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Post-Remediation Performance Assessment at a Petroleum Impacted Site

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Acronyms and Abbreviations

µg/L	microgram per liter
1,2-DCA	1,2-dichloroethane
1,2-DCE	1,2-dichloroethane
1,2-DCB	1,2-dibromoethane
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
CFR	Code of Federal Regulations
DCB	dichlorobenzene
DCC	dynamic closed chamber
DEQ	Department of Environmental Quality
DoD	U.S. Department of Defense
EPA	U.S. Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
EXWC	Engineering and Expeditionary Warfare Center
ft	feet
ITRC	Interstate Technology & Regulatory Council
JP	jet propellant
LIF	laser-induced fluorescence
LNAPL	light non-aqueous phase liquid
MCL	maximum contaminant level
mg/L	milligram per liter
MNA	monitored natural attenuation
MTBE	methyl tertiary butyl ether
NA	not applicable/not available
NAVFAC	Naval Facilities Engineering Command
NSZD	natural source zone depletion
PAH	polycyclic aromatic hydrocarbon
TPH	total petroleum hydrocarbon
U.S.	United States
VOC	volatile organic compound

1.0 Objectives

This document is intended to provide strategic guidance to managers responsible for petroleum hydrocarbon impacted sites. Significant and quite detailed technical guidance has been published by others and is widely available (Interstate Technology & Regulatory Council (ITRC), 2018). The intent here is not to duplicate that guidance but rather to help the user understand what technologies and know-how is available and where it can be found, and to put that information into a helpful management context.

The emphasis of this guidance is aligned with light non-aqueous phase liquid (LNAPL) management. However, issues related to dissolved and vapor phase hydrocarbons will also be discussed. This discussion will be limited to petroleum hydrocarbons derived from crude oil.¹

2.0 LNAPL Basics

Petroleum hydrocarbons are molecules comprised entirely of carbon and hydrogen. Crude oil is predominantly a petroleum hydrocarbon, and most of the petroleum hydrocarbons we work with are derivatives of crude oil. The most common petroleum products we work with are fuels, gasoline, diesel, jet fuels, etc. Other petroleum hydrocarbon products, such as lubricants and hydraulic fluids, may have relevance at some sites. It is important to understand that the petroleum products are made up of thousands of individual hydrocarbon molecules with varying properties, such as solubility, vapor pressure, and biodegradability. **Figure 1** shows the boiling point ranges (based on distillation in the refining process) for some commonly used petroleum products.

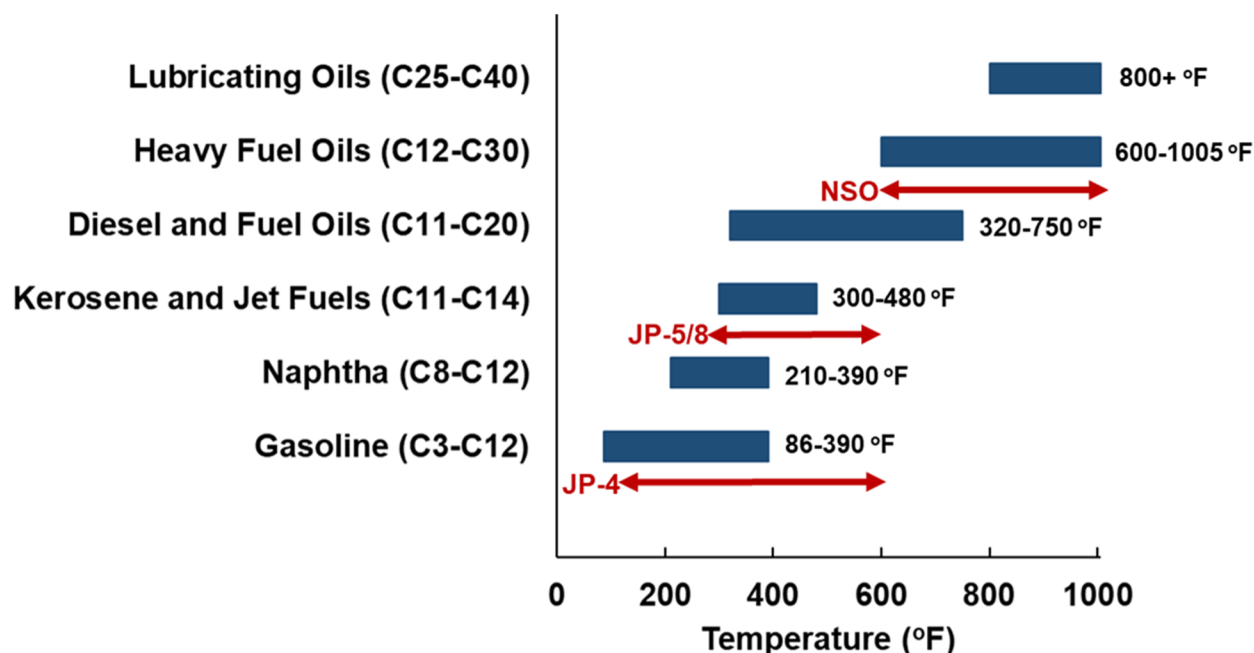


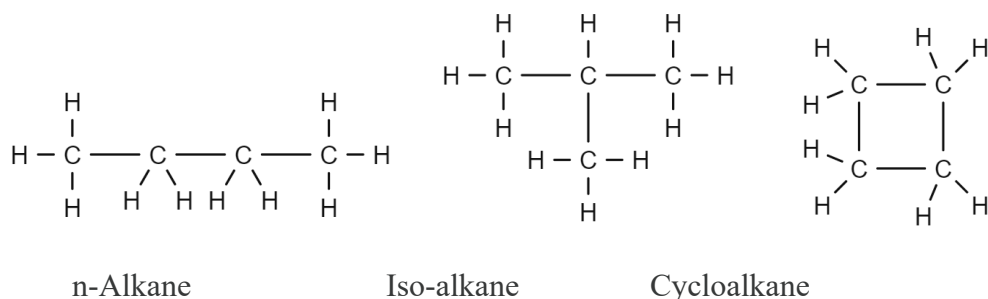
Figure 1 – Boiling Point Ranges for Various Petroleum Hydrocarbon Products (Data were adapted from ITRC, 2018)

¹Other LNAPLs such as vegetable oil and bio diesels exist, but are not addressed here.

Distillates are products that are boiled off from crude oil and decondensed, residuals are products that do not evaporate and are left behind after distillation. In general, lower boiling point petroleum products are less viscous, more soluble, more biodegradable, and more volatile than heavier products.

Petroleum products contain two primary groups of petroleum hydrocarbons, aromatics and aliphatics. Aromatics contain an aromatic ring, benzene is the smallest aromatic, heavier aromatics can contain many rings and are polycyclic aromatic hydrocarbon (PAH). Aliphatics do not contain an aromatic ring and can consist of straight, branched, or cyclic compounds. The distinction is important, because although aromatics typically make up well less than half of petroleum products, they are often the most soluble and toxic fraction. **Figure 2** shows some typical smaller hydrocarbon molecules.

