recovery of remaining LNAPL is impracticable).
Decline curve analysis	Analysis of unit volume of LNAPL recovery or recovery rate per unit of time. Endpoint reached when decline curve analysis indicates that the remaining LNAPL volume is below threshold of concern, or the time and effort to recover the remaining volume is impracticable.
Dissolved-phase concentration	Concentrations stable or decreasing; endpoint reached when reduced to regulatory standards at a compliance point.
Dissolved-phase plume stabilized	If exhibited, then it is also an indication of a stable LNAPL body.
Limited/infrequent in-well LNAPL thickness	Stated LNAPL thickness objective or LNAPL thickness typically not observed in monitoring well under average site conditions. Indicative that LNAPL is not consistently recoverable and the majority of remaining impacts are residual.
LNAPL body footprint stabilized	Assesses whether technology effectively counters existing LNAPL driving gradient and/or captures migrating LNAPL. Comparison of LNAPL body footprint before and after treatment to demonstrate stable or shrinking footprint.

Example performance metrics and remediation endpoints	Description
LNAPL composition	Reduce mole fraction of volatile or soluble LNAPL constituents. Endpoint reached when volatile or soluble constituents of concern reduced to risk-based regulatory standards in media of concern.
Enhanced biodegradation rate	Assure remedial performance by maintaining threshold oxygen concentration in zone targeted by air sparging, soil vapor extraction, or bioventing. Endpoint reached when soil respiration rate or CO ₂ production declines below established threshold.
LNAPL recovery rate vs. estimated LNAPL flux	The recovery system either diminishes the driving LNAPL gradient and/or achieves a higher recovery rate than the estimated LNAPL flux across the width of the LNAPL body front. Endpoint reached when LNAPL flux diminishes to zero, or another target threshold.
LNAPL saturation profile	Comparison of saturations before and after treatment to demonstrate reduced saturations. Endpoint reached when saturation-based concerns have been abated.
LNAPL transmissivity	Use reduction of transmissivity over time to assess technology performance. Endpoint reached when LNAPL transmissivity indicates recovery has reached its practicable limit, or concern has been abated.
LNAPL/vapor recovery ratio	Ratio of unit volume of LNAPL recovered per unit volume of vapor. Decreasing ratio indicates decreasing recovery effectiveness. Endpoint reached when further reduction of this ratio is impracticable, or concern has been abated.
LNAPL/water recovery ratio	Ratio of unit volume of LNAPL recovered per unit volume of water. Decreasing ratio indicates decreasing recovery effectiveness. Endpoint reached when further reduction of this ratio is impracticable, or concern has been abated.
No first LNAPL occurrence in downgradient well	Performance metric to address/limit LNAPL migration. LNAPL never enters a monitoring well installed outside of LNAPL body.
Soil saturation for soil stability	LNAPL saturation reduced to yield acceptable soil bearing capacity.
Soil concentrations	Concentrations stable or decreasing; endpoint reached when reduced to regulatory limits.
Vapor-phase concentration	Concentrations reduced until regulatory standards are met at a compliance point.
Unit cost of incremental mass removal	Increasing cost per unit LNAPL recovered indicates decreasing cost- effectiveness (cost may not always be in line with regulatory requirements; however, in certain circumstances this metric can be useful for assessing practicable limits).

Ideally, each performance metric has a measurable predetermined value that describes when the technology has reached its limits of beneficial application. That is the remediation endpoint for the technology chosen. It is important to note that the remediation endpoint is technology specific, and may not fully eliminate the LNAPL concern or achieve the LNAPL remedial goal. For example, air sparging and soil vapor extraction may be applied with the objective of changing the LNAPL composition to address risk concerns. The remediation endpoint may be a practicable mass removal rate, or a target soil respiration rate, or some other measure(s) of the beneficial limits of the technology. If risk concerns still exist when these beneficial limits have been reached, then another remedial technology is needed. A transition to another technology such as NSZD is then implemented, with the intent of fully addressing the remaining risk concerns by further reducing the concentrations of risk-driving LNAPL components in soil vapor or groundwater to levels that no longer pose a risk.

5.6 Integration of the LCSM and LNAPL Remedial Technology Selection

The development of an Initial LCSM ([Section 4](#)) aids in the effective identification of potential LNAPL concerns. Once potential LNAPL concerns have been identified, threshold metrics, such as comparison to generic numerical screening levels, can be applied to confirm whether a potential concern can be screened out from further evaluation or consideration. SMART remediation objectives can be developed specific to the identified LNAPL concerns by establishing remedial goals, selecting

one or more appropriate remedial technologies, and identifying remedial technology-specific endpoints and performance metrics. [Section 6](#) of this document provides more detailed information to aid in the selection of an appropriate remedial technology, or combination of technologies, to meet the defined remedial goals.

¹ More detailed verification of risk concerns can be made via risk assessment, which evaluates potential exposure and toxicity concerns associated with the presence of LNAPL, considers LNAPL composition, and accounts for the attenuation of mobile LNAPL constituents. Evaluation of risk is not dependent on the abatement of mobile LNAPL, and may be initiated at any point in the project life cycle.

6. LNAPL Remedial Technology Selection

6.1 Process Overview

This section provides a summary of the remedial technology selection process. *This process is NOT appropriate for emergency response situations.*

Figure 6-1 illustrates the technology selection process and how it relates to coincidental, ongoing LCSM development. Note that Figure 6-1 assumes the LCSM was developed sufficiently in [Section 4](#) and that all LNAPL concerns were identified in [Section 5](#) prior to beginning remedial technology screening in this chapter.

Technology selection is a stepwise and linear process for addressing each LNAPL concern; however, remedy selection is seldom linear. The initial focus in technology selection, therefore, should not be when (i.e., in what sequence) each concern is addressed or step is performed, but rather that each is addressed/performed sufficiently. If all concerns are addressed, then the regulating authority can be confident that a complete remedial strategy is being proposed, and the proposing entity can be confident that the proposal is likely to be effective and acceptable to regulators and stakeholders alike. However, some concerns ultimately may take precedence over others and thus dictate the order of technology implementation.

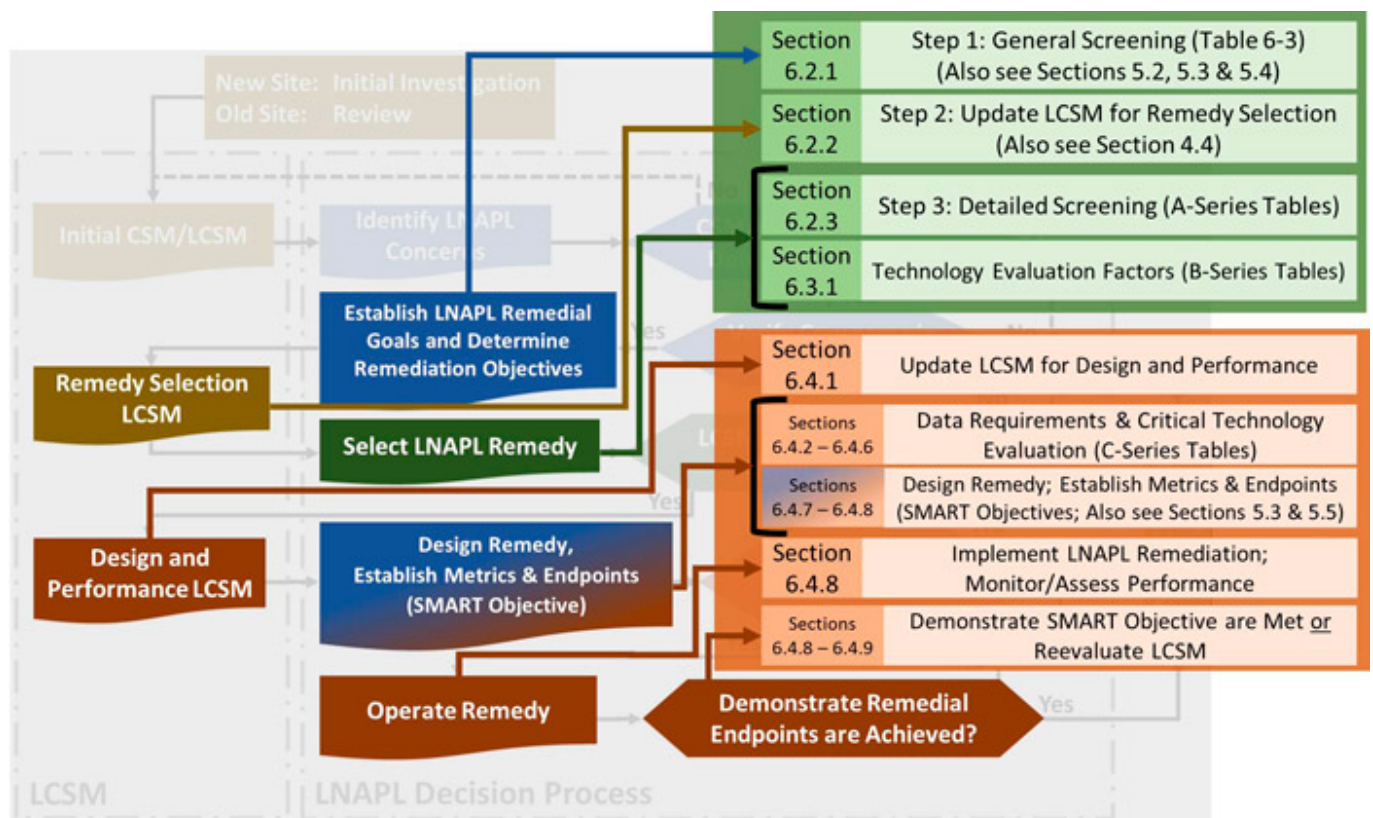


Figure 6-1. LNAPL technology screening and selection coincident with LCSM development.

Before screening and selecting LNAPL technologies, the user should be familiar with the variety of LNAPL remediation technologies currently available as described in this document and elsewhere (e.g., Enviro Wiki, http://erwiki.net/index.php?title=Main_Page). Familiarity with technologies will assist in screening. Useful elements of this document for remedial technology screening include:

- Table 6-1 provides a brief description of each of the technologies addressed in this guidance. The technologies listed are based upon a survey of the LNAPL team's experience and knowledge; some are more innovative or

have a better record of accomplishment than others.

Please note that less intensive LNAPL recovery technologies such as the use of adsorbent socks, manual bailing, passive skimmers, or (periodic, short-term) vacuum trucks are not included in the technology tables. These methods generally are not very effective to recover significant LNAPL. However, depending on the expected or measured yield of recoverable LNAPL, these technologies may be appropriate when dictated by local regulations, aesthetic concerns, or emergency response actions not included in this process.

- Table 6-2 provides categorical information about each technology, including assignation to a technology group (refer to [Section 5](#)), applicable site conditions, relative rate of cleanup, and a quick reference to specific [Appendix A](#)
- [Appendix A](#) provides detailed information on each of the technologies presented in this guidance through a series of three tables (A-, B-, and C-series tables) that correlate to the screening process in [Section 6.2](#) through [Section 6.4](#), respectively.

Because of the number of potential technology candidates and the wide array of applicability of the technologies, selection of an appropriate technology is multifaceted. The selection process must consider the LNAPL remedial goals in light of the overall site use (current and future), LNAPL remediation objectives, site conditions, LNAPL type, and non-technical factors.

Table 6-1. Overview of LNAPL remedial technologies

LNAPL Technology	Description of Technology
Excavation	LNAPL body is physically removed and properly treated or disposed. Accomplishes removal and/or reduction of all phases including LNAPL, adsorbed, dissolved, and vapor.
Fluid recovery (4 variations; excludes SVE or groundwater-only recovery)	• Skimming: LNAPL is the only fluid removed using a pump or similar continuous mechanical device. There may be incidental, small volume water recovery.
	• Vacuum Enhanced Skimming: LNAPL and vapor are the fluids removed. LNAPL drawdown via skimming and vacuum induce an LNAPL gradient toward the recovery point. Also referred to as bioslurping or vacuum enhanced fluid recovery (VEFR).
	• Total Liquid Extraction: LNAPL and water are the fluids removed. Drawdown of LNAPL and groundwater induce an LNAPL gradient toward the recovery point. Groundwater drawdown may expose submerged LNAPL thereby increasing LNAPL mobility and recovery rate. Groundwater extraction may also provide hydraulic containment of potentially migrating LNAPL. Also referred to as dual pump liquid extraction (DPLE) (ITRC 2009a).
	• Multi-Phase Extraction (MPE): LNAPL, water, and vapor are the fluids removed. LNAPL drawdown, groundwater drawdown, and vacuum induce an LNAPL gradient toward the recovery point. Groundwater drawdown may expose submerged LNAPL thereby increasing LNAPL recovery rate. Groundwater extraction may also provide hydraulic containment of potentially migrating LNAPL. Also referred to as dual-phase extraction (DPE) or two-phase extraction (TPE) (USACE 1999). MPE is also often used as a phase-change technology to expose submerged LNAPL (as well as LNAPL in the vadose zone) to volatilization and enhanced aerobic biodegradation with hydraulic LNAPL removal as a secondary remediation objective.
Enhanced LNAPL recovery (3 variations)	• Water flooding (incl. hot water flooding): Water is injected to enhance the LNAPL gradient toward recovery wells. Hot water may be injected to reduce LNAPL viscosity and interfacial tension and further enhance LNAPL removal by hydraulic recovery.
	• Surfactant-enhanced subsurface remediation (SESR): A surfactant is injected to decrease interfacial tension and increase solubility. LNAPL and water are recovered hydraulically.
	• Cosolvent flushing: A solvent is injected to increase LNAPL solubility and mobility. LNAPL and water are recovered hydraulically.

LNAPL Technology	Description of Technology
In situ thermal remediation (4 variations)	• Steam injection: LNAPL is removed by forcing steam into the aquifer to vaporize and solubilize LNAPL, increase LNAPL recovery by reducing the viscosity and interfacial tension of LNAPL, and enhance LNAPL gradient. Vapors, impacted groundwater, and LNAPL are recovered via vapor extraction and hydraulic recovery.
	• Thermal conduction heating: Soil is heated using heating elements to vaporize and solubilize LNAPL and increase LNAPL recovery by reducing the viscosity and interfacial tension of LNAPL. Vapors, impacted groundwater, and LNAPL are recovered via vapor extraction and hydraulic recovery.
	• Electrical resistance heating: Electrical current is used to heat soil and groundwater through subsurface electrodes to vaporize and solubilize LNAPL and increase LNAPL recovery by reducing the viscosity and interfacial tension of LNAPL. Vapors, impacted groundwater, and LNAPL are recovered via vapor extraction and hydraulic recovery.
	• In situ smoldering: Initiated through a short duration, low energy “ignition event.” Combustion is sustained by the addition of air through a well to the target treatment zone. The energy of the reacting contaminants is used to pre-heat and initiate combustion of contaminants in adjacent areas, propagating a combustion front through the LNAPL-impacted zone in a self-sustaining manner, provided a sufficient flux of oxygen is supplied.
Air sparging/ soil vapor extraction (AS/SVE)	AS injects air into the saturated zone to solubilize (turbulence), biodegrade (aerobic), and volatilize LNAPL constituents from the submerged and overlying portions of the LNAPL body where airflow occurs. SVE also enhances aerobic biodegradation and volatilization of the LNAPL constituents from the vadose zone and collects vapors created by AS. AS or SVE can also be used individually if conditions are appropriate. A significant portion of the LNAPL depletion accomplished by AS/SVE is due to enhancement of aerobic biodegradation. Depletion of LNAPL in the vadose zone is enhanced by SVE because it can draw continuous LNAPL from the saturated zone into the vadose zone via capillary processes (wicking).
Biosparging/ bioventing	Similar processes to AS/SVE, except air/oxygen is injected more slowly with the main goal being stimulation of aerobic biological degradation of LNAPL in the saturated and unsaturated zones. Various configurations are possible including inducing airflow into the unsaturated zone by extraction of soil vapors.
In situ chemical oxidation	LNAPL is depleted by enhanced solubilization and chemical destruction through the addition of a chemical oxidant into the LNAPL zone (e.g., hydrogen peroxide and persulfate). Chemical oxidation typically requires the addition of catalysts, stabilizers, and/or activators to control the rates of oxidation. Oxidation reactions with LNAPL can be vigorous and require controls for off-gas, for example.
Enhanced anaerobic biodegradation	Enhanced anaerobic biodegradation involves supplying electron acceptors other than oxygen (e.g., nitrate and sulfate). Anaerobic biodegradation can also be achieved by increasing the subsurface temperature to increase natural biodegradation rates.
Natural source zone depletion (NSZD)	LNAPL is degraded via naturally occurring processes of biodegradation, volatilization, and dissolution. The predominant process is biodegradation, including direct LNAPL-contact biodegradation. LNAPL constituents dissolve, biodegrade, volatilize, solubilize in soil moisture, and also subsequently biodegrade in the vadose zone. Biodegradation produces gaseous products, such as methane and carbon dioxide and ultimately completely mineralize the LNAPL.
Activated carbon	Activated carbon with electron acceptors or chemical oxidants is injected or placed into excavations to enhance biodegradation or destruction processes. The activated carbon adsorbs organic compounds and provides a substrate for biomass growth. The added reagents support enhanced (aerobic or anaerobic) bioremediation or destruction by chemical oxidation.

LNAPL Technology	Description of Technology
Phytotechnology	Phytotechnologies use plants to remediate or contain contaminants in the soil, groundwater, surface water, or sediments. Phytoremediation is generally considered a phase-change technology, enhancing subsurface biodegradation, but, to a lesser extent, can also be considered mass control technology if designed for hydraulic control.
Physical or hydraulic containment	Subsurface barriers (e.g., sheet piles, French drain, slurry wall, groundwater extraction, trenches, and permeable absorptive barrier) are constructed to prevent, impede, or divert LNAPL migration. It is generally a mass control technology and does not significantly reduce LNAPL mass.
In situ soil mixing (stabilization)	LNAPL is immobilized by reducing the permeability of the LNAPL zone through in situ mixing of amendments (e.g., addition of bentonite clay or cement). In addition to reducing LNAPL mobility, it also reduces the leachability and volatility of the LNAPL constituents.
<i>Notes:</i> 1 – Enhanced aerobic biodegradation is not listed in this table separately because aerobic biodegradation occurs during many of the other technologies including all aeration methods and ISCO.	

Table 6-2. Summary information for LNAPL remediation technologies

[View Table 6-2 in Adobe PDF format.](#)

As shown on the upper right side of Figure 6-1 (modified from Figure 4-1), the technology selection process begins with a preliminary screening of LNAPL and site conditions as described in [Section 6.2](#). The user will first screen the technologies based on their potential to achieve the LNAPL remedial goals and objectives given the general site and LNAPL conditions. Table 6-3 rearranges the technologies by applicability to LNAPL goals and objectives. Leaving Section 6.2, the user will have a shortened (screened) list of technologies that have the potential to achieve the LNAPL remediation objectives, given the geologic conditions at the site.

Further evaluation of screened technologies is performed using [Section 6.3](#). Table 6-4 and the B-series tables in [Appendix A](#) list miscellaneous technology evaluation factors (including remedial timeframe, public concern, carbon footprint, and site use) that carry varying degrees of significance with respect to the site and to stakeholders in choosing a final technology to implement.

The final evaluation step is to select a technology based on engineering data requirements. [Section 6.4](#) and the C-series tables in [Appendix A](#) will assist the user in recognizing the critical site-specific requirements that must be evaluated, along with the Design and Performance LCSM, for selecting the final technology(ies) and establishing LNAPL remediation milestones and performance metrics.

Although it is beyond the scope of this document, technology implementation (i.e., construction and execution/operation) is important. First, even if the proper technology is selected, poor implementation will guarantee non-optimum performance and increase the likelihood of technology failure. It may not become apparent to stakeholders until later that implementation, not technology selection, was the reason for failure. Second, there is often more than one way to implement a technology (e.g., horizontal vs. vertical wells; constant vs. pulsed system operation). When dictated by site-specific needs, creativity and innovation by the environmental professional, contractors, and vendors are critical to remedial success.

6.2 Preliminary Technology Screening

This section describes a preliminary site-evaluation process to narrow the list of LNAPL remedial technologies (introduced in Tables 6-1 and 6-2). As illustrated in Figure 6-2, the screening process uses three steps to evaluate site-specific input parameters:

1. Consider LNAPL remedial goals and LNAPL remediation objectives to generate a reduced list of feasible LNAPL remedial technologies (see Table 6-3). Table 6-3 is a restatement of technologies from Table 6-2 in relation to remediation objectives and goals. This table has the advantage of providing the user with technology choices or alternatives to address specific concerns and is critical to screening technologies. Examples of possible

performance metrics are also provided.

The potentially applicable technologies listed in Table 6-3 are limited to those most likely to be selected from, in the opinion of the ITRC LNAPL Team. Other technologies may be conceptually applicable; however, they are considerably less likely to pass screening and are not listed.

2. Revisit the LCSM to collate data and, as necessary, collect additional site characterization data that will be used in Step 3 to screen out technologies that are not likely to be effective for the geologic and LNAPL conditions specific to the site being evaluated—and, in [Section 6.3](#), to further screen out technologies that are likely to be more difficult to implement due to other site-specific factors.
3. Take the results from Steps 1 and 2 and, using [Appendix A](#) tables, apply site-specific geologic and hydrogeologic characteristics to focus the list of applicable remedial technologies.

Each of these steps is described in more detail below.

Screening Step 1: Identify remedial goals and site/ LNAPL conditions to screen technologies using Table 6-3 (Section 6.2.1).

Table 6-3. Preliminary Screening Matrix

LNAPL remedial goal	LNAPL remediation objective	Technology group	LNAPL technology	Applicable Site Conditions			Example performance metrics (d)
				Geology (a)	Zone (b)	LNAPL type (c)	

Screening Step 2: Remedy Selection LCSM (Section 6.2.2)

Screening Step 3: Detailed screening of technologies with geologic factors in A-series Tables (Section 6.2.3)

Appendix A, Table A-XX.A.

Technology			
Remediation process	Physical mass recovery		
	Phase change		
	In situ destruction		
	Stabilization/ binding		
Objective applicability	LNAPL saturation		
		Example performance metrics	
	LNAPL composition		
		Example performance metrics	
Applicable LNAPL type			
Geologic factors	Unsaturated zone	Permeability	
		Grain size	
		Heterogeneity	
		Consolidation	
	Saturated zone	Permeability	
		Grain size	
		Heterogeneity	
		Consolidation	

Figure 6-2. Process overview of Steps 1 through 3.

Table 6-3. Preliminary screening matrix

6.2.1 Step 1: General Screening [▼Read more](#)

The screening process begins with the first (left) column of Table 6-3, which lists LNAPL remedial goals covering the typical spectrum of site-specific LNAPL concerns. The user should note that some remedial goals might have more than one LNAPL remediation objective (column 2), which means more than one technology can be utilized to achieve the identified remedial goal. The remediation objective is basically a restatement of the remedial goal in the context of remediation technology. The Technology group (column 3) describes the general method by which the remediation objective can be achieved. A suite of potentially applicable technologies (column 4) is associated with each LNAPL remediation objective. Applicable site conditions (columns 5, 6, and 7) assist in choosing a technology.

Repeat the procedures above for each applicable LNAPL remedial goal. You may find that some technologies already identified are capable of addressing more than one LNAPL objective. The LNAPL technologies that pass Step 1 will be further evaluated in Step 3.

6.2.2 Step 2: Refinement of the Remedy Selection LCSM [▼Read more](#)

The Initial LCSM that was developed through the application of questions in [Section 4](#) was sufficient for identification of LNAPL concerns developed in [Section 5](#). However, at this point, the user may find there is not enough information available from the assessment phase to continue the technology selection process. For example, it may be that the lateral extent of LNAPL is defined, but the vertical distribution is not. This is where the Remedy Selection LCSM becomes important, and the questions in [Section 4.4](#) should be answered. The key aspect of this step is to assess additional site-specific parameters to further screen technologies.

6.2.3 Step 3: Detailed Screening [▼Read more](#)

Screening Step 3 uses the A-series tables provided in [Appendix A](#) to further screen and eliminate technologies that fail after a more detailed assessment of technology-specific factors. For some technologies (e.g., excavation, some heating technologies), geologic factors do not affect the suitability of the technology; however, success for other technologies may depend significantly on certain geologic conditions being present at the site. For example, ISCO and enhanced anaerobic biodegradation may not be a primary technology choice when soils are impermeable or highly heterogeneous.

Technologies carried forward from Step 3 will be evaluated as explained in [Section 6.3](#) and [Section 6.4](#). If no remedial technology passes by this point, repeat the process for Step 1, but select a different LNAPL remedial goal. If no technology can be identified to achieve the required objective, consider discussing this outcome with the regulatory authority (see [Section 6.3.2](#)).

6.3 Technology Evaluation

After the user has completed [Section 6.2](#) and identified a list of technologies (at least two) that are applicable to the site, these technologies are further evaluated to identify which might be successfully implemented at the site. Preferences for specific remediation objectives may be apparent upon reviewing the list of applicable technologies. Alternatively, if the most suitable remediation objective is not apparent from [Section 6.2](#), then review of additional evaluation factors may clarify which remediation objective is best suited. Then the user can return to [Section 6.2](#) and complete the initial technology screening process.

6.3.1 Technology Evaluation Factors

Table 6-4 provides nine factors specific to LNAPL remediation to consider when selecting key evaluation factors for the project. Based on the LCSM and remediation objectives, identify a short list of factors (typically four to six) that are likely to be most relevant for technology selection. To ensure acceptance of the technology selection process, this set of factors should be selected in consultation with all of the site stakeholders.

Once a set of factors has been determined for the project, the B-series tables in [Appendix A](#) should be reviewed for the screened technologies from [Section 6.2](#). These factors should be considered for each technology in the short list to confirm that the technology is feasible for the project. Figure 6-3 provides an example of this evaluation process for excavation.

Table 6-4. Evaluation factors^(a).

Remedial timeframe	Defined	The timeframe by which the LNAPL remediation objective is to be met. The timeframe may be a regulatory or non-regulatory evaluation factor. Any one LNAPL remediation project may have different timeframes to meet different LNAPL remedial goals or remedial objectives.
	Impact	Holding all other variables the same, the shorter the timeframe, the more aggressive the effort required, which often increases costs. For a given technology, the time required to meet an end point increases with the size of the LNAPL body unless the remediation system scale increases. Increased permitting requirements for one technology over another increases the time that lapses before technology implementation. Increased infrastructure/site barriers commonly slow technology implementation because of the need to avoid infrastructure impacts and compensate for barriers.
Safety	Defined	Safety issues at a particular site that may present a particular challenge to a technology, and safety considerations unique or particular to a technology. This guidance presumes that all construction activities will be in compliance with Occupational Safety and Health Administration (OSHA) health and safety requirements, and that system operation will be within applicable regulations. In addition, it is presumed that any engineered technology has inherent basic safety issues, but the technology may involve the addition of electricity, heat, or chemicals that may pose a particular operational risk if applied at large field scale or in close proximity to workers or the public. Published accident rates for the construction or operational activities may suffice for screening.
	Impact	Safety considerations at urban and rural sites may be different or more intensive. At public access, non-restricted access facilities, it may be more difficult to reliably manage safety issues. Infrastructure issues may be more critical for certain technologies than others. Some technologies may produce waste streams or conditions that are particularly difficult to manage at a particular site or that potentially escalate quickly to a critical state.
Waste stream generation and management	Defined	Level of effort required to manage any waste stream from the remediation.
	Impact	Increased permitting generally increases the time before a technology can be deployed. Waste streams may be more toxic or more difficult to control than the parent LNAPL. Larger waste streams present more of a challenge for disposal or treatment and on-site management pending disposal or treatment.
Community concerns	Defined	Concerns expressed by the community, nearby homeowners, civic organizations, elected officials, or concerns that are likely to be expressed as the LNAPL remediation progresses.
	Impact	• The technology poses a particular societal risk. • The completion of the remediation causes more harm than good or renders a site less fit for active and productive use or reduces the existing level of ecological use. • The LNAPL remediation is applied to public lands possibly controlling the degree or timing of public participation or requiring additional permits (National Environmental Policy Act). • The remedy is not, or is not perceived to be, consistent with current and future planned land use, reducing property value or use. • LNAPL site is in close proximity to sensitive receptors. • LNAPL technology is particularly vulnerable to environmental justice considerations.
Environmental factors (carbon footprint/ energy requirements/ waste generation)	Defined	Resource (e.g. energy and water) usage and availability, and waste generation (amount, toxicity and treatment/disposal) options.
	Impact	• The energy usage or waste generated is disproportionate to other technologies. • An energy source is not reliably or amply available to power the technology as required. • Natural passive energy sources (solar, wind) can power the technology adequately.

Site restrictions	Defined	Physical, logistical, or legal obstacles to system deployment at the site (e.g., building locations, high-traffic areas, small property size, noise ordinances, site geology [e.g., depth to bedrock, presence of bedrock, depth to groundwater], or nearby sensitive receptors, such as schools, day cares, hospitals, etc.)
	Impact	Site restrictions and limitations impact the implementation of some technologies more than others, due to equipment size, degree of surface disruption, etc. At sites with more potential physical, logistical, or legal site restrictions, the physically larger, more “disruptive” technologies may be less feasible to implement.
LNAPL body size	Defined	The three-dimensional limits (volume distribution) of the LNAPL body.
	Impact	The larger the LNAPL body, the larger the scale of remedial effort required. The feasibility of some technologies may be limited to small-scale application, while others are more feasible for small- and large-scale application. Treatment of larger sites may be complicated by access limitations, physical barriers, cost constraints, or technology limitations.
Regulations and permits	Defined	Some technologies require specific permitting to deploy (e.g., underground injection control [UIC], air, waste management, remediation, maximum available air control technology [air emissions], or OSHA compliance).
	Impact	The greater degree of the permitting required for technology deployment, the higher the costs and more likely the delays to system deployment.
Cost	Defined	Monetary value of expenditures for supplies, services, labor, products, equipment, and other items purchased for both implementation and operational phases.
	Impact	Each technology has different costs, and those costs vary widely depending on the site conditions, inflation, and time it takes to remediate. Reasonably accurate planning-level cost estimates (+100%/-50%) would be required for each technology based on knowledge of the treatment area, key physical constraints, and unit cost rates. Design level costs (i.e., +30%) typically are not available at the screening stage. Consider capital costs vs. life cycle costs, even at the screening level. (AACE Cost Estimate classification system, https://web.aacei.org/resources/publications)
Other	Defined	(user defined)
	Impact	(user defined)
(a) These factors are used in the B-series tables in Appendix A. Some factors are weighted High, Moderate, or Low. “High” means the technology has high sensitivity or contribution to the factor. “Low” means the technology has low sensitivity or contribution to the factor.		

Short list feasibility evaluation (Section 6.3.1)

Determine evaluation factors to consider for the project from the list in Table 6-4.

Review those evaluation factors in the B-series Tables to determine feasibility of each technology in the short list.

Table 6-4. Evaluation factors

Remedial time frame	Defined	The time frame by which the LNAPL remedial objective...
	Impact	Holding all other variables the same, the shorter the time...
Safety	Defined	Safety issues at a particular site that may present...
	Impact	Safety considerations at urban and rural sites may be...
Waste stream generation/management	Defined	Level of effort required to manage any waste stream from...
	Impact	Increased permitting generally increases the time before...
Community concerns	Defined	Concerns expressed by the community, nearby homeowners
	Impact	- The technology poses a particular societal risk...
Carbon footprint/energy requirements	Defined	Source energy usage and carbon emission/greenhouse gas...
	Impact	-The energy usage or carbon emissions are disproportionate...
Site restrictions	Defined	Physical, logistical, or legal obstacles to system deployment
	Impact	Site restrictions and limitations impact the implementation
LNAPL body size	Defined	The three-dimensional limits (volume distribution) of the.
	Impact	The larger the LNAPL body, the larger the scale of remedial
Other regulations	Defined	Some technologies require specific permitting to deploy...
	Impact	The greater degree of the permitting required for...
Cost	Defined	Monetary value of expenditures for supplies, services,...
	Impact	
Other	Defined	
	Impact	

Table A-1.B. Evaluation factors for excavation

Remedial time frame	Concern	Low
	Discussion	Very short. The size of the LNAPL...
Safety	Concern	Moderate
	Discussion	Some potentially significant safety...
Waste management	Concern	Moderate to high
	Discussion	Significant waste stream may be...
Community concerns	Concern	Low to moderate
	Discussion	Public generally familiar with an...
Carbon footprint/energy requirements	Concern	High
	Discussion	Equipment emissions and...
Site restrictions	Concern	High
	Discussion	Disruptive technology. physical...
LNAPL body size	Concern	Small to moderate
	Discussion	Very large LNAPL bodies may be...
Other regulations	Concern	Low to moderate
	Discussion	Waste management characterization.
Cost	Concern	High
	Discussion	May be a high-cost alternative.
Other	Concern	
	Discussion	

Figure 6-3. Evaluation factors for determining feasibility of technologies: example for excavation.

6.3.2 Scenarios with No Feasible Remedial Options

At some sites, evaluation using the available remediation objectives and the selected key factors may result in elimination of all retained technologies. In these cases, the user either identifies additional technologies for evaluation, modifies the remedial goals so that one or more technologies are retained through the evaluation process, reconsiders the evaluation factors, and/or seeks guidance from the regulatory authority. For example, if no active LNAPL remediation technologies can achieve all of the remedial goals, then risk mitigation may need to be addressed through the use of controls (i.e., administrative, engineering, and/or institutional) in addition to or as an alternative to active remediation. Alternatively, one might consider a combination of technologies that might collectively achieve the goal.

6.4 Technology Selection, Implementation, and Evaluation

After one or more technologies have been evaluated through the processes described in [Section 6.3](#), minimum data requirements need to be defined to support the following:

- selecting the final technology,
- engineering the technology to meet remedial goals / remediation objectives, and
- evaluating remedial progress toward those goals.

This section describes these minimum data requirements. The C-series tables in [Appendix A](#) describe the data requirements for each technology in more detail, to the extent information is available. Coincidentally, the LCSM should again be reviewed to identify data gaps and the need for additional site data to further technology selection.

Information provided in this section does not replace the services of qualified professionals in the technology selection, engineering, and evaluation process. The information provided in this section is designed to support review of site-specific plans and indicate the types of data that are typically used for the required evaluations. Federal, state, and local requirements should be researched and understood by those individuals

implementing the technology selection and design.

When developing the minimum data requirements and critical considerations for a technology, the mode(s) of action should be considered. For example, multi-phase extraction can function as an LNAPL mass-recovery technology or a phase-change technology. Testing, design, and remedial performance and progress metrics should be developed to assess the mode(s) of action to be relied upon to reach remediation objectives and, ultimately, the remedial goals.

6.4.1 Design and Performance LCSM

Example performance metrics for the different objectives to identify what type of data are needed to evaluate performance for the chosen technology(ies) are provided in Table 6-3 (far right column). Together, the technology group and performance metrics columns (columns 3 and 8, Table 6-3) explain how the LNAPL can be addressed in the context of that objective and how achievement of the objective can be demonstrated. The performance metrics are different for the different LNAPL remediation objectives, but all measure progress toward the LNAPL remedial goal.

1. What are the conditions to be created by the selected technology(s) that will accelerate LNAPL depletion? [▼Read more](#)

The goal of implementing a technology is to change subsurface conditions to accelerate depletion of LNAPL beyond the natural rate of depletion (i.e., the rate of NSZD). As technology selection enters the design and performance phase, a detailed understanding of whether and how the remaining screened technology(ies) can maintain intended changes to subsurface conditions is the final check that the technology will be effective and implementable before full-scale installation and operation is undertaken.

For a remedial goal requiring a LNAPL mass recovery technology, one of the most important conditions to change is the LNAPL gradient toward the extraction point (e.g., well, trench, etc.). Using the LCSM already developed, consider where in the hydrostratigraphy (position relative to formation layering and the water table) it will be most effective to induce an LNAPL gradient. Inducing gradients in other fluid phases present in the same interval as the mobile LNAPL can enhance the LNAPL gradient. For example, when implementing vacuum-enhanced fluid recovery for a perched LNAPL body, it is most effective to focus the vacuum and soil vapor flow on the permeable layer containing the mobile LNAPL on top of the perching layer. Applying vacuum to and inducing soil vapor flow from layers underlying and/or overlying the mobile LNAPL will not directly enhance the LNAPL gradient.

For a remedial goal requiring a phase-change technology, conditions for which the technology is intended may include one or more of the following:

- increased air flow through the LNAPL zone to enhance depletion of volatile LNAPL constituents;
- increased oxygen concentration (in soil vapor and/or groundwater) in the LNAPL zone to enhance aerobic biodegradation of the LNAPL;
- groundwater flow through the LNAPL zone to enhance depletion of soluble LNAPL constituents;
- increased non-oxygen electron acceptor concentrations (e.g., nitrate or sulfate) in the LNAPL zone to enhance anaerobic biodegradation of the LNAPL; or
- increased temperature in the LNAPL zone to enhance volatility and solubility of LNAPL constituents as well as, up to moderate temperatures, microbial activity, and biodegradation rates.

The technology(ies) undergoing final screening (i.e., laboratory and/or pilot-scale testing) and design must be able to maintain the conditions intended to accelerate LNAPL depletion and should focus those conditions on the LNAPL zone or at least the target portion of the LNAPL zone. These conditions should be:

- the focus of laboratory and/or pilot-scale testing (this is also known as the primary failure criteria for technology testing);
- the main criteria for remedial design (for example, the criteria that determine well spacing); and
- the primary metric(s) of operational performance.

Using the existing LCSM to understand how geological heterogeneity and LNAPL distribution will complicate or simplify establishing and maintaining the intended conditions throughout the target zone is integral to this LCSM question.

2. What conditions will demonstrate the desired LNAPL changes? [▼Read more](#)

As the LNAPL is depleted, the LNAPL condition(s) in the subsurface will change. The conditions in the aqueous and vapor phases in and around the LNAPL may change too. Some of these changes will directly relate to the LNAPL remediation objectives and the LNAPL remediation endpoints. Some will relate indirectly. For example, when the remediation objective is reduction of LNAPL mobility, LNAPL transmissivity can provide a direct measure, and LNAPL saturation (soil concentration) may provide an indirect measure, of the mobility changes (which are also likely to be subject to a high degree of uncertainty).

The ability to measure changes in the LNAPL conditions targeted by remediation is central to demonstrating that:

1. remediation is changing the LNAPL as intended (e.g., reducing mobility or depleting a constituent of concern from the LNAPL);
2. the spatial extent of those changes is as intended;
3. the rate of those changes is as intended; and
4. remediation objectives are met and remediation endpoints achieved.

The changing LNAPL condition(s) are the performance metrics by which remedial progress is measured. During remediation, these performance metrics will confirm that the remedial technology selected is appropriate, given its site-specific effectiveness and implementability for the remediation objective. Further, these metrics will provide insight into whether the remedial design is sufficient to reach the intended remediation endpoints. If they indicate that the implemented technology is not likely to be sufficient to meet the remediation endpoints, then reevaluation of the LCSM and remedial technology selection decision may be warranted. However, the first step should be updating the LCSM with the operation and progress information gained from full-scale operation of the remedial technology. Reevaluation of the design using this updated LCSM may reveal that with design, installation, and/or operation modifications, the selected technology can accomplish the remediation objectives and meet the remediation endpoints.

The performance metrics of remedial progress will also be used to demonstrate that the remediation endpoints have been achieved. For some remedial technologies, “rebound” may occur after termination of activity. For example, groundwater concentrations may initially be reduced by ISCO and then increase again after all the oxidant is depleted. Similarly, while SVE is running, hydrocarbon concentrations in soil vapor may be low and then increase again after SVE is shut down. Remediation objectives and endpoints should be compared to these rebounded conditions to evaluate true progress and update the LCSM. Understanding the site-specific processes that will cause rebound and a remedial technology’s ability to mitigate those site-specific processes provides additional final technology screening, design, and performance information. Note also that those metrics typically subject to rebound, while simpler to measure, may be the most robust metrics available. In the preceding examples, a more robust metric might be leachability or volatility of LNAPL in soil samples. These would provide a more direct measure of the potential for the LNAPL zone to continue to act as a source for elevated concentrations of hydrocarbon in groundwater and/or soil vapor.

6.4.2 Minimum Data for Final Evaluation of Technology Suitability

The technology(ies) that are selected through the processes in [Sections 6.2](#) and [6.3](#) require final screening and site-specific testing to confirm the suitability of the technology to the site, the remediation objectives, and the remediation endpoints. It is important to conduct this screening and testing with several purposes in mind, including data collection for full-scale engineering design and site-specific technology testing. Even though considerable effort may have been exerted to get to the point of conducting a site-specific test, it is important to allow negative test results (if any) to prompt reconsideration of the LCSM, the technology, and/or the LNAPL remedial goals. That is, if a test result is unfavorable to the selected technology, then it may be necessary to conclude that the selected technology will not be able to achieve the LNAPL remediation objectives and reach the remediation endpoints.

The data collection and testing recommended should allow a 90% design cost estimate to be developed, which is an important step in evaluating the feasibility of a selected technology. Accurate costing for application of the selected remedial technology(ies) may provide a final discriminating factor between technologies or as a go/no-go point for a single

selected technology.

6.4.3 Site-Specific Data for Technology Evaluation

These basic data are likely to have been collected already as part of the technology selection process. For the most part, these are measurements of site-specific hydrogeological or LNAPL characteristics. The representativeness of the measured characteristics is a factor that should be carefully considered. For example, for the results of a pumping test to be relevant to the design of an MPE system, it should have been conducted in the area where the system will be implemented or in an area where the LCSM indicates that hydrogeologic conditions are similar. Similarly, the coincident effects of two technologies (e.g., air sparging and SVE) on each other need to be assessed; pilot testing each separately may not reveal their interaction. Use of non-representative data may lead to erroneous design calculations.

6.4.4 Bench-Scale Testing

Bench-scale testing of a remedial technology can be an important step toward evaluating feasibility. It can provide initial estimates of important data and parameters for engineering a remedial technology. In general, bench-scale tests are most useful when applied to investigate the feasibility of technologies in which reagent injection or biodegradation is a key element. For example, bench-scale testing of a chemical oxidant provides information about its effectiveness in destroying the target LNAPL constituents, allows estimates of the portion of the chemical oxidant required just to overcome the natural oxidant demand of the soil, and produces information regarding potential occurrence of unfavorable by-products. In this example, if the natural soil oxidant demand is very high, then feasibility of ISCO may be called into question because of cost and deliverability factors (while it may be hydraulically feasible to deliver the oxidant, the oxidant demand may be such that the oxidant is depleted before it reaches all the target LNAPL constituents).

6.4.5 Pilot Testing

Pilot testing a remedial technology provides data to evaluate field-scale application and remedial technology design. In many cases, a pilot test involves collecting more data (spatially and temporally) than during full-scale remediation. For example, SVE system pilot testing includes pressure and soil-vapor concentration observations at varying distances and directions to determine the ROI, which is then used to estimate the SVE well spacing. This expanded data set provides both a final feasibility step and important information for successful engineering, design, and operation of the selected technology. As mentioned in [Section 6.4.3](#), if two technologies will be implemented simultaneously in the same area, pilot testing of the combined remedy as it will be implemented is recommended.

Pilot testing is recommended for almost all technologies and can often be implemented as a portion of the full-scale design. It is important to gather data that allow evaluation of whether the technology will perform as expected and is capable of achieving the LNAPL remediation objectives. It is also important to consider what data are needed if computer models ([Section 6.4.6](#)) will be utilized later. If it does not perform as expected, the technology and its selection process should be carefully reevaluated, including updating the LCSM and acknowledging the infeasibility of the technology as warranted. While much effort and capital may have been invested in a selected technology to get it through pilot testing, one of the main reasons for pilot testing is to provide a final confirmation of the remedial approach before investing “full-scale” effort and capital. Ideally, the equipment installed for the pilot test (e.g., monitoring wells, injection wells) can be used as part of the full-scale system.

6.4.6 Applicable Models

In some cases, semi-analytical and/or numerical models are a useful technology evaluation tool. They may be used to assist in a feasibility study for a selected technology, engineering design of a remedial system, remedial progress evaluation, and/or development of metrics for technology application to the extent practicable. Models can be very powerful tools and give relevant insights into the application of a technology. They also have uncertainty, however, that is inherent in the simplifications necessary to implement modeling, such as simplification of the heterogeneity of the actual hydrogeologic system or simplification of LNAPL behavior. Recognition of this uncertainty and appropriate quantification, such as sensitivity studies, allows model results to be used to their fullest extent and, just as importantly, limit their use to what is reasonable. Care should be taken to calibrate the model against known site conditions and site data. Implementation of models, and in particular, implementation of numerical models for simulation of multiphase flow and behavior, is another area where relevant professional skills and experience are considered particularly important.

6.4.7 Engineering for Full-Scale Design

Full-scale design of the selected technology should consider the data and parameters developed during site investigation and bench- and pilot-scale technology testing. The data and parameters in this section of the C-series tables in [Appendix A](#) are crucial to a successful full-scale design. Professional expertise (skill and experience) is particularly critical at this stage.

As mentioned in [Section 6.1](#), technology implementation (i.e., construction and execution/operation) considerations become important at this point in the process. Practitioners should work with competent and trustworthy contractors and vendors.

6.4.8 Performance Metrics for Monitoring Operation and Remediation Progress

During full-scale operation of the selected remedial technology, monitoring both the operational performance of the technology and the progress of remedial efforts is necessary to determine the effectiveness of remediation. Thus, it is crucial to establish performance metrics for operations and remediation progress for each given technology prior to full-scale implementation. These metrics are necessary for demonstrating when a technology has been applied successfully, and/or to the extent practicable, evaluating progress toward remedial goals. See ASTM ([ASTM 2014b](#)) for additional performance metric examples.

Operational performance monitoring allows for efficient and optimized operation of the remedial system/technology. Careful monitoring of specific data (referred to here as operational performance metrics) during technology implementation is important for gauging whether the technology continues to perform as expected. For example, operational performance monitoring for a multi-phase extraction system would include monitoring parameters such as the flow rate, differential pressure and static pressure to verify that these parameters are within acceptable ranges previously determined during previous projects and pilot testing.

Performance metrics for remediation progress allow interpretation of the progress toward a remediation objective. If progress appears to be too slow, the design and operation of the remedial technology should be reevaluated, either throughout the site or in the portion of the site where performance is inadequate. For example, if the performance metric of LNAPL transmissivity at the downgradient edge of an LNAPL body does not demonstrate sufficient reduction in the LNAPL body's migration potential in one particular segment of the body front for an LNAPL skimming system, then additional skimming wells in that segment may be warranted. It is also possible that the segment contains a previously unrecognized preferential flow channel and that skimming will not work in that particular location. Performance metrics for remediation progress may also be useful in determining if and when the remediation objectives and remedial goals have been met. This skimmer example also highlights the importance of reevaluating the LCSM throughout the life of the remedial operations, particularly whenever unexpected data are observed (and results confirmed). A complete and up-to-date LCSM allows the best possible decisions about application and operation of remedial technology(ies) to be made. See ASTM ([ASTM 2014b](#)) for additional insights in updating the LCSM.

6.4.9 Evaluating the LCSM During Remediation

It is important to note that after implementation of a selected technology(ies), the LCSM should continue to be evaluated, particularly if the selected technology is not performing as anticipated and there are no mechanical or execution issues. The effects of remedial efforts on the subsurface (in general) and LNAPL concentrations (more specifically) should be monitored and recorded to confirm efforts are effective. For example, if ISCO fails to meet intended remediation objectives, it may be that unidentified geological conditions (e.g., lithology changes or fractures) or pockets of LNAPL are responsible. Additionally, data gathered from operations should be reviewed for abnormalities if the selected technology is not performing as anticipated, for example, if vacuum from SVE operations is not affecting a targeted area. If these types of situations develop and there is no apparent cause, it should be considered that the LCSM is incomplete or inaccurate and may need to be corrected before continuing.

6.4.10 References and Further Information

The technologies briefly described in this document have been more fully documented in other sources; some of these sources are listed in a later section of this document. After initial technology selection, it is strongly recommended that these additional sources, as well as others that are available (or become available after this document is published), be consulted. This process will allow the practitioner and regulator to develop a good, working understanding of the technology so that the most appropriate decisions for application of the LNAPL remedial technology can be made.



Appendix A-LNAPL Technologies Appendix

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[Table A-1-B. Evaluation factors for Excavation](#)

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Skimming A-2

[Table A-2-A. Skimming](#)

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Vacuum Enhanced Skimming A-3

[Table A-3-A. Vacuum Enhanced Skimming](#)

[Table A-3-B. Evaluation factors for Vacuum Enhanced Skimming](#)

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[Table A-3. Illustrations](#)

Total Fluid Extraction A-4

[Table A-4-A. Total Fluid Extraction](#)

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[Table A-5-A. Multi-Phase Extraction](#)

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[Table A-6-B. Evaluation factors for Water Flooding](#)

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[Table A-7-B. Evaluation factors for SESR](#)

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Steam Injection A-9

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Thermal Conduction Heating A-10

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[Table A-11-A. Electrical Resistance Heating](#)

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Appendix B-Natural Source Zone Depletion (NSZD) Appendix

Executive Summary

Numerous sites across the country are impacted with light, nonaqueous-phase liquids (LNAPL). LNAPL Natural Source Zone Depletion (NSZD) occurs through the combined action of natural processes that reduce the mass of LNAPL in the subsurface. Key NSZD processes include volatilization, dissolution, and biodegradation; these processes reduce LNAPL mass, saturation, and mobility over time. NSZD rates (i.e., the rates of bulk LNAPL mass depletion) are often higher than historically acknowledged.

This document updates and supersedes earlier ITRC guidance on NSZD ([ITRC 2009b](#)), reflecting advances in the intervening years in understanding NSZD mechanisms (including direct biodegradation of LNAPL) and methods to confirm the occurrence and/or quantify the rate of NSZD. This appendix discusses key mechanisms and several frequently-used NSZD assessment methods, including:

- The **gradient method**, based on soil gas composition,
- **Carbon dioxide flux based-methods**, including CO₂ traps and flux chambers, and
- The **biogenic heat monitoring method**.

This appendix discusses the importance of incorporating NSZD into the three stages of the LNAPL Conceptual Site Model (LCSM) development process (the Initial LCSM, Remedy Selection LCSM, and Design and Performance LCSM). NSZD is a fundamental aspect of understanding issues such as LNAPL mobility, distribution, and longevity, and thus is a key part of the Initial LCSM. In later LCSM stages, NSZD can be evaluated as a remedial alternative, with NSZD serving in one or more of the following roles:

- A **baseline** to evaluate the relative benefit of other technologies (e.g., by comparing an LNAPL skimming system's removal rates to NSZD rates);
- A **stand-alone remedy** at sites where LNAPL-related impacts are stable, potential receptors are not at risk, and NSZD timeframes are consistent with the goals of the site owner and with regulatory requirements;
- A **component of a remedy**, where NSZD is primary remedy component for portions of the LNAPL zone, and engineered remediation systems are focused on those portions of the LNAPL footprint where more aggressive removal is appropriate to meet remedial goals; and
- A final step in a treatment train, where there is **remedy transition** to NSZD as a long-term risk management approach after other remedial technologies have achieved their design objectives.

NSZD is an underlying driver of progress toward remedial goals at almost all LNAPL sites, through reductions in LNAPL mobility and LNAPL body longevity, and changes in LNAPL composition. Research continues into developing and refining methods to confirm NSZD activity and quantify NSZD rates.

1.0 Introduction

Numerous sites across the country are impacted with light, nonaqueous-phase liquids (LNAPL). LNAPL Natural Source Zone Depletion (NSZD) occurs through the combined action of natural processes that reduce the mass of LNAPL in the subsurface. Key processes include volatilization, dissolution, and biodegradation. At LNAPL release sites where LNAPL still exists, NSZD over time depletes LNAPL mass and reduces LNAPL saturation and mobility.

This document provides a technical overview of NSZD for LNAPL and the methods by which rates can be measured. The NSZD rate, when appropriately assessed, can serve as an objective benchmark to compare the relative effectiveness of different remedial alternatives, a metric to gauge the declining performance of active remediation systems, and the basis for consideration of NSZD as a remedy. It is assumed that the NSZD evaluation process described herein is conducted within the framework of the overarching LNAPL site management process described in the main body of the ITRC report ("the parent document").

