Flint Hills Resources Alaska, LLC

Onsite Site Characterization Report – 2013 Addendum

North Pole Refinery
North Pole, Alaska
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ARCADIS

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Acronyms and Abbreviations

1,3,5-TMB	1,3,5-trimethylbenzene
3-D	three-dimensional
AAC	Alaska Administrative Code
ACL	alternative cleanup level
ADEC	Alaska Department of Environmental Conservation
AEM	airborne electromagnetic
APH	aliphatic hydrocarbon
API	American Petroleum Institute
API Workbook	Draft API LNAPL Transmissivity Workbook
ARCADIS	ARCADIS U.S., Inc.
AS	air sparge
ASTM	ASTM International
atm*m^3/mol	atmospheres-cubic meters per mole
AWS	alternative water solution
Barr	Barr Engineering Company
bgs	below ground surface
BOD	biological oxygen demand
BTEX	benzene, toluene, ethylbenzene, and total xylenes
btl	below the liner
CCV	continuing calibration verification
CD Support Work Plan	Work Plan for Additional Site Monitoring Activities During Construction Dewatering
cfs	cubic feet per second
city	North Pole, Alaska
cm/s	centimeters per second
cm^2/s	square centimeters per second
cm^3/L	cubic centimeters per liter

cm^3/mole	cubic centimeters per mole
C_{max}	maximum concentration after injection
COC	constituent of concern
COPC	constituent of potential concern
Core Labs	Core Laboratories
CSM	Conceptual Site Model
Cu	uniformity coefficient
CU #1 Wash Area	Crude Unit #1 Wash Area
CU #2 EU	Crude Unit #2 Extraction Unit
D_{60}/D_{10}	sample heterogeneity
diesel #2	No. 2 diesel fuel
DLC	dioxin-like compound
DO	dissolved oxygen
DPE	dual-phase extraction
DRO	diesel range organics
Ecological CSM	Ecological Conceptual Site Model
ERI	electrical resistivity imaging
ESI	Environmental Standards, Inc.
ET	evapotranspirate
EU	extraction unit
FDEM	frequency domain electromagnetic induction
FHRA	Flint Hills Resources Alaska, LLC
FOSA	perfluorooctane sulfonamide
FPM-C	Free Product Mobility – Centrifuge
FPM-WD	Free Product Mobility – Water Drive
FRC	flame-resistant clothing
Friedman and Bruya	Friedman and Bruya, Inc.

ft/day	feet per day
ft/ft	foot per foot
ft^2/day	square foot per day
ft^3/day	cubic feet per day
FTA	Fire Training Area
g/cm^3	grams per cubic centimeter
$g\text{-}HC/g\text{-}O_2$	grams of hydrocarbon to grams of oxygen for mineralization
GAC	granular activated carbon
gasoline-P	premium unleaded gasoline
gasoline-R	87-octane regular unleaded gasoline
GC/MS	gas chromatography/mass spectrometry
Geomega	Geomega, Inc.
GPS	global positioning system
GRO	gasoline range organics
GSA	grain size analysis
GVEA	Golden Valley Electric Association
HDPE	high-density polyethylene
HSA	hollow-stem auger
IFT	interfacial tension
IRAP	Interim Remedial Action Plan
ITRC	Interstate Technology & Regulatory Council
Jet A	Jet A fuel
kg	kilograms
kg/g	kilograms per gram
kg/m^3	kilogram per cubic meter
LCS	laboratory control sample
LCSD	laboratory control sample duplicate

LEL	lower explosive limit
LIF	laser-induced fluorescence
LNAPL	light nonaqueous phase liquid
LOD	limit of detection
LOQ	limit of quantitation
m	meters
m^3	cubic meters
$m^3\ H_2O/m^2/sec$	cubic meters of water per square meter per second
MAROS	Monitoring and Remediation Optimization System
mg/kg	milligrams per kilogram
mg/L	milligrams per liter
mL	milliliters
mL/min	milliliters per minute
mm	millimeters
mmHg	millimeter of mercury
MS	matrix spike
MSD	matrix spike duplicate
MSDS	Material Safety Data Sheet
MSL	mean sea level
NA	not available
naphtha	petroleum naphtha
NGP	North Gravel Pit
NGP Work Plan	Work Plan for Additional Site Characterization Activities and Remedial Evaluation at the North Gravel Pit
NPB	north property boundary
NPR	North Pole Refinery
NSZD	natural source zone depletion

offsite	area located outside the property boundary, primarily in the downgradient north-northwest direction
Offsite Addendum	Offsite Site Characterization Report – 2013 Addendum
Offsite SCWP	2013 Offsite Site Characterization Work Plan
onsite	area that is located within the property boundary of the FHRA NPR
Onsite Addendum	Draft Onsite Site Characterization Report – 2013 Addendum
Onsite FS	Draft Final Onsite Feasibility Study
Onsite SCWP	Revised 2013 Onsite Site Characterization Work Plan
PAH	polyaromatic hydrocarbon
PCB	polychlorinated biphenyl
PCDD	polychlorinated dibenzo-p-dioxin
PCDF	polychlorinated dibenzofuran
PFBS	perfluorobutane sulfonate
PFC	perfluorinated compound
PFDA	perfluorodecanoic acid
PFDS	perfluorodecane sulfonate
PFHxA	perfluorohexanoic acid
PFHxS	perfluorohexane sulfonate
PFNA	perfluorononanoic acid
PFOA	perfluorooctanoic acid
PFOS	perfluorooctane sulfonate
PFTriA	perfluorotridecanoic acid
PFUnA	perfluoroundecanoic acid
PIANO	paraffins, isoparaffins, aromatics, naphthenes, and olefins
PID	photo ionization detector

POE	point of entry
power plant	electrical generating facility
ppm	parts per million
ppmv	parts per million by volume
PPRTV	provisional peer-reviewed toxicity value
probe valve	gas-tight two-way ball valve installed closest to the soil gas probe
purge valve	gas-tight two-way ball valve installed on the opposite end of the sampling train
PVC	polyvinyl chloride
QA	quality assurance
QC	quality control
RCRA	Resource Conservation and Recovery Act
Revised Draft Final HHRA	Revised Draft Final Human Health Risk Assessment
Revised IRAP Addendum	Revised Interim Remedial Action Plan Addendum
RFA	RCRA Facility Assessment
RPD	relative percent difference
RRO	residual range organics
RSAP	Revised Sampling and Analysis Plan
RSL	regional screening level
SCR – 2011	Site Characterization Report – Through 2011
SCR – 2012	Site Characterization Report – 2012 Addendum
SGS	SGS Laboratories in Anchorage, Alaska
SGP	South Gravel Pit
site	FHRA North Pole Refinery, an active petroleum refinery located on H and H Lane in North Pole, Alaska
SOP	standard operating procedure

SPB	south property boundary
SPE	solid-phase extraction
SVE	soil vapor extraction
SVOC	semivolatile organic compound
SWA	Southwest Former Wash Area
SWI	Shannon and Wilson, Inc.
TCDD	2,3,7,8-tetrachlorodibenzo-p-dioxin
TDR	time-domain reflectometry
TEF	toxicity equivalence factor
TestAmerica	TestAmerica, Inc. laboratory in Denver, Colorado
TIN	Triangular Irregular Network
TKN	total Kjeldahl nitrogen
TOC	total organic carbon
TPH	total petroleum hydrocarbon
TTA-1	Tracer Test Area 1
TTA-2	Tracer Test Area 2
TVH	total volatile hydrocarbons
UAF	University of Alaska – Fairbanks
USCS	Unified Soil Classification System
USEPA	United States Environmental Protection Agency
USGS	U.S. Geological Survey
VES	vacuum-enhanced skimming
VOC	volatile organic compound
vol%	percent by volume
VPH	volatile petroleum hydrocarbons
VPT	vertical profile transect
WHO	World Health Organization

WO	work order
WWTP	wastewater treatment plant
YSI	Yellow Springs Instruments
µg/kg	micrograms per kilogram
µg/L	micrograms per liter
µm	micrometers
°C	degrees Celsius
°F	degrees Fahrenheit

Executive Summary

This Onsite Site Characterization Report – 2013 Addendum (Onsite Addendum) for the Flint Hills Resources Alaska, LLC (FHRA) North Pole Refinery (NPR) presents site characterization data collected in 2013 and the results of technical analyses based on these data. The technical analyses and discussions in this Onsite Addendum are informed by the full data set collected over the total site history and by historical findings.

This Onsite Addendum is the last of a series of site characterization reports that collectively present an extensive body of information that has been gathered to ascertain the physical characteristics of the site, define the sources of contamination, and determine the nature and extent of contamination present at the site. The companion reports are:

- Site Characterization Report – Through 2011 (SCR – 2011; Barr Engineering Company [Barr] 2012)
- Site Characterization Report – 2012 Addendum (SCR – 2012; ARCADIS U.S., Inc. [ARCADIS] 2013b)
- Offsite Site Characterization Report – 2013 Addendum (ARCADIS 2013m)

This document and the companion reports, in conjunction with the Revised Draft Final Human Health Risk Assessment (ARCADIS 2012), are sufficient to support a risk-based evaluation of appropriate remedial alternatives for the site.

This Onsite Addendum outlines results from field activities conducted in 2013, including the technical background and rationale for each activity proposed in the Revised 2013 Onsite Site Characterization Work Plan (Onsite SCWP; ARCADIS 2013e) and additional work agreed to in electronic communication with Alaska Department of Environmental Conservation. It also presents additional interpretations and conclusions based on ongoing monitoring well sampling and a review of the full data set for the site. Field activities completed in 2013 were also partially discussed and documented during periodic technical meetings with ADEC. This Onsite Addendum documents the following key characterization initiatives that were completed during 2013, along with related site characterization activities approved in the Onsite SCWP:

- Installation of additional Phase 8 monitoring, observation, and light nonaqueous phase liquid (LNAPL) assessment wells and well nests for further site characterization and delineation.
- LNAPL investigation, including LNAPL transmissivity and compositional testing.

- Collection of routine benzene, toluene, ethylbenzene, total xylenes (BTEX) and sulfolane groundwater analytical data from monitoring wells.

- Collection of groundwater samples for sulfolane and BTEX analysis from hydropunch borings, and hand-driven sampling points.

- Collection of soil samples for sulfolane and BTEX analysis for additional delineation of source areas.

- Collection of soil samples at a high resolution to evaluate storage of sulfolane in the capillary fringe and vadose zone.

- Collection of soil samples to evaluate grain size distribution, verify visual observations of soil types recorded during borehole drilling, assess aquifer heterogeneity and estimate hydraulic conductivity.

- Collection of soil and groundwater samples for total organic carbon analysis.

- Measurement of water levels using automated and manual methods.

- Capture zone analysis and vertical gradient data collection in conjunction with surveying (hydrologic studies).

- Implementation of an aquifer pumping test using the onsite recovery wells.

- Execution of two tracer tests onsite, including installation of nearby monitoring wells, conducting single-well pumping tests, and high-frequency collection of water level and tracer data.

- Collection of soil gas analytical and diffusivity testing data to evaluate bioventing feasibility, explosion risk, natural source zone depletion, and volatile hydrocarbon distribution.

- Phase III perfluorinated compound investigation including sampling groundwater and Fire Training Area (FTA) soil (including additional analytes).

- Collection of subsurface data using geophysical field surveys that included airborne, ground-based and down-hole methods to characterize permafrost.

- Tracer testing to assess hydrogeologic properties of fine- and coarse-grained soil.

- Collection of data from an onsite air sparge (AS) pilot test.

- In-situ respiration pilot testing.

- Collection of bathymetric, water and sediment data for remedial evaluation of the North Gravel Pit (NGP).

The culmination of site characterization activities and evaluations resulted in the following summarized conclusions:

- Groundwater flow and transport at the site is dynamic and extremely complex due to a combination of factors including heterogeneously distributed soil types, discontinuous permafrost, seasonal fluctuations in surface water elevations at the Tanana and Chena rivers, and annual freeze-thaw cycles that extend well below ground.

- Geological information collected from soil borings advanced in 2013 was consistent with historical observations. Peat/high organic soil and plastic silts were identified in 2013 using detailed geologic assessment techniques intended to identify these and other soil types.

- Permafrost is largely absent under the developed portions of the site. Discontinuous permafrost is present in the northern, undeveloped portions of the site.

- The extent of LNAPL impacts is known, LNAPL is not a significant source of sulfolane to groundwater, the LNAPL plume is stable, LNAPL is readily recoverable in some areas of the site, and natural processes are depleting the LNAPL at a significant rate.

- The distribution of volatile petroleum hydrocarbons in soil gas is consistent with the reported LNAPL types at the site. Methane was below 100 percent lower explosive limit (LEL) in all 6 shallow soil gas samples collected at the approximate midpoint between the groundwater table and surface and 5 out of 6 deep soil gas samples collected near the groundwater table within the LNAPL smear zone. At the location where methane exceeded the LEL, the methane concentration in soil gas decreased 90 percent between the deep and shallow soil gas sample, which is likely attributable to aerobic consumption of methane in the vadose zone by methanotrophic bacteria.

- Sulfolane concentrations in groundwater exceeding the ACL of 362 micrograms per liter (µg/L) are found onsite, generally upgradient from the groundwater extraction wells.

- Benzene concentrations exceeding the 590 µg/L ACL are limited to the developed portions of the site. Some benzene is present downgradient of the groundwater recovery system capture zone, but site data show that benzene attenuates rapidly downgradient and is not present off site.

- Perfluorinated compounds (PFCs) were found at low levels in soil above the Fire Training Area liner and slightly above the ACL in one monitoring well and in one hydropunch boring. The PFCs detected in the soil are contained within a lined and bermed area and the recent groundwater results are consistent with the previous sampling data indicating no further investigation is warranted.

- Historical records indicate that there are six primary source locations of sulfolane to groundwater at the NPR. The largest sources have been identified as Lagoon B and the Crude Unit #2 Extraction Unit (CU #2 EU) Area. Other sources include the Southwest Former Wash Area (SWA), South Gravel Pit (SGP), Sump 908, and Crude Unit #1 Wash Area (CU #1 Wash Area).

- Soil and groundwater quality data collected in 2013 confirm the historical source records. Significant sulfolane concentrations were found in soil collected from under Lagoon B, within the CU #2 EU, SWA, and CU #1 Wash Area soil. These soil impacts are the primary source of sulfolane currently observed in groundwater. Less significant impacts were found in soil samples collected in the area of Sump 908 and the south gravel pit.

- Pilot testing and remedial investigation activities were completed at the site in 2013 to support future feasibility study (FS) evaluations. This testing included continuation of an air sparge (AS) pilot test, North Gravel Pit investigations, and in-situ respiration pilot testing. AS is effective for *in-situ* sulfolane treatment. Bioventing or similar oxygenation remedies would be effective for *in-situ* treatment of petroleum hydrocarbons.

- FHRA continued to implement ADEC-approved corrective actions to address sulfolane and petroleum hydrocarbon impacts. These response actions included continuation of the Alternative Water Solutions Program, continued operation of the onsite groundwater recovery system, and continued operation of onsite LNAPL recovery systems. The corrective actions have collectively prevented exposure to sulfolane in excess of the 362 µg/L ACL for sulfolane.

- The groundwater recovery system was expanded in 2013. Field data collected to evaluate the capture zone extent indicate that the groundwater recovery system is capturing groundwater as designed, and the system is effectively preventing migration of dissolved-phase COCs at concentrations above the respective ACLs beyond the capture zone of the recovery system.

A Conceptual Site Model (CSM) was prepared for the site that summarizes how chemicals were historically released to the environment at the NPR, how the released chemicals move through the environment, how those chemicals affect people and other living things, and ongoing efforts to protect people from being exposed to those chemicals. The CSM is based on extensive environmental assessment activities that have been conducted at the NPR during the past 26 years, with the majority of activities occurring since 2009. The assessment included a thorough review of historical chemical use at the NPR, collection of water and soil samples from the surface and subsurface, monitoring of groundwater data over time, hydrologic studies of groundwater gradients and movement, geophysical studies of permafrost in the area, and computer-based simulations of the movement of sulfolane in the subsurface. The CSM will support evaluation of potential remedial technologies in a future feasibility study and development of the final cleanup plan for the site. The extensive LNAPL, soil, groundwater, and soil-gas data collected to date and the CSM are sufficient to support a risk-based evaluation of appropriate remedial alternatives for the site. The CSM is attached as Appendix 1-A.

1. Introduction

On behalf of Flint Hills Resources Alaska, LLC (FHRA), ARCADIS U.S., Inc. (ARCADIS) prepared this Onsite Site Characterization Report – 2013 Addendum (Onsite Addendum) for the FHRA North Pole Refinery (NPR), an active petroleum refinery located on H and H Lane in North Pole, Alaska (site). The data, analyses, and conclusions in this report are the product of a collaborative effort among FHRA's consulting team members. That team includes qualified professionals in a variety of technical disciplines from four environmental consulting firms; ARCADIS, Shannon & Wilson, Inc. (SWI), Barr Engineering Company (Barr), and Geomega, Inc. (Geomega). FHRA has engaged these consulting firms to perform various tasks on the project. This report, therefore, encompasses contributions from professionals from each firm in the text and figures presented.

The North Pole Refinery (NPR) was built in 1976 and 77 by Earth Resources Corporation of Alaska and refinery operations began in August 1977. Earth Resources leased the refinery property from the State of Alaska, which owned the refinery land. MAPCO, Inc. acquired Earth Resources Corporation in 1980, and continued operations under a newly formed company, MAPCO Alaska Petroleum, Inc. In 1998, Williams Alaska Petroleum, Inc. acquired MAPCO through a stock purchase, thereby succeeding to MAPCO's operations. Williams and its predecessor MAPCO operated the NPR on State-owned land for almost 25 years, up until 2004. FHRA purchased the refinery assets from Williams effective April 1, 2004, along with the refinery land, which Williams had acquired from the State of Alaska shortly before the transaction with FHRA. FHRA has owned and operated the refinery since then.

This Onsite Addendum is the last of a series of site characterization reports that collectively present an extensive body of information that has been gathered to ascertain the physical characteristics of the site, define the sources of contamination, and determine the nature and extent of contamination present at the site. The companion reports are:

- Site Characterization Report – Through 2011 (SCR – 2011; Barr Engineering Company [Barr] 2012), submitted in December 2012

- Site Characterization Report – 2012 Addendum (SCR – 2012; ARCADIS U.S., Inc. [ARCADIS] 2013b), submitted in January 2013

- Offsite Site Characterization Report – 2013 Addendum (ARCADIS 2013m)

The information collected to date in conjunction with the Revised Draft Final Human Health Risk Assessment (Revised Draft Final HHRA; ARCADIS 2012) are sufficient to support a risk-based evaluation of appropriate remedial alternatives for the site.

The onsite site characterization activities discussed in this Onsite Addendum were proposed in multiple 2013 work plans and technical memoranda. The Alaska Department of Environmental Conservation (ADEC) approved the work plans and technical memoranda subject to incorporation of ADEC comments. The two primary documents proposing work were the Revised 2013 Onsite Site Characterization Work Plan (Onsite SCWP; ARCADIS 2013e2013e) and the Additional Scope of Work for Site Characterization Activities to Refine the Evaluation of Fate and Transport of Sulfolane (ARCADIS 2013g). The additional field activities were proposed to further refine the Conceptual Site Model (CSM) and were developed based on recommendations presented in previous site characterization reports prepared by FHRA that summarized work completed in the onsite area. In addition, the scope of work includes investigation activities completed at the request of the Alaska Department of Environmental Conservation (ADEC) and provided to FHRA in comments to the Onsite SCWP (ARCADIS 2013e2013e) and in general communications between ADEC and FHRA. Throughout the 2013 site investigation activities, FHRA maintained an adaptive management strategy to ensure that site characterization was completed to the necessary extent to support feasibility study (FS) development.

It is acknowledged that in 18 Alaska Administrative Code (AAC) 75.990(115), ADEC defines the term “site” as an “area that is impacted, including areas impacted by the migration of hazardous substances from a source area, regardless of property ownership.” For this Onsite Addendum, the term “onsite” is the area that is located within the property boundary of the FHRA NPR, and the term “offsite” is the area located outside the property boundary, primarily in the downgradient north-northwest direction, based on the approximate extent of the dissolved-phase sulfolane plume detected at concentrations above the detection limit (approximately 3.1 micrograms per liter [µg/L]).

Site conditions were previously evaluated in the Site Characterization and First Quarter 2011 Groundwater Monitoring Report (Barr 2011), Site Characterization Work Plan Addendum (ARCADIS 2011b), SCR – 2011 (Barr 2012), and SCR – 2012 (ARCADIS 2013a). The Revised Draft Final HHRA (ARCADIS 2012) evaluated whether concentrations of site-related constituents in soil and groundwater pose a risk to onsite and offsite receptors.

FHRA developed a hydrogeologic conceptual site model that describes the distribution of the conductive saturated aquifer, the distribution of permafrost and its influence on groundwater flow, and the sources and sinks of groundwater. Fourteen geologic cross-sections were prepared to show the stratigraphy and permafrost in the upper 350 feet in the onsite and offsite areas using information from boring logs, private wells, geophysical data, and land surface information. The cross sections are presented in Section 5 and the onsite hydrogeology in Section 6. The hydrogeologic conceptual site model is a component of the CSM presented in Appendix 1-A

FHRA submitted an Ecological Conceptual Site Model (Ecological CSM; ARCADIS 2011a) to ADEC in June 2011. The purpose of the Ecological CSM (ARCADIS 2011a) was to establish whether environmental contaminants related to site operations that are present onsite, or that have migrated offsite, will come in contact with ecological receptors. The Ecological CSM (ARCADIS 2011a) found that there were no complete exposure pathways for ecological receptors and concluded that no further evaluation is warranted.

ARCADIS, Barr, Geomega, SWI, and other technical specialists completed or directed the field activities summarized below during 2013. Field activities were completed by qualified persons as defined by 18 AAC 75.990.

1.1 Purpose

This Onsite Addendum outlines results from field activities conducted in 2013, including the technical background and rationale for each activity proposed in the Onsite SCWP (ARCADIS 2013e) and a technical memorandum (ARCADIS 2013g). It also presents additional interpretations and conclusions based on ongoing groundwater monitoring well sampling and a review of the full data set for the site. In some instances as noted in this Onsite Addendum, data collection and evaluation are ongoing. In these cases, this Onsite Addendum indicates where the data analysis and recommendations will be presented. Field activities completed in 2013 were partially documented during Technical Project Team and other meetings. This Onsite Addendum summarizes the following characterization initiatives that were completed during 2013:

- Installation of additional Phase 8 monitoring, observation, and light nonaqueous phase liquid (LNAPL) recovery wells and well nests for further site characterization and contaminant delineation.

- LNAPL investigation, including LNAPL transmissivity and compositional testing.

- Collection of routine benzene, toluene, ethylbenzene, total xylenes (BTEX) and sulfolane groundwater analytical data from monitoring wells screened across and below the groundwater table.

- Collection of groundwater samples for sulfolane and BTEX analysis from new monitoring wells, hydropunch borings, and hand-driven sampling points.

- Collection of soil samples for sulfolane and BTEX analysis for additional delineation of source areas.

- Collection of soil samples at a high resolution to evaluate storage of sulfolane in the capillary fringe and vadose zone.

- Collection of soil samples to evaluate grain size distribution, verify visual observations of soil types recorded during borehole drilling, assess aquifer heterogeneity and estimate hydraulic conductivity.

- Collection of soil and groundwater samples for total organic carbon analysis.

- Measurement of water levels using automated and manual methods.

- Capture zone analysis and vertical gradient data collection in conjunction with surveying (hydrologic studies).

- Implementation of an aquifer pumping test using the onsite recovery wells.

- Execution of two tracer tests onsite, including installation of nearby monitoring wells, conducting single-well pumping tests, and high-frequency collection of water level and tracer data.

- Collection of soil gas analytical and diffusivity testing data to evaluate bioventing feasibility, explosion risk, natural source zone depletion, and volatile hydrocarbon distribution.

- Phase III perfluorinated compound investigation including sampling groundwater and Fire Training Area (FTA) soil (including additional analytes).

- Collection of subsurface data using geophysical field surveys that included airborne, ground-based and down-hole methods to characterize permafrost.

- Tracer testing to assess hydrogeologic properties of fine- and coarse-grained soil.

- Collection of data from an onsite air sparge (AS) pilot test.

- In-situ respiration pilot testing.

- Collection of bathymetric, water and sediment data for remedial evaluation of the North Gravel Pit (NGP).

The scope of the geochemical parameter monitoring program was also revised (ARCADIS 2013); those results will be reported in quarterly groundwater monitoring reports.

Additional data collected and summarized in this Onsite Addendum were used to validate and refine the CSM presented in Appendix 1-A.

Remedial evaluations completed in 2012 and 2013 include:

- Air sparge (AS) pilot testing
- Revisions to the previously completed NSZD evaluation (Barr 2012)
- Soil vapor extraction (SVE) pilot testing
- In-situ respiration (bioventing) testing
- NGP remedial evaluation

1.2 Proposed Cleanup Levels

In correspondence dated July 19, 2012, the ADEC indicated that FHRA should use an alternative cleanup level (ACL) of 14 µg/L for dissolved-phase sulfolane at the site in the development of remedial action objectives and in evaluation of remedial alternatives. This ACL was based on a provisional peer-reviewed toxicity value (PPRTV) for sulfolane that was derived by the United States Environmental Protection Agency (USEPA) in January 2012, and on exposure assumptions developed by ADEC. In the May 2012 Revised Draft Final HHRA (ARCADIS 2012), the PPRTV used with the ADEC-selected exposure parameters was called the PPRTV Scenario. The Revised Draft Final HHRA (ARCADIS 2012) also presented the ARCADIS Scenario, using scientifically supported toxicity value and exposure parameters selected by ARCADIS after data and literature review. The toxicity value and many of the exposure parameters differed between scenarios. Using the ARCADIS Scenario, there were no current or future offsite receptors identified through the risk assessment who exceed the acceptable hazard index or excess lifetime cancer risk, and the sulfolane ACL is 362 µg/L.

FHRA concludes that an ACL of 362 µg/L is the most appropriate and data-supported ACL for the site. Accordingly, sulfolane concentrations in groundwater in the onsite and offsite areas are compared to an ACL of 362 µg/L for this Onsite Addendum and screening of remedies in the feasibility studies also will be based on this ACL.

In this Onsite Addendum, sulfolane in soil concentrations are compared to a migration-to-groundwater cleanup value (0.999 milligram per kilogram [mg/kg]) derived using the USEPA Calculator for Regional Screening Levels for Chemical Contaminants at Superfund Sites (http://epa-prgs.ornl.gov/cgi-bin/chemicals/csl_search [RSL calculator]) and a target groundwater ACL of 362 µg/L. This is the same calculator that ADEC used to calculate the soil ACL of 0.038 mg/kg using the target groundwater ACL of 14 µg/L. ADEC-specific parameters were used in the calculator, including the dilution attenuation factor and fraction organic carbon of 13.2 and 0.001, respectively.

Based on the Revised Draft Final HHRA (ARCADIS 2012), the other constituents of concern (COCs) at the site in addition to sulfolane are benzene, xylenes, naphthalene, and 1,3,5-trimethylbenzene (1,3,5-TMB). Groundwater ACLs for these COCs were calculated using ADEC-accepted exposure scenarios in the Revised Draft Final HHRA (ARCADIS 2012). Soil migration to groundwater ACLs for the other COCs were calculated using the risk-based groundwater ACLs and the USEPA regional screening level (RSL) calculator.

Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) were detected at the site following the completion of the Revised Draft Final HHRA (ARCADIS 2012) and, therefore, also are identified as COCs. Groundwater ACLs for PFOS and PFOA are not site-specific and were developed by ADEC using the USEPA RSL calculator. In correspondence dated August 16, 2013, ADEC issued ACLs for PFOS and PFOA in soil based on the migration to groundwater pathway, also using the USEPA RSL calculator. Following further review, in ADEC email correspondence dated December 5, 2013, the migration to groundwater ACLs for PFOS and PFOA were confirmed to be 1.2 and 1.1 mg/kg, respectively (equivalent to 1,200 and 1,100 µg/kg, respectively, for comparison with the site data). However, because PFOS and PFOA were detected in a soil-lined containment area where the impacts will not come in contact with groundwater, PFOS and PFOA soil results were compared to ACLs based on USEPA Region 4 recommended residential soil screening levels (for direct contact).

Soil and groundwater ACLs for COCs are summarized in the table below.

COC	Groundwater ACL (µg/L)	Soil ACL (mg/kg)
Sulfolane	362	0.999
Benzene	590	2.85
Xylenes	3,470	27.6
Naphthalene	31.8	0.731
1,3,5-TMB	92.4	1.02
PFOS	1.3	54.7*
PFOA	3.1	137*

*PFOS and PFOA soil ACLs calculated for onsite outdoor workers (direct-contact) using the USEPA Regional Screening Level Calculator (USEPA 2013).

2. Site Setting

2.1 Property Description

The 240-acre site is located inside the city limits of North Pole, Alaska (the city). The city is located approximately 13 miles southeast of Fairbanks, Alaska, within the Fairbanks North Star Borough (Figure 2-1). NPR is an active petroleum refinery that receives crude oil feedstock from the Trans-Alaska Pipeline.

Three crude oil processing units are located in the southern portion of the site, making up the process area. Only one of the processing units is currently operating. Tank farms are located in the central portion of the site. Truck-loading racks are located immediately north of the tank farms and a railcar-loading rack is located west of the tank farms. Wastewater treatment lagoons, storage areas, and two flooded gravel pits (the North and South Gravel pits) are located in the western portion of the site. Rail lines and access roads are located in the northernmost portion of the site.

Along the southern site boundary, partially surrounded by the NPR, is an electrical generating facility (power plant) operated by Golden Valley Electric Association (GVEA). FHRA representatives indicated that the power plant burns heavy aromatic gas oil (diesel 4) or other fuels produced at the site. The property south of the site and the GVEA power plant is occupied by the Petro Star, Inc. Refinery. Site features are presented on Figure 2-2.

North of the site are residential properties and the city’s wastewater treatment plant (WWTP). The North Pole High School is located immediately north and west of the WWTP and residential properties. An undeveloped parcel, owned by the Alaska Department of Natural Resources, lies between the site and the WWTP. The Tanana River is located to the south and west, flowing in a northwesterly direction toward Fairbanks. Surrounding the site is property that is residential or undeveloped. East of the site and crossing the offsite area running southeast to northwest are the Old Richardson Highway, and the Alaska Railroad right-of-way. Current site features are presented on Figure 2-2. Onsite and offsite site plans are presented on Figures 2-3 and 2-4, respectively.

2.2 Physical Setting

The site and the surrounding North Pole area are located on a relatively flat-lying alluvial plain that is situated between the Tanana River and Chena River. The site is located on the Tanana River Floodplain. Up to 2 feet of organic soil is typically found in the undeveloped portions of the site. Silt and silty sand layers varying in thickness from 0 to 10 feet typically occur beneath the organic soil. Alluvial sand and gravel associated with the Tanana River are present below the organic soil and silty layers. Depth to bedrock has been estimated at 400 to 600 feet below ground surface (bgs).

The city is located within an area of Alaska characterized by discontinuous permafrost (Ferrians 1965). Permafrost tends to act as a confining unit, impeding and redirecting the flow direction of groundwater (Glass et al. 1996). Based on regional information (Williams 1970, Miller et al. 1999), permafrost is assumed to be absent beneath the Tanana River.

The aquifer beneath the alluvial plain between the Tanana River and Chena River generally consists of highly transmissive sand and gravel under water table conditions (Cederstrom 1963, Glass et al. 1996). The Tanana River has a drainage area of approximately 20,000 square miles upstream of Fairbanks (Glass et al. 1996). Near the site, this aquifer is reportedly greater than 600 feet thick (at least 616 feet thick near Moose Creek Dam) (Glass et al. 1996). Beyond the zones of influence of the site groundwater recovery system, groundwater flow directions are controlled by discharge from the Tanana River to the aquifer and from the aquifer to the Chena River, as described by Glass et al. (1996). Variations in river stage through time are believed to be the primary cause of variations in groundwater flow direction in the aquifer between the rivers (Lilly et al. 1996, Nakanishi and Lilly 1998). Based on data from U.S. Geological Survey water table wells, the groundwater flow direction generally varies from a north-northwesterly direction to a few degrees east of north. The groundwater flow direction trends to the north-northwest in spring and more northerly in the summer and fall (Glass et al. 1996).

2.3 Onsite Constituents of Concern

Extensive sampling of groundwater and soil was completed for numerous constituents of potential concern (COPCs) to develop a list of COCs for the site. The process of identifying COCs is documented in the SCR – 2011 (Barr 2012) and the Revised Draft Final HHRA (ARCADIS 2012). In general, COCs were identified as those chemicals detected in media samples above the respective regulatory criteria. Impacted media are described in Section 5. COCs identified through the human health risk assessment process are discussed below:

- *Sulfolane*. Sulfolane is used at the NPR in the refining process as detailed in the SCR – 2011 (Barr 2012).

- *Naphthalene*. Naphthalene is generally present in crude stock and refined petroleum products.

- *Benzene*. Benzene is generally present in crude stock and refined lighter-end petroleum products (e.g., gasoline).

- *Xylenes*. Xylenes are present in crude stock and refined petroleum products as three different isomers (para-, iso-, and ortho-xylene). The three isomers have similar fate and transport characteristics and are regulated similarly. Therefore, xylenes are lumped into a single category.

- *1,3,5-TMB*. 1,3,5-TMB is generally present in crude stock and refined petroleum products.

At ADEC's request, the following additional COPCs, which were not included in the Revised Draft Final HHRA (ARCADIS 2012), were also evaluated at the site:

- *Gasoline range organics (GRO)*. GRO represents a grouping of hydrocarbon compounds typically found in gasoline.

- *Diesel range organics (DRO)*. DRO represents a grouping of hydrocarbon compounds typically found in diesel fuel.

- *PFCs including PFOS and PFOA*. Certain formulations of firefighting foams manufactured before 2002 included PFOS and PFOA chemistry.

- *Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs).* These compound classes are generally created as byproducts of industrial and combustion processes. These compound classes are also commonly referred to as dioxins and furans.

From the above list of COPCs, the additional COCs identified are PFOS and PFOA. Sulfolane is the only COC identified in the offsite area; the remaining COCs are limited to the onsite area.

3. Onsite Phase 8 Well Installation

Onsite Phase 8 wells were installed in 2013 to provide additional characterization of the nature and extent of LNAPL and COC impacts onsite as proposed in the Onsite SCWP (ARCADIS 2013e) and the Revised Interim Remedial Action Plan Addendum (Revised IRAP Addendum; ARCADIS 2013h). Onsite Phase 8 monitoring wells are shown on Figure 3-1 and Phase 8 well construction information is presented in Table 3-1. Upon installation, monitoring well names were modified from the temporary well name proposed in the Onsite SCWP (ARCADIS 2013e).

Onsite site characterization was managed in an adaptive manner and 80 additional wells as proposed in the Onsite SCWP (ARCADIS 2013e) and the Revised IRAP Addendum (ARCADIS 2013h) were installed in 2013. The majority of all planned work was completed, although soil conditions, weather, finalization of scopes of work, and access limitations associated with working in an active refinery did affect the schedule of the field work, in some cases pushing field work into the late fall. Accordingly, approximately 33 wells installed are pending analytical results and ten of the proposed wells are pending installation. The pending laboratory results are not expected to be affect the reliability of this document and its conclusions and the data will be supplemented in subsequent routine monitoring reports. The pending well installations were related to the pending expansion of the groundwater extraction and treatment system, and therefore not critical in the completion of the site characterization scope of work.

Monitoring and observation wells were installed to define the nature and extent of COCs, provide a record of groundwater elevations at the site, monitor groundwater treatment system performance, and further characterize permafrost. At select locations, well nests were installed with screened intervals set at different depths to vertically delineate sulfolane and monitor vertical groundwater concentrations. The objectives set forth for the proposed Phase 8 well installations were as follows:

- *Phase 8 Observation Wells for Groundwater Capture Monitoring*. Additional monitoring wells were installed to monitor groundwater capture at the recovery wells installed in 2013.

- *Phase 8 North Property Boundary (NPB) Well*. Define the horizontal and vertical extent of sulfolane concentrations along the NPB and identify depth to permafrost.

- *Phase 8 Upgradient Groundwater Delineation Wells*. Define the extent of the sulfolane plume upgradient of the Crude Unit #1 Wash Area (CU #1 Wash Area) and Crude Unit #2 Extraction Unit (CU #2 EU) source areas.

- *Phase 8 LNAPL Observation Well Installation*. Define LNAPL extent within the LNAPL plume footprint and provide additional spatial LNAPL transmissivity data.

- *Phase 8 Wells for Groundwater Capture.* Evaluate trends and improve monitoring of COC capture.

The following sections summarize installation methods and observations made during installation.

3.1 Well Construction Methodology

3.1.1 Phase 8 Monitoring Wells

Onsite Phase 8 well construction was completed according to the Revised Sampling and Analysis Plan (RSAP; ARCADIS 2013c) consistent with historical well construction methods. Onsite monitoring wells were designed, constructed, and installed in accordance with ADEC's Monitoring Well Guidance (ADEC 2013). Monitoring wells were constructed of 2-inch-diameter Schedule 40 polyvinyl chloride (PVC) blank casing from the ground surface to the screened interval.

Monitoring wells screened across the water table were screened from approximately 5 to 15 feet bgs; wells with submerged well screens were installed with 5-foot screens placed at the desired depth. Screens were constructed of Schedule 40 PVC 0.01-inch slotted casing. Well construction information is summarized in Table 3-1.

Monitoring wells constructed in this manner include site monitoring wells, wells along the NPB, and BTEX monitoring wells. Proposed wells pending installation include 10 groundwater treatment system performance monitoring wells at proposed well locations EGWRT-1, EGWRT-2, and EGWRT-6. These outstanding wells are not material to completing the site characterization process, but will be installed in the spring of 2014 to coincide with the operation of the expanded groundwater extraction and treatment system.

Well development and initial sampling results from the following wells were not completed in time to report in this Onsite Addendum: MW-142-65, MW-142-150, MW-334-15, MW-337-20, MW-344-55, MW-345-55, MW-351-15, MW-351-55, MW-351-75, MW-351-150, MW-359-15, MW-359-35, MW-359-80, MW-361-15, MW-362-15, MW-362-25, MW-362-35, MW-362-50, MW-362-80, MW-364-15, MW-364-30, MW-364-90, MW-365-15, MW-366-15, MW-367-15, MW-368-15, O-19-55, O-19-90, O-26-65, O-27-65, O-27-150 and S-41R. These wells are discussed further in Section 10. Results from these wells are not expected to affect the reliability of this document and its conclusions and will be reported in future groundwater monitoring submittals when the data become available.

3.1.2 Light Nonaqueous Phase Liquid Observation and Recovery Wells

Onsite Phase 8 LNAPL observation and recovery wells were completed according to the RSAP consistent with historical well construction methods. In addition, these wells were generally designed, constructed, and installed in accordance with ADEC's Monitoring Well Guidance (ADEC 2013). LNAPL observation and recovery wells were constructed of 4-inch-diameter Schedule 40 PVC blank casing from the ground surface to the screened interval.

LNAPL observation and recovery wells screened across the water table were screened from approximately 5 to 15 feet bgs. Screens were constructed of 0.01-inch slotted stainless steel wire-wrapped casing. Well construction information for wells at the site is summarized in Table 3-1.

3.2 Soil Classification

Soil classification was completed according to the Unified Soil Classification System (USCS), as summarized in the RSAP. The soil conditions encountered onsite are generally consistent with historical soil classification data at the site, as documented in the SCR – 2011 (Barr 2012) and the SCR – 2012 (ARCADIS 2013a). Also, the soil conditions encountered are consistent with previous observations that the regional geology is highly heterogeneous. Groundwater was encountered at approximately 7 to 13 feet bgs in the onsite Phase 8 monitoring wells. Boring logs summarizing the soil observed are included in Appendix 3-A. A general summary of typical conditions observed is presented below.

Soils encountered from ground surface to approximately 2.5 feet bgs consisted of sand, gravel, and silt with no apparent bedding. These earth materials are likely fill.

The majority of soil borings encountered a distinct layer of fine-grained materials beneath the fill. This layer was approximately 2.5 to 5 feet thick and consisted of fine-grained materials classified as dense silt with some plasticity. These materials are native and may represent a low-energy depositional environment such as a floodplain, overbank or slackwater. A distinct layer of fine-grained materials was not observed in well clusters MW-359 and MW-360 near the NPB.

A 2- to 4-foot-thick silty sand layer was encountered beneath the fine-grained materials. This layer consisted of alternating bedding of silt and sand, with sand as the predominant constituent present. At well cluster MW-359, trace organic material interbedded with the silty sand was observed in this interval. A 1-foot-thick layer of peat was observed beneath the silty sand at well cluster MW-360. These materials are native and may represent a low-energy depositional environment such as bog or abandoned portion of a meander channel.

At locations MW-359 and MW-363, near the NPB, frozen soils were logged in shallow soil (up to 2 feet bgs) and are interpreted to be associated with seasonal freezing. Due to the relatively shallow depths of ice observed at these locations, borings were continued through the frozen soils. Ice was not observed at depths below 2 feet bgs In addition, these wells are located in an undeveloped part of the site where seasonally frozen soils are more likely to extend deeper and persist longer during the water season. For comparison, permafrost is defined as soil or ground that is frozen (i.e., below 32 degrees Fahrenheit [°F]) for two or more consecutive years. Otherwise, permafrost was generally not encountered in onsite areas during the installation of Phase 8 monitoring wells; permafrost observations made during Phase 8 monitoring well installations and hand auger borings are summarized in Section 5.1.1.

The remaining soil borings not summarized above consisted of sand and gravel to boring termination (15 to 150 feet bgs). The pore spaces of the gravel deposits are commonly filled with finer grained soil such as sand and silt-sized particles. Fine-grained materials (e.g., silt) and intermittent lenses with silty material were identified. Sand lenses with thickness of up to 2.5 feet were observed within the sand and gravel layer, and were identified as being comprised of 95 percent or greater sand. The heterogeneous soil in the zone between 15 and 150 feet is discussed in greater detail in Section 4.5.

3.3 Soil Screening and Sampling

Split spoon soil samples were screened according to the RSAP using a photo ionization detector (PID); soil samples with readings exceeding 20 parts per million (ppm) organic vapor concentrations were submitted to SGS Laboratories in Anchorage, Alaska (SGS). Soil sampling during installation of the onsite Phase 8 wells was completed as proposed in the Onsite SCWP (ARCADIS 2013e) and in subsequent discussions with ADEC. Sampling and documentation were completed according to the RSAP. Due to heaving sands in saturated zones, the sampling frequency was not always continuous at depths below the groundwater table. Soil samples were collected and analyzed for specified parameters that may include the following:

- Grain size analysis (GSA) by ASTM International (ASTM) D422-63
- TOC by USEPA Method 9060
- Sulfolane by USEPA modified Method 8270D with isotope dilution
- BTEX by USEPA Method 8021
- GRO by Alaska Method AK101

- DRO by Alaska Method AK102

- Polyaromatic hydrocarbons (PAHs) by USEPA Method 8270

GSA data are discussed in Section 6.1.2.2. Analytical results for TOC, sulfolane and petroleum COCs are aggregated with other site data and discussed in Section 9.

3.4 Well Decommissioning

Recovery wells R-4, R-3, R-5, R-14, and R-38 were slated for decommissioning in 2013. These wells were no longer useful for LNAPL recovery and were proposed for decommissioning according to procedures outlined in the RSAP. Recovery well R-4 was decommissioned according to the RSAP in 2013; R-38 was not found and is considered destroyed. Wells R-3, R-5, and R-14 were not decommissioned in 2013. These wells will be decommissioned according to the procedures outlined in the RSAP in the future.

4. Onsite Geology

4.1 Regional Geologic Setting

NPR and the surrounding North Pole, Alaska area are located on the Tanana River floodplain, a relatively flat-lying alluvial plain situated between the Tanana and Chena rivers (Figure 2-1). The elevation of the floodplain is between 400 and 630 feet mean sea level (MSL) and the surface slopes downward to the northwest approximately 1 foot to 10 feet per mile.

The Tanana River is a glacially fed braided river that drains the northern Alaska Range; it exhibits an anastomosing pattern of channels separated by bars and islands. The Chena River is a meandering tributary to the Tanana River, discharging into the Tanana River near Fairbanks.

The geology of the area is dominated by a thick sequence of unconsolidated alluvial deposits. Depth to bedrock in the area of the NPR is estimated at 500 to 600 feet bgs (Péwé 1982). An injection well on the GVEA property adjacent to NPR was drilled to a depth of 450 feet and did not encounter bedrock, and no borings placed during site characterization have encountered bedrock. Bedrock crops out as low relief hills on the flanks of the Tanana River valley to the northwest, north, northeast, and east. A detailed review of regional geology is provided in the SCR – 2011 (Barr 2012).

4.2 Site-Specific Geologic Data

A total of 227 soil borings and 339 monitoring wells have been installed on the NPR site to date. These borings and wells are more densely located in areas of interest (e.g., near source areas, and the groundwater recovery system capture zone). The soil onsite is well described and characterized as noted in the following sections.

4.3 Grain Size Analysis Results

Grain size analyses (GSAs) were performed on 325 soil samples collected during the site characterization. Sieve, hydrometer, and laser diffraction tests have been performed to determine the gradations of samples collected from depths ranging from ground surface to. The results show that soil on site primarily consists of sand and gravel with some finer-grained units in the vadose zone and upper portion of the saturated zone.

4.4 Cross-section Development

Fourteen geologic cross-sections were prepared to show the stratigraphy and permafrost in the upper 350 feet in the onsite and offsite areas using information from boring logs, private wells, geophysical data, and land surface information. These cross-sections span the onsite and offsite areas and the seven cross-sections applicable to the onsite area are included in this Onsite Addendum (Figure 5-2 and Appendix 5-E).

Due to the broad scale and resulting limitations in presenting detailed geological information, additional cross-sections were prepared to illustrate the onsite geology (Figure 4-1 and Figures 4-2A through -2D).

Additional cross-sections summarizing soil and groundwater analytical data are presented in Sections 9 and 10, respectively. Geological information is included on these cross-sections to provide context for the observed COC distribution.