Aliphatics



Aromatics

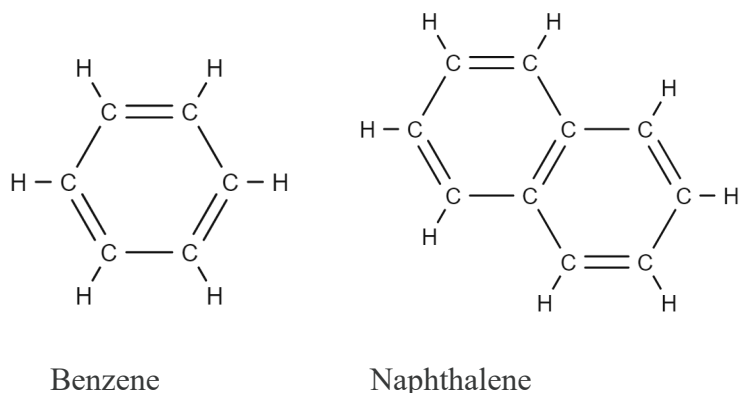


Figure 2 – Examples of Smaller Molecular Molecular Weight Aromatic and Aliphatic Petroleum Hydrocarbons

Non-petroleum hydrocarbons are sometimes added to petroleum products (particularly gasoline). Some non-petroleum hydrocarbon additives have become environmental problems, most notably methyl tertiary butyl ether (MTBE) and related oxygenates, and 1,2-dichloroethane (1,2-DCA). MTBE was a gasoline additive mostly used from the early 80s until recently. MTBE is more soluble and tends to migrate further in groundwater than petroleum hydrocarbons and has been a

contaminant requiring remediation at some sites. 1,2-DCA was an additive to leaded gasoline. It was phased out for on-road vehicles with lead in the 1980s. Lead continues to be used in some aviation gasoline formulations, but 1,2-dibromoethane (1,2-DCB) has mostly replaced 1,2-DCA. Like MTBE, 1,2-dichloroethane (1,2-DCE) may also be found in groundwater associated with gasoline release; 1,2-DCB may also be found, but it appears to be a less frequent concern.

When a petroleum hydrocarbon release migrates downwards (if sufficient quantity is released), it may encounter and disperse onto the water table, sometimes migrating according to the slope of the surface onto which it disperses. Petroleum hydrocarbons are only sparingly soluble in water, and as a result, most of the material may remain in a separate oil phase. Being “lighter” than water, it is referred to as Light Non-Aqueous Phase Liquid (LNAPL). **Figure 3** illustrates this process.

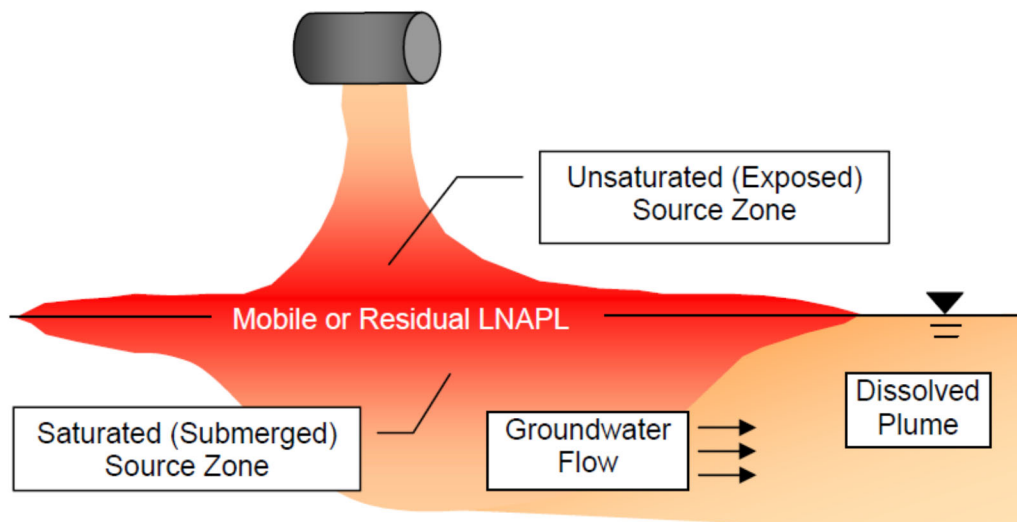


Figure 3 – Example of a Petroleum Hydrocarbon Release and Subsurface Behavior (ITRC, 2009)

Many processes can affect petroleum hydrocarbons after release, notably:

LNAPL Migration – migration of the oil phase – this refers to the movement of LNAPL either downward to the water table or on the surface of the water table. Migration is defined as the expansion of LNAPL area, which is different from mobility discussed below. Although the LNAPL migrates under its own head and is not transported by groundwater, in most cases, LNAPL migration on the surface of the water table occurs in the same direction as groundwater. LNAPL Migration is limited by interfacial tension, meaning that the LNAPL will only migrate so long as there is sufficient pressure within the LNAPL body to overcome the capillary forces created by water holding it back. As a result of this, migration does not occur at many LNAPL sites although significant thicknesses of LNAPL may be measurable in wells. At most LNAPL sites, LNAPL migration has ceased.

LNAPL Mobility, is movement of LNAPL that may or may not be related to migration. In order for LNAPL to be mobile, it must be present in a concentration above what is called the residual capacity of soil. LNAPL can be present below its residual capacity – Physically, this is in the form of LNAPL droplets or ganglia. The residual capacity of soil

for LNAPL can vary, but is typically in the thousands or tens of thousands of mg/L. Mobile LNAPL² can enter a monitoring well where it can be measured and possibly extracted or recovered. LNAPL does not migrate at most sites where mobile LNAPL is observed. To migrate, LNAPL must exceed its residual capacity at the down gradient extreme of the plume and must have sufficient head or pressure to drive migration. Many LNAPL sites are quite mature, and therefore, LNAPL impacts may have reached the maximum extent years ago when there was pressure within the LNAPL body as a result of the release.

Dissolution and Migration in Groundwater, particularly the lighter and aromatic petroleum hydrocarbons will dissolve at some concentration into groundwater and migrate with groundwater. Dissolved petroleum hydrocarbons are biodegradable, and this biodegradation is what usually limits the extent of migration of a dissolved hydrocarbon plume. As a rule of thumb, the dissolved plume rarely extends more than about 200 feet beyond the LNAPL plume. This dissolution and biodegradation also slowly depletes the LNAPL mass.

Volatilization and Migration in the Vapor Phase, lighter weight petroleum hydrocarbons, in particular, will volatilize from the LNAPL and migrate in the vadose zone, primarily as a result of diffusion. At most sites, this volatile migration is limited by biodegradation, and vapor phase petroleum hydrocarbons rarely reach the ground surface. This process also slowly reduces the LNAPL mass.