This document reflects the tremendous advances that have occurred in understanding and measuring NSZD in the intervening years, which have resulted in a shift in the conceptualization of NSZD, moving away from an emphasis on processes exhibited through electron acceptors and lateral groundwater transport, toward a fuller appreciation of the importance of methanogenesis, direct biodegradation of LNAPL, and vadose zone transport of biogenic gases. As this new conceptual model has been embraced, it has become evident that the rate of LNAPL depletion had historically been greatly underestimated ([Garg et al. 2017](#)).

1.1 LNAPL Source Zones

“LNAPL” is a term given to an organic compound that is immiscible with, and lighter than, water (e.g., crude oil, gasoline, diesel fuel, heating oil). When an LNAPL is released to the subsurface, it can migrate downward and laterally. The resulting LNAPL distribution depends on lithology and soil properties (such as grain size, porosity, and water saturation), LNAPL properties (such as viscosity), and the LNAPL release volume and head.

Small LNAPL releases may become trapped in the soil pores as an immobile, residual phase before it is able to reach the water table. Larger LNAPL releases may migrate to the water table while leaving immobile, residual LNAPL along the migration path. At the water table, LNAPL can accumulate and spread across the surface of the saturated zone in all directions, partially influenced by the direction of decreasing hydraulic gradient. The constituents, or chemicals, that compose the LNAPL may be removed over time by various mechanisms, such as sorption, volatilization, dissolution, and direct biodegradation. The LNAPL “body” can function as a potentially long-lived source of secondary impacts to adjacent soil, soil gas, and groundwater. This document refers to such an LNAPL body as a “source zone.” Figure NSZD-1 shows an example LNAPL source zone in cross section. The portion of the source zone in the unsaturated zone is referred to as the unsaturated (or exposed) source zone. The portion of the source zone in the groundwater-saturated zone or below the water table is referred to as the saturated (or submerged) source zone.

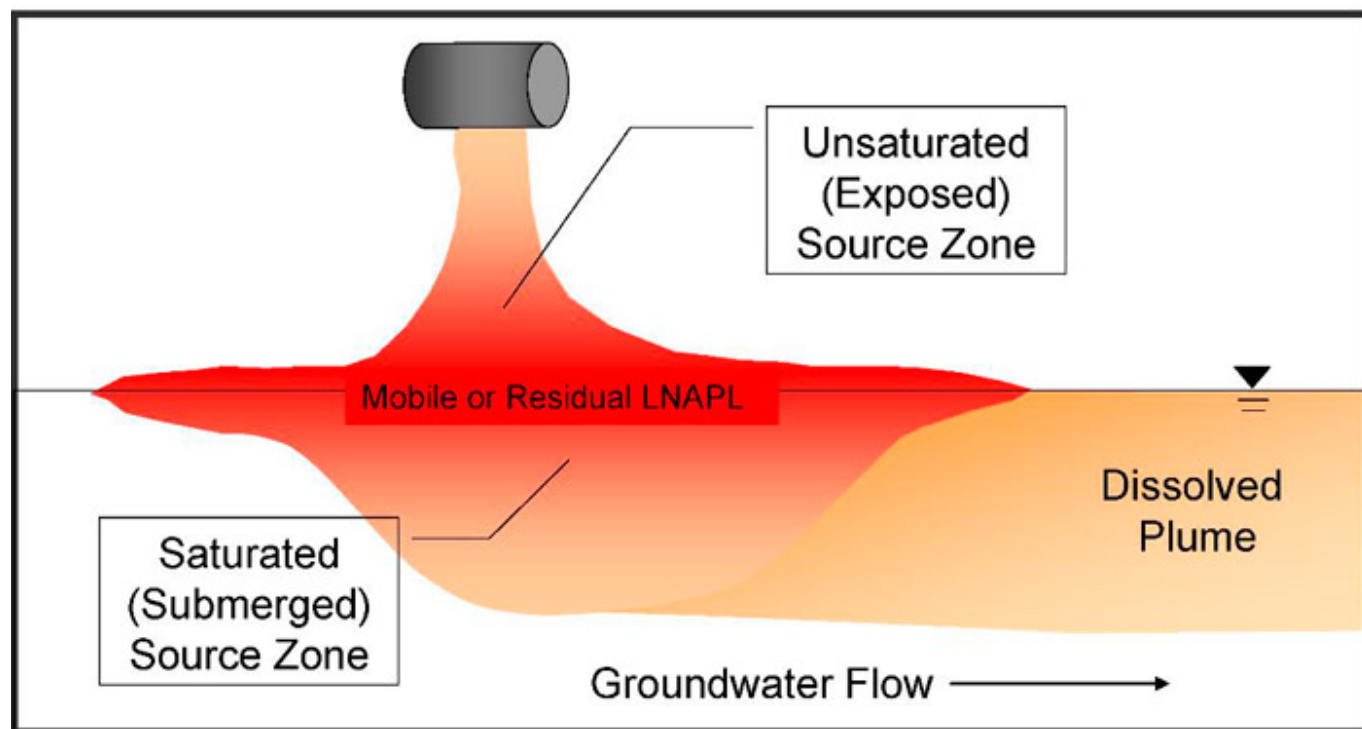


Figure NSZD-1. Example LNAPL source zone.

1.2 Natural Source Zone Depletion

The naturally occurring processes of partitioning and biodegradation result in mass loss from the LNAPL source zone. This document addresses several questions associated with NSZD:

- What are the processes involved in NSZD?
- How can the NSZD rate be measured, and what are typical NSZD rates?
- What are the long-term implications of NSZD on LNAPL source zone longevity and composition?

2.0 NSZD Processes and Theory

Once released into the subsurface, hydrocarbon constituents in LNAPL undergo various processes that reduce the total LNAPL mass. LNAPL NSZD occurs when certain processes act to (a) physically redistribute (partition) LNAPL components to the mineral, aqueous and gaseous phases and (b) biologically break down NAPL components. Specifically, these processes involve: i) sorption onto subsurface solids; ii) dissolution of LNAPL constituents into pore water; iii) volatilization of LNAPL constituents into the vadose zone; and iv) biodegradation of LNAPL constituents within the LNAPL body and adjacent vadose and saturated zones.

At the core of NSZD are the biodegradation processes described in this section. The ways that these reactions determine LNAPL fate and transport in the vadose zone and the groundwater (saturated zone) are addressed in separate subsections.

2.1 Biogeochemical Principles

The biodegradation of petroleum is an oxidation process (releases electrons). Microbes couple such electron-generating reactions to electron-accepting (reduction) reactions. Reduction reactants are known as terminal electron acceptors (TEAs). Where multiple TEAs are available in soil, thermodynamic considerations favor microbial use of the TEAs that generate more energy, starting with oxygen ([Bethke et al. 2011](#)). This concept is known as the electron acceptor ladder. This concept is illustrated in Figure NSZD-2, which shows the electron potential (pE), a thermodynamic property of the electron acceptors related to their ability to accept electrons ([Stumm and Morgan 1981](#)).

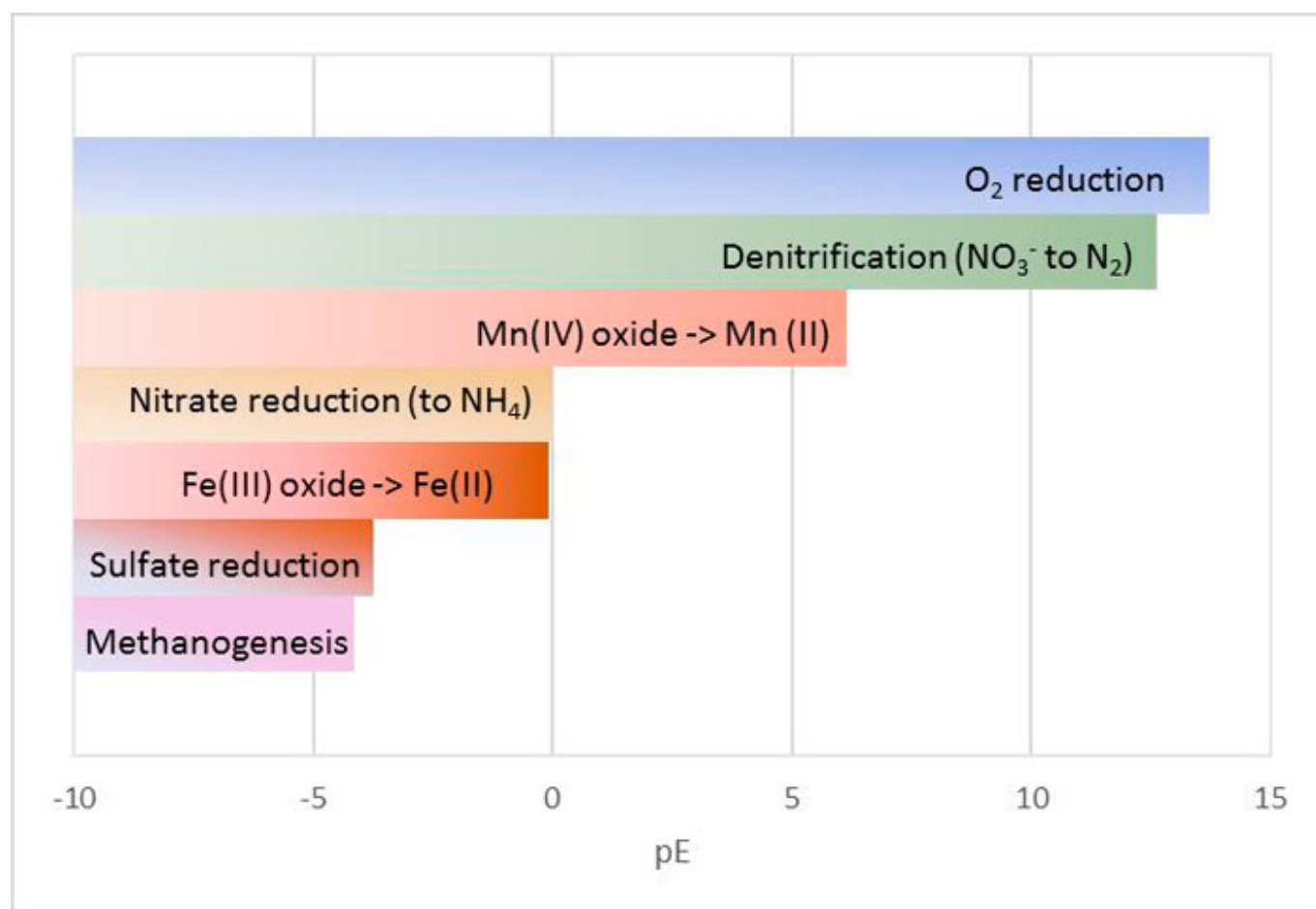


Figure NSZD-2. Electron acceptor ladder.

The sequence of reactions shown in Figure NSZD-2 is determined by how much energy is derived from each of these processes. To the extent possible, microorganisms will follow oxidation processes in the order of decreasing energy gain. For example, if oxygen is present, it will likely be used first, as it is more energetically favorable. This is known as aerobic biodegradation. However, while oxygen is present in ambient air, it can be scarce in the subsurface, so aerobic biodegradation is often limited to shallow depths or fringe areas of the plume where recharge occurs.

Following the concept of the electron acceptor ladder, as oxygen is depleted, microbes sequentially shift to nitrate, then to

manganese and iron oxides, and then sulfate as TEAs (Figure NSZD-2). These TEAs might be initially available in limited amounts in all soils and/or groundwater. The oxidation of petroleum (the reaction coupled to the TEA reduction) produces CO_2 . As the LNAPL spill weathers and TEAs are consumed, they are depleted at the contaminant source, and these TEA-based processes rely on the influx of additional TEAs. Concentration gradients across these geochemical zones are often observable in the dissolved contaminant plume (groundwater surrounding the source, for example see ([Lovley, Chapelle, and Woodward 1994](#)), and vadose zone (e.g., ([Sihota et al. 2016](#))). Zones where different geochemical processes occur sometimes overlap (for example methanogenic and sulfate-reducing conditions might co-exist) [([Bethke et al. 2011](#)); ([Irrianni-Renno et al. 2016](#))]. See [Section 2.3.2](#) for more details on the TEA processes and the associated mass losses of petroleum hydrocarbons.

Methanogenesis lies near the bottom of the electron acceptor ladder, since it generates relatively little energy compared to reactions driven by other TEAs. While the implication is that methanogenesis occurs after other TEAs have been depleted, this does not necessarily mean that the rate of methanogenesis will be slow nor that it rarely occurs. To the contrary, methanogenic zones are common in LNAPL source zones, methanogenesis is increasingly acknowledged as a dominant NSZD process ([Garg et al. 2017](#)), and the fate of biogas that it generates can be a significant aspect of NSZD assessment. The biogases that methanogenesis produces include methane and carbon dioxide (CH_4 and CO_2 , respectively). See [Section 2.3.3](#) for more details on methanogenesis and the associated mass losses of petroleum hydrocarbons.

2.2 NSZD Processes Expressed Through Vertical Gas Transport

As generally depicted in Figure NSZD-3, the overall NSZD processes expressed primarily via vertical gas transport involve:

- volatilization of LNAPL (early stage sites where there is petroleum hydrocarbon with high volatility);
- shallow aerobic biodegradation of petroleum hydrocarbons, resulting in the consumption of O_2 and production of CO_2 ;
- methanogenesis of petroleum hydrocarbons in the anaerobic portion of the saturated, capillary or vadose zones, resulting in the production and vertical transport of CH_4 and, to a lesser extent, CO_2 ;
- aerobic oxidation of CH_4 produced from methanogenesis, resulting in the consumption of O_2 and production of CO_2 ; and
- transport of gases via diffusion, advection and ebullition from the saturated zone.

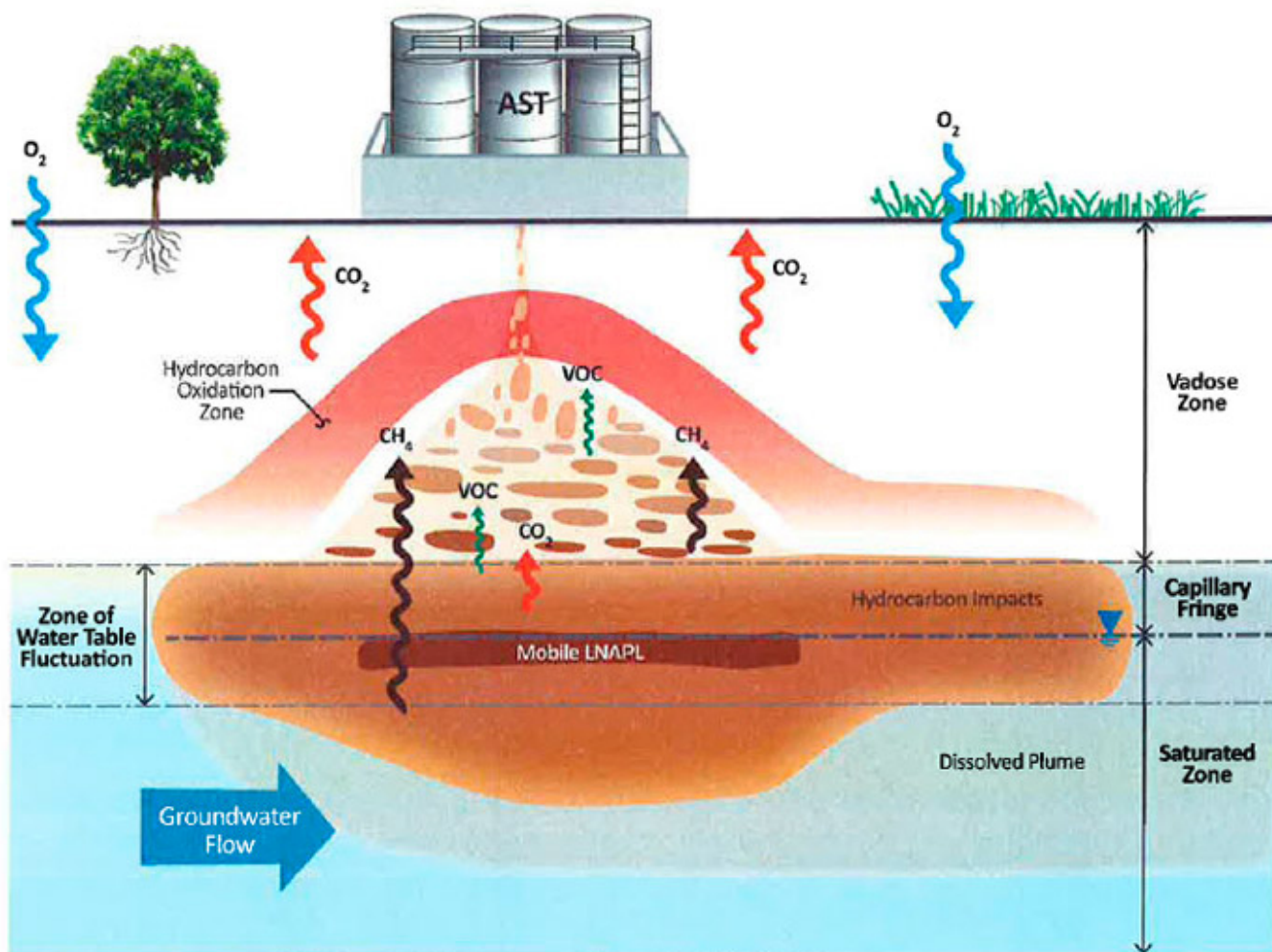


Figure NSZD-3. Vapor transport-related NSZD processes (API 2017).

2.2.1 Volatilization

LNAPL source mass within the vadose zone is subject to redistribution as soil gas due to volatilization of hydrocarbon constituents. These constituents will volatilize into soil vapor based on their mole fraction and pure chemical vapor pressure. Volatilization of hydrocarbon constituents is most important for lighter molecular weight releases such as gasoline or lighter crude oil fractions and early time after a release into the environment, and becomes a less significant process as the LNAPL ages and the fraction of the most volatile components in the LNAPL becomes smaller.

By-products of NSZD processes are present both in groundwater and the vadose zone. In many cases, it may be appropriate to focus NSZD rate measurements on the vertical, soil gas flux processes because of their dominance of the total NSZD rate. For example, a study at the former Guadalupe oil field in California showed that LNAPL mass loss expressed through changes in aqueous phase geochemistry were two orders of magnitude lower than loss expressed through gas flux ([Johnson, Lundegard, and Liu 2006](#)).

2.2.2 Gas Transport Processes

With diffusion, volatile constituents or gaseous biodegradation byproducts move from areas of higher concentration to areas of lower concentration. Oxygen utilized in aerobic biodegradation moves from the atmosphere at ground surface to the depth of biodegradation. In contrast, LNAPL constituent vapors or soil gases preferentially migrate from subsurface contaminant source areas towards the ground surface and atmosphere. Migration of these gases via diffusion is driven by concentration gradients. Diffusion is a function of a constituent's air diffusion coefficient and the air-filled porosity of the soil, and it is faster in soils with more air-filled effective porosity, such as sand with low moisture content. The rate of aerobic biodegradation (e.g., methane oxidation) is predominantly a function of diffusive O₂ flux through the soil.

Advection is the movement of bulk soil gas from areas of higher pressure to areas of lower pressure due to the presence of a pressure gradient. For NSZD, advection may become important when the rate of gas generation from methanogenic

biodegradation (CH_4 and CO_2) is high. Research is ongoing on the relative contribution of advection, however results to date suggest most systems to be diffusion dominated. Studies at the National Crude Oil Spill Fate and Natural Attenuation Research Site near Bemidji, Minnesota, show that for a crude oil release exhibiting an NSZD rate of approximately 1,500 gallons per acre-year ([Sihota and Mayer 2011](#)), advection was responsible for approximately 15 percent of the net flux of methane ([Molins et al. 2010](#)). All other factors being equal, higher NSZD rates (and higher rates of biogenic gas production) would result in a greater advective contribution to biogenic gas flux. Advection of biogenic gasses in the vadose zone can be assessed by measuring nitrogen, argon and/or pressure differentials in soil gas ([Amos et al. 2005](#)).

If methanogenesis occurs in the capillary fringe, then advective transport conditions could develop at the base of the vadose zone. Additionally, if methanogenesis is occurring in the saturated zone then, after the groundwater becomes super-saturated with gas, bubble formation will occur that could lead to gas transport to the vadose zone ([Amos et al. 2005](#)). Bubble formation is termed degassing. Bubble transport of gas from groundwater to the vadose zone is termed ebullition and occurs episodically ([Sihota et al. 2013](#)) along fractures in the soil. Relatively thin soil layers with different soil properties (e.g., a layer of silty soil in medium-grained sand) can have a significant effect on the transport of vapors through unsaturated soils.

Simultaneously to this biogas transport process, oxygen diffuses downward from the atmosphere, and meets the upward migration of methane and petroleum hydrocarbon vapors (if present), creating a hydrocarbon oxidation zone (also termed a methanotrophic zone for the scenario of methane oxidation or the aerobic/anaerobic interface) that produces CO_2 and heat [([Sweeney and Ririe 2014](#)); ([Warren and Bekins 2015](#))] according to the overall reaction shown in Equation NSZD-2-1.



The location of the oxidation zone is controlled by the ingress of O_2 through the ground surface and soil and the gas transport of upward-diffusing VOCs and/or methane (from the methanogenic zone).

2.3 NSZD Processes Expressed Through Lateral Groundwater Transport

Source zone mass is lost as the dissolved-phase constituents and biodegradation by-products leave the source zone via groundwater transport. Figure NSZD-4 depicts the basic elements of NSZD in the saturated source zone including dissolution and biodegradation mass depletion processes that result in changes in groundwater concentrations. Although biodegradation processes in the saturated zone also result in gaseous by-products they are not shown here for simplicity.

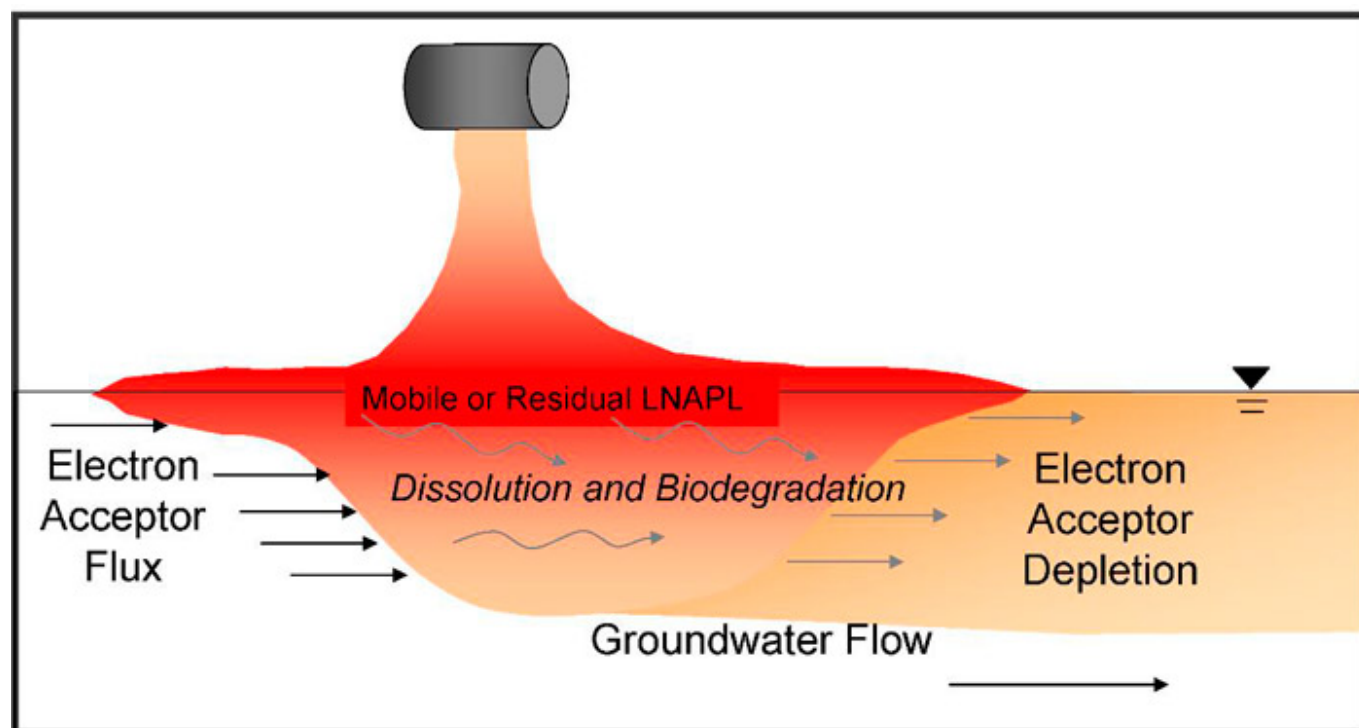


Figure NSZD-4. Groundwater transport-related NSZD processes.

Overall, NSZD processes expressed via lateral groundwater transport involve:

- Dissolution of petroleum constituents in the saturated zone. (Dissolution in this discussion is conceptualized as a saturated zone process, however, it is noted that dissolution can also occur in pore water within the unsaturated zone.)
- Biodegradation via dissolved electron acceptors, resulting in the depletion of oxygen (O₂), nitrate (NO₃), manganese (Mn⁴⁺), ferric iron (Fe³⁺), and sulfate (SO₄²⁻). These reactions result in the production of carbon dioxide (CO₂), as well as the reduced forms of these electron acceptors.
- Biodegradation generally proceeds down the electron acceptor ladder (see Figure NSZD-2) to methanogenesis, resulting in the production of CH₄ and, to a lesser extent, CO₂.
- Significantly smaller mass loss is expressed through changes in groundwater geochemistry and lateral transport than expressed through vapor-phase changes and vertical gas transport.

2.3.1 Dissolution

Portions of source zones that are submerged or in contact with pore water in general are subject to dissolution of LNAPL constituents into groundwater according to the constituents' aqueous solubility. "Effective solubility" represents the maximum equilibrium concentration of a constituent from a multicomponent NAPL mixture in groundwater at a specific temperature and pressure (EPA 1995). Effective solubility (S_i^e) of an individual NAPL constituent is a product of its mole fraction in the NAPL (X_i) and solubility of the constituents in its pure phase (S_i):

$$S_i^e = X_i S_i \quad [\text{Eq. NSZD-2-2}]$$

(Zemo et al. 2013) reported average theoretical effective solubilities of gasoline and diesel, as well as averages from several studies by other authors. Other studies reporting effective solubility estimates for gasoline include, (EPA 1996) and (Falta, Ahsanuzzaman, and Wilson 2012). In some cases, it may be appropriate to determine a site-specific effective solubility value of actual on-site LNAPL using standard test methods (e.g., ASTM Standard E1148) and Equation NSZD-2-2.

While dissolution facilitates NSZD, it is not an absolute prerequisite to biotic LNAPL mass depletion processes (see Section 2.4).

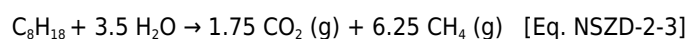
2.3.2 Biodegradation: Dissolved Electron Acceptors in the Saturated Zone

As groundwater flows through the submerged source zone, petroleum hydrocarbon constituents dissolve into the groundwater, where they are available for biodegradation. Biodegradation of dissolved petroleum hydrocarbon plumes in groundwater by naturally-occurring microbial populations has been well documented. This biodegradation in the saturated zone is reflected in spatial changes in concentrations of dissolved electron acceptors and dissolved biodegradation by-products. The magnitude of mass loss from these various biodegradation reactions can be determined through monitoring of corresponding changes in groundwater chemistry. Procedures for estimating mass loss expressed through changes in groundwater chemistry are specified in existing guidance documents [(ITRC 2009b) and (NRC 2000)].

Regarding Figure NSZD-4, it is important to acknowledge that not all reaction by-products will remain soluble and leave the source zone. Some reduced by-products will react with soil minerals and create solids. For example, (Ng et al. 2015) found that 91% of iron reduction may not be detected in dissolved phase; the dissolved ferrous iron by-product from biodegradation reacted with naturally occurring sulfur to create iron sulfide solids. Therefore, the estimates of the portion of NSZD as manifested as changes in the aqueous phase using results of groundwater sampling and analysis may underestimate the mass losses.

2.3.3 Biodegradation: Methanogenesis

At sites under anaerobic conditions, methanogenic microorganisms facilitate the degradation of hydrocarbons (e.g., octane C₈H₁₈) to create CO₂ and CH₄, as seen in Equation NSZD-2-3 below.



The soluble portions of the biodegradation byproducts migrate away from the source with groundwater flow, while the remainder of the CO₂ and CH₄ partition and transport into the unsaturated phase (vadose zone). Methanogenesis is not limited by external electron acceptors, unlike other anaerobic biodegradation reactions, but may be limited by hydrogen, acetate buildup, availability of nutrients, or temperature [(Wilson, Hers, and Jourabchi 2016) and (Zeman et al. 2014)].

Based on studies of the Bemidji and Guadalupe oil field sites, methanogenesis was demonstrated to be an important NSZD process.

2.4 Direct Biodegradation of LNAPL

Biodegradation of LNAPL source zones via microbial activity in the aqueous phase and vapor phase has been thoroughly described and documented in the technical literature. Although it is commonly assumed that biodegradation or mineralization of source zone constituent mass is limited by the rate of partitioning from the LNAPL to aqueous phase, direct biodegradation of the nonaqueous phase in the subsurface is becoming increasingly recognized as an important NSZD process.

A carefully constructed mass balance on the crude oil released at the National Crude Oil Spill Fate and Natural Attenuation Research Site near Bemidji, Minnesota, by (Ng et al. 2014) pointed to an important gap in the CH₄ and CO₂ mass balance at the site. The conventional conceptual model, where hydrocarbon constituents must be dissolved in groundwater before they can biodegrade, was unable to explain the magnitude of the measured carbon surface efflux from the LNAPL in the source zone. A new component of the conceptual model was proposed, *“Direct outgassing of CH₄ and CO₂ produced from oil constituents that degrade within the pore space adjacent to the entrapped oil (outgassing mechanism).”*

The direct outgassing process involved low solubility compounds (e.g., alkanes) that biodegraded within the LNAPL body “without an intermediate aqueous phase.” Numerical reactive transport modelling of the LNAPL body at Bemidji, (Ng et al. 2014)

) showed direct outgassing was a critical part of the site model, with about 70% of carbon loss from the oil attributed to direct outgassing. In a follow-up paper, (Ng et al. 2015) concluded that: *“These mass balance results suggest a conceptual framework in which some patches of the oil body are relatively isolated from the flow system, thereby allowing oil-contact biodegradation of low solubility degradable oil constituents, with most biodegradation products (CH₄) directly outgassing without first entering aqueous solution.”*

Other researchers have investigated the mechanisms for non-aqueous phase biodegradation processes and its application to NSZD. (Ng et al. 2014) cited work by (Meckenstock et al. 2014) who observed high rates of biodegradation in a bulk oil body that contained minuscule water droplets only 1 to 3 uL in size. (Hua and Wang 2014) described very low solubility NAPL phase hydrocarbons that were pseudosolubilized by biosurfactants, and microorganisms that grow in fatty acids and therefore are not in the water phase. The direct outgassing concept is now emerging in the NSZD community; (Garg et al. 2017) described how biodegradation of oil constituents could occur without solubilization into bulk groundwater in a 2017 review paper of NSZD processes and controls.

3.0 Incorporating NSZD into the LNAPL Site Management Process

This section provides an overview of how NSZD concepts fit within the overall evaluation and management of LNAPL sites. NSZD assessments can be conducted at differing levels of complexity and accuracy, and on a range of time scales, based on the stage of the project and the nature of the LCSM.

3.1 NSZD and the LNAPL Conceptual Site Model

As site stakeholders develop an LNAPL Conceptual Site Model (LCSM) in accordance with the guidance in [Section 4](#) of the parent document, the LCSM will typically progress through a series of stages and likely revisions. The initial LCSM will characterize LNAPL concerns and identify drivers for further action, if any. This initial LCSM will evolve into a Remedy Selection LCSM that, based on those drivers, informs selection of a remedial technology (or technologies). Next, a Design and Performance LCSM will guide remedy implementation and performance monitoring until overall remedial objectives have been reached.

NSZD assessment informs the LCSM, but also depends on the overall LCSM for accuracy and representativeness. For example, accurate interpretations of the extent of the overall LNAPL body (including residual LNAPL), the extent and aerobic/anaerobic nature of the vadose zone, and the magnitude of seasonal groundwater fluctuation can be helpful in interpreting the representativeness of individual NSZD measurements relative to a site-wide, annualized degradation rate. Other LCSM components and considerations pertinent to NSZD processes and measurements are covered elsewhere ([API 2017](#)).

NSZD assessments can involve varying degrees of complexity, and a range of data quality objectives, in a manner parallel

with the evolution and maturation of the LCSM—as illustrated in Figure NSZD-5. Early in the LCSM development and site management process, a screening-level NSZD assessment can confirm that NSZD is active and provide evidence supporting overall stability of the LNAPL body. LNAPL mass loss via NSZD can act to offset/balance the spreading effects caused by localized accumulations of LNAPL/elevated LNAPL saturation and pressure heads. Even though high LNAPL saturations in the release area may cause LNAPL migration laterally toward the periphery of the LNAPL zone, depletion processes concurrently act to reduce LNAPL mass and diminish saturations, thereby balancing the movement ([Mahler, Sale, and Lyverse 2012](#)). A qualitative, screening-level NSZD assessment may be all that is needed over the course of the LCSM development (e.g., when NSZD supports continue mass depletion in a risk-based program).

[View Figure NSZD-5 in Adobe PDF format.](#)

Figure NSZD-5. NSZD-LCSM relationship.

In the later stages of LCSM development, more quantitative or spatial- and time-integrated NSZD assessments may be used to evaluate the relative benefit of remedial options, to track performance of NSZD relative to other components of a remedial strategy, and to confirm that NSZD continues to contribute to plume stability or contraction. This range of objectives is discussed in the following section.

3.2 Data Quality Objectives for NSZD Assessment

As described in [Section 3.1](#), the role of NSZD assessment in the overall LCSM may vary significantly over the course of a project. Correspondingly, NSZD assessments may target a range of data quality objectives, depending on the anticipated role of the results in the refinement of the LCSM and selection or implementation of remedies.

As depicted on Figure NSZD-6, at the initial stage of a project, NSZD assessment may simply seek to verify that NSZD processes are active and are a potentially viable component of a future site strategy. Data regarding geochemistry, vadose zone characteristics, or hydrogeology may support an understanding of NSZD as well as other aspects of the LCSM. In this case, the objectives of data collection would be focused on verifying that NSZD is contributing to site remediation progress, rather than quantifying that contribution. As an example, an initial assessment may include:

- field-screening of soil gas composition from existing monitoring wells screened across the water table to identify areas of elevated methane or carbon dioxide and depleted oxygen [([Sweeney and Ririe 2017](#)) and ([Jewell and Wilson 2011](#))];
- groundwater sampling to identify areas of increased dissolved-phase hydrocarbons, dissolved iron, manganese, methane, and carbon dioxide, and decreased dissolved oxygen, sulfate, and/or nitrate;
- one-time or “snapshot” measurements of carbon dioxide soil gas flux to identify elevated flux within LNAPL-impacted areas; or
- one-time or “snapshot” vertical profiles of temperatures in existing monitoring wells (spanning both the vadose and saturated zones) to identify biogenic heat contributions within LNAPL-impacted areas.

At sites with extensive investigation and monitoring histories, substantial data for some of these assessment methods may already be available, or additional data could possibly be collected relatively quickly using existing monitoring wells. When a quantitative, time- and/or spatial-integrated NSZD estimate is desired—for example, when evaluating seasonal variability of NSZD rates or comparing NSZD contributions to active recovery measures—data quality objectives may dictate different investigation methods or different temporal applications of measurement methods.

Following completion of the remedy selection and implementation, and transition to a performance LCSM, a different approach to NSZD monitoring could be appropriate. This could include periodic monitoring of CO₂ flux, temperature, soil gas composition, or other indicators of NSZD on an annual, biannual, or similar basis, at a small number of representative locations to confirm that NSZD processes remain active and consistent with previous measurements.

Overall, whether the project and LCSM are in an initial stage, a data-intensive remedy selection and implementation stage, or a later performance monitoring stage, the selection of assessment methods should be guided by the LCSM. In many cases, not all methods might be viable—for example, sites covered by concrete might not follow a simple, vertical gas and heat transport model assumed by most of the NSZD quantitation methods. The data quality objectives for each stage of the assessment should be identified before field work is planned, and appropriate to answer the key questions (e.g., verifying NSZD activity, accurately measuring rates, or confirming long-term sustainability of NSZD processes) that are relevant to the project at the time of assessment.

Additional information on data quality objectives for NSZD assessments may be found in the recent American Petroleum Institute guidance document ([API 2017](#)).

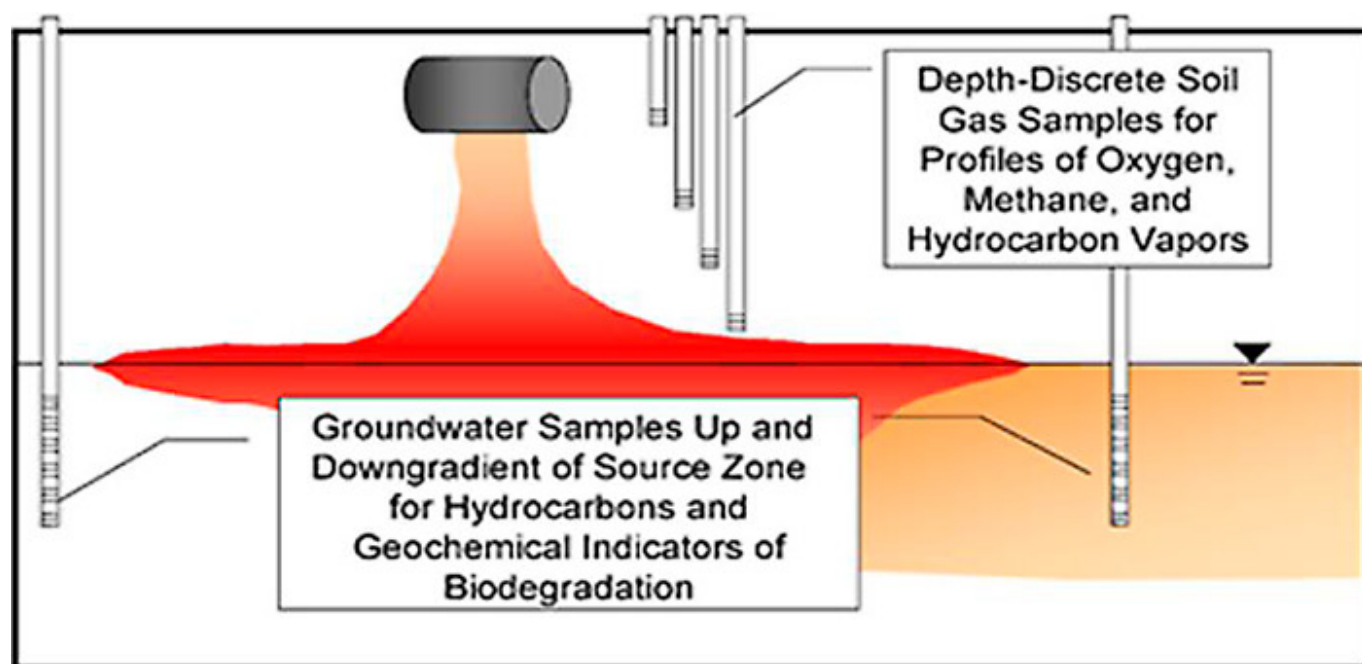


Figure NSZD-6. Data for establishing NSZD occurrence.

3.3 NSZD and LNAPL Compositional Changes

If a remedy contains an LNAPL composition-based remedial objective, then monitoring chemical concentrations within the source zone LNAPL is appropriate. Initial characterization of LNAPL composition should be accomplished as early as possible to establish baseline concentrations. The LNAPL baseline composition can then be used in comparisons with subsequent measurements to evaluate the magnitude and type of changes to the source zone that may have occurred.

Petroleum-based LNAPLs comprise complex mixtures of many chemical constituents (e.g., ([ITRC 2018](#)) ; ([TPHCWG 1998](#))). While it is important to characterize the source zone with as much detail as possible, routine NSZD monitoring may be based on fewer reference constituents. The analysis of magnitudes and trends of just a few appropriately selected constituents (e.g., the chemicals driving risk at the site) can provide a robust, long-term NSZD evaluation with minimal laboratory analytical demands.

For example, if the performance metrics are aqueous in nature, then monitoring the TPH fractions (or the contaminant of groundwater concern) in the LNAPL with high aqueous solubility would be important. Since such constituents possess a greater propensity to dissolve in groundwater, they are likely to be a reasonably representative indicator of LNAPL constituent mass transfer. Likewise, monitoring of TPH fractions in the LNAPL with greatest volatility (e.g., vapor pressure) may be used as an indicator of remedial effectiveness at sites with concerns involving volatilization to soil gas. Similarly, LNAPL fractions with high toxicities may be used as reference constituents when evaluating potential health risks associated with progress of an NSZD project. ([TPHCWG 1997](#)) provides additional discussion selection criteria for TPH reference constituents. Additionally, an Alaskan guidance document contains a useful summary of representative properties of various hydrocarbon fractions ([ASCWG 2006](#)).

Over time, as certain TPH fractions are preferentially depleted from the source zone based on their physical and/or chemical properties, the remaining LNAPL composition will change as the remaining constituents become relatively enriched compared to the depleted ones. Such changes in composition are persuasive evidence for the activity of NSZD processes and should be considered in long-term NSZD demonstrations.

3.4 Quantifying NSZD Rates

3.4.1 Methods

NSZD processes expressed through either vertical gas flux or lateral groundwater flow are quantified using a mass balance approach on a control volume. Such control volume includes the zones of the subsurface where the processes analyzed

occur (i.e., NSZD reactions). The control volume is defined by a surrounding perimeter known as the control surface. The flow across such control surface of either reactants or reaction by-products is quantified as a mass flux having the units of mass (of the chemical species of interest) per unit control surface area per unit time. Such fluxes provide a way of quantifying what enters and/or leaves the control volume, and thus constitute the metrics by which a reaction rate inside the control volume is derived. Figure NSZD-7 below includes a schematic diagram of such fluxes for both groundwater and gas-transport related processes. All NSZD rate measurement methods rely on derivation of the reaction rate based on a constituent flux.

Procedures for estimating mass loss expressed through lateral changes in groundwater geochemistry are specified in existing guidance documents [(ITRC 2009b); (NRC 2000)].

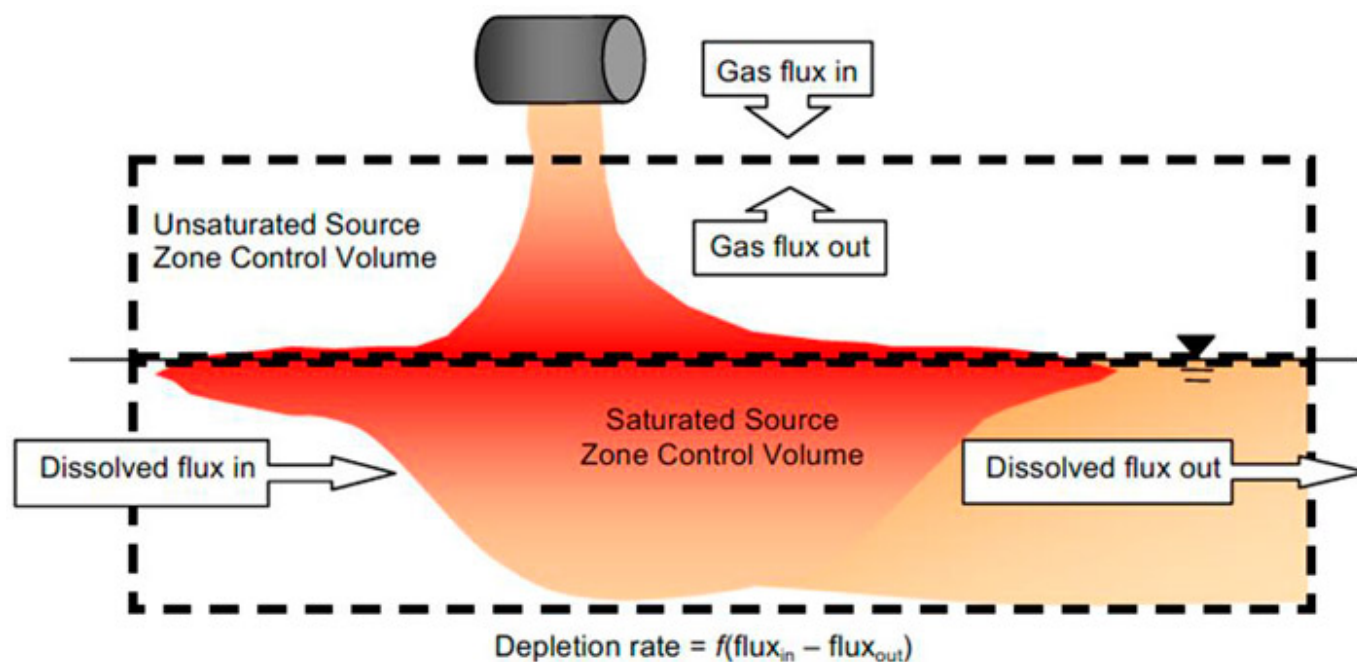


Figure NSZD-7. Example control volume “box” for quantitative assessment of NSZD.

As discussed previously, the component of NSZD expressed in the vertical transport of soil gas typically dominates the total NSZD rate; therefore, the principal methods currently used to quantify the NSZD rate focus on vertical gas flux and are briefly described below. A more detailed discussion of each of these methods is presented in [Section 4](#).

- The **gradient method** involves the assessment of changes in the vertical distribution of soil gas constituents (principally oxygen and CO₂) over the LNAPL source zone footprint, combined with estimates or measurements of the effective diffusion coefficient for the soil gas. The gas flux is calculated using Fick’s first law of diffusion, which can then be stoichiometrically converted to equivalent LNAPL mass loss rates.
- The **dynamic closed chamber (DCC)** method uses field instrumentation to measure the real-time, short-term (typically a few minutes) direct measurement of soil gas efflux of CO₂.
- The **passive CO₂ flux trap** method uses a chemical “trap” that captures CO₂ emanating from the soil. This method is designed to be deployed over multiple days, thus avoiding short term efflux variations.
- **Biogenic heat** methods are based on the principle that hydrocarbon biodegradation is an exothermic process that produces energy. By quantifying the heat signal in the subsurface and assessing the temperature data in an energy balance that accounts for heat transport and microbial heat production (or enthalpy), temperature data can be converted into biodegradation rates.

These methods, all based on the vertical flux of biogenic gases, are compared and contrasted in Table NSZD-1.

Table NSZD-1. Method comparison table

[View Table NSZD-1 in Adobe PDF format.](#)

In various ways, each of the methods described above relies on the assumption that methane is oxidized. Depending on site conditions which are generally atypical, the rate of methane generation can sometimes exceed the site’s methane oxidation

capacity. In this case, the above methods will result in under-estimation of the NSZD rate if methane efflux from the subsurface is incorrectly assumed to be zero.

3.4.2 General NSZD Rate Measurement Considerations

Temporal Variability and Frequency of Measurements ▼[Read more](#)

A variety of factors can result in variability in NSZD rate measurements over time. Some of these factors (e.g., temperature) can impact the actual rate of NSZD processes in the LNAPL zone, while other factors (variability in soil moisture, episodic ebullition of methane) impact the NSZD rate measurement rather than the underlying NSZD rate ([Garg et al. 2017](#)).

For shallow LNAPL zones, the annual highest soil temperatures are observed after the highest ambient air temperatures, due to a time delay required for the ambient heat to propagate downward and reach the depths of interest and for travel-time of subsurface gas migration ([Sihota et al. 2016](#)). Accordingly, for shallow LNAPL zones (e.g., approximately 15-feet below grade), NSZD rates tend to be higher during the late summer and early fall. For deeper LNAPL zones, the timing of shallow soil expressions (e.g., CO₂ flux measurements at the ground surface) of temperature-related variations in the rate of methanogenic activity in deeper soils is complicated by longer lag times between seasonal air and soil temperature cycles, the dampening of temperature variations with depth, and the biogenic gas transport time from deeper soils to shallow soils.

Shallow soil gas locations can be subject to hourly soil gas transport fluctuations due to diurnal fluctuations in ambient temperatures and barometric pressures. Such short-term fluctuations tend to be dampened at depth. Among the variables that affect vertical gas transport in the vadose zone, soil moisture is both difficult to characterize and significant to gas transport ([Shen, Pennell, and Suuberg 2013](#)). The number of NSZD rates measurements needed to reflect site conditions will be a function of data use objectives, site conditions, and observed variability in the parameters that can impact rate measurements.

Spatial Variability and Number of Measurements ▼[Read more](#)

Available methodologies consist of point (XY) estimations. Extrapolating these to the full site scale requires the use of statistical methodologies. The required data density depends on multiple variables: site heterogeneity (including ground cover, soil type and stratigraphy, depth to groundwater/NAPL) across the LNAPL footprint, LNAPL distribution, as well as the data use objectives and costs. The practitioner might consider an iterative process in which the LCSM is informed in earlier stages with higher data density of lower data quality, and lower data density of higher quality at later stages. This is a common practice in environmental remediation, as exemplified by the EPA Triad Approach (for example, see ([Johnson 2010](#))).

Background Considerations ▼[Read more](#)

As in most disciplines, NSZD measurement methods are subject to interferences. The gradient method is subject to uncertainties due to variabilities in the soil vapor diffusion properties. Methods that rely on the estimation of soil gas CO₂ flux (i.e., DCC and passive flux trap) are subject to interferences due to its natural presence in soils as part of the carbon cycle, as well as potential flow reversals associated with diurnal pressure fluctuations (barometric pumping) as well as temperature changes and alkalinity conditions [([Lowry, Dunn, and Neeper 1996](#)); ([Ma et al. 2013](#))]. The shallow soil is subject to natural processes that result in the assimilation of CO₂ through photosynthesis and natural organic matter decay that releases CO₂ back into the atmosphere through respiration. This shallow soil zone is often referred as the root zone. Abiotic and biotic factors affect photosynthesis and respiration resulting in seasonal and diurnal variability in CO₂ effluxes. Despite these interferences, most sites show a differentiable CO₂ flux signature in the LNAPL-impacted vadose zone and root zone. Soil gas flux methods need to account for these potential CO₂ sources. The two methods available to do this are:

1. background correction using measurements at unimpacted locations
2. radiocarbon isotopic (¹⁴C) correction to differentiate CO₂ associated with modern (i.e., natural) and fossil (i.e., petroleum NSZD) carbon

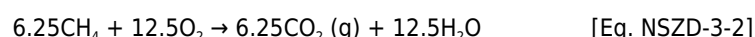
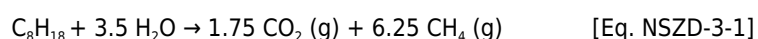
For total CO₂ efflux, the background correction consists of conducting measurements at unimpacted locations and subtracting them from the total CO₂ efflux at LNAPL-impacted locations. This methodology is standard in many disciplines

(i.e., ecology), but was first proposed to NSZD measurements by Sihota et al. 2010. This method assumes that the ambient CO₂ and modern CO₂ production in the root zone at background location(s) is similar to that over impacted locations. Because natural CO₂ production varies diurnally and spatially, the sampling design should consider repeat testing or time series data and consistency in the time when measurements are conducted for sites where diurnal fluctuations are significant ([Sihota et al. 2016](#)).

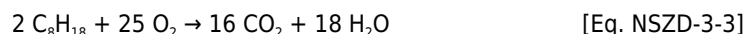
For NSZD assessment methodologies based on biogenic heat measurements, a background correction is required in order to account for natural temperature changes in the subsurface. Temperature anomalies can also occur from subgrade utilities, storm water recharge, snow melt, foundations, and topography. Generally, the background correction is achieved by conducting measurements at a location outside of the LNAPL body with similar geology and surface types. Additional information on background temperature measurements is provided in Section 4.4.2.

