TECHNICAL REPORT
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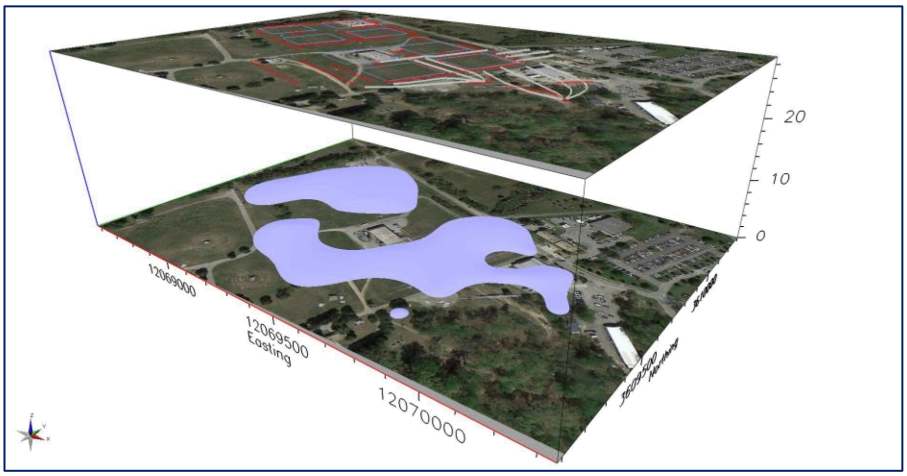
CASE STUDY REVIEW OF OPTIMIZATION PRACTICES AT NAVY PETROLEUM SITES



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14. ABSTRACT
Optimization helps to set petroleum sites on the most fitting path toward meeting remedial action objectives (RAOs) and achieving response complete (RC). Optimization can be applied across all phases of the cleanup process. Optimization helps to expedite the cleanup process by increasing efficiency, reducing costs, accelerating cleanup timeframes, and improving sustainability metrics. This report provides an overview of optimization concepts as applied to the cleanup of Department of the Navy (DON) petroleum sites. This case study review was conducted to identify specific examples where optimization concepts and best practices advocated for petroleum site management were successfully implemented at DON sites.

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ACRONYMS AND ABBREVIATIONS

API	American Petroleum Institute
ARAR	applicable or relevant and appropriate requirement
bgs	below ground surface
BTEX	benzene, toluene, ethylbenzene and total xylenes
C8H18	octane
CAP	corrective action plan
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFR	Code of Federal Regulations
CO_2	carbon dioxide
CSM	conceptual site model
DCA	dichloroethane
DCE	dichloroethane
DEQ	Department of Environmental Quality
DFSP	Defense Fuel Supply Point
DO	dissolved oxygen
DON	Department of the Navy
DRO	diesel range organics
DTSC	Department of Toxic Substances Control
EPH	extractable petroleum hydrocarbon
ERP	Environmental Restoration Program
FFSRA	Federal Facilities Site Remediation Agreement
FID	flame ionization detector
FL-PRO	Florida Residual Petroleum Organic
FPRS	free product recovery system
GRO	gasoline range organics
HHRA	Human Health Risk Assessment
HRO	heave range organics
IRP	Installation Restoration Program
ITRC	Interstate Technology and Regulatory Council
JP	jet petroleum
LIF	laser induced fluorescence
LNAPL	light non-aqueous phase liquid
LUC	land use control
MADEP	Massachusetts Department of Environmental Protection

MCAS	Marine Corps Air Station
MDEQ	Michigan Department of Environmental Quality
MNA	monitored natural attenuation
MPE	multiphase extraction
MPRS	mobile product recovery system
MTBE	methyl tert butyl ether
NAVFAC	Naval Facilities Engineering Systems Command
NAVFAC EXWC	Naval Facilities Engineering and Expeditionary Warfare Center
NAWS	Naval Air Weapons Station
NFSO	Navy Special Fuel Oil
NOU	Northern Operable Unit
NSZD	natural source zone depletion
O&M	operations and maintenance
OM&M	operation, maintenance, and monitoring
ORP	oxidation reduction potential
OU	operable unit
OWS	oil-water separator
PIANO	paraffins, iso-paraffins, aromatics, naphthenes, and olefins
PID	photoionization detector
RAA	remedial alternative analysis
RAO	Remedial Action Objective
RAP	Remedial Action Plan
ROD	Record of Decision
RPM	Remedial Project Manager
RSE	remedial system evaluation
RWQCB	Regional Water Quality Control Board
SESR	surfactant-enhanced subsurface remediation
SGC	silica gel cleanup
STAR	self-sustaining treatment for active remediation
SVE	soil vapor extraction
SVOC	semi-volatile organic compound
TCE	trichloroethene
TFR	total fluids recovery
TPH	total petroleum hydrocarbon
TPHCWG	TPH Criteria Working Group Method
U.S. EPA	United States Environmental Protection Agency
UST	underground storage tank
VC	vinyl chloride
VES	vacuum-enhanced skimming

VOC	volatile organic compound
VPH	volatile petroleum hydrocarbon
VRP	Voluntary Remediation Program
WSDETCM	Washington State Department of Ecology Toxics Cleanup Method

1.0 INTRODUCTION

Optimization helps to set petroleum sites on the most fitting path toward meeting remedial action objectives (RAOs) and achieving response complete (RC). Optimization can be applied across all phases of the cleanup process. Optimization helps to expedite the cleanup process by increasing efficiency, reducing costs, accelerating cleanup timeframes, and improving sustainability metrics. This report provides an overview of optimization concepts as applied to the cleanup of Department of the Navy (DON) petroleum sites. This case study review was conducted to identify specific examples where optimization concepts and best practices advocated for petroleum site management were successfully implemented at DON sites. Supplemental information regarding petroleum site management can be found in the Naval Facilities Engineering and Expeditionary Warfare Center (NAVFAC EXWC) Technical Report - Transition of Petroleum Sites to Closure or Passive Remedies: Evaluating Natural Source Zone Depletion (NSZD) and Other Methods (NAVFAC EXWC, 2021).

1.1 Overview

The Navy's optimization policies and guidance provide a framework for evaluating site information and collecting new information to close data gaps. The Navy's optimization approach involves the following key components: conducting independent optimization reviews; utilizing a continually updated conceptual site model (CSM); ensuring the remedy is targeting appropriate locations or zones; incorporating a treatment train approach to adapt to changing site conditions; and developing an exit strategy to minimize prolonged operations and maintenance (O&M). At petroleum sites, the need for an optimized remedial approach is often triggered by diminishing returns in efforts to recover light non-aqueous phase liquid (LNAPL) from the subsurface. State-specific low-threat and risk-based closure guidance can be utilized as part of the evaluation process to determine if LNAPL may remain in place, while maintaining protectiveness of human health and the environment. This case study review identified Navy petroleum cleanup sites where various optimization strategies were applied. Documentation was collected and reviewed on the remedy status and optimization approaches from 10 Navy sites located nationwide. Two Navy sites were then selected to further highlight optimization concepts based on: 1) closely following optimization principles and a multiple lines of evidence approach; 2) determining stable and/or decreasing LNAPL source zones and associated groundwater plumes; and 3) supporting an evaluation that LNAPL recovery efforts were yielding diminishing returns.

1.2 Report Organization

This report provides an overview of optimization concepts presented in Navy policy and guidance with a focus on the strategies most applicable to petroleum sites. The report is organized into the following sections:

- Section 2.0 Background: Includes a summary of the Navy's recommended optimization practices and their application to petroleum sites, as well as an overview of federal and state regulations related to petroleum site assessment and closure.
- Section 3.0 Case Study Review: Includes a summary of the types of Navy petroleum sites identified, along with two case studies that demonstrate the application of petroleum site management and optimization strategies.

- Section 4.0 Key Findings: Presents the overall conclusions in relation to the specific optimization strategies employed, LNAPL recovery effectiveness, and the use and acceptance of NSZD.

2.0 BACKGROUND

Several optimization strategies can be applied at DON petroleum sites with a major focus on keeping an updated CSM and understanding the LNAPL source behavior. The recommended optimization steps are utilized within the framework of applicable federal and state regulations for petroleum sites. This section reviews petroleum site management concepts, optimization strategies, and regulations specific to petroleum sites.

2.1 Overview of Navy's Optimization Concepts Used at Petroleum Sites

Optimization can be applied across all phases of the cleanup process. This includes the early phases when RAOs are developed and remedies are selected. The optimization efforts continue to focus on the latest site conditions and remediation system performance over time. These ongoing efforts help to guide changes to achieve RAOs more efficiently and effectively. The CSM is reviewed and updated to ensure that it accurately reflects current site conditions and identifies all sources and exposure pathways. The remedial action is then evaluated with respect to the CSM to determine if continued operation will further mitigate risk and/or if changes are warranted to improve performance to reduce lifecycle cost or reduce the remedial timeframe. Following these optimization practices helps to ensure that the remedy is reducing site risk and achieving RAOs, while generating the data and lines of evidence required to achieve RC and/or site closure.

Optimization of remedial actions at petroleum sites follows this general approach, supplemented by tracking specific metrics to reach RC and/or site closure. One challenge faced at petroleum sites is the presence of LNAPL, which must be recovered to the "maximum extent practicable." Fortunately, with an improved understanding of LNAPL behavior in the subsurface and actual risk posed by residual LNAPL, interpretation of what is "practical" to recover at a site is evolving and does not always require that LNAPL be removed to a pre-defined minimum measurement (e.g., to less than 0.01 ft). Several states, such as California, Massachusetts, and Virginia, have developed low-threat or risk-based closure criteria and guidance that allow for site closure with LNAPL in place.

A successful management strategy to achieve site closure at a low-risk petroleum site requires a comprehensive and up-to-date CSM, which will serve as a foundation for optimizing remedial actions. Often, an adequate CSM is developed during the early phases of the environmental restoration process. However, as site restoration progresses, important changes related to the nature and extent of contamination and other site features are not always captured in revisions to the CSM, which can impede optimization approaches and decision making. Hence, it is necessary to continuously update the CSM throughout the environmental restoration process.

The CSM must adequately characterize the extent of the impact, identify all sources of contamination, and include exposure pathways, receptors, and associated risks. Of particular importance, LNAPL "composition-based" risks are the potential for toxic chemicals from LNAPL to form dissolved plumes and vapor-phase impacts, while "saturation-based" risks are related to the likelihood of LNAPL to migrate in the subsurface. Both "composition-based" and "saturation-based" risks must be investigated and incorporated into the CSM. These risks should be re-evaluated as site conditions change and the CSM should be updated accordingly to allow site decisions and remedial approaches to be based on the most current data. For instance, multiphase extraction (MPE) may be performed at a site to reduce saturation risk by recovering a large volume of LNAPL in a short timeframe. Simultaneously, composition risks also may be diminished via extraction and biodegradation of aromatic (e.g., benzene) and shorter chain hydrocarbons, which tend to be more volatile. A CSM that incorporates changes in composition and saturation can be used to demonstrate risks have been reduced or mitigated (Tomlinson et al., 2017). It also may be used to justify transitioning to a less aggressive and less costly remedy or potentially provide the lines of evidence required by the state's low threat guidance to close a site with LNAPL in place.

A successful site management strategy will control sources and mitigate any risks through demonstration of the long-term protectiveness of human health and the environment. Low threat and risk-based closure guidance generally requires answers to four main questions concerning the presence of LNAPL including:

- Is the LNAPL at risk of migrating?
- Are there any potential risk exposure scenarios if LNAPL remains?
- How much of the LNAPL is recoverable?
- Will naturally occurring processes serve to attenuate the remaining LNAPL and dissolved phase constituents in a reasonable timeframe?

In addition to these questions, the low threat and risk-based closure must assess the risks associated with the dissolved groundwater plume, soil contamination, and soil gas (i.e., vapor intrusion to existing or future buildings). At some sites, land use controls (LUCs) may be warranted to further mitigate the risk of contact with impacted media. The cost of the remedy should also be considered as what is "practical" to recover is highly dependent on the incurred cost. For example, it may not be practical to recover a small fraction of LNAPL at a high cost, if leaving the LNAPL in place does not pose a risk to human health or the environment.

Therefore, remedial action optimization for petroleum sites must focus on evaluating and/or generating site data to answer these questions. The optimization process should identify sampling procedures and/or alternate technologies that may be implemented at a reduced lifecycle cost and data collected to establish that the risk has been mitigated to achieve site closure. An overview of strategies for assessing and answering these questions is provided below.

2.1.1 Is the LNAPL at Risk of Migrating?

LNAPL migration (a saturation-based risk) occurs when LNAPL saturation is sufficiently high to cause it to spread laterally (or vertically). It is important to understand the difference between migrating LNAPL and mobile LNAPL. All migrating LNAPL is mobile, but not all mobile LNAPL is migrating. Although mobile LNAPL exceeding a residual saturation can cause movement; the volume of fluid may not be sufficient to cause migration. An example of mobile LNAPL is an observed change in thickness in a well caused by changing groundwater elevation (i.e., barometric or tidal effects), in conjunction with the absence of LNAPL appearing in nearby sentinel wells. A common optimization approach is to collect time series data (as shown in Figure 2-1). An increase in the areal extent of the LNAPL plume over time is indicative of migration, whereas a decrease such as shown in Figure 2-1 is a strong line of evidence that the LNAPL extent is shrinking or stable.

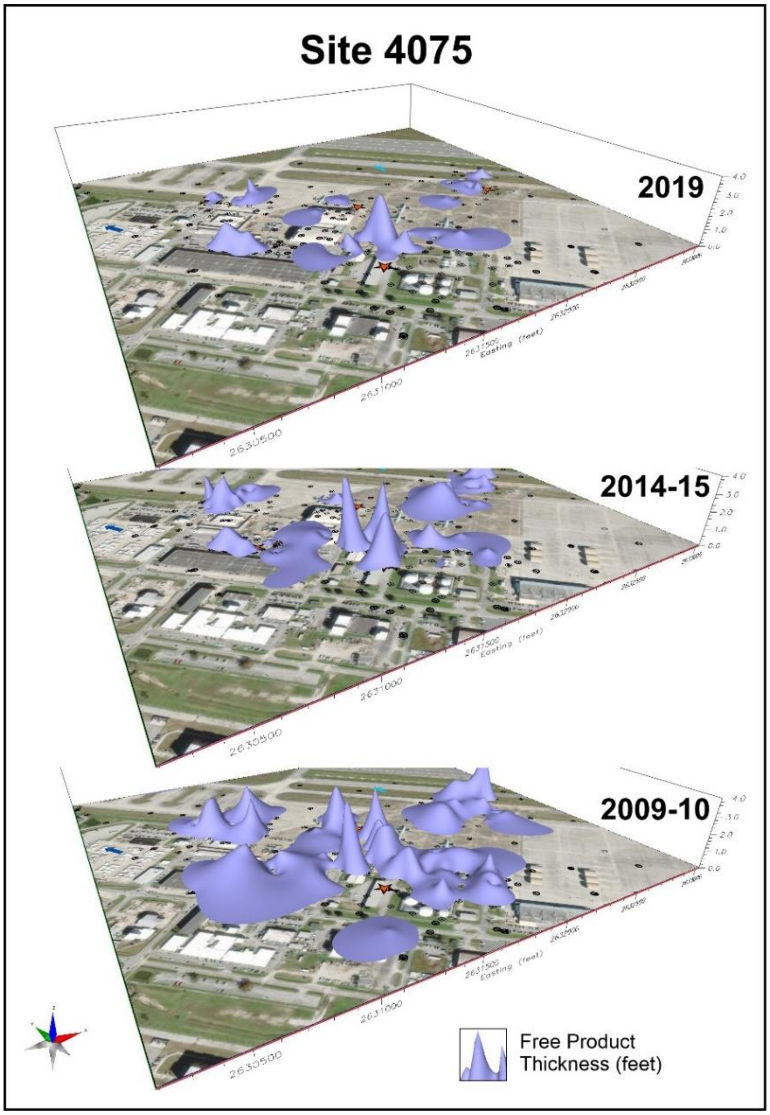

Figure 2-1. Reduction of LNAPL Thickness in Monitoring Wells at Site 4075, MCAS Cherry Point (Courtesy of NAVFAC)

2.1.2 Are There Any Potential Risk Exposure Scenarios if LNAPL Remains?

Risk exposure at LNAPL sites arises from the toxicity of the chemicals that dissolve from the LNAPL (composition-based risk) and subsequently migrate along exposure routes to human or ecological receptors. Composition-based risks are determined by analysis of groundwater, soil, and soil vapor for identified contaminants of concern and comparing results to cleanup levels that presumably have been established using a risk-based approach. Optimization activities should focus on ensuring that the monitoring network remains appropriate for addressing any identified risk exposure scenarios and that those scenarios have not changed. As site conditions and contaminant concentrations change, wells may be removed from or added to the monitoring network and sampling frequency may be reduced (or increased) to ensure site risks are adequately addressed.

