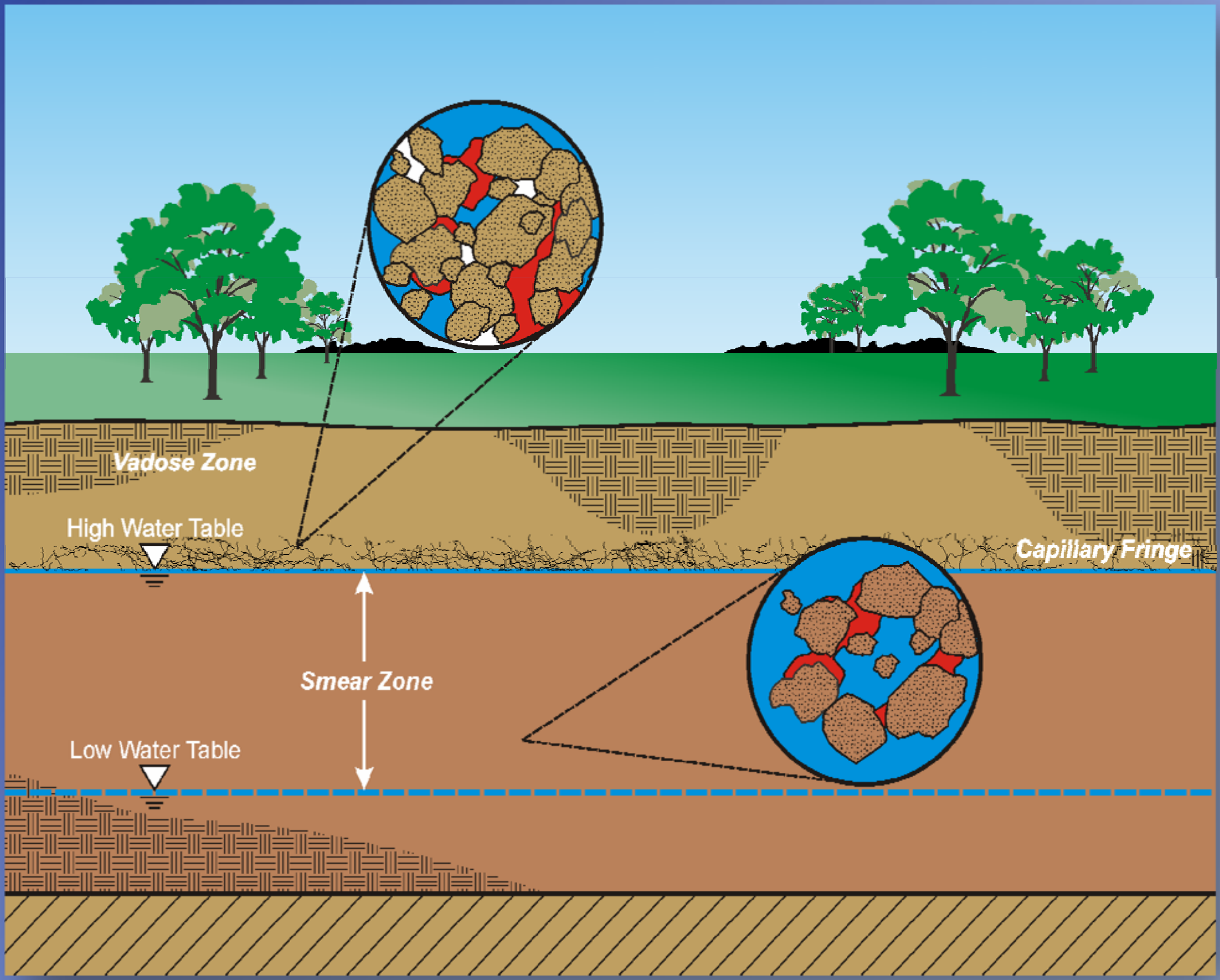
LNAPL Site Management Handbook



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Introduction

This *Light Non-aqueous Phase Liquid (LNAPL) Site Management Handbook* provides an overview of effective strategies for managing LNAPL-contaminated sites to ensure protectiveness of human health and the environment, while simultaneously avoiding unnecessary and prolonged remedial efforts. Concepts presented in this document can be applied throughout the life-cycle of an LNAPL remediation project; therefore, the information provided in this handbook can be useful regardless of the stage of the project.

LNAPL-contaminated sites can be very challenging to assess, remediate, and ultimately close out due to both technical and regulatory issues. Therefore, if possible, it is essential to develop a strategic action plan early in the process to establish goals, specify a remedy, and chart a clear course to achieve site closure. It should be noted that even if a strategic action plan was not developed early on, this exercise is still recommended even in the latter stages of a project. LNAPL can be technically challenging to recover from the subsurface due to high residual saturation, low mobility/recoverability, and continuous changes in the LNAPL saturation profile with water table fluctuations. In addition, LNAPL weathering can create other environmental problems including vapor and dissolved-phase contaminant plumes. Furthermore, other than the common "recover LNAPL to the maximum extent practicable" requirement, most state or federal regulatory programs address saturation concerns on a site-specific basis, with few specifics provided. This handbook presents two case studies (Appendices A and B) to highlight different approaches for managing sites impacted with LNAPL.

The information provided in this handbook is based on the Navy Remediation Innovative Technology Seminar (RITS) presentation given in Spring 2009 (CH2M Hill, 2009), the Interstate Technology Regulatory Council (ITRC) guidance documents for *Evaluating LNAPL Remedial Technologies for Achieving Project Goals* (ITRC, 2009a) and *Evaluating Natural Source Zone Depletion at Sites with LNAPL* (ITRC, 2009b), and *A Decision-Making Framework for Cleanup of Sites Impacted with Light Non-Aqueous Phase Liquid* (U.S. Environmental Protection Agency [EPA], 2004).

What is LNAPL and where is it found?

LNAPL is a mixture of hydrocarbons existing as a separate immiscible phase occurring within the unsaturated (vadose) and saturated (groundwater) zones of the subsurface. The density of LNAPL is less than that of water, making it generally buoyant in water-saturated media and readily observed in monitoring wells as a discrete layer residing above groundwater.

LNAPL is one of the most common groups of contaminants found in the environment. The majority of LNAPL consists of petroleum hydrocarbons that have been released to the environment from aboveground storage tanks (ASTs), underground storage tanks (USTs), pipelines, and associated handling and transfer equipment. Some examples of LNAPL include jet fuel (JP-4, JP-5, and JP-8), bunker fuel, diesel fuel, kerosene, and gasoline.

In the past, LNAPL was conceptualized as existing as a thin, continuous lens of hydrocarbons residing on top of the water table. This is referred to as the "pancake-layer" concept. It assumed that the pore space in the formation immediately above the water table was completely filled with LNAPL. Based on this concept, the volumes of LNAPL present at sites were estimated and the recoverable portion and ease of recovery were predicted. More recently, LNAPL has been conceptualized to coexist with other fluids (water and air) in the subsurface. This "multiphase" conceptualization assumes that LNAPL saturation is variable with a saturation peak near the top of the capillary fringe. As shown in Figure 1 (Highlight 1), in the capillary fringe located immediately above the groundwater table, small volumes of LNAPL coexist with groundwater and air in the pore space. At the air-water interface, LNAPL that accumulates will gradually push out a portion of the water (and air) and occupy a greater fraction of the pore space. Changes in LNAPL pressure head and natural groundwater fluctuations result in a mixture of LNAPL and water that will occupy the pore space across a vertical LNAPL smear zone, as shown in Figure 1 (Highlight 2). The amount of interconnected LNAPL and its associated pressure head available to displace the groundwater decreases with increasing depth beneath the water table. As such, the LNAPL saturation decreases and the pore space becomes predominantly saturated with water. The degree of saturation at any depth is dependent on many site-specific factors; including the volume of LNAPL released, soil lithology, the age of the release, the magnitude of water table fluctuation, and fluid properties.

