Attenuation Evaluation Plan, Investigation and Remediation of Releases and Groundwater Protection and Evaluation, Red Hill Bulk Fuel Storage Facility

JOINT BASE PEARL HARBOR-HICKAM, OʻAHU, HAWAIʻI

Administrative Order on Consent in the Matter of Red Hill Bulk Fuel Storage Facility, EPA Docket Number RCRA 7003-R9-2015-01 and DOH Docket Number 15-UST-EA-01, Attachment A, Statement of Work Section 6.2, Section 7.1.2, Section 7.2.2, and Section 7.3.2

September 1, 2017
Revision 00

NAVFAC
Naval Facilities Engineering Command
NAVFAC HAWAII

Comprehensive Long-Term Environmental Action Navy
Contract Number N62742-12-D-1829, CTO 0053

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September 1, 2017
Revision 00

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Contract Number N62742-12-D-1829, CTO 0053

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CONTENTS

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ACRONYMS AND ABBREVIATIONS

AOC	Administrative Order on Consent
BTEX	benzene, toluene, ethylene, and xylene
CF&T	contaminant fate and transport
CLEAN	Comprehensive Long-Term Environmental Action Navy
COPC	chemical of potential of concern
CSIA	compound-specific isotope analysis
CSM	conceptual site model
CTO	contract task order
DLA	Defense Logistics Agency
DOH	Department of Health, State of Hawai'i
DON	Department of the Navy, United States
EAL	Environmental Action Level
EC	equivalent carbon
EPA	Environmental Protection Agency, United States
ft	foot/feet
GC/FID	gas chromatography/flame ionization detector
GC/MS	gas chromatography/mass spectrometry
HSSM	Hydrocarbon Spill Screening Model
JP	Jet Fuel Propellant
LNAPL	light non-aqueous-phase liquid
LOE	line of evidence
MNA	monitored natural attenuation
NAP	natural attenuation parameter
NAPL	non-aqueous-phase liquid
NATO	North American Treaty Organization
NAVFAC	Naval Facilities Engineering Command
no.	number
NSZD	natural source-zone depletion
ORP	oxidation reduction potential
PAH	polynuclear aromatic hydrocarbon
SAP	sampling and analysis plan
SC	specific conductance
SIP	stable isotope probing
SOW	scope of work
SRB	sulfate-reducing bacteria
SSRBL	Site-Specific Risk-Based Level
SVEET	Soil Vapor Extraction Endstate Tool
SVOC	semivolatile organic compound
TIC	tentatively identified compound
TOC	total organic carbon
TPH	total petroleum hydrocarbons
TPH-d	total petroleum hydrocarbons – diesel range organics
U.S.	United States
UV	ultraviolet
VOC	volatile organic compound
WP	work plan

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Attenuation Evaluation Plan, Investigation and Remediation
of Releases and Groundwater Protection and Evaluation
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1.   Introduction

This document presents the plan for collecting and analyzing data to evaluate and bound the rate of fuel attenuation in the subsurface from the range of fuel releases that could occur at the Red Hill Bulk Fuel Storage Facility ("the Facility") at Joint Base Pearl Harbor-Hickam, Hawaiʻi. The Facility is owned and operated by the United States (U.S.) Navy (DON; Navy) and is funded by Defense Logistics Agency (DLA).

This *Attenuation Evaluation Plan* (AEP) has been prepared for the Facility's Investigation and Remediation of Petroleum Product Releases and Groundwater Protection and Evaluation project. The project *Work Plan / Scope of Work* (WP/SOW) (DON 2017a) presents the process, tasks, and deliverables that address the goals and requirements of Statement of Work Sections 6 and 7 of the *Administrative Order on Consent* (AOC) *In the Matter of Red Hill Bulk Fuel Storage Facility* (EPA Docket No: RCRA 7003-R9-2015-01; DOH Docket No: 15-UST-EA-01). The AOC was issued by the U.S. Environmental Protection Agency (EPA) Region 9 and State of Hawaiʻi Department of Health (DOH) (EPA Region 9 and DOH 2015) to the Navy/DLA in response to a release of an estimated 27,000 gallons of Jet Fuel Propellant (JP)-8 from one of the Facility's 12.5-million-gallon underground fuel storage tanks (Tank 5) that was confirmed and reported to DOH on January 23, 2014. The bottoms of the Facility's 20 tanks are located approximately 100 feet (ft) above a major groundwater aquifer, which is used to supply both Navy and the City and County of Honolulu drinking water sources.

The planning activities described in the project WP/SOW (DON 2017a) include the preparation of nine documents (including this AEP), referred to as derivative deliverables, that will address specific aspects of the planning process. The flowchart presented on Figure 1 shows the sequencing of the derivative deliverables, and further detail is provided in the WP/SOW. The project study area and modeling domain are shown on Figure 2.

This AEP was prepared for DLA under Naval Facilities Engineering Command (NAVFAC) Hawaii. This document was prepared under contract number (no.) N62742-12-D-1829, contract task order (CTO) no. 0053 of the Comprehensive Long-Term Environmental Action Navy (CLEAN) IV program.

2.   Purpose

The overall objective of this project is to evaluate the potential current and future risk to human health and the environment from the release of jet fuel (JP-8) from Tank 5 in January 2014 and any potential future releases from the Facility. To achieve this objective, additional data collection is underway, and further evaluation is planned as outlined in the following plans and reports:

- *Sampling and Analysis Plan* (SAP)*, Revision 01,* April 2017 (DON 2017c)

- *Existing Data Summary and Evaluation Report,* March 2017 (DON 2017b)

- *Data Gap Analysis Report,* April 2017 (DON 2017d)

- *Monitoring Well Installation Work Plan Addendum 02,* August 2017 (DON 2017f)

- *Attenuation Evaluation Plan,* September 2017

- *Conceptual Site Model* (CSM) *Development and Update Plan,* September 2017 (DON 2017h)

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1   •   *Groundwater Model Evaluation Plan,* September 2017 (DON 2017g)

2   •   *SAP Addendum 01,* September 2017 (DON 2017i)

3   •   *Sentinel Well Network Development Plan* (forthcoming)

4   •   *Risk-Based Decision Criteria Development Plan* (forthcoming)

5   Contaminant fate and transport modeling (CF&T), one of seven project tasks identified in the project
6   WP/SOW (DON 2017a), requires a thorough understanding of the natural attenuation processes at
7   this site. EPA defines natural attenuation as a variety of physical, chemical, or biological processes
8   that, under favorable conditions, act without human intervention to reduce the mass, toxicity,
9   mobility, volume, or concentration of contaminants in soil or groundwater (EPA 1999). These in situ
10   processes include biodegradation; dispersion; dilution; sorption; volatilization; and chemical or
11   biological stabilization, transformation, or destruction of contaminants.

12   The purpose of this document is to describe the work scope and technical approach for evaluating the
13   attenuation processes in the contaminant source area (typically referred to as natural source-zone
14   depletion [NSZD]) and along potential groundwater migration pathways (typically referred to as
15   monitored natural attenuation [MNA]).

16   This AEP contains elements of both NSZD and MNA to address the Red Hill AOC project
17   objectives. NSZD studies typically focus on collecting data to evaluate the time needed for natural
18   processes to attenuate the source (NAVFAC 2017). On the other hand, MNA studies typically focus
19   on collecting data to evaluate how far the dissolved plume will migrate away from the source.

20   Differences between MNA and NSZD studies for remediation are clarified by a recently published
21   paper by Garg et al. (2017), which are summarized in Table 1:

22   **Table 1: MNA vs. NSZD (adapted from Garg et al. 2017)**

Information Type	Monitored Natural Attenuation (MNA) of Dissolved Plume	Natural Source Zone Depletion (NSZD) of LNAPL Body
Management Focus	How far plume will migrate	How long will sources last
Key Constituents	Dissolved BTEX, N, SNs*	All LNAPL Constituents
Key Biodegradation Process	Electron-acceptor mediated biodegradation	Methanogenesis
Key Unsaturated Zone Biodegradation Process	Volatilization of LNAPL Followed by Aerobic Biodegradation of Hydrocarbon Vapors	Anaerobic Biodegradation (Methanogenesis) of LNAPL followed by aerobic methane oxidation
Key Saturated Zone Biodegradation Process	Anaerobic biodegradation of dissolved BTEX, N, SNs*	Anaerobic biodegradation of LNAPL by methanogenesis with off-gassing and ebullition
Key Metric	"Biodegradation Capacity" (BIOSCREEN mass balance)	"NSZD Rate"
Key Measurement	Upgradient vs. Downgradient electron acceptors and by-products	Carbon dioxide efflux; gradient of oxygen consumption in unsaturated zone; thermal flux
Representative Attenuation Rates	Half-life of months to years	NSZD rate of 100s to 1000s of gallons per acre per year