4.5 Soil Encountered

The data show that the site is underlain by a heterogeneous sequence of unconsolidated deposits. To demonstrate this, cross-sections 4-2A through 4-2D display the geology and predominant soil types described below.

Up to 2 feet of organic soil is present at the surface of undeveloped portions of the NPR and surrounding area. The natural surficial organic soil was often removed during construction and replaced with sand and gravel fill derived from local sources to facilitate site development. Gravel fill is present at developed areas onsite at depths of up to 6 feet bgs (Figures 4-2A through 4-2D).

Discontinuous, shallow peat layers are observed intermittently beneath the NPR at depths ranging from 2 to 15 feet bgs (Figures 4-2A, 4-2C, and 4-2D). Peat is a deposit typical in this portion of Alaska that is formed from decaying plant material, often moss and reeds. Peat forms in water-saturated or wetland conditions that would be expected in areas such as the NPR because it is on the Tanana River floodplain. Flooding obstructs oxygen from the atmosphere, slowing rates of decomposition. Peat typically forms in amorphic, colloidal masses. The peat is thinner or nonexistent in areas at NPR where the soil was likely removed to a deeper depth and replaced with stable fill for construction of facility infrastructure.

Interbedded discontinuous layers of silt, fine sandy silt, and silty fine sand are present in the upper 10 to 15 feet of the unconsolidated sequence. The colors of these deposits vary considerably from black to brown to gray, occasionally exhibiting gray and brown mottling near the water table. This soil is believed to have been deposited in sloughs and meander-cutoff channels, and as overbank flood deposits. Historical topographic maps and aerial photographs predating NPR construction show a slough and meander scar near the current truck-loading area. Silty deposits were encountered during construction of the current truck-loading rack. An additional meander scar is located near the current location of the Southwest Area Former Wash Area (SWA). The braided anastomosing nature of the Tanana River suggests that many such meander-cutoff channels and overbank deposits exist below the surface within this depth interval.

Coarser-grained alluvial sand and gravel with varying fines content are present below the surficial silt/sand deposits. The upper surface of these coarse-grained alluvial deposits is typically encountered within 8 to 12 feet of the ground surface. These deposits are predominantly sandy gravel and gravelly sand with fines, with discontinuous lenses of sand, silt, and intermittently thin lenses of peat. The gravel is fine to coarse and the sand is commonly fine- to medium-grained with a relatively low fraction of coarse sand. The pore spaces of the gravel deposits are commonly filled with finer grained soil such as sand and silt-sized particles. Color varies from brown to gray, although, as grain size increases, colors become dominated by the lithology of the individual clasts.

4.6 Fine-Grained Soil

Some fine-grained soil (greater than 50 percent by weight passing the No. 200 [75-micrometer] sieve) at the NPR exhibit clay-like properties in the field. Fine-grained soils such as silts that exhibit clay-like properties can significantly influence the hydraulic conductivity and other transport properties of soil. These soils were observed in borings O-32, O-35 and O-38.

Dry strength, dilatancy, toughness, and plasticity tests are used in the field to determine if the fine-grained soil should be classified a clay or silt. As noted in ASTM D2488, Standard Procedure of Description and Identification of Soils (Visual-Manual Procedure), the organic content of fine-grained soil may influence these field tests. The Atterberg Limit test described in ASTM D2487, Standard Practice for Classification of Soil for Engineering Purposes (USCS), is a laboratory procedure used to determine if a fine-grained soil is a silt or clay.

The fine-grained soil collected during the installation of observation well O-32, from a depth of 6.25 to 6.5 feet bgs, was subjected to the Atterberg Limit test; the sample fell below the “A Line” due to a low-plasticity index (13) and a liquid limit of 45 (Appendix 4-A). The organic content of this sample was determined to be 3.95 percent by weight, which is sufficient to classify this sample as a silt. Although a GSA was not completed for this sample, the GSA for another similar sample from MW-175-15 (2.5 to 5.4 feet bgs) is presented in Appendix 4-A. More than 50 percent of the sample passed the No. 200 sieve, indicating the grains are considered silt/clay-sized particles; however, because this fine-grained soil does not exhibit the required plastic properties of clay the soil is also classified as silt. A down-hole geophysical assessment conducted at the site in 2013 determined that clay minerals are likely nominal to nonexistent at the site and that most of the fine grained soils should be classified as silt. The down-hole geophysical assessment is described in Section 5.1.2.

4.7 Stratigraphy and Heterogeneity

Soil at NPR is heterogeneous at a variety of scales, reflecting the dynamic environment in which these soils were deposited. Soil is not mixed evenly throughout the alluvial deposits and the peat, other organics, sand particles, clay-sized particles, silt particles, and other material are all found in varying amounts at different locations. The soil varies vertically as well as horizontally across the NPR as observed in soil boring logs presented in Appendix 3-A. This heterogeneity is evident on Figure 4-3, which displays GSA breakdown of soil for boring DR-2, a tracer test area dose-response well (Section 6.1.3). The GSA that was completed on the sample collected from 21.1 feet bgs shows a mixture of both coarse-grained gravel and sand and silt-sized particles, indicating that the finer grained material is filling the pore spaces in between the coarse-grained gravel.

5. Onsite Permafrost

Permafrost is defined as subsurface soil or ground that is frozen (i.e., below 32 degrees F) for two or more consecutive years (Bates and Jackson 1997). Permafrost has been observed in the subsurface in the vicinity of NPR during the installation of monitoring wells and private wells. Its presence has also been inferred through the interpretation of geophysical data.

Alaska has two primary regions of permafrost (Williams 1970):

1. Continuous permafrost zone, where permafrost is present nearly everywhere
2. Discontinuous permafrost zone, where permafrost occurs at significant thicknesses locally, but is broken by unfrozen zones

North Pole is located within an area of Alaska characterized by discontinuous permafrost (Ferrians 1965).

Because permafrost does not transmit groundwater, it exerts strong control on groundwater flow and COC transport patterns by creating localized regions of converging and diverging horizontal and vertical flow around permafrost bodies (Carlson and Barnes 2011). Defining the extent of permafrost has been a primary goal of site characterization at NPR and is critical to the site conceptual model.

5.1 2013 Permafrost Delineation Methods

Several of the site characterization activities completed during 2013 included work to further define permafrost. These activities included monitoring well installation, geophysical surveys, and hand auger borings. Evaluation of hydrographs from the data-logging groundwater pressure transducer program (Appendix 6-B) provided an additional line of evidence for the interaction of the suprapermafrost and subpermafrost aquifers near a thawed zone. Additional work completed by the University of Alaska-Fairbanks (UAF) supported the identification of suprapermafrost and subpermafrost groundwater flow regimes, which further enhanced the understanding of how permafrost interacts with groundwater.

5.1.1 Phase 8 Well Installation

During previous phases of site characterization, several Phase 8 monitoring wells were advanced either to the top of permafrost or to a maximum depth of 150 feet bgs, whichever was encountered first. The hollow-stem auger (HSA) drilling method used for site investigations is limited to a total depth of 150 feet bgs. Well installation is described in Section 3. Phase 8 well locations are shown on Figure 3-1.

When encountered, permafrost was sampled to determine the nature of the frozen soil. The presence of permafrost in soil borings and monitoring wells has been evaluated using several types of information, including direct observation, drill action, and penetration resistance (i.e., blow counts). If frozen soils were suspected, samples were collected from undisturbed soil, then immediately retrieved for visual classification (i.e., the sampler was not floated to the next sample interval before retrieval). Drilling was ceased once frozen soil was confirmed.

The permafrost samples were classified using the ADOT&PF system, based on ASTM D4083 and Linnell and Kaplar, Description and Classification of Frozen Soils (1966) in accordance with Section 3.2.5 of the RSAP. Depth to permafrost is listed in Table 3-1 and on the individual borings logs provided in Appendix 3-A. The permafrost ranged from poorly to well-bonded. The permafrost encountered during installation of the well borings is described on the boring logs in Appendix 3-A.

If the boring was advanced to a total depth of 150 feet bgs, then permafrost was inferred to be thawed/absent at this location, unless otherwise indicated by geophysical data.

Two Phase 8 monitoring well borings encountered permafrost. These wells were located on the NPB along Transfer Road, and were MW-148-100 (permafrost at 110 feet bgs) and MW-363-15 (permafrost at 20 feet bgs). Permafrost was not encountered within 150 feet of the ground surface at wells MW-142-150, O-27-150, MW-351-150, MW-358-150, MW-359-150, MW-360-150, MW-362-150, and MW-364-150 (Figure 3-1).

5.1.2 Geophysical Surveys

An airborne electromagnetic (AEM) geophysical survey was completed in five areas near NPR between August 21 and August 24, 2013 (Appendix 5-A). The purpose of the survey was to provide supporting evidence for the delineation of the top and bottom of permafrost within unconsolidated aquifer materials of the five areas. Total coverage of the five survey blocks was approximately 227 miles (365 km). The flight path of the airborne geophysical survey was limited to undeveloped areas due to the Federal Aviation Administration rules.

AEM data were acquired using a RESOLVE electromagnetic system, supplemented by a single high-sensitivity cesium magnetometer. The electromagnetic data collected using the sensors was processed to produce maps and images that display the magnetic and conductive properties of the survey area. A GPS electronic navigation system ensured accurate positioning of the geophysical data. A detailed report summarizing the AEM survey, including a discussion on restrictions and data interference, is included in Appendix 5-A.

Ground-based frequency domain electromagnetic induction (FDEM) and electrical resistivity imaging (ERI) data were collected from October 2 to October 16, 2013 to supplement the AEM survey. A follow-up survey including a down-hole geophysical evaluation was conducted from October 30 to November 5, 2013. The ground-based FDEM survey was performed using a Geonics EM-34. The ERI equipment used during this investigation consisted of an Advanced Geosciences, Inc. (Austin, Texas), SuperSting™ R8/IP earth resistivity system with a 112 electrode switch box, electrode cables with 6-meter connector spacing, and stainless steel electrodes. Equipment for the down-hole geophysical survey included a Mount Sopris Model 5MCA-1000 MGX-II console portable logger mounted to a 4305-1000 Mini-winch with 200 meters of 1/8” single-conductor cable. Ground-based methodology is described in Appendix 5-B.

The ground-based surveys were collected in the wooded north of the truck rack and south of the north property boundary, as well as in areas where the AEM survey could not be flown due to the presence of residences (Appendix 5-A). A detailed report of the ground-based geophysical survey, including a discussion of limitations and potential data interference, is included in Appendix 5-B.

The geophysical surveys conducted for the NPR site were successful at delineating the top and bottom of permafrost in many areas of the study. The data from the four geophysical surveys (AEM, FDEM, ERI, and down-hole geophysical) were coupled with private, municipal, industrial, and monitoring well bore log information. These combined data sets confirmed areas of known permafrost, and the geophysical data provided additional insight as to the extent and structure of the permafrost in areas without bore log data.

5.1.1 Hand Auger Borings

Results from the geophysical surveys and the installation of Phase 8 monitoring wells along the property boundary (MW-149 and MW-363) indicated a potential shallow permafrost body in the northern portion of the site between the vertical profile transect (VPT) wells and Transfer Road. Fourteen hand auger borings were advanced with the goal of confirming the shallow top of permafrost in this area, as indicated by the geophysical data (Figure 5-1). Eight of the borings met refusal at depths varying from 1.7 to 5.6 feet bgs. The field staff indicated that the sound and action of the hand auger bucket scraping on the refusal surface was consistent with the presence of permafrost, based on previous experience. The remaining borings did not encounter permafrost to a depth of approximately 7 feet. Hand auger logs are included in Appendix 5-C.

5.1.2 Hydrograph Evaluation

The results of an evaluation of monitoring well hydrographs (Appendix 6-B) identified two characteristic trends that are exhibited by the vast majority of wells completed in the suprapermafrost aquifer that are monitored using data-logging groundwater pressure transducers. One trend, referred to as the “Tanana River” trend consists of groundwater levels that are closely related to seasonal discharge and stage variation of the Tanana River. The “Tanana River” trend was noted in wells south of the NPR, onsite, and offsite west of Chena Slough (locally known as the Badger Slough). Details on the evaluation are presented in Section 5 of Appendix 6-B.

Average groundwater flow directions for the period record of each pressure transducer data logger are plotted at the centroid of each group of wells used to calculate the flow directions presented on Figure 8 of Appendix 6-B. The average flow directions indicate divergence in the mid-plume area near well MW-156A-15 where the plume widens at the water table. The flow direction in the group of wells including MW 156A-15, MW-157A-15, and MW-158A-15 indicate flow toward MW-157A-15.

5.1.3 Groundwater Stable Isotope Study

UAF collected and analyzed groundwater samples from several monitoring wells to evaluate groundwater temperatures and isotopic signatures of different groundwater flow regimes related to the presence and interaction of subpermafrost and suprapermafrost aquifers. Resulting data were used to infer areas of permafrost presence and absence. The study distinguished areas in the suprapermafrost aquifer that are connected with the subpermafrost portion of the aquifer, differentiating suprapermafrost groundwater from subpermafrost groundwater, and also areas of potential mixing between the two aquifers. The mixing process is presumed to occur in or near areas lacking permafrost. (Barnes and Barnes 2013).

5.2 Permafrost Data Evaluation

The geophysical data were correlated with the monitoring well logs, available private well boring logs (see Section 2.3.3.2 of the SCR-2011 [Barr, 2012]), and land use information from historical aerial photographs to produce a three-dimensional (3-D) permafrost model from which generalized cross-sections and a depth to top of permafrost contour map were constructed. The 3-D permafrost model is a visual depiction of the outer surface of the permafrost within the aquifer system and was constructed using the geological modeling software Leapfrog (Cowan et. al. 2002).

The depth to the top of permafrost contour map is shown on Figure 5-2 and images of the 3-D permafrost model are included as Figures 5-3 and 5-4. Additional views of the permafrost model are provided in Appendix 5-D. The generalized cross-sections are presented in Appendix 5-E. Cross-section locations are indicated on Figure 5-2.

The geophysical data indicate that transitions from frozen to thawed soils can include interlayered zones of frozen and thawed soil; however, these transitions are depicted as sharp contacts on the cross-sections. Similarly, permafrost interpreted to be isolated masses is depicted with clean edges and discrete shapes, although the breaks between the masses could be more gradual and also include interlayering of frozen and thawed soil. A vertical exaggeration of 25 times has been used on the cross-sections since the horizontal distances covered are significantly greater than the vertical distances. This allows subsurface features to be shown with an adequate amount of detail; however, sloped contacts become distorted and appear to be much steeper than they actually are.

The sulfolane plume is depicted on the cross-sections; discussion of sulfolane distribution in groundwater is presented in Section 10 and transport mechanisms are discussed in Section 12.

The three-dimensional permafrost model supports the overall site characterization efforts and is a useful tool to help understand potential pathways for suprapermafrost and subpermafrost transport mechanisms. The permafrost model will be used as a guide for constructing the permafrost zones within the numerical groundwater flow and transport model.

5.3 Onsite Permafrost Occurrences

The extent of permafrost is discussed from southeast to northwest, starting at NPR and moving in the downgradient direction (northwest). For simplicity, full monitoring well names are not used, rather, the well designator number is listed (e.g., MW-154 refers to the permafrost results for MW-154B-95).

5.3.1 Process Areas, Tank Farms, and Western portion of the Site

Permafrost is generally absent under the process areas, tank farms, and western portion of the site (wastewater treatment lagoons, storage areas, and South Gravel Pit) (Figure 5-2). To date, permafrost has been encountered only at MW-154-95 (102 feet bgs) and MW-179-135 (140.5 feet bgs) as shown on Cross-Sections I-I’, II-II’, and IV-IV’ (Appendix 5-E). No additional permafrost was encountered during Phase 8 well installation in the process areas, tank farms or western portion of the site. The geophysical surveys conducted in these areas did not identify significant permafrost bodies. However, there is a lower confidence in the geophysical data from this portion of the site due to the presence of refinery infrastructure.

5.3.2 Truck Rack and Vertical Profiling Transect Areas

Permafrost appears to be discontinuous in the area from the tank farms to the VPT and parallel with the railroad tracks. The top of permafrost has been identified at some of the wells along the VPT at depths ranging from 70 feet bgs at the MW-301 nest to 130 feet bgs at the MW-303 nest; it was not encountered to a depth of 150 feet at the MW-304 and MW-306 nests. The geophysical data indicates that permafrost in this area is likely discontinuous. Four Phase 8 wells installed downgradient of the VPT (MW-358, MW-359, MW-360 and MW-362 wells nests) support discontinuous permafrost, because no permafrost was encountered within 150 feet of the ground surface (Figure 5-2). Cross-Sections I-I', II-II', and VI-VI' (Appendix 5-E) illustrate the discontinuous nature of the permafrost onsite.

5.3.3 Undeveloped Area North of Railroad Tracks

In the undeveloped wooded area between the railroad tracks and Transfer Road at the northern property boundary, the geophysical data indicates a potential shallow, significant permafrost body present from the ground surface to depths greater than 100 feet bgs. The hand augers confirmed shallow frozen soils at the eight locations (Figure 5-2). If the top of this permafrost body extends above the water table, then no suprapermafrost aquifer exists, and groundwater flow is diverted around the body.

Permafrost appears to be highly variable along Transfer Road, as shown on Figure 5-2 and Cross-section VII-VII'. It was encountered at depths of 19 and 20 feet bgs at wells MW-149 and MW-363, respectively. It was not encountered within 150 feet of the ground surface at MW-364, a well nest located 450 feet west of MW-149. At the MW-148 well nest, approximately 400 feet further west of MW-149, permafrost was encountered at a depth of 110 feet bgs at MW-148-100 and 151.5 feet bgs at adjacent well MW-148D-150. At the MW-153 nest, approximately 400 feet west of the MW-148 nest, permafrost was observed at 59 feet bgs. No permafrost was encountered within 135 feet of the ground surface at MW-318-135, a well located adjacent to the Tanana River. Cross-section VII-VII' shows the permafrost along Transfer Road as two separate masses separated between wells MW-148 and MW-364, however Figure 5-2 shows that the masses join as part of a larger offsite permafrost mass north of NPR. The base of the masses is interpreted to be highly irregular with a depth that varies between 90 and 160 feet bgs. The geophysical surveys also indicated that a portion of the soil within the permafrost may be thawed, as shown on Cross-section VII-VII'. This area along Transfer Road appears to be the southern edge of large permafrost mass that is present under much of the offsite area, as discussed in the Offsite Addendum (ARCADIS 2013m).

As shown on Cross-Sections I-I’, II-II’, and VI-VI’ (Appendix 5-E), the current sulfolane plume, based on detectable concentrations, extends to a maximum depth of approximately 90 feet bgs at the vertical profile transect (VPT [MW-302]). At this depth, it is possible that the plume encountered the edge of permafrost near the NPB. Advective groundwater flow around the permafrost mass may have caused the plume to bifurcate vertically, leading to separate suprapermafrost and subpermafrost plumes offsite, although this mechanism has not been fully identified during site characterization. This mechanism is probable; however, it was not shown on the cross-sections based on the plume data because all of the groundwater samples collected at depth in this area were nondetect for sulfolane.

5.3.4 Summary

Permafrost is largely absent under the developed portions of the site. Discontinuous permafrost is present in the northern portions of the site. Installed monitoring wells along with geophysical data suggest small discontinuous masses are present at MW-154, MW-179 and along the VPT. An irregular, shallow permafrost body is present in the wooded area south of Transfer Road. The southern edge of a large, relatively continuous permafrost mass is present near the NPB; the mass extends to the north and west under the offsite plume.

6. Onsite Hydrogeology

The site is located east and northeast of the Tanana River and southwest of the Chena River, both of which act as a groundwater source and sink to the hydrogeologic system (Figure 6-1). The hydrogeologic system for the North Pole area comprises unconsolidated alluvium and valley fill deposits in the Tanana Valley Basin, and is located between the Yukon-Tanana Uplands and the Northern Foothills of the Alaska Range (Figure 6-1). The Tanana River has a drainage area of approximately 20,000 square miles upstream of Fairbanks (Glass et al. 1996).

Key hydrogeologic concepts for the site are:

- General distribution of the conductive saturated aquifer
- General distribution of permafrost and its influence on groundwater flow
- Sources and sinks of groundwater

This section discusses these concepts. In some instances this section takes into account both onsite and offsite data to provide the most complete discussion.

6.1 Aquifer Characteristics

The alluvial aquifer material was deposited primarily by a high-energy, braided stream system (Nakanishi and Lilly 1998). Although the uppermost deposits in some areas are finer-grained, consisting of silt and fine sand, the primary aquifer material consists of gravel and sand with a fine-grained silt matrix. The aquifer material is a complex system of alternating lenses of sand, gravel, and silt (Cederstrom 1963). The lenses are thin (typically less than 20 feet thick) and individual units cannot be traced for great distances in the subsurface (Cederstrom 1963, Nakanishi and Lilly 1998). Cederstrom (1963) provides the following evaluation of the heterogeneity of the alluvial aquifer:

> *“The deposits apparently consist of every gradation and combination of fine and coarse material. No lens appears to be more than 15 or 20 feet thick, and ordinarily the lenses are thinner. Apparently no bed can be traced in the subsurface for any great distance, and marker beds of any kind are unknown. In brief, the heterogeneity of the formation is its outstanding characteristic.”*

6.1.1 Aquifer Thickness

Saturated alluvial deposits within the area defined by Geomega (2013b) range in thickness from less than 1 foot to more than 600 feet bgs, based on bore log information. In some locations where permafrost extends above the water table, saturated alluvium may not exist. Several discontinuous bodies of permafrost have been identified within the area defined by Geomega (2013b), which limits the lateral and vertical extent of alluvial materials through which groundwater flows. The permafrost bodies divide the aquifer into two or more units: suprapermafrost (above), intrapermafrost (between or within), and subpermafrost (below) aquifers. The presence of permafrost bodies can also significantly influence the groundwater flow directions.

The suprapermafrost aquifer generally consists of highly-transmissive sand and gravel under water table conditions (Cederstrom 1963, Glass et al. 1996). In the Tanana Valley, the alluvial aquifer is reportedly more than 600 feet thick (at least 616 feet near Moose Creek Dam [Glass et al. 1996]); however, the deepest known well near the site is the GVEA injection well, which is 450 feet deep and did not encounter bedrock. This well is located at the GVEA substation near the NPR south property boundary (SPB [Figure 2-3]).

Isolated, discontinuous masses of permafrost were identified during installation of several well nests north of the groundwater extraction system (Figure 5-2). A large mass of permafrost extending above the water table was delineated by recent hand augering and geophysical data (see Figure 5-2 near MW-149B-19 and the eastern end of Cross-Section VII-VII'). Permafrost was also encountered in an isolated area south of the recovery system during installation of well MW-179D-135 at a depth of approximately 140.5 feet below the water table. With the exception of this location, none of the 150-foot deep borings in the developed portion of the NPR encountered permafrost (from the SPB to areas northeast of the extraction wells [see Figure 5-2. Northwest of the extraction wells, the tops of what the geophysical data identified as apparently isolated masses of permafrost were found from depths of 70 to 130 feet bgs (see wells MW-301-70, MW-154B, MW-302-110, MW-303-130, and MW-305-110) to greater than 150 feet bgs near the recovery wells and throughout the developed area (Figure 5-2). Aside from the locations discussed above, permafrost is not known to be present beneath the rest of the NPR.

6.1.2 Hydraulic Conductivity

Hydraulic conductivity estimates from the literature and various site characterization activities are summarized below. The aquifer is demonstrated to be extremely heterogeneous based on multiple lines of evidence described below, and is presumed to have similar heterogeneity beneath the permafrost due to similarity in the depositional environment.

6.1.2.1 Literature Values and Previous Studies

Downey and Sinton (1990) estimated the hydraulic conductivity of the alluvial aquifer near the Fairbanks North Star Borough to be 1,000 feet per day (ft/day). Reported hydraulic conductivity values of the suprapermafrost aquifer in the region range from 8 to 2,400 ft/day (Nakanishi and Lilly 1998). These results are primarily from relatively shallow wells. However, the GVEA injection well, which is perforated from 412 to 432 feet bgs, had a specific capacity of approximately 80 gallons per minute (gpm) per foot of drawdown, indicating that relatively permeable materials were present at that depth. No permafrost is known to be present near the GVEA injection well; however, the air rotary drilling method used to drill the well did not allow for positive identification of frozen material. The GVEA well is at a depth similar to the depth of the subpermafrost aquifer identified in residential wells to the north and northwest.

A study in 1987 (SWI 1987) concluded that hydraulic conductivity of the sand and gravel ranged from 100 to 1,000 ft/day based on GSAs of samples collected from the NPR.

A 1995 recovery well optimization study pump test at the NPR found variability in aquifer characteristics over small distances (i.e., tens of feet) based on differences in measured drawdown in wells at similar distances from a pumped well (SWI 1995). The 1995 testing consisted of a step-drawdown test of recovery well R-34. The well was pumped at rates of 50, 100, 150, and 170 gpm for 6 hours at each rate. Quantitative analysis of the 1995 data is not possible because the rate was not constant and drawdowns were calculated only at the end of each step. The steps were not long enough to allow application of the Jacob method for distance-drawdown analysis.

Aquifer testing at the NPR in 2009 indicated a range of hydraulic conductivity values from 130 to 580 ft/day, based on an estimated saturated thickness of 590 feet and pumping of wells penetrating the upper 15 feet of the aquifer (Barr 2010b). These estimates were developed with an understanding that no permafrost was present beneath developed areas of the NPR based on the timing of NPR development and proximity of the Tanana River. As noted in Section 5, subsequent investigations have encountered permafrost at multiple monitoring well locations beneath the NPR at depths of less than 150 feet. Using the current estimated representative saturated thickness of the suprapermafrost aquifer of 150 feet (see Section 6.1.1), the 2009 aquifer testing results indicate a hydraulic conductivity range of approximately 500 to 2,300 ft/day.

Aquifer testing of the new North Pole water supply wells in July 2010 indicated a hydraulic conductivity ranging from approximately 700 to 1,100 ft/day based on pumping of wells screened from approximately 120 to 150 feet below the water table (Barr 2010c and 2010d).

6.1.2.2 Site Characterization Grain Size Analyses

GSAs were performed on 325 soil samples collected during the site characterization; 216 of these tests were performed on samples collected since completing the SCR – 2011 (Barr 2012b). Sampling methods are described in the RSAP. Both sieve and hydrometer tests were performed to determine the gradations of samples collected from depths ranging from ground surface to 152 feet bgs. Table 6-1 presents the following information:

- Blow count (the number of hammer blows required to advance the sampler 6 inches).
- Density classification based on the blow count.
- Breakdown of the sample size distribution based on the following size categories:
  - Percent gravel (grains greater than 4.75 millimeters [mm] in diameter)
  - Percent sand (grains between 4.75 and 0.075 mm in diameter)
  - Percent fines (grains less than 0.075 mm in diameter)
- Indications of representative grain sizes as defined below:
  - D_{10}, 10 percent of the sample is finer than this size (mm).
  - D_{20}, 20 percent of the sample is finer than this size (mm).
  - D_{50}, 50 percent of the sample is finer than this size (mm).
  - D_{60}, 60 percent of the sample is finer than this size (mm).
- Uniformity coefficient (Cu), an indication of sample heterogeneity, defined as D_{60}/D_{10}.
- Soil type based on method ASTM D2487.
- Estimates of hydraulic conductivity of the sample based on up to three different methods:
  - Hazen's method (Hazen 1911, Fetter 1988), which is applicable to soil with a Cu of less than 5 and D_{10} ranging from 0.1 to 3 mm. Hazen's method was applicable to 18 samples.

- Prugh's method (as presented on Figures 3.7a, 3.7b, and 3.7c of Powers et al. 2007), which depends on sample density, D_{50}, and Cu. Prugh's method was applicable to 41 samples.

- The Barr (2001) method, which uses all of the gradation information and is applicable to all of the samples.

Ternary plots show the percentage of gravel, sand, and fines (silt) in each sample based on the depth of the sample interval (Figure 6-2). A sample consisting entirely of sand would plot at the top vertex, a sample consisting entirely of gravel would plot at the right vertex, and a sample consisting entirely of silt would plot at the left vertex. The individual plots correspond to the depth ranges used to evaluate groundwater results, assuming a nominal water table depth of approximately 10 feet bgs. Soil samples were collected at depths less than 10 feet bgs. Different symbols are used for samples collected onsite versus offsite. The samples from 20 feet bgs or less have higher silt contents (up to almost 90 percent) than samples from greater depths, where silt content ranges up to 15 percent. The spread of the samples on all of the grain size subplots demonstrates the extreme heterogeneity of the aquifer materials.

Hydraulic conductivity values were estimated from the sieve samples in Table 6-1 with Cu values less than 5 using Hazen's method with a value of the C coefficient estimated based on the sample description (see Equation 1 below, from Fetter [1988], Equation 4-10, p. 81).

$$K = C(D_{10})^2 \qquad \text{Equation 1}$$

Where:

K = hydraulic conductivity in centimeters per second (cm/s)

D_{10} = effective grain size in centimeters (10 percent of the sample is finer than this size)

C = coefficient that accounts for grain size and sample sorting at typical shallow groundwater temperatures, as listed below:

Very fine sand, poorly sorted	40 to 80
Fine sand with appreciable fines	40 to 80
Medium sand, well sorted	80 to 120
Coarse sand, poorly sorted	80 to 120
Coarse sand, well sorted, clean	120 to 150

Hydraulic conductivity was also estimated using the Prugh method (Powers et al. 2007). This involved manually looking up values from the appropriate chart and plot based on relative density, Cu, and D_{50} for each sample.

The Barr method (Barr 2001) relates the surface area of soil particles as determined from GSA data to the coefficient of permeability based on the theory that pressure loss is proportional to viscous resistance and viscous resistance is caused by drag at the particle surfaces.

Hydraulic conductivity values for Hazen's (1911) method versus Barr's (2001) and Prugh's (Powers et al. 2007) methods versus Barr's (2001) method are plotted on Figure 6-3. As shown, the Prugh (Powers et al. 2007) method gives larger values than the Barr (2001) method. Hydraulic conductivity of the samples based on Barr's (2001) method is plotted versus the depth of the midpoint of the sample interval on Figure 6-4. The symbol type on this plot indicates whether the samples are from onsite or offsite, and exhibit similar distributions with depth.

As shown, hydraulic conductivity estimated based on GSAs from samples of aquifer material collected during well installation have a range of more than five orders of magnitude, from 0.1 to 17,000 ft/day (Table 6-2). Hydraulic conductivity values estimated from individual soil samples from a heterogeneous aquifer can show great variability due to the small size of a given sample; the samples are essentially point estimates. A given sample may not be representative of a significant volume of the aquifer. Figure 6-5 shows a histogram of the log (base 10) of the hydraulic conductivity values based on Barr (2001). This histogram approximates a log-normal distribution, which would be expected for hydraulic conductivity that typically exhibits a log-normal distribution in granular porous media (Freeze and Cherry 1979). Results for nearly 70 percent of the samples fall between 10 and 100 ft/day, and approximately 99 percent are less than 1,000 ft/day (Table 6-2).

The lowest hydraulic conductivity values were reported for samples collected from the shallow silty layers located near the water table (see Table 6-1 and Figure 6-4). Aside from the shallow results, these hydraulic conductivity data do not show an apparent trend with depth (Figure 6-4).

The Cu of a soil sample is defined as the D_{60} value (60 percent of the grains in the sample have a smaller diameter than this value) divided by the D_{10} value. The sample is more uniform in particle size distribution if the Cu number is smaller. A Cu value of 5 is considered the practical upper limit for typical analyses such as filter pack and screen design (Driscoll 1986), although the charts for soil with intermediate density based on the

Prugh (Powers et al. 2007) method apply to soil with Cu values as high as 10 (Powers et al. 2007).

Thirty-nine of the 326 samples listed in Table 6-1 have Cu values of less than 5. The Cu values were sorted from smallest to largest and plotted on Figure 6-6 along with the corresponding D_{10} and D_{60} values. Based on this plot, the extremely high Cu values are from finer-grained samples, and the vast majority of the high Cu values stem primarily from samples with high D_{60} values. The high amount of nonuniformity for the majority of the samples can be interpreted as the finer fraction of the formation filling the interstices between the coarser grains. This finer-grained matrix creates a material with a lower specific yield, higher specific retention, lower hydraulic conductivity, and lower mobile porosity than more uniform materials. Such nonuniform deposits are formed in fluvial settings during or shortly after deposition through the process of vertical winnowing (the loss of fine particles to the subsurface during transport [Parker and Klingeman 1982]).

6.1.2.3 2011 Recovery Well Pumping Test

An aquifer test was performed on the NPR groundwater recovery system in August 2011 and is described in Sections 2.3.4.3 and 3.5.1.1 of the SCR-2011 (Barr 2012). The groundwater recovery system was comprised of five wells at that time (R-21, R-35R, R-39, R-40, and R-42). The aquifer testing was completed by turning off all five extraction wells within approximately 4 minutes of each other on August 30, 2011, then turning them back on approximately 24 hours later. The combined recovery and pumping phases were analyzed to evaluate aquifer parameters and system performance.

No indication of a recharge boundary caused by infiltration from the Tanana River or North Gravel Pit (NGP) was noted during the test, and a barrier boundary was not apparent in the aquifer test data. A response indicative of a barrier would be expected if a large mass of shallow permafrost is located close to the extraction system.

Analyses at multiple well clusters were performed using the Moench (1997) solution and are summarized in Table 6-3. Copies of the AQTESOLV analyses are presented in Appendix T of the SCR-2011 (Barr 2012). The storage coefficient typically went to its lower bound during the parameter estimation process. Variation of the storage coefficient parameter did not appreciably affect the data fitting process if the storage coefficient was set at any value in the allowed range of 1.5×10^{-5} to 1.5×10^{-3}. Some of the analyses produced storage coefficients at the upper bound allowed in the analyses. The elastic response to the testing is apparently so rapid and so small in magnitude that it could not be measured.

The specific yield values are relatively low, which reflects the heterogeneity of the aquifer system (Moench 1994) and the influence of silty and sandy material within the gravel deposits at the water table, which retain a significant fraction of water (e.g. Pool and Eychaner 1995).

The estimated hydraulic conductivity near the recovery well system was found to range from 1,000 to 1,500 ft/day. This estimate was based on an assumed saturated thickness of the suprapermafrost aquifer of 150 feet.

6.1.2.4 Single-Well Pumping Test Results

Transmissivity and hydraulic conductivity values were measured during several single-well pumping tests conducted in 2011 (Table 6-4). The AQTESOLV well test analysis summaries are included in Appendix H of the SCR – 2011 (Barr 2012). Hydraulic conductivity values were calculated from the transmissivity and well screen length for each well and varied between 50 and 10,700 ft/day (Table 6-5).

The transmissivity and hydraulic conductivity values measured during these short-duration single-well tests demonstrate that significant heterogeneity exists within the geologic formation around the test wells, as indicated by the nearly three order of magnitude range in values estimated.

6.1.2.5 2012 Tracer Test

A tracer test was performed at the site in March 2012 to evaluate the feasibility of in-situ remediation technologies that rely on injection of remediation reagents below the water table (ARCADIS 2013a). As part of the tracer test, step injection testing was performed at the injection well to evaluate a range of possible tracer injection rates and assess hydraulic properties of the water-bearing zone.

The modified Theis Solution for unconfined aquifers was used to analyze the injection test data based on observed water-level responses at the injection and observation wells. These data were used to estimate transmissivity and hydraulic conductivity of the water-bearing zone, using a saturated thickness equal to the well screen interval. Hydraulic conductivity values measured during the step injection test varied between 140 and 1,100 ft/day, and had a geometric mean of 400 ft/day.

6.1.2.6 2013 Recovery Well Pumping Tests

In late May/early June 2013, a pumping test was conducted for the expanded recovery system. As of 2012, the groundwater recovery system at NPR consisted of five wells (R-21, R-35R, R-39, R-40, and R-42). Four new recovery wells were added to the system in 2013 (R-43, R-44, R-45, and R-46) and two of the existing wells (R-39 and R-40) were removed from service upon startup of R-45 and R-46 (which serve as replacement wells for R-39 and R-40) (Figure 2-3).

The startup testing for the 2013 expanded recovery system consisted of a two day shutdown period, four single-well tests (one well pumping at a time with multiple observation wells), and monitoring of the expanded system restart for three days (Barr 2013b). This testing provided additional aquifer parameter estimates and field measurements of groundwater elevations and drawdown caused by the recovery system.

Well interference was noted in many of the observation wells due to cycling of NPR’s production wells NPR-1 and NPR-2 (Figure 2-3). Data logger monitoring frequency was increased to one reading every 5 seconds at MW-109. A data logger was temporarily installed in MW-116 and water levels were recorded every 2 seconds for approximately 24 hours to provide better resolution of the aquifer response to pumping cycles near the production wells. These data were analyzed using the methods discussed in Section 3.2 of Evaluation of Recovery Well Replacement, Start-up Aquifer Testing for Recovery System Hydraulic Capture Performance Monitoring (Barr 2013b).

Aquifer properties (transmissivity, storage coefficient, specific yield, and vertical anisotropy [ratio of vertical to horizontal hydraulic conductivity]) were determined using composite analyses for wells screened at differing depths, as recommended by Moench (1994) (Table 6-6). Hydraulic conductivity values for the analyses ranged from 200 to 1,600 ft/day, using an assumed aquifer thickness of 150 feet. Storage coefficient values ranged from 0.0011 to 0.088, which translates to a range of specific storage values of 2.4×10^{-5} m^{-1} to 1.9×10^{-3} m^{-1}. The anisotropy in vertical to horizontal hydraulic conductivity in the solutions ranges from 0.0033 to 0.12.

6.1.2.7 2013 Tracer Tests

Two additional tracer tests were performed in fall 2013 to validate the dual-porosity conceptual model for COC transport and to further characterize site hydrogeologic properties (Appendix 6-A). One tracer test was performed at an area of the site containing fine-grained soil, designated as Tracer Test Area 1 (TTA-1). The second tracer test was performed at an area of the site containing coarse-grained soil, designated as Tracer Test Area 2 (TTA-2). As part of the tracer testing procedures, hydraulic conductivity of the soil immediately surrounding the injection and monitoring wells was measured by performing a series of single-well short-duration pumping tests. Hydraulic conductivity values for the fine-grained soil in TTA-1 were found to vary between approximately 19 and 54 ft/day and had a geometric mean of 33 ft/day. Hydraulic conductivity values for the coarse-grained soil in TTA-2 were found to vary between approximately 28 and 455 ft/day and had a geometric mean of 100 ft/day.

6.1.2.8 Hydraulic Conductivity Estimates and Applications

The hydraulic conductivity of saturated soil within the suprapermafrost aquifer has been estimated using numerous techniques presented previously in this section. As would be expected of an aquifer formed primarily in a braided stream environment of deposition, and as documented in the literature regarding the region cited above, the hydraulic conductivity estimates varied over several orders of magnitude in both the horizontal and vertical directions, exhibiting an extremely high degree of heterogeneity. Site-specific hydraulic conductivity estimates range from 0.1 to 17,000 ft/day. A summary of the estimates is below.

- Estimates based on GSAs ranged from 0.1 to 17,000 ft/day. Three of the 324 samples tested had hydraulic conductivity values that exceeded 1,500 ft/day.
- Estimates based on 2009 testing of the recovery well system ranged from 500 to 2,300 ft/day with a geometric mean of 1,100 ft/day.
- Estimates based on the single-well pumping tests ranged from 50 to 10,700 ft/day, with a geometric mean of 270 ft/day.
- Estimates based on 2010 aquifer testing of the new City of North Pole water supply wells ranged from 700 to 1,100 ft/day, with a geometric mean of 880 ft/day.
- Estimates based on 2011 testing of the recovery well system ranged from 1,000 to 1,500 ft/day, with a geometric mean of 1,300 ft/day.
- Estimates based on single-well pumping tests performed during the 2012 tracer test ranged from 140 to 1,100 ft/day, with a geometric mean of 400 ft/day.
- Estimates based on 2013 testing of the recovery well system ranged from 200 to 1,600 ft/day, with a geometric mean of 100 ft/day.
- Estimates based on single-well pumping tests performed during the 2013 tracer tests ranged from 19 to 54 ft/day for finer-grained soil with a geometric mean of 33 ft/day, and 28 to 455 ft/day for coarser-grained soil with a geometric mean of 100 ft/day.

The hydraulic conductivity values listed above were estimated using methods that sample the aquifer at various scales, with long-term pumping tests covering the largest scale (i.e., tens to hundreds of feet), single-well pumping tests covering an intermediate scale (i.e., 5 to 10 feet), and GSAs covering the smallest scale (i.e., pore scale). Results of the various hydraulic conductivity tests demonstrate a more than five order magnitude range of hydraulic conductivity at the site and underscore the extreme heterogeneity of site soil.

Understanding the variability of hydraulic conductivity in the subsurface is critical in the evaluation of many aspects of the site characterization and potential remedial alternatives because the degree and pattern of heterogeneity at a site dictates the feasibility and effectiveness of remedial technologies. To the extent possible, site-specific data have been used in all aspects of the site characterization as summarized below:

- *Mass flux estimates at the VPT*. Data from aquifer tests within and near the VPT were used in this estimate (ARCADIS 2013l).

- *Recovery system capture zone evaluation using the groundwater flow model*. Aquifer testing results and geologic and water-level information available as of the end of 2012 were used to calibrate the groundwater flow model and to evaluate the extent of capture of the groundwater recovery system (Geomega 2013b).

- *Density of available data for the groundwater flow model*, which covers approximately 150 square miles, varies widely with location due to the nature of the investigation and locations of wells installed. Horizontal hydraulic conductivity values in the groundwater flow model range from 85 to 1,530 ft/day (Geomega 2013b [Table 5]). Geomega (2013b [Figures 5-3b 1 to 37) presents the spatial distribution of hydraulic conductivities in the groundwater flow model. The lowest values in the model represent the silty units found at or near the water table.

- *Recovery system capture zone evaluation based on field measurements*. The lateral extent of the capture zone was determined based on potentiometric surface maps of groundwater levels measured in monitoring wells. Vertical anisotropy (the ratio of vertical hydraulic conductivity to radial hydraulic conductivity) is used to delineate the vertical extent of the capture zone in cross-section view (Barr 2013b [Section 4.3.4]).

- *Light Nonaqueous Phase Liquid (LNAPL) mobility*. Modifications to the relative permeability of the aquifer materials with respect to LNAPL and LNAPL transmissivity were estimated using site-specific testing (see Section 7).

6.1.3 2013 Tracer Tests

Two tracer tests were performed at the site in fall 2013 to validate the dual-porosity conceptual model for COC transport in groundwater and its potential influence on plume transport, further characterize hydrogeologic conditions at the site, estimate hydraulic conductivity and hydraulic gradients in the tracer test areas, and to support risk assessments and remedial evaluations. The tracer tests were performed in accordance with the Onsite SCWP (ARCADIS 2013e) at two different areas of the site. The first tracer test was performed in an area with relatively fine-grained soil (TTA-1). The second tracer test was performed in an area with relatively coarse-grained soil (TTA-2). Appendix 6-A describes the activities conducted during both tracer tests, including well installation, single-well pumping test results, baseline sampling results, step injection testing, tracer injection activities, and groundwater monitoring.

The purpose of the tracer tests was to collect data necessary to further validate the dual-porosity conceptual model for COC transport in groundwater and to more thoroughly characterize the hydrogeologic and fate and transport properties of saturated soil beneath the site.

Specific objectives of the tracer tests included:

- Provide additional data to augment the data from the 2012 tracer testing (ARCADIS 2013a). Results of the 2012 tracer testing showed characteristics that suggested rapid transport and tailing of a tracer breakthrough curves consistent with dual porosity transport.
- Validate the dual-porosity fate and transport conceptual model and its potential influence on plume transport.
- Obtain quantitative information to estimate mobile porosity, total porosity, and mass transfer coefficient model parameters.
- Through injection step testing in each area, determine well-specific injection flow rates to be used during tracer testing.
- Estimate hydraulic conductivity and hydraulic gradients in both areas.

Information collected during the tracer tests provides insights regarding the fate and transport behavior of chemicals in groundwater at the site. The conclusions presented below are based on results of the tracer tests:

- Dual-porosity transport of tracers in site groundwater was demonstrated by comparing tracer breakthrough curves at the two areas. In TTA-1, the tracer breakthrough curves show long, gradual increases in concentration through time that indicate significant storage of tracers in the fine-grained soil. In fact, tracer concentrations in almost all TTA-1 monitoring wells were continuing to increase at the end of the approximate 2-

month monitoring period. The fine-grained soil in TTA-1 represents one porosity regime in which tracers are stored for relatively long periods of time.

In TTA-2, the tracer breakthrough curves show relatively rapid increases and decreases in concentration through time that indicate relatively rapid transport and much less storage of tracers in the coarse-grained soil. In fact, tracer concentrations in almost all TTA-2 monitoring wells decreased to background conditions within approximately 1 to 2 weeks after tracer injection. The coarse-grained soil in TTA-2 represents a second porosity regime in which significant advective transport occurs. Mass transfer of tracers between the mobile and immobile porosity regimes due to advection and diffusion provides a primary control on the timing of tracer transport, chemical plume evolution, plume longevity, plume stability, and ultimately, the feasibility of remediation technologies. Furthermore, there is some evidence of pore-scale dual-porosity transport associated with presence of immobile porosity (i.e., dead-end pore spaces) within the coarse-grained soil, which is demonstrated by tailing evident in some of the TTA-2 breakthrough curves.

- Data collected during the tracer tests were used to estimate dual-porosity transport parameters for each area, including mobile porosity, total porosity, and mass transfer coefficients. For TTA-1, total porosity was estimated between approximately 29 and 36 percent based on laboratory analytical results of three undisturbed soil core samples, and mobile porosity was estimated between approximately 4 and 13 percent. The median mobile porosity estimated at TTA-1 was approximately 9 percent. For TTA-2, total porosity measurements will be reported to ADEC, and mobile porosity was estimated between approximately 2 and 21 percent. However, this range is considered to be biased high due to an assumption of strictly two-dimensional tracer transport; a more accurate estimate of mobile porosity likely ranges between 9 and 11 percent, with a median value of 10 percent. The mass transfer coefficient at TTA-2 was estimated between approximately 4×10^{-2} and 2×10^{-7} per day based on quantitative analysis of breakthrough curves using the dual-porosity fate and transport model curve-fitting procedure. The absolute values of these parameters should be used with caution due to uncertainties in the assumptions of the data analysis methods.