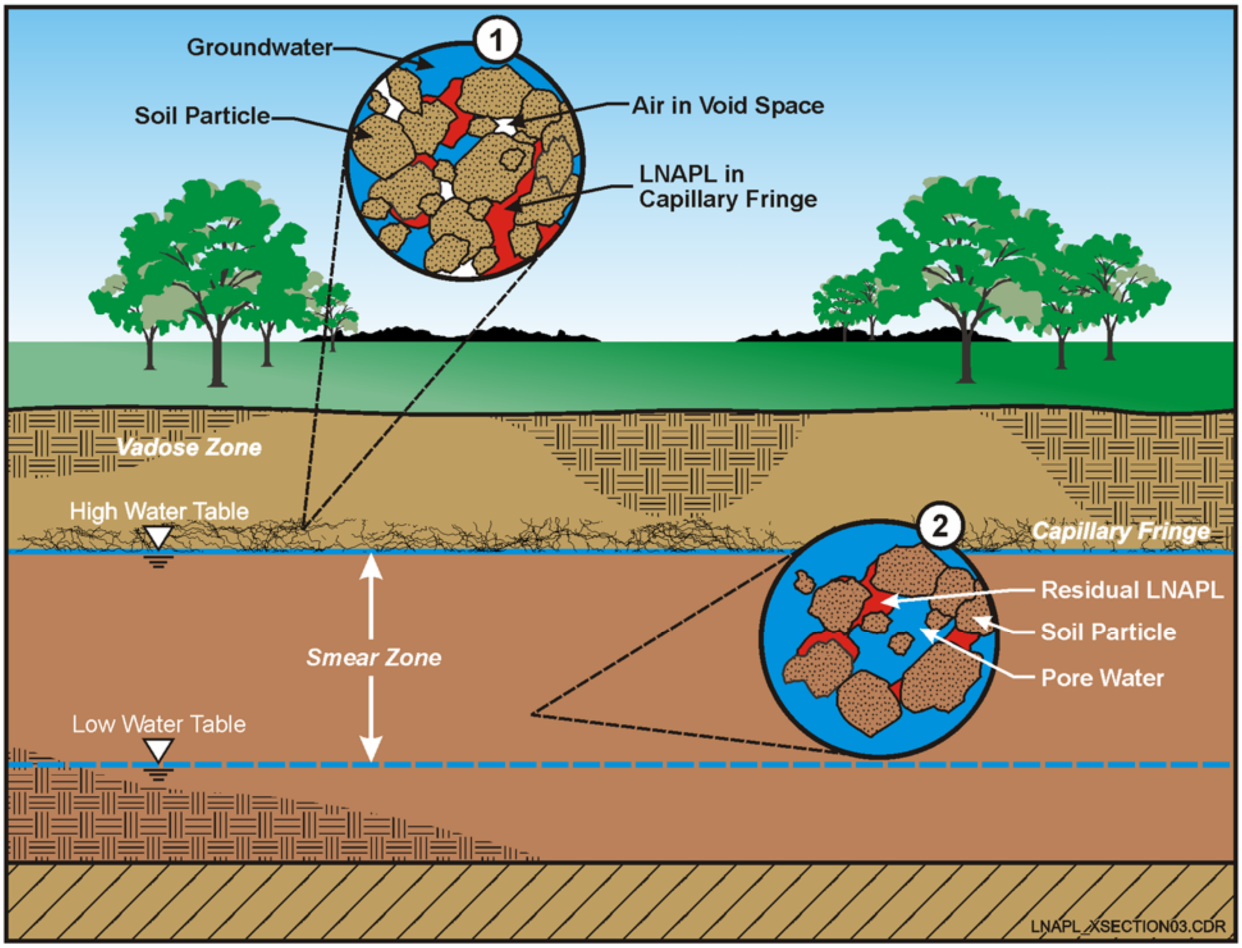

Figure 1. Conceptual Depiction of LNAPL in the Subsurface

The properties of LNAPL affect its distribution in the subsurface and impact the selection and success of a technology to recover or degrade it. Critical properties include density, viscosity, interfacial tension, and chemical composition. These values vary considerably depending on LNAPL type (see Tables 1a through 1c). It should be noted that weathering, which includes processes such as dissolution, biodegradation, volatilization, and retardation, will change the characteristics of LNAPL (principally the chemical composition) and these key properties.

Table 1a. Common Properties of LNAPL

Fuel Type	Specific Gravity (g/mL)[7]	Viscosity (Centipoise)[7]	Boiling Point Range (ºC)	Flash Point (ºC)	Interfacial Tension (mN/m)[7]
Gasoline[1]	0.67 to 0.8 @ 15ºC	0.62 at 15°C	38 to 204	-43 to -38	52 @ 20°C
AVGAS[2]	0.711 @ 16ºC	2.3 @ 15°C	33 to 170	-46	37 @ 20°C
JP-4[3]	0.75 @ 15ºC	1.0 @ 15°C	60 to 270	-29	50 @ 15°C
JP-5	0.82 @ 15ºC	2.0 @ 15°C	176	60	-
JP-8	0.78 to 0.84 @ 15ºC	2.0 @ 20°C[8]	205 to 300	38	-
Diesel (#2)[4]	0.87 @ 15ºC	2.7 @ 15°C	150 to 370	52 to 96	50 @ 20°C
Kerosene[5]	0.81 @ 15ºC	2.3@ 15°C	151 to 301	>38	47-49 @ 20°C
Bunker C[6]	0.9 to 1.1 @ 15ºC	45,030 @ 15°C	>177	>166	40 @ 23°C

1 ChemADVISOR, 2010a
2 ChemADVISOR, 2010b
3 ChemADVISOR, 2010c
4 ChemADVISOR, 2010d
5 ChemADVISOR, 2009
6 ChemADVISOR, 20010e
7 API Interactive LNAPL guide, July 2004 (accessed through www.api.org)
8 U.S. Air Force Defense Quality and Standardization Office "TURBINE FUELS, AVIATION, KEROSENE TYPES, NATO F-34 (JP-8), NATO F-35, AND JP-8+100" MIL-DTL-83133, 1999. Wright-Patterson AFB
9 EPA – OSWER June 2000. Accessed via http://www.clu-in.org/download/studentpapers/strbak_flushing.pdf

Table 1b. Composition of Selected Fuels[1]

Fuel Type	Mass Fractions (%)				
	Paraffins	Isoparaffins	Aromatic	Naphtha	Olefins
Gasoline	9.1	38.1	43.4	3.8	5.6
AVGAS	3.3	74.2	22.0	0.5	0.001
JP-4	29.3	31.0	43.4	3.3	6.2
JP-5	-	-	-	-	-
JP-8[2]	79.7	-	20.3	-	-
Diesel (#2)	55.0	12.0	24.0	-	5.0
Bunker C	21	21	34	-	-

1 Morrison, Robert D. 1999. Environmental Forensics: Principles & Applications.
2 API Interactive LNAPL guide, July 2004 (accessed through www.api.org)

Table 1c. Effective Solubility of BTEX components from different LNAPL fuels[1]

Fuel Type	BTEX component solubility (mg/L)			
	Benzene	Toluene	Ethylbenzene	Xylenes
Gasoline	42.0	25.1	3.2	15.1
JP-4	-	22.2	8.6	-
JP-8[2]	-	27.8	-	-
Diesel (#2)	4.17	7.15	0.62	1.51
Kerosene	3.56	12.2	0.79	2.3

1 API Interactive LNAPL guide, July 2004 (accessed through www.api.org)

What is an LNAPL Management Strategy?

An LNAPL management strategy is the primary toolkit for decision-making at an environmental remediation site where LNAPL is present. Having such a strategy in place provides the Navy Remedial Project Manager (RPM) with a framework to measure progress throughout the life of the project. Benefits of implementing an LNAPL management strategy include: (1) garnering regulatory pre-approval for a site management approach that explicitly acknowledges the inherent challenge of LNAPL remediation and incorporates an adaptive remediation process; (2) recognizing the ability of intrinsic processes (e.g., natural attenuation) to contain or reduce LNAPL; and (3) helping to achieve a cost-effective and more environmentally-sustainable remediation program.

What steps are taken to develop an LNAPL Management Strategy?

