Naval Facilities Engineering Systems Command

Naval Facilities Engineering Systems Command Pacific
JBPHH HI

Draft

Natural Source-Zone Depletion Work Plan

Red Hill Bulk Fuel Storage Facility

JOINT BASE PEARL HARBOR-HICKAM O‘AHU HI

February 2023

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Natural Source-Zone Depletion Work Plan
Red Hill Bulk Fuel Storage Facility
JOINT BASE PEARL HARBOR-HICKAM O‘AHU HI

February 2023

Prepared for NAVFAC Pacific by
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N62742-17-D-1800
CTO N6274222F0212

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ACRONYMS AND ABBREVIATIONS

CH_4	methane
CO_2	carbon dioxide
COC	chain of custody
DSVMP	deep soil vapor monitoring point
ft	foot or feet
ID	identification
JP-5	Jet Propellant 5
LNAPL	light nonaqueous-phase liquid
NSZD	natural source-zone depletion
O_2	oxygen gas
PID	photoionization detector
RAA	Remedial Alternatives Analysis
SOP	standard operating procedure
SVMP	soil vapor monitoring point
TPH	total petroleum hydrocarbons
TW	temporary well
QC	quality control
VOC	volatile organic compound
WP	work plan

1. Introduction and Purpose

This Natural Source-Zone Depletion (NSZD) Work Plan (WP) is provided to document the scope of work proposed to evaluate and quantify NSZD processes attenuating petroleum hydrocarbons impacting U.S. Navy Well 2254-01 (also known as Red Hill Shaft). This NSZD WP is prepared under Contract N62742-17-D-1800, Contract Task Order N6274222F0212. The information collected will assist in the evaluation of potential future remediation activities for Red Hill Fuel Storage Facility.

AECOM will conduct this NSZD monitoring program over 24 months, which involves the following:

- Analysis of baseline and periodic (semi-annual) soil vapor analytical samples (oxygen gas [O_2], carbon dioxide [CO_2], methane [CH_4], volatile organic compounds [VOCs], and total petroleum hydrocarbons [TPH])
- Monthly monitoring of soil vapor composition (O_2, CO_2, CH_4, and VOCs)
- Monthly monitoring of temperature

The purpose of the NSZD study is to:

- Evaluate and quantify NSZD processes as measured in the vadose zone
- Support understanding of NSZD processes over time
- Determine changes in light nonaqueous-phase liquid (LNAPL) composition over time
- Support effectiveness of the deep soil vapor extraction pilot study (WP to be submitted under separate cover)

This NSZD WP is intended to provide the framework and sampling methods for an NSZD evaluation. The NSZD monitoring program is planned for 24 months, with site characterization work ongoing. The study is planned for 24 months for multiple reasons:

- One objective of the study is to evaluate if NSZD processes change the soil vapor composition over time, and since half-lives of LNAPL have been reported to be 7 to 14 years (DeVaull et al. 2020), it is expected that two years would be required to observe a change in composition
- The heat signal is likely a lagging indicator as the biogenic heat warms the formation, the monthly readings provide temperature data to build a robust thermal model
- Because site characterization is ongoing, the 24-month timeframe provides the flexibility to evaluate new locations as site characterization continues

It is expected that additional monitoring locations (wells, soil vapor) may be constructed as part of the overall site characterization work being conducted under separate WPs and that data may be collected from these additional locations following the same procedures and analysis methods outlined in this WP.

2. Roles and Responsibilities

This contract is being conducted for Naval Facilities Engineering Systems Command Contract N62742-17-D-1800, Contract Task Order N6274222F0212. Table 1 lists the project personnel roles and responsibilities.

Table 1: Roles and Responsibilities

Role	Name
AECOM Project Manager	Ed Sloan
AECOM Quality Manager	Robin Boyd
AECOM CLEAN Health and Safety Manager	Devon Molitor
AECOM Operations Manager	Skyler Pauli
AECOM Task Manager	George Sauer
AECOM Technical Subject Matter Expert	Brad Koons
AECOM Project Chemist	John Fong
AECOM Field Team Leader	Rachel Tucci
AECOM Site Safety Manager	George Sauer
AECOM Site Safety and Health Officers	• George Sauer • Stuart Anderson • Justin Wood • Petros Paulos • Andy Burkemper • Chris Beza
AECOM Site Geologist/Sampling Technicians	• Rachel Tucci • Collin Ferguson • Gita Datt
Subcontractors	None

3. Conceptual Site Model

Adit 3 site characterization began immediately after the November 20, 2021, Jet Propellant 5 (JP-5) release. Investigation activities to determine the nature and extent of JP-5 impacts in the study area are ongoing. The network of completed and proposed subsurface characterization locations as of October 17, 2022, including boreholes, temporary wells (TWs), and soil vapor monitoring points (SVMPs), is presented on Figure 1. Locations in the Adit 3 tunnel (“A3”) are identified using a coordinate system with the origin at the eastern edge of the United States Department of the Navy Well 2254-01 pumping station doorway. Coordinates represent the distance in feet from the origin, with positive (+) values to the west, in the direction of the Adit 3 tunnel entrance, and negative (-) values to the east. The JP-5 release occurred from an overhead pipe near station A3-375, and fuel moved along the tunnel floor toward the Adit 3 sump, approximately 750 feet west of the release point (Figure 1). The approximate location of the Hume Line, a 6-inch diameter concrete drainage pipe that runs beneath the tunnel floor, is shown on Figure 1. and Figure 2, in plan and cross section view, respectively. The Hume Line was initially installed as a water management system and set at approximately 2.5 to 3 feet below the tunnel floor to act as a conduit for groundwater to migrate to the sump and limit tunnel flooding. The Hume Line was constructed with a loose connecting bell piping configuration. The top of the pipe was left unsealed to allow groundwater to enter the pipe, while the bottom of the pipe appears to have been grouted to limit vertical seepage and to direct fluids to the sump. During the release, the sump likely filled to a level above the Hume Line connection, allowing fuel to travel east within the Hume Line beneath the tunnel floor and into the subsurface through the openings along the upper portion of the pipe, or through other cracks and imperfections in the concrete pipe. The extent and condition of the Hume Line is not fully understood. Based on sewer camera footage, the Hume Line appears to have a blockage at approximately A3-60.

The distribution of JP-5 impacts in shallow subsurface materials is presented on Figure 1 and Figure 2, based on fluid level gauging data (i.e., accumulations of LNAPL or sheen in boreholes and TWs), results of hydrophobic dye testing (i.e., oil in soil), and concentrations of petroleum hydrocarbons detected in soil and groundwater. Additionally, Figure 2 includes a summary of soil headspace screening results obtained during borehole installation using a photoionization detector (PID) to indicate the approximate distribution of hydrocarbon impacts in the shallow subsurface. Shallow subsurface impacts beneath the Adit 3 tunnel appear to be concentrated in the vicinity of the pumping station entrance, from approximately A3+050 to A3-110. LNAPL accumulations have consistently been observed in A3-01-TW and A3-040-TW, indicating that LNAPL is present in shallow subsurface materials at saturation greater than residual levels in this area. The extent of LNAPL appears to extend to the west at least as far as A3+050, where concentrations of diesel range total petroleum hydrocarbons (total petroleum hydrocarbons-diesel; C10 to C24) in soil and groundwater (1,200 milligrams per kilograms and 1,200 micrograms per liter, respectively) indicate the presence of LNAPL.

To the east, LNAPL has been observed at the bottom of borehole A3-110-BH, consistent with total petroleum hydrocarbons-diesel analytical results in soil collected from this location. The extent of LNAPL may extend further to the east of A3-110 at depths greater than approximately 6 feet below tunnel floor (the maximum depth characterized using the hammer drill rig). The lateral and vertical extent of impacts will be refined based on data collected during future investigation activities. For that purpose, a network of intermediate-depth SVMPs (Figure 1) and monitoring wells (Figure 3) is proposed to be installed (DON 2017; 2022). Monitoring wells and/or SVMPs installed during the timeframe of the proposed NSZD study may be incorporated into the monitoring program.

4. NSZD Background

NSZD is the combination of naturally-occurring processes that decrease the mass of LNAPL in the subsurface over time. The mechanisms responsible for LNAPL depletion include volatilization, dissolution, and biodegradation (ITRC 2018). The significance that these mechanisms play in depleting LNAPL depends on the LNAPL composition (e.g., the volatility, solubility, and biodegradability of LNAPL constituents) and the site setting, which includes the site geochemistry, microbial ecology, and subsurface characteristics that control the movement of soil gas and groundwater into and out of the source zone.

The efficacy of natural attenuation for degrading petroleum hydrocarbons in groundwater has been well established since the early 1990s (NRC 1993; Rice et al. 1995). While there has long been evidence that microbiological degradation processes responsible for natural attenuation in dissolved phase plumes were also occurring within LNAPL source zones to 'weather' or change the composition of LNAPL (Christensen and Larsen 1993), there was a common historical perception that biodegradation of the source material itself was limited (Lyman, Reidy, and Levy 1992; Newell et al. 1995). More recent research on NSZD at petroleum LNAPL sites has demonstrated that the rate of natural LNAPL depletion is often on the order of hundreds to thousands of gallons of LNAPL per acre per year (Johnson, Lundegard, and Liu 2006; Garg et al. 2017; CRC CARE 2020a). This has highlighted the importance of including NSZD in the LNAPL conceptual site model development and site management decision making (Mahler, Sale, and Lyverse 2012; Lundy 2014). NSZD measurements are more frequently being collected to better understand the relative benefit of active LNAPL remediation alternatives at LNAPL sites as potentially an alternative or supplement to approaches such as LNAPL skimming or bailing (ITRC 2018; CL:AIRE 2019; CRC CARE 2020b).

Increased focus on NSZD in recent years has led to the development of guidance on data collection and interpretation approaches by several institutions around the world (ITRC 2009; 2018; API 2017; CRC CARE 2018; CL:AIRE 2019). Several methods have been developed to evaluate NSZD rates (API 2017; ITRC 2018). While methods have been developed to estimate relative hydrocarbon mass losses based on changes in LNAPL composition (Douglas et al. 1996; Lundy 2014; DeVaull et al. 2020), the prevailing methods for quantifying NSZD rates rely on mass and/or energy balance approaches, and involve measurements of the flux of electron acceptors (e.g., O_2) into the source zone (Johnson, Lundegard, and Liu 2006) and/or measuring the flux of petroleum biodegradation products such as CO_2 (Sihota, Singurindy, and Mayer 2011; McCoy et al. 2014) or excess heat (Sweeney and Ririe 2014; Warren and Bekins 2015) out of the source zone. The overall rate of depletion is expressed in terms of mass or volume of hydrocarbon degraded per unit area, per unit time (e.g., gallons per acre, per year).

4.1 PREVIOUS NSZD STUDY

An NSZD study was conducted in the vicinity of the tank farm of the Red Hill Bulk Fuel Storage Facility in 2017 (DON 2019) using multiple lines of evidence to evaluate NSZD. The NSZD study included a soil vapor study as a qualitative evaluation to determine if there was evidence of NSZD occurring and a qualitative study using the carbon dioxide efflux and thermal methods. Below is a summary of the NSZD study provided in the *Conceptual Site Model, Investigation and Remediation of Releases and Groundwater Protection and Evaluation* (DON 2019).

The 2017 soil gas study included collection of soil vapor samples from shallow, middle, and deep soil vapor probes underneath the fuel storage tanks and vapor pins installed in the upper access tunnel. The VOC concentrations in the vapor samples showed differences in the alkane composition indicating NSZD processes were active. The oxygen concentrations were generally high (13.7 to 20.6 percent) and carbon dioxide was low (0.1 to 3.2 percent). The aerobic environment was attributed to soil vapor probes not installed within LNAPL impact areas and a hypothesis that the tunnel ventilation system is providing atmospheric air to the formation (further discussion below). The vertical interval for the soil vapor monitoring probes installed for this study were selected based on elevated PID readings during installation.

NSZD rates were estimated using the carbon dioxide efflux method, which consisted of carbon dioxide efflux analysis including the use of carbon dioxide traps (devices placed on the ground surface to capture the CO_2 generated from biodegradation of hydrocarbons fluxing across the ground surface) and measurement of CO_2 in the tunnel ventilation system exhaust. These carbon dioxide fluxes were converted to petroleum hydrocarbon degradation rates (NSZD rates). The NSZD rates over the tank farm area were estimated at 4,400 to 7,400 gallons per year. The study indicated that the tunnel is ventilated, operates at a lower air pressure than the basalt, and behaves like a soil vapor extraction (SVE) system, pulling soil vapors out of and adding atmospheric air to the basalt underlying the tunnel, thereby resulting in the aerobic environment observed in the soil vapor study.

The thermal method included vertical temperature profiling of three existing wells within the LNAPL footprint and one background well (outside of the LNAPL footprint). Temperature anomalies (elevated temperatures in the wells within the LNAPL footprint compared to the background well) were converted to NSZD rates. The NSZD rates from the thermal method over the tank farm area were estimated at 2,600 to 17,300 gallons per year.

The lessons learned from the 2017 study were used to inform this NSZD study, which includes the collection of soil vapor samples and temperature profiles. Although deemed successful in the previous study, the carbon dioxide flux method is not included in this NSZD study because the tunnel floor is an impervious surface, which would impede soil vapor flux through the tunnel, required for CO_2 trap placement. Measurement of CO_2 in the tunnel ventilation system exhaust would not be specific to the November 2021 JP-5 release because the ventilation system aggregates petroleum degradation from all areas of the site. Therefore, the NSZD study will focus on local data collection using the temperature profiling method (Sweeney and Ririe 2014; Warren and Bekins 2015), along with soil gas composition (Johnson, Lundegard, and Liu 2006). The sampling and analysis methods are further discussed in Sections 5 and 8, respectively.