- Results of the quantitative breakthrough curve fitting procedure indicate that there is a statistically significant basis for accepting the dual-porosity fate and transport model and rejecting the advection-dispersion fate and transport model at two out of three drift-phase monitoring well locations analyzed. At the third location, there is no statistically significant basis for rejecting either model.

- Hydraulic conductivity was measured at seven monitoring wells in TTA-1 and found to vary between approximately 19 and 54 ft/day, indicating the presence of hydraulic heterogeneity within the fine-grained soil in TTA-1. Hydraulic conductivity measurements made using single-well, short-duration pumping tests in this manner result in accurate estimates of the hydraulic conductivity of saturated soil within approximately 5 feet of the well screen, providing a high level of confidence in the results. The hydraulic conductivity measurements at the TTA-1 groundwater monitoring network exhibited a spatial trend that is consistent with an alluvial depositional environment characterized by meandering stream channels. In this environment, high hydraulic conductivity units are deposited within lower hydraulic conductivity units. This depositional heterogeneity may result in apparent trending in hydraulic conductivity. The TTA-1 hydraulic conductivity measurements result in a horizontal hydraulic conductivity ellipse with a 4:1 ratio that is oriented toward the northwest-southeast.

- Hydraulic conductivity was measured at four monitoring wells in TTA-2 and found to vary between approximately 28 and 455 ft/day, indicating the presence of significant geologic heterogeneity within the coarse-grained soil in TTA-2. Hydraulic conductivity measurements made using single-well short-duration pumping tests in this manner result in accurate estimates of the hydraulic conductivity of saturated soil within approximately 5 feet of the well screen, providing a high level of confidence in the results. Similar to TTA-1, the hydraulic conductivity measurements at the TTA-2 groundwater monitoring network also appeared to exhibit a spatial trend that is consistent with an alluvial depositional environment characterized by meandering stream channels. However, the horizontal hydraulic conductivity ellipse at TTA-2 could not be resolved to the same degree of certainty as TTA-1 because fewer measurements were made at TTA-2. Nonetheless, tracer test results suggest that the hydraulic conductivity ellipse at TTA-2 may have a 3.4:1 ratio and be oriented toward the north-northwest to south-southeast.

6.1.4 Sources and Sinks for Groundwater

Sources for groundwater in the Tanana Valley aquifer system include rivers, regional underflow through unconsolidated alluvium, and precipitation. Sinks for the groundwater include rivers, underflow through unconsolidated alluvium, evapotranspiration, and artificial discharge via wells. The recharge from rivers, precipitation, and regional groundwater underflow comprise the major inflows to the groundwater system, while evapotranspiration, rivers, regional groundwater underflow, and well pumping comprise the major outflows.

Precipitation on portions of the Tanana basin at elevations less than 1,000 feet mean sea level (MSL) is estimated to be 12.5 inches per year (Anderson 1970). Actual evapotranspiration over the same area is estimated to be 9.8 inches per year (Anderson 1970). The balance of the precipitation is believed to recharge the shallow water table, and then discharge to rivers within the basin. This portion of the basin (at elevations less than

1,000 feet MSL) has an area of approximately 12,000 square miles. Therefore, the annual average rate of precipitation infiltration is estimated to be 2.7 inches per year. This cycling of recharge to the area rivers occurs above the permafrost. Lakes and swamps in the basin act as flow-through features for groundwater, with some loss to evaporation when they are not frozen.

The major surface water features in the area consist of the Tanana River, Chena River, Badger Slough, and a drainage ditch known as Ditch C. Ditch C is connected to Badger Slough. Shallow groundwater discharges to Ditch C, particularly north of Richardson Highway. The Badger Slough is a tributary to the Chena River, which is a tributary to the Tanana River. Discharge and stage data for the Chena and Tanana rivers were obtained from the U.S. Geological Survey (USGS) water data web site to construct the groundwater model (Geomega 2013b), values are summarized in the table below.

River	Mean Annual Discharge (cfs)
Tanana River	20,546
Chena River	814 to approximately 1,300 cfs (increasing in the downstream direction)

Note:
cfs = cubic feet per second

A key characteristic of rivers in the region is the large seasonal variations in flow and stage due primarily to spring snow melt. For example, the Tanana and Chena rivers have spring flows that can be four to six times the October flows, with annual changes in stage of 6 to 10 feet (USGS 2011). When the discharge is high, water from the Tanana River recharges the aquifer and discharges to the Chena River and associated tributaries (Nelson 1978). During seasonal high flows, the Chena River also locally recharges the aquifer. Both the Tanana and Chena rivers gain discharge from the alluvial aquifer when the discharge rates are lower. This seasonal fluctuation influences groundwater flow, as discussed in Section 10.5.

Two flood-control structures have been built in the study area: the Moose Creek Dam on the Chena River approximately 2 miles upstream from the NPR, and a levee along the northern side of the Tanana River extending from the Moose Creek Dam to Fairbanks (Geomega 2013b [Figure 1-1]). The floodgates on Moose Creek Dam are only used during high flow to ensure that the Chena River flow through Fairbanks is controlled at a maximum of 12,000 cfs. If the Chena River flow is sufficiently high at the dam, water will flow to the Tanana River along a constructed sill. Between 1979 and summer 1993, the dam was only used during eight periods of high flow and the sill was only used once (Glass et al. 1996).

The flood control structures have not been demonstrated to have any effect on groundwater flow at the site.

Three basic types of discharge occur via wells in the area:

1. FHRA production and remedial wells
2. Municipal supply and/or industrial wells
3. Domestic wells

6.1.5 Gravel Pits

The North Gravel Pit (NGP), which was excavated below the water table on the western portion of the site, is believed to be a surface expression of the water table. An investigation of the NGP groundwater/surface water interaction is discussed in Section 14.3. The water level in the South Gravel Pit is several feet above the water table in the adjacent aquifer, presumably due to resistance to flow from the pit caused by fine-grained sediments that have been deposited in that pit over time.

6.1.6 Water Table Configuration

The water table at the NPR and offsite is shallow, typically occurring within 5 to 10 feet of the ground surface. The water table typically occurs within the alluvial sand and gravel; however, during seasonal high water conditions the water table may occur within the finer-grained soils above the alluvial sands and gravels.

Onsite, the elevation of the water table ranges from approximately 480 to 490 feet MSL, decreasing from southeast to northwest. Offsite, the water table elevation varies from approximately 460 to 485 feet MSL, and decreases in elevation to the northwest, mimicking the gradually decreasing elevation of the ground surface (ARACADIS 2013n). The elevation of the potentiometric surface associated with deeper portions of the aquifer, as indicated by wells completed in the interval from 15 to 55 feet below the water table is similar to the water table (ARCDIS 2013n).

The water table fluctuates in elevation seasonally. Historical data indicate that it may fluctuate up to 9 feet at some locations (SWI 2002). This is consistent with values reported by Glass et al. (1996). Hydrographs for well MW-138 (Barr 2012 [Figure 48]) and R-20 (Barr 2012 [Figure 49]) show that the water table has fluctuated up to 4 feet since 2007. The groundwater elevation typically decreases during winter and early spring, with the lowest elevations occurring from late March through May. Groundwater elevations appear to increase during June and July, peaking during late July or August. Groundwater elevations then typically decrease through the remainder of the year. These variations are similar to those observed at three shallow observation wells maintained by the USGS as part of its Active Groundwater Level Network as shown the SCR-2011 (Appendix W, Barr 2012). Water levels in these wells have been observed to fluctuate from 3 to more than 4 feet in the period of record (2001 to 2011). Only one of these wells was monitored by the USGS in 2012 and 2013.

6.1.7 Horizontal Hydraulic Gradient – Magnitude and Flow Direction

Beyond the zones of influence of the NPR groundwater recovery system, groundwater flow directions are controlled by recharge from the Tanana River to the aquifer and discharge from the aquifer to the Chena River, as described by Glass et al. (1996). Variations in river stage through time are believed to be the primary cause of variations in groundwater flow direction through the aquifer between the rivers (Appendix 6-C, Lilly et al. 1996). The groundwater flow direction varies up to 19 degrees from a north-northwesterly direction to a few degrees east of north based on data from USGS water table wells (Appendix 6-C). The flow direction trends to the north-northwest in spring and more northerly in the summer and fall (Appendix 6-B).

Data from the three USGS wells located near the Tanana River, southeast of NPR, indicate a slope on the water table ranging from 4.5 to 6.5 feet per mile. Data from the USGS Active Groundwater Level Network wells were included in the SCR-2012 (Appendix 6-C).

Groundwater elevations are currently measured using data loggers suspended from the tops of the casings in monitoring wells at the NPR. Details on the data logger program results are presented in the SCR-2011 (Appendix 6-B). Horizontal hydraulic gradients (magnitude and direction of flow) were estimated using groups of three wells completed at similar depths in the suprapermafrost aquifer.

The direction of groundwater flow determined between 49 triangular groups of wells screened at or near the water table and monitored with data loggers is shown on Figure 6-7. Variations in groundwater flow directions were calculated throughout the period of record and were plotted in units of degrees counterclockwise from due east (Attachment A of Appendix 6-B). The groundwater flow direction in the suprapermafrost aquifer was found to have the greatest easterly component during summer months when the Tanana River stage is higher, and was found to have a more westerly orientation in other seasons when the Tanana River stage is lower. These findings are consistent with data collected at the USGS wells discussed above.

The flow direction data are also summarized using rose diagrams (Attachment B of Appendix 6-B). The flow directions are presented with the average value for the period of record plotted at the centroid of each group of wells (Figure 6-8). This figure also includes the extent of the sulfolane plume and a color flood and contours of the depth to permafrost below ground surface. Significant features in the permafrost distribution include the overall lack of detected permafrost beneath the NPR and the inferred thawed zone beneath Badger Slough where permafrost was not encountered to depths of 150 feet bgs and where geophysical and stable isotope data indicate a connection between the subpermafrost and suprapermafrost aquifers. The relationship between the average flow direction and the shape of the plume is clear when average flow directions are presented with the sulfolane isopleths (Figure 6-9).

The average flow directions indicate divergence in the mid-plume area near well MW-156A-15 at the water table where the plume widens. The flow direction measured in the group of wells comprising MW-156A-15, MW-157A-15, and MW-158A-15 indicate flow toward MW-157A-15, which may be caused by taliks or undulations in the permafrost surface in that area (Section 4.2 of the Offsite Addendum; ARCADIS 2013m).

The magnitude of the hydraulic gradients was also calculated between the groups of wells shown on Figure 6-7 (Attachment C of Appendix 6-B). The gradients are primarily the greatest in the summer when the Tanana River stage is high and recharge from the river to the alluvial aquifer is greatest. Excluding outliers, the expected values of horizontal hydraulic gradients range from approximately 0.0004 to 0.002.

6.1.8 Vertical Hydraulic Gradients

Vertical gradients are calculated within well nests for wells that are equipped with water level data loggers and based on manual measurements. Locations of the well nests with data loggers are shown on Figure 6-10. Calculated vertical gradients based on the data logger program and on manual measurements are evaluated below.

6.1.8.1 Data Logger Program

The vertical hydraulic gradients were calculated as the water elevation measured in the well with the shallower screen minus the water elevation measured in the well with the deeper screen, divided by the vertical separation between the screen midpoints. Based on this definition, negative vertical hydraulic gradients indicate an increasing hydraulic head with depth in the aquifer and suggest movement of water from deeper in the formation toward the shallower portion of the formation (upward gradient). Conversely, positive vertical hydraulic gradients indicate a decreasing hydraulic head with depth in the aquifer and suggest movement of water from shallower in the formation toward the deeper portion of the formation (downward gradient).

All combinations of nested wells with data loggers were considered in this analysis. Details on the calculation of errors associated with these gradient estimates are presented in the SCR – 2011 (Appendix G, Barr 2012). The complete set of plots for each well nest with data loggers is shown in the SCR – 2011(Attachment D of Appendix G, Barr 2012). Due to the small head differences that typically occur in nested wells and relatively large errors introduced through using the data loggers and by frost jacking of the well casings, the direction of the gradient is within the margin of error in many cases.

Table 6-7 summarizes nested wells monitored with data loggers in which the vertical gradient is quantified during at least some portion of the period of record. For comparison, the results of manual measurements of the vertical gradient described in Section 6.1.8.2 are compared with the data logger results. The manual and data logger evaluations agree in terms of the sense of flow (whether it has an upward component or a downward component based on the vertical head differences).

6.1.8.2 Manual Measurements

Manual water level measurements collected concurrently with surveys of the elevations of tops of well casings have been obtained at selected nested wells both offsite (Tables 6-8a and 6-8b and Figure 6-10) and onsite (Tables 6-9a and 6-9b and Figure 6-11) since March 2013. This manual measurement program was implemented to obtain information on frost jacking of the well casings and to provide accurate hydraulic head difference calculations for a small number of well nests while the data logger standard operating procedure (SOP) was under development (SWI 2013, Barr 2013a). The random errors associated with each hydraulic head calculation are the quadratic sum of the water-level measurement error (±0.01 foot) and the top of casing survey error (±0.01 foot) for a total error of ±0.014 foot. The error associated with a calculated hydraulic head difference is the quadratic sum of the random errors associated with the two hydraulic head values, or 0.02 foot.

Significant findings from the offsite vertical gradient observations based on monthly manual measurements are summarized below:

- The vertical head difference between wells MW-148A-15 and MW-148B-30 was downward or within the margin of error on the estimate. The vertical head difference between wells MW 148B-30 and MW-148C-55 was upward or within the estimated margin of error. This is consistent with the concentration trends, which are highest in MW 148B-30. These head and concentration trends likely reflect the preferential flow path of groundwater to a more conductive zone focusing flow at this location.

- The vertical head difference between wells MW-160AR-15 and MW-160B-90 was upward, except for the May measurement. This is consistent with topography on top of permafrost, which is higher at this location than to the south. Such a sloping surface in the direction of groundwater flow would tend to create an upward gradient. The vertical head difference between MW-160AR-15 and MW-160B-90 is not consistent with the higher sulfolane concentrations measured in MW-160B-90. The lower sulfolane concentrations in MW-160AR-15 likely reflect degradation of sulfolane in the gravel pit south of that well nest and recharge to the shallow portion of the suprapermafrost aquifer.

- The vertical head difference between wells MW-162A-15 and MW-162B-65 were downward when the well could be measured. This is consistent with the relatively higher sulfolane concentrations measured in MW-162B-65.

- The vertical head difference in the MW-318 well nest (the well nest closest to the Tanana River) was oriented downward at all times when the required measurements could be made. This was likely caused by the Tanana River recharging the shallow aquifer. Note that the isotopic signature at this well nest was interpreted to represent a mixture of water types (i.e., was found to be dissimilar from the Tanana River signature) (Barnes and Barnes 2013).

Significant findings from the onsite vertical gradient observations based on monthly manual measurements are as follows:

- Head differences in the MW-186 well nest are consistently upward. This is primarily caused by the location of this well nest in the recovery well network. This is further discussed below.

- Vertical head differences in the MW-304 well nest indicate upward flow between MW-304-15 and MW-304-80. This is consistent with the sulfolane concentrations in these wells. Head differences between MW-304-80 and MW-304-125 and between MW 304-125 and MW-304-150 are within the margin of error on the estimate.

- Vertical head differences in the MW-306 nest indicate a downward hydraulic gradient or head differences within the margin of error of the calculation. This well nest is located east of the sulfolane plume; therefore, sulfolane concentrations are not present and thus cannot be compared.

In addition to the monthly measurements, manual measurements of water levels and top of well casing surveys were made during the 2013 aquifer testing (Barr 2013b). Hydraulic head differences calculated with the recovery system off (June 3, 2013) and after the recovery system had been pumping for 3 days (June 6, 2013) are presented in Table 6-10.

The changes in head difference between these two dates are due primarily to pumping of the recovery system. Significant findings in these data are summarized below:

- Head differences in the MW-174 well nest are oriented downward or within the margin of error of the calculation. The downward head difference between wells MW 174-15 and MW-174A-50 without the recovery system pumping (on June 3, 2013) was reduced to less than the margin of error on the calculation by June 6, 2013, likely due to operation of the recovery system.

- Vertical head differences in the MW-186 nest indicated a convergence of flow toward the MW 186E-75 screen from above and below when the recovery system was not pumping, but a continuous upward gradient throughout the well nest when the recovery system was pumping. This suggests that preferential flow might occur at the elevation of the MW 186E-75 screen, if the recovery well system did not influence flow.

- As noted above, vertical head differences in the MW-306 nest indicate a downward hydraulic gradient with and without the recovery system pumping. No permafrost was encountered in this well nest to a depth of 150 feet bgs although shallow permafrost was observed directly downgradient. This well nest is located east of the sulfolane plume.

- A relatively large, upward head difference of -0.32 ft was measured between MW 310-15 and MW-310-110. This may reflect convergence of flow in the shallower portion of the aquifer toward the NGP. The head difference was still upward, but reduced to -0.21 ft after 3 days of pumping of the recovery system. This likely reflects the discharge of treated water from the recovery system to the NGP, raising the head in the pit and adjacent shallow portions of the aquifer relative to the higher heads deeper in the aquifer.

6.1.9 Analyses of Hydrographs from the Suprapermafrost Aquifer

The continuous records of depth to water measurements recorded by the data loggers from late 2010 through 2013 provide insight into the hydraulic responses of the aquifer system. Overall trends were evaluated along with seasonal variation in responses of groundwater elevations to barometric pressure variations. Results of these evaluations are presented in the following subsections.

6.1.9.1 Overall Hydrograph Trend Evaluation

Methods used to evaluate hydrograph trends are presented in Section 5 of Appendix 6-B. Two characteristic trends were identified that are exhibited by the vast majority of wells completed in the suprapermafrost aquifer. The characteristics that differentiate these trends and the spatial distribution of wells exhibiting the trends are summarized below.

The magnitude of the groundwater elevation rise caused by the 2013 spring breakup event, which peaked in early June, was markedly larger at wells onsite and offsite west of Badger Slough that those wells close to Badger Slough. This is primarily due to the greater distance from the Tanana River to the wells near Badger Slough. In addition, the hydrographs for wells near Badger Slough (e.g., MW-325-18) exhibit marked increases in groundwater elevation from December 2012 through April 2013, whereas the groundwater elevation in wells further from Badger Slough show no such rise in groundwater elevation in the same time period.

The cause of increase in groundwater elevation from December 2012 through April 2013 in wells near Badger Slough is likely related to recharge of the suprapermafrost aquifer from the subpermafrost aquifer through the thawed zone beneath Badger Slough. This is based on the similarity of hydrographs of other wells near the slough to that of MW-325-18 and vertical gradients at the MW-181 well nest (Table 6-7), and is consistent with preliminary stable isotope results that indicate mixing of subpermafrost and suprapermafrost water in this area (Barnes and Barnes 2013).

Three wells have hydrographs that do not fit in the categories described above: MW-166A-15 and MW-194A-15, which resemble each other, and MW-320-20, which does not resemble any of the other wells. Appendix 6-B presents additional information on these three wells. Figure 6-12 shows the spatial relationships between wells with data loggers classified into the three groups described below:

- **T** symbolizes wells that exhibit a trend dominated by the influence of the Tanana River as described above. This group includes wells at the NPR beneath which no permafrost is known to exist.

- **O** symbolizes wells that exhibit increases in groundwater elevation over the winter and are less dominated by the influence of the Tanana River. All of the wells in this group are in or near the area beneath Badger Slough where permafrost was not encountered to depths of 150 feet bgs and where geophysical data indicate a thawed zone potentially connecting the subpermafrost and suprapermafrost aquifers.

- **166/194** indicates wells MW-166A-15 and MW-194A-15, whose hydrographs resemble each other and no other wells. These wells are adjacent to Ditch C, which may explain the observed trends.

6.1.9.2 Barometric Pressure Effects

Seasonal variations in the barometric efficiency are apparent in of many of the wells monitored using data loggers. For example, Figure 6-13 shows the recorded barometric pressure and hydrographs for wells MW 162A-15, MW-325-18, and MW-325-150. Barometric pressure in feet of water is plotted such that variations in groundwater elevation caused by variations in barometric pressure will have the same response. The scale of the barometric pressure plot is half of that of the groundwater elevation. Two peaks in barometric pressure are indicated with arrows on Figure 6-13. These events occurred in December 2012 and January 2013, when seasonal frost would have been in place. The hydrographs of the three wells on Figure 6-13 and many other wells with data loggers showed sudden, corresponding drops in water level. This correlation is believed to be a reflection of seasonal frost temporarily creating confined conditions and increasing the barometric efficiency of the suprapermafrost aquifer.

The indication of seasonal frost creating temporarily confining conditions is consistent with the response to pumping noted during the expanded recovery system startup aquifer testing (Barr 2013b). Time-drawdown data from observation wells gathered during the sequential pumping of four separate recovery wells did not show a characteristic unconfined aquifer response. The observed responses are believed to have been caused by seasonal frost penetrating below the water table elevation, creating confining conditions. Downward extension of seasonal frost into the suprapermafrost aquifer is described by Williams (1970). Seasonal frost acting as a confining layer above shallow groundwater is described by Kane et al. (1973).

7. Light Nonaqueous Phase Liquid Investigation

Appendix O of the SCR – 2011 (Barr 2012) discusses a comprehensive LNAPL assessment conducted in 2011. Additional LNAPL data have been collected since the 2011 assessment that re-affirms the findings of the 2011 assessment. This section summarizes LNAPL data collected to date and evaluates that data.

7.1 Methodology

7.1.1 Light Nonaqueous Phase Liquid Nature and Extent

The LNAPL nature and extent has been extensively characterized by advancing soil borings and conducting both *in*- and *ex-situ* evaluation of the soil, installation of monitoring wells, collection of fluid-level data during the past 26 years, and collection of LNAPL samples for laboratory analysis of physical and chemical properties. The specific methodologies used to evaluate those data are described in Sections 7.1.1.1 and 7.1.1.2.

7.1.1.1 Light Nonaqueous Phase Liquid Composition Evaluation

LNAPL samples were collected and submitted to Friedman and Bruya, Inc. for sulfolane and paraffins, isoparaffins, aromatics, naphthenes, and olefins (PIANO) analyses by gas chromatography/mass spectrometry (GC/MS). PIANO analysis is a detailed evaluation of 149 compounds in the 3- to 15-carbon (C3 to C15) range. Compounds are divided into five main groups: paraffins (normal alkanes [e.g., hexane, octane]), isoparaffins (branched or isoalkanes [e.g., isooctane]), aromatics (e.g., benzene, toluene), naphthenes (cyclo-alkanes [e.g., cyclohexane]), and olefins (alkenes [e.g., 1-pentene]). In addition to these petroleum hydrocarbons, the PIANO analyses included 11 oxygenated compounds such as ethanol and methyl tert-butyl ether.

The PIANO data were evaluated for each sample for C3 to C15 petroleum hydrocarbon classes. Stacked bar charts were generated showing the distribution of PIANO compounds as a relative percent of the total PIANO compound pool by petroleum hydrocarbon class. These bar charts allow for interpretation of the distribution of different PIANO groups within each hydrocarbon class. PIANO bar charts generated from 2013 LNAPL samples were directly compared against PIANO bar charts from refined product samples that were provided by FHRA in 2011 (Barr 2012). LNAPL composition was determined assuming that the FHRA-provided refined product samples were representative of the predominant sources of LNAPL at the NPR.

7.1.1.2 Light Nonaqueous Phase Liquid Indicators

A vast amount of soil quality data have been generated for the site since environmental assessments began in 1987. These data were used to determine the areal and vertical extent of LNAPL-impacted soil at the site. Soil boring logs, soil total petroleum hydrocarbon (TPH) analytical data, monitoring well fluid-level data, and laser-induced fluorescence (LIF) data were reviewed for evidence of LNAPL impacts. The following observations were considered representative of LNAPL impacts:

- *Soil boring logs*. Elevated PID readings (above 20 ppm), visual observations of LNAPL recorded in soil borings, and/or olfactory observations consistent with petroleum impacts.
- *Soil TPH data*. A calculated LNAPL saturation of 1 percent.
- *Fluid-level data*. Current or historical observations of LNAPL accumulation in wells; documentation of historical LNAPL recovery from wells was considered evidence that LNAPL accumulated in those wells in the past.
- *LIF*. Fluorescence response above background soil fluorescence.

LNAPL saturation was calculated from soil TPH analytical data using the following equation (American Petroleum Institute [API] 2004):

$$S_O = TPH \times \frac{\rho_b}{\emptyset\, \rho_o} \times 10^{-6} \qquad \text{Equation 1}$$

Where:

S_o = total hydrocarbon saturation in pore space, dimensionless

$\emptyset$ = total porosity, dimensionless

TPH = soil TPH concentration, mg/kg

ρ_b = bulk density, grams per cubic centimeter (g/cm^3)

ρ_o = LNAPL density, g/cm^3

Details on the LIF data evaluation methodology are presented in the SCR – 2012 (ARCADIS 2013a).

7.1.2 Light Nonaqueous Phase Liquid Mobility Assessment

A comprehensive LNAPL mobility assessment uses multiple lines of evidence to determine LNAPL mobility and the potential for future LNAPL migration. Immobile LNAPL is functionally locked in pore spaces. Mobile LNAPL is capable of moving laterally and vertically within the existing LNAPL plume footprint. Migrating LNAPL moves outside of the existing LNAPL plume footprint, thereby causing expansion of the footprint. The following lines of evidence were used to assess LNAPL mobility and migration potential at the site:

- LNAPL observations in monitoring wells
- LNAPL field and residual saturation
- LNAPL pore velocity
- LNAPL pore-entry pressure
- Dissolved-phase plume stability

Appendix O of the SCR – 2011 (Barr 2012) presents detailed information on the data analysis methodology.

7.1.3 Light Nonaqueous Phase Liquid Recoverability

LNAPL recoverability was evaluated to determine the practicality of extracting LNAPL from the subsurface. The LNAPL recoverability assessment is based on calculation of the fraction of recoverable LNAPL and LNAPL transmissivity measurement. Several methods were applied to calculate LNAPL transmissivity using data generated during data collection to calculate LNAPL transmissivity, and from ongoing LNAPL recovery system operations. Those methods include:

- LNAPL manual skimming tests
- LNAPL baildown tests
- Water-enhanced recovery (dual-phase extraction [DPE])
- LNAPL pneumatic skimming tests

The methodologies used to calculate the fraction of recoverable LNAPL are included in Appendix O of the SCR – 2011 (Barr 2012). The methodology for LNAPL transmissivity data and collection and analysis are consistent with the ASTM Standard Guide for Estimation of LNAPL Transmissivity, E2856-11 (ASTM 2012).

7.1.3.1 Light Nonaqueous Phase Liquid Transmissivity

The recoverability of LNAPL is influenced by many factors, including LNAPL saturation in the impacted soil, soil permeability, and physical properties of the LNAPL. LNAPL transmissivity represents the volumetric rate of LNAPL flow through a unit width of porous media per unit time, under a unit hydraulic gradient. A direct mathematical relationship exists between LNAPL transmissivity and the rate of LNAPL flow into a well; therefore, it is an ideal parameter for assessing LNAPL recoverability. LNAPL transmissivity calculations inherently account for the combined effects of aquifer matrix permeability, LNAPL physical properties, and the relative proportion of pore space occupied by LNAPL within a specified vertical interval of aquifer material.

LNAPL transmissivity is commonly characterized using LNAPL manual skimming tests, LNAPL baildown tests, and evaluation of data from LNAPL recovery systems. Data can be used to quantitatively characterize LNAPL recoverability in the area surrounding the test locations. LNAPL recovery using hydraulic methods yields negligible LNAPL volume when the LNAPL transmissivity is less than 0.1 to 0.8 square foot per day (ft^2/day) (Interstate Technology & Regulatory Council [ITRC] 2009a).

7.1.3.1.1 Light Nonaqueous Phase Liquid Manual Skimming Tests

Manual LNAPL skimming tests involve repeated LNAPL recovery periods relative to baildown testing (which consists of one near-instantaneous LNAPL removal at test initiation), and thus represent a larger portion of the LNAPL-impacted formation. LNAPL Transmissivity results calculated using manual LNAPL skimming tests are expected to correlate more strongly to results that would be expected for LNAPL recovery system operation.

A manual skimming test consists of removing all LNAPL from a well, gauging the well as the LNAPL recharges, and removing LNAPL again before the recharge reaches 25 percent of the pre-test LNAPL thickness. This process is repeated until the LNAPL removal rate stabilizes.

Analysis of the manual LNAPL skimming test data can be completed using Equation 2 per ASTM standards:

$$T_n = Q_n \cdot \frac{\ln\left(R_{OI} / r_w \right)}{2 \cdot \pi \cdot s_n} \qquad \text{Equation 2}$$

Where:

T_n = transmissivity, ft^2/day

Q_n = measured LNAPL recovery rate, cubic feet per day (ft^3/day)

R_{OI} = radius of influence, feet

r_w = well radius, feet

s_n = LNAPL drawdown, feet

The radius of influence is difficult to estimate for a manual skimming test; however, because the term occurs within a logarithmic function in Equation 2, the value is not critical for estimating LNAPL transmissivity. For this evaluation, the value of the term “ln (R_{OI}/r_w)” was assumed to be 4.6 per ASTM guidance (ASTM 2012).

An LNAPL drawdown was not measured during the manual skimming testing; therefore, LNAPL drawdown was calculated from the static LNAPL thickness using Equation 3:

$$S_n = b_n \times (1 - \rho_r) \qquad \text{Equation 3}$$

Where:

b_n = LNAPL thickness, feet

ρr = LNAPL density ratio, dimensionless

7.1.3.1.2 Light Nonaqueous Phase Liquid Baildown Test Analyses

An LNAPL baildown test is initiated by quickly removing accumulated LNAPL from a well. The rate of LNAPL flow into the well is a function of soil and LNAPL properties discussed above and the magnitude of the initial hydraulic gradient toward the well developed during LNAPL removal. The baildown test response is influenced by the prevalent fluid levels at the time of testing. Multiple baildown tests have been performed at the site to describe the range of LNAPL transmissivities under different fluid-level conditions.

Baildown tests are analyzed in the Draft API LNAPL Transmissivity Workbook (API Workbook [API 2012]) using a modified slug test method by Bouwer and Rice (1976). Assumptions for the modified Bouwer and Rice method include quasi-steady-state recharge to the well, with drawdown dependent on rate and no storage effects. To ensure recharge from the formation, estimation of the ratio between radius of influence and effective radius must be greater than 2.0.

Some baildown tests do not generate data that can be analyzed quantitatively. This generally occurs when there is limited LNAPL thickness to begin with, the LNAPL in the well is not in equilibrium with the formation, or the LNAPL discharge into the well cannot be related to the LNAPL drawdown induced during the test because heterogeneities within the soil matrix do not conform to simplifying assumptions on hydraulic response to induced stress. When baildown test data cannot be analyzed quantitatively, the data are evaluated quantitatively with respect to the amount of LNAPL recharge into the well during the test.

Data analysis options in the API Workbook (API 2012) include a data time cut and drawdown adjustment that can be applied as needed. A data time cut is required for nearly every test, where early-time data due to filter pack drainage is removed from analysis. Initial filter pack drainage does not represent formation drainage, and analysis will lead to erroneous results. A drawdown adjustment may also be applied to tests where the fluid levels in the well did not fully recover to initial conditions. The drawdown adjustment is only applied if LNAPL in the well at the time of test initiation is not in equilibrium with LNAPL in the formation. This results in a clear trend of zero LNAPL discharge at a non-zero value for LNAPL drawdown. Further information on the data time cut and drawdown adjustment is provided in the user guide for the API Workbook (API 2012).

7.1.3.1.3 Water-Enhanced Recovery

LNAPL transmissivity can be estimated based on analysis of long-term LNAPL recovery system performance data. For total fluids recovery systems, such as the DPE system in place at the site, LNAPL transmissivity can be estimated based on water and LNAPL discharge data using Equations 4 and 5, below (ASTM 2012):

$$T_n = T_w \cdot \rho_r \cdot \frac{Q_n}{Q_w} \qquad \text{Equation 4}$$

Where:

T_n = LNAPL transmissivity (ft^2/day)

T_w = aquifer transmissivity to groundwater (ft^2/day)

Q_n = average LNAPL recovery rate (ft^3/day)

Q_w = groundwater recovery rate (ft^3/day)

ρ_r = LNAPL-water density ratio (dimensionless)

In instances where the skimming drawdown is greater than $^1/_{10}$ of the water extraction induced drawdown, then Equation 5 is more appropriate.

$$T_n = \frac{Q_n T_w}{Q_w}(\rho_r + \frac{S_{skim}}{S_w}) \qquad \text{Equation 5}$$

Where:

S_{skim} = unconfined LNAPL drawdown (feet)

S_w = groundwater drawdown (feet)

Equations 4 and 5 are applicable for estimating LNAPL transmissivity from a single DPE LNAPL recovery well. The analysis is based on an assumption that LNAPL and groundwater both flow horizontally to the extraction well.

Three extraction wells were operated in the current LNAPL recovery system (R-21, R-35R, and R-40) in 2013. R-40 was only operated as a DPE well through May 2013. LNAPL and groundwater recovery is routinely recorded for the combined system performance, and fluid discharge is measured from individual wells. Therefore, LNAPL transmissivity calculations for these data are representative of each well location.

7.1.3.1.4 Light Nonaqueous Phase Liquid Pneumatic Skimming

LNAPL recovery data from LNAPL skimming systems can be used to calculate LNAPL transmissivity if the automated LNAPL skimming pump operates continuously, or at a high enough frequency to maintain LNAPL drawdown in the recovery well. The data that are necessary to complete the LNAPL transmissivity calculations include LNAPL drawdown induced by the skimming pump and volume recovery rates from each test well, which can be collected as a part of routine operation and maintenance activities. Longer-term automated LNAPL skimming transmissivity calculations were completed at two wells (MW-138 and R-20R) from January 2010 to October 2013.

Continuous automated LNAPL skimming data were analyzed using Equation 2, in the same manner as the manual LNAPL skimming tests (ASTM 2012). A baseline condition of LNAPL thickness could not be determined due to existing ongoing LNAPL skimming. LNAPL drawdown was calculated using Equation 3 and the LNAPL thickness in the well during gauging. The LNAPL skimming pumps used at the site require a minimum LNAPL thickness of 0.10 foot in order for LNAPL to enter the pump and be evacuated from the well. In instances where the reported in-well thickness of LNAPL was less than 0.10 foot, an assumed thickness of 0.10 foot was used for the LNAPL drawdown calculation. Smaller reported LNAPL thicknesses in MW-138-20 and R-20R likely represent conditions in the well shortly after pump actuation.

7.1.4 Natural Source Zone Depletion

NSZD is a combination of natural processes that reduce the mass of LNAPL in the subsurface through time. NSZD occurs when processes act to physically redistribute LNAPL components to the aqueous phase via dissolution, or to the gaseous phase via volatilization. In turn, dissolved or volatilized LNAPL constituents are biologically degraded by microbial activity. Biodegradation rates of LNAPL constituents dissolved in groundwater or volatilized in soil gas depend on the type and availability of electron acceptors (e.g., oxygen, nitrate, sulfate, ferrous iron) in the subsurface soil and groundwater. In most

LNAPL-impacted aquifers, the electron acceptors discussed above are depleted in shallow intervals and the shallow aquifer is deeply anaerobic. In the absence of electron acceptors, fermentation of hydrocarbons and subsequent conversion of the fermentation byproducts to methane by methanogens becomes a significant pathway for hydrocarbon depletion. NSZD preferentially depletes the most soluble and volatile constituents of the LNAPL.

An evaluation of the potential efficacy of NSZD as a means of reducing LNAPL mass, which through time will further reduce LNAPL mobility, was conducted following protocols outlined in the Technology Overview for Evaluating Natural Source Zone Depletion at Sites with LNAPL (ITRC 2009b).

The rate of LNAPL depletion in groundwater can be determined through inspection of upgradient and downgradient hydrocarbon and electron acceptor concentrations in groundwater and understanding the volumetric flow rate of groundwater through the LNAPL plume. An observation of increased dissolved-phase petroleum hydrocarbon constituent concentrations between upgradient and downgradient groundwater monitoring locations provide evidence that LNAPL dissolution is occurring. Depletion of electron acceptors (oxygen, nitrate, sulfate), production of electron acceptor reduction products (ferrous iron, manganese, methane), or generation of hydrocarbon fermentation byproducts (acetate, methane) demonstrates that microbial metabolism of hydrocarbons is ongoing.

In the vadose zone, LNAPL components may volatilize and redistribute into soil gas. Methane generated in the saturated zone may be expressed in the vadose zone via ebullition due to the low aqueous solubility of methane. Volatilized petroleum hydrocarbon compounds and methane then migrate through vadose zone soil from areas of higher concentrations to lower concentrations via diffusive transport processes. Diffusion is typically the dominant gas transport mechanism under most natural conditions. Soil gas advection may be an important process in high-activity methanogenic zones. Diffusive mass flux of soil gas in the vadose zone is directly related to soil permeability and air-filled effective porosity of the soil matrix. Soil gas flux is lower in lower-permeability materials and soil with a high water content that reduces the air-filled porosity.

Biodegradation of methane and volatile petroleum hydrocarbons (VPH) occurs in the vadose zone where oxygen is present. This biological activity results in a characteristic soil gas profile in the vadose zone. Oxygen is depleted within the LNAPL smear zone and elevated VPH, methane, and carbon dioxide are observed. The soil gas composition trends to atmospheric conditions vertically within the soil column.

The rate of hydrocarbon depletion within the vadose zone can be determined through calculation of oxygen mass flux into the vadose zone and conversion of that mass flux into equivalent hydrocarbon depletion. The mass flux is determined using the oxygen concentration gradient, which is the driving force, and the gas diffusion properties of the soil (ITRC 2009b). The oxygen content of the soil gas is typically used to complete the LNAPL depletion rate calculations because it accounts for all aerobic biodegradation within the vadose zone. Oxygen does not participate in the carbonate cycle, which can be a sink or source of carbon dioxide in soil gas.

7.1.5 Source Zone Mass Depletion by Dissolution to Groundwater in the Saturated Zone

As groundwater moves through the subsurface it will contact LNAPL-impacted soil within the saturated zone, and infiltrating precipitation may contact LNAPL-impacted soil within the vadose zone. In both cases, petroleum hydrocarbons will partition into the water and result in a loss of mass from the LNAPL body. When infiltration of precipitation is insignificant and clean groundwater enters the LNAPL source zone, the rate of LNAPL source mass loss by dissolution can be simplified to consider only dissolved hydrocarbons exiting the submerged portion of the source zone. The rate of source zone mass loss by dissolution to groundwater (R_{Dis}) can thus be determined by Equation 6 (ITRC 2009b):

$$R_{Dis} = q_d \cdot h \cdot w \cdot C_d \qquad \text{Equation 6}$$

Where:

q_d = groundwater-specific discharge (cubic meters of water per square meter per second [m^3 $H_2O/m^2/sec$])

h = thickness of submerged source zone (m)

w = width of submerged source zone (m)

C_d = average groundwater concentration (milligrams per liter [mg/L])

CF = conversion factor (1,000 mg/L per kilograms per cubic meter [kg/m^3] of water)

7.1.6 Source Zone Mass Depletion Rate by Biodegradation in the Saturated Zone

Biodegradation of LNAPL in the saturated zone results in decreasing concentrations of dissolved electron acceptors (oxygen, nitrate, sulfate) in influent groundwater and precipitation recharge, and increasing concentrations of biodegradation transformation products (dissolved iron and methane). Comparison of the loss of electron acceptors and formation of transformation products supports estimation of the rate of LNAPL biodegradation in the submerged source zone (R_{BioSat}). An estimate of the biodegradation rate was completed using Equation 7.

$$R_{BioSat} = q_d \cdot h \cdot w \cdot AC \qquad \text{Equation 7}$$

Where:

q_d = groundwater specific discharge (m^3 $H_2O/m^2/sec$)

h = thickness of submerged source zone (m)

w = width of submerged source zone (m)

AC = assimilative capacity, the difference between upgradient and downgradient concentrations of each natural attenuation indicator species multiplied by a representative stoichiometric coefficient (ITRC 2009b)

7.1.7 Source Zone Mass Depletion Rate by Volatilization and Biodegradation in the Unsaturated Zone

Volatile hydrocarbons are depleted by partitioning to soil gas and subsequent aerobic biodegradation of the liberated hydrocarbons. Additionally, methane may be discharged into the vadose zone by methanogenic activity within the saturated portion of the LNAPL plume. Methane gas discharged to the vadose zone is rapidly consumed by aerobic methanotrophs. Carbon dioxide is generated by aerobic biodegradation of the volatile hydrocarbons and methane.

A qualitative assessment of NSZD is conducted by evaluating the vertical profile of oxygen, carbon dioxide, petroleum hydrocarbon, and methane content in soil gas:

- Methane detected in soil gas is evidence of methanogenic degradation of hydrocarbons. Methane is rapidly degraded in the presence of oxygen through aerobic processes; therefore, methane concentrations are expected to decrease from the water table to the surface.

- The presence of hydrocarbons in soil gas, increasing with depth, indicates that volatilization and degradation of the LNAPL is occurring.

- Carbon dioxide is a product of aerobic biodegradation of hydrocarbons (including methane). Carbon dioxide concentrations are expected to increase with depth in areas where aerobic biodegradation is occurring.

- Oxygen is consumed during aerobic biodegradation; therefore, oxygen concentrations are expected to decrease with depth in zones with active aerobic biodegradation.

NSZD rates can be estimated by evaluating vertical soil gas fluxes across a theoretical horizontal plane placed above the source zone (Johnson et al. 2006, ITRC 2009b). The horizontal plane is located above the source zone and, if possible, placed at a depth where there is an apparent transition from an aerobic to anaerobic regime in the vadose zone. This is done to focus the evaluation on the zone of most vigorous aerobic bioremediation to reduce the NSZD rate calculation to the oxygen flux across the plane.

The NSZD rate in the vadose zone is quantified by determining the rate that oxygen enters the vadose zone and converting that mass flux to equivalent hydrocarbon mass depleted. The NSZD rate in the unsaturated zone (R_{Vapor}) can be calculated based on oxygen content in soil gas using Equation 8:

$$R_{Vapor} = A \cdot \frac{S_{O_2} \cdot D_{O_2}\left(C_{O_2}^{atm} - C_{O_2}^{d}\right)}{d}$$

Equation 8

Where:

A = area of LNAPL footprint

So_2 = stoichiometric mass ratio of grams of hydrocarbon to grams of oxygen for mineralization (0.25 g-HC/g-O_2)

Do_2 = diffusion coefficient for oxygen (square meter per second); the site-specific diffusion coefficient was calculated in Section 8.0

Co_2^{atm} = atmospheric concentration of oxygen (0.295 kg/m^3)

Co_2^{d} = concentration of oxygen at depth d (kg/m^3)

d = thickness of the zone where vapor transport is occurring (m)

7.2 Data

LNAPL data collected through 2011 were presented in Appendix O of the SCR – 2011 (Barr 2012). This appendix included hydrogeologic parameters of fluid gauging and hydraulic gradient, LNAPL fluid collection with physical property analyses for LNAPL density, LNAPL viscosity, and interfacial tension (IFT), and collection of 60 feet of undisturbed soil core and analysis of those soil cores for free product mobility, air-water capillary drainage, and laser particle size analysis. These data were used for the LNAPL mobility assessment analyses, also presented in Appendix O of the SCR – 2011 (Barr 2012).

Additional LNAPL data have been collected since the 2011 assessment; these data reinforce the findings of the 2011 assessment. This section summarizes the LNAPL data collected to date and evaluates that data.

7.2.1 Hydrogeologic Parameters

LNAPL accumulations or detections have been observed in 37 observation and monitoring wells (excluding recovery wells) at the site since 2006. Potentiometric surface elevations and LNAPL thicknesses (i.e., hydrographs) are graphed vs. time on Figures 7-1A through 7-1H for 30 monitoring wells with consistent LNAPL accumulations. The hydrographs also present monitoring well screened interval information when available for the wells. LNAPL recovery has been conducted in R-34 and S-50, but extended nonrecovery periods made data from these wells appropriate for hydrograph generation.

Hydrographs were not generated for wells in which LNAPL has never accumulated or has not been measured at thicknesses greater than 0.01 foot (MW-176B-50, O-1, O-14, R-22, S-32, or S-43). Hydrographs were not generated for abandoned wells with historical data. Lastly, hydrographs were not made for recovery-only wells or the recovery operation period of observation wells, because groundwater and LNAPL levels in recovery wells are not representative of nonpumping site conditions.

7.2.2 Light Nonaqueous Phase Liquid Physical Properties

LNAPL and groundwater samples were collected from one monitoring well (O-27) in April 2012 to further supplement data collect for the LNAPL Assessment presented as Appendix O of the SCR – 2011 (Barr 2012). The sample was sent to Core Laboratories of Bakersfield, California for analysis of density, viscosity, and three IFT pairs. Each test and the pertinent information generated from each test are described below:

- *LNAPL Density, ASTM D1481.* This test provides basic information on the density of the LNAPL, which is compared to that of water and used when modeling the distribution and mobility of the LNAPL.

- *LNAPL Viscosity, ASTM D445.* This test assesses fluid viscosity at a controlled temperature, representative of groundwater temperature. LNAPL is typically more viscous than groundwater and LNAPL viscosity is used to translate hydraulic conductivity to LNAPL conductivity.

- *IFT, ASTM D971.* This test assesses IFT between air-water, air-LNAPL, and water-LNAPL fluids. This information is used as input for LNAPL modeling to determine the distribution and mobility of LNAPL in the subsurface.

All fluid property tests were performed at 1 degree Celsius (°C) (i.e., 34 °F), which is representative of the average annual groundwater temperature at the site. The fluid physical properties are presented in Table 7-1. Laboratory data reports are included in

Appendix 7-A. Data for fluid properties that were collected in September and October 2011 were reported in Appendix O of the SCR – 2011 (Barr 2012).