Stoichiometry and Units of Measurement ▼ [Read more](#)

The gas flux measured by the gradient, DCC, and passive flux trap NSZD rate measurement methods is converted into units of NSZD by assuming the stoichiometry of the reaction. Following from [Section 2](#), a generic example is presented below, which reflects the methanogenic degradation of octane, followed by the oxidation of methane. The two reactions in this sequence are shown in Equations NSZD-3-1 and 3-2.



Although these two reactions occur in different zones, defining a control volume that includes both zones, and assuming that both reactions are complete (i.e., all CH₄ is converted to CO₂) result in the overall reaction in Equation NSZD-3-3 (equivalent to the aerobic petroleum degradation process). The concept behind this reaction is that each mole of hydrocarbon undergoing mineralization by NSZD results in a stoichiometrically proportional number of moles of CO₂ produced.



The assumption that the CO₂ produced by NSZD mineralization does not accumulate within the soil is the basis to use of soil gas CO₂ efflux to measure NSZD. Such assumption seems reasonable and has been validated by geochemical modeling (for example, ([Molins et al. 2010](#)); ([Sihota et al. 2013](#)); and ([Sihota et al. 2016](#))).

Using the overall Equation NSZD-3-3 (i.e., for both degradation steps shown as one) as the basis, the CO₂ flux estimate attributable to LNAPL degradation (i.e., after correcting from background processes) can be converted to the NSZD rate. The rate can be expressed on a molar basis (i.e., moles LNAPL per unit area per time), or on a mass basis (i.e., grams of LNAPL per unit area per time). If the LNAPL density is assumed, such losses can also be expressed as a volumetric loss rate (i.e., LNAPL volume per unit area per time, such as gallons per acre per year). The latter are often used, as they match the units commonly used to determine the performance of active remedies, such as hydraulic recovery (to which NSZD might be compared).

Such unit conversions require assumptions related to the chemical composition and density of the LNAPL. Values for these are often available from site-specific laboratory results; generalized assumptions can also be used. Calculations to convert CO₂ flux to equivalent volumetric loss rates are relatively insensitive to LNAPL chemical composition ([API 2017](#)). In general, due to uncertainty related to measurement methods, gas transport assumptions, and unit conversion assumptions, derived NSZD loss rates should be reported to no more than two significant figures, consistent with the order-of-magnitude nature of typical NSZD rate estimates.

Similar unit conversion considerations are important for other NSZD assessment methods. For example, in an aqueous-phase mass budget assessment, stoichiometric conversions are used to convert changes in flux of terminal electron acceptors to a mass of hydrocarbons degraded, and LNAPL density values would be used to develop an equivalent volumetric LNAPL loss rate.

4.0 Methods of NSZD Rate Quantification

The following sections summarize the methods to measure NSZD rates as expressed through vertical gas flux. It presents details of the gradient, passive flux trap, DCC, and biogenic heat methods. It should be noted that the API document titled Quantification of Vapor Phase-Related Natural Source Zone Depletion Processes is a comprehensive assessment of the current state of NSZD measurement methodologies and presents the best practices regarding implementation of the gradient and CO₂ efflux methods ([API 2017](#)).

4.1 Gradient Method

4.1.1 Method Description

Petroleum hydrocarbon mass loss by volatilization and biodegradation can be evaluated by assessing changes in the vertical distribution of soil gas constituents (O₂, CO₂, methane, and vapor phase petroleum hydrocarbons) in the soil gas above the LNAPL-impacted soil. Changes in the vertical profile of soil gas composition are combined with measurements of the effective soil vapor diffusion coefficient in order to estimate the downward flux of oxygen, or the upward flux of CO₂ (and methane and hydrocarbons, if present). As discussed in [Section 2.2](#), these fluxes may be equated stoichiometrically to equivalent LNAPL mass loss rates ([Johnson, Lundegard, and Liu 2006](#)).

This approach relies on a one-dimensional application of Fick's first law as shown in Equation NSZD-4-1 and is generally referred to as the gradient method.

$$J = D_v^{eff} \frac{dC}{dz} \quad [\text{Eq. NSZD-4-1}]$$

It typically uses depth-discrete soil gas sampling results to estimate concentration gradients (dC/dz), and field testing data to estimate the vapor-phase diffusion coefficient (). The resulting flux (J) is then used to stoichiometrically estimate a rate of hydrocarbon mass loss. The approach relies on several simplifying assumptions:

- Diffusion is the only significant transport mechanism (e.g., advection of soil gas is insignificant and the species of interest is not reactive within the monitoring points used for the measurement—while oxygen flux is typically dominated by diffusion, advective transport of biogenic gasses may be important at depth due to methanogenesis (e.g., Molins et al. 2010),
- Migration processes are predominantly vertical and in a quasi-steady-state (i.e., temporal variations are insignificant), and
- Biodegradation of hydrocarbons (including CH₄) is the dominant sink for oxygen, and the dominant source of carbon dioxide and methane (i.e., background soil respiration is negligible or can be accounted for separately).

4.1.2 Measurement Methodology

The effective vapor phase diffusion coefficient may be measured in the field ([Johnson et al. 1998](#)) or estimated from soil moisture and total porosity ([Millington and Quirk 1961](#)). Soil gas concentration profiles can also be measured in the field using multi-depth soil gas probes. Further information on selection of horizontal and vertical locations of soil gas probes is described in the API NSZD guidance document ([API 2017](#)).

4.1.3 Method Limitations and Interferences

The gradient method is based on an assumption of diffusive gas transport (with the corollary that advection is negligible). It is currently believed that diffusion is dominant at many sites, with advection theoretically contributing more to biogenic gas transport at sites with higher NSZD rates. Additional information on diffusion versus advection is presented in [Section 2.3](#).

A critical parameter in analysis of the soil gas data is the vapor phase diffusion coefficient. At heterogeneous sites, the value of this coefficient can vary by several orders of magnitude, making this a difficult parameter to estimate for quantitative calculation of NSZD rates ([Garg et al. 2017](#)). The coefficient varies not only spatially, but also temporally along with changes in soil moisture content. Spatial variability can occur both laterally and vertically; establishment of a representative coefficient for layered soil is particularly challenging. Use of an assumed value, or extrapolation of a field testing-derived value to other locations or points in time, introduces a degree of inaccuracy into the derived loss rates. Location-specific measurement of the soil gas diffusivity concurrent to the time that gas samples are collected is recommended.

Conceptually, the simplifying assumptions involved in this method's application of Fick's law ([Section 4.1.1](#)) are not valid at

all subsurface locations, but might be validated if applied to a linear section of the gradient that experiences minimal changes in time (at steady state). Judicious positioning of a gradient “control plane” can enhance the validity of these assumptions and reduce the potential for error. The reactant flux (hydrocarbon mass loss) can be quantified by locating a horizontal reference plane above the source zone at a height (z) (Figure NSZD-8). The ideal location (z) for this reference plane is below the root zone (where natural soil respiration is most significant), and above the zone of methane oxidation. This depth typically corresponds to the aerobic/anaerobic interface ([Sweeney and Ririe 2014](#)). Oxygen tends to be near zero below this interface, and methane tends to be near zero above this interface.

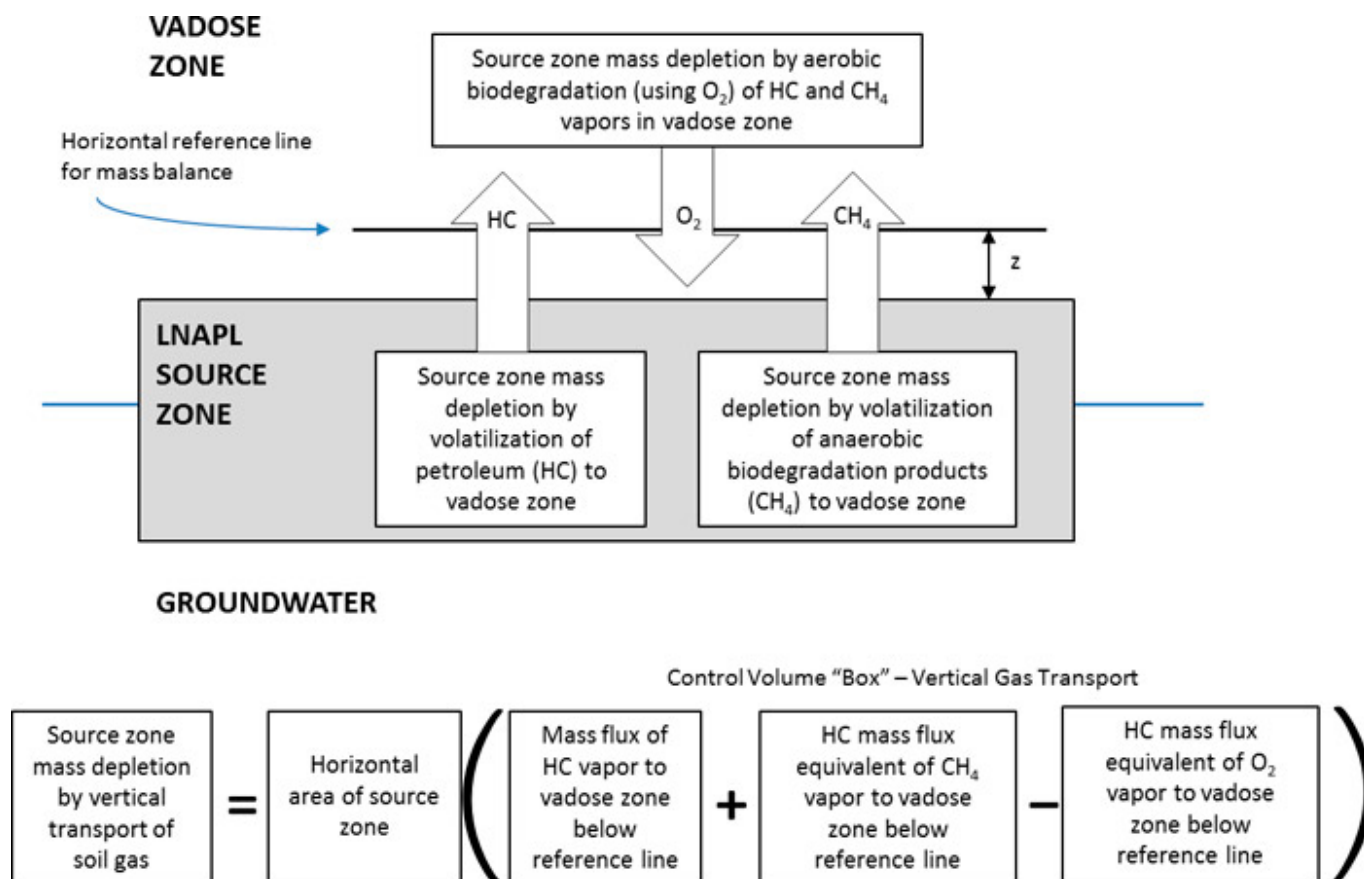


Figure NSZD-8. Reference diagram for NSZD mass depletion processes.

4.1.4 Gradient Method Nomograms

Gradient method nomograms, described below, are useful tools for designing an NSZD assessment program, predicting a range of potential results, and assessing and communicating results. The nomograms are for screening-level purposes only. The nomogram method is not recommended to serve as a substitute for site-specific NSZD field assessments.

Where natural soil respiration is negligible, the calculation of oxygen flux is often driven by two points: the concentration of oxygen at the soil surface, and the depth where the oxygen concentration diminishes to (near) zero. A simplified NSZD assessment may be conducted using a nomogram that assumes that depth and oxygen diffusion coefficient are the dominant inputs for NSZD. Nomograms are drawn using established theoretical analytical equations and a set of known existing or assumed parameters. Because some site-specific parameters may not yet have been measured, they are typically run using a range of values that could be representative of field conditions. Nomograms are also typically graphical in nature, have one axis that is the desired value (i.e., the NSZD rate), and the other axis uses a parameter that is readily available. Inherent to theoretical analysis, they make many simplifying assumptions and as a result, their data quality is considered screening-level.

Figure NSZD-9 represents an example NSZD rate estimate nomogram based on application of Fick’s first law (Equation NSZD-4-1). The nomogram plots estimated hydrocarbon degradation rates for generic soil types with effective O_2 diffusion coefficients derived from the Millington-Quirk equation with porosity and moisture contents summarized in Table NSZD-2. These plots assume:

- a single homogeneous and isotropic clean soil exists above the LNAPL smear zone;

- no soil O₂ consumption occurs due to natural soil respiration;
- the horizontal reference plane exists where O₂ is zero and oxidation of CH₄ is complete; and
- the O₂ gradient is linear and estimated from atmosphere to the depth of the horizontal reference plane.

The user selects a horizontal reference plane above the LNAPL smear zone using available site knowledge, such as depth to LNAPL affected soils identified in boring logs, zero O₂ concentrations identified in soil gas profiles or monitoring well screening samples (Section 3.2), or a historic high LNAPL-water interface elevation. Figure NSZD-9 indicates that for a site with clean sand above the LNAPL smear zone with an average depth to the LNAPL-water interface of 6 meters below ground, a hydrocarbon biodegradation rate of 2.6 g/m²/day may be expected.

The diffusion coefficient (as estimated using the (Millington and Quirk 1961) relation) can vary an order of magnitude based on porosity and moisture content, as evidenced in the two clay examples shown below, with 40 and 60 percent water saturation. Site-specific nomograms may be developed to narrow the range of estimated NSZD rates. Nomograms can be developed for more complex soil distributions by developing an overall diffusion coefficient for the soil column using summation methods described in (Johnson et al. 1998).

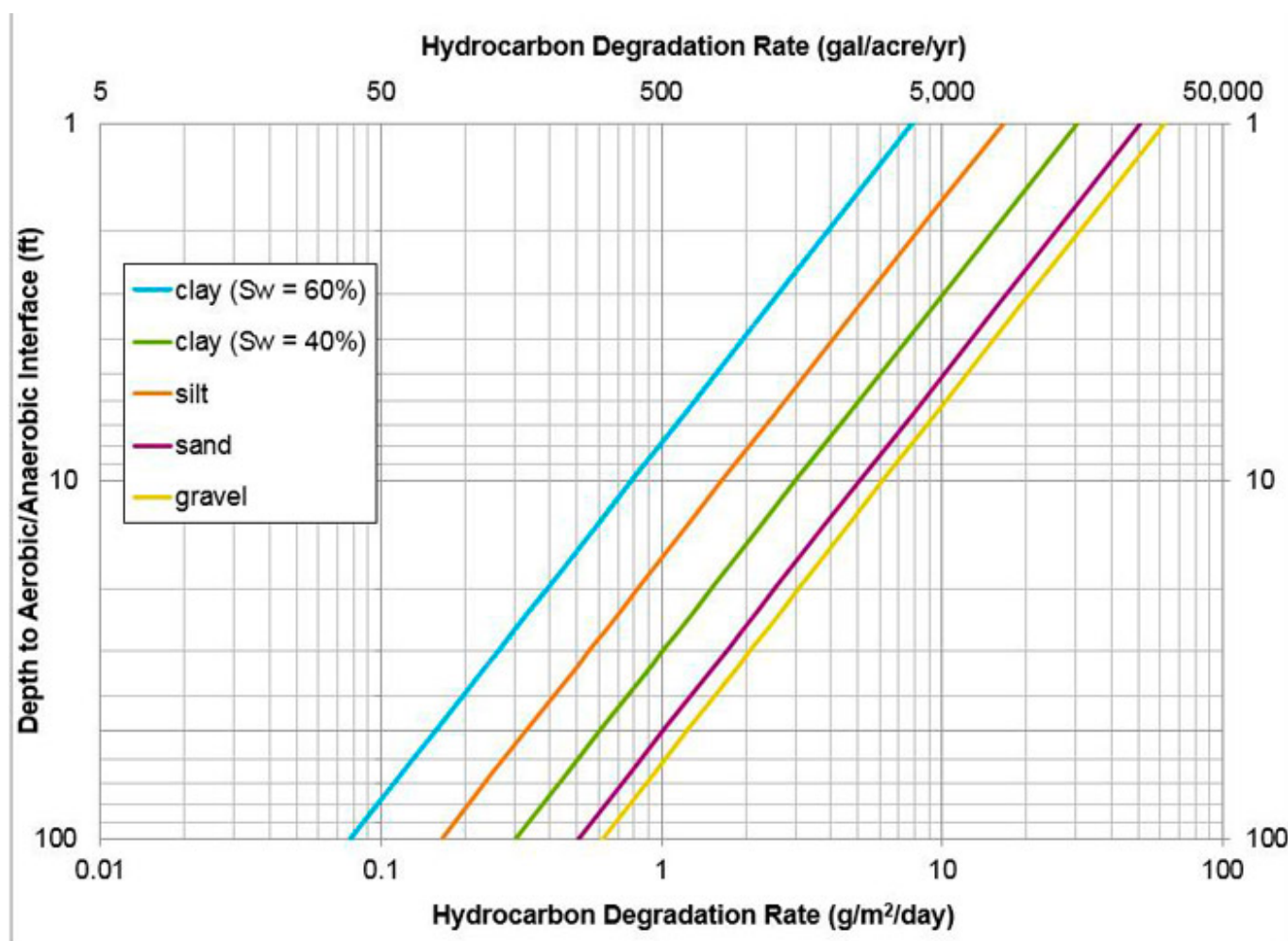


Figure NSZD-9. Example of nomogram to estimate NSZD rates. Note that typical aerobic/anaerobic interface depths and hydrocarbon degradation rates would fall toward the center of the plot area shown.

Table NSZD-2. Porosity and water content inputs and Millington-Quirk diffusion coefficient estimates for Figure NSZD-9 Example Nomogram

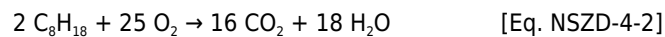
Soil type	Porosity	Soil moisture content (percent)	Effective O ₂ diffusion coefficient (cm ² /sec)
Clay	0.5	60	0.003
Clay	0.5	40	0.013

Soil type	Porosity	Soil moisture content (percent)	Effective O ₂ diffusion coefficient (cm ² /sec)
Silt	0.5	50	0.007
Sand	0.36	20	0.021
Gravel	0.31	10	0.026

4.2 Passive CO₂ Flux Trap Method

4.2.1 Method Description

The passive CO₂ flux trap method was developed specifically to monitor NSZD using a stoichiometric conversion of the rate of CO₂ efflux from LNAPL degradation ([McCoy et al. 2014](#)), according to Equation NSZD-4-2 for a representative petroleum hydrocarbon (the equation may be modified to suit site-specific hydrocarbon composition):



This method was co-developed and patented by Colorado State University and Chevron U.S.A. (U.S. Patent No. 8,714,034). This technology is licensed and commercialized by E-Flux, LLC (Fort Collins, CO, USA).

The passive CO₂ flux trap captures the CO₂ emanating from the soil surface over a multi-day duration of time. After field deployment, the traps are collected, capped, and then shipped back to the vendor for laboratory analysis. Knowing the cross-sectional capture area and the deployment time, the cumulative CO₂ mass released by the soil (and captured by the trap) is then used to calculate the flux. The standard practice for passive flux traps is to analyze both total carbon and ¹⁴C (radiocarbon dating by atomic mass spectroscopy) to differentiate the contributions to the sample from modern CO₂ (background generated from natural organic matter in the soil) and fossil fuel CO₂ (generated from biodegradation of LNAPL contaminants).

4.2.2 Measurement Methodology

As shown on Figure NSZD-10, the passive CO₂ trap setup consists of a cartridge with CO₂ sorbent (a strong base) that is coupled to a receiver (pipe) preinstalled into the soil. The receiver is a short section of pipe that is driven into the ground, to a depth of a couple inches, just enough to make a seal with the soil. During receiver installation, care is taken to minimize soil disturbance by recompacting soil within and around the receiver back to its original level. A rain cover is attached to the cartridge to protect the sorbent material from unexpected rain during deployment. The traps are deployed for multiple days, typically 2 weeks, to capture the CO₂ emanating from the soil. The deployment time is limited to avoid saturation of the sorbent (in the order of 30% content in weight, as mass CO₂/mass of sorbent).

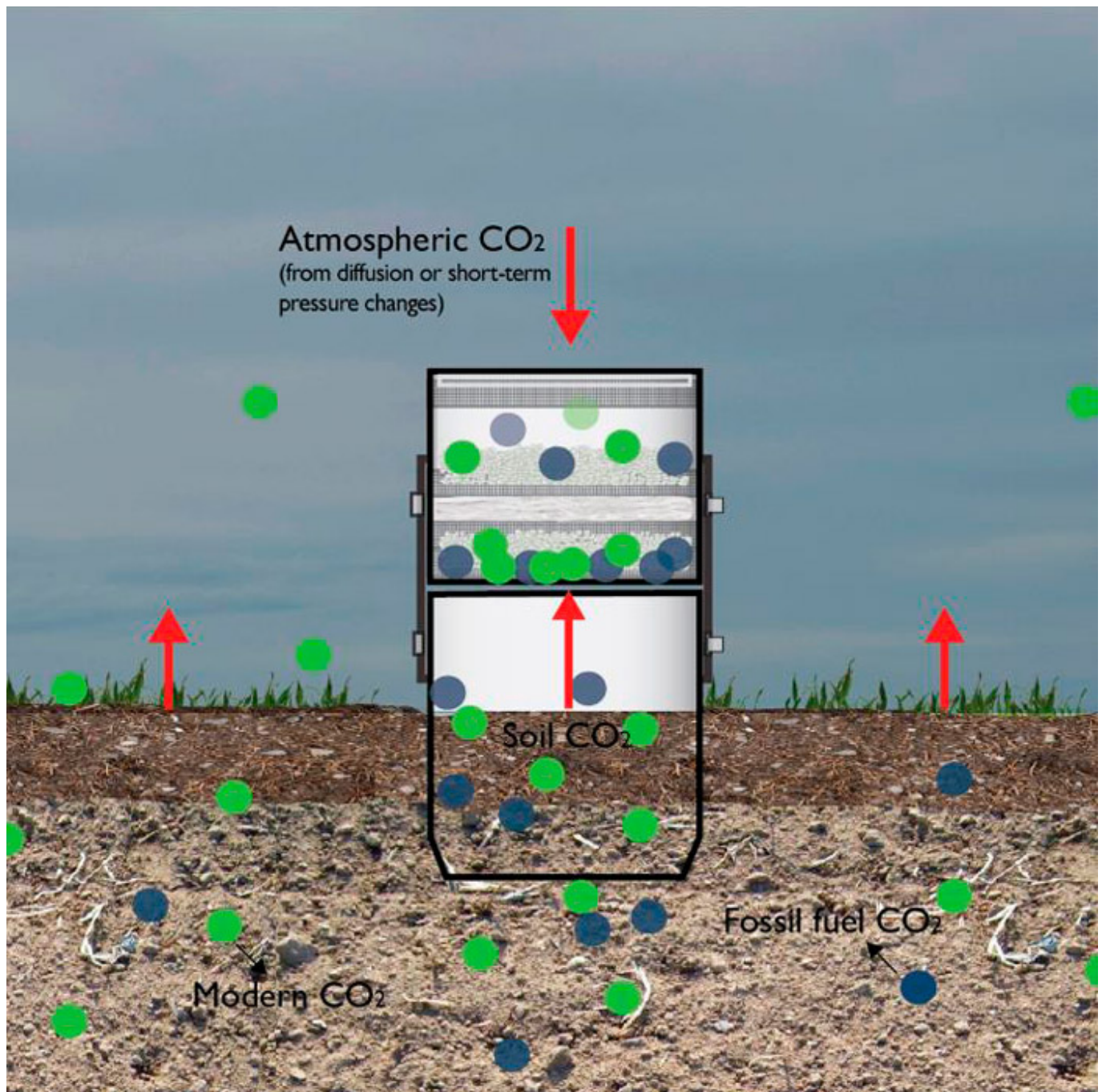


Figure NSZD-10. Schematic of the passive CO₂ trap, and the separate capture of CO₂ leaving the soil (associated with the soil gas efflux) and the ambient CO₂ interference (Figure provided by vendor E-Flux, used with permission).

The traps have a two-layered design, to differentiate soil gas effluxes (i.e., CO₂ leaving the soil into the atmosphere) from that atmospheric CO₂ that either diffuses into the cartridge or flows downward (i.e., due to atmospheric pressure changes driving ambient gas into the soil). Short-term fluctuations in total soil gas flux, including flow reversals are known to occur ([Ma et al. 2013](#)), either due to barometric pumping (changes in ambient pressure), ambient temperature changes, and/or the CO₂ production rates associated with shallow soil production processes. Such processes are diurnal and climatological in nature, and the total soil gas flux (inclusive of natural organic matter respiration) often follows a diurnal pattern.

As the reaction between CO₂ and the sorbent is fast and no breakthrough occurs (i.e., deployment duration does not allow for sorbent saturation), the two trap elements permit capture of the mass of CO₂ associated with the average soil gas efflux while preventing the influx of atmospheric CO₂ into the sample during the period of deployment. The CO₂ mass associated with the soil gas efflux is reported by the vendor as the basis to estimate NSZD rates.

Additional features of the passive CO₂ traps are:

- The sorbent is porous, so it allows for free gas exchange between soil and atmosphere through the trap, avoiding pressure buildup within the device.
- The traps have no moving parts and require no power, so can be deployed in remote areas.
- The capture area corresponds to either a 4" diameter receiver pipe (standard) or 8" diameter (for added sensitivity).
- The analysis of the trap is performed in the lab, after traps are returned to the vendor. This includes total CO₂ analysis (to calculate the total CO₂ efflux), as well as radiocarbon isotopic analysis (¹⁴C) as described below.
- Results are travel blank corrected, using an extra cartridge that is not deployed (a travel blank). This is necessary to account for the initial measurable low amount of CO₂ (and its ¹⁴C isotopic contribution) inherently contained in the sorbent from the manufacturer.
- The lab analysis typically requires four weeks to receive results.

The radiocarbon isotopic background correction relies on measuring ¹⁴C concentrations in the CO₂ efflux. Ambient air is ¹⁴C rich, as this isotope is created by the cosmic rays on the atmosphere. Ambient CO₂ is incorporated into the food chain through photosynthesis, preserving the atmospheric ¹⁴C ratio. This isotope is not stable, decaying with a half-life of ~5,700 years ([Aelion, Kirtland, and Stone 1997](#)). As LNAPL is millions of years old, it is completely depleted of ¹⁴C. Based on this, a two-source model is available to allocate contributions from both sources to an environmental sample, assuming that modern carbon has ¹⁴C levels near atmospheric, and fossil fuel has no ¹⁴C ([ASTM 2014b](#)). This technique is often referred to as radiocarbon dating. Applications to NSZD were reported in one of the first case studies of the passive CO₂ traps ([McCoy et al. 2014](#)), and now are standard for this technique. As this correction is location-specific, it obviates the need for CO₂ efflux monitoring from background locations.

4.2.3 Method Limitations and Interferences

As with other methods to measure gaseous efflux at ground surface (e.g., DCC), passive flux trap locations need to be located in soils that can permit gas transport. If they are installed within impervious, compacted, or low permeability zones and penetrate a layer confining to the underlying soil vapor, then a preferential flow path (i.e., a chimney) will be created and results will be non-representative of natural gas efflux. As such, these surface methods should not be installed in concrete or asphalt pavement, or very hard compacted soils.

Installation of passive flux traps in background locations is not necessary, as a ¹⁴C correction is used. This isotopic correction is performed on the traps atop the LNAPL footprint and eliminate the need for separate traps in background, unimpacted areas.

The detection limit of the passive flux trap method is based on the detection limits of the analytical method used. For a capture area corresponding to a 4" diameter receiver, a deployment time of 4 days, and a trap with 40 grams of sorbent, the resulting detection limit for total CO₂ flux is 0.5 μmol/m²/s. A typical deployment of two weeks results in a total CO₂ flux detection limit of approximately 0.1 μmol/m²/s (sufficient to detect most field-observed fluxes). The high sensitivity of the two source model on which ASTM D6686-12 is based can detect even small fossil fuel contributions to the sample (in the order of 1-2%) on the captured CO₂. The sensitivities described can be lowered by a factor of 4 by changing to an 8" diameter receiver.

Additional factors to be considered affecting the trap measurements (and some of the other methods as well) include wind and rain:

- Wind has been shown to affect all methods to estimate NSZD based on gas transport, although the particular bias reported in that work were not realistic, as the conditions were not representative of field conditions. Strong wind might bias the DCC results low, whereas for the trap, a high wind has been shown to bias results high. The latest trap design has a reduced top view footprint and height (with respect to the original design), modifications proven to reduce bias. Other things being equal, the bias is proportional to wind velocity. For example, if sustained for the period of measurement, a moderate breeze of 15 miles per hour (mph) (as measured at an elevation of 10 m above ground, a level sufficient to raise dust from the ground and move small branches on

trees) was shown to create a high bias on the CO₂ traps of +7% and a loss bias of -30% for the DCC (E-Flux 2015). If unusually windy conditions are expected at a field site during CO₂ trap use, additional efforts should be made to understand the magnitude of this bias and mitigating measures (E-Flux 2015).

- Heavy or persistent rain might result in either soil saturation during trap deployment or different soil moisture levels between the site and under the trap. If this results in saturated soil conditions, it may shut down gas transport, even if microbial activity at the contamination depth is unaltered, creating a low bias on the results. Small amounts of moisture that do not saturate the soil might result in preferential flow towards the trap, resulting in a potential high bias. The magnitude of such high bias has not been determined. If possible, it is best to avoid significant rain events during trap deployment, even if this result in needing an 8" trap diameter (see above discussion on detection limits).

4.3 Dynamic Closed Chamber Method

4.3.1 Method Description

The dynamic closed chamber (DCC) method was adapted by researchers at University of British Columbia for estimation of NSZD rates ([Sihota and Mayer 2011](#)). The DCC method involves measurement of the CO₂ efflux using a shallow-embedded, ground surface-based flux chamber, typically equipped with a circulation pump and real time gas detector (i.e., an infrared gas analyzer). DCC systems use the rate of increase of CO₂ concentration in a measurement chamber to estimate the efflux. For such an estimate to be valid and representative, pressure and temperature conditions must be similar inside and outside the chamber. Similarly to the passive CO₂ flux trap method, it is assumed that all petroleum hydrocarbon vapors including methane in the unsaturated soil zone are converted to CO₂ and that the LNAPL degradation rate can be estimated from stoichiometric considerations for the biodegradation of representative petroleum hydrocarbon compound.

4.3.2 Measurement Methodology

One example of a DCC system is the LI-8100A analyzer, manufactured by LI-COR Biosciences (Lincoln, NE, USA). It is a fully automated system dedicated to making measurements of soil CO₂ flux (see Figure NSZD-11). The analyzer control unit powers either a survey or long-term measurement chamber, and houses the system electronics and the infrared gas analyzer (IRGA) used to measure the change in CO₂ concentration in the flux chamber (along with other parameters important for accurate CO₂ efflux calculations—e.g., water vapor (LI-COR 2014)). The LI-8100A survey chamber allows for rapid measurements to be made at many locations (20 – 50 per day, depending on site size), and the long-term measurement chamber supports automated, sequential measurements at a single location over time (hours to months). Both chambers have engineered pressure vents to prevent pressure gradients and wind incursion from outside the chamber. To date, the survey chamber has been more frequently used in NSZD assessments than the long-term chamber.



Figure NSZD-11. LI-8100A Automated Soil Gas Flux System with survey chamber (left) and infrared gas analyzer (right).

The LI-8100A survey chamber is placed on a collar that consists of an 8-inch diameter section of plastic pipe, approximately 4 inches long. This collar is similar to the receiver pipe described for the CO₂ trap method in [Section 4.2](#). The collar is pushed or driven approximately 2 to 3 inches into the soil, and is typically installed at least 24 hours prior to flux measurement. As with CO₂ sorbent traps, the method assumes that upward soil gas flux into the collar is representative of an equivalent area of the subsurface, and that flux into the collar and DCC is not increased by formation of preferential pathways or decreased by permeability reductions from collar installation. Therefore, disturbance of soil within and around the collar should be minimized; however, shallow organic material (e.g., plant litter) to reduce sources of non-petroleum related CO₂. Coarse-grained surficial material such as gravel and cobbles should also be removed prior to collar placement to prevent short-circuiting of flow from the atmosphere into the chamber.

The efflux is estimated using a linear or exponential regression of the increase in CO₂ concentration within the chamber headspace, typically using software provided by the chamber manufacturer. This makes it possible to estimate the initial rate of CO₂ increase that occurred immediately after the chamber closed, and minimize the degree to which elevated

concentrations of CO₂ in the chamber affect flux. Accordingly, measurement times should typically be limited to about 1½ to 3 minutes in order to keep chamber CO₂ concentration changes small.

4.3.3 Method Limitations and Interferences

There are similar limitations with the DCC method as compared to other flux-based soil gas methods. DCC measurements should be conducted in soils that permit gas transport. To address natural soil respiration and the influence from background sources of CO₂, DCC measurements in background locations and/or ¹⁴C correction should be performed.

Use of ¹⁴C isotopic analysis is documented for the DCC method [([Sihota and Mayer 2011](#)) and ([Eichert et al. 2017](#))]. As the flux measurements of the DCC are short term, such application is considered a method in development ([API 2017](#)).

Additional research on ¹⁴C correction for the DCC method is ongoing.

A limitation of the DCC survey-chamber method is that it provides for a snapshot measurement. Because production of CO₂ from both NSZD and natural soil respiration varies temporally on varying timescales (diurnally to seasonally) and is influenced by external factors (e.g., soil moisture and temperature), it is important to include these considerations and factors in the LCSM development and advisable to conduct repeat measurements at a subset of locations, which can readily be incorporated in the overall sampling strategy.

Soil moisture can affect soil gas transport, and gas exchange at ground surface and microbial processes and rates are affected by temperature; although, based on cold climate studies, the effect of temperature is typically relatively small ([Hers et al. 2014](#)). ([Sihota et al. 2016](#)) demonstrates the seasonal variability in DCC measurements of CO₂ efflux with peak measurements during late spring and summer at a crude oil spill site (Bemidji, MN). This study also found that frozen soils acted to inhibit gas transport and resulted in decreased CO₂ efflux measurements. NSZD rates estimated from DCC CO₂ efflux measurements may vary over orders of magnitude depending on site conditions. Variations associated with near-surface soil conditions are not necessarily related to or concurrent with variations in the actual rate of NSZD occurring at greater depth; rather, these variations affect the ability to observe NSZD indicators through soil gas flux. Consequently, CO₂ efflux measurements should be avoided during and shortly after rainfall events. Soil physical properties including water retention may be used to assess the effect of rainfall events and infiltration on soil moisture.

4.4 Biogenic Heat Methods

4.4.1 Method Description

NSZD thermal signatures are closely related to the NSZD processes expressed through vertical gas transport (Section 2.2), described as part of the oxidation of methane and petroleum hydrocarbons in the vadose zone. The concept of biogenic heat from NSZD processes in the subsurface is analogous to a compost pile which generates heat, with heat being transferred to its surroundings.

Local soil temperatures at a petroleum release site will be impacted by surrounding ambient temperatures, heat released from biodegradation, and the subsurface heat transfer processes. For instance, ([Warren and Bekins 2015](#)) investigated thermal signatures from NSZD at the Bemidji, Minnesota site and found temperatures above the crude oil body in the vadose zone were up to 2.7 °C higher than temperatures outside the LNAPL footprint. CO₂ efflux data acquired from an independent study were found to be comparable to rates estimated from biogenic heat measurements. Additionally, ([Sweeney and Ririe 2014](#)) found that the subsurface temperatures in an LNAPL-impacted location were consistently higher than a background area, typically ranging from 2 to 2.5 °C.

- Microbial degradation is an exothermic process that produces energy. By quantifying the heat signal in the subsurface and assessing the temperature data in an energy balance that accounts for heat transport, a measure of biodegradation rates of petroleum hydrocarbons can be achieved ([Warren and Bekins 2015](#)). These microbial reactions can occur in either the unsaturated or saturated zone, and in some cases involve a two-step process such as: 1) methane generation in anaerobic zones above and below the water table, and 2) the methane oxidation in the unsaturated zone by naturally occurring bacteria utilizing oxygen diffusing in from the surface. For the various biodegradation reactions of interest, the heat of reaction (DH), as approximated by the change in enthalpy, is summarized in Table NSZD-3.

Table NSZD-3: Heats of reaction (change in enthalpy) for biodegradation of a model hydrocarbon constituent

Biodegradation Reaction (Decane as Model Petroleum Hydrocarbon Constituent)	Approximate Change in Enthalpy*	
	kJ/mole	kJ/g
Aerobic Respiration $C_{10}H_{22} + 15.5 O_2 \rightarrow 10 CO_2 + 11 H_2O$	-6790	-48
Denitrification $C_{10}H_{22} + 12.4 NO_3^- + 12.4 H^+ \rightarrow 10 CO_2 + 17 H_2O + 12.4 N_2$	-6320	-44
Manganese Reduction $C_{10}H_{22} + 31 MnO_2 + 62 H^+ \rightarrow 10 CO_2 + 31 Mn^{2+} + 42 H_2O$	-6560	-46
Iron Reduction $C_{10}H_{22} + 62 Fe(OH)_3 + 124 H^+ \rightarrow 10 CO_2 + 62 Fe^{2+} + 166 H_2O$	-5160	-36
Sulfate Reduction $C_{10}H_{22} + 7.75 SO_4^{2-} + 15.5 H^+ \rightarrow 10 CO_2 + 7.75 H_2S + 11 H_2O$	-230	-2
Methanogenesis $C_{10}H_{22} + 4.5 H_2O \rightarrow 2.25 CO_2 + 7.75 CH_4$	-25	-0.2
Methane Oxidation (methane from 1 mole decane) $7.75 CH_4 + 15.5 O_2 \rightarrow 7.75 CO_2 + 15.5 H_2O$	-6770**	-48**
Biodegradation reactions based on (Wiedemeier et al. 1998). Reactant and product enthalpies (input parameters for calculation change in enthalpy for the complete reaction) from compilation in (Stockwell 2015). * Negative value signifies release of heat in the reaction. ** Enthalpy denominator is on decane basis.		

If pseudo steady-state biomass levels exist in soil, then the rate of heat release will equal the rate of hydrocarbon degradation multiplied by the heat of reaction (DH). Since the heat of reactions for both methane oxidation and aerobic biodegradation are similar, sole use of the methane oxidation heat of reaction may be used to account for the majority of the mass of degradation (assuming that reaction mechanisms based on external electron acceptors are negligible).

Quantification of the NSZD rate from the heat signal of biodegradation involves two key steps: i) evaluation of the heat flux; and ii) conversion to a biodegradation rate using the heat released from the biodegradation reaction.

The evaluation of heat flux is essentially comprised of an energy balance on a control volume and recognition of heat conduction as the mechanism of heat transfer in the subsurface. Figure NSZD-12 illustrates the hydrocarbon oxidation zone (where the majority of biogenic heat is produced) and Figure NSZD-13 illustrates the corresponding depth vs. temperature profile of background-corrected temperatures.

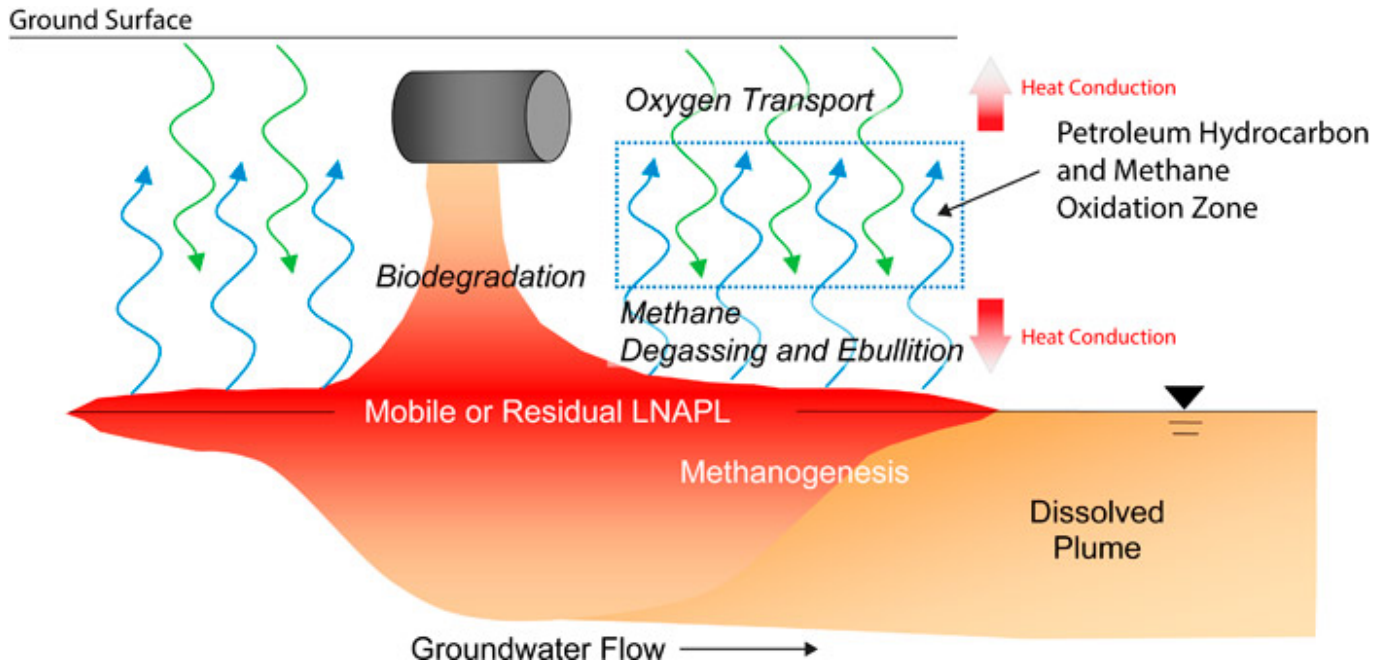


Figure NSZD-12. Petroleum hydrocarbon and methane oxidation zone.

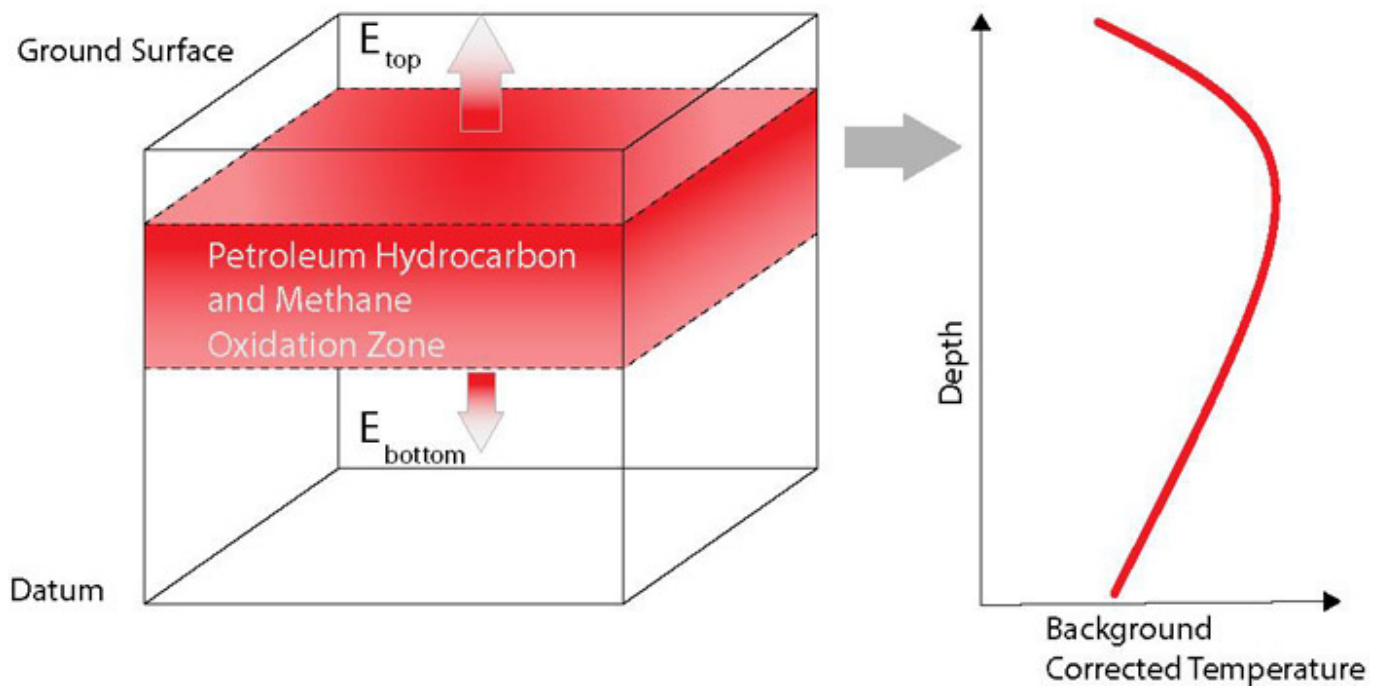


Figure NSZD-13. Vertical profile of background-corrected temperature.

Heat conduction in the subsurface follows Fourier's Law and can be simplified to a one-dimensional heat flux in the vertical direction as follows:

$$q_h = -K_T (\Delta T / \Delta z) \quad [\text{Eq. NSZD-4-3}]$$

where q_h is the heat flux ($\text{J/m}^2/\text{s}$), K_T is the thermal conductivity of the soil ($\text{J/s/m/}^\circ\text{C}$), ΔT is the change in background-corrected temperature ($^\circ\text{C}$), and Δz (m) is the depth interval across which heat flux is calculated. The soil thermal conductivity is a volume-weighted average from different lithologies in the vadose zone. Soil thermal conductivity can range from $0.1 \text{ J/s/m/}^\circ\text{C}$ (for dry fine-medium textured soil) up to $4 \text{ J/s/m/}^\circ\text{C}$ (for water saturated sand) and is dependent on soil moisture content ([Sweeney and Ririe 2014](#)).

The total heat flux in the energy balance of the control volume includes the sum of the upward heat flux (to the ground surface), as well as downward heat flux (to the saturated zone).

$$q_T = -K_T (\Delta T/\Delta z)_{\text{upward}} - K_T (\Delta T/\Delta z)_{\text{downward}} \quad [\text{Eq. NSZD-4-4}]$$

An NSZD rate is then obtained by using the total heat flux as well as the heat released from the biodegradation reaction, as seen in the following expression:

$$R_{\text{NSZD}} = q_T / \Delta H_{\text{rxn}} \quad [\text{Eq. NSZD-4-5}]$$

where R_{NSZD} is the NSZD rate in units of (g-HC/m²/s), q_T is the heat flux (J/m²/s), and ΔH_{rxn} is the heat of reaction of hydrocarbon biodegradation.

4.4.2 Measurement Methodology

The essential component of the thermal approach is a temperature monitoring device such as a thermocouple, thermistor, or Resistance Temperature Detectors (RTDs), with off-the shelf thermocouples being used in most applications to date. However, it should be noted that this is an emerging methodology and, to date, a standard approach has not been developed. Once installed, thermocouples can provide temperature data for an extended period (likely several years at a minimum). These thermocouples can either be manually handled or, analogous to remote acquisition of continuous water elevation data from a transducer, also be easily connected to a data logger and cell phone for remote acquisition of continuous temperature data. Self-contained temperature data loggers can be deployed in existing monitoring wells following a similar principal ([Sweeney and Ririe 2014](#)). Once downloaded, the data can be evaluated to isolate the biogenic heat and ultimately converted to cumulative LNAPL loss rates through use of an energy balance. A network of multi-depth temperature sensors (which must be evaluated relative to a representative background temperature profile) can provide for:

- continuous NSZD rate monitoring, thus mitigating concerns with temporal variability and associated uncertainty on the representativeness of other methods relying on a “snapshot” of site conditions; and
- long-term performance monitoring in those situations where NSZD is serving as a long-term remedy and tracking of LNAPL mass depletion over time is appropriate.

Different methods can be used for obtaining subsurface temperature measurements. Temperature gradients have been estimated by using probes or temperature data loggers installed in existing groundwater monitoring wells ([Sweeney and Ririe 2014](#)). In a USGS study conducted at the national Crude Oil Spill Fate and Natural Attenuation site in Bemidji, MN, vadose zone temperature measurements were collected with temperature data loggers housed in a water-filled PVC pipe ([Warren and Bekins 2015](#)). This installation method achieved the objectives of not having any above-ground equipment and allowing instrumentation retrieval/redeployment; the pipes were filled with water and polyester filling “plugs” to mitigate convection. Measurement of subsurface temperatures can also be achieved by installing thermocouples directly in the ground so that there is direct thermal communication with subsurface media (soil and groundwater). A vertical array of thermocouples can be attached to a PVC rod, and can then be installed using conventional drilling techniques.

A background correction is required in order to account for natural temperature changes in the subsurface. Generally, the background correction is achieved by conducting measurements at a location outside of the LNAPL body with similar geology and surface types. The temperatures at specific depths of the background location are then subtracted from those of the LNAPL-impacted location. The background correction is a sensitive and critical step in the application of the biogenic heat method. When selecting measurement locations, care should also be taken to avoid potential thermal interferences, such as anthropogenic heat sources or sinks and non-representative locations with temperature-altering conditions (utilities, persistent shadows, concentration of runoff/infiltration, foundations). Additional considerations are presented in [Section 4.4.3](#). This is an area where the best practices are still evolving.

Representative background temperature measurements may not be available or reliable at all sites; in these cases, it is possible to estimate background temperature using mathematical models, and compare measured temperatures to the modeled background to evaluate biogenic heat production. One model is described by ([Sweeney and Ririe 2014](#)), and uses annual temperature data and soil thermal properties to predict subsurface temperature as a function of depth and time of year. When using this approach, care should be taken to ensure that the site measurements collected are not subject to interferences not reflected in the background model.

4.4.3 Method Limitations and Interferences

Limitations of the biogenic heat method and design considerations include:

- As with the other methods that measure vadose zone gas transport and reaction processes, the biogenic heat method requires background correction. Background locations should be placed in a clean area on-site with similar surface cover, soil stratigraphy, and depth to groundwater as the measurement point within the LNAPL zone. Significant differences in soil type, surface temperatures, and vegetation cover might introduce significant errors through this assumption, sometimes evidenced by higher background temperatures than those at the impacted ones. Additional factors should be considered in selecting a background location for thermal NSZD measurements. Sources of subsurface heat other than hydrocarbon-impacted soil (e.g., active pipelines, high surface water recharge, etc.) can affect interpretation of subsurface temperatures. As such, thermal monitoring locations within both the LNAPL-impacted and background locations should be selected after detailed evaluation of other heat sources.
- Temperatures used for temperature gradient measurements should be located outside of the reactive zone. The depth of the methane oxidation zone (typically the primary source of biogenic heat) can vary and is affected by soil moisture and atmospheric exchange of oxygen. However, proper placement of temperature measurement points along the vertical transect (and equivalent depths in background-correction), allow for identification of the depth of the oxidation zone.
- The reactions occurring within the reactive zone need to be known, in order to calculate the corresponding heat of reaction. When NSZD is dominated by methanogenesis as is often the case, this aspect does not result in significant uncertainty in data interpretation considering the similar heats of reaction for methane oxidation and hydrocarbon oxidation.

5.0 Considerations in Long-term LNAPL site Management

5.1 Evolution of the LNAPL Source Zone

The combination of NSZD in the LNAPL source zone and MNA in the associated aqueous phase plume, with appropriate monitoring to assure attainment of performance objectives, will often constitute the final step in remediation of an LNAPL release site. In some cases, NSZD may be evaluated as the primary remedy at late-stage release site where LNAPL is no longer mobile, the LNAPL mass continues to be depleted, and the aqueous phase plume is in stable-shrinking status. In considering NSZD as a long-term remedy, pertinent issues and questions include the following:

- With the significant rates of LNAPL mass loss that are being measured at many sites (rates as high as thousands of gallons per acre per year), how long will the LNAPL zone persist?
- The NSZD rate measurement methods described herein provide bulk LNAPL loss rates. How does NSZD change the composition of residual LNAPL over time?
- The driver on the required duration of LNAPL release site monitoring is the restoration of groundwater to specified criteria for individual LNAPL constituents of concern (e.g., attainment of drinking water standards for benzene). As NSZD proceeds and residual LNAPL is depleted, how does that translate into changes in LNAPL-groundwater partitioning and improvement in groundwater quality?