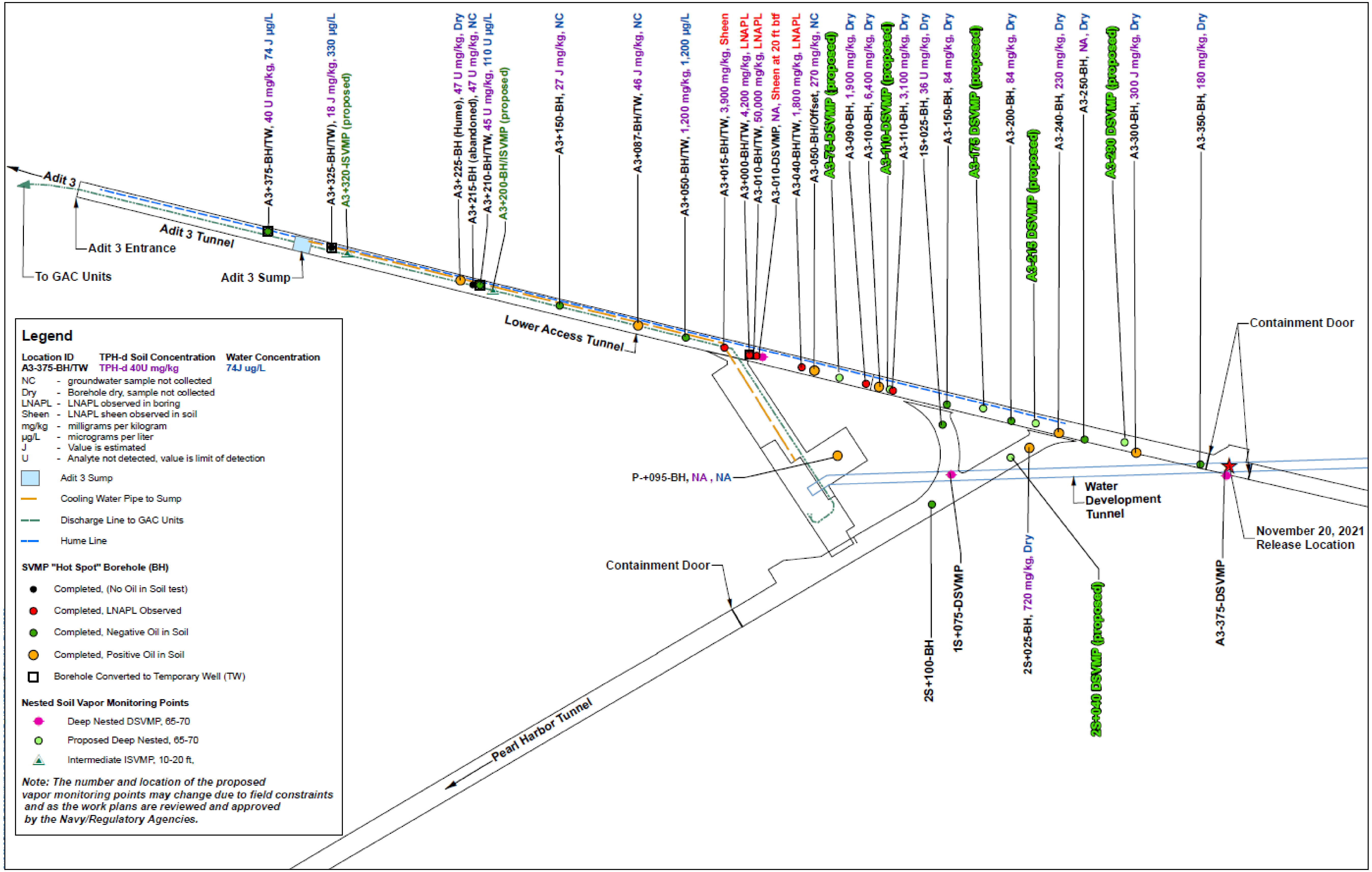
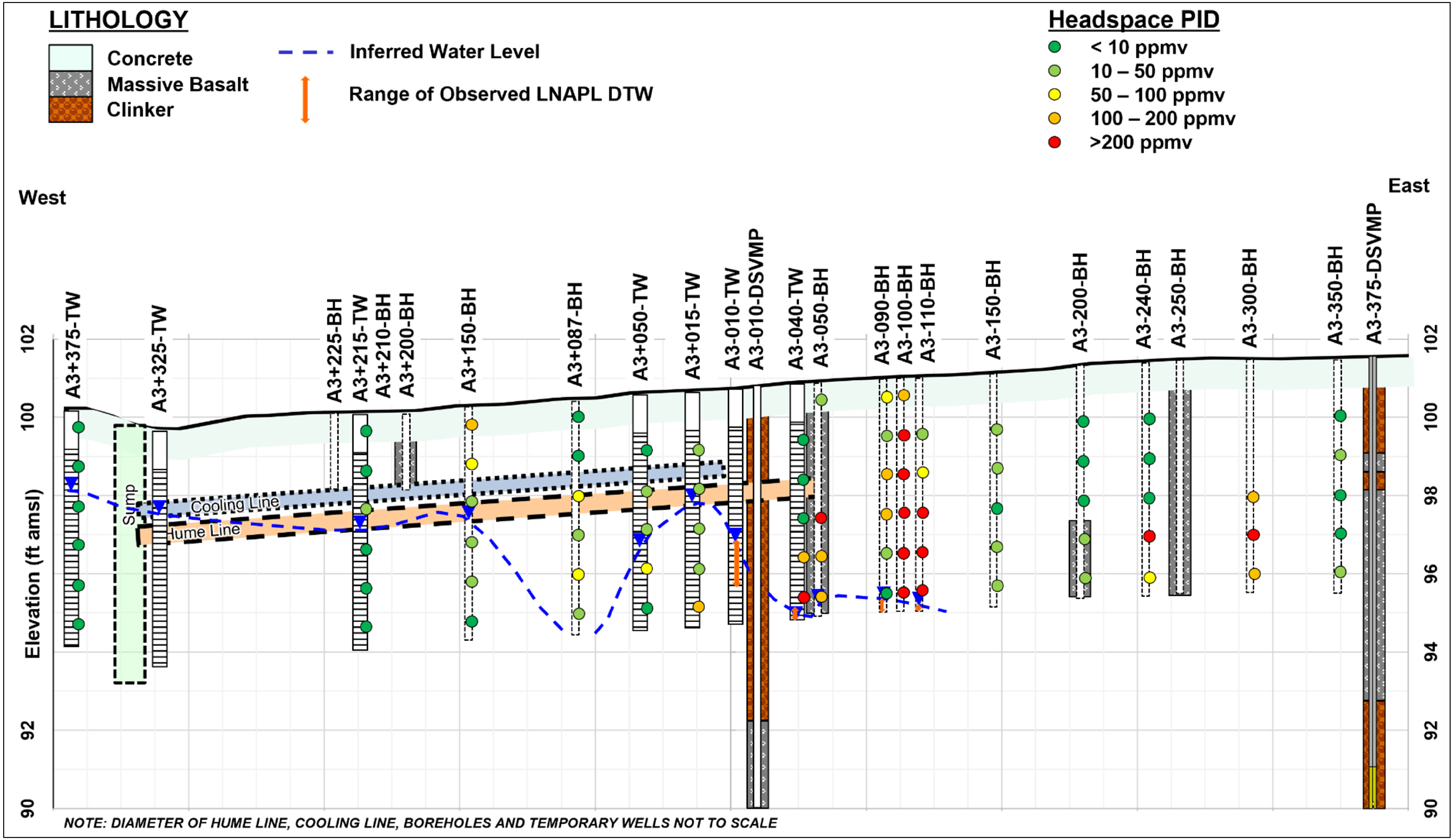
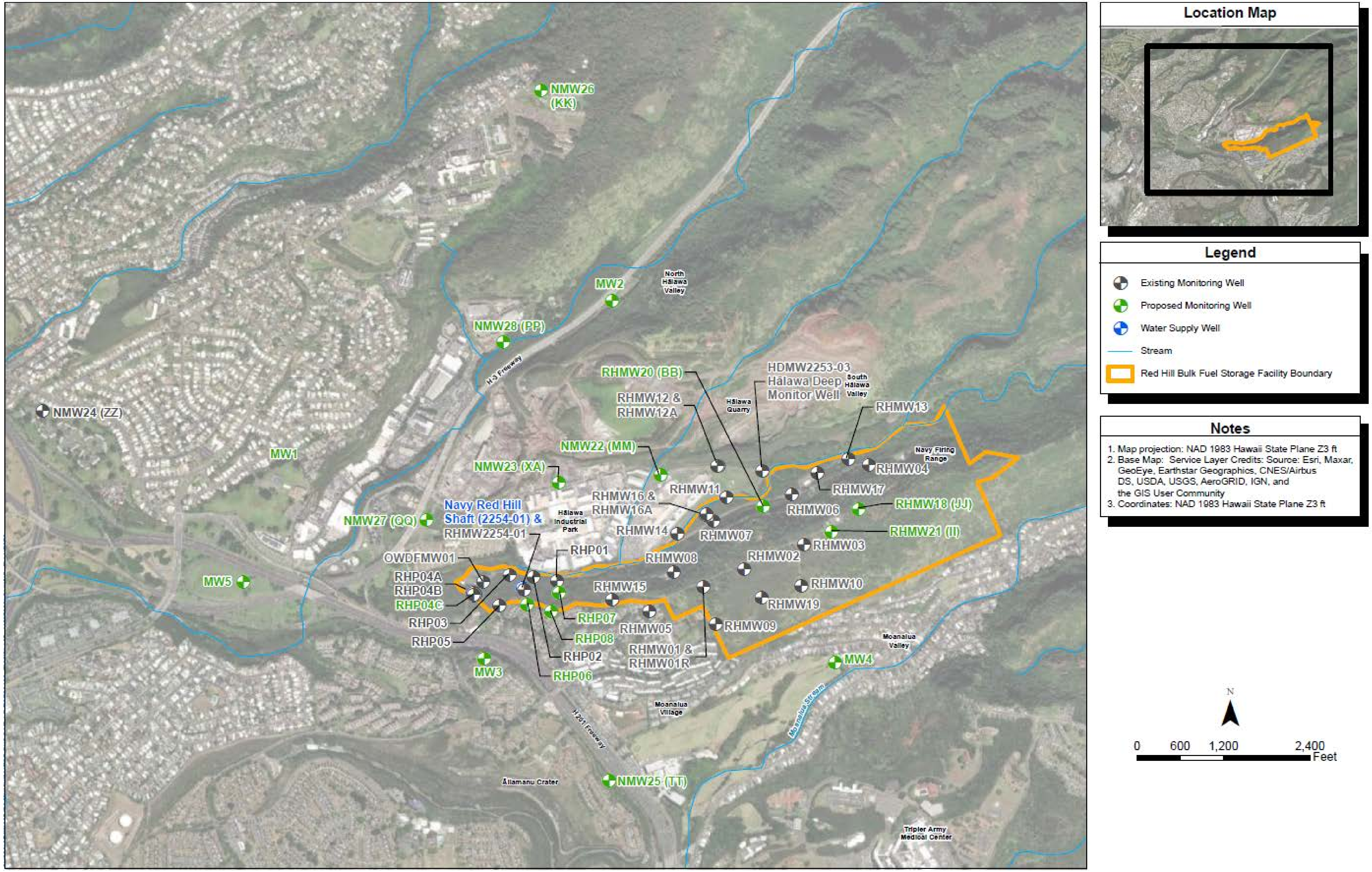


Figure 1: In-Progress Field Map (as of October 17, 2022), Adit 3 LNAPL Site Characterization, November 20, 2021 JP-5 Release



NOTE: DIAMETER OF HUME LINE, COOLING LINE, BOREHOLES AND TEMPORARY WELLS NOT TO SCALE

Figure 2: Investigation Area Cross Section



Notes
1. Map projection: NAD 1983 Hawaii State Plane Z3 ft
2. Base Map: Service Layer Credits: Source: Esri, Maxar, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community
3. Coordinates: NAD 1983 Hawaii State Plane Z3 ft

Figure 3: Proposed and Existing Monitoring Well Network (As of December 2022)

5. Project Quality Objectives

As a component of preparing this work plan, project quality objectives (PQOs) were developed for the study following Standard Operating Procedure I-A-1 “Development of Project Quality Objectives”. The PQOs (Steps 1 through 5) are presented in Table 2 for reference and were used to guide work plan development. PQO achievement for the pilot studies are presented in Section 8 and in other applicable sections of the work plan.

Table 2: Project Quality Objectives for NSZD Work Plan

Problem Statement (Step 1)	NSZD processes and depletion rates have not been quantified in the vicinity of the November 2021 release, Adit 3. NSZD is a proven in situ remediation technology that has been shown to reduce the mass and change the composition of petroleum hydrocarbons in the subsurface.			
Study Goals (Step 2)	**Study Questions (Step 2)**	**Data Needs and Schedule (Step 3)**	**Study Area (Step 4)**	**Analytical Approach (Step 5)**
Determine if NSZD processes are active	Is there evidence of oxygen utilization or carbon dioxide and methane generation?	Collect monthly: • VOCs, oxygen, carbon dioxide, and methane • Temperature profiles	Unsaturated zone beneath the tunnel floor where hydrocarbon impacts are present	Compare soil vapor composition to atmospheric conditions to determine if there is evidence of NSZD: The presence of VOCs, methane and/or carbon dioxide in soil vapor at concentrations greater than atmospheric conditions, and/or The presence oxygen at concentrations less than atmospheric conditions (approximately 20.9 percent by volume). Compare temperature profiles within the inferred LNAPL extent to background location to determine if a thermal anomaly is present.
Estimate NSZD Rates	What is the estimated rate of petroleum degradation through natural processes?	Conduct once: • Diffusivity Testing Collect monthly: • VOCs, oxygen, carbon dioxide, and methane • Temperature profiles		Use calculations outlined in Section 8.2 to quantify NSZD rates using the gradient (soil gas concentrations and diffusivity test data) and biogenic heat methods.
LNAPL Composition over Time	Is there evidence that the LNAPL composition is changing?	Semiannual analytical sampling of VOCs and TPH		Soil vapor composition will be analyzed semiannually, and the composition data will be evaluated temporally to determine if there is a change in the composition (assume a decrease in volatile and biodegradable compounds).

6. Field Work Activities

Field work activities include repeated soil vapor and temperature measurements over a 24-month period as summarized below and in Table 3:

- Soil vapor monitoring of three deep soil vapor monitoring points (DSVMP) as shown on Figure 1 (A3-10-DSVMP, AS-375-DSVMP, and 1S+075-DSVMP)
  - – Monthly soil vapor screening of differential pressure (tunnel and SVMP), O_2, CO_2, CH_4, and VOCs
  - – Semiannual analytical soil vapor sampling for O_2, CO_2, CH_4, VOCs, and TPH
  - – Diffusivity testing during initial field event
- Temperature profiling
  - – Monthly temperature readings from buried thermistors at DSVMPs
  - – Monthly vertical profiling at background monitoring wells RHMW05 and proposed RHP07 (currently being installed) as shown on Figure 3
  - – Logging of temperature inside tunnel with data logger

Table 3: Summary of Field Work Activities

	One-Time	Continuous	Monthly		Semiannually
Location	Diffusivity Testing	Temperature Logging	Soil Vapor Screening	Temperature Profiling	Soil Vapor Analytical Testing
Deep SVMP (at each Interval)	X		X	X	X
Monitoring Wells				X	
Tunnel Temperature		X			

The NSZD study is scheduled to be conducted over a period of 24 months, and it is expected that additional borings, monitoring wells, SVMPs will be installed as part of the overall site characterization work being conducted under separate WPs. The NSZD study may expand to additional locations if they may provide value to the study using the field methodologies described below. Conversely, locations may be removed if they are not providing value to the study.

6.1 SOIL VAPOR MONITORING

The soil vapor monitoring portion of the NSZD study will include semi-annual analytical sampling and monthly screening. Soil vapor results will be evaluated for the following, in accordance with Johnson et al. (2006) and ITRC (2018) guidance, for qualitative lines of evidence that NSZD is occurring:

- The presence of VOCs, CH_4 and/or CO_2 in soil vapor greater than atmospheric conditions (e.g., detectable concentrations of CH_4, and CO_2 greater than approximately 400 parts per million by volume)
- The presence of O_2 less than atmospheric conditions (approximately 20.9 percent by volume)

Additionally, the analytical samples will provide insight into the compositional change of the LNAPL.

Section 6.2 describes the procedures to be used to record vertical temperature profiles at SVMPs instrumented with temperature probes and monitoring wells to support the NSZD evaluation.

6.1.1 Soil Vapor Analytical Sampling Procedure

Subsurface SVMP probes will be sampled semi-annually for laboratory analysis of total VOCs by TO-3, individual VOC constituents by TO-15, and fixed gases (O_2, CO_2, CH_4, and nitrogen). The Summa canister samples will be shipped at ambient temperature under chain of custody (COC) control to the selected laboratory.

Samples will be collected in accordance with Active Soil Gas Sampling SOP I-B-3, provided in Appendix A.