These data are included in the LNAPL and groundwater density ratio calculations used for LNAPL transmissivity analyses.

7.2.3 Light Nonaqueous Phase Liquid Compositional Analysis

7.2.3.1 Light Nonaqueous Phase Liquid Forensics

LNAPL samples were collected from 10 observation and recovery wells at the site in 2011 (O-2, O-7, O-9, O-11, O-13, R-14A, R-39, R-40, S-21, and S-22). Five refined product samples produced at the NPR were collected by FHRA laboratory staff in 2011 to provide a direct comparison for interpreting forensics results from LNAPL samples. The refined product samples included 87-octane regular unleaded gasoline (gasoline-R), premium unleaded gasoline (gasoline-P), petroleum naphtha (naphtha), Jet A fuel (Jet A), and No. 2 diesel fuel (diesel #2). The 2011 LNAPL composition results are discussed in the SCR – 2011 (Barr 2012).

In 2013, additional LNAPL samples were collected for compositional analysis from 12 monitoring, observation, and recovery wells (MW-138-20, MW-176A-15, MW-186A-15, MW-334-15, MW-115-15, O-19, O-27, O-31, O-34, R-32, S-39, and S-51) per the Onsite SCWP (ARCADIS 2013d). In deviation from the Onsite SCWP, six observation and recovery wells included in the Onsite SCWP (R-32R, O-33, and O-35 through O-38) were not sampled due to insufficient LNAPL in the wells (ARCADIS 2013d). LNAPL has been not been measured in one observation well (O-32).

The 2011 and 2013 LNAPL sampling locations are shown on Figure 7-2. LNAPL sampling locations are spatially distributed across the site.

LNAPL and FHRA-provided refined product samples collected in 2011 and 2013 were submitted under chain of custody documentation to Friedman and Bruya, Inc. (Friedman and Bruya), a forensics laboratory in Seattle, Washington. PIANO analysis by GC/MS was performed on the LNAPL and refined product samples.

7.2.3.2 Sulfolane in Light Nonaqueous Phase Liquid

Nine LNAPL samples were collected for sulfolane analysis from monitoring, observation, and recovery wells (S-21, S-22, S-33, S-39, S-51, R-32, R-33, MW-115-15, and MW-138-20) between March 12 and December 6, 2010. SGS analyzed the LNAPL samples for sulfolane using USEPA Method 8270D. Upon review of 2010 analytical results, SGS, in consultation with Environmental Standards, Inc. (ESI), developed an additional SOP that outlines the method for analyzing sulfolane in LNAPL. Three monitoring, observation, and recovery wells (S-51, R-32, and MW-138-20) were resampled on April 18, 2011 and analyzed according to the SOP using USEPA Method 1625B with isotope dilution. Sulfolane concentrations in LNAPL samples collected from March 12, 2010 to April 18, 2011 are presented in the SCR – 2011 (Barr 2012b).

The analytical results for LNAPL samples collected in 2010 were below detection limits for sulfolane. However due to the high laboratory detection limits with USEPA Method 8270D, the results were not definitive regarding the presence or absence of sulfolane in LNAPL. Lower analytical detection limits were achieved with USEPA Method 1625B with isotope dilution. One sample from MW-138-20 was above analytical detection limits during the resampling event on April 18, 2011 using this method. Additional LNAPL sampling was completed as described in the Onsite SCWP (ARCADIS 2013d) to determine sulfolane concentrations in LNAPL using USEPA 1625B with isotope dilution. LNAPL samples were collected from 12 monitoring, observation, and recovery wells (MW-138-20, MW-176A-15, MW-186A-15, MW-334-15, O-19, O-27, R-32, S-21, S-22, S-51, O-31, and O-34) in 2013. In deviation from the Onsite SCWP, six observation and recovery wells included in the Onsite SCWP (R-32R, O-33, and O-35 through O-38) were not sampled due to insufficient LNAPL thickness in the wells (ARCADIS 2013d). LNAPL has not been measured in one observation well (O-32).

The spatial distribution of sample locations from the 2010, 2011, and 2013 sample events cover the LNAPL-affected areas of the site. The locations are shown on Figure 7-3.

7.2.4 Groundwater Quality Data

Groundwater quality data were used to assess the stability of dissolved-phase petroleum constituents in groundwater as part of the LNAPL mobility assessment. Analytical data for groundwater samples collected between April 1987 and September 2013 from 66 onsite monitoring and observation wells screened at or near the water table were available for the dissolved-phase plume stability analysis. Monitoring wells that currently have or historically have had LNAPL accumulations greater than 0.01 foot or a sheen were not considered for this analysis. This dissolved-phase trend analysis included analytical data for benzene and xylenes. These historical data were presented in the Third Quarter 2013 Groundwater Monitoring Report (ARCADIS 2013i).

7.2.5 Light Nonaqueous Phase Liquid Manual Skimming Test Data

Although not a part of the Onsite SCWP (ARCADIS 2013d) or RSAP, FHRA completed a manual skimming test at MW-334-15 in October 2013. Monitoring well MW-334-15 was slated for LNAPL baildown testing as part of the site-wide baildown test program. However, when the test was attempted, the observed LNAPL discharge into the well was high and LNAPL could not effectively be purged to initiate the test. Based on this observation and consultation with ARCADIS experts, the field staff discontinued the baildown test and instead conducted a manual skimming test at MW-334-15.

Forty-eight gallons of LNAPL were removed during the 3-hour manual skimming test. An LNAPL recovery rate was calculated for each LNAPL removal step, which was in turn used to calculate the transmissivity for that period. Field data for the LNAPL manual skimming test at MW-334-15 are included in Appendix 7-B. An additional 95 gallons of LNAPL were recovered from well MW-334-15 between October 31 and November 19, 2013 resulting in a total of 143 gallons of LNAPL recovered from this well.

7.2.6 Light Nonaqueous Phase Liquid Baildown Test Data

ARCADIS completed LNAPL baildown tests at the site in October 2013 at seven monitoring wells in which LNAPL was observed (MW-176A, O-27, O-31, O-33, O-34, S-21, and S-39). One test was completed per well (except for wells O-34 and S-21, where two tests were completed). LNAPL recovery in wells after test completion ranged from 3 to 100 percent of the initial LNAPL thickness for the wells.

LNAPL baildown testing was conducted according to procedures outlined in the RSAP. Appendix 7-C presents the field LNAPL baildown test data.

7.2.7 Water-Enhanced Recovery

FHRA completed LNAPL transmissivity calculations for recovery wells R-21 and R-40 using remediation system data collected from January 2010 through October 2013. Transmissivity calculations for recovery well R-40 were completed using data collected from January 2010 through May 2013. Since May 2013, R-40 is no longer a recovery well. System data include water flow rate, depth to water and LNAPL, and LNAPL removed weekly.

As discussed above, groundwater transmissivity is a required input calculation of LNAPL transmissivity from a groundwater and LNAPL recovery system. Average groundwater transmissivity values for the recovery wells were calculated from hydrogeologic analyses presented in the Evaluation of Recovery Well Replacement, Start-up Aquifer Testing for Recovery System Hydraulic Capture Performance Monitoring Report (Barr 2013a). Groundwater transmissivity values were based on groundwater pump tests conducted at the NPR. The groundwater transmissivity values used for the LNAPL transmissivity calculations were chosen based on the spatial location of wells in relation to each other, screen intervals, and similar geology. The average groundwater transmissivity used for

LNAPL transmissivity calculations for R-35R and R-40 was based on data from R-40. Similarly, groundwater transmissivity values from R-43 and R-44 were averaged and used for LNAPL transmissivity calculations for R-21. An average groundwater transmissivity of 8,000 ft^2/day was used for R-35R and R-40, and 13,600 ft^2/day was used for R-21.

LNAPL/water density ratios were calculated for R-21, R-35R, and R-40 from laboratory fluid physical properties discussed the in SCR – 2011 (Barr 2012b). Data collected from S-20 were used for R-40 due to the availability of data and location of wells relative to each other. R-21 and R-35R have specific fluids properties data.

LNAPL and groundwater drawdowns are also required input values for the LNAPL transmissivity calculation. Ideally, these drawdown values would be based on a difference between fluid levels under non-pumping, equilibrium conditions. However, the fluid-level data were collected while the DPE systems were running because routine recovery system shutdown and equilibration are not feasible. Therefore, two simplifying assumptions were made to facilitate the LNAPL transmissivity calculations:

1. LNAPL drawdown used in the calculations was based on the observed thickness of LNAPL in the well during gauging and system data collection.

2. Groundwater drawdown could reasonably be calculated for each well (R-21, R-35R, and R-40) by pairing the recovery well with a monitoring well outside the zone of capture.

These assumptions introduce a small degree of error into the calculation, but the results are representative of the magnitude of LNAPL transmissivity.

The following wells were paired together to complete the calculation: R-21:O-5, R-35R:MW-130-25, and R-40:MW-135-25. Groundwater drawdown was calculated for each pair based on fluid gauging data from the quarterly reports. Data collected from each well along with calculated groundwater drawdown is presented in Appendix 7-D.

7.2.8 Light Nonaqueous Phase Liquid Pneumatic Skimming

LNAPL transmissivity can be calculated from an LNAPL skimming system if periodic LNAPL drawdown and LNAPL volume recovery rate data are collected from each test well. Longer-term automated LNAPL skimming transmissivity calculations were completed for two wells (MW-138 and R-20R) from January 2010 to October 2013. The data used in the LNAPL transmissivity calculations are presented in Appendix 7-E.

7.2.9 Natural Source Zone Depletion Evaluation

Data presented in the following sections were used to evaluate NSZD processes and to calculate rates of LNAPL mass reduction at the NPR.

7.2.9.1 Data for Dissolution Rate in Saturated Zone

A significant portion of the LNAPL-impacted area of the site is covered with low-permeability surfaces, as shown on Figure 7-4. Based on that observation, infiltration of precipitation was not considered a significant contribution of dissolved oxygen (DO) to the subsurface. This assumption simplifies the dissolution rate equation used in the NSZD evaluation.

Another assumption in the dissolution calculations is that groundwater entering the LNAPL source zone is clean. Monitoring well MW-105A was selected as the representative background well for the NSZD evaluation. MW-105A is outside and upgradient from the LNAPL and dissolved-phase plumes. Table 7-2 presents dissolved-phase petroleum hydrocarbon constituent concentrations found in a groundwater sample collected from MW-105A in May 2013. GRO and DRO data were not available for this well; however, a total BTEX concentration of 0.002 mg/L was detected in the groundwater sample, indicating that influent groundwater contains only trace amounts of petroleum hydrocarbons. Therefore, the LNAPL mass loss rate by dissolution can be simplified to consider only dissolved hydrocarbons exiting the submerged portion of the source zone.

A change in dissolved-phase petroleum hydrocarbon constituent concentrations between groundwater monitoring locations upgradient and within or downgradient from the LNAPL plume provide evidence that LNAPL dissolution is occurring. Source zone monitoring well MW-176A was selected to represent groundwater quality within the LNAPL plume because the well is located an area of the site where LNAPL is characterized as a mixture of Jet A and diesel #2, which is generally representative of the majority of LNAPL at the site. Dissolved-phase GRO and DRO concentrations were 4.5 and 5.4 mg/L, respectively, in a groundwater sample collected from MW-176A on April 2, 2013 (Table 7-2). The concentration of dissolved-phase TPH, which is the sum of the GRO and DRO values, was 9.9 mg/L. These concentrations are consistent with concentrations used in the 2012 NSZD assessment.

7.2.9.2 Data for Biodegradation Rate in Saturated Zone

Quantification of biodegradation in the saturated zone uses biogeochemical parameters (oxygen, nitrate, sulfate, dissolved iron and manganese, and methane). Monitoring well MW-176A was selected for use as the source zone for the NSZD evaluation. Monitoring well MW-105A was used as the background monitoring well. Biogeochemical data from the second quarter 2013 sampling events at MW-105A and MW-176A are provided in Table 7-3.

7.2.9.3 Data for Volatilization and Biodegradation in the Unsaturated Zone

LNAPL depletion is quantified by determining the rate of oxygen consumption in the subsurface. Soil gas samples were collected from two discreet depths at six locations within the LNAPL footprint and analyzed for oxygen, carbon dioxide, methane, and volatile organic compounds (VOCs) as discussed in Section 9. The vapor-phase soil diffusivity to oxygen is required to determine the oxygen flux into the subsurface. Push-pull diffusivity testing was completed at the site to determine site-specific vapor-phase soil diffusivity to oxygen for use in the evaluation.

Data used to calculate LNAPL depletion rates in the unsaturated zone are summarized in Table 7-4; information regarding soil gas data collection and vapor-phase soil diffusivity are summarized in Section 9.

7.3 Light Nonaqueous Phase Liquid Nature and Extent

7.3.1 Sources and Release Mechanisms

The potential sources of LNAPL and historically documented petroleum hydrocarbon releases are summarized in the SCR – 2011 (Barr 2012). During preparation of the SCR – 2011 (Barr 2012), FHRA and ADEC files were reviewed to evaluate known historical releases and to obtain information regarding the release volumes, locations, and cleanup actions performed in response to the releases. Historical records indicate that more LNAPL has historically been recovered than was reportedly released. Therefore, it is likely that releases of petroleum products to the environment were not well documented prior to NPR ownership of the facility. FHRA is not in a position to verify the completeness or accuracy of records that were maintained prior to their ownership of the NPR (Barr 2011). Since FHRA purchased the NPR in 2004, FHRA's policy has been to document the volume of all releases regardless of volume. Historical documented petroleum product releases occurred from various aboveground storage tanks, sumps, distribution piping, loading racks, and other site infrastructure (Barr 2011).

7.3.1.1 Spill Events and Releases since Submittal of the Site Characterization Report 2012

Additional releases of petroleum products were documented by FHRA staff and reported to ADEC since completion of the SCR – 2011 (Barr 2012). Documented releases greater than 10 gallons that were not contained or remediated include (Appendix 7-F):

- No. 2 fuel oil (540 gallons)
- Oily water (675 gallons)
- Light atmospheric gas oil (200 gallons)
- Crude oil/kerosene (25 gallons)

7.3.2 Light Nonaqueous Phase Liquid Composition Evaluation

7.3.2.1 Light Nonaqueous Phase Liquid Forensics - 2013 Results

PIANO bar charts from the FHRA-provided refined product samples were used to evaluate 2013 LNAPL sample composition. PIANO bar charts for the refined product samples are provided on Figure 7-5. PIANO results for the refined product samples are summarized below:

- The gasoline-R and gasoline-P samples have similar PIANO bar charts, with hydrocarbons in the C4 to C8 range dominating the PIANO compound pool. The PIANO bar charts show higher relative proportions of paraffins and naphthenes in the gasoline-R sample compared to the gasoline-P sample, reflecting the difference in grade.

- The naphtha sample shows a similar distribution to gasoline, although it is slightly heavier and contains a greater proportion of paraffins and naphthenes, and lower proportion of aromatics than gasoline.

- The Jet A PIANO data are characterized by a broader and heavier range of hydrocarbons (C6 to C15) respective to gasoline (C4 to C10). Jet A is dominated by paraffins and aromatics.

- Diesel fuel is the heaviest of the FHRA-provided refined product samples; aromatics and paraffins were the dominant classes detected in the PIANO analysis (note that isoparaffins are not measured above the C10 range). The relative contribution of paraffins to the total PIANO pool increases with increasing carbon class, a trend that is indicative of a diesel-type product.

PIANO bar charts for 2013 LNAPL samples are provided on Figures 7-6A, 7-6B, and 7-6C. PIANO data for LNAPL samples collected from O-31 and O-34 are currently pending at Friedman and Bruya, and will be reported in the Final Onsite Site Characterization Report. PIANO laboratory reports for 2013 LNAPL samples are provided in Appendix 7-G.

Based on available PIANO results, the LNAPL samples collected in 2013 can be broadly segregated into the following groups:

- Jet A-dominated samples (R-32, O-19, MW-186A-15, S-51, MW-138-20, and O-27)
- Jet A/naphtha-dominated mixtures (MW-334-15 and S-39)
- Diesel #2-dominated samples (MW-115-15)
- Jet A/diesel #2-dominated mixtures (MW-176A-15 and MW-276A-15)

Jet-A dominated samples predominantly comprise paraffins and aromatics in the C7 to C10 range, with minor contributions of paraffins in the C11 to C15 range.

Two samples (MW-334-15 and S-39) appear to be mixtures of naphtha and Jet A. The PIANO results for samples MW-334-15 and S-39 display a distribution of paraffins, isoparaffins, aromatics, and naphthenes in the C6 to C11 range, with minor contributions of paraffins in the heavier hydrocarbon range (C12 to C15). MW-334-15 includes lighter hydrocarbons down to the C4 range. This suggests that gasoline may have a minor contribution to the LNAPL composition at this monitoring well.

One sample (MW-115-15) appears to have a diesel #2-dominated composition. The PIANO bar chart for this sample shows that heavier hydrocarbons dominate the carbon class distribution. Unlike Jet A-dominated samples, where the contribution of heavy paraffins decreases with increasing carbon class, heavy paraffins in the MW-115-15 sample increase with increasing carbon class (from C13 to C15). This trend is indicative of a diesel #2-type product.

Two samples (MW-176A-15 and MW-276A-15) appear to be mixtures of Jet A and diesel #2. The distribution of paraffins, isoparaffins, aromatics, and napthenes in the C6 to C11 range are indicative of a Jet A-based product. Similar to MW-115-15, the contribution of heavier paraffins in these samples increases with increasing carbon class. This indicates that diesel #2 is a component of the samples.

7.3.2.2 Light Nonaqueous Phase Liquid Sulfolane Concentration Results

Sulfolane concentrations in the 2013 LNAPL samples are provided in Table 7-5 and shown on Figure 7-7. Sulfolane concentrations from 2010 and 2011 are displayed on Figure 7-7 for comparison. Concentrations were below analytical detection limits, except for one sample collected from MW-138-20 on April 18, 2011 (573 µg/kg) and the parent and duplicate from MW-176A-15, which was collected on April 2, 2013 (37.2J and 39.5J µg/kg, respectively). LNAPL sulfolane concentrations in MW-138-20 were below 80.4 µg/kg (laboratory detection limit for that sample) when the well was resampled on April 2, 2013.

LNAPL and groundwater are immiscible. Within LNAPL-impacted soil, LNAPL and groundwater are in direct contact and the LNAPL constituents partition from the LNAPL into groundwater based on aqueous solubility and the mole fraction of each constituent in the LNAPL. Based on the maximum sulfolane detection of 39.5J µg/kg in LNAPL samples collected in 2013, it is apparent that LNAPL is not a significant source or sink of sulfolane found in groundwater.

7.3.3 Light Nonaqueous Phase Liquid Indicators

Areal and vertical delineation of LNAPL is complete at the site. Soil borings not affected by LNAPL have been advanced in all directions and soil borings have extended beyond the bottom of the LNAPL impacts. The areal extent of LNAPL impacts based on historical soil quality data collected for the site are shown on Figure 7-8

7.3.3.1 Areal Distribution of Light Nonaqueous Phase Liquid

Elevated PID readings, olfactory observations, LNAPL presence as noted on soil boring and monitoring well logs, and/or LNAPL accumulations in monitoring wells were considered to indicate LNAPL impacts. Qualitative indications of LNAPL during installation of soil boring and monitoring well measurements are presented as red triangles on Figure 7-8. Monitoring wells and soil boring locations where LNAPL was not observed from boring logs and gauging data are identified with black triangles.

LNAPL accumulations in monitoring wells, both current and historical, were also used to assess the areal and vertical distribution of LNAPL at the site. Gauging data from 45 of 125 wells indicated LNAPL accumulations (MW-115-15, MW-135-20, MW-136-20, MW-138-20, MW-176A-15, MW-186A-15, MW-334-15, O-2, O-7, O-9, O-10, O-11, O-13, O-19, O-21, O-22, O-27, O-31, O-33 through O-38, R-5, R-14, R-14A, R-18, R-20, R-20R, R-21, R-32 through R-35, R-32R, R-35R, R-39, R-40, R-44, R-45, S-21, S-22, S-39, S-43, S-44, S-50, and S-51). LNAPL sheens have been detected in the following wells: O-1, O-14, R-4, R-22, and S-32. These locations were also presented as red triangles on Figure 7-8.

TPH soil analytical data were used to calculate hydrocarbon pore saturation at each location using the procedure outlined in Section 7.1.1.2. Soil borings with a calculated hydrocarbon pore saturation of 1 percent or greater were considered to be affected by LNAPL. These results are presented on Figure 7-8 and calculations are presented in Appendix 7-H.

LNAPL impacts identified using LIF were observed toward the center of the investigation area, in the sand and gravel alluvium on both sides of the railroad tracks (e.g., L-6, L-37, L-40, and L-46), as described in the SCR – 2012 (ARCADIS 2013a). LIF results provide areal delineation of LNAPL in the truck-loading rack area to the north, which is the direction of groundwater flow, and to the southwest. LIF locations near monitoring wells without LNAPL impacts based on boring logs (i.e., MW-113 and O-12) confirm the absence of LNAPL in these areas. These data confirm and improve the current understanding of the horizontal extent of LNAPL in the areas investigated. LIF results are based on percent reflectance, and are included on Figure 7-8.

Collectively, these data were used to generate Figure 7-8, which shows the areal distribution of LNAPL impacts at the site and provides an understanding of the data density. Horizontal delineation of LNAPL impacts is complete at the site, with clean borings advanced in all directions, as described in the SCR – 2012 (ARCADIS 2013a).

7.3.3.2 Vertical Distribution of Impacts

Boring logs for monitoring wells and soil borings were reviewed for vertical distribution of LNAPL impacts under the same criteria as areal extents. Cross-sections were generated along the A-A’, B-B’, C-C’, and D-D’ transects shown on Figure 4-1. Vertical LNAPL impacts are presented in the geologic cross-sections included on Figures 4-2A, 4-2B, 4-2C, and 4-2D. Data summarizing the vertical extent of LNAPL impacts for soil borings and monitoring wells onsite in the water table zone are included in Tables 7-6 and 7-7. LIF results with maximum fluorescence are included in Table 7-8. Further data analysis for LIF is included in the SCR – 2012 (ARCADIS 2013a).

Most LNAPL impacts occurred in the gravelly sand unit, which is the deepest and largest unit observed in the subsurface. Generally, the LNAPL smear zone spanned 5 to 10 feet and is located from approximately 488 to 482 feet above MSL (approximately 5 to 12 feet bgs, which is consistent with historical groundwater fluctuations), as shown on the cross-sections. Most soil borings were advanced to depths greater than observed LNAPL impacts, as shown on the geologic cross-sections and Table 7-8.

Based on a review of the LIF logs, a fluorescence response greater than 3 percent was used as an indication of LNAPL depending on the depth and waveform observed. Each waveform was inspected to determine if it was indicative of site LNAPL. LIF detection occurred at depths ranging primarily from 6 to 11 feet bgs, as indicated in Table 7-8. This depth range corresponds well with impacts noted on soil boring logs.

Vertical delineation of LNAPL is complete at the site. The vertical extent of the LNAPL is consistent with a conceptual LNAPL smear zone generated by seasonal groundwater table fluctuations at the site.

7.4 Light Nonaqueous Phase Liquid Mobility Assessment

7.4.1 Light Nonaqueous Phase Liquid Observations in Monitoring Wells

LNAPL accumulations or detections have been observed in 45 observation, recovery, and monitoring wells at the site since 2006. The historical maximum LNAPL thickness measured in observation and monitoring wells (not recovery wells) at the NPR was 4.40 feet in MW-176A in April 2012. In general, maximum LNAPL thicknesses were observed in spring 2012 because the groundwater table was at a historical measured low at the site. In an unconfined aquifer system, an inverse relationship between the groundwater potentiometric surface elevation and LNAPL thickness observations is expected (i.e., LNAPL thicknesses in wells decrease as the groundwater elevation increases). Unconfined or semiconfined aquifer behavior is apparent on most of the hydrographs presented on Figures 7-1A through 7-1H. Hydrographs for monitoring wells MW-135-20, MW-138-20, MW-176A-15, MW-186A-15, O-2, O-11, O-19, R-5, R-14A, S-21, S-44, S-50, and S-51 clearly show this characteristic relationship between groundwater elevation and LNAPL thickness.

Wells MW-115-15, MW-135-20, MW-136-20, R-33, and S-39 have corrected groundwater elevations that are at or above the elevation of the top of well screening. In S-39, LNAPL accumulations in the wells are present only when the corrected groundwater elevation is below the top of well screen, thereby allowing LNAPL to enter the well. LNAPL accumulates in wells MW-115-15, MW-135-20, MW-136-20, and R-33 when the corrected groundwater elevation is above the screened interval, which indicates that the wells are screened in the LNAPL smear zone and the LNAPL saturation below the water table is sufficiently high to allow LNAPL to discharge into the well even though the LNAPL is submerged.

LNAPL thickness in wells has remained fairly constant during the fluid-level monitoring program and the observed variations in LNAPL thickness are due to seasonal groundwater table fluctuations. The potential for LNAPL to migrate is dependent upon the presence of sufficient LNAPL driving head for pore entry, and hydraulic gradient. LNAPL has not been observed in any wells installed downgradient, upgradient, or sidegradient from the existing LNAPL plume impacted areas since the extent was delineated. These observations indicate that the LNAPL plume is not migrating beyond the current footprint.

7.4.2 Light Nonaqueous Phase Liquid Field and Residual Saturations

LNAPL field and residual saturations in soil cores collected from the site were determined through the petrophysical laboratory analyses Free Product Mobility – Water Drive (FPM-WD) Method and Free Product Mobility – Centrifuge (FPM-C) Method. LNAPL is mobile when field saturation exceeds residual saturation (ITRC 2009a). Field saturations from FPM-WD tests were above residual saturation at ASB-02 and ASB-05, which are located near MW-138 and S-20, respectively (see Figure 1 in Appendix O of the SCR – 2011 [Barr 2012b]), indicating that LNAPL is mobile as defined by ITRC (2009a) under saturated conditions. Field saturations exceeded residual saturations for FPM-C testing in ASB-04, ASB-07, and ASB-08, indicating that LNAPL is mobile at the pore scale near these soil core locations during unsaturated conditions. Additional results for LNAPL field and residual saturations are included in Appendix O of the SCR – 2011 (Barr 2012).

7.4.3 Light Nonaqueous Phase Liquid Pore Velocity

The potential for LNAPL movement exists in the subsurface at the pore scale wherever field LNAPL saturations exceed residual saturation; therefore, LNAPL pore velocity was calculated at locations where residual saturation was exceeded to determine the degree of mobility. ASTM suggests that LNAPL pore velocities less than 1 x 10^{-6} cm/s indicate that LNAPL in the formation is functionally immobile (ASTM 2006).

The LNAPL pore velocities calculated at sample depths where field saturation exceeded residual saturation using a calculated LNAPL relative permeability ranged from 2.34 x 10^{-5} to 8.07 x 10^{-4} cm/s. All LNAPL pore velocities exceeded the ASTM functional-immobility criterion. Additional results and detailed output of LNAPL pore velocity calculations are included in Appendix O of the SCR – 2011 (Barr 2012).

7.4.4 Light Nonaqueous Phase Liquid Pore-Entry Pressure

LNAPL migration into pristine soil occurs when sufficient LNAPL head pressure is present in the subsurface at the fringe of the LNAPL plume to displace groundwater from the soil pores. The required LNAPL head pressure to facilitate migration was calculated as critical LNAPL thickness, a more easily measured indicator than head pressure.

The October 2011 LNAPL thicknesses in monitoring wells near six of the eight soil borings were less than the critical head pressures required for plume expansion, indicating limited potential for LNAPL plume expansion . LNAPL thicknesses in monitoring wells near core locations ASB-01 and ASB-04 were greater than the calculated critical LNAPL thicknesses. However, monitoring wells downgradient from ASB-01, and historical thicknesses in the monitoring well near ASB-04, did not exceed the critical LNAPL thicknesses. This indicates there is the potential for LNAPL movement in the core of the LNAPL plume near those locations, but limited potential for LNAPL plume migration into pristine soil at the fringes of the LNAPL plume. Additional information regarding the LNAPL pore entry pressure analysis is included in Appendix O of the SCR – 2011 (Barr 2012).

7.4.5 Dissolved-Phase Plume Stability

Stable or decreasing groundwater concentrations of dissolved LNAPL compounds indicate that the LNAPL plume is stable or decreasing in size. Mann-Kendall statistical analyses can be completed on groundwater quality data to determine trends of dissolved-phase plume stability, as described in Appendix O of the SCR – 2011 (Barr 2012). Mann-Kendall statistical analysis is a component of the Monitoring and Remediation Optimization System (MAROS) computer software package that was developed to analyze groundwater quality data from environmental sites. Mann-Kendall trends presented in the Third Quarter 2013 Groundwater Monitoring Report (ARCADIS 2013i) were not used by the LNAPL assessment. Mann-Kendall analysis completed for the LNAPL assessment using the MAROS program included a broader historical groundwater analytical dataset than the trends presented in the Third Quarter 2013 Groundwater Monitoring Report (ARCADIS 2013i).

Historical groundwater analytical data from April 1987 through September 2013 were analyzed for benzene and xylenes at each onsite well screened at or near the water table. Data were compared to ADEC ACL of 590 µg/L for benzene and 3,450 µg/L for xylenes.

Mann-Kendall statistical analysis was completed using MAROS for wells where benzene and xylenes concentrations exceeded ADEC ACLs during the last four groundwater sampling events. For wells where individual benzene and xylenes did not exceed ACLs, Mann-Kendall statistical analyses were not completed. Additionally, wells with historical exceedances greater than ADEC ACLs, but with at least four consecutive groundwater samples below cleanup levels, were not considered for Mann-Kendall statistical analysis. Wells with less than four historical groundwater samples were not considered in the dissolved-phase plume analysis.

Monitoring well MW-116-15 is the only location that exceeds ACLs during the last four groundwater sampling events and the data was analyzed in MAROS.

Results of the dissolved-phase plume stability analysis are presented on Figure 7-9 as two-sector pie charts, color-coded to indicate the analytical result per benzene and xylenes constituent. Wells without historical exceedances of ADEC ACLs for each constituent are represented with a blue semi-circle. Wells with historical ACL exceedances, but having four consecutive groundwater samples below cleanup levels since the last exceedance, are represented with a black semi-circle and are labeled with the year of last historical exceedance. Wells where the Mann-Kendall statistical analysis was completed are also included on Figure 7-9 and color-coded based on the trend analysis result. Mann-Kendall statistical analysis input and output are included in Appendix 7-I. In addition, the benzene isopleth contour is also plotted on Figure 7-9. Appendix 7-I also includes a summary of the wells considered for the dissolved-phase plume analysis and historical minimum and maximum exceedances for benzene and xylenes compounds.

The majority of groundwater samples collected from these wells have exhibited concentrations of benzene and xylenes constituents below ADEC ACLs. Various wells with historical benzene, toluene, and ethylbenzene exceedances of ACLs have been below these cleanup levels for more than 3 years, further supporting that the dissolved-phase plume is stable or decreasing as established in Appendix 7-I. These trends are influenced by the onsite recovery system, which aids in removal of impacted groundwater.

Mann-Kendall statistical trend results for benzene and xylene are decreasing for MW-116-15.The overall prevalence of groundwater samples below ACLs and decreasing trends of benzene and xylenes in upgradient well MW-116-15 demonstrates that the dissolved–phase plume is stable, which indicates that the LNAPL plume is also stable.

7.5 Light Nonaqueous Phase Liquid Recoverability Assessment

7.5.1 Fraction of Recoverable Light Nonaqueous Phase Liquid

The fractions of recoverable LNAPL were calculated at the eight ASB soil boring locations using site-specific LNAPL field and residual saturations derived from the undisturbed soil core petrophysical testing. In homogeneous settings, LNAPL thickness in a well indicates LNAPL saturation in the adjacent formation. Mobile, and therefore theoretically recoverable, LNAPL is present when field LNAPL saturation exceeds residual saturation. Residual saturation was not exceeded at soil boring locations ASB-01, ASB-03, and ASB-06, which indicates that there is negligible recoverable LNAPL near those boring locations. These locations are show on figures in Appendix O of the SCR – 2011 (Barr 2012).

Fractions of recoverable LNAPL ranged from 1.1 to 31.6 percent for the five soil cores with field LNAPL saturations exceeding residual saturations. The high proportion of recoverable LNAPL at ASB-05 (27.9 percent) and ASB-07 (31.6 percent) located in the central and western areas, respectively, of the LNAPL impacts is corroborated by the productive LNAPL recovery systems located near these soil core locations. Recoverable LNAPL at the lower end of this range (1.1 to 6 percent) in soil cores ASB-08 in the western area of LNAPL impacts and ASB-02 and ASB-04 in the southern area of LNAPL impacts is inconsistent with LNAPL thicknesses accumulating in nearby wells. These data are discussed in Appendix O of the SCR – 2011 (Barr 2012). Boring locations are located on Figure 1 in Appendix O of the SCR – 2011 (Barr 2012).

7.5.2 Light Nonaqueous Phase Liquid Transmissivity

The recoverability of LNAPL is influenced by many factors, including LNAPL saturation in the impacted soil, soil permeability, and physical properties of the LNAPL. LNAPL transmissivity represents the volumetric rate of LNAPL flow through a unit width of porous media per unit time under a unit hydraulic gradient. A direct mathematical relationship exists between LNAPL transmissivity and the rate of LNAPL flow into a well; therefore, it is an ideal parameter for assessing LNAPL recoverability. LNAPL transmissivity calculations inherently account for the combined effects of aquifer matrix permeability, LNAPL physical properties, and the relative proportion of pore space occupied by LNAPL within a specified vertical interval of aquifer material.

7.5.2.1 Light Nonaqueous Phase Liquid Manual Skimming Tests Results

On October 15, 2013, the LNAPL transmissivity determined through manual LNAPL skimming testing at MW-344-15 was 141 ft^2/day, which is three magnitudes greater than the suggested lower limit of the practicable recoverability criterion range of 0.1 to 0.8 ft^2/day (ITRC 2009a). Based on this result, LNAPL recovery by hydraulic methods at this well is feasible and will lead to beneficial reduction of overall LNAPL mass. Recovery well R-45 was installed adjacent to this location and water-enhanced LNAPL recovery is ongoing. Additionally, MW-334-15 was over-drilled and a 4-inch well was installed to allow more effective LNAPL recovery. The LNAPL manual skimming test results are included in Table 7-9 and on Figure 7-10. Appendix 7-J includes data analysis output.

7.5.2.2 Light Nonaqueous Phase Liquid Baildown Test Analyses Results

LNAPL baildown tests have been completed semiannually since October 2011 in wells with sufficient LNAPL accumulation to support testing. Data from the LNAPL baildown tests completed at MW-176A, O-27, O-31, O-33, O-34, S-21, and S-39 in October 2013 are included in Table 7-10. API Workbook (API 2012) output data for LNAPL baildown tests are included as Appendix 7-K. Figure 7-10 contains current and historical LNAPL transmissivity results for monitoring wells where LNAPL baildown tests were completed.

LNAPL baildown tests at MW-176A, O-31, O-34, S-21, and S-39 were analyzed using the modified Bouwer and Rice (1976) method. Calculated LNAPL transmissivities at monitoring wells MW-176A, O-31, O-34, and S-39 are below or on the lower end of the transmissivity criterion range of 0.1 to 0.8 ft^2/day (ITRC 2009a). This indicates that LNAPL recovery via hydraulic methods is negligible and these wells will not produce sufficient LNAPL to beneficially reduce the overall LNAPL mass. LNAPL transmissivities for both tests completed at S-21 are greater than the transmissivity criterion range with transmissivities of 1 and 1.6 ft^2/day. While these results still exceed the LNAPL transmissivity criterion range, comparing these results to the analyzed tests at S-21 in May 2012 shows a significant decrease in LNAPL transmissivity. LNAPL recovery at this well via hydraulic means may be beneficial in overall reduction of the LNAPL plume.

LNAPL transmissivities for the LNAPL baildown tests completed at O-27 and O-33 in October 2013 could not be resolved quantitatively due to poor LNAPL recovery into the well after fluid removal. These tests could not be analyzed using the API Workbook (API 2012) based on these results. Qualitative assessment of these tests indicates low LNAPL transmissivity. Well O-27 only recovered to 10 percent of the initial LNAPL thickness in more than 6.75 hours of fluid-level gauging and O-33 only recovered to 36 percent of the initial LNAPL thickness in more than 3 days of fluid-level gauging.

7.5.2.3 Water-Enhanced Recovery Results

LNAPL transmissivity was calculated through analysis of water-enhanced recovery data for R-21 from January 2010 through October 2013, R-35R from January 2010 through June 2012, and R-40 from January 2010 through April 2013. The analysis method includes an underlying assumption that the fluid recovery rate is low enough that LNAPL and groundwater move horizontally through the aquifer to the recovery well. The groundwater pumping rates at these wells creates localized drawdown that violates the horizontal LNAPL flow assumption. While this likely results in error in the transmissivity results, the calculation was pursued to provide an approximation of the LNAPL transmissivity observed at these locations.

The average quarterly LNAPL transmissivity ranged from 0.02 to 1.4 ft^2/day for R-21 when transmissivity was greater than zero. The overall average transmissivity for R-21 was 0.32 ft^2/day from January 2010 through October 2013. The average LNAPL transmissivity ranged from 1.07×10^{-3} to 0.07 ft^2/day for R-35R, with an overall transmissivity average of 0.03 ft^2/day from January 2010 through June 2012. The average LNAPL transmissivity ranged from 0.01 to 0.16 ft^2/day for R-40, with an overall transmissivity average of 0.07 ft^2/day from January 2010 through April 2013. Results from the water-enhanced recovery systems are shown in Tables 7-11, 7-12, and 7-13 and summarized in Table 7-14. Appendix 7-D includes data analysis output.

The 2013 LNAPL transmissivities in R-21, R-35R, and R-40 are generally lower than the lower limit of the ITRC criterion range, but historically have been above the lower limit. These wells have produced a significant volume of LNAPL through time and this finding may indicate that the calculated LNAPL transmissivities for the recovery wells are skewed low due to the large drawdown. LNAPL transmissivity fluctuates in all three wells during the time periods specified above, and at times is greater than the suggested lower limit of the practicable recoverability criterion range of 0.1 to 0.8 ft^2/day (ITRC 2009a).

7.5.2.4 Pneumatic Skimming Results

LNAPL transmissivity was calculated through analysis of the continuous automated LNAPL pneumatic skimming data for MW-138 from January 2010 through October 2013, and for R-20R from August 2011 through October 2013 (Table 7-15). The average LNAPL transmissivity ranged from 0.4 to 1.6 ft^2/day for R-20R from August 2011 through October 2013. The average LNAPL transmissivity ranged from 0 to 17.5 ft^2/day for MW-138 from January 2010 through October 2013. Results from automated LNAPL pneumatic skimming are summarized in Table 7-16. Appendix 7-E includes data analysis output.

LNAPL transmissivity in both MW-138 and R-20R is predominately greater than the suggested upper limit of the practicable recoverability criterion range of 0.1 to 0.8 ft^2/day (ITRC 2009a). Based on these results, LNAPL recovery at these wells is feasible and will continue because it will lead to beneficial reduction of overall LNAPL mass.

7.6 Natural Source Zone Depletion

An NSZD evaluation conducted as part of the SCR – 2011 (Barr 2012) used site-specific data from 2011 in the saturated zone and assumptions to estimate the mass loss in the unsaturated zone because site-specific soil gas quality and diffusivity data were not available at that time. This NSZD evaluation update includes soil gas quality and site-specific soil gas diffusivity data that were collected in 2013. Details regarding the collection of soil gas samples and calculation of soil gas diffusivity data are presented in Section 9. The saturated zone NSZD evaluation also includes groundwater data collected in April, May, and June 2013.

7.6.1 Qualitative Assessment of Natural Source Zone Depletion

Biodegradation and dissolution of the submerged portion of the LNAPL can be assessed by comparing the chemical composition of groundwater upgradient from the source zone with groundwater immediately downgradient. Biodegradation of petroleum hydrocarbons results in a decrease in electron acceptor concentrations and a corresponding increase in biodegradation transformation products between upgradient, and within and/or downgradient from the LNAPL plume. The relevant biogeochemical data (oxygen, nitrate, sulfate, dissolved iron, dissolved manganese, and methane) are presented in Table 7-2. A comparison of the upgradient (MW-105A) and source zone/downgradient (MW-116 and MW-176A) data indicates the following:

- Sulfate decreased from 39 mg/L at the upgradient monitoring location to an average of 1.9 mg/L in the source zone monitoring locations, indicating sulfate reduction from anaerobic degradation.

- Dissolved iron increased from 1.24 mg/L at the upgradient monitoring location to an average of 37.6 mg/L in the source zone monitoring locations, indicating iron reduction from anaerobic degradation.

- Dissolved manganese increased from 0.428 mg/L at the upgradient monitoring location to 7.5 mg/L in the source zone monitoring locations, indicating manganese reduction from anaerobic degradation.

- The methane concentration increased from 0.06 mg/L at the upgradient location to 6.7 mg/L at in the source zone monitoring locations, indicating carbon dioxide reduction or organic acid fermentation from anaerobic degradation.

- There was no significant change in DO or nitrate concentrations across the LNAPL source zone. This observation is a result of the fact that the aquifer is naturally anoxic and nitrate is present in the aquifer at nominal levels; therefore, neither oxygen nor nitrate are readily available electron acceptors at the site.

The above spatial comparison of upgradient and source zone/downgradient natural attenuation parameters shows a clear decrease in electron acceptor concentrations and an increase in biodegradation transformation product concentrations, which demonstrates that biodegradation of LNAPL is occurring.

Soil gas samples were used to construct soil gas content profiles for SG-01 through SG-06, as shown on Figure 7-11. The soil gas profiles provide evidence of NSZD via vapor-phase transport. Inspection of the soil gas content profiles shows that:

- Methane was detected in all soil gas samples and increased with depth, indicating that methanogenesis is occurring in the saturated zone, methane is transferred to the vadose zone via ebullition (due to low aqueous solubility of methane), and the gaseous methane is consumed in the vadose zone by methanotrophs.

- Volatile hydrocarbons were found in soil gas and increased with depth, indicating that LNAPL is being depleted via volatilization and the volatile hydrocarbons in soil gas are being consumed in the vadose zone by soil microorganisms.

- Carbon dioxide, which is a product of aerobic biodegradation of hydrocarbons and methane, was greater than atmospheric conditions and increased with depth at all locations.

- Oxygen content decreased with depth at all soil gas locations.

These observations indicate that LNAPL depletion is occurring and biodegradation of hydrocarbons and methane is occurring in the vadose zone.

7.6.2 Quantitative Estimate of Natural Source Zone Depletion

The extent of LNAPL-affected soil was determined from historical observations of LNAPL at the site. The NSZD evaluation uses an LNAPL source plume total area estimate of 23 acres, based on the spatial distribution of monitoring wells with historical LNAPL accumulations, soil borings with indications of LNAPL, and LIF data (Figure 7-8). The cross-sectional area of the saturated zone affected by LNAPL, perpendicular to the groundwater flow direction, was estimated to be 1,050 feet based on historical observations of LNAPL in R-8 on the west side of the site and SB-129 and O-29 on the east side of the site (Figure 7-8). The saturated LNAPL source zone (i.e., thickness of dissolved-phase-impacted groundwater in the LNAPL footprint) is approximately 10 feet thick, based on LIF, LNAPL indicators in soil and monitoring well borings, LNAPL observations in monitoring wells, and dissolved-phase concentrations.

LNAPL impacts are evident extending 13 to 18 feet below ground, approximately 5 feet into the groundwater table, on average, as discussed in Section 9 and shown in Table 7-6. Dissolved-phase impacts generally extend into groundwater below the bottom of LNAPL. For example, in May 2011, petroleum-impacted groundwater was detected in MW-125. Monitoring well MW-125 has a screened interval from 19.5 to 24 bgs and the measured depth to water on that day was 12.5 bgs, indicating that dissolved-phase impacts exist at least to 19.5 bgs, which is 7.5 feet into the water table. Parameters used in the analysis are presented in Table 7-17 and NSZD calculations are detailed in Appendix 7-L.

7.6.2.1 Estimate of Source Zone Mass Depletion by Dissolution to Groundwater in the Saturated Zone

LNAPL mass loss occurs via dissolution of hydrocarbons into water as groundwater moves through the subsurface and contacts LNAPL-impacted soil within the saturated zone. The flux of groundwater exiting the LNAPL source area and the concentrations of hydrocarbons that dissolve into groundwater dictates the mass loss. Based on the average hydraulic conductivity, site groundwater gradient, and cross-sectional area of the impacted groundwater, approximately 280 cubic meters (m^3) of groundwater exits the source area every day. The average dissolved-phase concentration of petroleum compounds in the wells immediately downgradient from the source areas (but upgradient from the groundwater recovery system) was 9.9 mg/L.

Using Equation 5 and the plume parameters presented in Table 7-17, the LNAPL mass depletion rate as a result of dissolution is estimated to be between 200 and 1,000 kilograms (kg) TPH per year based on the range of water hydraulic conductivities reported by Barr (2013a). This equates to between 100 and 300 gallons of LNAPL depleted per year.

7.6.2.2 Estimate of Source Zone Mass Depletion Rate by Biodegradation in the Saturated Zone

Mass loss of LNAPL via biodegradation of hydrocarbons is controlled by groundwater flux into the LNAPL source zone, as discussed above, and the availability of electron acceptors in groundwater or the aquifer matrix. The assimilative capacity of the aquifer is 1.6 x 10^{-2} kg TPH per m^3 of groundwater. This capacity comprises approximately 43 percent sulfate reduction, 44 percent methanogenesis, 9 percent iron reduction, and less than 4 percent manganese reduction.

Using Equation 6 and the plume parameters presented in Table 7-17, the mass depletion rate due to biodegradation in the saturated zone is estimated to be between 500 and 2,900 kg TPH per year based on the range of water hydraulic conductivities reported by Barr (2013a). This equates to between 200 and 900 gallons of LNAPL depleted per year.