Groundwater samples generally are collected and analyzed for volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) using U.S. Environmental Protection Agency (U.S. EPA) Methods 8260B and 8270C, respectively. Concentrations are compared to remedial goals to ascertain risks, plume maps are generated, and time-series data can be compared to evaluate plume stability. Statistical software, such as MAROS (GSI, 2012) or equivalent may be useful for evaluating groundwater concentration trends (i.e., decreasing, stable, increasing).

Many states have specific requirements for analysis of total petroleum hydrocarbons (TPH), which must be adhered to for use in site investigations and risk assessment. Common methods include U.S. EPA Method 8015, the Washington State Department of Ecology Toxics Cleanup Method (WSDETCM), and the Massachusetts Department of Environmental Protection Method (MADEP). Less common methods include the Florida Residual Petroleum Organic (FL-PRO) Method and the TPH Criteria Working Group Method (TPHCWG). Results reported using each of these methods include slightly different carbon ranges (Table 2-1); hence, care should be taken when comparing results.

Table 2-1. Carbon Fractions and Silica Gel Cleanup Requirements for Several TPH Analytical Methods

Method	Reportable TPH Ranges	Silica Gel Cleanup
8015	GRO $C_6 - C_{10}$ DRO $C_{10} - C_{28}$	Optional for DRO[1]
WSDETCM	GRO $C_7 - C_{12}$ DRO $C_{12} - C_{24}$ HRO $C_{24} - C_{40}$	Optional for DRO and HRO[1]
MADEP VPH[2]	$C_5 - C_8$ Aliphatics $C_9 - C_{10}$ Aromatics $C_9 - C_{12}$ Aliphatics	No[1]
MADEP EPH	$C_{11} - C_{22}$ Aromatics $C_{19} - C_{36}$ Aliphatics $C_9 - C_{18}$ Aliphatics	Yes
FL-PRO	$C_8 - C_{40}$	Yes
TPHCWG	*Aliphatics* TPH Range 1 $C_5 - C_6$ TPH Range 2 $>C_6 - C_8$ TPH Range 3 $>C_8 - C_{10}$ TPH Range 4 $>C_{10} - C_{12}$ TPH Range 5 $>C_{12} - C_{16}$ TPH Range 6 $>C_{16} - C_{35}$ *Aromatics* TPH Range 1 $C_6 - C_7$ TPH Range 2 $>C_7 - C_8$ TPH Range 3 $>C_8 - C_{10}$ TPH Range 4 $>C_{10} - C_{12}$ TPH Range 5 $>C_{12} - C_{16}$ TPH Range 6 $>C_{16} - C_{21}$ TPH Range 7 $>C_{21} - C_{35}$	Yes

1. Silica gel cleanup is only used on the extractable fraction.
2. Provides fractionation using instrument detectors: flame ionization detector (FID) for aliphatics; photoionization detector (PID) for aromatics.
DRO – diesel range organics; EPH – extractable petroleum hydrocarbons; GRO – gasoline range organics
HRO – heavy range organics; VPH – volatile petroleum hydrocarbons

TPH analytical methods may or may not use silica gel cleanup (SGC) as an option (Table 2-1), which is required by some states and prohibited by others. SGC is used to remove polar organics from the sample matrix, a portion of which is attributed to naturally occurring organic matter and degradation byproducts. If not removed, the polar compounds can contribute to the total TPH result, even though they are not necessarily part of the TPH or a degradation product. However, some localities are concerned that the toxicity of the polar metabolites that are TPH degradation products is unknown and therefore prefer that they are included as part of the TPH value. As a result, TPH values can vary substantially from method to method, which can impact LNAPL management decisions. It is important to understand local requirements pertaining to the TPH analytical method to be used.

Paraffins, iso-paraffins, aromatics, naphthenes, and olefins (PIANO) analyses may be performed on LNAPL samples to evaluate chemical constituents that are typically found in residual LNAPL. This information can be useful for fingerprinting or forensics to identify the nature of the product. If available, it is useful to compare results to historical (or future) data to help understand the degree of weathering that has occurred. The PIANO results can reveal the impact a remedy has on LNAPL composition over time (which relates to risk) and can identify which processes appear to be dominant (e.g., biodegradation, dissolution, and volatilization).

2.1.3 How Much of the LNAPL is Recoverable?

Regulatory agencies require that a good faith effort be made to recover LNAPL to permit site closure with LNAPL in place and to transition to a less aggressive technology such as NSZD. In some states, such as Virginia, it is recognized that "*continued attempts to reduce free product to an arbitrarily measured thickness (e.g., 0.01 ft. or less) in a monitoring well is neither practicable nor even necessary"* and "*continued recovery of product beyond a "practicable" achievable thickness may provide little or no positive environmental protection"* (Virginia Department of Environmental Quality [Virginia DEQ], 2012).

Optimization activities should focus on collecting data necessary to demonstrate that LNAPL recovery is approaching an asymptotic level and that it is no longer practical to recover remaining LNAPL. Optimization of the recovery system (adjusting flowrates, installing additional wells, etc.) may be required in order to achieve these objectives. In addition, it may be necessary to demonstrate that alternative and sometimes innovative technologies have been considered. Optimization techniques may consist of plotting and evaluating cumulative recovery over time and performing decline curve analyses to demonstrate that the majority of recoverable LNAPL has been removed from a site (Figure 2-2).

LNAPL transmissivity is a useful optimization metric, recognized by the Interstate Technology and Regulatory Council (ITRC) for evaluating LNAPL recoverability (ITRC, 2009). It is a function of soil type and associated properties such as porosity and conductivity, the chemical and physical properties of the LNAPL itself, and degree of LNAPL saturation. LNAPL transmissivity may be measured by one or more of several methods including the baildown method, skimming method, system recovery method, and tracer test method (ASTM, 2013). The ITRC has indicated that below a LNAPL transmissivity of 0.1 to 0.8 ft^2/day, it may not be practical to continue LNAPL recovery at a site. Some states also are recognizing the importance of LNAPL transmissivity and include guidance for applying it at sites. For instance, the Michigan Department of Environmental Quality (MDEQ) states that "*if LNAPL remaining at a site has a transmissivity greater than 0.5 ft^2/day, it is* *likely that additional recovery would be beneficial and that the LNAPL may be recovered in a cost-effective and efficient manner"* (MDEQ, 2014). LNAPL transmissivity should be measured at regular intervals (e.g., semi-annually, annually) as a line of evidence to provide a basis for demonstrating when it is no longer practical to recover LNAPL. The acceptance of LNAPL transmissivity as a metric for petroleum sites is still evolving at the state level. Some states offer specific guidance on its use, while others permit its use as one line of evidence regarding LNAPL recoverability.

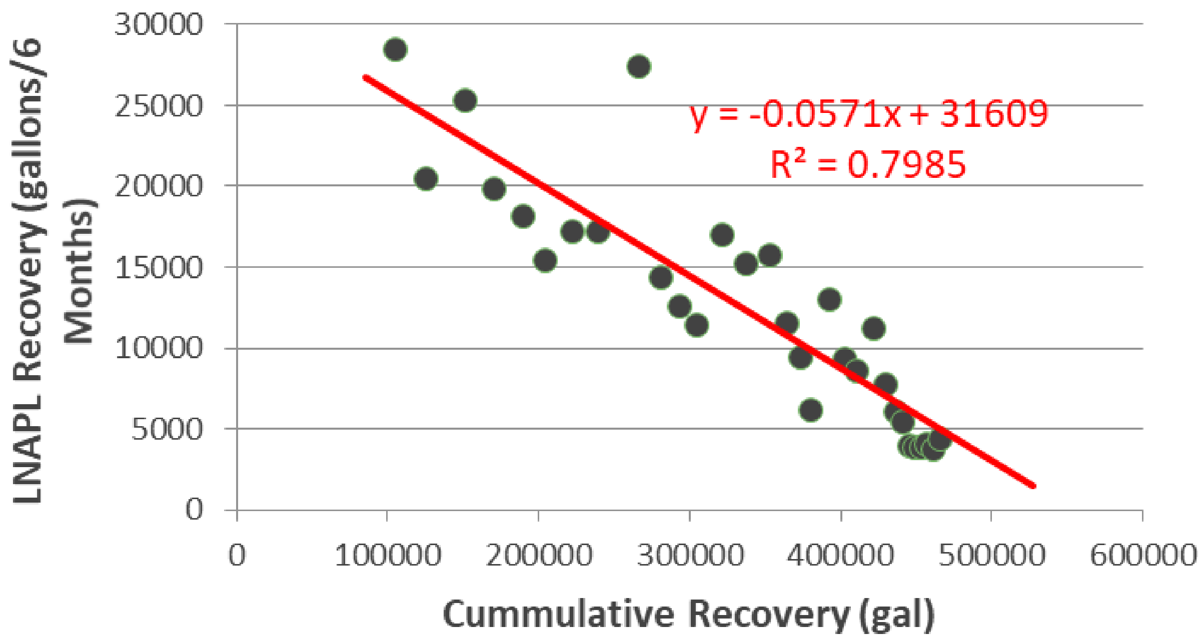

Figure 2-2. Decline Curve Analysis at the Yorktown Defense Fuel Supply Point (Courtesy of NAVFAC)

2.1.4 Will Naturally Occurring Processes Serve to Attenuate the Remaining LNAPL and Dissolved Phase Constituents in a Reasonable Timeframe?

Monitored natural attenuation (MNA) is a widely accepted technique to demonstrate that dissolved phase groundwater constituents are being attenuated and should be included as part of most strategies for managing petroleum-impacted sites. Similarly, NSZD is gaining acceptance for attenuating residual LNAPL at sites that pose little or no risks or at sites where active LNAPL recovery technologies have reached a point of diminishing return. NSZD requires an evaluation of naturally occurring LNAPL degradation rates. A variety of methods are available including using flux chambers, carbon traps, and temperature measurements. Sampling should be performed at different times of the year to establish rates during warmer and colder seasons. Samples should be collected at multiple locations at a site since rates will vary depending on LNAPL composition and saturation at a location and distance from the original source. Rates should continue to be monitored periodically (e.g., annually) to evaluate changes over time as the more easily degradable fractions of petroleum products are eliminated. Hydrocarbon measurements such as the PIANO analysis may be performed to further assess compositional change of the remaining hydrocarbons. The acceptance of NSZD as an allowable remedy is still evolving at the state level. More information on how to conduct NSZD investigations is provided by the ITRC (ITRC, 2018).

2.1.5 What is the Expected Cost to Recover Additional LNAPL?

The cost to remove LNAPL from a site should be considered as part of the remedial action optimization process. Although cost may be less of a concern to regulatory stakeholders, it is an important site management consideration. Calculations should consider all O&M costs including monitoring and reporting. As shown in Figure 2-3, the cost per gallon of LNAPL recovered can be determined and used as a line of evidence to demonstrate it is no longer practical to continue recovery. It also may be used to aid decision making to optimize the existing remedy to enhance removal of contaminants (if possible) or transition to an alternate, passive technology.

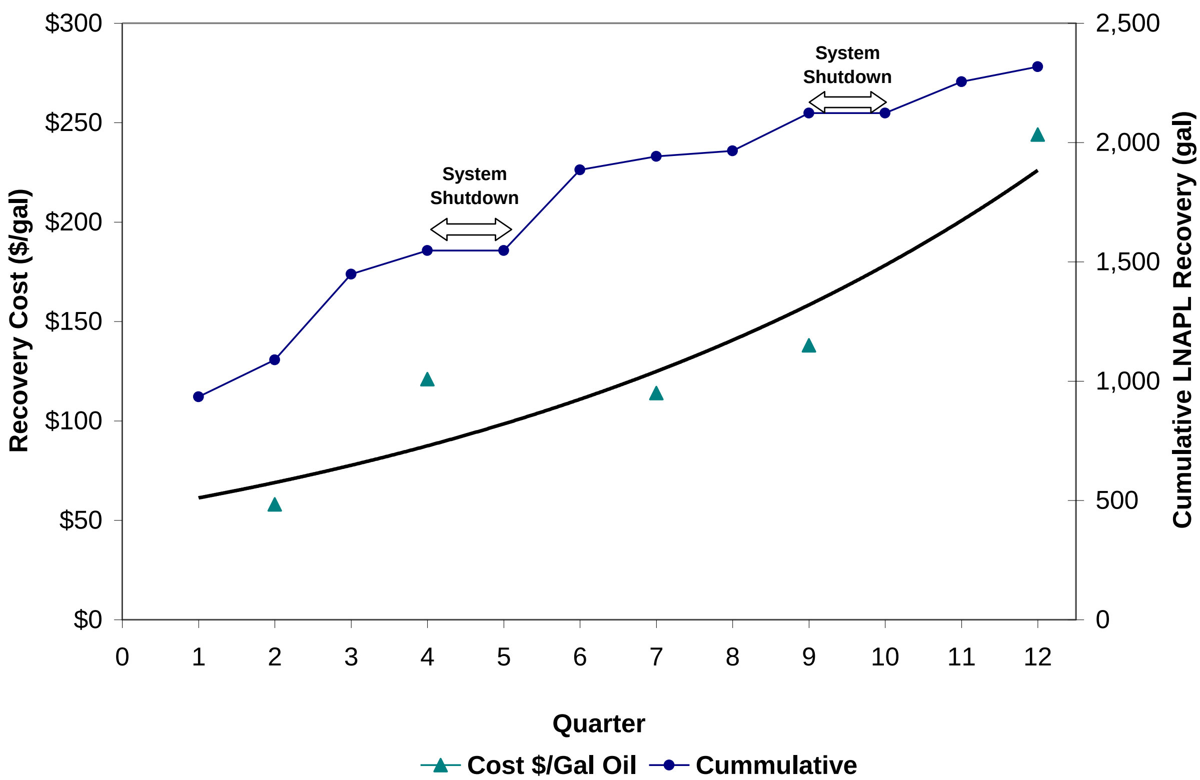

Figure 2-3. Normalized Cost of a Multiphase Extraction System at Site 6, Naval Construction Battalion Center Gulfport (Courtesy of NAVFAC)

2.1.6 Additional Resources for the Optimization of Petroleum Sites

NAVFAC has developed several resources to help Remedial Project Managers (RPMs) and their consultants to understand the unique aspects of petroleum sites and appropriate strategies to manage them. These include:

- Petroleum Site Management Update – A Roadmap to Closure (NAVFAC, 2015)
- Complex Challenges at LNAPL Sites (NAVFAC, 2017)

- New Developments in Petroleum Site Management (NAVFAC, 2017)
- The LNAPL Site Management Handbook (NAVFAC, 2010)

These petroleum-related resources and more can be found on the NAVFAC ERB Web site:

- Petroleum Focus Area Webpage https://www.navfac.navy.mil/navfac_worldwide/specialty_centers/exwc/products_and_services/ev/go_erb/focus-areas/petroleum-sites.html

In addition, NAVFAC has developed several guidance documents that provide procedures and best practices for optimizing remedial actions at DON sites. These include:

- Guidance for Optimizing the Remedy Evaluation, Selection, and Design (NAVFAC, 2010b)
- Guidance for Optimizing Remedial Action Operation (NAVFAC, 2012).
- Guidance for Planning and Optimizing Monitoring Strategies (NAVFAC, 2010a)
- Guidance on Green and Sustainable Remediation (NAVFAC, 2011) .
- Policy for Optimizing Remedial and Removal Actions at all DON Environmental Restoration Program (ERP) Sites (DON, 2012).