6.1.2 Soil Vapor Screening Procedure

Monthly soil gas screening will be completed at each of the DSVMPs. The pressure differential will be measured at each DSVMP using a Magnehelic pressure differential gauge, or similar, to evaluate the potential for advective flux to/from the DSVMP. Soil gas composition screening will be completed using a PID with a 10.6 electron volt lamp and a landfill gas meter to measure concentrations of VOCs, O_2, CH_4, CO_2 in soil gas. A water trap and a particulate filter will be installed between the tubing and the gas meter to protect the instruments from water and dust, and an activated carbon filter will be used on the landfill gas meter intake to remove VOCs from the gas sample to prevent VOCs from triggering a false or elevated CH_4 reading. Soil gas will be purged using the internal pump on the field gas analyzers, and readings will be recorded every 30 seconds until stable concentrations are achieved (defined as three consecutive readings within 10 percent of each other with no consistent increasing or decreasing trend).

This soil vapor screening procedure is a modification of the Active Soil Gas Sampling SOP I-B-3, provided along with field data entry logs in Appendix B.

6.1.3 Diffusivity Testing

Gas diffusion coefficients are required to calculate oxygen flux into the subsurface. Gas diffusion coefficients can be estimated from literature values, the Millington-Quirk equation (1961), or through field testing. The field approach described in *In Situ Measurement of Effective Vapor-Phase Porous Media* (Johnson et al. 1998) will be followed. This method evaluates transient changes of tracer gas to determine site-specific effective porous medium gas diffusion coefficients. The tracer gas (sulfur hexafluoride, SF_6) is introduced to the subsurface at a known concentration through a soil gas probe. The tracer gas is allowed to diffuse into the soil matrix for a predefined time period (residence time). At the end of the time period, a grab sample is collected from the soil gas probe and the tracer gas concentration is measured. The process is repeated for several diffusion time intervals, generally 0, 15, 60, and 120 minutes.

Diffusivity testing will be conducted once during the NSZD field program. This test is recommended to be conducted during the initial soil vapor sampling field event after temperature and soil vapor samples have been collected, however it can be done in any monthly event during the first three months. This procedure is provided along with field data entry logs in Appendix C.

6.2 TEMPERATURE PROFILING

Temperature data will be used to construct vertical profiles of temperature with depth at each test well location to determine whether thermal anomalies (i.e., zones of elevated temperature relative to background conditions) associated with LNAPL biodegradation processes can be identified as a qualitative line of evidence that NSZD via biodegradation is occurring at the Site. Additionally, temperature data, along with estimated thermal conductivity values for subsurface materials, will be used to estimate steady state heat flux away from thermal anomalies identified in the subsurface. Heat flux estimates will be used to estimate equivalent hydrocarbon mass loss rates based on stoichiometric relationships for the prevailing biodegradation reactions along with the heat of reaction (determined using published data for the standard enthalpy of formation [e.g., Haynes, Lide, and Bruno 2012]) in accordance with methods presented in Sweeney and Ririe (2014).

The following sections describe the procedures to be used to record vertical temperature profiles at SVMPs, instrumented with temperature probes and monitoring wells to support the NSZD evaluation.

6.2.1 Temperature Profiling at SVMPs Procedure

The SVMPs have been implemented with Physitemp temperature probe with 0.1 degree Celsius accuracy (Physitemp 2022) that are read with a BAT12 thermometer. Temperature readings will be collected at each depth interval during each monthly event. Additionally, temperature data will be collected monthly from the open borehole above the nested SVMPs, if possible, using the procedure outlined in Section 6.2.2.

Field data entry logs are provided in Appendix D.

6.2.2 Temperature Profiling in Monitoring Wells Procedure

Temperature measurements will be collected at five-foot increments from approximately five feet below ground surface to a total depth of approximately 100 feet or to the total depth of the well, whichever is less. The top of the well(s) will be sealed to limit heat exchange with the atmosphere during data collection, and sufficient time will be allowed for the temperature probe to reach equilibrium with the surrounding subsurface materials. Equilibration typically takes 30 to 60 minutes in the unsaturated zone but is likely achieved more rapidly in the saturated zone. All temperature measurements will be made while lowering the probe into the wells. Temperature data, along with fluid level gauging data (i.e., depth to water), will be recorded at each screening location on separate field data-entry logs.

An SOP and field data entry logs are provided in Appendix D.

6.2.3 Tunnel Temperature Logging

AECOM will deploy three temperature loggers (Onset HOBO Pendant, Thermohron iButton, Madgetech Temp1000IS, or similar) in each of the DSVMPs (A3-10-DSVMP, AS-375-DSVMP, and 1S+075-DSVMP) to understand the ambient temperature of the tunnel. The loggers will be set to collect temperature readings every 6 hours.

Data will be downloaded during the monthly monitoring events.

7. Sample Details

Additional details about collecting subsurface gas samples are presented in Appendix E.

7.1 SAMPLE CUSTODY REQUIREMENTS

Each sample will be assigned a COC sample identification (ID) number and a descriptive ID number in accordance with Naval Facilities Engineering Systems Command Pacific Environmental Restoration Program Procedure I-A-8, Sample Naming (DON 2015). All sample ID numbers will be recorded in the field logbook in accordance with Procedure III-D, Logbooks (DON 2015). The COC sample ID number (the only ID number submitted to the analytical laboratory) is used to facilitate data tracking and storage. The COC sample ID number allows all samples to be submitted to the laboratory without providing information on the sample type or source. The descriptive ID number is linked to the COC sample ID number, which provides information regarding sample type, origin, and source.

Table 4: Sample Type and Matrix Identifiers

Identifier	Sample Type	Matrix
GS	Soil Vapor	Gas

Table 5: Field Quality Control (SACODE) Type Identifiers

Identifier	Field or QC Sample Type	Description
N	Primary Sample	All field samples, except QC samples
FD	Duplicate	Co-located for unconsolidated material

QC quality control

Table 6: Sample Date

Identifier	Field or QC Sample Type	Description
MMDDYY	Sample Collection Date	MM month, DD day, YY year

QC quality control

7.1.1 Handling, Shipping, and Custody

All samples collected for analysis will be recorded in the field logbook in accordance with Procedure III-D, *Logbooks* (DON 2015). All samples will be labeled and recorded on COC forms in accordance with Procedure III-E, *Record Keeping, Sample Labeling, and Chain-of-Custody* (DON 2015). Samples will be handled, stored, and shipped in accordance with Procedure III-F, *Sample Handling, Storage, and Shipping* (DON 2015). All samples collected on this project will be shipped to the analytical laboratory via overnight airfreight.

All samples received at the analytical laboratory will be managed in accordance with laboratory SOPs for receiving samples, archiving data, and sample disposal and waste collection, as well as storage and disposal per Section 5.8, “Handling of Samples” of the Department of Defense *Quality Systems Manual (QSM)* v. 5.4 (DoD and DOE 2021).

7.2 LABORATORY QC SAMPLES

Laboratory quality control samples will be prepared and analyzed in accordance with the methods and procedures listed in Appendix E.

7.3 FIELD EQUIPMENT CALIBRATION, MAINTENANCE, TESTING, AND INSPECTION TABLE

Table 7 provides equipment calibration, maintenance, testing, and inspection information.

Table 7: Field Equipment Calibration, Maintenance, Testing and Inspection

Field Equipment	Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference
Photoionization Detector	Inspection and calibration	Daily prior to commencing field activities and as needed throughout the day	Calibrate using site air and isobutylene gas following the instrument manufacturer’s specifications. Isobutylene concentration at 100 ppm.	If PID cannot be calibrated per specifications, replace PID.	Field Lead	Follow manufacturer’s instructions and NAVFAC Northwest SOP III-J.
Four gas meter	Inspection and calibration	Daily prior to commencing field activities and as needed throughout the day	Calibrate using site air and 4-gas calibration mix gas following the instrument manufacturer’s specifications.	If meter cannot be calibrated per specifications, replace four gas meter.	Field Lead	Follow manufacturer’s instructions and NAVFAC Northwest SOP III-J.

ppm	part per million
NAVFAC	Naval Facilities Engineering Systems Command
SOP	standard operating procedure

8. Data Analysis

NSZD rates will be quantified in terms of volume of hydrocarbon degraded per unit area per unit time (e.g., gallons per acre per year). The rates will be evaluated spatially to determine the average NSZD rate across the study area.

8.1 QUALITATIVE EVALUATION OF NSZD PROCESSES

Soil gas results will be evaluated in accordance with Johnson, Lundegard, and Liu (2006), API (2017), and ITRC (2018) guidance for qualitative lines of evidence that NSZD is occurring, including:

- The presence of VOCs, CH_4 and/or CO_2 in soil vapor at concentrations greater than atmospheric conditions (e.g., detectable concentrations of CH_4, and CO_2 greater than approximately 400 parts per million by volume [ppmv]), and/or
- The presence O_2 at concentrations less than atmospheric conditions (approximately 20.9 percent by volume).

Temperature data will be used to construct vertical profiles of temperature with depth at each test well location to determine whether thermal anomalies (i.e., zones of elevated temperature relative to background conditions) associated with LNAPL biodegradation processes can be identified as a qualitative line of evidence that NSZD is occurring via biodegradation.

8.2 QUANTITATIVE EVALUATION NSZD DATA

The following sections describe the methodology of the data analysis used to estimate NSZD rates at the site.

8.2.1 Stoichiometry and Conversion Factors Utilized in NSZD Data Interpretation

The methods utilized to estimate NSZD rates rely on stoichiometric relationships derived from the prevailing biodegradation reactions that are observed at most LNAPL sites. Following Johnson et al. (2006) and Garg et al. (2017), the dominant biodegradation reactions involved in NSZD are assumed to be methanogenesis (Equation 1) followed by aerobic oxidation of methane (Equation 2), or direct aerobic oxidation of hydrocarbon constituents that comprise the LNAPL (Equation 3), as indicated below, where “a” and “b” represent the number of carbon and hydrogen atoms in a given hydrocarbon compound, respectively.

$$C_aH_b + \left(a - \frac{b}{4}\right) \cdot H_2O \rightarrow \left(\frac{a}{2} + \frac{b}{8}\right) \cdot CH_4 + \left(\frac{a}{2} - \frac{b}{8}\right) \cdot CO_2$$ **Equation 1**

$$\left(\frac{a}{2} + \frac{b}{8}\right) \cdot (CH_4 + 2 \cdot O_2 \rightarrow CO_2 + 2 \cdot H_2O)$$ **Equation 2**

$$C_aH_b + \left(a + \frac{b}{4}\right) \cdot O_2 \rightarrow a \cdot CO_2 + \left(\frac{b}{2}\right) \cdot H_2O$$ **Equation 3**

These equations provide a basis for estimating NSZD rates by measuring the flux of oxygen (O_2) into a source zone, or by measuring the flux of hydrocarbon degradation products such as carbon dioxide (CO_2) out of the source zone. Additionally, the change in enthalpy, or heat of reaction, can be calculated from the internal energy of the products and reactants in Equations 1 to 3. The heat of reaction can then be used to convert measurements of subsurface heat flux associated with LNAPL degradation into NSZD rates.

Whether degradation occurs through methanogenic degradation followed by methane oxidation (Equation 1 followed by Equation 2) or through direct aerobic oxidation (Equation 3), the reactants and products are ultimately the same. The stoichiometric relationships can be expressed in terms of the mass of hydrocarbon degraded per unit mass of O_2 consumed, the mass of hydrocarbon degraded per unit mass of CO_2 produced, or the amount of heat energy released per unit mass of hydrocarbon degraded. NSZD rates for this study will be calculated using decane ($C_{10}H_{22}$) as a representative hydrocarbon compound. The resulting stoichiometric coefficients for O_2 utilization (S_{O_2}; 0.29 g-$C_{10}H_{22}$/g-O_2), CO_2 production (S_{CO_2}; 0.32 g-$C_{10}H_{22}$/g-CO_2), or heat released to the subsurface (ΔH_{rxn}; 47.6 kJ/g-$C_{10}H_{22}$) was calculated using molecular weights and standard heigh of formation for each of the compounds represented in Equations 1 and 3, presented in Table 8 (Haynes, Lide, and Bruno 2012).

Table 8: Molecular Weights and Standard Enthalpy of Formation for Constituents Involved in NSZD Biodegradation Reactions

Constituent	Molecular Weight (g/mol)	Standard Enthalpy of Formation (kJ/mol)
Decane ($C_{10}H_{22}$)	142.3	-300.9
Water (H_2O)	18.0	-285.8
Carbon Dioxide (CO_2)	44.0	-393.5
Oxygen (O_2)	32.0	0.0
Methane (CH_4)	16.0	-74.6

8.2.2 Quantitative Evaluation of Soil Vapor Data

Natural depletion of petroleum consumes O_2 and produces CO_2, which creates a chemical gradient that drives diffusive gas flux. The mass flux of O_2 into the subsurface or transport of CO_2 from an LNAPL source at depth toward ground surface can be estimated using Fick’s first law (Equation 4; Johnson, Lundegard, and Liu 2006). The soil gas data provide a direct measurement of soil gas concentration gradients that will be coupled with gas diffusion coefficients to calculate rates of volatilization, O_2 ingress and utilization, and/or CO_2 efflux to quantify natural depletion rates.

$$J_i = D_i^{eff} \cdot \left(\frac{\Delta C}{\Delta z}\right) \qquad \textbf{Equation 4}$$

Where:

J_i = Mass flux of O_2 or CO_2 (grams per square meter per second)

D_i^{eff} = The effective gas diffusion coefficient (square meter per second [m^2/s])

ΔC = Concentration difference between two sample depths of O_2 or CO_2 (grams per cubic meter [g/m^3])

Δz = Differ depth at which soil gas composition was measured (m)

Gas diffusion coefficients for subsurface materials in the vicinity of the soil vapor probes (and similar formation materials) will be derived using field tests, as described in Section 6.1.3 with calculations detailed in Appendix C. Literature estimates and/or estimates using Millington and Quirk (1961) will be used for rock types where SVMP screen intervals were not installed, i.e., there is not a field derived diffusivity, when calculating the effective diffusion coefficient.

O_2 and CO_2 mass flux values are converted into equivalent hydrocarbon depletion rates (R_{NSZD}) in units of gal/ac/yr using stoichiometric coefficients (S_{O_2}; 0.29 g-$C_{10}H_{22}$/g-O_2, S_{CO_2}; 0.32 g-$C_{10}H_{22}$/g-CO_2, ITRC 2009) and LNAPL density, using Equation 5:

$$R_{NSZD} = \frac{S_i \cdot J_i}{\rho_n} \cdot C \qquad \textbf{Equation 5}$$

Where:

R_{NSZD} = Equivalent hydrocarbon depletion rate (gal/ac/yr)

S_i = Stoichiometric coefficient for compound *i* (kg-HC/kg-compound *i*)

ρ_n = Density of LNAPL (kilogram per liter)

C = Unit conversion factor

8.2.3 Quantitative Evaluation of Temperature Profiling

Temperature data, along with estimated thermal conductivity values for subsurface materials, will be used to estimate steady state heat flux away from thermal anomalies identified in the subsurface. Heat flux estimates will be used to estimate equivalent hydrocarbon mass loss rates based on stoichiometric relationships for the prevailing biodegradation reactions along with the heat of reaction (determined using published data for the standard enthalpy of formation [e.g., Haynes, Lide, and Bruno 2012]) in accordance with methods presented in Sweeney and Ririe (2014).