The state-of-the-science on these issues is discussed below. Given the rapid rate at which NSZD is evolving and maturing as an LNAPL site management tool, the user is encouraged to check the current literature for the latest developments if these issues are deemed critical to LNAPL site management decision-making.

With the current state-of-the practice, NSZD rate measurements provide a measurement of the bulk hydrocarbon depletion rate. To date, most measurements have provided NSZD rates in a relatively narrow range. An analysis of rate information from 25 sites revealed the middle 50 percent of sites exhibited NSZD rates falling between 700 and 2,800 gallons/acre/year, with a median of approximately 1,700 gallons/acre/year ([Garg et al. 2017](#)).

Projecting LNAPL zone longevity requires an estimate of the current LNAPL mass, an understanding of average annual NSZD rates across the LNAPL body, and a projection of how NSZD rates will change over time. Understanding an average annual NSZD rate will typically require enough measurements to assess and account for shorter-term rate variability resulting from factors that may include seasonal patterns in temperature, vadose zone soil moisture content, and water table fluctuations.

In the absence of long-term NSZD studies, there is uncertainty about the changes in the NSZD rate over time. Based on several lines of evidence, a zero-order depletion rate can be assumed for much of the life of an LNAPL release, until only a

low saturation or LNAPL or a relatively recalcitrant fraction is left ([Garg et al. 2017](#)).

It is sometimes assumed that the bulk NSZD rate will eventually decrease as the LNAPL is depleted of its more volatile, soluble, and bioreactive constituents. It has been further hypothesized that LNAPL depletion will reach a 'break point', where LNAPL depletion and/or compositional change results in a reduction of rates and transition to first-order rate kinetics. ([Siddique et al. 2008](#)) report zero-order rates when naphtha concentration oil sands was over 5,000 mg/Kg in, soil and first order for lower concentrations.

Similar to the issue of changes in bulk NSZD rates over time, there is currently insufficient information to allow quantitative projections of the long-term changes in LNAPL composition and associated COC partitioning to groundwater. Specific hydrocarbon compound degradation is highly dependent upon dissolved concentration, microbial diversity, and subsurface heterogeneity ([Zeman et al. 2014](#)). In a study of the volatile hydrocarbon content of an LNAPL over a 21-year period, depletion of individual volatile hydrocarbons from the LNAPL ranged from 13 to 64 percent ([Baedecker et al. 2011](#)). Earlier studies by the U.S. Department of Defense showed BTEX weathering from oil varied based on spill age, relative solubility, LNAPL geometry, and the rate at which groundwater and precipitation contact the mobile LNAPL ([Parsons 2003](#)). The average observed total BTEX, first-order weathering rate for jet fuel number 4 (JP-4, a 50:50 kerosene-gasoline blend) was 15 percent by mass per year, with the lowest rates occurring at sites with low groundwater velocities.

The biodegradation processes of NSZD do not reduce LNAPL mass solely via dissolution into the aqueous phase. LNAPL mass may also be depleted by direct oil contact biodegradation and outgassing without dissolution. The known microbial biodegradation mechanisms are:

1. Uptake of soluble LNAPL constituents in the aqueous phase.
2. Uptake of hydrocarbon microdroplets that have been pseudosolubilized by microbial biosurfactants.
3. Uptake of hydrocarbons by microorganisms that grow in fatty acids that are in direct contact with LNAPL.

The second and third mechanisms may also deplete less soluble and insoluble hydrocarbons. Together, these mechanisms may contribute to zero-order NSZD rates ([Garg et al. 2017](#)); ([Hua and Wang 2014](#)); ([Meckenstock et al. 2014](#)).

In the evolution of an LNAPL release, reductions of an order-of-magnitude or more in concentrations of COCs such as benzene are often seen in the aqueous phase plumes that emanate in the down-gradient direction from an LNAPL zone. However, within and immediately adjacent to the LNAPL body, aqueous phase COC concentrations are typically more persistent and stable. NSZD weathering effects and associated improvements to water quality within or close to the LNAPL are too complex for accurate, quantitative projections with current models. Better understanding of these long-term effects will require long-term field studies or comparative studies of similar release sites at different stages of evolution. However, this detailed information is not necessarily required for implementation of NSZD as a remedy. In situations where potential receptors are not at risk, risk management measures such as a groundwater management zone are available (see [Section 5.3.2](#)), and where site conditions generally remain the same, then an understanding of bulk LNAPL mass loss rates will often be sufficient for purposes of assessing the appropriate role of NSZD in site remediation and risk management.

5.2 NSZD Side-Effects

As described in [Section 2](#), NSZD processes result in changes to groundwater geochemistry. Intrinsic bioremediation processes in the core of the LNAPL zone will drive geochemical conditions to a lower oxidation-reduction potential (ORP) than in the background, surrounding zone of saturation. As a result, groundwater within and downgradient of the LNAPL zone often exhibits higher concentrations of total dissolved solids and reduced metals (e.g., iron, manganese, and in some cases, arsenic). Within and near the LNAPL zone, these changes to inorganic groundwater geochemistry will persist for as long as the LNAPL continues to undergo NSZD. Experience has shown that most mobilized metals oxidize and precipitate when groundwater conditions downgradient of the LNAPL/NSZD zone return to background ([ITRC 2008](#)) and ([EPA 2013](#)).

It is often presumed that the carcinogenic indicator compounds (e.g., benzene, ethylbenzene, and naphthalene), rather than other petroleum compounds that may be present at petroleum release sites, drive risk-based decision making. Through

NSZD processes, hydrocarbons undergo “weathering” and biotransformation, and a current topic of inquiry is the extent to which degradation products, particularly polar metabolites, should be considered in LNAPL site risk assessment and risk-based site management decision-making. The polar metabolites that have been detected in petroleum release sites consist almost entirely of hydrocarbon oxygenates (Zemo et al. 2013); (Bekins et al. 2016) that include alcohols, phenols, aldehydes, ketones, and acids/esters. The chemistry and toxicity of these petroleum metabolites are issues of current interest. The ITRC TPH Risk project is evaluating this issue, and the work product from this ongoing project should be consulted for additional information on this topic.

5.3 Remedy Considerations

The following list discusses key considerations for making decisions related to NSZD and incorporating NSZD into an LNAPL site management strategy.

1. LNAPL mass depletion occurs through a combination of natural processes (volatilization, dissolution, and biodegradation) that change the composition and reduce the saturation of the source LNAPL. These natural processes are observable at all LNAPL release sites with mobile or residual LNAPL. The rate that these processes deplete LNAPL mass, the bulk NSZD rate, can be quantitatively estimated through a variety of methods. The NSZD rate serves as the basis by which NSZD may be evaluated as a remediation alternative.
2. NSZD is an important component in each step of the LCSM including the Initial, Remedy Selection, and Design and Performance LCSMs (see also Figure NSZD-5):
 1. Initial LCSM: The NSZD processes are one reason LNAPL plumes are typically stable (not migrating).
 2. Remedy Selection LCSM: There are a variety of ways in which NSZD may appropriately be incorporated into an LNAPL site remedy: i) as a benchmark to compare the effectiveness or efficiency of other remedies, ii) as the final step in a treatment train to achieve remedial objectives, iii) as an “up front” remedy for a portion of the site, or iv) as the primary remedy for older, stable LNAPL sites.
 3. Design and Performance LCSM: An NSZD monitoring program that is designed to evaluate progress toward meeting the remedial goals will often be appropriate. These goals could include: i) reducing mass within the LNAPL source zone to achieve LNAPL body stability (saturation objective), ii) maintaining effective NSZD processes in the LNAPL source zone to achieve mass losses that are comparable or better than LNAPL fluid recovery systems (saturation objective), and/or iii) mitigating dissolved contaminant plume migration (composition objective).
3. If NSZD is selected as a remedy, it is important to establish SMART (specific, measurable, attainable, relevant, and timely) performance metrics. Examples include i) sustained NSZD mass loss rates in core areas of the LNAPL body, ii) NSZD mass loss rates in excess of measured lateral LNAPL flux through monitoring wells, iii) stable lateral footprint of the LNAPL body as indicated by maintained absence of in-well LNAPL in select perimeter sentinel wells, iv) stable and/or receding geospatial distribution of the dissolved phase contaminant plume, or v) reduced mole fraction of COCs in the LNAPL.
4. At sites where the LCSM establishes the role of NSZD processes in the evolution of the LNAPL release, and NSZD processes have progressed to a point where both composition and saturation concerns are eliminated, aqueous and vapor phase plume and LNAPL footprint have stabilized and are contracting, and potential receptors are not at risk, NSZD merits consideration as the primary remedy component.
5. At some sites, NSZD may be the primary remedy component for portions of the LNAPL zone, allowing engineered remediation systems, including enhanced-NSZD, to be focused on those portions of the LNAPL footprint where achieving remedial goals requires more aggressive remedies and will provide the most benefit to reduce or mitigate saturation concerns (e.g., LNAPL recovery near the release area where significant volumes of recoverable LNAPL still exist, or where the LNAPL footprint extends to a receptor exposure point [e.g., sheen discharge to surface water]).
6. NSZD will often be implemented as the final step in a treatment train, whereby an initial remedy has achieved its endpoint prior to achieving the site-wide remedial objectives, and the remedy then transitions to NSZD for long-term risk management. With appropriate evaluation of NSZD and incorporation into the Design and Performance LCSM, the transition to NSZD can be a part of the specified remedy, implemented within the framework of a performance monitoring plan, and triggered by achievement of a pre-established performance metric (e.g., a specified mass removal/recovery rate, LNAPL transmissivity, or plume stability demonstration).
7. At many sites that are already in the remediation and performance monitoring phase, the decision framework for determining the endpoint of the implemented remedial technology is not often well prescribed or technically

achievable. For these sites, practice has evolved to use multiple lines-of-evidence to justify transition. For example, the (NRC 2013) proposes taking risk reduction, life-cycle costs, and technical feasibility into account during a transition process that is transparent, reduces long-term risks to an acceptable level, and is practical and cost effective. Based on these considerations, transition to NSZD as the final remediation component will merit consideration at many sites.

8. When the remedy transitions to NSZD, LNAPL composition and/or saturation concerns may still be present (e.g., dissolved-phase concentrations above cleanup standards or mobile LNAPL is present in monitoring wells). In some regulatory settings, a demonstration that LNAPL concerns are controlled and NSZD continues to deplete the LNAPL source may be adequate to support a No Further Action decision.
9. In other regulatory settings, the implementation of NSZD to remedy LNAPL concerns requires performance monitoring to assure protection of potentially exposed populations and assess progress toward meeting the remedial goals. Depending on site-specific considerations, NSZD performance metrics could include the SMART performance metrics discussed in Item 3. The monitoring program could include one or more of the methods described in [Section 3](#) and [Section 4](#), or could incorporate more traditional long-term monitoring methods (see Figure NSZD-5).
10. To provide an appropriate level of protectiveness and ensure NSZD remedy performance, it will often be appropriate to include contingency planning in the NSZD remedy. If the performance of NSZD is not adequate, and the monitoring data indicates that the remedy fails to meet one of the performance metrics, then the remedy must be adjusted or optimized to achieve remedial goals. (ITRC 2006) prescribes decision logic for optimization and contingency planning to achieve the stated performance monitoring objectives.

5.3.1 Remedy Transition to NSZD and Case Studies

Often, there comes a time during remedy implementation (i.e., of an LNAPL fluid recovery system) when the monitoring data indicates that a change or remedy optimization is needed. A remedy transition is a process by which an ineffective and/or inefficient remedy is stopped and another remedy is started or an ongoing remedy such as NSZD is put in the lead role to more effectively and efficiently achieve remedial objectives. LNAPL remedial technology transition is discussed in the main body text, [Section 5.4.5](#). NSZD will often be a component of an LNAPL site remedy and in some cases part of a treatment train approach (as discussed in [Section 5.4.4](#) of the main body text), whereby an initial remedy is deployed to reduce mass and after it has achieved its goal, will transition to NSZD.

Remedy Transition

Almost all remedial technologies (e.g., LNAPL fluid recovery, multiphase extraction) will progress to a point where mass removal rates become relatively low, and continued operations will remove small additional amounts of mass that are insignificant relative to the cumulative mass reduction previously achieved. At this point, the level-of-effort in continued operation will not provide commensurate value in terms of increased environmental protection and/or risk reduction, and the practical endpoint of the engineered mass removal technology will have been achieved. This is the appropriate point for transition.

The basis for remedy transition is well founded in the existing literature. The National Research Council (NRC) realized that complex sites, inclusive of LNAPL, require an adaptation to the post-remedy-selection decision-making process that incorporates alternative protective end states other than clean closure (ITRC 2017a) and (NRC 2013). For example, NRC states “Specifically, if data indicate that contaminant concentrations are approaching an asymptote [and optimization has been exhausted], resulting in exponential increases in the unit cost of the remedy, then there is limited benefit in its continued operation. At this point of diminishing returns, it is appropriate to assess whether to take additional remedial action (if legally possible) or whether to transition to more passive long-term management.” The NRC goes on to provide recommendations for a transition assessment that can accelerate the transition of sites to several end states, one of which includes “...long-term passive management (e.g., using natural attenuation [NSZD for LNAPL] with or without monitoring, physical containment, permeable reactive barriers, institutional controls, or some combination thereof)...” Additionally, the ASTM Standard Guide for Greener Cleanups (ASTM 2014c) recommends switching to a less energy intensive technology for the final steps of remediation when possible (for example, suspend pump and treat or SVE and initiate bioremediation or phytotechnology) when overall energy balance supports the concept.

A flowchart that illustrates the decision logic leading to remedy transition to NSZD (modified from ITRC’s Complex Sites guidance document (ITRC 2017b) is presented in Figure NSZD-14. This flowchart addresses the common scenario where a specified remedy contains both NSZD and an interim active remedy, and assumes performance and endpoint metrics were established for both remedy components. These metrics allow for clear decision making during the monitoring phase of the

project. Similar flow charts may be found in other guidance documents ([LALWG 2015](#)); see Figure 8-1).

The impetus for transition to NSZD is typically triggered by achievement of a pre-established performance metric such as:

- a specified LNAPL recovery rate (e.g., a rate that is not significantly greater than the NSZD rate, or that a feasibility study establishes as not providing commensurate value relative to NSZD considering various aspects of effectiveness and cost)
- a specified LNAPL transmissivity
- demonstration of LNAPL plume stability for a specified period of time
- remedy performance has reached its practical limit (e.g., steady COC concentrations in groundwater or negligible rate of rise in an active recovery system cumulative mass removal curve)

In many cases, the active (interim) remedy will have achieved its performance metric, but COC concentrations in environmental media (most typically groundwater) in excess of remedial objectives will still persist. As shown on Figure NSZD-14, when the performance metric for the active remedy is met, it is time to transition.

For the scenario when no transition criteria have been established, the decision logic in Figure NSZD-15 can also be used. In these situations, an additional step is needed. When the decision criteria or logic for transition to NSZD is not well prescribed in decision documents, but the need emerges for remedy transition to a more effective and efficient approach (e.g., when a mass removal plateau is observed), practice has generally evolved to use multiple lines-of-evidence to justify transition. For example, the ([NRC 2013](#)) proposes taking risk reduction, life-cycle costs, and technical feasibility into account during a transition process that is transparent, reduces long-term risks to an acceptable level, and is practical and cost effective. Figure NSZD-15 presents a flowchart that can be used to assess a newly defined need for remedy transition. In this scenario of a newly defined need for remedy transition, the decision-making process will be a site-specific judgment involving input from all key stakeholders.

Figure Note:

This is a modified version of Figure 5-4 from the main body text of LNAPL-3 intended to illustrate a scenario whereby an active remedy and NSZD are selected and ultimately used to achieve site closure.

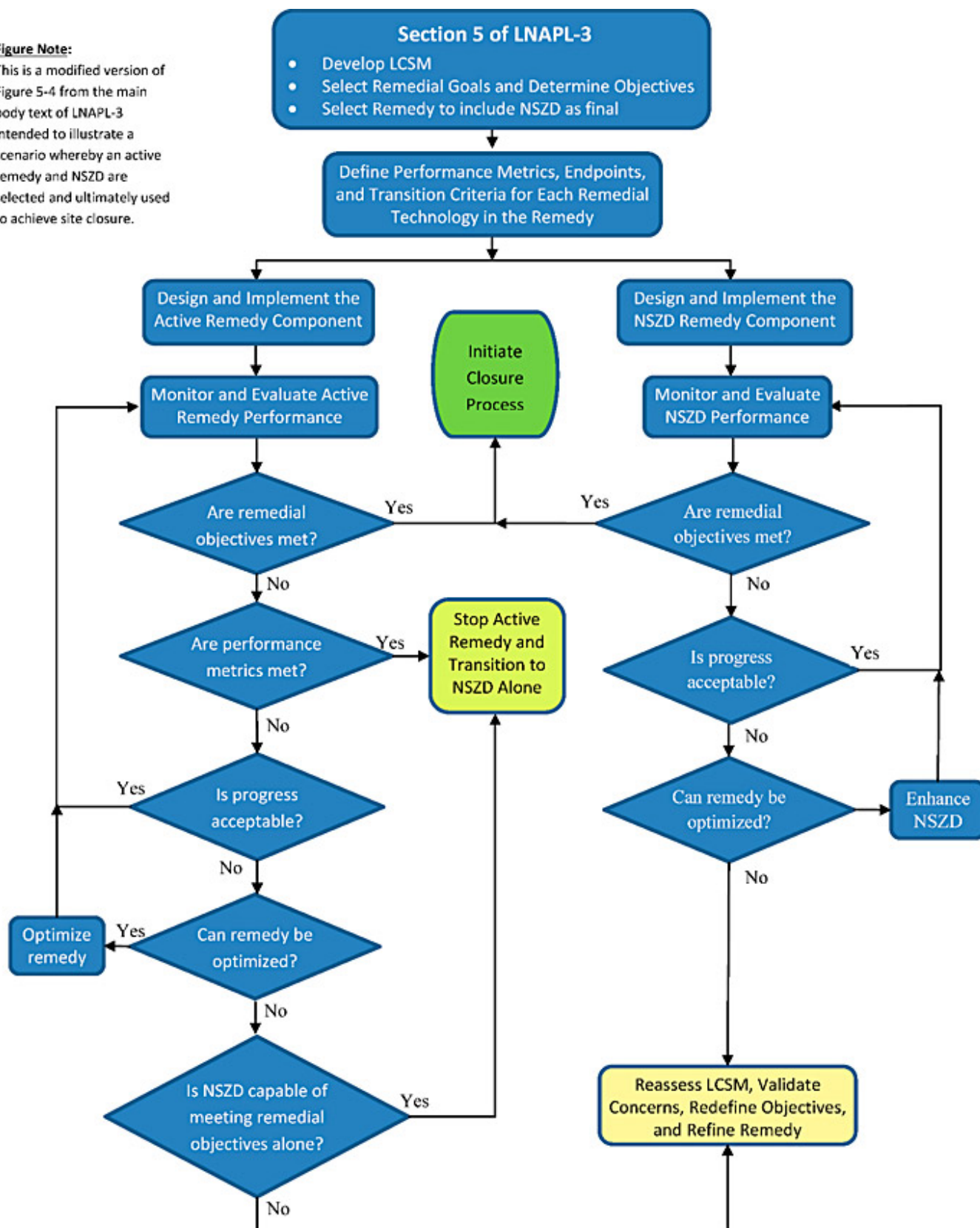


Figure 6-1. Combined Active-NSZD remedy management flowchart.
NSZD Appendix to 2017 ITRC LNAPL TechReg Guidance

Figure NSZD-14. Combined active-NSZD remedy management flowchart.

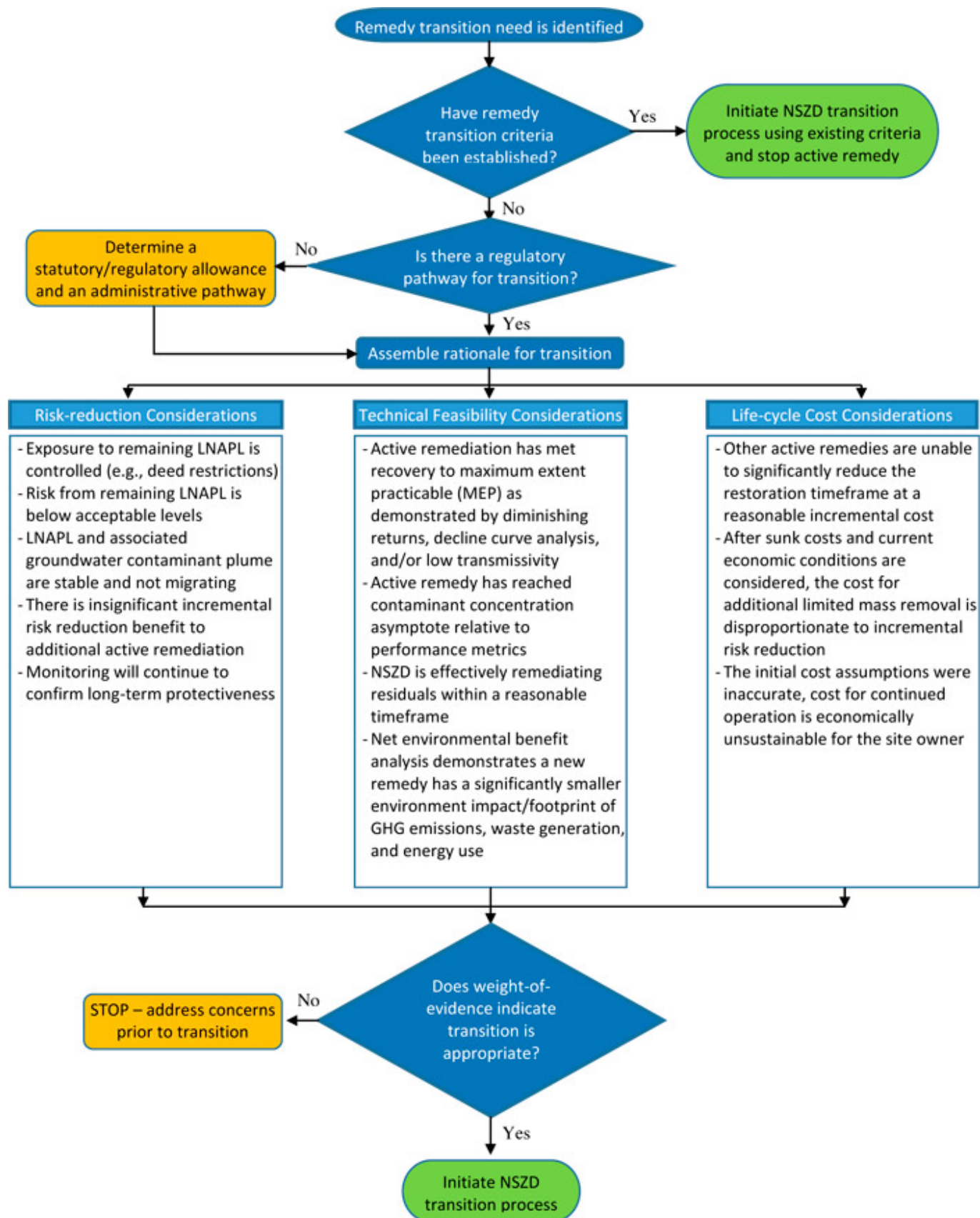


Figure NSZD-15. New transition need flow chart.

To illustrate the use of multiple lines-of-evidence to justify transition from LNAPL fluid recovery to NSZD, three case studies are presented on Insets NSZD-1 through NSZD-3.

Inset NSZD-1. Case Study 1 - Selection of NSZD Remedy [Read more](#)

- Former used oil recycler
 - Old, viscous, highly degraded mixture of oils
 - LNAPL in highly heterogeneous natural and man-made fill surrounded by native clay
- Measured LNAPL transmissivity and MPE operations indicate recovery is impractical
 - LNAPL recharge rate following bailing **slow**
 - No significant LNAPL recharge 70 days post-bailing
 - Negligible recoverability confirmed during short-term MPE pilot-testing
 - Approximately 0.0007 and 1 gal at two wells

- Exposures Assessment
 - Groundwater quality: no exceedances of relevant risk-based criteria
 - Engineered cap and Restrictive Covenant (non-residential land use, groundwater use prohibition) ensure future protectiveness



- Drivers for Ongoing Remediation
 - LNAPL stable on-site and negligible recoverability = no saturation-based driver for active remediation
 - No compositional driver for active remediation

Full-Scale MPE Performance		Risk-Reduction	Technical Feasibility	Life-Cycle Cost
Total LNAPL recovered	104 gal 784 lb	No threat of LNAPL migration	Extent of LNAPL in wells stable onsite	Continued mass removal using active remedy would cost >\$10,000/gal LNAPL recovered
Average LNAPL recovery rate	0.5 lb/hour			
Cost	>\$1 M >\$10,000/gal LNAPL >\$1,200/lb LNAPL	No COC exceedances in groundwater	Impractical recoverability	>315,000 lb CO ₂ e (USEPA SEFA estimate)
GHG emissions – CO ₂ , CH ₄ , N ₂ O (based on electrical power consumption, USEPA eGRID emission factor)	> 330,000 lb (>230 lb/hour)	Restrictive covenant restricts exposure	Significant environmental footprint of active remedy	
Environmental Footprint (based on USEPA SEFA spreadsheets, power consumption, manufacturing of materials, groundwater extraction, etc.)	315,000 lb CO₂e 16,000 lb NO_x+SO_x+PM 80 lb HAPs			

Initiate NSZD Transition

(Credit: Matthew Rousseau, GHD, matthew.rousseau@ghd.com)

Inset NSZD-2. Case Study 2 - Transition from LNAPL Fluid Recovery to NSZD [Read more](#)

- Jet fuel pipeline release site
- Silt and clay overly silty, fine-grained sand, K~11 ft/day
 - Depth to water 54-61 ft bgs, rose 16-ft since release in 1995
 - Smear zone is submerged >10 ft below water table and LNAPL is immobilized
- Source excavation (500 tons to 18 ft bgs) performed after release discovery, did not reach vertical extent
- An LNAPL skimmer recovery system (10 yrs O&M) removed 10,140 gallons of LNAPL
 - Recovery rates dropped from 6,000 to 100 gallons/yr
- An SVE system (5 yrs O&M) operated to maximum extent practical and removed 9,600 gallons of LNAPL
- An NSZD evaluation quantified:
 - Groundwater COCs above MCLs within source zone, no dissolved phase plume downgradient of LNAPL footprint
 - Biogeochemical mass budgeting shows 9-12 gallons per year of LNAPL depletion via aqueous processes
 - CO₂ efflux monitoring showed an additional 700-1,300 gallons per year of LNAPL mass losses via NSZD

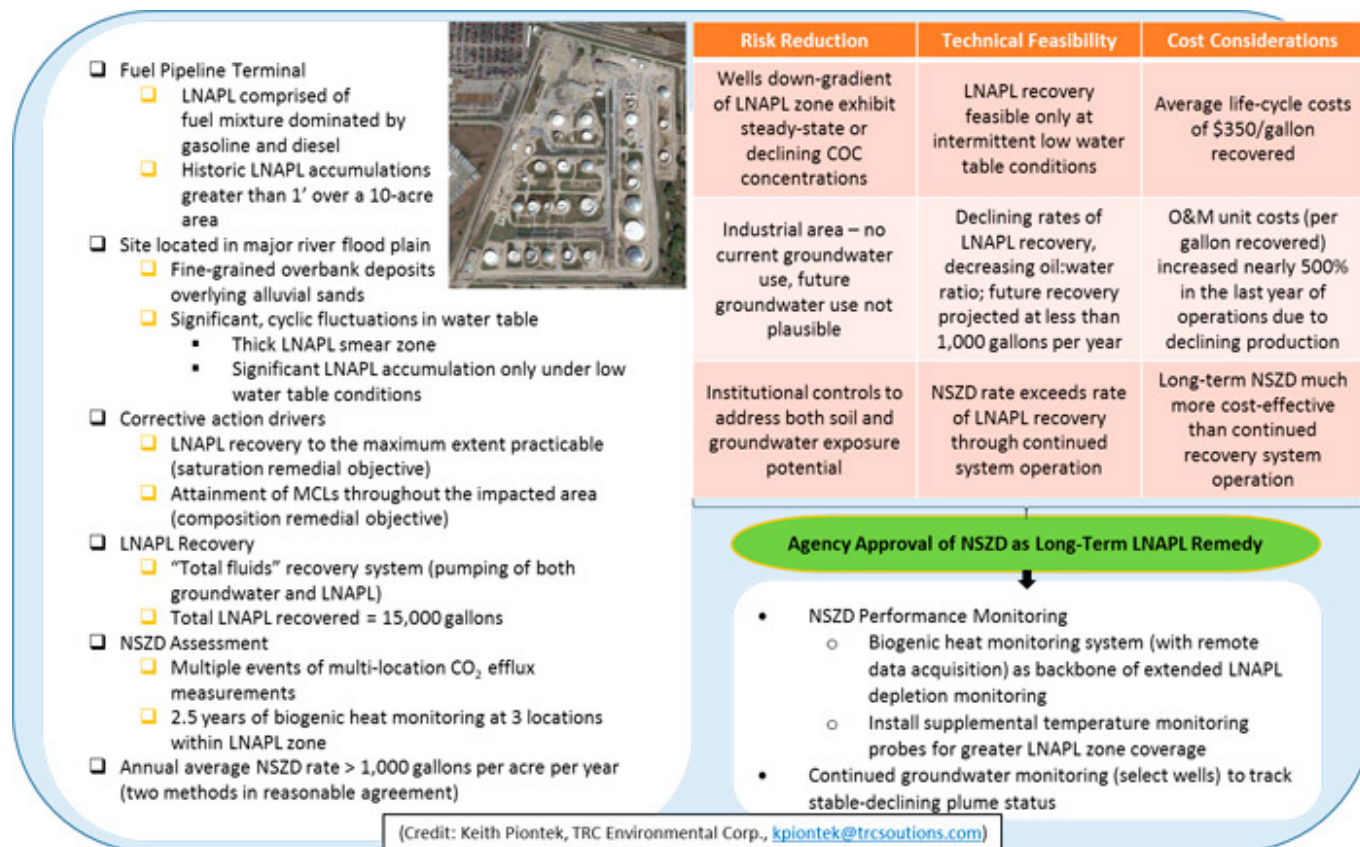


- Exposure assessment
 - Multiple observations indicate the LNAPL plume is stable
 - Industrial land use surrounding, site is within utility R.O.W.
 - Water Table aquifer is not used for potable purposes, within an area served by a POTW, and groundwater rights are strictly legally controlled
 - Nearest downgradient groundwater use associated with refineries process supply, municipal supply is 1/2 mile upgradient in XXX-ft deeper formation
 - No current unacceptable exposure scenario
 - No indoor or ambient health risks identified
 - Soil impacts >18 ft bgs

Risk-reduction	Technical Feasibility	Life-cycle Cost
No threat of LNAPL nor dissolved plume migration	Active remediation was effective, but NSZD is now most effective (1,000 vs 100 gals/yr)	None needed.
Industrial land use and no receptors	Impractical LNAPL recovery, $T \sim 0.05$ ft ² /day	
Groundwater is within a legally enforced use area	LNAPL and dissolved plumes are stable	

INITIATE NSZD TRANSITION

Inset NSZD-3. Case Study 3 - Agency Approval of NSZD as Long-Term LNAPL Remedy [Read more](#)



5.3.2 NSZD Implementation and Remedy Endpoint

There will come a time during the performance monitoring phase when the remedial goals and objectives are met. When this occurs, the remedy may be discontinued and the site proceeds to a no further action (NFA) or closure state.

The ITRC (2006) has documented the advantages of an exit strategy for remediation. A key component of the exit strategy is the decision logic to terminate a response action. Firm endpoint criteria are necessary to determine when an LNAPL remedy is complete and avoid perpetual remediation without compensatory environmental benefit. It is most productive if the shutdown and endpoint criteria and decision logic leading to them are documented and agreed upon by the project stakeholders in advance of remedy implementation. Gaining up-front consensus on the process that will be used to determine when the LNAPL remedy will be deemed complete is invaluable to the efficiency of remedy completion. Each remediation technology/system should have its own endpoints.

The endpoint of an NSZD remedy will vary based on site-specific conditions, the governing regulatory program, and how NSZD is used as a remedial technology. Table NSZD-4 lists viable NSZD remedial endpoints for various regulatory programs and the monitoring data that can be used to support NFA or closure proceedings.

Generally, when the remedy transitions to NSZD, LNAPL composition and/or saturation concerns may still be present (e.g., dissolved-phase concentrations above cleanup standards or mobile LNAPL is present in monitoring wells). In some regulatory

Enhancing NSZD

NSZD performance monitoring and evaluation could potentially identify situations in which NSZD is not maintaining sufficient progress toward attainment of remedial objectives. In such a situation, alternatives for enhancing the rate of biotic mass removal processes should be considered. Alternatives could include enhancing the rate of prevailing biotic reactions (thermal enhancement of methanogenesis) or switching to faster processes (e.g., bioventing to support aerobic biodegradation in zones that are currently methanogenic).

settings, the implementation of NSZD to address remaining LNAPL concerns will require performance monitoring to assure protection of potentially exposed populations, assess progress toward meeting the remedial goals, and/or demonstrate continued LNAPL depletion through NSZD for a period of time. Depending on site-specific considerations, NSZD performance metrics could include the SMART performance metrics (see “key considerations” item 3 at the beginning of Section 5.3). The monitoring program could include one or more of the methods described in Sections 3 and 4, or could incorporate more traditional long-term monitoring methods (see Figure NSZD-5).

To provide an appropriate level of protectiveness and ensure NSZD remedy performance, it may be appropriate to include contingency planning in the NSZD remedy. If the performance of NSZD is not adequate, and the monitoring data indicates that the remedy fails to meet one of the performance metrics, then the remedy must be adjusted or optimized to achieve remedial goals. (ITRC 2006) prescribes decision logic for optimization and contingency planning to achieve the stated performance monitoring objectives.

If NSZD is used as a terminal remedy (i.e., the final step in a combined remedy), then its endpoint will often be defined as attainment of the remedial objectives. In some regulatory settings, a demonstration that LNAPL concerns are controlled and NSZD will continue to deplete the LNAPL source may be adequate to support a No Further Action decision. For a detailed example of the development of a remediation process endpoint for situations where a significant mass of residual LNAPL in the subsurface cannot or is technically impracticable to remove, see the “Residual Management Zone” concept (LALWG 2015).

Table NSZD-4. Example NSZD remedial endpoints associated with various regulatory considerations

Regulatory Framework or Scenario	Possible Remedial Endpoint for NSZD¹	Indicator Data²
LNAPL removal to the maximum extent practicable (MEP)	Sustained NSZD mass loss rates	Periodic or continuous NSZD rate measurements for a demonstration period of sufficient duration (will vary)
Risk-based corrective action (RBCA)	No unacceptable risk to human health or the environment	COC concentrations at potential receptor locations are below risk-based criteria LNAPL is being degraded and the aqueous phase plume is at steady-state or declining status
Attainment of specified water quality criteria throughout the zone of impact	In some jurisdictions and for some sites, the criteria may be based on potable groundwater use (e.g., Maximum Contaminant Levels)	Groundwater samples and analysis for COCs
LNAPL Residual Management Zone or similar	LNAPL is residual in nature and not migrating and NSZD is documented as occurring and ongoing	No detection of LNAPL outside the limits of the management zone

Notes:

1. The remedial endpoint for NSZD is defined as the criteria required to obtain a No Further Action (or equivalent) determination from the governing regulatory agency.
2. It is important to note that the indicator data for compliance with endpoint criteria may or may not include NSZD monitoring as documented in this appendix. For example, if NSZD is adequately quantified and established to be effective, then performance monitoring may be as simple as monitoring groundwater COC concentrations over time. Ongoing NSZD rate measurements may be unnecessary if all other indicators are progressing as expected.



Appendix C - Transmissivity (T_n) Appendix

1. Introduction

In the simplest terms, LNAPL transmissivity (T_n) quantifies the rate that LNAPL can be pumped from a well. LNAPL transmissivity can readily be measured and compared to a threshold standard established by regulatory authority or site stakeholders. However, as discussed in this appendix, there is a broader spectrum of uses for LNAPL transmissivity: planning for LNAPL recovery pilot tests, optimizing and tracking LNAPL recovery remedies, designing LNAPL recovery systems, and making a case for compliance with policy requirements for LNAPL recovery to the maximum extent practicable.

LNAPL transmissivity describes the capacity of aquifer materials to transmit LNAPL. It is analogous to groundwater or aquifer transmissivity and is expressed in units of square length over time, which represents the flowrate of LNAPL through a unit width of aquifer under a unit gradient.

$$T = Q / (w \cdot i)$$

Where:

T = LNAPL transmissivity, L^2/T

Q = LNAPL flow rate, L^3/T

W = unit width of aquifer, L

i = LNAPL gradient, L/L

A key difference as compared to the basic concept of groundwater transmissivity is that LNAPL moves in a multiphase (LNAPL, groundwater, and soil gas) flow regimes and, therefore, LNAPL transmissivity is a function of the LNAPL saturation and relative permeability of porous media to LNAPL flow. Groundwater transmissivity is also affected by the presence of LNAPL and is a function of the water and LNAPL saturation and the relative permeability of the porous media to groundwater flow. LNAPL transmissivity is not an intrinsic property of the media alone, but also depends on the multiphase conditions and the properties of the LNAPL.

LNAPL recoverability is not directly proportional to the thickness of LNAPL that accumulates in a well ([Kirkman, Adamski, and Hawthorne 2013](#)). However, LNAPL recoverability is directly proportional to LNAPL transmissivity. Therefore, LNAPL transmissivity can be used as a threshold metric to evaluate LNAPL migration concerns or a performance metric for LNAPL recovery evaluation.

Top Three Things to Know about LNAPL Transmissivity (T_n)

1. T_n describes a basic relationship between LNAPL drawdown in a well and LNAPL flow to that well. This makes it a representative metric for LNAPL recoverability by any hydraulic method—including skimming, pumping, vacuum extraction, or manual bailing.
2. T_n measurements must be used in context of the overall LCSM; identifying potentially confined or perched conditions and understanding seasonal changes are important to accurately measuring and appropriately using T_n as a metric.
3. T_n measurements are relevant to LNAPL saturation remedial objectives (e.g., recovering LNAPL to the maximum extent practicable, or controlling LNAPL migration) and are not directly relevant to composition-based remedial objectives (e.g., meeting dissolved-phase groundwater standards).

Historical and recent research substantiates the use of LNAPL transmissivity as a reliable indicator of LNAPL recovery potential [([Kolhatkar et al. 1999](#)); ([Lundy and Zimmerman 1996](#)); ([Kirkman 2013](#)); ([ASTM 2013](#)); ([API 2016](#)); ([Palmier et al. 2000](#))]. This research identifies the theory that underpins LNAPL transmissivity and how data analysis practices have evolved over time [([Lundy and Zimmerman 1996](#)); ([Huntley 2000](#)); ([Kirkman 2013](#))] as well as model and field validation of various methodologies ([Kolhatkar et al. 1999](#)) and ([Palmier et al. 2000](#)).

1.1 LNAPL Transmissivity Application

LNAPL transmissivity was initially used in the 1990s to evaluate hydraulic recovery of LNAPL ([Lundy and Zimmerman 1996](#)); ([Kolhatkar et al. 1999](#)). Since that time LNAPL transmissivity has been applied throughout the life cycle of LNAPL projects. Some examples of the broader use of LNAPL transmissivity are:

- LNAPL CSM: During development of the LNAPL conceptual site model, existing information on transmissivity and related parameters should be reviewed, and LNAPL transmissivity can be used as one line of evidence to evaluate LNAPL migration concerns.
- Pilot Testing: LNAPL transmissivity measurements can be used to plan pilot tests. Depending on scale and type of test, the LNAPL transmissivity measurements on their own may be considered a pilot test of LNAPL recovery.
- Technology Selection and Design: The results of LNAPL transmissivity testing can be used to guide selection of remediation technology, determine equipment sizing, and establish appropriate recovery well density.
- Remedy Optimization and Progress Tracking: LNAPL transmissivity may be used to track and optimize remediation, identify areas to focus remediation, and estimate remediation timelines.
- Technology Threshold Metric: An LNAPL transmissivity between the range of 0.1 to 0.8 ft²/day may be used as a decision point for remedial system operation or technology transitions.
- Defining maximum extent practicable (MEP): LNAPL transmissivity can be an indication of whether an MEP endpoint has been reached and may be interpreted within a framework that includes other complementary metrics. [Section 1.2](#) discusses this further.

While LNAPL transmissivity is useful for evaluating LNAPL hydraulic recovery potential, it should not be used as a sole means to determine whether an LNAPL remedy for a site is necessary or unnecessary. LNAPL transmissivity does not characterize LNAPL composition concerns (e.g., human health or environmental risk as defined by RBCA ASTM and regulatory programs developed for sorbed, dissolved and vapor phase chemicals of concern). Another constraint is that LNAPL transmissivity is useful as part of an overall LNAPL plume stability evaluation, but a low transmissivity condition does not eliminate potential for sheen generation to a nearby surface water body. The decision on whether to implement an LNAPL remedial action should be based on the broader site LNAPL CSM rather than LNAPL transmissivity alone.

If a decision has been made to pursue LNAPL recovery, LNAPL transmissivity is one of several metrics that can be used to evaluate remediation technology performance. Site conditions and remediation stage dictate whether LNAPL hydraulic recovery, vapor extraction (if applicable), or biodegradation are the dominant mass removal mechanisms. Calculation of mass removal rates using common units (e.g., gallons per acre per year removed) facilitates removal mechanism comparison.

If LNAPL mass recovery is ongoing, LNAPL transmissivity can provide a metric to understand remedy progress and define the point at which hydraulic LNAPL recovery is no longer beneficial. LNAPL transmissivity directly varies with LNAPL saturation and thus offers a direct measure of the effect of LNAPL recovery on mobile LNAPL. LNAPL transmissivity measures the recoverability of the mobile LNAPL present and provides a metric to measure progress towards residual saturation (defined by zero LNAPL transmissivity). A threshold LNAPL transmissivity value, typically representative of an LNAPL saturation that is nominally above the residual LNAPL saturation for the formation, may be established at the outset of the LNAPL recovery action and used as a trigger for stopping LNAPL recovery. This can be useful as an optimization strategy to discontinue LNAPL recovery from wells or trenches where little recoverable LNAPL is present and focus recovery efforts on locations with higher transmissivity and more recoverable LNAPL.

It should be noted that LNAPL transmissivity measurements often vary in both space and time. For example, groundwater fluctuations can occur such that the LNAPL fluctuates from unconfined to confined conditions. In that situation, it may be necessary to measure LNAPL transmissivity values under both conditions. Repeated LNAPL transmissivity measurements may produce consistent values or result in extremes for some sites. In the case of extremes, spatial and temporal averaging of LNAPL transmissivity values can produce a more reliable understanding of LNAPL recoverability for use in site decision making.

The LNAPL transmissivity testing and estimation methods presented in the following sections provide a well-established framework to evaluate transmissivity for a wide variety of site conditions. This testing framework has been expanded based on recent experience to properly select and scale the testing and analysis to an individual site. Discussions of specific scenarios have been provided to support application and considerations of LNAPL transmissivity.

1.2 Maximum Extent Practicable

The United States federal government set an expectation in the Code of Federal Regulations (40 CFR 280.64 subpart F) that at underground storage tank sites where a petroleum release occurred and LNAPL is present, “*owners and operators must remove free product to the maximum extent practicable as determined by the implementing agency.*” The regulation further states that abatement of free product migration should be used as a minimum objective for design of an LNAPL recovery system.

State environmental regulators are typically the implementing agencies and there has been variability in state definitions of MEP. Historically, many state environmental regulatory agencies used *de minimus* LNAPL thicknesses, e.g., 0.01 foot, in wells as evidence of compliance with the federal MEP mandate. Some jurisdictions allow(ed) a pragmatic definition of MEP based on operation of an intensive LNAPL recovery action to the point that the remediation system was no longer producing meaningful volumes of LNAPL. This approach is effectively a site-specific, empirical definition of recovery to the MEP.

There are a number of methods that can be used individually or in combination to demonstrate compliance with the MEP requirement. These include:

- comparing mobile LNAPL mass to the mass of LNAPL in the smear zone,
- analyzing LNAPL recovery data and determining that future recovery will not be meaningful,
- showing that LNAPL thicknesses are small and/or intermittently observed,
- modeling future potential LNAPL recovery using a multiphase model,
- demonstrating that the LNAPL body is stable and that stability will not change in the future, and
- presenting information that shows an unreasonable cost per gallon or pound of LNAPL recovered.

This section is not intended to be a full discourse on MEP and but rather a discussion of how LNAPL transmissivity can be used for demonstration of compliance with MEP.

As of 2017, several state regulatory agencies have formally adopted MEP definitions that incorporate LNAPL transmissivity and many others have accepted LNAPL transmissivity in when considering remediation system shut down and site closure decisions. Colorado, Kansas, Massachusetts, Michigan, and Virginia have published technical guidance stating that LNAPL transmissivity will be considered in making decisions on the need for LNAPL recovery actions. Michigan and Kansas explicitly linked LNAPL transmissivity to their interpretation of MEP. Michigan LNAPL guidance defines MEP as “*recovery of all NAPL that can be recovered in a cost effective and efficient manner*”. The guidance further states that “*if the NAPL has a transmissivity greater than 0.5 ft²/day, it is likely that the NAPL can be recovered in a cost-effective and efficient manner unless a demonstration is made to show otherwise.*” Kansas LNAPL guidance defines MEP as “*recovery of all LNAPL with a transmissivity greater than 0.8 ft²/day that can be recovered in an efficient, cost-effective manner.*”

One meaningful advantage to the use of LNAPL transmissivity in determining compliance with MEP is avoiding implementing recovery actions that will not remove a meaningful amount of the source mass based on industry experience. This is useful if there is an overall objective of maximizing the environmental net benefit in relation to (often limited) remediation resources.

1.3 LNAPL transmissivity range in the 2009 ITRC LNAPL document

The LNAPL transmissivity range of 0.1 to 0.8 ft²/day has been referenced by many site owners and practitioners, and has been incorporated into LNAPL technical guidance by some state environmental regulatory agencies. Given the degree to which this range has been adopted by many stakeholders, the ITRC team has assembled background information on the origin of the 0.1 to 0.8 ft²/day range. The following presents conditions at the sites that were used as the basis for the range.

Site One [▼Read more](#)

Following a Site Phase II and Phase III ESA, the site conceptual model identified two areas with LNAPL impacts. Area 1 is summarized with the following key points:

- The subsurface consisted of silty clay with sand lenses that contained hydrocarbon impacts based on laser induced fluorescence investigation.
- Impacted sand lenses frequently occurred below the water table and represented residual and/or confined mobile LNAPL.
- The mobile LNAPL exhibited LNAPL transmissivity values of 0.1 to 4 ft²/day.

- LNAPL distribution was understood through soil borings, fluid gauging data and CPT /LIF data.
- Hydrocarbon fingerprint analysis indicated that the LNAPL was an aged diesel indicating the release was not recent nor likely ongoing at the active facility.
- LNAPL stability was documented based on delineation activities and over 8 years of monitoring LNAPL extent.

The location exhibiting 4 ft²/day LNAPL transmissivity was selected for LNAPL skimming, which was conducted over a 4-year period. LNAPL recovery rates started at 2 gallons per day (gpd) and quickly decreased to less than 0.2 gpd. A total of 215 gallons of LNAPL was recovered over 1,500 days. The API LNAPL Distribution and Recovery model was utilized to forecast LNAPL recovery rates over time for an ideal isotropic condition in a sandy soil (of the same type as the impacted sand lenses). A point representing asymptotic recovery was selected based on 90 percent of the recoverable LNAPL (mobile fraction) being removed in a given time frame that was one-fifth of the time to recover the remaining 10 percent. The remaining 10 percent of mobile LNAPL also represented less than 25 percent of the residual mass in place. The LNAPL transmissivity representative of this asymptote was 0.8 ft²/day. This LNAPL transmissivity value was selected as the endpoint for the site. LNAPL recovery from the fluvial channel depositional-environment reduced LNAPL transmissivity to less than 0.2 ft²/day over the first 4 months of recovery highlighting the limited extent of sand at the site. LNAPL recovery rates remained low and LNAPL transmissivity remained low for the remainder of the 4-year recovery period.

Conditions in the second area of the site are summarized as follows:

- LNAPL was perched in gravelly material overlying moist to wet clay. The LNAPL likely occurred in depressions of the clay and distribution centered around the clay surface rather than the water table.
- Soil core analyses indicated an LNAPL saturation of 0.2 percent of the pore space in the silty clay, confirming that LNAPL impact to the silty clay was minimal. Collection of cores from the overlying gravel was not feasible.
- Baildown test analysis combined with the soil profile confirmed the perched LNAPL conditions ([Kirkman, Adamski, and Hawthorne 2013](#)).
- Although there was up to 7 feet of LNAPL gauged in wells screened across the gravel and the silty clay, less than 0.5 feet actually occurred as mobile LNAPL in the overlying gravel.
- Initial LNAPL transmissivity results indicated values of 1.4 ft²/day and skimming recovery rates near 0.8 gpd as a result of the LNAPL occurring in the coarse gravel rather than the silty clay.
- The water-table occurred in the clay although infiltrating water likely was seasonally perched on the clay or flowed through the gravel.
- Four years of LNAPL recovery at two well locations resulted in less than 50 gallons of LNAPL removed.
- Initial LNAPL skimming rates were near 0.5 gpd, and declined to near 0.1 gpd; rates also decreased seasonally to less than 0.001 gpd.
- Maximum LNAPL transmissivity post recovery was estimated to be 0.4 ft²/day.
- LNAPL recovery rates were no longer observed to decline following initial 6 months of recovery; rather, seasonal fluctuations occurred.
- LNAPL recovery and downgradient monitoring confirmed that the LNAPL extent was limited and stable. No impacts to groundwater or other receptors were identified.

The overall conceptual model represented minimal mobile LNAPL impacts being stable and occurring in a surficial gravelly unit. Relatively large gauged thicknesses were not indicative of the need for recovery, but rather represented perched LNAPL. LNAPL recovery and soil profiles versus fluid levels confirmed the presence of perched LNAPL. LNAPL recovery rates quickly reached asymptotic conditions, under which skimming was not substantially changing the mobility or overall quantity of LNAPL present. Groundwater and fluid level monitoring identified that the LNAPL was stable and no dissolved phase exceedances were migrating off-site.

An agreement was reached with the agency to cease LNAPL skimming and conduct two years of groundwater monitoring, fluid level monitoring and periodic removal. The two years of monitoring confirmed the conceptual model and resulted in closure.

Site Two [▼Read more](#)

Site two is a railroad facility where LNAPL existed in secondary porosity of a fine grained soil based on soil cores and monitoring well gauging data. No dissolved or vapor phase risks were identified related to the LNAPL, which consisted of

weathered diesel and lubricating oils. The remedial objective was to prevent LNAPL from reaching and impacting a nearby creek; therefore, LNAPL stability was the primary concern. Occurrences of LNAPL in the creek were historically observed but had not been seen in over a decade. In 2004 the LNAPL body was delineated and LNAPL physical properties measured from soil cores were used to estimate the hydraulic head that would be needed to drive the LNAPL towards the creek. The capillary properties of the soil, accounting for secondary porosity, were used in this calculation, which concluded that 1.5 to 1.9 ft. of hydraulic head would be required to cause LNAPL migration. Neither existing hydraulic head at the LNAPL body (0.64 to 0.05 ft.) nor natural infiltration-based events were sufficient to create a head similar to the required head to displace LNAPL, resulting in the conclusion that LNAPL was stable and would not impact the creek. The site achieved closure based on lack of impacts to receptors, stable LNAPL and lack of recoverability.

