FINAL REPORT
LA LNAPL RECOVERABILITY STUDY

Issued: October 2015

Prepared by:
The LA LNAPL Workgroup

LA LNAPL RECOVERABILITY STUDY

Final Report of the LA Basin LNAPL Recoverability Study

Prepared by the LA LNAPL Workgroup:

Western States Petroleum Association
BP
Tesoro
Chevron
Phillips 66
ExxonMobil
Shell
Los Angeles Regional Water Quality Control Board
Water Replenishment District of Southern California

TECHNICAL CONSULTANT

GSI Environmental Inc.

PILOT TEST CONSULTANTS

AECOM Technical Services, Inc.
Colorado State University
Surbec Environmental

Funding for this project was provided by the Western States Petroleum Association.

TO CITE THIS DOCUMENT:

Los Angeles LNAPL Workgroup, 2015. Final Report for the LA Basin LNAPL Recoverability Study Western States Petroleum Association, Torrance, California.

Core LA LNAPL Workgroup Members:

Andrew Kirkman	BP
Mark Adamski	BP
Bradley Rogers	Chevron
Darrell Fah	Tesoro
David Harris	Phillips 66
Dok Choe	ExxonMobil
John Amato	Chevron
Joseph Lentini	Shell
Kwang Lee	LARWQCB
Paul Cho	LARWQCB
Mark Lyverse	Chevron
Mark Malander	ExxonMobil
Mike Wang	WSPA
Mohammad Zaidi	LARWQCB
Sam Unger	LARWQCB
Sanjay Garg	Shell
Tom Rinehart	Chevron
Natasha Sihota	Chevron

Other LA LNAPL Workgroup Members:

Arthur Heath	LARWQCB
Patty Senecal	WSPA
Paula Sime	Tesoro
Phuong Ly	Water Replenishment District
Ted Johnson	WRDSC
Steve Turner	URS
Becky Frend	URS
Eddie Yuen	ExxonMobil
Matthew Small	USEPA
Karen Lyons	Shell
Kateri Luka	BP
Gene Freed	Shell
Roger Hahn	Chevron
Christian Osterberg	URS
Jeff Bunce	ExxonMobil
Paula Rasmussen	LARWQCB
Holly Saffold	ExxonMobil

Consultants and Technical Experts:

Project Coordinator

Charles Newell	GSI Environmental

Pulsed Oxygen Biosparge (POBs) Pilot Test

Michal Rysz	GSI Environmental
Roy Patterson	AECOM
Matt Himmelstein	AECOM

Natural Source Zone Depletion (NSZD) Pilot Test

Natasha Sihota	Chevron
Poonam Kulkarni	GSI Environmental
Julio Zimbron	E-Flux
Thomas Sale	Colorado State University

Surfactant Enhanced Aquifer Remediation (SEAR) Pilot Test

Travis McGuire	GSI Environmental
Poonam Kulkarni	GSI Environmental
Faraneh Chamran	AECOM
Frank Muramoto	AECOM
Laura Wesson	Oklahoma State University
Jeffrey Harwell	Surbec

LA LNAPL Management Decision Tree

Mark Lyverse	Chevron
Mark Malander	ExxonMobil
Mike Wang	WSPA
Mohammad Zaidi	LARWQCB
Sam Unger	LARWQCB
Sanjay Garg	Shell
Kwang Lee	LARWQCB
Darrell Fah	Tesoro
David Harris	Phillips 66
Dok Choe	ExxonMobil
John Amato	Chevron

Final Report of the LA Basin LNAPL Recoverability Study

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF APPENDICES

SOURCE REPORTS

LIST OF ACRONYMS

ASTM	American Society for Testing and Materials
BAT	Best Available Technology
BTEX	Benzene, Toluene, Ethylbenzene, and Xylenes
BGS	Below Ground Surface
CSU	Colorado State University
DCC	Dynamic Closed Chamber
DO	Dissolved Oxygen
EPA	Environmental Protection Agency
FID	Flame Ionization Detector
GC	Gas Chromatogram
ITRC	Interstate Technology Regulatory Council
LARWQCB	Los Angeles Regional Water Quality Control Board
LCSM	LNAPL Conceptual Site Model
LDRM	LNAPL Distribution and Recovery Model by API
LMC	LNAPL Mass Control
LMR	LNAPL Mass Recovery
LNAPL	Light Non-aqueous Phase Liquids
LPC	LNAPL Phase Change
NRC	National Research Council
NSZD	Natural Source Zone Depletion
OPIS	Oxygen Pulse Injection System
PC	Pathway Control
PIANO	Paraffin, Isoparaffins, Aromatics, Naphthalene and Olefins
POBs	Pulsed Oxygen Biosparging
ROST	Rapid Optical Screening Tool
RMZ	Residual Management Zone
RWQCB-LA	Regional Water Quality Control Board Los Angeles
SCF	Standard Cubic Feet
SEAR	Surfactant Enhanced Aquifer Remediation
TCEQ	Texas Commission on Environmental Quality
UVOST	UltraViolet Optical Screening Tool
WRD	Water Replenishment District
WSPA	Western States Petroleum Association

FACT SHEET
Los Angeles Light Non-Aqueous Phase Liquid (LNAPL) Recoverability Study

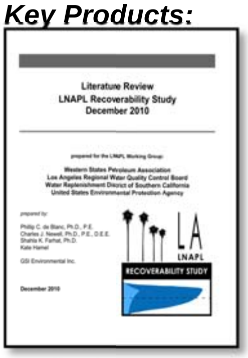
Non-aqueous phase liquids (NAPLs) are liquids that are immiscible with water and that form a separate phase when released into the subsurface. Light non-aqueous phase liquids (LNAPLs) exhibit a liquid density less than that of water. LNAPLs can consist of one or more compounds, and are typically a mixture of petroleum hydrocarbons. LNAPLs released into the subsurface are of environmental concern because they can provide a source of long-term release of constituents of concern to the environment. Because LNAPLs form a separate phase in the subsurface, LNAPLs pose many challenges to effective characterization and remediation.

The Los Angeles Light Non-Aqueous Phase Liquid (LNAPL) Recoverability Study (**"LA LNAPL Project")** is a 7-year collaborative research effort joining agencies and industry to identify and better understand technologies and techniques suitable for treating and managing LNAPL at sites in the LA Basin. The LA LNAPL Workgroup and their contractors included: *Western States Petroleum Association (WSPA), Water Replenishment District (WRD), Regional Water Quality Control Board Los Angeles (RWQCB-L.A.), Shell, ExxonMobil, Phillips 66, Chevron, Tesoro, Colorado State University, AECOM, and GSI Environmental Inc.*

After a comprehensive literature review, the Workgroup evaluated over 20 LNAPL remediation technologies. Based on an analysis of potential technologies for the available research sites, the Workgroup then conducted Pilot Tests of three very different technologies, ranging from passive to more intensive approaches, and obtained valuable information on how each technology could perform in the LA Basin.

Using information from the detailed literature review of recent science combined with the Pilot Test results, the LA LNAPL Workgroup outlined a Decision Tree for managing LNAPL sites based on risk, previous LNAPL removal efforts, technical practicability, and other factors.

Key Products:



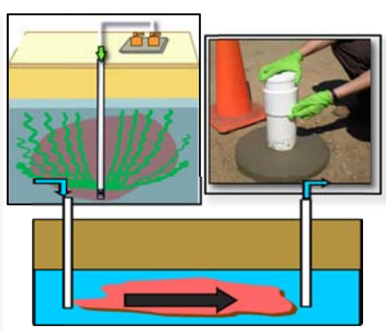
LNAPL Literature Review

Evaluated 21 LNAPL Recovery Technologies

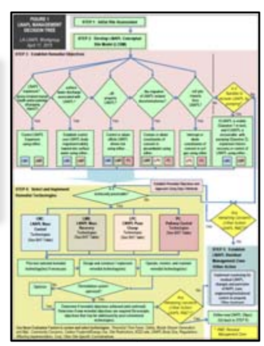
- -Thermal Conductive Treatment
- -Steam Heating
- -Chemical Oxidation
- -Deep Soil Mixing
- -Natural Source Zone Depletion
- -Surfactant Treatment
- -Biosparging

Evaluation based on *effectiveness, unit cost, operational issues at active sites, track record at other sites, ability to treat large sites, land use*

Evaluation of Over 20 LNAPL Remediation Technologies



Conducted Pilot Tests of Three Post-Conventional Technologies (Pulsed Oxygen Biosparging; Surfactant Flushing; and Natural Source Zone Depletion)



LNAPL Management Strategy Decision Tree

1.0 EXECUTIVE SUMMARY

1.1 Origin and Objectives of the LA LNAPL Workgroup

The Western States Petroleum Association (WSPA) and Los Angeles Regional Water Quality Control Board (LARWQCB) have, along with other parties, established an LNAPL Workgroup to develop a cooperative approach to addressing LNAPL problems in the Los Angeles Basin. The project began on October 11, 2007 and ended on September 15, 2015.

A series of detailed objectives for the LA LNAPL Workgroup were developed in 2007, and have been addressed in the different Workgroup products as shown below and described in Table 2.1. While not every objective was addressed, in many cases very detailed specifications were developed when a consensus on complicated technical issues was reached.

1.2 Conceptual Model for LNAPL Treatment / Recovery in LA Basin

The LA LNAPL Workgroup started with an existing methodology published by the American Society for Testing and Materials (ASTM, 2007) for developing an LNAPL Conceptual Site Model (LCSM) and evaluating potential LNAPL remediation strategies (Figure 3.1). This information was then refined and customized based on the experiences of the LA LNAPL Workgroup members. The key concepts for developing an LCSM were identified and summarized in six questions:

Question 1: What was the nature and locations of the LNAPL release(s)?
Question 2A: What are the objectives of characterization?
Question 2B: How much detail do I need to build a site conceptual model?
Question 3: Where and how large is the LNAPL body?
Question 4: Is the LNAPL mobile? Is the LNAPL recoverable?
Question 5: What are the estimated chemical fluxes or concentrations?
Question 6: How should I manage the LNAPL at my site?

1.3 Post-Conventional LNAPL Remediation Technologies

The LA LNAPL Workgroup developed an LNAPL Remediation Technology Matrix (Table 4.1) in order to evaluate more than 20 conventional and post-conventional remediation technologies (i.e., remedial technologies incorporated into site remediation after the initial LNAPL removal effort has been completed or the LNAPL has been determined to have low hydraulic recoverability).

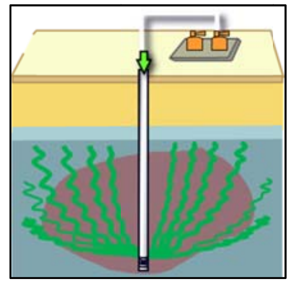
The Workgroup decided to test post-conventional technologies that address residual LNAPL, either as LNAPL left after conventional recovery efforts are no longer efficient or as residual in the form of submerged LNAPL. To this effect, three Pilot Tests were conducted:

- Pulsed Oxygen Biosparging (POBs, see Section 5).
- Low Pore Volume Surfactant Enhanced Aquifer Remediation (SEAR, see Section 6).
- Natural Source Zone Depletion (NSZD, see Section 7).

The POBs and SEAR Pilot Tests were designed to extend these technologies to treat LNAPL in a difficult hydrogeologic setting with high heterogeneity, submerged LNAPL, and at a scale that would be representative of a full refinery site-scale remediation system.

1.4 Pulsed Oxygen Biosparge (POBs) Pilot Test

1.4.1 Background



The Pulsed Oxygen Biosparging (POBs) technology was an extension of a technology researched by Shell referred to as Oxygen Pulse Injection System (OPIS) (Shell Global Solutions, 2007). A POBs system sparges high concentration (~90%) oxygen into the treatment zone, which promotes biodegradation of most soluble organic contaminants, like benzene and BTEX (benzene, toluene, ethylbenzene, and xylenes), without the need for a soil vapor extraction system.

The POBs Pilot Test was performed at the Shell Carson facility. This Pilot Test had the overall goal to "extend" the technology and test its ability to overcome difficult and/or novel applications in terms of:

- Applying POBs in a **difficult hydrogeologic setting** of a relatively thin (~5-foot-thick), potentially discontinuous, lower permeability sand/silty sand unit.
- Treating **submerged LNAPL** as opposed to the more common application of POBs to treat dissolved plumes or even LNAPL plumes encountered at the water-table surface.
- Designing the test in a way that an actual **large-scale deployment** of the POBs technology would be implemented, with large spacing (30 feet) between injection wells.
- Extending the technology and **measuring performance between injection points** (approximately 15 feet away) and not adjacent or close to the injection wells.

1.4.2 Key Results

It was difficult to inject into the thin, heterogeneous unit. In addition, several daylighting events (oxygen channels emerging at the surface) made operation of the biosparge system difficult during the year-long test. Units where LNAPL is present and can accumulate in the injection wells may be difficult or impossible to biosparge such as the deep wells in the Pilot Test. Submerged NAPL makes the applicability of this technology difficult to assess prior to drilling.

Over ***90%*** of the dissolved phase benzene and BTEX compounds were removed from the high-oxygen zone around the injection wells (Table 5.1.A), with lower removals for TPH (~30%), consistent with the aerobic biodegradation process. Lower oxygen levels at the monitoring wells located away from the injection wells likely caused lower removals of benzene (40%) and toluene (45%) and some removal of xylenes (19%) and ethylbenzene (9%) (Table 5.1.B).

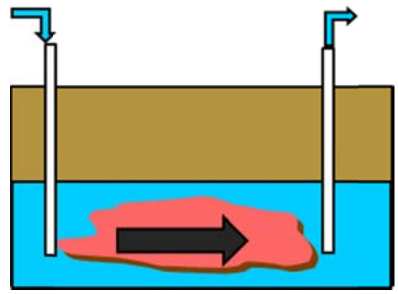
Rebound testing was conducted sixteen months after system shutdown and concentrations were compared to "After" concentrations at the wells. Some rebound occurred in the injection wells, with no rebound in the monitoring wells inside and outside the treatment area. Rebound did not affect the overall reduction in concentrations at these locations, and the overall reduction percentages were similar compared to the "Before" vs. "After" difference.

Both the decrease in benzene and BTEX *mass fractions* were statistically significant at the p=0.05 level, with p values of 0.01 and 0.03 respectively.

This confirms that the expected *composition change* (i.e., preferential removal of BTEX compounds as opposed to removal of LNAPL mass) was established by the oxygen biosparge system during the test. It would likely take several more years of biosparging to reduce the benzene and BTEX mass fractions by 90%.

1.5 Low Pore Volume Surfactant Enhanced Aquifer Remediation (SEAR) Pilot Test

1.5.1 Background



The low pore volume, low concentration SEAR technology was developed by researchers at the University of Oklahoma, and commercialized by Surbec Environmental, LLC (Surbec). The technology employs non-toxic, biodegradable chemical surfactants (SURFace ACTive AgeNTS) that, as a result of their chemical properties, are able to reduce the interfacial tension between water and LNAPL. When the interfacial tension is sufficiently reduced, NAPL mobility increases such that NAPL can be readily recovered and pumped to the surface. A survey of 12 different field demonstrations have shown the mass removal from well-designed surfactant projects was in "the mid-70 percent to the high 90% range" (National Research Council, 2005).

The SEAR Pilot Test was performed at the Tesoro Hynes facility. As with the Biosparge Pilot Test, the SEAR Pilot Test had the overall goal to extend the SEAR technology and test its ability to overcome difficult and/or novel applications in terms of the hydrogeological setting, source location, injection well spacing, and performance monitoring of the system, as described below:

- Apply SEAR in a **difficult hydrogeologic setting** of a relatively thin (~5-foot-thick), potentially discontinuous, lower permeability sand/silty sand unit.
- Treat **submerged LNAPL** as opposed to the more common application of SEAR technology to treat LNAPL plumes encountered at the water-table surface.
- Design the test in a way that an actual **large-scale deployment** of the SEAR technology could be evaluated with a "line drive" injection approach with a line of injection wells spaced ~25 feet apart that direct the surfactant solution towards a line of extraction wells located ~75 feet away.

1.5.2 Key Results

Soil concentrations were used as a key metric to evaluate if LNAPL had been mobilized and removed from the soil to the surface. No statistically significant difference in soil concentrations in the untreated zone surrounding the treatment zone was observed. The study documented that TPH concentrations in the treatment zone were higher than the surrounding untreated zone; this is likely due to sampling variability.

Overall the data indicated that 60 kilograms of TPH were removed during the entire test, and 34 kg removed from the push-pull test specifically, corresponding to about 21 gallons and 12 gallons of LNAPL, respectively. This amount is about 1% of the total LNAPL mass estimated to be in the entire treatment zone prior the Pilot Test. All of the removal was observed in the dissolved phase, and no free product LNAPL was recovered.

The post-test groundwater concentrations for benzene, BTEX, total TPH and chloride were greater than baseline values overall, though the increase was not statistically significant (i.e., $p>0.05$ using a two-tailed distribution t-test).

The technology was unsuccessful at removing LNAPL from the thin, highly heterogeneous sand unit at the Tesoro Hynes facility. These results suggest that successful implementation of this technology or related technologies (such as co-solvent addition) in the LA Basin, a treatment zone should have several of the following characteristics:

- relatively high permeability (e.g., ITRC, 2003, Table 2-1), in particular a hydraulic conductivity of 1.0×10^{-3} cm/sec or higher;
- a relatively continuous treatment zone with a thickness of ten feet or more;
- for submerged LNAPL, a treatment zone with laterally-continuous low-permeability units both above and below the treatment zone.

1.6 Natural Source Zone Depletion (NSZD) Pilot Test

1.6.1 Background

In the late 2000s there were rapid developments in the understanding and characterization of Natural Source Zone Depletion (NSZD; ITRC, 2009; Sihota et al., 2011). Because of the importance of NSZD processes to developing a Conceptual Site Model, the LA LNAPL Workgroup decided to measure NSZD rates at two sites in the LA Basin.

The LA LNAPL Workgroup, working with Colorado State University (CSU), deployed carbon traps at both the Shell Carson facility (Pilot Test 1) and the Tesoro Hynes facility (Pilot Test 2).

1.6.2 Key Results

NSZD is occurring at both the Shell Carson and Tesoro Hynes facilities at average site-wide rates of ***1,700 gal/acre/yr*** and ***1,100 gal/acre/yr*** respectively (based on results obtained from CO_2 trap measurements). These hydrocarbon biodegradation rates are comparable to those at six other field sites measured by CSU (McCoy, 2012), where the average rate was 3,500 gal/acre/yr, and ranged from 400 to 18,000 gal/acre/yr, but were greater than those reported for a crude oil release site (Sihota et al., 2011).

Figure E.1 below shows hydrocarbon degradation rates derived from Carbon-14 (^{14}C) analysis at each carbon trap location at the two sites. LNAPL extent at each site is also shown on both panels of the figure.

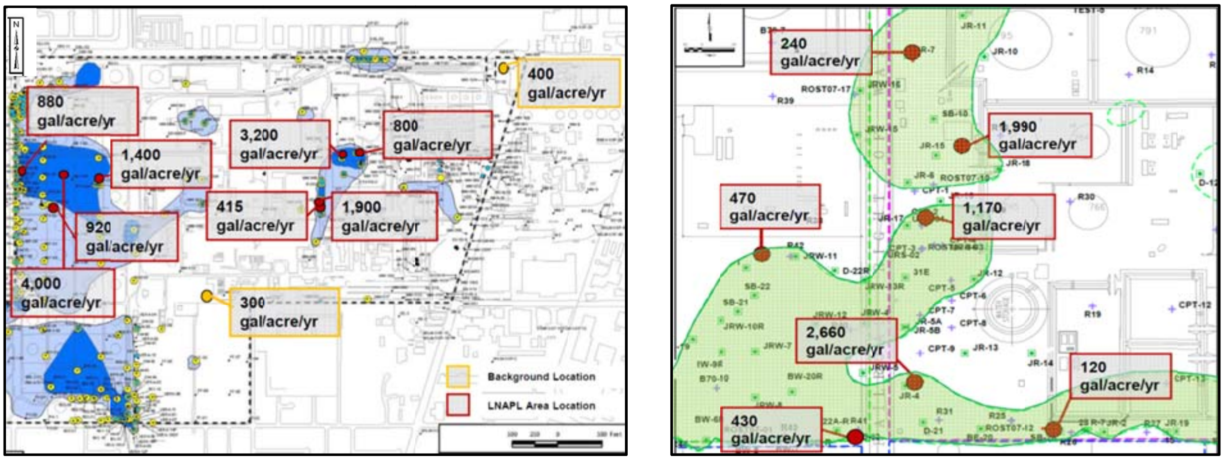


Figure E.1. Locations and Hydrocarbon Degradation Rates at Shell Carson Facility (Left Panel) and Tesoro Hynes Facility (Right Panel). *Values shown represent ^{14}C analysis results that automatically correct for background (i.e., soil respiration), and thus show hydrocarbon degradation rates at each location. Hydrocarbon was detected at background locations at the Shell Carson site, likely from migration of CO_2 flux from LNAPL zones in other areas due to geologic heterogeneity and other factors. Left Panel: light blue areas indicate inferred extent of residual LNAPL, and dark blue areas indicate measurable LNAPL in wells. Right Panel: light green areas represent LNAPL extent at site.*

1.7 LA LNAPL Management Decision Tree

The LA LNAPL Workgroup has developed an LNAPL Management Decision Tree that provides a framework that can be used to identify Remedial Objectives and a Best Available Treatment Technology for LNAPL remediation. The approach described in this Decision Tree is a generic framework intended to provide suggestions for developing an effective site-specific LNAPL management strategy. It is not intended to be a rigid plan that dictates which specific technologies should be used at a particular site.

Key elements of the Decision Tree are described in the following sections:

1. Flow Chart with Accompanying Text and Tables
2. Best Available Technology (BAT) Table

The flow chart (Figure E.2 below) contains five key steps for site-specific evaluation, and as explained in further detail in the accompanying text and tables, as follows:

- Step 1: Perform Initial Site Assessment.
- Step 2: Develop LNAPL Conceptual Site Model (LCSM).
- Step 3: Establish LNAPL Remedial Objectives.
- Step 4: Select and Implement Remedial Technologies
- Step 5: Establish LNAPL Residual Management Zone Once LNAPL Remedial Objectives are Met and/or Other Action

The Best Available Technology (BAT) table is intended to provide general suggestions for technology selection based on the research and experiences from pilot testing performed by the LA LNAPL Workgroup. The BAT tables include the following categories:

- Operating vs. non-operating facilities

- Conventional vs. post-conventional LNAPL recovery
- High, moderate, and low-intensity technologies
- Applicability to sites classified as either Type I (granular media with mild heterogeneity and moderate to high permeability) or Type III (granular media with moderate to high heterogeneity) sites

2.0 ORIGIN AND OBJECTIVES OF THE LA LNAPL WORKGROUP

Non-aqueous phase liquids (NAPLs) are liquids that are immiscible with water and that form a separate phase when released into the subsurface. Light non-aqueous phase liquids (LNAPLs) exhibit a liquid density less than that of water. LNAPLs can consist of one or more compounds, and are typically a mixture of petroleum hydrocarbons. LNAPLs released into the subsurface are of environmental concern because they can provide a source of long-term release of constituents of concern to the environment. Because LNAPLs form a separate phase in the subsurface, LNAPLs pose many challenges to effective characterization and remediation.

The Western States Petroleum Association (WSPA) and Los Angeles Regional Water Quality Control Board (LARWQCB), along with other parties, established an LNAPL Workgroup to develop a cooperative approach to addressing LNAPL problems in the Los Angeles basin. The general objectives of the LNAPL Recoverability Study are to:

- Establish methodologies to estimate LNAPL volume and distribution in the subsurface;
- Establish methodologies to assess LNAPL recoverability;
- Establish methodologies to assess LNAPL remediation performance; and
- Define the "best available treatment technology" (BAT) for LNAPL remediation.

2.1 Detailed Objectives from Scope of Work

The detailed objectives for the LA LNAPL Recoverability Study were presented in a Scope of Work developed in 2007 at the beginning of the project (see Appendix 1). Note these objectives represented a very ambitious set of goals for the consensus-based process that was used by the LA LNAPL Workgroup. While not every objective was addressed, in many cases very detailed specifications were developed when a consensus on complicated technical issues was reached. Table 2.1 presents each objective that was listed in the 2007 Scope of Work and shows where this objective is addressed in the LA LNAPL work products.

2.2 LA LNAPL Project Chronology

The overall LA LNAPL project's work since 2007 can be divided into several categories, as shown in Figure 2.1. As can be seen on Figure 2.1, the initial work focused on retention of Dr. Charles Newell as Project Coordinator and developing a collaborative process for development, review, and comment on two collaborative documents:

1. The LA LNAPL Literature Review
2. The LA LNAPL Conceptual Model

After an extended period of development, review, and revision, the Literature Review was approved and issued by the Workgroup in November 2011. Key elements of the draft Conceptual Model Document have been used to build the LA LNAPL Management Strategy Decision Tree document, and have also been used in sections 3.0 and 8.0 of this Final Report (see Table 2.1).

***Table 2.1**. Objectives in Original Scope of Work and How Addresses by LA LNAPL Study*

OBJECTIVE IN ORIGINAL SCOPE OF WORK	HOW ADDRESSED BY LA LNAPL STUDY
Literature Review and Data Collection	
Characterize methodology for LNAPL volume/mobility estimation.	*Literature Review Section 3.0*
Identify typical LNAPL types that may be encountered and their physical properties. LNAPLs to be considered will include both refined and unrefined LNAPLs.	*Literature Review Section 2.0*
Compile field data.	*Literature Review Section 6.0*
Methodology for Conceptual Model	
Create functional categories	*Final Report Section 3.0*
Establish accurate and reliable characterization tools	*Literature Review Section 3.0* *LNAPL Management Flowchart*
Evaluate existing methods/models for partitioning (to groundwater and to air)	*Final Report Section 3.0*
Evaluate and select LNAPL distribution model	*Literature Review Section 3.0*
Develop 3-D Conceptual Model for estimating LNAPL distribution • *Model LNAPL distribution in different settings and establish site-specific conceptual model* • *Model LNAPL distribution/mobility in different hydro-geologic set tings and establish the site-specific LNAPL conceptual model.* • *Conduct a sensitivity analysis to evaluate which soil and LNAPL properties contributed the greatest to variability in the LNAPL vo lume and mobility.*	*Literature Review Section 3.0* *LNAPL Management Flowchart* *Final Report Section 3.0*
Identify methods to delineate physical (three dimensional) masses of LNAPL and calculate actual LNAPL volume within a delineated LNAPL mass.	*Literature Review Section 3.0* *LNAPL Management Flowchart*
Literature Review and Data Collection	
Evaluate and select appropriate modeling program for LNAPL recovery/mobility prediction in the unsaturated and saturated zones as a function of basic soil and fluid properties (i.e., ASTM, TRRP, other studies).	*Literature Review Section 4.0*
Review current and emerging removal technologies.	*Literature Review Section 5.0*
Compile literature case studies that show accuracy of LNAPL recovery models from actual field sites (where data are available).	*Literature Review Section 4.0*
Compile data from any LNAPL recovery pilot tests performed in an appropriate hydrogeologic setting.	*Literature Review Section 6.0*
Determination of Recoverability	
Develop a methodology to evaluate LNAPL recoverability. This will include:	*Literature Review Section 4.1*
Evaluation of LNAPL mobility and aquifer characteristics using an accurate LNAPL site conceptual model • *Evaluation of LNAPL fluxes to other phases (i.e. dissolved phase in groundwater, and vapor phase in unsaturated soil).* • *Modeling of LNAPL recoverability with different geological characteristics, and refinery site conditions (safety risk, physical site limitations) and receptors (water protection and human health risk).* • *Choosing a set of suitable modeling techniques.*	*Final Report Section 3.0*

OBJECTIVE IN ORIGINAL SCOPE OF WORK	HOW ADDRESSED BY LA LNAPL STUDY
Develop an evaluation matrix of LNAPL recovery technologies and success metrics. Discussion of "endpoints" for LNAPL recovery will be based on technical feasibility and economics as opposed to a project endpoint that indicate when any further remediation will permanently cease. Select current and emerging technologies to be tested in the demonstration project.	*Final Report Section 8.0*
Strategically select appropriate demonstration sites.	*Final Report Section 4.0* *Individual Pilot Test Reports*
Design and conduct pilot tests of leading conventional and emerging technologies for removal of LNAPL.	*Final Report Sections 4.0. 5.0, 6.0, 7.0* *Individual Pilot Test Reports*
Evaluate the effectiveness of the pilot tests with confirming the reduced LNAPL, and cost analysis.	*Final Report Section 4.0. 5.0, 6.0, 7.0* *Individual Pilot Test Reports*
Develop LNAPL site conceptual model for pilot project(s) (and success metrics)	*Final Report Sections 3.0, 4.0* *Individual Pilot Test Reports*
Develop a feasibility summary table of technology (BATTs) versus selected variables such as hydrogeology, conductivity, saturation etc.	*Final Report Section 4.0*
Explain how other factors besides feasibility and economics (such as risk) might fit into the LNAPL recovery decision-making process.	*Final Report Section 8.0*

2.3 Key Objectives for Pilot Tests

The LA LNAPL Workgroup believed that hydraulic recovery of LNAPL via pumping or skimming technologies was relatively well understood and defined the suite of hydraulic recovery technologies as "conventional technologies." The Workgroup decided to invest its Pilot Test work on **post-conventional treatment technologies,** which were defined as *remedial technologies incorporated into site remediation after the initial LNAPL removal effort has been completed or the LNAPL has been determined to have low hydraulic recoverability (i.e., low LNAPL transmissivity).*

Over 20 conventional technologies and post-conventional treatment technologies were reviewed in detail, and three technologies were selected for detailed Pilot Tests in the LA Basin. Work on three Pilot Tests began in early 2010, with the actual Pilot Tests starting between mid-2011 to mid-2013, as follows (Figure 2.1):

1. Pulsed Oxygen Biosparge (POBs) Pilot Test: Started mid-2011Low Pore Volume Surfactant-Enhanced Aquifer Remediation (SEAR) Pilot Test: After three years of permitting and detailed design, started in mid-2013.
2. Natural Source Zone Depletion Pilot Test at Two Sites: Started mid-2011

These Pilot Tests were designed with these key features:

- Employed multiple LNAPL characterization technologies to evaluate several performance metrics;

- Included relatively high density of sampling to obtain good before vs. after performance data;

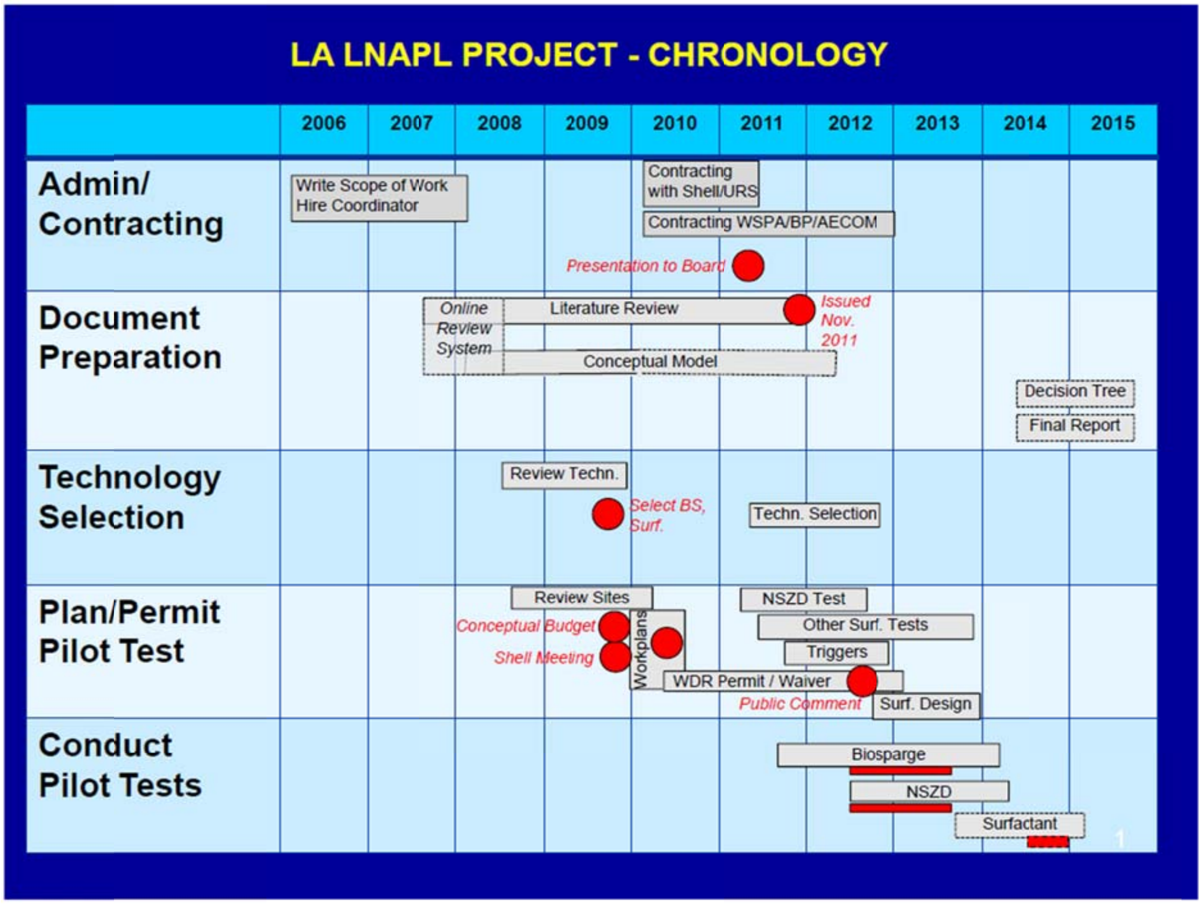


Figure 2.1. *LA LNAPL Project Chronology 2006 – 2015.*

One important feature associated with the LA LNAPL Pilot Tests is that each test attempted to extend an existing post-conventional remediation technology to test its ability to overcome difficult and/or novel applications in terms of the hydrogeological setting, source location, injection well spacing, and performance monitoring of the system:

- Each of the three pilot tests had to deal with **difficult hydrogeologic setting** of a relatively thin (~5-foot-thick), potentially discontinuous, lower permeability sand/silty sand unit. In the LA LNAPL Literature Review document (LA LNAPL Workgroup, 2011) this type of hydrogeologic setting was defined as a "*Type III – Granular Media with Moderate to High Heterogeneity*." This type of setting is different than the typical larger, thicker sand units in which many sparging systems are installed.
- Instead of being located near the water table, the LNAPL at each Pilot Test location shared a key feature of most of the LNAPL present in LA Basin refineries in that it was "submerged LNAPL", defined as *"LNAPL that is found well below the water table due to a historical release, followed by a rising water table. Most submerged LNAPL is in the residual form, and conceptual models for LNAPL located at or near the*

water table do not apply. Submerged LNAPL is found in the LA Basin at sites with older, historical releases of LNAPL due to rising water table since the 1950s." (LA LNAPL Literature Review). This submerged LNAPL presented additional challenges for applying and testing post-conventional technologies in the LA Basin.

- Some of the post-conventional technology could be subject to relatively stringent regulations due to their chemicals/systems to be used. For example, the application of the Low Pore Volume Surfactant Pilot Test had to meet specific requirements of no discharge of volatiles to the atmosphere; recovery of almost all of the chloride used as an electrolyte in the injection fluid due to regional groundwater regulatory limits, no injection of site groundwater without treatment, and limited in increase in dissolved benzene concentrations. These constraints, while necessary to meet the environmental goals for the LA Basin, greatly increased the cost and complexity of some of the Pilot Test work compared to typical applications performed in other states.

RESULTS: LA LNAPL Recoverability Study Objectives

- A series of detailed objectives for the LA LNAPL Workgroup were developed in 2007, and have been addressed in the different Workgroup products as shown in Table 2.1.
- While every objective was addressed, in some cases very detailed specifications were not developed due to the difficulty in achieving consensus on complicated technical issues and therefore the objective was met with more general discussion.
- The Workgroup has been active since 2006 and developed the LA LNAPL Literature Review document in 2011. This document summarizes the key state of knowledge about LNAPL distribution, mobility, and remediation.
- The Workgroup decided to invest its Pilot Test work on **post-conventional treatment technologies,** which are defined as *remedial technologies incorporated into site remediation after the initial LNAPL removal effort has been completed or the LNAPL has been determined to have low hydraulic recoverability (i.e., low LNAPL transmissivity) (LA LNAPL Literature Review).*
- Three Pilot Tests were performed: Natural Source Zone Depletion; Pulsed Oxygen Biosparging, and Low Pore Volume Surfactant treatment.
- The Pilot Tests included extensive characterization to obtain high-quality performance data. The applications were much more challenging than is typically associated with these remediation technologies, due to very heterogeneous hydrogeologic settings, the presence of submerged LNAPL, and a relatively complicated regulatory environment.

3.0 CONCEPTUAL MODEL FOR LNAPL TREATMENT/RECOVERY IN LA BASIN

As a result of the literature review and in order to meet the Conceptual Model objectives shown in Table 2.1, the LA LNAPL Workgroup developed the following clarifying themes:

- Develops a "How To" guide to answer several "Key Questions" regarding LNAPL releases, characterization, distribution, and remediation;
- Incorporates but does not repeat in testing, information from the LA LNAPL Scope of Work, the LA LNAPL Literature Review, the ASTM LNAPL Conceptual Site Model Standard Guide, EPA Guidance, and other key sources;
- Focuses on relatively large sites such as refineries and terminals (although some of the information is applicable to smaller sites such as retail gasoline stations):
- Emphasizes use within Los Angeles Basin hydrogeology, but some of the information applicable to other locations;
- Presents new thinking about LNAPL sites developed by the scientific community and practitioners over the past several years;
- Includes discussions about the level of detail needed based on site characteristics and potential methods for removing and managing LNAPL.

3.1 Underlying Conceptual Model Guidance

The LA LNAPL Workgroup started with an existing methodology published by the American Society for Testing and Materials (ASTM, 2007) for developing an LNAPL Conceptual Site Model (LCSM) and evaluating potential LNAPL remediation strategies. This information was then refined and customized based on the experiences of the LA LNAPL Workgroup members. The key concepts for developing a LCSM were then translated into six questions as shown below.

Question 1: What was the nature and locations of the LNAPL release(s)?

Question 2A: What are the objectives of characterization?

Question 2B: How much detail do I need to build a site conceptual model?

Question 3: Where and how large is the LNAPL body?

Question 4: Is the LNAPL mobile? Is the LNAPL recoverable?

Question 5: What are the estimated chemical fluxes or concentrations?

Question 6: How should I manage the LNAPL at my site?

Each of these questions is discussed below. Note that the development of an LCSM is an iterative process, and is particularly applicable to sites with longer management timeframes such as active refineries and terminal facilities. Therefore, even as an LNAPL remedial strategy is being implemented, the additional data obtained during remediation system operation can be used to revise the LCSM as well as to quantify the effectiveness of the remediation system.

3.2 Question 1: What was the nature and locations of the LNAPL release(s)?

If available, historic process information about facility operations and locations of "primary contaminant sources" (such as leaking tanks, pipelines, sewers, equipment, process units, etc.) is used to answer key questions such as:

- How much LNAPL was released? (This may be unknown. However, if it is known, an estimate of the range of potential volumes should be developed.)
- Was this a sudden release or a slower release over a longer period? (If known)
- When did the release start and end? (If known)
- Was the release from a surface or subsurface source? (If known)
- How much has the water table fluctuated since the time of the release?

This information could include evaluation of: spill reports, tank measurements, loss estimates from process mass balance calculations, interviews with plant personnel, and historical plant documents. A complete history of the primary source is unlikely to be reconstructed at most older refinery and terminal sites. However, locations of some of the historical releases can be estimated based on results of previous subsurface investigations.