23   *Benzene, toluene, ethylbenzene, xylenes (BTEX), naphthalene (N), and substituted naphthalenes (SNs).
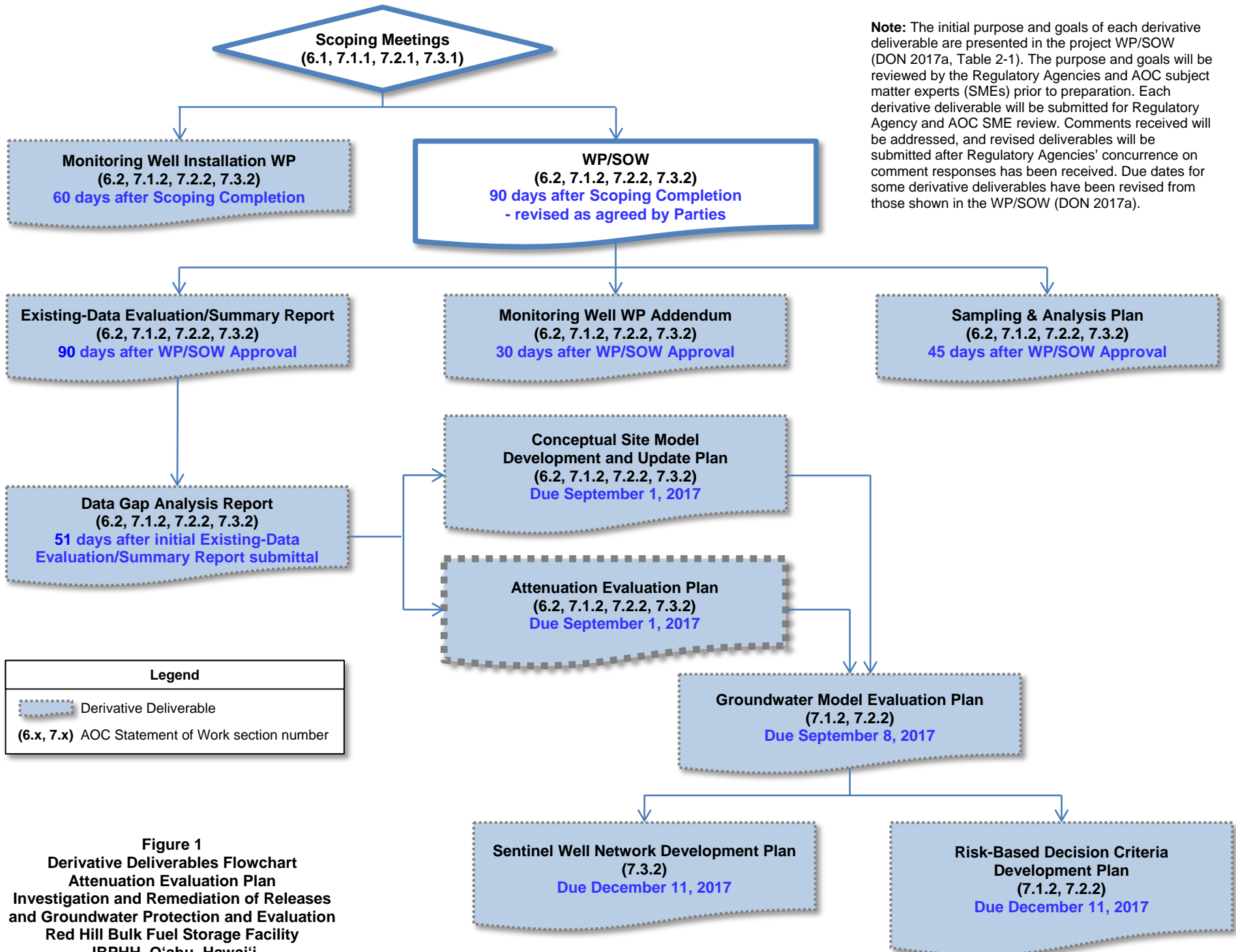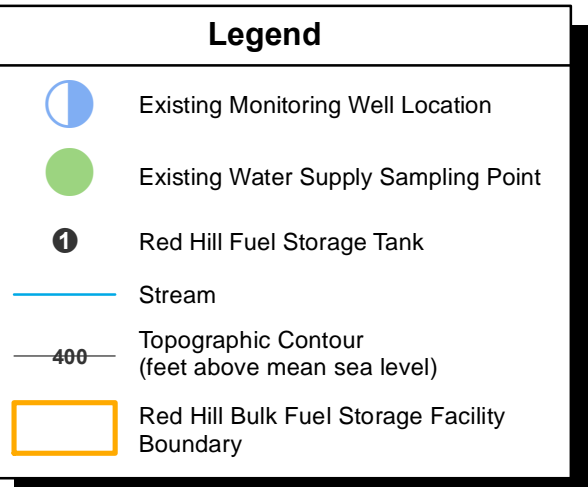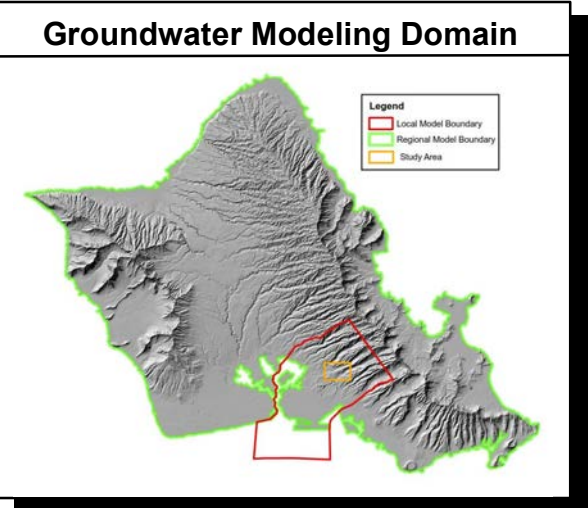
Scoping Meetings
(6.1, 7.1.1, 7.2.1, 7.3.1)

Note: The initial purpose and goals of each derivative deliverable are presented in the project WP/SOW (DON 2017a, Table 2-1). The purpose and goals will be reviewed by the Regulatory Agencies and AOC subject matter experts (SMEs) prior to preparation. Each derivative deliverable will be submitted for Regulatory Agency and AOC SME review. Comments received will be addressed, and revised deliverables will be submitted after Regulatory Agencies' concurrence on comment responses has been received. Due dates for some derivative deliverables have been revised from those shown in the WP/SOW (DON 2017a).

Monitoring Well Installation WP
(6.2, 7.1.2, 7.2.2, 7.3.2)
60 days after Scoping Completion

WP/SOW
(6.2, 7.1.2, 7.2.2, 7.3.2)
90 days after Scoping Completion
- revised as agreed by Parties

Existing-Data Evaluation/Summary Report
(6.2, 7.1.2, 7.2.2, 7.3.2)
90 days after WP/SOW Approval

Monitoring Well WP Addendum
(6.2, 7.1.2, 7.2.2, 7.3.2)
30 days after WP/SOW Approval

Sampling & Analysis Plan
(6.2, 7.1.2, 7.2.2, 7.3.2)
45 days after WP/SOW Approval

Conceptual Site Model Development and Update Plan
(6.2, 7.1.2, 7.2.2, 7.3.2)
Due September 1, 2017

Data Gap Analysis Report
(6.2, 7.1.2, 7.2.2, 7.3.2)
51 days after initial Existing-Data Evaluation/Summary Report submittal

Attenuation Evaluation Plan
(6.2, 7.1.2, 7.2.2, 7.3.2)
Due September 1, 2017

Legend

Derivative Deliverable

(6.x, 7.x) AOC Statement of Work section number

Groundwater Model Evaluation Plan
(7.1.2, 7.2.2)
Due September 8, 2017

Figure 1
Derivative Deliverables Flowchart
Attenuation Evaluation Plan
Investigation and Remediation of Releases and Groundwater Protection and Evaluation Red Hill Bulk Fuel Storage Facility
JBPHH, Oʻahu, Hawaiʻi

Sentinel Well Network Development Plan
(7.3.2)
Due December 11, 2017

Risk-Based Decision Criteria Development Plan
(7.1.2, 7.2.2)
Due December 11, 2017
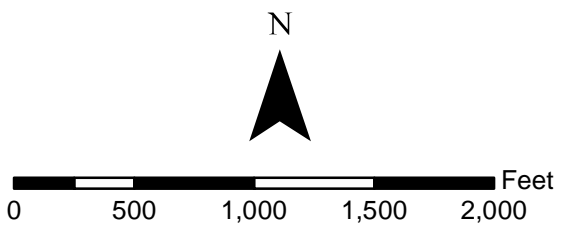
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Figure 2
Current Study Area and Modeling Domain
Attenuation Evaluation Plan
Investigation and Remediation of Releases
and Groundwater Protection and Evaluation
Red Hill Bulk Fuel Storage Facility
JBPHH, O'ahu, Hawai'i

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1   While data described in this plan may be later used to support the evaluation remedial alternatives
2   (NAVFAC 2010), the objective of this plan is to support development of the CSM, groundwater flow
3   model, and CF&T model. Figure 3 shows the key attenuation data to be collected for both the NSZD
4   and MNA processes, and Figure 4 shows the key calculations and modeling tasks to evaluate
5   attenuation. The data collected as described in this plan will be used to support the CF&T model to
6   evaluate the current 2014 Tank 5 release and hypothetical future release scenarios.

7   The CF&T model will be used to develop Site-Specific Risk-Based Levels (SSRBLs) that will be
8   derived for specific areas based on DOH Environmental Action Levels (EALs) and other criteria
9   (e.g., attenuation, solubility). The process for developing these SSRBLs will be described in the
10 forthcoming derivative deliverable *Risk-Based Decision Criteria Development Plan*.

11 While data described in this plan are oriented to support the CF&T model, the data set will later be
12 used to support the evaluation of remedial alternatives, including MNA, as outlined in guidance
13 (Adamson and Newell 2014; DOH 1998).

3.   Technical Approach and Attenuation Data Overview

15 This section provides an overview of the physical, chemical, and biological nature of attenuation
16 processes at the Facility, and presents a general description of the types of information to be
17 evaluated.

3.1   NATURAL ATTENUATION OF PETROLEUM FUELS AND DISSOLVED COMPOUNDS

19 Petroleum fuels released into the environment are affected by physical, chemical, and biological
20 processes that change the fuel composition and decrease the petroleum mass. In the contaminant
21 source zone, this process is referred to as NSZD. NSZD occurs when petroleum components in the
22 aqueous or gaseous phase are physically redistributed and/or biologically degraded (ITRC 2009).
23 Processes that attenuate dissolved groundwater plumes are included in MNA. For both NSZD and
24 MNA, attenuation processes include evaporation (i.e., volatilization), dissolution by water, and
25 microbial degradation:

26 •   *Volatilization:* Fuel releases lose volatile compounds to gas-filled pore space in the vadose
27   zone, and to a lesser extent, volatile compounds are lost from the surface of dissolved
28   plumes into the vadose zone.

29 •   *Dissolution:* Petroleum fuels are composed of hundreds of compounds. These fuel chemical
30   compounds dissolve from the non-aqueous-phase liquid (NAPL) into water that contacts the
31   NAPL. The concentration of petroleum compounds in water in contact with NAPL is a
32   function of the molar concentration of a given compound in the NAPL and the relative
33   solubility of the compound in water versus its solubility in the NAPL. In the saturated zone,
34   the rate of NAPL depletion via dissolution is controlled by rate of groundwater flow through
35   the NAPL-affected area. In the unsaturated zone, the rate of NAPL depletion via dissolution
36   is controlled by the rate of groundwater recharge by direct infiltration of precipitation and
37   the biodegradation of the vadose zone fuels.

38 •   *Microbial degradation:* Microbial populations degrade petroleum fuels. Dissolved and
39   volatilized petroleum compounds are biologically degraded by microbial activity. Some
40   bacteria can also directly metabolize petroleum compounds without dissolution through
41   direct contact with the NAPL via cellular wall transfer. Biodegradation rates of petroleum
42   compounds depend on the types and availability of electron acceptors (e.g., oxygen, nitrate,
43   sulfate, ferrous iron) in the subsurface soil and groundwater. In most aquifers impacted by

1　light non-aqueous-phase liquid (LNAPL), electron acceptors are depleted in both the vadose
2　and saturated zones where the NAPL resides. In the absence of electron acceptors,
3　fermentation of hydrocarbons and subsequent conversion of the fermentation byproducts to
4　methane by methanogens becomes the dominant pathway for petroleum depletion. It is
5　typical to find gaseous methane in the vadose zone and dissolved methane in the
6　groundwater at petroleum NAPL sites. The methane is aerobically consumed in the vadose
7　zone by methanotrophs. Biological oxidation of volatile petroleum hydrocarbons and
8　methane is exothermic.

9　Effects of these NSZD fuel processes (also known as fuel weathering processes) are discernable on
10　gas chromatography/mass spectrometry (GC/MS) patterns and gas chromatography/flame ionization
11　detector (GC/FID) chromatograms (Murphy and Morrison 2002) and by reductions in source zone
12　dissolved-phase concentrations over time.

13　MNA processes in the dissolved plume are demonstrated by reductions in contaminant mass
14　downgradient of the source, consumption of electron acceptors, and generation of metabolic
15　byproducts such as ferrous iron and methane. The previous CF&T modeling study for the Facility
16　(DON 2007) showed that both aerobic and anaerobic degradation are occurring in the groundwater
17　system in the basal aquifer beneath the Facility. Natural attenuation was quantitatively evaluated in
18　that study as part of establishing SSRBLs for chemicals using a numerical transport model (DON
19　2007).