7.6.2.3 Estimate of Source Zone Mass Depletion Rate by Volatilization and Biodegradation in the Unsaturated Zone

Source zone depletion through volatilization and biodegradation is determined by the rate of oxygen consumption in the subsurface. Inspection of the soil gas profiles (Figure 7-12), indicates that aerobic activity primarily occurs in the shallow vadose zone for soil gas probe locations SG-02 through SG-06. This observation is based on the vertical change in oxygen content with increasing depth, which shows a greater change in oxygen content between surface and the shallow soil gas point than between the shallow and deep soil gas point. Based on this observation, the horizontal mass-balance control plane was placed at the shallow soil gas probe for these locations and the difference between oxygen in atmospheric gas and measured oxygen concentration at the shallow probe was used to determine the NSZD rate.

Oxygen content in soil gas at SG-01 was higher and methane and VOC contents were lower than the observations at other soil gas probes. Review of the SG-01 soil boring log indicates that SG-01 was not installed in a location with LNAPL impacts; the maximum PID reading at that location was 1.2 ppm. The soil gas sample collected from SG-01 had elevated carbon dioxide, methane, and volatile hydrocarbons compared to atmospheric air. This result may indicate that minor hydrocarbon impacts are present and aerobic consumption of those hydrocarbons is occurring or may be a result of lateral movement of soil gas from known LNAPL-impacted areas near SG-01. An NSZD rate was not calculated for SG-01 because it is not representative of NSZD in the LNAPL-impacted areas.

Because the theoretical horizontal plane was placed at the shallow soil gas probes, the effective diffusivity for the shallow soil gas probes, representing the shallow lithology, were used in Equation 7. The hydrocarbon depletion rate at the five locations ranges from 3,400 to 15,000 kg hydrocarbon per acre per year, or approximately 1,100 to 4,700 gallons of LNAPL per acre per year (Figure 7-12). Recent literature publications (Lundegard and Johnson 2006, Sihota et al. 2011) and ARCADIS' experience suggest that the magnitudes of petroleum hydrocarbon LNAPL losses through NSZD often fall within the range of hundreds to thousands of gallons per acre per year, which is consistent with these results.

The highest NSZD rate of 4,700 gallons per acre per year was found at SG-03. The oxygen content in the soil gas sample from SG-03 was similar to that observed in SG-02, SG-04, SG-05, and SG-06; however, the VOC and methane contents were low compared to other locations. This soil gas probe is in a Jet A-/naphtha-mixed LNAPL, with a large portion of VOCs and alkanes as indicated in the PIANO analysis. The PIANO data indicate that the LNAPL at this location is highly volatile and would readily partition into soil gas. The low VOC and methane concentrations at SG-03 compared to other locations may be explained by the gas diffusivity properties of the soil at SG-03, which was 2 to 5 times the value calculated at the other shallow soil gas probes. The higher gas diffusivity suggests that the rate of oxygen diffusion into the formation near SG-03 is higher than other locations, which supports a higher rate of aerobic biodegradation, thereby preventing accumulation of VOCs and methane.

Based on the average estimated mass loss rate and the LNAPL footprint of 23 acres, the total estimated mass loss rate due to natural processes as measured in the unsaturated zone is approximately 51,000 gallons per year. This annual estimate does not reflect the fact that LNAPL depletion may be slower in the winter due to soil diffusivity changes from soil freezing and/or decreases in subsurface temperature that may affect biological activity. However, even if this depletion rate is only representative for a few months of the year, the overall finding that natural LNAPL depletion is occurring at a rate of tens of thousands of gallons per year is significant.

7.7 Summary of Results

7.7.1 Light Nonaqueous Phase Liquid Delineation and Characterization

The areal and vertical extents of LNAPL impacts are delineated at the site. This determination is based on observations made during well and soil boring installation, including: olfactory observances, staining/sheen observances, and elevated PID readings. LIF and hydrocarbon pore saturations were also considered for horizontal delineation.

7.7.2 Light Nonaqueous Phase Liquid Composition Summary

The composition of LNAPL at the site is consistent with refined products that have historically been produced at the NPR. Jet A appears to be the primary refined product type in LNAPL samples at the site (Figure 7-13). Secondary product types include naphtha (in the northeastern portion of the site) and diesel #2 (in the southern portion of the site). Mixtures of refined products (e.g., Jet A/naphtha; Jet A/diesel #2 mixtures) are present at the interface of primary and secondary product types.

LNAPL is not a significant source or sink of sulfolane to groundwater based on 24 LNAPL samples collected from 16 wells. The highest LNAPL sulfolane concentration observed was 573 µg/kg in a sample collected from MW-138-20 in April 2011. However, a subsequent sample collected from this monitoring well in April 2013, and analyzed by an updated laboratory method, was less than analytical reporting limits (<80 µg/kg).

7.7.3 Light Nonaqueous Phase Liquid Mobility

LNAPL at the site is mobile within the interior and fringe of the LNAPL plume and has the potential to migrate if LNAPL recovery ceases or hydrogeologic conditions change at the site. These findings are supported by multiple LNAPL mobility assessment lines of evidence:

- Petrophysical testing of undisturbed soil cores collected from the site showed that field saturations exceeded residual saturations at two locations in the southern area of LNAPL impacts, at one soil boring located in the central area of LNAPL impacts, and at two soil borings located in the western area of LNAPL impacts. LNAPL is mobile in these areas, meaning that LNAPL can redistribute vertically and horizontally within the existing LNAPL footprint.

- Pore velocity potentials were calculated using LNAPL relative permeability from API equations at five soil core locations where field saturation exceeded residual saturation. All calculated pore velocities exceeded the ASTM mobility criterion of 1×10^{-6} cm/s. LNAPL mobility is significant as demonstrated by pore velocities and the degree to which the mobility criterion is exceeded.

- The LNAPL pore-entry pressure analysis showed current and historical observed LNAPL thicknesses exceeding the critical LNAPL thicknesses calculated. This conservative analysis indicates that sufficient head pressure is present for potential LNAPL migration into pristine soil at all eight soil core locations. LNAPL migration can be confirmed by monitoring for LNAPL in sentry wells (wells installed downgradient from LNAPL impacts).

However, while the LNAPL is mobile and has the potential to migrate, the following mobility analyses indicate that the LNAPL plume is stable and not migrating:

- Overall trends between groundwater elevations and LNAPL thicknesses represent unconfined or semiconfined conditions with large seasonal fluctuations. LNAPL has not accumulated in any new wells downgradient, sidegradient, or upgradient from the existing LNAPL footprint. This indicates that the LNAPL plume is not migrating and is mostly contained within the recovery zone.

- Dissolved-phase benzene and xylenes concentrations are primarily below ACLs, especially in monitoring wells at the plume periphery. Where monitoring wells had exceedances above ACLs in the last four groundwater samples, Mann-Kendall statistical analysis was completed (which was on location: MW-116-15). Most results from the Mann-Kendall analysis indicated decreasing trends upgradient in the central part of LNAPL impacts at the site. These results suggest that the dissolved-phase benzene and xylenes plumes are stable, which indicates at the site-wide scale that the LNAPL plume is also likely stable.

- Petrophysical testing of undisturbed soil cores collected from the site showed field saturations at residual saturation at one location on the leading edge of the plume and at two locations in the eastern area of LNAPL impacts at the NPR, indicating that LNAPL is immobile in these fringe areas. This observation is tempered by the suspected fluid loss during soil core collection.

7.7.4 Light Nonaqueous Phase Liquid Recoverability

7.7.4.1 Fraction of Recoverable Light Nonaqueous Phase Liquid

Fractions of recoverable LNAPL ranging from 1.1 to 31.6 percent were calculated for the five soil cores with field LNAPL saturations exceeding residual saturations. The high proportion of recoverable LNAPL at ASB-05 (27.9 percent) and ASB-07 (31.6 percent) located in the central and western areas, respectively, of the LNAPL impacts, is well-supported by productive recovery systems located near these soil core locations.

7.7.4.2 Light Nonaqueous Phase Liquid Transmissivity

LNAPL transmissivity has been assessed at the site using multiple methods. Transmissivity data have been collected from several locations across the site to assess the variability of LNAPL transmissivity due to seasonal groundwater table fluctuations, as summarized below:

- An LNAPL manual skimming test conducted in October 2013 showed that LNAPL is readily recoverable at MW-334-15. The LNAPL transmissivity value from the 3-hour manual skimming test was four orders of magnitude greater than the ITRC (2009a) suggested lower criterion range for LNAPL recoverability.

- LNAPL baildown tests conducted at the site suggest that the LNAPL recoverability at individual well locations varies through time. This is the expected outcome because groundwater table fluctuations influence LNAPL transmissivity. LNAPL transmissivities measured in baildown tests conducted in October 2013 were generally below the ITRC (2009a) LNAPL transmissivity criterion, except for both baildown tests completed at S-21. However, baildown tests at several locations have resulted in LNAPL transmissivity above the ITRC (2009a) criterion in the past.

- LNAPL transmissivity in R-21, R-35R, and R-40 is generally lower than the lower limit of the ITRC (2009a) criterion range in 2013, but these results may be skewed low by the high pumping rates and groundwater table drawdown at these wells. These DPE wells have produced a substantial volume of LNAPL through time.

- LNAPL transmissivity in both MW-138 and R-20R is greater than the suggested upper limit of the practicable recoverability criterion range of 0.1 to 0.8 ft^2/day (ITRC 2009a) based on ongoing LNAPL skimming conducted at those wells. Based on these results, the ongoing LNAPL recovery will be continued and lead to beneficial reduction of overall LNAPL mass.

7.7.5 Natural Source Zone Depletion Evaluation Summary

A qualitative evaluation of the chemical composition of groundwater and soil gas indicates that LNAPL is being depleted through natural processes, including dissolution, volatilization, and biodegradation in the saturated and unsaturated zones. NSZD rates were quantified and the idealized total mass loss rate is 51,000 gallons per year in the saturated and unsaturated zones. This depletion rate may be biased high due to seasonal changes in soil diffusivity and biological activity. However, at a minimum, the natural LNAPL depletion rate at the site is on the order of tens of thousands of gallons per year.

7.8 Conclusions

The nature and extent of LNAPL has been thoroughly characterized through 26 years of data collection on petroleum impacts at the site, bolstered by intense efforts to assess LNAPL composition, mobility, and recoverability in the past 3 years. The extent of LNAPL impacts is known, LNAPL is not a significant source of sulfolane to groundwater, the LNAPL plume is stable, the dissolved-phase benzene and xylenes plumes are stable, LNAPL is readily recoverable in some areas of the site, and natural processes are depleting the LNAPL at a significant rate.

8. Soil Gas Investigation

FHRA conducted a soil gas investigation at the NPR on August 27 through 30, 2013 and September 16, 2013 as proposed in the Onsite SCWP (ARCADIS 2013d). The primary objective of this investigation was to evaluate soil gas composition to determine the viability of inducing air flow in the unsaturated zone to enhance microbial degradation (bioventing) as an LNAPL remediation technology. The secondary objectives of the soil gas investigation included the following:

- Quantify the fraction of soil gas that is composed of volatile hydrocarbons and/or methane and determine whether soil gas poses a potential explosion risk at the site.
- Refine the NSZD evaluation previously completed for the site (Appendix O of the SCR – 2011 [Barr 2012]).
- Assess the distribution of volatile hydrocarbons in relation to various petroleum LNAPLs that have been observed at the site.

Soil gas samples were collected from nested soil gas sampling probes at six locations within the LNAPL-impacted area at the site, as shown on Figure 7-11.

8.1 Field Methods

Vertically nested soil gas sampling probes were installed within LNAPL-impacted areas to capture conditions representative of different types of LNAPL identified at the site (Figure 7-11). Soil gas samples were collected from each of the nested soil gas sampling probes. Prior to sampling, the soil gas sampling probes were field screened for fixed gases and volatile hydrocarbons. Soil diffusivity testing was completed at each soil gas location after soil gas samples had been collected. The field methods used during this investigation are summarized below.

8.1.1 Soil Gas Probe Installation

Six permanent multilevel soil gas probes (SG-01 through SG-06) were installed at the NPR. The soil gas probe boring locations were manually cleared using vacuum truck and hand auger techniques to a final depth of approximately 6 to 8 feet bgs. The total depth of each borehole was determined based on observed soil moisture.

Soil samples were collected by advancing a hand auger at 1-foot intervals ahead of the vacuum-cleared depth for field screening. The soil was screened in the field using a PID, and described by the supervising field staff using visual methods of the USCS.

After advancing the borehole, a 6-inch-long, 0.375-inch-outer-diameter stainless steel soil vapor screen was set at the appropriate depth in a 1-foot interval of sand pack, allowing approximately 3 inches of sand above and below the screen. Teflon®-lined polyethylene tubing was connected to the vapor screen and capped with a gas-tight cap at the surface to eliminate the potential for gas transfer between the subsurface and the atmosphere, induced by barometric pressure fluctuations. The soil gas probe and sampling train connections were completed with compression fittings equivalent to Swagelok™ specifications.

A 1-foot interval of dry, granular bentonite was placed above the sand pack followed by an interval of hydrated bentonite grout to the depth of the next sample probe. Sand pack was used around the screened interval of each sample probe to allow soil gas from the adjacent soil to reach the probes. Dry granular bentonite was used above the sand pack to ensure that the hydrated bentonite did not enter the sand pack and to potentially inhibit soil gas flow. At the surface, the nested probe location was secured with a traffic-rated well box set in concrete. Soil gas probes were left to equilibrate for a minimum of 48 hours prior to field screening, sampling, and diffusivity testing. Typical soil gas probe construction is presented on Figure 8-1 and actual construction of the nested soil gas probes is summarized in the boring logs included in Appendix 8-A.

Two soil gas probes were installed in each of the nested soil gas probe locations because a minimum of 2 feet of bentonite is required to properly seal the soil gas probe, and the depth to groundwater is approximately 8 feet bgs. The depth of the deepest probe was determined in the field and was placed above the depth where soil moisture was visually observed. The shallow probe was installed at least 3.5 feet bgs to assure a proper seal with the ground surface. Soil gas probes were installed at the following depth intervals:

- SG-01: 3.5 and 6 feet bgs
- SG-02: 3.5 and 6.5 feet bgs
- SG-03: 3.5 and 6.5 feet bgs
- SG-04: 4 and 7 feet bgs
- SG-05: 4 and 8 feet bgs
- SG-06: 3.5 and 6.5 feet bgs

8.1.2 Leak Testing Methods

Leak testing was conducted to ensure the integrity of the soil gas samples. Three tests were conducted for each sample:

1. Monitored purge air during field parameter readings to ensure that the bentonite seals were competent at each of the soil gas probes.

2. Performed shut-in tests to ensure that the sample trains were airtight.

3. Conducted soil gas sampling in a helium shroud as a final quality check of the soil gas samples.

Leak testing was completed at each soil gas probe simultaneously with field screening in accordance with ARCADIS SOP #416199, Rev. 3, Administering Helium Tracer Gas for Leak Checks of Soil Gas or Sub-Slab Sampling Probes, which is included in Appendix 8-B. An enclosure was constructed around the well head. Helium, used as the tracer compound for the leak test, was metered into the enclosure and monitored for concentration stability with a helium detector. The helium content of the gas in the enclosure was maintained at approximately 10 to 20 percent during the screening at each location. Purged soil gas was screened for helium in the field using a helium detector. This testing was conducted to verify the integrity of the soil gas probe bentonite seal during the field screening procedures. The helium shroud enclosed the well head and the sampling train during the soil gas sampling field procedures.

A shut-in leak detection test was completed prior to purging and sampling to assure the integrity of the sampling train. One gas-tight two-way ball valve was installed closest to the soil gas probe (probe valve) and another gas-tight two-way ball valve was installed on the opposite end of the sampling train (purge valve). While the probe valve was left in the closed position, a laboratory-provided syringe was used to remove approximately 25 milliliters (mL) from the purge probe, inducing a vacuum of -8 inches of mercury (approximately -108 inches of water) within the sampling train. The purge valve was closed and the vacuum within the sampling train was monitored for a minimum of 2 minutes. If any observable loss occurred in the vacuum within the sampling train after 2 minutes, fittings were adjusted and the test repeated until the vacuum in the sampling train did not dissipate.

The final leak detection test included constructing a helium-filled enclosure around the well head and entire sampling train (valves, tubing, fittings, gauges, and SUMMA™ canister) to check for leaks during soil gas sample collection. Helium was analyzed in the laboratory and used as a leak tracer compound for each soil gas sample collected.

In the field, helium was screened with a Radioelectronics™ MGD-2002 helium detector that was calibrated by the manufacturer within the past 6 months. The field meter was zeroed with ambient air and checked against the helium source to ensure the calibration was accurate.

8.1.3 Field Measurement Methods

Field screening of soil gas was completed at each nested soil gas probe location. Soil gas was purged from each soil gas probe interval at a rate of less than (<) 200 milliliters per minute (mL/min) using a pre-calibrated air sampling pump. The effluent air from the air sampling pump was collected in a Tedlar® bag for screening.

Soil gas was screened with the following calibrated field meters: Landtec GEM™2000 Landfill meter, RKI Eagle™ 2, and a PID. Purged soil gas was screened for oxygen, carbon dioxide, methane (with and without a granular activated carbon [GAC] filter), total volatile hydrocarbons (TVH) with the RKI Eagle 2, and VOCs with a PID. Field measurements were recorded on field sheets and are included in Appendix 8-C.

The RKI Eagle 2 and PID field meters were calibrated in the field each day prior to screening with calibration gas mixtures. The Landtec GEM 2000 detector was calibrated by the manufacturer within the past 6 months. These field meters were zeroed with ambient air and checked against the appropriate calibration gases prior to use to ensure that the calibration was accurate.

Calibration gas mixtures that were used included fixed gases such as oxygen (12 percent), carbon dioxide (10 percent), hexane (0.48 percent), and methane (2.5 percent). VOCs and TVH were calibrated for the RKI Eagle 2 and PID using isobutylene (100 ppm) calibration gas. Calibration gases were administered to the respective meters using a gas cylinder regulator. Calibration was considered completed when measurements were within 10 percent of the calibration gas concentration.

8.1.4 Soil Gas Sampling Methods

Sampling procedures for the September 2013 soil gas sampling event were consistent with the procedures described in ARCADIS SOP #428199, Rev. 4, Soil Gas Sampling Using Single or Nested Probes, which is included in Appendix 8-B.

To minimize potential ambient air influence during purging, a gas-tight two-way valve was installed in the sampling train. Purging consisted of opening the two-way valve, then removing approximately 3 volumes of stagnant soil gas using a laboratory-provided syringe. The purge volume was determined by the dimensions of the aboveground gauges, tubing, sampling equipment, and below ground tubing. Effluent purged air was collected from the syringe in a Tedlar® bag and field measured for helium using a helium detector to assess sample train and soil gas probe bentonite seal integrity. Once purging was completed, the two-way valve was closed to prevent ambient air from entering the sample train.

The soil gas sample was then collected using a 1-liter SUMMA canister with a laboratory-provided flow regulator set to approximately 100 mL/min for 10 minutes. Laboratory-supplied SUMMA canisters were batch certified by the laboratory prior to field receipt. Initial and final vacuum gauge readings were taken for each sample and recorded on the soil gas sample collection logs included in Appendix 8-D.

Due to high concentrations of methane present at soil gas probe location SG-02 during field screening (Appendix 8-C), an alternative sampling method was implemented to allow for shipment of potentially flammable soil gas samples. The alternative sampling method uses Tedlar bags and sorbent tubes as described below instead of a single 1-liter SUMMA canister. Soil gas samples were collected from probe location SG-02 using a vacuum box and Tedlar bag. The vacuum box and Tedlar bag were connected to the SG-02 sampling train and all quality control (QC) procedures (shut-in and leak testing) were completed prior to collecting the sample. The soil gas samples were collected by evacuating air from the vacuum box that contained the Tedlar bag at a rate of approximately 100 mL/min using a precalibrated air sampling pump. The Tedlar bag was connected to the sampling train by compression fittings and Teflon®-lined poly tubing. As the vacuum box was evacuated, the Tedlar bag filled with soil gas due to the pressure differential.

Naphthalene has a low vapor pressure, which results in adsorption onto the Tedlar bag surface and low recovery during analysis. Due to the limitations of Tedlar bags for naphthalene sampling, sorbent tube sampling methods were also used at soil gas probe location SG-02. Soil gas was collected by attaching a laboratory-provided sorbent tube containing a multisorbent material to the sampling train two-way valve. Soil gas was actively pulled through the sorbent tube using a laboratory-provided syringe at a flow rate of ≤100 mL/min. The required volume of 60 mL was collected, as determined by the laboratory to achieve the required reporting limits. The effluent sampled air was collected in a Tedlar bag and field tested for the presence of helium using the helium detector. After sample collection, the sorbent tube was sealed using compression caps on both sides of the tube. ARCADIS SOP #112409, Rev. 1, Soil-Gas Sampling and Analysis Using USEPA Methods TO-17 and TO-15, is included as Appendix 8-B.

One duplicate sample was collected in-line with the parent sample for each sampling method used (SUMMA canisters, Tedlar bag, and sorbent tube). The parent and duplicate samples were collected concurrently using a laboratory-supplied duplicate tee fitting. Duplicate samples were collected as follows:

- BD-1 was collected from SG-05 at 8 feet bgs in a SUMMA canister and analyzed for TO-15 and fixed gases.

- BD-2 was collected from SG-02 at 6.5 feet bgs in a sorbent tube and analyzed for TO-17.

- BD-3 was collected from SG-02 at 6.5 feet bgs in a Tedlar bag and analyzed for TO-15 and fixed gases.

One equipment blank sample was collected by transferring the contents of a laboratory-provided 1-liter pressurized SUMMA canister to an evacuated 1-liter SUMMA canister during the soil gas sampling event. Transfer was achieved using a section of Teflon-lined polyethylene tubing attached to a decontaminated two-way valve assembly used during sampling.

One field blank was also collected in the field by opening a laboratory-provided sorbent tube and exposing it to current field conditions per ARCADIS SOP #112409 (Appendix 8-B). The sorbent tube was resealed with compression caps on both sides of the tube.

8.1.4.1 Analytical Methods

Each sorbent tube sample was retained in the laboratory-provided ice-chilled cooler, and transported to an Alaska-certified laboratory under chain of custody documentation for analysis. The SUMMA canister, Tedlar bag, and sorbent tube soil gas samples were shipped to Eurofins/AirToxics, Ltd. in Folsom, California for the following analyses:

- Benzene, toluene, ethylbenzene, m,p-xylene, o-xylene, 1,3,5-TMB, and naphthalene by USEPA Method TO-15.

- VPH by USEPA Method TO-15 for the following analytes:

  - C5 to C6 aliphatic hydrocarbons
  - Greater than C6 to C8 aliphatic hydrocarbons
  - Greater than C8 to C10 aliphatic hydrocarbons
  - Greater than C10 to C12 aliphatic hydrocarbons
  - Greater than C8 to C10 aromatic hydrocarbons
  - Greater than C10 to C12 aromatic hydrocarbons

- Naphthalene by USEPA Method TO-17.

- Fixed gases (oxygen, carbon dioxide, nitrogen, and methane) by ASTM Method D1946.

8.1.5 Diffusion Testing Methods

Porous medium gas diffusion coefficients are required to calculate oxygen flux into the subsurface. ARCADIS followed the approach described by Johnson et al. (1998), which evaluates transient changes of tracer gas to determine site-specific effective porous medium gas diffusion coefficients. The tracer gas (sulfur hexafluoride) is introduced to the subsurface at a known concentration through a soil gas probe. The tracer gas is allowed to diffuse 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 residence time intervals (generally 0, 15, 60, and 120 minutes).

Sulfur hexafluoride concentrations were measured in the field by using an IonScience™ SF_6 P1 detector (sulfur hexafluoride detector). The sulfur hexafluoride detector was factory calibrated and was checked in the field with a known concentration of sulfur hexafluoride.

A 5 percent sulfur hexafluoride mixture (injection mixture) was created by filling a 1-liter Tedlar bag with 950 mL of ambient air. Using a laboratory-provided syringe, 50 mL of sulfur hexafluoride gas was added to the 1-liter Tedlar bag. The sulfur hexafluoride detector has an upper measurement range of 1,000 ppm; therefore, the injection mixture was diluted by 10 percent to verify the concentration. The injection concentration was then calculated based on the dilution results. A new sulfur hexafluoride mixture was generated for each soil gas location.

To initiate the test, 50 mL of the injection mixture was injected into the soil gas probe using a laboratory-provided syringe and two-way ball valve. The soil gas probe tubing was then 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.

Immediately after the sulfur hexafluoride mixture was injected (0-minute time interval), an air sampling pump was connected to the probe tubing to purge the soil gas from the probe at a rate of less than 200 mL/min. The effluent air was collected from the air sampling pump and screened for concentrations of sulfur hexafluoride. This concentration was interpreted to be the maximum concentration after injection (C_{max}). After sample collection, 5 liters of soil gas were purged to eliminate any remaining sulfur hexafluoride gas within the sand pack and surrounding soil.

This injection procedure was repeated for 15-, 60-, and 120-minute residence time increments. The sulfur hexafluoride mixture was injected and allowed to diffuse into the surrounding soil for the specific time increment. After the time interval had elapsed, the soil gas was collected and screened for sulfur hexafluoride gas. The soil gas probe was then purged and the next time step was completed. Injected sulfur hexafluoride concentrations and extracted sulfur hexafluoride concentrations were recorded on field sheets and are included as Appendix 8-E.

8.2 Data

This section describes data collected from site activities to support the analyses conducted as part of the soil gas investigation.

8.2.1 Soil Borings

FHRA installed six permanent multilevel soil gas probes (SG-01 through SG-06) at the NPR on August 27 through 30 and September 16, 2013 as proposed in the Onsite SCWP (ARCADIS 2013d). A site map showing the approximate locations of soil gas probes SG-01 and SG-06 is included on Figure 7-11. The locations of the probes were selected within the area of known petroleum LNAPL observed at the site. Boring logs with PID readings and USCS soil descriptions for soil gas probes SG-01 through SG-06 are included in Appendix 8-A.

During advancement of the borehole for soil gas probe SG-01, an unidentified metal obstruction was encountered. The original borehole location selected for nested soil gas probe SG-01 was backfilled with native soil and abandoned. The new soil gas probe was offset approximately 17 feet to the east of the original location, approximately 7 feet west of an underground fire water utility.

During advancement of soil gas probe boring SG-03, significant moisture was encountered at 7.5 feet bgs. The borehole for SG-03 was backfilled with granular bentonite to a depth of 6.5 feet bgs to prevent saturation of the sand pack. Saturated soil was encountered during advancement of soil gas probe boring SG-04 at 8.5 feet bgs. The borehole for SG-04 was backfilled with granular bentonite to a depth of 7.5 feet bgs to prevent saturation of the sand pack.

8.2.2 Leak Detection

Three leak detection tests were conducted at each location to ensure the quality of soil gas samples, including field screening of helium during field parameter readings, shut-in leak testing of the sample train, and analytical sampling within a helium shroud. The results of the three tests are presented in Table 8-1.

The nested soil gas probes were leak tested while purging the soil gas probes inside of a helium shroud. The field screening leak test was conducted at all soil gas probes and helium was not detected in the purged soil gas with the following exceptions:

- Helium was detected during the field parameter collection leak detection test conducted while purging SG-02 at 6.5 feet bgs. Methane is known to interfere with helium detectors and methane was detected at greater than the lower explosive limit (LEL) in the soil gas. To confirm that methane was creating a false reading, the helium concentration inside the shroud was more than doubled, from approximately 20 to 50 percent helium, and purging continued. A corresponding increase in helium was not measured; therefore, the helium reading was concluded to be due to methane interference. Based on the methane interference and because the soil gas probe at 3.5 feet bgs passed the leak detection test, it was concluded that the bentonite seal of the deeper soil gas probe was also competent. Further, helium was not detected in the laboratory sample collected from SG-02 at 6.5 feet bgs.

- Field screening of helium was not completed at SG-06 at 6.5 feet bgs due to equipment malfunction. Helium was not detected in the laboratory sample collected from SG-06 at 6.5 feet bgs.

All sample trains constructed for soil gas sampling were considered tight. The sample trains were only used after they passed the shut-in test, meaning that the sample train held a vacuum for at least 2 minutes.

In the final leak test, the soil gas samples were collected inside a helium shroud to identify any leaks in well seals or the sample train. The soil gas samples were analyzed for helium at the laboratory; helium was not detected in any of the soil gas samples. The leak detection tests confirmed that the bentonite seals at each of the soil gas probes were competent, the sample trains were air-tight, and the soil gas samples were representative of soil gas from the subsurface.

8.2.3 Soil Gas Field Parameters

Soil gas was screened with a Landtec GEM 2000 Landfill meter, an RKI Eagle 2, and a PID for oxygen, carbon dioxide, methane (with and without a GAC filter), TVH with the RKI Eagle 2, and VOCs with a PID. Field parameter measurements are included in Appendix 8-C and the final measurements at each soil gas probe are summarized in Table 8-2.

Field screening results show that the concentrations of VOCs, carbon dioxide, and methane increase, and oxygen decreases with depth. The data from the GEM 2000 and the RKI Eagle 2 are well correlated to each other and to laboratory analytical results for oxygen, carbon dioxide, and methane (after being filtered with GAC); however, there are differences in the magnitude of each compound being detected. The average values for oxygen and carbon dioxide were calculated from all soil gas probe locations (12 in all) from the final field parameter readings (presented in Table 8-2) and the laboratory analytical results (presented in Table 8-3).

The average values from the field meters were compared to the laboratory results to evaluate which meter is more accurate. On average, the magnitude of the RKI Eagle 2 response was more consistent with laboratory data (16 percent difference for oxygen and 1 percent difference for carbon dioxide, versus 32 and 12 percent differences with the GEM 2000). Both meters underestimated methane concentrations; however, the RKI Eagle 2 only reports methane in percent of LEL, limiting the range of response.

8.2.4 Results of Laboratory Analytical Data

Soil gas samples were collected at the site on September 21, 2013 from soil gas probes SG-01 through SG-06, at the locations shown on Figure 7-11. Soil gas samples were collected from two depths at each sample location. The laboratory analytical results are presented in Table 8-3 and Appendix 8-F. Data qualifiers are defined in the data tables.

At all soil gas probe locations, the concentrations of VPH, carbon dioxide, and methane increase with depth, and oxygen decreases with depth. This is expected because VPH and methane are generated from the source zone at or around the water table and biodegrade in the vadose zone, generating carbon dioxide and depleting oxygen. Helium was not detected in any sample, which confirms sample integrity.

The highest concentrations of VPH are reported in SG-04 at the deep soil gas probe, which is located in an area of the LNAPL footprint reported as predominantly naphtha (Figure 7-11). These results are consistent with these petroleum products and their relative volatility.

The soil gas collected from SG-01, located in an area characterized as primarily diesel (Figure 7-11), exhibited the lowest concentrations of VPH, however, review of the SG-01 soil boring log indicates that SG-01 was not installed in a location with LNAPL impacts; the maximum PID reading at that location was 1.2 parts per million. Data for SG-01 will be presented, but will not be evaluated further.

8.2.5 Results of Vapor-Phase Soil Diffusion Testing

Porous medium gas diffusion coefficients are required to calculate NSZD rates. FHRA followed the approach described by Johnson et al. (1998), which evaluates transient changes of tracer gas to determine site-specific effective gas diffusion coefficients for soil. The analytical results are summarized in Table 8-4.

Concentrations of the recovered tracer gas generally decreased with longer residence time, which is expected as the tracer gas diffuses away from the injection point through time. At SG-05, the 1-liter sulfur hexafluoride mixture that was used for the 0-, 15-, and 60-minute residence time tests was depleted during completion of those tests. A replicate C_{max} (0-minute residence time) test and a 120-minute test were conducted using a new sulfur hexafluoride injection mixture. The vapor-phase soil diffusion coefficient evaluates the fraction of recovered tracer gas; therefore, use of two sulfur hexafluoride injection mixtures satisfies the requirements of the procedure.

8.3 Data Evaluations

8.3.1 Bioventing Evaluation

Oxygen serves as an electron acceptor for the biologically mediated oxidation of hydrocarbons, which results in production of carbon dioxide. If active microbial populations are present, soil gas oxygen concentrations are usually low (typically less than 5 percent by volume [vol%]) and soil gas carbon dioxide concentrations are high, typically greater than 10 vol% (Leeson and Hinchee 1996).

The gas composition observed at five locations (SG-02 through SG-06) indicates that oxygen is depleted within the vadose zone and carbon dioxide is present. Concentrations of respiration gasses from the deeper soil gas probe at these five locations were less than 5 vol% oxygen, greater than 16 vol% carbon dioxide, and methane was detected from 0.031 to 17 vol%. Volatile compounds were also detected in the extracted gases at concentrations ranging from 214 to 4,700 parts per million by volume (ppmv).

The gas composition observed at SG-02 through SG-06 indicates that natural biodegradation of the LNAPL is occurring and aerobic biodegradation within the LNAPL smear zone is oxygen-limited. These data indicate that technologies that provide additional oxygen to the vadose zone, such as bioventing, could be successful as a remedial technique to increase contaminant mass depletion rates within the vadose zone, depending on the remedial action objectives.

8.3.2 Explosion Risk Evaluation

Methane and VPH concentrations in soil gas were compared to representative refined petroleum product LEL concentrations to evaluate the explosion risk potential at the site. VPH concentrations were compared to LELs for LNAPL that was identified near the soil gas probe through analytical forensics sampling (Figure 7-11 and Section 7). LELs published in Material Safety Data Sheets (MSDSs) for LNAPL produced by the facility (Appendix 8-G) were used for the evaluation. The LEL for No. 1 diesel fuel and gasoline were considered representative of Jet A and naphtha, respectively, because the composition of these fuels are similar and LELs for Jet A and naphtha were not available. At locations with a mixture of fuel types, the lower LEL was used to evaluate the explosion risk.

Methane and VPH concentrations shown as percent LEL are presented in Table 8-5, and detections that exceed the 10 percent LEL threshold identified in the Onsite SCWP (ARCADIS 2013e) are highlighted.

8.3.2.1 Shallow Sampling Interval (0 to 5 feet bgs)

VPH was detected at 23 and 25 percent of the LEL at shallow soil gas probes SG-04 and SG-06, respectively. All other shallow soil gas samples were below 10 percent of the LEL. Methane concentrations in the shallow samples collected from soil gas probes SG-02 (34 percent LEL) and SG-06 (24 percent LEL) exceeded the potential risk threshold. Methane concentrations in the shallow samples collected from the remaining soil gas probes were below 10 percent of the LEL.

8.3.2.2 Deep Sampling Interval (5 to 8 feet bgs)

VPH was detected at soil gas probes SG-02 (80 percent LEL), SG-04 (69 percent LEL), SG-05 (31 percent LEL), and SG-06 (57 percent LEL). Methane concentrations were detected above 100 percent of the LEL in the deep sample at soil gas probe SG-02 and above 10 percent of the LEL in the deep samples at soil gas probes SG-03 (56 percent LEL) and SG-06 (54 percent LEL).

8.3.2.3 Observations in Concentration Relative to Depth Intervals

At each of the soil gas sample locations, hydrocarbon and methane concentrations were substantially lower (SG-02, SG-03, and SG-05 were one order of magnitude or more lower) at the shallower depths of 3 to 4 feet bgs versus the deeper samples collected from 6 to 8 feet bgs. This reduction in concentration, in conjunction with the associated reduction in oxygen, indicates that attenuation of petroleum hydrocarbons and methane is ongoing within the vadose zone at the soil gas sample locations. The processes attenuating the petroleum hydrocarbons and methane are discussed in Section 7.

8.3.2.4 FHRA Vapor Intrusion Mitigation

Refinery operations create explosive gas concerns that are independent of soil gas quality. Because of this, FHRA has a long-standing program to protect workers from explosive gases. FHRA detailed the explosive gas mitigation measures in place at the refinery in a letter to ADEC dated November 1, 2013 (Appendix 8-H):

> *"FHRA stresses worker safety through implementation of the Safe Work program. As additional risk mitigation measures, buildings within electrically classified areas were already designed to be pressurized, which provides protection from vapor intrusion into the buildings. For the non-pressurized buildings in the known contamination area, FHRA has instituted a periodic monitoring program of indoor air for VOCs and %LEL."*

8.3.3 Vapor-Phase Soil Diffusion

Results of the tracer gas injection tests were used to calculate site-specific vapor-phase soil diffusivity to oxygen, using the approach described by Johnson et al. (1998).

8.3.3.1 Vapor-Phase Soil Diffusivity Calculation

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 mass recovered after diffusing into the formation for a period of time (residence time) compared to the mass recovered with no residence time period (0 minutes, or C_{max}). The fraction of the initial injected tracer gas recovered, η, is described as:

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

Where:

C_{ts} = 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:

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

Where:

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

erf() = error function

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

Where:

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

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

V_s = volume of sample (mL)

t_s = time between injection and extraction (seconds)

The effective vapor-phase diffusion coefficient is solved by calculating η using Equation 1 and the results from the tracer gas injection tests at each soil gas probe for each residence time period. The relational parameter, β, is solved through an iterative solver in Microsoft™ Excel and Equation 2. Finally, the effective vapor-phase diffusion coefficient is calculated using Equation 3. For each soil gas probe, 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 probe.

In this investigation, sulfur hexafluoride was 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 4.

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

Where:

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

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

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

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

Diffusion coefficients in air can be calculated for specific compounds using Equation 5 (American Chemical Society 1982).

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

Where:

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

T = temperature (Kelvin)

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

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

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)

P = pressure (1 atmosphere)

8.3.3.2 *Effective Diffusion Coefficient for Oxygen*

Site-specific effective diffusion coefficients for oxygen were calculated at both depths for the six soil gas probes. The calculations are included in Appendix 8-I and results are summarized in Table 8-6. In general, the diffusion coefficient decreases with depth at each location, which is expected as water occupies a greater percentage of the pore space.

The calculated effective diffusion coefficients ranged approximately one order of magnitude, from 0.0016 cm^2/sec at the deep probe at SG-01 to 0.02 cm^2/sec at the shallow probe at SG-03. The soil at the soil gas probes comprises predominantly sand and gravel, with lenses of silty sand. The diffusion coefficients are consistent with literature values (Johnson et al. 1998, ITRC 2009b) and ARCADIS' experience at other sites.

8.3.4 Natural Source Zone Depletion Evaluation Update

Soil gas concentrations and results of the diffusivity testing were used to evaluate the rate of NSZD via soil gas transport. LNAPL constituents and the associated degradation products (e.g., methane) volatilize and diffuse away from source zones, and oxygen used for aerobic biodegradation diffuses down through the soil profile from the atmosphere. NSZD rates associated with these soil gas transport processes in the unsaturated zone can be estimated by evaluating vertical gas fluxes across a theoretical horizontal plane placed above the source zone (Johnson et al. 2006, ITRC 2009b). Results of the soil gas investigation are coupled with other site data to complete the NSZD evaluation as presented in Section 7.

8.3.5 Distribution of Volatile Hydrocarbons

The TVH concentrations in the deep soil gas probes were compared with LNAPL types identified through analytical testing (LNAPL forensics data in Section 7). Soil gas concentrations from the deep samples were compared because the samples were closest to the LNAPL (located at the water table) and likely were less affected by biodegradation in the vadose zone. TVH concentrations reported in the deep soil gas probes are summarized in Table 8-3 and shown on Figure 8-2.

The concentrations of TVH in soil gas are not consistent with the identified LNAPL types. The highest concentration of TVH in soil gas was measured in the area with naphtha-dominated LNAPL (SG-04), however, SG-03, a mixture of Jet A and naphtha LNAPL, had the lowest concentrations of TVH in soil gas (omitting SG-01, as noted in section 9.2.4). The lack of a correlation between TVH in soil gas and LNAPL type may be due to variability in the biodegradation rates in the unsaturated zone. As presented in the NSZD evaluation in Section 7, the NSZD rate is directly related to the gas diffusivity of the soil. The highest gas diffusivity was calculated at SG-03, which supports a higher rate of aerobic biodegradation, thereby preventing accumulation TVH.

Although, the deepest soil gas samples were evaluated, the effects of biodegradation are apparent at these depths. It is likely that LNAPL type and area specific biodegradation rates result in the variable concentrations of TVH in soil gas.

8.4 Summary

The soil gas investigation met the primary and secondary objectives, and results of the investigation indicate:

- Methane was below 100 percent lower explosive limit (LEL) in all 6 shallow soil gas samples collected at the approximate midpoint between the groundwater table and surface and 5 out of 6 deep soil gas samples collected near the groundwater table within the LNAPL smear zone. At the location where methane exceeded the LEL, the methane concentration in soil gas decreased 90 percent between the deep and shallow soil gas sample, which is likely attributable to aerobic consumption of methane in the vadose zone by methanotrophic bacteria.

- Bioventing, or other methods of increasing oxygen in the subsurface, may be beneficial and appropriate potential remediation technologies for some portions of the site for enhanced reduction of contaminant mass in the vadose zone.

- Site-specific soil diffusion coefficients were determined from tracer gas injection tests that were used in conjunction with the soil gas data to update the 2012 NSZD evaluation (Section 7).

The distribution of TVH in soil gas is dependent on the LNAPL type and area specific biodegradation.

9. Soil Investigation

9.1 2013 Soil Characterization

An extensive onsite soil investigation was conducted in 2011 to evaluate soil impacts at the site. Results from the 2011 investigation and specific recommendations for further soil characterization activities are summarized in the SCR – 2011 (Barr 2012). Additional soil characterization activities were conducted in 2012 at locations with elevated sulfolane and/or benzene concentrations in soil. Results for the 2012 investigation are presented in the SCR – 2012 (ARCADIS 2013a).

The Onsite SCWP (ARCADIS 2013d) presented recommendations for further soil characterization at potential and known sulfolane source areas, including those identified by Geomega in the History of Sulfolane Releases to the Environment at the Flint Hills Refinery, North Pole, Alaska (Appendix A SCR-2012; ARCADIS 2013a). Section 13 of this report provides an updated summary of the primary sources of sulfolane at the site, including the areas described further in this section. Soil characterization activities proposed in the Onsite SCWP (ARCADIS 2013d) supplement the soil sampling data summarized in the SCR – 2011 (Barr 2012) and SCR – 2012 (ARCADIS 2013a).

Areas proposed for additional soil investigation in 2013 included:

- SWA
- Lagoon B
- SGP (former lagoon overflow ditch)
- CU #1 Wash Area
- CU #2 EU (with a specific focus on the immediate area around Sump 02/04-02 as discussed in Section 9.1.7)
- Sump 908
- Tank 194 Area

FHRA collected 218 soil samples from 47 soil borings located within or near areas proposed in the Onsite SCWP (ARCADIS 2013d) for sulfolane and/or BTEX analysis. The soil samples were collected between August 14 and November 8, 2013. Boring locations are shown on Figure 9-1.

In addition to soil samples collected from designated soil borings, FHRA collected 199 soil samples for sulfolane and/or BTEX analysis from July 11 to November 19, 2013 during the installation of 46 onsite Phase 8 monitoring wells, six soil gas sampling point nests, and four high-resolution vertical soil sampling boring clusters CF13-01 through CF13-04. Additional soil samples were collected for other petroleum hydrocarbon analyses from onsite Phase 8 monitoring wells and soil gas investigation borings. Seventy-seven soil samples from 24 onsite Phase 8 monitoring wells were analyzed for GRO, DRO, and PAHs. Twenty-nine soil samples from the six soil gas monitoring points were analyzed for GRO, DRO, 1,3,5-TMB, and naphthalene. The locations of onsite Phase 8 monitoring wells, soil gas investigation wells, and high-resolution vertical soil sampling borings are shown on Figure 9-1. Data qualifiers are defined in the data tables.

9.1.1 Soil Sample Collection Methodology

Soil sample collection methods presented below pertain to soil borings advanced in the areas proposed for additional soil investigation. Sample collection from onsite Phase 8 monitoring well borings, soil gas investigation borings, and high-resolution vertical soil sampling borings is discussed in Sections 3, 8, and 9.3, respectively.

9.1.1.1 Direct-Push Borings

Soil borings located in the target areas discussed above were advanced using direct-push technology. Soil samples were collected from immediately above the air-groundwater interface and the bottom of the boring. Additional soil samples for benzene analysis were collected based on field observations or elevated PID measurements. Finer-grained units were targeted for sulfolane sampling, as recommended in the Onsite SCWP (ARCADIS 2013d).

Boring advancement, soil sampling, soil classification, soil screening, and field QC measures were completed in accordance with the procedures described in the RSAP. Boring logs were prepared for each boring and are included in Appendix 9-A.

Soil samples collected from the soil borings were submitted to SGS for sulfolane analysis by USEPA modified Method 8270D with isotope dilution. Samples collected in the following areas were also analyzed for BTEX by USEPA Method 8021, as proposed in the Onsite SCWP (ARCADIS 2013d):

- CU #1 Wash Area
- CU #2 EU
- Sump 908 Area
- Tank 194 Area

Five soil samples (SB13-01 [2.9-3.2], SB13-01 [5.0-5.4], SB13-01 [13.0-14.5], SB13-06 [2.0-4.0], and SB13-06 [14.0-15.0]) from the SGP were also analyzed for BTEX by USEPA Method 8021, although this analysis was not originally considered in the Onsite SCWP (ARCADIS 2013d).

Data validation for soil samples is discussed in Section 16 of this Onsite Addendum. Soil analytical laboratory reports are included as Appendix 9-B.

9.1.1.2 Hand Auger Soil Borings

Four soil borings in Lagoon B (SB13-31, SB13-32, SB13-33, and SB13-34) were advanced using hand auger techniques. Additional hand-augered soil samples were collected from the FTA. The methodology and results for this sampling are discussed in Section 11. Boring locations are presented on Figure 9-1.

Lagoon B, which has been closed since 2006, has a liner system consisting of a top primary liner and bottom secondary liner with PVC spacers between the two liners. The primary and secondary liners were cut to expose the underlying soil at the proposed boring locations and sandbags were laid out along the exposed soil. The hand auger was then advanced at each location until immediately above the water table or until refusal. Total boring depths ranged from approximately 3.2 to 3.5 feet bgs.