Biodegradation, already mentioned above, is a very important process in understanding the limited migration and long-term fate of petroleum hydrocarbons in the environment. Petroleum hydrocarbons are naturally occurring compounds, and it has been estimated that natural petroleum seeps still account for as much (or more) release to the environment as manmade spills (Kvenvolden and Cooper, 2003). As a result, many naturally occurring organisms have evolved to use petroleum hydrocarbons as a food source, and over time, most petroleum hydrocarbon spills will eventually biodegrade. This is not to say that in many cases remediation is unnecessary, but rather, the natural effects of biodegradation need to be considered in any remedial strategy. Our present understanding of these processes indicate that biodegradation only occurs in association with water (such as the dissolved fraction in groundwater) and in pore water in the vadose zone, with some biodegradation occurring at water/oil interfaces. More recent Natural Source Zone Depletion (NSZD) research indicates that rapid biodegradation of low-solubility compounds can also occur in the pores directly in contact with LNAPL (e.g., Garg et al., 2017 for a summary), explaining the high NSZD rates observed in most LNAPL source zones.

Petroleum hydrocarbons biodegrade in the presence and absence of oxygen. Aerobic biodegradation, in which oxygen acts as an electron acceptor, usually occurs most rapidly. However, significant rates of anaerobic biodegradation are often observed. Anaerobic biodegradation can occur using electron acceptors such as nitrate, sulfate, or carbon dioxide. Biodegradation reduces hydrocarbon mass, and limits dissolved and vapor phase migration. One important biodegradation process is methanogenesis, an anaerobic process

² The term free product is commonly used to refer to mobile LNAPL; in most cases the terms are interchangeable.

that produces methane. This occurs in the pore water found in the LNAPL body, the methane is then typically released to the vadose zone where it encounters oxygen diffusing in from the atmosphere and biodegrades. This process is responsible for most of the petroleum hydrocarbon mass reduction at many sites.

3.0 Petroleum Hydrocarbon Site Management

Petroleum Hydrocarbon site management is driven by a wide variety of factors including:

Risk to Human Health or the Environment. Some petroleum constituents are known to be toxic. This has resulted in standards being set for some of the petroleum hydrocarbon constituents. For example, the U.S. Environmental Protection Agency (EPA) has set a drinking water standard for benzene of 5 µg/L. Benzene can be present in gasoline or JP-4 jet fuel in the 1% range, and can result in groundwater concentrations well in excess of 1,000 µg/L. For an actual risk to occur some route of exposure is required. Actual exposure to LNAPL is rare. More commonly, the concern is exposure to its dissolved components in drinking water, or its vapor constituents in vapor.

LNAPL Recovery – the extraction and removal of LNAPL – is often done, at times, independent of risk. It is not uncommon for site owners to implement some form of LNAPL recovery whenever measurable LNAPL (mobile LNAPL) is encountered in monitoring wells. Oftentimes, LNAPL mass is recovered for a set duration, rarely until all measurable LNAPL is removed. While this does remove mass, this typically does little to reduce risk unless the LNAPL is migrating³.

Historically, agencies have required removal of mobile LNAPL to the maximum extent practicable based on 40 Code of Federal Regulations (CFR) §280.64. Unfortunately, “extent practicable or practical” is not defined in the CFR and has been subject to many different interpretations. Some example endpoints are shown in **Table 1**. The authors do not advocate the application of many of these endpoints, these are simply exemplifying of endpoints that have been applied.

³ Migrating LNAPL does not always represent a risk, but at most sites where LNAPL is migrating some action to stop the migration is required.

Table 1 – Example endpoints, or definitions of “to the extent practical which have been applied.” (Adapted in part from ITRC, 2018a)

Metric	Example Endpoints
LNAPL Transmissivity , a measure of LNAPL mobility.	LNAPL Transmissivity < practicable recovery limit (0.1 to 0.8 ft ² /day)
Stable or controlled LNAPL plume	LNAPL plume no longer migrating.
Stable dissolved plume	Dissolved concentrations no longer migrating.
Relative removal rates compared to natural removal processes.	Engineered recovery rate similar to or less NSZD rate
Water/oil recovery ratio	250 gals:1 gal
Cost of LNAPL recovered	\$10 to \$100/gallon recovered
Decline in recovery rates	Less than 2 gallons/month. Less than 10% of initial recovery rates.
Measured LNAPL thickness in a well	0.1 inches to greater than 1 ft
Hydrocarbon concentration in soil	Usually based on some calculated estimate of residual capacity.

The authors advocate for selection of endpoints that are achievable and risk based. This is not always consistent with regulations, and the authors do not advocate ignoring regulation. To the contrary, site managers must comply with all applicable regulation. However, it has been the authors’ experience that most regulators are open to consideration of risk and many will make exceptions to normal policy and practice if a risk-based case can be made. Requirements vary from state to state. Some states do not generally allow measurable LNAPL to be left in place (such as Washington Department of Ecology and Montana Department of Environmental Quality (DEQ)). Some states like California have low-threat closure policies which outline general criteria to be satisfied in order to achieve closure at a site with presence of LNAPL. Other states like Texas have developed Risk Based LNAPL Management guidance. **Figure 4** summarizes the LNAPL recovery requirements of some select states (NAVFAC EXWC, 2017a). The requirements include in **Figure 4** are necessarily briefly summarized; actual requirements may vary on a site-specific basis.

State	Measurable Level that Permits Closure	Closed Sites with LNAPL Greater Than Measurable Level? If So, Additional Criteria Used?	Source
CA	Removed to extent practicable	Yes. "LUST sites can be closed if the required level of water quality will be attained within a reasonable period of time. California has closed several sites with LNAPL."	Menatti, 2010; NEIWPC, 2006; Lund et al., 2014
FL	0.01 ft	Yes. "A site with residual soil contamination or groundwater contamination above cleanup target levels can only receive No Further Action if there are institutional controls (deed restrictions) on the property."	NEIWPC, 2006
HI		Yes. "Only if BTEX and PAHs are ND or well below action levels and no other receptors."	NEIWPC, 2006
IA	<0.01 ft	Yes. "Following NAPL recovery activities, a site may be closed if product does not return in a monitoring well in excess of 0.02 ft for a period of one year."	NEIWPC, 2006
IL		Yes. Obtained closures in Illinois with notable NAPL thicknesses. Site-specific basis, essentially along the same lines as Massachusetts.	Payne, 2016
MA		Yes. "Non-Stable NAPL is not present under current site conditions and for the foreseeable future, and all NAPL with Micro-Scale Mobility is removed if and to the extent feasible based upon consideration of CSM principles."(*)	Marra, 2014
MI		Yes. "Recovery of all LNAPL with a transmissivity greater than 0.5 ft ² /day and that can be recovered in a cost-effective and efficient manner."	Lund et al., 2014
MO	Maximum extent practicable	Yes. "Site-specific criteria."	NEIWPC, 2006
NC	< 0.01 ft	No. "No receptors and removal is technically and economically infeasible."	NEIWPC, 2006; Lund et al., 2014
NV	0.5 inch	Yes. "If a risk-based analysis was performed showing no vulnerable receptors and a fate and transport analysis performed showing that there was little potential for migration."	NEIWPC, 2006
RI		No	Lund et al., 2014
TX	Unrecoverable or impractical	Yes "Closure can be granted when recoverable NAPL is still present if there are no receptors and the plume is stable."	NEIWPC, 2006
UT	1/8-inch	Yes. "RBCA-based approach considered on site-specific basis."	Menatti, 2010
VA	<0.01 ft	Yes. "The data should support the claim that the technologies used and/or evaluated are no longer effective and that additional recovery is not practicable. If >0.01 ft exists also have to show: a) Remaining LNAPL and dissolved-phase constituents are not a risk to human health or the environment, and b) NSZD of the LNAPL body and natural attenuation of the dissolved-phase plume are documented as occurring at the site and are expected to further mitigate risk from the release, and c) The areal extent of the free phase plume at the site is shown to be stable or decreasing"	NEIWPC, 2006; Steers, J., 2012; Lund et al., 2014
WA	<0.01 ft	No. "Ecology won't close LUST sites with measurable free product"	NEIWPC, 2006

