EXECUTIVE SUMMARY

Post-Remediation Performance Assessment at a Petroleum Impacted Site

ESTCP Project ER-201582

MAY 2020

Jovan Popovic, Ph.D.
Jennifer Segura, P.E.
Travis Lewis, P.E.
NAVFAC

Charles Newell, Ph.D., P.E.
Poonam Kulkarni, P.E.
GSI Environmental

Distribution Statement A
This document has been cleared for public release

This report was prepared under contract to the Department of Defense Environmental Security Technology Certification Program (ESTCP). The publication of this report does not indicate endorsement by the Department of Defense, nor should the contents be construed as reflecting the official policy or position of the Department of Defense. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the Department of Defense.

EXECUTIVE SUMMARY

Project: ER-201582

TABLE OF CONTENTS

Page

1.0 INTRODUCTION 1
2.0 OBJECTIVES 1
3.0 TECHNOLOGY DESCRIPTION 2
3.1 TPH-CWG RISK-BASED METHOD 2
3.2 TRANSMISSIVITY MEASUREMENTS 3
4.0 PERFORMANCE ASSESSMENT AND GUIDANCE 4
5.0 COST ASSESSMENT 4
6.0 IMPLEMENTATION ISSUES 4
7.0 LITERATURE CITED 5

ACRONYMS AND ABBREVIATIONS

API	American Petroleum Institute
ASTM	American Society for Testing and Materials
BTEX	Benzene, toluene, ethylbenzene, xylene
CO_2	Carbon dioxide
CSM	Conceptual site model
DoD	U.S. Department of Defense
DPE	Dual-phase extraction
EC	Equivalent carbon
e.g.	Exempli gratia
EPA	U.S. Environmental Protection Agency
ER	Environmental Restoration
ESTCP	Environmental Security Technology Certification Program
EXWC	Expeditionary Warfare Center
ft	Feet
ft^2/day	Feet squared per day
gpm	Gallon per minute
IC	Institutional Controls
i.e.	Id est
ITRC	Interstate Technology & Regulatory Council
LNAPL	Light non-aqueous phase liquid
LTM	Long-term monitoring
LUC	Land Use Control
MNA	Monitored natural attenuation
MPE	Multi-phase extraction
NAS	Naval Air Station
NAVFAC	Naval Facilities Engineering Command
NSZD	Natural Source Zone Depletion
O&M	Operation and maintenance
RBSL	Risk-based screening level
RPM	Remedial project manager
SERDP	Strategic Environmental Research and Development Program
SCAPS	Site Characterization and Analysis Penetrometer System
SSHP	Site Safety and Health Plan
SW	Southwest

TPH-CWG	Total Petroleum Hydrocarbon Criteria Working Group
U.S.	United States

ACKNOWLEDGMENTS

Funding for this work was provided by the U.S. Department of Defense's (DoD) Environmental Security Technology Certification Program (ESTCP).

The project team consists of the following organizations:

- Naval Facilities Engineering Command (NAVFAC) and Expeditionary Warfare Center (EXWC)
  - Jovan Popovic (Principal Investigator)
  - Jennifer Segura
  - Travis Lewis
- GSI Environmental, Inc.
  - Charles Newell
  - Poonam Kulkarni

In addition, the project team would like to acknowledge the participation of the following individuals and/or organizations:

- Geothermal Resource Group, Inc.
- Broadbent & Associates, Inc.

The project team would also like to thank the project manager Marie Dreyer at NAVFAC SW, Steve Bonaker and Scott Emmons at Naval Air Station (NAS) Fallon, and the other site personnel and contractors associated with the demonstration site for the support during the project. Their time and efforts associated with the project are greatly appreciated.

1.0 INTRODUCTION

Environmental Security Technology Certification Program (ESTCP) Project Number ER-201582, Post-Remediation Performance Assessment at a Petroleum Impacted Site, involves the demonstration and evaluation of multiple methods to assess residual light non-aqueous phase liquid (LNAPL) remaining at legacy sites. This executive summary briefly describes the methods being assessed, field activities, data evaluation and guidance developed in support of this project.