These resources and more can be found on the NAVFAC ERB Web site:

- Optimization Webpage https://www.navfac.navy.mil/navfac_worldwide/specialty_centers/exwc/products_and_services/ev/go_erb/program-support/optimization.html

2.2 Overview of Federal and State Regulations Related to Petroleum Site Assessment and Closure

The Navy sites addressed in this petroleum case study review include underground storage tanks (USTs) used for fuel storage, USTs at fuel dispensing stations, fuel farms consisting of multiple aboveground storage tanks (ASTs), and petroleum pipelines. Environmental regulations related to the cleanup of these petroleum sites are generally covered under federal and state regulations that apply to corrective actions at UST sites. Several other types of Navy petroleum cleanup sites are not represented in this case study review, including firefighting training areas and marine-related releases (ships/fuel transfer stations).

2.2.1 Overview of Federal Regulations Related to Petroleum Sites

The federal regulations covering corrective actions associated with USTs are contained in the Code of Federal Regulations (CFR), Title 40, Part 280 (40 CFR 280), "Technical Standards and Corrective Action Requirements for Owners and Operators of Underground Storage Tanks" under the Resource Conservation and Recovery Act (RCRA).

These federal UST regulations include (but are not limited to) reporting on releases or leaks from the UST system, investigating for free product, free product removal, investigating the full extent of contaminated soil and groundwater, and developing a site-specific corrective action plan (CAP). The regulations require the CAP to account for the hydrogeologic setting and potential effects of residual contamination on nearby surface water and groundwater and also require that an exposure assessment be performed. Upon approval of the CAP, the corrective action must be implemented, and the results must be monitored and reported. In addition, federal UST regulations (40 CFR 280.64) require that free product removal be conducted in a manner that minimizes the spread of contamination into previously uncontaminated zones by using recovery and disposal techniques appropriate to the hydrogeologic conditions at the site.

Federal regulations promulgated under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) have historically excluded environmental cleanup associated with petroleum products or wastes. The scope of the CERCLA petroleum exclusion is provided under CERCLA Sections 101(14) and 104(a)(2). However, petroleum sites that also include a mixture of CERCLA contaminants (e.g., halogenated VOCs) do not fall under the CERCLA petroleum exclusion, and in these instances, CERCLA regulations are applicable.

Subtitle I of the Solid Waste Disposal Act allows individual state UST programs approved by the U.S. EPA to operate in lieu of the federal program. The U.S. EPA has established criteria under CFR, Title 40, Part 281 "Approval of State Underground Storage Tank Programs" that need to be achieved by state UST programs to obtain the authority to operate in lieu of the federal program. The state UST programs must be at least as stringent as U.S. EPA's requirements (see Figure 2-4 for approved programs). As discussed in Section 2.2.2, the Navy installations follow applicable local and state UST regulations.

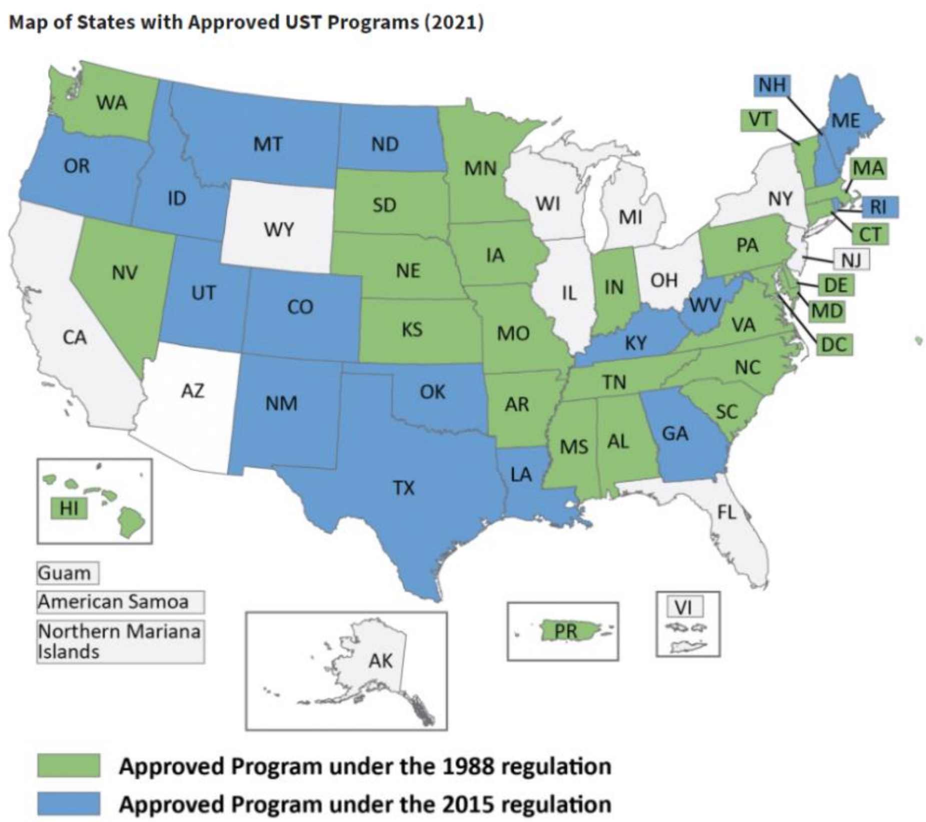

Figure 2-4. Individual States with Approved UST Programs to Operate in lieu of U.S. EPA (Courtesy of U.S. EPA, 2021)

2.2.2 Overview of State Regulations Related to Petroleum Sites

DON installations conduct remediation projects under state-led UST cleanup programs. State UST programs guide cleanup at most petroleum hydrocarbon-contaminated sites. UST programs are delegated to the state level, as part of RCRA, and may incorporate requirements that are more stringent than federal UST regulations. The Navy strives to implement consistent cost-effective remediation and management approaches across all of these regulatory-driven processes (NAVFAC, 2010a).

Optimization strategies for petroleum sites often incorporate low-threat or risk-based closure criteria allowed under state-specific provisions. The acceptance and use of various petroleum site cleanup and management approaches varies from state to state. For a given site, it is important to determine the state-specific adoption of various practices including the use of LNAPL transmissivity metrics, NSZD, and specialized TPH analytical techniques. RPMs should review and understand state-specific site closure requirements and other related metrics for petroleum sites. Several states have accepted optimized practices with respect to the use of LNAPL transmissivity and NSZD as established as a best practice by ITRC. As the acceptance of these practices is still evolving, RPMs should confer with their regulatory stakeholders on current approaches for their petroleum cleanup sites in order to advocate for the use of optimized approaches where feasible and allowed under state-specific provisions.

3.0 CASE STUDY REVIEW

A case study review was conducted to identify representative Navy petroleum cleanup sites where optimization strategies were leveraged to decrease costs, reduce cleanup timeframes, and move towards more sustainable technologies.

3.1 Types of Petroleum Sites Included in the Review

This case study review evaluated information from 10 Navy sites involving a petroleum release to surrounding environmental media (soil, groundwater, and potentially surface water) followed by environmental cleanup (Table 3-1). The ten sites are located within seven states and the District of Columbia (including CA, DC, FL, MS, NC, NV, RI, VA).

The petroleum products included jet fuel (JP-4 and JP-5), aviation gas, gasoline, diesel, and heavy oil (or bunker oil or Navy Special Fuel Oil). These products were released from USTs, tank farms, and/or pipelines, contaminating surrounding environmental media (Table 3-1). Sites involving the release of heavy fuel oils to the subsurface present the greatest challenge for recovery of LNAPL due to the viscous nature of these materials and inherently low biodegradation rates. In addition, some of the 10 sites reviewed for the case study have been contaminated by CERCLA contaminants such as halogenated VOCs (solvents, degreasers, and refrigerants [Freon™]). These CERCLA contaminants are generally understood to have been released from separate sources but were later commingled. These mixed plumes result in more complicated recovery of mobile LNAPL and treatment of dissolved phase contaminants.

To various degrees, each of the 10 Navy petroleum sites reviewed in Table 3-1 exhibited use of the optimization concepts described in Section 2. The types of practices employed included: 1) continually updating the CSM; 2) evaluating the degree of risk from contaminant migration and risk of exposure to human or ecological receptors; 3) establishing technology transition metrics and/or exit strategies; 4) tracking on the feasibility of LNAPL recovery; 5) relying on the ability of naturally occurring processes to attenuate the remaining LNAPL and dissolved phase constituents (e.g., MNA or NSZD); and 6) utilizing cost considerations of the remediation process over the lifecycle of the remediation system.

From this collection of petroleum sites, two Navy sites were then selected to further highlight optimization concepts with site-specific data. These sites represent the adoption of the optimization best practices advocated for in Navy policy and guidance for petroleum sites. These two sites are highlighted in more detail for installations located in Yorktown, Virginia (Section 3.2) and China Lake, California (Section 3.3).

Table 3-1. DON Petroleum Site Summary of Site Remedies, Challenges, and Optimization Strategies (Status as of April 2021)

No.	Site Name and Location	Site Type	Petroleum Product Released	LNAPL Present? Yes/No/NA	Most Recent LNAPL Readings Available (feet) / Date	Selected Remedies	Site Challenges	Optimization Strategies/Benefits
1	Site UST-5, Marine Corps Recruit Depot San Diego, California	Gas Station UST	Gasoline	Yes Sheen in 2009. Minor amount of LNAPL in 1996.	<0.01 feet / 2009. Max of 0.01 feet (1/8 inches) observed in 1996	Use of absorbent socks and vacuum truck.	• Required evaluation of the vapor intrusion pathway to buildings near the UST site. • Methyl tert butyl ether (MTBE) plume with a larger footprint than the benzene, toluene, ethylbenzene and total xylenes (BTEX) plume.	Strategies: • Used optimization concepts to select the optimal location for groundwater monitoring wells and soil gas monitoring points. • Used a multiple lines of evidence approach to demonstrate that site contaminants do not pose risks to human health or the environment following the California Low-Threat UST Case Closure Policy. • Applied fate and transport modeling to assess the MTBE plume. Concluded that the MTBE plume was stable; will not discharge to downgradient marine surface water; and a continuing source of MTBE was not present at the site. Benefits: • Accelerated time to site closure. A no further action letter was issued based on regulatory approval of the application of the Low-Threat UST Case Closure Policy for this site.
2	Site 1 , Armitage Field Operable Unit, Naval Air Weapons Station China Lake, California	UST Site	Various grades of jet fuel and aviation gas	Yes	Max of 1.73 feet / 2019	Soil vapor extraction (SVE); solar-powered skimmer-based free product recovery system (FPRS); and submersible pumping using a mobile product recovery system (MPRS)	• Complex, commingled plume of contaminants: jet fuels/aviation gas, gasoline, and chlorinated VOCs. • High heterogeneity in geology and presence of caliche layers affecting LNAPL transport and distribution.	Strategies: • Resolved data gaps to improve understanding of the target treatment zones. • Measured LNAPL transmissivity to determine recoverability of remaining LNAPL. • Determined NSZD bioattenuation rates and mechanisms using carbon dioxide (CO_2) flux measurement and thermal monitoring. Calculated NSZD degradation rates ranged from 36 to 99 gallons/acre/year based on CO_2 flux measurements, and average degradation rates based on thermal monitoring ranged from 147 to 190 gallons/acre/year. • Demonstrated biological degradation was occurring through NSZD. • Re-evaluated remedial action objectives, remedial goals, and closure strategies. • Assessed the overall protectiveness of the current remedy. Benefits: • Identified opportunities for improving cost efficiency of operations and established metrics for future shutdown. • Data provided lines of evidence to evaluate remedial approaches and future transition to NSZD.
3	Sites 111, 225, Building 71, Washington Navy Yard, District of Columbia	UST Sites	Gasoline, diesel, used oil, and possibly fuel oil, and unknown petroleum products	Yes	0.01 to 1.78 feet / 2017	MNA	• Discovery of previously undocumented LNAPL, requiring additional treatment during supplemental data gap investigations. • LNAPL and dissolved impacts threaten adjacent Anacostia River, leading to 2017 recommendation for LNAPL removal by excavation. • Due to diminishing LNAPL recoveries and technological inefficiencies, it was necessary to change LNAPL recovery technologies several times.	Strategies: • Used a multiple lines of evidence approach to show that additional LNAPL recovery is impractical and that LTM for MNA is appropriate for the site. • Performed LNAPL mobility assessments to indicate LNAPL was neither mobile nor migrating. • Performed supplemental LNAPL characterization to address data gaps. Findings were that the dissolved phase hydrocarbon plume present at the site remains stable and is expected to further decline as a result of natural attenuation, based on geochemical changes in the surficial groundwater. • Optimized the groundwater monitoring network and included the recommendation to limit monitoring to sentinel wells. • Recommended a path forward that includes performing a soil removal action, implementing LUCs, and conducting annual monitoring to track LNAPL and dissolved plume stability and progress in natural attenuation. Benefits: • Addressed data gaps in the LNAPL CSM and developed recommendations that could result in cost savings from a transition to a passive treatment approach.
4	UST 20/Site 19 and UST 24, Naval Air Station Pensacola, Florida	Petroleum Pipeline Leak	Jet Fuel (JP-4)	UST 20/Site 19. NA. UST 24, Yes LNAPL was present.	At UST 20/Site 19 - NA. At UST 24, Max of 1.64 feet / 2002.	Biosparging systems at both UST 20/Site 19 and at UST 24	• UST site CSMs have not been integrated - flow mapping discrepancies exist. • Remaining hydrocarbons in soil at UST 24 or UST 20/Site 19 has not been estimated since 2000s; needed to estimate the remaining treatment timeframe for groundwater. • Difficulties in operating Site 19 air sparging system due to surface water inundation and preferential pathways in some sparging wells; required lowering of flow rates.	Strategies: • Revisited the CSM at UST 20/Site 19 to develop a revised remedial strategy. The technology selection changed from low-volume air sparging and chemical addition (PHOSter II™) to traditional air sparging in concert with MNA and eventually to biosparging. • Re-examined the Remedial Action Plan (RAP) at UST 24 because of data gaps. Additional investigation results led to a transition from bioslurping to biosparging as an interim measure, which was implemented in concert with the air sparging system at UST 20/Site 19. • Operated sparging systems as pulsed or cycled system to reduce the formation of preferential pathways. • Screened vadose zone soil gas for CO_2 and methane to monitor petroleum biodegradation. Benefits: • Provided cost savings based on transition to passive technologies (e.g., biosparging).