In addition to the information above, the type of LNAPL can be described using functional categories, or discrete LNAPL sub-types. Instead of developing physical and chemical characteristics for every LNAPL area at a site, several general LNAPL types can be identified based on site characterization data. Examples of likely functional categories include:

a. Low viscosity with significant mobile fraction (such as gasoline)
b. High viscosity with significant mobile fraction (such as diesel)
c. Low viscosity without significant mobile fraction (such as light crude)
d. High viscosity without significant mobile fraction (such as a heavy crude)

3.3 Question 2A: What are the Objectives of Characterization?

Different types of LNAPL releases may require different types of characterization. For example, a new and relatively small, shallow release from a pipeline or UST may be easy to access and remediate. In this case an **Initial Response** consisting of delineation via soil borings followed by a proven remedial technology such as excavation or soil vapor extraction (SVE) could be feasible, cost-effective and reach closure criteria and/or significantly reduce long-term footprint in under a one-year time frame. Other examples of releases amenable to an Initial Response would be historic impacts only existing in the vadose zone.

An **Initial Response** characterization program would have these data objectives:

1. Delineate LNAPL
2. General knowledge of LNAPL type for health and safety concerns during initial response
3. Knowledge of immediate risk to down gradient receptors
4. Evaluate potential for LNAPL spreading/migration.

Other characterization activities would be used for sites in an **Active Remediation Phase** where a potential LNAPL remediation project is either being considered or an existing remediation project is being monitored. An **Active Remediation** characterization program would have these data objectives:

1. Use Initial Response data
2. Quantify LNAPL recoverability
3. Assess LNAPL compositional risk (i.e., potential for down-gradient dissolved mass flux and vapor mass flux)
4. Evaluate LNAPL migration risk

Last are sites passive phase characterization such as the Natural Source Zone Depletion Phase (**NSZD Phase**). This phase would be applicable to sites where NSZD Phase would be applicable to sites 1) after active LNAPL remediation efforts have been implemented and completed (either conventional recovery or conventional followed by active post-conventional technologies), 2) where there is no risk to down-gradient and off-site/on-site receptors, and 3) where institutional controls are in place that prevent land use change and/or prevent use of affected groundwater-bearing zones.

An NSZD Phase characterization program would have these data objectives:

1. Use Initial Response and Active Remediation Phase data
2. Quantify source area vapor mass flux
3. Quantify source area dissolved mass flux
4. Quantify mass removal to biodegradation

3.4 Question 2B: How Much Detail Do I Need to Build a Site Conceptual Model?

The ASTM's *"Development of Conceptual Site Models and Remediation Strategies for Light Nonaqueous-Phase Liquids Released to the Subsurface"* guide (ASTM, 2006) provides examples of factors that determine the level of information needed for development of an LNAPL Conceptual Site Model (**Figure 3.1).** As shown on Figure 3.1, the ASTM guide outlines a qualitative tiered approach, in which the relative level of effort or tier increases based on potential risk factors as well as hydrogeologic and plume factors. While subjective, the figure does show key factors that drive the level of complexity for a Site Conceptual Model:

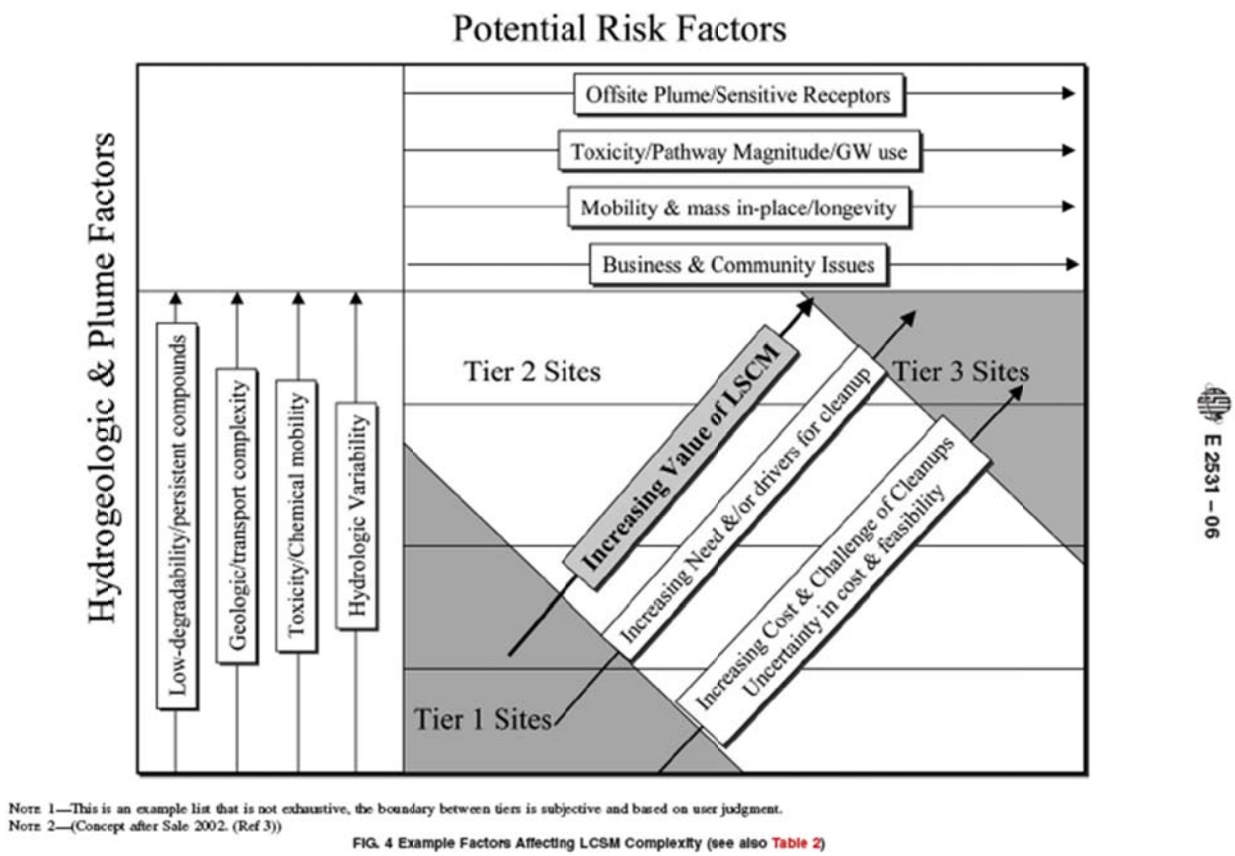


Figure 3.1. *Example Factors Affecting LCSM Complexity (ASTM, 2006)*

The ASTM approach is useful for understanding relative levels of effort required to characterize a site and develop a robust LNAPL CSM. However, the definition of the different Tiers is subjective and cannot be used in a prescriptive manner (where each site is analyzed and defined to fit into one of the three Tiers). The Tiered system is shown here to illustrate that several factors will guide the type and level of site characterization detail that will be needed to build an LNAPL Conceptual Site Model.

3.5 Question 3: Where and How Large is The LNAPL Body?

The location and distribution of LNAPL at a particular site is an important component of the LNAPL Conceptual Site Model. Characterization data is used at each site to determine the lateral and vertical extent of the LNAPL body as well as provide input data for an LNAPL mobility evaluation. LNAPL characterization data types, and a list of potential LNAPL Assessment Components are shown in **Table 3.1**. Note that this is not a list of required tasks, but a list of potential data analysis tasks that may be applied at LNAPL sites. Different sites will likely have a different set of LNAPL assessment components, with lower Tier sites having fewer and less sophisticated components and higher Tier sites having more of these components (see Question 2b).

Answering Question 3 involves the following steps:

Step 1. Assemble existing historical hydrogeologic and sampling data from the site and identify data gaps. One useful concept for characterizing the site is to define its Hydrogeologic Setting. A simplified 5-Category system based on a National Research Council publication is described in Section 7.0 (page 67) of the LA LNAPL Literature Review.

Step 2. Site Characterization: If site characterization is required (either at a new LNAPL release site or an existing LNAPL release site has data gaps), design and implement a supplemental LNAPL characterization program based on the data types needed, and then use some or all of the LNAPL Assessment Components listed in **Table 3.1** for the needed data types.

Table 3.1. *Summary of Data Types and LNAPL Assessment Components. Note that this is not a list of required tasks, but a list of potential data analysis tasks that may be applied at LNAPL sites. Different sites will likely have a different set of LNAPL assessment components, with lower Tier sites having fewer and less sophisticated components and higher Tier sites having more of these components (see Question 2b).*

Data Type	List of LNAPL Assessment Components
Basic Field Program	• Maps showing locations of borings and wells; • Boring logs showing total depth drilled, USCS soil classification, and OVA readings obtained on head space of soil samples collected during drilling; • Identify and log thickness of LNAPL zones in formation while drilling and soil sampling / coring above and below the water table (through field screening by visual observations of soil samples, exposure of soil cores to UV light, shake tests, dye tests, and paint filter tests); • Construct well-design diagrams.
Groundwater elevation and hydraulic information	• Groundwater elevation contour maps adjusted for LNAPL apparent thickness/density showing flow directions, horizontal and (if relevant/available) vertical hydraulic gradients; • Hydraulic conductivity and groundwater transmissivity distribution maps (for sites with just a few data points just show well locations with posted data; if enough data, draw iso-contours); • LNAPL apparent thickness distribution maps based on well measurements.
Soil, soil vapor, and groundwater samples collected	• Groundwater dissolved-phase plume maps; tables showing analytical results for significant site-specific contaminants (e.g. TPH, BTEX, oxygenates); • Isoconcentration maps for each significant vadose zone contaminant in soil and soil gas component (show concentrations at several depths) • Site-wide cross-section(s) should show lateral and vertical extent of various soil types (including underlying aquifers and aquitards and grain size data), LNAPL intervals both in the vadose and saturated zone, soil concentrations at sample depths, and fluctuations in water table.
Vertical LNAPL Distribution	• Use of CPT/LIF testing and/or high-frequency soil sampling and analysis for TPH to identify LNAPL zones, soil core photography under UV and visible light, and soil core fluid saturations (Dean-Stark), before installing recovery wells; • Figure of LNAPL and groundwater elevations vs. time at a well (equilibrium concentrations); • Cross-sections with well screens, LNAPL apparent thickness representing equilibrium conditions, groundwater elevation and vertical profiling data for LNAPL impacts. These are useful for illustrating that detailed concepts at one location based on scatter plots and hydrographs occur on a much larger scale at the site; • Scatter plots of LNAPL apparent thickness vs. groundwater elevation; • Soil core photography under UV and visible light; • Soil core fluid (water and LNAPL) saturations (Dean-Stark or TPH over range of LNAPL).
Aerial LNAPL Distribution	• Maps showing distribution of apparent LNAPL thickness (measured from recovery wells) and LNAPL zone thickness in the formation observed in soil cores from the formation adjacent to a recovery well and all other LNAPL observations (visual, dye formation adjacent to a recovery well and all other LNAPL observations (visual, dye test, LIF, etc.); • Specific volume of LNAPL from models such as LDRM[1].
Define LNAPL Scenario (also called LNAPL Type-Area)	LNAPL Scenario as defined using these types of terms: • confined or unconfined; • associated with a perched groundwater layer; • dune sand versus in an interbedded formation with significant silts and clays; • smeared around the water table or historical water tables; • submerged below the current water table (define the vertical interval containing LNAPL).

Table 3.1 (cont'd)

Data Type	List of LNAPL Assessment Components
LNAPL Characterization Physical Fluid Properties	● Site maps that delineate LNAPL type (e.g. diesel, gasoline, weathered diesel, etc.) and/or the concentrations of specific constituents within LNAPL (e.g., oxygenates). LNAPL type data plotted aerially and vertically help distinguish between separate plumes, identify sources, and set up modeling boundaries; ● LNAPL physical laboratory analysis (density, viscosity, air/water interfacial tension, air/LNAPL interfacial tension); ● LIF fluorescence spectrum analysis (shorter or longer wavelength response), GC (gas chromatogram) FID, GC mass spectrometry, Lead speciation, PIANO[2] Analysis.
Quantification of LNAPL Mobility and Recoverability via Conventional Technologies	● For existing conventional recovery systems: LNAPL recovery rate, volume over time charts, and decline-curve analyses (i.e., recovery rate versus cumulative recovered volume). These can be used in conjunction with water-table elevation, applied vacuum and/or water recovery rate to evaluate optimum water extraction rates and applied vacuum and to estimate LNAPL transmissivity over time. Can also incorporate routine LNAPL removal events (i.e., passive opportunistic recovery); ● Maps or figures of LNAPL footprint vs. time; ● For evaluation of mobility at edge of LNAPL body: Pore entry pressure analysis; ● For evaluation of new or expanded conventional recovery system: tables or site maps that are contoured to show LNAPL "mobility term"; and/or LNAPL seepage velocity; and/or LNAPL transmissivity. ASTM 2856-13 Standard Guide for Estimation of LNAPL Transmissivity describes methods, interpretation, and applicability of various test methods. Note that oil and water saturations determined by analyses of the soil cores collected from the LNAPL intervals in a boring located adjacent to a new or historical recovery well can serve as a cross-check to confirm the accuracy of the LNAPL transmissivity calculated from a baildown test conducted at the well location; ● Upgrade existing system to evaluate each well's individual performance and monitor operational parameters (i.e. better data collection and management); ● LNAPL tracer tests; ● Pilot testing different technologies (e.g. skimming, dual-phase extraction, vacuum-enhanced extraction, etc.); ● Other mobility analysis using techniques.
LNAPL Mass	● Maps or tables of LNAPL-specific volume, total recoverable LNAPL, and a total mass estimate using LNAPL models such as LDRM[1]. The uncertainty in any mass estimate should be shown; at some sites this could be several orders of magnitude range or more.

1. LDRM: the API LNAPL Distribution and Recovery Model
2. PIANO: the amount of paraffin, iso-paraffins, aromatics, naphthalene and olefins

Key Point Regarding Table 3.1: This list represents a broad range of LNAPL characterization data types. Larger, more complex sites will likely require more data types while smaller, simpler sites may only require a few data types.

3.6 Question 4: Is the LNAPL Mobile? Is the LNAPL Recoverable?

This section summarizes methods to evaluate LNAPL mobility and recoverability using conventional technologies. The terms “mobility” and “recoverability” therefore represent “yes/no” answers to these two key questions typically asked at an LNAPL site:

Question 1: Can the LNAPL move under the influence of an existing or likely hydraulic gradient; i.e., is the LNAPL “mobile?”

Question 2: Can the LNAPL be recovered using conventional pumping technologies; i.e., is the LNAPL “recoverable?

To answer these two questions, the assessment of LNAPL mobility can be either empirical (i.e., based on observations of LNAPL in the field), or quantitative (i.e., based on calculations of rates of LNAPL movement or potential movement). Our review has led to five methods that have been used or proposed by different groups to answer Questions A and B posed above. These methods are summarized in the table below and are described at length in the subsequent sections. At small, simple sites, a single method may provide sufficient information for moving forward, while at other larger, more complex sites a “weight of evidence” approach may be advantageous.

The five methods of assessing LNAPL migration and recoverability that the Workgroup found in the technical literature are listed on Table 3.2.

***Table 3.2.** Methods that Have Been Used to Evaluate LNAPL Mobility (Slightly Modified from LA LNAPL Lit. Review Section 4.0)*

Method	Metric	Which Question?	Where Usually Applied?	How These Methods Are Applied (or Proposed to be Applied)
Evaluate site temporal data	Change in LNAPL footprint over time; consistent, large-scale changes in apparent thickness in LNAPL; and changes in the dissolved plume footprint.	1	Edge of LNAPL Zone	If the data show an expanding LNAPL footprint then LNAPL is considered to be mobile.
Dye Tracer Test	A fluorescent dye is injected into a well containing LNAPL. The rate of disappearance of the dye is then used to estimate the LNAPL migration rate (LNAPL Darcy velocity). To convert these LNAPL Darcy velocity to LNAPL seepage velocity one divides by the LNAPL content (mobile LNAPL saturation times porosity).	1	Core and edge of LNAPL zone covering range of LNAPL types and transmissivity conditions anticipated at the site	Low LNAPL flux measurements demonstrate limited LNAPL mobility and recoverability.
Apply Darcy's Law and Related Methods	LNAPL Mobility Term (from calculations of LNAPL properties and soil characteristics)	1 or 2	Either core or edge of LNAPL Zone	If LNAPL Mobility > 10^{-7} $cm^3 sec/g$ then LNAPL "can be presumed to be effectively immobile" (Massachusetts LSPA, 2008).
	LNAPL Seepage Velocity (from calculations of LNAPL properties and soil characteristics or from LNAPL tracer tests)	1 or 2	Either core or edge of LNAPL Zone	ASTM (2007) provides example where LNAPL Seepage Velocity > 0.3 meters per year (1 foot per year) means recovery by hydraulic skimming may be feasible.
	LNAPL Transmissivity (from calculations of LNAPL properties and soil characteristics; recovery data; or from LNAPL baildown test)	1 or 2	Either core or edge of LNAPL Zone	Practical limit of hydraulic and pneumatic recovery systems is LNAPL Transmissivity > 1.1 to 8.6 x 10^{-7} m^2/s (0.1 to 0.8 ft^2/day) (ITRC, 2009).
Evaluate Pore Entry Pressure	Apparent LNAPL thickness	1	Edge of LNAPL Zone	If apparent LNAPL thickness in well > than pore entry head, then LNAPL has potential to move (and be removed by pumping).
Compare Measured LNAPL Saturation to Residual Saturation	LNAPL Saturation	1 or 2	Edge and Core of LNAPL Zone	If saturation > residual saturation (determined by one of several methods) then LNAPL has potential to move (and be removed by pumping).
Apply LNAPL Computer Models	Computed rate of LNAPL movement or rate/volume of recovery	1 or 2	Edge and Core of LNAPL Zone	Assess significance of LNAPL movement or recovery relative to site remedial objectives.

Note to Table 3.2: The LA LNAPL project is not advocating using any of the metrics above as strict numerical standards to be applied to a specific site. Site-specific issues such as risk, site conditions and status, regulatory agency's acceptance, and other factors need to be considered in addition to these general guidelines to determine LNAPL mobility issues. This table was developed in an attempt to summarize the key methods used to define LNAPL mobility in the technical literature. There are differing opinions about the applicability and accuracy of different methods, particularly regarding the need for collection of LNAPL saturation verification samples to confirm that LNAPL recovery efforts via conventional extraction technologies can be terminated. As described above, the definition of LNAPL mobility and recoverability will likely be defined on a site-specific basis.

3.7 Question 5: What Are The Estimated Chemical Fluxes or Concentrations?

Effective management of an LNAPL body often requires knowledge of the contaminant concentrations and fluxes (i.e., the rate of flow of contaminants) at certain points or zones. The term "flux" has been used in two ways: as a mass flux (in units of mass per area per time) and as mass discharge (the mass flowing through a certain zone or across a transect line in units of mass per day). The Interstate Technology Regulatory Council (ITRC) provides a detailed definition of these two terms.

To calculate the contaminant mass flux and/or mass discharge from LNAPL bodies to groundwater, the following steps should be performed:

1. Review and apply one of the five general approaches for estimating mass flux and mass discharge. (ITRC, 2010) shown below. The pros and cons of each method are described in the ITRC document.
   - Transect method (i.e., high resolution sampling and use of calculation tools such as the Mass Flux Toolkit to calculate mass discharge)
   - Well capture methods
   - Passive flux meters
   - Isoconcentration contour map data
   - Computer models. These include source-specific models such as BIOSCREEN (Newell et al., 1996), REMFuel (when available), SourceDK (Farhat et al. 2004), Mass Flux Toolkit (Farhat et al., 2006), API's LNAST (Huntley and Beckett, 2002 and API, 2004), Natural Attenuation Software (Widdowson et al, 2005), and others.
2. The mass flux/mass discharge can be calculated at a location of interest. For example, consider the following four cases:
   - If the change in mass discharge before and after remediation is of interest, then mass discharge measurements are appropriate.
   - If attenuation of the plume is of interest, then mass discharge estimates at different transects in the plume should be performed.
   - If understanding which areas within a source area are contributing the most to the groundwater loading to groundwater, then a transect showing the mass flux in a vertical plan near the source is useful.
   - If the relative strength of the plume is of interest, then the Plume Magnitude can be determined using the Mag 1 to Mag 10 scale described in Newell et al. (2011).

3. Concentrations at certain points of interest in groundwater can be determined using actual measurements (such as wells at the boundary of a facility), using models such as REMFuel, or in certain cases, calculated using mass discharge data and the assumed flowrate from the receptor well or stream (see ITRC, 2010).
4. Estimating fluxes and concentrations in the vapor phase requires different approaches, such as the approaches presented in the NSZD Pilot Test discussed in Section 7.

3.8 Question 6: How should I manage the LNAPL at my site?

Section 8 provides the LNAPL Management Decision Tree developed by the LA LNAPL Workgroup. The decision tree provides a framework that can be used to identify Remedial Objectives and "**Best Available Treatment Technology**" for LNAPL remediation

RESULTS: Conceptual Model For LNAPL Treatment/recovery in LA Basin
The LA LNAPL Workgroup started with an existing methodology published by the American Society for Testing and Materials (ASTM, 2007) for developing an LNAPL Conceptual Site Model (LCSM) and evaluating potential LNAPL remediation strategies (**Figure 3.1**). This information was then refined and customized based on the experiences of the LA LNAPL Workgroup members. The key concepts for developing a LCSM were then translated into six different questions as shown below. ***Question 1: What was the nature and locations of the LNAPL release(s)?*** ***Question 2A: What are the objectives of characterization?*** ***Question 2B: How much detail do I need to build a site conceptual model?*** ***Question 3: Where and how large is the LNAPL body?*** ***Question 4: Is the LNAPL mobile? Is the LNAPL recoverable?*** ***Question 5: What are the estimated chemical fluxes or concentrations?*** ***Question 6: How should I manage the LNAPL at my site?***

4.0 POST-CONVENTIONAL LNAPL REMEDIATION TECHNOLOGIES

4.1 Overview

This section provides an overview of key LNAPL treatment and recovery technologies and is extracted from Section 5 of the LA LNAPL Literature Review (LA LNAPL, 2011). For ease of reference, LNAPL treatment and recovery technologies for LNAPL have been divided into the general categories used by the Texas Commission on Environmental Quality (TCEQ) NAPL workgroup:

- **Current, conventional** technology - A proven technology that removes LNAPL by physical means, including excavation, hydraulic, or pneumatic remedial measures.
- **Current, alternative** technology - A technology that removes, mobilizes, or destroys LNAPL using biological, chemical, electromagnetic, or thermal processes. Some of these technologies have not been proven at the field scale. Alternative technologies are often used for post-conventional recovery.
- **Containment t**echnology - A technology that contains, rather than destroys or removes, LNAPL and/or an associated dissolved phase plume.
- **Assisting** technology - A technology that is used to enhance the effectiveness of another remedial technology.
- **Emerging** technology - A technology that is under development for LNAPL remediation, but has not been proven to be effective on a large scale. Some emerging technologies can also be used as a **Post-Conventional** technology for removing residual LNAPL.
- **Post-Conventional** technology - A technology can be applied for removing residual LNAPL as opposed to removing LNAPL using a conventional technology.

The LA LNAPL Workgroup was primarily interested in testing Post-Conventional technologies that address residual LNAPL, either as LNAPL left after conventional recovery efforts are no longer efficient or as residual in the form of submerged LNAPL.

4.2 LNAPL Remediation Technology Overview

A number of Conventional and Post-Conventional LNAPL remedial technologies are listed by these categories in Table 4.1. Where available, the limitations, general cost and/or efficiency, and additional technical notes about each technology are provided in the table. The Interstate Technology & Regulatory Council (ITRC) team led by Pam Trowbridge (Pennsylvania Dept. of Environmental Protection) and Lily Barkau (Wyoming Dept. of Environmental Quality) developed a Technical/Regulatory Guidance document "Evaluating LNAPL Remedial Technologies for Achieving Project Goals." (ITRC, 2009) and also provided a screening matrix of remediation technologies; these are provided in Appendix A.

Table 4.1. Current and Emerging LNAPL Remediation Technologies

Remediation Strategy	Description	Classification	Frequency of Use for LNAPL Recovery in LA Basin	Applicable Geology (fine, coarse)/ Applicable Zone (saturated, unsaturated) (ITRC, 2009B)	Potential Timeframe (ITRC, 2009B)	Objective	Strengths/Limitations
Physical excavation	Contaminated soil is removed by an established excavation method and disposal or treatment of soil.	Current Conventional	Frequent	F,C/ S,U	Very short (<1 year)	Recover all LNAPL in excavation zone (typically in vadose zone)	High initial cost, but no operation/maintenance costs; established and proven method. Reliable method for removing all LNAPL from excavation zone. In practice, limited to zones above the water table with contamination in upper 40 feet.
Soil vapor extraction	Also called SVE or soil venting. A vacuum is applied to the subsurface to remove volatile constituent vapors. One of the most commonly used techniques and can be used in combination with other technologies (air sparging, steam injection, surfactant flushing, dense brine containment and others)	Current Conventional	Frequent	C / S, U	Short to medium (1-5 years)	Remove volatile constituents in LNAPL in vadose zone	Proven technology and best remedy for LNAPL in the vadose zone in most hydrogeologic settings. Limited by low-permeability, high-soil water content and heterogeneities. High initial recovery rates followed by long periods of low recovery.
Combined fluids	One pump that removes both LNAPL and water phase	Current Conventional	Frequent	C / S, U	Medium (2-5 years)	Recover free LNAPL	Well-understood technology. Most commonly used technology with reliable design tools. Limited by low permeability, high soil water content and heterogeneities. Relatively slow technology.
Floating LNAPL extraction	FLE uses an LNAPL skimming pump with LNAPL inlet set at the water-LNAPL interface for removal	Current Conventional	Frequent	F, C/ S	Long to very long (5-10+ years)	Recover free LNAPL	Well understood technology with reliable design tools. May be limited by site geology.

Table 4.1. Current and Emerging LNAPL Remediation Technologies (cont'd)

Remediation Strategy	Description	Classification	Frequency of Use for LNAPL Recovery in LA Basin	Applicable Geology (fine, coarse)/ Applicable Zone (saturated, unsaturated) (ITRC, 2009B)	Potential Timeframe (ITRC, 2009B)	Objective	Strengths/Limitations
Dual-pump liquid extraction	DPLE uses two pumps, one set below the water table to create drawdown, and a second pump set at the water-LNAPL interface to recover LNAPL.	Current Conventional	Frequent	C / S	Long to very long (5-10+ years)	Recover free LNAPL	Well-understood technology. Most commonly used technology with reliable design tools. Limited by low permeability, high soil water content and heterogeneities. Relatively slow technology. Dewatering is one variant, but there are limitations to the degree of dewatering that can be achieved.
Multi-phase extraction (Dual phase extraction variant)	Uses one pump below the water table and a suction-tube from vacuum pump set above the cone of depression to remove LNAPL	Current Conventional	Frequent	C / S	Medium (2-5 years)	Recover free LNAPL	Effective method for increasing LNAPL flow rate to well when available water drawdown is limited. Vacuum increases hydraulic head without increasing drawdown. Removes NAPL, and water simultaneously. Vapor treatment is expensive.
Multi-phase extraction (Two-phase extraction variant)	Also called Bioslurping. Uses a single high-vacuum pump, suction-tube set at air-liquid interface for removal of undifferentiated LNAPL and vapor phase LNAPL	Current Conventional	Infrequent	F,C/ S,U	Long to very long (5-10+ years)	Recover free LNAPL; remove volatile constituents in LNAPL in vadose zone and dewatered sat. zone	Well-understood technology. Addresses capillary fringe, lower vadose zone, and upper saturated zone simultaneously. Relatively high cost due to need to separate LNAPL and water, and need to treat both water and vapor streams. Energy intensive. Vapor treatment is expensive.
Waterflood	Extraction of NAPLs via waterflood with wells or trenches, using fluid gradients to push NAPLs toward an area for extraction	Current Conventional	Infrequent	C / S	Short (1-3 years)	Recover free LNAPL	Not effective when available drawdown is small and/or permeability of formation is low. Produces large quantities of groundwater that require treatment.

Table 4.1. Current and Emerging LNAPL Remediation Technologies (cont'd)

Remediation Strategy	Description	Classification	Frequency of Use for LNAPL Recovery in LA Basin	Applicable Geology (fine, coarse)/ Applicable Zone (saturated, unsaturated) (ITRC, 2009B)	Potential Timeframe (ITRC, 2009B)	Objective	Strengths/Limitations
Air sparging	The injection of clean air into the saturated zone of a porous medium to volatilize and transport contaminants for removal by SVE The SVE prevents the contaminated air from reaching uncontaminated areas Used for LNAPL and DNAPL	Current Alternative	Infrequent	C / S, U	Short to medium (1-5 years)	Remove volatile/ soluble components from saturated zone LNAPL via volatilization and (indirectly) aerobic biodeg.	Proven technology. Uses two processes to remove volatile/soluble compounds: volatilization and biodegradation. Commonly combined with SVE to capture vapors. Inexpensive. Limited by low permeability, high soil water content and heterogeneities. Relatively low radius of influence (~15 feet).
In-situ chemical oxidation	Increases the mass flux from a source zone by breaking up organic chemicals in place. Can provide rapid containment and destruction of readily oxidized contaminants	Current Alternative	Infrequent	C / S, U (ozone oxidant)	Very short to short (< 1-3 years)	Destroy LNAPL in residual and free phases (as well as dissolved and sorbed constituents). Used primarily for saturated zone but some vadose zone applications	Addresses both residual and free phase. Can destroy LNAPL but large quantities of oxidant are needed. May result in further cleanup issues (such as elevated metals). Success depends on the degree of contact of the NAPL solution and the injected substance. Limited effectiveness in low permeability settings. Typical spacing for injections range from 2.5 feet for tight clays to 25 feet in permeable saturated soils. Also done with soil mixing.
Surfactant flushing for LNAPL mobilization	Surfactants (typically anionic) are delivered to pooled or trapped NAPL. Primary purpose is to decrease NAPL-water interfacial tension, which promotes mobilization	Current Alternative	Infrequent	C / S	Very short to short (< 1-3 years)	Remove free LNAPL and some residual LNAPL from saturated zone	Removes LNAPL through mobilization and demobilization in the subsurface. Success depends on contact. Relatively expensive technology. Difficult to apply on large scale.

Table 4.1. Current and Emerging LNAPL Remediation Technologies (cont'd)

Remediation Strategy	Description	Classification	Frequency of Use for LNAPL Recovery in LA Basin	Applicable Geology (fine, coarse)/ Applicable Zone (saturated, unsaturated) (ITRC, 2009B)	Potential Timeframe (ITRC, 2009B)	Objective	Strengths/Limitations
Surfactant flushing for LNAPL solubilization	Surfactants (typically non-ionic) are delivered to pooled or trapped NAPL. Primary purpose is to increase solubility of LNAPL constituents and extract resulting dissolved phase mass	Current Alternative	Infrequent	C / S	Very short to short (< 1-3 years)	Remove free LNAPL and some residual LNAPL from saturated zone	Removes LNAPL through solubilization. May be inefficient for removing significant LNAPL mass due to need to solubilize LNAPL. Success depends on contact. Relatively expensive technology. Difficult to apply on large scale.
Thermal remediation	Involves the injection of steam, electromagnetic energy, or conductive heat to heat the NAPL zone and volatilize contaminants. Often used in combination with SVE to capture vapors	Current Alternative/ Emerging technology	Infrequent	F,C/ S,U	Very long (10+ years)	Volatilize and destroy free and residual LNAPL for both vadose and unsaturated zone	Relatively high removal performance if high temperature can be maintained. More effective in low-permeability media than most other technologies. High water inflow can compromise project effectiveness. Careful monitoring is required. Not typically performed at retail sites due to health/safety concerns. High cost. Typical well spacing for conductive heating: 7 to 20 feet. Energy intensive.
Alcohol flushing	Similar to surfactant flushing. Derived from a crude oil recovery technique in which miscible, low-molecular weight alcohols are delivered to NAPL regions to solubilize and mobilize pure phase NAPLs. Alcohols are also used as co-solvents with other surfactants	Emerging Technology	Very few applications nationwide	C / S	Very short to short (< 1-3 years)	Remove free LNAPL and some residual LNAPL from saturated zone	Addresses both residual and free phase. Addition of chemicals that may require further cleanup. Success depends on the complete contact of the NAPL solution and the injected substance. High cost.

Table 4.1. Current and Emerging LNAPL Remediation Technologies (cont'd)

Remediation Strategy	Description	Classification	Frequency of Use for LNAPL Recovery in LA Basin	Applicable Geology (fine, coarse)/ Applicable Zone (saturated, unsaturated) (ITRC, 2009B)	Potential Timeframe (ITRC, 2009B)	Objective	Strengths/Limitations
Electrokinetics	A DC electrical field is established in the NAPL zone that induces water and NAPL migration to a recovery area. NAPL flow through a treatment zone can be induced	Emerging Technology	Very few applications nationwide	F / S, U	--	Recover free LNAPL and some residual LNAPL from vadose zone	In theory, can mobilize some residual LNAPL. Designed for fine-grained soils where other technologies are ineffective. Oxidation/ reduction reactions can form undesirable products. Not proven effective at many sites.
Denitrification	Soybean oil coated particles can be used to denitrify NO2 and NO3. Particles can be used as a permeable barrier in a trench. Oils can also be injected through a well to avoid digging trenches.	Emerging Technology	Very few applications nationwide	--	--	Remove and destroy soluble components from free and residual LNAPL in the saturated zone	Can indirectly destroy LNAPL so no surface treatment is necessary. Most effective during the first 10 weeks then declines in efficiency. Very limited field data.
Dense brine strategies	Displacement or containment using dense brines. Used primarily for DNAPL	Emerging Technology	Very few applications nationwide	--	--	Remove free LNAPL and some residual LNAPL from saturated zone	Displacement technologies are well understood. Likely not to be applicable to most LNAPL sites. Brine can cause secondary water quality impact.
Humic acid enhanced remediation	Humic acid solutions can be used to increase the solubility of petroleum-derived compounds	Emerging Technology	Very few applications nationwide	--	--	Remove free LNAPL and some residual LNAPL from saturated zone	Based on natural compounds. May be some problems with clogging. Only addresses soluble LNAPL constituents.

Table 4.1. Current and Emerging LNAPL Remediation Technologies (cont'd)

Remediation Strategy	Description	Classification	Frequency of Use for LNAPL Recovery in LA Basin	Applicable Geology (fine, coarse)/ Applicable Zone (saturated, unsaturated) (ITRC, 2009B)	Potential Timeframe (ITRC, 2009B)	Objective	Strengths/Limitations
Bioventing/ biosparging	A form of bio-stimulation that enhances natural in-situ biodegradation of aerobically degradable compounds in NAPL by providing additional oxygen to soil microorganisms	Emerging Technology	Moderate	C / S, U	Short to medium (1-5 years)	Remove/ destroy volatile components from free and residual LNAPL in the vadose zone	Can indirectly destroy LNAPL so no surface treatment is necessary. Reduced or no vapor treatment cost. Slower technology than SVE.
Fracturing	Not a clean-up method in itself; used to break up dense soil or clay below ground to assist other cleanup methods	Assisting Technology	Infrequent	--	--	Increase permeability for both vadose and unsaturated zone	Can help address problems with clean-up of low permeability units. Cannot be used in high seismic activity areas where it might open up new pathways for contaminants.
Low permeability barriers and containment	Uses trenches, chemical, or physical barriers to isolate or limit NAPL sources and reduce risks by managing the plume	Containment Technology	Infrequent	F,C/ S	Very long (10+ years)	Stop or reduce mobile LNAPL	Only addresses dissolved phase. Passive technology that can be less expensive than active technologies.
Natural Source Zone Depletion	Physical, chemical and biological processes that under the right conditions will reduce the mass, volume, toxicity or concentration of a contaminant in the soil/groundwater without human intervention	Containment Technology	Infrequent	F,C/ S,U	Very long (10+ years)	Remove volatile/ soluble components from LNAPL via volatilization and (indirectly) aerobic bio-degradation	Destroys LNAPL indirectly by biodegrading soluble components. Cost is low. Likely to be much slower than most other remediation technologies. Not effective for long-chained hydrocarbons (i.e., C-20 and higher).

4.3 ITRC LNAPL Screening Matrix for LNAPL

The ITRC Technical/Regulatory Guidance document (ITRC, 2009b) that was mentioned above in Section 4.2 also provided a screening matrix for comparing technologies based on the following decision-making criteria:

- LNAPL Remedial Objective
- LNAPL Remediation Goal
- Technology Group
- Example Performance Metrics
- LNAPL Technology and LNAPL/Site Conditions

The screening matrix includes a total of 17 LNAPL remediation technologies, and is reproduced in Appendix A of this document.

4.4 LNAPL Mass Removal vs. Composition Change Technologies

In addition to the categories developed by the TCEQ, LNAPL remediation technologies can be divided into those that are implemented for the purpose of: (i) mass-recovery, (ii) mass-control, and (iii) phase-change (ITRC, 2009b). Mass-recovery and mass-control strategies are mainly aimed at addressing remedial objectives defined by the LNAPL saturation goals. Phase-change approaches focus on targeting the composition of the LNAPL and “exploit the tendencies of LNAPLs to partition to other phases by increasing the rates of volatilization or dissolution of the LNAPL constituents” (ITRC, 2009b). Degradation of the LNAPL fractions also affects LNAPL composition and weathering. Biodegradation of LNAPL constituents in the groundwater and vapor phase (volatilized components) has been widely accepted. Direct biodegradation of LNAPL, although likely to be a slow process, in part due to microbial toxicity effects, has also been suggested as a mechanism for LNAPL composition change in source zones (see ITRC, 2009 for a more detailed discussion).

Active engineered LNAPL remediation technologies and their remedial objectives, including composition changes, are described in the Table 4.2 below. Even though NSZD has not traditionally been thought of as a stand-alone remediation technology for application at LNAPL sites, the processes involved in the physical redistribution (dissolution and volatilization) and breakdown (biodegradation) of LNAPL constituents are integral part of this technology and are thus included in the discussion. NSZD is also significant “because engineered remedial actions typically do not always completely remediate soil and NSZD may be useful to address the residual hydrocarbon” (ITRC, 2009b).

Table 4.2. *LNAPL Remediation Technologies and Remedial Objectives*

Technology	**Remedial Objective** (primary shown in bold)
Excavation	**Saturation** + Composition
Physical or hydraulic containment	**Saturation** + Composition
In-situ soil mixing	**Saturation** + Composition
Natural source zone depletion (NSZD)	**Composition** + Saturation
Air sparging /soil vapor extraction	**Composition** + Saturation
LNAPL skimming	**Saturation**
Bioslurping/enhanced fluid recovery	**Composition** + Saturation
Dual-pump liquid extraction	**Saturation**
Multiphase extraction (single and dual pump)	**Saturation** + Composition
Water flooding	**Saturation**
In-situ chemical oxidation	**Composition**
Surfactant enhanced subsurface remediation*	**Saturation** + **Composition**
Cosolvent flushing	**Saturation** + **Composition**
Steam/hot-air injection	**Saturation** + **Composition**
Radio frequency heating	**Saturation** + Composition
Three-and-six phase electrical resistance heating	**Saturation** + **Composition**
	Source: ITRC, 2009b

* Note there are two main surfactant technology variants: 1) surfactant addition for LNAPL mobilization (often an anionic surfactant); and 2) surfactant addition of LNAPL solubilization (often a non-ionic surfactant). See Table 4 for more discussion of these two methods.

4.5 Natural Source Zone Depletion (NSZD) Benchmark

The LA LNAPL Literature Review document summarized the emergence of Natural Source Zone Depletion (NSZD) as an important process at LNAPL Sites (LA LNAPL, 2011) and provided the following summary of NSZD.