The first step involved in developing a sound LNAPL management strategy is collecting key data to develop an understanding of the nature (i.e., geologic and geospatial distribution of LNAPL saturation) and extent of the LNAPL problem. The next step is to perform an LNAPL natural attenuation (NA) evaluation to determine the effects of natural weathering (e.g., dissolution, volatilization, and biodegradation) on the fate and transport (e.g., concentration, mobility, and stability) of the LNAPL. The term LNAPL NA is analogous with what is often referred to as source zone natural attenuation (SZNA) or natural source zone depletion (NSZD). However, for this handbook, it will be referred to as LNAPL NA. An evaluation of risk to human health and the environment should also be performed for the media and exposure routes of concern. At this point, an LNAPL conceptual site model (LCSM) can be developed. The LCSM provides the basis for understanding the LNAPL condition and characterizes the extent of the problem. Once all of the relevant information has been gathered and incorporated into an LCSM, the overall risk management strategy should be developed to define realistic LNAPL remedial action objectives (RAOs) that maintain protectiveness of human health and the environment and comply with regulatory requirements. The final step taken during development of an LNAPL management strategy is to establish an execution plan that details RAOs, performance metrics, milestones, and endpoints. This plan serves as a road map for remedy implementation and optimization. It should be flexible, dynamic, and chart a clear course for achieving site closure, which may include long-term management (LTMgt). Figure 2 illustrates the sequence of activities recommended when developing a comprehensive LNAPL management strategy.

Figure 2. Activity Sequencing for Development of an LNAPL Management Strategy

What is an LCSM and how is it prepared?

The LCSM is the body of information describing multiple facets of the LNAPL and site setting that is necessary for use as a basis to identify the LNAPL RAOs (ITRC, 2009a). A simplified example is shown in Figure 3. The LCSM is a conceptual site model, which includes the source, pathway, and receptors, with a focus on the source component (e.g., the LNAPL). Overall, the level of detail required for an LCSM is site-specific and influenced by a number of factors such as the RAOs of the LNAPL site management strategy, site complexity, and regulatory framework. The LCSM can comprise some or all of the following scientific and technological inputs (ITRC, 2009a):

- Site setting (historical and current) – includes land use, groundwater classification, presence and proximity of receptors, exposure pathways, etc.
- Geological and hydrogeological information/setting
- LNAPL properties (specific gravity, viscosity, boiling and flash points, interfacial tensions)
- LNAPL chemical properties (concentration, constituent solubilities, fractionation/speciation of mole fractions of TPH constituents, and half lives)
- LNAPL spatial distribution (vertical and horizontal delineation)
- LNAPL mobility and body stability information
- LNAPL recoverability information
- Associated dissolved-phase and vapor-phase plume information
- LNAPL natural attenuation processes

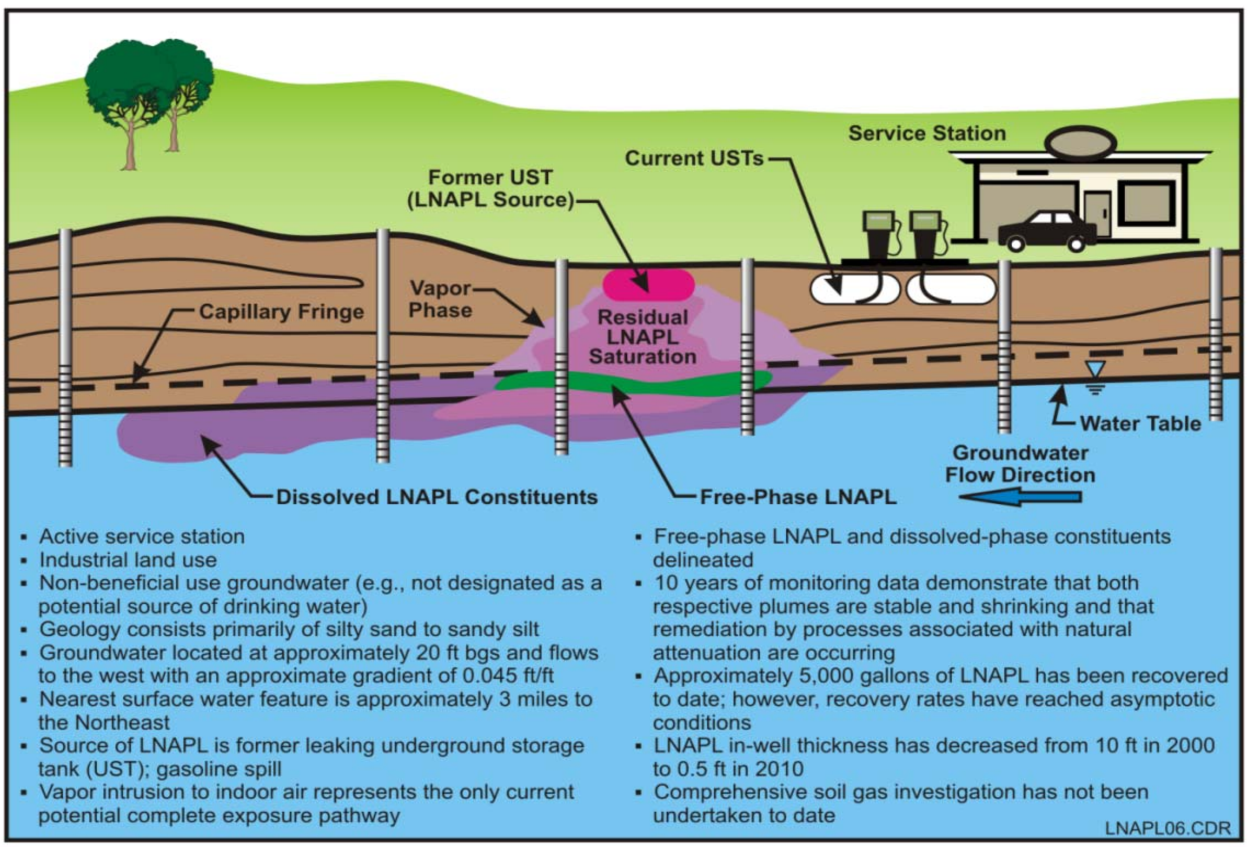

Figure 3. Example of an LNAPL Conceptual Site Model

As the project progresses, the LCSM should be regularly reevaluated in light of additional site/LNAPL data assessment, pilot test data, remedial technology performance metrics, and monitoring data. A complete and up-to-date LCSM allows the best possible decisions regarding application and operation of remedial technologies to be made (see ASTM, 2007).

What is an LNAPL NA evaluation?

LNAPL NA consists of the processes/ mechanisms by which the concentration of constituents (or chemicals) that comprise the LNAPL may be decreased naturally over time in situ. Examples of these mechanisms include dissolution, volatilization, and biodegradation. Once key data are collected to support development of the site-specific LCSM, an LNAPL NA evaluation should be performed to help determine the most appropriate LNAPL management approach for the site (e.g., no further action [NFA], LTMgt, or treatment).

> Tools and techniques are available to determine LNAPL NA at petroleum sites. As part of the LCSM, it is important to understand the natural rate of intrinsic mass destruction under site-specific redox conditions. This information can be used to estimate the amount of mass removed each year, and also compared to mass removal from an active engineered system. Two examples are listed below:
>
> *Modeling* – Natural Attenuation Software (NAS v2) was developed by Virginia Tech, United States Geological Survey (USGS), and NAVFAC and is available for download at http://www.nas.cee.vt.edu/. This software can be used to estimate overall natural attenuation remediation timeframes for a given source mass.
>
> *Mass Budgeting* – A mass budget can be established to evaluate the rate at which dissolved contaminants partitioning from the LNAPL are being destroyed based on the given redox conditions. Example calculations can be found in *Natural Attenuation for Groundwater Remediation* (National Research Council [NRC], 2000). http://www.nap.edu/catalog.php?record_id=9792.

LNAPL NA evaluations can be either qualitative or quantitative, depending on the site-specific needs. A qualitative assessment typically involves identifying the processes/mechanisms that are contributing to LNAPL NA and/or gathering data which demonstrate that the source zone is redistributing contaminant mass to groundwater or the vadose zone or both. A quantitative assessment involves collection and evaluation of site data that can be used to determine mass flux rates for each of the processes/mechanisms that are naturally decreasing LNAPL source zones. Typically, toxic chemical content (benzene, toluene, ethylbenzene and total xylenes [BTEX] and polycyclic aromatic hydrocarbons [PAHs]), degree of weathering, leachability, and degradation rates are determined as part of this process. Detailed technical descriptions and sample calculations for quantitatively assessing LNAPL NA are presented in a recent document prepared by the ITRC's LNAPL Team entitled *Evaluating Natural Source Zone Depletion at Sites with LNAPL* (ITRC, 2009b).

Once completed, a comprehensive LNAPL NA evaluation will allow the following questions to be answered:

- What is the rate at which LNAPL is being depleted from the source zone?
- What processes are primarily driving LNAPL NA?
- What will LNAPL NA look like in the future?