Table 3-1 (Continued). DON Petroleum Site Summary of Site Remedies, Challenges, and Optimization Strategies (Status as of April 2021)

No.	Site Name and Location	Site Type	Petroleum Product Released	LNAPL Present? Yes/No/NA	Most Recent LNAPL Readings Available (feet) / Date	Selected Remedies	Site Challenges	Optimization Strategies/Benefits
5	Trumbo Point Tank Farm, Naval Air Station Key West, Florida	Tank farm with ASTs	Jet fuel (JP-5) and marine diesel fuel, Bunker C Fuel, and Navy Special Fuel Oil	Yes	1.64 feet / 2015	Various LNAPL product recovery techniques: use of vacuum truck at wells; skimmer traps inside wells; a portable extraction system for LNAPL recovery; bailers.	• Concrete fragments were used to backfill some of the former tank locations following demolition, limiting use of drilling equipment in those areas. • Product recharge was noted in some monitoring points in the area near the abandoned tank bottom that was left in place. • The 2010 NAPL delineation (using laser induced fluorescence [LIF]) indicated that the extent of free product at the site was not bounded by the existing well networks.	Strategies: • Combined LNAPL cleanup with soil hot spot removal where the open excavation was used to pump out LNAPL. • Refined CSM through additional investigations, including a 2010 LIF investigation to assess the in situ distribution of LNAPL. • Performed an evaluation of natural attenuation processes. • Recommended continuing with free product recovery methods and groundwater monitoring until a technology transition can occur as noted below. • Performed an evaluation that shows decreasing size of mobile LNAPL plume and probably decreasing size of the dissolved plume, making this site a good candidate for application of NSZD (GSI, 2019). Benefits: • Addressed data gaps in the LNAPL CSM and developed recommendations that could result in cost savings from a transition to a passive treatment approach.
6	Site 228, Naval Air Station Meridian, Mississippi	UST Site, Navy Exchange Filling Station	Gasoline	No	Not Applicable	Biosparge system from 2013 -2018	• Several biosparge wells have air flows below design parameters. Dissolved oxygen (DO) distribution is much less efficient during times of lower groundwater elevations in the fall and winter.	Strategies: • Performed an optimization evaluation and advanced modeling effort which concluded: ○ Modifying groundwater sampling frequency from quarterly to semi-annually; ○ Optimizing biosparge system operation (e.g., additional or modified sparge points). ○ Evaluating other remedial alternatives based on the likelihood of free product reoccurring and the estimated time period for achieving the cleanup goals. ○ Ending active remediation and transitioning to MNA/NSZD until cleanup goals are achieved. Benefits: Addressed data gaps in the LNAPL CSM and developed recommendations that could result in cost savings from a transition to a passive treatment approach.
7	Tank Farm "B" Site, Marine Corps Air Station (MCAS) Cherry Point, North Carolina	Tank Farm "B"	Fuel release was JP-5 (Jet Fuel).	Yes	0.02 and 0.79 feet in 2017 (two wells had LNAPL) <0.10 feet in 2020 and 2021 (three well had detected LNAPL)	SVE system with 48 SVE wells and of 31 total fluids pumps.	• MCAS temporarily assigned high risk due to proximity to Potable Wells 1 and 8. • Horizontal SVE wells have taken in shallow groundwater and become inundated periodically. LNAPL measurements between events varied significantly, which may be related to which wells were gauged in each event.	Strategies: • Prepared an Optimization Plan and conducted an SVE system optimization evaluation. This effort addressed additional delineation of free product, updated the CSM, and provided data from a pulsed-sparging pilot test. • Performed an evaluation that shows decreasing size of mobile LNAPL plume and probably decreasing size of dissolved plume, making this site a good candidate for application of NSZD (GSI, 2019). • Modeling of the dissolved-phase groundwater contamination was completed in early 2021 which demonstrates that the dissolved-phase plume will continue to decrease in size and concentrations and receptor impacts are unlikely. Benefits: Improved delineation and strategy for future transition to a passive treatment approach.
8	Northern Operable Unit (NOU) Site 2, New Fuel Farm and NOU Site 4, Transportation Yard, Naval Air Station Fallon, Nevada	Tank Farm ASTs [Note: Site 2 and Site 4 are reported together].	Jet fuel (JP-5 and JP-8), diesel fuel, aviation gas, and gasoline, mixed paint wastes and other waste fluids	Yes	Max of 1.46 feet / 2013 In 2007, average sitewide at 0.93 feet, and in 2013 at 0.65 feet in 2013	Since 2014, LNAPL recovery has been conducted using a truck-mounted diaphragm pump powered by an air compressor to skim off free product, moving between wells as needed.	• Occurrence of mixed chlorinated VOCs (trichloroethene [TCE] and vinyl chloride [VC]) and hydrocarbon plume. • Soil gas screening level exceedances for chlorinated VOCs that require the use of LUCs to prevent construction of residential buildings. • Revised Human Health Risk Assessment (HHRA) in 2015 identifies VC in groundwater as a new constituent of concern (COC) for the hypothetical future residential scenario for vapor intrusion only. • Compliance with Nevada requirement for removal of free product at thicknesses >0.5 inches. (NAC § 445A.22735[1][a]).	Strategies: • Addressed a number of data gaps during the Remedial Investigation/Feasibility Study Addendum and presented remedial alternatives for additional LNAPL recovery. Data gaps resolved included: ○ Updated the CSM for Site 2 and Site 4 ○ Collected updated groundwater quality data and further defined LNAPL extent. ○ Collected soil gas data to evaluate human health risk to indoor air. • Revised the HHRA to incorporate risks from dermal contact with groundwater and from exposure to VC for the vapor intrusion pathway. • Identified the preferred remedial alternative for additional LNAPL recovery (manual/automated bailing/skimming and long-term monitoring with LUCs). Benefits: • Addressed data gaps and optimized LNAPL recovery efforts.

Table 3-1 (Continued). DON Petroleum Site Summary of Site Remedies, Challenges, and Optimization Strategies (Status as of April 2021)

No.	Site Name and Location	Site Type	Petroleum Product Released	LNAPL Present? Yes/No/NA	Most Recent LNAPL Readings Available (feet) / Date	Selected Remedies	Site Challenges	Optimization Strategies/Benefits
9	Tank Farm 1 (Site 7), Naval Station Newport, Middleton, Rhode Island	Tank Farm, ASTs	Fuel oil, jet fuel (JP-4), diesel fuel, aviation gasoline, and motor gasoline	No	Not Applicable	Soil remediation performed only (excavation).	• Mixture of CERCLA contaminants (metals) and petroleum fuels in soils, which is the only media in the Record of Decision (ROD). • Isolated groundwater results in 2017 exceed Rhode Island standards for drinking water. • There is inaccessible soil under structures. • Challenging geologic conditions, with weathered and/or metamorphosed shale exposed at ground surface or shallow depths, and groundwater occurring in the bedrock.	Strategies: • Selected the remedial alternative in the ROD to address soil contamination to protect against migration of soil contaminants to groundwater. The remedy selected was limited soil excavation with LUCs. MNA is anticipated to be the remedy for site-wide groundwater at Tank Farm 1; however, additional action may be necessary as per- and polyfluoroalkyl substances (PFAS) analytes were recently added to monitoring plan. • Designed and optimized soil sampling for the soil excavation to meet data quality objectives. Benefits: • Source removal via soil excavation will reduce leaching/migration of contaminants and therefore the overall timeframe for groundwater restoration.
10	Yorktown Defense Fuel Supply Point, Yorktown, Virginia	Tank Farm, USTs	Navy Special Fuel Oil	Yes	0.5 feet / 2016	Heat-enhanced pump-and-treat system for LNAPL recovery. Pump-and-treat system has now been permanently shut down and NSZD used in lieu of manual free product recovery.	• High O&M cost for the heat-enhanced system with diminishing returns. • LNAPL recovery leveling off before the maximum theoretical recovery had been achieved. • Presence of crushed concrete debris complicates recovery well installation. Plume has migrated off-site.	Strategies: • Performed a remedial alternative analysis to identify suitable technologies (including NSZD). • Performed an NSZD study using a lines of evidence approach to assess suitability of technology at the site, which included: evaluating LNAPL transmissivity; confirming LNAPL recovery was approaching asymptotic levels; and monitoring of LNAPL thickness. • Performed a study with the use of CO_2 flux traps to assess degradation rates. Removal rates due to NSZD were calculated to range from about 1,230 to 2,200 gallons per year (NAVFAC Mid-Atlantic, 2020). • Future pilot studies to support the effectiveness of several free product recovery methods (bailing, socks, solar skimmers with heater, etc.) Benefits: Cost savings resulting from transition to passive treatment approach with NSZD.

3.2 Case Study 1: Yorktown Defense Fuel Supply Point, Yorktown, Virginia

The Yorktown Defense Fuel Supply Point (DFSP) site in Virginia was selected as a case study to highlight best practices for the application of LNAPL site management and optimization concepts. The state of Virginia has well-defined guidance for evaluating sites for closure with LNAPL remaining in place. The Virginia DEQ recognizes that the presence of LNAPL may not represent a human health risk and identifies several lines of evidence that, if demonstrated, may allow a site to be closed with LNAPL in place (Virginia DEQ, 2012). The data collected from the DFSP site illustrate how these strategies can facilitate the transition from an active to a passive approach that will eventually lead to site closure at a reduced lifecycle cost.

3.2.1 Site Background

The DFSP occupies approximately 110 acres in central York County, Yorktown, Virginia (Figure 3-1). Beginning in 1918, Navy Special Fuel Oil (NSFO) was stored at the former Tank Farm Area in eight 90,000-barrel capacity, concrete USTs. Storage and use of NSFO was discontinued in 1972 and the USTs were abandoned in place in 1998. Historic releases of NSFO resulted in soil and groundwater contamination and large quantities of LNAPL in the aquifer. The extent of the LNAPL plume is estimated to underlie an area of approximately 13 to 14 acres, centered under the former USTs (NAVFAC, 2017a). Quantities released were estimated between 4.4 and 7.9 million gallons, of which 1.2 to 3.0 million gallons were estimated to have been mobile LNAPL and theoretically recoverable, with the remaining LNAPL (up to 4.9 million gallons) estimated to be residual and non-recoverable (NAVFAC, 2017a). NSFO is very viscous, relatively dense, making it challenging to recover using conventional technologies.

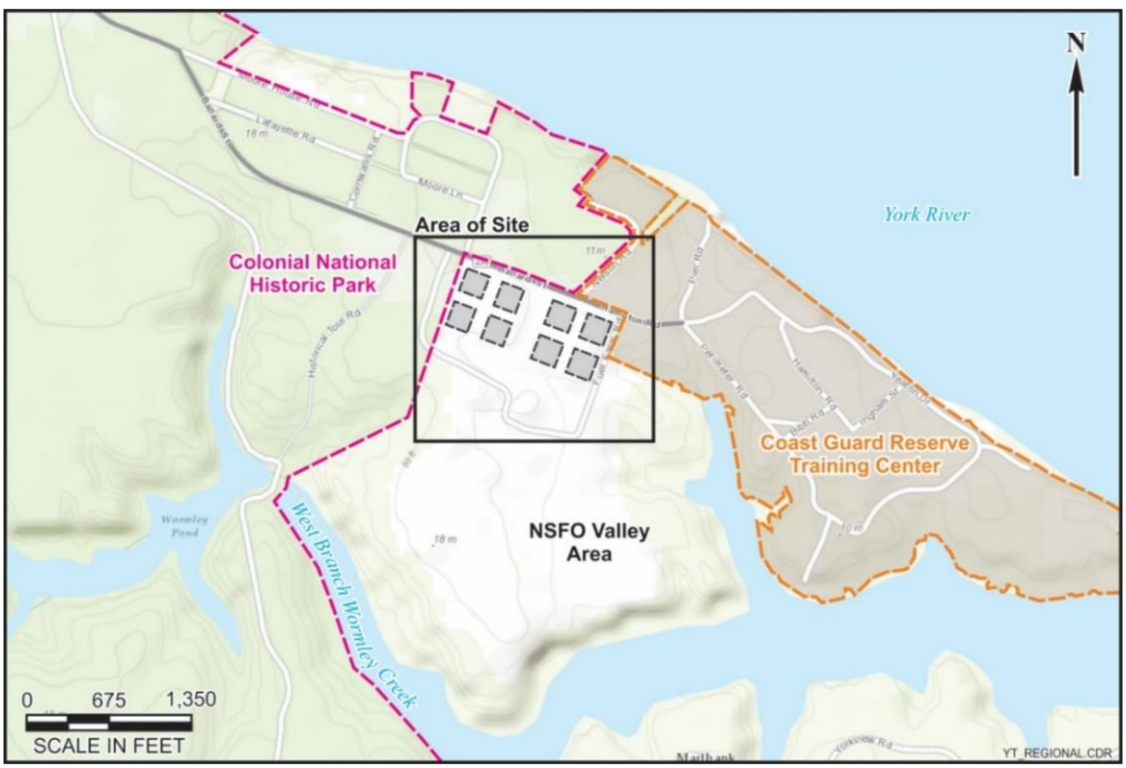

Figure 3-1. Regional Location Map for Yorktown DFSP, Virginia (Courtesy of NAVFAC)

A full-scale, heat-enhanced, total fluids recovery (TFR) system was operated from 2001 to 2019.[1] It was originally installed to prevent the migration of LNAPL toward a nearby creek. The TFR system was operated with a heating component from 2001 to August 2013 to heat the LNAPL to reduce its viscosity and increase its mobility. After this date, use of the heating component was discontinued while fluid recovery efforts continued through 2019. Although the system recovered an average of about 680 gallons/month during the 2016 calendar year, LNAPL recovery was leveling off, with the expectation that the operating cost (cost/gallon recovered) would become increasingly expensive and ultimately prohibitive. Approximately 470,000 gallons of LNAPL were recovered through 2017.

3.2.2 Technology Description

The steam-enhanced recovery system is comprised of 28 recovery trenches, multiple recovery wells, and groundwater depression and skimming pumps. The treatment system was designed to achieve 7 ft of drawdown of groundwater in each recovery trench operating in extraction mode to provide a pressure gradient to induce migration of the LNAPL into the trenches.

A closed-loop underground steam grid network indirectly heats the LNAPL, reduces its viscosity, and thereby enhances its recovery. The recovery system includes an aboveground plant to treat the recovered water to remove hydrocarbons and metals. LNAPL and water are separated, water is chemically treated and used in conjunction with dissolved air flotation to remove emulsified oil and solids. Water is further treated using clay absorbers, filter bags, and activated carbon. A portion of the water can be heated and introduced into the aquifer to facilitate recovery of viscous LNAPL, while the remainder is discharged to the York River.

LNAPL that is separated from groundwater in the oil-water separator (OWS) is pumped to a 20,000-gallon tank and then to an 8,000-gallon tank in series. Any residual water that settles out from the LNAPL in these tanks periodically is manually drained from the tanks and pumped back to the treatment plant through a sump. The recovered LNAPL in the 8,000-gallon tank periodically is removed by a tanker truck and transported to a processing facility to be recycled.

The steam generation system consists of a gas-fired boiler, a condensate return tank, two water softeners, two chemical feed systems, a boiler blowdown separator tank, and blowdown water holding tank and transfer pumps. The system is designed to provide saturated steam to the delivery system and ultimately to the below grade heating grids, heating coils located in the groundwater infiltration holding tank, heating coils in the LNAPL recovery tanks, and heating the condensate returns from the steam heating piping network.

3.2.3 State Regulatory Framework and Remedial Action Objectives and Goals

The lead regulatory agency overseeing the corrective action at the DFSP is the Virginia DEQ. The DFSP is regulated under Virginia's UST regulations and guidance for implementing corrective action. Section 9VAC 25-580-270 of Virginia UST regulation requires that LNAPL be recovered to the maximum extent practicable and Virginia's Storage Tank Program Technical Manual (Virginia DEQ, 2011) indicates that, in most instances, free product thickness should be 0.01 feet

[1] Operation of the system was discontinued to perform an NSZD investigation.

or less unless continued recovery efforts cannot attain this minimum and more aggressive recovery methods are not warranted.

However, in 2012, Virginia DEQ issued the memorandum “Case Closure Evaluation of Sites with Free Product” (Virginia DEQ, 2012) that provided guidance for evaluating the feasibility and practicality of LNAPL removal and recognizes when a site can be closed with LNAPL present (thicknesses greater than 0.01 ft) without increased risk to human health and the environment.

The 2012 Virginia DEQ guidance incorporates a line-of-evidence approach to evaluate if active LNAPL recovery is no longer necessary and to determine if a site containing LNAPL can be recommended for site closure. Specific lines of evidence include:

- Treatment system data indicate an asymptotic rate of LNAPL recovery (a line of evidence for achieving recovery to the maximum extent practical);
- The remaining LNAPL is not recoverable or has a low mobility/recovery as determined by transmissivity tests;
- Various LNAPL technologies have been used and/or evaluated;
- LNAPL and dissolved-phase constituents do not pose a risk to human health and the environment;
- The areal extent of the LNAPL plume is stable or decreasing;
- NSZD of the LNAPL is occurring and will serve to further mitigate risk; and
- Natural attenuation of the groundwater plume is occurring, will mitigate risk, and prevent further migration of the dissolved phase plume.

3.2.4 Petroleum Management Strategies and Practices Employed

In accordance with Navy policy, the Navy performed an optimization review of the remedial action in 2016 (Battelle, 2018). The review included a remedial alternative analysis (RAA) to compare the efficacy of the current remedy to other conventional and innovative technologies that could be implemented taking into consideration all site-specific factors. NSZD was recommended as a viable remedy and the Virginia DEQ issued a response letter concurring with the Navy’s recommendation (Virginia DEQ, 2018). The Virginia DEQ also approved to permanently discontinue operation of the heating portion of the system at DFSP (NAVFAC, 2017a). However, the Virginia DEQ requested that the fluid recovery portion of the system (i.e., operation without the heating component) continue to operate for one to two more years to demonstrate that the LNAPL recovery rate continued to approach an asymptotic value prior to transitioning to a passive technology.