Notes: *Non-Stable NAPL: a NAPL with a footprint that is expanding laterally or vertically by: (a) migrating along or within a preferred flow path; (b) discharging or periodically discharging to a building, utility, drinking water supply well, or surface water body; or (c) spreading as a bulk fluid through or from subsurface strata; and NAPL with Micro-Scale Mobility: a NAPL with a footprint that is not expanding, but which is visibly present in the subsurface in sufficient quantities to migrate or potentially migrate as a separate phase over a short distance and visibility impact an excavation, boring, or monitoring well. (Marra, 2014).

Figure 4 – Summary of LNAPL Recovery Limits for Site Closure for Key Navy States, (NAVFAE EXWC, 2017)

In managing LNAPL remediation, the authors advocate for the most cost-effective approach that will satisfy applicable regulatory requirements. At many sites this can be a demonstration that risk-based end points have been achieved. At other sites, additional remediation may be required. In situations where regulation requires additional remediation without risk basis, the authors recommend the lowest cost actions that will satisfy regulation.

LNAPL remediation endpoints advocated by the authors include:

- Mandatory or baseline endpoints:
 - No unacceptable risk. This is a minimal endpoint; **the authors do not ever advocate ignoring unacceptable risk.**
 - No LNAPL migration or potential for migration. Although it is possible that a migrating LNAPL plume does not present risk, no further migration means no further environmental impact, and most regulatory agencies and responsible site owners accept nothing less.
 - Compliance with regulatory requirements. Note that the authors have listed this as a mandatory endpoint, and we know from experience that many regulators are open to negotiation and discussion as to what is acceptable. We recommend setting technical endpoints first and then working with regulators to achieve the most cost-effective solution possible.
- Practicability endpoints, to be applied only after the baseline endpoints have been addressed:
 - No unacceptable risk may be sufficient, even if LNAPL recovery is possible or practical, this should always be considered.
 - Engineered active remediation does not significantly improve on the removal rates due to natural processes (NSZD). A rational case can be made that it is not practical to expend additional remediation dollars if no great improvement is possible
 - Cost – the cost of LNAPL removal is within a reasonable range. In practice a cost of \$10/gallon of recovered LNAPL is often used, a higher cost of \$100/gallon is sometimes also used. There is a consensus amongst practitioners that higher per gallon costs are not reasonable. Other cost factors should be considered, for example, at some shallow or small sites the cost of excavation may be less than the cost of longer-term management. And there is the rare exception where the cost of LNAPL recovery is less than the value of the recovered LNAPL, which can at times be sold.

4.0 LNAPL Site Management Tools

In this section, we discuss tools recommended to site managers to develop risk-based approaches to manage and close LNAPL sites. These tools are well described in the literature, particularly in ITRC and American Petroleum Institute (API) websites and documents. It is not the intent of the authors to provide the details that can be found on those sites. Rather, this document intends to direct site managers to those sources throughout the text.

5.0 Natural Source Zone Depletion (NSZD)

NSZD is the sum of various processes that reduce LNAPL mass over time. This is also called natural attenuation (typically abbreviated as monitored natural attenuation [MNA]). Some authors distinguish the terms using MNA to refer to processes that occur in groundwater which limit hydrocarbon plume growth, and NSZD to refer to processes that are expressed in the vadose zone and tend to be rates that can be used to estimate mass removal over time. We will adhere to that practice.

NSZD is the reduction in LNAPL mass over time due to natural processes. For petroleum hydrocarbons, this primarily results from aerobic and anaerobic biodegradation, and there are multiple tools available for measuring these rates. Methanogenesis is generally regarded as one of the more predominant anaerobic LNAPL biodegradation processes during NSZD. Under these conditions, gaseous, low-solubility methane migrates upwards in the vadose zone until it encounters aerobic conditions where it may biodegrade to carbon dioxide. Other petroleum hydrocarbon degrading processes, both anaerobic and aerobic, also produce carbon dioxide. These degradation processes are all heat generating. Measurement of NSZD depends on the measurement of carbon dioxide production, oxygen depletion or heat generation. Tools currently available and in use today include:

- Oxygen consumption – the rate of oxygen consumption can be determined from the vertical distribution of oxygen and other gases in the vadose zone. This was the original NSZD technique first published by the ITRC in 2009 (ITRC, 2009b). It requires soil vapor monitoring at various depths, as well as some measure or estimate of oxygen diffusion rates. While less used than other methods now, it is still in practice and a method to be considered, particularly at sites where the vapor monitoring points may already exist.
- Carbon dioxide production can be measured and used to determine petroleum hydrocarbon biodegradation rates. Techniques include:
 - Carbon Traps, such as those used at the Fallon site, are typically a device placed on the ground surface that is left in place for a time, typically a few weeks and carbon dioxide is trapped in a solid hydroxide-based media. The traps are then returned to a laboratory where the mass of accumulated carbon dioxide is determined.
 - Flux chambers can be placed on the ground measuring directly the more or less instantaneous carbon dioxide flux. This is a shorter-term measurement typically requiring less time and often providing real time data. A common approach is based on the Dynamic Closed Chamber (DCC) illustrated in **Figure 5** below.

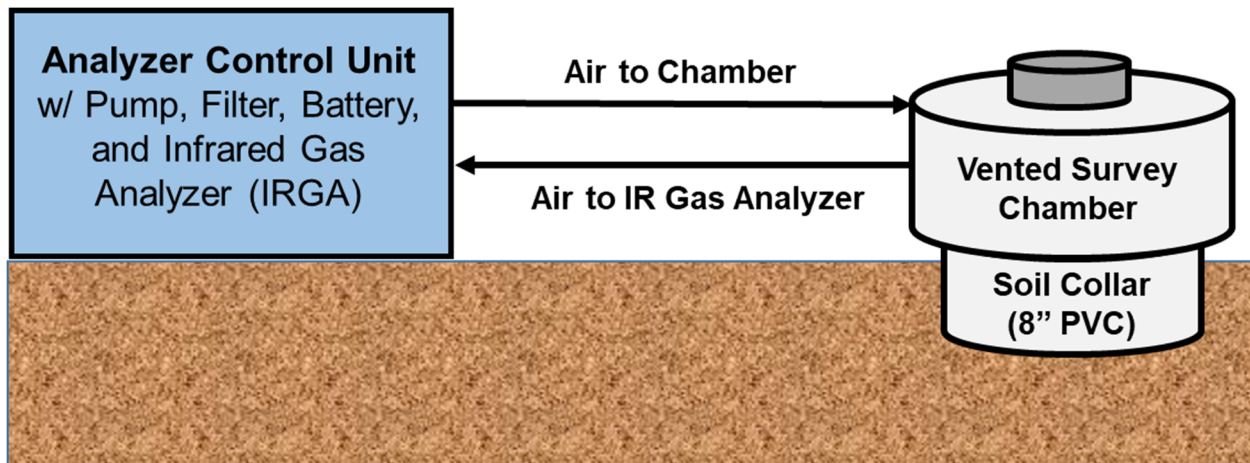


Figure 5 – Animation Depicting DCC Apparatus and Setup

- Temperature based methods depend on measurements of temperature increases due to petroleum hydrocarbon biodegradation (Zeman et al., 2014; Karimi et al., 2018). This can be as simple as lowering a temperature probe in a well and comparing temperature profiles in contaminated and uncontaminated locations to a more complex array of temperature probes continuously monitored (Sweeney and Ririe, 2014).