When the answers to these questions are understood, a more informed decision can be made with respect to selection of an approach for LNAPL remediation. By itself, LNAPL NA can be a viable remedial option, but must be compared with the relative benefit of more aggressive treatment options. Of course, the regulatory environment will also play into the determination regarding the LNAPL management approach, as well as if LNAPL NA is suitable as a stand-alone remedial option at any point during the life-cycle of the project.

What is the Multiple Lines of Evidence Approach?

The NA analyses are combined with others to develop multiple lines of evidence that will provide strong technical support for the most appropriate LNAPL management approach. This multiple lines of evidence approach is especially important when recommending NFA or LTMgt, for example, as presentation of weighted evidence (e.g., findings from various evaluations pointing to the same conclusion) that the LNAPL is naturally attenuating will ultimately generate a much stronger case. The multiple lines of evidence approach to supporting an NFA or LTMgt LNAPL site management strategy is described in more detail below.

First Line of Evidence – LNAPL Mobility Evaluation

According to *Evaluating LNAPL Remedial Technologies for Achieving Project Goals* (ITRC, 2009a), LNAPL is considered mobile when it will accumulate in wells and LNAPL saturation is greater than the residual saturation. LNAPL is migrating when it can be observed to move over time. It is important to note that not all mobile LNAPL necessarily migrates, but LNAPL must be mobile in order to migrate. When developing an NFA or LTMgt LNAPL site management strategy, it is critical to demonstrate that the LNAPL is not migrating and doesn't pose a threat of additional contamination to surface water or groundwater. LNAPL stability can be demonstrated by collecting data that show:

- LNAPL is at residual saturation (i.e., it's disconnected) and can't migrate
- LNAPL is mobile (i.e., occurs at various thicknesses in-well), but is no longer spreading laterally
- The associated dissolved-phase plume, if present, is stable or shrinking (incorporates results from the NA evaluation)
- Surface water is not impacted
- LNAPL mass is stable or decreasing (incorporates results from the NA evaluation)

Second Line of Evidence – LNAPL Risk Evaluation

Another key piece of information for developing an NFA or LTMgt LNAPL management strategy is demonstrating that LNAPL presents no risk to human health or the environment under current and reasonably anticipated future scenarios. This can be accomplished by showing that:

- Impacted groundwater is not a current or future risk when groundwater use restrictions are in place
- Soil gas above the LNAPL area is not a current or future risk with or without engineering controls
- The associated dissolved-phase plume, if present, is stable or shrinking (incorporates results from the NA evaluation)
- LNAPL toxicity is decreasing over time based on LNAPL NA evaluations

Third Line of Evidence – LNAPL Removal to Maximum Extent Practicable
Demonstrating that LNAPL recovery has been completed to the maximum extent practicable is important in developing the overall weight of evidence argument for an NFA or LTMgt site management strategy. This can be accomplished by:

- Charting cumulative LNAPL recovery versus time to show asymptotic removal
- Performing a decline curve analysis to show actual recovery that is near the maximum predicted LNAPL recovery volume
- Using simple bail down tests to determine slow recoverability and low LNAPL transmissivity
- Presenting environmental sustainability arguments demonstrating net negative environmental benefits of continued recovery
- Comparing LNAPL NA rates to active fluid recovery rates

Historically, poor LNAPL remediation practices resulted from the ambiguous "recover LNAPL to the maximum extent practicable" requirements. This requirement stems largely from a provision in the Code of Federal Regulations (40 CFR §280.64). For example, many regulatory agencies require a somewhat arbitrary maximum in-well LNAPL thickness that completely ignores risk to human health and the environment, the LCSM, and has limited or no correlation with LNAPL mobility, recoverability, or dissolved-phase or vapor-phase soil gas concentrations (ITRC, 2009a). Thus, it is important to develop realistic LNAPL remedial objectives and goals that are consistent with the LCSM and in conjunction with local regulatory agency requirements (e.g., define "extent practicable" using site-specific parameters).

How to develop an LNAPL Management Strategy

Long-Term Vision
Development of an LNAPL management strategy begins by defining the long-term vision and goals for site restoration. The LCSM is carefully reviewed by key project stakeholders to ensure that they have a common reference for understanding the problems posed by the contamination. This information becomes the foundation on which the LNAPL management strategy is based. The long-term vision for the site is developed using a consensus-based approach, which considers and integrates the interests of each key stakeholder. It should be noted that although stakeholders will have many interests in common, there will be specific needs and requirements imposed by individual stakeholders. For instance, primary objectives of a facility owner may be to limit disruptions to operations and minimize treatment costs, whereas the interests of regulatory agencies likely would be to achieve protection of human health and the environment within a reasonable timeframe. These varying interests could lead to dramatically different approaches for managing the site; hence, it is important that they are all understood and considered as the LNAPL management strategy is being developed.

Remedial Action Objectives and Remedial Goals
Site-wide RAOs and remedy-specific remedial goals (RGs) are developed based on the specific contaminant remediation requirements associated with achieving the long-term vision for the site. The RAOs are site-specific, site-wide goals which are formed based on the contaminants of concern (COCs), the impacted media, fate and transport of COCs and those potential exposure routes, and receptors identified in the LCSM (U.S. Navy, 2006). The RAOs must provide a clear and concise description of what the remedial action(s) should accomplish at a

given site. RAOs should express how to protect human health and the environment rather than requiring a particular remedial technology to be operated until final cleanup goals are achieved. Examples of RAOs include:

- Protect human health by preventing exposure of potential residents and occupational workers to volatile organic compounds (VOCs) in indoor air that have migrated from contaminated groundwater beneath the site
- Protect human health for future recreational receptors
- Protect existing beneficial uses of the shallow aquifer underlying the site to the extent practicable while minimizing VOC migration beyond the current boundaries of the facility at concentrations that exceed cleanup goals

RGs define an endpoint for a component of the remedy that must be met for each phase of the remedy in order to achieve the RAOs. Although, in some cases numerical RGs may be dictated by specific regulatory requirements, in general the RGs should relate to criteria that ensure that the LNAPL plume is no longer migrating, the dissolved phase plume is stable, chemicals within the LNAPL are no longer contributing to soil gas, and that the recoverability of the remaining LNAPL is no longer necessary or practicable (see Multiple Lines of Evidence above). Achieving the RGs will ensure compliance with RAOs. Examples of RGs include:

- Remove LNAPL to the maximum extent practicable (required by many states)
- Reduce benzene concentrations in groundwater to an agreed upon level, which is expected to mitigate risk to down-gradient receptors
- Heat the aquifer and/or vadose zone to a specified temperature. Perform vacuum recovery of hydrocarbons until asymptotic recovery is achieved

Key Considerations

The LNAPL management strategy must consider the various management options available to achieve the RAOs and RGs. Choices include active, passive, and natural remediation technologies, engineering controls, and institutional controls. The selected management strategy might be comprised of a combination of two or more of these options, which could be applied simultaneously to address different exposure pathways or be applied sequentially as a treatment train to first remove the bulk contamination, followed by a polishing phase to achieve the RAOs. The optimum strategy will be one that achieves the long-term vision for the site and best accommodates the requirements and interests of the individual stakeholders.

Selection of the management approach is an iterative process. It begins with screening a wide range of options. Potential technologies and management approaches should be identified and, if necessary, site investigations should be performed to collect any additional data required to justify a particular technology or approach and to develop the design of the remedy. Bench- and pilot-scale tests also might be performed to support technologies that appear to be likely candidates for effectively achieving the RAOs for the site. At any point in this process, additional information learned about the site-specific conditions may require that the LCSM and/or management approach be revisited and revised. In addition, during execution of the management strategy and treatment of the LNAPL, changing site conditions, changes to regulatory requirements, and other unforeseen changes may necessitate changes to the LCSM and/or management strategy.