A supplemental investigation was performed in 2019 and 2020 to collect data to evaluate NSZD (NAVFAC Mid-Atlantic, 2020). Operation of the TFR system was discontinued on March 1, 2019 to prevent any interference with the investigation. CO_2 flux traps were deployed in March 2019, September 2019, and July 2020 to quantify the rate of NSZD and concentrations of vapors in wells were measured to support the trap measurements; LNAPL thicknesses in wells were measured quarterly to assess LNAPL stability; quarterly groundwater monitoring was performed to assess temporal and spatial changes of the dissolved phase hydrocarbon plume and geochemical parameters associated with biodegradation; and LNAPL transmissivity testing was performed. The evaluation demonstrated that NSZD is an appropriate technology in lieu of active LNAPL recovery and is being recommended for application at the site. The findings from both studies were consistent in determining that an NSZD approach was feasible as described below (Battelle, 2018; NAVFAC Mid-Atlantic, 2020).

Optimization approaches at the site have consisted of the following: 1) continuously optimizing the operation, maintenance, and monitoring (OM&M) of the TFR system to increase the rate of LNAPL recovery and/or reduce operating costs and 2) collecting data necessary to address the lines of evidence as described in Section 3.2.3 in accordance with Virginia DEQ guidance.

Optimization of the OM&M has focused on making modifications to equipment, materials, and procedures including eliminating heating, using fewer or different treatment chemicals, reducing monitoring, and other process changes to reduce annual operating costs while maintaining or improving performance. More recently, as understanding of LNAPL behavior and LNAPL site management practices have evolved and NSZD has gained greater regulatory acceptance, optimization activities have focused on addressing those criteria necessary to demonstrate that remaining LNAPL does not pose a risk to human health and the environment and that NSZD can attenuate the LNAPL remaining at the site.

Recent activities have consisted of compiling information from reports to develop an updated and relevant CSM and identifying data gaps. Additional site investigations include supplemental site characterization, a demonstration of an innovative smoldering technology to remove LNAPL, and an NSZD study that was performed to address data gaps. Results have been used to refine the CSM and address the lines of evidence required by the Virginia DEQ to demonstrate that the site poses minimal risk and can be transitioned to a passive remedy and/or apply for closure while LNAPL remains in place. These lines of evidence and the associated activities and data used to justify them are summarized below.

Does Treatment System Data Indicate an Asymptotic Level of LNAPL Recovery?

The closed-loop steam enhanced treatment system recovered more than 470,000 gallons of LNAPL between 2001 and March 2017. As shown in Figure 3-2, LNAPL recovery was beginning to approach an asymptotic value by 2017. Figure 2-2 (in Section 2) depicts the results of the decline curve analysis for this site. It shows that LNAPL recovery was rapidly decreasing and that the theoretical maximum recoverable LNAPL (x-intercept) was approximately 554,000 gallons, assuming no modifications to the system (additional well trenches, improved heating, vacuum-enhanced recovery, etc.). Although this analysis predicted that 80,000 gallons of LNAPL could theoretically still be recovered from the site, the cost to continue recovery would become prohibitive before the maximum theoretical recovery would be achieved. Hence, it is not reasonable to assume that operation would continue until the recovery rate decreased to zero gallons per month. As agreed between the Navy and the Virginia DEQ (Virginia DEQ, 2017), the TFR system remained operational for about two more years to demonstrate a continued reduction in the LNAPL recovery rate. Operation was discontinued on March 1, 2019 to perform the NSZD investigation.

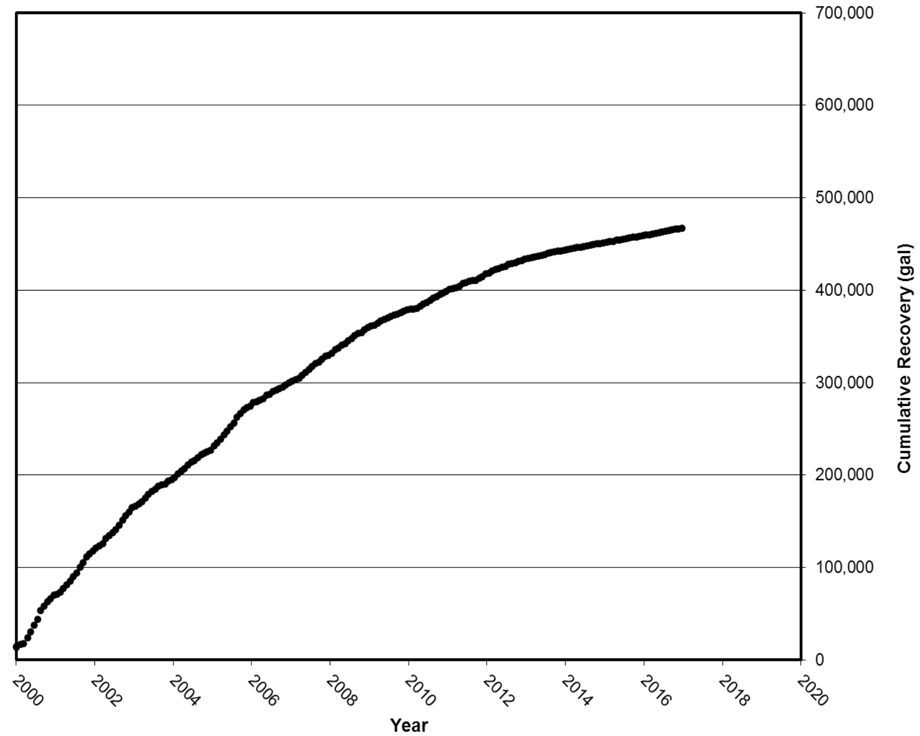

Figure 3-2. Cumulative LNAPL Recovery (Courtesy of NAVFAC)

To What Extent is the Remaining LNAPL Mobile?

LNAPL transmissivity was determined as part of the 2017 optimization study (Battelle, 2018) using data generated by the recovery system as described in ASTM E2856-13 (ASTM, 2013). Figure 3-3 shows three transmissivity curves as a function of time generated from a sensitivity analysis using estimated low, high and mode values of aquifer transmissivity. LNAPL transmissivity was very high during the early years of operation but has decreased over the last several years. The dashed lines shown in the figure represent a guideline range of values suggested by the ITRC, below which additional LNAPL recovery may not be practicable (ITRC, 2009). The curves generated using the mode and minimum aquifer transmissivity values fall below the 0.1 ft^2/day minimum value, while the curve generated using the highest transmissivity value falls within this range. These data indicate that this criterion has been met and thus provides a line of evidence that LNAPL recovery using the existing system may be approaching a diminishing point of return and may no longer be necessary.

Transmissivity also was measured as part of the recent NSZD investigation. Testing was performed at select wells in accordance with ASTM E2856-13. However, LNAPL transmissivity could not be measured because the viscous LNAPL either did not enter and/or could not be observed and removed from the well indicating that the formation is not transmissive with respect to LNAPL at these locations, which is suggestive that the LNAPL at those locations is not mobile (NAVFAC Mid-Atlantic, 2020).

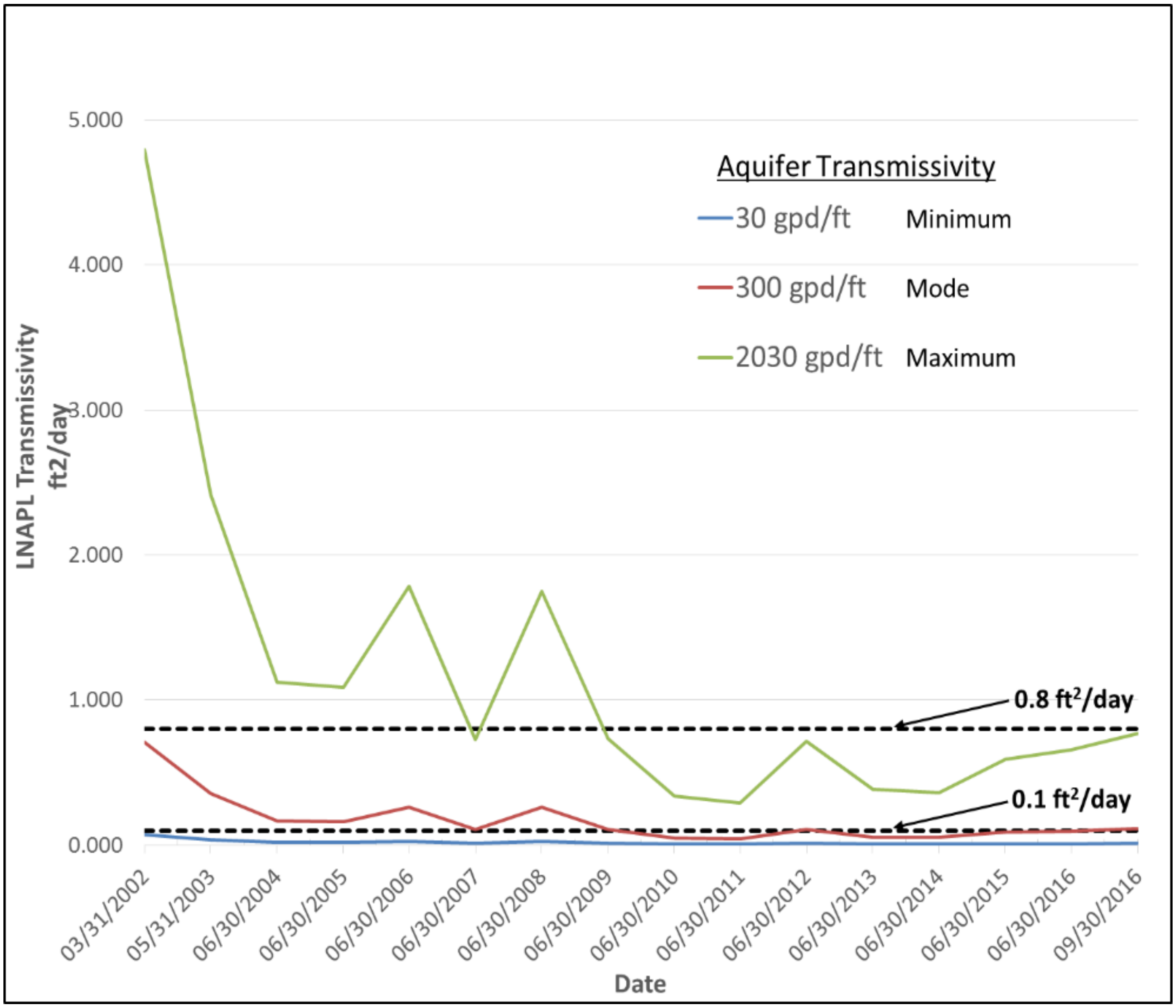

Figure 3-3. LNAPL Transmissivity as a Function of Time (Courtesy of NAVFAC)

Have Other LNAPL Treatment Technologies Been Evaluated and/or Tested?

As part of the CAP, a remedial technology screening was performed that included various excavation options, product recovery with and without heat enhancement (hot water and steam), and MNA (Baker, 1996). In 2005, this prior screening was reassessed as part of an optimization study (URS, 2005), which considered an updated CSM and new technology developments and refinements. Two additional technologies including surfactant-enhanced subsurface remediation (SESR) and excavation with on-site treatment with beneficial reuse of materials using a batch asphalt plant were considered. SESR was carried forward in the evaluation and was recommended as a potential alternative to the existing treatment system but was not implemented.

As part of a more recent optimization study (Battelle, 2018), the previous technology screenings and analyses were re-evaluated based on current site conditions and LNAPL site management practices and recent advances in technologies to address viscous LNAPL. A literature search was performed to identify technologies that could be suitable to remediate the type of LNAPL present. Technologies including excavation, electrical resistance heating, surfactant-enhanced recovery, and in situ chemical oxidation were considered for application at the site; however, they were determined either to be technically impractical due to existing site conditions, would be excessively difficult to implement, or result in prohibitively high cost.

Three technologies including NSZD, MPE, and self-sustaining treatment for active remediation (STAR), an aggressive in situ combustion technology used to treat viscous LNAPLs such as creosote and Bunker C fuel, were determined to be possible candidates for application at the site. However, further evaluation of MPE (with and without heat) indicated that although it could be effective, various site-specific limitations and challenges would make this alternative challenging and/or costly to implement.

A pilot-scale demonstration of STAR was performed since STAR was a new and innovative technology for which the availability of data from previously applications were limited. Although STAR effectively treated contaminated soil in the immediate vicinity of the ignition well, the average treatment efficiency declined at short distances from the well, which likely was a result of the discontinuous nature of the LNAPL as well as the presence of a low permeability clay lens located at about 17 to 18 feet beneath the ground surface that may have hindered the distribution of air and propagation of the smoldering front. Because many closely spaced ignition wells would be required to treat the remaining NFSO, it was deemed to not be a cost effective solution based on the site-specific pilot test results.

Do LNAPL and Dissolved-Phase Constituents Pose a Risk to Human Health and the Environment?

Human health and ecological risk assessments have been performed for the site. The HHRA concluded that "*carcinogenic risks associated with the site and the surrounding properties were within the U.S. EPA's acceptable target risk range for the exposure scenarios evaluated and that the potential for an adverse (non-carcinogenic) system effect is minimal*" (URS, 2005). The ecological risk assessment concluded that there was no impact to the terrestrial population on the adjacent Colonial Historic National Park property to the west (URS, 2005). Potential impacts, but no major risks, were identified to terrestrial populations at the NSFO Area and adjacent United States Coast Guard property to the north. Potential impacts also were identified to the terrestrial and aquatic ecosystems in the Wormley Pond Valley Area (URS, 2005); however, updates to the risk assessments demonstrated that the LNAPL constituents do not present a risk to human health or the environment due to the absence of a complete exposure pathway and because the viscosity of the LNAPL renders it immobile (URS, 2005).

During the NSZD investigation, the concentrations of dissolved hydrocarbon constituents were compared against the Virginia Voluntary Remediation Program (VRP) Groundwater screening levels, which are based on U.S. EPA Region 3 Risk Screening Level updated June 2019 (NAVFAC Mid-Atlantic, 2020). Naphthalene was the only compound found to exceed its standard, which occurred in three isolated locations, when compared to the "construction direct contact" scenario. The construction direct contact exposure scenario applies to soil intrusive activities, the exposure to which can be easily controlled with various health and safety precautions. Hence, the site would not pose unacceptable risks if operation of the recovery system is permanently discontinued (NAVFAC Mid-Atlantic, 2020).

Is the Areal Extent of the LNAPL Plume Stable or Decreasing?

The areal extent of the LNAPL plume is decreasing as illustrated in Figure 3-4. The thickness of the plume has varied across the site from less than 0.01 feet to about 15 feet. LNAPL thicknesses were measured in December 2018 prior to turning off the recovery system, and again in March, June, and August 2019 and July 2020. The perimeter monitoring wells did not show evidence of an increase in LNAPL indicating that the plume remained stable after turning off the system, although some variations were noted within the LNAPL body, presumably due to LNAPL re-equilibrating and seasonal variations (i.e., change in groundwater elevations) (NAVFAC Mid-Atlantic, 2020).

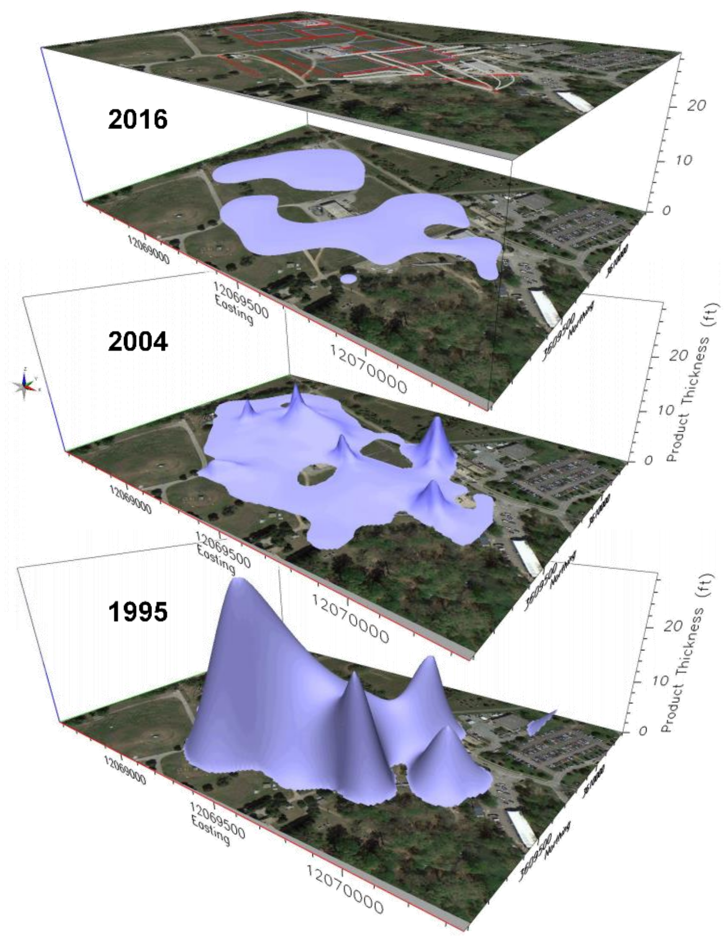

Figure 3-4. Reduction of LNAPL in Monitoring Wells (Courtesy of NAVFAC)

Is NSZD Occurring and Will it Continue to Mitigate Risk?