The temperature increase from NSZD at a given depth and time of year is calculated using Equation 6:

$$\Delta T_{NSZD}(z,t)=T_{SZ}(z,t)-T_{BKGD}(z,t) \qquad \textbf{Equation 6}$$

Where:

$\Delta T_{NSZD}(z,t)$ = The difference in temperature at depth “z” and time “t” attributable to NSZD (°C)

$T_{SZ}(z,t)$ = Temperature at depth “z” and time “t” within the LNAPL source zone (°C)

$T_{BKGD}(z,t)$ = Background temperature at depth “z” and time “t” outside of the LNAPL source zone (°C)

The upward and downward conductive heat flux away from the depth at which the maximum temperature difference is observed at each source zone monitoring location is calculated using Fourier’s law of heat conduction. The upward and downward heat flux are then added to calculate the total conductive heat flux attributable to biodegradation (Equation 7):

$$q_T = K_u \cdot \left(\frac{\Delta T}{\Delta z}\right)_u + K_d \cdot \left(\frac{\Delta T}{\Delta z}\right)_d \qquad \textbf{Equation 7}$$

Where:

q_T = Total conductive heat flux upward and downward from the depth of the maximum observed increase in temperature relative to background (watts per square meter [W/m^2])

K_u = Effective thermal conductivity of subsurface materials from depth of maximum observed increase in temperature to ground surface (watts per meter, per Kelvin [W/m/K])

$\left(\frac{\Delta T}{\Delta z}\right)_u$ = Upward temperature gradient (°C/m)

K_d = Effective thermal conductivity of subsurface materials from depth of maximum observed increase in temperature to total depth of temperature measurement (W/m/K)

$\left(\frac{\Delta T}{\Delta z}\right)_d$ = Downward temperature gradient (°C/m)

Heat flux estimates are used to calculate equivalent LNAPL depletion rates based on stoichiometric relationships for the prevailing biodegradation reactions (Equations 1 to 3) along with the heat of reaction (determined using published data for the standard enthalpy of formation, Table 8) using Equation 8:

$$R_{NSZD} = \frac{q_T}{\Delta H_{rxn} \cdot \rho_n} \qquad \textbf{Equation 8}$$

9. Reporting

AECOM plans to initiate the NSZD evaluation upon approval of this WP and provide informal monthly updates to the Navy on the progress of the NSZD study. The monthly update will be a bullet-point updates via email that describes the qualitative evidence of NSZD (soil vapor composition) along with a table or chart with monthly NSZD rates derived from the soil vapor and temperature profiling data. The temperature profiling data may take up to 3 months of data collection to develop an appropriate background correction model to derive rates and this model may be modified over the course of the NSZD study period.

An NSZD progress report will be prepared after one year to support the evaluation of NSZD effectiveness and be included as an attachment in the Remedial Alternatives Analysis (RAA) report. Included in the one-year progress report will be a recommendation to collect additional NSZD data or terminate the study, if evidence of NSZD is adequate to meet the RAA recommendations. At the conclusion of the NSZD study, AECOM will prepare a final NSZD report summarizing the data collected. It is anticipated that the NSZD report will present the soil gas and temperature data collection methods, locations where data were collected, data analysis methods, qualitative evidence of ongoing NSZD, and quantitative calculation of NSZD biodegradation rates.

10. References

American Petroleum Institute (API). 2017. *Qualification of Vapor Phase-Related Natural Source Zone Depletion Processes*. 1st ed. API PUBL 4784. Washington, DC: API Publishing Services. May.

Christensen, L. B., and T. H. Larsen. 1993. “Method for Determining the Age of Diesel Oil Spills in the Soil.” *Ground Water Monitoring and Remediation* 23: 142–49.

Contaminated Land: Applications in Real Environments (CL:AIRE). 2019. *An Introduction to Natural Source Zone Depletion at LNAPL Sites*. London, UK. www.claire.co.uk/LNAPL.

CRC CARE. 2018. *Technical Measurement Guidance for LNAPL Natural Source Zone Depletion*. Newcastle, AU: CRC CARE Technical Report No. 47. Cooperative Research Centre for Contamination Assessment and Remediation of the Environment, 2018.

———. 2020a. *Australian Case Studies of Light Non-Aqueous Phase Liquid (LNAPL) Natural Source Zone Depletion Rates Compared with Conventional Active Recovery Efforts*. Newcastle, AU: CRC CARE Technical Report No. 47. Cooperative Research Centre for Contamination Assessment and Remediation of the Environment, 2020.

———. 2020b. *The Role of Natural Source Zone Depletion in the Management of Light Non-Aqueous Phase Liquid (LNAPL) Contaminated Sites*. Newcastle, AU: CRC CARE Technical Report No. 47. Cooperative Research Centre for Contamination Assessment and Remediation of the Environment, 2020.

DeVaull, George, Rhodes, Ileana, Hinojosa, Emiliano, and C. Bruce. 2020. “Petroleum NAPL Depletion Estimates and Selection of Marker Constituents from Compositional Analysis.” *Groundwater Monitoring & Remediation*. https://doi.org/40. 10.1111/gwmr.12410.

Department of Defense and Department of Energy, United States (DoD and DOE). 2021. *Department of Defense (DoD) and Department of Energy (DOE) Consolidated Quality Systems Manual (QSM)* *for Environmental Laboratories*. DoD/DOE QSM Ver. 5.4. Prepared by DoD Environmental Data Quality Workgroup and DOE Consolidated Audit Program Operations Team.

Department of the Navy (DON). 2015. *Final Project Procedures Manual, U.S. Navy Environmental Restoration Program, NAVFAC Pacific*. JBPHH HI: Naval Facilities Engineering Command, Pacific. May.

———. 2017. *Monitoring Well Installation Work Plan Addendum 02, Investigation and Remediation of Releases and Groundwater Protection and Evaluation, Red Hill Bulk Fuel Storage Facility, Joint Base Pearl Harbor-Hickam, O‘ahu, Hawai‘i; August 25, 2017, Revision 00*. Prepared by AECOM Technical Services, Inc., Honolulu, HI. Prepared for Defense Logistics Agency Energy, Fort Belvoir, VA, under Naval Facilities Engineering Command, Hawaii, JBPHH HI.

———. 2019. *Conceptual Site Model, Investigation and Remediation of Releases and Groundwater Protection and Evaluation, Red Hill Bulk Fuel Storage Facility, Joint Base Pearl Harbor-Hickam, O‘ahu, Hawai‘i; June 30, 2019, Revision 01*. Prepared by AECOM Technical Services, Inc., Honolulu, HI. Prepared for Defense Logistics Agency Energy, Fort Belvoir, VA, under Naval Facilities Engineering Command, Hawaii, JBPHH HI.

———. 2022. *Site Characterization Plan, Moderate Depth SVMP Addendum Red Hill Bulk Fuel Storage Facility (November 2021 Release, U.S. Navy Well 2254-01) Joint Base Pearl Harbor-Hickam Oahu HI*. Prepared by AECOM Technical Services, Inc. JBPHH HI: Naval Facilities Engineering Systems Command, Hawaii. May.

Douglas, G. S., A. E. Bence, R. C. Prince, S. J. McMillen, and E. Butler. 1996. “Environmental Stability of Selected Petroleum Hydrocarbon Source and Weathering Ratios.” *Environmental Science and Technology* 30: 2332–39.

Garg, S., C. J. Newell, P. R. Kulkarni, D. C. King, D. T. Adamson, M. I. Renno, and T. Sale. 2017. “Overview of Natural Source Zone Depletion: Processes, Controlling Factors, and Composition Change.” *Groundwater Monitoring & Remediation* 37 (3): 62–81. https://doi.org/10.1111/gwmr.12219.

Haynes, W.M., David R. Lide, and Thomas J. Bruno, eds. 2012. *CRC Handbook of Chemistry and Physics*. 93rd ed. Boca Raton, FL: CRC Press.

Interstate Technology & Regulatory Council (ITRC). 2009. *Evaluating Natural Source Zone Depletion at Sites with LNAPL*. LNAPL-1. Prepared by the ITRC LNAPLs Team. April.

———. 2018. *Light Non-Aqueous Phase Liquid (LNAPL) Site Management: LCSM Evolution, Decision Process, and Remedial Technologies*. LNAPL-3. Washington, DC: LNAPL Update Team. March.

Johnson, Paul C., Cristin Bruce, Richard L. Johnson, and Mariush W. Kemblowski. 1998. “In Situ Measurement of Effective Vapor-Phase Porous Media Diffusion Coefficients.” *Environmental Science & Technology* 32 (21): 3405–9. https://doi.org/10.1021/es980186q.

Johnson, Paul C., Paul D. Lundegard, and Zhuang Liu. 2006. “Source Zone Natural Attenuation at Petroleum Hydrocarbon Spill Sites: I. Site-Specific Assessment Approach.” *Groundwater Monitoring & Remediation* 26: 82–92.

Lundy, D. 2014. *An Investigation of the Relationship Between Lateral Spreading and Mass Depletion of an LNAPL Body in Contact with Groundwater at the Bemidji, MN Crude Oil Release Site. In Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy*. Athens, GA: University of Georgia, 2014.

Lyman, W. J., P. J. Reidy, and B. Levy. 1992. *Mobility and Degradation of Organic Contaminants in Subsurface Environments*. Chelsea, MI: C.K. Smoley, Inc., 1992.

Mahler, N., T. Sale, and M. Lyverse. 2012. “A Mass Balance Approach to Resolving LNAPL Stability.” *Ground Water* 50: 861–71. https://doi.org/10.1111/j.1745-6584.2012.00949.x.

McCoy, K., J. Zimbron, T. Sale, and M. Lyverse. 2014. “Measurement of Natural Losses of LNAPL Using CO_2 Traps.” *Groundwater* 53: 658–67.

Millington, R. J., and J. M. Quirk. 1961. “Permeability of Porous Solids.” *Transaction of the Faraday Society* 57: 1200–1207. https://doi.org/10.1039/TF9615701200.

Newell, C. J., S. D. Acree, R. R. Ross, and S. G. Huling. 1995. *Groundwater Issue: Light Non-Aqueous Phase Liquids*. Washington, DC: OSWER, 1995.

National Research Council (NRC). 1993. *Ground Water Vulnerability Assessment: Predicting Relative Contamination Potential Under Conditions of Uncertainty*. Washington, DC: The National Academies Press, 1993.

Physitemp. 2022. “Precision Temperature Specialists.” November 2022. https://www.physitemp.com/.

Rice, D. W., R. D. Grose, J. C. Michaelsen, B. Dooher, D. H. MacQueen, S. J. Cullen, W. E. Kastenberg, L. G. Everett, and M. A. Marino. 1995. *California Underground Leaking Fuel Tank (LUFT) Historical Case Analyses*. Report submitted to the California State Water Resources Control Board and Senate Bill 1764 Advisory Committee, 1995.

Sihota, N. J., O. Singurindy, and K. U. Mayer. 2011. “CO_2-Efflux Measurements for Evaluating Source Zone Natural Attenuation Rates in a Petroleum Hydrocarbon Contaminated Aquifer.” *Environmental Science & Technology* 45 (2): 482–88. https://doi.org/10.1021/es1032585.

Sweeney, R.E., and G.T. Ririe. 2014. “Temperature as a Tool to Evaluate Aerobic Biodegradation in Hydrocarbon Contaminated Soil.” *Groundwater Monitoring & Remediation* 34 (3): 41–50.

Warren, Ean, and Barbara A. Bekins. 2015. “Relating Subsurface Temperature Changes to Microbial Activity at a Crude Oil-Contaminated Site.” *Journal of Contaminant Hydrology* 182 (November): 183–93. https://doi.org/10.1016/j.jconhyd.2015.09.007.

Appendix A:
Active Soil Gas Sampling SOP I-B-3

Active Soil Gas Sampling

1. Purpose

This standard operating procedure describes recommended soil gas sampling procedures for use by the United States (U.S.) Navy Environmental Restoration (ER) Program, Naval Facilities Engineering Command (NAVFAC), Pacific personnel.

2. Scope

This procedure applies to all Navy ER projects performed in the NAVFAC Pacific Area of Responsibility.

This procedure shall serve as management-approved professional guidance for the ER Program and is consistent with protocol in most recent version of the the Uniform Federal Policy-Quality Assurance Project Plan (DoD 2005). As professional guidance for specific activities, this procedure is not intended to obviate the need for professional judgment during unforeseen circumstances. Deviations from this procedure while planning or executing planned activities must be approved and documented by the following prime contractor representatives: the CTO Manager and the Quality Assurance (QA) Manager or Technical Director. A Navy project representative (i.e., Remedial Project Manager or QA Manager) shall also concur with any deviations.

3. Definitions

3.1 ACTIVE SOIL GAS SAMPLING

The process of collecting a soil gas sample using mechanical equipment to create a hole, typically to a depth of 3 feet (or greater), and then using a vacuum pump to “actively” withdraw a soil-gas sample through stainless steel probes or plastic tubing. For whole gas sampling, the soil-gas sample is collected in a container that generally has a volume of 0.025 to 6.0 liters; for sorbent tube sampling, a volume of soil gas is drawn through a sorbent-packed tube, trapping contaminants onto the sorbent material. The gas/sorbent sample is then analyzed onsite by a mobile laboratory or sent to a fixed laboratory for analysis. The results provided by active soil-gas systems are most often reported in volume of gas per unit volume of air (e.g., parts per million by volume or part per billion by volume) or in units of mass per unit volume (e.g., milligrams per liter or micrograms per cubic meter).

3.2 PERMEABILITY

Permeability is the resistance of fluids, air, and gases to flow through a porous medium.

3.3 SATURATED ZONE

The saturated zone is the zone in which the voids in the rock (consolidated) or soil (unconsolidated) are filled with water at a pressure greater than atmospheric.

3.4 SOIL GAS

Soil gas is the atmospheric gases, vapor, and gaseous compounds present between soil particles in the subsurface. It can flow and migrate in response to pumping or pressure differentials.

3.5 VADOSE ZONE

The vadose zone is the unsaturated zone between the land surface and the water table. It includes the root zone, intermediate zone, and capillary fringe. The pore spaces contain water at less than atmospheric pressure, as well as air and other gases. Saturated bodies, such as perched groundwater, may exist in the unsaturated zone

3.6 FIXED GAS

Fixed gases are gases that are considered permanent by percent in the atmosphere (e.g. nitrogen gas [N_2] and oxygen gas [O_2]).

3.7 BIOGENIC GAS

Biogenic gas is a gas that is synthesized by biological activity (e.g. methane [CH_4] and carbon dioxide [CO_2]).

4. Responsibilities

The prime contractor CTO Manager is responsible for ensuring that the soil gas survey activities conducted during the NAVFAC Pacific ER Program comply with this procedure. It is recommended that supervisory personnel have an understanding of the principles of soil gas and the physical characteristics of the vadose zone. This should be determined in consultation with the QA Manager or Technical Director. To a certain extent, adequate understanding of the physical characteristics of the vadose zone by field supervisory personnel is site specific and is subject to the judgment of the QA Manager or Technical Director. The CTO Manager is responsible for ensuring that all personnel involved in sampling and/or testing shall have the appropriate education, experience, and training to perform their assigned tasks as specified in Chief of Naval Operations Instruction 5090.1, under *Specific Training Requirements* (DON 2014).

The prime contractor QA Manager or Technical Director is responsible for ensuring overall compliance with this procedure.

The Field Manager is responsible for ensuring that all project field staff are familiar with these procedures.

Field sampling personnel are responsible for the implementation of this procedure.

5. Procedures

5.1 CONSIDERATIONS FOR MUNITIONS AND EXPLOSIVES OF CONCERN

Potential Munitions and Explosives of Concern (MEC) hazards may be encountered in any area formerly or currently occupied or used by the Department of Defense (DoD). MEC hazards may occur on the ground surface, in the subsurface, and within bodies of water, and may not always be readily observable, or identifiable. As a result, whether or not munitions-related activities ever occurred on the specific work area or within waters in which Navy operations/activities will take place, special care should always be taken when conducting field operations, especially intrusive activities, in the event that MEC may be encountered.