20　Aromatic hydrocarbons, such as the benzene, toluene, ethylbenzene, and xylene (BTEX) group, and
21　many polynuclear aromatic hydrocarbons (PAHs) are broken down by microbes that are usually
22　indigenous to the aquifer. These microbes require a carbon source (provided by the fuel
23　hydrocarbons), electron donors and acceptors, mineral nutrients, and water (Wiedemeier et al. 1999).
24　An emphasis of the previous modeling effort (DON 2007) was to simulate the role of electron
25　acceptors in the degradation of hydrocarbons. The electron acceptors are part of complex oxidation-
26　reduction reactions involving transfer of electrons from one compound to another. The electron
27　acceptors oxidize fuel hydrocarbons, thus reducing their oxidation state.

28　Common electron acceptors include:

29　　• Oxygen

30　　• Nitrate

31　　• Ferric iron

32　　• Sulfate

33　　• Carbon dioxide

34　Natural attenuation of hydrocarbons also produces byproducts, which include:

35　　• Ferrous iron

36　　• Methane

37　　• Carbon dioxide

Natural Source Zone Depletion (NSZD)

How long will it take to attenuate the source?

NSZD parameters:

1. Sampling of dissolved constituents (VOC, SVOC, TPH, NAPs)
2. Soil gas measurements for VOC, SVOC, O_2, CO_2, CH_4
3. Sampling of dissolved gases in groundwater
4. Temperature survey to measure heat generation
5. Sheen sampler deployment (if possible)
6. Carbon Trap deployment (if possible)
7. Recharge measurements for leaching analysis

Monitored Natural Attenuation (MNA)

How far will the dissolved plume migrate?

8. Stable isotope probing (SIP) in groundwater
9. Bacterial species identification
10. Laboratory microcosm studies
11. Borehole flowmeter analysis (if needed)

Gas Exchange At Surface

Recharge from Surface to Groundwater

Aerobic Zone

Methane Oxidation

Anaerobic Zone

Soil Vapor Monitoring Point

Tunnel

Tunnel

Near Source Monitoring Well(s)

Plume Monitoring Well(s)

Unsaturated Zone

Leaching dissolved hydrocarbons to groundwater

Saturated Zone

Electron Acceptors in Soil (Ferric iron)

Electron Acceptors in Groundwater (Dissolved Oxygen, Nitrate, Sulfate)

Consumed Electrons Acceptors (Dissolved oxygen, Nitrate, Sulfate)

Biodegration Products (Ferrous Iron, Methane)

Fluxes Key

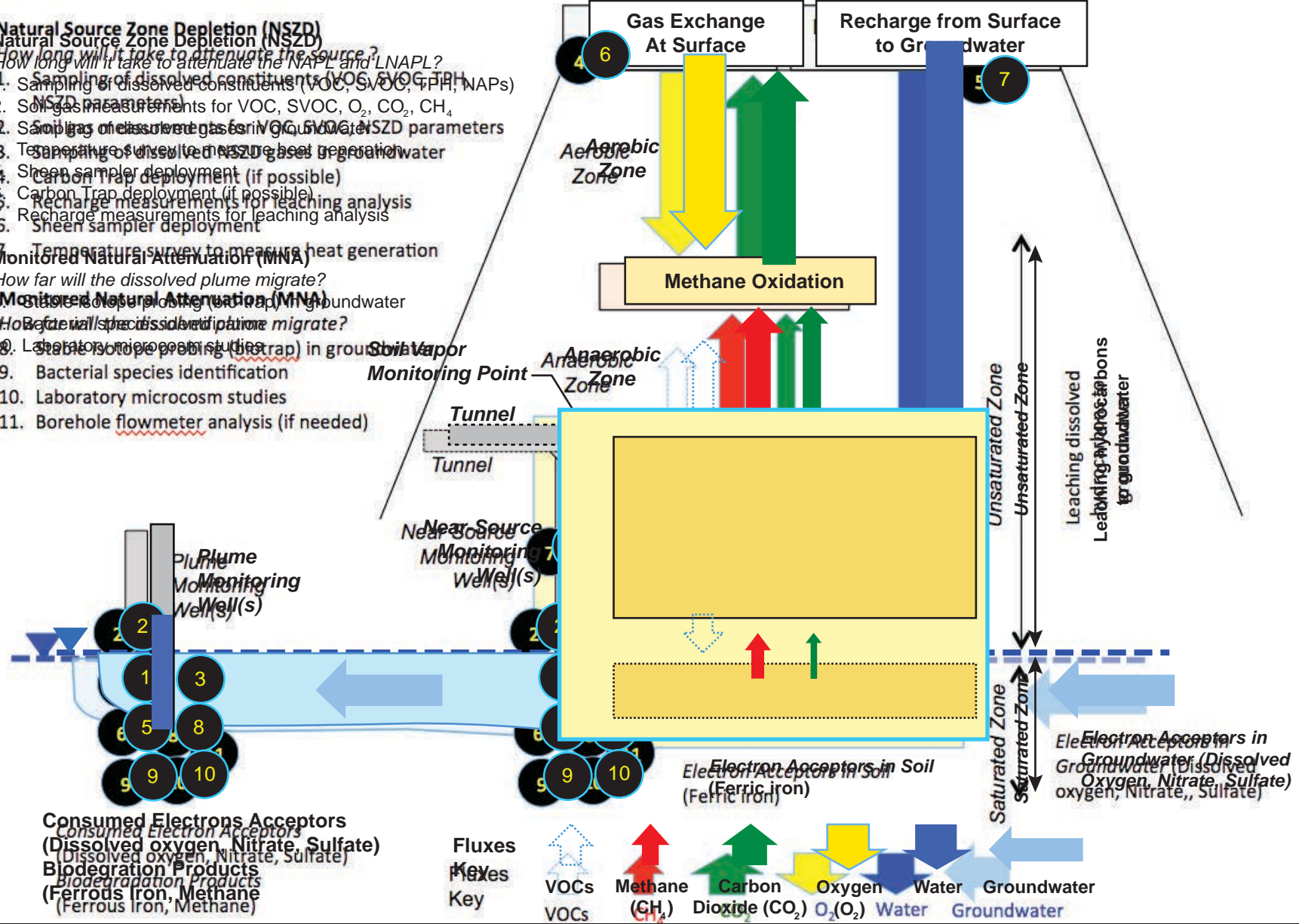|	
VOCs	Methane (CH_4)
Carbon Dioxide (CO_2)	Oxygen O_2 (O_2)
Water	Groundwater

Figure 3
Key Monitoring Tasks
Attenuation Evaluation Plan
Investigation and Remediation of Releases and Groundwater Protection and Evaluation
Red Hill Bulk Fuel Storage Facility
JBPHH, Oʻahu, Hawaiʻi

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Figure 4
Key Calculations and Supporting Modeling Tasks
Attenuation Evaluation Plan
Investigation and Remediation of Releases and Groundwater Protection and Evaluation
Red Hill Bulk Fuel Storage Facility
JBPHH, Oʻahu, Hawaiʻi

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1   The electron acceptors and natural attenuation byproducts are collectively referred to as natural
2   attenuation parameters (NAPs), since their presence and concentrations can be used to demonstrate
3   that natural attenuation is occurring and estimate the mass of hydrocarbons being reduced by these
4   processes. Dissolved oxygen is an important NAP because it indicates the potential for degradation
5   of fuel hydrocarbons.

6   Dissolved hydrocarbons migrate primarily along groundwater flow lines. Transport processes
7   include advection with moving groundwater, hydrodynamic dispersion causing mixing with the basal
8   aquifer, retardation due to equilibrium partitioning between solid and liquid phases, and degradation
9   due to natural processes (i.e., natural attenuation). Other natural processes that cause attenuation of
10   the dissolved chemicals of potential of concern (COPCs) are briefly summarized below as a prelude
11   to further description of the technical approach for evaluating attenuation in Section 4:

12   •   *Sorption:* Sorption of a compound to the material through which it migrates substantially
13   retards the migration rate. For CF&T modeling, the term sorption encompasses adsorption,
14   ion exchange, and chemisorption. Sorption was not simulated in the previous CF&T
15   modeling conducted for the Facility (DON 2007) because basalt has very low reactivity with
16   dissolved constituents, and advection and dispersion are the dominant contaminant migration
17   processes for groundwater.

18   •   *Dispersion:* Groundwater flows though the interconnected pores of an aquifer through the
19   process of advection, which is a function of the groundwater flow rate through
20   interconnected pore space, often referred to as the pore velocity. Pore velocity is a function
21   of the hydraulic conductivity, hydraulic gradient, and effective porosity of the aquifer.
22   Groundwater flow by advection causes hydrodynamic dispersion, which is often simply
23   referred to as dispersion. Dispersion is the product of dispersivity and groundwater flow
24   velocity. Dispersion causes dissolved constituents to spread out with distance as
25   groundwater flows, which reduces dissolved contaminant concentrations in the plume.
26   Values of dispersivity typically vary in the longitudinal, transverse, and vertical directions.
27   Dispersivity also depends on the plume's length, width, and thickness, as well as the aquifer
28   matrix properties.

29   •   *Biodegradation:* Biodegradation refers to transformation of NAPL in the vadose zone and on
30   the groundwater, and of dissolved petroleum compounds in groundwater, into simpler
31   substances by bacteria, fungi, and yeast. As described above for microbial degradation of
32   fuels, the microbe populations reduce the mass and concentrations of dissolved
33   hydrocarbons if sufficient nutrients and energy sources are available. Biodegradation of
34   dissolved hydrocarbons typically proceeds at higher rates in an aerobic environment.

35   •   *Effective Porosity:* Effective porosity is important for solute transport because this parameter
36   represents the interconnected pore space in the aquifer through which groundwater can flow.
37   However, the total porosity is not important because many pore spaces in certain types of
38   rock and sediment are not interconnected and thus do not transmit or store water. For
39   instance, the total porosity of basaltic rocks includes bubble-like openings in the rock called
40   vesicles, which were created by degassing from the lava as it cooled. Not all vesicles are
41   interconnected, but they contribute to total porosity. Total porosity of lava on Oʻahu ranges
42   between 5 and 50 percent, but the effective porosity is approximately 4–5 percent (Oki 1998;
43   Whittier et al. 2004; Oki 2005).