The LNAPL management plan must incorporate risk reduction metrics. These metrics will be used to gauge the success of the management approach and the progress toward achieving site closeout. Many metrics are available and will, to a large extent, be based on stakeholder requirements and the long-term vision for the site. Common risk-reduction metrics (CH2M Hill, 2009) include:

- Reduction of the LNAPL gradient
- Reduction of LNAPL saturation and mobility
- Reduction of LNAPL mass to a level at which NA can assimilate the dissolved-phase plume
- Reduction of BTEX and PAH content in LNAPL to eliminate vapor intrusion and leachability to groundwater
- Reduction of aromatic and aliphatic components in LNAPL to reduce risk of direct exposure

Valuable Tools and Techniques

These metrics relate to changes (reduction) in the distribution, mobility, recoverability and composition of the LNAPL. Hence, it is important to understand these characteristics and how they change during implementation of the LNAPL management approach. A number of tools and techniques are available to evaluate these characteristics. For instance, changes to the distribution, volume, and mobility of LNAPL can be determined by monitoring various site-specific parameters such as LNAPL thickness and groundwater table elevations, and measuring various parameters from LNAPL and soil core samples collected from the site. Visualization and modeling software, such as the relatively simple calculation spreadsheets provided by the American Petroleum Institute (API, 2004) or more complex multi-phase numerical modeling software such as UTCHEM (University of Texas Chemical Compositional Simulator), can be used to evaluate the data and determine volumes and distribution of the LNAPL at the site. A number of field measurement methods to determine geotechnical and chemical properties, such a laser-induced fluorescence (LIF) and electro resistive tomography (ERT), also are available to assess the distribution of the LNAPL.

During LNAPL recovery activities, recovery rate data must be evaluated. Bail down tests can be performed to evaluate passive recovery of LNAPL into the wells. During active recovery (using in-well pumps or a multiphase extraction [MPE] system), the recovery rate is easily tracked by plotting the cumulative LNAPL recovery volume over time or by performing a decline curve analysis as shown in Figure 4. Additional information pertaining to decline curve analysis is provided by the ITRC (2009a).

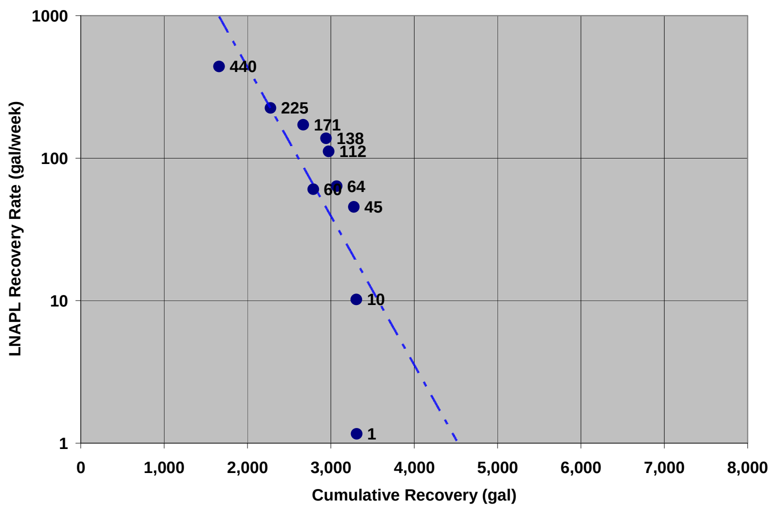

Figure 4. Decline Curve Analysis

The risk reduction metrics and associated tools and techniques that will be used to evaluate progress must be agreed upon by project stakeholders and incorporated into the LNAPL management plan. The resulting data are used to develop the lines of evidence discussed above (e.g., no risk, not migrating, and not recoverable) that will demonstrate if NFA or LTMgt is appropriate for the site, or if transition to a less active phase of the treatment train is necessary.

How do performance metrics measure LNAPL RGs?

As previously mentioned, LNAPL RGs typically define the limits to which a component of the remedy will be utilized to achieve the RAO. Performance metrics are units of measure that can be used to quantify LNAPL remediation performance, as well as risk management. Performance metrics vary based on the technology selected, and essentially establish endpoints describing when that technology has reached its limits of beneficial application or not-to-exceed thresholds that may indicate when implementation of a technology has created an unacceptable risk. The endpoints will vary considerably based on local regulatory requirements and site-specific objectives. Many states and municipalities have specific guidance that should be referred to while formulating the remediation endpoints for the site. In most cases, the endpoint will involve performing the activities necessary to demonstrate the three lines of evidence discussed above. For example, at a site located in northern Florida, in addition to demonstrating that the cost per gallon of LNAPL recovered had become cost prohibitive, a protocol for bailing the wells was implemented (Figure 5) to further demonstrate that LNAPL was immobile and could not be effectively recovered.

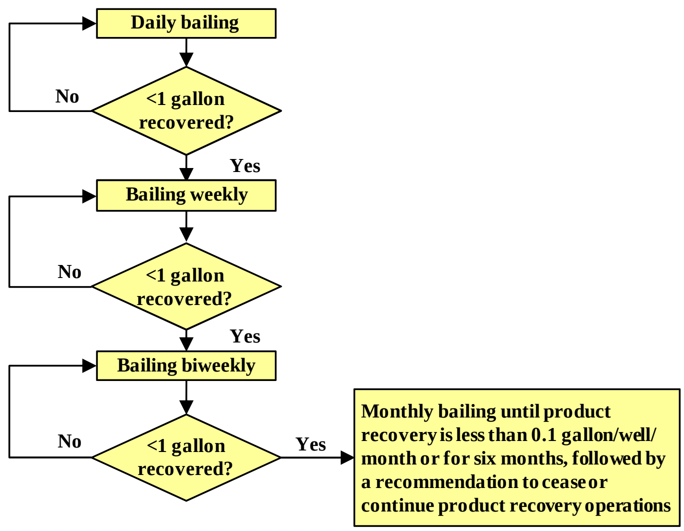

Figure 5. Example Bailing Protocol to Demonstrate LNAPL had been Recovered to the Extent Practical

Remediation system operational metrics that can be used to gauge progress toward achieving an endpoint include:

- Recovery rate asymptote as determined by LNAPL recovery versus time curves to determine if asymptotic conditions have been reached
- LNAPL/water recovery or LNAPL/vapor recovery ratio to determine if recovery effectiveness is decreasing
- LNAPL in-well thickness

Compliance or risk management metrics might include:

- Dissolved-phase contaminant concentrations in downgradient wells to ensure remedial processes are not causing groundwater plume migration
- Vapor-phase concentrations at specific compliance points to ensure remedial processes are not creating a vapor migration issue

- Water level measurements to ensure that groundwater mounding is not occurring which might promote LNAPL migration and smearing

Finally, performance metrics can also be incorporated to measure the sustainability of the remedial technology selected for LNAPL abatement. For example, comparison of the non-renewable energy use to the quantity of fuel recovered from the subsurface on an equivalent unit basis (i.e., pounds of diesel) can be used as a rough measure of the environmental sustainability or net environmental benefit of an LNAPL remedy.

When to consider treatment?

The LCSM provides the information necessary to determine if LNAPL remediation is warranted, and provides a basis for LNAPL remediation (e.g., level of concern, portion/condition of LNAPL body needing remediation, and urgency) (ITRC, 2009a). If it can be demonstrated that the three lines of evidence discussed above are satisfied (i.e., LNAPL is not migrating, does not pose current or future risk, and cannot be effectively recovered) and regulation does not require the continuation of monitoring, then NFA (with or without controls) can be an appropriate management approach for the site. At sites with controlled contaminant exposure and limited active migration within a controlled property boundary, LTMgt, which may incorporate a combination of long-term monitoring and land-use controls, may be required. The controls must remain in place until monitoring demonstrates that the three lines of evidence discussed above are satisfied. However, treatment should be considered if all three lines of evidence do not indicate that NFA would be appropriate. Furthermore, it should be performed only when mobility or toxicity reductions are required in order to be protective of human health and the environment and/or to comply with regulatory requirements.

What types of treatment are available?

Treatment can be divided into two types: passive and active. At many sites, both active and passive treatments are applied, simultaneously or in sequence, to achieve the RAOs.

Passive treatment methods are typically designed to treat contaminants in the dissolved-phase plume that emanate from an LNAPL source zone. They consist of technologies such as monitored natural attenuation (MNA) and permeable reactive barriers (PRBs).

Active treatments are most appropriate to address LNAPL that is either migrating, poses immediate risk, or can be cost-effectively recovered. They are divided into three categories of technologies including mass-recovery, phase-change, and mass control (ITRC, 2009a). These technology groups are intended to associate the specific technologies within each group to the mechanism by which the technology predominantly would be used to remediate LNAPL and achieve site-specific RGs. In some instances, a particular technology can fall into multiple groups (Table 2).