If the site is currently recognized as belonging in the Military Munitions Response Program and has a current, Naval Ordnance Safety and Security-accepted, site-specific Explosives Safety Submission (ESS) (per DON 2010), then field activities, especially intrusive activities, shall adhere to the safety procedures outlined within the ESS.

If suspected MEC is encountered on an active DoD installation, immediately notify your supervisor, DoD Point of Contact, and installation Point of Contact, who will contact and facilitate military Explosive Ordnance Disposal response.

5.2 BACKGROUND INFORMATION

The soil gas survey is a semi-quantitative technique for evaluating the distribution of contaminants in soil gas. The resulting data can be used to qualitatively evaluate the potential for, and extent of, certain types of contamination in soil and groundwater.

Soil gas sampling is most often used to:

- Help locate and characterize areas of contaminated soil or groundwater.
- Evaluate subsurface contaminant vapor concentrations in areas where significant concentrations of volatile or semivolatile contaminants are known to be present.
- Identify the potential for contaminated vapor migration and intrusion into overlying and nearby buildings or structures.

If the extent of contamination in soil and groundwater is already known, then soil gas samples are typically not required for site characterization. Soil gas is also not an appropriate characterization technique for non-volatile contaminants such as metals.

There are two broad categories of active soil gas:

1. *Whole air sampling* is the collection of a volume of gas in a sample container. As the name implies, “whole air” samples remain in a gas matrix while in the sample container, thus concentrations of targeted compounds are directly reported. Sample containers associated with whole air sampling are the sample bag (e.g., Tedlar bag) and the canister (e.g. Summa canister).
2. *Sorbent tube sampling* is the drawing a volume of air through a sorbent tube using a pump or other vacuum source and trapping contaminants onto the sorbent material. Unlike whole air sampling, concentrations of targeted compounds are measured by determining the mass of contaminant on the sorbent material, and dividing that mass by the volume of air that was drawn through the sorbent material.

The use of active soil gas surveying to locate potential source areas of subsurface contamination is based on aqueous phase/vapor phase equilibrium in the subsurface. Volatile organic compounds (VOCs) have a tendency to partition from the aqueous phase into the soil vapor phase because of their relatively low solubilities and high vapor pressures. Certain semivolatile compounds also behave in this manner. Generally, an organic compound with a relatively high Henry’s Law constant (i.e., the ratio of a compound’s equilibrium concentration in air to its equilibrium concentration in water) is likely to partition from soil or groundwater into soil gas. The presence of VOCs in shallow soil gas depends on the following factors: (1) the volatilization of VOCs from soil or groundwater into the soil gas, (2) the presence of a chemical gradient in soil gas between the contaminant source and the ground surface, and (3) the physical properties of the soil. If VOCs are present in the soil gas in large enough quantities, they can be detected during a soil gas survey.

Typical compounds detected in soil gas include aromatic hydrocarbons (benzene, toluene, ethylbenzene, xylenes), aliphatic hydrocarbons with carbon ranges from C_1 – C_{10} (methane, butane, pentane), mixtures (gasoline, jet propellant-4), and chlorinated hydrocarbons (chloroform, carbon tetrachloride, vinyl chloride).

Fixed gas (i.e., O_2 and N_2) and biogenic gas (i.e., CO_2, CH_4, nitrous oxide, and hydrogen sulfide) data obtained during a soil gas investigation also provide an indication of potential subsurface contamination. A concurrent increase in CO_2 and decrease in O_2 often indicates increased chemical or biological breakdown of organic compounds. This phenomenon is usually associated with the degradation of petroleum hydrocarbons; however, moisture content, natural organic content, and reduction/oxidation (redox) conditions in the soil can also affect fixed gas/biogenic gas ratios.

5.3 EQUIPMENT AND SUPPLIES

Soil gas sampling requires specialized equipment to install sampling points and obtain air samples. The following equipment and supplies are typically required to conduct soil vapor sampling:

- Hydraulic driving/hammering system designed to drill through pavement and install sampling probes and soil vapor extraction wells at depth
- Stainless steel drive points for setting vapor probes at depth
- For installation of sub-slab vapor probes: a hammer drill and various sized drill bits to establish sampling locations through concrete
- Vapor probes (permanent or temporary)
- Tubing (Teflon preferably for sample lines directly in contact with vapor sample) and fittings
- Oil-less air pump, syringe or evacuation chamber for purging sample lines of ambient air, checking for air leaks in the sampling train, etc.
- Sample containers: Summa canister, sorbent tubes, vials etc.
- Photoionization Detector
- Fittings, tools, syringes
- Helium gas and a Helium Detector (if used for field leak-testing)

The following sections discuss the equipment considerations for whole air sampling and sorbent cartridge sampling.

5.3.1 Whole Air Sampling Equipment and Supplies

Whole air samples may be collected in Summa canisters, gas-tight vials, or sample bags. Canisters are the preferred sampling containers, as gas-tight vials can contain only small sample volumes and sample bags should not be air shipped because the bags may be compromised due to pressure/temperature differentials during transport and tend to sorb contaminants. When low-level definitive data is required, it is recommended that canisters be used. Consideration to the canister volume should be taken when low-level data is required or re-analysis is anticipated. For the purposes of this standard operating procedure, discussion of whole air samples will be focused on air samples collected using canisters. Refer to the State of Hawaii Department of Health (DOH) Technical Guidance Manual for the Implementation of the Hawaii State Contingency Plan (TGM) for guidance on using other sampling containers (DOH 2009).

5.3.1.1 SUMMA CANISTER

A Summa canister is a stainless steel container that has had the internal surfaces chemically deactivated to produce a surface that is nearly chemically inert which is important for minimizing reactions with the sample and maximizing recovery of target analytes from the container. Recovery of compounds from canisters is limited to 10 carbon aromatic hydrocarbons compounds and 12 carbon aliphatic compounds.

Canister Certification for Cleanliness

The Summa canister is provided by a vendor, who certifies that the canister is clean. It is important to verify that the certificate sufficiently documents that project contaminants are not present in the canister at a detection limit appropriate for the site investigation.

Typically, Summa canisters are either “batched” or “individually” certified clean. The definitions of cleanliness will vary among vendors, thus it is important to review the project goals with the vendor providing the Summa canisters. In general, the cleaning process involves a combination of dilution, heat, and high vacuum.

For a “batched” certified clean canister, a canister within the same “batch” has been certified for a subset of VOCs using a gas chromatography/mass spectrophotometer (GC/MS) to have less than a specified concentration. Canisters that are “batch” certified are appropriate for collecting samples with anticipated high concentrations and routine ambient air applications. U.S. Environmental Protection Agency (EPA) methods TO-14 or TO-15 are the analytical methods used to analyze air samples where low level detections are not required (EPA 1999).

For an “individually” certified clean canister, each canister is certified clean for a client-specified list of target analytes below the laboratory’s specified detection limits. Canisters that are “individually” certified are appropriate for collecting ambient and indoor air samples which are driven by risk or litigation. When collecting air samples with an individually certified clean canister, it is important to use the flow controller and pressure gauge associated with the canister. EPA method TO-15 selective ion monitoring (SIM) analysis is the analytical method used to analyze air samples requiring low level detection.

Canister Holding Times

Once a canister is certified clean, the recommend time for sample collection is within 30 days of certification. Following sampling, laboratories prefer to have canisters returned within 14 days of air sampling although 30 days has been recognized by the EPA as acceptable. However, the stability of the chemicals of concern should be the driver on the number of days to analysis. Consult the laboratory for appropriate holding times.

Canister Volumes (Sizes)

Summa canisters are available in various volumes, but the most commonly used sizes are 1 liter and 6 liters. Six liter volumes are typically used for collecting ambient or indoor air samples that require low levels of detection. Ambient and indoor air samples are usually collected over an 8 hour or 24 hour period. One liter canister volumes are typically used for soil vapor sampling and is the minimum volume the State of Hawaii recommends for final decision making purposes. Sample collection periods will ultimately define the size of the Summa canister used.

Associated Canister Hardware

Hardware associated with Summa canisters includes vacuum gauges, flow controllers (critical orifice) and particulate filters.

The flow controller limits the rate that a sample can be drawn into the Summa canister and ensures the sample flow rate over the targeted sampling period (i.e., time-integrated sampling). In general, sampling flow rates should not exceed 200 milliliters per minute (mL/min) or sampling pressures greater than 7 inches of mercury. The vacuum drawn should not strip vapor from the soil but rather sample the vapor within the pore spaces of the subsurface at equilibrium.

Built into most flow controllers are 2 micron particulate filters which eliminate particulates larger than two microns. Grab air samples are usually fitted with a 7 micron particulate filter which removes particles larger than 7 microns.

The vacuum gauge is used to indicate the initial pressure of the canister before sampling and the final pressure after sampling. Laboratories typically prepare Summa canisters with a vacuum of approximately 30 inches of mercury. The vacuum gauges provided by the supplier are typically not calibrated and are meant to provide relative measures of change. Summa canister providers should be consulted to ensure the appropriate size canister and appropriate critical orifice is used to meet project requirements. In addition, if more stringent requirements are needed to monitor the canister pressure, then the canister supplier should be consulted for alternative pressure gauges.

5.3.2 Sorbent Tube Sampling Equipment and Supplies

Sorbent tube sampling may be used for short-chain VOCs or longer chained VOC and semivolatile compounds with molecular weights up to 200 grams per mole which cannot be recovered from canisters. Sorbent tubes are typically stored and shipped chilled (prior to and after sampling) at 4 degrees Celsius but should be brought to ambient temperatures prior to use.

Flow rates drawn through the sorbent tubes should be no more than 200 mL/min. A syringe or a pump may be used to draw air through the sorbent tubes. A pump is used when large volumes of air are required for sampling.

5.3.2.1 SELECTION OF SORBENT TUBES

Selection of sorbent cartridges, solid phase sorbent and the evacuating system used to draw air through the sorbent will depend upon the target analytes of interest and the intent of data use. Sorbent tubes have a maximum sorption capacity before break through occurs. Consideration to the level of contamination will also influence the sorbent tube assembly. Consult with the analytical laboratory for selection of the appropriate sorbent material for the project analytes.

5.4 SELECTION OF SAMPLING LOCATIONS AND ANALYSES

The design of a soil gas survey program depends on the objectives of the program and the types of contaminants anticipated being present. The following items shall be considered when designing a soil gas program.

Number of Samples: This depends upon the extent of anticipated contamination, the size of the site, and the selected sample spacing.

Soil Types Expected to be Encountered (if known): The lithology of the subsurface must be considered when determining sampling locations, distance between samples, and sampling depth.

Depth of Samples: This will depend on the type of contamination, the depth to groundwater, and the objectives of the survey. For instance, evaluation of surface contamination may require only a 3- to 5-foot sampling depth whereas evaluation of deeper soil gas quality may require penetration to 20 feet. Samples may also be collected at several discrete intervals to provide a depth profile. Some flexibility exists in choosing a sampling depth or depths; however, once chosen, consistency across the site should be used.

Distance between Samples: For detecting the limits of plumes, spacing may be 50 to 100 feet or greater. Around a buried tank, spacing may be a few feet. Also consider the relative air permeability of the soil type(s) present. Soils with low air permeability (i.e., clays) may require closer sample spacing. Select spacing based on the objective(s) of the survey, subsurface conditions, and the nature of the target compounds. These factors shall be addressed in the project-specific work plan (WP).

Sampling Point Selection: Large spills, leaks, or plumes are often sampled on a predetermined sampling grid or by using real-time field data. Sample point selection for vapor intrusion concerns suggest locating subslab sample points within a building in areas where utilities or cracks serve as conduits for vapor intrusion, or commonly used spaces. Location access may also be an important factor.

Objectives of the Survey: If the objective is to define and delineate a soil vapor plume, then locate points throughout the suspected area. If the objective is to evaluate the potential for vapor intrusion into a building, then strategically locate subslab sampling locations within the building, at the source areas or around the building. In addressing vapor intrusion concerns, soil gas sample collection generally focuses in and around buildings within 100 feet of the source area. Point samples are used during the initial phases of an investigation to determine the extent and magnitude of subsurface vapor contamination and to assess potential exposure pathways. Soil gas samples are recommended from beneath the building slab and the potential source area. The depth beneath the subsurface and the target analytes should be taken into consideration when developing a soil vapor sampling strategy.

Timing of Sampling: Probe locations can be sampled in stages to meet the objectives of the survey. The first stage of sampling may involve widespread spacing of the probes. Later sampling should focus on areas where VOCs were detected during the first stage of sampling to define the lateral extent of soil gas contaminants, or delineate a source area. Later sampling events should include some overlap with earlier sampling points in order to provide a basis for correlation between data sets.

The frequency of a soil vapor investigation may also depend upon the objectives of the investigation. If vapor intrusion is a concern, collection of a soil vapor sample may occur in two distinct events to determine if seasonal/temporal variations change the soil vapor concentration beneath the slab or within the subsurface.

Selection of Analytes: Generally, only contaminants with relatively high Henry's Law constants are amenable to detection using soil gas; thus, analysis should focus on known indicator compounds at the site. Analytes should be selected to sample the compounds necessary to meet the objectives of the study and to maximize the number of locations sampled in a given period of time.

5.5 SAMPLING PROCEDURES

Summary Overview

Insert the soil gas probes into the ground using a hydraulic ram, pneumatic hammer, or other similar device. When the soil gas probe is at the desired sampling depth, a section of inert tubing is fitted to the top of the probe and connected to an air withdrawal system. The air withdrawal system is used to apply a vacuum to the system and draw soil gas from the surrounding formation into the probe. Purge the system for a sufficient amount of time to allow all of the atmospheric air to be removed, and ensure that a representative soil gas sample can be obtained. The amount of air to be removed is proportional to the volume of the sampling probe. Maintain an airtight seal around the soil gas probe at the ground surface to help prevent possible short-circuiting from atmospheric air diluting soil vapor gas concentrations. Purging of approximately 1.5 volumes permits removal of atmospheric air from the system with a minimum disturbance of the soil gas around the probe tip. Unlike purging of a groundwater monitoring well, purging of a soil gas probe should remove only the ambient air in the system. If a vacuum pump is used, record vacuum pressure and time required to purge the prescribed volume of gas from each probe to permit estimation of relative soil permeabilities.

When purging is complete, end the air withdrawals and allow the sampling system to return to atmospheric pressure. Withdraw the appropriate soil gas sample volume from the system using the vacuum in a Summa canister or pull soil gas through a sorbent tube using a vacuum pump.

Other methods of sample withdrawal and collection are acceptable as long as approval is obtained from the CTO Manager and QA Manager or Technical Director.

As part of the sampling procedure, record probe locations on a site map in accordance with Procedure I-I, *Land Surveying*. In addition, use field data forms (and chain-of-custody forms if necessary) to record observations regarding vapor sampling and probe installation. These field data forms may include, but are not limited to, vacuum pressures corresponding to steady flow, time required for the sampling system to reach atmospheric pressure, sampling depth, volume of soil gas extracted, soil characteristics, and procedures that are necessary to drive sampling probes to the target depth.

For additional information on the installation of temporary and permanent sample probes, please refer to the DOH TGM (DOH 2009, Section 7.9).

5.5.1 Purging Vapor Probe Locations

Once the vapor probe has been installed at the designated sampling location, the vapor probe should be purged of ambient or stagnant air. The volume of air space in sand packs installed with the vapor point should be included in purging if less than 24 hours has lapsed since installation of the probe.