ITRC (2009a) discussed how Natural Source Zone Depletion (NSZD) can serve as a *control* or benchmark when comparing the effectiveness of remediation actions. NSZD is also important to consider as a solution to residual hydrocarbons that are likely to be left behind after treatment (ITRC, 2009a).

Accurate information on LNAPL distribution, LNAPL composition, and site hydrogeology are needed to evaluate NSZD. It may be helpful to consider NSZD processes when initially creating an LNAPL conceptual site model to ensure that the site characterization includes the necessary data. Mass-depletion calculations vary based on the location of the LNAPL; therefore, separate estimates of LNAPL in the vadose zone and in the saturated zone are necessary. The portion of the mobile LNAPL body within the vadose zone is subject to volatilization and biodegradation, whereas the LNAPL in the saturated zone is only subject to dissolution and biodegradation. (ITRC, 2009a).

The NSZD technology could be used as a benchmark by comparing natural degradation rates vs. active removal rates. For example, if attenuation rates determined from NSZD measurements indicate that NSZD is responsible for removing LNAPL quantities that are much higher than those removed by actively engineered remedies, then a case could be made for discontinuing the active treatment once it is demonstrated that the effectiveness of NSZD is sustainable. On the other hand, projected removal rates from an in-situ technology that are much higher than NSZD rates would indicate that in-situ remediation may be merited.

4.6 Post-Conventional Technology Review and Pilot Test Selection

The LA LNAPL Workgroup invested significant resources on testing Post-Conventional remediation technologies. The Workgroup felt there was considerable expertise and tools available for assessing and applying conventional hydraulic-based LNAPL recovery technologies, and that more information was needed to assess the effectiveness, implementability, and cost of Post-Conventional technologies.

The Workgroup's primary criterion for selecting technologies for pilot testing was that they should have the potential to be applied to sites in a hydrogeologic setting referred to as *"Type III – Granular Media with Moderate to High Heterogeneity",* as described in Section 7 of the LA LNAPL Literature Review. This hydrogeologic setting is common to most of the refineries in the LA Basin. (One exception is the Chevron El Segundo refinery, which has a hydrogeologic setting better described as a *"Type I – Granular Media with Mild Heterogeneity and Moderate to High Permeability").*

In addition, the Workgroup was interested in applying at least one Composition Change technology and one Saturation Reduction technology.

In 2009, after detailed evaluation of existing case studies, performance data, and the extensive remediation experience of the Workgroup members, two technologies were retained for possible testing to achieve saturation reduction or composition change:

- Saturation reduction: Low Pore Volume Surfactant-Enhanced Aquifer Remediation (SEAR) and Thermal Remediation (either thermal conductive heating, electrical resistivity, or steam addition).
- Composition change: Pulsed Oxygen Biosparging (POBs).

The Workgroup heard a detailed presentation by Dr. Paul Lundegard regarding a large-scale, well-characterized state-of-the-art thermal remediation pilot test involving the addition of steam that was conducted at the Chevron Guadalupe Oil Field. This test was directed by three remediation experts, Dr. Paul Johnson of the Arizona State University, Dr. David Huntley of San Diego State University, and Dr. Kent Udell of the University of California, Berkeley. Because the large scale of the pilot test, the high level of characterization, and the oversight of the three experts, the LA LNAPL Workgroup felt this pilot test provided a high-quality case study of thermal remediation of LNAPL distributed in a geologic formation consisting of fine to medium sand. In this case study the LNAPL was not "trapped" below the water table as found in some other parts of the LA Basin due to more recent rising water table conditions. Preliminary cost estimates of a thermal pilot test in the Los Angeles Basin indicated potentially high cost and posed challenges to implementation (such as very stringent air standards). Therefore, the Workgroup decided to summarize the data from the Guadalupe Steam Pilot Test in this report but not conduct a thermal pilot test. Instead the Workgroup conducted a pilot test using the SEAR technology at a refinery site in the Los Angeles Basin. A summary of the cost and performance of the Guadalupe Pilot Test is provided in the text box on the next page.

PERFORMANCE SUMMARY: GUADALUPE PILOT TEST (LUNDEGARD, 2008)

The Guadalupe pilot test was performed at an oil field operated by Union Oil of California (Unocal) from 1951 to 1994 in southern San Luis Obispo County and northern Santa Barbara County, California. The LNAPL was primarily comprised of diluent, a diesel range hydrocarbon used as a viscosity reduction agent to make the heavy oil produced at the site transportable by pipeline.

Hydrogeological setting:

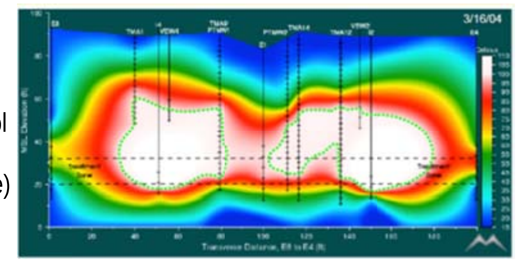
NRC's Type I *"Type I – Granular Media with Mild Heterogeneity and Moderate to High Permeability" setting, specifically,* relatively homogeneous and permeable unconsolidated sediments comprised of dune sands.

Operation:

Pilot test began in June 2003 and lasted till March 2004. Test cell was a 70 x 70 foot area bound by four injection wells that penetrated the groundwater table 70 feet below the ground surface, with an extraction well in the center. The test cell was located within the larger Pilot Test area that was bound by eight outer extraction wells (vapor and liquid) in an area 140 feet by 140 feet (approximately 0.5 acres). The outer extraction wells served to maintain the integrity of the pilot test cell. Steam was injected into the wells at a rate of 20,000 lb/hr. Steam was injected from one corner and extraction wells were used to pump the diluent, groundwater and condensed steam. The fluids collected through the extraction were separated, the recovered diluents stored to be transported off-site and the recovered water injected in the existing GRP process water system.

Summary:

- 9 months construction, 9 months operation
- 3.9 million gallons of water extracted from the treatment cell
- 25000 gallons of diluent recovered from cell
- 29.7 million gallons of water pumped for groundwater control
- 450000 gallons of propane burned
- As shown in image to right, design temperatures (pure white) reached through most, but not all of treatment zone



Operational Results:

- Diluent residuals and their associate mass contamination remains in soil after steam injection.
- Low volatility of the diluent limited the effectiveness of the steam technology
- Steam injection alone does not cleanup soil and groundwater as effectively as excavation
- Study also concluded that the impact on the ecology would be similar to large scale excavation.

Cost and Performance Results:

- Results of the pre-test and post-test change in NAPL Specific Volume are shown in the table below (see LA LNAPL Literature Review of definition).
- Approximately 46% of the LNAPL remained after the Pilot Test in the key target zone, and 14% in the zone that was known to have received steam throughout the Pilot Test
- The Pilot Test cost $6.3 million and treated 2240 cubic yards for a unit cost of $2,812 per cubic yard.
- Scaling the project to treat the entire 78 acre site within 8 year period was estimated to cost $390,000,000 for a unit cost of $260 per cubic yard.

Boring	Pre-Test Specific Vol.	Post-Test Specific Vol.	Pore Volumes of Steam	% remaining- Whole Target Zone	% remaining- "Steam Zone" Only
1	0.463	0.229	1.9	49%	13%
2	0.517	0.170	7.8	33%	16%
3	0.558	0.263	6.8	47%	15%
4	0.570	0.249	8.3	44%	10%
5	0.454	0.263	5.2	58%	18%
6	0.436	0.203	7.0	47%	15%
7	0.476	0.354	9.2	74%	16%
8	0.483	0.075	18.8	16%	2%
9	0.494	0.077	21.6	16%	5%
10	0.259	0.206	3.1	80%	32%
Mean	0.471	0.209	9.0	46%	14%

4.7 Pulsed Oxygen Biosparging (POBs)

The Pulsed Oxygen Biosparging (POBs) technology was an extension of a technology researched by Shell referred to as Oxygen Pulse Injection System (OPIS) (Shell Global Solutions, 2007). A POBs system sparges high concentration (~90%) oxygen into the treatment zone, which promotes biodegradation of most soluble organic contaminants, like benzene and BTEX (benzene, toluene, ethylbenzene, and xylenes), without the need for a soil vapor extraction system. The POBs Pilot Test was performed at the Shell Carson facility. The Pilot Test had the overall goal to extend the POBs technology and test its ability to overcome difficult and/or novel applications in terms of the hydrogeological setting, source location, injection well spacing, and performance monitoring of the system. Specific goals are described below:

- Apply POBs in a complex hydrogeologic setting of a relatively thin (~5-foot-thick), potentially discontinuous, lower permeability sand/silty sand unit. In the LA LNAPL Literature Review document (LA LNAPL Workgroup, 2011) this type of hydrogeologic setting was defined as a "*Type III – Granular Media with Moderate to High Heterogeneity*." This type of hydrogeological setting is different than the typical larger, thicker sand units in which many sparging systems are installed.
- Determine the ability of the POBs technology to treat submerged LNAPL as opposed to the more common application of POBs Extending or even water-table LNAPL. Submerged LNAPL is defined as *"LNAPL that is found well below the water table due to a historical release, followed by a rising water table. Most submerged LNAPL is in the residual form, and conventional floating LNAPL conceptual models do not apply. Submerged LNAPL is found in the LA Basin at sites with older, historical releases of LNAPL due to rising water table since the 1950s"* (LA LNAPL Workgroup, 2007). At the Shell Carson site, the submerged LNAPL in the treatment zone was located approximately 24 feet below ground surface and 17 feet below the water table. A successful project that employed "deep air sparging" (Klinchuch et al., 2007) provided some support for applying POBs to deeper units.
- Design the test in a way that an actual large-scale deployment of the POBs technology could be evaluated with large spacing (30 feet) between injection wells. For example, guidance developed by Shell suggested wells on 5-foot centers for barrier designs and wells on 10-foot centers for areal treatments (Shell Global Solutions, 2007). This spacing would not be practical for large treatment areas (tens or even hundreds of acres) of treatment zone containing submerged LNAPL. For this test, 30-foot spacing between injection wells was used. Again, the deep air sparging project by Klinchuch et al., (2007) indicated that larger spacing could be successful, but in a different hydrogeologic setting.
- Push the technology and measure performance between injection points (approximately 15 feet away) and not adjacent or close to the injection wells. The goal was to determine the ability of the POBs system to distribute the oxygen, and therefore the zone of biodegradation, throughout the treatment zone.

Section 5 of this report summarizes the design, operational history, and performance of the LA LNAPL Pulsed Oxygen Biosparge Pilot Test as a post-conventional LNAPL technology.

4.8 Low Pore Volume Surfactant-Enhanced Aquifer Remediation (SEAR)

The low pore volume, low concentration SEAR technology was developed by researchers at the University of Oklahoma, and commercialized by Surbec Environmental, LLC (Surbec). The technology employs non-toxic, biodegradable chemical surfactants (SURFace ACTive AgeNTS) that, as a result of their chemical properties, are able to reduce the interfacial tension between water and LNAPL. When the interfacial tension is sufficiently reduced, NAPL mobility increases such that NAPL can be readily recovered and pumped to the surface. A survey of 12 different field demonstrations have shown the mass removal from well-designed surfactant projects was in "the mid-70 percent to the high 90% range" (National Research Council, 2005). The patented surfactant formulations developed by Surbec yield such results using 10 times less surfactant than commonly used in other SEAR approaches (e.g., NAPL solubilization).

The SEAR Pilot Test was performed at the Tesoro Hynes facility. As with the Biosparge Pilot Test, the LA LNAPL SEAR Pilot Test had the overall goal to extend the SEAR technology and test its ability to overcome difficult and/or novel applications in terms of the hydrogeological setting, source location, injection well spacing, and performance monitoring of the system, as described below:

- Apply SEAR in a complex hydrogeologic setting of a relatively thin (~5-foot-thick), potentially discontinuous, lower permeability sand/silty sand unit. In the LA LNAPL Literature Review document (LA LNAPL Workgroup, 2011) this type of hydrogeologic setting was defined as a "*Type III – Granular Media with Moderate to High Heterogeneity*." This type of setting is different than the typical larger, thicker sand units in which the SEAR technology has typically been applied.
- Determine the ability of the SEAR technology to treat submerged LNAPL as opposed to the more common application of the SEAR technology to treat water-table LNAPL. Submerged LNAPL is defined as *"LNAPL that is found well below the water table due to a historical release, followed by a rising water table. Most submerged LNAPL is in the residual form, and conventional floating LNAPL conceptual models do not apply. Submerged LNAPL is found in the LA Basin at sites with older, historical releases of LNAPL due to rising water table since the 1950s"* (LA LNAPL Workgroup, 2007). At the Tesoro Hynes facility, the submerged LNAPL in the treatment zone was located approximately 24 feet below ground surface and 17 feet below the water table.
- Design the test in a way that an actual large-scale deployment of the SEAR technology could be evaluated with a "line drive" injection approach with lines of injection wells spaced 25 feet apart that direct the surfactant solution towards a companion line of production wells located 70 feet away. This type spacing would result in approximately 26 wells per acre; for a 50-acre site approximately 1300 wells would be required. (By comparison, closer spacing, such as 25 feet between injection and production wells instead of 70 feet, and 10 feet between injection wells instead of 25 feet, would have required 4300 wells for a 50-acre site).

Section 6 of this report summarizes the design, operational history, and performance of the LA LNAPL Low Pore Volume SEAR Pilot Test as a post-conventional LNAPL technology.

4.9 Natural Source Zone Depletion (NSZD) Pilot Test

In 2009 there were rapid developments in the understanding and characterization of Natural Source Zone Depletion (NSZD). The ITRC published a Technology Overview (ITRC, 2009a) and Colorado State University began to publish results from their carbon dioxide trap equipment. Because of the importance of NSZD processes to developing a Conceptual Site Model, and because of the recent availability of the carbon trap characterization technology, the LA LNAPL Workgroup decided to apply the carbon trap technology at two sites in the LA Basin. Section 7 of this report summarizes the design, installation, and results from the NSZD Pilot Test as a post-conventional LNAPL technology.

RESULTS: Post-Conventional LNAPL Remediation Technologies
• The LA LNAPL Workgroup developed an LNAPL Remediation Technology Matrix (Table 4.1) to evaluate conventional and, more importantly, Post-Conventional remediation technologies. • The Workgroup decided to test Post-Conventional technologies that address residual LNAPL, either as LNAPL left after conventional recovery efforts are no longer efficient or as residual in the form of submerged LNAPL. • Because considerable expertise and tools were already available for assessing and applying conventional hydraulic-based LNAPL recovery technologies, this Study stressed assessing the effectiveness, implementability, and cost of Post-Conventional technologies. • Thermal technologies were not tested for the LA LNAPL project because a large, well characterized Steam Pilot Test had been previously conducted at the Chevron (formerly Unocal) Guadalupe Oil Field. (Results of that pilot test are summarized in Section 4.6). • Three Pilot Tests were conducted: Pulsed Oxygen Biosparging (POBs, see Section 5); Low Pore Volume Surfactant-Enhanced Aquifer Remediation (SEAR, see Section 6); and Natural Source Zone Depletion (NSZD, see Section 7). • The POBs and SEAR Pilot Tests were designed to extend these technologies to treat LNAPL in a difficult hydrogeologic setting with high heterogeneity, submerged LNAPL, and at a scale that would be representative of a site-scale remediation system at a refinery site.

5.0 PULSED OXYGEN BIOSPARGING PILOT TEST RESULTS

5.1 Pilot Test Objectives

This pulsed oxygen biosparging (POBs) pilot test for remediation of LNAPL was conducted at the Shell Carson Terminal (Site) in Carson, California from June 2012 to June 2013. The pilot tests performed as part of the LA LNAPL Project tested **Post-Conventional treatment technologies,** which are defined as *remedial technologies incorporated into site remediation after the initial LNAPL removal effort has been completed or the LNAPL has been determined to have low hydraulic recoverability (i.e., low LNAPL transmissivity).* Key points regarding this Pilot Test are:

- The POBs technology sparges high concentration (~90%) oxygen into the treatment zone, which promotes biodegradation of most soluble organic contaminants, like benzene and BTEX (benzene, toluene, ethylbenzene, and xylenes), without the need for a soil vapor extraction system.
- This Pilot Test had the overall goal to extend the technology and test its ability to overcome difficult and/or novel applications in terms of:
    - Applying POBs in a complex hydrogeologic setting of a relatively thin (~5-foot-thick), potentially discontinuous, lower permeability sand/silty sand unit.
    - Treating submerged LNAPL as opposed to the more common application of POBs Extending or even LNAPL plumes encountered at the water-table surface.
    - Designing the test in a way that an actual large-scale deployment of the POBs technology would be implemented, with large spacing (30 feet) between injection wells.
    - “Extending” the technology and measuring performance between injection points (approximately 15 feet away) and not adjacent or close to the injection wells.
- The Pilot Test was designed to evaluate changes in mass, composition of LNAPL, concentrations in groundwater, and mass discharge of the dissolved plume, operational factors (such as how easy was the technology to implement), and cost.

5.2 Pilot Test Design

A mobile onsite pulsed oxygen sparging system (Matrix Environmental Technologies Inc.) was used for oxygen generation, storage, and delivery. Three injection wells were drilled in the triangular pattern shown in Figure 5.1. Originally, two separate transmissive units were targeted for treatment, but the planned treatment of the deeper unit had to be abandoned due to accumulation of several feet of LNAPL in the injection wells that would have been challenging to sparge safely with oxygen. Therefore, the scope of work for drilling the “P2” series of wells in Figure 5.1 was not completed, and no sparging or monitoring took place in the P2 zone.

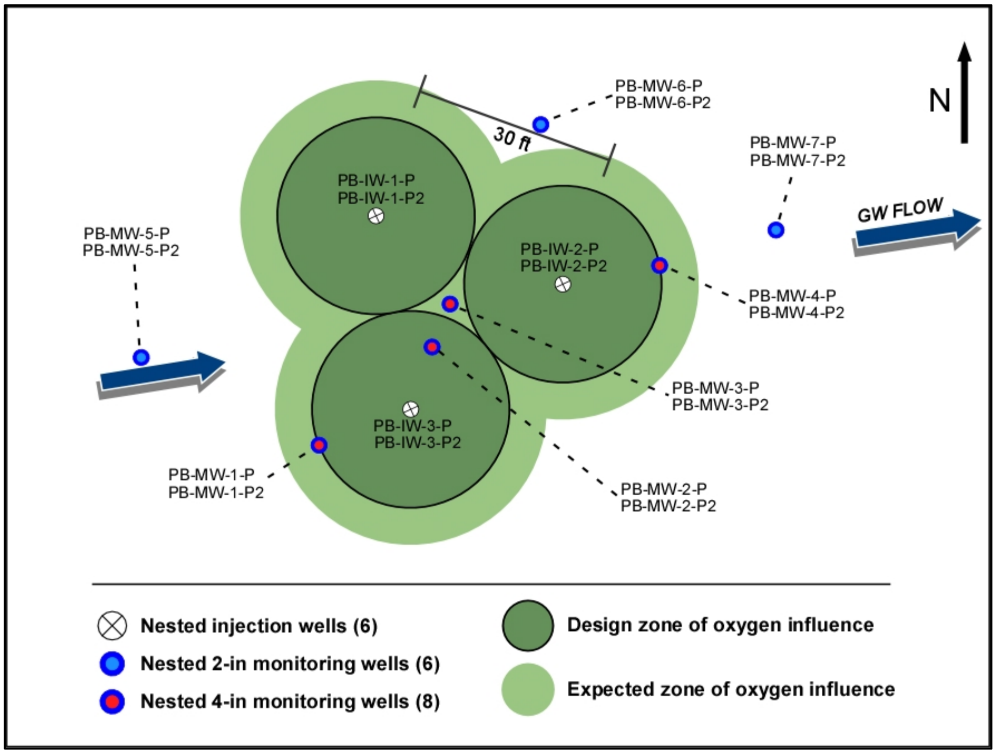


Figure 5.1. *Pilot Test Layout. Injection Wells (IW) were spaced 30 feet apart and Monitoring Wells (MW) were located at four locations within the test zone and two background locations. The Deeper unit wells (P2) were either not drilled or not used during the Pilot Test due to the accumulation of LNAPL in the wells.*

Note: Injection and monitoring wells are referenced by abbreviated names in this report, such as "IW-1P" for well PB-IW-1-P and "MW-1" for well PB-MW-1-P.

5.3 Pilot Test Operation

The POBs injection system experienced several operational difficulties during the 12-month testing period, as follows:

- High injection pressures were required to inject the oxygen in the treatment zone, demonstrating the difficulty of injecting into this type of formation.
- The lack of any dissolved oxygen (DO) change in the monitoring wells early in the test resulted in a decision to inject more oxygen than in the initial design parameters.
- The high injection pressures and/or large injection volumes, in turn, resulted in two daylighting events that required two injection wells to be abandoned. A short-circuiting event required one of these abandoned wells, well IW-3P, to be over-drilled and removed.
- A total of three injection well related drilling events were performed during the test: (1) drilling of the three original injection wells; (2) drilling of injection well IW-3R to replace injection well IW-3P, and (3) over-drilling/removal of injection well IW-3P. Additionally,

injection well IW-2P was taken out of service after seven months of biosparging and was not re-drilled.

- An approximate total of 38,600 standard cubic feet (SCF) of oxygen was injected during the test. The longest running injection well with no operational problems (IW-1P) was able to support an average injection rate of 41 SCF per day during the year-long test.

In general, the mechanical equipment functioned as designed during the test, requiring little maintenance; however, the relatively thin, heterogeneous formation made it difficult to inject oxygen in the subsurface.

- High DO concentrations were most apparent in the injection wells, and in one monitoring well where a short-circuiting event through the monitoring well screen was likely occurring. After about four months, small but statistically significant increases in DO (0.5 to 3 mg/L) were observed in the three working monitoring wells and (unexpectedly) in both background wells. The pattern of these increases suggests that after a year, the biosparging system was delivering low volumes of oxygen to the relatively large area represented by these wells.
- Over 90% of the dissolved phase benzene and BTEX compounds were removed from the high-oxygen zone around the injection wells (Table 5.1.A), with lower removals for TPH (~30%), which is consistent with the aerobic biodegradation process. Lower oxygen levels at the monitoring wells located away from the injection wells was the likely reason for much lower removals of benzene (28%) and toluene (30%) and no removal of ethylbenzene or xylenes (Table 5.1.B).
- The groundwater data were found to be log-normally distributed rendering the geometric mean concentration values meaningful for comparison.

Table 5.1.A *Geometric Means of Before and After Constituent Groundwater Concentrations for Injection Wells*

	Before Concentration (µg/L)	**After Concentration** (µg/L)	**Percent Reduction**
Benzene	795	16	98%
BTEX	2,737	154	94%
TPH – All Fractions	46,659	32,061	31%

Table 5.1.B *Geometric Means of Before and After Constituent Groundwater Concentrations for Monitoring Wells Inside Treatment Area*

	Before Concentration (µg/L)	**After Concentration** (µg/L)	**Percent Reduction**
Benzene	883	638	28%
BTEX	2,625	2,124	19%
TPH - All Fractions	54,919	34,269	38%

- Benzene concentrations **in soil** decreased slightly after the test (11% reduction using an arithmetic average). BTEX was unchanged (Table 5.2).
- The mass fraction of both **benzene and BTEX decreased by about 51% and 45% respectively** during the test, which is statistically significant at the p=0.05 level. However, the majority of the reduction was due to toluene and benzene with no change in concentration of xylene or ethylbenzene. This confirms that a significant composition change (removal of benzene and BTEX) did occur during the year-long test.
- The average concentration of the TPH-All Fractions *increased* by 82% before and after the test. This increase in TPH has two likely potential explanations: 1) an LNAPL inflow during the test, potentially due to the surging action of the oxygen pulses; and/or 2) random sampling variability. The UltraViolet Optical Screening Tool (UVOST) and core photography data do not indicate LNAPL inflow (Attachment 1: Figures 5.17 to 5.19).

Table 5.2. *Arithmetic Average Concentration in Soil Samples Before and After Pilot Test*

	Benzene (mg/kg)	**BTEX (mg/kg)**	**TPH – ALL (mg/kg)**	**GRO (mg/kg)**	**DRO (mg/kg)**
Pre-Test	9.1	86	5,151	2,600	2,481
Post-Test	8.1	86	9,361	4,722	4,536
% Reduction	11%	0%	-82%	-82%	-83%
Statistically Significant?	***Yes***	No	No	No	No

Notes: Negative % Reduction indicates an *<u>increase</u>* *in average concentrations. GRO = Gasoline Range Organics, DRO = Diesel Range Organics*

- Only two pairs of before and after LNAPL saturation data were available for analysis. These two pairs of LNAPL saturation data for MW-1 and MW-2 (Attachment 1: Figure 5.20) either decreased or stayed the same (12.3% to 5.5% and 7.7% to 7.6%). The before and after soil samples generally showed an *increase* in TPH concentration (Attachment 1: Figure 5.17 and 5.19); the reason for this trend is unknown. Insufficient LNAPL data collection and the heterogeneity of the soil analysis prevent any statistically significant conclusions.
- Benzene removed: between **3.6 – 6.5 kilograms** (51% removal based on mass fraction).
- BTEX removed: between **30 - 55 kilograms** (45% removal based on mass fraction).
- A mass balance estimate suggests that 1.9% to 10.6% of the oxygen delivered to the treatment zone was consumed for biodegradation of BTEX.
- Our analysis suggests that there is no evidence of LNAPL inflow, losses attributable to volatilization were not significant, and the soil sampling data accurately show a reduction in the mass fraction of benzene and BTEX during the test.

5.4 Pilot Test Performance Summary

Overall the key Pilot Test results are:

- It was difficult to inject into the thin, heterogeneous unit, and several daylighting events (oxygen channels emerging at the surface) made operation of the biosparge system difficult during the year-long test. Hydrogeologic units where LNAPL is present and can accumulate in the injection wells may be difficult or impossible to biosparge like the deep wells in the Pilot Test. Submerged NAPL makes the applicability of this technology difficult to assess prior to drilling.

- The mass fractions of benzene and BTEX in soil were reduced by **51% and 45%** respectively during the year-long test, a statistically significant change. This confirms that the expected *composition change** (preferential removal of BTEX compounds as opposed to removal of LNAPL mass) was established by the oxygen biosparge system during the test. It would likely take several more years of biosparging to reduce the benzene and BTEX mass fractions by 90%.

* The ITRC LNAPL Framework document (ITRC, 2009) also uses the term "*LNAPL Phase Change*" as well as composition change. LNAPL Phase Change is defined as "*Reliance on or application of a technology that indirectly remediates the LNAPL body via recovery and/or in situ destruction/degradation of vapor or dissolved-phase LNAPL constituents.*"

6.0 LOW PORE VOLUME SURFACTANT ENHANCED AQUIFER REMEDIATON PILOT TEST PERFORMANCE SUMMARY

6.1 Objective

In 2009, after detailed evaluation of existing case studies, performance data, and the extensive remediation experience of the Workgroup members, Low Pore Volume Surfactant Enhanced Aquifer Remediation (SEAR), which was developed by Dr. Jeff Harwell at the University of Oklahoma, was selected as the Saturation Reduction technology for testing by the LA LNAPL Workgroup. Dr. Harwell's company, Surbec Environmental, was hired to perform lab treatability studies and help with the design of the Pilot Test.

The mass removal from well-designed surfactant projects has been reported to be in "the mid-70 percent to the high 90% range" (National Research Council, 2005). However, application of this technology to submerged LNAPL sites in the Los Angeles basin is complicated by several factors:

- relatively low permeability, highly heterogeneous geologic conditions;
- the presence of LNAPL distributed as "submerged LNAPL" through a 30-foot thick interval below the water table, in contrast to LNAPL being confined to the near the water at most sites;
- the presence of operating process units on the surface at terminals and refineries on the surface over some of the LNAPL sites;
- test design with intent to implement Pulsed Oxygen Biosparge (POBS) technology with large spacing (30 feet) between injection wells.

In summary, the overall expectation was that these factors were extending the surfactant technology to untested and more difficult conditions in this Pilot Test.

A laboratory treatability test was conducted by Surbec Environmental (Surbec) using soil and LNAPL from the site. The treatability test concluded that:

> *"Tests with the simulated ground water allowed for developing a workable surfactant system capable of removing more than 90% of the NAPL. Based on the soil column results we have obtained, we would recommend a pilot test for this site in order to observe any soil heterogeneities and unforeseen obstacles that can happen when applying this technology in the field." (Surbec, 2010)*

Because real groundwater could not be shipped to the Surbec facility, Surbec produced "simulated groundwater" with the same chemical composition as site groundwater.

The original volume of LNAPL in place in the Deep Unit was estimated to be approximately 1,670 gallons of LNAPL based on soil core results from the two locations that were sampled. Assuming between 50% and 90% removed gave a range would have resulted in between 750 and 1,500 gallons of LNAPL removal. When the surfactant test was converted to a push pull test, the affected treatment zone was reduced by about 50%. Therefore the adjusted removal rate was between 370 to 750 gallons removed.

6.3 Pilot Test Design

The SEAR pilot test was conducted at the Tesoro East Hynes Terminal from April 15 to October 20, 2014. The treatment area was approximately 50 feet x 75 feet, and consisted of:

- six injection wells (IW-1B/C, IW-2B/C, IW-3B/C),
- three extraction wells (EW-1, EW-2, EW-3), and
- eight monitoring wells (SPT-1B/C, SPT-2B/C, SPT-3B/C, SPT-4B/C).

A low concentration surfactant and electrolyte solution was injected in the deepest of three units (IW-1/2/3C) from April 15, 2014 through June 4, 2014. Extraction from the same wells was conducted from June 19 through October 20, 2014 as part of a Push-Pull test.

The figure below summarizes the locations and characterization data acquired to assess the performance of this technology. Following the charge of the LA LNAPL Workgroup, the characterization efforts were more extensive than typical LNAPL remediation projects, and included all of the following:

- CPT/LIF testing
- Concurrent specific conductivity with depth at CPT/LIF locations
- Soil sampling and analysis in the treatment interval (26-31 ft bgs)
- Before/after core photography and testing
- Groundwater sampling and analysis

Additionally, soil sampling locations were categorized as either treated (red dots) or untreated (blue dots) depending on the estimated area of treatment due to surfactant flushing.

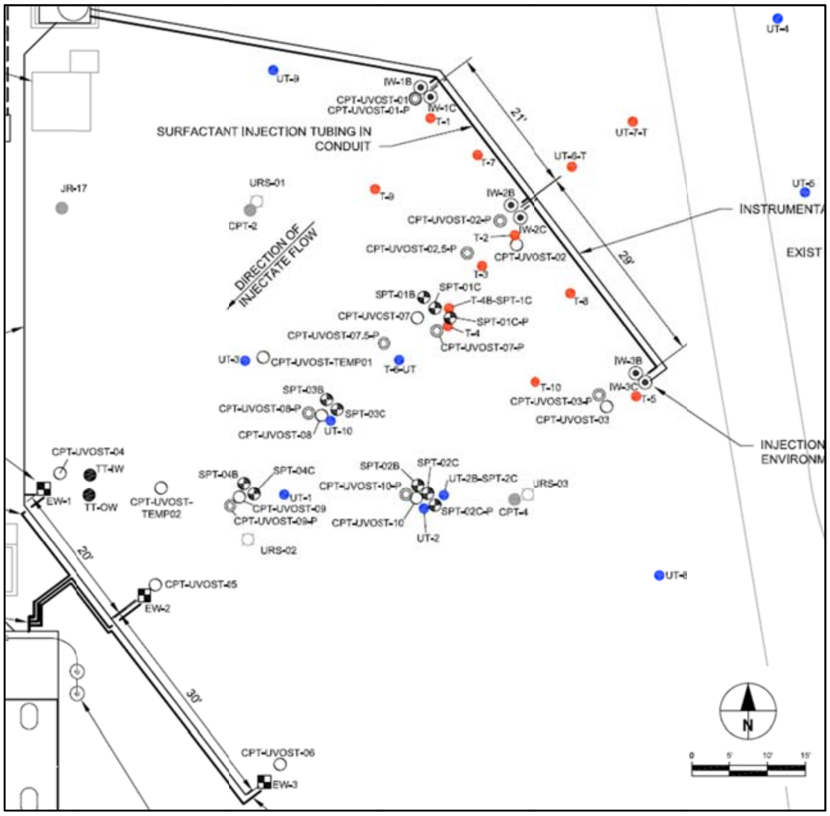


Figure 6.1. Surfactant Pilot Test Layout. Figure shows Untreated Soil Sampling Locations (blue circles); Soil Sampling Locations in the Treatment Zone (red circles); and Injection Extraction, and Monitoring Wells.

6.4 Pilot Test Operations

6.4.1 Where did the surfactant go? Did it go where we intended it to go? If not, why not?

Results from surfactant analysis of soil samples were submitted to Surbec from the post-test characterization soil cores. Due to complications during laboratory analysis, Surbec could not provide surfactant concentrations in the samples. However, concurrent specific conductivity probes used during post-test characterization at CPT/UVOST locations indicate that some chloride was detected between SPT-1C and SPT-3C in the treatment zone (approximately 25 ft from injection wells). Additionally, weekly sampling of chloride was conducted in the injection and monitoring wells in order to track the movement of injected surfactant solution through the treatment zone. These results indicated that breakthrough of chloride had occurred at SPT-1C with concentrations up to 2,400 mg/L.

Based on these data, the known volume of injection fluid and observed hydraulic gradients, the "footprint" of the surfactant solution within the treatment area is estimated to form a roughly oval injection shape with some downgradient migration that extended near monitoring well SPT-1C (about 25% of the original treatment zone).

6.4.2 How did regulatory factors affect the Pilot Test Design?

Several regulatory factors played an important role in this Pilot Test:

1) **The Waste Discharge Requirement (WDR) permit**. The LA LNAPL Workgroup spent considerable time working on a permit submittal, partly because of questions regarding the Workgroup performing the test, and the site owner serving as permit holder. To address this issue, the Regional Board provided the Study with a Waiver. Additionally, intra-group contracting issues with the LA LNAPL Workgroup required considerable time. Future applications of this technology either need to account for the time and cost of acquiring the WDR permit.
2) **Regional Board requirements not to degrade LA Basin groundwater with chloride that was contained in the injection fluid.** Electrolytes (most commonly sodium chloride) are a critical component of the low pore volume surfactant technology. To meet the non-degradation requirement, a chloride impact calculation was performed based an allowable fence line concentration. It indicated that the Pilot Test could leave an "allowable chloride mass" of 620 kilograms chloride in groundwater after the test was concluded. (In general it is very difficult to recover all of the injected fluid.) The allowable mass was used in turn to calculate a "trigger concentration" of 980 mg/L, which was the maximum allowable increase in the average concentration of chloride in the test zone. Because the injection fluid had chloride concentrations of several thousand mg/L, this chloride restriction played a large role in the operation of the Pilot Test because of the concern that it might be difficult to retrieve any injected chloride above the 620-kg level from these heterogeneous, low permeability units. This was a key factor that led to the conversion to a Push-Pull test once low injection rates were observed. Any future implementations of this technology may need to reserve project funds to remove excess chloride in case a chloride trigger is exceeded at the end of the project.
3) **Requirements to not significantly worsen dissolved phase hydrocarbon water quality after the test.** Although the surfactant technology was not expected to worsen groundwater water quality based on the experience of the technology developer (Dr. Jeff Harwell), concerns by the Regional Board led to the Workgroup to develop a "benzene trigger" where there would be no more than a 50% increase in average benzene concentrations over baseline conditions. In the end, benzene concentrations did increase by about 20% in the test zone after the test was concluded. However, the benzene trigger was not exceeded and no additional post-test pumping or treatment was required. Any future implementations of this technology may need to plan for removal of excess benzene in case this benzene trigger is exceeded at the end of the project.
4) **No discharge-to-air requirement.** This stipulation is inherent to almost any industrial process in the Los Angeles Basin. As expected, it led to increased costs to pay for daily air monitoring of the extracted fluids tank (approximately $1000 per day), and was one factor that made extending the test beyond the planned 6 months financially prohibitive. This is an important environmental regulation in the region, and any future consideration of using the low pore volume surfactant technology needs to account for this factor.
5) **Stipulation that the contaminated groundwater could not be used as the**

injection fluid without treatment. The technology developer recommended the use of groundwater from the plume or from background wells to be used as injection makeup water. This was not allowable in the LA Basin without treatment, leading to the use of firewater at the facility as the source of the injection water, and required the addition of additional electrolytes (calcium and magnesium chloride) in an attempt to mimic the groundwater geochemistry. The additional chloride complicated the test in terms of Water Replenishment District non-degradation requirements (see #2 above).

All told, these regulatory requirements/requests did not create insurmountable problems or negatively directly affect the results of the Low Pore Volume Surfactant Pilot Test. However, together these five important regulatory requirements significantly increased the cost and reduced the operational flexibility of the LA LNAPL Pilot Test. Future applications of the technology need to account for these five regulatory factors.

6.5 Pilot Test Performance

Originally, three separate treatment zones containing submerged LNAPL were to be tested: Upper Zone (12 to 18 feet bgs); Middle Zone (18 to 24 feet bgs); and a Deeper Zone (24 to 30 feet bgs). Based on soil core and cone penetrometer information taken before the Pilot Test was started, the Upper Unit appeared to have the lowest permeability while the Lower Unit had the highest. During construction of the injection system, a thermal tracer test was performed in the Upper Unit where cold water was injected into the formation. This test indicated the Upper Unit's permeability was too low to inject, and this unit was not tested (no injection, extraction, or monitoring wells drilled into this unit).

Because of low injection rates, the injection into the Middle Unit was halted on 9 May 2014. After this date, the test focused exclusively on the Lower Unit.

Before/After UVOST

CPT/UVOST data were collected before and after the pilot test next to the injection and monitoring wells. The data were divided into three key areas:

- A treated zone defined as the area where surfactant was injected and presence of surfactant is known (IW-1, IW-2 and IW-3),
- An untreated zone defined as the area not affected by injected surfactant (SPT-2, SPT-3 and SPT-4), and
- A transition zone defined as the area between the treated and untreated zones and potentially affected by injected surfactant (SPT-1).

Based on the review of CPT, UVOST and core fluorescence photograph data pre and post-injection, findings can be summarized as follows:

- Formation materials are coarser in Deeper Zone than the Upper Zone of the soil columns across the site.
- In the treated zone, LIF intensity suggests effects of surfactant on LNAPL removal in the lower zone, but not in the Middle Zone where surfactant injection was halted early in the test.

- In the untreated Deeper Zone, LIF intensity appears to be closely related to soil heterogeneity.
- In the transition Deeper Zone, LIF intensity is less certain, but possibly related to both surfactant and soil heterogeneity.

Soil Sampling (Untreated vs. Treated)

Soil sampling was conducted at both treated and untreated locations in the treatment zone (Deeper Zone, 26-31 ft bgs) as seen in Figure 6.1. The following table summarizes average soil concentrations both zones for benzene, BTEX, and total TPH. Concentrations were either similar (benzene and BTEX) or slightly higher in the treated zone (total TPH), though the differences were not statistically significant.

***Table 6.1**. Soil Sampling Results in Untreated vs. Treated Zones*

Constituent	Untreated Locations* Average Soil Concentration (mg/kg)	Locations in Treatment Zone* Average Post-Test Soil Concentration (mg/kg)	Statistically Significant?**
Benzene	50	50	No (p=0.8)
BTEX	820	860	No (p=0.9)
Total TPH	6,350	8,460	No (p=0.3)

* See Figure 6.1 for Untreated vs. Treated locations. 17 samples were used to develop the averages for the untreated locations, and 17 samples for the treated samples.

** Statistical significance determined using a two-tailed distribution t-test. A p-value less than or equal to 0.05 was defined as achieving statistical significance.