Site Three [▼Read more](#)

Several monitoring wells associated with a railroad facility exhibited mobile LNAPL. A multi-phase extraction (MPE) test was conducted over a period of 2 years. The recovery volumes were sufficiently low to demonstrate that LNAPL recovery would not significantly reduce the LNAPL saturation over a 10 year period. The site exhibited stable LNAPL, no dissolved or vapor risks to receptors, and was dominated by residual LNAPL. A report summarizing results demonstrating LNAPL stability, lack of risks to receptors and lack of effectiveness for LNAPL recovery was submitted to the agency requesting a no further action determination, which the agency subsequently granted. As part of development of the LNAPL transmissivity discussion in the 2009 ITRC LNAPL document, the data were reviewed and LNAPL transmissivity values were estimated using equations for MPE data analysis now included as part of ASTM E2856-13 ([ASTM 2013](#)). The results indicated that LNAPL transmissivity values were initially 0.1 ft²/day at the start of the MPE program and remained at 0.1 ft²/day at the termination of the program. The lack of change in transmissivity indicates that the two-year MPE test provided no material improvement in site conditions.

Site Four [▼Read more](#)

A railyard exhibiting two areas of mobile LNAPL had been through a corrective action strategy involving periodic LNAPL removal and installation of a recovery trench and vertical wall to prevent seeps to surface water. The LNAPL exhibited high viscosity values ranging from 3.75 to 25 centipoise and was representative of a weathered diesel and/or heavier petroleum. Groundwater monitoring had been discontinued, because the degree of weathering resulted in no detections of dissolved petroleum constituents in groundwater. The primary focus of LNAPL management was LNAPL removal to MEP and prevention of seeps to surface water. The first area of LNAPL exhibited LNAPL near a surface water body, and LNAPL transmissivity values were estimated to be on the order of 0.004 ft²/day. LNAPL distribution and recovery modeling was completed to evaluate the potential benefit of a 200 foot long skimming trench, and identified that the bulk of the mobile LNAPL could be recovered in 100 years. If water enhanced LNAPL recovery were implemented, the starting oil to water ratio was estimated to be 1 gallon of LNAPL to 1,000 gallons of water, which is often utilized as an endpoint for this technology rather than an optimal starting point. As LNAPL recovery was demonstrated to be ineffective, a cutoff wall was proposed in this area to ensure LNAPL would never reach surface water. No surface water impacts had previously been identified; however, this measure was implemented as a supplemental measure to prevent LNAPL migration, and provided secondary structural benefit to the railyard facility.

The second area of the site exhibited weathered diesel fuel in an area with a shallow water-table dominated by sand with a 1- to 2-inch clay seam. An LNAPL transmissivity test was conducted to evaluate LNAPL recoverability, and resulted in a value of 0.03 ft²/day. An LNAPL distribution and recovery model was calibrated using baildown test results and soil and LNAPL properties. The modeled scenario considered a 100-foot long skimming trench operated at maximum efficiency, and located in the area representing the maximum estimated LNAPL transmissivity value. Model results predicted that 50 years of LNAPL recovery would be required to recover the bulk of the remaining mobile LNAPL. Comparison of LNAPL transmissivity to aquifer transmissivity identified that if water enhanced recovery was utilized the initial oil to water production ratio would be 1:100. This ratio of oil to water would decrease during the life of recovery. The site also did not have existing infrastructure for water treatment. The lack of groundwater impacts, stability of the existing LNAPL in this area and distance to any surface water body or receptors, extended timeframes and large investments required for LNAPL recovery combined with residual LNAPL continuing to remain at the site provided the basis for the site closure.

Shortly after the report was submitted, LNAPL thickness began rising in one of the wells in Area 2. Upon review of adjacent cone penetrometer data, the clay seam was identified as potentially confining the LNAPL. A second baildown test was completed in the well when it exhibited the larger thickness. The analysis accounted for the confined LNAPL and resulted in a similar but lower LNAPL transmissivity value. The visualization of the soil profile adjacent to fluid levels identified the confined conditions and explained why the thickness rose with an increase in the water table. The second baildown test provided sufficient evidence that LNAPL was stable, not increasing in impact, and LNAPL remained non-recoverable.

Site Five [▼Read more](#)

An active petroleum facility had LNAPL in more than 50 wells where vacuum truck liquid recovery or skimming had been performed for over 20 years. The LNAPL occurred in silty sand layers confined by finer clays in an alluvial depositional environment. Although the wells accumulated LNAPL to thicknesses on the order of 4 feet or more, LNAPL transmissivity at those wells was consistently less than 0.8 ft²/day, with some transmissivity results up to 2 orders of magnitude lower than that value. Historical LNAPL recovery data were presented to illustrate the decline in LNAPL recovery that had occurred; current recovery efforts were not producing significant volumes compared to past recovery. Ten additional years of LNAPL recovery would produce less than ten percent of the historically recovered LNAPL volumes. Soil core and laser induced fluorescence data as compared to fluid levels illustrated that the majority of the LNAPL was residual and not mobile. LNAPL transmissivity values were used to forecast future recovery, which would have addressed a small fraction of remaining impacts at low rates. In 2009, agreement was reached with the agency that LNAPL recovery was no longer beneficial. This redirected the site focus towards technologies that would address groundwater impacts.

Overall, consistent observations among these scenarios included:

- LNAPL plumes were stable and delineated and generally were within the current facility property.
- There were no risks to receptors—rather than postponing risk-based decision making after LNAPL had been removed from wells, risks were evaluated concurrently with LNAPL removal.
- Volumes of LNAPL that were reasonably recoverable represented a small part of either the overall mass at the site, or the historically recovered LNAPL mass; future recovery of mobile LNAPL would reduce the LNAPL mass at the site by only a small amount.
- LNAPL transmissivity values had been reduced to values below 0.8 ft²/day with recovery, or initially existed at values of 0.1 ft²/day or lower.
- Gauged LNAPL thickness was not a primary criterion in demonstrating LNAPL recoverability or the potential benefit of LNAPL recovery.

Since the range of 0.1 to 0.8 ft²/day was presented by ITRC ([ITRC 2009a](#)), additional sites have used similar methods to determine the limits of hydraulic LNAPL recovery. Figure Tn-1 presents the empirical data from sites that were intensively studied to support the statement above. LNAPL recovery data from 11 different hydraulic recovery systems at four sites was analyzed. Site 1 represents a sand and gravel aquifer with hydraulic conductivity values on the order of 300 ft/day. Site 2 represents a medium sand of 30 ft/day conductivity that transitions into silt. Site 3 represents a silty sand exhibiting hydraulic conductivity near 3 ft/day, and Site 4 represents a sandy silt exhibiting less than 1 ft/day hydraulic conductivity.

The y-axis of Figure Tn-1 represents the fraction of LNAPL mass removed from the mobile interval after various time intervals of recovery operation. At the start of recovery, some fraction of mass was recoverable and some fraction was residual. Each data column represents recovery from a given well or group of wells. The number along the x-axis under each column represents the starting (baseline) LNAPL transmissivity. As LNAPL recovery operation progressed, the fraction of LNAPL recovered at systems with initial LNAPL transmissivity values above 0.3 to 0.8 ft²/day is represented in dark blue. Each of these dark blue bars is labelled with the time it took to achieve this recovery. The light blue represents the additional recovery achieved when the LNAPL transmissivity fell below 0.3 to 0.8 ft²/day along with the corresponding time. The solid gray represents the estimated remaining mobile LNAPL fraction. The marbled gray represents the residual mass remaining based on soil cores and soil TPH samples and use of an f-factor to estimate residual LNAPL.

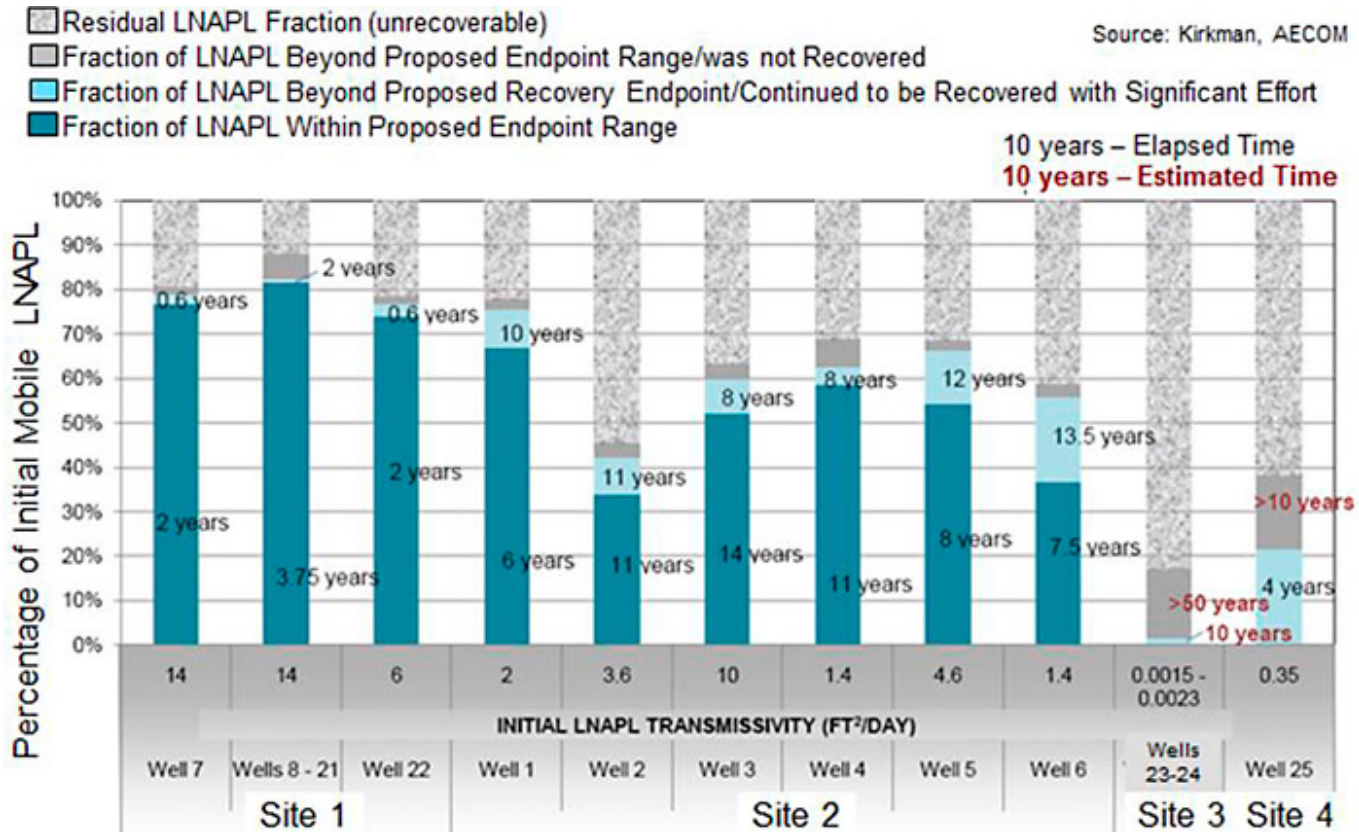


Figure Tn-1: Fraction of LNAPL recovered above 0.3 to 0.8 ft²/day.

As Sites 3 and 4 never exhibited LNAPL transmissivity values above 0.8 ft²/day, there are no dark blue bars and the majority of LNAPL was residual at the start of recovery. For Sites 1 and 2, at the point where LNAPL transmissivity fell into the range of 0.3 to 0.8 ft²/day, as indicated by the short light blue bars and often long durations, the majority of the mass was residual and continued recovery did not produce significant volumes of LNAPL relative to past volume recovered.

The recent site analyses affirmed the initially proposed transmissivity range of 0.1 to 0.8 ft²/day.

2.0 Field Methods to Measure T_n

LNAPL transmissivity is fundamentally a description of the relationship between LNAPL drawdown (or gradient) and LNAPL discharge (or flow). As such, most field test methods involve inducing an LNAPL drawdown at a well and measuring LNAPL discharge from the formation to that well. Field testing that correlates the volumetric rate of LNAPL discharge from the formation to LNAPL drawdown or the volume of water and LNAPL during pumping is the preferred way to measure LNAPL transmissivity. Both qualitative and quantitative methods for collecting and using field data to assess LNAPL transmissivity are presented in this section.

2.1 Qualitative - Recoverability

Purging LNAPL from a well and monitoring how quickly LNAPL returns to a well has been used for decades to assess LNAPL recoverability. It is intuitive that if the LNAPL returns quickly the LNAPL is more recoverable than if it recharges very slowly or does not recharge at all. It has become common to collect LNAPL recharge data over time in order to calculate LNAPL transmissivity, which is covered in the next section.

The Minnesota Pollution Control Agency (MPCA) has a structured approach to using qualitative recoverability data. The guidance provided by the MPCA states that if LNAPL in a well is purged, and less than one gallon of LNAPL recovers into the well within 24 hours; and if a repeat test shows the same recovery or lower; then LNAPL recoverability is considered low and automated LNAPL recovery methods are considered ineffective.

The MPCA approach is worthwhile for comparative behavior of LNAPL in wells. When considering a test represented by static potentiometric surface, the value of 1 gallon per day via bailing or skimming correlates well with the LNAPL transmissivity range of 0.1 to 0.8 ft²/day presented in ([ITRC 2009a](#)). Given an LNAPL transmissivity of 0.8 ft²/day and a similar skimming drawdown, 0.2 ft., as would be induced in baildown tests, the expected LNAPL recovery rate would be approximately 1.6 gallons per day. The MPCA method is useful for a broad range of sites because of the simplicity of the approach. However, it is difficult to utilize this method to project performance of an MPE or water enhanced recovery system, or for assessing LNAPL recovery performance for alternate technologies.

2.2 Quantitative - Transmissivity

Three testing methods are commonly used to measure LNAPL transmissivity. The data collection and data analysis procedures for these LNAPL transmissivity measurement methods are discussed in detail by ASTM E2856-13: ASTM Standard Guide for Estimation of LNAPL Transmissivity ([ASTM 2013](#)).

LNAPL Baildown Testing: An LNAPL baildown test is initiated by quickly removing accumulated LNAPL from a well. The rate of LNAPL flow into the well is a function of soil and LNAPL properties discussed above and the magnitude of the initial hydraulic gradient toward the well developed during LNAPL removal. The LNAPL discharge into the well is related to the LNAPL drawdown (both decrease during the test) to calculate LNAPL transmissivity. The baildown test response is influenced by prevalent fluid levels at the time of testing. Multiple baildown tests can be performed at a site to describe the range of LNAPL transmissivity values under different fluid-level conditions.

Manual LNAPL Skimming Testing: Manual LNAPL skimming tests involve repeated LNAPL recovery periods relative to baildown testing (which consists of one near-instantaneous LNAPL removal at test initiation), and thus represent a larger portion of the LNAPL-impacted formation. A manual skimming test consists of removing all LNAPL from a well, gauging the well as the LNAPL recharges, and repeatedly removing LNAPL before the recharge reaches 25 percent of pre-test LNAPL thickness. This process continues until the LNAPL removal rate stabilizes. The steady-state LNAPL discharge observed towards the end of the test is related to the induced drawdown to calculate LNAPL transmissivity.

LNAPL Recovery System Evaluation: This evaluation is commonly completed on historical LNAPL recovery system data, but it is becoming more common to configure new LNAPL recovery systems or retrofit existing LNAPL recovery systems to generate data that can be used to track LNAPL transmissivity over time. Multiple equations have been derived to calculate LNAPL transmissivity for LNAPL-only recovery, LNAPL and groundwater recovery, and multiphase (LNAPL, groundwater, and soil gas) recovery. For remedial systems operated over longer time frames, the average LNAPL volumetric recovery rate is related to the LNAPL drawdown induced by the extraction of fluids from the subsurface.

An element of the LNAPL Recovery System Evaluation approach in the ASTM guide is estimation of LNAPL transmissivity from the ratio of groundwater and LNAPL extracted from a well. This approach is easily calculated if the water drawdown induced during pumping is larger than 10 times the available LNAPL drawdown, but may also be calculated where this ratio threshold is not met ([ASTM 2013](#)). The oil/water ratio analysis can be applied to data collected during a short or long-term pumping test. A typical short-term oil/water ratio test might consist of pumping both LNAPL and water from a well for a period of several minutes to hours, with a pump intake set well below the mobile LNAPL interval, and measuring the ratio of LNAPL and water either through periodic samples or through observation of the collected liquids at the conclusion of the test. The oil/water ratio analysis can improve upon other transmissivity estimation methods when gauged LNAPL thickness is low and drawdown is similar in magnitude to gauging precision (e.g., 0.01 ft.) or where water tables exhibit frequent fluctuations such as tidally influenced cycles.

A fourth method that is less commonly performed is LNAPL Dye Trace Testing ([ASTM 2013](#)). A fluorescent dye that dissolves in petroleum but is not water soluble is added to LNAPL in a monitoring well. The dye concentration in the LNAPL in the well is measured over time and the rate of concentration decrease is used to calculate the LNAPL flux through the well. The time-averaged LNAPL transmissivity can be calculated from the LNAPL flux using site-specific data. This test is unique among transmissivity test methods because it measures LNAPL flow under ambient conditions (rather than an induced gradient); therefore, it can also be helpful for assessment of LNAPL mobility. Data collection and analysis methods for LNAPL Dye Trace Testing are also presented in the ASTM guide.

These approaches to LNAPL transmissivity measurement provide a sufficient degree of accuracy to characterize recoverability, changes in recoverability with remediation, and to calibrate models for forecasting LNAPL distribution and recovery performance. Comparative studies of multiple LNAPL transmissivity measurement techniques at the same location have shown that the different test methods generate similar results ([Palmier et al. 2000](#)); ([Kirkman 2013](#)). LNAPL recharge

behavior observed during baildown tests can be used as a diagnostic to determine whether LNAPL is unconfined, perched, or confined ([Kirkman, Adamski, and Hawthorne 2013](#)). When multiple tests are conducted at different locations, the influence of geologic heterogeneity is incorporated into the transmissivity results. Field testing can also be repeated to quantify the range of LNAPL transmissivities that may be observed due to water table fluctuations increasing the overall confidence in the transmissivity data.

3.0 Data evaluation and estimation of T_n - How do you estimate T_n ?

There are several methods to estimate LNAPL transmissivity. Selection of the appropriate field testing and data analysis approach is a function of how the transmissivity values will be used. A simple approximation of LNAPL transmissivity using known site parameters may be sufficient to support LCSM development for an LNAPL with small LNAPL thicknesses while a precise field-based method of determining LNAPL transmissivity would be appropriate for LNAPL model calibration at a site where LNAPL appears to be readily recoverable.

3.1 Standard methods and approaches

The ASTM Standard Guide for Estimation of LNAPL Transmissivity (ASTM E2856-13) provides data collection and data analysis procedures for estimating LNAPL transmissivity from baildown tests, manual skimming tests, LNAPL recovery system data, and LNAPL dye trace testing. API published an LNAPL Transmissivity Workbook (API Workbook) and companion user's manual that provides a spreadsheet-based user-friendly method to calculate LNAPL transmissivity from baildown test data ([API 2016](#)). The API Workbook is consistent with the data analysis practices in ASTM E2856-13.

3.2 Simplified approaches

The transmissivity data collection and analysis methods presented in ASTM E2856-13 were designed to provide a high degree of rigor for the purpose of ensuring that the LNAPL transmissivity values measured using the ASTM method represented current best practices ([ASTM 2013](#)). It was realized that compliance with the ASTM standard cannot be consistently achieved at all sites and may not be necessary for all sites. This section describes simplified methods that can provide approximations of LNAPL transmissivity.

3.2.1 Darcy's Law Calculation

LNAPL transmissivity can be estimated from Darcy's Law, with a correction to the water hydraulic conductivity to account for the difference in fluid properties between the LNAPL being considered and groundwater. This approach is a theoretical exercise and it should not be expected that the result of this calculation will match field tests that measure LNAPL transmissivity. Field tests inherently account for deviations from theory and account for multiphase fluid flow. However, this calculation method may provide an estimate of LNAPL transmissivity that is useful to understand what LNAPL transmissivity may be at a site where additional field data collection is deemed unnecessary.

The data required to complete the calculation are:

Groundwater hydraulic conductivity, K_w (feet/day)

LNAPL relative permeability, k_r (dimensionless)

Groundwater density, μ_w (grams/milliliter)

Groundwater viscosity, ρ_w (centipoise)

LNAPL density, ρ_n (grams/milliliter)

LNAPL viscosity, μ_n (centipoise)

The thickness of LNAPL accumulation in a well (unconfined) or the mobile LNAPL interval (confined), b_n (feet)

The groundwater density and viscosity are assumed to be 1 gram/liter and 1 centipoise, respectively, at 20 degrees Celsius.

LNAPL transmissivity, T_n (feet²/day) is calculated using the following equation:

$$T_n = K_w \cdot k_{rn} \cdot \frac{\rho_n \mu_w}{\rho_w \mu_n} \cdot b_n$$

It is preferential for the data used in the calculation, with the exception of the groundwater density and viscosity, to be site-specific parameters. The LNAPL density can be determined in the field using a hydrometer or through laboratory analysis. LNAPL viscosity measurement is typically conducted in an analytical laboratory. The water hydraulic conductivity can be determined via slug testing, pump testing, or another suitable method. However, several sources provide LNAPL density and viscosity data for unweathered crude oils and refined petroleum products, and representative water hydraulic conductivities can be selected based on an understanding of the soil type where the LNAPL resides.

The simplest direct calculation of LNAPL transmissivity is based on an assumption that LNAPL fills all soil pores within the mobile LNAPL zone and where the LNAPL relative permeability is one. This calculation is considered to be conservative because LNAPL does not reach 100 percent saturation at environmental sites. This conservative calculation can be useful for sites where the LNAPL thickness is very small and field testing is neither practical nor considered necessary.

LNAPL transmissivity can also be calculated with an additional correction for the fact that LNAPL does not fill all soil pores at an environmental site (relative permeability is less than one). Within the saturated zone, LNAPL fills only a portion of the pore space. Groundwater and, in some cases, trapped gasses fill the remaining pore space. Groundwater cannot move through LNAPL-filled pores and LNAPL cannot move through groundwater-filled pores. The reduction of available pore space for liquid flow is equivalent to a decrease in the permeability of the formation. Multiphase flow calculations include a relative permeability term, which ranges from 0 to 1, to account for this decrease in soil permeability.

While a relative permeability term is useful to decrease the degree of conservatism in the Darcy's Law calculation, there are no simple methods to estimate relative permeability without conducting field LNAPL transmissivity tests or collecting soil samples for lab analysis of petrophysical properties.

In light of this limitation, an analysis of LNAPL transmissivity data that were collected by API from member companies and compiled in a database was completed to determine a representative range of LNAPL relative permeability values. Ninety-four unique LNAPL transmissivity measurements that were entered in the database included sufficient ancillary site data to calculate relative permeability near the test well. Ninety percent of the relative permeability values were below 0.28; 80 percent were below 0.09.

The API data are provided as a potential basis for selection of a relative permeability value that represents the degree of conservatism that is appropriate for the site setting and conditions. The relative permeability may also be estimated from fluid retention models as described in API LDRM model ([API 2007](#)).

3.2.2 Bouwer and Rice Type Curves

When LNAPL discharge into a well during a baildown test does not follow ideal hydraulic response patterns, it is not possible to accurately estimate T_n using conventional methods. In these cases it may be reasonable to approximate LNAPL transmissivity through visual inspection of the recovery data versus an idealized hydraulic response. The API Workbook can be used to generate Bouwer and Rice type curves that show idealized LNAPL drawdown as a function of time. Note that a test-specific J-ratio term must be established in the workbook to support this approach. The user's guide for the API Workbook provides direction on how to set an appropriate J-ratio.

An example of the use of the Bouwer and Rice type curves for determination of LNAPL transmissivity is shown on Figure Tn-2. In this case inspection of where the data plot on the graph indicates that the LNAPL transmissivity is between 0.002 and 0.005 meters²/day. The Bouwer and Rice analytical calculation for these data was 0.003 meters²/day. All of the data points are to the left of the 0.005 meters²/day curve and it would be accurate to state that the LNAPL transmissivity is less than 0.005 meters²/day. For a theoretical scenario where an LNAPL transmissivity threshold of greater than 0.01 meters²/day had been established for initiating LNAPL recovery, this approach would provide a high degree of certainty that the transmissivity was less than the threshold value.

While this method for determining LNAPL transmissivity is straightforward, it can produce erroneous results. ([Kirkman, Adamski, and Hawthorne 2013](#)) demonstrated that while an estimate of LNAPL transmissivity can be made via type curves, those type curves rely on an accurate identification and elimination of the initial drawdown data, which is often higher than the formation response due to filter pack recharge effects. If the filter pack recharge data are dominant within the data set,

possibly due to incomplete LNAPL purging, this approach could in overestimation of LNAPL transmissivity.

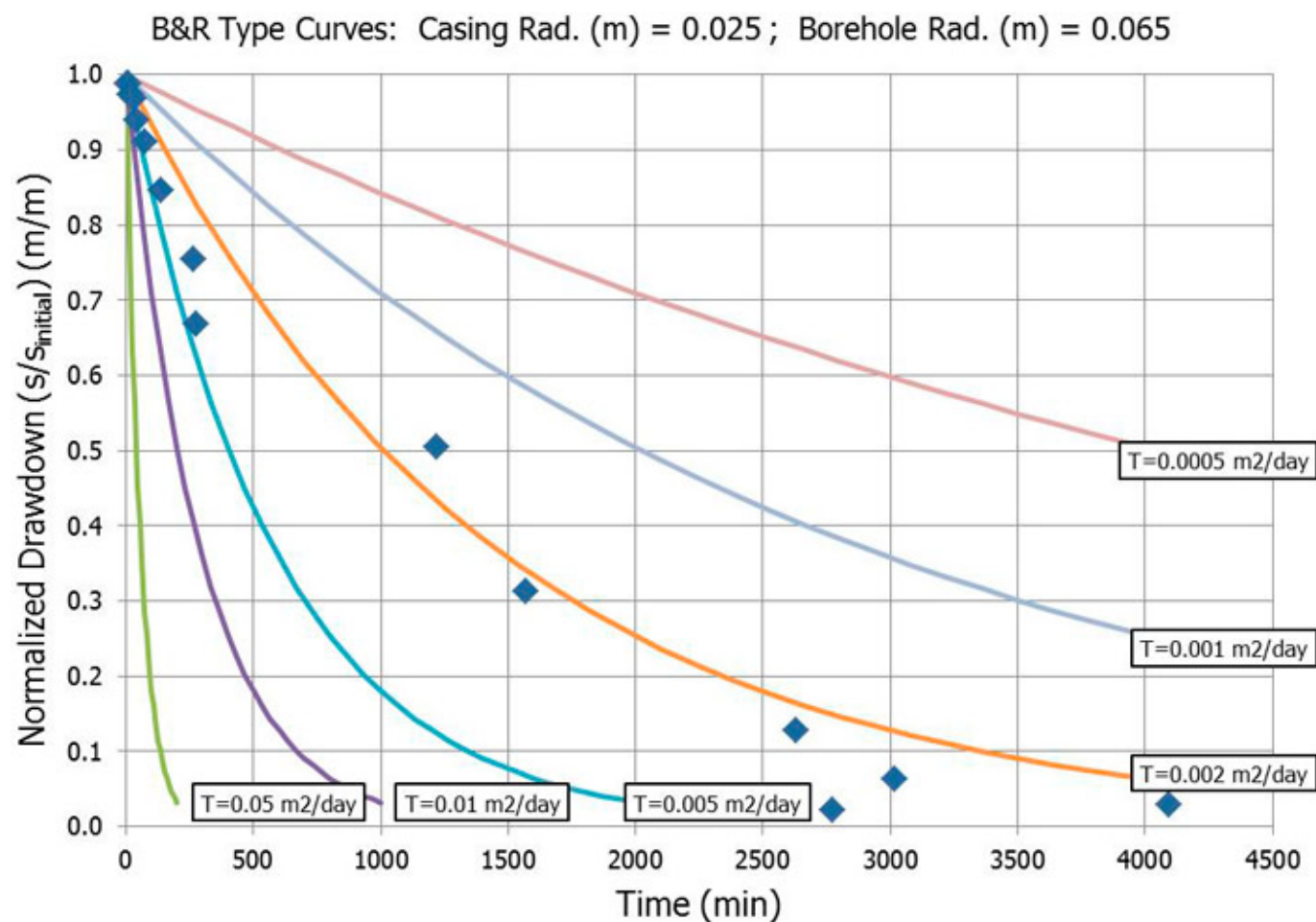


Figure Tn-2. Normalized drawdown data from a baildown test plotted with Bouwer and Rice type curves generated for the test well.

3.3 Common challenges in LNAPL Transmissivity Measurement

As LNAPL transmissivity has become more widely used and more frequently measured, several common challenges or complicating factors have emerged in transmissivity measurement. For example, at monitoring wells with small equilibrium in-well LNAPL thicknesses, LNAPL baildown testing involves significant uncertainty and is generally not recommended ([ASTM 2013](#)). A few frequently encountered challenging scenarios are summarized in the following table, along with potential solutions or suggestions to mitigate challenges.

Table Tn-1. LNAPL transmissivity measurement challenges and potential solutions

Challenge	Potential Causes	How should field activities be adjusted to get a more reliable T_n result?
Fluctuating water table during testing creates uncertainty in LNAPL drawdown	Tidal fluctuations, weather-related/regional influences	Consider oil-water ratio tests (which can induce additional drawdown and reduce significance of ambient fluctuations) or qualitative measurements. Consider using early-time data to generate an approximate or upper-bound result.

Challenge	Potential Causes	How should field activities be adjusted to get a more reliable T_n result?
Slow recovery	Low T_n (associated with low LNAPL saturation, submerged NAPL, etc.); Possibly poorly developed wells	Consider using data to estimate an upper-bound transmissivity result, even if data appear to represent filter pack recharge only. Evaluate data using Bouwer & Rice type curves to develop an upper-bound result. Consider redeveloping wells and re-testing, noting that significant time may be required for re-equilibration. Consider estimating maximum theoretical LNAPL transmissivity at 100% LNAPL saturation, using LNAPL viscosity data and Darcy's Law relationships described in Section 3.2.1 of this Appendix.
Difficult/imprecise Fluid Level Measurements; Difficulty in Gauging	High viscosity LNAPL Easily-emulsified LNAPL LNAPL optical properties	For high viscosity NAPL, consider using empirical data or desktop calculations. For emulsions or optically challenging NAPLs, consider using pressure transducers or other automated measurement solutions. Consider oil-water ratio tests where total fluids can be pumped from the test well and measured <i>ex situ</i> , with additional separation or settling time and/or different measurement methods.
Small in-well LNAPL thickness (below 0.2-0.5 ft. benchmarks for manual skimming or baildown testing in ASTM E2856-13)	Small mobile LNAPL interval in the surrounding formation Well not yet equilibrated with larger mobile LNAPL interval	Consider oil-water ratio tests where total fluids can be pumped from the test well and measured <i>ex situ</i> , with greater precision than down-well measurements. Consider estimating maximum theoretical LNAPL transmissivity at 100% LNAPL saturation, using LNAPL viscosity data and Darcy's Law relationships described in Section 3.2.1 of this Appendix.

3.4 Interpreting LNAPL Transmissivity and In-well LNAPL Thickness

As LNAPL transmissivity has been more broadly adopted as a tool for site evaluation, in-well LNAPL thickness, which was historically often relied upon as an indicator of the magnitude of LNAPL impact, has generally become less significant. However, in-well LNAPL thickness and the relation to the surrounding mobile LNAPL interval in the formation is still an important component of the LNAPL conceptual site model. Additionally, the relationship of in-well LNAPL thickness to LNAPL transmissivity results can highlight important considerations or cautions related to LNAPL transmissivity and LNAPL hydrogeologic conditions.

The following table summarizes general inferences that may be drawn from relationships between LNAPL transmissivity and in-well LNAPL thicknesses.

Table Tn-2. Interpretation of LNAPL thickness and transmissivity

In-Well LNAPL Thickness	LNAPL Transmissivity	What does this tell us?
High	High	Recoverability may be good; consider targeting this location if needed to reach saturation objectives.
	Low	LNAPL may be present in a confined or perched conditions or in fine-grained soils with a small mobile LNAPL interval. The large thickness in this case is observed only because the well is present and providing hydrostatic relief.

In-Well LNAPL Thickness	LNAPL Transmissivity	What does this tell us?
Low	High	Carefully evaluate LNAPL drawdown, which is a sensitive parameter for T_n . Measurement error for drawdown may be relatively large at small LNAPL thicknesses. Consider qualitative T_n test methods or oil-water ratio testing to reduce sensitivity to drawdown.
	Low	Recoverability is likely low; however, as with other low-thickness conditions, confirm LNAPL drawdown is accurately measured.

4.0 Case Studies

The following case studies were prepared to provide context on practical application of LNAPL transmissivity at LNAPL-affected sites. Case studies are presented for the following applications and topics:

- LNAPL transmissivity and recovery system design
- Averaging of LNAPL transmissivity results
- Tracking of LNAPL recovery system performance
- Assessment of LNAPL body stability
- Use of LNAPL transmissivity at small sites

4.1 LNAPL Recovery System Design

LNAPL transmissivity has direct application to recovery system design, and can be used to estimate LNAPL recovery rates and compare potential recovery approaches. The following case study of a site where LNAPL recovery was needed to reach LNAPL saturation objectives describes ways that LNAPL transmissivity data can be used for LNAPL recovery system design.

Background

The study site is a natural gas plant where a gas condensate release was identified during routine pipeline maintenance. Soil near the release area was heterogeneous with interbedded coarse-grained and fine-grained soils. Water-saturated hydraulic conductivities at the site range from 10^{-3} to 10^{-4} cm/sec, which are consistent with silty sands and fine sands. The average hydraulic gradient is 0.003 foot per foot.

LNAPL Nature and Extent

The natural gas condensate was found to be leaking from a buried pipeline. The pipeline was repaired and there is no longer an ongoing release. The natural gas condensate has a low density (0.701 grams per cubic centimeter) and low viscosity (0.504 centistokes). The horizontal and vertical extent of LNAPL was investigated using laser-induced fluorescence, photoionization detector screening of soil cuttings, and visual observations in soil borings and monitoring wells.

LNAPL Recoverability - Initial Baildown and Manual Skimming Tests

During the initial investigation, LNAPL transmissivity testing was conducted using short-term test methods. An LNAPL baildown or manual skimming test was conducted at three monitoring wells located adjacent to the source (monitoring well (MW)-1), downgradient of the source (MW-2) and at the leading edge of the LNAPL body (MW-3). Baildown tests were attempted and failed at MW-1 and MW-2 because LNAPL recharge was rapid and exceeded the maximum flow rate of the pump used to purge LNAPL. In response to this observation, modified skimming tests were conducted. As before, the LNAPL recharge rate was rapid, and only minimal LNAPL drawdown in the well could be achieved. The initial investigation calculated that transmissivities for wells MW-1 and MW-2 were subject to a high degree of uncertainty due to the minimal drawdown. To reduce this uncertainty, and provide greater accuracy to support LNAPL recovery system design, a LNAPL pumping test was pursued.

Table Tn-3. LNAPL transmissivity results from the first attempt at measurement. gpm = gallons per minute

Well ID	Well Location	Test Method	Measured LNAPL Thickness (ft.)	LNAPL Transmissivity (ft ² /day)	Maximum LNAPL Recovery Rate (gpm)
MW-1	Source	Manual Skimming	8.13	125 – 210	2.1-3.6
MW-2	Mid-point	Manual Skimming	4.39	60 – 95	0.5-0.9
MW-3	LNAPL fringe	Baildown Test	2.2	1.3	0.003

LNAPL Pump Tests

A series of 10-hour LNAPL pumping tests were completed at MW-1, MW-2, and MW-3 to more accurately determine LNAPL transmissivity and sustainable LNAPL recoverability for designing interim and longer-term LNAPL recovery at the site. This longer-term test (10 hours) approximated steady state LNAPL flow to the well, resulting in a more accurate estimate of LNAPL transmissivity. LNAPL pump tests were completed in general accordance with the manual skimming protocol included in the ASTM E2856-13, with the goal of achieving a consistent LNAPL drawdown with a stable, continuous LNAPL extraction rate for the duration of the test. Based on the initial LNAPL transmissivity testing, an appropriately sized pump was selected to maintain an LNAPL thickness in the well of no greater than 25 percent of the measured thickness. Pump intakes were placed within the accumulated LNAPL, approximately 0.5 feet above the potentiometric surface, to avoid recovery of groundwater. LNAPL thickness was continuously monitored in the early stages of the test, and LNAPL pumping rates were manually adjusted to reach a stable LNAPL drawdown.

LNAPL transmissivity was calculated following Equation 16 of ASTM E2856-13 ([ASTM 2013](#)). Results for the LNAPL pump tests are summarized in Table Tn-4.

Table Tn-4. LNAPL transmissivity results from 10-hour LNAPL pumping tests

Well ID	Total Test Time (hours)	Average LNAPL Recovery Rate (gallons/minute)	Average LNAPL Transmissivity (ft ² /day)
MW-1	80	1.2	100
MW-2	20	0.3	60
MW-3	10	0.1	20

LNAPL Recovery Design

The results of the LNAPL transmissivity testing were used to develop an LNAPL recovery action designed to recover mass, reduce LNAPL saturation, and mitigate LNAPL migration. Results from the LNAPL transmissivity testing were incorporated into the recovery system design, and informed the recovery method, well density and location, pump and pipe sizing, and recovered LNAPL handling requirements. Because LNAPL transmissivity values vary spatially and there is significant heterogeneity at the site, short-term pump tests were conducted at each recovery well that was installed to verify potential recovery rates and design aspects. Incorporating LNAPL transmissivity prior to remediation design resulted in appropriate sizing of the remediation system, supported logistics planning, and developed baseline transmissivity values that can be used to track remedy progress.

4.2 LNAPL Transmissivity Averaging

As discussed elsewhere in this Appendix, LNAPL transmissivity is a bulk parameter representing the combined effects of multiple parameters that control the capacity of the formation to transmit LNAPL, including:

- aquifer matrix characteristics,
- LNAPL physical properties,
- the fraction of pore space occupied by LNAPL (LNAPL saturation, or relative permeability to LNAPL), and
- the vertical interval of mobile LNAPL in the formation.

The fact that LNAPL transmissivity is inclusive of each of these parameters makes it a useful metric for assessing LNAPL recoverability, as it is directly proportional to recoverability under the ambient conditions during the time of testing. However, it is important to acknowledge that the parameters affecting LNAPL transmissivity can vary temporally under

certain conditions, resulting in a corresponding temporal variability of LNAPL transmissivity.

While aquifer matrix properties are typically assumed fixed, LNAPL properties and relative permeability to LNAPL often vary over time. For example, the physical properties of petroleum LNAPLs can be altered as the result of NSZD processes. These effects tend to increase the viscosity of LNAPLs, leading to a gradual decrease in LNAPL transmissivity. LNAPL saturation at a given location can also vary over time and space as the result of engineered LNAPL remediation efforts, NSZD processes, or redistribution of LNAPL through vertical and/or horizontal migration. In the early stages of LNAPL body development following a release, LNAPL saturation will increase near the leading edge of the LNAPL body and decrease in the area of the release. As LNAPL spreads into previously non-impacted formation materials, an increasing fraction of the LNAPL is trapped as a discontinuous non-wetting phase by capillary forces (becoming residual LNAPL). Thus, as the LNAPL body spreads or moves, an increasing volume of LNAPL becomes residual over time, resulting in an overall decrease in the volume of mobile LNAPL distributed over a larger volume of the subsurface.

Beyond the point where lateral LNAPL migration has ceased, water table fluctuations may continue to alter the interval of mobile LNAPL in the formation. Residual LNAPL saturation is generally higher under water saturated conditions (where LNAPL and water completely fill the pore space, and LNAPL is the non-wetting fluid phase) than unsaturated conditions (where pore space is occupied by water, LNAPL, and air, and LNAPL has intermediate wettability). As a result, LNAPL can transition from residual to mobile (or vice versa) as the water table rises and falls.

Fluctuating water levels are commonly observed in response to seasonal recharge patterns, or in some cases due to tidal influences, construction dewatering, or changes in nearby groundwater pumping schedules. Where LNAPL is present in the zone of water table fluctuation, the vertical redistribution of LNAPL will result in a corresponding temporal variability in LNAPL transmissivity. The impact of water table fluctuations on LNAPL recoverability should be evaluated on a site-specific basis to determine appropriate test methods, number of locations to be tested, and frequency of testing ([Kirkman 2013](#)). Case study examples of how LNAPL transmissivity was evaluated at sites with temporal variability in LNAPL transmissivity due to water table fluctuations are provided below.

Case 1: Tidally influenced site [▼Read more](#)

The case study site is near a tidally influenced river, and groundwater fluctuations are common at wells with LNAPL. During a typical tidal cycle the measured LNAPL thickness varies from near-zero to 2-3 feet. The water table fluctuations create a change in the vertical LNAPL saturation profile as shown in Figure Tn-3, where high water tables trap LNAPL in the formation and low water tables result in vadose zone drainage and increased LNAPL saturation in the mobile interval.

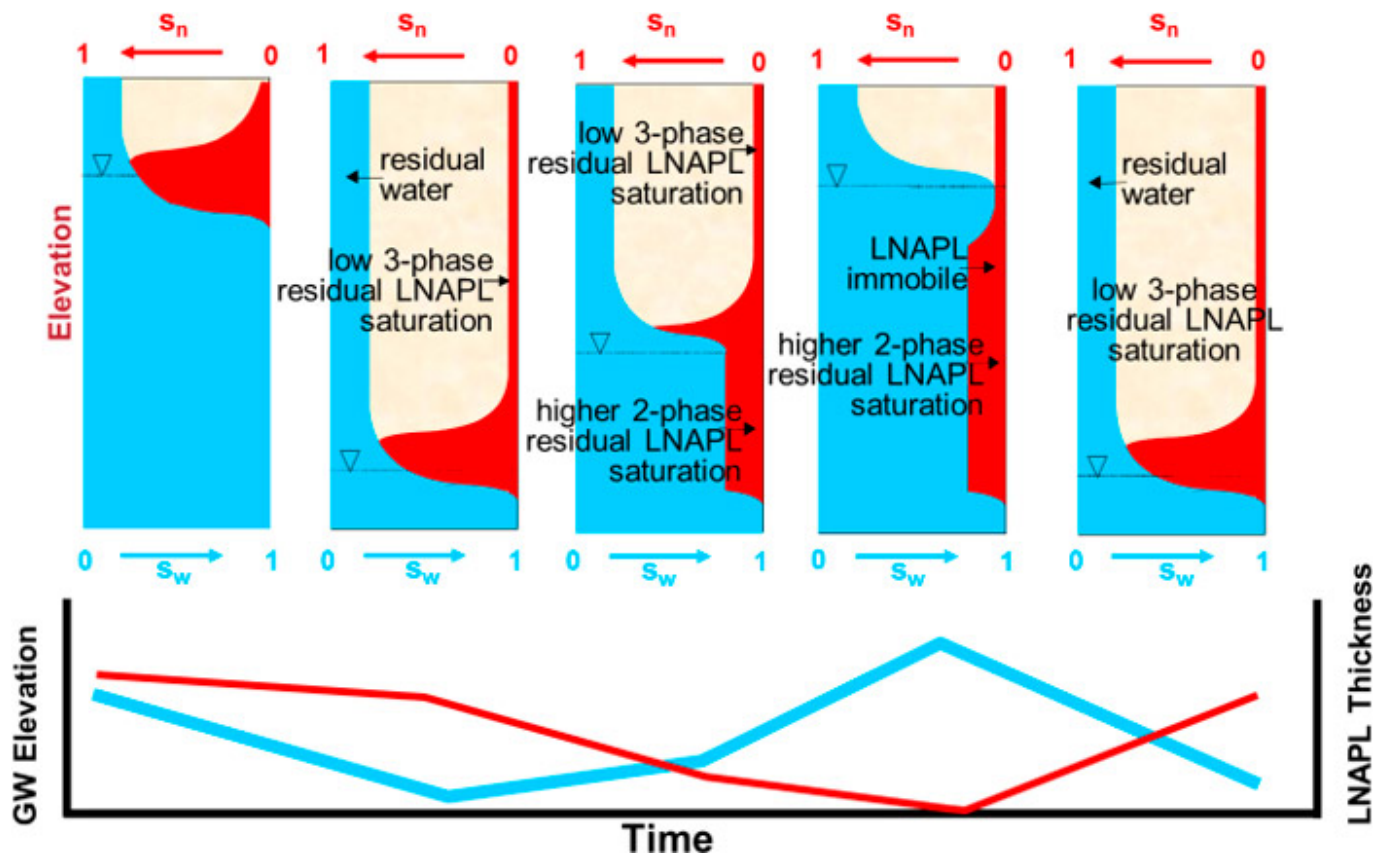


Figure Tn-3: LNAPL saturation profile variability under fluctuating water tables.

Conducting a baildown test under tidal cycles is complicated by the water table fluctuation. ASTM recommends baildown tests only if the LNAPL recovers fully during the low tide. However, this will likely over-predict LNAPL recovery, as the result represents only a fraction of the day when LNAPL transmissivity is highest. In contrast, manual skimming tests conducted over a full tidal cycle may produce a more representative result and capture how the LNAPL transmissivity varies over the cycle.

The average LNAPL transmissivity over the tidal cycle is more representative of overall site conditions and more valuable to remedial decision making. Therefore, instead of low-tide or high-tide baildown tests, results of manual skimming tests conducted across full tidal cycles (which provide temporally averaged measurements) were used to project potential LNAPL recovery rates and evaluate LNAPL recoverability relative to established metrics.

Case 2: Seasonal Variability [Read more](#)

Much like tidal cycles, seasonal groundwater fluctuations can create significant variations in LNAPL transmissivity. At a railroad facility in the Midwest, site groundwater elevations are affected by an adjacent river, and up to 15 feet of seasonal groundwater elevation fluctuation has been observed at the site. LNAPL transmissivity was measured across a range of groundwater elevation conditions to understand seasonal variability. Additional testing is underway to collect results reflecting the full range of groundwater elevation conditions. A time-weighted average LNAPL transmissivity will be calculated, with each LNAPL transmissivity result for a given well weighted based on the fraction of the year that the related groundwater elevation condition occurs. This time-weighted average will be compared to a 0.8 ft²/day LNAPL transmissivity standard in regulatory guidance published by the state environmental agency. This averaging approach has been discussed in concept with the state environmental regulator, but has not yet been officially endorsed.

Table Tn-5. Repeated LNAPL transmissivity measurements in 5 site wells over three years—the highlighted values exceed the 0.8 feet²/day LNAPL transmissivity evaluation criterion established by the state regulatory agency. ft. msl = feet above mean sea level

Date	LNAPL Transmissivity (ft ² /day)	Corrected GW Elevation (ft. msl)	River Elevation (ft. msl)
NM Not measured because of small LNAPL thickness — transmissivity near zero			
MW-A			
2012-12-17	11	717.17	713.27
2013-07-17	3.1	720.40	716.98
2015-02-07	NM	731.13	730.93
MW-B			
2012-12-21	0.40	716.80	713.27
2013-07-24	0.090	718.68	716.98
2015-02-07	NM	731.43	730.93
2012-12-17	0.060	717.61	713.27
MW-C			
2012-12-20	0.034	722.15	713.27
2013-07-23	1.5	723.00	716.98
2015-02-07	NM	730.09	730.93
MW-D			
2012-12-18	0.010	717.98	713.27
2013-07-24	8.3	720.07	716.98
2015-02-07	<0.08	731.83	730.93
MW-E			
2012-12-17	0.069	715.45	713.27
2013-07-18	2.4	718.55	716.98
2015-02-07	NM	731.81	730.93

Case 3: Active Recovery System [▼Read more](#)

In the case of an active recovery system, if the proper data are collected, LNAPL transmissivity can be calculated and tracked on a much greater frequency (e.g., with daily or weekly recovery totals). At the example site, a dual-phase (total fluids pumping) recovery system is operated continuously and LNAPL transmissivity is tracked weekly. The prescribed endpoint for LNAPL recovery is an LNAPL transmissivity of 0.8 ft²/day, and recent measurements show that LNAPL transmissivity values are fluctuating about that endpoint week to week. The overall trend indicates LNAPL transmissivity decreased from 10 to below 0.8 ft²/day; however, as a consequence of the fluctuations in LNAPL transmissivity around the threshold value established for the site, system operation continues. In this case, averaging the LNAPL transmissivity over a longer period (such as one month) or using trendlines fitted to the weekly data are reasonable approaches to develop an appropriate value for comparison to remedial goals.

4.3 LNAPL Transmissivity to Track LNAPL Recovery Progress

Short term transmissivity tests such as baildown and manual skimming tests evaluate LNAPL transmissivity by purging LNAPL from a well and observing the hydraulic response over the course of hours or days. In contrast, long-term recovery data represent sustained hydraulic recovery dynamic equilibrium conditions that reflect a larger radius of influence around a well than short-term test methods. Correspondingly, the average LNAPL transmissivity value calculated from long-term recovery data represents a larger volume of the subsurface than short-term test methods and better accounts for subsurface permeability and/or LNAPL saturation heterogeneities. Consequently, short-term testing methods are precise point

measurements while long-term recovery data measurements represent more accurate large-scale measurements.

It is possible to estimate LNAPL transmissivity values from recovery data for individual wells or trenches, groups of wells or trenches, or entire hydraulic recovery systems. As LNAPL is recovered from the subsurface, the LNAPL saturation decreases and it is expected that the LNAPL transmissivity will decrease as a result. An analysis of LNAPL transmissivity over time can provide a gauge of the progress towards completion of hydraulic recovery. The benefit to using LNAPL transmissivity as compared to tracking LNAPL recovery volumes is that LNAPL transmissivity can normalize changes in system operation that may result in increased LNAPL production. For example, if the overall pumping rate for a combined groundwater and LNAPL recovery system were increased, the volumetric rate of LNAPL recovery will likewise increase. However, an oil/water ratio analysis will show that the LNAPL transmissivity did not change and may show that the increased pumping rate results in a faster decrease in LNAPL transmissivity over time compared to the lower pumping rate.

An example transmissivity evaluation for an LNAPL recovery system showing recovery progress over time is presented in Figure Tn-4. The graph shows LNAPL and groundwater recovery trends over time for an LNAPL remediation system that was operated for eight years at a rail yard. There was a steady increase in the volume of both groundwater and LNAPL recovered at the site as a result of upgrades to groundwater treatment system equipment and improved management of system and well fouling. The LNAPL recovery profile shows that LNAPL recovery peaked in 2013 as a result of these efforts. However, the LNAPL transmissivity curve shows that the LNAPL transmissivity was decreasing throughout operation of the remediation system.