5.5.2 Equilibrating Vapor Probe Locations

Following purging, vapor probe locations should be allowed to equilibrate. Equilibration times will depend upon the method of installation. The DOH TGM indicates that temporary probes reach equilibrium within 2 hours or so of installation, while permanent probes installed with a direct push rig typically require 8 to 24 hours. Vapor probes installed with a hollow auger are expected to require 48 hours of equilibration time. Equilibration times should be clearly communicated in the planning phases of a project and agreed upon by all project stakeholders.

5.5.3 Purging Sampling Trains

Following equilibration, connect an airtight canister assembly or sorbent cartridge assembly to the vapor probe using inert, rigid-walled tubing (i.e., Teflon, nylon, or stainless steel) and appropriate fittings.

This sampling train should be purged from ambient air prior to sampling. The rule of thumb for purging sample tubing is three tubing-volumes. The goal of purging is to have the tubing and other equipment filled with soil vapor prior to sample collection. Purging sample tubing can be accomplished by using a syringe, a pump or a canister and a three way valve. The purging of sample lines should not cause an excess vacuum on the soil. Stripping of vapor from soil should be avoided. The DOH TGM recommends that purging flow rates should not exceed 200 milliliters (mL) per minute and vacuum pressures should not exceed 7 inches of mercury.

5.5.4 Permeability Testing

While evacuating sample tubing of ambient air, the permeability of the sample location can be tested with a 20 or 50 mL syringe. If the syringe has difficulty drawing air from the probe location, the flow rates for sampling soil vapor need to be lowered. Alternatively, the sample location could be abandoned and another sampling location installed.

5.5.5 Leak Testing

Prior to sampling, the sample train should be leak tested. Leaks in a sampling train and the vapor probe surface seal can result in dilution of the soil vapor samples with ambient air resulting in low biased reported values. There are two types of leak tests: 1) a tightness test which checks the tightness of the sampling train and 2) a tracer test which measures the presence/absence of a compound introduced near the vapor probe surface seal. The design of the system used to perform a leak test will depend upon the installation design of the vapor probe.

The design of the tightness test should include isolating the sample train from the soil vapor probe and drawing a vacuum on the sampling train. The applied vacuum should hold for at least 60 seconds. If the vacuum does not hold, retighten connections of the sampling train and perform tightness test again.

There are two options for performing the tracer test: 1) *surface seal testing*, where the tracer compound (i.e., isopropanol) is applied to an absorbing material and placed on the vapor probe surface seal *or* a tracer gas (i.e., helium or difluoroethane) is introduced into a small shroud which is placed over the vapor probe surface seal; and 2) *whole apparatus testing,* where a tracer gas is introduced into a shroud which covers the entire sampling apparatus.

Of the two options, the surface seal testing is the easiest to implement and uses less tracer material. Feed-back on the integrity of the vapor point is immediate if helium is used as the tracer gas because presence of helium can be tested for in the field with a hand-held helium detector. The whole apparatus tracer test option can be implemented if the integrity testing of the entire sampling apparatus is required. Selection of the option used for leak testing should be agreed upon by all stakeholders.

There are multiple tracer compounds that can be used for leak testing. Three of the commonly used compounds are isopropanol, helium and difluoroethane. Each has advantages and disadvantages. The advantages of using isopropanol and difluoroethane, are that they are both inexpensive, readily available, and isopropanol does not require a shroud. There are several disadvantages of using these tracer compounds: 1) there are no available field meters that are selective for these compounds, so the presence of a leak is not known until the samples are analyzed by the laboratory; 2) if the compounds are present in high concentrations in the sample, they may interfere with laboratory analysis and elevate reporting levels above project action levels; and 3) the quantification of a leak can only be estimated because the initial concentration of the compounds in the field are unknown. The advantage of using helium is that it can be detected and quantified in the field. As a result, leaks at the sampling point can be determined immediately and the size of the leak can be quantified if the sample is tested for helium in the laboratory and the concentration of helium under the shroud maintained for the duration of the sampling period.

5.5.6 Prepare Summa Canister (Whole Gas Sampling)

Prior to sampling, verify the evacuated pressure of the canister (typically 30 inches of mercury). Do not use the canister if the pressure is less than 25 inches of mercury (or as appropriate for canister volume) and contact canister supplier. Record the initial pressure on the sample chain of custody (COC).

For grab sampling, verify the canister valve is closed and attach particulate filter. For time integrated sampling, close canister value and assemble the canister, flow controller and pressure gauge. Close assembly by capping the sample inlet. Check for leaks in assembly by opening and quickly closing the canister valve. If the needle on the vacuum gauge drops the assembly is not air tight. Refit and/or tighten connection until the needle on the vacuum gauge remains steady. Do not use assembly if it is not air tight.

5.5.7 Prepare the Sorbent Tube (Sorbent Tube Sampling)

Prior to sampling, tubes should be kept in their storage and transportation container and allowed to equilibrate with ambient temperature. The flow rates should be set using a dummy tube of identical construction. Using clean gloves, the sample tubes should be removed from the container and attached to the sampling lines. Any flow rate adjustments should be made quickly to avoid sampling errors. Then the flow rate should be monitored throughout the sampling process.

5.5.8 Collect Soil Gas

To begin, open canister valve at a half turn or start vacuum pump for the sorbent tube assembly. Record start date and time. Periodically monitor the progress of the air sampling by verifying sufficient vacuum pressure remains for entire sampling period for canister sampling. Monitor and record the flow rate periodically stable over the sampling period for sorbent tube sampling.

For canister sampling, the final vacuum pressure should preferably be 5 inches of mercury but are acceptable between 2 to 10 inches of mercury. If the vacuum is less than 1 inch of mercury, the air sample integrity may have been compromised. Record the final pressure and end date and time as well as the canister, controller and gauge serial numbers.

For sorbent tube sampling, turn off pump at pre-defined times, and seal sorbent tubes. Record the final flow rate, end date and end time, and the sorbent serial number.

5.5.9 Analytical Methods

The analytical method for soil gas samples collected using a sorbent cartridge is EPA Method TO-17 (EPA 1999). The analytical method for soil gas samples collected using a Summa canister depends upon the project objectives. For projects requiring indoor air risk drivers is typically analyzed by EPA Method TO-15 GC/MS SIM. For soil-gas data, EPA TO-14 or TO-15 should be sufficient. However, ultimately, the analytical method used, will depend upon the project specific needs. Consult the analytical laboratory for recommended analytical method to use.

5.5.10 Active Soil Gas Sampling Field Quality Control Samples

Duplicate soil vapor samples must be collected from the same sample location, using the same equipment and procedure as used for the original. The percentage of duplicates submitted for laboratory analysis depends on project-specific objectives and regulatory specifications that shall be defined in the WP. Purge the pump between sampling locations and check for residual VOC contamination by collecting field blanks for analysis.

5.5.11 Active Soil Gas Sampling Equipment Decontamination

Soil gas samples should not contact potentially sorbing materials such as the pump diaphragm or soft tubing. Check all components of the sampling system randomly for contamination by drawing atmospheric air through the system, subjecting it to analysis, and comparing the resulting chromatogram with that of ambient air. Use pre-cleaned probes for each sampling location in order to minimize the possibility of cross-contamination among sampling locations.

Clean sampling components, such as the probes, using steam or pressurized water and detergent at the conclusion of each day and clean immediately after use with a portable sprayer as described in Procedure I-F, *Equipment Decontamination*. Sampling syringes can be decontaminated and reused only if GC analyses indicate no residual contamination is present. Drive points placed at the ends of the steel sampling tubes are dedicated to one sampling location. Note that this procedure assumes that syringe sampling will be conducted. If other sampling techniques are preferred or required, document them in the project-specific WP.

5.5.12 Active Soil Gas Analytical Quality Control Samples

Blanks shall be run at least once for every 20 samples and after “hot” samples with concentrations outside the calibration range. A quality control standard containing concentrations in the middle range of those expected at the site shall be run at least once for every 20 samples, or at a minimum of once per day. In addition, a minimum of two ambient air samples shall be collected over the course of each day and analyzed for background concentrations of target compounds.

6. Documentation/Records

The subcontractor shall document each soil gas sampling event in a bound logbook or appropriate field log sheets. The following information will be recorded for each soil gas sampling event:

- Sample number
- Project name and number
- Sampling location and depth
- Date and time
- Name(s) of sampling personnel
- Site location
- Miscellaneous observations
- Analytical equipment utilized (e.g., GC, column, detector)

Other documentation will be recorded on a daily basis in the bound field notebook, and will include:

- Calibration results
- Blank measurement results

The original field records will be placed in the project files immediately upon completion of fieldwork. Subcontractors will prepare a detailed report summarizing the methodologies used during the survey, the results obtained, and an interpretation of the results. This report will be incorporated into the site characterization report or equivalent document.

7. Health and Safety

Field Personnel shall perform work in accordance with the current (or as contractually obligated) United States Army Corps of Engineers Safety and Health Requirements Manual EM-385-1-1 (USACE 2008) and site-specific health and safety plan.

8. References

Department of Defense, United States (DoD). 2005. *Uniform Federal Policy for Quality Assurance Project Plans, Part 1: UFP-QAPP Manual*. Final Version 1. DoD: DTIC ADA 427785, EPA-505-B-04-900A. In conjunction with the U. S. Environmental Protection Agency and the Department of Energy. Washington: Intergovernmental Data Quality Task Force. March. On-line updates available at: http://www.epa.gov/fedfac/pdf/ufp_qapp_v1_0305.pdf.

Department of Health, State of Hawaii (DOH). 2009. *Technical Guidance Manual for the Implementation of the Hawaii State Contingency Plan*. Interim Final. Honolulu: Office of Hazard Evaluation and Emergency Response. 21 June. http://www.hawaiidoh.org/tgm.aspx.

Department of the Navy (DON). 2010. Ammunition and Explosives Safety Ashore. NAVSEA OP 5 Volume 1, 7th Revision, Change 11. 0640-LP-108-5790. Commander, Naval Sea Systems Command. July 1.

———.2014. *Environmental Readiness Program Manual*. OPNAV Instruction 5090.1D. 10 January.

Environmental Protection Agency, United States (EPA). 1999. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*. 2nd ed. EPA-625/R-96-010b. Center for Environmental Research Information. January.

United States Army Corps of Engineers (USACE). 2008. *Consolidated Safety and Health Requirements Manual*. EM-385-1-1. Includes Changes 1–7. 13 July 2012.

Procedure I-F, *Equipment Decontamination*

Procedure I-I, *Land Surveying.*

Procedure I-A-5, *Utility Clearance*.

9. Attachments

None.

Appendix B:
Soil Gas Screening SOP

Standard Operating Procedure
Down-Well Soil Gas Screening
Date: October 2022

Purpose and Applicability

This AECOM Standard Operation Procedure (SOP) describes how to conduct low purge volume soil gas sampling from groundwater monitoring wells screened in the vadose zone. Low-flow soil gas screening is performed to assess the composition of soil gas near the base of the vadose zone, which can be used to demonstrate natural source zone depletion (NSZD) processes are occurring and estimate rates of NSZD over a light nonaqueous phase liquid (LNAPL) source. The test is conducted by lowering sample tubing to the base of the vadose zone (just above the LNAPL source) in a standard screen/riser monitoring well, connecting the tubing to gas-tight fittings at the top-of-casing, and purging the tubing at a low flow rate to collect real-time gas measurements with a field gas analyzer.

Limitations

Low purge volume gas sampling is suitable for wells screened across the vadose zone. An adequate monitoring well network within the LNAPL footprint must be accessible for comparing the real-time analytical results across space. Additionally, it may be desirable to collect soil gas samples from one or more monitoring wells installed in similar geologic conditions located outside of the LNAPL source zone (i.e., upgradient) to assess background soil gas conditions. This data can be used to account for potential oxygen utilization and/or methane production that is not directly related to LNAPL biodegradation. The accuracy of and confidence in soil gas sample results are dependent upon the instrument calibration, seal around the top-of-casing, the condition of the well, and environmental factors (i.e., soil temperature). This small purge method utilizes the internal pump from the field gas analyzer to extract soil gas from base of the vadose zone at low flow rates (typically 1 L/min or less). The small purge rate limits potential for dilution from soil gas in shallower, more permeable layers in the soil that may intersect the screened interval of the monitoring well (Sweeney and Ririe, 2017). Leak testing using helium or other tracer gases may also be considered to ensure gas samples are not compromised by leaks in the sampling train or at the seal at the top of the well casing, as necessary.

Soil Gas Sampling Background

Conventional methods for soil gas (vapor) sampling typically involve intrusive installation of permanent soil gas sampling probes or temporary probes driven into the desired interval of the vadose zone at petroleum contaminated sites. Recent developments in vapor sampling indicate that representative soil gas composition data can be collected directly from existing groundwater monitoring wells screened across the water table. Field and numerical modeling studies suggest that data collected using the low purge volume method can be representative of subsurface soil gas conditions and are suitable for assessing petroleum vapor risk and evaluating natural source zone depletion (NSZD) processes (Sweeney and Ririe, 2017; Sookhak Lari et al., 2017).

Total petroleum hydrocarbon (TPH) concentrations from within the anaerobic region near the LNAPL source can be estimated using an O_2 correction factor made for data collected from monitoring wells (Wilson et al., 2014). O_2 concentrations (low near the LNAPL source; higher away from the source) are collected in-situ with the field gas analyzer. This method has been adapted from an agency accepted model to demonstrate effective aerobic biodegradation (Sweeney and Ririe, 2017; USEPA, 2012). A rate of degradation can be estimated from these data to predict point of compliance.

Responsibilities

The AECOM personnel performing the tests are responsible for contacting the AECOM project manager and/or project technical team if there are any uncertainties about the test procedure or unusual observations in the field. The project manager, technical lead, or their designee is responsible to oversee and ensure that the tests are performed in accordance with the project specific sampling program and this SOP.

Health and Safety

Specific project requirements as described in an approved Work Plan, Sampling Plan, Quality Assurance Project Plan, Job Hazard Analysis (JHA) or Site-Specific Health & Safety Plan (HASP) will take precedence over the procedures described in this document. The hazards associated with soil gas sampling from monitoring wells include, but are not limited to, the following:

- Slip, trips, and falls
    - Review terrain hazards prior to conducting these operations.
    - Ensure there is a safe means of access/egress to the wellhead.
- Dermal exposure to LNAPL
    - Ensure that proper personal protective equipment (PPE) is used to mitigate the impact of potential splashes of LNAPL to skin and/or eyes.
- Exposure to site contaminants
    - Take all precautions necessary to prevent fire/explosion and/or exposure to airborne vapors from product in the well; high volatility LNAPLS such as gasoline and condensate are of greater concern than low volatility LNAPL such as rail fuel or lubricating oils.
- Ergonomics
    - Use appropriate ergonomic techniques when inserting or retrieving equipment for the wells to preclude injury to the body.
- Static Electricity
    - While very rare, a static electricity source explosion hazard can result during field work when potential static electricity charge accumulations and ignition sources (i.e., flammable or combustible vapors/dust in atmosphere) exist.

Standard PPE includes safety glasses or goggles, hard hat, protective toe cap safety boots, and hand protection such as nitrile gloves. Specialized PPE may include reflective vests, fire retardant coveralls, Tyvek and face shield, and hearing protection.