As can be seen, no statistically significant difference in concentrations in the untreated zone surrounding the treatment zone was observed. Note that the TPH concentrations in the treatment zone were higher than the surrounding untreated zone; this is likely due to sampling variability.

Core Photography

Before and after core photos were taken at two locations: SPT-1 and SPT-2. Comparison of pre and post injection core photos is inconclusive due to utilizing different sampling methods. However, there is good correlation between the pre and post-injection core photo and associated pre and post LIF intensity.

Mass Removal

Mass removal calculations were performed using fluid evacuated volume from the tank that was used to store recovered fluids, and groundwater concentration results from the extraction wells during the five sampling events. Average Benzene, BTEX, and TPH concentration data for extraction wells EW-1, EW-2 and EW-3 were used for the first sampling date, while concentration data for the injection wells IW-1C, IW-2C and IW-3C were gathered from the second, third and final sampling dates.

Total mass removed during the entire pilot test for these constituents are listed below:

- Benzene: 7 kg (2 gal)
- BTEX: 21 kg (8 gal)
- Total TPH: 61 kg (21 gal)

Because the push-pull test included only extraction from the three injection wells IW-1/2/3C, the mass removed prior to conversion to a push-pull test was subtracted (i.e., mass removed from EW-1,2,3).

As such, the mass removed during the push-pull test for these constituents were:

- Benzene: 3 kg (1 gal)
- BTEX: 8 kg (3 gal)
- Total TPH: 34 kg (12 gal)

Overall the data indicated that 60 kg of TPH were removed during the entire test, and 34 kg removed from the push-pull test specifically, which correspond to about 21 gallons and 12 gallons of LNAPL, respectively. This is about 1% of the total LNAPL mass estimated to be in the entire treatment zone prior the Pilot Test. All of the removal was observed in the dissolved phase, and no free product LNAPL was recovered.

The TPH data collected from the soil samples in the untreated and post-treatment treated zones were used to estimate the hydrocarbon mass per acre. It was assumed that most of the TPH mass was in residual LNAPL form. In the zone treated by the push-pull test design, the estimated mass and volume of LNAPL after the Pilot Test was completed was estimated to be 4,900 kg or 1,700 gallons over this 0.4 acre treatment zone. This translated to approximately **42,900 gallons per acre** for this zone. In the untreated zone surrounding the push-pull treatment zone, the post-test volume was estimated to be **32,200 gallons LNAPL per acre.**

The reason the treated zone volume per acre was higher than the untreated zone is either: 1) the treatment zone had higher LNAPL concentrations to start with; and/or 2) during the pull portion of the test some LNAPL from what was considered the untreated zone was actually drawn into the treatment zone (but not removed by the pumping wells). The first reason (1) is the most likely explanation for the large gallons per acre figure for the post-test treatment zone.

Groundwater Monitoring

Groundwater sampling events were conducted five times during the pilot test duration: i) baseline (pre-test), ii) First during-test, iii) Second during-test, iv) Third during-test, and v) final (post-test). The following table summarizes the before/after groundwater conditions in the deeper treatment zone, which included wells IW-1/2/3C, SPT-1/2/3/4C and EW-1/2/3.

As shown in Table 6.2, the post-test groundwater concentrations for the constituents were greater than baseline values overall, though the increase was not statistically significant (i.e., $p>0.05$ using a two-tailed distribution t-test).

***Table 6.2**. Before and After Groundwater Monitoring Results*

Wells	Geomean of Before-Test Baseline Groundwater Samples (µg/L)	Geomean of After-Test Groundwater Samples (µg/L)	% Change	Statistically Significant?*
Benzene	15,360	17,120	11	No (p=0.14)
BTEX	42,800	55,520	30	No (p=0.08)
Total TPH	93,190	124,120	33	No (p=0.18)
Chloride	59,670	136,550	129	No (p=0.10)

(*) statistical significance determined using a two-tailed distribution t-test. A p-value less than or equal to 0.05 was defined as achieving statistical significance. 10 samples were used to develop the averages for the before-test samples, and 10 samples for the after-test samples.

Groundwater concentrations of site organic constituents increased over baseline conditions, but not to the extent to exceed the pre-test “trigger” level where a 50% increase in benzene concentrations would have required remedial measures. The increase in the organic compounds may be due to some solubilization of the LNAPL due to the surfactant mixture. Chloride concentrations also increased due the electrolytes that were a necessary part of the surfactant mixture, but did not exceed the post-test trigger concentrations.

6.6 Key Factors Affecting Performance

Permeability

The key factor that appears to have resulted in the low recovery of the surfactant test was the site stratigraphy. The low hydraulic conductivity (40% lower than the design value based on injection well slug tests) soils limited the ability to effectively inject the surfactant solution as demonstrated by the very low injection flow rates that were observed. Attempts to increase the injection flow rates by modifying the injection approach to a constant-head (as opposed to constant-flow) were unsuccessful. This resulted in a very small area around the injection wells where sufficient surfactant was injected to induce LNAPL mobilization. As demonstrated by the column tests performed by Surbec, 1.5 pore volumes of surfactant solution was required to produce a surfactant concentration high enough to overcome surfactant adsorption to soil and induce LNAPL mobilization. It is likely that any LNAPL that was mobilized during the extend portion of the test did not have sufficient surfactant concentration to mobilize the LNAPL back toward the well during the “pull” portion of the test. As such, no LNAPL was recovered.

Surfactant chemistry is unlikely to have resulted in the observed results. During startup of the test, the surfactant solution was tested on-site using a jar-test method recommended by Surbec. During this test, it was confirmed that the surfactant solution was able to achieve the microemulsion required for LNAPL mobilization. In addition, the surfactant solution, which used fire water as makeup water as opposed to groundwater, contained calcium and magnesium chloride in order to mimic the natural groundwater geochemistry and minimize the mobilization of fine-grained soils.

Microbial Analysis

Due to observed reductions in injection well hydraulic conductivity and changes in water coloration (i.e., black groundwater in the injection wells), the presence of biofouling was evaluated as a possible cause. Results suggest an increased likelihood that the interference in process performance is at least partially attributable to biofouling; however, it does not appear that presence of surfactant directly enhanced microbial activity.

6.7 Implications

The technology was unsuccessful at removing LNAPL from the relatively thin, highly heterogeneous interbedded sand, silt and clay unit at the Tesoro Hynes facility. The Workplan assumed an average hydraulic conductivity of 4.9×10^{-4} cm/sec, while the actual values measured from the field construction of the injection and monitoring wells was 1.3×10^{-4} cm/sec. For successful implementation of this technology or related technologies (such as cosolvent addition) in the LA Basin, a treatment zone should have several of the following characteristics:

- relatively high permeability (e.g., ITRC, 2003, Table 2-1), in particular a hydraulic conductivity of 1.0×10^{-3} cm/sec or higher;
- a relatively continuous thick treatment zone of ten feet or more;
- for submerged LNAPL, a treatment zone with good continuous low permeability units both above and below the treatment zone.

A tracer test is recommended prior to any full-scale application of the technology. If injection of tracer chemicals is of concern, injecting heat or cold water and using temperature as the tracer may be a good alternative (a tracer test was applied in the upper unit of the Surfactant Pilot Test, indicated very low permeability, and led to the decision not to perform the Pilot Test in this unit). Because construction of the Skid had already started and other scheduling issues, tracer tests were not performed in the middle or lower units prior to startup of the Pilot Test).

From an operational point of view, these complicating factors would reduce the cost of implementing this technology significantly:

- sites where native groundwater could be used for injection without any treatment;
- sites where on-site treatment via air strippers could be used rather than trucking contaminated water to an existing treatment system;
- sites where close review of the injected and recoverable chloride mass is not required.

The reduction in cost could also translate indirectly to better performance if more project resources could be applied to improved designs. However, based on our experience many potential surfactant projects in the LA Basin would be subject to some or all of the complicating factors listed above.

7.0 NATURAL SOURCE ZONE DEPLETION (NSZD) PILOT TEST

7.1 Background

In 2009 there were rapid developments in the understanding and characterization of Natural Source Zone Depletion (NSZD). Because of the importance of NSZD processes to developing a Conceptual Site Model, the LA LNAPL Workgroup decided to measure NSZD rates at two sites in the LA Basin. The Workgroup, working with Colorado State University (CSU), conducted the pilot tests at the Shell Carson facility (Pilot Test 1) and the Tesoro Hynes facility (Pilot Test 2). The tests were performed from mid-2012 to mid-2013.

7.2 Theory

Carbon dioxide (CO_2) is the product of hydrocarbon biodegradation, either from direct biodegradation (as shown in the formula below) or as an indirect product from methane formation that is then biodegraded to CO_2

$$C_{10}H_{22} + 31/2\ O_2 \rightarrow 10\ CO_2 + 11\ H_2O$$

As such, subsurface CO_2 generation above background levels is direct evidence of biodegradation of hydrocarbons and an acceptable indicator of NSZD (ITRC, 2009; Sihota et al., 2011; Sihota and Mayer 2012; Sihota et al., 2013; Warren et al., 2014). (See NSZD Conceptual Model to the right).

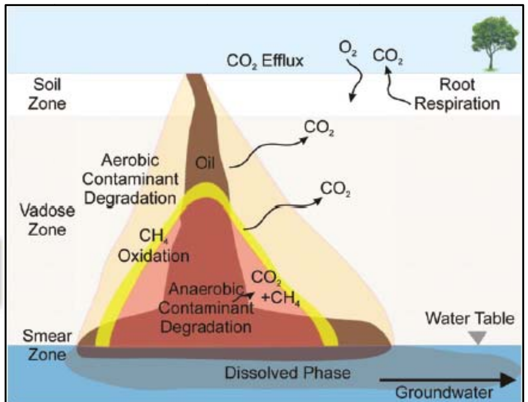


Fig. 1. Conceptual model of contamination in the vadose zone at the Bemidji site.

Sihota and Mayer, 2012. Reprinted by Permission, ASA, CSSA, SSSA.

7.3 Measuring NSZD Rates at LNAPL Sites

Three methods are often used to measure hydrocarbon degradation rates: an intrusive method requiring drilling and installation of soil gas monitoring wells, the **gradient method**; and two methods that measure the CO_2 flux at the surface: the **dynamic chamber method** and the **carbon trap** method.

Two ways to perform a background correction can be applied to exclude the CO_2 produced from plant respiration:

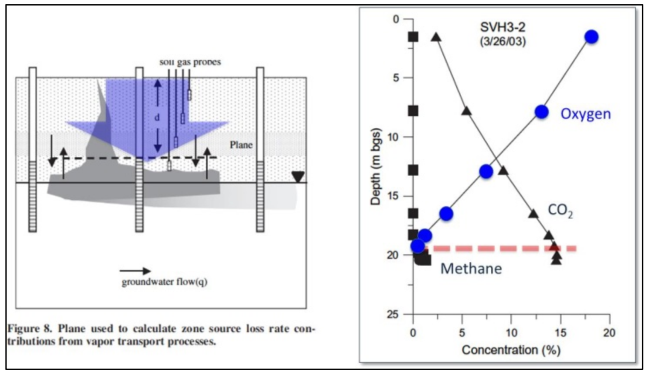
i) take the CO_2 flux measurements in a clean area (i.e., no LNAPL) and subtract from LNAPL-impacted area (Sihota et al., 2011) or

ii) use ^{14}C isotope analysis to determine contribution of CO_2 from hydrocarbons (Sihota and Mayer, 2012).

7.3.1 Gradient Method

In the unsaturated zone at LNAPL sites, the concentration of gaseous oxygen (O_2) *decrease with depth* because it is consumed in LNAPL degradation reactions in the unsaturated zone and with methane (CH_4) oxidation (as CH_4 is migrates upwards from the saturated zone or is generated during anaerobic degradation in the vadose zone (Lundegard and Johnson, 2006; ITRC, 2009)).

The gradient method is designed to measure the rate that O_2 is consumed (using the biodegradation formula presented in Section 7.2), and convert this consumption rate to a NSZD rate. This calculation also requires the results from in-situ diffusivity tests (or theoretical calculations) to develop effective diffusion coefficients (D_e) (Johnson et al., 1998); ideally these measurements should be conducted at the same time as gas compositional measurements are conducted to appropriately account for gas transport processes. The O_2 gradient (i.e., the change in concentration vs. change in depth) is multiplied with D_e to calculate an oxygen consumption flux using Fick's first law (Johnson et al., 2006; Lundegard and Johnson, 2006; Sihota, 2011).



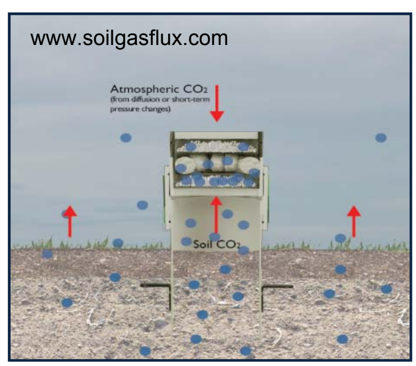
Johnson et al., 2006; Lundegard and Johnson, 2006; Reprinted by Permission.

7.3.2 Dynamic Chamber Method

The Dynamic Chamber Method involves the use of an infra-red gas analyzer (IRGA) connected to a robotic chamber (e.g., LI-COR). To determine the rate of CO_2 efflux, the chamber closes over a collar installed into the shallow surface soil (> 10 cm). Air recirculates between the chamber and the IRGA during the measurement period (~1.5 minutes), enabling measurement of the CO_2 accumulation rate. Using the linear increase in CO_2 concentration, the time of measurement, and environmental variables measured coincidentally enables calculation of a CO_2 efflux (Sihota et al., 2011; LICOR, 2014). Either snapshot readings or longer-term measurements (i.e., repeated measurements at the same location over days to months) can be taken with the devise (LI-COR, 2014). The NSZD rate is calculated by correcting for the naturally occurring CO_2 efflux using either the background CO_2 efflux correction (Sihota et al., 2011) or the radio-isotope of carbon (^{14}C; Sihota and Mayer, 2012).

7.3.3 Carbon Trap Method

The Carbon Trap Method involves the use of a receptacle containing a CO_2 adsorbent. It is placed in near-surface soil and traps CO_2 as it migrates from the NSZD zone to the surface. When returned to the lab, the amount of CO_2 that has entered the trap from the soil is measured to determine a CO_2 flux, which is converted to a NSZD rate.



Carbon traps are typically deployed for a two-week period and capture both naturally occurring CO_2 flux from organics in the soil and CO_2 that was generated by hydrocarbon biodegradation. The naturally occurring, background CO_2 signal can be removed from the trap data by analyzing for the carbon 14 isotope and adjusting the measurement of total CO_2 flux (see Frequently Asked Questions in Section 7.5 below; Eflux, 2014; McCoy et al., 2014).

7.4 Pilot Test Results

The LA LNAPL Workgroup, working with Colorado State University (CSU), deployed carbon traps at both the Shell Carson facility from September 20 to October 4, 2012 (Pilot Test 1) and the Tesoro Hynes facility from March 20 to April 4, 2013 (Pilot Test 2).

NSZD is occurring at both the Shell Carson and Tesoro Hynes facilities at average annualized site-wide rates of 1,700 gal/acre/yr and 1,100 gal/acre/yr respectively. These hydrocarbon biodegradation rates are comparable to those at 6 other field sites measured by CSU (McCoy, 2012), where the average rate was 3,500 gal/acre/yr, and ranged from 400 to 18,000 gal/acre/yr.

Note the LA LNAPL NSZD results are based on single two-week measurements. Actual long-term NSZD rates could be significantly different than the two week snapshots collected as part of this project.

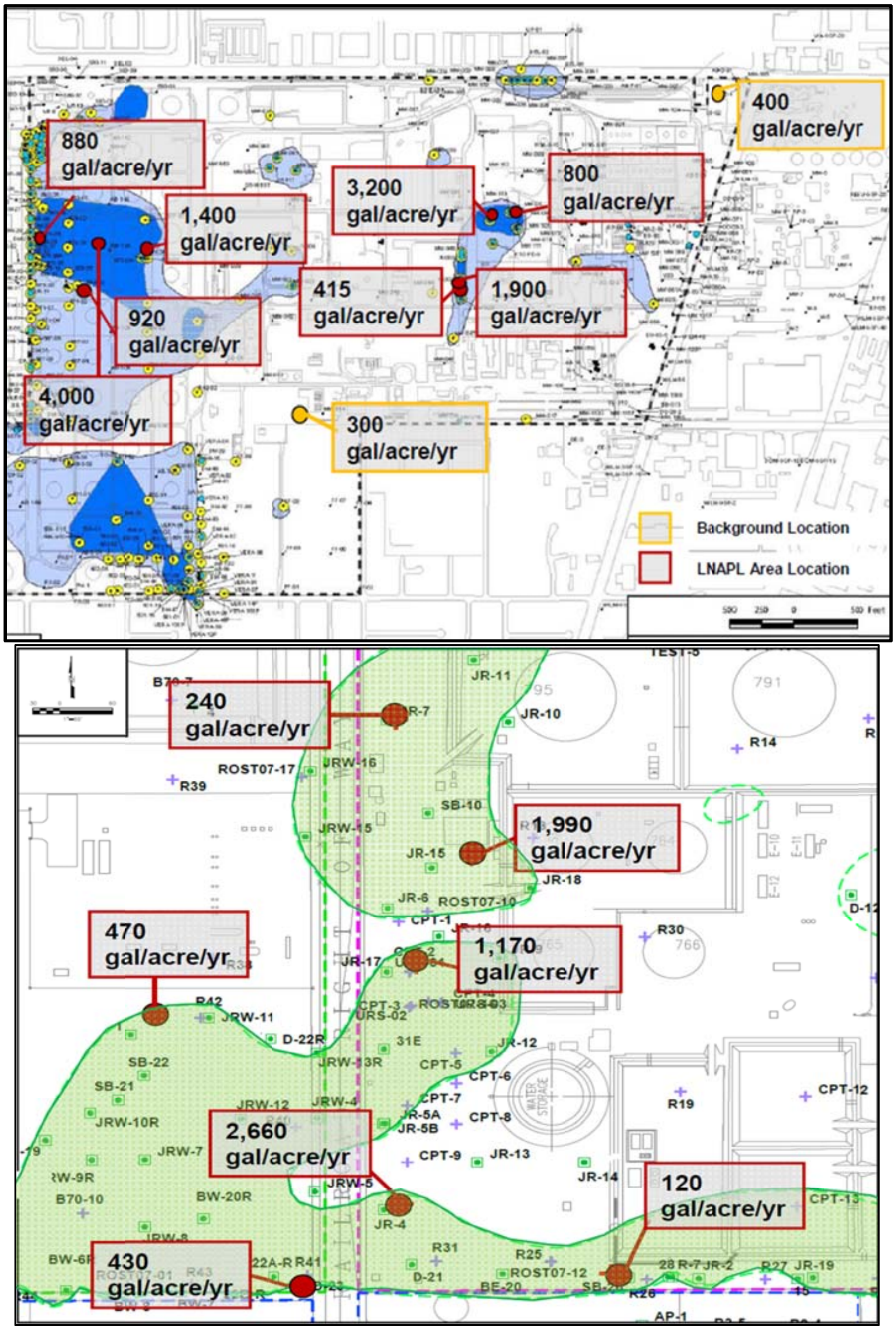


Figure 7.1. *Locations and Hydrocarbon Degradation Rates at Shell Carson Facility (Top Panel) and Tesoro Hynes Facility (Bottom Panel). Values shown represent* ^{14}C *analysis results that automatically correct for background (i.e., soil respiration), and thus show hydrocarbon degradation rates at each location. Hydrocarbon was detected at background locations at the Shell Carson site, likely from migration of* CO_2 *flux from LNAPL zones in other areas due to geologic heterogeneity and other factors. Left Panel: light blue areas indicate inferred extend of residual LNAPL, and dark blue areas indicate measurable LNAPL in wells. Right Panel: light green areas represent LNAPL extent at site.*

7.4.1 Pilot Test 1: Shell Carson Facility

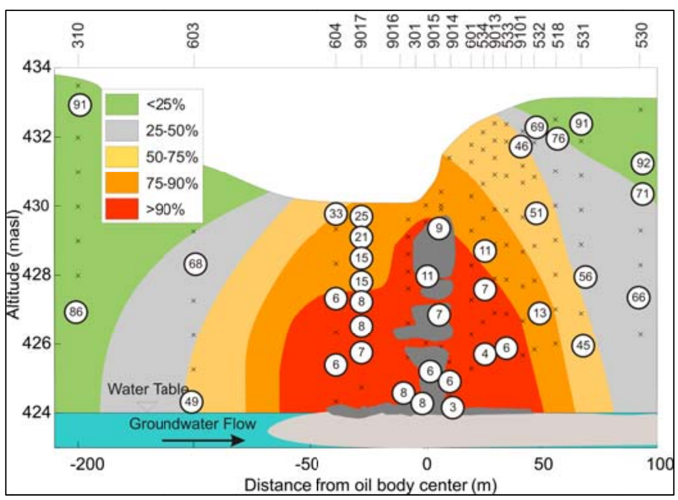
- The hydrocarbon biodegradation rate at the site averages approximately 1,700 gallons/acre/year equivalent. Two separate methods provided this same value: average for affected areas minus background (Method 1), and the average of the ^{14}C-adjusted degradation rates (Method 2).
- Locations with more prevalent and stronger ROST signals generally correlated with higher hydrocarbon biodegradation rates based on a qualitative study.
- Hydrocarbon biodegradation rates were strongly correlated to the total volume of LNAPL at each location as expressed by an LNAPL specific volume estimate derived from ROST data (r^2 of 0.8), but were not correlated to the amount of LNAPL in the vadose and saturated zones.
- No relationship was observed between geology and hydrocarbon degradation rates.

7.4.2 Pilot Test 2: Tesoro Hynes Facility

- The site average hydrocarbon (LNAPL) biodegradation rate is approximately 1,100 gallons/acre/year equivalent.
- Hydrocarbon degradation rates do not seem to correlate with the vertical distribution of hydrocarbons, according to ROST data.
- Compound categories (i.e. LNAPL composition) do not appear to have any correlation with CO_2, probably due to factors such as non-quantitative nature of the data and complicated microbial environment.

7.5 Frequently Asked Questions about NSZD

- ***How do you know the CO_2 is coming from LNAPL, and not from plants?*** A background correction is required to exclude the CO_2 produced from plant respiration: i) one can take the CO_2 flux measurements in a clean area and subtract from LNAPL-impacted area (Sihota et al., 2011) or ii) one can use ^{14}C isotope analysis to determine contribution of CO_2 from hydrocarbons (Sihota and Mayer, 2012). The colors in the figure to the right show the percentage of the CO_2 that was attributed to hydrocarbon degradation using the ^{14}C analysis. In the red zone, which is above and around the dark grey zones that indicate LNAPL, >90% of the CO_2 was generated via LNAPL biodegradation.



Sihota and Mayer (2012). Reprinted by Permission, ASA, CSSA, SSSA

- ***Do the carbon efflux methods measure NSZD in the vadose zone, saturated zone, or both?***
  They represent the contribution from any LNAPL in the vadose and any LNAPL in the saturated zone. In the figure above, the "red dome" represents a zone rich in hydrocarbon CO_2 (>90% hydrocarbon CO_2); it extends *over* LNAPL found at the water table, not just narrow zone containing vadose zone LNAPL, although deeper submerged LNAPL may not produce as clear a CO_2 signal at the surface.

- ***What factors affect the NSZD measurements?***
  Surficial measurements of carbon dioxide flux are affected by temperature, barometric pressure gradients, soil moisture content (i.e., rainfall), and wind. In addition, soil properties that influence gas transport (i.e., porosity) will also affect the ability to measure the CO_2 flux at ground surface. The gradient method is also sensitive to how much water fills the pore space in the vadose zone, which can change over time.

- ***Why can it be difficult to compare the different methods?***
  The different methods measure CO_2 flux over different time periods and some are snapshot measurements (gradient, DCC survey) as compared to an integrated average over an extended time period (DCC long-term, carbon traps). Moreover, small scale subsurface heterogeneities can have significant impacts on gas migration.

- ***Is the type of contaminant likely to affect the calculated NSZD rates?***
  Not significantly. Most of the NSZD research projects to date, and the carbon trap vendor, use octane or decane to represent the LNAPL in NSZD biodegradation calculations. In other words, because the effects are small, they do not use site-specific information about the LNAPL composition or density (e.g., the difference in rates between using octane and fresh gasoline is 1%, and between using octane and weathered gasoline is -12%).

- ***If NSZD is working, why is the LNAPL still there after all these years?***
  The LNAPL is degrading, but relatively slowly. For instance, a site-wide degradation rate of 1,400 gal/acre/yr, is equivalent to lowering LNAPL saturation (the percent of the pore space filled by LNAPL) by about 2% of pore space every 10 years. In some areas, the LNAPL saturation can fill much of the pore space.

- ***Will NSZD stop at some point?***
  NSZD is not likely to stop due to any geochemical limitations, but different compounds may be degraded at different times. At the Bemidji, MN crude oil research spill site, natural degradation was occurring and measured more than 30 years following the release (Sihota et al., 2011), consistent with other indicators of biodegradation (Warren et al., 2014).

8.0 LA LNAPL MANAGEMENT DECISION TREE

One of the work products from this effort is a **LNAPL Management Decision Tree** (see Figure 8.1). The decision tree provides a framework that can be used to identify Remedial Objectives and "**Best Available Treatment Technology**" for LNAPL remediation

Note that the approach described in this document is a generic framework intended to help develop an effective LNAPL management strategy on a site-specific basis. It is not intended to be a rigid plan that will dictate what specific technology will be used at every site. In addition to technical issues, it is important to note that cleanup sites in California are subject to regulatory oversight by the Regional Board under the authority of the Porter-Cologne Water Quality Control Act (Cal. Wat. Code §§ 13000 et seq.) (Water Code) and other statutory or regulatory requirements as described further below. Nothing in this document alters the statutory or regulatory authority of the Regional Board under the Water Code or any other provision of law, nor shall anything in this document limit the Participants' legal authority or responsibilities.

Step 1: Perform Initial Site Assessment (Based on Data in Table 8.1)

Table 8.1 is a summary of data gathering activities for Potential LNAPL Assessment Components. Different sites will likely have a different set of LNAPL assessment components depending on site complexity, potential risk, and other factors. At some sites, the need for one or more of the data types listed in Table 1 may be excluded depending on the site-specific condition and characteristics of the LNAPL.

Table 8.1. *List of Potential LNAPL Assessment Components*

Information Type	List of Potential LNAPL Assessment Components
Basic Field Program	• Maps showing locations of borings and wells, • Boring logs showing total depth drilled, USCS soil classification and OVA readings obtained on head space of soil samples collected during drilling • Identify and log thickness of LNAPL zones in formation while drilling and soil sampling / coring above and below the water table (through field screening by visual observations of soil samples, exposure of soil cores to UV light, shake tests, dye tests, paint filter tests). • Construct well design diagrams. • Contour maps of LNAPL thickness measured in wells.
Groundwater elevation and hydraulic information	• Groundwater elevation contour maps adjusted for LNAPL apparent thickness/density showing flow directions, horizontal and (if relevant/available) vertical hydraulic gradients. • Hydraulic conductivity and groundwater transmissivity distribution maps (for sites with just a few data points just show well locations with posted data; if enough data, draw iso-contours); • LNAPL apparent thickness distribution maps based on well measurements
Soil, soil vapor, and groundwater samples collected	• Groundwater dissolved-phase plume maps, tables showing analytical results for significant site-specific contaminants (e.g. TPH, BTEX, Oxygenate). • Iso-concentration map for each significant vadose zone contaminant in soil and soil gas (show concentrations at several depths if vadose zone is deep) • Site-wide cross-section(s) should show lateral and vertical extent of various soil types (including underlying aquifers and aquitards and grain size data) and LNAPL intervals both in the vadose and saturated zone, soil concentrations at sample depths, fluctuations in water table.
Vertical LNAPL Distribution	• Use CPT/LIF and/or high frequency TPH analysis to identify LNAPL zones, Soil core photography under UV and visible light, soil core fluid saturations (Dean-Stark), before installing recovery wells. • Figure of LNAPL and groundwater elevations vs. time at a well (equilibrium concentrations); • Cross-sections with well screens, LNAPL apparent thickness representing equilibrium conditions, groundwater elevation and vertical profiling data for LNAPL impacts. These are useful for illustrating that detailed concepts at one location based on scatter plots and hydrographs occur on a much larger scale at the site. • Scatter plots of LNAPL apparent thickness vs. groundwater elevation • Soil core photography under UV and visible light • Soil core fluid (water and LNAPL) saturations (Dean-Stark or TPH over range of LNAPL).

Aerial LNAPL Distribution	• Maps showing distribution of apparent LNAPL thickness (measured from recovery/monitoring wells) and LNAPL zone thickness in the formation observed in soil cores from the formation adjacent to a recovery well and all other LNAPL observations (visual, dye formation adjacent to a recovery well and all other LNAPL observations (visual, dye test, LIF, etc.). • Specific volume of LNAPL from models such as LDRM[1].
Define LNAPL Scenario (also called LNAPL Type-Area)	LNAPL Scenario as defined using these types of terms: • confined or unconfined • associated with a perched groundwater layer • dune sand versus in an interbedded formation with significant silts and clays • smeared around the water table or historical water tables • submerged below the current water table (define the vertical interval containing LNAPL)
LNAPL Character-ization Physical Fluid Properties	• Site maps that delineate LNAPL type (e.g. diesel, gasoline, weathered diesel, etc.) and/or the concentrations of specific constituents within LNAPL (e.g., BTEX, oxygenates). LNAPL type data plotted aerially and vertically help distinguish between separate plumes, identify sources, and set up modeling boundaries. • LNAPL physical laboratory analysis (density, viscosity, air/water interfacial tension, air/LNAPL interfacial tension), • LIF fluorescence spectrum analysis (shorter or longer wavelength response), GC (gas chromatogram) FID, GC mass spectrometry, Lead speciation, PIANO[2] Analysis
Quantification of LNAPL Mobility and Recoverability via Conventional Technologies	• For existing conventional recovery system: LNAPL Recovery Rate, volume over time charts as well as decline curve analyses (Recovery rate versus cumulative recovered volume). These can be used in conjunction with water-table elevation, applied vacuum and/or water recovery rate to evaluate optimum water extraction rates, applied vacuum and estimate LNAPL transmissivity over time. Can also incorporate routine LNAPL removal events (i.e., passive opportunistic recovery) • Maps or figures of LNAPL footprint vs. time • For evaluation of mobility at edge of LNAPL body: Pore entry pressure analysis • For evaluation of new or expanded conventional recovery system: tables or site maps that are contoured to show LNAPL "mobility term"; and/or LNAPL seepage velocity; and/or LNAPL transmissivity. ASTM 2856-13 Standard Guide for Estimation of LNAPL Transmissivity describes methods, interpretation, and applicability of various test methods. Note that oil and water saturations determined by analyses of the soil cores collected from the LNAPL intervals in a boring located adjacent to a new or historical recovery well can serve as a cross-check to confirm the accuracy of the LNAPL transmissivity calculated from a baildown test conducted at the well location. • Upgrade existing system to evaluate each well's individual performance and monitor operational parameters (i.e. better data collection and

	management) • LNAPL Tracer tests. • Pilot testing different technologies (e.g. skimming, dual phase, vacuum enhanced, etc.) • Other Mobility analysis techniques.
LNAPL Mass	• Maps or tables of LNAPL specific volume, total recoverable LNAPL, and a total mass estimate using LNAPL models such as LDRM including submerged LNAPL. The uncertainty in any mass estimate should be shown; at some sites this could be several orders of magnitude range or more.

1. LDRM: the API LNAPL Distribution and Recovery Model
2. PIANO: the amount of paraffin, isoparaffins, aromatics, naphthalene and olefins

Key Point: This list represents a broad range of LNAPL characterization data types. Larger, more complex sites will likely require more data types while smaller, simpler sites may only require a few data types. It is imperative in decision making that collected LNAPL assessment components should give comprehensive information for an adequate LNAPL conceptual site model development. The regulatory agency may require specific data types related to the assessment components.

Step 2: Develop LNAPL Conceptual Site Model

An **LNAPL Conceptual Site Model (LSCM)** describes LNAPL delineation in the subsurface, physical properties, chemical composition and the hydrogeologic setting of the site in order to assess flux, risk, and potential remedial action (see ASTM E 2531-06, *Standard Guide for Development of Conceptual Site Models and Remediation Strategies for LNAPL Released to the Subsurface*).

The following information (at a minimum) should be documented in the LCSM:

- LNAPL release location and timing, if known.
- LNAPL type.
- Horizontal and vertical extent of each LNAPL body.
- Product thickness measurements in monitoring/recovery wells.
- LNAPL physical and chemical characteristics.
- Geologic setting and hydrogeologic conditions.
- Groundwater quality.
- Groundwater beneficial uses, both existing and potential and distance to wells.
- Potential human exposure pathways (soil, vapor and water) and relevant ecological receptors and habitats under current and future use scenarios.
- Results of Interim actions (if conducted).

An LSCM is developed using a dynamic process where the LSCM is updated/modified as additional data are collected. The LSCM should identify any data gaps and evaluate what potential effects these data gaps have on selecting LNAPL remedies.

Step 3: Establish LNAPL Remedial Objectives

LNAPL remedial objectives are the LNAPL condition to be achieved by the remedial strategy or action that constitutes the end of LNAPL management for a specific LNAPL concern. While establishing LNAPL remedial objectives factors that need to be taken into account include: 1) the need for urgency to address a potential threat to human health and the environment, 2) any ongoing migration of mobile LNAPL/free product and waste constituents in the dissolved phase in and away from source areas, 3) technology applicability and regulatory acceptance, and 4) economic feasibility. Interim actions such as conventional recovery technologies must be considered for immediate threats to human health and the environment. If needed, post-conventional recovery technologies approved by the regulatory agency must be implemented to achieve reduction to regulatory levels. Because more than one LNAPL concern may need to be addressed to render the site protective, multiple objectives may be established so that the different LNAPL concerns are abated.

Remedial Objectives must be considered for both current and future land uses with respect to unacceptable risk associated with human health and the environment including any impairment of existing and reasonably anticipated beneficial uses of groundwater; key issues are presented in question form below:

1. Does LNAPL pose an unacceptable imminent onsite/offsite human health risk?
2. Is LNAPL footprint expanding? Does LNAPL expansion pose an unacceptable risk, e.g., potential off property impact?
3. Is there an unacceptable risk of surface water discharge?
4. Is there unacceptable risk to groundwater associated with the migration of LNAPL-related dissolved plumes?
5. Do onsite/offsite soil-gas impacts pose an unacceptable human health risk?

Through a remedial objective evaluation described above, it could be determined that the presence of LNAPL at the site does not pose a risks based on these scenarios. However, interim hydraulic recovery must be conducted if LNAPL is mobile and recoverable.

Requirement for Recovery of Mobile/Recoverable LNAPL. If no LNAPL Remedial Objectives need to be addressed (the five questions under Step 3 are answered as "NO"), you still must determine if LNAPL must be controlled or hydraulically recovered by evaluating LNAPL mobility and recoverability by answering two key questions typically asked at an LNAPL site (Figure 8.1):

Question 1: Can the LNAPL move under the influence of an existing or likely hydraulic gradient; i.e., is the LNAPL "mobile?"

Question 2: Can LNAPL can be recovered using conventional pumping technologies; i.e., is the LNAPL "recoverable?

To answer these two questions, the assessment of LNAPL mobility can be either empirical, based on observations of LNAPL in the field, or quantitative, based on calculations of LNAPL rates of movement or potential movement. Six different methods have been used or proposed by different groups to answer Questions 1 and 2 posed above. These methods are summarized in the LA LNAPL Literature Review. At small, simple sites, a single method may provide sufficient information for moving forward, while at other larger, more complex sites more than one methodology described in Table 8.2 should be considered.

Methods that have been used to evaluate LNAPL mobility and/ or recoverability are shown in Table 8.2.

If a Conventional (Hydraulic) Recovery technology is indicated ("Yes" answers to both questions 1 and 2 above), hydraulic recovery must be implemented and operated until the hydraulic recovery end point acceptable to the regulatory agency has been reached and all measures to reduce unacceptable risks were demonstrated to the regulatory agency's satisfaction**.** The hydraulic recovery technology selected must be optimized before considering hydraulic recovery complete. If the hydraulic recovery reaches its technical limit, the treatment zone should be evaluated to determine whether the treatment zone can go to Step 5 (Establish LNAPL Residual Management Zone – "RMZ") or if some form of Post-Conventional Recovery must be conducted. This decision should take into account the following factors: the risk posed by the residual LNAPL, changes of LNAPL characteristics and specific site conditions, current and future land use, and other factors including the regulatory guidance/enforcement orders/community concerns. In addition, environmental factors (i.e., potential seasonal changes/water table fluctuations) should be considered during the implementation of hydraulic recovery technologies. It must be noted that any changes to LNAPL recovery system(s) may be subject to the regulatory agency's review and approval. After interim recovery actions where LNAPL is no longer mobile or recoverable, the regulatory agency will require an LNAPL recovery system shutdown analysis and evaluation as to whether residual LNAPL poses foreseeable impacts to human health, the environment or future land/beneficial groundwater use. Regulatory decisions will consider any issues received from the public, stakeholders and the community.

Remediation Timeframe*.* Cleanup has to be completed in "a reasonable timeframe", which the Regional Board working with site stakeholders will determine on a site-specific basis. A regulatory agency considers a number of factors when addressing the reasonable timeframe for remediation. The factors include the anticipated effectiveness and sustainability of the selected remedial technology for the contaminated media (soil gas, soil, groundwater) and current and future demand on the impacted aquifer/land use. It is anticipated that short remediation time frames (e.g., a few years) may be driven by human health threat, aquifer uses, and social/land use concerns such as land development scenarios. Longer timeframes will likely be more appropriate for no-risk, stable plumes, and sites with demonstrated natural degradation with multiple lines of evidence.

***Table 8.2.** Methods that Have Been Used to Evaluate LNAPL Mobility (Slightly Modified from LA LNAPL Lit. Review Section 4.0)*

Method	Metric	Which Question?	Where Usually Applied?	How These Methods Are Applied (or Proposed to be Applied)
Evaluate site temporal data	Change in LNAPL footprint over time; consistent, large-scale changes in apparent thickness in LNAPL; and changes in the dissolved plume footprint.	1	Edge of LNAPL Zone	If the data show an expanding LNAPL footprint then LNAPL is considered to be mobile.
Dye Tracer Test	A fluorescent dye is injected into a well containing LNAPL. The rate of disappearance of the dye is then used to estimate the LNAPL migration rate (LNAPL Darcy velocity). To convert these LNAPL Darcy velocity to LNAPL seepage velocity one divides by the LNAPL content (mobile LNAPL saturation times porosity).	1	Core and edge of LNAPL zone covering range of LNAPL types and transmissivity conditions anticipated at the site	Low LNAPL flux measurements demonstrate limited LNAPL mobility and recoverability.
Apply Darcy's Law and Related Methods	LNAPL Mobility Term (from calculations of LNAPL properties and soil characteristics)	1 or 2	Either core or edge of LNAPL Zone	If LNAPL Mobility > 10^{-7} cm^3sec/g then LNAPL "can be presumed to be effectively immobile" (Massachusetts LSPA, 2008).
	LNAPL Seepage Velocity (from calculations of LNAPL properties and soil characteristics or from LNAPL tracer tests)	1 or 2	Either core or edge of LNAPL Zone	ASTM (2007) provides example where LNAPL Seepage Velocity > 0.3 meters per year (1 foot per year) means recovery by hydraulic skimming may be feasible.
	LNAPL Transmissivity (from calculations of LNAPL properties and soil characteristics; recovery data; or from LNAPL baildown test)	1 or 2	Either core or edge of LNAPL Zone	Practical limit of hydraulic and pneumatic recovery systems is LNAPL Transmissivity > 1.1 to 8.6 x 10^{-7} m^2/s (0.1 to 0.8 ft^2/day) (ITRC, 2009).