Since the 1990s, the Strategic Environmental Research and Development Program (SERDP) and ESTCP have conducted many demonstrations of LNAPL removal and plume treatment technologies. Technologies, such as bioventing, dual-phase extraction (DPE), air sparging and monitored natural attenuation (MNA), were demonstrated successfully to show that LNAPL could be removed and benzene, toluene, ethylbenzene, and xylenes (BTEX) plume migration could be controlled. DPE refers to the process of simultaneously extracting groundwater, soil vapor, and LNAPL. This process typically also results in significant biodegradation due to the vapor extraction aerating soil. The process has gone by many names including bioslurping and multi-phase extraction (MPE).

These technologies were successfully applied at many sites including U.S. Department of Defense (DoD) sites and considerable free product was removed. The expectation was that unlike chlorinated solvents, petroleum sites could be closed after a reasonable period of time. However, in the longer term, many of these sites are still struggling to remove enough free product to meet U.S. Environmental Protection Agency (EPA) and state requirements of source control (product mobility) as well as plume treatment and are continuing to face long-term management challenges. In a recent survey of Navy and Marine Corps site remedial project managers (RPMs), almost one-third reported continuing remediation and long-term management challenges at petroleum sites. A review of post-remediation and long-term monitoring (LTM) data and some selective additional monitoring to evaluate residual risk are needed to accelerate the closure of these sites.

2.0 OBJECTIVES

The overall objective of this demonstration is to help DoD make a stronger case for closure or transition to passive management of legacy petroleum sites and expand DoD's knowledge and use of alternative methods for characterizing LNAPL at petroleum-impacted sites in order to improve the conceptual site model (CSM) and make more informed decisions regarding remediation and site management. The technical objective of the demonstration was to implement three methods to assess any remaining LNAPL at DoD petroleum-impacted sites and demonstrate that the weathered product remaining at these sites poses little or no significant risk. These methods included: i) the American Petroleum Institute's (API) Total Petroleum Hydrocarbon Criteria Working Group (TPH-CWG) residual risk methodology using the TPH fraction method; ii) Natural Source Zone Depletion (NSZD) measurements using Carbon Traps to estimate LNAPL biodegradation rates; and iii) the LNAPL transmissivity of LNAPL bodies using historical recovery data.

3.0 TECHNOLOGY DESCRIPTION

The field demonstration was completed at Naval Air Station (NAS) Fallon located in Fallon, Nevada. Three methods were implemented to help assess the remaining LNAPL at a petroleum impacted site and provide guidance for future applications at other DoD sites. This included a NSZD assessment using Carbon Traps to estimate biodegradation rates, collection and analysis of soil, groundwater and LNAPL samples per the API TPH-CWG residual risk methodology using the Washington State TPH fractionation method, and calculation of transmissivity rates using historical recovery data. A brief summary of each method is included below.

3.1 TPH-CWG RISK-BASED METHOD

The TPH-CWG method treats complex petroleum mixtures as a combination of fractions for conducting environmental modeling and estimating non-cancer risk. Carcinogenic petroleum compounds are evaluated separately. This approach can be used within a tiered framework to estimate human health risk and to calculate risk-based screening levels (RBSLs) for guiding cleanup decisions.

Since TPH is composed of multiple types of hydrocarbons, the TPH-CWG approach relies on the analytical separation of petroleum into 13 fractions. The fractions are based on their aliphatic or aromatic nature and their equivalent carbon (EC) number, a function of boiling point. Additionally, they have been assigned toxicological and transport parameters, derived from extensive reviews of data from individual compounds in the fraction or from petroleum mixtures represented within the fraction. The TPH-CWG fractionation data results, fraction toxicity information, and transport parameters can be used to perform a risk-based analysis for each fraction present at the site being evaluated. The hypothetical risk and the resulting soil screening level (i.e., the RBSL) for the "whole TPH" mixture are calculated by combining the non-cancer risks from individual fractions weighted by their percent composition within the TPH mixture, meaning the total risk is apportioned over the different fractions present.