1 **3.2   ATTENUATION DATA TYPES**

2 Natural attenuation data are typically divided into three categories of information or lines of
3 evidence (LOEs): primary (LOE 1), secondary (LOE 2), and additional/other/optional (LOE 3).
4 Primary data include historical groundwater and/or soil data that demonstrate a clear and meaningful
5 trend of decreasing contaminant mass and/or concentration. Secondary data inputs are hydrogeologic
6 and geochemical data that can be used to demonstrate indirectly the type(s) of natural attenuation
7 processes and the rate at which such processes will reduce contaminant concentrations. Additional
8 data inputs (LOE 3) such as microbiological/microcosm studies are used to support the evidence that
9 natural attenuation is occurring (DOH 1998; ASTM 2015; Adamson and Newell 2014). These data
10 types are summarized as follows:

11 - **Primary data information / LOE 1: Historical Groundwater and/or Soil Chemistry**
12   **Data** – Historical COPC mass reduction based on monitoring data vs. time groundwater
13   and/or soil chemistry data that demonstrate a clear and meaningful trend of decreasing
14   contaminant mass and/or concentration. These data include all site analytical results for the
15   COPCs and their degradation by-products, or chemical components:

16   – Spatial and temporal variations and trends in COPC data from different times of the year
17   to determine if changes in contaminant concentrations, indicator parameters, or water
18   types are caused by natural attenuation or can be attributed to seasonal variability

19   – Spatial and temporal variations and trends in COPC data arising from variable pumping
20   rates at major water supply wells within the groundwater modeling domain

21   – Analysis of chemical composition of contaminants in the source area, and associated
22   spatial and temporal degradation during migration in the vadose and saturated zones

23 - **Secondary data information / LOE 2: Hydrological and/or Geochemical Data** –
24   Hydrogeologic and geochemical data that can be used to demonstrate indirectly the type(s)
25   of natural attenuation processes and the rate at which such processes will reduce contaminant
26   concentrations. Sampling locations should consider heterogeneities in geologic structures
27   and in the spatial distribution of contaminants. Groundwater flow paths and rates should be
28   fully and accurately defined, as this is one of the most important factors in evaluating the
29   applicability of natural attenuation. These data include:

30   – Physical and hydraulic properties of geologic features

31   – General water chemistry (major ions, including bromide, fluoride, calcium, magnesium,
32   manganese, potassium, sodium, and total and dissolved silica)

33   – COPCs and their potential degradation by-products as determined from literature
34   searches

35   – TPH-d and TPH-o with and without silica gel cleanup

36   – Field indicator parameters, including pH, dissolved oxygen, oxidation/reduction
37   potential (ORP; also known as redox or Eh), temperature, and specific conductance (SC)

38   – NAPs, such as alkalinity, chloride, nitrate, nitrate-nitrite as nitrogen, dissolved methane,
39   ferrous iron (iron II), sulfate, and total organic carbon

1 • **Additional data information / LOE 3: Field or Microcosm Studies** – Hydrogeologic and
2 geochemical data that can be used to demonstrate indirectly the type(s) of natural attenuation
3 processes and the rate at which such processes will reduce contaminant concentrations.
4 These data include:

5 – Microbial studies, including a general microbial community profile and petroleum-
6 degrading microbial community profile

7 – Site-specific carbon-labeled COPC degradation rates

8 – Nitrogen and sulfur isotope distribution

9 – Oxygen, carbon dioxide, methane, volatile organic compounds (VOCs), and semivolatile
10 organic compounds (SVOCs) in soil gas

11 – Vertical temperature profiles of the vadose and saturated zones using existing
12 groundwater wells

13 – Dissolved gases, including oxygen, carbon dioxide, and methane using IsoFlask
14 sampling

15 – Carbon traps to collect carbon dioxide in surface soil gas

16 All these data types will provide a solid basis to support the CSM and CF&T models, and will
17 provide a foundation to build the LOEs to support a natural attenuation and remedial alternatives
18 evaluation (ITRC 2009). The specific proposed procedures and approach are detailed in Section 4.

19 ## 4. Technical Approach for Evaluating Attenuation

20 The technical approach for evaluating attenuation at the Facility will include evaluation of much of
21 the data that exist and that are currently being collected at the site. However, additional data are
22 required as defined in the pertinent portions of the *Data Gap Analysis Report* (DON 2017d) and
23 within this plan. The comprehensive attenuation data (Table 2) will be used to develop a more
24 detailed CSM and perform and refine the CF&T model. Specifically, this attenuation evaluation will
25 employ multiple lines of evidence to document the level of contaminant attenuation that is occurring
26 at the site, identify the primary mechanisms of attenuation, and estimate the effects on the source
27 COPCs.

28 Attenuation processes and rates will be characterized by collecting and evaluating additional water
29 chemistry data, microbial data, and stable isotope data for selected COPCs. This information will be
30 incorporated into the CSM to better understand the attenuation processes within the geologic
31 framework and groundwater flow system. Figure 3 shows the key monitoring tasks (detailed in
32 Sections 4.1.2 and Section 4.2), and Figure 4 shows the key calculations and supporting modeling
33 tasks (detailed in Section 4.1) for the source studies.

34 Evaluations that will be conducted and additional data that will be collected are described in detail in
35 Sections 4.1 and 4.2. Primary data inputs include evaluation of spatial and temporal trends using
36 historical COPC concentration data and source studies. Secondary data inputs include biodegradation
37 studies, groundwater chemical analyses of natural attenuation parameters, vapor sampling, and
38 vertical temperature profiles. The evaluation of historical and new data will be used to establish
39 attenuation LOEs and to estimate rates of attenuation that can be used to support the CF&T model.

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1 **Table 2: Attenuation Data Types**

Data Type	Line of Evidence	Data	Attenuation Process	Input to	Data Source	Future Use
Primary	LOE 1: Historical COPC mass reduction over time and groundwater and/or soil chemistry data	COPC spatial and temporal trends	Dissolution	CSM, CF&T Model [a]	Historical and current COPC analytical data	Remedial alternative evaluation, SSRBL update
		Groundwater flow	Dispersion,	CSM, CF&T Model [a]	Groundwater flow model	Remedial alternative evaluation, SSRBL update
		Source/NAPL chemical composition	Dissolution, Biodegradation	CSM, CF&T Model [a]	Fuel chemical makeup literature review and analysis of sheen samplers and tank bottom water (or fuel/water shake test)	SSRBL update
		COPC plume variability	Dispersion, Dissolution	CSM, CF&T Model [a]	Historical COPC concentrations, groundwater flow model, precipitation records, water supply pumping rates	SSRBL update
Secondary	LOE 2: Hydrogeologic and geochemical data	Physical and hydraulic properties of geologic features	Dispersion,	CSM	Geologic mapping and dual-ring infiltrometer tests	Remedial alternative evaluation
		Geotechnical properties of the subsurface rocks and unconsolidated material	Sorption, Dispersion, Effective Porosity	CSM	Petrographic analysis of core	Remedial alternative evaluation
		General water chemistry	Dissolution, Sorption	CSM, CF&T Model [a]	Groundwater geochemistry analytical data	Remedial alternative evaluation
		COPC degradation by-products (e.g., methane, ferrous iron, CO_2)	Volatilization, Dissolution, Sorption	CF&T Model [a]	Literature review	Remedial alternative evaluation
		Field indicator parameters	Biodegradation	CF&T Model [a]	Field readings, including pH, dissolved oxygen, ORP, temperature, and SC	Remedial alternative evaluation
		NAPs	Biodegradation	CF&T Model [a]	Groundwater analytical data, including alkalinity, chloride, nitrate, nitrate-nitrite as N, dissolved methane, ferrous iron, sulfate, and TOC	Remedial alternative evaluation

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Data Type	Line of Evidence	Data	Attenuation Process	Input to	Data Source	Future Use
Additional	LOE 3: Field or microcosm studies	Microbial community studies	Biodegradation	CF&T Model [a]	General microbial community and petroleum-degradation microbial community profiles in select monitoring well locations	Remedial alternative evaluation
		COPC degradation rates	Biodegradation	CF&T Model [a]	Benzene and naphthalene degradation rates in select monitoring well locations	Remedial alternative evaluation
		Isotope distribution	Biodegradation	CF&T Model [a]	Nitrogen and sulfur isotope distribution in monitoring well network	Remedial alternative evaluation
		Vadose zone soil gas concentrations	Volatilization, Biodegradation	CF&T Model [a]	Gas concentrations from soil vapor monitoring, and air column in groundwater monitoring well locations, including oxygen, carbon dioxide, methane, VOCs, and SVOCs	Remedial alternative evaluation
		Subsurface temperature profiles	Biodegradation	CF&T Model [a]	Vertical temperature profiles of select wells in the monitoring well network	Remedial alternative evaluation
		Dissolved gases	Biodegradation, Leaching	CSM	Gas concentrations (oxygen, carbon dioxide, methane) from groundwater in select monitoring well locations using IsoFlask sampling	Remedial alternative evaluation
		Lab microcosm study	Biodegradation	CSM	Attenuation rates for select groundwater COPCs using site soil and water under lab conditions	Remedial alternative evaluation

TOC   total organic carbon
[a] Data input will be used for CF&T model, including modeling future release scenarios.

1   The new data to be collected include:

2   •   Source studies including collection of groundwater and tank bottom water for the following
3   analyses:

4   –   Forensic and total petroleum hydrocarbon (TPH) fractions analyses will be used to
5   evaluate the key components of TPH-diesel-range organics (TPH-d) beyond BTEX,
6   1-methylnaphthalene, 2-methylnaphathalene, and naphthalene at locations from the
7   source area to areas distant from the source.

8   •   Biodegradation studies will include collection of groundwater samples or biotraps for the
9   following analyses:

10   –   QuantArray-Petro method will be used to quantify key organisms and functional genes
11   responsible for biodegradation of the petroleum hydrocarbons, including BTEX, PAHs,
12   and other short- and long-chain alkanes.

13   –   Stable isotope probing (SIP) will be used to evaluate the rate of degradation of TPH
14   compounds, specifically naphthalene and benzene.

15   –   Next-generation DNA sequencing will be used to evaluate the composition of the
16   microbial community in groundwater.

17   –   Compound-specific isotope analysis (CSIA) will be used to further evaluate the nitrates
18   and sulfates in the groundwater as another attenuation LOE.

19   –   Microcosm study using site sediment and groundwater from near source monitoring
20   wells to evaluate microbial community under laboratory conditions (if feasible).

21   •   Analyses of NAPs will be conducted to evaluate whether biodegradation processes are active
22   in reducing the mass of COPCs.

23   •   Groundwater sampling activities field parameters, including dissolved oxygen, pH, ORP,
24   temperature, and SC.

25   •   Vapor samples for oxygen, carbon dioxide, methane, VOC, and SVOC concentrations will
26   be collected from the tanks' soil vapor monitoring points and from select groundwater
27   monitoring wells to further evaluate presence and degree of biodegradation activity.

28   •   Temperature profiles will be obtained to evaluate the biodegradation of NAPL compounds
29   and attenuation of NAPL in the vadose zone, and may provide information to evaluate
30   preferred pathways and/or groundwater flow directions in the saturated zone.

31   Samples for forensic analyses, TPH fractions, QuantArray-Petro, next-generation DNA sequencing,
32   and CSIA will be collected concurrently with the quarterly long-term monitoring events for at least
33   one sampling event, anticipated to be during the October 2017 groundwater monitoring event.
34   Samples will be collected from select wells in the current Red Hill long-term groundwater
35   monitoring network. Forensic and TPH fractions analyses will be conducted on samples from wells
36   RHMW01 through RHMW04, and any other wells that contain detectable concentrations of TPH or
37   other fuel-related COPCs.

38   Samples for SIP will be collected between long-term monitoring events and include at least one
39   event for naphthalene and one event for benzene. Samples will be collected from wells RHMW02
40   through RHMW04 for naphthalene, and RHMW02 and RHMW03 for benzene. SIP samples are
41   anticipated to be collected in early 2018.

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1 The collection vapor samples and temperature profiles will be conducted as one-time events in late
2 2017.

3 The analytical program for the source, biodegradation, and other studies described in this section is
4 listed in Table 3, and sampling locations are shown on Figure 5. The schedule, methods, and
5 procedures for the respective sampling events are detailed in the concurrently published *SAP*
6 *Addendum 01* (DON 2017i).

7 4.1   PRIMARY DATA INPUTS (LOE 1)

8 This subsection details the primary information as described in Section 3, and provides a rationale
9 and the intended data inputs supporting development of the CSM, groundwater flow model, and
10 CF&T model.