Soil samples were collected from continuous intervals for soil classification and screening starting at the lagoon surface. Soil screening included organic vapor measurements using a PID and visual observations of staining and odors. One soil sample was collected for laboratory analysis from each boring immediately above the water table or at the deepest interval achieved. Soil samples were submitted to SGS for sulfolane analysis by USEPA modified Method 8270D with isotope dilution. Soil boring logs are presented in Appendix 9-A. Data validation for soil samples is discussed in Section 16. Soil analytical laboratory reports are included as Appendix 9-B.

9.1.1.3 Vacuum-Cleared Soil Borings

Soil borings SB13-31 through SB13-34 were advanced using vacuum clearing techniques, where direct-push technology was not feasible due to limited access. The top 6 feet of soil borings SB13-20a and SB13-47 were also vacuum cleared. Soil was collected every foot in advance of the vacuum for soil sampling, characterization, and screening using a hand auger. Boring locations are shown on Figure 9-1. Boring logs were prepared for each boring and are included in Appendix 9-A.

9.1.2 Soil Analytical Results – Site-Wide

Locations of soil borings advanced during 2013 site characterization activities are shown on Figure 9-2. Figure 9-2 also displays 2011 and 2012 soil and monitoring well borings presented in the SCR-2011 (Barr 2012) and the SCR-2012 (ARCADIS 2013a). Soil sulfolane and benzene analytical results from 2011, 2012, and 2013 are presented on subsequent site-wide figures to evaluate historical and current soil impacts at the site. Other petroleum COCs (total xylenes, naphthalene, and 1,3,5-TMB) are discussed below. Discussions of the results within the context of the various source areas are presented in Section 9.1.3 through 9.1.9.

9.1.2.1 Sulfolane

Soil sulfolane concentrations (in µg/kg) from 2011, 2012, and 2013 soil investigation activities on a site-wide scale at specified depth intervals (0 to 2, 2 to 6.5, 6.5 to 10, 10 to 18, and greater than 18 feet bgs) are presented in Figures 9-3a through 9-3e. Concentrations of sulfolane in soil exceeding the calculated ACL (999 µg/kg) are present in the SWA, SGP, Lagoon B, CU #1 Wash Area and CU #2 EU. The soil sulfolane concentrations are generally below the calculated ACL at all depth intervals outside of these source areas. Soil sulfolane analytical results for 2013 are presented in Table 9-1a. Soil sulfolane analytical results for 2011 and 2012 are provided in Appendix 9-C.

9.1.2.2 Petroleum Hydrocarbons

Soil benzene concentrations (in µg/kg) from 2011, 2012, and 2013 soil investigation activities on a site-wide scale at specified depth intervals (0 to 2, 2 to 6.5, 6.5 to 10, 10 to 18, and greater than 18 feet bgs) are presented in Figures 9-4a through 9-4e. Soil benzene concentrations above the calculated ACL (2,580 µg/kg) in shallow soil (0 to 2 feet) are generally confined to areas near CU #1 Wash Area and the CU #2 EU. Detectable benzene concentrations are found across the site near the soil-groundwater interface (Figures 9-4b and 9-4c). Soil benzene concentrations are less pronounced in soil collected from depths greater than 10 feet bgs.

The presence and concentration of other petroleum hydrocarbons in soil, including delineated COCs (total xylenes, naphthalene, and 1,3,5-TMB), correlate with benzene concentrations on a site-wide scale. Overall, soil concentrations of total xylenes, naphthalene, and 1,3,5-TMB are highest and most widespread at the soil-groundwater interface and are likely a result of “smearing” of LNAPL during groundwater fluctuations. Soil petroleum hydrocarbon analytical results for 2013 are presented in Tables 9-1b through 9-1e. Soil petroleum hydrocarbon analytical results for 2011 and 2012 are provided in Appendix 9-C.

9.1.3 Soil Analytical Results – Southwest Former Wash Area

The SWA is currently used for materials storage. However, the SWA was previously used as a wash area where EU heat exchanger bundles were pressure washed during turnarounds, generating sulfolane-laden wastewater.

Additional soil investigation for the SWA was proposed in the Onsite SCWP (ARCADIS 2013d) based on findings presented in the SCR-2011 (Barr 2012) and SCR-2012 (ARCADIS 2013a).Sulfolane was detected at a maximum concentration of 18,000 µg/kg in one soil sample collected from 3 to 5 feet bgs (SB-143) in 2011. Subsequent samples collected in 2012 had soil sulfolane concentrations as high as 72,000 J µg/kg in shallow soil (SB-191 [0-2]) and as high as 724,000 µg/kg in the capillary zone directly above the soil-groundwater interface (SB-238 [5.8-6.8]). Borings SB-191 and SB-238 were advanced directly east of the former wash area, where sulfolane-laden wastewater was likely released.

Soil samples were collected in 2013 to further characterize soil sulfolane concentrations near the former wash skid and to delineate soil impacts in the SWA. Soil sulfolane concentrations at designated depth intervals (0 to 2, 2 to 6.5, 6.5 to 10, and 10 to 18 feet bgs) collected in 2013 are presented in Figures 9-5a through 9-5d. Soil analytical data from 2011 and 2012 site characterization activities are also presented on Figures 9-5a through 9-5d for historical reference. Soil analytical data for 2013 are provided in Table 9-1. SWA soil analytical data for 2011 and 2012 are provided in Appendix 9-C.

Soil sulfolane concentrations collected in 2013 ranged from 16.7 J µg/kg (SB13-13 [14-16]; duplicate sample) to 1,600,000 JL µg/kg (CF13-1A [5.9-6.0]). The highest soil sulfolane concentrations were detected directly east of the former wash area, which is consistent with previous soil analytical data collected from the SWA. The highest soil sulfolane concentrations detected to date at the site were found in soil boring CF13-1A, which was a high-resolution vertical soil sampling boring. A detailed evaluation of soil sulfolane concentrations detected in CF13-1A and the mechanisms for sulfolane retention in the SWA are presented in Section 9.3.

Two geologic cross-sections (E-E’, F-F’) were prepared to evaluate the lateral and vertical distribution of sulfolane in soil in the SWA. Figure 9-6 displays a plan view of the cross-section transects in the SWA. Cross-sections E-E’ and F-F’ illustrate the complexity of the geology in the SWA and the distribution of sulfolane in the soil profile (Figures 9-7 and 9-8). The highest concentrations of sulfolane in soil are generally in finer-grained soil (e.g., peat and silt) and are found above the average regional water table in the unsaturated zone and capillary fringe.

9.1.4 Soil Analytical Results – Lagoon B

Sulfolane was detected in the groundwater sample collected from monitoring well MW-110-20 during the third quarter 2013 at a concentration of 538 µg/L (Appendix 10-B). This monitoring well is located downgradient from Lagoon B and the high sulfolane result was identified as an indicator of historical sulfolane releases from Lagoon B. Soil samples collected downgradient from Lagoon B also contained sulfolane at concentrations exceeding laboratory detection limits. In response to these findings, 32 soil boring locations (SB-206 through SB-225 and SB-252 to SB-263) were advanced below the lagoon base during 2012 site characterization activities (Appendix A of ARCADIS 2013a). Sulfolane was detected at concentrations ranging from 15.1 JL µg/kg (SB-224) to 5,950 µg/kg (SB-216). The highest soil sulfolane concentrations were found in borings placed near the center of Lagoon B.

The Onsite SCWP (ARCADIS 2013d) proposed four soil borings (SB13-31, SB13-32, SB13-33, SB13-34) to further characterize sulfolane concentrations in soil near the center of Lagoon B. Sulfolane concentrations ranged from 3.91 J µg/kg (SB13-32 [1.5-2.0]) to 70.3 µg/kg (SB13-31 [1.5-2.0]). Figure 9-9 presents 2013 soil sulfolane concentrations in Lagoon B at all depths. Soil analytical data from 2011 and 2012 site characterization activities are also presented on Figure 9-9 for historical reference. Soil analytical data for 2013 are provided in Table 9-1a. Lagoon B soil analytical data for 2011 and 2012 are provided in Appendix 9-C.

Soil sulfolane concentrations were lower in SB13-31, SB13-32, SB13-33, and SB13-34 compared to sulfolane concentrations in soil samples previously collected at deeper intervals from the center of Lagoon B. For example, soil sulfolane concentrations in SB13-32 were 3.91 J µg/kg (1.5 to 2 feet bgs) and 10.2 J µg/kg (2.2 to 3.2 feet bgs). However, SB-216 was advanced approximately 18 feet southeast of this location and had a sulfolane concentration of 5,950 µg/kg in 2012. The soil sample collected from SB-216 was collected from a layer of silt with high organic content, which likely explains the elevated sulfolane concentrations in this sample (see Section 9.3). Samples from SB13-32 were collected from predominantly gravel and sand.

Sulfolane concentrations in soil samples collected in 2011, 2012, and 2013 from Lagoon B were highest in borings near the center of the lagoon. Soil samples collected along the sides of the lagoon contained lower sulfolane concentrations or concentrations less than detection limits. Soil sulfolane concentrations greater than the calculated ACL (999 µg/kg) were confined to within the lagoon. Borings were advanced to the top of the water table and soil samples were collected from these depths, allowing for vertical delineation of sulfolane in the unsaturated zone at Lagoon B.

9.1.5 Soil Analytical Results – South Gravel Pit

9.1.5.1 Sulfolane

The Onsite SCWP (ARCADIS 2013d) proposed soil borings in the SGP area to further delineate sulfolane impacts from a documented historical spill that occurred in a former overflow ditch between Lagoon B and the SGP. Section 13 presents information pertaining to this spill. During 2012 site characterization activities, one soil boring (SB-229) was advanced in the SGP (ARCADIS 2013a). Three soil borings (SB-230, SB-231, and SB-232) were advanced to the north and east of the SGP source area. Sulfolane was not detected in the vadose zone in SB-229 through SB-232, but was detected in the capillary zone at concentrations ranging from 14.3 µg/kg (SB-229 [5.0-6.0]) to 59 µg/kg (SB-231 [5.0-6.6]). Sulfolane was detected in one sample collected from the saturated zone (SB-230 [10.0-11.0]) at a concentration of 1,800 µg/kg.

Five soil borings (SB13-01, SB13-02, SB13-03, SB13-05, and SB13-06) were advanced during 2013 field activities, as proposed in the Onsite SCWP (ARCADIS 2013e). Sulfolane was detected in soil at concentrations ranging from 39.0 JL µg/kg (SB13-01 [5.0-5.4]) to 316 µg/kg (SB13-06 [5.0-6.0]). Soil sulfolane concentrations collected in 2013 in the SGP area at specific depth intervals (0 to 2, 2 to 6.5, 6.5 to 10, and 10 to 18 feet bgs) are presented on Figure 9-10. Soil analytical data from 2011 and 2012 site characterization activities are also presented on Figure 9-10 for historical reference. Soil analytical data for 2013 are provided in Table 9-1a. Soil analytical data for 2011 and 2012 are provided in Appendix 9-C.

The lateral extent of soil sulfolane impacts in the designated depth intervals are presented on Figure 9-10. The lateral extent of soil impacts in the SGP source area is limited. Soil sulfolane concentrations were below the proposed calculated ACL (999 µg/kg), except the soil concentration of 1,800 µg/kg detected in the saturated zone (SB-230 [10.0-11.0]).

9.1.5.2 Petroleum Hydrocarbons

Soil samples collected in 2012 from SB-229, SB-230, SB-231, and SB-232 were analyzed for BTEX. Toluene, ethylbenzene, and xylenes were not detected in samples collected from these borings. One soil sample collected from the saturated zone (SB-230 [10.0-11.0]) contained benzene at a concentration of 15.3 J µg/kg, which is below the calculated ACL of 2,850 µg/kg. Soil analytical results for 2011 are provided in Appendix 9-C.

Five samples were also analyzed for BTEX from SB-01 and SB-06 in 2013. Benzene concentrations in soil were below analytical detection limits. Total xylene concentrations in soil were below analytical detection limits, except for three samples (SB13-01 [2.9-3.2], SB13-01 [5.0-5.4], and SB13-06 [2.5-3.5]). Total xylene concentrations detected in these samples were below the calculated ACL (27,600 µg/kg), ranging from 150 µg/kg to 3,230 JL µg/kg. Soil analytical results for BTEX analyzed during 2013 are provided in Table 9-1b.

9.1.6 Soil Analytical Results – Crude Unit #1 Wash Area

9.1.6.1 Sulfolane

The Onsite SCWP (ARCADIS 2013d) proposed the investigation of the CU #1 Wash Area to assess sulfolane and BTEX impacts from overspray and other releases in this area. Prior to commencing development of the SWA in 1990, the CU #1 Wash Area was the only wash area at the NPR, and as such, was likely used to power wash EU bundles during turnarounds. The wash area has a 180-foot-long slotted drain, which channels wastewater to Sumps 901 and 901.5 (ARCADIS 2013a). The CU #1 Wash Area is sloped to the slotted drain but does not have curbs, which would have allowed overflow or overspray during EU equipment cleaning when the area was used for that purpose. Sulfolane-laden wastewater was likely released to soil by overflow and/or overspray during power washing. Potential releases may have also occurred from the slotted drain and Sump 901.5 (ARCADIS 2013a).

One soil boring (SB-146) was advanced during 2011 site characterization activities to assess soil impacts downgradient from the CU #1 Wash Area (Barr 2012). Seven soil borings (SB13-16, SB13-17, SB13-18, SB13-19, SB13-20, SB13-20a, and SB13-47) were advanced near the slotted drain in the CU #1 Wash Area during 2013 site characterization activities. One boring (SB13-20) was advanced 2 feet from ground surface and terminated after encountering concrete. Boring SB13-20a was advanced as a replacement boring approximately 18 feet from the abandoned boring. Soil boring locations are provided on Figure 9-2.

Sulfolane concentrations in soil at designated depth intervals (0 to 2, 2 to 6.5, 6.5 to 10, and 10 to 18 feet bgs) are presented on Figure 9-11. Soil sulfolane concentrations ranged from 5.42 J µg/kg (SB13-47 [5.0-5.5]) to 11,700 JL µg/kg (SB13-19 [0.0-2.0]). Laterally, soil sulfolane concentrations above the calculated ACL (999 µg/kg) are confined to the areas near SB13-16 and SB13-19 in the designated depth intervals. Sulfolane was detected in groundwater collected from SB13-16 at 42,000 JL* µg/L. A discussion on sulfolane concentrations in groundwater at the CU #1 Wash Area is provided in Section 10.3.9.

Cross-section G-G’ through the CU #1 Wash Area is displayed on Figure 9-12. The lithology below the CU #1 Wash Area is primarily poorly graded gravel and sand, with an isolated area of silty sand and silty gravel along the eastern edge of the area. Soil sulfolane concentrations above the calculated ACL (999 µg/kg) extend from below the ground surface (near the slotted drain) at SB13-19 to approximately 11 feet bgs at SB13-16. Soil sulfolane concentrations are below the calculated ACL or below detection limits at depths greater than 15 feet bgs along the cross-section transect.

Soil borings advanced during 2013 site characterization activities provide sufficient lateral and vertical delineation of soil sulfolane impacts in the CU #1 Wash Area. Historical records from the NPR provide evidence for a known, local source of sulfolane near this wash area where soil impacts are observed.

9.1.6.2 Petroleum Hydrocarbons

The SCR – 2011 (Barr 2012) documents several petroleum hydrocarbon releases in the CU #1 Wash Area. In response to these known releases, soil samples were collected for petroleum hydrocarbon analysis from soil borings collected during 2011 and 2013 site characterization activities. Soil analytical results for COCs (benzene, total xylenes, and naphthalene) are presented below.

In 2011, soil samples were collected from SB-146 for BTEX and PAH analysis. Benzene concentrations in soil ranged from 237 µg/kg (SB-146 [0.0 - 2.0]) to 34,000 µg/kg (SB-146 [5.0 - 6.4]; duplicate sample). Total xylene concentrations in soil ranged from 544 µg/kg (SB-146 [0.0 - 2.0]) to 281,000 µg/kg (SB-146 [5.0 - 6.4]; duplicate sample). Naphthalene concentrations in soil ranged from 19.8 J µg/kg (SB-146 [0.0 - 2.0]) to 17,400 µg/kg (SB-146 [5.0 - 6.4]). The highest benzene, xylene, and naphthalene soil concentrations were found in the smear zone at SB-146. Soil analytical results for SB-146 are provided in in Appendix 9-C.

Soil samples collected in 2013 from SB13-16, SB13-17, SB13-18, SB13-19, SB13-20, SB13-20a, and SB13-47 were analyzed for BTEX, as proposed in the Onsite SCWP (ARCADIS 2013e). Benzene concentrations in soil ranged from 3.89 J µg/kg (SB13-47 [0.3 - 1.0]) to 51,300 µg/kg (SB13-20a [6.0 - 7.2]). Soil benzene concentrations exceeded the calculated ACL of 2,850 µg/kg in five of the seven soil samples. Figure 9-13 presents 2011 and 2013 soil benzene concentrations at designated depth intervals (0 to 2, 2 to 6.5, 6.5 to 10, and 10 to 18 feet bgs). Benzene concentrations exceeding the calculated ACL were generally found in the vadose or smear zone. BTEX soil analytical results for SB13-16, SB13-17, SB13-18, SB13-19, SB13-20, SB13-20a, and SB13-47 are provided in Table 9-1b.

Total xylene concentrations in soil ranged from 18.3 J µg/kg (SB13-47 [0.3 - 1.0]) to 335,000 µg/kg (SB13-20a [6.0 - 7.2]). Total xylene concentrations exceeded the calculated ACL of 27,600 µg/kg in all soil borings, but the exceedances were generally found in the vadose or smear zone. BTEX soil analytical results for SB13-16, SB13-17, SB13-18, SB13-19, SB13-20, SB13-20a, and SB13-47 are provided in Table 9-1b.

9.1.7 Soil Analytical Results – Crude Unit #2 Extraction Unit Area

9.1.7.1 Sulfolane

Sulfolane has been used throughout the CU #2 EU Area since 1985. Several spills have occurred in this area (see Appendix 7-F); therefore, the presence of sulfolane in soil in and around the CU #2 EU was expected. The Onsite SCWP (ARCADIS 2013d) proposed additional soil investigation for the CU #2 EU based on findings presented in the SCR – 2011 (Barr 2012) and SCR – 2012 (ARCADIS 2013a) and analytical results from the lean solvent spill on May 5, 2011. The maximum soil sulfolane concentration in the CU #2 EU was 15,200 µg/kg (S-2; surface sample).

Thirteen soil borings (SB13-25 through SB13-29, SB13-39 through SB13-46) and five monitoring well borings (MW-336-15, MW-336-20, MW-336-35, MW-336-55, and MW-337-20) were installed within or near the CU #2 EU in 2013, per the Onsite SCWP (ARCADIS 2013e). Sulfolane concentrations in these borings ranged from 4.90 J µg/kg (SB13-46 [2.3-3.3]) to 21,600 µg/kg (SB13-43 [15-16.5]). Figures 9-14a through 9-14d present 2013 soil sulfolane concentrations at designated depth intervals (0 to 2, 2 to 6.5, 6.5 to 10, and 10 to 18 feet bgs). Soil analytical data from 2011 site characterization activities are included on Figures 9-14a through 9-14d for reference. Soil analytical data for 2013 are provided in Table 9-1a. Soil analytical data for 2011 are provided in Appendix 9-C.

Figures 9-14a through 9-14d show the lateral extent of soil sulfolane soil impacts in the CU #2 EU. From 0 to 2 feet bgs, soil sulfolane concentrations are generally low, except in the area near the sulfolane EU (near SB13-39). However, several soil borings have soil sulfolane concentrations exceeding the calculated ACL (999 µg/kg) from 6.5 to 18 feet bgs. From 10 to 18 feet bgs, sulfolane exceedances in soil extend from SB13-43 downgradient to the MW-336 monitoring well nest and MW-337. These elevated soil concentrations in the CU #2 EU Area are upgradient from observation well O-1, where the highest groundwater sulfolane concentration (6,590 µg/L) was reported in the Third Quarter 2013 Groundwater Monitoring Report (ARCADIS 2013i).

Figure 9-15 presents a geologic cross-section in the CU #2 EU. Soil is primarily classified as poorly graded gravel and sand in this area. Sulfolane concentrations in soil above the calculated ACL (999 µg/kg) are found near SB13-43 and SB13-44, and in areas downgradient from Sump 02/04-02. Grab groundwater samples were collected during the installation of select borings (see Section 10). Sulfolane concentrations in groundwater as high as 61,600 JL* µg/L were detected near SB13-43. These elevated groundwater concentrations, coupled with sulfolane exceedances in soil, demonstrate that the CU #2 EU is a primary source of sulfolane contamination in groundwater onsite and offsite.

The vertical extent of sulfolane impacts in the CU #2 EU is delineated by groundwater samples collected from the MW-336 well nest. High groundwater sulfolane concentrations were detected in shallow, impacted soil (MW-336-15 at 17,600 µg/L, MW-336-20 at 34,800 µg/L). However, sulfolane concentrations were lower in MW-335-35 (377 µg/L) and near analytical detection limits in MW-335-55 (4.32 J µg/L).

9.1.7.2 Petroleum Hydrocarbons

Historical records have documented petroleum hydrocarbon releases in the CU #2 EU (Barr 2012). Several large releases have occurred, including a 200-gallon spill of “benzene overhead product” in 1999. In response to these known releases, soil samples were collected from soil borings for petroleum hydrocarbon analysis during 2011 and 2013 site characterization activities. Soil analytical results for COCs (benzene, total xylenes, naphthalene, and 1,3,5-TMB) are presented below.

Eleven soil borings (SB-165 through SB-168, SB-172 through SB-178, and SB-180) and two observation well borings (O-15 and O-21) were advanced in or near the CU #2 EU in 2011 (Barr 2012). Boring locations are displayed on Figure 9-2. The soil samples collected from these borings were analyzed for BTEX and PAHs. A total of eight samples from SB-165, SB-172, and SB-175 were also analyzed for a suite of other petroleum hydrocarbons, including 1,3,5-TMB. Soil analytical data for samples collected in 2011 are provided in Appendix 9-C.

Five borings advanced in 2011 (O-21, SB-165, SB-173, SB-174, and SB-180) had soil benzene concentrations above the calculated ACL (2,580 µg/kg). Total xylene concentrations in soil exceeded the calculated ACL (27,600 µg/kg) in seven soil borings, including those with benzene exceedances and two additional borings (SB-167 and SB-175). Naphthalene concentrations in soil exceeded the calculated ACL (731 µg/kg) in six soil borings (O-21, SB-165, SB-173 through SB-175, SB-180) 1,3,5-TMB was only detected in one sample (SB-175 [7.0-9.0]) at a concentration of 4,800 µg/kg.

Soil samples collected in 2013 from 13 soil borings (SB13-25 through SB13-29, SB13-39 through SB13-46) and five monitoring well borings (MW-336-15, MW-336-20, MW-336-35, MW-336-55, and MW-337-20) were analyzed for BTEX. Soil samples collected from the monitoring well borings and four soil boring samples were also analyzed for a suite of other petroleum hydrocarbons, including PAHs. Soil analytical data for samples collected in 2013 are provided in Tables 9-1b and d.

Benzene concentrations in 2013 soil samples ranged from 6.21 J µg/kg (SB13-45 [0.5-2.3]) to 438,000 µg/kg (SB13-29 [7.0-8.0]), with nine soil borings (SB13-25 through SB13-29, SB13-39, SB13-40, SB13-43, SB13-44) exceeding the calculated ACL (2,580 µg/kg). All monitoring well borings had soil benzene concentrations exceeding the ACL. Total xylene concentrations in soil ranged from 20.4 J µg/kg (MW-336-55 [2.0-3.5]) to 2,510,000 µg/kg (SB13-29 [7.0-8.0]). All soil borings advanced in 2013 in this area had at least one sample exceeding the calculated ACL for total xylenes (27,600 µg/kg). Naphthalene concentrations in soil ranged from 2.77 J µg/kg (MW-336-35 [0.4-2.0]) to 38,400 µg/kg (SB13-26 [6.5-6.8]). One soil boring (SB13-26) and four monitoring well borings (MW-336-15, MW-336-20, MW-336-35, and MW-337-20) had naphthalene soil concentrations exceeding the calculated ACL (731 µg/kg).

The lateral extent of soil benzene impacts in the CU #2 EU at designated depth intervals (0 to 2, 2 to 6.5, 6.5 to 10, and 10 to 18 feet bgs) are presented on Figures 9-16a through 9-16d. Soil benzene concentrations are highest in the smear zone, directly above the regional water table (e.g., 2 to 6.5 and 6.5 to 10 feet bgs). Soil benzene concentrations exceeding the calculated ACL (2,580 µg/kg) are generally found in the northwest sector of the CU #2 EU. Total xylene and naphthalene soil concentrations are also highest in the smear zone in the CU #2 EU.

9.1.8 Soil Analytical Results – Sump 908

9.1.8.1 Sulfolane

Sump 908 (Figure 9-17) has historically received sulfolane-laden wastewater from the salt dryer at the site. As early as 1997, the sump was found to have heavy corrosion and structural integrity issues. (Geomega 2013a).

One soil boring (SB-160) was advanced in the Sump 908 area during 2011 site characterization activities (Figure 9-2; Barr 2012). Sulfolane concentrations in soil were reported as high as 590 J* µg/kg (SB-160 [4.5 - 6.4]; duplicate sample). Soil analytical results for 2011 are provided in Appendix 9-C.

Three soil borings (SB13-21, SB13-23, and SB13-24), one observation well boring (O-35), and two soil gas borings (SG-07 and SG-08) were advanced within or near the Sump 908 source area in 2013. Boring locations are shown on Figure 9-2. Soil samples collected from soil gas borings SG-07 and SG-08 were not analyzed for sulfolane, per the Onsite SCWP (ARCADIS 2013e). Soil sulfolane concentrations detected in SB13-21, SB13-23, SB13-24, and O-35 were below the calculated ACL (999 µg/kg), ranging from 4.44 JN* µg/kg (SB13-24 [6.0-6.6]) to 418 JL* µg/kg (SB13-21 [6.5-7.0]). Soil sulfolane analytical results for designated depth intervals (0 to 2, 2 to 6.5, 6.5 to 10, and 10 to 18 feet bgs) are shown on Figure 9-17. Soil analytical results for 2013 are provided in Table 9-1a.

9.1.8.2 Petroleum Hydrocarbons

Historical petroleum hydrocarbon releases have been reported in the Sump 908 area, including a spill of 100 gallons of oily water at Sump 908 in August 1997 (Barr 2012). Soil samples were collected for petroleum hydrocarbon analysis during 2011 and 2013 site characterization activities to delineate hydrocarbon impacts in the Sump 908 area. Soil analytical results for petroleum COCs (benzene, total xylenes, naphthalene, and 1,3,5-TMB) are presented below.

In 2011, soil samples were collected from SB-160 for BTEX and PAH analysis. Samples from this boring were also analyzed for a suite of other petroleum hydrocarbons, including 1,3,5-TMB. Benzene, total xylenes, naphthalene, and 1,3,5-TMB were detected in each of the soil samples collected from this boring. Soil concentrations exceeded calculated ACLs for the four COCs in the sample collected from 4.5 to 8.4 feet bgs. Soil analytical data for 2011 are provided in Appendix 9-C.

Soil samples were collected from SB13-21, SB13-23, SB13-24, O-35, SG-07, and SG-08 for BTEX analysis. Samples from O-35 were also analyzed for PAHs. Samples collected from soil gas borings SG-07 and SG-08 were analyzed for PAHs and a suite of other petroleum hydrocarbons, including 1,3,5-TMB.

Benzene concentrations in soil ranged from 46.7 µg/kg (SB13-21 [0.0-2.0]) to 10,000 µg/kg (SG-07 [8-8.5]). Four borings (SB13-21, SB13-23, SB13-24, and SG-07) had soil benzene concentrations above the calculated ACL (2,580 µg/kg). Figure 9-18 displays soil benzene concentrations in designated depth intervals (0 to 2, 2 to 6.5, 6.5 to10, and 10 to 18 feet bgs). Soil benzene concentrations were highest within the LNAPL smear zone near the regional water table in this area.

Total xylene concentrations in soil ranged from 50.0 J µg/kg (SG-07 [4-4.5]) to 197,000 µg/kg (SB13-23 [7-7.5]; duplicate sample). Four borings (SB13-21, SB13-23, SB13-24, and SG-07) had total xylene soil concentrations above the calculated ACL (26,700 µg/kg). Naphthalene concentrations in soil ranged from 1.72 J µg/kg (O-35 [17.5-18]) to 23,300 µg/kg (SG-07 [8-8.5]). Three borings (O-35, SG-07, and SG-08) had soil naphthalene concentrations above the calculated ACL (731 µg/kg). 1,3,5-TMB soil concentrations in SG-07 and SG-08 ranged from 1,740 µg/kg (SG-07 [5-5.5] to 20,400 µg/kg (SG-07 [8-8.5]). Samples collected from soil gas borings SG-07 and SG-08 had 1,3,5-TMB concentrations above the calculated ACL (1,020 µg/kg).

9.1.9 Soil Analytical Results – Tank 194 Area

9.1.9.1 Sulfolane

The Onsite SCWP (ARCADIS 2013e) proposed soil borings near the Tank 194 Area to assess the possibility of an additional sulfolane source area and to characterize sulfolane and BTEX soil impacts in the area. One soil boring (SB-148) and one observation well boring (O-28) were advanced in the area during 2011 site characterization activities. Soil samples were collected from the borings and analyzed for sulfolane; results were generally below analytical limits of detection, except for two samples (SB-148 [3.5 - 5.1], 7.21 J* µg/kg; O-28 [8-9], 309 J^* µg/kg).

Seven soil borings (SB13-07 through SB13-12, SB13-30) were advanced in the Tank 194 Area in 2013. Sulfolane was detected in soil at concentrations ranging from 3.51 J µg/kg (SB13-07 [1.2-2.3] to 555 µg/kg (SB13-30 [5-6]). Soil sulfolane concentrations in designated depth intervals (0 to 2, 2 to 6.5, 6.5 to 10, and 10 to 18 feet bgs) are presented on Figure 9-19. The 2013 soil sulfolane concentrations in the Tank 194 Area were below the calculated ACL (999 µg/kg). Therefore, the Tank 194 Area is not a primary source of sulfolane.

9.1.9.2 Petroleum Hydrocarbons

Soil samples collected from SB-148 and O-28 during 2011 site characterization activities were analyzed for BTEX and PAHs. Benzene and total xylene concentrations in soil were below analytical detection limits in these borings. One soil sample (O-28 [8-9]) had a naphthalene concentration of 11,040,000 JH* mg/kg. However, the other soil samples analyzed for naphthalene were below analytical detection limits.

Soil samples collected from SB13-07 through SB13-12 and SB13-30 were analyzed for BTEX. BTEX constituents were below the respective analytical detection limits in samples collected from 2013 borings in the Tank 194 Area.

9.2 2013 Soil Characterization Near the Vertical Profiling Transect and West of the Railcar Loading Rack

Soil borings were proposed near the VPT and west of the railcar loading rack to assess the possibility of an additional sulfolane source area (ARCADIS 2013g). Soil borings at the VPT were also proposed for high-resolution soil sampling for GSA to improve the understanding of the fate and transport of sulfolane at the site (ARCADIS 2013g). GSA data collected from the VPT are presented in Section 4.

9.2.1 Methodology

From August 29 to 31, 2013, FHRA advanced two soil borings (HP13-57 and HP13-59) along the VPT and 10 soil borings (HP13-66 through HP13-75) to the west of the railcar loading rack. Boring locations are displayed on Figure 9-20.

Soil boring advancement and soil classification were conducted in general accordance with the RSAP. Borings were continuously logged for lithology to approximately 35 feet bgs. Soil sampling was more comprehensive than the approach prescribed in the RSAP to allow for high-resolution soil sampling and to target finer-grained intervals, per the Onsite SCWP (ARCADIS 2013e). Boring logs for each boring are included in Appendix 9-A.

Soil samples collected from soil borings near the VPT and west of the railcar loading rack were submitted to SGS for sulfolane analysis by USEPA modified Method 8270D with isotope dilution. Soil samples from the VPT borings (HP13-57 and HP13-59) were also submitted to SWI for GSA by ASTM Method D422-63. The GSA data from these borings are discussed in Section 4.

9.2.2 Soil Results

Sulfolane concentrations in soil at designated depth intervals (0 to 2, 2 to 6.5, 6.5 to 10, and 10 to 18 feet bgs) at HP13-57, HP13-59, and HP13-66 through HP-75 are presented on Figures 9-21a through 9-21d. Sulfolane concentrations in soil were below analytical detection limits in samples collected from the 0- to 10-foot bgs depth intervals, except for two samples (HP13-59 [5-5.3], 8.08 J µg/kg; HP13-70 [7-8], 5.38 J µg/kg). Sulfolane concentrations near or below analytical detection limits in these samples confirm the absence of a sulfolane source area near the VPT or to the west of the railcar loading rack.

Sulfolane concentrations in soil from 10 to 18 feet bgs ranged from 13.4 µg/kg (HP13-57 [15.3-15.5]) to 47.6 µg/kg (HP13-74 [17.0-18.0]). Sulfolane in soil below 10 feet bgs is attributed to the soil being in contact with contaminated groundwater from upgradient sources.

9.3 High-Density Vertical Soil Sampling (Capillary Fringe Investigation)

The Onsite SCWP (ARCADIS 2013e) proposed high-resolution soil sampling to assess the vertical distribution of sulfolane in vadose zone soil in the SWA and to evaluate potential mechanisms for long-term persistence of sulfolane in soil that contributes sulfolane to groundwater. Soil sampling activities conducted during 2011 and 2012 identified high concentrations of sulfolane in soil in the SWA. Section 9.1.3 discusses potential historical sulfolane releases in the SWA.

Sulfolane is miscible in water and would not be expected, based on miscibility alone, to be a persistent source of groundwater contamination after a release to the environment. However, several studies at other sites have documented the persistence of another miscible contaminant (ethanol) for months to years after a release to unsaturated soil, suggesting that ethanol was stored in soil and slowly released to groundwater. The persistence of sulfolane in soil at the site may be attributable to mechanisms that are similar to those observed in the ethanol studies because sulfolane has physical characteristics that are similar to ethanol.

Researchers studying ethanol persistence at other sites found high concentrations of ethanol in soil pore water above the water table and within the capillary fringe (McDowell and Powers 2003, Freitas and Barker 2013). These observations have been linked to the miscibility and density of ethanol, which is lower than groundwater. While the latter mechanism would not be relevant to the sulfolane-laden wastewater that was released, which would be expected to be slightly more dense than groundwater, the solubility of sulfolane likely would have resulted in the transfer of sulfolane into soil pore water.

The persistence of sulfolane in unsaturated soil at the site may also be related to minimal infiltration in the impacted areas due to soil compaction in road and equipment areas, site plowing and grading, and construction of impermeable or low-permeability surfaces related to site improvements (e.g., Lagoon B and CU #2 EU). Water table fluctuations below these areas may result in the transfer of sulfolane from impacted soil in the capillary fringe and unsaturated zone to the regional groundwater.

The high-resolution soil sampling program completed in the SWA included data to assess the vertical distribution of soil sulfolane concentrations, organic content of the soil, soil moisture, and geotechnical properties of the unsaturated zone, capillary fringe, and saturated zone.

A modified high-resolution soil sampling program was adopted for three locations along the onsite VPT, as proposed in the Additional Scope of Work for Site Characterization Activities to Refine the Evaluation of Fate and Transport of Sulfolane (ARCADIS 2013g), which was submitted to ADEC on July 26, 2013. The purpose of this investigation was to collect data to assess the vertical distribution of sulfolane in vadose and capillary zone soil and to evaluate potential mechanisms for persistence of sulfolane in soil at those locations.

9.3.1 Data Collection

FHRA advanced 20 onsite high-density vertical soil borings to approximately 12 feet bgs using HSA drilling methods (CF13-1A through CF13-1E, CF13-2A through CF13-2E, CF13-3A through CF13-3E, and CF13-4A through CF13-4E) between August 16 and 27, 2013.

Borings CF13-1A through CF13-1E were advanced in the SWA. Borings CF13-2A through CF13-2E, CF13-3A through CF13-3E, and CF13-4A through CF13-4E were advanced along the VPT. The locations of these borings are shown on Figure 9-22.

Boreholes in each cluster had the following objectives:

- *Boring A*. Continuous lithologic documentation, measuring volumetric water content at 3-inch intervals, and collection of soil samples for analysis of sulfolane.
- *Boring B*. Continuous lithologic documentation, measuring volumetric water content at 3-inch intervals, and collection of soil samples for analysis of TOC.
- *Boring C*. Collection of soil samples for geotechnical analyses, including bulk density and GSA.
- *Boring D*. Collection of soil samples for geotechnical analyses, including bulk density, unsaturated hydraulic conductivity, air-water drainage capillary pressure-saturation testing, saturated porosity, and irreducible water saturation.
- *Boring E*. Continuous lithologic documentation, measuring volumetric water content at 3-inch intervals, and collection of soil samples for analysis of soil moisture content.

9.3.2 Soil Boring Advancement and Soil Characterization Methods

Soil boring advancement and soil classification were conducted in general accordance with the RSAP. Soil sampling was more comprehensive than the approach prescribed in the RSAP; therefore, sampling procedures detailed in the Onsite SCWP (ARCADIS 2013d) were not followed. Homestead Drilling Company advanced the borings with a truck-mounted HSA. Soil cores were collected from each boring with a 2-foot-long, 3-inch-diameter (approximately 2.5-inch-inner-diameter) split spoon sampler with a “sand catcher” (retainer). The Onsite SCWP (ARCADIS 2013e) proposed split-spoon samplers to be pushed into the subsurface to minimize soil disturbance and pore water displacement. Use of a 300-pound hammer was listed as a contingency in the event that pushing was unsuccessful. Due to poor soil recovery with the initial split spoon samples, a 300-pound hammer was required to maximize soil recovery during boring advancement.

Once collected, cores were carefully lifted from the respective boreholes and removed from the lead rod to avoid jarring. Split barrels were immediately handed to the supervising geologist and inspected for soil recovery. In Borings A, B, and E, soil volumetric water content was measured at 3-inch increments using the time-domain reflectometry (TDR) probe specified in the Onsite SCWP (ARCADIS 2013d). The TDR supplier initially provided a TDR probe that could not be used for small soil sample volumes, such as the soil cores; therefore, TDR probe measurements were not collected on the CF13-1 borings in the SWA. To mitigate the lack of TDR data, groundwater elevation was gauged in nearby monitoring wells prior to drilling. Gauging data from these wells were used to estimate the depth to capillary fringe and groundwater in the SWA. Soil moisture was observed visually by the supervising geologist during boring advancement as a secondary line of evidence for determining the depth to the capillary fringe and groundwater. Finally, analytical samples were collected for soil moisture content in Boring E to ensure that soil moisture data would be available for the SWA.

After measuring and documenting soil volumetric water content at 3-inch intervals, core lithology in Borings A, B, and E was documented by the supervising geologist per the RSAP. Boring logs for Borings A, B, and E at each location are provided in Appendix 9-A. TDR-based soil volumetric water content measurements are presented where available on boring logs.

Cores from Borings C and D at each location were collected in 2-foot acetate split barrel liners. Information on core advancement and recovery is documented in the boring logs. Boring logs for Borings C and D at each location are provided in Appendix 9-A.

9.3.3 Soil Sampling Methods

Soil sampling in Borings A through E at each location was consistent with the Onsite SCWP (ARCADIS 2013e). In Borings A, B, and E, at least one sample was collected per foot in the unsaturated zone where soil was recovered, with finer grained units targeted for sampling. Samples were collected continuously at 3-inch intervals from the capillary fringe. Depth to the capillary fringe was estimated from TDR probe measurements (CF13-2, CF13-3, and CF13-4 locations), visual observations of soil moisture, and depth to water in nearby monitoring wells (CF13-1 location). Below the groundwater table, at least one sample was collected per foot when soil was recovered. Finer grained units were targeted for sampling in the saturated zone. Soil sampling intervals in Borings A, B, and E at each location are displayed on the respective boring logs in Appendix 9-A.

Borings C and D at each location were collected in acetate split barrel liners in 2-foot intervals through the unsaturated zone, capillary fringe, and into the saturated zone. After inspection for recovery, acetate liners were capped and sealed. Soil recovery in Borings C and D at each location is displayed on the respective boring logs in Appendix 9-A.

Soil samples collected from Borings A and B at each location were submitted under direct chain of custody to SGS in Anchorage, Alaska. Samples from Borings A and B were analyzed for sulfolane by USEPA Method 8720D and TOC by USEPA Method 9060A, respectively. Isotope dilution was not used when analyzing for sulfolane in samples collected at CF13-1A due to the elevated sulfolane concentrations detected. Soil samples collected from Boring E at each location were submitted under direct chain of custody to SWI in Fairbanks, Alaska for soil moisture analysis by ASTM Method D2216.

Core sections from the C borings were slated for GSA by ASTM Method D422-63, per the Onsite SCWP (ARCADIS 2013d). ASTM Method D422-63 analyzes coarser material by sieve analysis (>75 micrometers [µm], No. 200 sieve) and finer material by a sedimentation process using a hydrometer (<75 µm, No. 200 sieve). Bulk density analysis was also proposed using ASTM Method 2434-68. Due to poor soil recovery in CF13-1C, samples from this core were not submitted for analysis. As discussed below, grain size analysis was completed using a different laboratory technique. Sulfolane soil concentrations at the CF13-2, CF13-3, and CF13-4 locations along the VPT were low. In response to these results, the C borings from these locations were not analyzed for grain size or bulk density. The geology in this area was adequately characterized by field logging.

Boring D at each location was submitted to Core Laboratories (Core Labs) in Bakersfield, California. Due to the low sulfolane concentrations at CF13-2, CF13-3, and CF13-4, these borings were not processed. CF13-1D was analyzed for the following:

- *Core Labs Saturated Zone Analysis Group*. Permeability to water (native-state), total and air-filled porosity, grain and bulk density, moisture content and total pore fluid saturation (water only) by Methods API RP40, ASTM 2216, and USEPA 9100.

- *Core Labs Capillarity – Air/Water Drainage Analysis Group*. Drainage capillary pressure curve (air displacing water) includes: air permeability, saturated hydraulic conductivity, fluid production vs. capillary pressure, total porosity, and dry bulk density by Methods ASTM D6836 and API RP40.

- GSA by ASTM D422 and D4464Mod.

The analytical methods listed above were expanded from those proposed in the Onsite SCWP (ARCADIS 2013e). The Core Labs Saturated Zone Analysis Group was selected to provide the necessary data for evaluating soil pore water concentrations. The Core Labs Capillarity – Air/Water Drainage Analysis Group was selected to estimate air-water capillary drainage parameters. GSA was performed on CF13-1D in place of the analysis that was proposed on the CF13-1C core to reduce variability introduced by processing different soil cores and to increase the vertical density of GSA data compared to what could be achieved with the CF13-1C core. ASTM Methods D422-63 and D4464 Mod were used, which analyzed coarser material by sieve analysis (>75 µm, No. 200 sieve) and finer material by laser diffraction methods (<75 µm, No. 200 sieve). This change was approved by ADEC.

9.3.4 Soil Analytical Results

9.3.4.1 Southwest Area – CF13-1

The soil quality data from the CF13-1A boring advanced in the SWA identify a high concentration of sulfolane in most of the vadose zone soil samples. The groundwater table at the time of installation of the soil borings was at approximately 8.4 feet below grade. The minimum, median, and maximum sulfolane concentrations in the 15 soil samples collected above the groundwater table were 48,300, 588,000 JL*, and 1,620,000 JL* µg/kg, respectively.

The maximum sulfolane concentration in CF13-1A was identified in a sample collected from 5.75 to 6 feet below grade (1,610,000 µg/kg). The soil that made up this sample was described as having high organic content and could be classified as peat. This sample was collected above the typical range of groundwater fluctuations in the SWA, which is estimated to range from 7.5 to 9.7 feet below grade, meaning that this sulfolane-bearing zone does not routinely come in contact with groundwater. A vertical profile of sulfolane concentrations in soil showing the groundwater table at the time the soil boring was advanced, the typical range of groundwater elevations in the SWA due to seasonal groundwater table fluctuations, and the maximum known high and low groundwater elevations in the SWA are presented on Figure 9-23. Soil analytical results for sulfolane, TOC, and soil moisture from the CF13-1 location are summarized in Table 9-2. Sulfolane, TOC, and soil moisture analytical results are provided in Appendix 9-D. Analytical laboratory reports are provided in Appendix 9-B.

Groundwater samples were collected from one soil boring in the SWA (CF13-1B) and two Phase 8 monitoring wells (MW-355-15 and MW-355-55) downgradient from the SWA. Sulfolane was detected in groundwater at 36.3 µg/L in CF13-1B at 12.7 ft bgs and at 4.90 J µg/L in MW-355-15. Sulfolane concentrations were below analytical detection limits in groundwater collected from MW-355-55. Groundwater sulfolane concentrations within and downgradient of the SWA were low relative to the high soil concentrations measured in vadose zone soils in the SWA. This suggests that sulfolane transport through and out of the vadose zone is the limiting factor in this historic source area.

9.3.4.2 Additional Areas – CF13-2, CF13-3, and CF13-4

Low soil sulfolane concentrations were measured at CF13-2, CF13-3, and CF13-4. Twenty-four of 42 soil samples collected for sulfolane at these locations were below analytical detection limits and four were qualified with data flags near analytical detection limits. Quantified soil sulfolane concentrations ranged from 4.90 J µg/kg (CF13-3A; 1.25-1.50 feet bgs) to 83.7 µg/kg (CF13-2A; 9.0-9.25 feet bgs). The CF13-2A sample collected from 9 to

9.25 feet bgs was characterized as sand and was collected below the approximate water table observed during boring advancement (8.8 feet bgs). Soil TOC and soil moisture varied throughout the CF13-2, CF13-3, and CF13-4 vertical profiles, with TOC and soil moisture highest in finer grained soil (e.g., peat and silt). Soil analytical results for sulfolane, TOC, and soil moisture from the CF13-2, CF13-3, and CF13-4 locations are summarized in Tables 9-3, 9-4, and 9-5. Sulfolane, TOC, and soil moisture analytical results are provided in Appendix 9-D. Analytical laboratory reports are provided in Appendix 9-B.