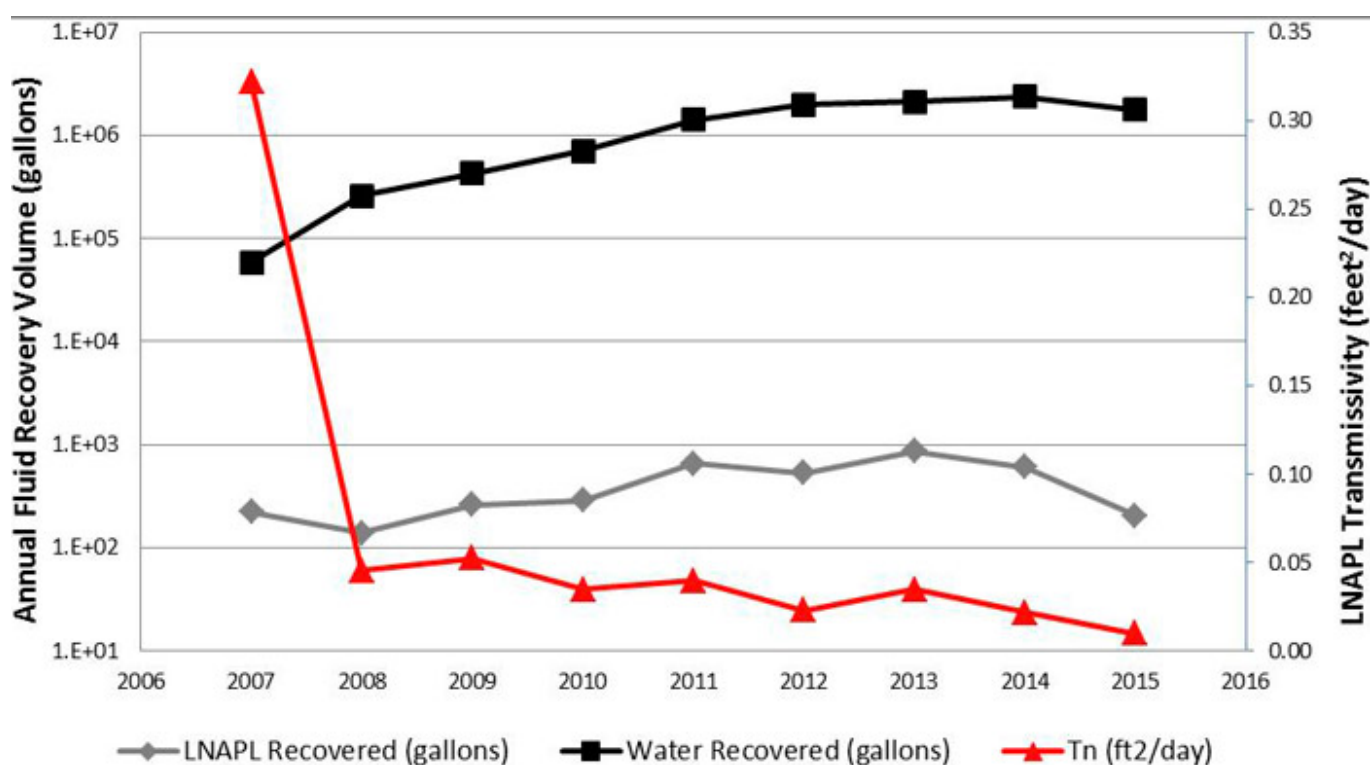


Figure Tn-4: LNAPL transmissivity and LNAPL and groundwater recovery volumes for a total fluids recovery system.

While LNAPL transmissivity is an excellent parameter to trace recovery system performance, additional lines of evidence may be useful to round out the evaluation. Complementary analyses include decline curve analysis, modeling of sustainable recovery curves, and calculation of specific LNAPL volume reductions as a result of LNAPL recovery.

Figure Tn-5 provides an empirical example of why LNAPL transmissivity is a better metric than using the thickness of LNAPL accumulation in wells for evaluating LNAPL recovery performance. The graph presents 10 years of vacuum truck recovery at an LNAPL site with little to no change in thickness as a result of recovery efforts. The dominant factor for LNAPL thicknesses illustrated by these data is the potentiometric surface elevation. If the LNAPL thickness was affected by the ongoing recovery action, a clear trend of smaller LNAPL thicknesses over time would have been observed, which would have resulted in clustering of early time data on the right side of the graph and late time data on the left.

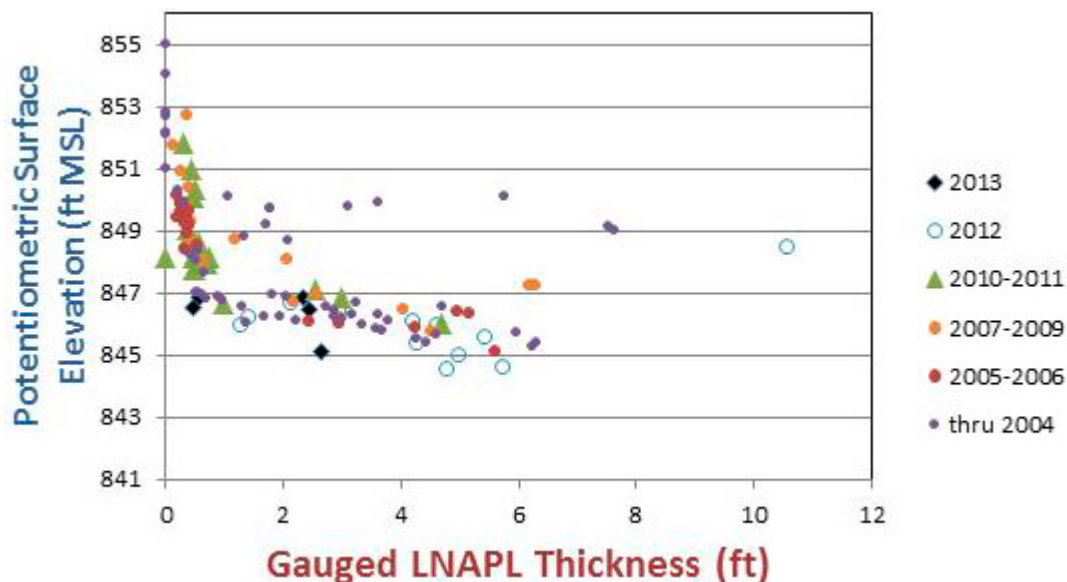


Figure Tn-5: Gauged LNAPL thickness vs. potentiometric surface elevation through time ([Kirkman, Adamski, and Hawthorne 2013](#)).

4.4 LNAPL Body Stability

LNAPL transmissivity can be used as a line of evidence to assess the overall stability and migration potential of an LNAPL body, supporting other evaluations based on time-series fluid level measurements and dissolved-phase concentration trends. Stability and migration potential are controlled by hydraulic gradients and LNAPL hydraulic conductivity, rather than the related concept of LNAPL transmissivity. LNAPL conductivity is governed by similar parameters (LNAPL saturation, LNAPL physical properties, and soil permeability), but does not incorporate the vertical thickness component of LNAPL transmissivity, making it suited to evaluate LNAPL migration potential rather than LNAPL recovery potential. LNAPL conductivity values can be calculated from transmissivity results, and it is also possible to directly measure LNAPL flux under ambient conditions through LNAPL tracer testing. An example use of transmissivity testing methods for evaluation of LNAPL body stability is provided below.

At this site, unconfined LNAPL is consistently present in three wells (MW-1, -2, and -3) within a larger residual LNAPL footprint. Each well typically contained 0.5 to 1 ft. of LNAPL under equilibrium conditions. Fluid level gauging data indicate that the mobile LNAPL footprint is consistent or decreasing in size over time, and monitoring data from downgradient wells indicate declining dissolved-phase concentration trends. LNAPL baildown tests completed at MW-1, MW-2, and MW-3 indicate the following:

- MW-1: Negligible LNAPL recharge occurred over a period of 5 days – Tn could not be well-quantified by baildown tests, but is qualitatively very low.
- MW-2: Tn of 1.5 ft²/d
- MW-3: Tn of 0.4 ft²/d

Based on these results, migration potential in the area of MW-1 was interpreted to be minimal; however, questions remained regarding the overall stability and migration potential of LNAPL in MW-2 and MW-3. To supplement the baildown test results, LNAPL dye trace tests (tracer tests) were conducted in each of the three wells containing LNAPL.

The LNAPL tracer test results indicated the following LNAPL flux over a six-month test period:

- MW-1: 0.008 ft./yr.
- MW-2: 0.9 ft./yr.
- MW-3: 0.4 ft./yr.

These data supported previous conclusions regarding MW-1, with LNAPL movement in the area of MW-1 minimal and hydraulic recovery of LNAPL at that location considered impractical. The tracer test results were used in conjunction with LNAPL hydraulic gradient measurements to calculate LNAPL transmissivity values, which were in general agreement with the previous baildown test results. The tracer test results also allowed calculation of LNAPL pore velocity, yielding:

- MW-1: 8×10^{-7} cm/s
- MW-2: 5×10^{-5} cm/s
- MW-3: 6×10^{-6} cm/s

The velocity estimates developed from tracer testing results are based on actual LNAPL flow, but do not account for NSZD mechanisms that are likely occurring around the perimeter of the LNAPL body, acting to reinforce overall LNAPL body stability. Therefore, the results should be considered a local measurement within the core of the area of mobile LNAPL, rather than a representative velocity for the LNAPL body as a whole. Flux measurements can also be combined with NSZD measurements to demonstrate overall LNAPL body stability following the approach of ([Mahler, Sale, and Lyverse 2012](#)).

Overall, review of these site data indicate that LNAPL transmissivity results correlate well to LNAPL mobility, and initial baildown test results could be used as a preliminary line of evidence to evaluate mobility and stability; however, by incorporating additional measurements and lines of evidence, including the LNAPL tracer testing method, an improved understanding of both LNAPL transmissivity and overall LNAPL body stability were developed.

4.5 Use of LNAPL Transmissivity at Small Sites

Several of the other case studies presented in this Appendix focus on aspects of LNAPL transmissivity application that are relevant to larger sites—for example, evaluation of data from large recovery systems. The following example (Figure Tn-6) presents an application of the same LNAPL transmissivity concepts to a site with a small LNAPL footprint.

The example site is a former service station and truck stop located in an area of commercial development that operated from the early 1980s through the mid-1990s. USTs previously used for storage of gasoline and diesel fuel were removed from the site in the late 1990s, and the site has been vacant since. Impacts to soil were noted during removal of a diesel UST, and a series of soil borings and monitoring wells installed in the late 1990s and early 2000s served to delineate the extent of diesel impacts in the subsurface. LNAPL accumulations were observed in as many as eight monitoring wells in an area of approximately 0.5 acres surrounding a former diesel UST.

Various LNAPL recovery technologies, including periodic removal technologies (manual bailing, vacuum truck extraction, and deployment of sorbent socks) and belt skimmers were implemented at the site from 2001 through 2005 in an attempt to reduce LNAPL thickness in wells to less than 1/8-inch, in accordance with regulatory policy. A total of approximately 500 gallons of LNAPL was recovered; however, LNAPL accumulations were still routinely observed in four monitoring wells at the site.

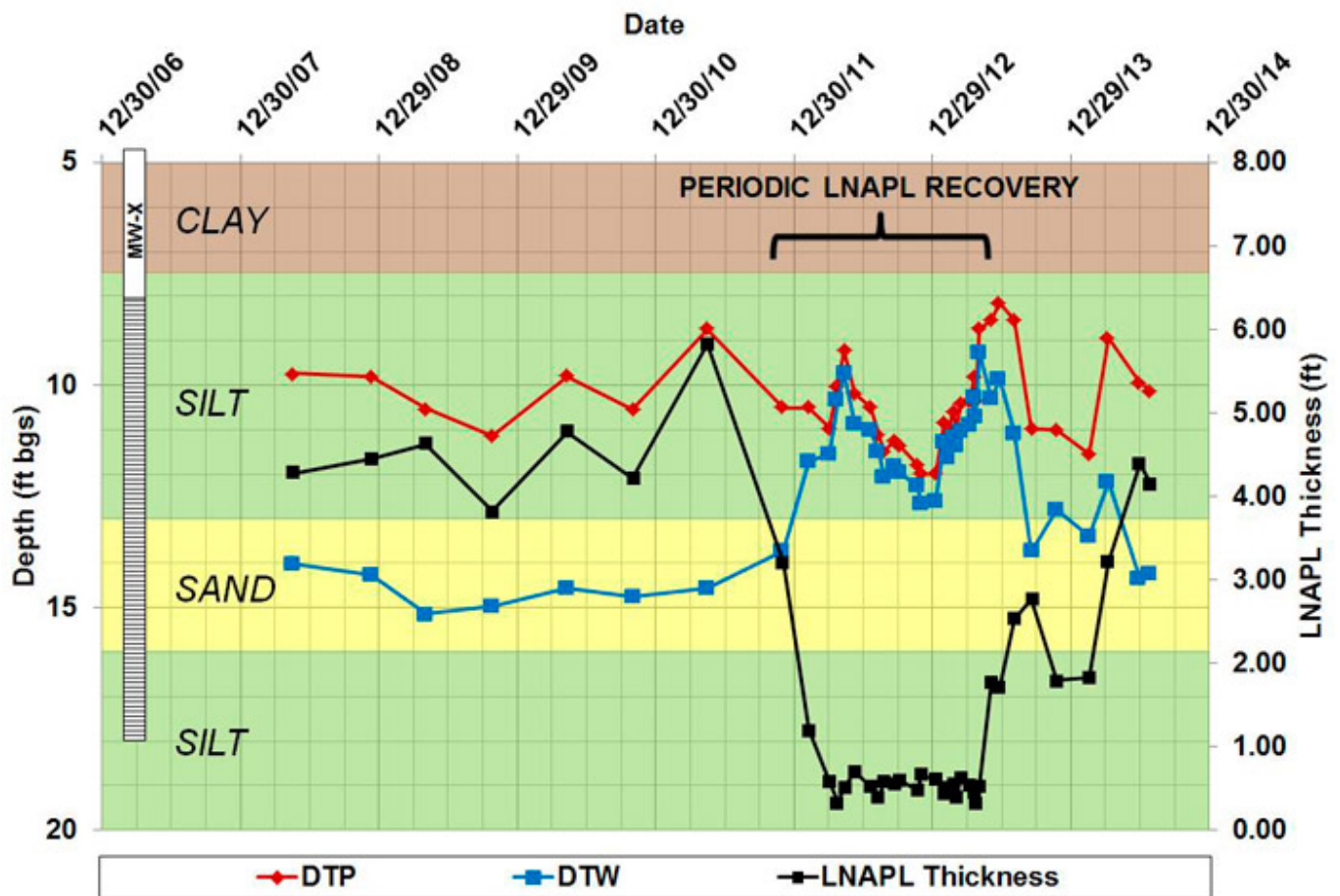


Figure Tn-6. Fluid levels and LNAPL thickness in MW-X before, during, and after periodic LNAPL recovery was conducted. DTP = Depth to Product, DTW = Depth to Groundwater.

LNAPL removal activities were temporarily halted from 2005 through 2011; however, fluid level gauging and groundwater monitoring activities continued on a biennial schedule. During this time, groundwater sampling results indicated stable to decreasing dissolved phase concentrations of TPH-D and naphthalene in wells surrounding the LNAPL source zone. This data, along with the observation that sentinel wells installed around the perimeter of the LNAPL body remained free of LNAPL, provided compelling evidence that the LNAPL body was stable and not migrating. However, LNAPL accumulations in one well (MW-X) reached a thickness of nearly six feet, which raised concerns that LNAPL migration could be occurring. Between December 2011 and August 2013, monthly LNAPL bailing was resumed in an effort to halt any potential LNAPL migration. While LNAPL thickness was maintained at approximately 0.5 ft., there was no evidence of any further progress toward the 1/8-inch criterion.

Beginning in 2013, a more informed approach to LNAPL management was adopted including LNAPL transmissivity testing, which at well MW-X was less than 0.1 ft²/d. Evaluation of historical soil boring logs and review of historical fluid level gauging data from 2008 through 2011 using up-to-date analysis approaches, such as diagnostic gauge plots, revealed that LNAPL in the vicinity of MW-X was present under confined conditions.

This finding provided an explanation for the historical LNAPL thickness trends observed at MW-X, and demonstrated that changes in LNAPL thickness had no bearing on LNAPL mobility. Other site data, including dissolved phase concentration trends and fluid level gauging data in wells located around the perimeter of the LNAPL body, provided compelling evidence that LNAPL was stable and not migrating. The low LNAPL transmissivity result at MW-X provided an additional line of evidence in support of a stable LNAPL body, and demonstrated that LNAPL recovery would not provide a meaningful reduction in LNAPL mass.



Appendix D - Fractured Rock Appendix

1.0 Introduction

The behavior of LNAPL in fractured bedrock is not necessarily intuitive and is not as easily described using the principles and techniques adopted for more homogeneous porous media. Differences have been observed and theorized for how LNAPL behaves in fractured bedrock formations. While the same physical principles apply for multiphase flow in fractured aquifers as in porous aquifers, unique characteristics of finite and restricted fluid flow paths can lead to unexpected results in fractured settings. Notable differences from unconsolidated materials include:

- Secondary porosity effects (bedrock fracture size and orientation) provide preferential flow pathways for LNAPL migration following a release.
- Fluid flow can be limited to fracture planes, thereby practically constricting aquifer bulk volume. As a result, LNAPL gradients can be greater than in porous media, resulting in increased lateral or vertical migration.
- Initial LNAPL head pressures focused on finite planar features can exceed those exerted on a more voluminous porous media aquifer and result in LNAPL propagation deep into the saturated zone via vertical and/or sub-vertical fractures ([Adamski 2005](#)); ([Hardisty 2010](#)).
- Fluctuations in groundwater elevation may cause “pumping” of LNAPL that result in greater lateral and vertical spread of LNAPL for longer time frames than for unconsolidated materials ([Hardisty 2010](#)).
- Similar to confined or perched LNAPL, the gauged thickness of LNAPL in a monitoring well may not accurately represent the mobile LNAPL interval in the formation.
- LNAPL penetration into the primary rock matrix may preferentially occur along fractures. Following removal of LNAPL from a fracture, there is the potential for LNAPL within the adjacent primary matrix to re-enter the fracture over time.

Approaches to characterization and specific investigation methods for fractured bedrock sites are provided in the ITRC Fractured Bedrock guidance ([ITRC 2017a](#)) and other documents. The purpose of this Appendix is to provide information that is focused on the understanding, approaches and methods that uniquely apply to LNAPL releases in fractured bedrock conditions.

2.0 Fractured Rock Concepts and Technical Background

Fractured bedrock can represent a wide variety of rock types with different primary matrix and secondary fracture porosity and permeability influencing the hydrogeologic behavior of groundwater and contaminants in bedrock. To simplify the discussion of how LNAPL behaves in various rock types, LNAPL behavior is discussed for four categories of fractured rock ([Nelson 2001](#)):

- Type 1 - minimal matrix permeability and porosity results in fluid flow and storage in the fractures (Single porosity).
- Type 2 - low matrix permeability but high porosity results in fluid flow in fractures, but storage in both the rock matrix and fractures (Dual porosity).
- Type 3 - high matrix permeability and porosity results in fluid flow and storage in both the rock matrix and fractures, but permeability is enhanced by the fractures (Dual permeability).
- Type 4 - high matrix permeability and porosity results in fluid flow and storage in both the rock matrix and fractures, with the fractures not significantly increasing flow (Single porosity or equivalent porous media analogue).

These simplified schematics (Figure FR-1) are intended to present conceptualized system behaviors, but the practitioner is cautioned to develop site-specific LNAPL Conceptual Site Models (LCSMs) as the range of conditions and behaviors is infinitely variable due to the unique setting of each site.

2.1 Fluid Entry Pressure

For LNAPL to migrate within fractured rock, the fluid entry pressure of a fracture must be overcome. This concept is equivalent to pore entry pressure for porous media, or the Type 4 category described above. Fracture entry pressure is a function of the difference in pressure between LNAPL and the other fluid(s) present, as well as the wetting angle, interfacial tension between the fluids, and the aperture of the fracture (i.e., the Laplace Equation) ([Corey 1990](#)).

$$Pe = \frac{2\sigma\cos\theta}{b}$$

Where:

Pe = Entry pressure

σ = Interfacial tension between LNAPL and water

b = Fracture aperture

θ = Contact angle with the wetting fluid

In the following sections, the concept of LNAPL head is directly related to this entry pressure, whether it is where LNAPL first enters a fractured rock system, or as it migrates through subsurface fractures of variable size ([Kueper and McWhorter 1991](#)).

2.2 Secondary Porosity Effects

LNAPL migration following a release in a fractured rock setting is driven primarily by fracture size (aperture) and orientation. However, where significant primary porosity and permeability of the bedrock matrix exists, fluid behavior similar to that which occurs in porous media can occur, resulting in what is commonly termed a dual porosity system. The range of behaviors is simplified into the Type 1 through Type 4 rock type hierarchy, with Type 1 units demonstrating the greatest departure from porous media fluid behavior and Type 4 units most closely following porous media behavior. The effect of variability in primary matrix permeability and porosity for the rock types is illustrated in Figure FR-1.

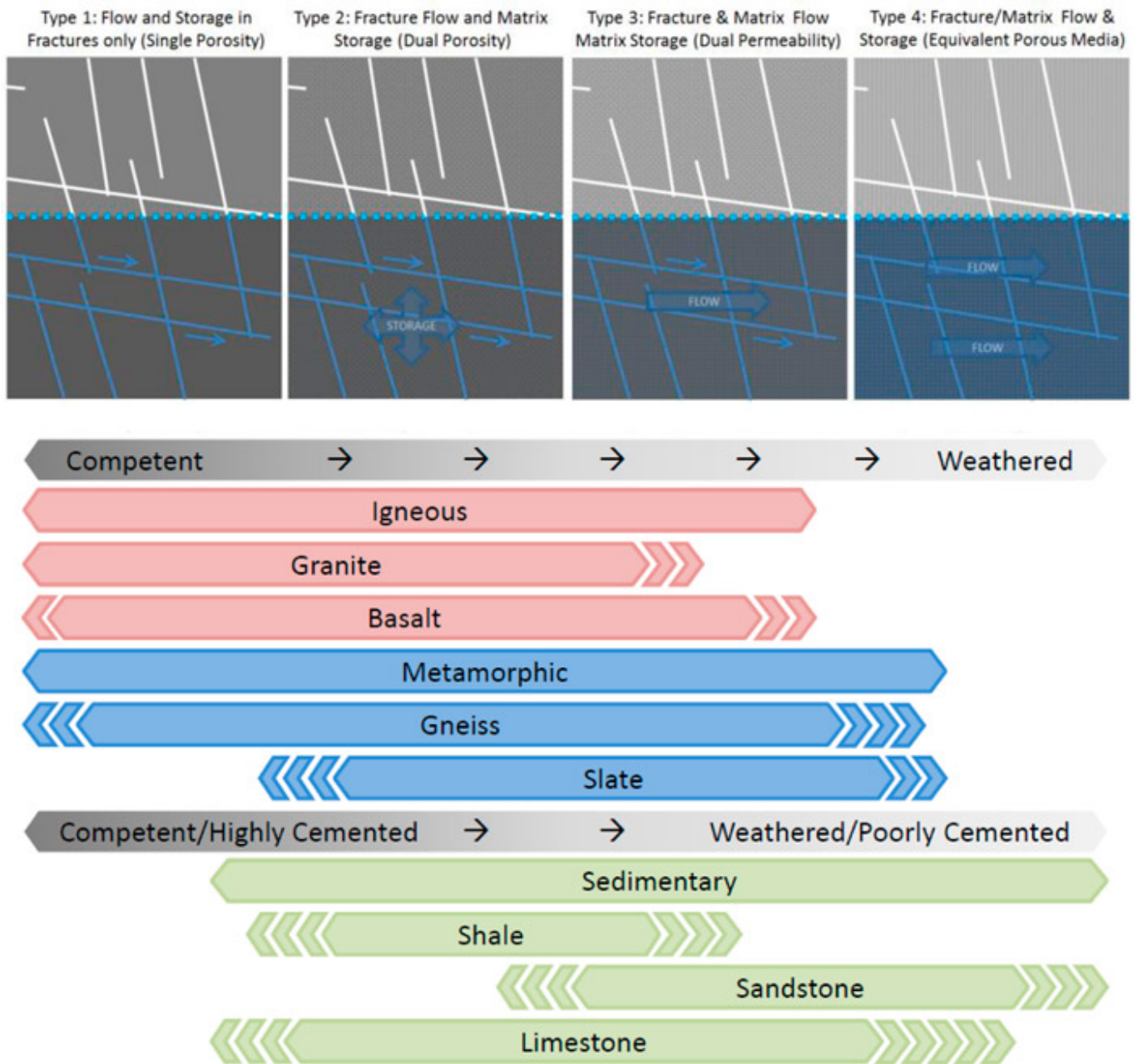


Figure FR-1. Rock type and characteristics.

LNAPL migration in Type 1 bedrock (e.g., crystalline bedrock), where primary matrix porosity is negligible, will allow for minimal LNAPL entry into the primary matrix. LNAPL will migrate preferentially along larger more transmissive fractures and can be hydraulically up-gradient from the release location. Increased porosity and permeability will result in increased entry of LNAPL into the rock matrix. For Type 2 and 3 bedrocks (e.g., limestone, sandstone), LNAPL will preferentially flow along fractures, but will increasingly penetrate into the primary matrix. Type 4 bedrock (e.g., highly weathered) can behave more similarly to unconsolidated formations. The effect of variability in primary matrix permeability and porosity on LNAPL distribution is illustrated in Figure FR-2.

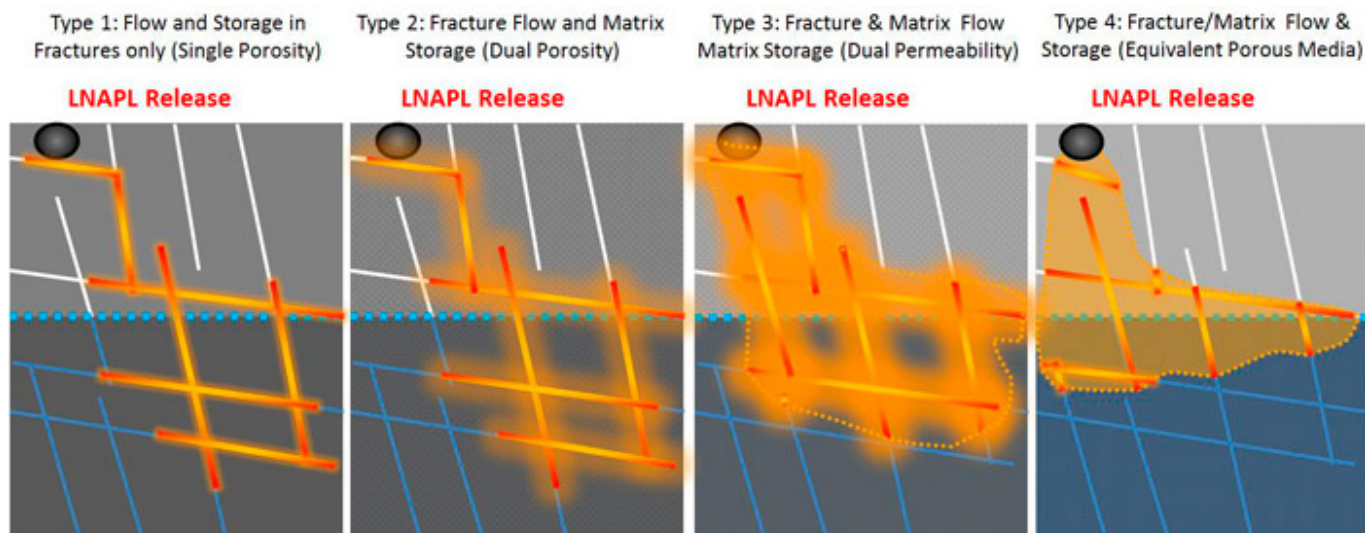


Figure FR-2. Rock type and LNAPL distribution.

2.3 Influence of Fracture Plane Angle on LNAPL Migration

The primary rock properties controlling LNAPL penetration and distribution in rock types 1 through 3 are fracture spacing and orientation. Where the volume of LNAPL released to the rock exceeds the volume of porosity near the spill, these properties will control LNAPL penetration and distribution. More steeply dipping fracture planes will allow for greater vertical penetration and lower fracture density (or larger spacing between fractures or lower “secondary porosity” relative to the bulk aquifer volume) will also promote deeper LNAPL penetration by focusing LNAPL head on those more discrete and finite preferential flow pathways. Fracture continuity and pervasiveness, which can be a function of weathering or depth, figure into both flow path direction and the continuum from Type 1 to Type 4 behavior.

In cases where shallow dip angle fracture or bedding planes are present above the water table and vertical fracturing is absent, lateral LNAPL migration will dominate the post-release plume distribution. The migration of the LNAPL body will predominantly occur in the direction of a fracture dip and follow fracture topography. Higher fracture dip angles, lower primary porosity, and open fractures can result in conditions that are not typically observed in unconsolidated formations (i.e., deep LNAPL penetration).

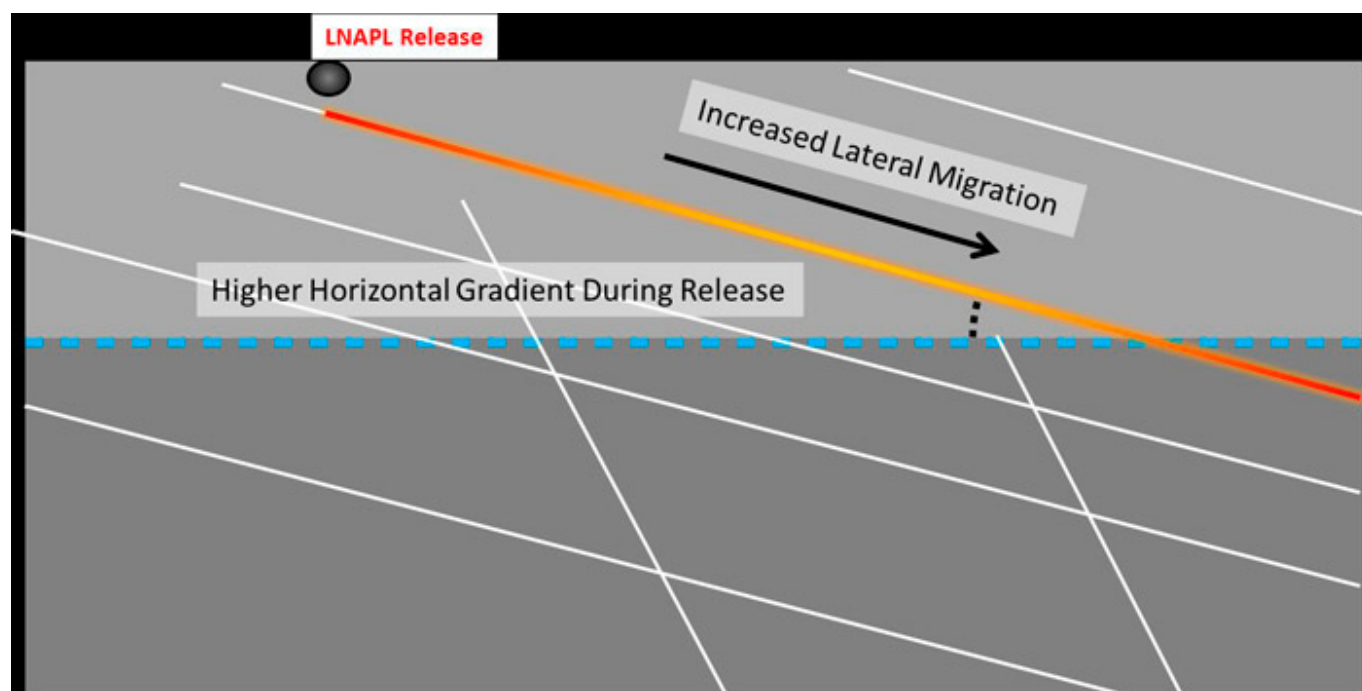


Figure FR-3. LNAPL lateral migration.

In cases where near-vertical fracture attitudes are present, LNAPL can be driven deep into the saturated zone due to the limited pathways for vertical migration and resultant buildup of LNAPL head. LNAPL may penetrate below the apparent groundwater elevation where the angle and aperture of a fracture, combined with the pressure head of the LNAPL (i.e., the height of the LNAPL source in the fracture above groundwater), can result in groundwater within the fracture being displaced to a significant depth ([Hardisty et al. 2003](#)). LNAPL has been observed at depths exceeding 30 feet (10m) below the water table in fractured rock settings.

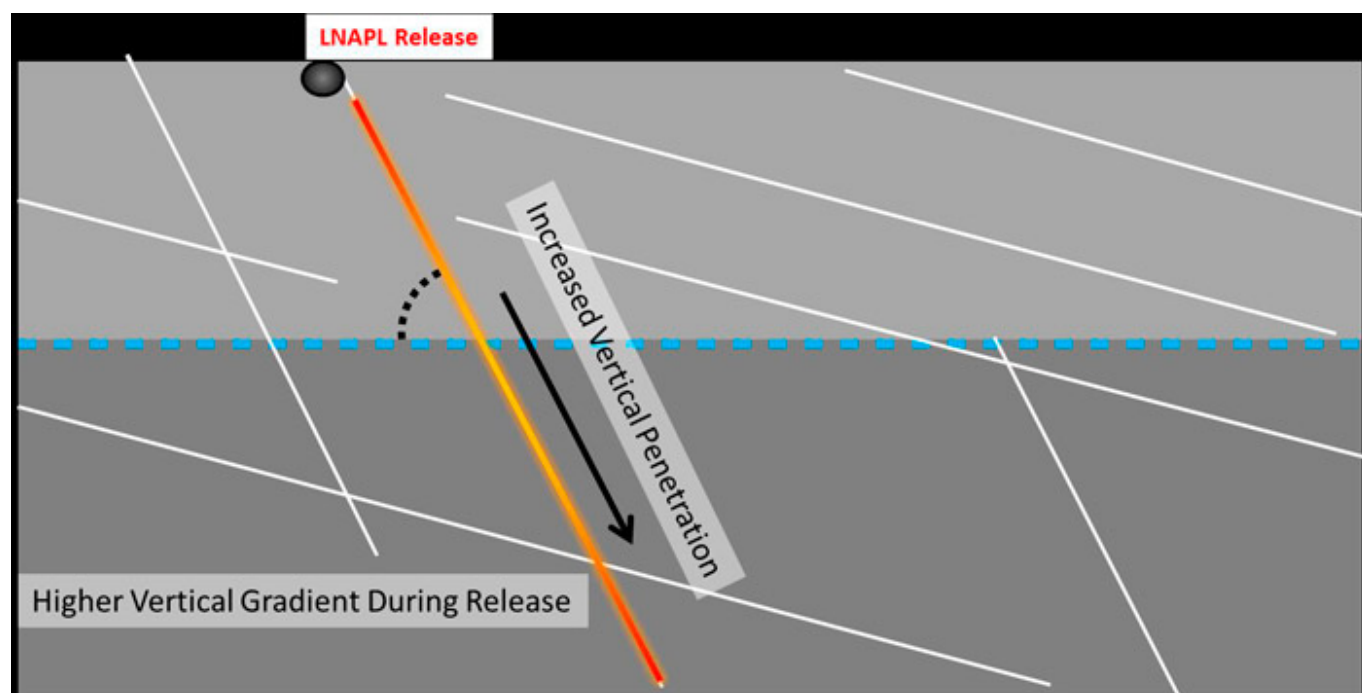


Figure FR-4. LNAPL vertical migration.

2.4 Influence of Groundwater Fluctuations on LNAPL Distribution

Even after reduction or elimination of an LNAPL driving head (i.e., post-release and stabilization), groundwater elevation fluctuations in fractured bedrock have the potential to cause both vertical and lateral redistribution of LNAPL ([Hardisty et al. 2003](#)). These effects are most critical in Type 1 and Type 2 bedrock where fracture orientation and frequency are within the zone of groundwater fluctuation.

As groundwater elevations fall, LNAPL will tend to migrate vertically downwards through sub-vertical transmissive fractures via gravity drainage. As groundwater elevations rise, LNAPL can migrate along any fracture that is no longer water saturated—including those with shallow or sub-horizontal dips. The result is that the fracture network could effectively act as a “pump” driving LNAPL in unexpected directions, including apparently up gradient, and may result in LNAPL being “trapped” potentially at significant depths below the static water level.

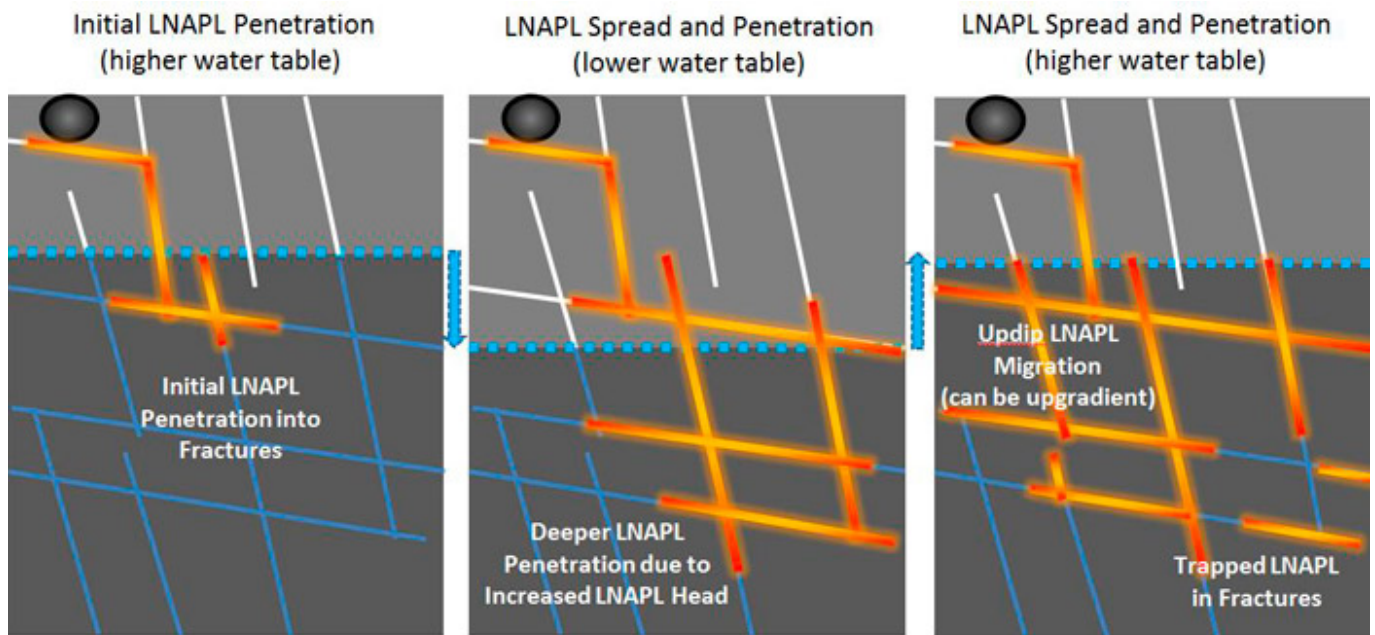


Figure FR-5. Changes in LNAPL distribution with groundwater fluctuation (modified from ([Hardisty et al. 2003](#))).

The difficulty in predicting these movements, combined with the inherent difficulty of constructing monitor wells that intersect the main fractures controlling LNAPL storage and movement, mean that establishing LNAPL body stability may be challenging. This requires a robust LCSM, longer-term monitoring data, and use of multiple lines of evidence.

As with porous media frameworks, changing water levels or saturations over time can also lead to further isolation of LNAPL bodies by alternately allowing for drainage from LNAPL-connected pores (or pathways) or trapping of LNAPL in pore or aperture openings too small for non-wetting fluid penetration absent a driving head—resulting in isolated LNAPL ganglia. These fluctuations can also be more pronounced in fractured rock aquifers with karst conditions being the most extreme ([CL:AIRE 2014](#)).

2.5 Gauged LNAPL Thickness in Fractured Bedrock

The gauged thickness of LNAPL in groundwater monitoring wells and open boreholes in fractured bedrock may result in exaggerated LNAPL thicknesses as compared to the mobile interval of LNAPL. These effects are most likely to occur in Type 1 and Type 2 bedrock and can result in confined or perched conditions resulting in exaggerated gauged thicknesses relative to what may be observed in unconsolidated formations (Figure FR-6).

There are several tools that may help to clarify these conditions for the LCSM. After well installation, use of diagnostic gauge plots and evaluation of constant LNAPL discharge during LNAPL baildown testing may help with understanding of the location of transmissive LNAPL fractures and the presence of perched or confined fractures. However, unlike unconsolidated formations, evaluation of diagnostic gauge plot data and LNAPL baildown testing can be complicated by 1) the presence of multiple transmissive fractures, each with different hydrogeologic conditions; and 2) the potential for both lateral and vertical redistribution of LNAPL with groundwater elevation changed as discussed above. If these conditions are expected prior to drilling, some techniques are available prior to well installation, such as NAPL Flexible Liner Underground Technologies (FLUTE™) systems, sampling with packers during drilling, etc.

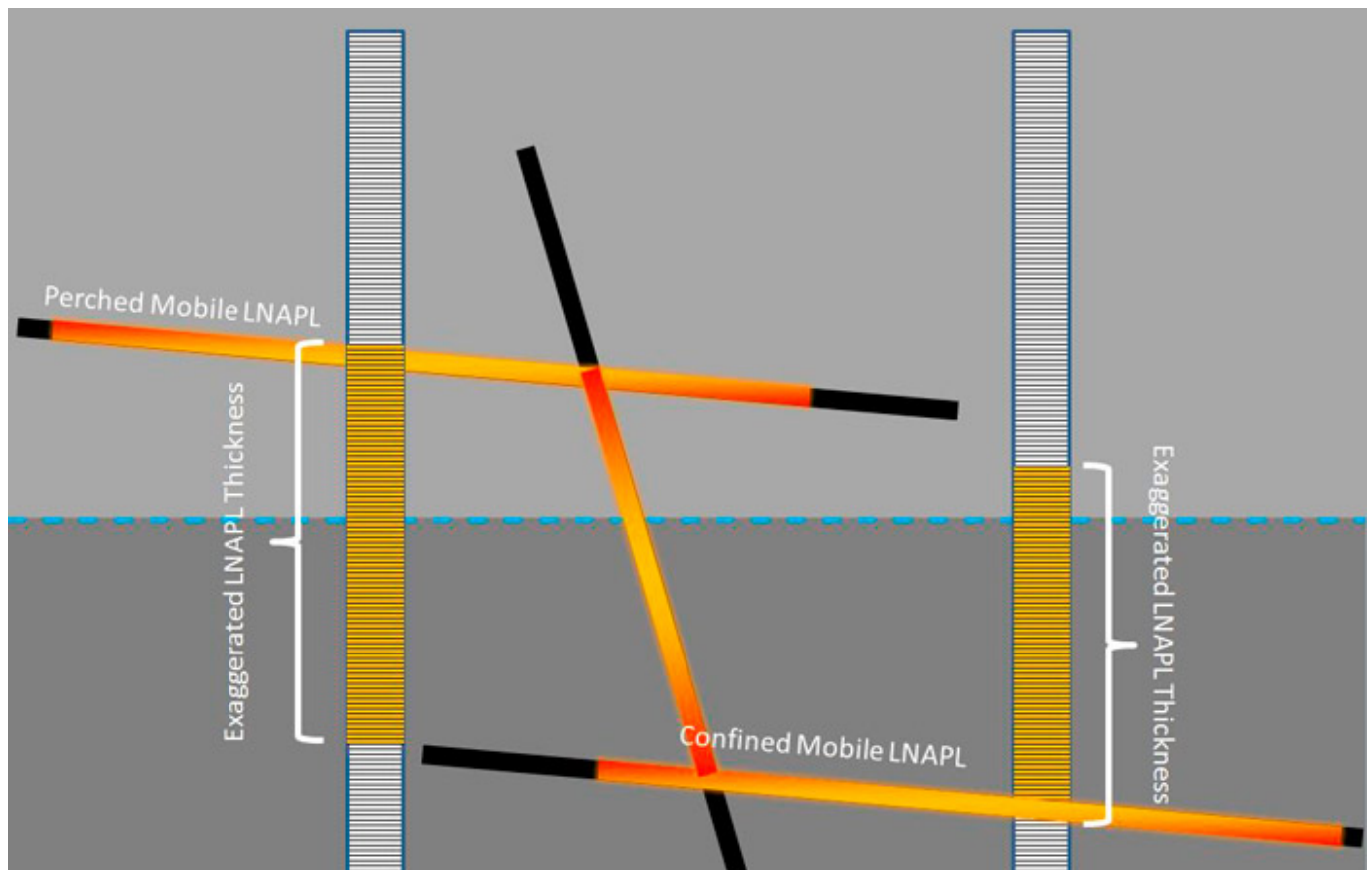


Figure FR-6. LNAPL vertical distribution and apparent monitoring well thickness.

These conditions illustrate why it is critical to develop the LCSM concurrent with the investigation process, to avoid connecting fractures that may not otherwise be connected. A well connecting two, previously unconnected near horizontal fractures, could cause LNAPL to migrate downward to lower fractured zones.

2.6 Re-Entry of LNAPL into Fractures from Primary Matrix

Entry of LNAPL into the rock matrix can occur where the primary matrix porosity and permeability is sufficiently high and is most likely to occur in Type 2, 3, and 4 bedrocks. In situations where the secondary porosity and permeability is higher than the primary porosity and permeability, mobile LNAPL will preferentially flow along the fractures, but may penetrate into the primary matrix over time as shown on the left side of the Figure FR-7. LNAPL recovery efforts will more readily remove the mobile LNAPL within the higher transmissivity fractures; however, mobile LNAPL may also remain in the primary matrix. After LNAPL recovery is stopped, re-entry of mobile LNAPL from the primary matrix back into the fractures may occur.

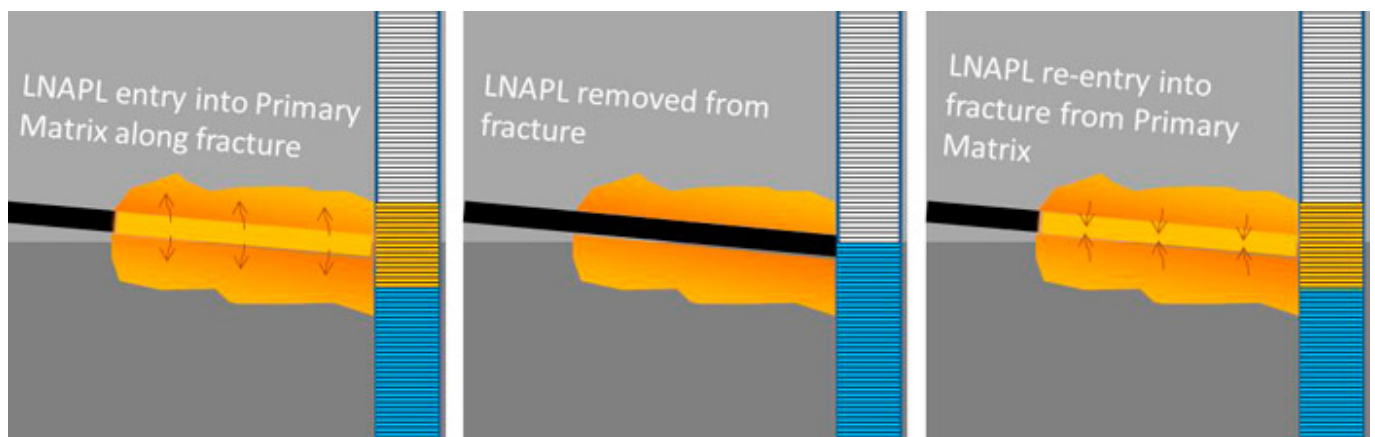


Figure FR-7. LNAPL re-entry into fracture from primary matrix.

Conceptually, this poses similar challenges as “back diffusion” of dissolved phase constituents in fractured rock

environments. In addition, LNAPL recovery rates and transmissivities may decline during active LNAPL recovery as mobile LNAPL is removed from the secondary porosity, but may rebound if re-entry of LNAPL into the fractures occurs.

3.0 LNAPL Conceptual Site Model

Development of an LNAPL Conceptual Site Model (LCSM) is described in detail in [Section 4](#) of the main body of this document. The level of detail required to develop an LCSM is in part a function of the complexity of environmental conditions. Although multiphase fluid relationships and flow in fractured rock settings are generally governed by the same physical principals as in unconsolidated media, more extreme ranges in quantification of physical properties are found in fractured rock, resulting in increased variability and complexity. Examples include fracture aperture (analogous to porosity) and bulk hydraulic conductivity, where ranges over multiple order of magnitude are common. In addition, the spacing, pervasiveness, amount of “interconnectedness” and attitudes of fractures (idealized as two-dimensional planes) imparts another layer of complexity to fractured rock fluid flow. The result is that an increased level of detail is typically required to develop an LCSM in fractured bedrock.

The ITRC Fractured Bedrock guidance ([ITRC 2017a](#)) and DNAPL guidance ([ITRC 2011](#)) provide a detailed discussion of the methods to develop a Conceptual Site Model in fractured bedrock. For LNAPL releases in fractured rock, practitioners are encouraged to review both ITRC guidance documents. Other tools for assessing fracture systems have been evaluated by the USGS in their Fractured Rock Geophysical Toolbox Method Selection Tool (FRGT-MST).

Introduction of an LNAPL with sufficient driving head into fractured bedrock often results in: an LNAPL plume distribution with anisotropic dimensions aligned with dip direction in the unsaturated zone, and aligned with bedding strike in the saturated zone; as well as vertical penetration to underlying beds proportional to bed thickness and/or cross-bed fracturing. In addition, LNAPL penetration into primary matrix pore space would be expected in these units and would increase with time and increased primary pore space of the various interbedded units.

Development of an LCSM should include conducting in-depth literature reviews and employing a multiple lines of evidence approach to developing and continually improving LCSMs to match empirical findings. Conventional investigation techniques (i.e., vertical borings and monitoring wells) are typically ill-suited to develop LCSMs in fractured bedrock. However, numerous alternative tools are available and can be used to develop LCSMs in fractured conditions. As real-world fractured aquifer systems exhibit behaviors along a continuum of the simplified Type 1 to Type 4 scenarios, a hybrid LCSM is often the best fit for managing site data and upon which future management decisions can be based.

Consistent with [Section 4](#) of this guidance on the development of the LCSM, the following questions are intended to guide LCSM development related to LNAPL in fractured rock. If all or part of a question is immaterial to matrix lithology, then the reader is directed to Section 4. Only those aspects of the questions that are specific to fractured rock are further discussed.

1. Is current and future land use known? [▼Read more](#)

This component of an LCSM is generally not specific to the lithology. However, because fractured rock tends to cause LNAPL to migrate farther from the source and in directions not necessarily dictated by the hydraulic gradient, the current and future land use of a larger area may be needed to complete the LCSM. In addition, more detailed information may be needed at an earlier stage in the LCSM process.

2. Does the potential for preferential pathways exist? [▼Read more](#)

LNAPL flow and transport in fractured bedrock is typically dominated by secondary porosity (fractures), but primary porosity provides a matrix for LNAPL intrusion. See Chapter 2 of ITRC’s Characterization and Remediation of Fractured Bedrock guidance ([ITRC 2017a](#)). The fracture orientation and spacing at an LNAPL release site can be challenging to define on a site level scale, and requires use of multiple lines of evidence in order to develop a detailed LCSM prior to implementation of remedial actions.

Karst features can vary from small voids to large caverns. These features can create conduits that are highly variable in flow direction, have flow velocities that can be orders of magnitude higher than the associated bedrock (e.g., limestone), and are often directly connected to groundwater and surface water features. Karst features can lead to potential contaminant discharges to streams, springs, and surface water bodies. Void spaces can also create collection points for LNAPL that can serve as persistent source areas for dissolution to groundwater and for LNAPL sources to the surrounding matrix.

It is important to thoroughly assess the potential for existence of preferential pathways that may impact LNAPL migration/distribution when developing the LCSM in fractured bedrock conditions.

3. How does stratigraphy relate to affecting impacts and potential migration? ▼[Read more](#)

Stratigraphy, or more generically, the structural fabric of a bedrock aquifer system, is the dominant element to determining contaminant migration direction. Fluid flow in fractured media encompasses study of the geometry and “connectedness” of planar features that offer preferential pathways for migration. These planar features may be bedding, foliation, fractures, joints or similar brittle features and in most cases, will define the direction(s) of the most rapid and significant contaminant migration.

Contrasts in hydraulic conductivity between fractures and rock matrix “blocks” are many orders of magnitude greater than those typically found between anisotropic features (i.e., sand lenses in a fine-grained matrix) in porous media aquifers. These extreme contrasts result in more discrete flow pathways in fractured rock systems. Physical properties of the rock matrix, particularly porosity and organic carbon content, can have a major impact on contaminant infiltration and storage in the rock matrix and subsequent back diffusion or re-entry of LNAPL into fractures.

Many of the system attributes (rock type, orientation of bedding or structural fabric, fracture type, fracture spacing, etc.) can be determined through evaluation of available geologic literature. The concept of preparing an initial Conceptual Site Model has been addressed in several ITRC documents, most recently including Petroleum Vapor Intrusion ([ITRC 2014](#)) and perhaps most germane to this topic, in the Characterization and Remediation of Fractured Rock ([ITRC 2017a](#)). Section 2 of the latter document is entitled “Terrain Analysis” and presents a high-level approach to evaluating known and/or anticipated structural and lithologic features of a given site. Much of this initial work should be done as a “desk top” evaluation and provides critical regional geologic characteristics to the LCSM.