11 4.1.1   Spatial Trends and Temporal Tends

12 Necessary components for evaluating COPC plumes include the plotting of COPC concentrations
13 over time at each monitoring location, as well as the spatial graphing of COPC concentrations versus
14 distance along the plume flow path over multiple sampling events (Newell et al. 2002). Temporal
15 trends will include at minimum, graphs of groundwater concentrations of COPCs collected from
16 each monitoring well from 2005 onward, and plots of ratios of TPH components (e.g., naphthalene)
17 normalized to TPH. The evaluation of spatial trends and temporal trends will consider shorter
18 variances that may be due to seasonal variation or recharge events, and longer-term effects that are
19 more typically aligned with natural attenuation processes. The geologic framework within the
20 groundwater aquifer will also be considered, since factors such as rock characteristics, hydrological
21 barriers, variable permeability zones, and structural geometry impede or facilitate plume migration
22 rates. Data that have been collected and continue to be collected within the Facility groundwater
23 monitoring network since 2007 will provide the basis for the trend analysis.

24 4.1.2   Source Studies

25 Kerosene-based jet fuels include Jet A-1, JP-4, JP-5, JP-8, and F-24. JP-8 was first introduced at
26 North American Treaty Organization (NATO) bases in 1978 and was extensively used by the
27 U.S. Air Force and the Navy prior to 2015. In January 2014, JP-8 was accidentally released from
28 Tank 5. After 2015, JP-8 usage was replaced by F-24, which the Navy considers the same as Jet A-1
29 fuel. For these kerosene-based fuels, weathering processes and the effects on fuel composition have
30 been reported in technical literature. As an early step in this attenuation study, published reports will
31 be compiled to characterize the composition of kerosene-based jet fuels including specific
32 compounds unique to the source fuel. Similarities and differences of these fuels will be described,
33 focusing on JP-5, JP-8, and F-24. Though these jet fuels are all kerosene-based, the fuel's exact
34 composition of aliphatic and aromatic hydrocarbons will vary depending on the crude oil source used
35 to refine the fuels (ATSDR 2017). Typical GC/MS chromatograms will be compiled to compare JP-8
36 to the other kerosene-based jet fuels stored at the Facility. Information from literature searches will
37 be used to characterize the fuel weathering processes and changes in NAPL composition with time.

38 4.1.2.1   FORENSIC ANALYSES

39 The elevated TPH concentrations in the groundwater monitoring wells near the tank source area
40 greatly exceed the sum of the individual compounds (i.e., BTEX, 1-methylnaphthalene,
41 2-methylnaphthalene, and naphthalene) analyzed to date. Thus, data from forensic analyses
42 (including full suite VOCs with tentatively identified compounds [TICs], full suite SVOCs with
43 TICS, TPH-d/o, and detailed hydrocarbon analyses) and TPH fractions (Section 4.1.2.2) will be used

1 to evaluate the components of TPH-d beyond BTEX, 1-methylnaphthalene, 2-methylnaphathalene,
2 and naphthalene.

3 Groundwater samples will be collected for forensic analyses from, at minimum, monitoring wells
4 that have a history of consistent detections of TPH compounds. Groundwater samples for forensic
5 analyses will be collected at minimum from RHMW01, RHMW02, and RHMW03 for at least one
6 sampling event. Tank bottom water (or water and fuel fractions from a fuel shake test [using JP-8 or
7 surrogate fuel and site groundwater] if tank bottom water is not available) will also be collected for
8 forensic analysis for at least one event. Sheen samplers collected from RHMW02 and RHMW03 will
9 also be collected for whole oil analysis for at least one event.

10 The data obtained from the fuel source, monitoring locations near the source, and monitoring
11 locations farther away from the source will be compared to evaluate any attenuation that occurs as
12 fuel travels away from the source (i.e., specific composition will be evaluated to determine which
13 specific fuel components are present at the source versus the specific fuel components present
14 increasingly distant from the source). A decrease of specific fuel components increasingly distant
15 from the source in the direction of transport indicates that attenuation has occurred.

16 *4.1.2.2   TPH FRACTIONS*

17 Migration and biodegradation of fuel-related COPCs in groundwater will be evaluated based on
18 additional analyses of the dissolved petroleum constituents in water samples from wells in the source
19 area and at monitoring well locations where COPCs have been detected. The available data for
20 COPC concentrations include lab analyses of specific compounds that are major components of
21 TPH, which include BTEX, 1-methylnaphthalene, 2-methylnaphathalene, and naphthalene, and
22 analysis of the polar and non-polar fractions of TPH-d and TPH-o using silica gel cleanup. These
23 data are applicable and useful for the CF&T model refinement. However, the elevated TPH
24 concentrations in the tank source area greatly exceed the sum of the individual compounds analyzed
25 to date. Thus, data from the forensic analyses, and the TPH fractions (see Table 3) will be used to
26 evaluate the components of TPH-d beyond BTEX, 1-methylnaphthalene, 2-methylnaphathalene, and
27 naphthalene.

28 This AEP includes performance of additional analyses of TPH-d in groundwater samples to define
29 the aliphatic and aromatic fractions of the TPH by EC number. In addition to the carbon fractionation
30 analysis, specific compounds in the TPH will also be quantified if sufficient TPH is present in the
31 samples. It is anticipated that carbon fractionation analysis will be performed on groundwater
32 samples from RHMW01, RHMW02, and RHMW03 at minimum, but also including groundwater
33 samples from any other wells that contain detectable concentrations of TPH or other fuel-related
34 COPCs. Groundwater samples from other monitoring wells in the network will be collected if TPH
35 is detected at these locations. These additional data will provide support to the conceptual model of
36 attenuation processes and a basis for specifying the attenuation parameters in the MODFLOW-USG
37 solute transport model (or MT3DMS). Subdividing TPH-d concentration values into components by
38 EC number will allow better estimates of the physical and chemical properties that affect fate and
39 transport (e.g., solubility, vapor pressure, and partition coefficients). Analyses that define the
40 components of TPH-d by EC number will also be used for evaluating sorption and degradation,
41 especially for the source area, and for assessing health risk following the technical approach
42 described by ATSDR (1999). Consequently, this plan includes collecting groundwater samples from
43 well RHMW02 and other wells where TPH is detected, and analyzing the samples to determine the
44 chemical composition of the dissolved TPH (e.g., forensic analysis) and the EC number fractions
45 (aromatic and aliphatic fractions) in the dissolved TPH-d.

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Table 3: Source and Biodegradation Studies Sample Analysis and Screening Criteria Summary

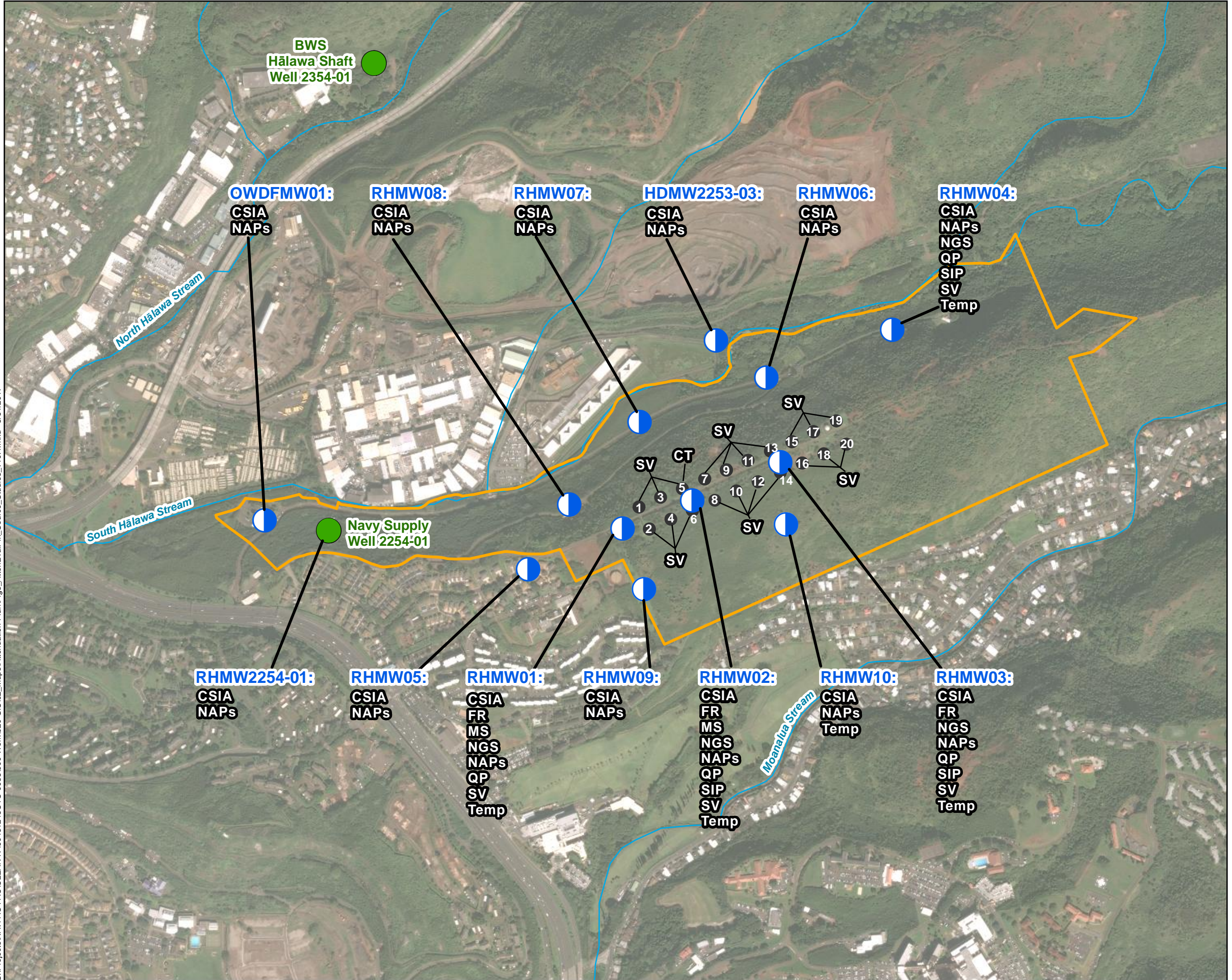| Type	Parameter	Analytical Method	Analyte(s)	Screening Criterion (µg/L)	SSRBL (µg/L)	RHMW2254-01	RHMW01	RHMW02	RHMW03	RHMW04	RHMW05	RHMW06	RHMW07	RHMW08	RHMW09	RHMW10	HDMW2253-03	OWDFMW01	Tank Bottom Water (or Shake Test)	Soil Vapor Monitoring Points	RHMW01R Vadose Zone Monitoring Points
Detailed and forensic analyses	VOCs	EPA 8260	Full Suite VOCs with TICs	—	—	C[a]	✓	✓	✓	C[a]	C[a]	C[a]	C[a]	C[a]	C[a]	C[a]	C[a]	C[a]	✓		
	SVOCs	EPA 8270	Full Suite SVOCs with TICs	—	—	C[a]	✓	✓	✓	C[a]	C[a]	C[a]	C[a]	C[a]	C[a]	C[a]	C[a]	C[a]	✓		
			Full Suite SVOCs with TICs (SGC extract)	—	—																
	TPH-d/o	EPA 8015	TPH-d, TPH-o	100	4,500	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓		
			TPH-d, TPH-o (SGC extract)	100	4,500	C[a]	✓	✓	✓	C[a]	C[a]	C[a]	C[a]	C[a]	C[a]	C[a]	C[a]	C[a]	✓		
	Detailed hydrocarbon analysis	EPA 8270 SIM Mod.	Parent and Alkylated PAHs	—	—	C[a]	✓	✓	✓	C[a]	C[a]	C[a]	C[a]	C[a]	C[a]	C[a]	C[a]	C[a]	✓		
	Sheen sampler	Shell procedure, ASTM D3328	C3–C44 Whole Oil	—	—		✓	✓													
TPH fractions	TPH fractions	MADEP VPH	C5–C8 Aliphatics, C9–C12 Aliphatics, C9–C10 Aromatics	—	—	C[a]	✓	✓	✓	C[a]	C[a]	C[a]	C[a]	C[a]	C[a]	C[a]	C[a]	C[a]	✓		
		MADEP EPH	C9–C18 Aliphatics, C13–C18 Aliphatics, C19–C36 Aliphatics, C11–C22 Aromatics	—	—																
		TX 1005, TX 1006	Aliphatic Fractions (nC6, >nC6-nC8, >nC8-nC10, >nC10-nC12, >nC12-nC16, >nC16-nC21, >nC21-nC35)	—	—																
			Aromatic Fractions (>C7-nC8, >nC8-nC10, >nC10-nC12, >nC12-nC16, >nC16-nC21, >nC21-nC35)	—	—																
Biodegradation studies	Petroleum degradation	QuantArray-Petro	RMO, RDEG, PHE, TOD, TOL, EDO BPH4, PM1, TBA, NAH, NIDA, PHN, ALK, ALMA, BCR, bssA, abcA, NMS, ANC, ASSA, EBAC, APS	—	—		✓	✓	✓	✓		C[b]		C[b]	C[b]	C[b]					
	DNA sequencing	Next generation sequencing	Bacterial Species Identification	—	—		✓	✓	✓	✓		C[b]		C[b]	C[b]	C[b]					
	Carbon degradation	Stable isotope probing	^{13}C-Naphthalene	—	—		✓	✓	✓			C[b]		C[b]	C[b]	C[b]					
			^{13}C-Benzene	—	—		✓	✓													
	Isotope analysis	Compound-specific isotope analysis	Nitrogen, Sulfur	—	—	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓			
	Microcosm study	Lab procedure	Microbial Community	—	—		✓	✓													
NAPs	NAPs	EPA 353.2	Nitrate-Nitrite as N	—	—	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓			
		EPA 300.0	Nitrate, Sulfate, Chloride	—	—																
		SM3500-Fe	Ferrous Iron	—	—																
		RSK 175M	Methane	—	—																
		SM2320B	Alkalinity (total, bicarbonate, carbonate)	—	—																
		IsoFlask	Dissolved oxygen, carbon dioxide, methane	—	—																
		EPA 415.1/9060	Total Organic Carbon	—	—	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓			
Field	Field parameters	Field (groundwater)	Dissolved Oxygen, pH, Specific Conductance, Redox Potential, Temperature	—	—	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓		
		Field (temperature probe)	Temperature (in-well casing measurement)	—	—		✓	✓	✓	✓							✓				
Soil Vapor [c]	Gases	ASTM D1946	Oxygen, Carbon Dioxide, Methane	—	—		✓	✓	✓	✓										✓	✓
	VOCs, SVOCs	TO-15/TO-17	VOCs, SVOCs	—	—		✓	✓	✓	✓										✓	✓
	Gases [d]	Lab procedure (carbon traps)	Carbon Flux	—	—	Lower access tunnel floor and ground surface on Red Hill ridge															