The measurements vary from technique to technique; however, all can be reduced to some unit of mass removed per unit area, a very convenient and widely used unit is gallons of LNAPL per acre per year.

When evaluating NSZD, many factors should be considered. A partially important factor is the background associated with the method. That is, for example what would the rate of carbon dioxide production or temperature profile be without petroleum hydrocarbon biodegradation. A variety of techniques have been developed to address this background issue. Detailing all of them is beyond the scope of this report, but can be found in the various documents cited. At some sites it is possible to find a background location, where no contamination has occurred, but at many locations, this is difficult. One particularly creative approach is to analyze the trapped carbon dioxide for ^{14}C content. ^{14}C is a naturally occurring (but unstable) carbon isotope found in atmospheric carbon dioxide. However, this is not found in ancient crude petroleum. By determining the ^{14}C content of the carbon dioxide, any effect of the decay of more recent plant-based material can be deduced leaving carbon dioxide produced by the petroleum hydrocarbons. Other background considerations relevant to other methods exist and are available in cited documents.

There are other considerations that need to be given to the interpretation of NSZD data, including timing (rates may vary seasonally and with water table elevation) and spatial variability. For example, surface carbon dioxide flux rates often vary considerably over short distances. This may be due to variable degradation rates; it can also be the result of differing underlying soils and the ability to transmit carbon dioxide vertically. At most sites, the measured rates are assumed to be representative of the footprint of the LNAPL plume. However, the gas production/consumption or thermal effects can be spread over a larger area, particularly at deeper sites. **Table 2** identifies some of the pros and cons of the various NSZD measurement methods.

Table 2 – Pros and Cons of Various NSZD Measurements and Methods

Method	Pros	Cons	Sources of more information
Gradient (typically oxygen consumption)	The original method; well understood. On sites where soil vapor probes already exist it can be low cost.	Requires multi depth soil vapor probes and a measure of estimate of soil vapor diffusivity.	Lundegard and Johnson, 2006; Sihota et al., 2011
Carbon Traps	Easy to deploy well understood method. Longer term data collection reduces variability.	Can be higher cost per location than flux chamber or thermal.	McCoy et al., 2014
Flux chambers	Typically, fast and lower cost per point. Well understood method.	Short term measurements can be subject to higher variability, due to factors such as barometric pressure changes.	Sihota et al., 2011
Thermal	Strong technical basis, becoming better understood.	The emerging technique, less well understood and accepted, but this is changing.	Stockwell, 2015

Before measuring NSZD rates, it is important to consider how the data will be used to support the site remediation and management strategy. This will often dictate the number of samples required as well as the frequency of sampling. It should also be noted that NSZD measurements are not precise and that rate measurements are not accurate as a forecasting tool. Rather, these are a means to help make site management decisions, often for comparison to what can be achieved with engineered remediation.

Additional information regarding Natural Source Zone Depletion can be found in ITRC LNAPL Guidance (ITRC, 2018a).

6.0 LNAPL Mobility, Migration Potential, and Recoverability

For any site, it is important to understand LNAPL mobility and to determine the potential for migration. The practicality of LNAPL recovery is related to mobility. LNAPL mobility and migration are complex processes. The intent of this section is to provide an overview of the principals of LNAPL movement and available tools for assessing LNAPL. More detailed and in-depth information is available in the resources cited.

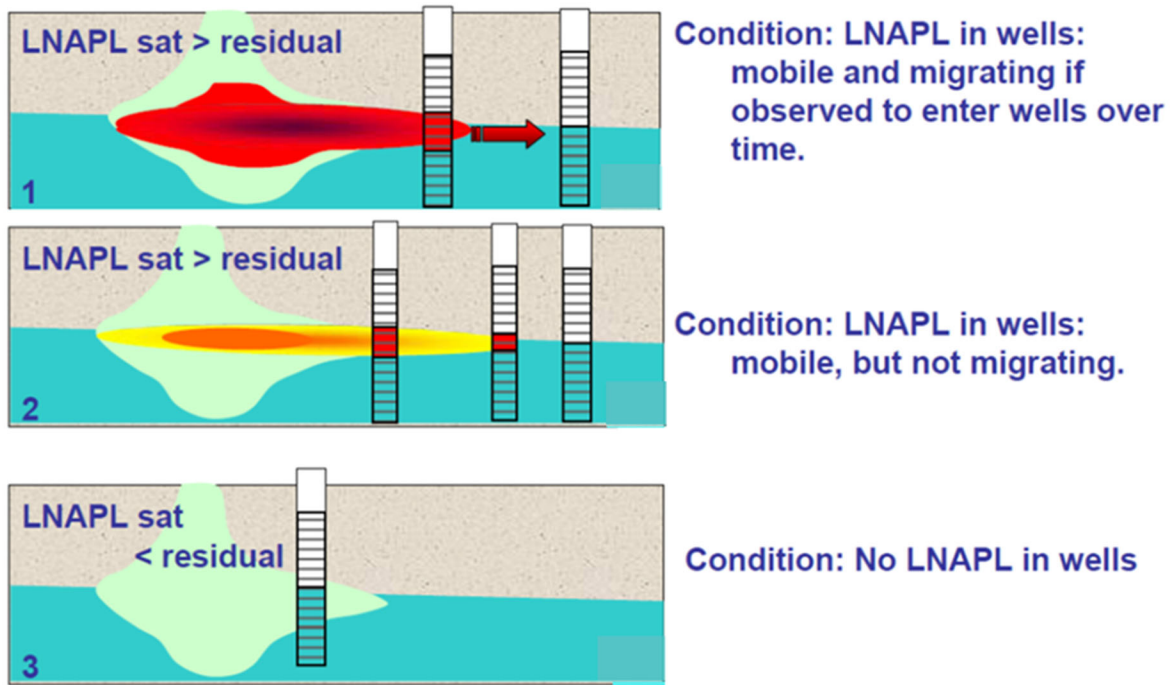


Figure 6 - Example of Petroleum Hydrocarbon Release and Subsurface Behavior (ITRC, 2009)

7.0 LNAPL Mobility

Mobile LNAPL is defined as LNAPL present in soil at concentrations above residual saturation – it will migrate into a monitoring well and can be measured. However, as discussed below, mobile LNAPL is not always the proper descriptor of migrating LNAPL.