Evaluate Pore Entry Pressure	Apparent LNAPL thickness	1	Edge of LNAPL Zone	If apparent LNAPL thickness in well > than pore entry head, then LNAPL has potential to move (and be removed by pumping).
Compare Measured LNAPL Saturation to Residual Saturation	LNAPL Saturation	1 or 2	Edge and Core of LNAPL Zone	If saturation > residual saturation (determined by one of several methods) then LNAPL has potential to move (and be removed by pumping).
Apply LNAPL Computer Models	Computed rate of LNAPL movement or rate/volume of recovery	1 or 2	Edge and Core of LNAPL Zone	Assess significance of LNAPL movement or recovery relative to site remedial objectives.

Note to Table 8.2: This Study is not advocating using any of the metrics above as strict numerical standards to be applied to a specific site. Site-specific issues such as risk, site conditions and status, regulatory agency's acceptance, and other factors need to be considered in addition to these general guidelines to determine LNAPL mobility issues. This table is an attempt to summarize the key methods used to define LNAPL mobility in the technical literature. There are differing opinions about the applicability and accuracy of different methods, particularly for the need for LNAPL saturation verification samples to confirm that LNAPL recovery efforts via conventional extraction technologies can be terminated. As described above, the definition of LNAPL mobility and recoverability will likely be defined on a site-specific basis.

Step 4: Select and Implement Remedial Technology (ies)

LNAPL remedial approaches fall under four categories: LNAPL Mass Control (LMC), LNAPL Mass Recovery (LMR), LNAPL Phase Change (LPC), and Pathway Control (PC) technologies (see ITRC's *Evaluating LNAPL Remedial Technologies for Achieving Project Goals Technical/Regulatory Guidance, 2009 LA LNAPL Literature Review, 2011).* LNAPL Mass Control technologies block or inhibit further LNAPL migration. LNAPL Mass Recovery technologies remove LNAPL via hydraulic recovery, physical removal, or in-situ destruction. LNAPL Phase Change technologies may increase the rate of volatilization or dissolution of LNAPL constituents. Pathway Control technologies interrupt or abate constituents of concern from downgradient risk receptors. The factors that should be considered to screen and select Remedial Technology(ies) and evaluate the necessity for more aggressive secondary or tertiary (intensive non-hydraulic remedies) remedial technologies include:

- Remedial Time Frame
- Safety
- Waste Stream Generation and Management
- Community Concerns
- Carbon Footprint/Energy Requirements
- Site Restrictions
- Natural Source Zone Depletion (NSZD)
- LNAPL Body Size
- Regulations Affecting Implementation

- Economic feasibility
- Other Site-Specific Considerations

For those LNAPL Remedial Objectives questions that are answered as "YES" at your site, a Remedial Technology may need to be selected and implemented. LNAPL mass control, mass recovery and/or phase change technologies must be evaluated and the best available technology selected if remediation is technically practicable. The best available remedial technology should be selected and implemented. Pilot testing might be necessary to help determine if implementation of the technology is technically practicable.

To help site stakeholders select technologies, Best Available Technology (BAT) tables for the LA Basin are provided in Table 8.3, in the following categories:

- *Large vs. small treatment zones (greater or smaller than 23,000 cubic yards).* The intention is to provide guidance on technologies that are likely suitable (and by omission, likely unsuitable) for large, multi-acre treatment zones containing LNAPL and smaller "hot spots" with higher LNAPL saturation or higher risk concerns. The 23,000 cubic yard number represents the upper 75th percentile of treatment zones from a study of 80 full-scale in-situ treatment systems.
- *Operating vs. non-operating facilities.* The intention is to differentiate the remediation systems in active operating refineries vs. non-operating areas. For example, technologies that potentially pose a safety risk, such as sites where breakthrough of oxygen biosparging to the ground surface, could be excluded from operating areas.
- *Conventional vs. post-conventional LNAPL recovery.* The intention is to guide the site stakeholders to technologies that are designed to remove mobile and recoverable LNAPL using pumping technologies (conventional) versus technologies that address non-mobile residual LNAPL (post-conventional). For example, skimming is a conventional BAT, and pulsed oxygen biosparging is a post-conventional BAT.
- *High, moderate, low intensity technologies.* The intention is to distinguish between high-cost, capital and O&M intensive technologies versus more passive, less costly technologies.

Note the BAT Table (Table 8.3) is intended to provide general suggestions for technology selection based on the research and experiences from pilot testing performed by the LA NAPL Workgroup. It is not intended to be a rigid system for permitting allowable LNAPL remediation technologies in the LA Basin.

After a technology(ies) has been selected, it is pilot tested (if needed), designed/implemented, and operated. The performance data from the remediation project will be evaluated and the remediation system optimized as needed.

When the LNAPL remediation objectives are met and any remaining regulatory concerns are addressed, the regulatory agency may determine that the site is eligible to be managed as an "LNAPL RMZ." If sequential LNAPL remediation technologies are applied, for example, intensive LNAPL pumping technologies then followed by skimming, or where conventional recovery is followed by post-conventional remediation technology, the site could be considered for the LNAPL RMZ.

***Table 8.3.** Potential Technologies For Managing On-Site LNAPL In the LA Basin*

For Treatment Zones in OPERATING AREAS				Special Conditions	
TECHNOLOGY TYPE	USED FOR LNAPL…	INTENSITY	Generally Applicable Any Conditions	Limited to Type I Hydrogeology (sand, little heterogeneity)	Limited to Small Treatment Sizes Due to Cost, Implementability (< 23,000 yd^3)
Conventional *(Removal of Free LNAPL)*	LMR LNAPL Mass Recovery	High	*Multi-phase extract. (e.g., water/LNAPL)*		
		Moderate	*Skimming*		
		Low	*Ads. Socks, Vac Truck, Natural Degrad.*		
	LMC LNAPL Mass Control	High	*Hydraulic Control*		
		Moderate	*Physical Barrier*		
Post-Conventional *(Removal of Residual LNAPL)*	LMR LNAPL Mass Recovery	Moderate			*STELA**
		Low	*Natural Degradation*		
	LMC LNAPL Mass Control	High	*Hydraulic Control*		
		Moderate	*Physical Barrier*		
	LPC LNAPL Phase Change	High		*Oxygen Biosparge*	
		Low	*Natural Degradation*		
	PC Pathway Control	High	*Hydraulic Control*		
		Moderate	*Permeable Barriers*		
		Low	*MNA, Engineering / Institutional Controls, Vapor Barriers, Sub-Slab Venting*		

For Treatment Zones in NON-OPERATING AREAS				Likely Limited to These Conditions:	
TECHNOLOGY TYPE	USED FOR LNAPL…	INTENSITY	Generally Applicable Any Conditions	Limited to Type I Hydrogeology (sand, little heterogeneity)	Limited to Small Treatment Sizes Due to Cost, Implementability (< 23,000 yd^3)
Conventional *(Removal of Free LNAPL)*	LMR LNAPL Mass Recovery	High	*Multi-phase extract. (e.g., water/LNAPL)*		
		Moderate	*Skimming*		
		Low	*Ads. Socks, Vac Truck, Natural Degrad.*		
	LMC LNAPL Mass Control	High	*Hydraulic Control*		
		Moderate	*Physical Barrier*		
Post-Conventional *(Removal of Residual LNAPL)*	LMR LNAPL Mass Recovery	Moderate	*STELA**		
		Low	*Natural Degradation*		
	LMC LNAPL Mass Control	High	*Hydraulic Control*		
		Moderate	*Physical Barrier*		
	LPC LNAPL Phase Change	High	*Oxygen Biosparge, Air Sparge + SVE*		*Thermal*
		Low	*Natural Degradation*		
	PC Pathway Control	High	*Hydraulic Control*		
		Moderate	*Permeable Barriers*		
		Low	*MNA, Engineering / Institutional Controls, Vapor Barriers, Sub-Slab Venting*		

(*) STELA: Sustainable Thermally Enhanced LNAPL Attenuation. *Disclosure: This technology was originally applied at a Chevron research site where the term STELA was developed. The technology is currently being further developed by Tom Sale (CSU) and Charles Newell at GSI Environmental (Newell serves as the LA LNAPL Project Coordinator).*

1. LMR: LNAPL Mass Recovery. LMC: LNAPL Mass Control. LPC: LNAPL Phase Change. PC: Pathway Control.

Note: Table 8.3 is a non-exclusive list of LNAPL remediation technologies that the LA LNAPL Workgroup felt are typically useful to consider for different types of applications in the LA Basin. It is **not intended to exclude** other technologies or to be the “last word” in the technology selection process. It is primarily designed for on-site applications with no unacceptable risk from the top five diamonds in Step 3 of the Decision Tree.

Table 8.4. Potential Expectations For In-Situ LNAPL Remediation Projects

TECHNOLOGY	TYPE I – GRANULAR MEDIA WITH MILD HETEROGENEITY & MODERATE TO HIGH PERMEABILITY (e.g. Dune Sand)	TYPE III – GRANULAR MEDIA WITH MODERATE TO HIGH HETEROGENEITY (e.g., interlayered sands, silts, clays)
Thermal Remediation (Electrical resistive heating (ERH), thermal conductive heating (TCH), steam injection	Steam Pilot Test, California: Removed 50-85% of submerged LNAPL (see Section 4.6)	Pemaco Chlorinated Solvent Site, Los Angeles: Average groundwater concentrations were reduced by >90%. In general, significant permitting, safety, and sustainability issues are likely, and intensive infrastructure will be required (close spacing, SVE system, etc.). More challenging at sites with submerged LNAPL.
Chemical Oxidation (multiple types of oxidants)	*Due to more favorable hydrogeology, potentially better than Type III sites described immediately to right*	39 Hydrocarbon Sites: 33% of sites achieved better than 90% reduction in groundwater concentrations, 67% of sites exhibited reduced groundwater concentrations between 0% and 90% (PERF, 2013)
Low Pore Volume Surfactant (anionic surfactant)	Several non-submerged LNAPL sites (LNAPL limited to near water table): >95% removal was attainable (Surbec). Average removal: ~7000 gallons per acre.	LA LNAPL Pilot Test: Effectively no removal of free-phase LNAPL due to low permeability, other factors. May be effective in thick (10 foot) LNAPL zones with minimum hydraulic conductivity of 10^{-3} cm/sec or better.
Surfactant Solubilization (nonionic surfactant)	Vendor information: Increases conventional pump-and-treat or multi-phase extraction by a factor of 4 to 8 times (Ivy). One solubilization Pilot Study increased dissolved phase removal via pumping by factor of 6.8; during the five day pilot test one pound of dissolved mass was removed (RMT, 2010) equivalent to <200 gallons LNAPL per acre per year over the treatment zone. Cosolvent flush expected to have similar performance.	
Pulsed Oxygen Biosparging	*Due to more favorable hydrogeology, potentially better than Type III sites described immediately to right, but with much reduced chance of occasional breakthrough to surface.*	LA LNAPL Pilot Test: BTEX concentrations in groundwater and soil were reduced by ~45% over one year. Considerable operational problems are likely, such as occasional breakthrough of intermittent oxygen pulse to surface at Type III sites, likely not be appropriate for operational areas.
Natural Source Zone Depletion (based on carbon traps).	Crude oil research site in Minnesota: 500 to 1700 gallons per acre per year (Sihota et al, 2011, 2013). Oil field site in California: 150 to 1500 gallons per acre per year (Lundedgard and Johnson, 2006). Six refinery sites around country: average 3500 gallons per acre per year (McCoy, 2012).	LA LNAPL Pilot Test: biodegradation of 1000 to 1700 gallons of LNAPL per acre per year from both vadose zone and saturated zone. Some high degradation zones may have up to 4000 gallons per acre per year.
Pneumatic and/or hydraulic fracturing	Not applicable	Both hydraulic and pneumatic fracturing can increase the recovery of pump & treat systems and SVE; described as "moderately good" technology for LNAPL recovery by USEPA (1994). Relatively few applications at LNAPL sites. Not mentioned in ITRC 2009 LNAPL Remedial Technologies guide. At Denmark clay till site pneumatic fracturing had distribution radius < 2 meters; hydraulic fracturing produced bowl-shaped fracture with approximately 3.5 meter radius (Christiansen et al, 2010).

Pilot Test Performed by LA LNAPL Workgroup.

Note: Table 8.4 is based on the experience and work performed by the LA LNAPL Workgroup. It is **not intended to exclude** other technologies or to be the "last word" in the technology selection process.

Step 5: Establish LNAPL Residual Management Zone Once LNAPL Remedial Objectives Are Met and/or Other Action

Despite implementing LNAPL remedial actions, there may remain an area where a significant mass of residual LNAPL in the subsurface cannot be removed or is technically impracticable to remove. Such an area is assumed to be a “Residual Management Zone (RMZ).” The RMZ is the area where non-recoverable LNAPL exists; the RMZ needs to be monitored and controlled for as long as required by the regulatory agency.

Before designating an LNAPL RMZ, it must be demonstrated that all risks have been appropriately mitigated and the designation is acceptable to the regulatory agency, supported by updated scientific data, and site-specific conditions including protection of receptors, groundwater, and current and future land uses.

The demonstration could include:

1. analysis for non-mobile, non-recoverable status and residual LNAPL levels, with soil gas and dissolved phase data; any change in the LNAPL zone;
2. engineering controls;
3. hydraulic containment or other mass flux control measures;
4. contingency plan if site conditions are changed and certain criteria (i.e., human health risk) are exceeded;
5. natural depletion/degradation of LNAPL including Natural Source Zone Depletion must be evaluated to demonstrate loss of LNAPL mass in the subsurface.

It must be noted that, despite establishment of the RMZ, the petroleum contaminated sites may be required to continue or update their on-going dissolved phase groundwater treatment and/or other treatment required by the regulatory agency.

Legal and Regulatory Requirements

Pursuant to the Water Code, the Regional Board is the principal state agency within the Los Angeles Region with primary responsibility for the coordination and control of water quality. The Regional Board implements the Water Code and applicable regulations and policies to protect the ground and surface waters of the state within the Los Angeles Region for their present and future beneficial uses and to protect human health that may be at risk due to the discharges of waste. The Regional Board adopted the Water Quality Control Plan for the Los Angeles Region (“Basin Plan”), which identifies beneficial uses, establishes water quality objectives to protect those uses, and identifies implementation programs to attain the water quality objectives. The Regional Board’s authority is provided, in part, by the following statutes and regulations:

a. Water Code section 13267 authorizes the Regional Board to require anyone who has discharged or is discharging waste or is suspected of discharging or having discharged waste that could affect the quality of the waters of the state, including surface and groundwater, to submit technical and monitoring reports.

b. Water Code section 13304 authorizes the Regional Board to require any person to clean up or abate the effects of discharges that could affect the quality of the waters of the state, including surface or groundwater, and to address nuisance conditions. Section 13304 orders are issued where the discharge has caused pollution or nuisance or threatens to cause pollution or nuisance. Abatement refers to actions such as providing alternative water or limiting exposure to the waste through land use restrictions.

c. State Water Resources Control Board Resolution No. 92-49 (Policies and Procedures for Investigation and Cleanup and Abatement of Discharges Under Water Code Section 13304) (Resolution 92-49) sets forth policies and procedures that apply to the investigation and cleanup and abatement activities conducted under the oversight of the Regional Board. Resolution 92-49 sets forth a progressive process of investigation, assessment, and cleanup and the requirements for determining cleanup levels in soil and water to protect the beneficial uses of surface water and groundwater affected by discharges into soil, groundwater, or surface water.

d. Water Code sections 13307.1, 13307.5 and 13307.6 establish required and optional public participation requirements that apply to investigation and cleanup actions.

As appropriate, the Regional Board will use its authority to require investigation and cleanup actions and the implementation of public participation requirements for each site. It will take into consideration the information developed through the use of this Decision Tree when reviewing and approving investigation and cleanup plans.

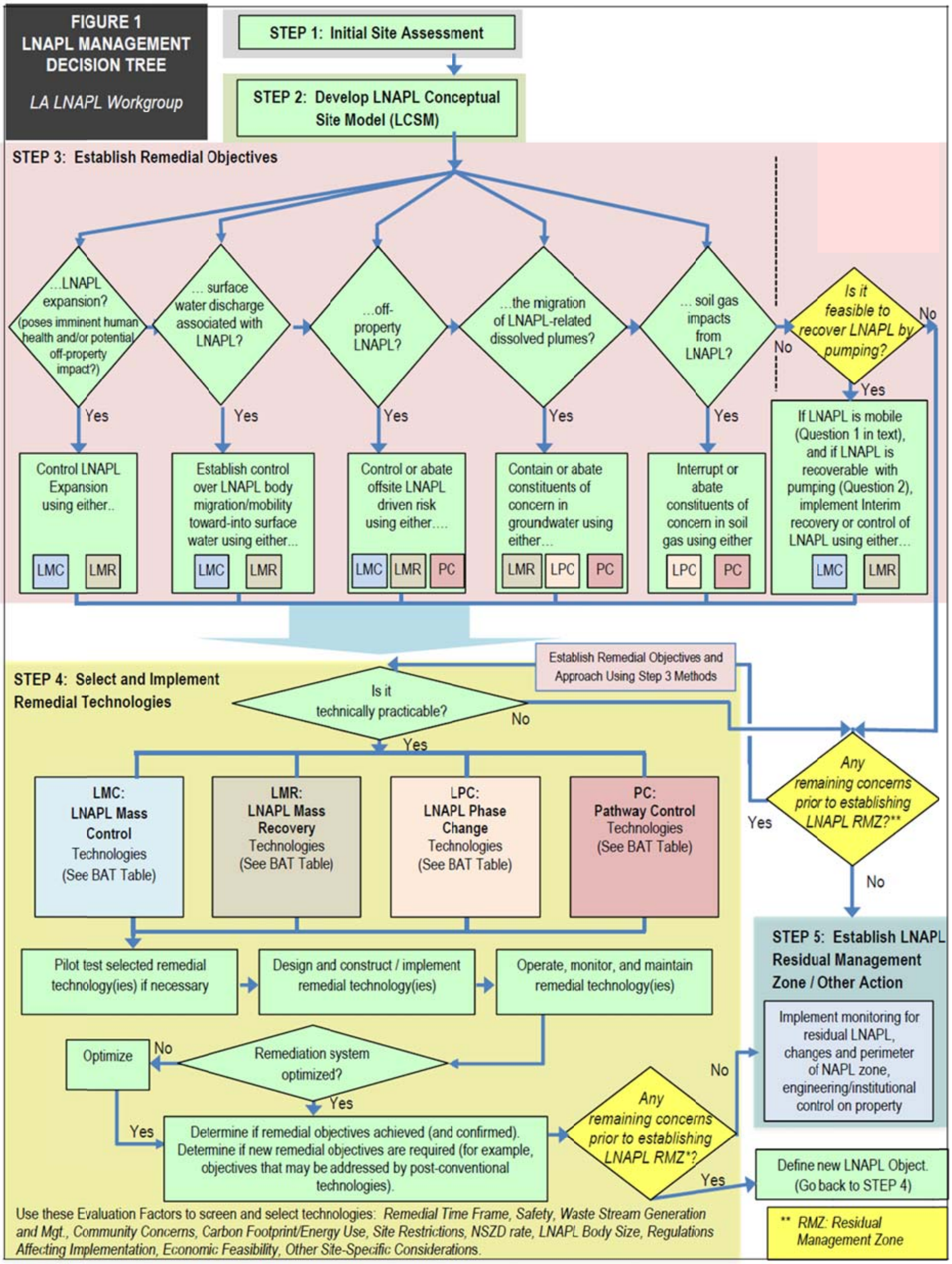


Figure 8.1. LNAPL Management Decision Tree Flow Chart

9.0 REFERENCES

ASTM, 2007. Standard Guide for Development of Conceptual Site Models and Remediation Strategies for Light Nonaqueous-Phase Liquids Released to the Subsurface. ASTM E2531-06.

API, 2004. "API Interactive LNAPL Guide, Version 2.0.4", prepared by Environmental Systems and Technologies and Aqua-Ver, Inc., July 2004.

American Society for Testing and Materials (ASTM), 2007. Standard Guide for Development of Conceptual Site Models and Remediation Strategies for Light Nonaqueous-Phase Liquids Released to the Subsurface guide (ASTM E 2531-06, 2007).

Arcadis, 2014. Natural Source Zone Depletion Assessment Report, Former Mobil Natural Gas Inc., La Gloria Gas Plant. Arcadis, Braintree Ma, Nov. 2014

Charbeneau, 2007. LNAPL Distribution and Recovery Model (LDRM), Randall J. Charbeneau, API Publication 4760, American Petroleum Institute, Washington, D.C., January 2007.

Christiansen, C. M., Damgaard, I., Broholm, M., Kessler, T., Klint, K. E., Nilsson, B., and Bjerg, P. L., 2010. Comparison of Delivery Methods for Enhanced In Situ Remediation in Clay Till. Ground Water Monitoring and Remediation. 30 (4), 107-122.

Farhat, S. K., C. J. Newell, and E. Nichols, 2006. "Mass Flux Toolkit, To Evaluate Groundwater Impacts, Attenuation, and Remediation Alternatives", developed for the Environmental Security Technology Certification Program (ESTCP) by Groundwater Services, Inc., Houston, Texas, March 2006. www.gsi-net.com

Farhat, S.K., P.C. de Blanc, C.J. Newell, J.R. Gonzales, and J. Perez, 2004. SourceDK Remediation Timeframe Decision Support System, User's Manual, April 2004. www.gsi-net.com

ITRC, 2009a. Technology Overview: Evaluating Natural Source Zone Depletion at Sites with LNAPL. April 2009. The Interstate Technology and Regulatory Council LNAPLs Team.

ITRC, 2009b. Technical/Regulatory Guidance: Evaluating LNAPL Remedial Technologies for Achieving Project Goals. December 2009. The Interstate Technology and Regulatory Council LNAPLs Team.

Lundegard, P.D., 2008. "Steam Pilot Test, Guadalupe Restoration Project", presentation to LA LNAPL Workgroup.

Lundegard, P. D. and Johnson, P. C. (2006), Source Zone Natural Attenuation at Petroleum Hydrocarbon Spill Sites—II: Application to a Former Oil Field. Ground Water Monitoring & Remediation, 26: 93–106. doi: 10.1111/j.1745-6592.2006.00115.x

Johnson, P.C.,M.W. Kemblowski, and J.D.Colthart. 1990. Quantitative Analysis of Cleanup of Hydrocarbon-Contaminated Soils by In-Situ Soil Venting. Ground Water, Vol. 28, No. 3. May - June, 1990, pp 413-429. LSPA, 2008. LNAPL and the Massachusetts Contingency Plan Part II, prepared by the Licensed Site Professional Association Technical Practices Committee, July, 2008.

McGuire, T. 2014. ESTCP Project ER-201120 Preliminary Results.

National Research Council (NRC), 2005. Contaminants in the Subsurface, The National Academies Press, Washington, D.C., USA

Newell, Charles J., Farhat, Shala K., Adamson, David T., and Looney, Brian B., 2011. "Contaminant Plume Classification System Based on Mass Discharge", Accepted for publication in *Ground Water*, (2011).

Newell, C.J., J. Gonzales, and R. McLeod, 1996. BIOSCREEN Natural Attenuation Decision Support System, U.S. Environmental Protection Agency. EPA/600/R-96/087, August 1996.

Newell, C.J., S.D. Acree, R.R. Ross, and S.G. Huling, 1995. *Light Nonaqueous Phase Liquids*, U.S. Environmental Protection Agency Ground Water Issue Paper, R.S. Kerr Environmental Research Laboratory, Ada OK. EPA/540/S-95/500, July 1995.

Sale, T., 2001. Methods for Determining Inputs to Environmental Petroleum Hydrocarbon Mobility and Recovery Models, API Publication number 4711, American Petroleum Institute, Washington, D.C.

Sihota, N.J., Mayer, K.U., 2012. Characterizing vadose zone hydrocarbon biodegradation using carbon dioxide effluxes, isotopes, and reactive transport modeling. Vadose Zone J. 11.

Sihota, N.J., Singurindy, O., Mayer, K.U., 2011. CO2-efflux measurements for evaluating source zone natural attenuation rates in a petroleum hydrocarbon contaminated aquifer. Environ. Sci. Technol. 45, 482–488.

Sihota, N. J., K. U. Mayer, M. A.Toso[b], J. F. Atwater, 2013. Methane emissions and contaminant degradation rates at sites affected by accidental releases of denatured fuel-grade ethanol, Journal of Contaminant Hydrology, Volume 151, August 2013, Pages 1–15

USEPA, 1994. Manual: Alternative Methods for Fluid Delivery and Recovery EPA/625/R-94/003, 96 pp

Warren, E.A, N. J. Sihota, F.s D. Hostettler, B. A. Bekins, 2014. Comparison of surficial CO2 efflux to other measures of subsurface crude oil degradation. Journal of Contaminant Hydrology, 164, pgs 275-284.

Widdowson, M.A., E. Mendez III, F. H. Chapelle, and C. C. Casey. 2005. Natural Attenuation Software (NAS) User's Manual Version 2. http://www.nas.cee.vt.edu/index.php

APPENDICES

Issued: October 2015

Prepared by:
The LA LNAPL Workgroup

LA LNAPL RECOVERABILITY STUDY

APPENDIX A:

Preliminary Screening Matrix and Technology Tables (ITRC, 2009b)

Table 6-1. Preliminary screening matrix

LNAPL remedial objective	LNAPL remediation goal	Technology group	Example performance metrics[a]	LNAPL technology and LNAPL/ site conditions[b,c]
		LNAPL saturation-based remedial objectives		
Reduce LNAPL saturation when LNAPL is above the residual range	Recover LNAPL to maximum extent practicable	LNAPL mass recovery	• LNAPL transmissivity • Limits of technology • Limited/infrequent well thickness • Decline curve analysis • Asymptotic performance of the recovery system • Cost of mass removal • Soil concentration at regulatory standard	• DPLE [C, S, LV, LS, HV, HS] • MPE (dual pump) [C, S, LV, LS, HV, HS] • MPE (single pump) [C, S, LV, LS, HV, HS] • Water flooding [C, S, LV, LS, HV, HS] • LNAPL skimming [F, C, S, LV, LS, HV, HS] • Bioslurping/EFR [F, C, U, S, LV, LS, HV, HS] • Excavation [F, C, U, S, LV, LS, HV, HS]
Reduce LNAPL when LNAPL is within residual saturation range	Further abate LNAPL beyond hydraulic or pneumatic recovery	LNAPL mass recovery	• Limits of technology • Asymptotic mass removal • Cost of mass removal • Soil concentration at regulatory standard	• Cosolvent flushing [C, S, LV, LS, HV, HS] • SESR [C, S, LV, LS, HV, HS] • AS/SVE [C, U, S, HV, HS] • ISCO [C, U**, S, HV, HS] • RFH [F, U, S, LV, LS, HV, HS] • Three- and six-phase heating [F, U, S, LV, LS, HV, HS] • Steam/hot-air injection [C, U, S, LV, LS, HV, HS] • NSZD [F, C, U, S, HV, HS]
Terminate LNAPL body migration and reduce potential for LNAPL migration	Abate LNAPL body migration by sufficient physical removal of mobile LNAPL mass	LNAPL mass recovery	• Total system recovery rate vs. background LNAPL flux • LNAPL saturation profile • LNAPL footprint/center of mass stabilization • Stable dissolved-phase plume concentrations, dissolved-plume shape	• Excavation [F, C, U, S, LV, LS, HV, HS] • DPLE [C, S, LV, LS, HV, HS] • MPE (dual pump) [C, S, LV, LS, HV, HS] • MPE (single pump) [C, S, LV, LS, HV, HS]
	Stop LNAPL migration by physical barrier	LNAPL mass control	• No first LNAPL occurrence downgradient	• Physical containment (barrier wall, French drain, slurry wall) [F, C, S, LV, LS, HV, HS]
	Sufficiently stabilize mobile LNAPL fraction to prevent migration	LNAPL mass control	• Stable dissolved-phase plume, dissolved-plume shape • No first LNAPL occurrence downgradient in LNAPL-unaffected soils	• In situ soil mixing (stabilization) [F, C, V, LV, LS, HV, HS]

LNAPL remedial objective	LNAPL remediation goal	Technology group	Example performance metrics[a]	LNAPL technology and LNAPL/ site conditions[b,c]
LNAPL compositional-based remedial objectives				
Abate accumulation of unacceptable constituent concentrations in soil vapor and/or dissolved phase from an LNAPL source[d]	Abate unacceptable vapor accumulations by sufficient depletion of volatile constituents in LNAPL	LNAPL phase change and LNAPL mass recovery	• LNAPL composition change • Soil volatile organic compound (VOC) concentrations to below regulatory standard • Soil vapor plume concentrations to below regulatory standard • Asymptotic performance of the recovery system • Cost of mass removal	• AS/SVE [C, U, S, HV, HS] • RFH [F, U, S, LV, LS, HV, HS] • Three- and six-phase heating [F, U, S, LV, LS, HV, HS] • Steam/hot-air injection [C, U, S, LV, LS, HV, HS]
	Abate unacceptable soil vapor concentrations by physical barrier or containment	LNAPL mass (vapor) control	• Soil VOC concentrations to below regulatory standard	• Physical or hydraulic containment (vapor barrier, barrier wall) [F, C, S, LV, LS, HV, HS] • SVE (vapor management and collection) [C, U, S, HV, HS]
	Control or treat soluble plume to abate unacceptable dissolved-phase concentrations at a specified compliance point	LNAPL mass control (interception of dissolved-phase plume)	• No first constituent occurrence at unacceptable levels downgradient • Dissolved-phase regulatory standard met at compliance point • Reduced dissolved-phase concentrations downgradient of the barrier	• Modified AS for enhanced biodegradation (e.g., oxygen injection) [C, U, S, HV, HS, LS, LV] • Physical or hydraulic containment (barrier wall, French drain, slurry wall, wells, trenches) [F, C, S, LV, LS, HV, HS] • DPLE [C, S, LV, LS, HV, HS] • MPE (dual pump) [C, S, LV, LS, HV, HS] • MPE (single pump) [C, S, LV, LS, HV, HS] • NSZD [F, C, U, S, HV, HS]
Reduce constituent concentrations in soil vapor and/or dissolved phase from an LNAPL source	Further reduction of groundwater and vapor concentration beyond acceptable levels	LNAPL phase change		• NSZD [F, C, U, S, HV, HS]

LNAPL remedial objective	LNAPL remediation goal	Technology group	Example performance metrics[a]	LNAPL technology and LNAPL/ site conditions[b,c]
LNAPL aesthetic-based remedial objectives				
Aesthetic LNAPL concern abated (saturation objective)	Geotechnical soil instability abated	LNAPL mass recovery	• Specific soil concentration that results in desired soil stability	• Excavation F, C, U, S, LV, LS, HV, HS • NSZD F, C, U, S, HV, HS
		LNAPL mass control	• Soil concentrations remain stable or decreasing • Acceptable structural strength	• In situ soil mixing (stabilization) F, C, U, S, LV, LS, HV, HS • NSZD F, C, U, S, HV, HS
Aesthetic LNAPL concern abated (composition objective)	Offensive odors abated	LNAPL mass (vapor) control	• Vapor concentrations (to below odor threshold) • Specific soil concentration	• Physical containment (barrier wall, French drain, slurry wall) F, C, S, LV, LS, HV, HS • SVE (vapor management and collection) C, U, S, HV, HS • AS (addition of oxygen)/SVE C, U, S, HV, HS • NSZD F, C, U, S, HV, HS

[a] Overall, until such time as the risks are mitigated by the LNAPL remedial technology(ies), risks should be managed via engineering or institutional controls.
[b] C = coarse soils, F = fine-grained soils, S = saturated zone, U = unsaturated zone, U** = unsaturated zone with ozone oxidant; LV = low volatility, LS = low solubility, HV = high volatility, HS = high solubility.
[c] If explosive conditions exist, emergency response approach is assumed to mitigate risk (i.e., immediate engineering control and abatement of vapors is assumed to reduce risk).
[d] Considered potentially most effective technology, without significant underutilization of technology capability.

TECHNOLOGY TABLES: SERIES A, B, C

NOTE: References begin on p. A-59.

Table A-1.A. Excavation

Technology	Excavation/large-diameter borings	The targeted LNAPL area is removed from the surface or subsurface via excavation or large diameter boring.	
Remediation process	Physical mass recovery	Yes	LNAPL physically removed.
	Phase change	No	Not the intended remedial process, but enhanced volatilization can occur as LNAPL exposed to atmosphere.
	In situ destruction	No	N/A
	Stabilization/ binding	No	N/A
Objective applicability	LNAPL saturation	Yes	LNAPL physically removed.
		Example performance metrics	Maximum soil concentration reduced to cleanup criteria, reduced LNAPL transmissivity, direct analysis of soil to measure changes in LNAPL saturation profile.
	LNAPL composition	No	N/A
		Example performance metrics	N/A
Applicable LNAPL type	All LNAPL types		
Geologic factors	Unsaturated zone	Permeability	Not typically a factor.
		Grain size	Not typically a factor.
		Heterogeneity	Not typically a factor.
		Consolidation	Unconsolidated easier to excavate; loosely consolidated may collapse; bedrock excavation has limited practicability.
	Saturated zone	Permeability	High permeability can maximize water inflow to excavation or "flowing sand" concerns destabilize side walls.
		Grain size	Not typically a factor.
		Heterogeneity	Not typically a factor.
		Consolidation	Unconsolidated easier to excavate; loosely consolidated may collapse; bedrock excavation has limited practicability.

Table A-1.B. Evaluation factors for excavation

Technology: Excavation		
Remedial time frame	Concern	Low
	Discussion	Very short. The size of the LNAPL source zone and depth of the source have an impact on the time to implement an excavation. Off-site disposal and handling may also factor in the time it takes to conduct an excavation project. Very large excavation projects may be slowed by the rate at which trucks can be moved from the site to disposal facility.
Safety	Concern	Moderate
	Discussion	Some potentially significant safety issues, but construction related and typically routine. Large excavations involve side-stability issues and the potential for collapse. In an area with dense infrastructure, these may significantly impact the safety concern for excavation. Traffic safety could also be an issue. Excavated material could come in contact with workers. Potential for worker exposure to contaminated soil, liquids, and vapors must be managed.
Waste management	Concern	Moderate to high
	Discussion	Significant waste stream may be generated. Excavation projects often involve off-site waste handling, waste characterization, and disposal.
Community concerns	Concern	Low to moderate
	Discussion	Public generally familiar with and accustomed to construction excavations. Concerns may be significant due to volatile emissions, dust, noise, odors, traffic, exhaust, visual/aesthetic, and safety impacts, etc.
Carbon footprint/energy requirements	Concern	High
	Discussion	Equipment emissions and short-term energy requirements large. Energy is used for the excavation machinery and trucks to haul the wastes off site. In addition, for volatile LNAPLs, the excavation generates emissions.
Site restrictions	Concern	High
	Discussion	Disruptive technology, physical space, and logistical demands significant. Often excavation is infeasible due to site improvements, buildings, structures, roads, etc. Due to the use of large, heavy equipment and the need for clearance on either side of the excavation, could be constrained due to buildings, facility requirements, utilities, and natural habitats.
LNAPL body size	Concern	Small to moderate
	Discussion	Very large LNAPL bodies may be infeasible to excavate. The size of the LNAPL body directly affects the cost and extent of the excavation. Smaller LNAPL bodies may be more amenable to excavation. If the LNAPL body is areally extensive, it will take longer to excavate or present more logistical challenges.
Other regulations	Concern	Low to moderate
	Discussion	Waste management characterization, waste manifesting, construction storm water protection plans, construction permits, and transport provisions applicable. Typically routine compliance with local and state regulations. Potential vapor emissions limits.
Cost	Concern	High
	Discussion	May be a high-cost alternative.
Other	Concern	
	Discussion	

Table A-1.C. Technical implementation considerations for excavation

Data requirements	Site-specific data for technology evaluation	Site access and subsurface utility and infrastructure locations	
	Bench-scale testing	N/A	
	Pilot-scale testing	N/A	
	Full-scale design	Soil type	
		Depth to LNAPL zone	
		Depth to water	
	Performance metrics	LNAPL thickness	Reduced LNAPL transmissivity.
		Soil concentration	Maximum soil concentration reduced to cleanup criteria.
		LNAPL saturation	Direct analysis of soil to measure changes in LNAPL saturation profile.
Modeling tools/applicable models			
Further information		USACE. 2003. *Engineering and Design: Safety and Health Aspects of HTRW Remediation Technologies,* Chap. 3, "Excavations." EM 1110-1-4007. http://140.194.76.129/publications/eng-manuals/em1110-1-4007/c-3.pdf	
		USACE. 1998. *Engineering and Design: Removal of Underground Storage Tanks (USTs)*, Chap. 15, "Soil Removal, Free-Product Product Removal, Backfilling Procedures." EM 1110-1-4006. http://140.194.76.129/publications/eng-manuals/em1110-1-4006/c-15.pdf	

Table A-2.A. Physical or hydraulic containment

Technology	Containment	Containment uses engineered barriers that either control horizontal migration of LNAPL, isolate LNAPL as a vapor or dissolved source, block physical access to LNAPL body, or prevent recharge infiltration through the LNAPL body (vertical barrier).	
Remediation process	Physical mass recovery	Potential	Not primary intent, but hydraulic control measures (interception wells or trenches) implemented as a containment system may remove some LNAPL.
	Phase change	No	N/A
	In situ destruction	No	Physical or hydraulic containment does not typically involve in situ treatment.
	Stabilization/ binding	Yes	Halts LNAPL migration.
Objective applicability	LNAPL saturation	Yes	Halts LNAPL movement.
		Example performance metrics	No first LNAPL occurrence downgradient of LNAPL containment, LNAPL constituent meets standard at point of compliance, reduced vapor concentrations.
	LNAPL composition	Yes	N/A
		Example performance metrics	N/A
Applicable LNAPL type	All LNAPL types		
Geologic factors	Unsaturated zone	Permeability	Soil permeability a factor when determining the amount of amendments (e.g., bentonite or cement) needed to achieve the desired permeability or for determining necessary hydraulic removal rates.
		Grain size	For backfill activities, large gravels or cobbles (>6 inches in diameter) typically not used in barrier wall construction.
		Heterogeneity	Not a factor for trenches; needs to be considered for wells.
		Consolidation	Consolidated material may be easier to trench because of side wall stability; cemented or indurated material may be difficult to excavate.
	Saturated zone	Permeability	Soil permeability a factor when determining the amount of amendments (e.g., bentonite or cement) needed to achieve the desired permeability or for determining necessary hydraulic removal rates.
		Grain size	Not typically a factor, although during backfill activities, large gravels or cobbles (>6 inches in diameter) not typically used in barrier wall construction.
		Heterogeneity	For keyed physical barriers, determine that a continuous aquitard or bedrock exists and determine its elevation along the alignment; barrier must intersect LNAPL vertical interval under all seasonal groundwater elevations.
		Consolidation	Consolidated material may be easier to trench because of side wall stability; cemented or indurated material may be difficult to excavate.