✓	to be analyzed	APS	sulfate reducing bacteria	DNA	deoxyribonucleic acid	NMS	naphthylmethylsuccinate synthase	SGC	silica gel cleanup
^{13}C	carbon-13 isotope	ASSA	alklysuccinate synthase	EBAC	total eubacteria	PAH	polynuclear aromatic hydrocarbon	TBA	tert-butyl alcohol monooxygenase
abcA	benzene carboxylase	BCR	benzoyl coenzyme A reductase	EDO	ethylbenzene/isopropylbenzene dioxygenase	PHE	phenol hydroxylase	TIC	tentatively identified compound
ALK	alkane monooxygenase	BPH4	biphenyl/isopropylbenzene dioxygenase	EPH	extractable petroleum hydrocarbon	PHN	phenanthrene dioxygenase	TOD	toluene/benzene dioxygenase
ALMA	alkane monooxygenase	bssA	benzylsuccinate synthase	NAH	naphthalene dioxygenase	PM1	methylibium petroliphilum	TOL	xylene/toluene monooxygenase
ANC	naphthalene carboxylase	C	contingent analysis	NIDA	naphthalene inducible dioxygenase	RMO	toluene ring hydroxylating monooxygenases	VPH	volatile petroleum hydrocarbon

[a] Contingent samples will be analyzed only if TPH-d and/or TPH-o are detected in the non-silica-gel-cleaned extract for EPA Method 8015.
[b] Contingent samples will be collected based on evaluation of groundwater geochemistry properties to determine appropriate background groundwater conditions.
[c] Soil vapor samples will be collected at soil vapor monitoring points under the tanks, and at the air column directly above the water table at all the groundwater monitoring wells.
[d] Carbon flux traps will be installed to the subgrade at several locations along the lower access tunnel.

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Legend

◐ (blue)	Existing Monitoring Well Location
● (green)	Existing Water Supply
①	Red Hill Fuel Storage Tank
― (blue line)	Stream
▭ (orange outline)	Red Hill Bulk Fuel Storage Facility Boundary

ACRONYMS:

CSIA	Compound-Specific Isotope Analysis
CT	Carbon Trap
FR	Forensic and TPH Fractions Analyses
MS	Microcosm Study
NGS	Next-Generation Sequencing
NAPs	Natural Attenuation Parameters
QP	QuantArray-Petro
SIP	Stable Isotope Probing
SV	Field Gases and VOCs
Temp	Temperature Probes

Notes

1. Map projection: NAD 1983 UTM Zone 4N
2. Base Map: DigitalGlobe, Inc. (DG) and NRCS. Publication_Date: 2015
3. SIP will be performed using ^{13}C-labeled Naphthalene and ^{13}C-labeled Benzene compounds conducted during separate sampling events. ^{13}C-labeled Benzene will not be sampled at RHMW04.
4. CSIA will be performed using nitrogen and sulfur isotopes.
5. Forensic and TPH fractions analyses will be performed at RHMW01, RHMW02, and RHMW03 at a minimum. Samples from other monitoring wells will be collected based on presence of TPH in the groundwater.
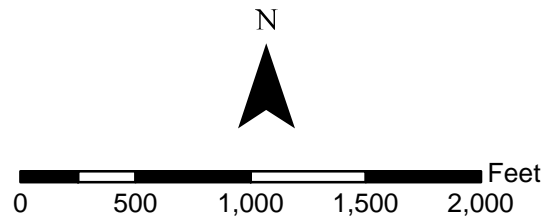
Figure 5
Source Study Sampling Locations
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Map labels:

BWS Hālawa Shaft Well 2354-01

OWDFMW01: CSIA NAPs

RHMW08: CSIA NAPs

RHMW07: CSIA NAPs

HDMW2253-03: CSIA NAPs

RHMW06: CSIA NAPs

RHMW04: CSIA NAPs NGS QP SIP SV Temp

Navy Supply Well 2254-01

RHMW2254-01: CSIA NAPs

RHMW05: CSIA NAPs

RHMW01: CSIA FR MS NGS NAPs QP SV Temp

RHMW09: CSIA NAPs

RHMW02: CSIA FR MS NGS NAPs QP SIP SV Temp

RHMW10: CSIA NAPs Temp

RHMW03: CSIA FR NGS NAPs QP SIP SV Temp

North Hālawa Stream

South Hālawa Stream

Moanalua Stream

Feet: 0 500 1,000 1,500 2,000

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1 *4.1.2.3* CONTAMINANT SOURCE MODELING

2 Existing information indicates that NAPL releases move through high-porosity clinker zones along
3 the top of low-porosity, low-permeability lava beds. Natural attenuation processes degrade the
4 NAPL within the vadose zone. This study will expand and refine the CSM for the fuel tank source
5 area based on examination of existing geologic data and borehole information. The assessment will
6 include the attenuation processes within the geologic framework of the vadose zone, focusing on the
7 geologic features that act as NAPL migration pathways or barriers. The CSM will describe the
8 physical characteristics of the basalt layers, intervening clinker beds, and mechanisms that affect
9 NAPL movement. Only information from existing bore log and well construction data will be used
10 for the evaluation since intrusive investigation activities in the immediate vicinity of the fuel tanks or
11 source area are not currently planned, as described in Section 4.1.2.1. The spatial distribution and
12 orientation of lava flows and clinker units will be shown on geologic cross sections of the tank farm
13 area. Detailed geologic descriptions will also be prepared, including estimates of the effective
14 porosity and permeability of each different geologic unit.

15 From the point NAPL moves into the rock around the tank, it will tend to migrate in the same
16 direction as the dip of the beds and spread laterally in clinker zones on top of the low-permeability
17 lava flows that restrict downward movement. Geologic mapping of surface outcrops and structural
18 geometry coupled with an evaluation of borehole logs and barrel logs will provide a means to refine
19 the CSM within the vadose zone. At a smaller scale, NAPL movement is restricted by capillary
20 forces in water-filled pore spaces; large NAPL head pressures are required for NAPL to displace
21 water from small pore spaces. Detailed geologic characterization in the source area, as noted above,
22 will also help develop a basis for estimating the volume of NAPL that could be retained in the
23 vadose zone (e.g., by residual saturation) and movement direction and extent of NAPL releases.

24 EPA's Hydrocarbon Spill Screening Model (HSSM) is a screening-level analytical program that can
25 simulate movement of LNAPL and dissolution of soluble components of the LNAPL in one
26 dimension (Charbeneau, Weaver, and Lien 1995). As part of the vadose characterization, it is
27 planned to estimate the movement of NAPL at the tank source release site by applying HSSM within
28 the updated geologic framework.

29 Consistent with the updated CSM, the source term will be input to and incorporated into the CF&T
30 groundwater model (MODFLOW-USG, and possibly MT3DMS), as described in the following
31 subsections.

32 **4.1.3** **Solute Transport Modeling**

33 The available time-series data show dissolved TPH-d and naphthalene increased in the nearby
34 monitoring well RHMW02 after the January 2014 JP-8 fuel release (DON 2017e). Subsequent
35 samples from a monitoring well located farther from the release location (RHMW01) detected the
36 same COPCs but at lower concentrations. With the exception of some concentrations exceeding
37 previous monitoring results, these data generally show decreasing concentrations in time with
38 distance from the source area. For example, concentrations of these constituents in monitoring wells
39 RHMW01 and RHMW02 decreased steadily from 2005 to 2013. After the fuel leak from Tank 5 in
40 January 2014, COPC concentrations increased at RHMW02 and RHMW01, then showed an overall
41 decline in subsequent sampling rounds with the exception of some fluctuations in concentrations
42 since January 2016. Together with the spatial distribution of NAP concentrations, these data indicate
43 natural attenuation mechanisms may be contributing to the decreases in the COPC concentrations in
44 the groundwater.