Equipment

The following is a list of field equipment needed to perform the down-well soil gas screening:

Equipment to be fitted to the top of well casing

- Appropriately sized PVC cap (2” or 4” diameter standard)
    - Alternative fittings include:
        - Campbell Well Seals: (https://www.envisupply.com/pdf/campbell_catalog.pdf)
        - Rubber Stoppers: (https://www.coleparmer.com/p/cole-parmer-two-hole-stoppers-rubber/48940)

        - Fernco Couplers: (https://in-situ.com/products/accessories/well-cap-cable-holder)
- Cordless drill and appropriate-sized bit (1/4” or 3/8” standard)
- Nylon or Teflon ® tubing (1/4” or 3/8” standard) of appropriate length to reach bottom of vadose zone
- Brass barbs to be threaded into the top of the PVC cap (1/2” diameter thread standard). **Optional**: Plumber’s putty or low VOC modeling clay equivalent
- Decontamination solutions and equipment
    - Liquinox
    - Deionized water
    - Paper towels
    - Garbage bags
    - Oil absorbent pads
    - Plastic sheeting to place around well before starting test
- PPE
    - Modified Level D PPE unless Site Specific requirements
    - Safety glasses or goggles
    - Hard hat
    - Safety toe boots
    - Abrasion resistant gloves under nitrile gloves
- Measuring devices
    - Air/LNAPL/Water interface probe
    - Field multi-gas analyzer for measuring **oxygen, carbon dioxide, and methane** concentrations in soil gas (e.g., GEM 2000 with internal pump capable of 0.3 LPM). **Install water trap and particulate filter between** well and gas analyzer to protect instrument, and where concentrations of hydrocarbon vapors other than methane (e.g., VOCs) are present at a concentration ≥ 100 ppmv, **install an activated carbon filter between the well and gas analyzer to prevent false positive methane readings**.
    - Photoionization detector (PID) or other gas analyzer for measuring concentrations of VOCs.
- Other tools
    - Time piece (e.g., digital watch or other device)
    - Tube cutter
    - Toolbox including socket wrench set for flush mount wells
    - Calculator
    - Well keys
    - Project field book for recording field observations
    - Site-specific permitting (if required)

- Work plan or field memo with site maps
- Soil boring logs and well construction diagrams for wells to be sampled

See **Figure 1** for an example of the equipment setup at the test well.

Procedures

Procedures for conducting low purge volume method are presented below. Procedures may vary depending on site specific needs and desired data.

Pre-Test Monitoring Procedures

Review well construction details along with other relevant data (e.g., historical fluid level gauging data and LNAPL footprint maps) prior to opening well-head. Required parameters for test implementation include:

- Ground surface and top of measuring point elevations
- Depth to water, or if LNAPL is present, depth to air-LNAPL and LNAPL-water interfaces
- Casing diameters
- Depth to top of well screened interval

Field Procedures

An outline of low purge volume procedures is included below:

1. Calibrate field gas analyzer according to manufacturer’s specification
2. Record pre-test monitoring information on the low purge volume data sheet (included in **Attachment A**).
3. Measure fluid levels (water and LNAPL) in each monitoring well where soil gas sampling is planned. Check to make sure top of well screen is above liquid interface(s) in all wells to be sampled.
4. Cut length of tubing so that when placed down the well the opening will be within one foot of LNAPL or water interface when connected to PVC cap.
5. Connect gas-tight fittings (see photo below) to the PVC well cap with a pass through for sample tubing that will connect directly to field gas analyzer.
6. Lower tubing into screened interval of well within a foot of the water table/LNAPL interface being careful not to bias opening toward wall of PVC.
7. Connect sealed fittings firmly on top of the well casing and connect field gas analyzer to tubing.
8. Begin purging gas from tubing using the multi-gas meter and record O_2, CO_2, and CH_4 readings every 30 seconds until stable readings are achieved (3 consecutive readings within 10% of each other with no consistent increasing/decreasing trend). Once readings have stabilized, seal tubing and swap out the multi-gas meter with PID or other gas sampling instruments and record VOC reading.
9. Dismantle set up and move to next monitoring point.

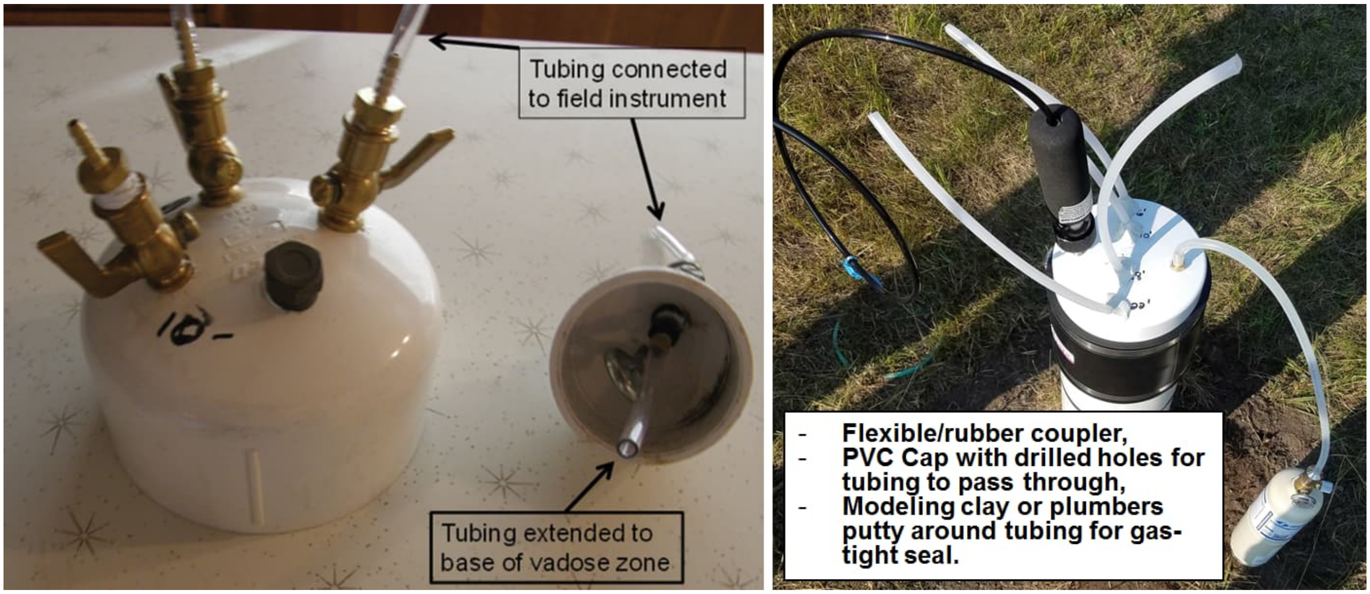


Figure 1: Photos of typical down-well sampling set-up.

Attachment A:
Low Purge Volume Data Sheet

Low Flow Purge Field Data Sheet

AECOM

WELL ID:

Site:

Proj. No.:

Sampler:

Date:

Weather:

Casing Diameter: (inches)

Depth to LNAPL: (feet TOC)

Depth to Water: (feet TOC)

Depth to Tubing Opening: (feet TOC)

Measurement Equipment:

Field Measurements

Time (t) *hh:mm:ss*	*O_2* *%v*	*CO_2* *%v*	*CH_4* *%v*	*Relative Pressure* *inches of water*		*Rate* *(L/min)*

Comments: Stabilization criteria are: ±10% for O_2, CO_2, and CH_4

Appendix C:
Effective Diffusion Coefficient Testing SOP

PURPOSE AND SUMMARY

Gas diffusion coefficients are required to calculate oxygen flux into the subsurface. Diffusivity can be estimated for porous media from literature values, using the Millington-Quirk (1961) equation, or through field testing. The method described below follows the approach described in *In Situ Measurement of Effective Vapor-Phase Porous Media* (Johnson et al. 1998). This method evaluates transient changes of tracer gas to determine site-specific effective porous media gas diffusion coefficients. The tracer gas (sulfur hexafluoride, SF_6) is introduced to the subsurface at a known concentration through a soil gas probe. The tracer gas is allowed to diffuse into the soil matrix for a predefined time period (residence time). At the end of the time period, a grab sample is collected from the soil gas probe and the tracer gas concentration is measured. The process is repeated for several diffusion time intervals, generally 0, 15, 60, and 120 minutes.

EQUIPMENT

- Sulfur hexafluoride (SF_6) gas
- ION Science SF_6 P1 detector (or similar)Calibration gas
- 1-liter Tedlar bags
- 50 mL syringe
- Two-way ball valve
- Tubing
- Purge pump

PROCEDURES

Sulfur hexafluoride (SF_6) will be used as a tracer gas for in situ soil diffusivity testing and measured in the field by using an ION Science SF_6 P1 detector. The SF_6 detector should be factory calibrated and calibrated each day in the field (and on an as-needed basis during each day) with a mixture of a known concentration of SF_6 and ambient air.

1. Create an injection mixture of 5 percent SF_6 by filling a 1-liter Tedlar bag with 950 mL of ambient air, then using a laboratory-provided syringe, 50 mL of SF_6 gas is added to the 1-liter Tedlar bag. Target injection concentration is 50,000 parts per million (ppm).
2. Test injection mixture: The ION Science SF_6 detector has an upper measurement range of 1,000 parts per million (ppm); therefore, the injection mixture must be diluted by 90 percent to verify the concentration by injecting 10 mL of the SF_6 injection mixture into a Tedlar bag with 990 mL of air. Test the diluted sample, multiply by 100 and compare to the target concentration. If not within 10 percent of target, restart at Step 1.
   a. Injection Mixture Target = 50,000 ppm
   b. Diluted Injection Mixture = 505 ppm
   c. Actual Injection Mixture = 505 × 100 = 50,500 ppm
   d. If the calculated concentration is within 10 percent (45,000 to 55,000 ppm) of the target, then proceed to next step.
3. To initiate the test, 50 mL of the injection mixture is injected into the soil gas probe using a laboratory-provided syringe and two-way ball valve.

4. The soil gas probe tubing is flushed with a volume of ambient air equal to the volume of the soil gas tubing to ensure that all of the injection mixture had been introduced into the pore space.
5. Immediately after the SF_6 mixture is injected (0-minute time interval), an air sampling pump is connected to the probe tubing to purge the soil gas from the probe at a rate of less than 200 mL/min.
6. The effluent air is collected from the air sampling pump and screened for concentrations of SF_6. This concentration is interpreted to be the maximum concentration after injection (C_{max}). After sample collection, soil gas is purged until SF_6 gas is no longer detected or concentrations were asymptotic (at least 5 L and up to 12 L of soil gas) to eliminate any remaining SF_6 gas within the sand pack and surrounding soil.
7. Repeat steps 3 through 6 for 15-, 60-, and 120-minute diffusion time increments.
    a. The SF_6 mixture is injected and allowed to diffuse into the surrounding soil for the specific time increment (15-, 60-, and 120-minute).
    b. After the time interval has elapsed, the soil gas is collected and screened for SF_6 gas.
    c. The soil gas probe is then purged, and the next time step is completed.
8. Injected sulfur hexafluoride concentrations and extracted SF_6 concentrations are recorded on the following field sheet.
9. The injection concentration was then calculated based on the dilution results. A new SF_6 mixture is generated for each soil gas location.

DERIVATION OF EFFECTIVE DIFFUSION COEFFICIENT FOR OXYGEN

The expected behavior of a tracer gas injected as a point source (volume injected is less than 10 percent of volume sampled) can be predicted using the gas diffusion properties of the soil. Site-specific measurements of gas diffusivity are completed by injecting a nonreactive tracer gas into the subsurface and measuring the concentration of tracer at the sampling interval after diffusing into the formation for a period of time (residence time) compared to the tracer concentration in a sample recovered with no residence time period, or C_{max}. The fraction of the initial injected tracer gas recovered, η, is described as:

$$\eta = \frac{C_{t_s}}{C_{max}} \qquad \textbf{Equation 1}$$

Where:

C_{t_s} = tracer gas concentration with residence time s (15, 60, or 120 minutes)

C_{max} = tracer gas concentration at time zero

The fraction recovered is related to the effective vapor-phase soil diffusion coefficient through Equations 2 and 3:

$$\eta = \operatorname{erf}\left(\beta^{1/2}\right) - \left(\frac{2\beta^{1/2}}{\sqrt{\pi}}\right) e^{-\beta} \qquad \textbf{Equation 2}$$

Where:

β = dimensionless, inverse time variable that relates η to diffusivity

$$\beta = \left[\frac{\theta_v^{1/3}}{D_v^{eff}}\right]\left[\frac{1}{4t_s}\right]\left[\frac{3V_s}{4\pi}\right]^{2/3}$$ **Equation 3**

Where:

θ_v = vapor filled porosity (soil porosity minus the irreducible water saturation)

D_v^{eff} = effective vapor-phase diffusion coefficient (square centimeters per second [cm^2/sec])

t_s = time between injection and extraction (seconds)

V_s = volume of sample (mL)

The effective vapor-phase diffusion coefficient is solved by calculating η using Equation 2 and the results from the tracer gas injection tests at each soil gas sampling point for each residence time period. The relational parameter, β, is identified using an iterative solver in Microsoft Excel and Equation 3. Finally, the effective vapor-phase diffusion coefficient is calculated using Equation 4. For each soil gas sampling point, three vapor-phase soil diffusivities are calculated (one for each of the three residence times [15, 60, and 120 minutes]). The geometric mean of these vapor-phase soil diffusivity values is taken as the effective vapor-phase soil diffusivity for that soil gas sampling point.

In this procedure, SF_6 is used as the tracer gas for the push-pull tests; therefore, the measured soil diffusivity is specific to sulfur hexafluoride. The soil diffusion coefficient for oxygen is calculated from the soil diffusion coefficient for sulfur hexafluoride by applying a correction based on the ratio of the compound-specific diffusion coefficient in air expressed in Equation 5.

$$D_{v,O_2}^{eff} = D_{v,SF_6}^{eff}\left(\frac{D_{O_2}^{air}}{D_{SF_6}^{air}}\right)$$ **Equation 4**

Where:

D_{v,O_2}^{eff} = effective vapor-phase diffusion coefficient for oxygen (cm^2/sec)

D_{v,SF_6}^{eff} = effective vapor-phase diffusion coefficient for sulfur hexafluoride (cm^2/sec)

$D_{O_2}^{air}$ = diffusion coefficient for oxygen in air (cm^2/sec)

$D_{SF_6}^{air}$ = diffusion coefficient for sulfur hexafluoride in air (cm^2/sec)

Diffusion coefficients in air can be calculated for specific compounds using Equation 5.

$$D_v^{air} = 0.001T^{1.75}\frac{\left(\frac{(M_a+M_b)}{M_aM_b}\right)^{1/2}}{\left(P\left(V_a^{1/3}+V_b^{1/3}\right)^2\right)}$$ **Equation 5**

Where:

D_v^{air} = diffusion coefficient of compound in air (cm^2/sec)

T = temperature (K)

M_a = molecular weight of air (28.97 grams/mole)

M_b = molecular weight of compound of interest (grams/mole)

P = pressure (1 atmosphere)

V_a = molar volume of air (20.1 cubic centimeters per mole [cm^3/mole])

V_b = molar volume of compound of interest (cm^3/mole)

The overall effective vapor phase diffusion coefficient across a depth interval spanning multiple soil gas sampling points is calculated using Equation 6.

$$\frac{D_{O_2}^{T}}{d} = \left[\sum_{i=1}^{n} \frac{d_i}{D_{O_2,i}}\right]^{-1}; d = \sum_{i=1}^{n} d_i$$ **Equation 6**

Where:

d_i = thickness of layer i having effective vapor phase diffusion coefficient $D_{O_2,i}$ (cm)

$D_{O_2,i}$ = effective vapor phase diffusion coefficient for oxygen in layer *i* (cm^2/sec)

AECOM

Soil Diffusivity Field Test

Well Construction Details/Flushing Volumes			Depth of Port	Length of Tubing above ground	Flushing Volume
			feet	feet	mL
Number of Soil Ports	4	Soil Port A			
Inner Diameter of soil port tubing (inches)	0.25	Soil Port B			
Volume of air per foot of tubing (mL)		Soil Port C			
Leak Check	P / F	Soil Port D			

SVMP ID:

Date:

Weather:

Site:

Proj. No.:

Sampler:

Source Gas Concentration Verification	Tracer Gas	Targeted Injection Concentration	Diluted Test Concentration	Calculated Injection Concentration	Difference	
		ppm	ppm	ppm	%	ppm
	SF_6	50,000				

Inject 10 mL of 5% solution into 1 L bag and fill with air. If >10% difference, retest or recreate Injection Solution.