Mass-recovery technologies are those technologies that physically remove LNAPL from the subsurface. Technologies include excavation and various pump and treat technologies, such as skimming, dual pump recovery, and MPE. As a less energy-intensive polishing step, mass recovery can also be accomplished to collect free product down to a sheen through the use of passive skimmers and absorbent socks.

Phase-change technologies are those that convert some components of the LNAPL to another form. They are designed to increase the rates of volatilization, degradation, and/or dissolution of the LNAPL constituents, thereby accelerating the weathering process. The contaminants are then degraded in situ or are captured in the vapor phase and treated aboveground. Examples of these technologies include air sparging, soil vapor extraction (SVE), in situ chemical oxidation (ISCO), surfactant-enhanced flushing, and thermal treatment technologies including electrical resistive heating (ERH), thermal conductive heating (TCH), radio frequency heating, and steam flushing.

It should be noted that ISCO does not treat the LNAPL directly, but rather reacts in the aqueous phase and treats the dissolved phase portion of the plume that emanates from the LNAPL. As a result, the concentration gradient between the LNAPL and groundwater is increased, which enhances dissolution of the LNAPL. Since the LNAPL is not directly treated, the time required to implement these technologies will be greater than those that treat the LNAPL directly because they are limited by the rate of dissolution of the individual LNAPL constituents.

Table 2. Active Treatment Technologies (Modified from ITRC, 2009a)

Technology Group	Technology
Mass Recovery	Excavation Multi-phase extraction Skimming Water flooding Dual-pump recovery Cosolvent flushing Thermal In-situ chemical oxidation (ISCO)
Phase-Change	In situ bioremediation (ISB) ISCO Thermal Air sparging/SVE
Mass Control	Physical barrier • Sheet pile • Slurry wall • French drain Stabilization Hydraulic containment SVE (vapor) LNAPL NA

Often, the phase-change technologies are used in conjunction with mass recovery technologies to enhance the recovery of the LNAPL. For instance, thermal treatment and surfactant flushing can be used to reduce the viscosity and increase the dissolution of the LNAPL, respectively, which reduces the residual soil saturation. Hence, the recoverability of LNAPL using these technologies in combination with hydraulic recovery technologies such as dual-pump extraction or MPE is increased.

The last category of active recovery technologies relate to mass control. These technologies stabilize LNAPL migration by applying physical controls or binding agents. Examples include in situ stabilization using a variety of mixing agents, permeable activated clay absorptive barriers, and hydraulic containment barriers including slurry walls and sheet piles. These control technologies can be used in conjunction with mass recovery and phase-change technologies depending on site-specific requirements.

How to select an appropriate technology?

The treatment technology selection process begins with an understanding of the long-term vision and RAOs for the site since site-specific requirements will greatly influence the technology that is selected. For instance, if a primary objective is to clean up a site quickly to allow property transfer without the need for institutional controls, a very aggressive technology such as excavation or TCH can be utilized to rapidly remove the LNAPL. However, at a comparable site, at which similar activities are expected to continue and cleanup duration is less of a concern because of the lack of risk to human health and the environment, a much less aggressive technology such as MNA or limited hydraulic recovery with skimming or dual-pump extraction may be appropriate.

Site-specific factors such as infrastructure impediments and LNAPL properties must also be considered during this phase of the screening process since they may preclude the use of some technologies and approaches. For example, at a shallow site where utility corridors are present that lead toward a sensitive receptor, it may not be practical to inject certain ISCO reagents. The groundwater may mound in the vicinity of the injection points and intercept the utility corridor, providing a conduit for the COCs to travel toward the receptor.

> **A Technology Screening Resource**
>
> The American Petroleum Institute (API) has developed an interactive LNAPL guide and LNAPL Recovery and Distribution Model (http://www.api.org/ehs/groundwater/lnapl/index.cfm) that provides useful tools to aid practitioners in selecting technologies and developing an LNAPL management approach for their sites. Both the guide and model support the quantitative prediction of LNAPL mobility and recovery at a site and allow the user to evaluate a number of common LNAPL recovery technologies including trenches, skimming, drawdown pumping, and vacuum-enhanced recovery. The interactive guide also provides a comprehensive list of reference parameters for various LNAPL and soil properties. In addition, field and laboratory methods to measure various parameters such as porosity, permeability, capillary pressure, oil and water saturations, interfacial tensions, product transmissivity, and relative permeability are provided, which can be incorporated into the mobility and recoverability models.

The technology screening process should also consider site-specific geologic factors that can limit the application of certain technologies. This step of the process eliminates technologies that would not be technically practical due to specific lithologic conditions. The screening process aims to identify those alternatives that would be the most likely to achieve the objectives for the site.

Sustainability is another factor that must be considered during the technology selection process. The management approach should be designed to minimize adverse effects to the environment caused by consumption of non-renewable natural resources and emission of greenhouse gases and criteria pollutants. Whenever possible, technologies and approaches that minimize detrimental environmental side-effects should be utilized. SiteWise™, which was specifically developed to support decision making during the remedy selection process and is now required as part of all Navy feasibility studies, is available at the Navy's Web site (http://www.ert2.org/t2gsrportal/).

The results of the technology screening process will generate a list of potential technologies. It may be necessary to perform bench- and/or pilot-scale tests to collect additional data to further refine the list. The nine evaluation criteria as defined by the EPA for feasibility studies (EPA, 1993) may be used to further evaluate each technology and determine those that would have the greatest likelihood of achieving the RAOs for the site. Detailed guidelines for performing a feasibility study as specified by the Department of the Navy are documented in Chapter 8 of the *Department of the Navy Environmental Restoration Program Manual* (U.S. Navy, 2006).

What is an LNAPL management execution plan?

An LNAPL management execution plan is essentially a work plan that combines RGs, performance metrics, milestones, and endpoints into a flexible implementation and optimization plan. The execution plan is used as a road map for remedy optimization and achieving NFA or LTMgt. It typically includes technology life-cycle evaluations and phase-out goals (as needed). Similar to the LCSM, the LNAPL management execution plan is intended to be a living document and to be revisited frequently. Furthermore, and analogous to a remedial/corrective action plan, it is crucial to obtain regulatory buy-in on this document prior to implementation of the plan.

What are common pitfalls at LNAPL sites?

The most common problem associated with LNAPL site management is a stagnation of LNAPL remediation. Specific regulations for cessation of LNAPL recovery vary from state to state, but typically require either that the LNAPL is recovered to the "maximum extent practicable" or less than 0.01 foot remains in the monitoring wells. For example, in the State of Florida, the risk-based corrective action rule requires that LNAPL be removed "to the extent practicable", where LNAPL is defined as free product that accumulates in excess of 0.01 ft on the surface of the water table. NFA, without institutional controls, is more difficult to obtain with more than 0.01 ft of LNAPL in site wells, but has been achieved in Florida through documentation of LNAPL removal efforts, as well as demonstrating that free product is no longer mobile and that LNAPL does not constitute a human health and/or environmental threat. In California, regulations require that removal also is performed "to the extent practicable," but non-degradation legislation makes it difficult to leave LNAPL in place. However, some Water Boards, such as the San Diego California Regional Water Quality Board, are distinguishing between mobile and immobile LNAPL and allowing long-term closure strategies with MNA for stable plumes.

In some cases, stagnation of LNAPL remediation refers to the inability to achieve site closeout or NFA; however, in other cases stagnation may refer to the inability to discontinue operation of an active remedy and transition to a less-costly passive remedy. As illustrated in Figure 6, this situation can result in high cost and an adverse impact to the environment with relatively little benefit with respect to removal of the LNAPL mass.

Stagnation of the remedy often occurs because stakeholders cannot achieve consensus as a result of a poorly defined exit strategy and lack of agreement on RGs and performance metrics. Although the requirement that the LNAPL be recovered to the "maximum extent practicable" allows needed flexibility for when to terminate recovery activities based on site-specific objectives and risks, there is a great deal of ambiguity with respect to what is practicable. As a result, needless operation of recovery systems occurs for an extended time while stakeholders try to demonstrate and agree that the data demonstrate that it is not practicable to continue LNAPL recovery.