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1   The initial CF&T model will be based on highly conservative assumptions (degradation rate = 0;
2   sorption rate = 0; and highest COPC concentrations measured in source area). This initial model will
3   simulate "maximum" concentrations at potential receptors, while subsequent CF&T runs will utilize
4   the estimated source decay and degradation rates based on the available data. In addition, a range of
5   potential values for degradation rates will be modeled to evaluate uncertainty.

6   Different methods are available to simulate contaminant source terms for the CF&T modeling. These
7   typically involve specifying a constant concentration source or an equivalent NAPL-water
8   partitioning. For instance, a contaminant source attenuation model, such as SourceDK (AFCEE
9   2011), may be used to evaluate concentrations of dissolved constituents in groundwater over time to
10   account for NAPL dissolution. The following approach is planned considering the currently available
11   information. However, as new information becomes available, the approach may be modified to
12   meet the modeling objectives.

13   For simplicity, a specific or constant concentration source will be used initially to generate
14   conservative CF&T simulation results. This will entail setting a continuous source term with either
15   constant or variable dissolved concentrations over time, without specifying the mass of the source.
16   Specifying the source term in this manner results in an infinite contaminant mass of constant
17   concentration and may over-predict contaminant concentrations in downgradient areas, which may
18   be overly conservative yet still provide useful information.

19   Truex et al. (2013) developed the SVEET (Soil Vapor Extraction Endstate Tool) model based on
20   their experience managing a large soil vapor extraction system at the Hanford Site. This tool matches
21   a non-Hanford site to a library of detailed numerical modeling runs from the STOMP model (PNNL
22   2015) to simulate recharge-controlled or gas-phase controlled transport of VOCs from the
23   unsaturated zone to groundwater. Truex et al. (2013) describe the underlying modeling approach as:

24   When vapor-phase transport is an important component of the overall
25   contaminant fate and transport from a vadose zone source, the contaminant
26   concentration expected in groundwater is controlled by a limited set of
27   parameters, including specific site dimensions, vadose zone properties, and
28   source characteristics. Under these circumstances, it is possible to pre-model
29   contaminant transport for a matrix of parameter value combinations that cover a
30   range of conditions and to estimate the results at a specific site by comparing the
31   site-specific characteristics to the characteristics of the pre-modeled scenarios.

32   As shown on Figure 6, the conceptual framework centers on a source area that is present at a
33   specified vertical location within the vadose zone. Additionally, a compliance well is located
34   downgradient from the source. Using site-specific parameters, SVEET predicts the contaminant
35   groundwater concentration at the compliance well, given the source strength (soil gas concentration)
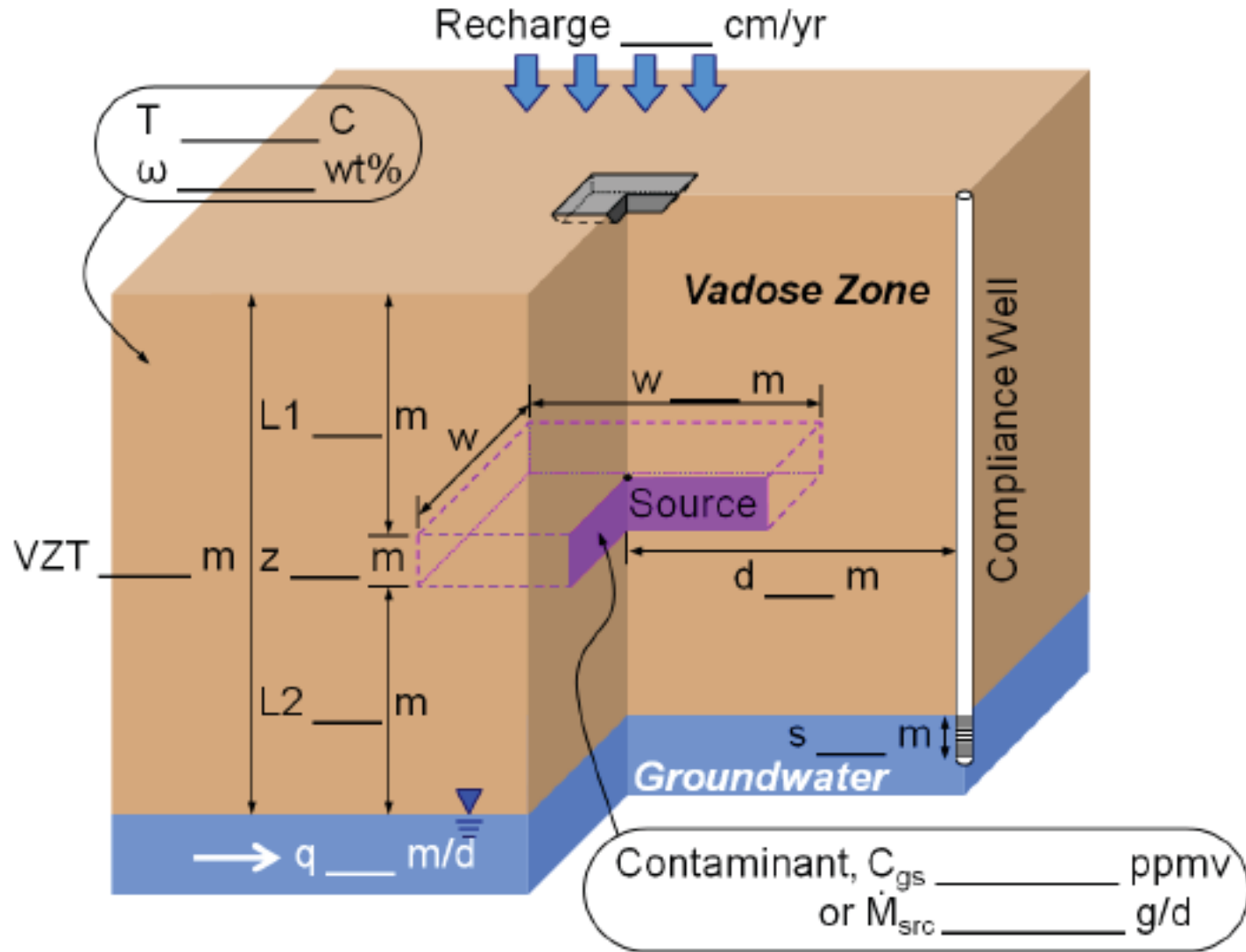36   and additional vadose zone parameters.

Figure 6
Key Model Inputs for SVEET
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1 The current version of MODFLOW-USG solute transport code, or MT3DMS, will be used to refine
2 the source term and obtain more realistic results based on site data. In Version 5 of MT3DMS
3 (Zheng 2010), the HSS Package directly links MT3DMS to the EPA HSSM (Charbeneau, Weaver,
4 and Lien 1995). The MT3DMS HSS Package (Zheng, Weaver, and Tonkin 2010) enables a
5 mass-loading time series to be specified in the source area, which is read directly into the MT3D
6 source term matrix (USGS 2016). The MODFLOW-USG solute transport code is anticipated to be
7 released in September 2018. If MODFLOW-USG has the same capability, it will be used to perform
8 a series of history matching simulations while adjusting source concentration and mass to reflect the
9 available COPC concentrations through time and equivalent NAPL-water partitioning. If not, the
10 MT3DMS will be used for this purpose. Unlike using a constant or variable-concentration source
11 term, using the equivalent NAPL-water partitioning approach will allow the MODFLOW-USG
12 model (or MT3DMS) to simulate release of COPCs from NAPL in the source zone. Specifically, this
13 approach allows the simulation of both:

14 • A finite mass of contaminant in a source zone

15 • Depletion of source mass through dissolution with time

16 NSZD is the dominant LNAPL depletion mechanism. If dissolution is the only mass depletion
17 parameter considered, it will greatly overestimate the source life and underestimate the cumulative
18 mass depletion rate. Thus, this approach is highly conservative, yet can often provide useful
19 information.

20 In addition to estimating the source term, history matching can be used to estimate transport
21 parameter values for porosity, dispersivity, and biodegradation half-life. The history-matching
22 simulation process is similar to the flow model calibration process. For solute transport, the
23 parameters are adjusted within reasonable ranges so that the simulated COPC concentrations in the
24 plume approximately match the measured values in monitoring wells.

25 Site-specific time series concentration data will be used to refine the CSM. Numerical CF&T
26 modeling will then be used to estimate the COPC decay rates. To estimate the decay rate, the
27 updated calibrated MODFLOW-USG model will be run using its solute transport module (similar
28 capability as MT3DMS), holding the advection and dispersion parameters constant while adjusting
29 the degradation rate in a series of iterative model runs to attain results comparable to the time-series
30 data from monitoring wells near the source and away from the source (e.g., RHMW02 and
31 RHMW01).

32 A new version of MT3DMS has recently been released by the U.S. Geological Survey, named
33 MT3D-USGS (USGS 2016). The MT3D-USGS model builds upon MT3DMS version 5.3 (Zheng
34 and Wang 1999) and integrates HSSM with the more sophisticated finite-difference, dissolved-phase
35 transport capabilities of MT3DMS. Time-varying mass-loading sources can thus be directly
36 incorporated into MT3D-USGS simulations. Before performing the CF&T modeling, MT3D-USGS
37 will be further evaluated and used for this project if it is found to provide advantages compared to
38 the other available CF&T modeling codes such as MODFLOW-USG solute transport.

39 ## 4.2   SECONDARY AND ADDITIONAL DATA INPUTS (LOE 2 AND LOE 3)

40 This subsection details the secondary and additional information as described in Section 3, and
41 provides a rationale and the intended data inputs supporting development of the CSM, groundwater
42 flow model, and CF&T model.

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4.2.1   Infiltration Rate Tests to Estimate Groundwater Recharge

Evaluation of NAPL movement in the vadose zone includes assessment of groundwater recharge through the vadose zone. The recharge rate of infiltrate through the caprock contributes to the rate of NAPL dissolution and mass transport of dissolved petroleum constituents through the vadose zone. Recharge will be estimated based on dual-ring infiltrometer tests at a minimum of three locations at different elevations within the Facility boundaries, mapped soil characteristics, and precipitation records. The calculated surface recharge rate will be used to inform the CSM and the numerical groundwater model.

4.2.2   Biodegradation Studies

This plan proposes collecting samples for microbiological analyses to identify bacterial species present in the source area and to describe how those species indicate active biodegradation processes to support the CF&T model. Data from the microbiological analyses will also provide inputs on biodegradation potential during modeling of possible future release scenarios. The following subsections describe the studies proposed to be employed to further refine the understanding of biodegradation.

4.2.2.1   QUANTARRAY – PETRO

To further evaluate biological processes contributing to natural attenuation at the Facility, data will be collected on the presence and quantity of microbial functional genes responsible for aerobic and anaerobic biodegradation of petroleum hydrocarbons. Petroleum products are complex mixtures of hundreds of aliphatic, aromatic, cyclic, and heterocyclic compounds. Biodegradation of these compounds can proceed along a multitude of pathways under both aerobic and anaerobic conditions. The QuantArray-Petro method will quantify key organisms and functional genes responsible for biodegradation of the petroleum hydrocarbons, including BTEX, PAHs, and other short- and long-chain alkanes. Data from the analysis also provide input for the evaluation of remedial alternatives for the site. Groundwater or bio-filter samples will be collected from RHMW01, RHMW02, RHMW03, and RHMW04 at minimum for QuantArray analysis for at least one sampling event.