The highest soil sulfolane concentrations measured at the VPT locations were in CF13-2A, at or below the approximate water table observed during boring advancement. This is consistent with the sulfolane groundwater plume delineated in the Third Quarter 2013 Groundwater Monitoring Report (ARCADIS 2013i), where groundwater concentrations were highest in the area of CF13-2 compared to the other VPT locations.

9.3.5 Data Evaluation

An analysis was completed to normalize the vertical sulfolane data collected at the CF13-1 location. The sulfolane data that were reported by the lab in terms of mass of sulfolane per mass of soil were converted to mass of sulfolane per volume of soil. This conversion was completed because the bulk soil density is expected to vary vertically based on the variable soil types found. The mass to volume conversion was completed where sulfolane and bulk density data were both available for the same vertical interval using the following calculation:

$$C_b = [C_s \times \rho_b] \text{ x } 1 \text{ x } 10^{-3} \text{ kg/g} \qquad \text{Equation 1}$$

Where:

C_b = bulk soil sulfolane concentration, micrograms per cubic centimeter

C_s = soil sulfolane concentration, µg/kg

ρ_b = bulk density, g/cm^3

kg/g = kilograms per gram

These normalized values were compared to soil properties to determine if the soil properties could be correlated to sulfolane concentration. The comparisons included sulfolane distribution as a function of soil TOC, pore water saturation, and silt- and clay-sized particle content. Vertical sulfolane concentration profiles compared to these soil properties, and sulfolane concentration plotted as a function of the soil properties are presented on Figure 9-24. Soil geotechnical data used to normalize the sulfolane soil data and determine pore water saturation are summarized in Table 9-2. The full geotechnical dataset obtained from Core Labs is presented in Appendix 9-D. Photographs from Core Labs are provided in Appendix 9-E.

The analysis indicates that sulfolane is not strongly correlated to soil TOC or pore water saturation. A strong correlation was found between sulfolane concentration and silt and clay-sized particle content of the soil samples. This observation is consistent with previous findings that suggest that fine-grained soil across the site retain sulfolane. The soil sample with the lowest sulfolane concentration in the vadose zone (48,300 µg/kg at 3.5 to 3.75 feet bgs) comprised 65 percent gravel and only 7 percent silt- and clay-sized particles.

The concentration of sulfolane in pore water within the soil column was also of interest. Due to the chemical properties of sulfolane, sulfolane is expected to minimally adsorb to soil grains or organic material within the soil matrix. Instead, sulfolane will be present almost exclusively in pore water within the soil matrix. Therefore, soil analytical results for sulfolane largely represent the mass of sulfolane that was present in pore water in the soil sample, which is incorporated into the laboratory sample during soil extraction in the laboratory. The sulfolane concentration in pore water was calculated using the following equation:

$$C_p = \left[\frac{C_s \times \rho_b}{\emptyset_w}\right] \text{ x 1 x } 10^{-3} \text{ kg/g x 1 x } 10^{3} \text{ cm}^3\text{/L} \qquad \text{Equation 2}$$

Where:

C_p = soil pore water sulfolane concentration (µg/L)

C_s = soil sulfolane concentration (µg/kg)

ρ_b = bulk density (g/cm^3)

Φ_w = water-filled porosity, dimensionless

cm^3/L = cubic centimeters per liter

The pore water calculation is of interest because the pore water sulfolane concentrations can be directly related to the sulfolane groundwater concentrations observed in the SWA and compared to the concentration of sulfolane in wash water that was the source of sulfolane impacts in the SWA.

Sulfolane pore water concentrations in CF13-1 are presented in Table 9-2. The maximum concentration of sulfolane in pore water was 5,870,000 µg/L and the median concentration was 2,740,000 µg/L. These concentrations exceed dissolved-phase sulfolane concentrations currently found in groundwater samples collected from the SWA (as of third quarter 2013). The maximum sulfolane concentration detected in groundwater samples collected immediately downgradient from the SWA was 298 µg/L at MW-330-20 during the third quarter 2013 groundwater sampling event (ARCADIS 2013i), which indicates that the remaining sulfolane found in soil pore water can reasonably be the source of the dissolved-phase impacts.

The conceptual model of sulfolane releases in this area is that sulfolane-laden wash water was oversprayed and/or splashed/overflowed out of the wash pad that was in place prior to 2002. This would have resulted in wash water with varying concentrations of sulfolane; however, in April 2000, the concentration was documented at 97,000,000 µg/L (Williams 2000c). Comparison of the maximum pore water concentration of 5,870,000 µg/L to the known concentration of sulfolane in wash water of 97,000,000 µg/L (Williams 2000c) suggests that the sulfolane concentrations in soil have decreased through time. It is expected that the pore water concentrations shortly after the release(s) would have been similar to the wash water, potentially with some dilution due to pore water in place at the time of the release. It is unlikely that all of the oversprayed wash water had a concentration of 97,000,000 µg/L (Williams 2000c); however, it is reasonable to assume that the sulfolane concentration of 5,870,000 µg/L in pore water represents a decrease from the historical high sulfolane concentration in pore water that was the likely result of historical releases in this area. The decrease in concentrations through time is likely attributable to sulfolane mass loss from leaching to groundwater and aerobic biodegradation in the vadose zone.

9.3.6 High-Density Vertical Soil Sampling Summary

The high-resolution soil sampling in the SWA resulted in several findings that are important to the conceptual model of sulfolane storage in unsaturated soil. These findings are based on soil data collected from the SWA, but the concepts can be reasonably applied to other areas where sulfolane was released at or near ground surface. The significant findings are:

- High concentrations of sulfolane were detected in vadose zone soil in the SWA, more than a decade after the last use of this area as a wash pad.

- The concentration of sulfolane in pore water is approximately one order of magnitude less than the one known concentration of sulfolane in recirculated wash water used in the SWA, which indicates that while the source has persisted, the sulfolane source has diminished through time.

- High concentrations of sulfolane are present in soil that does not continually interact with groundwater, which suggests that this soil may release sulfolane to groundwater as a result of seasonal groundwater fluctuations.

- The sulfolane in soil is strongly correlated to silt and clay content and relatively weakly correlated to pore water saturation and soil organic content.

9.4 Total Organic Carbon Analysis

9.4.1 Soil Sample Collection Methodology

As proposed in the Onsite SCWP (ARCADIS 2013d), soil samples were collected to characterize TOC spatially and with depth across the sulfolane plume. Soil samples collected for TOC were submitted to SGS and analyzed by USEPA Method 9060A. A total of 21 soil samples were collected for TOC analysis from 10 onsite wells (MW-110-65, MW-336-20, MW-336-55, MW-348-65, MW-355-55, MW-358-60, MW-359-60, MW-360-50, MW364-65, and O-5-65) and one soil boring (SB13-16). Soil samples were collected from the midpoint of the well screen (or total depth for soil boring SB13-16) and one sample from the midpoint between the water table and well screen midpoint. Sampling personnel targeted coarser-grained materials such as silty gravel and poorly graded gravel at each location to represent transport flow paths. Sample locations are distributed throughout the site as shown on Figure 9-25.

FHRA conducted additional TOC soil sampling onsite as part of the high-resolution vertical soil sampling discussed in Section 9.3. Sixty-seven soil samples were collected between one soil boring in the SWA (CF13-1B) and three soil borings at the VPT (CF13-2B, CF13-3B, CF13-4B). Soil sampling procedures in these borings are described in detail in Section 9.3.3. Sampling locations are shown on Figure 9-22.

FHRA conducted additional TOC soil sampling offsite. These results are presented in the Offsite Addendum (ARCADIS 2013m). A total of 33 TOC soil samples have been collected from 10 onsite well or soil borings and six offsite well borings.

9.4.2 Soil Results

Detectable TOC concentrations in onsite soil collected from monitoring wells and one standard soil boring (SB13-16) ranged from 0.0321 J percent at MW-336-20 (10.0-11.5 feet bgs) to 0.28 percent at O-5-65 (63.0-63.5 feet bgs). The average TOC concentration in onsite soil was 0.0904 percent. TOC concentrations are consistent with concentrations detected in offsite soil collected from the same depth range: 0.0594 in MW-347-65 (62.0-63.0) and 0.118 percent in MW-353-65 (62.0-63.5), with an average of 0.064 percent (ARCADIS 2013m). Onsite TOC results are summarized in Table 9-1e and shown on Figure 9-25.

TOC concentrations in high-resolution vertical soil sampling borings ranged from 0.0658 percent at CF13-4B (7.9-8.0 ft bgs) to 13.0 percent at CF13-3B (2.6-2.9 ft bgs). TOC soil concentrations were higher in the high-resolution vertical soil sampling borings relative to samples collected in other areas of the site. This is consistent with finer-grained units being targeted for sampling in the high-resolution vertical soil sampling borings and coarse-grained units being targeted for TOC sampling at other locations. The highest soil TOC concentrations in the high-resolution vertical soil sampling borings were generally in the vadose zone, reflecting the finer-grained soil documented in shallow soils at the site.

9.5 Summary

The nature and extent of COC impacts at the site have been thoroughly characterized through the collection of more than 1,000 samples during 2011, 2012, and 2013 site characterization activities. Significant findings of this investigation are:

- Sulfolane concentrations in soil exceeding the calculated ACL (999 µg/kg) are generally confined to delineated source areas (SWA, CU #1 Wash Area, and CU #2 EU). Elevated soil sulfolane concentrations in these areas, coupled with high groundwater concentrations reported in Section 10 and known historical releases summarized in Geomega (2013a) and Section 13 provide strong evidence for the ongoing secondary release of sulfolane to groundwater from contaminated soil in these areas.

- Petroleum hydrocarbon impacts in soil, including the COCs of interest (benzene, xylenes, 1,3,5-TMB, and naphthalene) are confined onsite. The highest concentrations of COCs are consistently found near the air-groundwater interface or the smear zone. Benzene, xylenes, 1,3,5-TMB, and naphthalene all have been reported above the respective soil ACLs in at the CU #1 Wash Area, CU #2 EU, and Sump 908.

- Retention of sulfolane in the unsaturated zone and capillary fringe was investigated in the SWA and along the VPT. The highest concentrations of sulfolane in soil were detected in the SWA in boring CF13-1A. High sulfolane concentrations were found to directly correlate with fine-grained soil and, in particular, the percent of silt and sand in the soil matrix.

- TOC concentrations in soil from below the water table are generally consistent with the concentrations detected in offsite soil. Samples collected as part of the capillary fringe investigation generally contained higher TOC concentrations than onsite and offsite samples collected below the water table. This is consistent with the finer-grained soils observed in the vadose and capillary fringe zones.

10. Groundwater Investigation and Constituent of Concern Distribution

10.1 Sampling Methods

As proposed in the Onsite SCWP and Additional Scope of Work for Site Characterization Activities to Refine the Evaluation of Fate and Transport of Sulfolane (ARCADIS 2013e and i, respectively) and subsequent comments and discussion with the ADEC, groundwater samples were collected from the following areas to further characterize dissolved-phase sulfolane concentrations at the site:

- Twenty-one Hydropunch™ borings along the VPT and the area west of the railcar loading rack at 8 to 10 feet below the water table (approximately 18 to 20 feet bgs)

- Sixteen temporary hand-driven well points at various soil boring locations at the water table, which is generally 10 feet bgs within the potential source areas.

10.1.1 Hydropunch Sampling

Groundwater samples were collected from discrete intervals to vertically delineate sulfolane concentrations in groundwater along the VPT, to identify any variability in sulfolane concentrations that was not detectable by the current layout of the VPT, and determine if a potential source area was present along the railroad tracks west of the railcar loading rack. The placement of these borings in strategic locations allows for a lateral profile of sulfolane impacts. Hydropunch boring locations at the VPT are shown on Figure 10-1.

A discrete interval groundwater sampler was driven through open-ended 1.25-inch-inner-diameter drill casing with a direct-push drill rig. The RSAP describes the discrete interval groundwater sampling procedures. In the VPT area, borings were advanced approximately 50 feet apart between VPT well nests MW-303 and MW-304 (HP13-55 through HP13-60). Four additional locations were spaced approximately 50 feet apart between VPT well nests MW-304 and MW-305 (HP13-62 through HP13-65). One additional location was established along the MW-304 VPT well nest, approximately 8 feet to the southwest of MW-304-125 (HP13-61). Borings were advanced to refusal (refusal being the mechanical limits of the direct-push technology versus a geologic feature such as permafrost) at each location, varying between 59 to 89 feet bgs, and between six and nine groundwater samples were collected at 10-foot intervals, beginning at the water table and extending to total depth.

An additional 10 borings (HP13-66 through HP13-75 shown on Figure 10-2) were advanced approximately 50 feet apart along the railroad tracks west of the railcar loading rack, upgradient from monitoring wells MW-139-25 and MW-142-20. The borings were advanced to approximately 10 feet below the water table (18 feet bgs), except for HP13-66, HP13-70, and HP13-75, which are located at the southern, midpoint, and northern end of the transect and were advanced to depths between 58 and 79 feet bgs. Groundwater samples were collected at the water table and 10 feet below the water table. Groundwater samples were collected at 10-foot intervals from deep borings HP13-66, HP13-70, and HP13-75.

Groundwater samples were collected using low-flow methods in accordance with micro-purge groundwater sampling procedures outlined in the RSAP. Water samples were submitted to SGS for sulfolane analysis. Data validation for these samples is discussed in Section 16 of this Onsite Addendum. Laboratory analytical reports for these samples are included as Appendix 10-A. Due to the nature of the sampling process, soil samples were not collected during this event for sampling or for lithological classification; however, soil samples were collected adjacent to borings near the railroad tracks and are described in Section 9.2.

Following groundwater sample collection at the final boring depth, the borings were decommissioned according to procedures described in the RSAP. The horizontal coordinates of each boring were obtained using a hand-held GPS unit.

10.1.2 Temporary Hand-Driven Point Investigation

Temporary hand-driven points were advanced to collect grab groundwater samples from the following areas:

- SWA
- CU #2 EU
- CU #1 Wash Area
- Tank 194 Area
- Sump 908

Temporary hand-driven points were completed using a hand-operated slide hammer to advance an expendable, stainless-steel screened well point fitted with new tubing. Once the well point reached the desired depth (between 8 and 12 feet bgs), the removable drive shaft was extracted.

Prior to sampling, the well points were developed using a peristaltic pump and measurements of temperature, conductivity, and pH were recorded using a hand-held meter; turbidity was noted visually. Pumping continued until the purge water ran clear, without visible sediment. In some cases, the pumping direction was reversed to surge the well point. Once the purge water was clear, a sample was collected from the well point using the peristaltic pump. Groundwater samples were submitted to SGS for sulfolane by modified USEPA Method 1625B with isotope dilution. Additionally, groundwater samples collected from borings in the CU #2 EU, CU #1 Wash Area, and Sump 908 were submitted for BTEX analysis by USEPA Method 8021. Purge water was managed according to procedures outlined in the RSAP.

10.1.3 Total Organic Carbon Sampling

As noted in the Offsite SCWP (ARCADIS 2013f), a sufficient amount of TOC in groundwater data are available from historical and ongoing groundwater monitoring activities. Since 2011, 109 groundwater samples have been collected from onsite wells for TOC analysis. Samples were collected as part of AS pilot monitoring, geochemical monitoring, and groundwater recovery system performance monitoring. Onsite sampling locations are shown on Figure 10-3.

FHRA conducted additional TOC groundwater monitoring offsite. These results are presented in the Offsite Addendum (ARCADIS 2013m). Since 2011, 496 TOC groundwater samples have been collected from onsite and offsite wells.

10.2 Petroleum Hydrocarbon Analytical Results

Based on the Revised Draft Final HHRA (ARCADIS 2012), COCs related to petroleum hydrocarbons at the site include benzene, total xylenes, naphthalene, and 1,3,5-TMB. Detected concentrations were compared to ACLs, as described in Section 1.2.

Petroleum hydrocarbon results are summarized below and data collected during 2013 characterization activities are included in Tables 10-1 and 10-2. Data qualifiers are defined in the data tables. Analytical laboratory reports are provided in Appendix 10-A.

10.2.1 Benzene and Total Xylenes

Benzene and total xylenes have been analyzed in samples collected at the site since 1987. Historical results are summarized in Appendix 10-B. During 2013 site characterization activities, groundwater samples were collected for BTEX analysis from the following areas:

- Water table:
  - Five newly installed monitoring wells (MW-174-15, MW-336-15, MW-348-15, MW-355-15, and O-32)

  - Two grab groundwater samples from temporary hand-driven points (SB13-16 and SB13-17) in the CU #1 Wash Area
  - Eleven grab groundwater samples from temporary hand-driven points (SB13-25 through SB13-29 and SB13-39 through SB13-44) in the CU #2 EU.
  - One grab groundwater sample from temporary hand-driven point SB13-23 at Sump 908
- 10 to 55 feet below water table:
  - Eleven newly installed monitoring wells (MW-110-65, MW-336-20, MW-336-35, MW-336-55, MW-348-65, MW-354-35, MW-354-60, MW-355-55, O-12-65, O-24-65, and O-5-65)
  - Six grab groundwater samples from temporary hand-driven points (SB13-39 through SB13-44) in the CU #2 EU

Benzene and total xylenes results are discussed below.

10.2.1.1 Water Table Zone Evaluation

Benzene was detected above the ACL of 590 µg/L in 13 of 14 groundwater samples collected from the CU #1 Wash Area, CU #2 EU, and Sump 908. Benzene was detected in both groundwater samples collected from borings in the CU #1 Wash Area at concentrations of 14,000 µg/L (SB13-16) and 14,900 µg/L (SB13-17). Benzene was detected in each of 11 groundwater samples collected from borings in the CU #2 EU at concentrations ranging from 5.80 µg/L (SB13-41) to 52,700 µg/L (SB13-43). Benzene was detected in the only groundwater sample collected from Sump 908 at a concentration of 4,190 µg/L (SB13-23). High benzene concentrations in groundwater such as 14,000 µg/L in the CU #1 Wash Area and 52,700 µg/L in the CU # 2 EU were likely in areas where LNAPL is present in soil.

Total xylenes were detected above the ACL of 3,470 µg/L in 12 groundwater samples collected from the CU #1 Wash Area and CU #2 EU. Total xylenes were detected in both groundwater samples collected from borings in the CU #1 Wash Area at concentrations of 7,880 µg/L (SB13-17) and 9,700 µg/L (SB13-16). Total xylenes were detected in each of 12 groundwater samples collected from borings in the CU #2 EU at concentrations ranging from 28.7 µg/L (SB13-41) to 16,800 µg/L (SB13-39 and SB13-43). Total xylenes were detected below the ACL in the only groundwater sample collected from the Sump 908 at a concentration of 1,750 µg/L (SB13-23). Wells with total xylenes concentrations detected above the ACL are located within the footprint of the benzene plume. Additionally, toluene and ethylbenzene detections were consistent with detections of benzene and total xylenes (Tables 10-1 and 10-2). These data are consistent with source area detections and LNAPL presence.

Groundwater samples collected during site characterization activities and second quarter 2013 routine groundwater monitoring showed that the benzene plume exceeds the calculated ACL of 590 µg/L at the water table beneath the CU #1 Wash Area and the CU #2 EU. An additional area exceeding the calculated ACL of 590 µg/L is present near recovery well R-45 and well O-13 near the truck loading rack. Concentrations of benzene and total xylenes do not exceed the respective ACLs beyond the capture zone of the groundwater treatment system. Historical data were used to support delineation of the plume boundary. The inferred extent of the benzene plume exceeding the calculated ACL of 590 µg/L is shown as an isopleth on Figure 10-4.

The detectable benzene plume at the water table is present beneath the tank farms, CU #1 Wash Area, and CU #2 EU, extending north under the current truck loading rack and west beneath Lagoons B and C. The detectable benzene plume extends past the capture zone of the groundwater treatment system; however, no detectable concentrations of petroleum hydrocarbons were found in groundwater samples collected beyond the developed portions of the site. This suggests that the benzene is rapidly attenuated by biodegradation downgradient from the capture zone. The inferred extent of the detectable benzene plume is shown as a nondetect isopleth on Figure 10-4.

10.2.1.2 Deep Groundwater Zone Evaluation

A hydropunch investigation completed in 2012 detected concentrations of petroleum hydrocarbons in groundwater samples collected below the water table zone in areas where LNAPL was observed (ARCADIS 2013a). Benzene was detected above the ACL of 590 µg/L in the groundwater sample collected at 53 feet bgs from boring HP-16 at a maximum concentration of 2,710 µg/L. Benzene was detected in 11 samples collected from depths ranging from 14 to 62 feet bgs. Borings HP-14 and HP-16 were located near well cluster MW-334, within the zone of observed LNAPL. A maximum benzene concentration of 11,300 µg/L was detected in the groundwater samples collected from boring HP-45 at 14 feet bgs. Benzene was detected in 10 samples collected from depths ranging from 14 to 54 feet bgs. Borings HP-45 and HP-46, located in the CU #2 EU, were also in the zone of observed LNAPL. HP-16 was the only hydropunch boring with increasing concentrations of benzene with depth. The unexpected benzene concentrations at depth were thought to be a result of drag down of LNAPL present at the water table. However, to further investigate the nature of these impacts, FHRA submitted groundwater samples from monitoring wells screened in the zones from 10 to 55 and 55 to 90 feet below the water table for laboratory analysis of BTEX.

FHRA collected groundwater samples from 21 monitoring wells between fourth quarter 2012 and third quarter 2013 as follows:

- Four wells near HP-14 and HP-16 (MW-175-90, MW-186B-60/C-100, and MW-334-65)
- Eight wells near HP-45 and HP-46 (MW-176B-50/C-90, MW-178B-50/C-90, MW-179B-50/C-90, and MW-180B-50/C-90)
- Three wells downgradient from impacted groundwater (MW-101-60 and MW-154A-75/B-95)
- Six additional wells to further refine the site characterization in groundwater below the water table: MW-129-40, MW-148B-30, MW-149B-20, MW-153B-55, MW-309-66 and MW-186E-75

Data collected from monitoring wells between fourth quarter 2012 and third quarter 2013 indicated that deep groundwater below the water table in these areas is not impacted with petroleum COCs. Benzene results collected from 2012 hydropunch borings ranged from 22.8 to 2,710 µg/L and total xylenes ranged from 224 to 11,990 µg/L. The majority of groundwater samples from monitoring wells did not contain detectable petroleum hydrocarbon concentrations; therefore, results from the 2012 hydropunch investigation do not correlate with the monitoring well data, specifically near borings HP-14 and HP-16. It is likely that, even though sampling precautions were taken, the concentrations observed in the 2012 hydropunch samples are the result of drag down of LNAPL present at the water table.

During 2013 characterization activities, samples were collected below the water table from 11 newly installed monitoring wells and six temporary hand-driven points in the site process area. Of these, one well cluster (including three wells and six hand-driven points) was installed near 2012 hydropunch borings HP-45 and HP-46 in the CU #2 EU. Monitoring well cluster MW-336 was installed in the CU #2 EU to vertically delineate impacts detected in groundwater samples collected from borings HP-45 and HP-46 during the 2012 hydropunch investigation.

Benzene and total xylenes were detected above the respective ACLs below the water table at concentrations of 15,300 and 4,720 µg/L, respectively, in the groundwater sample collected from newly installed monitoring well MW-336-20 located in the CU #2 EU. Concentrations were similar to those detected in MW-336-15. Two additional monitoring wells (MW-336-35 and MW-336-55) in this well cluster show decreasing concentrations of benzene to 28.1 µg/L at 35 feet bgs and 1.09 µg/L at 55 feet bgs and concentrations of total xylenes to 5.09 µg/L at 35 feet bgs. Total xylenes were not detected in samples collected deeper than 35 feet bgs. Decreasing concentrations to levels below the ACLs confirm that petroleum hydrocarbons detected in this area are vertically delineated. Additionally, toluene and ethylbenzene detections were consistent with detections of benzene and total xylenes. Petroleum hydrocarbon groundwater quality data are summarized in Tables 10-1 and 10-2. Benzene results from groundwater samples collected below the water table from second and third quarter 2013 and from 2013 characterization activities are shown on Figure 10-5.

Concentrations of benzene exceeded the ACL of 590 µg/L below the water table (at approximately 20 feet bgs) at three temporary hand-driven points (SB13-40, SB13-43, and SB13-44) advanced in the CU #2 EU (Figure 10-5). Concentrations of total xylenes exceeded the ACL of 3,470 µg/L below the water table (at approximately 20 feet bgs) at SB13-43 (Figure 10-5). Benzene was detected in five of six groundwater samples collected from these borings at concentrations ranging from 1.56 µg/L (SB13-41) to 22,000 µg/L (SB13-43). Total xylenes were detected in five of six groundwater samples collected from borings at concentrations ranging from 2.33 J µg/L (SB13-41) to 9,940 µg/L (SB13-43). Detected petroleum hydrocarbon concentrations are consistent with concentrations detected in monitoring well MW-336-20. Therefore, decreasing concentrations of petroleum hydrocarbons detected in wells MW-336-35 and MW-336-55 infer that hydrocarbon concentrations in groundwater near the CU #2 EU are vertically delineated to approximately the detection limit at 55 feet bgs or shallower.

Well cluster MW-354 was installed in the Former Bolted Tank Area (Figure 2-2) near hydropunch boring HP-34, where benzene concentrations were not delineated vertically during the 2012 hydropunch investigation (ARCADIS 2013a). Two wells were installed at depths of 35 and 65 feet bgs (Figure 10-5). Benzene was not detected in groundwater samples from either well. Total xylenes were detected at concentrations below the ACL in the groundwater sample collected from well MW-354-35 and were not detected in the groundwater sample collected from well MW-354-65. Therefore, petroleum hydrocarbon concentrations in this area are vertically delineated to 35 feet bgs or shallower.

Based on the petroleum hydrocarbon analytical data collected from wells below the water table zone in 2013, it is likely that smearing of LNAPL during boring installation resulted in detectable concentrations of hydrocarbons in the 2012 hydropunch results. Data collected from recently installed wells and temporary hand-driven points in the CU #2 EU are consistent with source area concentrations and areas with observed LNAPL. Based on the data collected, FHRA concludes that concentrations of petroleum hydrocarbons exceeding the respective ACLs are limited to groundwater upgradient from the groundwater treatment system and to groundwater within or near the water table zone near source areas and areas with observed LNAPL.

10.2.2 Naphthalene

Naphthalene was analyzed in groundwater samples collected from 38 wells between 2001 and 2012. Concentrations were detected above the ACL of 31.8 µg/L in groundwater samples collected from nine wells that are screened across the water table. Of these, four wells (MW-125-25, MW-130-25, MW-135-20, and MW-137-20) contained concentrations of naphthalene below the ACL in the most recent sample collected. The five remaining wells (MW-115-15, MW-116-15, MW-136-20, MW-138-20, and MW-139-25) contained concentrations of naphthalene above the ACL in the most recent groundwater samples collected, ranging from 37 µg/L (MW-136-20 collected in 2008) to 420 µg/L (MW-116-15 collected in 2008). Naphthalene was not detected in groundwater samples collected from wells screened below the water table. Naphthalene detections are limited to site process areas and areas where LNAPL has been observed. Historical naphthalene analytical results are summarized in Appendix 10-B. With the exception of MW-139-25, all of these wells are within the capture zone of the recovery system. No detections of naphthalene were found in groundwater samples collected from MW-142-20, which is downgradient of MW-139-25.

10.2.3 1,3,5-Trimethylbenzene

1,3,5-TMB was analyzed in groundwater samples collected from 18 wells between 2001 and 2012. Concentrations were detected above the ACL of 92.4 µg/L in groundwater samples collected from three wells screened across the water table. Of these, one well (MW-139-25) contained a concentration of 1,3,5,-TMB below the ACL in the most recent sample collected. The two remaining wells (MW-116-15 and MW-138-20) contained concentrations of 1,3,5-TMB above the ACL in the most recent groundwater samples at concentrations of 203 µg/L (collected in 2001) and 432 µg/L (collected in 2012), respectively. 1,3,5-TMB was not detected in groundwater samples collected from wells screened below the water table. 1,3,5-TMB detections are limited to site process areas and areas where LNAPL has been observed. Historical 1,3,5-TMB analytical results are summarized in Appendix 10-B.

10.3 Sulfolane

Sulfolane results are summarized below. Initial data collected during 2013 characterization activities are shown on Figures 10-6 through 10-11 and summarized in Tables 10-1 and 10-2. Data qualifiers are defined in the data tables. Additionally, third quarter 2013 monitoring well data and select 2012 hydropunch data for areas downgradient of the SWA are shown on Figures 10-8 and 10-9 to complete the interpretation of the extent of sulfolane concentrations in groundwater. Analytical laboratory reports are provided in Appendix 10-A. Historical data tables are included in Appendix 10-B.

10.3.1 Phase 8 Monitoring Wells

As proposed in the Onsite SCWP (ARCADIS 2013e), and in subsequent coordination with ADEC, 80 onsite wells were installed during 2013 characterization activities. Initial groundwater samples were collected from 47 wells and samples will be collected from the remaining 33 installed wells and reported in quarterly monitoring reports. Additionally, ten wells are pending installation and will be installed as weather permits. Initial groundwater sample results and wells with pending samples collected for sulfolane analysis are described below:

- Well MW-110-65 was installed near MW-110-20 to further characterize sulfolane concentrations in groundwater below the water table. Sulfolane concentrations were not detected in the sample collected from this well, indicating that detectable sulfolane is delineated above 65 feet bgs.

- Well MW-174-15 was a replacement for well MW-111-15. Sulfolane was detected at a concentration of 66.4 µg/L, which is consistent with historical data from MW-111-15.

- Well MW-334-85 was installed to delineate detectable sulfolane concentrations below well MW-334-65. Sulfolane concentrations were not detected in the sample collected from this well. Additionally, during the third quarter 2013, sulfolane was not detected in the sample collected from MW-334-65, indicating that detectable sulfolane is delineated above 65 feet bgs.

- Wells MW-344-15 and MW-344-75 were installed adjacent to well R-42 to evaluate hydraulic capture of the groundwater treatment system. Sulfolane was detected at a concentration of 104 µg/L in well MW-344-15, which is consistent with sulfolane concentrations in groundwater in this area. Sulfolane concentrations were not detected in the sample collected from well MW-344-75, indicating that detectable sulfolane is delineated above 75 feet bgs.

- Wells MW-348-15 and MW-348-65 were installed to evaluate sulfolane concentrations in the area northwest of observation well O-1. Sulfolane was detected at concentrations of 1,660 JL µg/L in well MW-348-15 and 6.04 J µg/L in well MW-348-65, confirming that sulfolane concentrations decrease downgradient from well O-1, which contained a sulfolane concentration of 6,590 µg/L in groundwater during third quarter 2013.

- Wells MW-354-15, MW-354-35, and MW-354-60 were installed to evaluate sulfolane concentrations detected during the 2012 hydropunch investigation in the Former Bolted Tanks Area. Sulfolane was detected at concentrations of 1,060 JL µg/L in well MW-354-15 and 849 µg/L in well MW-354-35. Sulfolane was not detected in well MW-354-60, confirming that sulfolane is delineated to approximately 60 feet bgs or shallower. Benzene and total xylenes concentrations detected in groundwater samples from this well are discussed in Section 10.2.1.

- Wells MW-355-15 and MW-355-55 were installed to evaluate sulfolane concentrations in the area downgradient from the SWA. Sulfolane was detected at a concentration of 4.60 J µg/L in well MW-355-15. Sulfolane was not detected in well MW-355-55. As described in Section 9.4, this area contains the highest sulfolane concentration in soil at the site (maximum sulfolane concentration of 1,620,000 JL* µg/kg); however, because this sulfolane-bearing zone is located above the typical range of groundwater fluctuations, it does not routinely come in contact with groundwater. Although the concentrations detected in groundwater samples are not indicative of a source area, the soil data discussed in Section 9.3 indicate that a significant amount of sulfolane is stored in the vadose zone beneath the SWA. A portion of the sulfolane historically released to this area continues to be retained in soil, creating an ongoing source of sulfolane to the aquifer.

Results are summarized in Table 10-1 and well locations are shown on Figure 3-1. Phase 8 monitoring wells that were installed with pending analytical results are shown on Figure 3-1 and include the following:

- Wells MW-142-65 and MW-142-150 were installed to evaluate sulfolane concentrations and the presence of permafrost in the area downgradient of the MW-154 well nest. Permafrost was not encountered at this location.

- Well MW-334-15 was re-installed as a 4-inch well to enhance LNAPL recovery at this location.

- Well MW-337-20 was installed just northeast of well MW-138 for further characterization of the sulfolane plume downgradient of the CU #2 EU. Well MW-337-20 was screened a few feet below seasonal LNAPL fluctuations (15 to 20 feet bgs) to monitor sulfolane concentrations without the presence of LNAPL during sampling.

- Well S-41R was installed as a replacement to decommissioned well S-41R to monitor sulfolane concentrations downgradient of the CU #1 Wash Area.

Analytical results collected from the above wells will be reported in quarterly monitoring reports.

10.3.2 Phase 8 – North Property Boundary Wells

As proposed in the Revised IRAP Addendum (ARCADIS 2013h), six new well nests (8-A through 8-E, installed as MW-358, MW-359, MW-360, MW-362, MW-363 and MW-364), including 5 wells completed up to 150 feet bgs, were installed near the NPB to confirm performance of the interim remedial activities. Initial and pending samples collected for sulfolane analysis are summarized below:

- Wells at location MW-358 were completed to depths of 15, 20, 40, 60, and 150 feet bgs. Sulfolane was detected at concentrations below the ACL of 362 µg/L in the groundwater sample collected from the 20- (24.7 µg/L), 40- (39.0 J µg/L), and 60-foot bgs (25.2 J µg/L) wells. Sulfolane was not detected in the sample collected from the 15- and 150-foot bgs wells.

- Wells at location MW-359 were completed to depths of 15, 35, 60, 80 and 150 feet bgs. Analytical results were available from samples collected at 60 and 150 feet bgs. Sulfolane was detected below the ACL of 362 µg/L in the groundwater sample collected from the 60-foot bgs (16.9 µg/L) well and was not detected in the sample collected from the 150-foot bgs well.

- Wells at location MW-360 were completed to depths of 15, 35, 50, 80, and 150 feet bgs. Sulfolane was detected at concentrations below the ACL of 362 µg/L in the groundwater sample collected from the 15- (21.7 µg/L), 35- (82.6 µg/L), 50- (92.7 µg/L), and 80-foot bgs (6.52 J µg/L) wells. Sulfolane was not detected in the sample collected from the 150-foot bgs well.

- Wells at location MW-362 were completed to a depths of 15, 25, 35, 50, 80 and 150 feet bgs. Analytical results were available from the sample collected at 150 feet bgs. Sulfolane was not detected in the sample collected from this well.

- One well was completed at location MW-363 to a depth of 15 feet bgs. Sulfolane was not detected in the sample collected from this well. Additional wells were not installed to deeper depths at this location because permafrost was encountered at approximately 20 feet bgs.

- Wells at location MW-364 were completed to depths of 15, 30, 65, 90 and 150 feet bgs. Analytical results were available from the samples collected at 65 and 150 feet bgs. Sulfolane was detected below the limit of detection (LOD) (9.60 J µg/L) in the groundwater sample collected from the 60-foot bgs well and was not detected in the sample collected from the 150-foot bgs well.

Results are summarized in Table 10-1 and shown on Figures 10-8 through 10-11. Pending analytical results collected from the above wells will be reported in quarterly monitoring reports.

10.3.3 Phase 8 – Observation and Replacement Recovery Wells

One replacement LNAPL recovery well (R-32R) and eight new LNAPL observation wells (O-31 through O-38), proposed in the Onsite SCWP (ARCADIS 2013d), were installed to further assess LNAPL transmissivity and potentially improve LNAPL recovery at the site if LNAPL accumulates in the wells. Sulfolane was detected above the ACL of 362 µg/L in groundwater samples collected from three wells at concentrations of 376 µg/L (O-32), 1,100 µg/L (R-32R), and 1,700 JL µg/L (O-34). The sample collected from O-31 was not successfully analyzed for sulfolane because of interference from petroleum hydrocarbons and is represented with an “R” to indicate a rejected result. Detected sulfolane concentrations are consistent with concentrations in surrounding groundwater. Results are summarized in Table 10-1 and well locations are shown on Figure 3-1.

10.3.4 Additional Groundwater Recovery Performance Monitoring Wells

Wells O-5-65, O-12-65, and O-24-65, proposed in the Revised IRAP Addendum (ARCADIS 2013h), were installed downgradient from the groundwater recovery system to further evaluate trends and improve monitoring of the groundwater treatment system. Sulfolane concentrations were not detected in the samples collected from these wells, indicating that detectable sulfolane is delineated above 65 feet bgs in these areas. Results are summarized in Table 10-1 and well locations are shown on Figure 3-1. Additionally, 16 wells were installed and analytical results are pending and will be reported in groundwater monitoring reports. Sulfolane results and wells with pending results for sulfolane analysis are described below:

- Well MW-344-55 was installed to evaluate hydraulic capture of the groundwater treatment system. Analytical results from this well were not available.

- Wells at location MW-345 were completed to depths of 15, 55, and 75 feet bgs near recovery well R-43 to evaluate hydraulic capture of the groundwater treatment system. Analytical results were available from samples collected from wells at 15 and 75 feet bgs. Sulfolane was detected at concentrations of 165 µg/L in well MW-345-15 and 7.03 J µg/L in well MW-345-75, which are consistent with sulfolane concentrations in groundwater in this area.

- Wells at location MW-351 were completed to depths of 15, 55, 75, and 150 feet bgs to evaluate hydraulic capture of the groundwater treatment system. Analytical results were available from samples collected from wells at 15 and 75 feet bgs. Sulfolane was detected at concentrations of 165 µg/L in well MW-345-15 and 7.03 J µg/L in well MW-345-75, which are consistent with sulfolane concentrations in groundwater in this area.

- Wells at location O-19 were installed to depths of 55 and 90 feet bgs to evaluate hydraulic capture of the groundwater treatment system. Analytical results from these wells were not available.

- Well O-26-65 was installed to evaluate hydraulic capture of the groundwater treatment system. Analytical results from these wells were not available.

- Wells at location O-27 were installed to depths of 65 and 150 feet bgs to evaluate hydraulic capture of the groundwater treatment system. Analytical results from these wells were not available.

- Wells MW-361-15, MW-365-15, MW-366-15, MW-367-15, and MW-368-15 were installed to better define conditions upgradient of CU #1, CU #2, and the EU.

Additionally, ten wells at locations EGWRT-1, EGWRT-2 and EGWRT-6 are pending installation and will be installed as weather permits. These wells were proposed to monitor hydraulic capture of the groundwater treatment system and are shown on Figure 3-1.

10.3.5 Hydropunch Near the Vertical Profile Transect

The Onsite SCWP (ARCADIS 2013d) proposed the advancement of hydropunch borings near the VPT to further characterize the spatial distribution of sulfolane concentrations in groundwater along the VPT. Eleven borings (HP13-55 through HP13-65) were advanced near the VPT (Figure 10-1) along a transect between the MW-303, MW-304, and MW-305 well clusters. Hydropunch groundwater samples were collected at 10-foot intervals at variable depths, typically between 9 and 89 feet bgs. Groundwater did not exceed the ACL of 362 µg/L in any sample collected from these hydropunch borings; concentrations ranged from below the detection limit to 292 µg/L (duplicate sample) at HP13-60 at 9 feet bgs (Table 10-2). As shown on the cross-section (Figure 10-6), an approximate 2-foot continuous layer of peat was found near the ground surface between VPT wells MW-303 and MW-305. Sand interbedded with layers of gravel was present from approximately 5 to 65 feet bgs. A continuous layer of sand was present at depths below 65 feet bgs to 90 feet bgs (total depth explored during the hydropunch investigation). Detectable sulfolane was found throughout the profile at concentrations below the ACL.

Sulfolane concentrations detected in hydropunch borings are consistent with concentrations detected in groundwater samples collected from nearby VPT wells. The highest detected sulfolane concentrations in most hydropunch borings at the VPT were found 10 feet below the water table and the sulfolane concentrations decrease with depth. This same pattern is seen in groundwater samples collected from the vertically nested VPT borings. Sulfolane was not detected below depths of 70 feet bgs in nearby VPT well MW-303, 95 feet bgs in VPT well MW-304, and 30 feet bgs in VPT well MW-305, which is consistent with hydropunch data. Therefore, data at the VPT are representative of concentrations across the transect and vertical delineation at the VPT has been achieved. Groundwater data collected from the VPT can be used to evaluate groundwater recovery performance.

10.3.6 Hydropunch West of the Railcar Loading Rack

Hydropunch borings were proposed west of the railcar loading rack to assess the possibility of an additional sulfolane source area (ARCADIS 2013g). Ten borings (HP13-66 through HP13-75) were advanced west of the railcar loading rack (Figure 10-2). These borings were advanced along the railroad upgradient from monitoring wells MW-139-25 and MW-142-20. Hydropunch groundwater samples were collected at 10-foot intervals at variable depths, typically between 8 and 79 feet bgs.

As shown on the cross-section (Figure 10-7), groundwater samples did not exceed the ACL of 362 µg/L in any sample collected from the hydropunch borings in this area; concentrations ranged from below the detection limit to 279 µg/L at HP13-74 at 18 feet bgs (Table 10-2). Sulfolane concentrations detected in groundwater samples collected from hydropunch borings are consistent with upgradient sulfolane concentrations (Figures 10-8 and 10-9). Therefore, the area west of the railcar loading rack is not considered a source area.

As shown on Figure 10-7, sulfolane concentrations detected in borings HP13-66, HP13-70, and HP13-75 generally decrease with depth. The remaining borings were only advanced to approximately 20 feet bgs; however, it is inferred that sulfolane concentrations also decrease with depth, similar to those detected in borings HP13-66, HP13-70, and HP13-75.

10.3.7 Southwest Former Wash Area

During 2013 characterization activities, soil in the SWA was evaluated as a potential secondary source of sulfolane in groundwater. Because of the elevated concentrations in vadose zone soil detected in the SWA in 2012, one grab groundwater sample was collected near the water table from boring CF13-1B. Sulfolane was detected below the ACL of 362 µg/L, at a concentration of 36.3 µg/L in the groundwater sample collected from this boring. Results are summarized in Table 10-2 and shown on Figure 10-8 within the detectable sulfolane plume and upgradient from the sulfolane plume within the area of the 2012 hydropunch borings. As discussed in Section 9.3.4, sulfolane concentrations in soil and pore water confirm that the SWA is contributing sulfolane impacts to groundwater, when groundwater contacts the historically impacted soil. Concentrations of sulfolane in soil in this area contributed to detectable sulfolane concentrations in downgradient groundwater during the 2012 hydropunch investigation and the third quarter 2013 concentration of 298 µg/L in well MW-330-20 (Figure 10-8).

10.3.8 Crude Unit #2 Extraction Unit

CU #2 EU soil was evaluated in 2013 as a source of sulfolane to groundwater. In addition to the soil sampling completed as described in Section 9.1.7, the following groundwater samples were collected and analyzed from the water table:

- One monitoring well MW-336-15

- Thirteen temporary hand-driven points at soil borings SB13-25 through SB13-29 and SB13-39 through SB13-46

Analytical results are pending from the groundwater sample collected at newly installed well MW-337-20 in the CU #2 EU Area.

Concentrations of sulfolane exceeded the ACL of 362 µg/L in 9 of 14 groundwater samples collected from the CU #2 EU, with concentrations ranging from 440 JL µg/L (SB13-40) to 61,600 JL µg/L (SB13-43). The concentration detected in the groundwater sample collected from boring SB13-43 is the highest sulfolane concentration detected in groundwater at the site (61,600 JL µg/L). Results are summarized in Tables 10-1 and 10-2 and shown on Figure 10-8.

Eight groundwater samples were collected approximately 10 feet below the water table from borings SB13-39 through SB13-46 in the CU #2 EU (Figure 10-9). Concentrations of sulfolane exceeded the ACL of 362 µg/L in the groundwater samples collected from borings SB13-43 (42,800 JL µg/L) and SB13-44 (2,250 JL µg/L). Additionally, monitoring well cluster MW-336 was installed near the CU #2 EU at depths of 15, 20, 35, and 55 feet bgs. Sulfolane concentrations detected in groundwater samples collected from these four wells decrease with depth from 17,600 µg/L (MW-336-15) to 4.32 J µg/L (MW-336-55). Therefore, the vertical extent of detectable sulfolane concentrations in this area is delineated to 55 feet bgs.

The concentrations detected in groundwater samples collected from this area coupled with the soil data discussed in Section 9 indicate that a significant amount of sulfolane is present beneath the CU #2 EU. A portion of the sulfolane historically released to this area is retained in soil and is an ongoing source of sulfolane to the aquifer. Groundwater and soil analytical data are discussed in Section 12.

10.3.9 Crude Unit #1 Wash Area

During 2013 characterization activities, soil in the CU #1 Wash Area was evaluated as a source of sulfolane in groundwater. In addition to the soil sampling completed as described in Section 9.1.6, two groundwater samples were collected at the water table from temporary hand-driven points at soil borings SB13-16 and SB13-17. The groundwater sample collected from boring SB13-16 exceeded the ACL of 362 µg/L, with a concentration of 42,000 JL* µg/L. Results are summarized in Table 10-2 and shown on Figure 10-8. The concentration detected in the groundwater sample collected from boring SB13-16 is consistent with other source area detections (MW-336-20 and SB13-43 in the CU #2 EU). Analytical results are pending from the groundwater sample collected from newly installed well S-41R located downgradient of the CU #1 Wash Area.

The sulfolane concentrations detected in groundwater samples collected from this area coupled with the soil data discussed in Section 9 indicate that a significant amount of sulfolane is stored in the vadose zone and present in groundwater beneath the CU #1 Wash Area. A portion of the sulfolane historically released to this area is retained in soil, creating an ongoing source of sulfolane to the aquifer. Groundwater and soil analytical data are discussed in Section 12.