Table A-2.B. Evaluation factors for physical or hydraulic containment

Technology: Physical containment		
Remedial time frame	Concern	Low
	Discussion	Very short to deploy, but potential long-term application. Time to construct containment structure varies with type, length, and depth, and other logistical factors. Time to achieve remedial goals depends on site-specific requirements (e.g., mitigate risk, remove LNAPL, reach regulatory standards in groundwater, etc.).
Safety	Concern	Low to moderate
	Discussion	Some potentially significant safety issues, but construction related and typically routine. The use of large, heavy equipment can be a factor. Potential side wall collapse during excavation and long-term geotechnical stability. In addition, if a slurry wall is the containment structure of choice, the excavated materials may come into contact with workers.
Waste management	Concern	Moderate
	Discussion	Significant liquid waste stream may be generated. Soils visibly saturated with LNAPL cannot be used in the slurry mix and are segregated. Excess slurry and soils not included in the slurry mix are waste materials. Pumping-based hydraulic interception may require treatment of effluent.
Community concerns	Concern	Low to moderate
	Discussion	Typically familiar with and accustomed to excavation/construction work. Concerns may be significant due to volatile emissions, odors, traffic, exhaust, etc. If a sheet pile containment structure or aboveground effluent treatment is used, noise could be a factor. Also, the public may see containment as not equal to cleanup.
Carbon footprint/ energy requirements	Concern	High
	Discussion	Equipment emissions and energy requirements large. Energy is used for the excavation machinery and trucks to haul the wastes off site. In addition, for volatile LNAPLs, the slurry trench generates volatile emissions. Active hydraulic interception requires energy for pumping and treatment.
Site restrictions	Concern	High
	Discussion	Disruptive technology, physical space, and logistical demands significant. Due to the use of large, heavy equipment and the need for approximately 20–30 feet of clearance on either side of the physical containment structure, could be limited due to buildings, utilities, and natural habitats.
LNAPL body size	Concern	Low to moderate
	Discussion	Applicable to only migrating portion of the LNAPL. The extent of the containment infrastructure depends on the LNAPL body needing to be contained.
Other regulations	Concern	Low to moderate
	Discussion	Normal construction, well, storm water, and discharge permitting. Other regulatory agencies may need to be included in decision making for the alignment of the containment infrastructure due to wetlands impacts; floodplain construction; water rights of adjacent land owners; or other federal, state, or local regulations.
Cost	Concern	Moderate to high
	Discussion	Depends on the length and depth of the physical containment structure, the type of physical containment structure chosen, and any possible site restrictions.
Other	Concern	
	Discussion	

Table A-2.C. Technical implementation considerations for physical or hydraulic containment

Data requirements	Site-specific data for technology evaluation	Soil type(s)/lithology	Soil type should be taken into account for physical or hydraulic design to ensure it meets performance metrics.
		Depth to LNAPL	
		Depth to water	Range of seasonal water level change needs to be defined.
		Hydraulic gradient	
		Site access	Including locations of utilities and foundations.
	Bench-scale testing	Soil column testing	
		Treatability testing	To test permeability of barrier wall mixes.
	Pilot-scale testing	N/A	
	Full-scale design	Soil type(s)/lithology	
		Depth to LNAPL	
		Depth to water	
		Hydraulic gradient	
	Performance metrics	LNAPL thickness	Monitoring wells downgradient of barrier to verify no occurrence of LNAPL.
		Depth to water	For hydraulic interception barriers (wells or trenches), maintain reversal of hydraulic gradient.
		Downgradient concentrations	LNAPL constituent meets standard at point of compliance.
Modeling tools/applicable models		MODFLOW	Other groundwater flow models may be applicable.
Further information		USACE. 1994. *Engineering and Design: Design of Sheet Pile Walls*. EM 1110-2-2504. http://140.194.76.129/publications/eng-manuals/em1110-2-2504/entire.pdf	
		EPA. n.d. "Technology Focus: Permeable Reactive Barriers, Permeable Treatment Zones, and Application of Zero-Valent Iron." http://clu-in.org/techfocus/default.focus/sec/Permeable_Reactive_Barriers,_Permeable_Treatment_Zones,_and_Application_of_Zero-Valent_Iron/cat/Overview	
		EPA. 1998. *Permeable Reactive Barrier Technologies for Contaminant Remediation*. EPA/600/R-98/125. http://clu-in.org/download/rtdf/prb/reactbar.pdf	
		EPA. 1998. *Evaluation of Subsurface Engineered Barriers at Waste Sites*. EPA 542-R-98-005. http://clu-in.org/download/remed/subsurf.pdf	

Table A-3.A. In situ soil mixing and stabilization

Technology	In situ soil mixing (stabilization)	Uses mechanical mixing of soil or aquifer materials with low-permeability materials such as clay and/or reactive media such as chemical oxidants or electron acceptors and/or stabilizing media such as Portland cement.	
Remediation process	Physical mass recovery	No	Manages mass in place by creating a homogenous zone of soil with a lower mass flux in the dissolved phase.
	Phase change	No	Soil mixing itself does not induce a phase change, but LNAPL is redistributed throughout the mixed interval; some incidental volatilization may occur.
	In situ destruction	Maybe	If reactive media added, some LNAPL constituents can be destroyed.
	Stabilization/ binding	Yes	Stabilization of LNAPLs in place is the primary mechanism of this technology.
Objective applicability	LNAPL saturation	Yes	Homogenizing LNAPL zone reducing LNAPL saturation level to immobile (residual) saturations.
		Example performance metrics	Reduced LNAPL mobility, direct analysis of soil to measure changes in LNAPL saturation profile, maximum soil concentration reduced to cleanup criteria, reduced or stable dissolved-mass flux downgradient.
	LNAPL composition	Maybe	If no reactive media added, no change in chemical composition expected; if reactive media added, destruction of some LNAPL constituents.
		Example performance metrics	Change in LNAPL constituent ratios or mass.
Applicable LNAPL type	All LNAPL types		
Geologic factors	Unsaturated zone	Permeability	Not typically a factor.
		Grain size	Not typically a factor.
		Heterogeneity	Most advantageous in heterogeneous settings where complex LNAPL saturation profiles due to geologic heterogeneities are homogenized due to soil mixing.
		Consolidation	Works well in all unconsolidated geologic settings.
	Saturated zone	Permeability	Not typically a factor.
		Grain size	Grain sizes including cobbles may be difficult to treat with soil mixing.
		Heterogeneity	Most advantageous in heterogeneous settings where complex LNAPL saturation profiles due to geologic heterogeneities are homogenized due to soil mixing.
		Consolidation	Works well in all unconsolidated geologic settings.

Table A-3.B. Evaluation factors for in situ soil mixing and stabilization

Technology: In situ soil mixing and stabilization		
Remedial time frame	Concern	Low
	Discussion	Very short to short. Area and depth of treatment are the major factors on time.
Safety	Concern	High to moderate
	Discussion	Some potentially significant safety issues, but construction related and typically routine. Large equipment on site to mix the soils. If chemical oxidants or other amendments are added, there may be chemical mixing and injecting under pressure. Potential temporary ground surface instability.
Waste management	Concern	Low
	Discussion	No to minimal waste streams; possibly no soils removed from the site.
Community concerns	Concern	Low to moderate
	Discussion	Public generally familiar with and accustomed to construction excavations. Concerns may be significant due to volatile emissions, odors, traffic, exhaust, etc. Also, the public may see stabilization as not equal to cleanup.
Carbon footprint/ energy requirements	Concern	Moderate to high
	Discussion	Equipment emissions and energy requirements large. Fuel is used to power machinery to mix soils, and there may be some reaction if oxidants are injected.
Site restrictions	Concern	High
	Discussion	Disruptive technology, physical space and logistical demands significant. Heavy equipment operating on site. Due to the use of large, heavy equipment and the need for clearance on either side of the target zone, the working area could be limited due to buildings, facility requirements, utilities, and natural habitats.
LNAPL body size	Concern	High
	Discussion	Physical obstructions such as buildings will be a limiting factor. If there is a significant depth requirement, special equipment may be required.
Other regulations	Concern	Low
	Discussion	May be required to monitor air quality.
Cost	Concern	Moderate to high
	Discussion	Costs increase with increasing volume of LNAPL-impacted soil to be mixed and stabilized. Depends on area and depth of treatment and any special restrictions.
Other	Concern	
	Discussion	

Table A-3.C. Technical implementation considerations for in situ soil mixing and stabilization

Data requirements	Site-specific data for technology evaluation	Soil type(s)/lithology	
		Depth to LNAPL zone	
		Site access	Including locations of utilities and foundations.
	Bench-scale testing	Leachability testing	
	Pilot-scale testing	N/A	
	Full-scale design	Soil type(s)/lithology	
		Homogeneity	
		Depth to LNAPL zone	
	Performance metrics	LNAPL thickness	Monitoring wells downgradient of barrier to verify no occurrence of LNAPL.
		Downgradient concentrations	LNAPL constituent meets standard at point of compliance.
		Mass flux	Estimated dissolved mass discharge less than goal.
		LNAPL saturation	Direct analysis of soil to measure changes in LNAPL saturation profile.
Modeling tools/ applicable models			
Further information		FRTR. n.d. “Remedial Technology Screening and Reference Guide, Version 4.0, “Solidification and Stabilization.” www.frtr.gov/matrix2/section4/4-8.html	
		Portland Cement Association. Information and resources about the use of solidification/stabilization with cement to treat wastes. www.cement.org/waste	
		USACE. 1999. *Engineering and Design: Solidification/Stabilization*. EM 1110-1-4010. http://140.194.76.129/publications/eng-manuals/em1110-1-4007/c-4.pdf	
		Larsson, S. 2004. *Mixing Processes for Ground Improvement by Deep Mixing*. Swedish Deep Stabilization Research Centre. http://kth.diva-portal.org/smash/record.jsf?pid=diva2:9502	

Table A-4.A. Natural source zone depletion

Technology	Natural source zone depletion	LNAPL mass reduction via naturally occurring volatilization (in the unsaturated zone), aqueous dissolution (in the saturated zone), and biodegradation (in both zones); site-specific LNAPL mass loss rates can be quantified empirically.	
Remediation process	Physical mass recovery	No	N/A
	Phase change	Yes	Volatile LNAPL fractions volatilize naturally to the gas phase in unsaturated soils; soluble LNAPL fractions dissolve to groundwater in the saturated zone.
	In situ destruction	Yes	In situ biodegradation processes destroy dissolved LNAPL in groundwater and volatilized LNAPL in unsaturated zone soil gas.
	Stabilization/binding	No	N/A
Objective applicability	LNAPL saturation	No	N/A
		Example performance metrics	N/A
	LNAPL composition	Yes	Modify LNAPL composition; can increase viscosity because of preferential loss of light fractions and will gradually concentrate in recalcitrant constituents as less recalcitrant constituents are depleted.
		Example performance metrics	Stable or reducing dissolved-phase plume, dissolved-phase plume shape, LNAPL composition change, soil VOC concentrations to below regulatory standard, soil vapor levels to regulatory standard.
Applicable LNAPL type	LNAPLs containing higher proportions of more soluble and more volatile hydrocarbon fractions deplete more efficiently via dissolution, volatilization, and biodegradation. As volatile LNAPL constituents are stripped, LNAPL can become more viscous, and more recalcitrant constituents can become more concentrated.		
Geologic factors	Unsaturated zone	Permeability	Unsaturated zone permeability, grain size, heterogeneity, consolidation, and soil moisture all affect the effective diffusivity rate of volatilized LNAPL soil gas in the subsurface. The effective diffusion rate of volatilized LNAPL soil gas greatly influences the LNAPL mass loss rate.
		Grain size	
		Heterogeneity	
		Soil moisture	
		Consolidation	Not typically a factor.
	Saturated zone	Permeability	Hydraulic properties that lead to higher groundwater velocities may result in higher LNAPL dissolution mass loss rates; lower groundwater velocities may limit the dissolution rate.
		Grain size	
		Heterogeneity	
		Consolidation	

Table A-4.B. Evaluation factors for natural source zone depletion

Technology: Natural source zone depletion		
Remedial time frame	Concern	High to very high
	Discussion	Very long term; natural volatilization and dissolution in unsaturated and saturation zones control the time frame.
Safety	Concern	Low
	Discussion	If there are no surface dangers.
Waste management	Concern	Low
	Discussion	No wastes generated; no waste removal from site.
Community concerns	Concern	Low to moderate
	Discussion	Potential perception of no action. Community may want active remediation and cleanup of site instead of monitoring. Need for more monitoring and reporting of results to educate the community on the improvements if achieved.
Carbon footprint/ energy requirements	Concern	Low
	Discussion	No emissions or energy requirements.
Site restrictions	Concern	Low
	Discussion	No constraints except to access monitoring network.
LNAPL body size	Concern	High
	Discussion	Large LNAPL plume will take significantly longer to remediate than smaller body.
Other regulations	Concern	Low
	Discussion	No additional regulatory or permitting requirements.
Cost	Concern	Low to moderate
	Discussion	Monitoring of the site is typically needed.
Other	Concern	
	Discussion	

Table A-4.C. Technical implementation considerations for natural source zone depletion

Data requirements	Site-specific data for NSZD evaluation	LCSM (saturated zone and unsaturated zone)	Detailed LCSM appropriate and verification of depletion mechanisms.
		Submerged LNAPL source zone distribution	Site-specific LNAPL distribution at and beneath the capillary fringe.
		Exposed LNAPL source zone distribution	Site-specific LNAPL distribution above the capillary fringe.
		LNAPL characteristics	Estimate volatile fraction of exposed LNAPL in unsaturated zone, estimate effective solubility of submerged LNAPL in saturated zone.
		Dissolved LNAPL concentrations	Dissolved LNAPL constituent fraction concentrations upgradient and downgradient of submerged LNAPL source zone.
		Dissolved electron acceptor/ biotransformation products	Dissolved cation and anion groundwater geochemical constituents used to quantify mass loss via biodegradation processes.
		Soil vapor LNAPL concentrations	Volatilized LNAPL constituent fraction concentrations at various depths in soil vapor originating in LNAPL source zone
		Soil gas oxygen/ methane concentrations	Oxygen and methane concentration profile vs. depth to LNAPL source zone to identify biodegradation zones
		Groundwater hydraulics of saturated zone	Hydraulic conductivity, groundwater-specific discharge.
	NSZD design parameters	Control volume determination	Establish three-dimensional boundaries for LNAPL source zone control volume.
		Saturated zone LNAPL mass loss rate	Calculate net mass flux in saturated zone by LNAPL dissolution and biodegradation leaving control volume based on dissolved-phase constituents.
		Unsaturated zone LNAPL mass loss rate	Calculate net mass flux in unsaturated zone by LNAPL volatilization and biodegradation leaving control volume based on volatilized LNAPL and oxygen/methane soil gas constituents.
	Bench-scale tests for NAPL longevity	Long-term soluble source mass loss	Serial batch equilibrium dissolution experimental measurements, scale lab-time LNAPL mass loss rates up to LNAPL field-time mass loss rates.
		Long-term volatile source mass	Serial batch equilibrium volatilization and diffusivity experimental measurements, scale lab-time LNAPL mass loss rates up to LNAPL field-time mass loss rates.
	Performance metrics	Saturated zone dissolution/ biodegradation mass loss rate	Current LNAPL source zone mass loss rate associated with LNAPL dissolution and subsequent biodegradation groundwater.
		Unsaturated zone volatilization/ biodegradation mass loss rate	Current LNAPL source zone mass loss rate associated with LNAPL volatilization and subsequent biodegradation in soil column.
		Long-term mass loss estimates	Extrapolation of short-term laboratory experiments (bench tests) to long-term LNAPL source zone mass loss.
Modeling tools/ applicable models		See ITRC 2009, etc.	Numerous computer simulation models exist that are capable of estimating the results of NSZD process parameters using equilibrium relationships; many models cannot account for site-specific kinetics.
Further information		ITRC. 2009. *Evaluating Natural Source Zone Depletion at Sites with LNAPL*. LNAPL-1. www.itrcweb.org/Documents/LNAPL-1.pdf	
		Johnson, P. C., P. Lundegard, and Z. Liu. 2006. "Source Zone Natural Attenuation at Petroleum Hydrocarbon Spill Sites: I. Site-Specific Assessment Approach," *Ground Water Monitoring and Remediation* **26**(4): 82–92.	
		Lundegard, P. D., and P. C. Johnson. 2006. "Source Zone Natural Attenuation at Petroleum Hydrocarbon Spill Sites: II. Application to a Former Oil Field," *Ground Water Monitoring and Remediation* **26**(4): 93–106.	

Table A-5.A. Air sparging/soil vapor extraction

Technology	Air sparging/ soil vapor extraction	AS injects ambient air or other gases (e.g., oxygen) down well bores or trenches below the groundwater table, aerating groundwater and volatilizing LNAPL. SVE induces a vacuum that volatilizes LNAPL if present above the water table and removes LNAPL vapors from the subsurface. AS and SVE may be used individually if conditions allow.	
Remediation process	Physical mass recovery	Yes	AS volatilizes LNAPL from saturated zone and capillary fringe; SVE extracts LNAPL vapors from unsaturated zone.
	Phase change	Yes	AS and SVE induce volatilization of the LNAPL.
	In situ destruction	Yes	Ambient air or oxygen sparging below the water table and vacuum induced circulation of atmospheric air into the unsaturated zone enhance in situ aerobic biodegradation.
	Stabilization/ binding	No	N/A
Objective applicability	LNAPL saturation	Yes	Can potentially reduce LNAPL saturations to below residual saturation.
		Example performance metrics	Mass removal to an asymptotic recovery of a well-operated and -maintained system (usually quantified in pounds of LNAPL constituent per day).
	LNAPL composition	Yes	Abate accumulation of unacceptable constituent concentrations in soil vapor and/or dissolved phase from an LNAPL source.
		Example performance metrics	LNAPL composition change, soil VOC concentrations to below regulatory standard, soil vapor plume concentrations to below regulatory standard.
Applicable LNAPL type	All LNAPL types although better-suited to more volatile LNAPLs (e.g., gasoline, kerosene). SVE-induced vacuum extracts volatile LNAPL from the pores and increases oxygen content of unsaturated zone which, enhances aerobic respiration of heavier-phase LNAPLs. AS helps volatilize LNAPL from the capillary fringe and saturated zone as well as enhancing aerobic degradation of heavier-phase LNAPLs. As volatile LNAPL constituents are stripped, LNAPL can become more viscous, and more recalcitrant constituents can become more concentrated.		
Geologic factors	Unsaturated zone	Permeability	SVE is more effective in higher permeability materials and where treatment zone capped with a confining layer or impermeable surface to increase the ROI.
		Grain size	Small to very small proportion of fine-grained soil.
		Heterogeneity	AS/SVE is more efficient in homogeneous soils; in heterogeneous soils, air flow will follow preferential pathways, possibly short-circuiting remediation coverage, but LNAPL may also be distributed along preferential pathways.
		Consolidation	Not typically a factor.
	Saturated zone	Permeability	AS may be most effective in moderate-permeability materials, which are less prone to severe air channeling but do not severely restrict air flow.
		Grain size	As above, medium grain size balances AS air flow rate with distribution (ROI); small grain size may require entry pressures that exceed confining pressure and result in soil heaving for shallow treatment zones.
		Heterogeneity	Fractured bedrock and more permeable zones will induce preferential flow.
		Consolidation	Not typically a factor.

Table A-5.B. Evaluation factors for air sparging/soil vapor extraction

Technology: Air sparging/soil vapor extraction		
Remedial time frame	Concern	Low to moderate
	Discussion	Short to medium—typically 1–5 years. Depends on soil type and LNAPL type. Low-permeability soils and heavier LNAPL require more time to remediate.
Safety	Concern	Low to moderate
	Discussion	Vapor releases and potential of volatilization due to sparging and vapor migration in the subsurface (if AS used without SVE). Pressurized piping systems. Low safety concern for SVE alone.
Waste management	Concern	Low to moderate
	Discussion	Vapors generated by SVE systems may require treatment. Recovered LNAPL should be recycled.
Community concerns	Concern	Low to moderate
	Discussion	Noise of treatment equipment may be an issue. AS-induced vapor migration in the subsurface can be controlled using SVE. Concern with technology unfamiliar to general public.
Carbon footprint/ energy requirement	Concern	Moderate to high
	Discussion	Carbon footprint depends on the energy required for treatment (e.g., thermal oxidation make-up fuel or energy for activated carbon regenerations) and energy used to power blowers/compressors, which can be significant.
Site restrictions	Concern	Low to moderate
	Discussion	Vertical AS/SVE wells can usually be spaced and located around site restrictions or accessed through the use of directional drilling equipment.
LNAPL body size	Concern	Moderate
	Discussion	The size and depth of the LNAPL body directly affect the cost and extent of the remediation system, although there is an economy of scale with the need for one blower and compressor to operate on multiple wells and sparge points.
Other regulations	Concern	Low to moderate
	Discussion	Air emissions permitting may be required.
Cost	Concern	Low to moderate
	Discussion	In general, AS/SVE is more cost-effective than other active LNAPL technologies and has been proven at many sites for over 20 years.
Other	Concern	
	Discussion	

Table A-5.C. Technical implementation considerations for air sparging/soil vapor extraction

Data requirements	Site-specific data for technology evaluation	Soil permeability (to air, e.g., in unsaturated zone) (k_{soil})	Permeability to air in the unsaturated zone directly affects the radius of treatment that can be developed around each SVE well for a given vapor extraction rate; lower-permeability soils require more SVE wells per unit area.
		Groundwater conductivity (K_{gw})	Hydraulic conductivity is an indicator of the potential effectiveness of AS. Lower hydraulic conductivity soils ($<10^{-4}$ cm/sec) are likely to restrict air flow and limit the mass removal rate of volatile LNAPL fraction. Very high hydraulic conductivity soils (10^{-1} cm/sec) are likely to require deeper AS wells and high air-flow rates to be effective.
		LNAPL characteristics ($LNAPL_c$)	AS/SVE is effective on only the volatile fraction of the LNAPL. AS/SVE performed on an LNAPL with a small volatile fraction (e.g., jet fuel or a strongly weathered gasoline) does not result in significant volatile mass removal, but may contribute to aerobic biodegradation.
	Bench-scale testing	N/A	
	Pilot-scale testing	AS air entry pressure	To evaluate safe injection pressures.
		AS pressure vs. flow	Safety and feasibility
		AS ROI (vs. flow)	Feasibility can be measured by observing transient groundwater mounding, monitoring a tracer gas added to sparge air, or monitoring vapor concentration changes or dissolved oxygen coincident with sparge operation.
		SVE vacuum vs. flow	Feasibility
		SVE ROI (vs. flow)	Feasibility
		SVE influent concentration	Treatment system type and sizing
	Full-scale design	AS pressure and flow	Compressor sizing
		AS ROI	AS well spacing
		SVE vacuum and flow	Blower sizing
		SVE ROI	SVE well spacing
		SVE influent concentration	Treatment system type and sizing
	Performance metrics	SVE well head and blower vacuum	Basic system performance—large differences can be an indicator of system problems, e.g., water in conveyance piping.
		AS well head and compressor pressure	Basic system performance
		SVE influent concentration	Tracking mass removal rate
		O_2 influent concentration	Indicator of aerobic biodegradation
		CO_2 influent concentration	Indicator of aerobic biodegradation
		Cumulative mass removed or mass removal rate	Treatment effectiveness
		AS dissolved oxygen	System performance
Modeling tools/ applicable models		SOILVENT	
Further information		NAVFAC. 2001. *Air Sparging Guidance Document*. NFESC TR-2193-ENV. www.clu-in.org/download/contaminantfocus/dnapl/Treatment_Technologies/Air_Sparg_TR-2193.pdf	
		Johnson, P. C., C. C. Stanley, M. W. Kemblowski, D. L. Byers, and J. D. Colthart. 1990. "A Practical Approach to the Design, Operation, and Monitoring of In Situ Soil Venting Systems," *Ground Water Monitoring Review* **10**(2): 159–78.	
		Johnson, P. C., M. W. Kemblowski, and J. D. Colthart. 1990. "Quantitative Analysis for the Cleanup of Hydrocarbon-Contaminated Soils by In Situ Soil Venting," *Ground Water Journal* **3**(28): 413–29.	
		Battelle. 2002. *Air Sparging Design Paradigm*. www.estcp.org/documents/techdocs/Air_Sparging.pdf	
		EPA. 1995. "Air Sparging." www.epa.gov/swerust1/cat/airsparg.htm	
		EPA. n.d. "Technology Focus: Soil Vapor Extraction." www.clu-in.org/techfocus/default.focus/sec/Soil_Vapor_Extraction/cat/Overview	

Table A-5.C. continued

Further information (continued)	AFCEE. n.d. "Soil Vapor Extraction." www.afcee.af.mil/resources/technologytransfer/programsandinitiatives/sourcezonetreatment/background/soilvaporextract/index.asp
	EPA. 1997. *Analysis of Selected Enhancements for Soil Vapor Extraction*. EPA-542-R-97-007. www.clu-in.org/download/remed/sveenhmt.pdf
	Ground Water Remediation Technologies Analysis Center. 1996. *Air Sparging Technology Overview Report*. http://clu-in.org/download/toolkit/sparge_o.pdf
	USACE. 2002. *Engineering and Design: Soil Vapor Extraction and Bioventing*. EM 1110-1-4001. http://140.194.76.129/publications/eng-manuals/em1110-1-4001/toc.htm
	USACE. 2008. *Engineering and Design: In Situ Air Sparging*. EM 1110-1-4005. http://140.194.76.129/publications/eng-manuals/em1110-1-4005/toc.htm
	EPA. 1994. *How To Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites, A Guide for Corrective Action Plan Reviewers*. EPA 510-B-94-003. www.epa.gov/oust/pubs/tums.htm

Table A-6.A. Skimming

Technology	Active LNAPL skimming	Uses a single pump or hydrophobic belt (e.g., bladder pump, pneumatic pump, or belt skimmer) to extract LNAPL from a well at air/LNAPL interface under natural gradients. The available drawdown is limited based on the LNAPL thickness, the density difference between LNAPL and water, and the heterogeneity of the adjacent soil. LNAPL skimming typically induces a limited ROI of <25 feet in unconfined conditions. LNAPL skimming is effective for confined, unconfined, and perched LNAPL.	
Remediation process	Physical mass recovery	Yes	Removes LNAPL at the groundwater surface; does not affect residual LNAPL mass.
	Phase change	No	LNAPL remains in liquid phase.
	In situ destruction	No	N/A
	Stabilization/binding	No	N/A
Objective applicability	LNAPL saturation	Yes	Active skimming drives LNAPL saturation towards residual saturation, decreasing LNAPL transmissivity and mobile LNAPL extent.
		Example performance metrics	Direct analysis of soil to indicate changes in formation LNAPL saturations; LNAPL transmissivity reduction/ LNAPL conductivity reduction, LNAPL/water ratio, asymptotic recovery of LNAPL from a well.
	LNAPL composition	No	N/A—Skimming recovers LNAPL as a fluid and does not exploit volatilization or dissolution, so it does not lead to a compositional change.
		Example performance metrics	N/A
Applicable LNAPL type	All LNAPL types; however, lower-viscosity LNAPL (0.5–1.5 cP) is much more recoverable than high-viscosity LNAPL (>6 cP).		
Geologic factors	Unsaturated zone	Permeability	Technology not applicable to LNAPL in the unsaturated zone.
		Grain size	
		Heterogeneity	
		Consolidation	
	Saturated zone	Permeability	Soil permeability is proportional to recovery rate—higher LNAPL recovery and saturation reduction in higher permeabilities. Permeability has significant effect on ROI of a skimming well. LNAPL permeability greater at lower water table levels when saturations are higher (smear zone opened).
		Grain size	Skimming can be effective in all grain size distributions; can achieve lower residual saturation in coarser materials where capillary pressures are less.
		Heterogeneity	Moderately sensitive to heterogeneity, affecting ROI; well screen location and pump depth can help overcome heterogeneities.
		Consolidation	Not typically a factor.
Cost	Per well, the capital costs of skimming wells are low compared to other technologies; however, to achieve a remedial time frame similar to that of dual pump or total fluids extraction, a denser well spacing is required due to the small ROC and lower per-well rate of LNAPL removal. Skimming wells typically need to be operated longer than DPLE because they can have lower recovery rates achieved compared to other mass recovery technologies.		

Table A-6.B. Evaluation factors for skimming

Technology: LNAPL skimming		
Remedial time frame	Concern	High
	Discussion	Long to very long. Depends on soil type, LNAPL type, release size, footprint, and end point (e.g., LNAPL thickness, sheen, or oil transmissivity goal). Low-permeability soils and heavier LNAPL require more time to remediate.
Safety concerns	Concern	Low
	Discussion	Potential release from primary containment into secondary containment. Overall skimmers represent a low safety risk.
Waste management	Concern	Low to moderate
	Discussion	Recovered LNAPL requires treatment, disposal, and/or recycling.
Community concerns	Concern	Low
	Discussion	Concern with noise, aesthetic, and access issues and length of operation vs. other methods.
Carbon footprint/ energy requirements	Concern	Low to moderate
	Discussion	Carbon footprint depends on time frame, duration, frequency of events, and the amount of volatiles generated.
Site restrictions	Concern	Low
	Discussion	LNAPL skimming can usually be implemented in wells located around site restrictions.
LNAPL body size	Concern	Moderate to high
	Discussion	The size of the LNAPL body directly affects the cost and extent of the well network required to implement LNAPL skimming. Skimming ROI affects the number of wells required to address the LNAPL body.
Other regulations	Concern	Low
	Discussion	No additional regulations.
Cost	Concern	Low to moderate
	Discussion	Low for capital costs and low to medium for operation and maintenance, depending on life span of the project.
Other	Concern	
	Discussion	

Table A-6.C. Technical implementation considerations for skimming

Data requirements	Site-specific data for technology evaluation	LNAPL conductivity (K_{LNAPL}), LNAPL transmissivity (T_{LNAPL})	LNAPL transmissivity data indicate the LNAPL extraction rate. Transmissivity data may be obtained from LNAPL baildown tests or predictive modeling.
		LNAPL characteristics ($LNAPL_c$)	Low-viscosity LNAPLs are more amenable to pumping than higher-viscosity LNAPLs. Hence, lighter-end, low-viscosity LNAPL such as gasoline, kerosene, jet fuel, diesel and No. 2 fuel oil are more amenable to dual-phase extraction than a No. 6 fuel oil or Bunker C.
		Soil type/grain size	Coarser-grained materials, homogeneous soils allow larger ROI to develop; finer-grained soils interbeds impede or lessen capture.
		Safety precautions	Explosivity of LNAPL—potential need for bonding and grounding of metal equipment/containers and other associated safety requirements.
		Available power/utilities	The power source must be determined. Drop-line power may be readily available. Alternatively, on-site sources such as generators or solar power may be needed. Power supply must be compatible with skimmer pump demand.
	Bench-scale testing	N/A	
	Pilot-scale testing	LNAPL ROI/ROC	Establish LNAPL ROI and capture zone based on LNAPL drawdown.
		LNAPL recovery rate, volume, chemical characteristics	Determine LNAPL recovery rate, volume, and chemical characteristics to assist with design of LNAPL storage, handling, and treatment/discharge options.
	Full-scale design	Number of extraction wells	Determine number of extraction wells necessary to achieve adequate zone of LNAPL recovery consistent with LNAPL site objective(s).
		Conveyance piping	Determine locations, lengths, materials for horizontal conveyance piping to/from wells to/from recovery/treatment system. Assess pipe insulation and heat tracing needs for winter conditions, if applicable.
		LNAPL ROI/ROC	Establish LNAPL ROI and capture zone based on LNAPL drawdown.
	Performance and optimization metrics	LNAPL recovery rates and volumes	Basic system performance monitoring.
		System uptime vs. downtime	
		LNAPL recovery vs. groundwater recovery	Quantity of LNAPL recovered as a percentage of incidental recovered groundwater.
		Total LNAPL equivalent recovery cost metric	Cost per gallon of LNAPL recovered.
Modeling tools/ applicable models		Projected future LNAPL recovery	Use of decline curve analysis, semi-log plots, etc. to predict future LNAPL recoveries and help determine when LNAPL recovery is approaching asymptotic.
Further information		EPA. 1996. *How to Effectively Recover Free Product at Leaking Underground Storage Tank Sites: A Guide for State Regulators.* Office of Underground Storage Tanks. EPA 510-R-96-001. www.epa.gov/oust/pubs/fprg.htm	
		EPA. 1994. *How To Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites: A Guide for Corrective Action Plan Reviewers*. EPA 510-B-94-003. www.epa.gov/oust/pubs/tums.htm	

Table A-7.A. Bioslurping/enhanced fluid recovery

Technology	Bioslurping/ enhanced fluid recovery	Bioslurping/EFR reduces LNAPL saturations in subsurface through applied vacuum in conjunction with up to two pumps (e.g., a vacuum with a downhole stinger tube or vacuum applied in conjunction with a positive-displacement pump). LNAPL is primarily removed as a liquid, but bioslurping/EFR also removes LNAPL through volatilization and aerobic biodegradation with an applied vacuum.	
Remediation process	Physical mass recovery	Yes (primary)	1. Bioslurping/EFR removes liquid LNAPL from saturated zone and perched LNAPL zones. 2. Induced vacuum extracts LNAPL vapors from unsaturated zone and capillary fringe.
	Phase change	Yes (secondary)	The EFR-induced vacuum volatilizes and evaporates the LNAPL.
	In situ destruction	Yes (secondary)	Infiltration of oxygenated air from the surface enhances in situ aerobic biodegradation of the LNAPL.
	Stabilization/ binding	No	
Objective applicability	LNAPL saturation	Yes	Bioslurping/EFR reduces LNAPL saturations.
		Example performance metrics	Direct analysis of soil to measure changes in LNAPL saturation; direct measurement of LNAPL thickness reduction in wells, reduced LNAPL transmissivity/LNAPL conductivity, LNAPL-to-water ratio for a given vacuum induced, asymptotic recovery of a well operated and maintained system, dissolved-phase stability, and LNAPL plume monitoring.
	LNAPL composition	Yes	Bioslurping/EFR reduces the volatile constituent fraction of the LNAPL. Volatilization loss and likely also the soluble fraction of the LNAPL. Aerobic degradation reduces LNAPL concentrations of degradable compounds in dissolved phase and drives preferential dissolution of those compounds from LNAPL. More volatilization occurs closer to the well(s) than at greater distance.
		Example performance metrics	Removal of VOC concentrations in extracted vapor to a concentration end point (e.g., 1 ppm-v), reduced dissolved-phase concentrations to regulatory standard at compliance point.
Applicable LNAPL type	All LNAPL types, although better suited to less viscous LNAPLs (e.g., gasoline, kerosene).		
Geologic factors	Unsaturated zone	Permeability	More effective in higher-permeability materials where gas-phase flow is easier but can also be applied in lower-permeability materials through the use of stronger vacuum.
		Grain size	More applicable to sands and gravels but can also be applied in silts and clays.
		Heterogeneity	In heterogeneous soils, vacuum extracts LNAPL from preferential pathways, possibly short-circuiting remediation coverage, but LNAPL is often also in preferential pathways.
		Consolidation	Not typically a factor.
	Saturated zone	Permeability	Can achieve faster LNAPL removal and lower LNAPL saturations in higher-permeability materials.
		Grain size	More applicable to sands and gravels but can also be applied in silts and clays.
		Heterogeneity	Fractured bedrock and more permeable zones will induce preferential flow. More applicable to perched LNAPL and unconfined LNAPL due to unsaturated zone exhibiting impacts and equivalent or higher permeability than saturated zone. Less applicable to confined conditions because the benefits of the applied vacuum are limited, although vapor treatment may still be necessary. The ratio of vacuum induced drawdown to water production–induced drawdown can be optimized for the given hydrogeologic scenario (e.g., perched LNAPL would require little to no water production, focusing the vacuum enhancement on the LNAPL recovery).
		Consolidation	Not typically a factor.

Table A-7.B. Evaluation factors for bioslurping/enhanced fluid recovery

Technology: Bioslurping/enhanced fluid recovery		
Remedial time frame	Concern	High to very high
	Discussion	Long to very long. Depends on soil type, LNAPL type, release size, footprint, and end point (e.g., LNAPL thickness, sheen, or transmissivity goal) and aggressiveness of pumping. Low-permeability soils and heavier LNAPL will require more time to remediate.
Safety	Concern	Low
	Discussion	Vapor releases and potential of volatilization due to vacuum operations.
Waste management	Concern	Moderate
	Discussion	Recovered fluids require treatment and LNAPL should be recycled. Can have an LNAPL/water/air emulsion that is difficult to break.
Community concerns	Concern	Low to medium
	Discussion	Concern with noise of treatment equipment and vapor releases from vacuum truck.
Carbon footprint/energy requirements	Concern	Low to moderate
	Discussion	Carbon footprint depends on time frame, duration, frequency of events, and the amount of volatiles generated. Energy source needed for vacuum.
Site restrictions	Concern	Low to moderate
	Discussion	Bioslurping/EFR can usually be implemented in wells located around site restrictions or in wells under obstructions through the use of directional drilling equipment.
LNAPL body size	Concern	Moderate to high
	Discussion	The size of the LNAPL body directly affects the cost and extent of the well network required to implemented bioslurping/EFR. ROI affects the number of wells required to address the LNAPL Body. Lower-permeability soils require closer well spacing. Intermittent operation may enhance overall recovery after initial saturation asymptote is reached.
Other regulations	Concern	Low
	Discussion	
Cost	Concern	Low to moderate
	Discussion	Overall, low for capital costs and low to medium for operation and maintenance, depending on life span of the project. In general, bioslurping/EFR are more cost-effective than other active LNAPL technologies and have been proven at many sites for over 20 years. Longer time frames may, however, not be cost-effective compared to other technologies.
Other	Concern	
	Discussion	

Table A-7.C. Technical implementation considerations for bioslurping/EFR

Data requirements	Site-specific data for technology evaluation	Hydraulic conductivity (K_w), transmissivity (T_w)	Hydraulic conductivity and transmissivity determine the appropriate groundwater extraction rate that may be sustained by the groundwater pump. Formations with low conductivities/ transmissivities may require the use of low-flow pneumatic pumps, as opposed to higher-flow submersible pumps.
		LNAPL conductivity (K_{LNAPL}), LNAPL transmissivity (T_{LNAPL})	LNAPL conductivity and transmissivity determine the LNAPL extraction rate that may be sustained by the LNAPL pump. These data may be obtained from LNAPL baildown tests or from predictive modeling.
		LNAPL characteristics ($LNAPL_c$)	Low-viscosity LNAPLs are more amenable to pumping than higher-viscosity LNAPLs.
		Soil type/grain size	Granular soils (sands and gravels) experience higher airflows with lower operating vacuums. Fine-grained soils (silts and clays) experience lower airflows with higher operating vacuums.
		Safety precautions	
		Available power/utilities	
	Bench-scale testing	N/A	
	Pilot-scale testing	Groundwater ROI/ROC	Establish groundwater ROI/capture for different groundwater pumping rates and determine acceptable pumping rate that may be sustained without creating unacceptable drawdown.
		LNAPL ROI/ROC	Establish LNAPL ROI/capture for different LNAPL pumping rates.
		Groundwater recovery rate, volume, and influent concentrations	Determine groundwater recovery rate, volume, and influent concentrations to assist with design of water handling, treatment, and discharge options.
		LNAPL recovery rate, volume, chemical characteristics	Determine LNAPL recovery rate, volume, and chemical characteristics to assist with design of LNAPL storage, handling, and treatment/discharge options.
		Airflow and vacuum	Determine system airflow and vacuum and individual extraction wellhead airflows and vacuums.
		Induced vacuum ROI	Determine vacuum ROI by measuring induced vacuums on adjacent monitoring wells.
		Influent vapor concentrations	Assess influent vapor concentrations and system airflow rates to determine potential off-gas treatment requirements/permitting issues and to calculate vapor-phase LNAPL recovery.
	Full-scale design	Number of extraction wells	Determine number of extraction wells required to achieve adequate zone of LNAPL recovery consistent with LNAPL site objective(s).
		Conveyance piping	Determine locations, lengths, and materials for all horizontal conveyance piping to/from recovery/treatment system. Assess pipe insulation and heat tracing needs for winter conditions, if applicable.
		Groundwater ROI/ROC	
		LNAPL ROI/ROC	
		Vacuum losses	Calculate potential vacuum losses due to conveyance pipe diameters, lengths, materials. Try to minimize losses between system and wellheads.
		Air permitting/off-gas treatment issues	Assess and design for air permitting and/or off-gas treatment requirements.
	Performance metrics	Groundwater/LNAPL recovery rates and volumes	Basic system performance monitoring.
		System uptime vs. downtime	
		Cumulative groundwater/ LNAPL recovery	
		LNAPL recovery vs. groundwater recovery	Quantity of LNAPL recovered as a percentage of recovered groundwater.
		Vapor-phase LNAPL recovery	
		Total LNAPL equivalent recovery cost metric	Cost per gallon of LNAPL recovered.