NSZD consists of multiple natural in situ degradation processes, including dissolution, volatilization, and biodegradation, which reduce the mass of LNAPL over time. Biodegradation has been shown to be the predominant mechanism by which LNAPL attenuates (ITRC, 2009). Dissolution and volatilization transfer LNAPL constituents into the aqueous and vapor phases, respectively, and biodegradation converts these constituents into innocuous byproducts including

CO_2 and water. As a remediation technology, NSZD focuses on monitoring and evaluating these processes, with the objective to determine their contributions to LNAPL attenuation and impact on the time to achieve remedial action objectives.

Virginia DEQ guidance requires that an assessment of NSZD processes be performed to demonstrate that NSZD is occurring and can serve to attenuate remaining LNAPL over time in order to transition and/or discontinue active remediation activities. To address this requirement, CO_2 fluxes were measured using aboveground CO_2 flux traps at 10 locations; nine placed in the LNAPL body and one placed at an upgradient location. Carbon trap deployment was performed in March 2019, September 2019, and July 2020 to understand temporal and seasonal variations. The traps were analyzed for CO_2 as well as the ^{14}C isotope in order distinguish the CO_2 that was produced from the degradation of LNAPL from that originates from potential non-LNAPL sources (NAVFAC Mid-Atlantic, 2020). NSZD rates were found to vary spatially and temporally (NAVFAC Mid-Atlantic, 2020). Higher concentrations (and therefore higher LNAPL degradation rates) were observed during months when soil temperatures were elevated, which is consistent with results observed at other sites. Soil borings also demonstrated a high degree of variability, with the highest values located in the southern portion of the site where the LNAPL smear zone begins at shallow depths at about 5 feet beneath ground surface and contains few or no clay lenses that could impact transport of vapors to the ground surface. The CO_2 flux data confirmed that NSZD is occurring with LNAPL depletion rates ranging between about 55.8 to 100 gal/acre/year. Assuming the LNAPL is spread across an area of 22 acres, based on these measurements, removal rates due to NSZD were calculated to range from about 1,230 to 2,200 gallons per year (NAVFAC Mid-Atlantic, 2020).

To address concern that clay lenses could have adversely impacted flux measurements, concentrations of CO_2 and methane in headspace in select wells were measured since vertical transport through a water column within a well is not impacted by surrounding lithology. Eleven locations out of 14 exhibit elevated levels, several of which were located adjacent to CO_2 traps that did not present elevated concentrations. From these results it was concluded that concentrations measured with the CO_2 traps may underestimate the NSZD rate (NAVFAC Mid-Atlantic, 2020).

Is Natural Attenuation of the Groundwater Plume Occurring and Will it Prevent Further Migration of the Dissolved-Phase Plume?

Monitoring of the dissolved phase plume was performed regularly during operation of the recovery system, the results of which confirm that the dissolved-phase plume is not migrating downgradient of the site. Groundwater monitoring has been continued since turning off the product recovery system on March 1, 2019. Data continue to indicate that the plume boundary is stable, although concentrations of naphthalene and benzene fluctuate within the body of the plume (NAVFAC Mid-Atlantic, 2020). Groundwater monitoring data measured after operation of the fluids recovery system was discontinued were used to calculate an LNAPL dissolution rate based on the ITRC NSZD guidance (ITRC, 2018) and using octane (C_8H_{18}) as a representative constituent of LNAPL, resulting in an average of 61.4 kg/yr with a range from 31.86 to 137 kg/yr (NAVFAC Mid-Atlantic, 2020). Since the dissolved phase plume is stable (not expanding), it can be assumed that the rate of degradation is at least equal to the rate of dissolution of hydrocarbons, indicating that the dissolved phase contaminants are attenuating. To further evaluate natural attenuation, a biodegradation rate was calculated using an electron budgeting approach that takes into consideration the consumption of electron acceptors including DO, nitrate, and sulfate and the production of degradation products including dissolved iron, manganese, and methane, using data collected during recent monitoring events. The resulting biodegradation rates were calculated to range from 55.8 to 119 kg/yr, which are similar to the calculated dissolution rates (NAVFAC Mid-Atlantic, 2020) providing another line of evidence that biodegradation and natural attenuation are occurring. Furthermore, since the dissolved phase plume is stable, it appears that the degradation rate is sufficient to prevent plume migration.

3.2.5 Conclusions

The optimization study and subsequent NSZD investigation resulted in regulatory approval to transition from active LNAPL recovery to NSZD with associated monitoring. This will result in a lower lifecycle cost and a more sustainable technology that has been well received by the regulatory stakeholders. Recent remedial action optimization activities have focused on demonstrating the lines of evidence as established by the Virginia DEQ to evaluate the feasibility and practicability of discontinuing active LNAPL recovery and transition to NSZD and eventually close the site with LNAPL in place. A summary of the Virginia DEQ lines of evidence, current status, and recommendations for future efforts are provided in Table 3-2.

Table 3-2. Summary Virginia DEQ Requirements as they Apply to the DFSP Site

Criterion	Key Metric	Result	Recommendations
Has LNAPL Recovery Diminished?	Cumulate Recovery/Decline Curve	Yes >470,000 gal out of a theoretical maximum of 554,000 gal	Operation of the system was discontinued in March 2019. Continue to monitor LNAPL thickness to determine if data indicate LNAPL is migrating.
Is LNAPL Immobile?	Transmissivity	Yes. Transmissivity is <0.8 ft^2/day^2 and the LNAPL plume footprint is stable	Continue to monitor LNAPL thickness and confirm LNAPL remains immobile.
Have Other Technologies Evaluated or Implemented?	RAA	Yes	No additional information needed.
Does the Site Pose Risk to Human Health and the Environment?	Risk Assessment	No unacceptable risk	No additional information needed.
Is the LNAPL Plume Stable or Decreasing?	LNAPL thickness	Stable	Continue to monitor quarterly (LNAPL thickness)
Is NSZD Occurring?	CO_2 flux measurements.	Yes (1,230 to 2,200 gal/yr)	Continue to monitor semi-annual to annual.
Is Natural Attenuation Occurring?	Natural attenuation parameters (concentrations of electron acceptors and degradation products)	Yes	Continue to monitor semi-annual to annual.

3.3 Case Study 2: IRP Site 1, Armitage Field Operable Unit, Naval Air Weapons Station, China Lake, California

Data were collected from July 2018 through April 2019 to support a remedial system evaluation (RSE) for IRP Site 1 located within the Armitage Field Operable Unit (OU) at Naval Air Weapons Station (NAWS) China Lake. This evaluation was conducted as part of a strategic project led by NAVFAC EXWC and documented in the Technical Report - Transition of Petroleum Sites to Closure or Passive Remedies: Evaluating Natural Source Zone Depletion and Other Methods (NAVFAC EXWC 2021). The RSE is being conducted to address changes in the nature and extent of the contaminant plume since remedial activities were first implemented at the site. The purpose of the RSE is to identify opportunities for improving remedy protectiveness, effectiveness, and cost efficiency and to facilitate progress toward site remediation completion.

3.3.1 Site Background

IRP Site 1 is located at the Armitage Field Former Fuel Farm (also called UST Site 10) approximately 3 miles north of the City of Ridgecrest, in the southern portion of NAWS China Lake. Six USTs were installed at the site from 1945 to 1957, including two 100,000-gallon and four 50,000-gallon USTs and one 4,000-gallon waste oil tank was installed in 1959. These USTs operated at the site until 1997 when fuel operations ceased, and the USTs and distribution systems were removed. Several types of aviation fuel were stored in these tanks including jet fuel (JP-3, JP-4, and JP-5) and aviation gas (avgas 115/145, and avgas 100/130). IRP Site 1 also included a series of 10-foot deep dry wells installed in 1945 that were used to dispose of off-specification aircraft fuels, used engine oils, fuel tank condensate, excess fuels and possibly solvents and degreasers, and sometimes these materials were released directly to the ground surface. These disposal practices were discontinued in 1982 and the dry wells were removed in 1997.

Multiple site investigations were performed, culminating in the Phase II remedial investigation in 1998 (Tetra Tech, 1998) and subsequent groundwater monitoring program to support the Armitage Field Feasibility Study (Tetra Tech, 2005). These investigations identified a floating free product plume composed of JP-5 and JP-4 range petroleum hydrocarbons covering approximately 14.3 acres at Site 1. This free product plume was found to be surrounded by a larger dissolved phase plume of petroleum-related VOCs, SVOCs, and PAHs covering approximately 38 acres (Tetra Tech, 2003).

In July 2000, a vacuum-enhanced skimming (VES) system was installed under the UST CAP, which preceded the ROD/RAP. The VES system was designed to induce a vacuum in the extraction wells to volatilize and then recover free product. These VES wells were screened across both the water table and the unsaturated zone. In 2003, some of the wells used by the VES system were converted for use as part of an SVE system, which is still currently in use at the site. The current SVE system includes 11 vapor extraction wells and a thermal oxidizer unit to burn hydrocarbons in the extracted soil vapor with a 99.9% destruction efficiency. Hydrocarbons recovered by the SVE system include contaminated soil vapor and volatilized hydrocarbon mass from the free product in the wells and surrounding formation (NAVFAC, 2017b). In addition, a MPRS is used to recover LNAPL from monitoring wells as needed based on periodic free product gauging. The MPRS is a trailer-mounted system consisting of a submersible product-only skimmer pump powered by compressed nitrogen gas or air and a steel LNAPL storage tank with secondary containment. The MPRS was first used at Site 1 as early as 1995 and has been regularly deployed since September 2006 (NAVFAC Southwest, 2016).

Under a 2014 optimization program, five pneumatic "Solar Sipper" systems were installed as a new solar-powered skimmer-based FPRS at IRP Site 1. These five skimmers are currently in use at IRP Site 1 and since being deployed have been periodically relocated to other on-site wells to take advantage of more favorable product recovery characteristics (NAVFAC, 2017b). Substantial amounts of free product have been recovered since initiating the corrective action, and estimates based on the partition coefficients of the contaminants and declining recovery rates indicate that as little as 1% of the original amount of free product may remain in the subsurface (NAVFAC Southwest, 2020).

3.3.2 State Regulatory Framework and Remedial Action Objectives and Goals

IRP Site 1 is part of the Armitage Field OU, which includes seven IRP sites (1, 2, 3, 44, 45, 50, and 58). The investigations and remedial activities for the Armitage Field OU are being conducted under the regulatory framework of CERCLA. The lead agency for these activities is the Navy with regulatory oversight from the California Department of Toxic Substances Control (DTSC) and the Region 6 California Regional Water Quality Control Board (RWQCB). The Navy, DTSC, and RWQCB signed a Federal Facilities Site Remediation Agreement (FFSRA) for NAWS China Lake in 2003. The FFSRA covers environmental cleanup activities under CERCLA at the entire NAWS China Lake facility and establishes a framework for the regulatory oversight and environmental management at the facility. Remedial activities, investigations, and evaluations for IRP Site 1 are being performed in accordance with the RAOs and applicable or relevant and appropriate requirements (ARARs) as described in the ROD/RAP for IRP Site 1 at the Armitage Field OU (NAVFAC Southwest, 2007). As presented in the ROD, the following RAOs apply to the petroleum contamination at IRP Site 1 and groundwater throughout the Armitage Field OU for the protection of human health and the environment:

- Free Product Mitigation - Remove free product (consisting of waste jet propellant [JP-5] fuel) to the maximum extent practicable.
- Human Health Protection from Groundwater - Prevent exposure to groundwater that contains trichloroethene, tetrachloroethene, benzene, and 1,2-dichloroethane at levels that exceed federal and state maximum contaminant levels.

These RAOs are appropriate given the site conditions when the ROD was prepared. The evaluation of achieving free product removal to the ″maximum extent practicable″ should consider the improved understanding of LNAPL behavior in the subsurface and actual risk posed by residual LNAPL, as discussed in Section 2.1. The data presented in this case study were collected with the goal of supporting multiple lines of evidence that demonstrate free product has been removed to the maximum extent practicable at Site 1.

3.3.3 Petroleum Management Strategies and Practices Employed

The RSE conducted at IRP Site 1 utilized many of the Navy's optimization concepts to begin developing a line of evidence approach to facilitate progress toward improving the cost effectiveness of the remedy. The RSE planning effort included the preparation of an RSE Workplan that provided the technical approach for applying these optimization concepts

(NAVFAC, 2017b). As part of the RSE, data were collected to understand: (1) the mobility of free product by means of assessing the current extent of the LNAPL plume; (2) the extent of recoverable free product based on transmissivity testing; and (3) if the LNAPL source zone is naturally attenuating based on an evaluation of NSZD (NAVFAC Southwest, 2020).

Mobility of LNAPL Product

Historically, the limits of the mobile LNAPL were inferred to a great extent due to significant data gaps in the monitoring network. Figure 3-5 shows the inferred extent of mobile LNAPL in 2008 (defined as greater than 0.01 feet thick) as the pink shaded area extending beyond the IRP site boundary to the east and to the north (NAVFAC, 2017b). As part of the RSE, measured product thickness data collected during the April 2019 O&M event (Figure 3-6) were evaluated along with UVOST® data collected in July 2018 (Figure 3-7) to update the CSM with respect to LNAPL extent (NAVFAC Southwest, 2020). The UVOST® system includes a down-hole tool equipped with a specialized laser that causes LIF in soil or groundwater that is contaminated with LNAPL. LIF responses were reported on wavelengths ranging from 350 nanometers (nm) to 500 nm (color coded from blue to orange in Figure 3-7). It is noted that calcareous sands, atypical organic soils, and other materials (e.g., seashells, peat, wood, septic) also fluoresce in response to the UVOST® system. To assist with data interpretation, recovered LNAPL free product was analyzed with UVOST® and the LIF response was noted as having a wavelength of 350 nm. Longer wavelength responses (i.e., LIF responses with wavelengths of 450 nm and longer) were interpreted to be caliche mineral deposits in the subsurface. Based on this, the UVOST® investigation indicates that petroleum contamination occurs at depths ranging from 37 feet below ground surface (bgs) to 42 feet bgs as shown in Figure 3-7, corresponding to the current depth to the water table at Site 1 (NAVFAC Southwest, 2020). A comparison of historical data to current site data, including the UVOST® investigation to fill data gaps at Site 1, shows that the overall aerial extent of LNAPL is decreasing over time. This decrease indicates that there is a low risk for future LNAPL migration.

Extent of Recoverable LNAPL

LNAPL transmissivity data were collected by baildown testing in accordance with the American Petroleum Institute (API) User Guide titled *API LNAPL Transmissivity Workbook: A Tool for Baildown Test Analysis* (API, 2016). Using this approach, LNAPL is rapidly removed from a well and the rate of fluid recovery is measured over time. Based on the hydrogeologic conditions at Site 1, data were evaluated using the API spreadsheet for an unconfined aquifer to calculate transmissivity. The LNAPL transmissivity tests were performed at well TT01-MW01 in the aviation gas plume and well MP-3 in the central portion of the main jet fuel plume (Figure 3-5). These wells were selected as they recently had measurable free product which is necessary to perform the test (3.5 feet at TT01-MW01 and 0.075 feet at MP-3). Results indicated similar results at both wells, with transmissivity measurements of 7.86 ft^2/day at TT01-MW01 and 7.35 ft^2/day at MP-3 (NAVFAC Southwest, 2020). These results are greater than the ITRC (ITRC, 2018)-recommended value of 0.8 ft^2/day as an indicator of recoverable LNAPL; however, the free product thickness at MP-3 (0.075 feet) is below the ITRC-recommended level of 0.2 feet and therefore may be error prone. Additionally, LNAPL transmissivities vary in space and time and should not be viewed as aquifer-wide properties. They are specific to that location at that time (NAVFAC Southwest, 2020).