Calculated Injection Concentration = diluted Test concentration x 100

Diffusivity Testing Results		Time between inject/sample	Baseline Concentration	Measured Sample Concentration	Diluted Sample Concentration	Dilution Factor	Purge Time		Purge Concentration (ppm)			Total Purge Volume
		minutes	ppm	ppm	ppm		Start	End	2.5L	5L	End	L
Soil Port A	C_{max}	0	0									
	C_{15}	15										
	C_{60}	60										
	C_{120}	120										
Soil Port B	C_{max}	0	0									
	C_{15}	15										
	C_{60}	60										
	C_{120}	120										
Soil Port C	C_{max}	0	0									
	C_{15}	15										
	C_{60}	60										
	C_{120}	120										
Soil Port D	C_{max}	0	0									
	C_{15}	15										
	C_{60}	60										
	C_{120}	120										

Baseline Concentration: For the 15, 60, and 120 minute tests, this is the final concetnration measured during the previous test (after the completed purge)

Measured Concentration: This is the maximum concentration observed during the test. Concentrations should decrease over time.

Diluted Sample Concentration: If the measured concentration exceeds the measurement range of the SF6 meter, dilute the sample, start with a 10x diultion (100 mL of the sample in a 1 L tedlar bag with 900 mL of ambient air). Use a lower dilution factor if possible

Appendix D:
Temperature Profiling SOP

AECOM

Temperature Profiling at SVMPs

Site:

Proj. No.: Date:

Sampler: Weather:

Measurement Equipment:

Field Data

Location ID	Depth Interval	Time Collected	Temperature °C or °F
			Stabilized Reading

Comments:

Standard Operating Procedure
Temperature Profiling

November 2022

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1. Purpose and Scope

This AECOM Standard Operating Procedure (SOP) describes how to collect temperature readings from temperature probes deployed in an existing monitoring well. Temperature profiling is conducted to construct a vertical temperature profile of the subsurface and identify zones of elevated temperature that arise from exothermic hydrocarbon biodegradation reactions, which can be used to demonstrate natural source zone depletion (NSZD) processes are occurring and estimate rates of NSZD of a light nonaqueous phase liquid (LNAPL) source.

2. Procedure

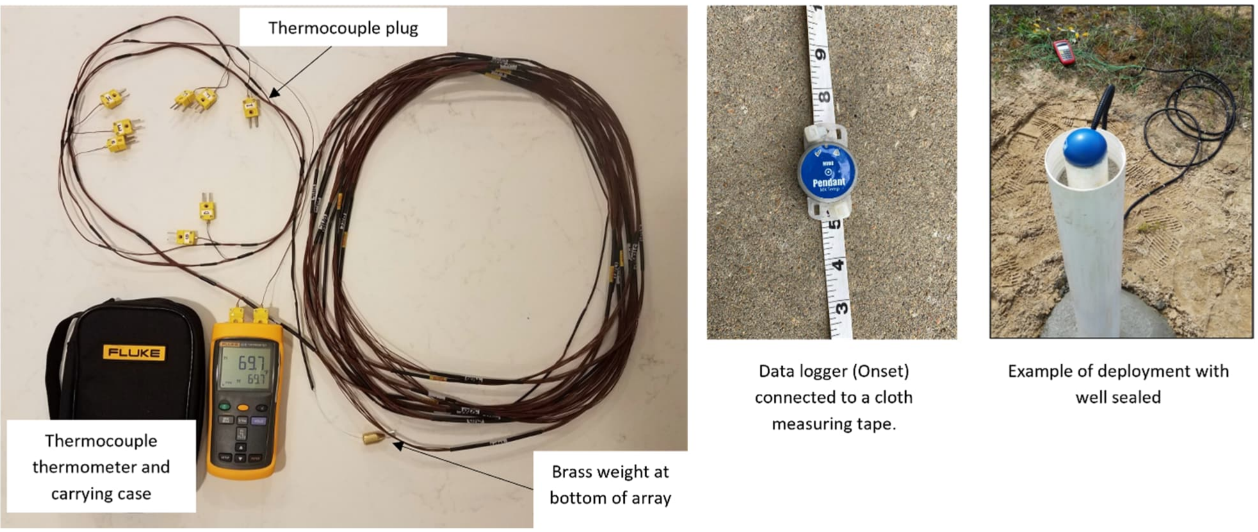
Microbial degradation of LNAPL constituents is exothermic, resulting in the release of heat to surrounding media. The heat released from biodegradation creates temperature gradients in the subsurface, and the overall heat transfer can be conceptualized as the superposition of heat flux from LNAPL depletion processes and background heat transport processes. The following procedures describe how to collect vertical temperature profile data from existing monitoring wells for the purpose of evaluating NSZD processes.

This procedure describes the deployment of an array of temperature probes in an existing well. Data is typically recorded in 1-foot or 2-foot intervals from approximately 1 to 2 feet below ground surface to the total depth of each well (the vertical interval and spacing of temperature probes can be modified depending on the depth of wells to be evaluated, the vertical extent of the source zone, and data needs of the project). An array of temperature sensors (typically a string of 10 or more thermocouples or data loggers fastened together) will be utilized for measuring temperatures in the well.

NOTE: To limit changes in temperature within the selected wells (e.g., due to heat exchange with the atmosphere), wells should not be left open to the atmosphere prior to or during temperature profile data collection. Temperature data should be recorded immediately following fluid level gauging and prior to soil gas sampling or any other planned data collection.

2.1 Equipment

- Oil-Water Interface Probe
- Array with temperature probes spaced according to project needs. Arrays may be constructed of either:
  - thermocouples with a hand-held meter to record temperature values or
  - data loggers (for example, Onset HOBO Pendant, Thermochron iButton, or Madgetech Temp1000IS) that are deployed in a well to record temperature data at regular time intervals, and data is downloaded after the field event
- Hand-held meter or datalogger software
- Well seal at top of casing to allow temperature sensor array down well while preventing heat exchange between the well and the atmosphere.



Data logger (Onset) connected to a cloth measuring tape.

Example of deployment with well sealed

Figure 1: Examples of temperature arrays and deployment in field.

2.2 Step by Step Procedure

If using data loggers, make sure the clocks on all data loggers are synchronized, and set them to collect data at regular time intervals (typically 2-to-5-minute intervals) before initiating data collection. The loggers can be deployed at numerous depths/wells over the duration of the field event and data downloaded at the end of the field event. Data collection during the field event involves detailed notes on the well, depth, and time the array is deployed.

1. Gauge the depth to LNAPL, depth to water, and total depth of the well.
2. Place the temperature probe array into the well so that the top temperature probe is located approximately 1 foot below ground surface.
    - Note that these measurements should be recorded from ground surface and not top of well casing for the purpose of comparing temperature profiles between background and source zone locations.
3. A seal should be placed at the top of the well casing to limit heat exchange between the well and the atmosphere.
4. For vadose zone readings, allow at least 90 minutes (unless temperature probe specific equilibration curves have been generated) to reach equilibrium with the surrounding formation materials.
    - Equilibration in the unsaturated zone takes much longer than for the saturated zone because the thermal conductivity of water is more than 20 times higher for water than air.
5. If using data loggers, after equilibration time, move to step 6. If using thermocouples and a hand-held meter, after allowing time for equilibration, connect the top thermocouple plug to the thermometer.
    - Verify that temperatures are stable with no consistent increasing or decreasing temperature trends, and record the time, depth, and temperature on the field log.
    - Repeat the above for the remaining thermocouple plugs.
6. If the total depth of the well is deeper the length of the array, lower the array deeper into the well such that the shallowest temperature probe is set 1 depth interval (1 or 2 feet) below the previous deepest temperature probe.
    - Repeat steps 3 – 5.
7. Continue lowering the temperature probe array into the well until the lower temperature probe is approximately 1 to 2 feet above the total depth of the well.
8. Remove the temperature sensor array from the well and decontaminate as needed.
    - It might be beneficial to have 2 temperature probe arrays, one for wells with LNAPL and one for wells without LNAPL to prevent cross-contamination.

For reference, example temperature profiles for a background and source zone location are provided below. Note that actual field-measured temperatures are likely to be different than those depicted in the chart. The shape of the example temperature profiles in the below chart are representative of data collected during the fall season from a site located in a temperate climate in the northern hemisphere. Characteristics of the temperature profiles include:

- Cooler temperatures at shallow depths in response to falling air temperatures in the fall/early winter, and
- Warmer temperatures at middle depths from the warmer summer air temperature signal.

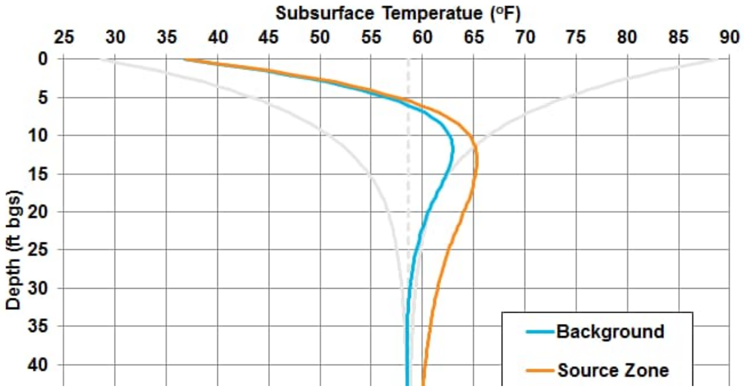


Chart showing example background and source zone temperature profiles.

Temperature Profiling in Well

Site:

WELL ID:

Proj. No.:

Date:

Sampler:

Weather:

Top of Casing Elevation: (feet)

Depth to LNAPL: (feet TOC)

Ground Surface Elevation: (feet)

Depth to Water: (feet TOC)

Difference: (feet)

Total Depth: (feet TOC)

Measurement Equipment:

Field Data

Depth (feet below ground)	Time Deployed	Time Collected	Temperature °C or °F			
			Reading 1	Reading 2	Reading 3	Average

Comments:

Appendix E:
Analytical Data Package Requirements for Chemical Analyses

GC-FID Stage 4 Deliverables

Item No.	Deliverable
1	Chain of Custody
2	Sample results with analysis and extraction/preparation dates
3	Summary of MS/MSD/Duplicate recoveries and control limits (listing or link with associated samples)
4	Summary of LCS/LCSD recoveries and control limits (listing or link with associated samples)
5	Method blanks (listing or link with associated samples)
6	Summary of surrogate recoveries
7	Summary of initial calibration data (RF and %RSD, or r if applicable)
8	Summary of continuing calibration (%D)
9	Injection logs
10	Extraction/preparation logs
11	Case narrative to discuss anomalies
12	Raw data associated with the summary forms listed above
13	Raw data for item #2 which includes chromatograms, logbooks, quantitation reports, and spectra

Note: The data deliverable package must have a table of contents and be paginated.

%D	percent difference
%RSD	percent relative standard deviation
GC-FID	gas chromatography-flame ionization detector
MS	matrix spike
MSD	matrix spike duplicate
LCS	laboratory control sample
LCSD	laboratory control sample duplicate
RF	response factor

GC-MS Stage 4 Deliverables

Item No.	Deliverable
1	Chain of Custody
2	Sample results with analysis and extraction/preparation dates
3	Summary of MS/MSD/Duplicate recoveries and control limits (listing or link with associated samples)
4	Summary of LCS/LCSD recoveries and control limits (listing or link with associated samples)
5	Method blanks (listing or link with associated samples)
6	Summary of instrument blanks - metals only (listing or link with associated samples)
7	Summary of surrogate recoveries
8	Summary of initial calibration data (RRF and %RSD, or r if applicable)
9	Summary of continuing calibration (%D and RRF)
10	Summary of internal standards (area response and retention time)
11	Summary of instrument tuning (listing or link with associated samples, must show 12-hour clock)
12	Injection logs
13	Extraction/preparation logs
14	Case narrative to discuss anomalies
15	Raw data associated with the summary forms listed above
16	Raw data for item #2 which includes chromatograms, logbooks, quantitation reports, and spectra

Note: The data deliverable package must have a table of contents and be paginated.

GC-MS	gas chromatography-mass spectrometry
RRF	relative response factor

General Chemistry Stage 4 Deliverables

Item No.	Deliverable
1	Chain of custody
2	Sample results with analysis and extraction/preparation dates
3	Summary of MS/MSD/Duplicate recoveries and control limits (listing or link with associated samples)
4	Summary of LCS/LCSD recoveries and control limits (listing or link with associated samples)
5	Method blanks (listing or link with associated samples)
6	Summary of initial calibration data (correlation coefficient, r)
7	Summary of continuing calibration (%D or % recovery), if applicable
8	Injection logs
9	Extraction/preparation logs, if applicable
10	Case narrative to discuss anomalies
11	Raw data associated with the summary forms listed above
12	Raw data for item #2, which includes logbooks, quantitation reports, and spectra

Note: The data deliverable package must contain a table of contents and be paginated.

Appendix E.1:
Field Sampling, Analytical, and Quality Management Reference Tables

- Table E-1: Location-Specific Sampling Methods/SOP Requirements
- Table E-2: Analyte List and Reference Limits
- Table E-3: Analytical Services

Table E-1: Location-Specific Sampling Methods/SOP Requirements

Sampling Location/ID Number	Matrix	Depth (ft bgs)	Analytical Group	Number of Samples	Sampling SOP Reference
TBD	Soil Gas	12-63.5 ft	VOCs, TPH, Fixed Gases	TBD	Procedure I-B-3 Soil Gas Sampling

Notes:
Procedures are from the *Project Procedures Manua*l (DON 2015).
Actual depth and number of soil gas samples will be dependent on investigation activities (additional SVMP installation) over the 2-year program.

bgs	below ground surface
ft	foot or feet
TBD	to be determined
TPH	total petroleum hydrocarbons

Table E-2: Preparation and Analytical Requirements for Field and QC Samples

Matrix	Analytical Group	Preparation Reference/Method SOP Analytical Reference/Method SOP	Containers	Sample Volume	Preservation Requirement	Maximum Holding Time (preparation/analysis)
Soil gas	Petroleum hydrocarbons viaTO-15	TBD	TBD	TBD	NA	Samples to be analyzed within 14 days
	VOCs via TO-3	TBD	TBD	TBD	NA	Samples to be analyzed within 14 days
	Fixed Gases	TBD	TBD	TBD	NA	Samples to be analyzed within 14 days

g	gram
HCl	hydrochloric acid
L	liter
mL	milliliter
oz	ounce

Table E-3: Analytical Services

Matrix	Analytical Group	Sampling Locations/ ID Numbers	Analytical SOP	Data Package Turnaround Time	Laboratory/Organization[a] (name and address)
Soil Gas	VOCs, TPH	TBD	TBD	14 business days after samples are received at laboratory	TBD

TPH	total petroleum hydrocarbons

[a] Laboratory meets Department of Defense Environmental Laboratory Accreditation Program or American Association of State Highway and Transportation Officials accreditation requirements, as applicable, to support project needs.