4.2.2.2   STABLE ISOTOPE PROBING

To evaluate the rate of degradation of TPH compounds, SIP analysis will be performed using a passive sampler (i.e., bio-trap) containing activated carbon amended with a 13C-labeled COPC. Groundwater COPC data show that naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene are the specific petroleum-related compounds found consistently in RHMW02, where TPH concentrations exceed the project screening criteria. SIP analysis using 13C-labeled naphthalene will quantify the current rates of naphthalene degradation in the groundwater. Though the COPC benzene is currently not detected in the groundwater, benzene is the most mobile COPC and has higher drinking water toxicity than the other COPCs. Thus, SIP analysis using 13C-labeled benzene will be used to quantify the rates of benzene degradation, which will be used to inform the biodegradation potential in possible future release scenarios.

Bio-traps with "biosep" beads amended with 13C-naphthalene or 13C-benzene will be deployed below the water level at the same depth as the sample pumps are set. The bio-traps will be deployed during one wet-season and one dry-season event for approximately 30 days each event. SIP with 13C-naphthalene will be performed at RHMW02, RHMW03, and RHMW04, at minimum, for at least one sampling event; SIP with 13C-benzene will be performed at RHMW02 and RHMW03 for at least one sampling event. The data obtained will be used to refine estimates of the biodegradation rate used in the CF&T model.

1 *4.2.2.3 NEXT-GENERATION DNA SEQUENCING*

2 To further evaluate the natural attenuation potential occurring at the site, the composition of the
3 microbial community will be evaluated at select locations using DNA sequencing technologies,
4 which provide identification of microbes down to the genus level. Groundwater or bio-filter samples
5 will be collected at RHMW01, RHMW02, RHMW03, and RHMW04 at minimum for at least one
6 sampling event. Comparisons of the microbial communities between all locations in the monitoring
7 network may provide information on differences in microbial communities that possibly relate to the
8 TPH attenuation potential at the Facility and inform the evaluation of possible remedial alternatives.

9 *4.2.2.4 COMPOUND-SPECIFIC ISOTOPE ANALYSIS*

10 Biodegradation of petroleum uses nitrate and sulfate as electron donors after oxygen has been
11 depleted. Groundwater NAP results indicate that depressed concentrations of nitrate and sulfate at
12 select monitoring locations, which provides evidence for natural attenuation. To further evaluate the
13 groundwater aquifer and the nitrates and sulfates in the groundwater, compound-specific isotope
14 analysis (CSIA) will be performed on nitrogen and sulfur isotopes in the groundwater. Naturally
15 occurring nitrogen exists mostly as 14N and with a small percentage existing as 15N. Similarly,
16 natural occurring sulfur exists mostly as 32S, and the remaining as small percentage of 34S, and
17 almost trace amounts of 33S and 36S. CSIA provides the ratio of 14N/15N and the ratio of 32S/34S.
18 During biodegradation, the lighter isotope (e.g., 14N) requires less energy to use than the heavy
19 isotope (e.g., 15N). Thus, groundwater chemistry at locations where biodegradation is occurring will
20 show an enriched ratio of the heavier isotope compared to locations where there is no
21 biodegradation. Groundwater samples for CSIA will be performed at all locations in the monitoring
22 network for a minimum of one sampling event. Data from the CSIA will quantify the extent of
23 nitrate and sulfate degradation at each monitoring location, and provide inputs to evaluate the rate of
24 nitrate and sulfate at the site. Sampling locations include all wells in the Red Hill monitoring well
25 network.

26 *4.2.2.5 MICROCOSM STUDY*

27 To further support data collected from the QuantArray-Petro, SIP, and Next-Generation DNA
28 Sequencing, a laboratory-conducted microcosm study will estimate the bulk attenuation rate due to
29 biodegradation for select COPCs in both aerobic and anaerobic conditions. COPC concentration
30 trends and the abundance of the biomarkers over time from the microcosms will be evaluated.

31 Sediment and groundwater from RHMW01 and RHMW02 will be collected during one sampling
32 event and sent to a laboratory to construct microcosms. The media from each monitoring well will be
33 used to create two replicates of three redox conditions (i.e., aerobic, anaerobic, and sterile). The
34 microcosms will be modified initially with benzene and/or naphthalene to a target concentration.
35 Aerobic microcosms will be incubated for up to 4 months; anaerobic microcosms will be incubated
36 for up to 8 months. Aqueous samples from each microcosm will be collected at the beginning of the
37 study, end of the study, and at set intervals during the incubation period. Samples will be analyzed
38 for BTEX, TPH-d, naphthalene, dissolved gases, anions, pH, and ORP. Sacrificial microcosms will
39 also be sampled for biomarkers Gene-Trac ORM-2 (gene responsible for anaerobic metabolic
40 degradation of benzene to non-toxic end products) and Gene-Trac SRB (sulfate-reducing bacteria,
41 which are often implicated in anaerobic petroleum hydrocarbon degradation).

42 **4.2.3 Groundwater Chemical Analyses of Natural Attenuation Parameters**

43 The project WP/SOW includes collecting and evaluating additional NAP data from Red Hill
44 monitoring wells to show biodegradation processes are active in reducing the mass of COPCs. These

1 data will support development of the CSM for attenuation processes and facilitate the CF&T
2 modeling. Currently the NAPs collected at the site include the following:

3 • *Field indicator parameters:* pH, dissolved oxygen, ORP (i.e., redox, Eh), temperature, and
4   SC

5 • *NAPs:* alkalinity, chloride, nitrate, nitrate-nitrite as nitrogen, dissolved methane, ferrous iron
6   (iron II), sulfate, total organic carbon (TOC), and dissolved gases (oxygen, carbon dioxide,
7   and methane using IsoFlask samplers)

8 Additional laboratory analytical NAPs will be collected to provide more data for the evaluation of
9 natural attenuation. Groundwater samples for NAPs will be collected for all locations in the
10 monitoring network for a minimum of one sampling event.

4.2.4   Vapor Sampling

12 Biodegradation of petroleum in the vadose zone is expected to generate carbon dioxide and methane
13 and to deplete oxygen. Vapor samples for oxygen, carbon dioxide, VOCs, SVOCs, and methane
14 concentrations will be collected from Red Hill soil vapor monitoring locations during one event at a
15 minimum. Data from these soil vapor sampling points will be used to determine the relative
16 concentrations of gases within the shallow, middle, and deep probes underneath the tanks and
17 evaluate presence and degree of biodegradation activity.

18 It is anticipated that gases generated during biodegradation occurring at the capillary fringe and
19 vadose zone will flow from the surrounding formation through the monitoring well screen. Gas
20 samples will also be collected from directly above the groundwater table in the monitoring locations
21 during one event at a minimum. The gas concentrations will be evaluated with the soil vapor
22 monitoring points' results and groundwater COPC and NAP data. Samples will be collected at
23 monitoring locations RHMW01, RHMW02, and RHMW03.

4.2.5   Vertical Temperature Profiles

25 Temperature in the subsurface is especially informative in evaluating biologically generated heat in
26 the unsaturated zone due to NSZD. Additionally, subsurface temperature profiles may provide
27 information to evaluate preferred pathways and/or groundwater flow directions. Temperature profiles
28 of the subsurface will be collected by lowering a string of thermistors or thermocouples down the
29 monitoring well locations to contact the sensor against the well casing and recording the temperature
30 readings from the bottom of the well to the top of the monitoring well. Additionally, temperatures
31 will be allowed to equilibrate at each depth before a final measurement is taken (approximately
32 10-15 minutes per depth). The temperature survey will be conducted in wells near potential LNAPL
33 zones and background wells where a "background corrected temperature" curve can be generated. If
34 no suitable background well can be used, then a simple seasonal thermodynamic model (such as the
35 Hillel model) will be used to obtain background corrected temperatures. Temperature profiles will be
36 collected at monitoring wells RHMW01, RHMW02, RHMW03, RHMW04, and RHMW10.

4.2.6   Carbon Traps

38 Carbon dioxide is a by-product of microbial biodegradation of NAPL in the subsurface. Carbon
39 dioxide concentrations emitted by the biodegradation of NAPL can be measured by installing carbon
40 traps along the lower access tunnel floor and on the surface adjacent to the tank farm. Two carbon
41 traps will be installed below the subgrade (into bedrock) of the lower access tunnel floor near
42 Tank 5; two additional carbon traps will be installed in the upper access tunnel floor near Tank 5.

Additionally, six surface traps will be installed at the ground surface above Tank 5. The traps will capture the carbon dioxide from the subsurface and also monitor the ambient conditions in the lower access tunnel and at the surface. Traps will be left in place for up to 4 weeks prior to retrieval and lab analysis of the sorbent material in the traps, which will provide an estimate of the NAPL degradation rate for the area.

4.2.7 Petrographic Studies

Petrographic analysis of the entire vadose zone core at RHMW01R (DON 2017f) will be conducted in a laboratory to 1) scan for hydrocarbons using white light and ultraviolet (UV) light for hydrocarbon fluorescence throughout the entire core; 2) perform analysis of trapped hydrocarbons, if identified in the core; and 3) perform tests of the NAPL mobility of the fuel and effective porosity within various rock types within the core. Analysis will include testing mobility of fuel in the core both found in situ and from fuel introduced to core samples at the laboratory. Additionally, sections of core within the Red Hill core inventory will be selected for the "introduced" fuel mobility testing, based on results from the RHMW01R core UV hydrocarbon fluorescence imaging and/or the necessity of the characterizing other rock types. These tests have a direct application to providing refinement to the CSM and CF&T models. Specifically, these tests will support an assessment of the capacity of NAPL to be immobilized by capillary forces (often referred to as residual saturation or residual NAPL).

4.3 ATTENUATION EVALUATION DATA USE

Attenuation will be evaluated along multiple LOEs from both primary and secondary information data sets. These data sets are focused on how the mass, toxicity, mobility, volume, or concentration of contaminants in the vadose zone and groundwater are potentially decreased by in-situ processes that include biodegradation, dispersion, dilution, sorption, and volatilization. The following attenuation data inputs have been identified in this plan:

Primary data inputs (LOE 1):

- Spatial and temporal trends of COPC data in the known groundwater plume
- Source studies
  - Forensic analysis
  - TPH fractions
  - Contaminant source modeling
- Solute transport modeling

Secondary and additional data inputs (LOE 2, LOE 3):

- Biodegradation studies
  - QuantArray – Petro
  - Stable isotope probing (SIP)
  - Next-generation DNA sequencing
  - Compound-specific isotope analysis (CSIA)
  - Microcosm study

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1   •   Field indicator parameters

2   •   Groundwater chemical analyses of NAPs

3   •   Vapor sampling

4   •   Vertical temperature profiles

5   •   Carbon traps

6   •   Petrographic studies

7   •   SVEET Model

8 9 10 11 Acquisition of these data sets will be used to support the development of the comprehensive CSM and groundwater flow model, and have a particular relevance to development of the CF&T model. The modeling is an iterative process and will be calibrated to align with the empirical data associated with the site.

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