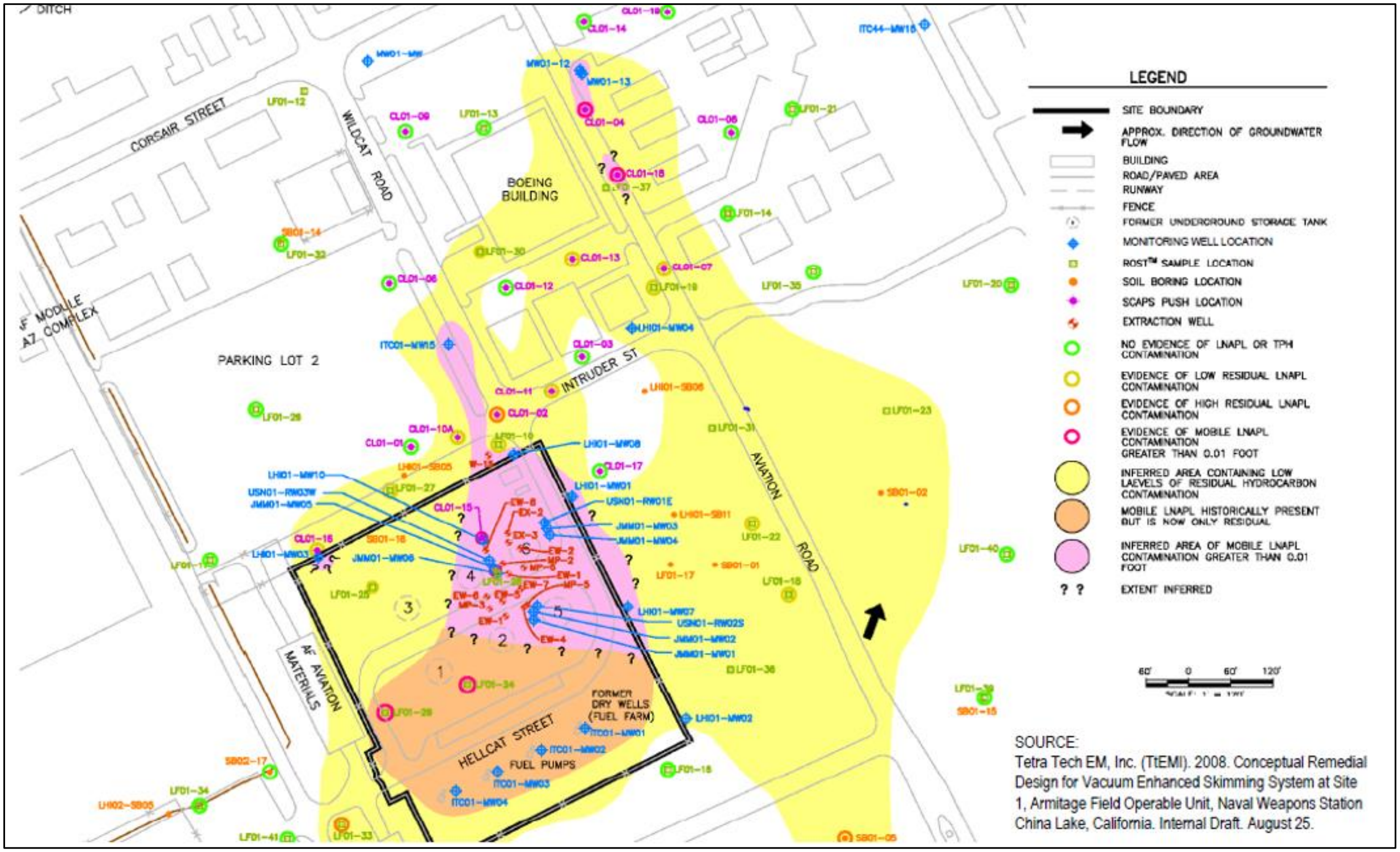

Figure 3-5. LNAPL Historic Extent at NAWS China Lake (Courtesy of NAVFAC)

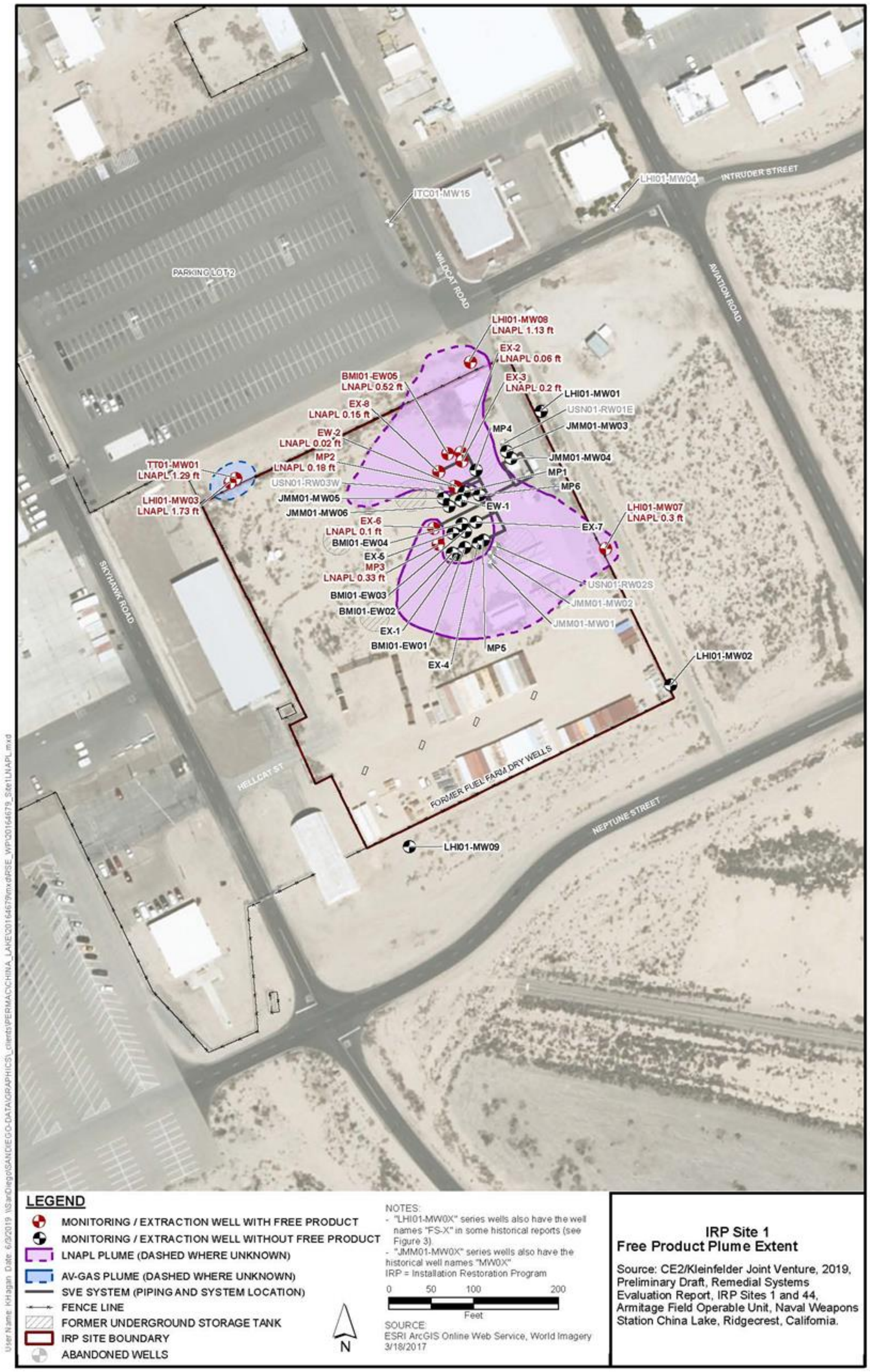

Figure 3-6. Free Product Plume Extent (July 2018) (Courtesy of NAVFAC)

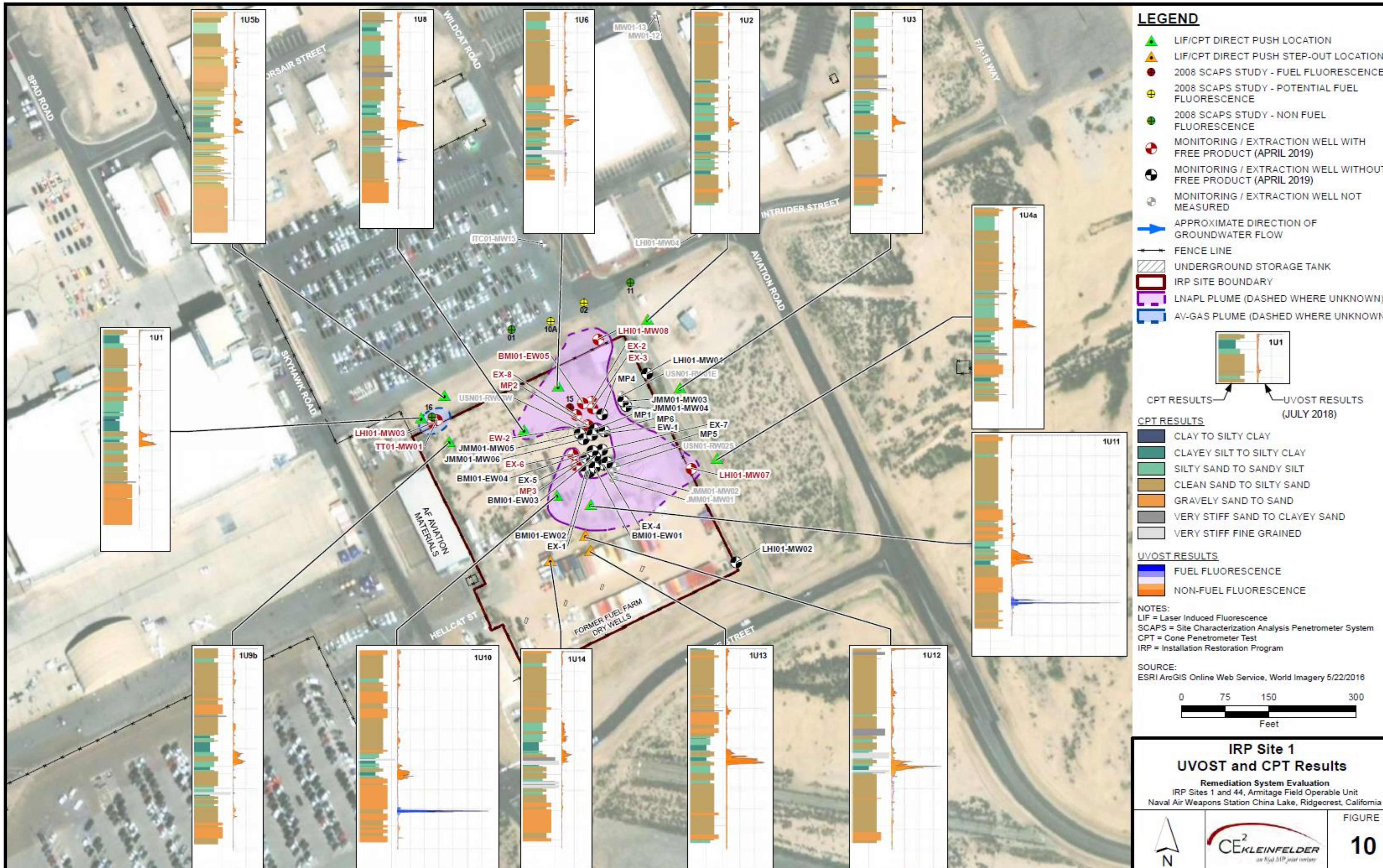

Figure 3-7. UVOST® Results for IRP Site 1 (Courtesy of NAVFAC)

Natural Attenuation of LNAPL

The natural attenuation evaluation focused on NSZD processes applicable to LNAPL; however, a summary of the groundwater MNA monitoring program was also presented. Analytical results from the groundwater monitoring program indicate that contaminant concentrations continue to attenuate toward levels below or near endpoint criteria. Low DO and negative oxidation reduction potential (ORP) values indicate a reducing environment at Site 1, suggesting that the naturally occurring microbial population is actively metabolizing dissolved phase contaminants (NAVFAC, 2020).

The evaluation of NSZD at IRP Site 1 was conducted using two innovative monitoring approaches, CO_2 traps and thermal monitoring. The data obtained from each of these techniques were used to calculate LNAPL biodegradation rates. A total of 10 CO_2 traps and three thermal monitoring stations were installed at Site 1 (Figure 3-8). All CO_2 traps and two thermal monitoring locations were located within or adjacent to the LNAPL plume area based on the UVOST® investigation results. The third thermal monitoring location was located outside of the LNAPL plume area to serve as a background station. The CO_2 traps were deployed in unpaved areas across the site for a total of 20 days, and the thermal monitoring points collected continuous real-time data for approximately 6 months (NAVFAC Southwest, 2020).

Carbon trapping is a method to estimate the depletion of LNAPL resulting from biodegradation by measuring the amount of CO_2 leaving the subsurface. Analysis of the traps quantifies the CO_2 flux, which is the rate of CO_2 produced from biodegradation measured as the mass of CO_2 emitted from the subsurface over a given area for a defined time period. Specifically, the CO_2 flux is calculated by dividing the mass of CO_2 measured to have accumulated in the trap by the cross-sectional area of the trap (4-inch diameter) and the time period the trap was deployed (20 days). The resulting CO_2 flux is then converted to mass of hydrocarbons removed by selecting an appropriate stoichiometric ratio between CO_2 and LNAPL.

A travel blank was analyzed to measure the fossil-fuel carbon content of unexposed CO_2 trap sorbent material. The mass of fossil fuel CO_2 from the travel blank was subtracted from the mass of CO_2 from field-deployed traps. This is reported as the "Blank-Corrected" CO_2 flux in Table 3-1. This blank-corrected CO_2 flux is then representative of the sum of CO_2 flux related to the LNAPL degradation and that produced from natural soil respiration processes at each sample location. The LNAPL degradation-derived CO_2 flux is obtained through the "background correction" by subtracting the natural respiration CO_2 flux from the measured CO_2 flux. The natural respiration CO_2 flux is measured by radiocarbon (^{14}C) analysis of each carbon trap.

Following the two corrective steps described above, the LNAPL-derived CO_2 flux was converted to mass/volume of LNAPL removed by selecting an appropriate stoichiometric ratio between CO_2 and LNAPL. For the application at IRP Site 1, LNAPL was assumed to be octane/C_8H_{18} with a representative specific density of 0.77 gram/centimeter^3. When the trip blank-corrected CO_2 flux is not statistically different from the "background" CO_2 flux, then the LNAPL loss rate is considered non-detectable.