4. Is the extent of the source areas known? ▼[Read more](#)

The lateral and vertical migration of LNAPL in fractured rock is highly influenced by preferential flow pathways and LNAPL can penetrate deeper into the aquifer than typically observed in unconsolidated conditions. Wells have been drilled into fracture systems that can yield water at rates in excess of 275 m³/day ([Kasenow 2006](#)). LNAPL introduced into such fractures can result in significant LNAPL migration. The weight of a LNAPL mass may displace water, causing LNAPL to be forced to depth and into permeable zones far below the potentiometric surface. Where possible, the investigator needs to recognize these conditions prior to constructing wells or open borings that may create these connections. This can be prevalent in areas of thin saprolite or thin sediments overlying fractured bedrock. Due to these conditions, reliance on multiple lines of evidence is generally required to determine the lateral and vertical extents of LNAPL in fractured rock.

5. Are dissolved or vapor issues expected based on LNAPL composition? ▼[Read more](#)

In many cases, CSMs will also need to include areas of the site that may not be bedrock—even if the source is known to exist in a bedrock setting. At any site where soil or non-lithified material overlies a contaminated bedrock aquifer, practitioners must consider the interplay and potential fluid flow (including vapor phase) between the bedrock and overlying media. Not only is the bedrock/overburden interface a critical surface that denotes a marked contrast in hydraulic properties between the juxtaposed media (therefore offering enhanced contaminant flow or storage capability), but vapor phase transport through porous media may still offer clues to the underlying bedrock structure.

Due to the marked contrast in fluid conductivities between fractured and non-fractured rock matrices, fluid flow will occur preferentially in fractures (or planar features of significantly higher conductivity than the surrounding rock matrix). This can result in more rapid and laterally extensive contaminant transport for a given hydraulic head. Similar behavior is realized with vapor phase transport.

Therefore, investigations to determine the lateral extent of subsurface impact from a contaminant release in a fractured rock setting may encompass a larger area than a porous media setting. Also, vapor phase transport from a fractured rock source through an overlying porous media cover may provide clues as to the bedrock fracture geometry as concentrations of near-surface soil gas may be correlated to deeper source configuration.

6. Are dissolved or vapor plumes characterized? ▼[Read more](#)

Soil and groundwater criteria for LNAPL are often based on mobility, measurable thickness, and contact with groundwater from an aesthetic perspective. Because LNAPL in fractured rock may be more difficult to intersect with traditional investigation techniques, indirect measurement tools may be used to develop the LCSM. These indirect tools and techniques target the vapor or dissolved phase and are based on the theoretical solubility of an LNAPL. Direct measurements may include hydrophobic dyes that can detect small amounts of LNAPL in the matrix or groundwater, or analysis of pulverized rock for presence of sorbed LNAPL.

7. Do soil or groundwater concentrations exceed criteria? ▼[Read more](#)

There are no unique differences in fractured bedrock.

8. Are exposure pathways complete or incomplete? ▼[Read more](#)

Methods to evaluate receptors and pathways of potential LNAPL migration are mostly consistent with LNAPL present in unconsolidated formation, but several additional considerations need to be made in fractured rock conditions:

1. The area in which to evaluate receptors and pathways may need to be increased, especially in directions parallel to preferential fracturing, due to the increased potential for LNAPL migration along preferential pathways.
2. Receptors such as groundwater extraction wells in the vicinity of an LNAPL release can have a greater radius of influence in fractured rock conditions, and these effects should be considered when establishing the area in which to evaluate receptors and pathways.
3. The duration of monitoring of sensitive receptors should consider the effects of migration in fractured rock that can impact LNAPL body stability.

9. Is the LNAPL body stable? ▼[Read more](#)

As described in [Section 2](#), even after reduction or elimination of an LNAPL driving head (i.e., post-release and stabilization), groundwater elevation fluctuations in fractured bedrock have the potential to cause both vertical and lateral redistribution of LNAPL ([Hardisty et al. 2003](#)). Fractures are also more susceptible to seasonal groundwater potentiometric surface variation. These include significant vertical smear of LNAPL along fracture walls, introduction of LNAPL to permeable zones at depth that may be “trapped” in stratigraphic and structural features. This would be most prevalent in areas that experience high seasonal variation in groundwater levels or in coastal areas that experience significant tidal ranges.

10. Is mobile LNAPL hydrogeologic condition known? ▼[Read more](#)

LNAPL present in fracture rock conditions can behave similarly to confined/perched LNAPL in unconsolidated formations. Gauging data collected in equilibrium conditions can be evaluated and interpreted using diagnostic gauge plots to inform understanding of the hydrogeologic condition of the LNAPL, and may provide insights into the rock type. In Type 1 and 2 bedrocks LNAPL present in transmissive fractures is likely to behave more similarly to confining/perched conditions.

11. What “tools” are available to develop an LCSM in fractured Bedrock? ▼[Read more](#)

Development of LCSMs in fractured rock requires similar approaches and tools as for investigation of general fractured bedrock Sites ([ITRC 2017a](#)) – Fractured Rock Tools Tables) as well as DNAPL ([ITRC 2011](#)) — [Click for DNAPL Tools Tables](#)). A summary of the most applicable tools to development of an LCSM is provided in Table FR-1.

Table FR-1. Summary information for LNAPL investigation tools applicable in fractured bedrock

[View Table FR-1 in Adobe PDF format.](#)

4.0 Remedial Technologies

Remediation in fractured bedrock is subject to the same constraints as porous media, with the added challenge that

explicitly mapping the transport pathways (fractures) and mass distribution is more difficult, or in some cases, impossible. This is one of the primary reasons that pump-and-treat remediation is commonly selected in complex fractured rock systems.

A key limitation in fractured bedrock remediation is access to the target compounds and distribution of reagents, when injection-based in-situ remedies are applied. The second matrix in [Appendix A](#) summarizes data requirements and data collection methods to evaluate remedial alternatives at fractured rock sites.

An important factor regarding the efficacy and cost for treatment, particularly in source areas, is the degree to which mass has diffused into the matrix and the potential significance of “rebound” that may occur due to back diffusion. When COCs are contained primarily in the fractures, remediation can have significant benefits in a relatively short period of time and pump and treat can be applied as a remedy, not just a containment measure.

In cases where a significant mass of recalcitrant compounds has diffused into the matrix, access to the source material can be inefficient, commonly resulting in rebound after in-situ treatment, or extended duration of pump and treat.

The reverse-diffusion effect on remedial timeframe may not be as significant for contaminants that may degrade in the matrix (e.g., aromatic hydrocarbons) if conditions are conducive for decay in the matrix or upon reverse-diffusion back into the fractures. Mature plumes of recalcitrant compounds, however, often require the most aggressive measures of remediation, such as thermal treatment or chemical oxidation to significantly reduce mass. Table FR-2 summarizes the applicability of conventional remedial technologies and provides a relative ranking as to their cost, reliability and period of performance.

Table FR-2. Summary information for LNAPL remediation technologies in fractured bedrock

[View Table FR-2 in Adobe PDF format.](#)



Appendix E-LNAPL Sheens Appendix

1.0 Introduction-What Are LNAPL Sheens?

Petroleum sheens (Figure S-1) can be encountered in surface water near facilities where historical subsurface petroleum releases have occurred. The occurrence of petroleum sheens may result in notices of violation and fines issued by regulatory agencies, as well as undesired publicity and aesthetic issues. In some cases, a rapid response is necessary.

Typical remedies for petroleum sheens in surface water may include adsorbent booms, physical barriers, hydraulic controls, or excavation of impacted soils. Though successful in some cases where deployed, these remedies may be less effective than desired, can conflict with other facility goals, and/or may have high cost of implementation.

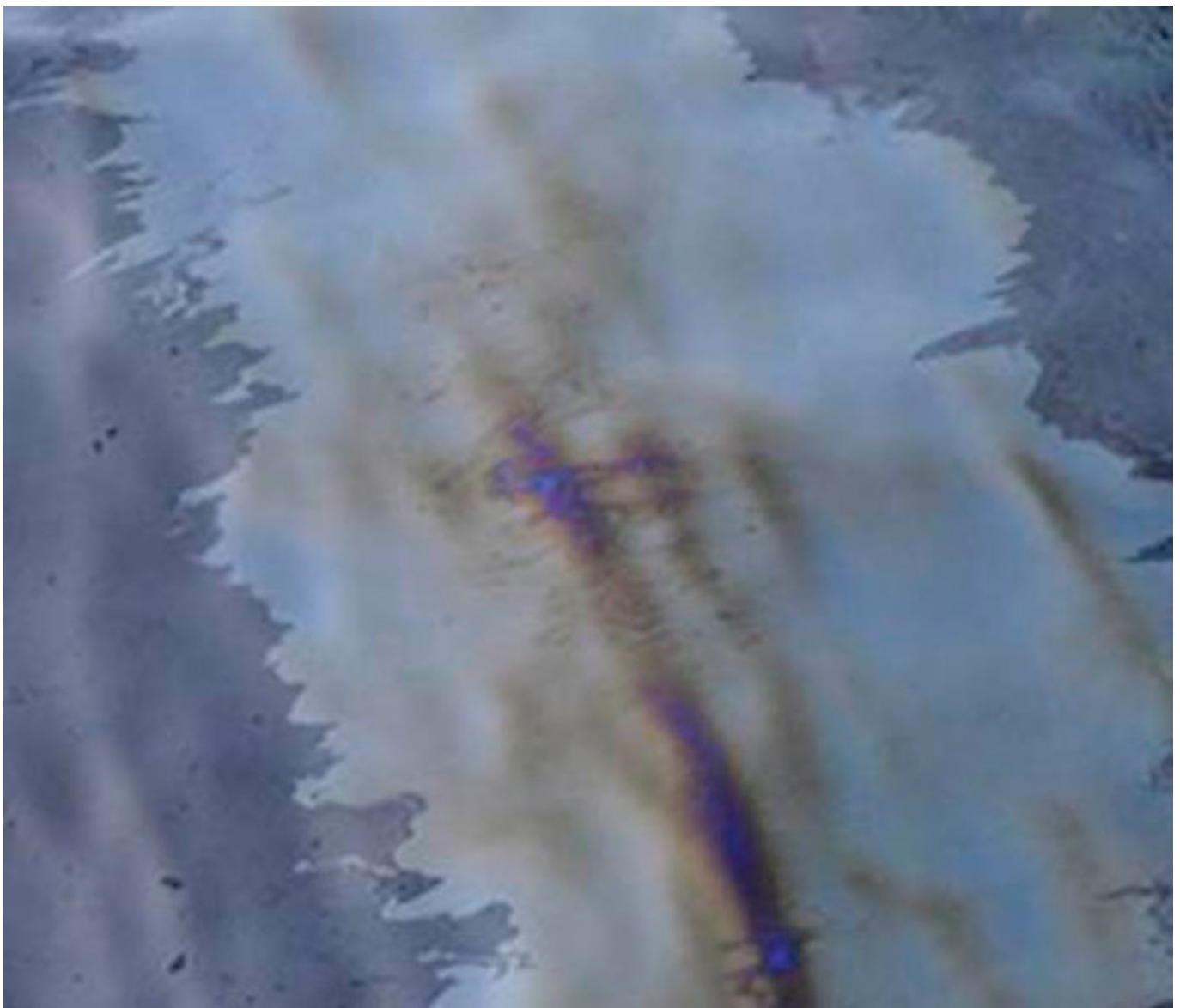


Figure S-1. Petroleum sheen on surface water ([Sale and Lyverse 2014](#)).

Governing Processes

Effective management of sheens begins with an understanding of governing processes.

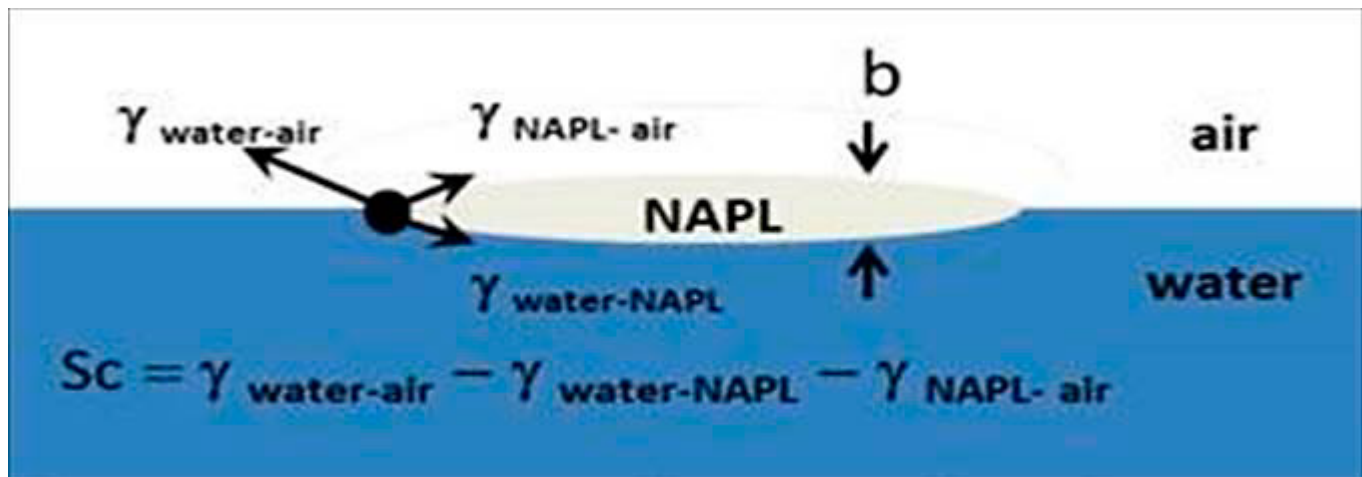


Figure S-2. Forces controlling spreading of LNAPL across air-water interfaces (Adamson, A. 1990).

Spreading—Petroleum sheens occur when petroleum liquids (referred to as Non-aqueous Phase Liquids—NAPLs) spread across air-water interfaces. The potential for a NAPL to spread is defined by the spreading coefficient (S_c). This concept is presented in Figure S-2. NAPLs spread across air-water interfaces until interfacial forces (γ) at the leading edge of the sheen are balanced or natural processes (e.g., dissolution and volatilization) deplete the petroleum liquids. Most petroleum NAPLs (crude oil, fuels, and lubricants) will spread across surface water as described above. Spreading may be enhanced by biosurfactants that are associated with biological degradation of NAPLs in subsurface media including sediments, soils, and rock.

Characteristics

Thin films—Sheens are so thin that the equivalent amount of petroleum liquids can be as low as a few liters per square kilometer (ten liters per square kilometer equates to a thickness of 0.00001 mm).

Appearance—The iridescent color of sheens is due to refraction of light through thin NAPL layers with varied thicknesses.

Origin—Sheens are commonly associated with releases of petroleum liquids near surface water bodies. They can also be due to biological degradation of naturally occurring organics (i.e., plant material). Natural sheens can occur in stagnant water associated with organic rich sediments (e.g., swamps).

Natural Losses—Hydrocarbons associated with petroleum are subject to a diverse set of natural loss processes. In the case of sheens on surface water, natural loss processes include volatilization, microbially mediated aerobic degradation, and dissolution into water. In sediments and groundwater systems, microbially mediated anaerobic processes can also play an important role in mitigating impacts associated with petroleum at groundwater-surface water interfaces. Depending on the composition of released petroleum and environmental conditions, sheens can persist for minutes to days. Critically, natural losses prevent sheens from being more common. Enhancing natural losses of petroleum hydrocarbons at groundwater-surface water interfaces (GSIs) is an emerging strategy for managing sheens.

Sheen Occurrence—Sheen occurrence can correspond to low surface water stage, high surface water stage, seasonal temperatures (Chalfant 2015) or ebullition (McLinn and Stolzenburg 2009). Understanding processes controlling sheens at individual sites can be difficult. With study, mechanisms governing the cause of a sheen can usually be resolved. In general, sheen appearance is dependent on a) the mechanism of releases and b) seasonally varying factors controlling natural losses of NAPLs at groundwater-surface water interfaces.

2.0 What are Some Important Regulatory Requirements Concerning Sheens?

According to Clean Water Act, 40 CFR, Chapter I, Subchapter D, Part 110, Section 110.1, a sheen is defined as “an iridescent appearance on the surface of water”. https://www.epa.gov/sites/production/files/2014-04/documents/b_40cfr110.pdf

Part 110.3 discusses the types of discharge of oil that the EPA Administrator has determined may be harmful to the public health or welfare or the environment. One is a discharge oil that may “cause a film or sheen upon or discoloration of the

surface of the water or adjoining shorelines.” Section 110.6 states that any person in charge of a facility, as soon as he or she has knowledge of a sheen that is in violation, shall immediately notify the National Response Center (NRC) at 800-424-8802. The NRC will relay the information to the On-Scene Coordinator (OSC) of the US EPA or U.S. Coast Guard, depending on the location. After receiving the report, the OSC will determine if federal emergency response action is necessary.

<https://www.epa.gov/sites/production/files/2014-06/documents/spccfactsheetspillreportingdec06-1.pdf>

If direct reporting to the NRC is not practical, reports may be made directly to the Coast Guard or a designated EPA OSC in the geographic area where the discharge occurs.

In addition to reporting to the NRC, some states also have separate reporting requirements for sheens. For example, some states have reporting requirements for spills or discharges directly into state waters if the quantity is sufficient to create a sheen (example: Texas). Other states have reporting requirements for sheens in navigable waters (example: Ohio). In addition, depending on the state, the responsible person may be required to: immediately abate and contain the spill or discharge that caused the sheen, cooperate fully with local and state authorities, and submit various documentation to state authorities. If a sheen occurs, the responsible party should check with state authorities to determine what additional requirements may be necessary.

3.0 What Are the Common Sheen Forming Scenarios and Processes?

Understanding mechanisms of releases and factors controlling natural losses of NAPL is central to developing remedies. As described below, it is not unusual for the occurrence of sheens to be episodic and related to hydrologic, atmospheric (i.e., changes in barometric pressure) or water stage/level conditions as described below. At any site, one or more of these mechanisms might be at play.

Scenarios

Seeps—Groundwater typically discharges from river banks or shorelines to surface water during falling surface water levels. Given NAPL near the GSIs, discharge of groundwater can drive NAPL sheen into surface water (Figure S-3). Most often, NAPL seeps appear at low surface water stages. As shown in Figure S-3, seeps are generally oriented parallel to the shoreline.

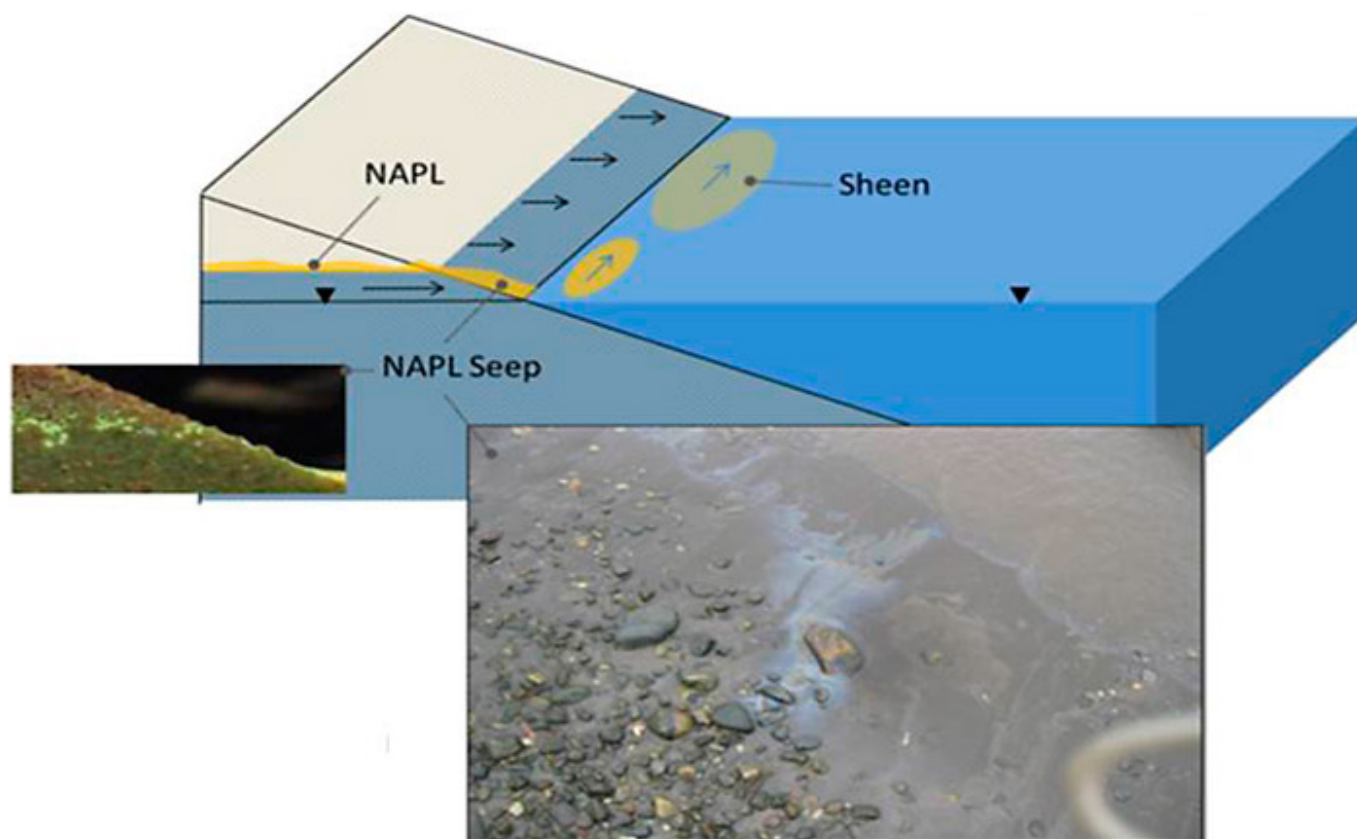


Figure S-3. Sheen from NAPL seep (Drawings by [Sale and Lyverse 2014](#)).

Ebullition—The term “ebullition” ([Conger 1943](#)); ([Amos et al. 2005](#)) has been used to describe the process of gas generation and discharge from sediments. Biodegradation of naturally-occurring organic compounds or of the petroleum itself that is affecting sediments, can generate gases that migrate upward through sediments due to buoyancy. NAPLs are hydrophobic and preferentially attach to the surface of a gas bubble passing through, which subsequently transports the NAPL to the air-water interface. NAPL-coated bubbles reaching the surface of a water body yield a sheen because the surface tension of water is much higher than petroleum. This process was described by ([McLinn and Stolzenburg 2009](#)).

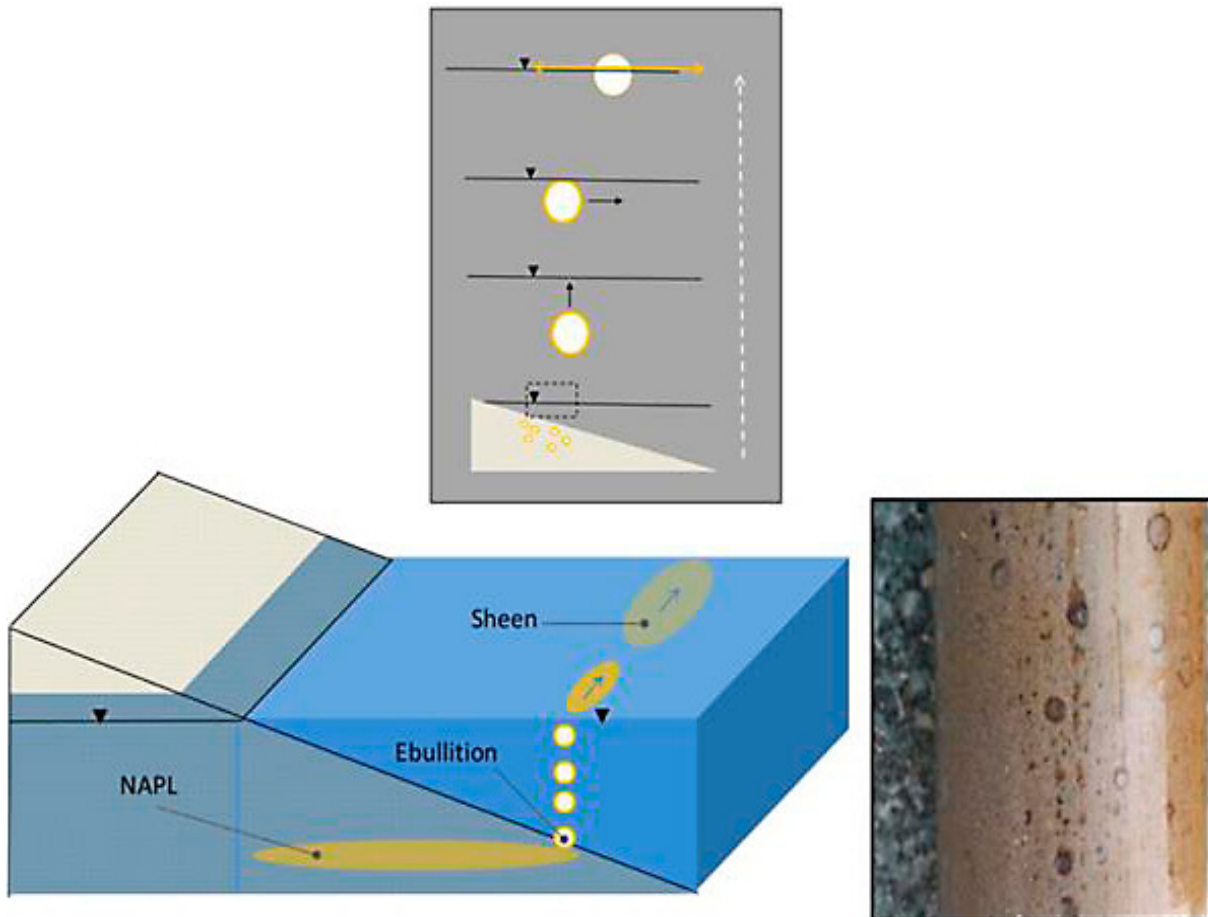


Figure S-4. Sheen from ebullition (Drawings by [Sale and Lyverse 2014](#)).

(Photograph provided by Dr. Julio Zimbron, authorization to use by Author/Colorado State University)

Sheens created from ebullition are episodic. The processes that trigger the coalescing of gas bubbles that move out of sediments and migrate upward to the surface of a water body are an area of current research. Conceptual models for conditions that can trigger ebullition include rising, water levels, falling water levels, temperature changes, and certain tidal conditions. Figure S-4 illustrates sheens generated from ebullition process. The lower right photo in Figure S-4 shows gas bubble formation within a core sample.

Erosion—Another mechanism driving sheens is erosion of sediments and soils. Erosion can occur at high flows along rivers, due to storm-related wave actions, construction activities, and/or ice scour. Soils containing residual LNAPL are now placed in direct contact with the air/water interface at the sediment surface (Figure S-5).

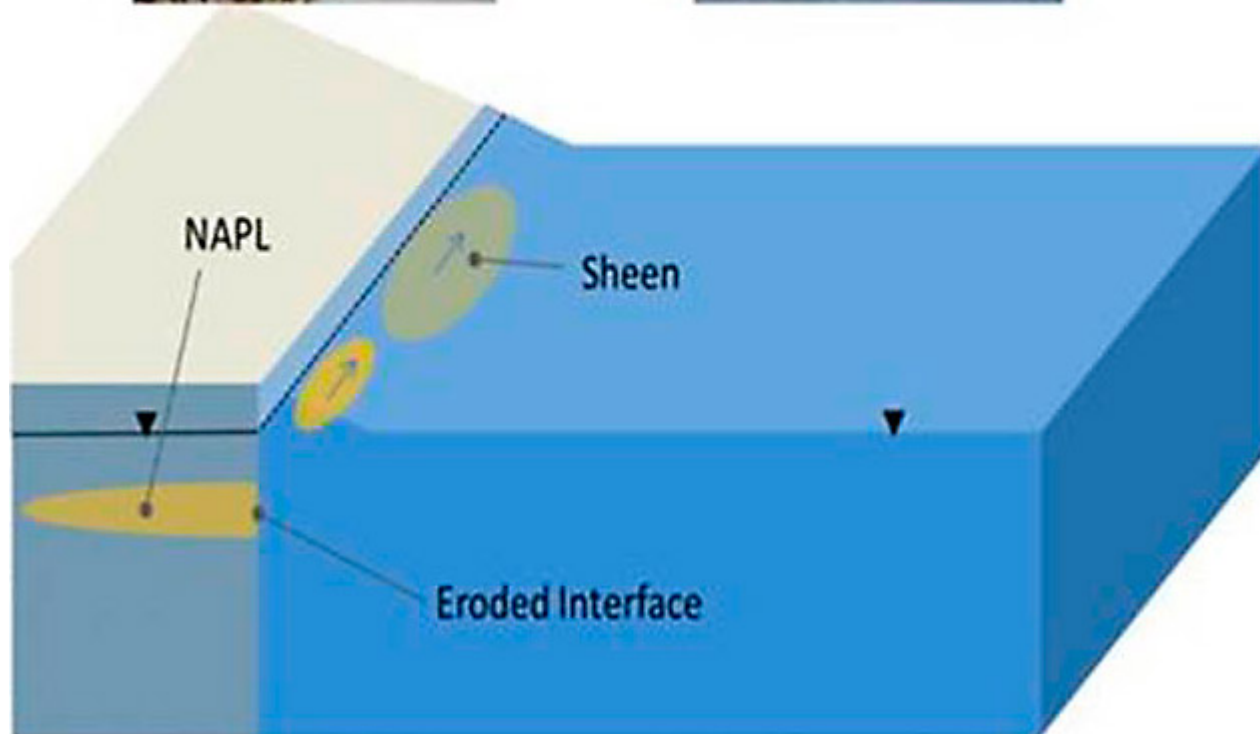


Figure S-5. Sheen from shore or bank erosion (Drawings by [Sale and Lyverse 2014](#)).

[Animations of the scenarios described above can be found here.](#) (courtesy of ACRADIS USA.)

Processes

Process-based insights developed from laboratory studies are described in the following text.

Sheens in Porous Media—NAPLs can move across the air-water interface in porous media (at the top of the capillary fringe) in a manner similar to the spreading of sheens on surface water (Figure S-6). Initial spreading rates as high as meters per minute were observed. With time, rates of spreading slowed as the NAPL was attenuated by dissolution. Visual observations suggest that sheen releases at the GSI can occur due to NAPL spreading along air-water interfaces in porous media as shown in Figure S-6.

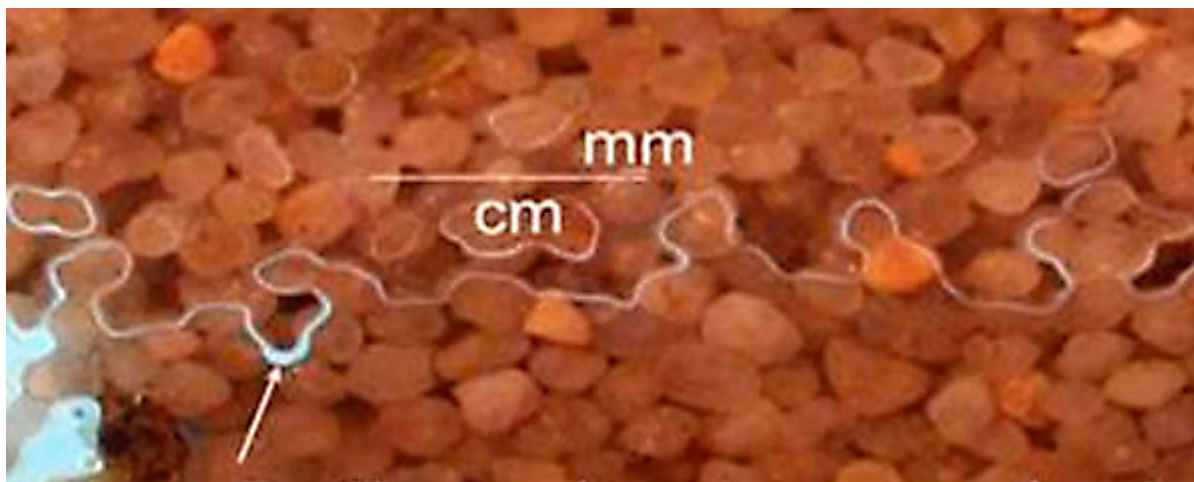


Figure S-6. Sheen advancing across the air-water interface at the top of the capillary fringe.

(Provided by Dr. Julio Zimbron, authorization to use by Author/Colorado State University.)

Ebullition—As previously introduced, where gases are generated in sediments adjacent to NAPLs, rising gas bubbles can carry coatings of NAPL (much like an outer coating on chocolate candy) to the water surface, forming sheens (Figure S-4). Laboratory studies and field observations provide the basis for the prior discussion of ebullition-based release mechanism for sheens. Ebullition associated with NAPLs has been discussed in various papers including [(Amos et al. 2005); (Yuan et al. 2007); (Yuan, Valsaraj, and Reible 2009); (McLinn and Stolzenburg 2009); (Viana et al. 2007)].

Water Level Fluctuation—In most cases, the mobility of NAPL in a geologic formation depends upon water level stage in the media. At high water levels, NAPL in porous media is occluded by the rising water and can be present as discontinuous ganglia and blobs of NAPL that are effectively immobile. Correspondingly, at low water stages, some of the NAPL can be mobile as either a continuous non-wetting phase in the saturated zone or as an intermediate wetting phase in the unsaturated zone. The capacity of the porous media to release NAPL is (generally) much greater at low water stages. Common factors controlling water levels at groundwater-surface water interfaces include tides, seasonal variation in stream flows, local groundwater extraction, and extreme weather.

4.0 What Are Methods to Identify Petroleum Derived Sheens?

Sheen Observation

As part of periodic monitoring, the locations of visually identified sheens should be recorded on field maps, photographed or observed with and without polarizing filters, and physical characteristics of the sheens recorded in a field form. While visual observations of sheens cannot be used to definitively determine sheen composition, important properties and characteristics of sheens can be visually assessed. Sheens observed during monitoring can be characterized based on visually observable physical properties:

- approximate size/dimensions of the sheen
- percentage of the water surface with visible sheen in the general area containing the sheen
- color of the sheen
- sheen structure (no structure, angular, patch, streamers, windrows, oil spots)
- orientation of sheen streamers, if present
- sheen blossom frequency, if applicable
- sheen brittleness based on how the sheen responds when disturbed (Figure S-7)
 - Brittle: sheen that cracks, breaks apart, or disaggregates upon disturbance. Brittle sheens are often of natural biogenic origin indicating that the sheens may be associated with microbial activity.
 - Non-brittle: sheen that rapidly coalesces upon disturbance. Non-brittle sheens are often related to anthropogenic sources, including petrogenic sources (e.g., petroleum hydrocarbons such as crude oil, gasoline, diesel fuel, and asphalt) and pyrogenic sources (e.g., combustion-related materials such as coal tar and creosote). Sheens can also be derived from petrogenic source materials that have been subjected to pyrogenic processes, such as used motor or used hydraulic oil.

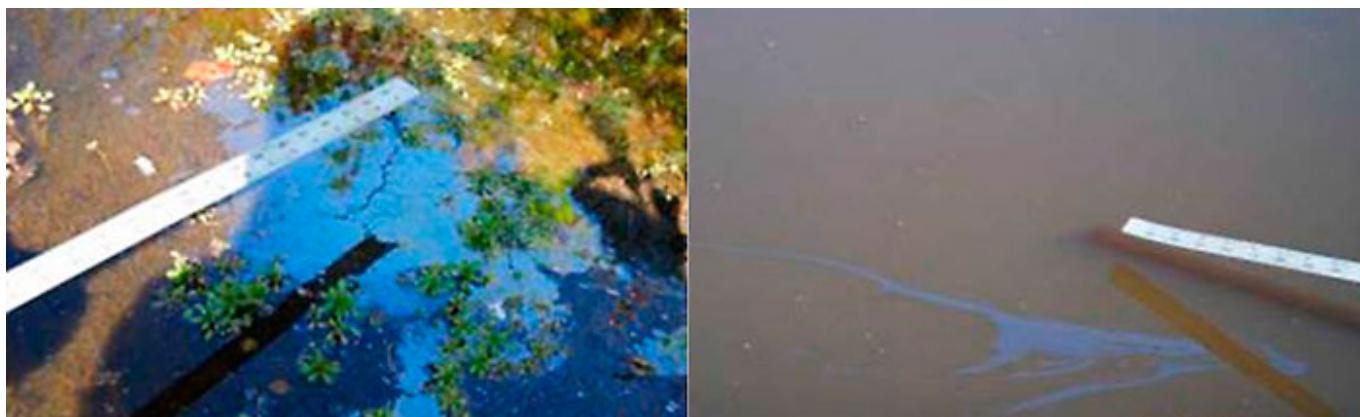


Figure S-7. Brittle sheen (left) and non-brittle sheen (right) ([Stout and Uhler 2016](#)).

In addition, surface water flow conditions and actions taken to remove the sheens should be noted.

The National Oceanographic and Atmospheric Administration (NOAA) published a document to assist responders in describing and characterizing oil spills on open water ([NOAA 2016](#)), and for consistency observed sheens should be characterized using NOAA specified terminology (e.g., color, structure).

When observing and photographing sheens, a polarizing filter can be used to provide a line of evidence regarding the source of the sheen. When rotating the polarizing filter through 180°, the sheen appearance will change. Biogenic sheens may appear blue to bluish purple at one orientation of the polarizing filter.

Sheen Sampling

In addition to periodic sheen monitoring activities, sheen sampling may be conducted. Sheen samples may be collected using an oil spill net sampler with a highly porous TFE-fluorocarbon polymer net attached to a disposable ring. The net is passed through the surface sheen to collect the sample. The net is then removed from the disposable ring and placed into a 4-ounce glass sample jar with a Teflon®-lined cap. Samples are placed into a cooler and shipped under appropriate chain of custody procedures to the analytical laboratory.

The objectives of the sheen sampling are to:

- Compare the composition of the sheen to known LNAPL release material.
- Assess potential additional sources of sheens based on chemical characteristics.
- Evaluate the possible relationship between sheen chemical properties and observed physical characteristics.

Sheen sampling should include the collection of sheens identified during monitoring as both as brittle and non-brittle. Sheen sampling locations should be identified on the field form.

In addition to the above sheen sampling activities, it is suggested that a sheen net blank and a laboratory generated sheen sample be analyzed. The analysis of a sheen net blank is conducted to determine whether sheen samples are affected by constituents derived from sheen net material. Analysis of a sheen generated under controlled (laboratory) conditions using suspected source material is conducted for comparison and potential identification of sheen samples.

To facilitate correlation of sheens to their sources, it is recommended that sheen samples, a sheen net blank sample, and a laboratory-generated sheen sample be analyzed for the following parameters:

- polycyclic aromatic hydrocarbons (PAHs) and biomarkers by USEPA Modified Method 8270 Select Ion Monitoring
- aliphatic and total petroleum hydrocarbons (TPH) by USEPA Modified Method 8015

Interpretation of Sheen Sample Results

Petroleum hydrocarbon forensics, or “fingerprinting,” is an important tool used to evaluate the chemical composition and source of sheens. Analytical results can then be used to identify the type(s) of petroleum hydrocarbons present, assess potential source(s), and evaluate the extent of weathering of petroleum hydrocarbons at environmental sites.

Petroleum hydrocarbon products, including gasoline, diesel fuel, motor oil, and crude oil, are complex mixtures consisting of 100s to 1,000s of different compounds. The chemical composition of petroleum hydrocarbon products varies due to several

factors including crude oil source, subsequent refining processes, and weathering processes (e.g., volatilization, dissolution, and biodegradation). Because of the complex composition of petroleum hydrocarbons, numerous analytical “forensic” techniques have been developed to characterize petroleum hydrocarbons based on the molecular mass and structure of compounds.

As part of a petroleum hydrocarbon forensic assessment, analytical results from samples are compared to analytical results and chromatograms for known or suspected sources. Analytical results from sheen samples can be compared with the analytical results from a sample of suspected source material, a laboratory generated sheen, a sheen net blank, and literature values for other potential sources of sheens or hydrocarbon constituents. Table S-1 summarizes the sources of PAHs in the environment.

Table S-1. Potential sources of PAHs in the environment

Petroleum Products	Combustion Products	Coal Derived	Plant Derived
Crude Oil Kerosene Jet Fuel Diesel Fuel Heating Oil Engine Oil Used Engine Oil Used Hydraulic Oil Asphalt	Coal Tar Creosote Petroleum-Derived Soot Forest Fire Ash Used Engine Oil Used Hydraulic Oil Asphalt	Coal Tar Creosote Coal Coal Ash Coal-Derived Soot	Peat Lignins Pine Forest Fire Ash
Sample comparisons are based primarily on direct comparison of chromatograms generated from the laboratory analysis of samples as well as bar charts generated from the distributions of detected concentrations of PAH and aliphatic petroleum hydrocarbon compounds. Figure S-8 illustrates an example where chromatograms and plots of PAH and biomarker ratios were used to confirm the source of a sheen-forming seep.			

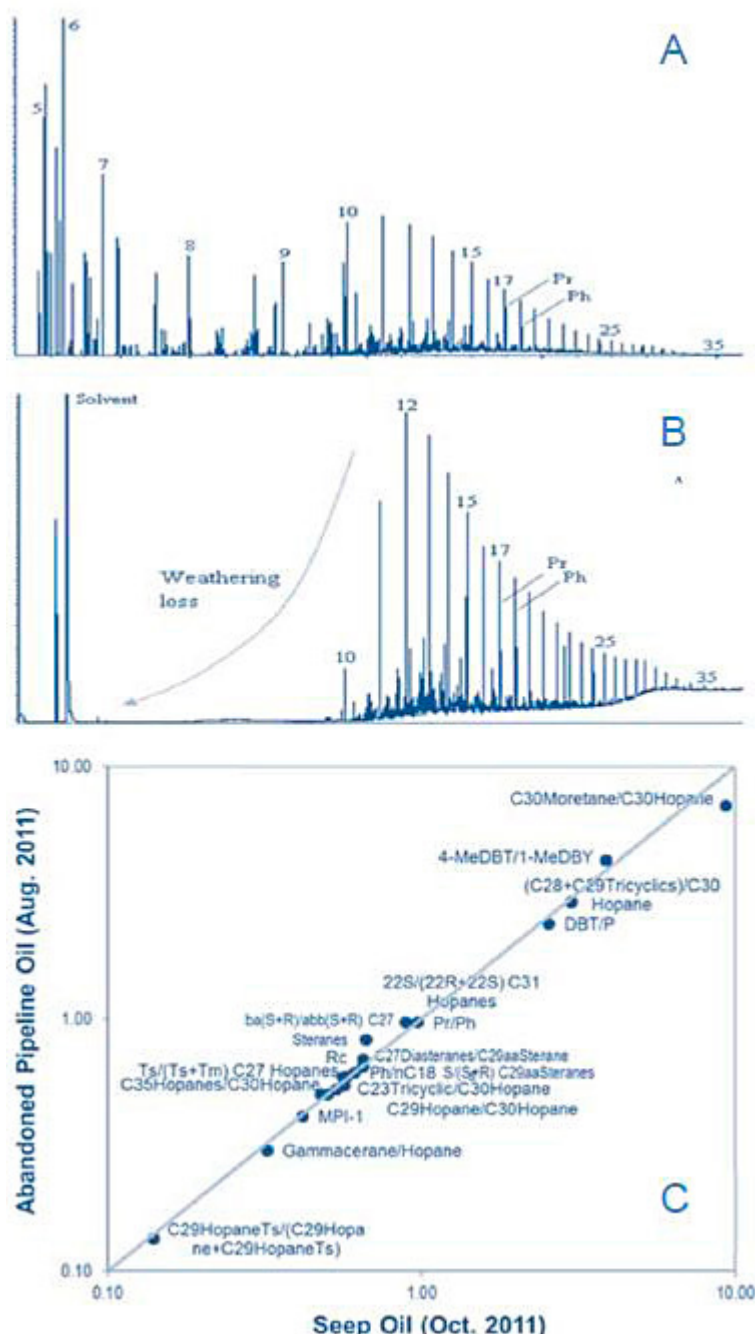


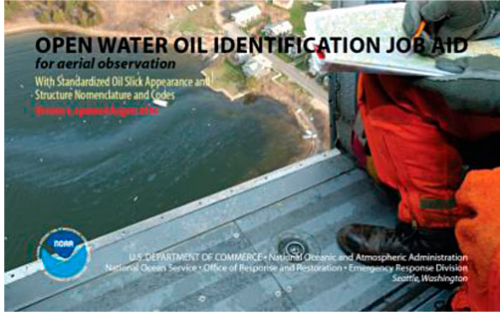
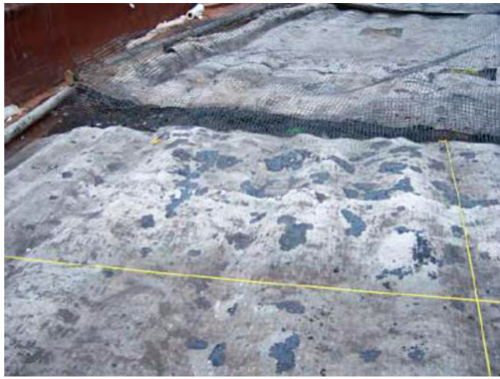
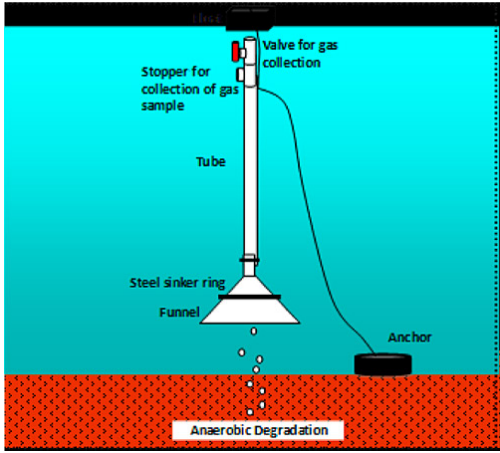
Figure S-8. Tier 1 GC/FID chromatograms of (A) 2011 pipeline oil and (B) 2011 mystery oil seep. (C) shows a high correlation ($r^2=0.99$) between 18 of these oils' diagnostic ratios based on PAHs and biomarkers. These oils "match." Numbers in (A) and (B) refer to n-alkane carbon numbers, Pr-pristane, Ph-phytane ([Hawkins 2012](#)).

Additional information on petroleum analyses and petroleum forensic chemistry is available in ITRC TPH-Risk ([ITRC 2018](#)).

5.0 What Tools are Available to Assess Flux from Seeps?

The measurement of seep fluxes and seep occurrence is complicated by their episodic nature, which makes observation challenging. Technological solutions including remote monitoring may improve this process in the near future. Table S-2 summarizes some manual techniques for measuring seep mass flux.

Table S-2. Methods for assessing seep flux

Method	Example	Description
Direct Methods	Visual Observation / Surveillance 	Direct aerial observation. (NOAA 2016) tools can also be used to classify sheens observed from land. Video surveillance can be used in areas prone to sheening due to ebullition.
	Corral Sampler 	A "corral" sampler, to quantify sheen generation. (Stolzenburg, Rice, and Vater 2012)
	Sorbents 	Cover area susceptible to seeps. Collect and measure mass of hydrocarbons collected. Reactive Core Mats (RCM) are deployed on the bed of the water body. Sorbent pads and sheen nets are used on the surface of the water body. (EPRI 2011)
	Collection Trench 	An impermeable collection device (e.g., 4" PVC pipe cut in half) of known dimensions will be placed in the trench, so that the lip of the collection pipe is flush with the mudflat and the pipe intercepts the water/LNAPL seeps flow. Observations will be made at regular intervals, depending on collection rate, to observe the accumulation of water/LNAPL within the pipe.
	Submerged Gas Collection Devices 	Devices deployed underwater to collect gas bubbles for the estimation of ebullition mass flux. (Viana et al. 2007)

Method	Example	Description
Indirect Methods	Distributed Temperature Sensing	Temperature sensing fiber optic cables deployed on a sediment bed. Detects thermal anomalies that are attributed to seep zones. (Selker et al. 2014)

6.0 Potential Sheen Mitigation Technologies

Remedy selection for sheen mitigation is a complex process that is dependent on site-specific factors. During site characterization and conceptual site model development, the potential source(s) of LNAPL causing sheens should be identified, particularly considering the dynamic nature of coastal or river environments, and multiple potential sources of oil or sheens given this setting. This is important to avoid potentially costly remedies to address sources not associated with the upland site. Certain remedies, if located in the wrong area (for example, in an upland area when source contamination is in the foreshore), will not be effective.

With a good LNAPL site conceptual model (LCSM) in hand, a site-specific remedial objective can be developed, and technologies described below in Table S-3 are options for consideration. As in the case of upland LNAPL remediation, more than one sheen mitigation technology may be used in a given situation.

Table S-3. Sheen remedies

Remedy	Primary Niche	Technology Status	Potential Advantages	Potential Limitations
Adsorbent Booms	Early response	Proven—well understood	- Simple deployment - Low cost	- Chronic maintenance - Declining regulatory acceptance
Sheet Pile Wall	Large-scale subsurface releases	Proven—well understood	Effective if maintained	- Large capital cost - Time to implement - Aesthetic impact - Constrained oxygen reduces natural losses of LNAPL
Subsurface Hydraulic Recovery of LNAPL	Sites with limited access to GSIs	Proven—well understood	- Depletion of mobile NAPL - Flushing of water may increase natural losses of NAPL	- Large O&M costs - Need to treat produced water
Organoclay Barriers	Sites with depleted NAPL sources	Proven—Multiple sites	- Relatively simple Deployment - Moderate capital and low O&M costs	- Potential LNAPL by-pass through organoclay - Constrained oxygen reduces natural losses of LNAPL - O&M increases when NAPL sorbing capacity is reached
Sediment Caps	Sites with on-going NAPL releases	Proven—Full-scale caps in place	Durable, can be used with LNAPL & DNAPL	O&M (periodic removal of accumulated NAPL may be needed)

Remedy	Primary Niche	Technology Status	Potential Advantages	Potential Limitations
Capillary Barriers	Sites with depleted NAPL sources	Innovative—a few well studied field applications	• Limited upgradient mounding of groundwater • Moderate capital and low O&M costs	• Access to large volumes of well-sorted fine sand • Effective compaction of capillary sand • Finite capacity to retain LNAPL
Oleophilic Bio-Barriers	Sites with depleted NAPL sources	Emerging—one well-studied field application	• Active depletion of NAPL (reactive barrier) • Moderate capital and low O&M costs	• Not appropriate for large LNAPL loads • Limited knowledge regarding long-term performance

In this document, sheen mitigation technologies are divided into three categories: Temporary, Conventional and Emerging. The technologies discussed here are limited to the mitigation of sheens. Oil spill recovery involves additional technologies and techniques that are beyond the scope of this document. Readers should refer to references by the US Coast Guard, NOAA, and the Marine Oil Spill Response Corporation.

Historically, the conventional sheen mitigation technologies described below have proven to be effective. However, associated costs for capital and operations and maintenance (O&M) have been large.

Decision makers and stakeholders should be aware of factors that can lead to failure of mitigation technologies over extended time periods. Factors leading to failure include incomplete characterization of affected soils/sediments, LNAPL bypass around or through remedy components, finite life-times of remedy components, and/or excessive LNAPL loading. Hopefully, emerging technologies will provide more sustainable and resilient solutions to mitigate low-mass-flux sheens. Such technologies, when they also incorporate biodegradation processes, are potentially more sustainable than conventional approaches based on physical controls.

Booms—Constructed of absorbent material, booms are devices deployed to the surface of waterways to divert, deflect or contain sheens or serve as a preventive measure for intermittent sheens ([NOAA 1994](#)). Relative to other technologies, booms are less rugged over the long term and must be carefully maintained. Due to inhalation and flammability hazards, booms are generally not used to contain gasoline ([NOAA 1994](#)). Oil skimmers can be deployed within boomed areas when sufficient amounts of oil are present.

Subsurface Hydraulic Recovery—Adjacent to shorelines, hydraulic LNAPL control can be deployed to abate LNAPL movement. The technology attempts to reverse the LNAPL hydraulic gradient away from the water body and reduce LNAPL saturation levels towards residual saturation. The effectiveness of this technology depends upon the quality of the LCSM and a sound system design that ensures capture.