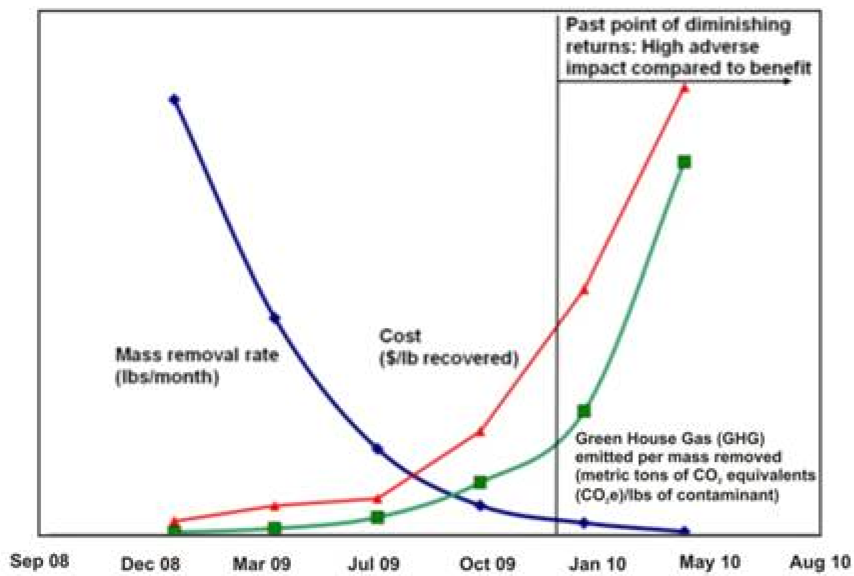

Figure 6. Relationship Between LNAPL Recovery, Cost and Environmental Impact

Other problems commonly encountered at LNAPL sites include:

- Inadequate understanding of the site conditions (i.e., poor LCSM)
- Inadequate definition of LNAPL terminology (i.e., what is migrating, mobile, and residual LNAPL) and how they relate to terminology in the regulations
- Unrealistic endpoints for site cleanup
- Lack of flexibility to transition to another remedy

Although these problems commonly occur at sites, they can be avoided by developing the consensus-based LNAPL management strategy discussed in this document. The strategy must clearly define the remedial objectives and the specific endpoints that must be achieved to ensure that the RAOs are cost-effectively attained. The performance metrics that outline which data will be collected and how they will be used to demonstrate progress to achieving the remedial objectives must be included in the execution plan. Furthermore, this management strategy must be developed in conjunction with consensus-based input from all key project stakeholders, ideally during the initial phase of the project.

Where can additional guidance be obtained?

Interstate Technology and Regulatory Council (ITRC) LNAPL documents:
http://www.itrcweb.org/teampublic_LNAPLs.asp

American Petroleum Institute (API) LNAPL Resource Center:
http:///www.api.org/ehs/groundwater/lnapl/index.cfm

Remediation Technologies Development Forum NAPL Cleanup Alliance:
http://www.rtdf.org/public/napl/about.htm

Department of the Navy Environmental Restoration Manual
https://portal.navfac.navy.mil/portal/page/portal/navfac/navfac_ww_pp/navfac_nfesc_pp/environmental/erb/resourceerb/nerp_manual_2006(20070710).pdf

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Appendix A: Case Study I — Marine Corps Base Camp Pendleton Former Underground Storage Tank Site 21478: Solar Powered Skimming for Free Product Recovery Followed by Subsequent Polishing via Absorbent Socks

Site Description:

Former underground storage tank (UST) Site 21478 at Marine Corps Base (MCB) Camp Pendleton previously contained a single-walled concrete UST, which was used to store heating oil for former Building 21478. On July 7, 1994, the UST was removed and subsequent investigations indicated that an LNAPL (i.e., free-phase hydrocarbon) plume was present. The geology at the site consists primarily of interbedded layers of sand, silty-sand, silt, clay, clayey-sand, and gravely-sand. Depth to groundwater ranged from approximately 35 to 45 ft below ground surface (bgs), with maximum in-well LNAPL thicknesses between 1 and 4 feet (ft) in source area wells.

Selected Remedy:

To remediate the in-well LNAPL, free product recovery efforts were initiated in 1998. Initially, passive free product filter canisters were installed in each recovery well. Subsequently, operation of a bioventing system for soil remediation was implemented. When it was determined that the bioventing system had reached its limits of effectiveness, solar-powered skimmers were installed in free product recovery wells to expedite LNAPL removal, as well as employ a less energy-intensive remedy (see Figure A-1).

Figure A-1. Solar Powered Skimming System for LNAPL Recovery (see blue equipment)

Once free product was removed from each recovery well to the maximum extent practicable (e.g., product no longer recovered to >0.01-ft in-well, but product sheen remained), absorbent socks were placed in each well as a polishing step.

Groundwater monitoring was performed in conjunction with free product recovery activities to monitor the stability of the dissolved-phase total petroleum hydrocarbon (TPH) plume, as well as indicator parameters associated with natural attenuation.

Results:

A total of 341 gallons of free product was removed from the subsurface at former UST Site 21478, primarily via solar-powered skimmers. Following removal of the absorbent socks, no free product or product sheen was observed for a period of four months. Subsequent monitoring indicated that LNAPL rebound occurred eight months later in site wells at in-well thicknesses ranging from a product sheen to 0.80-ft.

TPH constituents have not been detected in any downgradient monitoring wells for approximately 4 years. These results indicate that the dissolved phase petroleum hydrocarbon plume and likely the LNAPL plume are stable (i.e., not migrating) and primarily limited to the source area. Furthermore, specific chemical indicators of biodegradation (e.g., dissolved oxygen, nitrate, nitrite, sulfate, ferrous iron, manganese, and methane) clearly indicate that natural attenuation of dissolved-phase petroleum hydrocarbons is occurring at the site. For example, electron acceptors including dissolved oxygen and nitrate are lower in the source area well containing elevated TPH-D concentrations when compared to site wells with no measurable TPH-D. Conversely, metabolic byproducts of petroleum hydrocarbon biodegradation (ferrous iron, manganese, and methane) are elevated in the source area well containing elevated levels of TPH-D relative to the non-contaminated wells.

Conclusion:

For this particular site, solar-powered skimming of free product proved to be effective from a technical, cost, and sustainability perspective. Initially, closure and NFA was recommended for the site to the local regulatory agency based on (1) free product appeared to have been removed at former UST Site 21478 to the maximum extent practicable via solar-powered skimming and absorbent socks, (2) subsequent in-well LNAPL thickness rebound testing demonstrated that free product was not reoccurring for over three months, (3) the dissolved-phase TPH plume was not migrating downgradient, (4) natural attenuation of dissolved-phase TPH was occurring, and (5) no potable drinking wells are located within 5 miles of the site. The multiple lines of evidence to support the site closure request (e.g., no mobility, no unacceptable risk, and removal to the maximum extent practicable) illustrate the recommended approach to LNAPL risk management, as presented in this handbook.

However, as documented above, in-well LNAPL rebound was observed during a monitoring event performed approximately eight months following removal of all active and passive remedial systems. The occurrence demonstrates one aspect of the inherent challenges at LNAPL sites and the importance of rebound monitoring over an extended period of one year or more. Currently, the LNAPL remediation system previously used at the site is on back on-line, and a Tier 2 risk assessment is being discussed among the stakeholders as a means to potentially substantiate closure for the site.

Appendix B: Case Study II — Former Fire Fighting Training Area (NCBC Gulfport): Source Removal and Closure Plan

Site Description:

A former fire-fighting training area located at the Naval Construction Battalion Center (NCBC) Gulfport was the site of a CERCLA non-time critical removal action as part of the Navy's Installation Restoration program. The site, approximately ½ acre in size, was contaminated with LNAPL consisting of a variety of waste oils that were spilled and ignited during fire-fighting training exercises. The goal of the source removal action was to remove the LNAPL present in the subsurface, which served as a source of contamination to the groundwater, to the maximum extent practicable. The surficial aquifer was unconfined and composed of sands and fine-grained gravel ranging from 13 to 50 ft thick, underlain by a clay layer containing some silt and sand ranging from 28 ft to more than 150 ft thick. The depth to groundwater, which varied seasonally, ranged from 4 to 8 ft bgs.

Selected Remedy:

The initial interim remedy consisted of an interceptor trench recovery system. The trench was located on the east side of Colby Avenue. The main objective of the recovery trench was to prevent further migration of LNAPL. After about four years of operation, a more aggressive approach, consisting of MPE, was then implemented to remove the remaining recoverable LNAPL. The MPE system used 23 extraction wells and an aboveground extraction manifold (Figure B-1).