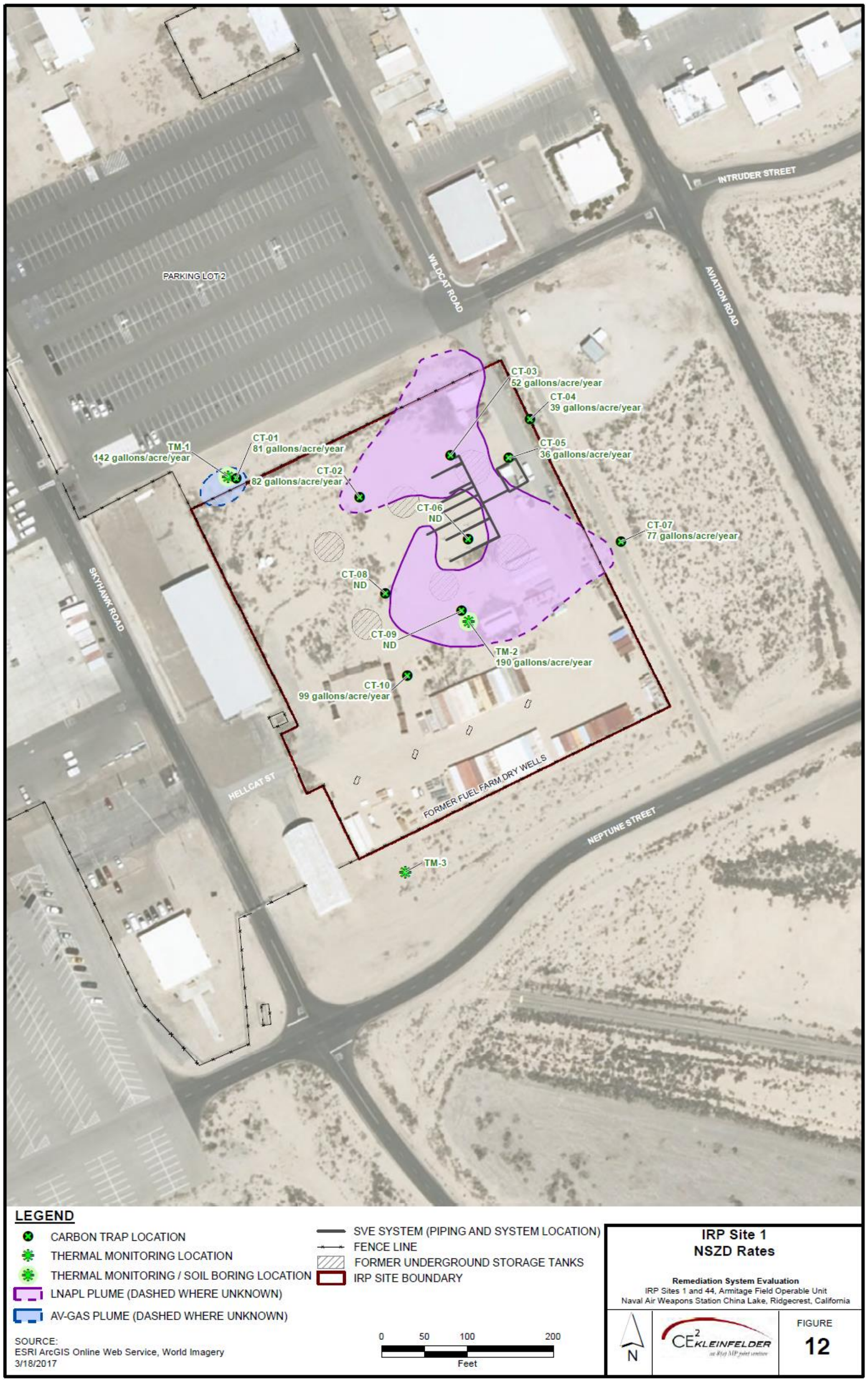

Figure 3-8. NSZD Rates at IRP Site 1 (Courtesy of NAVFAC)

The CO_2 fluxes and measured NSZD rates for IRP Site 1 are summarized in Table 3-1 and shown on Figure 3-8. The measured NSZD rate ranged from non-detect to 99 gallons of LNAPL per acre per year (gallons/acre/year). Assuming non-detect as zero, the CO_2 flux-based average NSZD rate for the site is approximately 47 gallons/acre/year. Excluding the three non-detect results, the average NSZD rate of the remaining seven locations is approximately 67 gallons/acre/year. Spatial variability of the NSZD rates is likely due to variability in the presence and concentration of LNAPL found in the subsurface, which is a result of both prior SVE treatment in portions of Site 1 and the heterogenous nature of the subsurface geology. Nevertheless, evidence of NSZD occurring at Site 1 exists despite the observed spatial variability (NAVFAC Southwest, 2020).

Table 3-1. CO_2 Flux Measurements and Estimated NSZD Rates at Site 1

Location	Blank-Corrected CO_2 Flux (μmol/m^2/s)	Natural Respiration CO_2 Flux (μmol/m^2/s)	Fossil Fuel CO_2 Flux (μmol/m^2/s)	NSZD Rate (gal/acre/year)
CT-01	0.65	0.52	0.13	81
CT-02	0.74	0.61	0.13	82
CT-03	0.88	0.79	0.08	52
CT-04	1.33	1.27	0.06	39
CT-05	0.68	0.62	0.06	36
CT-06	0.68	0.65	ND	ND
CT-07	0.93	0.81	0.12	77
CT-08	0.67	0.63	ND	ND
CT-09	0.59	0.57	ND	ND
CT-10	0.88	0.72	0.16	99

ND = non-detect

NSZD rates were also measured using thermal monitoring based on the understanding that heat is generated when the LNAPL degradation product, methane, is oxidized in the vadose zone above the LNAPL source. Recent research has found that anaerobic biodegradation of LNAPL generating methane is the primary mechanism of NSZD (Garg et al., 2017). As such, measuring the heat generated by this biodegradation process in an LNAPL source zone through temperature monitoring provides an indirect measurement of the NSZD rate. The measured heat flux was converted to an NSZD rate using the thermodynamics of the reactions involved in biodegradation.

The Thermal NSZD® technology by Thermal NSZD LLC was applied at Site 1. Thermal NSZD® is a continuous thermal monitoring system that measures the heat generated by biodegradation processes using a vertical series of thermocouples and converts the heat to daily and cumulative mass of LNAPL destruction in the subsurface. Three thermal monitoring locations were installed at Site 1: one in the aviation gas plume near the northeast corner of the site (TM-1), one in the jet fuel plume near the center of the site (TM-2), and one outside of the LNAPL plume area to serve as a background location (TM-3). Each thermal monitoring station was comprised of a 3/8-inch diameter solid polyvinyl chloride rod with eight thermocouples attached at depths of 6, 11, 16, 21, 26, 36, 41, and 46 feet bgs, respectively.

Temperature data from the thermal monitoring stations were remotely transmitted and recorded daily to a Thermal NSZD Dashboard during system operation. Temperature data were corrected for background (i.e., the difference between the raw temperature reading and the background temperature reading) and converted to NSZD rates at each LNAPL-impacted location via automated algorithms. Outputs from the Thermal NSZD Dashboard included daily NSZD rates, temperature versus time/depth data (both raw data and background corrected data), and calculation parameters.

Vertically, the background-corrected average temperatures were highest at 26 and 36 bgs at TM-1 and TM-2, respectively, and decreased upward towards the ground surface and downward towards the saturated zone (Figure 3-9). These appear to be the depth zones that contributed the most to the methane oxidation and are located above the mobile or residual LNAPL sources, as expected.

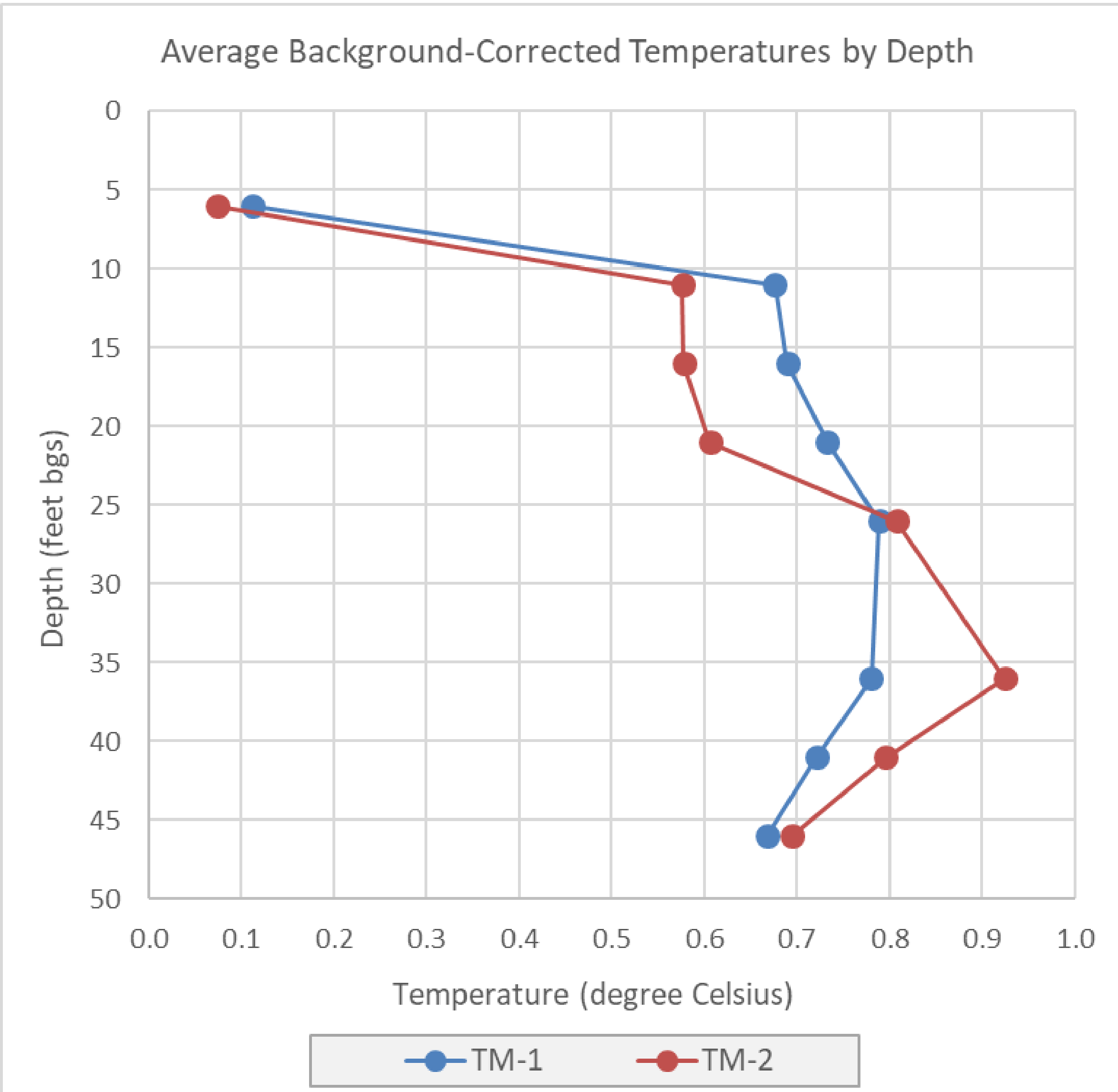

Figure 3-9. Average Background-Corrected Temperatures by Depth (Courtesy of NAVFAC)

The daily and average NSZD rates at locations TM-1 and TM-2 are shown in Figure 3-10. In general, the NSZD rates were highest in October, decreased towards the low in January/February, and started rising in March. This is largely consistent with seasonal temperature changes in the region and is likely reflective of the temperature dependency of the LNAPL biodegradation. The average NSZD rates were 142 gallons/acre/year at TM-1 and 190 gallons/acre/year at TM-2, with an overall average of 166 gallons/acre/year at Site 1. In comparison, the measured NSZD rates for carbon trap locations CT-01 and CT-09, which are collocated with thermal monitoring locations TM-1 and TM-2, are 81 gallons/acre/year and non-detect, respectively (NAVFAC Southwest, 2020).

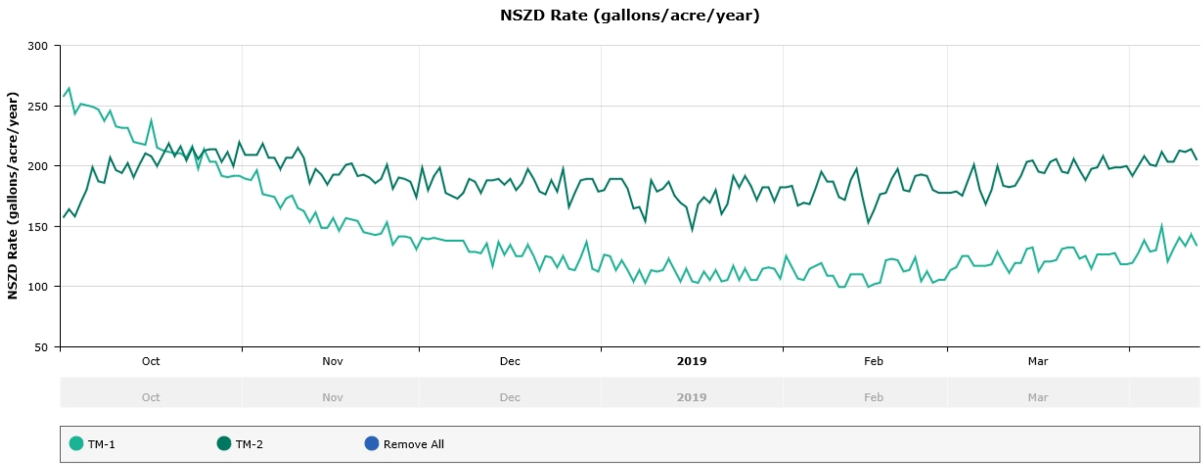

Figure 3-10. Measured Daily NSZD Rates (Courtesy of NAVFAC)

A likely explanation for the low CO_2 trap NSZD rate is that the fine-grained beds and caliche are inhibiting discharge of CO_2 to the atmosphere. This is demonstrated by data obtained from co-located monitoring points CT-09 and TM-2. A caliche layer was observed at 29 to 33 feet bgs near carbon trap location CT-09 and the highest average temperatures at TM-2 were recorded at 36 feet bgs, which is below this caliche layer. The thermal monitoring data indicate that LNAPL biodegradation is occurring at this location and CO_2 flux measurements were non-detect because upward migration of the degradation gases is inhibited in this area. Despite the differences, both the CO_2-based and thermal-based approaches show that NSZD is occurring at the site, and the site-wide NSZD rate is on the order of 47 to 166 gallons/acre/year (NAVFAC Southwest, 2020). With current data indicating that the LNAPL plume area is approximately 2 acres, the NSZD rate is estimated to be 94 to 332 gallons/year at Site 1. Total product recovery rates using active methods including SVE, MPRS, and solar-powered skimmers were reportedly 535 gallons in 2017 and 419 gallons in 2018 (NAVFAC Southwest, 2020).

3.3.4 Conclusions

The calculated LNAPL transmissivity values may suggest favorable free product recovery based on ITRC guidance (ITRC, 2018); however, there is so little product accumulating in the wells that the transmissivity tests were difficult to perform accurately. Additionally, gradients are low, inhibiting plume migration via advection and a comparison of the historical and current extent of

LNAPL indicates that the LNAPL plume is not migrating. The NSZD studies indicate that LNAPL is naturally degrading at rates similar to the recovery rates achieved by active removal measures.

The purpose of the RSE was to evaluate the effectiveness of free product recovery at the site. The data presented are examples of lines of evidence which can be used to support discussions with the regulatory agencies in transitioning from active treatment to a more passive treatment approach over time as the next phase of remedial action. As next steps are further evaluated, future approaches under consideration include NSZD, manual or passive free product recovery in select wells, and maintaining availability of the MPRS for use in select locations.

4.0 KEY FINDINGS

Key findings for optimization best practices at petroleum sites include the following:

- Well-defined state guidance for obtaining site closure with LNAPL in place and/or transitioning to NSZD are critical for achieving DON ERP objectives to reduce restoration lifecycle costs, reduce environmental liabilities, and close out sites. Available state guidance must be understood and incorporated into the LNAPL site management strategy as applicable. Regular communication with regulatory stakeholders supports the ability to achieve site objectives.
- The CSM should be regularly updated based on current site conditions, technological advances, and applicable regulations to form the basis of site decision making. Data gaps will change over time and must be identified and addressed, possibly by performing additional investigations. The level of detail should be sufficient to provide the foundation for all site decisions.
- A multiple lines of evidence approach that considers site risks, contaminant mobility, and rates of attenuation can be a useful tool to justify a transition from a costly active LNAPL recovery technology to a less costly passive technology such as NSZD. Trend analyses for parameters such as LNAPL mass/volume removal, dissolved plume stability, and removal costs should be tracked over time. As part of considering site risks, note that vapor intrusion should be evaluated where there is a completed pathway. Unless previously ruled out as an issue, vapor intrusion risk has the potential to be a focus of regulatory stakeholders whenever updates are undertaken to LNAPL CSMs.
- LNAPL transmissivity tests may be difficult to perform accurately at sites with little product accumulating in the wells. In those cases, it may be necessary to demonstrate that the LNAPL is no longer recoverable via asymptotic removal and that it is not migrating based on the historical and current extent of LNAPL.
- Carbon traps may underestimate NSZD rates. Interferences noted included caliche layers, clay lenses, or other surface seals (e.g., asphalt concrete, debris). These site conditions may prevent the transport of vapors to the surface and, therefore, may provide conservative values for CO_2 flux and the corresponding NSZD rates. Thermal monitoring and/or monitoring of concentrations of CO_2 and methane measured in the headspace of wells can help to further understand this limitation.

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