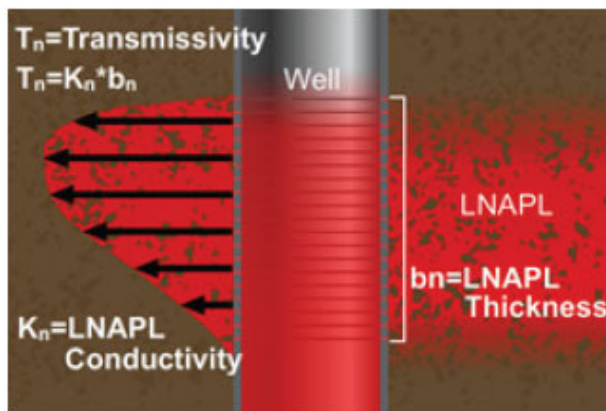


Figure 7 – Transmissivity Schematic (NAVFAC, 2015)

LNAPL Transmissivity has been emerging as the standard for measuring free product mobility and assessing recoverability. It has largely replaced measurement of LNAPL thickness in wells.⁴ Transmissivity is defined as the volume of LNAPL movement through a unit width of aquifer per unit time per unit drawdown. Units for this measurement are length²/time. Transmissivity can be calculated using American Society for Testing and Materials (ASTM) LNAPL Transmissivity Standard (E2856-13). Additional technical guidance can be found in the ITRC LNAPL Updated Guidance (ITRC, 2018) and API LNAPL Transmissivity and other Guidance.

⁴ LNAPL thickness in wells, commonly called free product thickness is still measured at LNAPL sites and has utility, sometimes as a remedial goal or standard. However, it is not clear that LNAPL thickness does not directly relate to LNAPL mass, recoverability, or migration potential.

Transmissivity rates are dependent on multiple parameters including soil type and properties (e.g. porosity, conductivity), chemical and physical properties of the LNAPL (e.g. density, viscosity, composition), LNAPL saturation in the formation, and thickness of the mobile LNAPL. As such, this measurement provides a much more comprehensive evaluation of product mobility and recoverability at a site.

LNAPL transmissivity can be measured using a variety of methods including:

- The short term **baildown or slug test**, LNAPL is removed from a well, and the rate of its recovery measured over time. This is probably the most common technique.
- The **manual skimming** method is accomplished by achieving steady state LNAPL recovery at a rate that maintains a consistent drawdown.
- Long term **LNAPL recovery data** can be used to determine transmissivity. This can be a convenient technique on sites where long term LNAPL recovery operations have been in place and the data are available.
- A less commonly used but effective approach is based on the use of an **LNAPL tracer** placed in a well and the rate of tracer disappearance is observed to derive LNAPL transmissivity.

A discussion of the application of these methods is beyond the scope of this document, but there are many quite informative guidance documents available.

Based on ITRC's LNAPL Transmissivity Guidance (ITRC, 2018a), LNAPL recovery is considered practical if transmissivity is greater than 0.1 to 0.8 ft²/day, it is not considered practical at lower transmissivities. Some states have set remedial goals based on transmissivity.

Other techniques including laboratory analysis are available to determine LNAPL mobility. For example, one test involves a centrifuge test where a centrifugal force of 1,000 times gravity is used to evaluate product mobility (ASTM D425M). An issue of concern with these laboratory tests is that they test only a small sample of aquifer material and are less likely to provide useful mobility data than the field-based transmissivity measurements.

8.0 LNAPL Recoverability

The ITRC based guidance that LNAPL is recoverable above the transmissivity range of 0.1 to 0.8 ft/day range (but not below) is widely accepted. This does not mean that LNAPL recovery is always necessary above that range if there is no unacceptable risk – if the LNAPL is not migrating, recovery may not be necessary. On the other hand, in some regulatory jurisdictions there are requirements to recover LNAPL at lower transmissivities. When this is the case, the potential for removing sufficient mass to provide any cost-effective benefit is limited.

Ultimately, the decision to recover or not to recover and the level of effort expended if recovery is chosen is a cost benefit analysis constrained by regulatory requirements. Technical guidance can inform that decision.

9.0 LNAPL Migration

It is important to understand the migration or potential for migration of an LNAPL plume. Most of the LNAPL plumes encountered at U.S. Department of Defense (DoD) sites have long past the potential for mobility, however plumes with new or ongoing LNAPL releases do have the potential to migrate.

LNAPL can migrate after release until capillary forces stop the migration. Over time, as LNAPL weathers and concentrations are reduced, the potential for migration also becomes reduced, and under most cases, once migration stops, it will not restart. There are exceptions to this, however. Since LNAPL has a lower residual saturation, it is therefore mobile at lower concentrations in unsaturated soil than in saturated soil, and at some sites and under certain conditions, a falling water table can remobilize immobile LNAPL.⁵

Tools available to determine LNAPL migration and migration potential include:

- Historic plume data when available is the most definitive tool. There are a number of approaches to evaluating plume data:
 - Extent of LNAPL and dissolved phase plume – if these are stable or being reduced over time, this is clear evidence of no migration.
 - Declining transmissivity and/or LNAPL thickness – (less effective than transmissivity) in wells over time, particularly when coupled with a stable extent.
 - Measuring mobile LNAPL in wells over a smaller area is a very effective means of evaluating whether there is a lack of migration. At many sites, the maximum historic extent of LNAPL migration can only be understood through observation of LNAPL concentrations in soil downgradient of the existing mobile LNAPL plume. Signs of LNAPL migration would most closely be aligned with high LNAPL concentrations in soil samples, detection of LNAPL downgradient of existing LNAPL via laser-induced fluorescence (LIF) probing, as well as observing strong hydrocarbon odors or texture in soil samples collected downgradient of the LNAPL Plume.
- Lower LNAPL transmissivity near the downgradient extent of the LNAPL plume can be evidence of limited migration; high LNAPL transmissivity near the downgradient extent of the LNAPL plume can be evidence of potential for migration.
- The API (1998) has published a technique to determine the critical LNAPL thickness above which spreading or migration can occur and below which the LNAPL will not migrate.

10.0 Risk Assessment

LNAPL can create a number of risks, **Figure 8** illustrates most of these.

⁵ This is most likely to occur at sites where during the migratory phase of plume development migration was halted by a rising water table, then when the water table falls to or below its former level migration may restart. This is not common and depends on trapped LNAPL below the water table at concentrations below the saturated residual capacity and above the unsaturated residual capacity.