Table A-7.C. continued

Modeling tools/ applicable models	Projected future LNAPL recovery	Use of decline curve analysis, semi-log plots, etc. to predict future LNAPL recoveries and help determine when LNAPL recovery is approaching asymptotic.
Further information	Ground-Water Remediation Technologies Analysis Center. 1996. *Bioslurping Technology Overview Report*. TO-96-05. http://clu-in.org/download/toolkit/slurp_o.pdf	
	Naval Facilities Engineering Service Center. 1996. *Best Practice Manual for Bioslurping*. https://portal.navfac.navy.mil/portal/page/portal/navfac/navfac_ww_pp/navfac_nfesc_pp/environmental/erb/bioslurp-old/bestprac.pdf	
	AFCEE. "Bioslurping." www.afcee.af.mil/resources/technologytransfer/programsandinitiatives/bioslurping/index.asp	
	NAVFAC. 1998. *Application Guide for Bioslurping. Volume 1: Summary of the Principles and Practices of Bioslurping*. NFESC TM-2300-ENV. https://portal.navfac.navy.mil/portal/page/portal/navfac/navfac_ww_pp/navfac_nfesc_pp/environmental/erb/resourceerb/tm-2300.pdf	
	NAVFAC. 1998. *Application Guide for Bioslurping. Volume II: Principles and Practices of Bioslurping*. NFSEC TM-2301-ENV https://portal.navfac.navy.mil/portal/page/portal/navfac/navfac_ww_pp/navfac_nfesc_pp/environmental/erb/resourceerb/tm-2301.pdf	
	EPA. 1996. *How to Effectively Recover Free Product at Leaking Underground Storage Tank Sites: A Guide for State Regulators.* EPA 510-R-96-001. www.epa.gov/oust/pubs/fprg.htm	

Table A-8.A. Dual-pump liquid extraction

Technology	Dual-pump liquid extraction	LNAPL recovered using two pumps (one dedicated to removing LNAPL and one dedicated to remove groundwater). The groundwater pump creates a cone of depression that induces LNAPL flow into the well through an increased hydraulic gradient. The LNAPL pump then recovers the LNAPL as it accumulates in the well. The LNAPL pump can be a bladder pump, pneumatic pump, or belt skimmer that extracts LNAPL only via a floating inlet at the air/LNAPL interface, while the groundwater pump is typically a submersible positive displacement pump. Each phase (LNAPL, groundwater) is typically treated separately.	
Remediation process	Physical mass recovery	Yes	Removes mobile LNAPL with a capture zone dictated by the cone of groundwater depression; does not affect residual LNAPL mass.
	Phase change	No	N/A. LNAPL remains in original liquid phase.
	In situ destruction	No	N/A
	Stabilization/ binding	No	N/A
Objective applicability	LNAPL saturation	Yes	LNAPL recovery reduces LNAPL saturation toward residual saturation; does not typically improve dissolved-phase concentrations due to residual LNAPL mass left behind.
		Example performance metrics	Direct analysis of soil to indicate changes in formation LNAPL saturations; LNAPL transmissivity/LNAPL conductivity, LNAPL/water ratio, asymptotic recovery of a well-operated and -maintained system.
	LNAPL composition	No	N/A. Skimming recovers LNAPL as a fluid and does exploit volatilization or dissolution, so it does not lead to a compositional change.
		Example performance metrics	N/A
Applicable LNAPL type	All LNAPL types; however, lower-viscosity LNAPL (0.5–1.5 cP) is much more recoverable than high-viscosity LNAPL (>6 cP).		
Geologic factors	Unsaturated zone	Permeability	Technology is not applicable to LNAPL in the unsaturated zone.
		Grain size	
		Heterogeneity	
		Consolidation	
	Saturated zone	Permeability	Soil permeability is proportional to LNAPL recovery rate—higher LNAPL recovery and saturation reduction in higher-permeability soils; permeability affects the ROI of a recovery well. A second key factor is the ratio between LNAPL transmissivity to aquifer transmissivity; low-conductivity materials (K_w <10^{-6} cm/sec) may experience poor total fluid recovery.
		Grain size	LNAPL within fine-grained soils may not be feasible to remove by DPLE.

Table A-8.B. Evaluation factors for dual-pump liquid extraction

Technology: Dual-pump liquid extraction		
Remedial time frame	Concern	Moderate
	Discussion	Medium. Depends on soil type, LNAPL type, release size, footprint, and end point (e.g., LNAPL thickness, sheen, or oil transmissivity goal). Low-permeability soils and heavier LNAPL require more time to remediate.
Safety	Concern	Moderate
	Discussion	There may electrical concerns with a submersible pump in a well with LNAPL and confined-space entry issues with access to well vaults.
Waste management	Concern	Moderate
	Discussion	Recovered LNAPL and groundwater water need to be properly disposed. LNAPL should be recycled. Need construction of wastewater treatment.
Community concerns	Concern	Low to moderate
	Discussion	Concern with noise, potential odors, and volatile emissions.
Carbon footprint/energy requirements	Concern	Moderate
	Discussion	Remediation runs continuously or cycles.
Site restrictions	Concern	Moderate
	Discussion	Typically all equipment is in a compound and piping is below ground. Equipment typically can be deployed to accommodate many site restrictions.
LNAPL body size	Concern	Low
	Discussion	Capable of remediating large and small LNAPL plumes. Lithology and permeability determine the spacing between recovery wells.
Other regulations	Concern	High
	Discussion	May need permits for discharge of water.
Cost	Concern	Moderate
	Discussion	Capital costs are higher than skimmer pumps, and operation and maintenance are much higher to maintain the system potentially for a shorter time frame.
Other	Concern	
	Discussion	

Table A-8.C. Technical implementation considerations for dual-pump liquid extraction

Data requirements	Site-specific data for technology evaluation	Hydraulic conductivity (K_w), transmissivity (T_w)	Hydraulic conductivity and transmissivity data help determine the appropriate groundwater extraction rate that may be sustained by the groundwater pump. These data may be obtained from slug tests or groundwater pumping tests or from predictive modeling. Relatively tight formations with low-conductivity/transmissivity soils may require the use of low-flow pneumatic pumps, as opposed to higher-flow submersible pumps.
		LNAPL conductivity (K_{LNAPL}), LNAPL transmissivity (T_{LNAPL})	LNAPL transmissivity data indicate the LNAPL extraction rate. Transmissivity data may be obtained from LNAPL baildown tests or predictive modeling.
		LNAPL characteristics ($LNAPL_c$)	Low-viscosity LNAPLs are more amenable to pumping than higher-viscosity LNAPLs. Hence, lighter-end, low-viscosity LNAPL such as gasoline, kerosene, jet fuel, diesel and No. 2 fuel oil are more amenable to DPLE than a No. 6 fuel oil or Bunker C.
		Soil type/grain size	Coarser-grained, more-homogeneous soils allow larger ROI to develop. Finer-grained soil interbeds impede or lessen capture.
		Safety precautions	Explosivity of LNAPL—potential need for bonding and grounding of metal equipment/containers and other associated safety requirements.
		Available power/utilities	The power source must be determined. Drop-line power may be readily available. Alternatively, on-site sources such as generators or solar power may be needed. Power supply must be compatible with skimmer pump demand.
	Bench-scale testing	N/A	
	Pilot-scale testing	Groundwater ROI/ROC	Establish groundwater ROI/ROC for different groundwater pumping rates. For continuous pumping systems, determine acceptable pumping rate that may be sustained for design groundwater drawdown.
		LNAPL ROI/ROC	Establish LNAPL capture for different LNAPL pumping rates. For continuous pumping systems, determine acceptable pumping rate that may be sustained without creating unacceptable drawdown.
		Groundwater recovery rate, volume, and influent concentrations	Determine groundwater recovery rate, volume, and influent concentrations to assist with design of water handling, treatment, and discharge options.
		LNAPL recovery rate, volume and chemical characteristics	Determine LNAPL recovery rate, volume and chemical characteristics to assist with design of LNAPL storage, handling, treatment, and discharge options.
	Full-scale design	Number of extraction wells	Determine number of required DPLE wells necessary to achieve adequate zone of LNAPL recovery consistent with LNAPL site objective(s).
		Conveyance piping	Determine locations, lengths, materials for all horizontal conveyance piping to/from DPLE wells to/from recovery/treatment system. Assess pipe insulation and heat tracing needs for winter conditions, if applicable.
		Groundwater ROC	Establish groundwater capture for different groundwater pumping rates. For continuous pumping systems, determine acceptable pumping rate that may be sustained without creating unacceptable drawdown.
		LNAPL ROC	Establish LNAPL capture for different LNAPL pumping rates. For continuous pumping systems, determine acceptable pumping rate that may be sustained without creating unacceptable drawdown.

Table A-8.C. continued

Data requirements (cont.)	Performance metrics	Groundwater/LNAPL recovery rates and volume	Basic system performance monitoring
		System uptime vs. downtime	
		Cumulative groundwater/LNAPL recovery	
		LNAPL recovery vs. groundwater recovery	LNAPL/water ratio
		LNAPL recovery cost metric	Cost per gallon of LNAPL recovered
		LNAPL thickness	
		Mass removed	
Modeling tools/ applicable models		API LDRM	
Further information		EPA. 2005. *Cost and Performance Report for LNAPL Recovery: Multi-Phase Extraction and Dual-Pump Recovery of LNAPL at the BP Former Amoco Refinery, Sugar Creek, MO*. EPA-542-R-05-016.	
		API. 1999. *Free-Product Recovery of Petroleum Hydrocarbon Liquids*. API PUBL 4682.	
		EPA. 1996. *How to Effectively Recover Free Product at Leaking Underground Storage Tank Sites: A Guide for State Regulators.* EPA 510-R-96-001. www.epa.gov/oust/pubs/fprg.htm	

Table A-9.A. Multiphase extraction (dual pump)

Technology	Multi-phase extraction (dual pump)	MPE technology employs vacuum-enhancement as well as two dedicated pumps to extract liquids (LNAPL through a bladder pump, pneumatic pump, or belt skimmer and groundwater typically through a positive-displacement submersible pump) from an extraction well simultaneously. It can also be known as total fluids excavation or vacuum-enhanced, dual-phase extraction. One dedicated pump targets LNAPL located at the groundwater surface; the second pump enhances LNAPL recovery with groundwater extraction, as well as vacuum enhancement at the wellhead. The groundwater extraction induces additional drawdown into the well over and beyond what skimming alone can induce. Because each fluid is recovered by an exclusive pump, emulsification of LNAPL is limited to that which may occur in the formation as a result of LNAPL weathering and dissolved-phase impacts within groundwater. MPE using dual pumps and vacuum enhancement is more applicable to cases where LNAPL is recovered at a rate sufficient to require the continuous operation of a dedicated LNAPL pump or where minimization of emulsification is desired and cycling of the LNAPL recovery pump is feasible. The cycling of the LNAPL pump allows LNAPL exhibiting lower recovery rates to build up substantial LNAPL thickness in the well, which can then be pumped off during a pump cycle.	
Remediation process	Physical mass recovery	Yes	Removes mobile LNAPL at the groundwater surface.
	Phase change	No	Vacuum induces volatilization, which changes the LNAPL constituent composition.
	In situ destruction	No	N/A
	Stabilization/ binding	No	N/A
Objective applicability	LNAPL saturation	Yes	LNAPL recovery reduces LNAPL saturation toward residual saturation; does not typically improve dissolved-phase concentrations due to residual LNAPL mass left behind.
		Example performance metrics	Direct analysis of soil to indicate changes in formation LNAPL saturations, LNAPL transmissivity/LNAPL conductivity, LNAPL/water ratio, asymptotic recovery of a well-operated and -maintained system.
	LNAPL composition	Yes	Yes
		Example performance metrics	Removal of VOC concentrations in extracted vapor to a concentration end point (e.g., 1 ppm-v); vapor-phase or dissolved-phase concentrations meet regulatory standard at compliance point; reduced volatile or soluble LNAPL constituent mass fraction.
Applicable LNAPL type	All LNAPL types; however, lower-viscosity LNAPL (0.5–1.5 cP) is much more recoverable than high-viscosity LNAPL (>6 cP).		
Geologic factors	Unsaturated zone	Technology is not applicable to LNAPL in the unsaturated zone.	
	Saturated zone	Permeability	Soil permeability is proportional to LNAPL recovery rate; higher LNAPL recovery and saturation reduction in higher-permeability soils. Permeability affects the ROI of a recovery well. A low-permeability setting maximizes drawdown, exposing the LNAPL smear zone for LNAPL recovery via vapor extraction, and reduced groundwater recovery minimizes groundwater treatment costs. The higher the permeability (or conductivity), the greater the water production will be to dewater the smear zone.
		Grain size	LNAPL in fine-grained soils may not be feasible to remove by MPE.
		Heterogeneity	Moderately sensitive to heterogeneity; affects the ROI of a recovery well. Focuses on LNAPL at the groundwater surface and LNAPL that can drain with a depressed groundwater surface. MPE is not applicable to thin, perched LNAPL layers, from which drawdown is limited; moderately applicable to unconfined LNAPL conditions; however, in low-permeability settings, smearing could occur due to excessive drawdowns. Excellent applicability for confined LNAPL since little to no additional smearing will occur. Well screen location and submersible pump depth can help overcome heterogeneities.
		Consolidation	Not typically a factor.

Table A-9.A. continued

Cost	Per well, the capital costs of MPE dual-pump wells are higher than skimming but lower than DPLE wells and bioslurping/EFR. Fewer wells are required to achieve the same goal within the same time frame as skimming.

Table A-9.B. Evaluation factors for multiphase extraction (dual pump)

Technology: Multiphase extraction (dual pump)		
Remedial time frame	Concern	Moderate
	Discussion	Medium. Depends on soil type, LNAPL type, release size, footprint, and end point (e.g., LNAPL thickness, sheen, or oil transmissivity goal). Low-permeability soils and heavier LNAPL require more time to remediate.
Safety	Concern	Moderate
	Discussion	The remediation equipment is either placed in a compound or trailer mounted. There are moving parts, piping under pressure and vacuum, and potential for vapor accumulation in remediation trailers.
Waste management	Concern	Moderate
	Discussion	Recovered LNAPL and water need to be properly recycled or disposed. Recovered vapors have to be managed or destroyed.
Community concerns	Concern	Moderate
	Discussion	Although equipment is usually out of sight, there is a potential for concerns with noise, potential odors, volatile emissions, aesthetic, and access issues.
Carbon footprint/energy requirements	Concern	Moderate
	Discussion	Remediation runs continuously or cycles. Little recovered vapors that need treatment.
Site restrictions	Concern	Moderate
	Discussion	Typically all equipment is in a compound and piping is below ground. Equipment can typically be deployed in manner to accommodate many site restrictions. Power needs to be supplied to the system, and produced water needs treatment.
LNAPL body size	Concern	High
	Discussion	The size of the LNAPL body directly affects the cost and extent of the well network required to implement MPE. MPE ROI affects the number of wells required to address the LNAPL body.
Other regulations	Concern	Moderate
	Discussion	May need permits to discharge water and vapors.
Cost	Concern	Moderate
	Discussion	Capital costs are higher than skimmer pumps, and operation and maintenance are much higher to maintain the system potentially for a shorter time frame.
Other	Concern	
	Discussion	

Table A-9.C. Technical implementation considerations for multiphase extraction (dual pump)

Data requirements	Site-specific data for technology evaluation	Hydraulic conductivity (K_w), transmissivity (T_w)	Hydraulic conductivity and transmissivity data help determine the appropriate groundwater extraction rate that may be sustained by the groundwater pump. These data may be obtained from slug tests, groundwater pumping tests, or predictive modeling. Relatively tight formations with low-conductivity/transmissivity soils may require the use of low-flow pneumatic pumps, as opposed to higher-flow submersible pumps.
		LNAPL conductivity (K_{LNAPL}), LNAPL transmissivity (T_{LNAPL})	LNAPL conductivity and transmissivity data help determine the appropriate LNAPL extraction rate that may be sustained by the LNAPL pump. These data may be obtained from LNAPL baildown tests, pumping tests, or predictive modeling. Relatively tight formations or sites with low LNAPL transmissivity/LNAPL conductivity may require the use of low-flow pneumatic pumps, as opposed to higher-flow submersible pumps.
		LNAPL characteristics ($LNAPL_c$)	Low-viscosity LNAPLs are more amenable to pumping than higher viscosity LNAPLs. Hence, lighter-end, low-viscosity LNAPL such as gasoline, kerosene, jet fuel, diesel and No. 2 fuel oil are more amenable to MPE than a No. 6 fuel oil or Bunker C.
		Soil permeability (to air, e.g., in unsaturated zone) (k_{soil})	Permeability to air in the unsaturated zone directly affects the radius of treatment that can be developed around each SVE well for a given vapor extraction rate. Lower-permeability soils require more SVE wells per unit area.
		Safety precautions	Explosivity of LNAPL—potential need for bonding and grounding of metal equipment/containers and other associated safety requirements.
		Available power/utilities	System needs three-phase power.
	Bench-scale testing	N/A	
	Pilot-scale testing	Groundwater ROC	Establish groundwater ROI/ROC for different groundwater pumping rates. For continuous pumping systems, determine acceptable pumping rate that may be sustained for design groundwater drawdown.
		LNAPL ROC	Establish LNAPL ROI/ROC for different LNAPL pumping rates. For continuous pumping systems, determine acceptable pumping rate that may be sustained without creating unacceptable drawdown.
		Groundwater recovery rate, volume, and influent concentrations	Determine groundwater recovery rate, volume, and influent concentrations to assist with design of water handling, treatment, and discharge options.
		LNAPL recovery rate, volume, and chemical characteristics	Determine LNAPL recovery rate, volume, and chemical characteristics to assist with design of LNAPL storage, handling, treatment, and discharge options.
		Vacuum and flow	Blower sizing
		Vacuum ROI	Well spacing
		Vacuum influent concentration	Treatment system type and sizing
	Full-scale design	Number of extraction wells	Determine number of required MPE wells necessary to achieve adequate zone of LNAPL recovery consistent with LNAPL site objective(s).
		Conveyance piping	Determine locations, lengths, materials for all horizontal conveyance piping to/from MPE wells to/from recovery/treatment system. Assess pipe insulation and heat tracing needs for winter conditions, if applicable.
		Groundwater ROC	Establish groundwater ROI/ROC for different groundwater pumping rates. For continuous pumping systems, determine acceptable pumping rate that may be sustained without creating unacceptable drawdown.
		LNAPL ROC	Establish LNAPL ROI/ROC for different LNAPL pumping rates. For continuous pumping systems, determine acceptable pumping rate that may be sustained without creating unacceptable drawdown.

Table A-9.C. continued

Data requirements (cont.)	Performance metrics	Groundwater/LNAPL recovery rates and volumes	Basic system performance monitoring
		System uptime vs. downtime	
		Cumulative groundwater/LNAPL recovery	
		LNAPL recovery vs. groundwater recovery	LNAPL/water ratio
		LNAPL recovery cost metric	Cost per gallon of LNAPL recovered
Modeling tools/ applicable models		Projected future LNAPL recovery	Use of decline curve analysis, semi-log plots, etc. to predict future LNAPL recoveries and help determine when LNAPL recovery is approaching asymptotic.
Further information		FRTR. n.d. "Remedial Technology Screening and Reference Guide, Version 4.0, Dual Phase Extraction." www.frtr.gov/matrix2/section4/4-37.html	
		EPA. 1996. *How to Effectively Recover Free Product at Leaking Underground Storage Tank Sites: A Guide for State Regulators.* EPA 510-R-96-001. www.epa.gov/oust/pubs/fprg.htm	
		EPA. 1995. *How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites: A Guide for Corrective Action Plan Reviewers,* Chap. 11, "Dual-Phase Extraction." EPA 510-R-04-002. www.epa.gov/swerust1/pubs/tum_ch11.pdf	
		API. 1999. *Free-Product Recovery of Petroleum Hydrocarbon Liquids*. API PUBL 4682.	
		EPA. 1997. *Presumptive Remedy: Supplemental Bulletin Multi-Phase Extraction (MPE) Technology for VOCs in Soil and Groundwater*. EPA-540-F-97-004. www.epa.gov/superfund/health/conmedia/gwdocs/voc/index.htm	
		USACE. 1999. *Engineering and Design: Multi-Phase Extraction*. EM 1110-1-4010. http://140.194.76.129/publications/eng-manuals/em1110-1-4010/toc.htm	
		EPA. 1999. *Multi-Phase Extraction. State of the Practice*. EPA 542-R-99-004. http://clu-in.org/download/remed/mpe2.pdf	
		EPA. n.d. "Technology Focus: Multi-Phase Extraction Overview." http://clu-in.org/techfocus/default.focus/sec/Multi%2DPhase%5FExtraction/cat/Overview	

Table A-10.A. Multiphase extraction (single pump)

Technology	Multiphase extraction (single pump)	MPE single-pump technology employs a single pump to extract fluids (e.g., a downhole pneumatic pump that removes groundwater and LNAPL, or a high-vacuum stinger tube to remove groundwater, LNAPL, and vapor) from an extraction well. MPE induces additional drawdown into the well over and beyond what skimming alone can induce. This additional drawdown in turn results in increased LNAPL recovery. MPE may emulsify LNAPL and requires LNAPL/water separation. MPE usually involves lower capital than DPLE. MPE becomes more favorable than DPLE when aboveground LNAPL/water treatment is feasible, LNAPL thicknesses are low, and LNAPL-to-water production ratios are low (e.g., <1:500).	
Remediation process	Physical mass recovery	Yes	Removes LNAPL at the groundwater surface; does not generally affect residual LNAPL mass.
	Phase change	No	Vacuum induces volatilization, which changes the LNAPL constituent composition.
	In situ destruction	No	N/A
	Stabilization/binding	No	N/A
Objective applicability	LNAPL saturation	Yes	LNAPL recovery reduces LNAPL saturation toward residual saturation; does not typically improve dissolved-phase concentrations due to residual LNAPL mass left behind.
		Example performance metrics	Direct analysis of soil to indicate changes in formation LNAPL saturations, LNAPL transmissivity, LNAPL transmissivity/LNAPL conductivity, LNAPL-to-water ratio, asymptotic recovery of a well-operated and -maintained system.
	LNAPL composition	Yes	
		Example performance metrics	Removal of VOC concentrations in extracted vapor to a concentration end point (e.g., 1 ppm-v); vapor-phase or dissolved-phase concentrations meet regulatory standard at compliance point; reduced volatile or soluble LNAPL constituent mass fraction.
Applicable LNAPL type	All LNAPL types; however, lower-viscosity LNAPL (0.5–1.5 cP) is much more recoverable than high-viscosity LNAPL (>6 cP).		
Geologic factors	Unsaturated zone	Technology is not applicable to LNAPL in the unsaturated zone.	
	Saturated zone	Permeability	A low-permeability setting maximizes drawdown, exposing the LNAPL smear zone for LNAPL recovery via vapor extraction, and reduced groundwater recovery minimizes groundwater treatment costs. The higher the permeability (or conductivity), the greater the water production is to dewater the smear zone.
		Grain size	LNAPL within fine-grained soils may not be feasible to remove by MPE.
		Heterogeneity	Moderately sensitive to heterogeneity; affects the ROI of a recovery well. Focuses on LNAPL at the groundwater surface and LNAPL that can drain with a depressed groundwater surface. MPE is not applicable to thin, perched LNAPL layers, from which drawdown is limited; moderately applicable to unconfined LNAPL conditions; however, additional LNAPL smearing could occur due to excessive drawdowns. Excellent applicability for confined LNAPL conditions since little to no additional smearing occurs. Well screen location and submersible pump depth can help overcome heterogeneities.
		Consolidation	Not typically a factor
Cost	Per well, the capital costs of MPE wells are higher than those of active skimming but lower than those of DPLE and bioslurping/EFR. Fewer wells are required to achieve the same goal within the same time frame as skimming. The costs of aboveground oil/water separation should be considered over and above the dual-pump aboveground fluid treatment.		

Table A-10.B. Evaluation factors for multiphase extraction

Technology: Multiphase extraction (single pump)		
Remedial time frame	Concern	Moderate
	Discussion	Medium. Depends on soil type, LNAPL type, release size, footprint, and end point (e.g., LNAPL thickness, sheen, or oil transmissivity goal). Low-permeability soils and heavier LNAPL require more time to remediate.
Safety	Concern	Moderate
	Discussion	The remediation equipment is either placed in a compound or trailer mounted. There are moving parts, piping under pressure and vacuum, and potential for vapor accumulation in remediation trailers.
Waste management	Concern	Moderate to high
	Discussion	Recovered LNAPL and water need to be properly disposed. Recovered vapors have to be managed or destroyed. LNAPL/water/air emulsion may be difficult to break and manage.
Community concerns	Concern	Moderate
	Discussion	Although, equipment is usually out of sight, there is a potential for concerns with noise, potential odors, volatile emissions, aesthetic, and access issues.
Carbon footprint/energy requirements	Concern	Moderate
	Discussion	Remediation runs continuously or cycles. Little off-gas needs treatment.
Site restrictions	Concern	Moderate
	Discussion	Typically, all equipment is in a compound, and piping is below ground. Equipment can typically be deployed in manner to accommodate many site restrictions. Power needs to be supplied to the system, and produced water needs treatment.
LNAPL body size	Concern	High
	Discussion	The size of the LNAPL body directly affects the cost and extent of the well network required to implement MPE. MPE ROI affects the number of wells required to address the LNAPL body.
Other regulations	Concern	Moderate
	Discussion	May need a permit to discharge water and vapor.
Cost	Concern	Moderate
	Discussion	Capital costs are higher than skimmer pumps, and operation and maintenance are much higher to maintain the system.
Other	Concern	
	Discussion	

Table A-10.C. Technical implementation considerations for multiphase extraction (single pump)

Data requirements	Site-specific data for technology evaluation	Hydraulic conductivity (K_w), transmissivity (T_w)	Hydraulic conductivity and transmissivity data help determine the appropriate groundwater extraction rate that may be sustained by the single pump. These data may be obtained from slug tests, groundwater pumping tests, or predictive modeling. Relatively tight formations with low-conductivity/transmissivity soils may require the use of low-flow pneumatic pumps, as opposed to higher-flow submersible pumps.
		LNAPL conductivity (K_{LNAPL}), LNAPL transmissivity (T_{LNAPL})	LNAPL conductivity and transmissivity data help determine the appropriate LNAPL extraction rate that may be sustained by the single pump. These data may be obtained from LNAPL baildown tests, pumping tests, or predictive modeling. Relatively tight formations or sites with low LNAPL conductivity/transmissivity may require the use of low-flow pneumatic pumps, as opposed to higher-flow submersible pumps.
		LNAPL characteristics ($LNAPL_c$)	Low-viscosity LNAPLs are more amenable to pumping than higher-viscosity LNAPLs. Hence, lighter-end, low-viscosity LNAPL such as gasoline, kerosene, jet fuel, diesel and No. 2 fuel oil are more amenable to MPE than a No. 6 fuel oil or Bunker C.
		Soil permeability (to air, e.g., in unsaturated zone) (k_{soil})	Permeability to air in the unsaturated zone directly affects the radius of treatment that can be developed around each SVE well for a given vapor extraction rate. Lower-permeability soils require more SVE wells per unit area.
		Safety precautions	Explosivity of LNAPL—potential need for bonding and grounding of metal equipment/containers and other associated safety requirements.
		Available power/utilities	
	Bench-scale testing	N/A	
	Pilot-scale testing	Groundwater ROI/ROC	Establish groundwater ROI/ROC for different groundwater pumping rates. For continuous pumping systems, determine acceptable pumping rate that may be sustained without creating unacceptable drawdown.
		LNAPL ROI/ROC	Establish LNAPL ROI/ROC for different LNAPL pumping rates. For continuous pumping systems, determine acceptable pumping rate that may be sustained without creating unacceptable drawdown.
		Groundwater recovery rate, volume, and influent concentrations	Determine groundwater recovery rate, volume, and influent concentrations to assist with design of water handling, treatment, and discharge options.
		LNAPL recovery rate, volume, and chemical characteristics	Determine LNAPL recovery rate, volume, and chemical characteristics to assist with design of LNAPL storage, handling, treatment, and discharge options.
		LNAPL emulsification issues	Determine level of emulsification occurring, feasibility of LNAPL/water separation, required residence time for LNAPL/water separation.
		Vacuum and flow	Blower sizing
		Vacuum ROI	Well spacing
		Vacuum influent concentration	Treatment system type and sizing
	Full-scale design	Number of extraction wells	Determine number of MPE wells required to achieve adequate zone of LNAPL recovery consistent with LNAPL site objective(s).
		Conveyance piping	Determine locations, lengths, materials for all horizontal conveyance piping to/from MPE wells to/from recovery/treatment system. Assess pipe insulation and heat tracing needs for winter conditions, if applicable.
		Groundwater ROI/ROC	Establish groundwater ROI/ROC for different groundwater pumping rates. For continuous pumping systems, determine acceptable pumping rate that may be sustained for design groundwater drawdown.
		LNAPL ROI/ROC	Establish LNAPL ROI/capture for different LNAPL pumping rates. For continuous pumping systems, determine acceptable pumping rate that may be sustained without creating unacceptable drawdown.
		LNAPL emulsification issues	Determine level of emulsification occurring, feasibility of LNAPL/water separation, required residence time for LNAPL/water separation.

Table A-10.C. continued

Data requirements (cont.)	Performance metrics	Groundwater/LNAPL recovery rates and volumes	Basic system performance monitoring
		System uptime vs. downtime	
		Cumulative groundwater/LNAPL recovery	
		LNAPL recovery vs. groundwater recovery	Quantity of LNAPL recovered as a percentage of recovered groundwater
		LNAPL recovery cost metric	Cost per gallon of LNAPL recovered
Modeling tools/ applicable models		Projected future LNAPL recovery	Use of decline curve analysis, semi-log plots, etc. to predict future LNAPL recoveries and help determine when LNAPL recovery is approaching asymptotic.
Further information		FRTR. n.d. "Remedial Technology Screening and Reference Guide, Version 4.0, Dual Phase Extraction." www.frtr.gov/matrix2/section4/4-37.html	
		EPA. 1996. *How to Effectively Recover Free Product at Leaking Underground Storage Tank Sites: A Guide for State Regulators.* EPA 510-R-96-001. www.epa.gov/oust/pubs/fprg.htm	
		EPA. 1995. *How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites A Guide for Corrective Action Plan Reviewers*. "Chapter 11. Dual-Phase Extraction." EPA 510-R-04-002. www.epa.gov/swerust1/pubs/tum_ch11.pdf	
		API. 1999. *Free-Product Recovery of Petroleum Hydrocarbon Liquids*. API PUBL 4682.	
		USACE. 1999. *Engineering and Design: Multi-Phase Extraction*. EM 1110-1-4010. http://140.194.76.129/publications/eng-manuals/em1110-1-4010/toc.htm	
		EPA. 1999. *Multi-Phase Extraction. State of the Practice*. EPA 542-R-99-004. http://clu-in.org/download/remed/mpe2.pdf	
		EPA. n.d. "Technology Focus: Multi-Phase Extraction Overview." http://clu-in.org/techfocus/default.focus/sec/Multi%2DPhase%5FExtraction/cat/Overview	

Table A-11.A. Water flooding (including hot-water flooding)

Technology	Water flooding (including hot-water flooding)	Water flooding involves groundwater recirculation in a combined injection/ extraction well configuration, where groundwater flow is directed through the LNAPL zone to increase the hydraulic gradient and enhance LNAPL flow, displacement, and removal. The mobilized LNAPL is recovered via hydraulic recovery. Water flooding causes a faster rate of LNAPL flow toward recovery wells. The important process factor in water flooding is the enhanced hydraulic gradient. The recirculated water can be heated prior to injection to decrease the viscosity and interfacial tension of the LNAPL, thereby further facilitating its recovery. Injection and extraction wells can be installed in lines on either side of the LNAPL zone (line-drive approach) or interspersed in a multispot grid pattern.	
Remediation process	Physical mass recovery	Yes	Water flooding enhances LNAPL extraction by increasing the hydraulic gradient toward extraction wells; heating the injected water can further increase the LNAPL extraction rate.
	Phase change	No	Hot-water flooding may slightly increase the solubility of LNAPL components.
	In situ destruction	No	N/A
	Stabilization/ binding	No	N/A
Objective applicability	LNAPL saturation	Yes	Enhances LNAPL fluid flow and recovery and can reduce LNAPL to residual saturation. Hot-water injection can reduce the LNAPL saturation more quickly and may reach a lower residual saturation level than DPLE or skimming.
		Example performance metrics	Reduced LNAPL thickness in wells and extent of wells containing LNAPL; reduced LNAPL saturation in soil samples.
	LNAPL composition	No	N/A
		Example performance metrics	N/A
Applicable LNAPL type	Water flooding applies to all LNAPL types. Hot-water flooding is most beneficial for viscous LNAPLs but can accelerate recovery of any LNAPL.		
Geologic factors	Unsaturated zone	Technology is typically not applicable to LNAPL in the unsaturated zone unless saturated conditions can be achieved by first raising the water table.	
	Saturated zone	Permeability	Higher-permeability materials may allow lower residual saturations to be achieved but require higher injection/extraction flow rates to significantly increase the hydraulic gradient. Moderate-permeability materials may facilitate an increase in the hydraulic gradient at a manageable flow rate. Low-permeability materials may exhibit limited enhancement in LNAPL flow using water flooding.
		Grain size	Can achieve lower residual saturation in coarser-grain materials where displacement pressures are lower; see related discussion on permeability, above.
		Heterogeneity	Moderately sensitive to heterogeneity.
		Consolidation	Consolidated media may affect water flooding effectiveness, primarily by heterogeneity that is introduced and the reduction in pore size.

Table A-11.B. Evaluation factors for water flooding (including hot water flooding)

Technology: Water flood		
Remedial time frame	Concern	Moderate
	Discussion	Short to medium. Use of hot water reduces the required time for remediation.
Safety	Concern	Moderate to high
	Discussion	Water-handling equipment to inject, extract, and treat; water-heating equipment, if used, has additional risks.
Waste management	Concern	Moderate
	Discussion	Need to recycle or dispose of LNAPL and potentially treat water source prior to injection.
Community concerns	Concern	Low to moderate
	Discussion	Concerns with noise, potential odors, aesthetics, and volatile emissions. Potentially significant equipment requirements on site.
Carbon footprint/energy requirements	Concern	Moderate
	Discussion	Equipment to inject and extract groundwater. Water-heating equipment, if used, increases energy use.
Site restrictions	Concern	Moderate to high
	Discussion	Potentially significant equipment requirements on site.
LNAPL body size	Concern	Moderate
	Discussion	Applicable to any size of LNAPL zone; size can be scaled.
Other regulations	Concern	Moderate
	Discussion	May need a permit to reinject groundwater.
Cost	Concern	High
	Discussion	Continuous injection and circulation of water, high operation and maintenance costs, heating the water prior to reinjection further increase cost over a relatively short time period.
Other	Concern	
	Discussion	

Table A-11.C. Technical implementation considerations for water flooding (including hot-water flooding)

Data requirements	Site-specific data for technology evaluation	Transmissivity of hydrogeologic unit containing LNAPL	Transmissivity data helps determine compatibility of formation for injection, potential injection rates, and sweep efficiency. Injected water flows preferentially through higher-permeability layers. Ideally, a confining unit is present above and below the LNAPL zone to better control the injected water.
		LNAPL fluid characteristics	Includes temperature-sensitive changes if hot-water flooding is applied.
	Bench-scale testing	LNAPL changes with temperature	If hot-water flooding is applied.
	Pilot-scale testing	Groundwater/LNAPL ROC	Aquifer tests to determine the ROC so can target water injection within the ROC to enable control of the injected water to maximize the efficiency of the sweep through the LNAPL body.
		Groundwater recovery rate, volume, and influent concentrations	Determine groundwater recovery rate, volume, and influent concentrations to assist with design of water handling, treatment, and discharge options.
		LNAPL recovery rate and volume	Determine LNAPL recovery rate and volume to assist with design of LNAPL storage, handling, treatment, and discharge options.
		Field test	Hot-water flooding may require closer well spacing due to heat loss to the formation after injection. Also, hot-water buoyancy effects should be considered in the design process.
	Full-scale design	Number of injection/ extraction wells	Determine number of required injection/extraction (e.g., DPLE) wells necessary to achieve adequate zone of LNAPL recovery consistent with LNAPL site objective(s).
		Conveyance piping	Determine locations, lengths, materials for all horizontal conveyance piping to/from extraction (e.g., DPLE) wells to/from recovery/treatment system. Assess pipe insulation and heat tracing needs for winter conditions, if applicable.
		Groundwater ROC	Establish groundwater capture for different groundwater pumping rates. For continuous pumping systems, determine acceptable pumping rate that may be sustained without creating unacceptable drawdown.
		LNAPL ROC	Establish LNAPL capture for different LNAPL pumping rates. For continuous pumping systems, determine acceptable pumping rate that may be sustained without creating unacceptable drawdown.
	Performance metrics	LNAPL thickness	
		Mass removed	
Further information		Ground-Water Remediation Technologies Analysis Center. 1997. *In Situ Soil Flushing Technology Overview Report*. TO-97-02. http://clu-in.org/download/remed/flush_o.pdf	
		EPA. n.d. "Technology Focus: In Situ Soil Flushing." www.clu-in.net/techfocus/default.focus/sec/In_Situ_Flushing/cat/Overview	
		EPA. 1992. *Chemical Enhancements to Pump and Treat Remediation.* EPA/540/S-92/001. www.epa.gov/tio/tsp/download/chemen.pdf	
		INDOT. 2007. *INDOT Guidance Document for In Situ Soil Flushing*. http://rebar.ecn.purdue.edu/JTRP_Completed_Project_Documents/SPR_2335/FinalReport/SPR_2335_Final/SPR_0628_2.pdf	

Table A-12.A. In situ chemical oxidation

Technology	In situ chemical oxidation	ISCO involves injecting an oxidant to react with and destroy organic compounds. Treatment of LNAPL sites using ISCO may focus on treatment of the dissolved plume, soils, or LNAPL; however, oxidation reactions occur in the dissolved phase. The oxidant must be matched to the site conditions and the project objectives. Effective oxidant delivery and contact with the target treatment media, as well as delivery of an adequately aggressive and stoichiometrically correct oxidant dose, are requisites for effective ISCO application.	
Remediation process	Physical mass recovery	No	N/A
	Phase change	Yes	Mass destruction in the dissolved-phase drives mass transfer from the LNAPL phase.
	In situ destruction	Yes	Under appropriate conditions, ISCO acts to break the hydrocarbon molecular bonds, producing CO_2 and water as by-products.
	Stabilization/ binding	No	N/A
Objective applicability	LNAPL saturation	No	N/A
		Example performance metrics	N/A
	LNAPL composition	Yes	Abate accumulation of unacceptable constituent concentrations in soil vapor and/or dissolved phase from an LNAPL source.
		Example performance metrics	LNAPL composition change; soil VOC concentrations to below regulatory standard; soil vapor plume concentrations to below regulatory standard.
Applicable LNAPL type	Applicability depends on the chemical oxidation susceptibility of the chemicals in the LNAPL or of the LNAPL constituents in either soil or groundwater.		
Geologic factors	Unsaturated zone	Geologic factors for ISCO application in the unsaturated zone are dominated by oxidant transport and delivery requirements. It is very difficult to deliver aqueous-phase oxidants to the unsaturated zone due to the limitations of unsaturated flow. Ozone, a gaseous oxidant, is amenable to delivery in the unsaturated zone, although its high rate of reaction is a transport limitation which often dictates relatively close injection-well spacing. More homogeneity and higher permeability result in more effective treatment.	
	Saturated zone	Low permeability and heterogeneity are challenging for amendment delivery and reduce efficiency and effectiveness. Delivery of gaseous oxidants to the saturated zone involves gas sparging, which is strongly affected by geologic heterogeneity and grain size and permeability distributions. High natural oxidant demand exerted by the native aquifer matrix, including both reduced minerals and soil organics, reduces ISCO efficiency.	