The importance of this method is that it differentiates between risks posed by fresh petroleum spills and weathered product. Compared to weathered product, fresh spills typically contain relatively higher risk factors (i.e., greater fraction of lower molecular weight compounds with higher vapor pressure, greater fraction of more toxic aromatics, greater proportion of soluble compounds, and lower proportion of compounds with strong sorption characteristics). By comparison, weathered product typically contains lower proportion of the more toxic aromatic fractions, lower soluble fractions, lower volatile fractions, and higher fractions that sorb well to soil.

The resulting risk-based information on the reduced presence of the more toxic fractions and reduced leachability and volatility characteristics of the weathered fuel product will be placed in context of the state's petroleum program. Here, most states have similar rules, with minor differences, such as thickness of free product allowed in monitoring wells. Some states (e.g., Massachusetts, Texas, and Washington) created similar TPH risk screening methods based on the one developed by API's TPH-CWG NSZD Measurements Using Carbon Traps.

NSZD is the reduction in LNAPL mass over time due to natural processes (ITRC, 2018a). For petroleum hydrocarbons, this is primarily driven by biodegradation, and currently-available tools can measure these biodegradation rates. Petroleum hydrocarbons can biodegrade either anaerobically or aerobically.

At sites dominated by anaerobic processes (i.e., most sites), hydrocarbons are converted to methane and carbon dioxide. Methane gas bubbles then migrate upwards in the vadose zone until oxygen is encountered. Here, methane and oxygen react to form additional carbon dioxide, as well as heat (Garg et al., 2017). Subsequently, NSZD measurements can be based on either the capture of carbon dioxide at the ground surface, the subsurface oxygen depletion profile, or measurement of the heat generation.

MNA is now an accepted remedial approach for managing dissolved contaminant plumes in groundwater. However, since 2006 there has been a growing realization that LNAPL itself is biodegrading at 10 or 100 times the rates previously thought. Therefore, there is a general distinction that NSZD is natural attenuation of the source (actually the LNAPL in the source) while MNA is the natural attenuation of the plume (Garg et al., 2017).

For this demonstration project, Carbon Traps were utilized to measure the carbon dioxide flux at the ground surface in order to determine the NSZD rate. Note, however, that NSZD rates can also be determined via other methods: i) flux chambers to measure CO_2 flux at the ground surface; ii) subsurface temperature monitoring (Thermal Monitoring); and iii) vertical subsurface gas profiles (Gradient Method). The specific measurements as well as measurement locations vary between methods, however, all can be reduced to units of mass removed per unit area per time. Specifically, a convenient and widely-used unit is gallons of LNAPL per acre per year.

3.2 TRANSMISSIVITY MEASUREMENTS

LNAPL transmissivity is an emerging standard for measuring free product mobility and recoverability, replacing measuring LNAPL thickness in wells. Transmissivity is defined as the volume of LNAPL through a unit width of aquifer per unit time per unit drawdown. Transmissivity can be calculated using American Society for Testing and Materials' (ASTM) LNAPL Transmissivity Standard ASTM E2856-13 (ASTM, Method E2856-13). Additional technical guidance can be found in the Interstate Technology & Regulatory Council (ITRC) LNAPL Updated Guidance (ITRC, 2018a) and API LNAPL Transmissivity Guidance (API, 2012; Charbeneau et al., 2016). For this demonstration project, historical free product recovery measurements were utilized to calculate transmissivity. However, there are multiple methods available to quantify free product recovery measurements to determine transmissivity rates including Baildown/Slug Test, Manual Skimming Tests, or Tracer Tests.

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

LNAPL transmissivity is now a widely accepted metric for assessing if conventional hydraulic recovery of LNAPL via pumping, skimming, etc. is practical. Empirical data suggest that LNAPL transmissivity values below a certain range indicate low recoverability and, therefore, the majority of the LNAPL at a site is in a state of lesser mobile and residual saturation. Based on ITRC's LNAPL Guidance (ITRC, 2009; ITRC, 2018), LNAPL recovery is considered practicable if LNAPL transmissivity is greater than a range of 0.1 to 0.8 ft^2/day. If transmissivity is less than a range of 0.1 to 0.8 ft^2/day though, LNAPL recovery is not considered practicable.