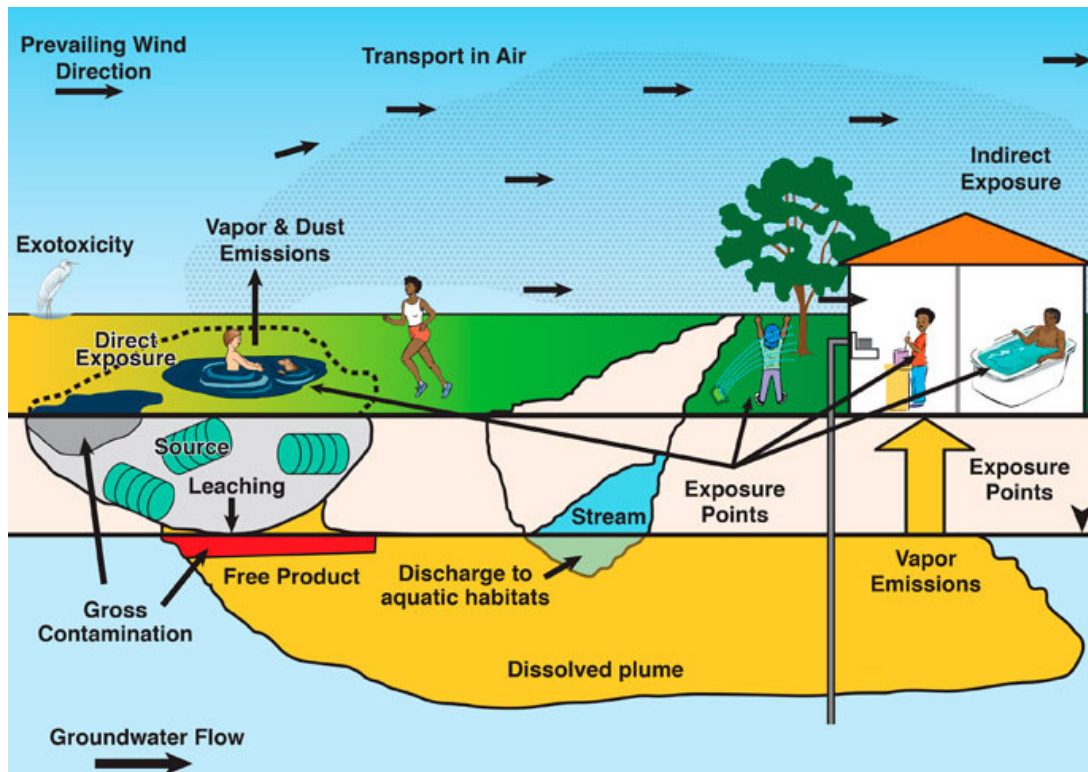


Figure 8 – Possible Exposure Routes Associated with LNAPL (ITRC, 2018b)

At most DoD sites, the exposure routes of greatest concern are related to groundwater, soil, and vapor intrusion, but other risks should be considered. Explosive risk from vapors is rare as petroleum hydrocarbons typically biodegrade before becoming problematic in buildings. At some sites, methane generated as the result of anaerobic degradation of LNAPL constituents has been raised as a concern. ASTM (E2993 – 16) has published guidance for assessing this risk, but the actual risk at most petroleum hydrocarbon sites has been found to be quite low. Migration to surface water, in the form of sheens, can occur but is rare at DoD sites and will not be addressed here.

Vapor intrusion can present a risk due to the biodegradability of LNAPL constituents. However, this risk is lower than for comparably volatile chlorinated solvents. As a rule of thumb ITRC guidance suggests vapor intrusion may be a risk if LNAPL is present within about 15 to 20 feet of a structure. Many DoD LNAPLs are heavier products containing little of the volatile organic compound (VOCs) (such as benzene) that are of vapor intrusion concern.

Risk based on exposure to contaminated soil or groundwater is the concern that drives remediation at most DoD LNAPL sites. Risk of exposure to individual petroleum hydrocarbon compounds such as benzene or naphthalene can be managed using conventional risk assessment techniques. However, since LNAPLs are a mixture of many different petroleum hydrocarbons (most of which are never individually quantified as a mixture), assessing chemical risk can be more challenging. Fortunately, many regulatory agencies recognize this and base cleanup standards on individual compounds, such as the drinking water maximum contaminant level (MCL) for benzene.

Most regulatory agencies do not require addressing the LNAPL as a whole. However, some do require total petroleum hydrocarbon (TPH) analysis, and some even set cleanup standards for soil or groundwater based on TPH. This is not risk based, however there is an approach originally published by the TPH working group to estimate risk associated with TPH. The method basically involves analyzing different TPH fractions (aromatic and aliphatic, carbon number, etc.), and then assigning risk to these individual categories based on the assumption of some surrogate compound representative of the fraction. This approach, though not as quantitatively risk based as setting standards for individual hydrocarbons, can represent a significant improvement on simple TPH standards.

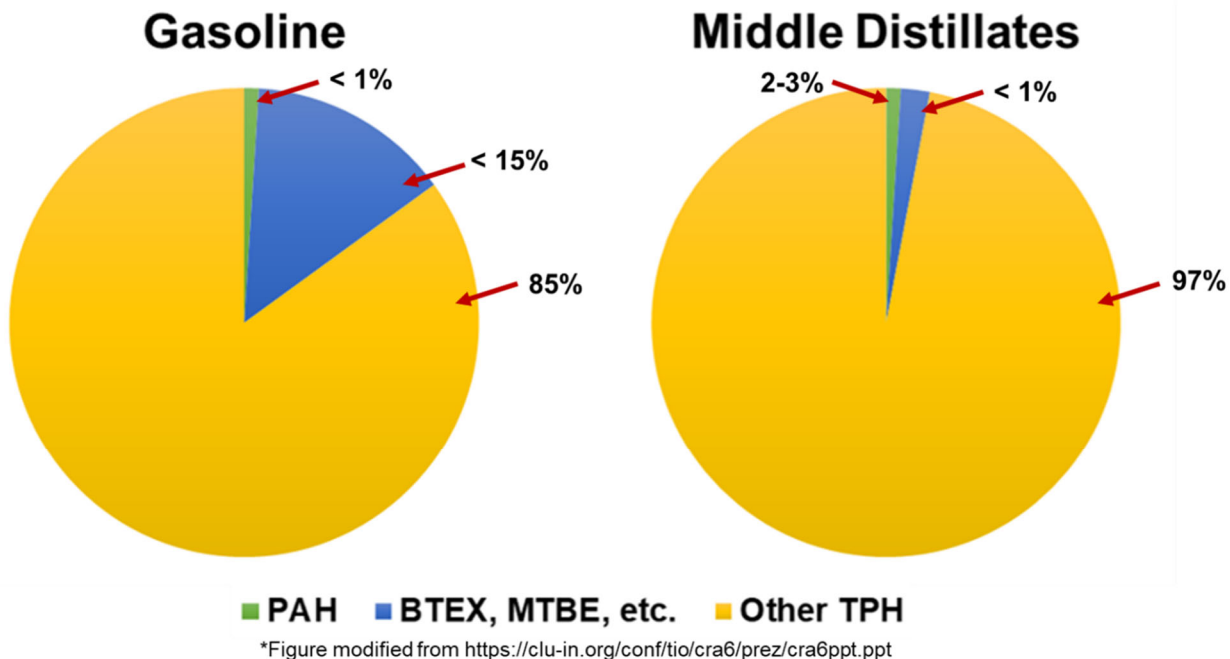


Figure 9 – Comparison of Gasoline and Middle Distillates Petroleum Hydrocarbon Component Distribution. These data indicate that most petroleum hydrocarbons in LNAPL are not identified and not of toxic concern (Data adapted from Brewer, 2009)

Since the original TPH working group method was published in 1999, other versions of the method have been adopted. For example, the state of Massachusetts has an approach that is widely used, as do the states of Texas and Alaska. The ITRC has recently published guidance updating the approach (ITRC, 2018b).