Table A-12.B. Evaluation factors for in situ chemical oxidation

Technology: In situ chemical oxidation		
Remedial time frame	Concern	Very low to low
	Discussion	Very short to short—typically less than one year. Best used on residual LNAPL. Not unusual for two or three injection applications for dissolved phase only; many more may be needed depending on LNAPL volume and desired end point.
Safety	Concern	High
	Discussion	Oxidants reactions can be very rapid and exothermic. Oxidant handling requires personal protective equipment (PPE). Infrastructure materials (e.g., piping and valves for injection) must be compatible with the oxidant.
Waste management	Concern	Low
	Discussion	All reactions are in situ. Recirculation type delivery requires waste management.
Community concerns	Concern	Low to moderate
	Discussion	Concerns with noise, potential odors, aesthetics, and volatile emissions. Personnel in protective clothing may give public some concern.
Carbon footprint/energy requirements	Concern	Low
	Discussion	Low external energy requirements. Recirculation type delivery requires more energy.
Site restrictions	Concern	Moderate
	Discussion	Injected down well bores, so generally not hampered by site restrictions, but may have to restrict public access during application of the oxidants.
LNAPL body size	Concern	Moderate to high
	Discussion	Higher success rate on small areas with minor LNAPL in-well thickness of a few inches or less. Free-product remediation is safe and accessible to solid peroxygens.
Other regulations	Concern	Moderate
	Discussion	May need an injection permit. Fracturing of the formation is a potential concern, which could impede UIC authorization for injection.
Cost	Concern	Moderate to high
	Discussion	May be cost-effective where LNAPL body is small or impact localized.
Other	Concern	
	Discussion	

Table A-12.C. Technical implementation considerations for in situ chemical oxidation

Data requirements	Site-specific data for technology evaluation	Site size and soil characteristics	Soil permeability, plasticity (classification), bulk density, total organic carbon and other natural oxidant sinks, site boundary.
		Groundwater characteristics	Hydraulic, gradient, geochemistry (buffering capacity).
		LNAPL characteristics ($LNAPL_c$)	LNAPL volume, chemical properties, concentrations, co-contaminants. LNAPL type affects oxidant selection.
		LNAPL depth	Affects delivery method(s).
		LNAPL location	Open area or under building, near utilities, source area identified and removed?
		Permit consideration	Permit may be needed for oxidant injection.
	Bench-scale testing	Soil characteristics	Permeability, natural oxidant demand, classification, bulk density, acid demand.
		Destruction efficiency	Determine efficiency of oxidant selected for destruction of contaminant(s) at site, by-products, oxidant dose.
		Delivery mechanism	Use of soil properties to determine best delivery/oxidant.
	Pilot-scale testing	Injection pressure	If injecting under pressure.
		Placement/number of monitoring wells	Highly recommended ROI be determined.
		Groundwater characteristics	Reducing conditions, oxidation reduction potential (ORP), pH, alkalinity, chloride, etc.
		Number of injection points	Delivery volume, oxidant destruction rate.
		Site conditions	Ability of site to accept oxidant, ROI, heterogeneities. Aquifer metals reactions (mobilization) to high-oxidized conditions.
	Full-scale design	Injection pressure	If injecting under pressure requires care.
		Placement/number of monitoring wells	
		Groundwater characteristics	Reducing conditions, ORP, pH, alkalinity, chloride, dissolved oxygen, etc.
		Number of injection points	Delivery volume, oxidant destruction rate
		Site conditions	Ability of site to accept oxidant, ROI, heterogeneities
	Performance metrics	Post monitoring	Reducing conditions, ORP, pH, alkalinity, chloride, injected oxidant, contaminant, daughter products, and groundwater elevations.
		Delivered amount	
		Daylighting observed	
		Oxidant distribution	
		Contaminant reduction	Long-term monitoring
		Contingency plan	Rebound effects
Modeling tools/ applicable models		Models being developed for predictive capabilities, stoichiometries, etc.	
Further information		EPA. 2006. *Engineering Issue: Chemical Oxidation*. EPA/600/R-06/072. www.epa.gov/ahaazvuc/download/issue/600R06072.pdf	
		Brown, R. A. 2003. "In Situ Chemical Oxidation: Performance, Practice, and Pitfalls." AFCEE Technology Transfer Workshop, Feb. 24–27, San Antonio. www.afcee.af.mil/shared/media/document/AFD-071031-150.pdf	
		Carus Chemical Company. 2004. "Material Safety Data Sheet for CAIROX® Potassium Permanganate." www.caruschem.com/pdf/new_files/CAIROX_MSDS.pdf	
		FMC. 2005. "Bulletin 1. General Efficacy Chart." FMC Environmental Resource Center, Environmental Solutions. http://envsolutions.fmc.com/Portals/fao/Content/Docs/klozurTechBulletin1%20-%20Activation%20chemistries%20Selection%20Guide%20(updated%201-08).pdf	
		FMC. 2006. "Persulfates Technical Information." www.fmcchemicals.com/LinkClick.aspx?fileticket=y%2f0DZcxPM4w%3d&tabid=1468&mid=2563	
		ITRC. 2005. *Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater*, 2nd ed. ISCO-2. www.itrcweb.org/Documents/ISCO-2.pdf	
		EPA. 1994. *How To Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites: A Guide for Corrective Action Plan Reviewers.* EPA 510-B-94-003. www.epa.gov/oust/pubs/tums.htm	
		Ground-Water Remediation Technologies Analysis Center. 1999. *In Situ Chemical Treatment Technology Evaluation Report.* TE-99-01. http://clu-in.org/download/toolkit/inchem.pdf	

Table A-12.C. continued

Further information (continued)	ITRC. 2001. *Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater*. ISCO-1. www.itrcweb.org/Documents/ISCO-1.pdf
	ESTP. 2006. *In Situ Chemical Oxidation for Groundwater Remediation—Technology Practices Manual*. ESTCP ER-06. www.serdp-estcp.org/ISCO.cfm

Table A-13.A. Surfactant-enhanced subsurface remediation

Technology	Surfactant-enhanced subsurface remediation	Injection wells deliver surfactant solution to LNAPL zone while extraction wells capture mobilized/solubilized LNAPL.	
Remediation process	Physical mass recovery	Yes	Surfactant enhances LNAPL mobility and recovery by significantly reducing LNAPL/water interfacial tension.
	Phase change	No	LNAPL is solubilized above its typical aqueous solubility.
	In situ destruction	No	Surfactants are cometabolites and may enhance aerobic and anaerobic microbial hydrocarbon digestion.
	Stabilization/ binding	No	N/A
Objective applicability	LNAPL saturation	Yes	SESR reduces LNAPL saturation and even mobilizes otherwise residual LNAPL from pores. Properly designed surfactant systems enhance removal efficiency of residual LNAPL potentially by several orders of magnitude compared to extraction remediation approach alone, which rely on standard dissolution to remove residual LNAPL.
		Example performance metrics	Reduced LNAPL transmissivity; reduction or elimination of measurable LNAPL in wells.
	LNAPL composition	Yes	Abate accumulation of unacceptable constituent concentrations in soil vapor and/or dissolved phase from an LNAPL source.
		Example performance metrics	LNAPL composition change; soil VOC concentrations to below regulatory standard; soil vapor plume concentrations to below regulatory standard.
Applicable LNAPL type	All LNAPL types, though mobility enhancement for those with higher oil-water interfacial tension are less efficient.		
Geologic factors	Unsaturated zone	When unsaturated zone LNAPL is near water table, water table can be raised (via mounding effect) to flood the zone with surfactant. When unsaturated zone LNAPL is far above water table, infiltration techniques may be used to flush the zone with surfactant but are not as effective as saturated zone treatment. More homogeneity and moderate permeability result in more effective treatment through even distribution of surfactant. See saturated zone geologic factors.	
	Saturated zone	Permeability	Surfactant delivery and LNAPL recovery are more rapid and more effective in higher-permeability soil.
		Grain size	LNAPL recovery is more rapid and effective in larger-grained soils (sands) than in smaller-grained soils (e.g., silt and clay).
		Heterogeneity	High levels of heterogeneity can reduce surfactant solution delivery efficiency, which increase the required number of pore volumes.
		Consolidation	High consolidation may reduce pore sizes, permeability, and injection feasibility; unconsolidated/loosely consolidated may allow larger spacing within well network (i.e., tend to be more favorable for recovery).

Table A-13.B. Evaluation factors for surfactant-enhanced subsurface remediation

Technology: Surfactant-enhanced subsurface remediation		
Remedial time frame	Concern	Very low to low
	Discussion	Very short to short. Bench-testing can be used to determine the number of pore volumes needed to remove the LNAPL. Typically, with finer-grained material, additional pore volumes are needed. Generally faster than DPLE and AS/SVE.
Safety	Concern	Low to moderate
	Discussion	Surfactants are not dangerous, but there may be safety issues due to the equipment used to inject the surfactant and treat the extracted mixture. LNAPL may be extracted and handled.
Waste management	Concern	Moderate
	Discussion	The recovered surfactant and LNAPL need to be disposed of as nonhazardous waste. Depending on what is recovered, may be able to dispose into sanitary sewer or transport to a disposal facility. Surfactants cause the aqueous waste stream to contain very high dissolved concentrations of LNAPL constituents and can pose challenges for aqueous-phase treatment systems.
Community concerns	Concern	Low to moderate
	Discussion	Concern with use of chemical treatment, volatile emissions, odors, noise. Trucks and equipment may be on site for some time.
Carbon footprint/ energy requirement	Concern	Low to moderate
	Discussion	Depends on whether the surfactant is gravity fed or injected. Mixing as well as extraction and treatment of waste require energy source.
Site restrictions	Concern	Moderate
	Discussion	No major construction activity or subsurface disruption but may need to restrict application area access while injecting and recovering fluids. Field team on site during application of technology.
LNAPL body size	Concern	Moderate to high
	Discussion	The success rate is higher for very small areas. As the treatment area increases in size, the chance for success decreases. May consider the technology as a follow-up to a traditional technology such as DPLE or MPE to remediate areas missed.
Other regulations	Concern	Moderate
	Discussion	May need a permit to inject and discharge permit.
Cost	Concern	Moderate to high
	Discussion	
Other	Concern	
	Discussion	

Table A-13.C. Technical implementation considerations for surfactant-enhanced subsurface remediation

Data requirements	Site-specific data for technology evaluation	Groundwater hydraulic conductivity	
		LNAPL characteristics	
		Contaminants of concern	
		Groundwater quality/geochemistry	
	Bench-scale testing	Soil cores for column tests	
		Contaminants of concern	
		LNAPL characteristics	
		Surfactant selection	
	Pilot-scale testing	Contaminants of concern	
		LNAPL characteristics	
		Delivery of surfactant solutions(wells)	
		Treatment of extracted mixture	
	Full-scale design	Groundwater hydraulic conductivity	
		Sweep volume	
		Soil type(s)/lithology	
		Homogeneity	
		Treatment system	
	Performance metrics	LNAPL thickness	
		Mass recovered	
		Achieve remedial objective	
Modeling tools/applicable models		UTCHEM	
Further information		EPA. 1995. *Surfactant Injection for Ground Water Remediation: State Regulators' Perspectives and Experiences*. EPA 542-R-95-011. www.epa.gov/tio/download/remed/surfact.pdf	
		Ground-Water Remediation Technologies Analysis Center. 1997*. In Situ Flushing Technology Overview Report*. TO-97-02. http://clu-in.org/download/remed/flush_o.pdf	
		NAVFAC. 2006. *Surfactant-Enhanced Aquifer Remediation (SEAR) Design Manual*. TR-2206-ENV. http://74.125.93.132/search?q=cache:CcfUkrCwimAJ:www.clu-in.org/download/contaminantfocus/dnapl/Treatment_Technologies/SEAR_Design.pdf+Surfactant-Enhanced+Aquifer+Remediation+(SEAR)+Design+Manual&cd=1&hl=en&ct=clnk&gl=us	
		NAVFAC. 2003. *Surfactant-Enhanced Aquifer Remediation (SEAR) Implementation Manual*. NFESC TR-2219-ENV. www.clu-in.org/download/techdrct/td-tr-2219-sear.pdf	
		AFCEE. n.d. "Cosolvent or Surfactant-Enhanced Remediation." www.afcee.af.mil/resources/technologytransfer/programsandinitiatives/sourcezonetreatment/background/cosolvent-surfac/index.asp	
		EPA. 1991. *In Situ Soil Flushing*. EPA 540-2-91-021.	

Table A-14.A. Cosolvent flushing

Technology	Cosolvent flushing	Cosolvent flushing involves the injection and subsequent extraction of a cosolvent (e.g., an alcohol) to solubilize and/or mobilize LNAPL.	
Remediation process	Physical mass recovery	Yes	Cosolvents enhance LNAPL mobility and removal by reducing the LNAPL/water interfacial tension.
	Phase change	No	Cosolvents allow LNAPL to be solubilized above its typical aqueous solubility limit, thereby enhancing removal.
	In situ destruction	No	N/A
	Stabilization/binding	No	N/A
Objective applicability	LNAPL saturation	Yes	LNAPL saturation decreases due to direct recovery and enhanced solubilization.
		Example performance metrics	Reduced LNAPL transmissivity, reduction, or elimination of measurable LNAPL in wells.
	LNAPL composition	Yes	Abate accumulation of unacceptable constituent concentrations in soil vapor and/or dissolved phase from an LNAPL source.
		Example performance metrics	LNAPL composition change; soil VOC concentrations to below regulatory standard; soil vapor plume concentrations to below regulatory standard.
Applicable LNAPL type	Assuming the primary mechanism is solubilization, cosolvents are most effective with lighter-molecular-weight LNAPLs (ITRC 2003) and become less effective as the molecular weight of the LNAPL increases.		
Geologic factors	Unsaturated zone	When unsaturated zone LNAPL is near the water table, the water table can be raised (via mounding effect) to flood the zone with cosolvent. When unsaturated zone LNAPL is far above water table, infiltration techniques may be used to flush the zone with cosolvent but are not as effective as saturated zone treatment. More homogeneity and moderate permeability results in more effective treatment through even distribution of cosolvent. See saturated zone geologic factors.	
	Saturated zone	Permeability	The overall cosolvent delivery and LNAPL recovery are more rapid in higher-permeability soils, but cosolvent can be delivered to lower-permeability soils; however, the time to complete the flushing process is longer with lower permeability.
		Grain size	The overall LNAPL mass recovery is effective in coarser-grain soils (sands) and finer-grain soils (e.g. silt and clay); however, the time to complete the flushing process is longer in the finer-grain soils.
		Heterogeneity	In highly heterogeneous soils, separate flow network may be required (e.g., one to treat the more permeable zone and another to treat the less permeable zone) if LNAPL is distributed in both zones. In some cases, short-circuiting of flushing is unavoidable. Higher heterogeneity can also reduce cosolvent delivery efficiency, which increases the required number of pore volumes.
		Consolidation	High consolidation may reduce pore sizes, permeability, and injection feasibility. Unconsolidated/loosely consolidated soil may allow larger grids on flow network (i.e., tend to be more favorable for recovery).

Table A-14.B. Evaluation factors for cosolvent flushing

Technology: Cosolvent flushing		
Remedial time frame	Concern	Very low to low
	Discussion	Very short to short. Cosolvent flushing is ideal to address the removal of residual LNAPLs that have become trapped in the pore spaces of a water-bearing unit. Need to be able to sweep the LNAPL by infiltrating or injecting the cosolvent and extracting simultaneously downgradient to maintain hydraulic control.
Safety	Concern	Moderate
	Discussion	A number of chemicals on site along with mechanical equipment; flammability awareness on some alcohols.
Waste management	Concern	Moderate
	Discussion	Wastewater, cosolvent, and LNAPL need to be properly disposed.
Community concerns	Concern	Moderate
	Discussion	There is a series of injection and extraction wells, mixing tanks, fluid separation, and wastewater-handling equipment. Personnel in PPE. Concern with use of chemical treatment, volatile emissions, odors, noise.
Carbon footprint/energy requirements	Concern	Moderate
	Discussion	Depends on whether the cosolvent is gravity fed or injected. Extraction and treatment of waste require energy source.
Site restrictions	Concern	Moderate to high
	Discussion	No significant construction activity or subsurface disruption but may need to limit access to application area while injecting and recovering fluids (possibly more safeguards than for SESR). Field team on site during application of technology.
LNAPL body size	Concern	Moderate
	Discussion	The success rate is higher for very small areas. As the treatment area increases in size, the chance for success decreases. May consider the technology as a follow-up to a traditional technology such as DPLE or MPE to remediate areas missed.
Other regulations	Concern	Moderate to high
	Discussion	May need variance or permits for discharge of wastewater and injection permit.
Cost	Concern	High
	Discussion	The ability to remove COCs from recovered fluid for recycling and injecting back into the subsurface is a major factor in controlling the cost of cosolvent flushing.
Other	Concern	
	Discussion	

Table A-14.C. Technical implementation considerations for cosolvent flushing

Data requirements	Site-specific data for technology evaluation	Groundwater hydraulic conductivity	
		LNAPL characteristics	
		Bench-scale testing	
	Bench-scale testing	Soil cores for column testing	
		Contaminants of concern	
		LNAPL characteristics	
		Cosolvent selection	
	Pilot-scale testing	Field test	
		Cosolvent delivery and recovery	
		Waste treatment/recycle of solvent solution	
	Full-scale design	Groundwater hydraulic conductivity	
		Sweep volume	
	Performance metrics	Groundwater concentration	
		LNAPL thickness	
		Mass recovered	
Modeling tools/applicable models		UTCHEM	
Further information		ITRC. 2003. *Technical and Regulatory Guidance for Surfactant/Cosolvent Flushing of DNAPL Source Zones*. DNAPL-3. www.itrcweb.org/Documents/DNAPLs-3.pdf	
		Ground-Water Remediation Technologies Analysis Center. 1997. *In Situ Flushing Technology Overview Report*. TO-97-02. http://clu-in.org/download/remed/flush_o.pdf	
		AFCEE. n.d. "Cosolvent or Surfactant-Enhanced Remediation." www.afcee.af.mil/resources/technologytransfer/programsandinitiatives/sourcezonetreatment/background/cosolvent-surfac/index.asp	

Table A-15.A. Steam/hot-air injection

Technology	Steam/hot-air injection	Steam and/or hot air is injected into wells to heat the formation and LNAPL. Steam injection induces a pressure gradient that pushes ahead of it, in sequence, a cold water (ambient temperature) front, a hot water front, and a steam front through the LNAPL zone. In the unsaturated zone, a steam and condensation front develops. The mobilized LNAPL is recovered from extraction wells, and volatilized LNAPL is collected via vapor extraction wells.	
Remediation process	Physical mass recovery	Yes	1. Cold water front flushes some of the remaining mobile LNAPL from pores. 2. Hot water and steam fronts or hot air reduce viscosity of LNAPL increasing mobility and recoverability.
	Phase change	Yes	The steam/hot air front volatilizes the LNAPL.
	In situ destruction	Yes	Steam/hot air front potentially causes the LNAPL to undergo thermal destruction or hydrous pyrolysis.
	Stabilization/ binding	No	N/A
Objective applicability	LNAPL saturation	Yes	Enhances LNAPL fluid flow by reducing interfacial tension and LNAPL viscosity, potentially reducing LNAPL saturations to below residual saturation achieved by standard hydraulic methods. Mass loss also occurs by volatilization and in situ destruction.
		Example performance metrics	Reduced LNAPL transmissivity; reduction or elimination of measurable LNAPL in wells.
	LNAPL composition	Yes	Abate accumulation of unacceptable constituent concentrations in soil vapor and/or dissolved phase from an LNAPL source.
		Example performance metrics	LNAPL composition change; soil VOC concentrations to below regulatory standard; soil vapor plume concentrations to below regulatory standard
Applicable LNAPL type	All LNAPL types, though higher-viscosity and/or lower-volatility LNAPL takes longer to treat and/or achieves less remedial effectiveness.		
Geologic factors	Unsaturated zone	Permeability	Steam injection is effective only in relatively permeable materials, where there is less resistance to flow; also, more effective in stratified LNAPL settings, where a low-permeability layer can help to control steam distribution.
		Grain size	Steam injection can achieve more effective saturation reduction in coarser-grain materials.
		Heterogeneity	Steam injection is more efficient in permeable pathways, but LNAPL is also distributed mainly in these pathways.
		Consolidation	High consolidation may reduce pore sizes, permeability, and injection feasibility.
	Saturated zone	Permeability	Steam injection is effective only in relatively permeable materials where there is less resistance to flow; also, more effective in confined LNAPL settings where a low-permeability layer can help to control steam distribution.
		Grain size	Steam injection can achieve more effective saturation reduction in coarser-grain materials.
		Heterogeneity	Steam injection is more efficient in permeable pathways, but LNAPL is also distributed mainly in these pathways.
		Consolidation	High consolidation may reduce pore sizes, permeability, and injection feasibility.

Table A-15.B. Evaluation factors for steam/hot-air injection

Technology: Steam/hot-air injection		
Remedial time frame	Concern	Very low
	Discussion	Very short. A steam front is developed and mobilizes the LNAPL to extraction wells or volatilizes the LNAPL, which is then collected by vapor extraction.
Safety	Concern	High
	Discussion	Steam under pressure and hot water and LNAPL extracted. Possible steam eruption from wells.
Waste management	Concern	Moderate
	Discussion	Collect LNAPL and groundwater with high dissolved concentrations from recovery wells and treat the off-gas.
Community concerns	Concern	Low to moderate
	Discussion	Process equipment, high temperature warnings, and personnel in PPE may be cause for concern. Also, noise, odor, and potential public exposure if steam is not effectively captured and treated.
Carbon footprint/energy requirement	Concern	Moderate
	Discussion	Equipment needed to generate steam requires large supply of energy. VOC emissions, but for a short duration. Extraction and treatment of waste. Footprint lessened by short duration.
Site restrictions	Concern	High
	Discussion	Large amount of equipment, piping, and control of vapor emissions. Field team on site during technology application. Application area restrictions during technology application.
LNAPL body size	Concern	Moderate
	Discussion	The heterogeneity and permeability of the soils greatly determine whether the steam front is successful and may limit the size that can be remediated.
Other regulations	Concern	Moderate
	Discussion	May need an injection permit. For treated groundwater may need a permit to discharge and VOC emissions.
Cost	Concern	Moderate to high
	Discussion	High costs to generate and maintain steam and high operation and maintenance costs. Short duration can make present value cost-competitive.
Other	Concern	
	Discussion	

Table A-15.C. Technical implementation considerations for steam/hot-air injection

Data requirements	Site-specific data for technology evaluation	Site size and soil characteristics	Permeability—venting of vapors to atmosphere (technology works in conjunction with AS/SVE).
		Groundwater characteristics	Hydraulic gradient, geochemistry (buffering capacity—scaling/fouling).
		LNAPL characteristics ($LNAPL_c$)	Chemical properties (composition vapor pressure, boiling point, octanol-water partitioning coefficient, viscosity, etc.).
		LNAPL depth	Lateral extent and vertical depth needed to estimate total soil volume to be heated, steam-generation needs, etc.
		LNAPL location	Open area or under building, near utilities, any other obstructions to injection well placement need special consideration.
		Off-gas treatment	Concentrations and types of contaminants affect loading and off-gas technology selection.
	Bench-scale testing	Similar to AS/SVE	See Table A-5.C.
		Soil characteristics	Permeability, moisture, classification.
		LNAPL characteristics	LNAPL viscosity reduction as a function of temperature.
		Groundwater geochemistry	pH, buffering capacity, O2, etc.
	Pilot-scale testing	Similar to AS/SVE	See Table A-5.C.
		Injection locations	Determine placement of injection and extraction wells.
		Injection rates	Determine required injection pressure rate to ensure overall coverage and minimize short-circuiting to the surface.
		Injection pressures	Increased injection pressure requirements limit mass flux to vapor phase and could result in soil instability.
		Off-gas treatment	Selection of off-gas treatment depends on concentration, contaminants, regulations, etc.
		LNAPL mass recovery	Volume recovered and rate.
		Piping concerns	High temperatures and pressures.
		Boiler capacity	Steam-generation issues.
	Full-scale design	Similar to AS/SVE	See Table A-5.C.
		Injection rates	Determine feasible injection rates on site to ensure overall coverage and minimize short circuiting to the surface.
		Injection pressures	Increased injection pressure requirements limits mass flux to vapor phase and could result in soil instability.
		Off-gas treatment	Selection of off-gas treatment depend on concentration, contaminants, regulations, etc.
		Piping concerns	High temperatures and pressures.
		Steam quality	Higher quality, better transfer of heat into treatment area (quality is measure of liquid in vapor; 100% = 0 liquid), condensation considerations.
		Boiler size, maintenance	Ability to generate and keep generation continuing for duration of injection.
	Performance metrics	Similar to AS/SVE	See Table A-5.C.
		Effluent measurements	
Modeling tools/applicable models			
Further information		EPA. 1998. *Steam Injection for Soil and Aquifer Remediation*. EPA/540/S-97/505. www.epa.gov/tio/tsp/download/steaminj.pdf	
		FRTR. n.d. "Remedial Technology Screening and Reference Guide, Version 4.0, In Situ Thermal Treatment." www.frtr.gov/matrix2/section4/4-9.html	
		EPA. n.d. "Technology Focus: In Situ Thermal Heating." www.clu-in.org/techfocus/default.focus/sec/Thermal_Treatment:_In_Situ/cat/Overview	
		EPA. 1995. *In Situ Remediation Technology Status Report: Thermal Enhancements*. EPA/542-K-94-009. www.clu-in.org/download/remed/thermal.pdf	
		USACE. 2009. *Engineering and Design: In Situ Thermal Remediation*. EM-1110-1-4015. http://140.194.76.129/publications/eng-manuals/em1110-1-4015/entire.pdf	

Table A-16.A. Radio-frequency heating

Technology	Radio-frequency heating	RFH energy is introduced into the subsurface via heating antennae. The subsurface is maintained at temperatures low enough to mainly influence the viscosity of the LNAPL, but temperature can be raised to increase volatilization or to result in hydrous pyrolysis. The mobilized LNAPL is recovered hydraulically.	
Remediation process	Physical mass recovery	Yes	Increased subsurface temperatures reduce LNAPL viscosity and increase mobility and recoverability.
	Phase change	Yes	Higher-temperature applications can volatilize LNAPL, which can then be recovered via SVE.
	In situ destruction	Yes	At high temperatures, LNAPL may undergo thermal destruction or hydrous pyrolysis.
	Stabilization/binding	No	N/A
Objective applicability	LNAPL saturation	Yes	Enhances LNAPL recovery, which reduces LNAPL saturations; mass loss by volatilization and in situ destruction may also reduce LNAPL saturation.
		Example performance metrics	Reduced LNAPL transmissivity; reduction or elimination of measurable LNAPL in wells.
	LNAPL composition	Yes	Abate accumulation of unacceptable constituent concentrations in soil vapor and/or dissolved phase from an LNAPL source.
		Example performance metrics	LNAPL composition change; soil VOC concentrations to below regulatory standard; soil vapor plume concentrations to below regulatory standard.
Applicable LNAPL type	All LNAPL types, though higher-viscosity and/or-lower volatility LNAPL take longer to treat and/or achieve less remedial effectiveness.		
Geologic factors	Unsaturated zone	Permeability	Most effective in locations with high permeability.
		Grain size	Can achieve more effective saturation reduction in coarser-grain materials.
		Heterogeneity	Heat flow can occur through heterogeneous areas, but LNAPL flow is most enhanced in permeable pathways.
		Consolidation	Not typically a factor.
	Saturated zone	Permeability	Most effective in locations with sand lenses that provide a layer through which fluid flow can occur.
		Grain size	Most effective in locations with sand lenses that provide a layer through which fluid flow can occur.
		Heterogeneity	Heat flow can occur through heterogeneous areas, but LNAPL flow is most enhanced in homogenous settings.
		Consolidation	Not typically a factor.

Table A-16.B. Evaluation factors for radio-frequency heating

Technology: Radio-frequency heating		
Remedial time frame	Concern	Very low
	Discussion	Very short. Temperature is increased for LNAPL removal by extraction wells.
Safety	Concern	Moderate
	Discussion	In moderate-temperature applications, electrical equipment on site and LNAPL recovery containers. In high-temperature applications, potential steam eruptions from wells.
Waste management	Concern	Moderate
	Discussion	Recovered LNAPL and water need to be properly disposed. May need to treat vapors recovered.
Community concerns	Concern	Moderate
	Discussion	Concern with technology that is unfamiliar to general public. The name "radio-frequency heating" may alarm some people. Will need to educate the community on the process and safety.
Carbon footprint/energy requirements	Concern	Moderate
	Discussion	AC current used in the radio-frequency generator. Trying to keep volatilization to a minimum.
Site restrictions	Concern	High
	Discussion	Damage to utilities. Could be hampered by need to prohibit site access during application. Access restrictions to application area may be needed.
LNAPL body size	Concern	High
	Discussion	Not known whether it will work on large sites.
Other regulations	Concern	Low
	Discussion	
Cost	Concern	High
	Discussion	Potentially high operation and maintenance costs to keep the system going because it is not a fully proven technology.
Other	Concern	
	Discussion	Radio frequency is not as thoroughly tested and proven as other thermal methods.

Table A-16.C. Technical implementation considerations for radio-frequency heating

Data requirements	Site-specific data for technology evaluation	Site size and soil characteristics	Soil-permeability (venting of vapors to atmosphere—technology works in conjunction with AS/SVE, MPE), plasticity (classification), bulk density, heat capacity.
		Groundwater characteristics	Gradient, aquifer permeability, geochemistry (buffering capacity), depth to water table.
		LNAPL characteristics ($LNAPL_c$)	Chemical properties (vapor pressure, boiling point, solubility, octanol-water partitioning coefficient, viscosity, etc.), concentrations of LNAPL constituents.
		LNAPL depth	Shallow contaminants may require use of surface cover/cap.
		LNAPL location	Accessibility and depth.
		Off-gas treatment	Concentrations of target and nontarget contaminants that may affect loading and off-gas technology selection.
	Bench-scale testing	Similar to AS/SVE	See Table A-5.C.
		Soil characteristics	Permeability, moisture, classification, bulk density, humic portion, heat capacity.
		GW geochemistry/ location	pH, buffering capacity, O_2, etc. Location of the water table.
	Pilot-scale testing	Similar to AS/SVE	See Table A-5.C.
		placement of heating probes	Optimize heating at specific levels and areas of largest contamination.
		Define possible groundwater recharge issues	Minimizing water recharge into thermal zone important. Use of hydraulic barriers, if needed.
		Off-gas treatment	Selection of off-gas treatment dependent upon concentration, contaminants, regulations, etc.
		Power consumption vs. active bed temperature	Basis to justify destruction/removal per unit energy used.
	Full-scale design	Similar to AS/SVE	See Table A-5.C.
		Placement of heating probes	Optimize heating at specific levels and areas of greatest LNAPL core area.
		Define possible groundwater recharge issues	Minimizing water recharge into thermal zone important. Use of hydraulic barriers, if needed.
		Off-gas treatment	Selection of off-gas treatment depends on concentration, contaminants, regulations, etc.
		End-point concentration	Negotiated concentration level.
	Performance metrics	Similar to AS/SVE	See Table A-5.C.
		Power consumption vs. active bed temperature	Active bed temperature is the temperature of the stratigraphic unit(s) targeted by the RFH. Compare to pilot study assessment.
Modeling tools/applicable models			
Further information		U.S. Department of Energy. 1994. *Final Report: In Situ Radio Frequency Heating Demonstration (U)*. www.osti.gov/bridge/servlets/purl/10133397-hP84ua/native/10133397.pdf	
		FRTR. n.d. "Remedial Technology Screening and Reference Guide, Version 4.0, In Situ Thermal Treatment." www.frtr.gov/matrix2/section4/4-9.html	
		EPA. n.d. "Technology Focus: In Situ Thermal Heating." www.clu-in.org/techfocus/default.focus/sec/Thermal_Treatment:_In_Situ/cat/Overview	
		EPA. 1995. *In Situ Remediation Technology Status Report: Thermal Enhancements*. EPA/542-K-94-009. www.clu-in.org/download/remed/thermal.pdf	
		USACE. 2009. *Engineering and Design: In Situ Thermal Remediation*. EM-1110-1-4015. http://140.194.76.129/publications/eng-manuals/em1110-1-4015/entire.pdf	

Table A-17.A. Three- and six-phase electric resistance heating

Technology	Three- and six-phase electric resistance heating	Electric resistance heating is a polyphase electrical technique used to resistively heat soil and mobilize and volatilize LNAPL. Electrodes are typically installed using standard drilling techniques to carry the electrical power to the subsurface. Electrical current flows from each electrode to the other electrodes out of phase with it. The soil matrix is heated due to the resistance to electric flow. The mobilized LNAPL is recovered from extraction wells, and volatilized LNAPL is collected via vapor extraction wells.	
Remediation process	Physical mass recovery	Yes	Heating reduces viscosity of LNAPL and increases mobility and recoverability.
	Phase change	Yes	The heating volatilizes the LNAPL.
	In situ destruction	Yes	LNAPL may undergo thermal degradation or hydrous pyrolysis.
	Stabilization/ binding	No	N/A
Objective applicability	LNAPL saturation	Yes	Enhances LNAPL fluid flow, reducing LNAPL saturations to residual saturation; mass loss also by volatilization and in situ destruction.
		Example performance metrics	Reduced LNAPL transmissivity; reduction or elimination of measurable LNAPL in wells.
	LNAPL composition	Yes	Abate accumulation of unacceptable constituent concentrations in soil vapor and/or dissolved phase from an LNAPL source.
		Example performance metrics	LNAPL composition change; soil VOC concentrations to below regulatory standard; soil vapor plume concentrations to below regulatory standard.
Applicable LNAPL type	All LNAPL types, though higher-viscosity and/or lower-volatility LNAPL will take longer to treat and/or achieve less remedial effectiveness.		
Geologic factors	Unsaturated zone	Permeability	Can be effective even in lower-permeability materials where heat loss to groundwater flux is low but electrical conductivity is high.
		Grain size	Fine-grained soils (silts and clays) are typically more electrically conductive than coarse-grained soils and can be more efficiently heated.
		Heterogeneity	Can be employed at sites with widely varying heterogeneity. Moisture content of the individual layers is the key determining factor for soil heating efficiency. LNAPL mobilization along preferential pathways is most likely.
		Consolidation	Not typically a factor.
	Saturated zone	Permeability	Most effective in lower-permeability materials, where fluid flow is reduced.
		Grain size	Fine-grained soils (silts and clays) are typically more electrically conductive than coarse-grained soils and can be more efficiently heated.
		Heterogeneity	Can be employed at sites with widely varying heterogeneity. Increased moisture content of the individual coarse layers and the electrical conductivity of fine-grained soils layers result in heating and increasing mobility over a wide range of soil conditions.
		Consolidation	Not typically a factor.

Table A-17.B. Evaluation factors for three- and six-phase heating

Technology: Three- and six-phase heating		
Remedial time frame	Concern	Very low
	Discussion	Very short. The soil matrix is heated to mobilize the LNAPL from the pores and collected by extraction wells and the volatilized LNAPL are removed by vapor extraction wells.
Safety	Concern	High
	Discussion	Electric equipment and cables on the ground. Possible steam eruption from wells.
Waste management	Concern	Moderate
	Discussion	Collect LNAPL from recovery wells and treat the vapors.
Community concerns	Concern	Low to moderate
	Discussion	Concern with technology that is unfamiliar to general public. Electrical and process equipment, high-voltage and high-temperature warnings, piping, and electrical cables are likely to cause concern. Potential concerns over odors and volatile emissions.
Carbon footprint/energy requirements	Concern	Moderate
	Discussion	Electric generation and vapor treatment offset by short duration of remediation.
Site restrictions	Concern	High
	Discussion	Electric cables on the ground; subsurface utility concerns, and need to restrict access during application.
LNAPL body size	Concern	Moderate
	Discussion	Capable of remediating large LNAPL plumes. Lithology and permeability determine the spacing between electrodes and placement of recovery wells and vapor extraction wells.
Other regulations	Concern	Moderate
	Discussion	Permit to inject water, vapor emissions.
Cost	Concern	Moderate to high
	Discussion	High electric costs and high operation and maintenance costs. Short duration can make present value cost-competitive.
Other	Concern	Low
	Discussion	Need to keep electrodes moist to maintain current. Some water injection is required.

Table A-17.C. Technical implementation considerations for three- and six-phase electrical resistance heating

Data requirements	Site-specific data for technology evaluation	Site size and soil characteristics	Soil resistivity, buried debris, and subsurface utilities. Soil permeability (venting of vapors to atmosphere—technology works in conjunction with AS/SVE, MPE), soil conductivity, plasticity (classification), bulk density, heat capacity, total organic carbon, site boundary—problems of scale.
		Groundwater characteristics	Conductivity, gradient, aquifer permeability, geochemistry (buffering capacity).
		LNAPL characteristics ($LNAPL_c$)	Chemical properties (vapor pressure, boiling point, octanol-water partitioning coefficient, viscosity, etc.), concentrations.
		LNAPL depth	Shallow contaminants may need to implement surface cover/cap.
		LNAPL location	Open area or under building, near utilities.
		Off-gas treatment	Concentrations of nontarget contaminants that may affect loading and vapor technology selection.
	Bench-scale testing	Similar to AS/SVE	See Table A-5.C.
		Soil characteristics	Permeability, moisture, classification.
		Heating effectiveness/ mass recovery	Relationship between heating time and mass recovery.
		Groundwater geochemistry	pH, buffering capacity, O_2, etc.
	Pilot-scale testing	Similar to AS/SVE	See Table A-5.C.
		Define boundary of treatment zone	Six/three-phase heating generally imparts uniform heating to the treatment zone.
		Steam generation	Determine amount of in situ steam generated by subsurface heating.
		Off-gas treatment	Selection of vapor treatment depends on concentration, contaminants, regulations, etc.
		Heating rate	Time needed to reach optimal/maximum temperature in treatment zone.
		Water injection	Possibility of water addition into the treatment zone to maintain conductivity of soil.
		Safety concerns	High voltage, electrical connections, buried metal objects, vapor/ lower explosive limit, others similar to AS/SVE, community concerns.
	Full-scale design	Similar to AS/SVE	See Table A-5.C.
		Power application/ consumption	
		Steam generation	Record amount of in situ steam generated by subsurface heating.
		Off-gas treatment	Selection of off-gas treatment dependent upon concentration, contaminants, regulations, etc.
		Heating rate	Time needed to reach optimal/maximum temperature in treatment zone.
		Water injection	Possibility of water addition into the treatment zone to maintain conductivity of soil.
		Safety concerns	High voltage, electrical connections, buried metal objects, vapor/ lower explosive limit, others similar to AS/SVE, community concerns.
	Performance metrics	Similar to AS/SVE	See Table A-5.C.
		Temperature in treatment zone	How quickly maximum/optimum temperature was reached and held constant.
		Temperature outside of treatment zone	Determine extent of heating at edge of treatment zone.
		Steam generation	Record amount of in situ steam generated by subsurface heating; measure of effective drying and volatilization occurring in treatment zone.
		Water addition	Record amount of water needed to be applied in the treatment zone.
		Mass removal rates	
		Off-gas concentrations	