Figure B-1. MPE Extraction Wells

Both systems utilized an aboveground treatment system consisting of an oil/water separator, an oil storage tank, an air stripper, and associated pumps, blowers, and controls. After demonstrating to the regulatory agencies that LNAPL was recovered to the "maximum extent practicable" in accordance with Mississippi Department of Environmental Quality (MDEQ) regulations, MNA was implemented to remediate the remaining dissolved-phase groundwater contamination. The endpoint for MPE was defined by:

- Asymptotic reduction in LNAPL recovery over time
- Asymptotic reduction of LNAPL thickness inside wells
- Prohibitive cost/gallon of LNAPL recovered

Results:

The interceptor trench prevented the migration of LNAPL west of Colby Avenue. However, the volume of LNAPL recovered was not reported. The MPE system recovered 2,330 gallons of LNAPL during approximately three years of operation. In addition, the MPE system treated the vadose zone through soil-vapor extraction and enhanced biodegradation of residual hydrocarbons in the vadose zone and capillary fringe. LNAPL recovery decreased significantly after the first few months of operation of the MPE system and the cost per gallon of LNAPL recovered increased substantially (Figure B-2). During operation, LNAPL thickness decreased in many of the wells located at the site; however, some rebound was observed post operation (Figure B-3). The data demonstrated that LNAPL was recovered and was not migrating off site. Water table fluctuations are smearing a few inches of LNAPL over a five vertical foot depth interval (i.e., LNAPL is mobile), thus allowing slight amounts of LNAPL to appear and disappear in the monitoring wells. Under these conditions, horizontal movement of LNAPL will not occur (i.e., LNAPL is not migrating), and recovery of LNAPL will be negligible.

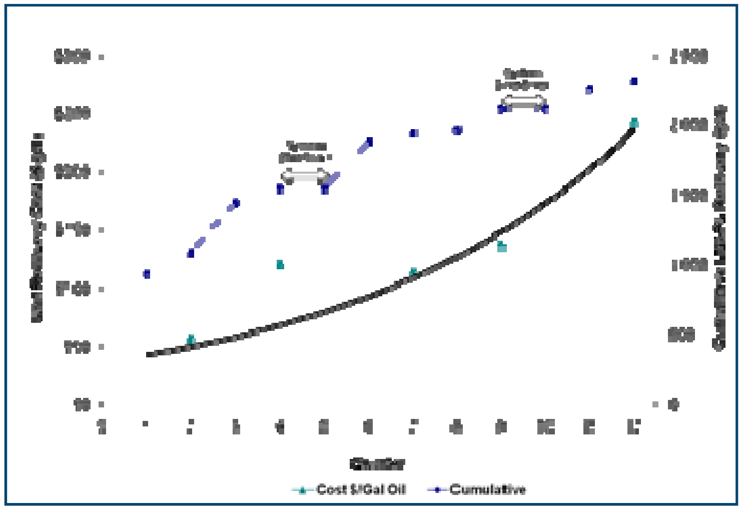

Figure B-2. Cumulative Recovery and Cost

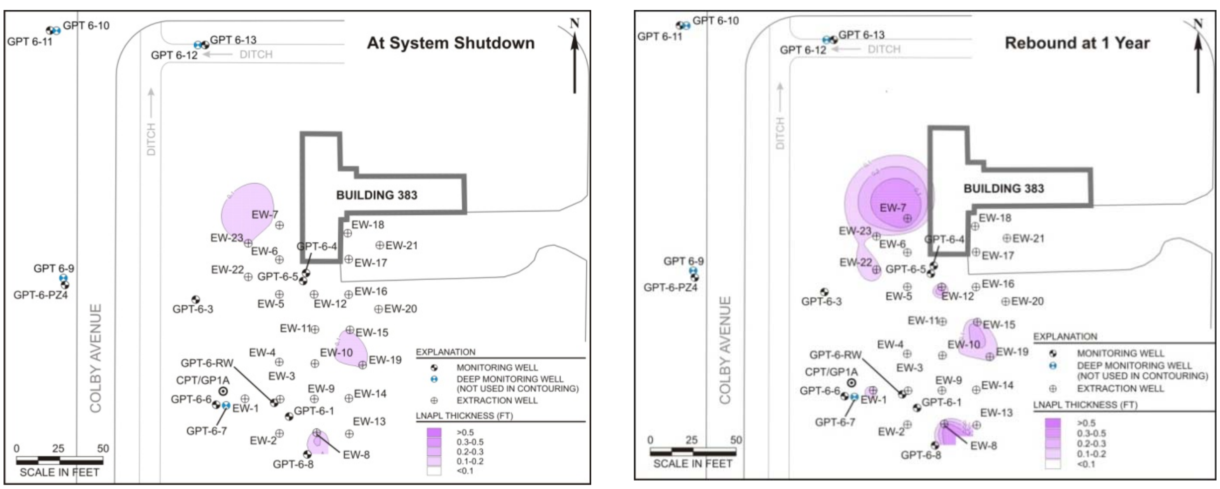

Figure B-3. Reduction of LNAPL in Site Wells

Groundwater monitoring was performed to evaluate the feasibility of MNA. Additional data on groundwater COCs were collected and used data to identify locations for additional long-term monitoring wells. TPH and naphthalene were found to be the only two constituents that exceeded the MDEQ Tier 1 Target RGs. A correlation of MNA parameters including dissolved oxygen, dissolved iron, sulfate, and manganese collected from wells located within the area of contamination to perimeter and background wells was made to further evaluate whether MNA was occurring.

BIOSCREEN, a natural attenuation screening tool, was used as a predictive tool to investigate the feasibility of MNA of the groundwater plume (http://www.epa.gov/ada/csmos/models/bioscrn.html). The model simulated the TPH and naphthalene groundwater plumes using site-specific parameters (Figure B-4).

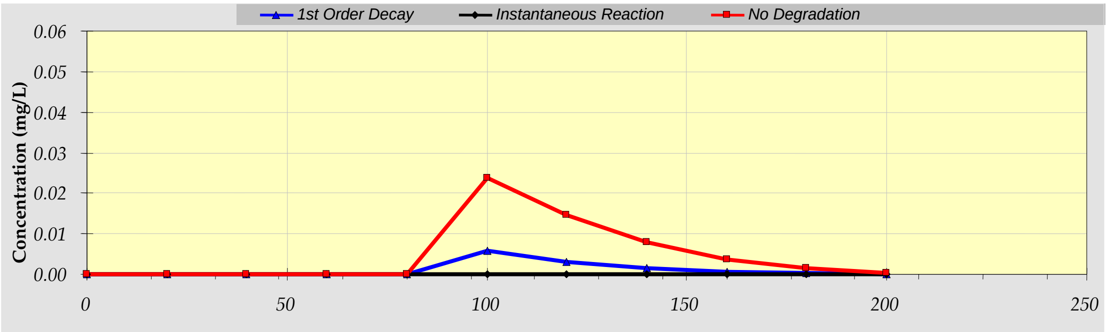

Figure B-4. BIOSCREEN Output for Naphthalene Simulation at 30 Years

Conclusions:

Obtaining regulatory concurrence to stop remedial action is challenging, in particular at LNAPL sites where the regulatory standard is to remove LNAPL "to the maximum extent practicable". This issue was resolved at this site in two stages. (1) Data collection and analysis first demonstrated that this goal was achieved in a manner that was agreeable to both the Navy and MDEQ. The work plan included the metrics that would be used to monitor compliance with this goal, which was developed based on previous experience on similar projects. (2) Partnering meetings with the regulatory agencies and other stakeholders were conducted, which facilitated obtaining regulatory input, and, ultimately, buy-in for the decision that remedial action was completed.

A decision document was developed for the site and approved by all stakeholders. The document proposed to implement institutional controls at the site including land use restrictions. No source removal was warranted based on the following lines of evidence:

1) Monitoring data indicate that horizontal movement of the remaining LNAPL would not occur and that the remaining LNAPL would not be recoverable.
2) The LNAPL had been present at the site for over 40 years. It was not expected that the groundwater plume would expand in the future, which is substantiated by the groundwater monitoring data collected thus far indicating that the dissolved-phase plume exhibits no migration.
3) Groundwater contaminant concentrations were below regulatory standards except for naphthalene and TPH-DRO. MNA, which had been demonstrated to be occurring at the site, appears to have limited contaminant migration. Soil contaminant concentrations also decreased compared with historical concentrations. All soil contaminant concentrations were below regulatory standards except for TPH-DRO.