Barriers/Berms—Intended to be more permanent structures to control or divert sheens. Sheet pile walls are a common engineered physical barrier. Life-cycle planning is a consideration for physical barriers because they can alter the hydraulics of the water body and are not easily removed once installed. Further, although relatively resilient, there is a finite lifespan to sheet pile barriers. Other types of barriers include trenches that can collect LNAPL for recovery, or bubble barriers that can promote volatilization and biodegradation ([NOAA 1994](#)).

Organoclay Barriers—Organoclay is an expansive clay in which charged organic compounds (organic amines) are introduced between the silicate sheets (layers) in the clay. Organic compounds make the clay surfaces oleophilic (oil-loving). Either pure organoclay, mixtures of organoclay and sand, or organoclay in a geotextile mat have been placed at GSIs.

Sediment Caps—Sediment caps that reliably and effectively trap and sequester ongoing LNAPL or DNAPL releases from sediments have been described ([Rice et al. 2013](#)), and designed and constructed at several locations. The design features of these caps can incorporate the Oleophilic Bio Barrier (OBB) technology (see below) and/or reactive treatment material for addressing the accumulating NAPL. Long-term effectiveness and adaptability to a wide variety of site conditions are two significant advantages of these caps.

Emerging-Two promising technologies for managing sheens are described in the following section. One has been studied in laboratory experiments (Capillary Barriers), the second has been piloted (Oleophilic Bio Barriers).

Capillary Barriers-Unpublished research conducted by Dr. Tissa Illangasekare, Colorado School of Mines and G.D. Beckett, Aquiver Inc. indicates that vertical walls of well-sorted fine-grained sand can preclude lateral movement of NAPL while allowing water to pass. Given water as the wetting fluid and NAPL as the non-wetting fluid, pressure in the NAPL relative to pressure in the water (a function of NAPL head, density and interfacial tension) needs to be great enough to exceed the displacement pressure of the water in the porous media. Given these conditions, the application of capillary barriers would most commonly be under conditions of sub-horizontal groundwater and/or NAPL movement. Capillary barriers should also be designed to address potential ebullition of gases, if occurring.

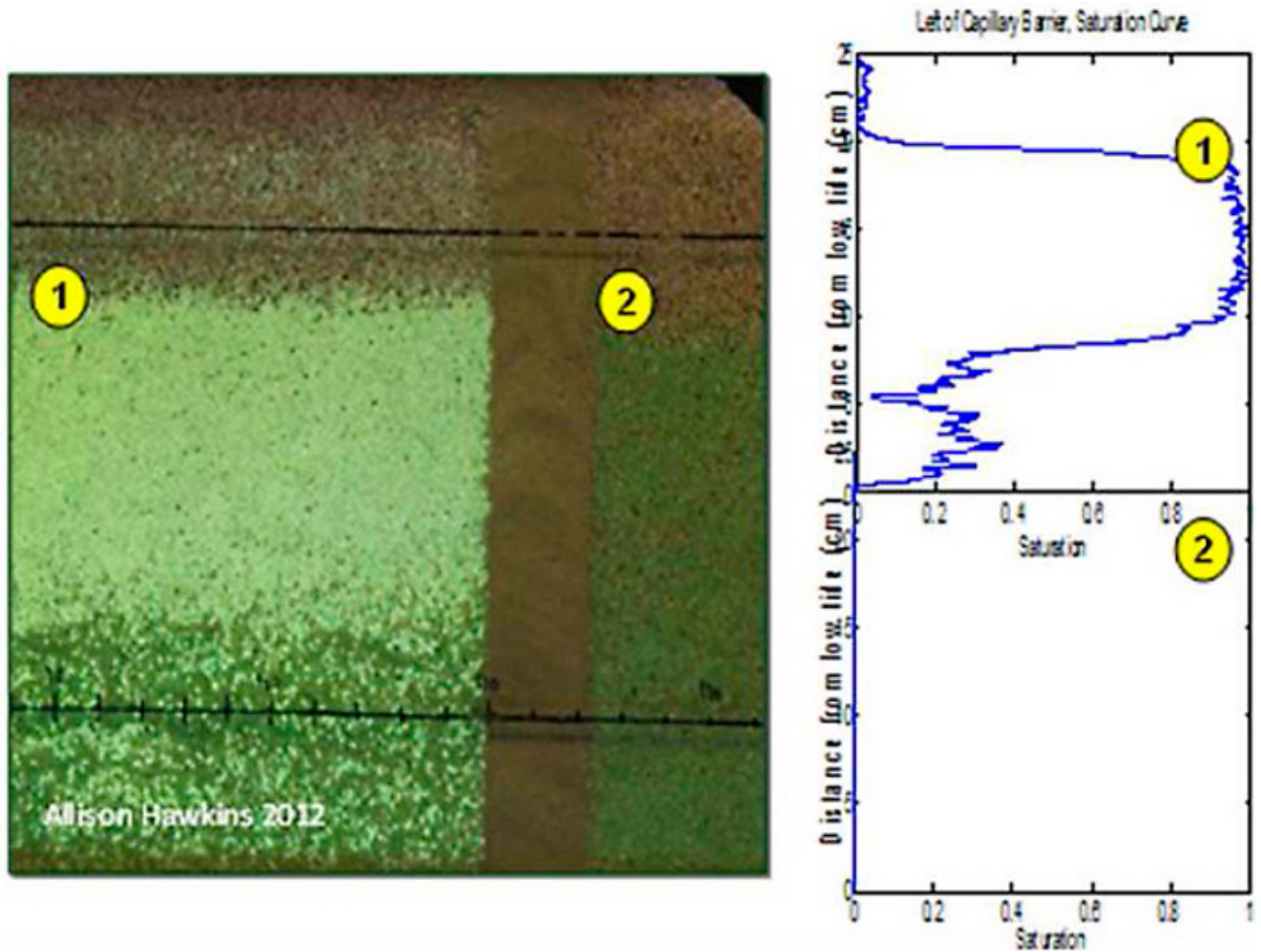


Figure S-9. 1) NAPL retention upgradient of a fine-sand capillary barrier. 2) downgradient NAPL free zone (Hawkins 2012).

Laboratory studies show that, up to a threshold NAPL thickness, capillary barriers can prevent NAPL migration while allowing water to pass (Figure S-9). The availability of large sources of sand suitable for capillary barriers can be challenging and that emplacement of fine-sand in the saturated zone, with the proper compaction and uniformity, can be difficult. Additional concerns include:

- Capillary barriers may limit cycling of aerobic water and atmospheric oxygen to the NAPL, limiting natural losses of NAPL at GSIs.
- Given a condition of constant NAPL loading and limited natural depletion, capillary barriers will fail when their capacity to retain NAPL is exceeded (i.e., LNAPL head exceeds capillary entry pressure).

Oleophilic Bio Barriers-The principle of an Oleophilic Bio Barrier is to place a composite of sorptive material at a GSI that readily conducts water and promotes aerobic degradation of the intercepted LNAPL (i.e., increase of residence time on the OBB material). Aerobic degradation is enhanced by natural cycling of aerobic surface water (e.g., tidal-driven water level

changes and resultant changes in pore gas oxygen content) and/or atmospheric oxygen through the OBB. Furthermore, OBBs include an upper structural cover (i.e., rock gabions) to control erosion. Potential mechanisms for erosion (wave, current, ice, boat-induced wash) and armor requirements should be evaluated. Collectively, OBBs can address sheen releases via seeps, ebullition, and/or erosion. Sand tank images of the geocomposite are presented in Figure S-10 and Figure S-11. Figure S-12 presents an OBB with a structural cover to control erosion.



Figure S-10. Oleophilic geocomposite set at the GSI shown retaining NAPL that has migrated in a left to right direction. Surface water is dyed bright green for easy identification. Note: Photo is taken under ultraviolet light which results in fluorescence of the NAPL in the granular media on the left side of the image ([Sale and Lyverse 2014](#)).

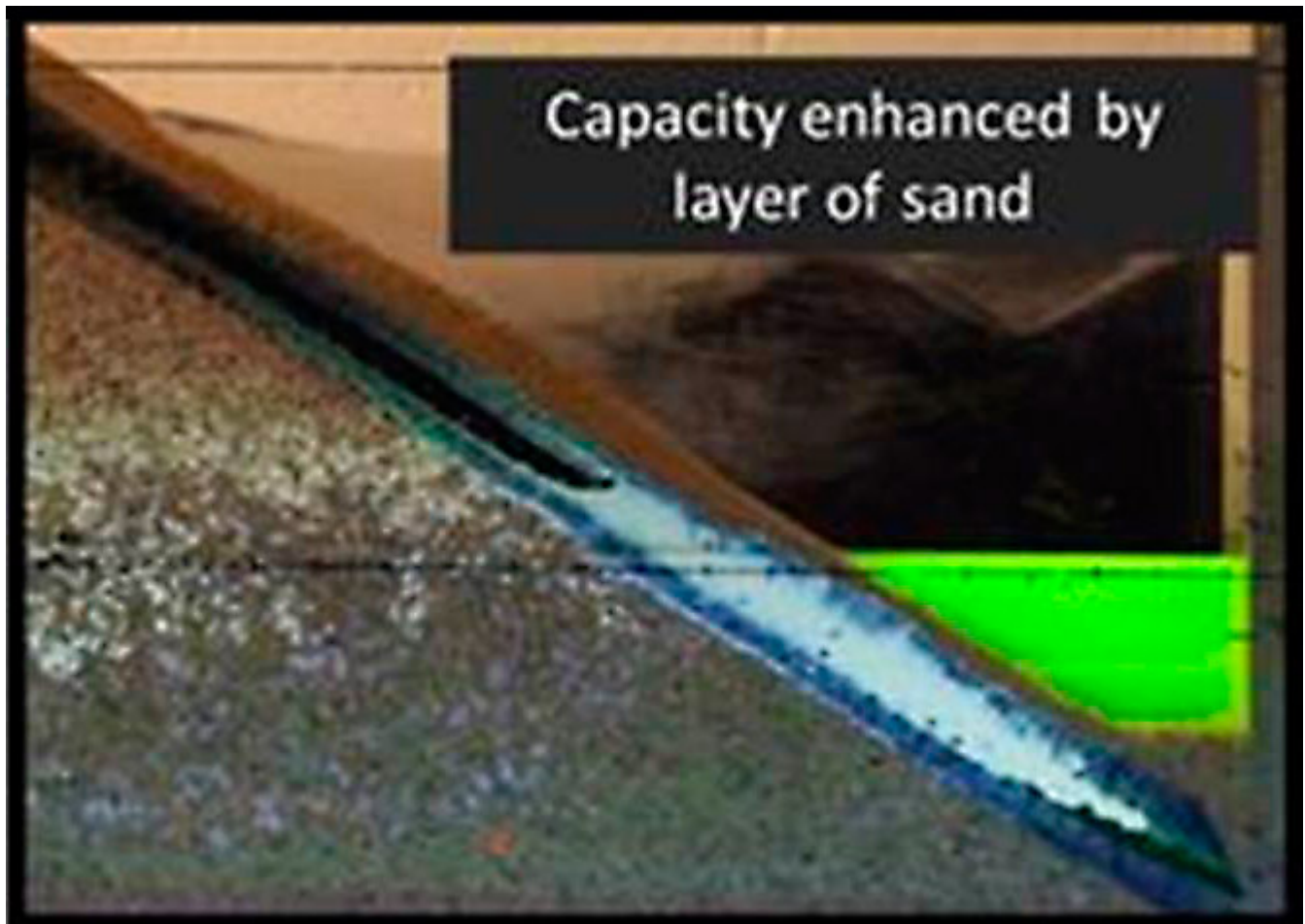


Figure S-11. Oleophilic geocomposite at NAPL-impacted GSI overlain with a sand layer to enhance the holding capacity of the barrier. Photographed under the same conditions as Figure 10 ([Sale and Lyverse 2014](#)).

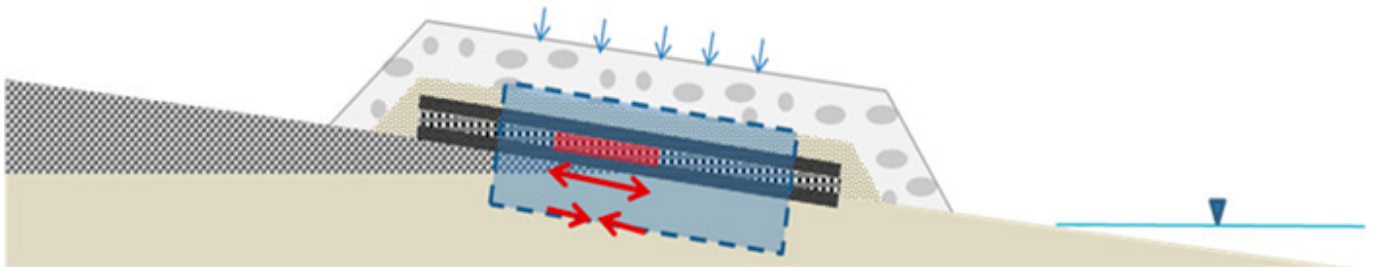


Figure S-12. Oleophilic Biobarrier including geocomposite (in black) and structural cover. Dashed grey area is an aerobic NAPL attenuation zone. Red arrows indicate lateral spreading and distribution of NAPL once it reaches the geocomposite ([Sale and Lyverse 2014](#)).

The fundamental difference between sheet pile, capillary, and organoclay barriers is that OBBs are reactive barriers. Like organoclay barriers, OBBs can last for extended periods, as long as the loading is less than their assimilative capacity. An additional concern with OBBs is fouling of the interior of the OBB with sediments. Information regarding a field application of an OBB is presented in ([Biondolillo, Chalfant, and Vogel 2017](#)) and ([Chalfant 2015](#)).



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Acronyms

API	American Petroleum Institute
AS	air sparging
ASTM	American Society for Testing Materials
ATSDR	Agency for Toxic Substance and Disease Registry
BTEX	benzene, toluene, ethylbenzene, and xylenes
CFR	Code of Federal Regulations
CL:AIRE	Contaminated Land: Applications in Real Environments
COC	constituents of concern
CPT	cone penetrometer testing
CSM	conceptual site model
CSU	Colorado State University
DCC	dynamic closed chamber
DNAPL	dense, non-aqueous phase liquid
DO	dissolved oxygen
DPE	dual-phase extraction
DPLE	dual pump liquid extraction
DRO	diesel range organics
EPA	Environmental Protection Agency
EPRI	Electric Power Research Institute
ERI	electrical resistivity imaging
ERT	electrical resistivity tomography
ESA	environmental site assessment
FID	flame ionization detector
FRGT-MST	Fractured Rock Geophysical Toolbox Method Selection Tool
GPR	ground penetrating radar
GSI	groundwater-surface water interface
ISC	Institute for Sustainable Communities
ITRC	Interstate Technology and Regulatory Council
LCSM	LNAPL Conceptual Site Model
LIF	laser induced fluorescence
LNAPL	light, non-aqueous phase liquid
LUST	leaking underground storage tank
MCL	maximum contaminant level
MPCA	Minnesota Pollution Control Agency

MIP	membrane interface probe
MNA	monitoring natural attenuation
MPE	multi-phase extraction
MW	monitoring well
NAPL	non-aqueous phase liquid
NOAA	National Oceanographic and Atmospheric Administration
NRC	National Response Center
NSZD	natural source zone depletion
OBB	oleophilic biobarrier
O&M	operations and maintenance
ORP	oxidation-reduction potential
OSC	on-scene coordinator
PAH	polycyclic aromatic hydrocarbons
PHC	petroleum hydrocarbon compound
PID	photoionization detector
PVI	petroleum vapor intrusion
RCM	reactive core mat
RCRA	Resource Conservation and Recovery Act
RTDF	Remediation Technologies Development Forum
SESR	surfactant-enhanced subsurface remediation
SMART	specific, measurable, attainable, relevant, and timely
SVE	soil vapor extraction
SVOC	semi-volatile organic compound
TEA	terminal electron acceptor
TI	technical impracticability
T_n	transmissivity
TPE	two-phase extraction
TPH	total petroleum hydrocarbon
TPHCWG	Total Petroleum Hydrocarbon Criteria Working Group
USACE	U.S. Army Corps of Engineers
USAEC	U.S. Army Environmental Center
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
UST	underground storage tank
UV	ultraviolet fluorescence
VEFR	vacuum enhanced fluid recovery
VOC	volatile organic compound



Glossary

A

Apparent NAPL Thickness

The gauged thickness of LNAPL in a well that is screened across the Mobile NAPL Interval. The Apparent NAPL Thickness may be equivalent to the Mobile NAPL Interval in a well at equilibrium under unconfined conditions. Under confined and perched conditions, the Apparent NAPL Thickness may be exaggerated compared to the Mobile NAPL Interval.

B

Biosurfactant

A surface active agent, produced through biological degradation of organic compounds (including petroleum hydrocarbons), that reduced interfacial tension between fluids.

C

C_{Sat}

Threshold bulk soil concentration, which when exceeded, indicates that a non-aqueous NAPL phase is likely to be present in the soil matrix.

C_{Res}

The bulk soil concentration at residual LNAPL saturation.

Capillary Pressure

The pressure difference between the non-wetting phase (i.e., LNAPL) and the wetting phase (i.e., groundwater) in a multiphase system such as an LNAPL-groundwater system.

D

Dual Phase Flow

Dual phase flow refers to the simultaneous flow of two phases, most commonly LNAPL and groundwater within an aquifer, for the purposes of this guidance document. The ability of each phase to flow is impeded by the presence of the other.

E

Effective Solubility

The solubility of an individual compound (e.g., benzene) that will dissolve from a chemical mixture (e.g., gasoline) into water. Effective solubility is usually significantly less than the compound's pure phase solubility. Effective solubility is described by Raoult's Law, which indicates that the solubility limit of any individual component of a complex mixture will be limited by the simultaneous dissolution of the other components of the mixture and will be equal to a component's pure phase solubility multiplied by the mole fraction of the component in the mixture.^[1]

I

Interfacial Forces

Forces that arise at interfaces between liquids and/or solids due to differences in the chemical properties (i.e., polarity) of the liquids/solids.

Intermediate Wetting Phase

Fluid phase that occurs between the wetting and the non-wetting phases (i.e. NAPL in a water wet unsaturated media).

In-Well LNAPL Thickness

The observed thickness of LNAPL in a monitoring well, which relates to the pressure and spatial distribution of LNAPL in the subsurface. In-well LNAPL thicknesses in monitoring wells vary with changes in groundwater elevations.

L

LNAPL

A light non-aqueous phase liquid (e.g., petroleum oil, gasoline, diesel fuel) that has a density less than water and is immiscible with water.

LNAPL Concern

An LNAPL condition or potential condition that could: pose a risk to health or safety (composition-based), result in additional LNAPL migration (saturation-based), address an LNAPL-specific regulatory requirement (regulatory-based), or otherwise create some physical or aesthetic impact or require a specific regulatory or stakeholder response.

LNAPL Control

Application of a technology that stabilizes an LNAPL body or impedes LNAPL migration without reliance on a mass recovery or phase change.

LNAPL Hydraulic Recoverability

Historically, a conceptual representation of hydraulic recovery/potential recovery. The concept of volume of LNAPL that can be hydraulically extracted under a particular pressure differential. Potential hydraulic recoverability reflects the volume of LNAPL above the residual saturation; however, due to inherent inefficiencies in extraction, recoverability typically reaches near zero values *before* residual saturations are attained. Not quantitative – points to metrics of recoverability.

LNAPL Management

A process that includes LNAPL site assessment and monitoring, LNAPL Conceptual Site Model development, identification and validation of LNAPL concerns, and application of remediation technologies, if needed to address any LNAPL concerns.

LNAPL Mass Recovery

Application of a technology that physically removes LNAPL without significant reliance on phase change.

LNAPL Phase Change Remediation

Application of a technology that indirectly remediates the LNAPL body via recovery and/or in-situ destruction or degradation of vapor or dissolved-phase LNAPL constituents.

LNAPL Remedial Goal

The desired LNAPL condition to be achieved by the remedial strategy or action that constitutes the end of LNAPL management for a specific LNAPL concern.

LNAPL Remediation

Application of an LNAPL mass recovery, phase change, and/or control technology to achieve a saturation, compositional, and/or aesthetic remediation objective.

LNAPL Remediation Objective

A statement describing how the remedial goal will be accomplished by the technology(ies) to be used. Combined with performance metrics and remedial end points, LNAPL remediation objectives become “SMART” (Specific, Measurable, Attainable, Relevant and Timely).

LNAPL Remediation Endpoint

Achievement of the remediation objective(s) described by the associated specific performance metric(s).

LNAPL Saturation

The LNAPL-filled fraction of the total porosity (e.g., 10% LNAPL saturation indicates that 10 percent of the total porosity is filled with LNAPL).

LNAPL Smear Zone

The zone within the upper portion of the saturated zone and the lower portion of the vadose zone containing LNAPL at variable saturation due to water table fluctuation.

LNAPL Transmissivity

LNAPL transmissivity is a proportionality coefficient that describes the ability of a porous media to transmit a specific LNAPL and is defined as the volume of LNAPL that may pass through a unit width of aquifer per unit time per unit gradient. It is a measure of the potential for LNAPL to flow and thus its potential recoverability.

M

Maximum Extent Practicable (MEP)

Regulatory endpoint concept for UST sites set forth in 40 CFR §280.64 that states “At sites where investigations... indicate the presence of free product, owners and operators must remove free product to the maximum extent practicable as determined by the implementing agency.” The determination of what constitutes MEP varies between regulatory entities and has changed over time.

Migrating LNAPL

An LNAPL body that is expanding laterally or vertically into areas previously un-impacted by LNAPL. The term ‘migration’ describes LNAPL movement on a macro or plume scale, which can occur only if the LNAPL driving mechanisms (e.g., LNAPL head) exceed the resistive mechanisms, and thus displace water in adjacent pore spaces. Natural and manmade preferential pathways may exist at a given site that could allow migration to occur where it would not otherwise be expected.

Mobile LNAPL

LNAPL that exists above residual saturation levels such that it may be observed in wells. Mobile LNAPL has the *potential* to migrate, but not all mobile LNAPL is migrating LNAPL.

Mobile NAPL Interval

The vertical interval of LNAPL that is above residual saturation.

Monitored Natural Attenuation (MNA)

Natural attenuation is the combination of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater. In the context of petroleum releases, MNA typically focuses on the documentation of the attenuation of petroleum constituents in the dissolved phase via monitoring over some duration of time.

N

Natural Attenuation

The combination of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater. In the context of petroleum releases, MNA typically focuses on the attenuation of petroleum constituents in the dissolved phase, in contrast to NSZD, which focuses on the depletion of mass within the LNAPL source zone.

Natural Source Zone Depletion

The combined action of natural processes that reduce the mass of LNAPL in the subsurface. Key processes include volatilization, dissolution, and biodegradation. Over time, depletion of LNAPL mass will reduce LNAPL saturation and mobility. Natural Source Zone Depletion is an LNAPL phase change remediation technology.

Non-Wetting Phase

Fluid phase that fills the largest pores and is not in direct contact with the solids in porous media (i.e., gases).

P

Performance Metric

The measured data or demonstrated change in site condition(s) that indicates progress toward or achievement of a remediation goal.

Phase Change

Natural or induced partitioning of LNAPL constituents from the LNAPL phase to a sorbed, vapor, or dissolved phase.

Pore Entry Pressure

The capillary pressure that must be exceeded before a non-wetting fluid (e.g., LNAPL) can invade pore space saturated with a wetting fluid (e.g., groundwater).

R

Relative LNAPL Permeability

The ratio between the effective permeability to LNAPL at a partial LNAPL saturation to its absolute permeability at maximum saturation. Typically referenced in terms of dual phase flow (i.e., LNAPL permeability in the presence of GW), and in such systems is inversely related to the relative permeability of GW.

Residual

Saturation in a non-wetting phase that is discontinuous (present as blob and ganglia). The relative permeability of a residual non-wetting phase is zero and correspondingly, the fluid is immobile under typical gradients of pressure or head.

Residual LNAPL

The fraction of an LNAPL body that will remain immobile and hydraulically unrecoverable under prevailing hydraulic conditions (i.e., will not flow into a well).

Residual LNAPL Saturation

The saturation at and below which LNAPL will no longer flow in an aquifer even under applied gradients. Residual LNAPL is immobile/unrecoverable and therefore does not contribute to migration risk; however, it will continue to act as a source of dissolved and vapor phase contamination.

S

Spreading Coefficient

A parameter based on the sum of interfacial forces at the water-NAPL- air contact point describing the potential of a NAPL to spread across water.

Stable LNAPL

An LNAPL body that no longer possesses the potential to migrate or expand into areas previously un-impacted by LNAPL (i.e., a stable LNAPL body is not migrating). Stability is judged by time-series data and controlled by physical processes (capillary pressure and volatilization) and biodegradation.

T

Threshold Metric

Measured data or site condition(s) that can indicate whether an initial LNAPL concern may be eliminated, or carried forward to select remediation objectives.

W

Wetting Phase

Fluid phase that is in direct contact with the solids in a porous media.

^[1] Effective solubility values can be calculated on a site-specific basis where LNAPL composition is known, or can be found in reference material such as the API Interactive LNAPL Guide (2004).



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References

- Adamski, M., V. Kremesec, R. Kolhatkar, C. Pearson, and B. Rowan. 2005. "LNAPL in fine-grained soils: Conceptualization of saturation, distribution, recovery, and their modeling." *Ground Water Monitoring & Remediation* 25:100-112.
- Adamson, A. 1990. *Physical Chemistry of Surfaces – Fifth Edition*. John Wiley & Sons. p777. ISBN 0-471-61019-4
- Aelion, C.M., B.C. Kirtland, and P.A. Stone. 1997. "Radiocarbon assessment of aerobic petroleum bioremediation in the vadose zone and groundwater at an AS/SVE site." *Environ. Sci. Technology* 31:3363-3370. doi: 10.1021/es960857.
- AFCEE. 2004. Procedures for Conducting Bioventing Pilot Tests and Long-Term Monitoring of Bioventing Systems. Air Force Center for Engineering and the Environment – US Air Force Center of Excellence.
- Amos, R.T., K.U. Mayer, B.A. Bekins, G.N. Delin, and R.L. Williams. 2005. "Use of dissolved and vapor-phase gases to investigate methanogenic degradation of petroleum hydrocarbon contamination in the subsurface." *Water Resources Research* 41. doi: 10.1029/2004WR003433.
- ANSR. 2012. "Mechanisms for LNAPL to Enter Confined Conditions." *Applied NAPL Science Review* 2 (4).
- API. 2003. Models for Design of Free-Product Recovery Systems for Petroleum Hydrocarbon Liquids: A User's Guide and Model Documentation. American Petroleum Institute.
- API. 2006. API Interactive LNAPL Guide Version 2.0.4. edited by Soil and Groundwater Technical Task Force: American Petroleum Institute.
- API. 2007. LNAPL Distribution and Recovery Model (LDRM) – Volume 2: User and Parameter Selection Guide. American Petroleum Institute.
- API. 2010. BIOVAPOR – A 1-D Vapor Intrusion Model with Oxygen-Limited Biodegradation (Version 2.0). American Petroleum Institute.
- API. 2016. LNAPL Transmissivity Workbook: A Tool for Baildown Test Analysis – User Guide. American Petroleum Institute.
- API. 2017. Quantification of Vapor Phase- Related Natural Source Zone Depletion Processes. American Petroleum Institute.
- ASCWG. 2006. Hydrocarbon Characterization for Use in the Hydrocarbon Risk Calculator and Example Characterizations of Selected Alaskan Fuels.: Alaska Statement of Cooperation Working Group.
- ASTM. 2013. Standard Guide for Estimation of LNAPL Transmissivity. ASTM International.
- ASTM. 2014a. Standard Guide for Developing Conceptual Site Models for Contaminated Sites. ASTM International.
- ASTM. 2014b. Standard Guide for Development of Conceptual Site Models and Remediation Strategies for Light Nonaqueous-Phase Liquids Released to the Subsurface. ASTM International.
- ASTM. 2014c. Standard Guide for Greener Cleanups. ASTM International.
- ASTM. 2015. Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites.: ASTM International.
- ATSDR. 2005. Public Health Assessment Guidance Manual (Update). In *U.S. Department of Health and Human Services: Agency for Toxic Substance and Disease Registry*.
- Baedecker, M.J., R.P. Eganhouse, B.A. Bekins, and G.N. Delin. 2011. "Loss of volatile hydrocarbons from an LNAPL oil source." *Journal of Contaminant Hydrology* 126:140-152.
- Bear, J. 1972. *Dynamics of Fluids in Porous Media*. New York: Dover Publications, Inc.

- Beckett, G.D., and P. Lundegard. 1997. "Practically Impractical – The Limits of LNAPL Recovery and Relationship to Risk, ." *Petroleum Hydrocarbons and Organic Chemicals in Groundwater: Prevention, Detection and Remediation Conference*.
- Bekins, B.A., I.M. Cozzarelli, M.L. Erickson, R.A. Steenson, and K.A. Thorn. 2016. "Crude Oil Metabolites in Groundwater at Two Spill Sites." *Ground Water* 51 (5):681-691.
- Bethke, C., R. Sandford, M. Kirk, Q. Jin, and T. Flynn. 2011. "The thermodynamic ladder in geomicrobiology." *AJS Online* 311 (3).
- Biondolillo, M., M. Chalfant, and L. Vogel. 2017. "The Oleophilic Biobarrier: Sustainably Preventing Oil Sheens on Waterways." *Proceedings of the Ninth International Conference on Remediation of Contaminated Sediments*, New Orleans, LA, January 9-12, 2017.
- Chalfant, M.W. . 2015. "Oleophilic bio barriers (OBBs) for control of hydrocarbon sheens at groundwater-surface water interfaces." *Colorado State University Libraries*.
- CL:AIRE. 2014. *An illustrated handbook of LNAPL transport and fate in the subsurface*. London: Contaminated Land: Applications in Real Environments (CL:AIRE).
- Conger, P. S. 1943. "Ebullition of gases from marsh and lake waters." *Chesapeake Biological Laboratory Publication* No. 59 (November).
- Corey, A.T. 1990. "Mechanics of immiscible fluids in porous media." In. Littleton, Colorado: Water Resources Publications.
- Dullien, F.A. 1979. *Porous media fluid transport and pore structure*: Academic Press.
- Eichert, J., B. McAlexander, M. Lyverse, P. Michalski, and N. Sihota. 2017. "Spatial and Temporal Variation in Natural Source Zone Depletion Rates at a Former Oil Refinery." *Vadose Zone J. 0*. doi: 10.2136/vzj2016.12.0131.
- EPA. 1995. *Light Nonaqueous Phase Liquids*. In *USEPA Ground Water Issue*. Washington, D.C.: OSWER Office of Research and Development.
- EPA. 1996. *How to Effectively Recover Free Product at Leaking Underground Storage Tank Sites: A Guide for State Regulators*. In *Office of Underground Storage Tanks*. Washington, D.C.: U.S. Environmental Protection Agency
- EPA. 1997. *Hydrocarbon Spill Screening Model (HSSM)*. In *Water Research*. Washington, D.C.: U.S. Environmental Protection Agency.
- EPA. 2004. *Handbook of Groundwater Protection and Cleanup Policies for the Resource Conservation and Recovery Act (RCRA) Corrective Action*. Washington, D.C.: U.S. Environmental Protection Agency
- EPA. 2010. *Underground Storage Tank Flood Guide*. Washington, D.C.: U.S. Environmental Protection Agency
- EPA. 2013. *Introduction to In situ Bioremediation of Groundwater*. Washington, D.C.: U.S. Environmental Protection Agency
- EPA. 2015. *RCRA (Resource Conservation and Recovery Act) Facilities Investigation Remedy Selection Track (FIRST)*.
- EPRI. 2011. *Reactive Capping for Coal-Tar Impacted Sediments An In Situ Evaluation of Effectiveness and Implementability (Phase II—Design, Installation, and Monitoring)*. In *Technical Update*. Palo Alto, California: Electric Power Research Institute.
- Falta, R.W., A.N.M Ahsanuzzaman, and J.T. Wilson. 2012. *REMFuel, remediation evaluation model for fuel hydrocarbons. In Version 1*.
- Fetter Jr., C.W. . 1992. "Contaminant hydrogeology." *Macmillan Publishing Company*.
- Freeze, R. A., and D.B McWhorter. 1997. "A Framework for Assessing Risk Reduction Due to DNAPL Mass Removal from Low-Permeability Soils." *Ground Water* 35:111-123.
- Garg, S., C.J. Newell, P.R. Kulkarni, D.C. King, D.T. Adamson, M.I. Renno, and T. Sale. 2017. "Overview of Natural Source

Zone Depletion: Processes, Controlling Factors, and Composition Change." *Groundwater Monitoring & Remediation* Wiley Online Library Version of Record. doi: 10.1111/gwmr.12219.

Hardisty, P.E. 2010. Environmental and Economic Sustainability. In *CRC Press*. Boca Raton, FL. .

Hardisty, P.E., S. Howard, D.B. Wheeler, and J. Dottridge. 2003. "Characterization of LNAPL in Fractured Rock." *Quarterly Journal of Engineering Geology and Hydrogeology* (November 2003).

Hawkins, A. . 2012. "Processes controlling the behavior of LNAPLs at groundwater surface water interfaces." Masters, Colorado State University.

Hers, I., P. Jourabchi, M. A. Lahvis, P. Dahlen, E. Hong Luo, P. Johnson, G.E. DeVaul, and K.U. Mayer. 2014. "Evaluation of Seasonal Factors on Petroleum Hydrocarbon Vapor Biodegradation and Intrusion Potential in a Cold Climate." *Groundwater Monitoring & Remediation* 34:60-78.

Hoag, G., and M. Marley. 1986. "Gasoline Residual Saturation in Unsaturated Uniform Aquifer Materials." *Journal of Environmental Engineering* 112 (10).

Hua, F., and H.Q. Wang. 2014. "Uptake and trans-membrane transport of petroleum hydrocarbons by microorganisms." *Biotechnology & Biotechnological Equipment*. 28:165-175.

Huntley, D. . 2000. "Analytic Determination of Hydrocarbon Transmissivity from Baildown Tests." *Groundwater* 38 (1):46-54.

Huntley, D., R.N. Hawk, and H.P. Corley. 1994. "Nonaqueous phase hydrocarbon in a fine-grained sandstone: 1. Comparison between measured and predicted saturations and mobility." *Ground Water* 32 (4):626-634.

Huntley, D., J.W. Wallace, and R.N. Hawk. 1994. "Nonaqueous Phase Hydrocarbon in a fine-grained sandstone: 2. Effect of local sediment variability on the estimation of hydrocarbon volumes." *Ground Water* 32:778-783.

Irriani-Renno, M., D. Akhbari, M.R. Olson, A.P. Byrne, E. Lefevre, J. Zimbron, M. Lyverse, T. Sale, and S.K. DeLong. 2016. "Comparison of bacterial and archaeal communities in depth-resolved zones in an LNAPL body." *Applied Microbiology and Biotechnology*. doi: 100:3347-3360.

ITRC. 2006. Exit Strategy – Seeing the Forest Beyond the Trees, Technology Overview. In *Remediation Process Optimization Team*. Washington, D.C. : Interstate Technology Regulatory Council.

ITRC. 2007. Vapor Intrusion Pathway: Investigation Approaches for Typical Scenarios (A Supplement to VI-1). Washington, D.C.: Interstate Technology Regulatory Council.

ITRC. 2008. In Situ Bioremediation of Chlorinated Ethene: DNAPL Source Zones. Washington, D.C.: Interstate Technology Regulatory Council.

ITRC. 2009a. Evaluating LNAPL Remedial Technologies for Achieving Project Goals. Washinton, D.C.: Interstate Technology Regulatory Council.

ITRC. 2009b. Evaluating Natural Source Zone Depletion at Sites with LNAPL. Washington, D.C.: Interstate Technology Regulatory Council.

ITRC. 2010. Use and Measurement of Mass Flux and Mass Discharge Information. Washington, D.C.: Interstate Technology Regulatory Council.

ITRC. 2011. Integrated DNAPL Site Strategy. Washington, D.C.: Interstate Technology Regulatory Council.

ITRC. 2014. Petroleum Vapor Intrusion Guidance Document, Fundamentals of Screening, Investigation, and Management. Washington, D.C.: Interstate Technology Regulatory Council.

ITRC. 2017a. Characterization and Remediation of Fractured Bedrock Washington, D.C. : Interstate Technology Regulatory Council.

ITRC. 2017b. Remediation Management of Complex Sites – Guidance Document. Washthington, D.C.: Interstate Technology and Regulatory Council.

- ITRC. 2018. TPH Risk Evaluation at Petroleum-Contaminated Sites. Washington, D.C.: Interstate Technology Regulatory Council.
- Jewell, K. P., and J.T. Wilson. 2011. "A new screening method for methane in soil gas using existing groundwater monitoring wells." *Groundwater Monitoring & Remediation* 33 (3):82-94.
- Johnson, P. C., C. Bruce, R. L. Johnson, and M. W. Klemblowski. 1998. "In Situ Measurement of Effective Vapor-Phase Porous Medium Diffusion Coefficients." *Environmental Science and Technology* 32 (21):3405-09.
- Johnson, P. C., P. Lundegard, and Z. Liu. 2006. "Source Zone Natural Attenuation at Petroleum Hydrocarbon Spill Sites: I. Site-Specific Assessment Approach." *Ground Water Monitoring & Remediation* 26:82-92.
- Johnson, R. 2010. Overview of the Triad Approach.
- Johnston, C.D., and M. Adamski. 2005. Relationship between Initial and Residual LNAPL Saturation for Different Soil Types. CLU-IN.org.
- Kasenow, M. 2006. Aquifer Test Data: Analysis and Evaluation. In *Water Resources Publications*. Littleton, CO.
- Kemblowski, M. W., and C.Y. Chiang. 1990. "Hydrocarbon Thickness Fluctuations in Monitoring Wells." *Ground Water* 28:244-252.
- Kirkman, A.J. . 2013. "Refinement of Bouwer-Rice Baildown Test Analysis." *Ground Water Monitoring & Remediation* 33 (1):105.
- Kirkman, A.J., M. Adamski, and M. Hawthorne. 2013. "Identification and Assessment of Confined and Perched LNAPL Conditions." *Groundwater Monitoring Review* 33 (1):75-86.
- Kolhatkar, R., V. Kremesec, S. Rubin, C. Yukawa, and R. Senn. 1999. "Application of field and analytical techniques to evaluate recoverability of subsurface free phase hydrocarbons." 1:5-15.
- Kueper, B.H., and D.B. McWhorter. 1991. "The behavior of dense, nonaqueous phase liquids in fractured clay and rock." *Groundwater* 29:716-728.
- Lahvis, M. A., I. Hers, R. V. Davis, J. Wright, and G. E. DeVauil. 2013. "Vapor Intrusion Screening at Petroleum UST Sites." *Groundwater Monitoring & Remediation* 33 (2):53-67.
- Lahvis, M.A., and I. Hers. 2013. "Evaluation of Source-Receptor Separation Distances as a Screening Methodology for Petroleum Vapor Intrusion Risk Assessment." The 2nd International Symposium on Bioremediation and Sustainable Environmental Technologies, Jacksonville, Florida, June 10-13.
- LALWG. 2015. Final Report of the LA Basin LNAPL Recoverability Study. LA LNAPL Work Group.
- Lenhard, R.J., J.L. Rayner, and G.B. Davis. 2017. "A practical tool for estimating subsurface LNAPL distributions and transmissivity using current and historical fluid levels in groundwater wells: Effects of entrapped and residual LNAPL." *Journal of Contaminant Hydrology* 205:1-11.
- Lovley, D., F. Chapelle, and J. C. Woodward. 1994. "Use of dissolved H₂ concentrations to determine distribution of microbially catalyzed redox reactions in anoxic groundwater." *Environmental Science Technology* 28 (7):1205-1210.
- Lowry, W., S.D. Dunn, and D. Neeper. 1996. "Barometric Pumping With a Twist: VOC Containment and Remediation without Boreholes." Conference on Industry Partnerships to Deploy Environmental Technology, Morgantown, WV.
- Lundy, D.A., and L.M. Zimmerman. 1996. "Assessing the Recoverability of LNAPL Plumes for Recovery System Conceptual Design." Proceedings of the 10th NGWA National Outdoor Action Conference/Exposition, May.
- Ma, J., Z.Y. Wang, B.A. Stevenson, X.J. Zheng, and Y. Li. 2013. "An inorganic CO₂ diffusion and dissolution process explains negative CO₂ fluxes in saline/alkaline soils." *Scientific Reports* 3 (2025).
- Mahler, N., T. Sale, and M. Lyverse. 2012. "A Mass Balance Approach to Resolving LNAPL Stability." *Ground Water* 50 (6):861-71.

- Marinelli, F., and D.S. Durnford. 1996. "LNAPL Thickness in Monitoring Wells Considering Hysteresis and Entrapment." *Ground Water* 34:405-414.
- McCoy, K., J. Zimbron, T. Sale, and M. Lyverse. 2014. "Measurement of Natural Losses of LNAPL Using CO₂ Traps." *Ground Water*. doi: 10.1111/gwat.12240.
- McLinn, E., and T.R. Stolzenburg. 2009. "Ebullition-facilitated transport of manufactured gas plant tar from contaminated sediments." *Journal of Environmental Toxicology and Chemistry*. 28 (11):2290-2306.
- Meckenstock, R.U., F. von Netzer, C. Stumpp, T. Lueders, A.M. Himmelberg, N. Hertkorn, P. Schmitt-Kopplin, M. Harir, R. Hosein, S. Haque, and D. Schulze-Makuch. 2014. "Water droplets in oil are microhabitats for microbial life." *Science* 345:673-676.
- Mercer, J. W., and R. M. Cohen. 1990. "A Review of Immiscible Fluids in the Subsurface: Properties, Models, Characterization and Remediation." *Journal of Contaminant Hydrology* 6:107-163.
- Millington, R. J., and J. M. Quirk. 1961. "Permeability of Porous Solids." *Transactions of the Faraday Society* 57:1200-07.
- Molins, S., K.U. Mayer, R.T. Amos, and B.A. Bekins. 2010. "Vadose zone attenuation of organic compounds at a crude oil spill site—Interactions between biogeochemical reactions and multicomponent gas transport." *Journal of Contaminant Hydrology* 112 (1):15-29.
- Nelson, R. 2001. "Geologic Analysis of Naturally Fractured Reservoirs, 2nd Edition." In.: Gulf Professional Publishing.
- Ng, G.-H.C., B.A. Bekins, I.M. Cozzarelli, M.J. Baedecker, P.C. Bennett, R.T. Amos, and W.N. Herkelrath. 2015. "Reactive transport modeling of geochemical controls on secondary water quality impacts at a crude oil spill site near Bemidji, MN." *Water Resources Research* 51:4156-4183.
- Ng, G.-H.C., B.A. Bekins, I.M. Cozzarelli, M.J. Baedecker, P.C. Bennett, and R.T. Amos. 2014. "A mass balance approach to investigating geochemical controls on secondary water quality impacts at a crude oil spill site near Bemidji, MN." *Journal of Contaminant Hydrology* 164:1-15.
- NOAA. 1994. Options for Minimizing Environmental Impacts of Freshwater Spill Response. In *Hazardous Materials Response Division and American Petroleum Institute*: National Oceanic and Atmospheric Administration.
- NOAA. 2016. NOAA Open Water Oil Identification Job Aid.: National Oceanic and Atmospheric Administration.
- NRC. 2000. Natural Attenuation for Groundwater Remediation. In *Committee on Intrinsic Remediation, Water Science and Technology Board, Board on Radioactive Waste Management, Commission on Geosciences, Environment, and Resources*. Washington, D.C.: National Research Council.
- NRC. 2013. Alternatives for Managing the Nation's Complex Contaminated Groundwater Sites. In *Division on Earth and Life Studies. National Academy of Sciences*, edited by Water Science and Technology Board Committee on Future Options for Management in the Nation's Subsurface Remediation Effort. Washington, D.C.: National Research Council.
- Palmier, C., D. Palmier, M. Olivier, and A. Olivier. 2000. "Comparison of Oil Transmissivity Methods Using Bail-Down Test Data." *Groundwater Monitoring & Remediation* 36:73-83.
- Parsons. 2003. Light Nonaqueous-Phase Liquid Weathering at Various Fuel Release Sites – 2003 Update. In *Prepared for the Air Force Center for Environmental Excellence*, edited by Brooks City-Base. San Antonio, Texas.
- Peargin, T., and R. Kolhatkar. 2011. "Empirical Data Supporting Groundwater Benzene Concentration Exclusion Criteria for Petroleum Vapor Intrusion Investigations." Proc. of Battelle Presentation at International Symposium on Bioremediation and Sustainable Environmental Technologies, Reno, NV, June 27-30, 2011.
- Pickell, J.J, B.F. Swanson, and W.B. Hickman. 1966. "Application of Air-Mercury and Oil-Air Capillary Pressure Data in the Study of Pore Structure and Fluid Distribution " *Society of Petroleum Engineers Journal*:55-61.
- Rice, J., H. Hinke, S. McAnulty, A. Sellwood, and J. Papez. 2013. "Design of a sediment cap to control ebullition-facilitated NAPL transport." Platform presentation at Seventh International Conference on Remediation of Contaminated

Sediments, Dallas, TX, February 4-7.

- Sale, T., and M. Lyverse. 2014. Sheens Associated with Subsurface Petroleum Releases – Current Knowledge and Best Practices. Chevron USA, Inc.
- Sale, T., N. Mahler, and T. Smith. 2016. "Reply to Lago et al. Comment on "Use of Single-Well Tracer Dilution Tests to Evaluate LNAPL Flux at Seven Field Sites and Measurement of LNAPL Flux Using Single-Well Intermittent Mixing Traces Dilution Tests." *Ground Water* 54 (5):624.
- Schmidt, G.W., D.D. Beckmann, and B.E. Torkelson. 2003. "Gas Chromatography Technique for Estimating the Octane Rating of Fresh and Weathered Gasolines Released to Soils and Groundwater." *Environmental Forensics* 4:75-80.
- Selker, J., F. Selker, J. Huff, R. Short, D. Edwards, P. Nicholson, and A. Chin. 2014. "Practical strategies for identifying groundwater discharges into sediment and surface water with fiber optic temperature measurement." *Environmental Science: Processes Impacts* 16:1772-1778.
- Shen, R., K.G. Pennell, and E.M. Suuberg. 2013. "Influence of Soil Moisture on Soil Gas Vapor Concentration for Vapor Intrusion." *Environmental Engineering Science* 30 (10):628-637.
- Siddique, T., R. Gupta, P.M. Fedorak, M.D. MacKinnon, and J.M. Foght. 2008. "A first approximation kinetic model to predict methane generation from an oil sands tailings settling basin." *Chemosphere* 72:1573-1580.
- Sihota, N.J., and K.U. Mayer. 2011. "Determination of vadose zone hydrocarbon degradation rates using CO₂ efflux measurements and isotopic analysis." *American Chemical Society* 242.
- Sihota, N.J., K.U. Mayer, M.A. Toso, and J.F. Atwater. 2013. "Methane Emissions and Contaminant Degradation Rates at Sites Affected by Accidental Releases of Denatured Fuel-Grade Ethanol." *Journal of Contaminant Hydrology* 151:1-15.
- Sihota, N.J., J.J. Trost, B.A. Bekins, A. Berg, G.N. Delin, B. Mason, E. Warren, and K.U. Mayer. 2016. "Seasonal Variability in Vadose Zone Biodegradation at a Crude Oil Pipeline Rupture Site." *Vadose Zone J.* 15 (5). doi: 10.2136/vzj2015.09.0125.
- Skinner, A., and T. Sale. 2013. "Analysis of Subsurface LNAPL Body Evolution." American Geophysical Union Hydrology Days, March 25-27, 2013.
- Stockwell, E.B. 2015. Continuous NAPL Loss Rates Using Subsurface Temperatures. edited by ProQuest Dissertations Publishing: Colorado State University.
- Stolzenburg, T, J. Rice, and K. Vater. 2012. "Migration of coal tar and PAHs from sediment by ebullition vs. dissolved/advection." Poster presentation at the MGP 2012 Symposium, Chicago, Illinois, March 27-29.
- Stout, S., and A. Uhler. 2016. Primer on Petroleum Forensic Chemistry. Houston, TX: ExxonMobil Environmental Services Company.
- Stumm, W., and J. Morgan. 1981. *Aquatic Chemistry-An Introduction to Chemical Equilibria in Natural Waters*. New York: John Wiley and Sons.
- Sweeney, R. E., and G.T. Ririe. 2014. "Temperature as a tool to evaluate aerobic biodegradation in hydrocarbon contaminated soil." *Groundwater Monitoring & Remediation* 34 (3):41-50.
- Sweeney, R.E., and G.T. Ririe. 2017. "Small Purge Method to Sample Vapor from Groundwater Monitoring Wells Screened Across the Water Table." *Groundwater Monitoring & Remediation* 37:51-59. doi: 10.1111/gwmr.12230.
- Tomlinson, D.W., M.O. Rivett, G.P. Wealthall, and R.E.H. Sweeney. 2017. "Understanding complex LNAPL sites: Illustrated handbook of LNAPL transport and fate in the subsurface." *Journal of Environmental Management* 204 (2):748-756.
- TPHCWG. 1997. A risk-based approach for the management of total petroleum hydrocarbons in soil. Total Petroleum Hydrocarbon Criteria Working Group.
- TPHCWG. 1998. Composition of petroleum mixtures. edited by Volume 2. Amherst, MA: Total Petroleum Hydrocarbon

Criteria Working Group.

USACE. 1999. Multi-Phase Extraction – Engineering Manual. U.S. Army Corps of Engineers.

USAEC. 2002. Remediation Technologies Screening Matrix and Reference Guide – 4th Edition. Aberdeen, MD: U.S. Army Environmental Center,.

Viana, P., K. Yin, X. Zhao, and K. Rockne. 2007. “Active sediment capping for pollutant mixtures: control of biogenic gas production under highly intermittent flows.” *Land Contamination and Reclamation* 15 (4):413.

Warren, E., and B.A. Bekins. 2015. “Relating subsurface temperature changes to microbial activity at a crude oil-contaminated site.” *Journal of Contaminant Hydrology* 182:183-193.

Wiedemeier, T.H., M.A. Swanson, D.E. Moutoux, E.K. Gordon, J.T. Wilson, B.H. Wilson, D.H. Kampbell, P. Haas, R.N. Miller, J.E. Hansen, and F.H. Chapelle. 1998. Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater. Washington, D.C.

Wilson, J. T., I. Hers, and P. Jourabchi. 2016. “A Simple Spreadsheet Model to Simulate the Natural Attenuation of Residual NAPL-Phase Hydrocarbons in the Subsurface.” Battelle 10th International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Palm Springs, CA, May 23-26.

Yuan, Q., K.T. Valsaraj, and D.D. Reible. 2009. “A Model for Contaminant and Sediment Transport via Gas Ebullition through a Sediment Cap.” *Environmental Engineering Science* 26 (9):1381-1391.

Yuan, Q., K.T. Valsaraj, D.D. Reible, and C.S. Wilson. 2007. “A laboratory study of sediment and contaminant release during gas ebullition.” *Journal of the Air and Waste Management Association* 59 (9).

Zeman, N., M. Renno, M. Olson, L. Wilson, T. Sale, and S. Long. 2014. “Temperature impacts on anaerobic biotransformation of LNAPL and concurrent shifts in microbial community structure.” *Biodegradation* 25:569-585.

Zemo, D.A, K.T. O'Reilly, R.E. Mohler, A.K. Tiwary, R.I. Magaw, and K.A. Synowiec. 2013. “Nature and Estimated Human Toxicity of Polar Metabolite Mixtures in Groundwater Quantified as TPHd/DRO at Biodegrading Fuel Release Sites.” *Groundwater Monitoring & Remediation* 33 (4):44-56.

Zytner, R.G., N. Biswas, and J.K. Bewtra. 1993. “Retention Capacity of Dry Soils for NAPLs.” *Environmental Technology* 14:1073-1080.