4.0 PERFORMANCE ASSESSMENT AND GUIDANCE

This project assessed multiple methodologies to better characterize any remaining LNAPL at petroleum impacted sites and the evaluation of the residual risk remaining at these sites. The naturally occurring biodegradation can be determined by measuring the CO_2 flux and determining the rates of degradation; and transmissivity rates can be used to help assess the recoverability of free product and LNAPL mobility at a site, while TPH fractionation data can be used to better assess the residual risk of the weathered free product. These tools can be used to supplement additional lines of evidence to help transition sites from active to passive recovery or even transition to site closure. Based on the results of this field investigation, active LNAPL recovery could potentially be discontinued without changing the low risk profile at the site.

5.0 COST ASSESSMENT

As part of the project, costs were evaluated to determine what a similar investigation would cost in order to assess the residual LNAPL at a site and determine a more cost-effective path forward. Based on the demonstration, it is estimated that a similar investigation and assessment completed for a comparable site would be approximately $100,000.

Additionally, transition to NSZD/MNA was compared with traditional free product recovery methods implemented for the recovery and management of LNAPL at impacted sites. The assessment included a comparison of implementing Land Use Controls/Institutional Controls (LUCs/ICs), transition to MNA with monitoring, and continued free product recovery efforts via manual methods such as bailing, skimming, and DPE. The estimated total costs for the various alternatives, compared over a duration of 15 years, range from approximately $500,000 to $4,700,000 -- including capital and annual operation and maintenance (O&M) costs. Based on these estimated project costs, transition of a site to a more passive approach could result in significant cost savings over the lifetime of a project. However, it should be noted that costs are site-specific and depend on many factors including the current/anticipated land use, regulatory requirements, when a site may be able to transition, etc. and therefore may vary from the costs presented.

6.0 IMPLEMENTATION ISSUES

This project demonstrated three approaches for assessing residual LNAPL at petroleum impacted sites after many years of various free product recovery efforts. The project identified best practices and guidance regarding the characterization and assessment of residual LNAPL in order to make more informed decisions regarding LNAPL remediation and site management strategies. In general, these methods could be implemented at most LNAPL impacted sites in order to help refine the CSM and evaluate the residual risk posed by the remaining LNAPL at legacy sites. However, it would be imperative to evaluate specific regulations and regulatory acceptance of various lines of evidence, analytical methods, and analytical results. Details on the implementation of the various methodologies/tools previously described and specific considerations are included in the Supplemental Guidance incorporated into Section 6 of the Final Report.

7.0 LITERATURE CITED

API, 2012. *User Guide for the API LNAPL Transmissivity Workbook: A Tool for Baildown Test Analysis*. API Publication. September 2012.

ASTM, Standard Guide for Estimation of LNAPL Transmissivity ASTM E2856 – 13.

Charbeneau, R.J., Kirkman, A. and Rangaramanujam, M., 2016. *API LNAPL Transmissivity Workbook: A Tool for Baildown Test Analysis-User Guide*. American Petroleum Institute, API Publication 4762, April 2016.

Garg, S., Newell, C. J., Kulkarni, P. R., King, D. C., Adamson, D. T., Renno, M. I., & Sale, T. (2017). Overview of natural source zone depletion: processes, controlling factors, and composition change. Groundwater Monitoring & Remediation, 37(3), 62-81.

ITRC. 2009. E*valuating LNAPL Remedial Technologies for Achieving Project Goals. LNAPL-2*.

Washington, D.C.: Interstate Technology Regulatory Council, LNAPL Team.

ITRC. 2018. *LNAPL Site Management: LCSM Evolution, Decision Process, and Remedial Technologies. LNAPL-3*. Washington, D.C.: Interstate Technology and Regulatory Council, LNAPL Update Team.