If compounds other than those typically analyzed with known risk factors are to be considered in a remedial strategy, the TPH working group approach to estimating risk is recommended. Many of the compounds of greatest risk are only present in relatively low concentrations in LNAPL; this method takes that into account.

11.0 Resources

LNAPL site management requires reliance on many tools and underlying guidance documents. In this report our objective is to inform site managers of the state of the practice for LNAPL site

management and the tools available that site managers should be aware of and consider using. **Table 3** lists many of the resources that can be accessed for technical guidance and support.

Table 3 – Resources for Technical Guidance and Support

Source	Applications	Link or full citation
API	API has a resource center with links to many useful tools	https://www.api.org/oil-and-natural-gas/environment/clean-water/ground-water/lnapl
	LNAPL Transmissivity Workbook: A Tool for Baildown Test Analysis	https://www.api.org/~/-media/4762%20LNAPL%20Tn%20wkbk%20Baildown%20userguide%20Apr2016%20(2).pdf
	LNAPL Distribution and Recovery Model (LDRM)	https://www.api.org/oil-and-natural-gas/environment/clean-water/ground-water/lnapl/ldrm
	Evaluating Hydrocarbon Removal From Source Zones And Its Effect On Dissolved Plume Longevity And Concentration	https://www.api.org/oil-and-natural-gas/environment/clean-water/ground-water/lnapl/evaluating-hydrocarbon-removal
	Interactive LNAPL Guide	https://www.api.org/oil-and-natural-gas/environment/clean-water/ground-water/lnapl/interactive-guide
	Methods For Determining Inputs To Environmental Petroleum Hydrocarbon Mobility And Recovery Models	https://www.api.org/oil-and-natural-gas/environment/clean-water/ground-water/lnapl/mobility-recovery
ASTM	E2856 - 13 Standard Guide for Estimation of LNAPL Transmissivity	https://www.astm.org/Standards/E2856.htm
ITRC	LNAPL Site Management: LCSM Evolution, Decision Process, and Remedial Technologies	https://lnapl-3.itrcweb.org

12.0 References

- American Petroleum Institute (API). 1998. *Recommended Practices for Core Analysis*. Recommended Practice 40. February 1998.
- American Petroleum Institute (API), 2001. *Risk-Based Methodologies for Evaluating Petroleum Hydrocarbon Impacts at Oil and Natural Gas E&P Sites*. API Publication Number 4709. February 2001.
- American Petroleum Institute (API), 2012. *User Guide for the API LNAPL Transmissivity Workbook: A Tool for Bardown Test Analysis*. API Publication. September 2012.
- ASTM Standard Guide for Estimation of LNAPL Transmissivity. ASTM E2856 – 13
- ASTM Standard Guide for Evaluating Potential Hazard as a Result of Methane in the Unsaturated Zone. ASTM E2993-16
- Garg, S., Newell, C.J., Kulkarni, P.R., King, D.C., Adamson, D.T., Renno, M.I. and Sale, T. 2017. *Overview of Natural Source Zone Depletion: Processes, Controlling Factors, and Composition Change*. *Groundwater Monitoring & Remediation*, 37(3), pp.62-81.
- ITRC. 2009a. *Evaluating LNAPL Remedial Technologies for Achieving Project Goals. LNAPL-2*. Washinton, D.C.: Interstate Technology Regulatory Council, LNAPL Team.
- ITRC. 2009b. *Evaluating Natural Source Zone Depletion at Sites with LNAPL*. Washington, D.C.: Interstate Technology Regulatory Council, LNAPL Team.
- ITRC. 2018a. *LNAPL Site Management: LCSM Evolution, Decision Process, and Remedial Technologies. LNAPL-3*. Washington, D.C.: Interstate Technology and Regulatory Council, LNAPL Update Team.
- ITRC. 2018b. *TPH Risk Evaluation at Petroleum-Contaminated Sites. Washington, D.C.: Interstate Technology and Regulatory Council, TPH Risk Evaluation Team*.
- Karimi A.K., Stockwell, E.B., Piontek, K.R. and Sale, T.C. 2018. *Thermal Monitoring of Natural Source Zone Depletion*. *Groundwater Monitoring & Remediation*, 38(3), pp.43-52.
- Kvenvolden, K.A. and Cooper, C.K., 2003. *Natural seepage of crude oil into the marine Environment*. *Geo-Marine Letters*, 23, pp.140-146.
- Lundegard, P. D. and Johnson, P. C., 2006. *Source Zone Natural Attenuation at Petroleum Hydrocarbon Spill Sites—II: Application to a Former Oil Field*. *Ground Water Monitoring & Remediation*. 26: 93–106.
- McCoy, K., Zimbron, J., Sale, T., Lyverse, M., 2014. *Measurement of Natural Losses of LNAPL Using Carbon Traps*. *Groundwater. Methods Note*. 2014.

- NAVFAC, 2015. Petroleum Site Management Update – A Roadmap to Closure. Oak Ridge National Laboratory (ORNL). 1994. *Remedial Investigation Report, Naval Air Station Fallon, Fallon, Nevada*. Final. September.
- NAVFAC EXWC. 2017a. *New Developments in LNAPL Site Management Fact Sheet*. https://www.navfac.navy.mil/content/dam/navfac/Specialty%20Centers/Engineering%20and%20Expeditionary%20Warfare%20Center/Environmental/Restoration/er_pdfs/1/navfacexwc-ev-fs-1709-newdev-lnapl-201704.pdf
- NAVFAC EXWC. 2017b. *Complex Challenges at Light Non-Aqueous Phase Liquid Sites*. https://www.navfac.navy.mil/navfac_worldwide/specialty_centers/exwc/products_and_services/ev/go_erb/focus-areas/petroleum-sites.html
- Shaw Group Inc. (Shaw). 2012. *Status Report, Second Quarter 2012, Free Product Recovery at Installation Restoration Sites 2 and 4, Underground Storage Tank-Restoration Site 1 (395), NAS Fallon, Nevada*. Final. September.
- Sihota, N.J., Singurindy, O., Mayer, K.U., 2011. *CO₂-Efflux Measurements for Evaluating Source Zone Natural Attenuation Rates in a Petroleum Hydrocarbon Contaminated Aquifer*. *Environmental Science and Technology*. 45, 482–488
- Stockwell, E., 2015. *Continuous NAPL Loss Rates Using Subsurface Temperatures*. Thesis. Department of Civil and Environmental Engineering. Colorado State University.
- Sweeney, R.E. and Ririe, G.T., 2014. *Temperature as a tool to evaluate aerobic biodegradation in hydrocarbon contaminated soil*. *Groundwater Monitoring & Remediation*, 34, pp.41-50.
- Zeman, N.R., Renno, M.I., Olson, M.R., Wilson, L.P., Sale, T.C. and Susan, K. 2014. *Temperature Impacts on Anaerobic Biotransformation of LNAPL and Concurrent Shifts in Microbial Community Structure*. *Biodegradation*, 25(4), pp.569-585.

Appendix A: Points of Contact

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