10.3.10 Tank 194 Area

During 2013 characterization activities, the soil around Tank 194 was evaluated as a potential source of sulfolane in groundwater. Two grab groundwater samples were collected at the water table from temporary hand-driven points at soil borings SB13-07 and SB13-10 in the Tank 194 Area. Concentrations of sulfolane in groundwater collected from these borings were detected below the detection limit. Soil results discussed in Section 9.1.9 from seven borings advanced this area include detections of sulfolane ranging in concentrations from 3.51 J µg/kg (SB13-07 [1.2-2.3] to 555 µg/kg (SB13-30 [5-6]). Because sulfolane was detected in soil, but was below the detection limit in groundwater, this area is not considered a significant source for sulfolane impacts to groundwater. Results are summarized in Table 10-2 and shown on Figure 10-8 at the southern boundary of the zone of detectable sulfolane concentrations represented by a nondetect isopleth.

10.3.11 Sump 908

During 2013 characterization activities, the soil around Sump 908 was evaluated as a potential source of sulfolane in groundwater. Sulfolane is routinely detected above the ACL of 362 µg/L in groundwater samples collected from monitoring well MW-176A-15, located near Sump 908 (Figure 10-8; Appendix 10-B). One groundwater sample was collected at the water table from the temporary hand-driven point at soil boring SB13-23 near Sump 908. Sulfolane was detected below the ACL of 362 µg/L, at a concentration of 180 µg/L in the groundwater sample collected from this boring. The most recent groundwater sample (third quarter 2013) collected from well MW-176A-15 contained a sulfolane concentration of 1,660 JL µg/L. Soil results discussed in Section 9.1.8 indicate that sulfolane concentrations in soil near Sump 908 were detected below the ACL of 999 µg/kg, ranging from 4.44 JN* µg/kg (SB13-24 [6.0-6.6]) to 418 JL* µg/kg (SB13-21 [6.5-7.0]). Therefore, soil and groundwater concentrations confirm historical minor releases from this sump and the area is considered a secondary source for sulfolane impacts to groundwater. Results are summarized in Table 10-2 and shown on Figure 10-8. The sulfolane plume above the ACL extends from the CU #2 EU, includes well MW-176A-15, and is delineated by boring SB13-23, which is included within the zone of detectable sulfolane concentrations.

10.3.12 Water Table Zone

The highest sulfolane concentrations in groundwater that currently exceed the ACL of 362 µg/L were found in samples collected from the CU #2 EU, CU #1 Wash Area, and downgradient from the SWA. However, it is important to note that these elevated sulfolane concentrations are significantly less than the historical record of concentrations in the sentinel well for Lagoon B (MW-110).

As shown on Figure 10-8, the sulfolane plume exceeding the calculated ACL of 362 µg/L at the water table begins from three of the identified source areas: CU #2 EU, CU #1 Wash Area, and Lagoon B (well MW-110-20), and extends north to include the Sump 908 (MW-176A-15) area. The plume continues north through the tank farm area until it intersects the groundwater recovery system capture zone, where it is captured. The sulfolane plume exceeding the ACL does not extend past the groundwater recovery system, except for a localized downgradient sulfolane concentration of 376 µg/L detected in well O-26. However, concentrations at the VPT (downgradient from O-26) do not exceed the ACL.

Well O-26 also has a consistently decreasing trend in sulfolane concentrations since sampling started in the first quarter 2012. This is due to optimization and expansion of the groundwater recovery system. A separate sulfolane plume exceeding the ACL is located in the area downgradient from the SWA, as detected during the 2012 hydropunch evaluation.

The detectable sulfolane plume in the water table extends offsite beyond the NPB and is defined upgradient by groundwater collected from borings SB13-42 and SB13-46, which did not contain detectable concentrations of sulfolane (Figure 10-8). This zone is defined to the east by wells MW-180A-15, MW-133-20, MW-125-25, O-24, MW-306-10, and MW-149A and to the west by wells MW-355-15, MW-301-CMT-10, and MW-358-15.

10.3.13 10 to 55 Feet Below Water Table

Sulfolane concentrations exceed the ACL of 362 µg/L in four groundwater samples collected from 10 to 55 feet below the water table in the CU #2 EU. Additionally, the sample collected from well MW-354-35 near the Former Bolted Tank Area exceeded the ACL at a depth of 35 feet bgs. Figure 10-9 shows the sulfolane data collected from 2013 characterization activities and from wells during the third quarter 2013 monitoring event. Sulfolane concentrations exceed the ACL in the CU #2 EU and the Former Bolted Tank Area and are shown on Figure 10-9 with isopleths of 362 µg/L. The plume in the Former Bolted Tank Area is likely influenced by sulfolane concentrations in the CU #2 EU. Sulfolane impacts in the CU #2 EU and Former Bolted Tank Area were delineated vertically to 60 feet bgs by wells MW-336-55 and MW-354-60.

The southern extent of the detectable sulfolane plume that extends from the CU #2 EU is inferred around the CU #1 Wash Area and joins the area downgradient of the SWA to include the 2012 hydropunch investigation results. The extent of the detectable sulfolane plume extends offsite beyond the NPB. Sulfolane initial analytical results are summarized in Tables 10-1 and 10-2 and historical data tables are included as Appendix 10-B.

10.3.14 55 to 90 Feet Below Water Table

Sulfolane concentrations in groundwater samples collected from onsite wells screened between 55 and 90 feet bgs have never exceeded the ACL of 362 µg/L. The maximum sulfolane concentration detected in this zone was 67.1 µg/L from well MW-154B-95 (historical maximum of 103 µg/L in 2012). Sulfolane concentrations at 2013 hydropunch borings located downgradient from well MW-154B-95 contained estimated sulfolane concentrations detected above the detection limit. Figure 10-10 shows the sulfolane data collected from wells during the third quarter 2013 monitoring event. The zone of detectable sulfolane concentrations begins at well MW-186E-75 and extends offsite past the NPB. Sulfolane analytical results are summarized in the historical data tables included as Appendix 10-A. Despite the lack of sulfolane detections exceeding the 362 µg/L ACL in this area, the groundwater capture zone extends to depths of approximately 80 feet bgs as discussed in Section 15.3.

10.3.15 90 to 160 Feet Below Water Table

Sulfolane was not detected in any groundwater samples collected from onsite wells screened at depths between 90 and 160 feet below the water table. Sulfolane was historically detected in one groundwater sample (the initial sample collected in 2011) in this zone from well MW-305-100, at an estimated concentration of 4.45 J µg/L. Sulfolane has not been detected in samples collected from this well during the six subsequent sampling events. Figure 10-11 shows the sulfolane data collected from wells during the third quarter 2013 monitoring event. Sulfolane analytical results are summarized in the historical data tables included as Appendix 10-B.

10.4 Total Organic Carbon Analytical Results

Detectable TOC concentrations in onsite groundwater ranged from 0.99 to 103 mg/L. The average TOC concentration in onsite groundwater was 5.42 percent. The highest TOC concentration (103 percent on May 31, 2012) was detected in a sample from well MW-138-20, which also has intermittent LNAPL and elevated dissolved-phase petroleum hydrocarbon and sulfolane concentrations present. Wells sampled for TOC are shown on Figure 10-3 and historical data are included in Appendix 10-B. Except for MW-138-20, the concentrations are consistent with concentrations detected in offsite monitoring wells, which ranged from 1.42 to 34.4 mg/L with an average of 2.53 mg/L (ARCADIS 2013m).

10.5 Temporal Variations in Sulfolane Concentration

Temporal sulfolane concentration trend analyses for groundwater samples collected at suprapermafrost monitoring wells have been completed using the Mann-Kendall method as described in ARCADIS (2013n). This section presents conclusions based on qualitative analyses intended to augment the Mann-Kendall analyses in order to evaluate temporal trends in sulfolane concentrations in onsite, suprapermafrost aquifer monitoring wells. Temporal trends include variations within a given year and over two or more years. Details on the evaluation of sulfolane concentration trends are presented in Appendix 10-C.

Sulfolane concentration data were evaluated with respect to seasonal variations in such factors as the horizontal hydraulic gradient (magnitude and direction of groundwater flow), and groundwater elevation. Seasonal trends that are repeated year after year that cannot be related to the factors listed in the previous section are also described. This evaluation also serves to identify wells where concentration trends were masked by seasonal variations.

Spatial trends, such as concentration trends in nested monitoring wells throughout the plume, and the overall concentration trends in monitoring wells throughout the plume were evaluated.

Possible influences of longer-term spatial and temporal trends were also considered; factors considered include concentration trends that may be related to multi-year trends in maximum groundwater elevation, expansion of the recovery well system, sulfolane release history, and source controls.

10.5.1 Evaluation of Seasonal Trends in Sulfolane Concentrations in Wells

Sulfolane concentration trends in samples from all wells with sufficient data (approximately four or more data points) and a period of record of two years or more were reviewed in light of available groundwater flow direction data. Locations of the onsite wells evaluated are shown in Figure 10-12. The database of sulfolane concentrations in groundwater dates back to 2001; however, frequent measurements are only available since 2006 and the pre-2006 MDL was significantly higher (2.0 mg/L), using a different analytical method (gas chromatograph / flame ionization detector) that has since been changed. Only data since 2006 were used in this analysis because these data were based on similar analytical methods.

Groundwater elevation data from the USGS wells described in Appendix 6-C and the NPR monitoring wells equipped with data loggers described in Appendix 6-B were utilized to develop horizontal plots of the direction and magnitude of horizontal hydraulic gradient (gradient plots) at or near NPR since 2006. The time-concentration plots for 79 monitoring wells were compared with the gradient plots to qualitatively determine if the plots were correlated. This includes 37 onsite and 42 offsite wells. In the context of this evaluation, a qualitative correlation means that the “timing of the peaks and valleys matches up” based on visual comparison of graphs, or the change in concentration is offset to a later time than the observed change in the gradient plot. See Appendix 10-C for more details.

Trends were categorized with respect to the question of whether the data exhibit a correlation between recorded seasonal variations in flow direction, magnitude of hydraulic gradient, or other unidentified factors. The following categories were used:

- “Yes” means a correlation was identified.
- “Possible” means a correlation was noted in some but not all years.
- “Inconclusive” means that the data appeared to show seasonality one year but not another year or, in the case of a nested well included with other wells in the nest, too few data points were available to draw a conclusion.

- "No" means that sufficient data are available to lead to a conclusion that no correlation with known factors or other seasonal trend is apparent in the data. Such data sets are typically from wells that are nested with wells where more data are available.

Of the 37 onsite suprapermafrost monitoring well time-concentration datasets evaluated, four show an apparent seasonal variation in sulfolane that can be related to variations in horizontal hydraulic gradients, 15 show a possible seasonal variation, and six are inconclusive or show no apparent seasonal variation (Figure 10-13).

Four onsite wells show a definite seasonal trend (MW-110-20 and MW-138-20 are located in source areas; MW-111-15 was located north of Lagoon A and MW-143-20 is in the VPT area).

10.5.2 Overall Temporal Trends

The concentration-time plots were also evaluated to determine if they exhibit an overall increasing or decreasing trend based on visual inspection of the graph. This evaluation takes seasonality and other factors into account to identify trend indications that would not be detected by the Mann Kendall analysis; that is, the seasonal fluctuations lead to a "no trend" determination. The following categories were established. The symbols indicated in the list below are posted on Figure 10-14.

- Decreasing trends
  - D Plots that show a steadily decreasing trend over time.
  - DsPlots that show a seasonal maximum concentration that decreases over time.
  - Di Plots that show a steadily decreasing trend over time if the initial value(s) are not considered.
- Increasing trends
  - I Plots that show a steadily increasing trend over time.
  - Is Plots that show a seasonal maximum concentration that increases over time.

The majority of onsite wells (24/37) fall into the decreasing categories. Onsite, this is likely due to source controls and the influence of the recovery system. Only onsite monitoring well MW-178B-50 showed an increase in sulfolane concentration over time. This well is in the capture zone of the recovery well system, and the trend is likely due to operation of the recovery well system. Sulfolane concentrations in MW-178B-50 were below the ACL.

10.5.3 Other Sulfolane Concentration Trends

Other findings described in more detail in Appendix 10-C are listed below.

Eleven of the 37 onsite wells evaluated exhibited trends in which a peak concentration that was markedly higher than other values within the same year occurred each year. These peak concentrations occurred at different times of the year. Wells exhibiting the yearly peak concentration in winter, prior to breakup are located both onsite and offsite, in all portions of the plume. Four of the six wells exhibiting the yearly peak concentration in summer to fall are located onsite and near the western portion of the site (MW-101-60, MW-110-20, MW-111-15, and MW-113-15), which is attributed to seasonal rises in the water table which mobilizes sulfolane contained in the capillary fringe or vadose zone.

Sulfolane concentration trends in nested monitoring wells show a decrease with depth in many well nests in the upgradient and mid-portion of the affected area (see Figure 48 of Appendix 10-C). This is expected for a solute that enters the suprapermafrost aquifer at or near the water table. Well nests that exhibit an increasing concentration trend with depth are distributed throughout the plume (see Figure 49 of Appendix 10-C). Those in the distal portion of the plume likely reflect the influence of recharge, which displaces groundwater and sulfolane downward. Those nests at and near NPR that exhibit increasing sulfolane concentrations with depth (such as wells MW-154B-95 and MW-178B-50) likely reflect downward vertical gradients causing transport of sulfolane deeper in these areas. This may contribute to vertical bifurcation of the sulfolane around permafrost masses north of the source areas and represents a mechanism for sulfolane transport from source areas at the NPR to the subpermafrost aquifer. Increasing concentrations at depth in the suprapermafrost aquifer offsite likely contribute to the mechanism of transport of sulfolane to the subpermafrost aquifer through taliks.

Longer-term trends such as abnormally high groundwater elevations in 2008 followed by several years with a trend of lower maximum groundwater elevation each year may be causing the sulfolane concentration trends seen in wells completed near the water table in areas with residual sources in the vadose zone. Wells that exhibit this trend include MW-113-15, MW-116-15, and MW-127-25.

10.6 Summary

The nature and extent of COCs including benzene, total xylenes, naphthalene, 1,3,5-TMB, and sulfolane has been thoroughly characterized through a tremendous amount of data collected, including approximately 2,737 groundwater samples from 339 onsite wells since 2009. The extent of petroleum hydrocarbons and sulfolane impacts are known and data collected during 2013 are consistent with previous data.

As anticipated based on previous research, investigations, and predictive/regressive calculations, sulfolane concentrations detected in groundwater coupled with the soil data discussed in Section 9 confirm that a significant amount of this COC is present beneath the CU #2 EU, CU #1 Wash Area, and SWA. A portion of the sulfolane historically released to these areas is retained in soil, creating an ongoing source of sulfolane to the aquifer. However, sulfolane concentrations are generally stable or decreasing; indicating that there are no ongoing sources from refinery operations and source mass is captured by the groundwater recovery system.

The benzene plume is confined to the developed portion of the NPR, and does not extend to the north property boundary or beyond. The majority of benzene concentrations detected above the calculated ACL of 590 µg/L are likely in areas where LNAPL is present in soil. Wells with total xylenes, naphthalene, and 1,3,5-TMB detections are located within the footprint of the benzene plume. Both the benzene and sulfolane plumes above the respective ACLs are delineated laterally and vertically to approximately 60 feet bgs or shallower and are captured by the groundwater recovery system, except for a small localized area of dissolved sulfolane near the water table at well O-26. Once the final expansion of the groundwater extraction and treatment system is complete to the west of the current system, hydraulic control will be in place controlling the residual sulfolane concentrations in groundwater associated with the more recently identified Southwest Former Wash Area source. Sulfolane concentrations exceeding 362 µg/L do not extend to the VPT. Hydropunch data collected near the VPT was consistent with sulfolane data gathered from the VPT, which demonstrates that the density of groundwater data collected from the VPT is sufficient to monitor groundwater recovery system performance.

11. Fire Training Area Investigation

The Onsite SCWP (ARCADIS 2013e) proposed Phase III PFC sampling. Results of previous PFC investigations are summarized in the Perfluorinated Compounds Investigation Report (ARCADIS 2013b). PFOA and PFOS were previously detected above ADEC site-specific ACLs of 3.1 µg/L for PFOA and 1.3 µg/L for PFOS. PFOA and PFOS were detected at concentrations of up to 28 J and 128 J µg/L, respectively in groundwater samples collected from monitoring well MW-321-15 during the Phase I and Phase II investigations. PFOS was also detected above the ADEC risk-based screening level at a concentration of 1.4 µg/L in a groundwater sample from one hydropunch location along the northern boundary of the FTA (HP-58, 10 feet bgs) during the Phase I investigation.

Phase III PFC sampling was proposed for both soil within the FTA and groundwater at MW-321-15 to supplement the Phase I and Phase II groundwater investigations of PFCs at the site. It is inferred that PFCs may be present in FTA soil due to the historical use of firefighting foams in this area of the site. The FTA is designed with an impervious liner that prevents rainwater or water used during firefighting training from infiltrating to groundwater. At ADEC's request, additional analytes were included in the soil investigation, including VOCs, semi-volatile organic compounds (SVOCs), GRO, DRO, residual range organics (RRO), polychlorinated biphenyls (PCBs), PCDDs and PCDFs.

11.1 Groundwater Sampling

FHRA collected one groundwater sample from monitoring well MW-321-15. The groundwater sample was submitted for analysis for the standard list of PFCs and for perfluorooctane sulfonamide (FOSA). The standard list of PFCs includes:

- Perfluorobutane sulfonate (PFBS)
- Perfluorobutanoic acid
- Perfluorodecane sulfonate (PFDS)
- Perfluorodecanoic acid (PFDA)
- Perfluorododecanoic acid
- Perfluoroheptanoic acid
- Perfluorohexane sulfonate (PFHxS)
- Perfluorohexanoic acid (PFHxA)
- Perfluorononanoic acid (PFNA)
- PFOA
- PFOS
- Perfluoropentanoic acid
- Perfluorotetradecanoic acid
- Perfluorotridecanoic acid (PFTriA)

- Perfluoroundecanoic acid (PFUnA)

11.2 Soil Sampling

FHRA collected seven soil samples from above the FTA liner, directly under or adjacent to the firefighting training structures and in the drainage area along the southern border of the FTA (PFC13-01 through PFC13-07). Groundwater and soil sampling locations are shown on Figures 11-1 and 11-2, respectively. Soil samples from the FTA were analyzed for PFCs, VOCs, SVOCs, GRO, DRO, and RRO. At ADEC's request, soil samples were also analyzed for a suite of PCBs and PCDDs and PCDFs.

11.3 Analytical Methods

11.3.1 Groundwater

Groundwater samples were submitted to the TestAmerica, Inc. laboratory in Denver, Colorado (TestAmerica). Groundwater samples were analyzed for PFCs using a modified version of USEPA Method 537, designated as DV-LC-0012. DV-LC-0012 uses a liquid chromatography/tandem mass spectrometry method to test for PFCs in water. FOSA was analyzed using Method PFC-FOSA. While it was not originally proposed, groundwater samples were also analyzed for PCBs using USEPA Method SW 8082A.

11.3.2 Soil

TestAmerica analyzed soil samples for PFCs by Method DV-LC-0012 and for PCBs by USEPA Method SW 8082A. Other analyses were performed by SGS in Anchorage, Alaska. VOCs and SVOCs in soil were analyzed using USEPA Methods 8260B and 8270D, respectively. FOSA was analyzed at TestAmerica using Method PFC-FOSA. PCDDs/ PCDFs were analyzed using USEPA Method 8290; soil sampling and analysis for the remaining analytes (GRO, DRO, RRO, SVOCs, and VOCs) were completed per the RSAP.

11.4 Sampling Methodology

Groundwater and soil sample collection were generally conducted in accordance with the RSAP. Because sampling for PFCs requires specific sampling methods to monitor for cross-contamination, specific quality assurance (QA)/ QC methods were followed, as described in the Onsite SCWP (ARCADIS 2013e) and summarized below.

11.4.1 Groundwater Sampling

Monitoring well MW-321-15 was purged and sampled per the RSAP. The field staff that collected the groundwater samples were required to wear flame-resistant clothing (FRC) during field activities to comply with NPR health and safety requirements. Precautions were taken to ensure that the groundwater samples did not come in contact with FRC or other personal protective equipment, because some FRC are known to include PFC-containing materials.

Samples for PFOA and PFOS analysis were collected in four 250-mL high-density polyethylene (HDPE) bottles fitted with HDPE screw-caps (1 liter total volume per sample). The collected groundwater samples were also inadvertently submitted for laboratory analysis to determine concentrations of PCBs. Groundwater samples were labeled by location and sample depth, date, and time, and were placed under chain of custody control for shipping, per the RSAP.

11.4.2 Soil Sampling

Shallow soil borings in the FTA were advanced slowly via hand auger to ensure that the liner below the FTA was not damaged. The soil samples were field screened with a PID readings were noted to evaluate hydrocarbon soil impacts and for general health and safety during boring advancement, per the RSAP. PID readings are shown on the soil boring logs included as Appendix 11-A.

Soil samples were collected from seven locations and analyzed for PFCs. This includes five locations (PFC13-01 through PFC13-05) adjacent to structures in the FTA and two locations (PFC13-06 and PFC13-07) in the drainage area along the south border of the FTA (Figure 11-2). Soil borings were advanced using a hand auger to a total depth of up to 2 feet bgs. The field staff visually verified the depth of the liner in boring PFC13-04 at approximately 1.6 feet bgs.

PFC soil samples were placed in 16-ounce unpreserved HDPE jars. PCB and PCDD/ PCDF soil samples were placed in unpreserved 4-ounce amber glass jars. Soil samples for additional analyses were collected in general accordance with the RSAP. Soil samples were labeled by location and sample depth, date, and time, and were placed under chain of custody control for shipping, per the RSAP.

11.4.3 Quality Assurance/Quality Control Samples

The field QA/QC program includes collection of equipment blanks and duplicate samples, in accordance with the RSAP. The duplicate soil sample labeled PFC13-08 was collected from PFC13-02. A duplicate groundwater sample was not collected from MW-321-15. One equipment blank (EB-1) was collected during groundwater sampling.

11.5 Results

This section summarizes the FTA investigation results. As part of the investigation, FHRA collected soil samples from the lined area of the FTA. Based on the analytical results of the samples and the presence of a liner in the FTA, soil in the FTA does not pose a risk for migration of COPCs to groundwater at the site. Laboratory analytical results are included in Appendix 11-B.

11.5.1 Polychlorinated Biphenyls

Soil samples collected from the FTA were submitted for laboratory analysis to determine concentrations of PCBs. Additionally, although not proposed in the work plan, the groundwater sample collected from monitoring well MW-321-15 was inadvertently submitted for laboratory analysis of PCBS. PCBs were not detected above the respective detection limits in either soil or groundwater. Analytical detection limits for soil samples were below the respective ADEC cleanup levels (CULs; Table B2 18 AAC 75.341,) of 1 mg/kg. PCBs were not detected in groundwater. Even though the method reporting limits exceeded the ADEC CUL of 0.5 µg/L, the method detection limits for PCB analysis for MW-321-15 samples were below the CULs for groundwater, and the laboratory has confirmed that PCBs were not present to the method detection limits, as shown in Table 11-1. PCBs have not been identified as a COC for the site.

11.5.2 Groundwater Perfluorinated Compounds

Groundwater PFC analytical results are summarized in Table 11-2 and on Figure 11-1. The ADEC risk-based groundwater ACL, which is based on ingestion, was exceeded for PFOS (1.3 µg/L), but was not exceeded for PFOA (3.1 µg/L) in the groundwater sample collected from MW-321-15. PFOS was detected at 7.6 J µg/L and PFOA was detected at 1.3 µg/L. Results from Phase III sampling are consistent with Phase II results (PFOS: 2.6 J µg/L and PFOA: 0.92 J µg/L) and confirm that Phase I results (PFOS: 120 J µg/L and PFOA: 28 J µg/L) are biased high due to matrix interferences. ADEC checklists and data validation reports for Phase III PFC sampling are discussed in Section 16 and included as Appendices 16-A and 16-B, respectively.

11.5.3 Soil

11.5.3.1 Perfluorinated Compounds

Soil PFC analytical results are included in Table 11-1 and on Figure 11-2. PFOA and PFOS concentrations ranged from 6.9 to 110 J µg/kg and 250 J to 2,500 J µg/kg, respectively. Concentrations of long-chain PFCs (more than eight carbons), such as PFNA, PFTriA, and PFUnA were detected in soil samples. This aligns with the understanding that long-chain PFCs are predominantly found in solid matrices due to the high tendency of these compounds to adsorb to solid matrices, whereas short-chain PFCs are more likely found in aqueous solution.

In correspondence dated August 16, 2013, ADEC issued ACLs for PFOS and PFOA for the soil to groundwater migration pathway. Following FHRA's review, ADEC confirmed in email correspondence dated December 5, 2013, that the correct migration to groundwater ACLs for PFOS and PFOA were confirmed to be 1.2 and 1.1 mg/kg, respectively (equivalent to 1,200 and 1,100 µg/kg, respectively, for comparison with the site data)..

As noted above, the FTA is lined; the liner was encountered at a depth of approximately 1.6 feet during installation of PFC13-04. The liner prevents PFCs from migrating to groundwater; therefore, an ACLs based on the migration to groundwater exposure pathway, is not appropriate for the exposure scenario for the FTA. The likely exposure scenario for PFCs in the lined FTA would be through incidental direct contact during excavation activities. Accordingly, an ACL based on direct contact would be an appropriate comparison.

Because an ADEC-established ACL for direct contact has not been established, the soil concentrations observed at the site were compared to sub-chronic construction worker exposure values derived from the USEPA Calculator for Regional Screening Levels for Chemical Contaminants at Superfund Sites (http://epa-prgs.ornl.gov/cgi-bin/chemicals/csl_search [RSL calculator]) soil screening levels for PFOS (54.7 mg/kg) and PFOA (137 mg/kg) (USEPA 2012) and the Minnesota risk-based industrial soil reference values for PFOS (14 mg/kg) and PFOA (13 mg/kg) (Minnesota Pollution Control Agency 2007]). PFOS and PFOA concentrations at all seven locations were below both the screening criteria.

11.5.3.2 Petroleum Hydrocarbons

Analytical results for soil petroleum hydrocarbons (GRO, DRO, VOCs, and SVOCs) are included in Table 11-3 and on Figure 11-3. Because these soil samples were collected from a lined area, concentrations were not compared to the most stringent ACLs for migration to groundwater. Instead, soil concentrations of GRO, DRO, and RRO, which were detected in the FTA, were compared to the ACLs established for ingestion (18 AAC 75.341, Table B2). Ingestion ACLs were exceeded for DRO at only one location (PFC13-06).

Concentrations of other petroleum hydrocarbons (VOCs and SVOCs) detected in the soil samples collected from the FTA were compared to the direct-contact ACLs established in Table B1 of 18 AAC 75.341. Direct-contact ACLs were not exceeded at any of the seven sample locations at the FTA.

11.5.3.3 Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans

PCDD and PCDF results are included in Table 11-1 and on Figure 11-4. The term dioxin commonly refers to the reference compound within its group, 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). Due to the similarity to TCDD in chemical structures, physical-chemical properties, and toxic responses, PCDDs and PCDFs are referred to as dioxin-like compounds (DLCs; USEPA 2013). ADEC administrative code indicates that PCDD and PCDF cleanup values should be established on a site-specific basis (18 AAC75.341). Consistent with this, the toxicity of DLCs can be assessed by evaluating their toxicity relative to TCDD by using toxicity equivalence factors (TEFs). The USEPA recommends the use of the 2005 World Health Organization (WHO) TEF values for TCDD and the DLCs. The TEQ calculation provides a means of determining the toxicity of a mixture by considering each compound’s toxicity relative to TCDD and summing the product of the individual TEF and its concentration in the mixture as shown below (USEPA 2013):

$$\mathrm{TEQ} = \sum_{i=0}^{n} C_i \mathrm{x}\, TEF_i$$

Where:

C_i = DLC concentration

TEF_i = toxicity equivalence factor assigned for dioxin or furan (WHO 2005)

TEQ = TCDD toxicity equivalence

The TEQs for the FTA soil samples ranged from 1.53×10^{-6} to 5.64×10^{-6} mg/kg. All TEQs were below both the ADEC direct-contact ACL ($4.7\ 10^{-5}$ mg/kg) and the migration to groundwater ACL (5.8×10^{-5} mg/kg) for dioxin, though this pathway, as previously noted is not complete or applicable for the FTA. TEQ calculations are summarized in Table 11-4.

11.6 Conclusions

PFCs are adequately characterized in groundwater at the site. The impacts are limited to MW-321-15 and groundwater immediately adjacent to the FTA, as determined during the Phase II investigation (ARCADIS 2013b). PFC impacts exceeding the site-specific ACLs for PFOS and PFOA in groundwater do not extend downgradient from these two locations. The higher PFOS and PFOA concentrations detected in the initial October 2012 groundwater sample from MW-321-15 were not observed during follow-up sampling events and are considered anomalous. The October 2012 sample from this well was turbid and issues were encountered during analysis, including clogging of the solid-phase extraction (SPE) cartridge with particulates. The laboratory reported a matrix interference, and independent level IV validation of the results recommended flagging the results as estimated. Two subsequent follow-up sampling events, plus analysis by a second laboratory using a slightly different method, have failed to repeat concentrations on this order of magnitude. Based on the results of these repeated sampling events, and with concentrations exceeding the ACL at only one location, further groundwater investigation for PFCs is not warranted.

The soil investigation identified PFC concentrations exceeding the site-specific ACLs in FTA soil located above the FTA liner. An ACL based on direct contact would be an appropriate comparison. In the absence of ADEC-derived ACLs for direct contact, the soil results were compared to USEPA and MPCA-established values. The detected soil concentrations did not exceed these values.

In addition, one sample exceeded the ADEC ingestion ACL for DRO and, while PCDD and PCDF concentrations were detected, the cumulative risk did not exceed the ADEC direct-contact ACL for the reference compound TCDD. Consistent with Footnote 8 to ADEC Table B1 Method Two – Soil Cleanup Levels Table (18 AAC 75.341), which indicates that “all cleanup levels for PCDD and PCDF congeners must be determined on a site-specific basis,” TEQ risk calculations were prepared to evaluate PCDD and PCDF risk at the site. The calculations, which are consistent with USEPA guidance (USEPA 2000), show that these compounds do not present an unacceptable risk through direct contact so these compounds are not identified as COCs for the site.

12. Fate and Transport Mechanisms

This section discusses the relevant fate-and-transport mechanisms governing COC transport in the offsite portion of the affected area. Onsite COCs may occur as LNAPLs, dissolved chemicals in water, sorbed to the soil matrix, or in the form of a gas. This section discusses the fate and transport of COCs in these four phases in the subsurface at onsite locations. Offsite fate and transport mechanisms influencing COC migration are discussed in the Offsite Addendum (ARCADIS 2013x).

Historical COC releases at the site have entered the subsurface directly from subsurface pipes or sumps, or through infiltration from releases to the surface at the source areas. Once in the subsurface, they are subject to transport in the vadose zone via pore water and soil gas migration (depending on volatility) and transport at and below the water table via groundwater migration. The predominant naturally occurring fate and transport mechanisms in the vadose and saturated zones include: advection, dispersion, and diffusion, storage within low-permeability zones, adsorption to soil grains, and degradation. Collectively, these processes are known to attenuate COC concentrations in groundwater over time and distance.

Differences between transport in the vadose and saturated zones are related to the amount of soil pore space that is filled with water, air, or other fluids (i.e., saturation). Saturation is defined as the amount of soil pore space filled with a particular fluid on a volumetric basis, and can vary between 0 and 100 percent (Freeze and Cherry 1979). In the vadose zone, soil pores are filled with a combination of water and air (i.e., soil vapor), which means that air and water saturations in the vadose are each less than 100 percent. When soil pores are not completely saturated with water, the water adheres to the soil so the migration of dissolved materials in water is slowed considerably. Seasonal freezing of soil water may stop dissolved-phase migration. Therefore, transport of COCs via both pore water and air migration are important transport pathways in the vadose zone.

Another key difference between transport in the vadose and saturated zones is that the hydraulic gradient direction in the vadose zone tends to be primarily downward due to the presence of air in the soil pores and the resulting contrast between the density of air and water. Conversely, hydraulic gradients below the water table (the surface in an unconfined aquifer at which the pressure equal atmospheric pressure) tend to be primarily horizontal.

The capillary fringe is a third zone of saturation, located between the water table and the vadose zone, and is defined as the zone above the water table where soil pores are approximately 100 percent saturated with groundwater that is held above the water table by the effects of surface tension, also known as soil suction (Stephens 1996). Pressure in the capillary zones is less than atmospheric. COC fate and transport processes in the capillary fringe may be different than in either the vadose zone or below the water table, and are therefore discussed separately.

The three main zones where COC transport may occur onsite include: vadose zone, capillary fringe, and saturated zone below the water table. Transport mechanisms through these zones are described below.

12.1 Sources of Sulfolane Onsite

Sulfolane is a clear liquid solvent that is used at the NPR in the production of gasoline products. It is denser than water, fully miscible with water and hydrocarbons, and has a freezing point of approximately 50 °F as it is typically used (see MSDS sheet). Under typical conditions in Alaska, if concentrated sulfolane is removed from the heated system, it may form a clear/gray gel or solid. Once an appreciable amount of water is mixed with the sulfolane, it remains a liquid at ambient temperatures. Therefore, sulfolane-containing wastewater does not gel or freeze.

Sulfolane is used in the refining process to extract lighter hydrocarbon constituents such as benzene and toluene from the refined product stream so they can be blended back in the correct proportions to meet the required specifications for gasoline products. The sulfolane is mixed with refined petroleum distillates in the EU where the lighter ends are extracted. In the stripper and recovery units, the petroleum is boiled off for use in final product blending and the sulfolane solvent is recovered for reuse within the EU in a continuous process. The sulfolane cycles to and from Tank 194 in response to changes in volume in the system.

Sulfolane arrives at NPR in truck-mounted intermodal shipping tanks of approximately 4,000 gallons capacity, which have been warmed so the sulfolane will remain liquid as it is offloaded directly into Tank 194. The material is cycled into the process system through piping and is used in the EU. All piping and vessels containing sulfolane are located aboveground and inspectable, and the EU towers are within concrete containment structures. Over time, heat causes polymerization of a portion of the sulfolane, which reduces its effectiveness in the process. Periodically, a portion of the sulfolane containing the most polymer is decanted off the bottom of the recovery unit into metal totes and disposed of properly.

From time to time, FHRA performs large-scale maintenance events within the NPR known as “turnarounds.” These events sometimes involve the EU, requiring shut-down of the unit, de-inventorying of vessels and piping in the unit, and proper management of these materials. Sulfolane mismanagement during past turnaround practices by Williams and its predecessors were significant sources of releases of sulfolane to the environment. FHRA has changed those practices to prevent releases. During an EU turnaround, equipment is de-inventoried by transferring sulfolane in three ways, listed by priority:

1. Using existing aboveground process piping to transfer material to process vessels having capacity to store the material

2. Using existing aboveground process piping to transfer material back to sulfolane Tank 194

3. Using temporary aboveground piping with secondary containment under each connection point to direct material to holding tanks (i.e., "frac" tanks) staged in a secondary containment area.

Fluids from turnaround cleaning activities are also transferred to frac tanks using aboveground piping and secondary containment practices noted above. Any sumps that are used during a turnaround for the collection of sulfolane-containing materials or wash water are first inspected and hydrostatically tested to ensure full integrity of the structures. Once a turnaround is complete, process materials are returned to the EU in reverse fashion, and any sulfolane-containing wastes are handled through the NPR's wastewater treatment system or disposed of offsite.

12.2 Transport through the Vadose Zone

Mechanisms governing COC transport through the vadose zone include: transport in the dissolved phase as infiltrating precipitation migrates vertically downward from ground surface to the water table, transport in the gas phase as soil vapor, and LNAPL transport.

12.2.1 Infiltration and Groundwater Recharge

The rate and distribution of infiltration into onsite soil are important because they control mass transport to the water table in source areas, and ultimately determine the COC mass loading rate to groundwater.

Infiltration is defined as the downward percolation of precipitation into soil due to a combination of gravity and capillary forces (Stephens 1996). Once water has infiltrated soil, it can remain in the soil as pore water due to the natural water retention properties of the soil, it may evapotranspire (ET) as water vapor upward into the atmosphere, be taken up in plant roots, or it may percolate deeper downward in the soil and enter the water table as groundwater recharge. Pore water also freezes seasonally, with the depth of frozen soil water extending to the water table in some locations and years. Recharge to the groundwater system is therefore the result of excess precipitation.

Recharge due to precipitation onsite was estimated through calibration of the site groundwater model to be approximately 1.44 inches per year (Geomega 2013b). The regional recharge rate due to precipitation is reported to be approximately 2.7 inches per year (Anderson, 1970).

12.2.2 Locational Influences on Infiltration and Recharge

The rate and distribution of infiltrating precipitation, and ultimately groundwater recharge, may vary with location and are governed by such factors as:

- Ground surface cover exerts an important influence on the rate and distribution of infiltration. Ground surfaces of different permeability can influence infiltration and recharge rates because different ground surface cover types allow for infiltration of differing amounts of precipitation. For example, ground surface covers with natural vegetation patterns have higher infiltration rates than ground surface covers with developed materials such as asphalt, concrete, buildings, and compacted soil. The relative influence of ground surface cover types on the rate and distribution of precipitation infiltration can be indicated by visual evaluation of aerial photographs (Geomega 2013a). Ground surface cover types onsite include a mixture of buildings, process units, roads, parking lots, railroad tracks, gravel-covered areas, hard-packed (graded) soil, vegetated areas, and surface water features. Evaluation of precipitation infiltration and mass transport in potential COC source areas onsite is discussed in Section 6.1.4. Ground surface cover and site features also influence where snow is plowed. Plowing snow from an area can reduce the amount of infiltration to site roadways or parking lots, while piling plowed snow can focus infiltration in other areas of the site.

- Soil hydraulic conductivity exerts an important influence on the rate and distribution of infiltration. Hydraulic conductivity is greater in coarse-grained soils such as sand and gravel and lower in fine-grained soils such as fine sand and silt. Hydraulic conductivity of soil at the site has been determined to be highly heterogeneous and may vary over many orders of magnitude. Specifically, hydraulic conductivity of soil samples including several samples collected from the vadose zone, has been estimated to vary over five orders of magnitude (Section 6). This information demonstrates that precipitation infiltration onsite is both highly variable and heterogeneously distributed, and must therefore be accounted for when estimating mass flux of COCs through the vadose zone.

- Soil moisture content exerts an important influence on the rate and distribution of infiltration because soil moisture is correlated with water saturation and hydraulic conductivity in the vadose zone depends on the degree of water saturation. As a result, soil with low moisture content and low water saturation have lower infiltration rates compared to soil with high moisture content and high water saturation. As soil approaches 100 percent moisture content and water saturation, the infiltration rate will approach a maximum value proportional to the saturated hydraulic conductivity (Kressic 2007). Thus it can be seen that mobility of water in the vadose zone depends strongly on moisture content and the degree of water saturation. Infiltration can also occur through preferential flow pathways or macropores (e.g., cracks in dry soil, void spaces adjacent to building foundations, root holes) where gravity is the primary driving force for flow (Ward and Stanley 2004). FHRA measured volumetric water content in selected soil samples as described in Section 10.1. Volumetric water content in samples collected ranged from 5.1 to 85.7 percent.

Other soil hydraulic properties such as soil texture, density, clay content, silt content, organic matter content, and porosity (Ward and Stanley 2004) can exert an important influence on the rate and distribution of infiltration. Once water has infiltrated the soil, it can remain trapped in the soil as pore water due to the natural hydraulic properties of the soil. FHRA measured grain size distribution, as discussed in Section 6. GSAs were performed on 325 soil samples collected during the site characterization. Sieve, hydrometer tests, and laser diffraction evaluations were performed to determine the gradations of samples collected from depths ranging from ground surface to 152 feet bgs (Table 6-1). Figure 12-1 shows ternary plots of the percentage of gravel, sand, and fines (silt) in each sample based on the depth of the sample interval. The majority of the samples contain a mixture of sand and gravel with little silt (Figure 12-1).

Topography exerts an important influence on the rate and distribution of infiltration. For example, topographically low areas tend to collect precipitation and snowmelt and can function as areas of focused infiltration and recharge. Alternatively, topographically high areas tend to shed precipitation and snowmelt and may exhibit lower rates of infiltration and recharge. The site topography naturally slopes to the northwest; however, much of the site has been regraded and is now relatively flat. The low spots are generally associated with water features such as Lagoon B and the gravel pits.

Other physical conditions can influence the rate and distribution of infiltration into soil such as the absence of naturally occurring plant matter that resists rewetting, and the presence of seasonal frost. If soil is saturated at the time of an intense freezing period, the soil can become a “concrete frost” through which almost no infiltration would occur (Ward and Stanley 2004).

12.2.3 Temporal Influences on Infiltration and Recharge

Infiltration rates and distributions may be highly variable due to the factors listed above, and may also vary temporally as well due to a combination of short-term events such as storms, seasonal events such as droughts, as well as long-term processes such as the annual freeze-thaw cycle. Varying rates of recharge throughout the year have been documented to cause temporal variations in groundwater quality (Pettyjohn 1982, Montgomery et al. 1987). Recharge varies seasonally due to seasonal variability in temperature, precipitation, and vegetative consumption. In addition, seasonal variations of surface water levels in the Tanana River can influence recharge rates. As water levels in the river rise or fall in response to seasonal climate changes, hydraulic gradients may increase or decrease, thereby producing seasonal changes in the amount of recharge. The majority of recharge at the site occurs in spring after the ground thaws and before ET becomes significant. Recharge to the aquifer begins soon after accumulated snow begins to melt (Cederstrom 1963). During the summer months, much of the precipitation is intercepted and returned to the atmosphere through ET. With the return of freezing temperatures in the later fall, infiltration is inhibited by frozen ground. For the site, aquifer recharge from precipitation was estimated to be approximately 1.44 inches per year (Geomega 2013b).

One implication of temporally variable infiltration rates is that the COC mass loading rate from soil to groundwater may vary daily, monthly, seasonally, and even annually, which causes COC concentrations measured in groundwater monitoring wells to fluctuate through time. Another implication of temporal variations in infiltration rates is that seasonal freezing and thawing of the vadose zone can result in storage of COC mass above the water table for a relatively long period of time, thereby retarding the rate at which COCs leach downward to the water table. A third implication of temporal variations in infiltration rates is that larger recharge events can provide an influx of electron acceptors to the shallow groundwater system, thereby temporarily enhancing aerobic COC degradation rates (McGuire et al. 2005).

Another factor influencing the rate and distribution of infiltration is that infiltration processes tend to differ between undisturbed and disturbed soil (Ireson et al. 2013). Infiltration through undisturbed soil tends to be more uniform whereas, in disturbed soil, snowmelt will flow on the ground surface to topographic depressions that focus infiltration. The relative proportions of topographically focused versus distributed infiltration of snowmelt vary spatially and from year to year, depending on soil type and local topography, soil moisture content, soil disturbance, snow accumulation, progression of the snowmelt, and other factors.

12.2.4 Vapor-Phase Transport

Volatilization of COCs to the vapor phase is controlled by COC-specific vapor pressure and Henry's constant values. The relevant values are summarized in the table below.

COC	Vapor Pressure (mmHg)	Henry's Constant (atm*m^3/mol)
Sulfolane	0.01	8.9×10^{-10}
Naphthalene	0.054	4.8×10^{-4}
Benzene	74.6	5.6×10^{-3}
Xylenes[2]	7 – 9	5.2×10^{-3} – 7.7×10^{-3}
1,3,5-TMB	2.48	8.8×10^{-3}
GRO	220 – 450	---
DRO	0.5	---
PFOA	0.017	NA
PFOS	2.48×10^{-6}	3.7×10^{-9}

Notes:

1. Vapor pressures are given for temperatures ranging from 20 to 25 °C.
2. Xylenes vapor pressure representative of m, p and o isomers.
3. mmHg = millimeter of mercury
4. atm*m^3/mol = atmospheres of cubic meters per mole
5. NA = not available

As shown, sulfolane, PFOA, and PFOS have low to negligible vapor pressures and Henry's Constant values, and are nonvolatile. Therefore, these COCs are not transported in the vapor phase. Petroleum hydrocarbon-related COCs such as benzene, total xylenes and naphthalene, on the other hand, are volatile and semivolatile, and can exist in the vapor phase at significant concentrations. The concentration, transport, and distribution of vapor-phase petroleum-related COCs in the subsurface will be limited to the vadose zone and will be influenced in varying degrees based on the individual vapor pressures and Henry's Constants. The site data indicate that benzene and xylene isomers in particular were present in soil gas. The distribution of these compounds in the vadose zone will be influenced by some combination of vapor diffusion, preferential pathways (e.g., from buried utilities), vapor-phase advection from changes in groundwater levels and barometric pressure, and biogedradation.

12.2.5 Light Nonaqueous Phase Liquid-Phase Transport

LNAPL may flow in the subsurface from areas of higher LNAPL pressure to areas of lower LNAPL pressure. However, several naturally occurring factors and subsurface phenomenon combine to limit the mobility of LNAPL.

The rate of LNAPL transport when mobile, for example when flowing into a recovery well, is a function of LNAPL saturation, soil permeability, physical properties of the LNAPL (density, viscosity, IFT between LNAPL and water), and magnitude of the LNAPL pressure gradient. The factors that influence LNAPL fate and transport in the subsurface are discussed below.

12.2.5.1 Light Nonaqueous Phase Liquid Density, Viscosity, and Interfacial Tension with Groundwater

Density, viscosity, and IFT of LNAPL are the three main properties that control the fate and transport of LNAPL in the subsurface, as summarized below:

- *Density.* The density of LNAPL was measured in 10 samples in October 2011 and April 2012 and ranged from approximately 0.82 and 0.85 g/cm^3 (SCR – 2011; Barr 2012 and SCR – 2012 ARCADIS 2013a). Therefore, the implications are that:

    - The water table forms a natural barrier for vertical LNAPL migration, and LNAPL cannot physically sink below the water table to any great extent, unless a high LNAPL head pressure is present related to a release event.

    - Pressure gradients in the LNAPL will be slightly lower than in water.

    - Mobile LNAPL will move vertically in response to groundwater elevation changes, resulting in an LNAPL smear zone.

- *Viscosity*. The viscosity of LNAPL controls the rate at which mobile LNAPL moves, with highly viscous LNAPLs flowing slowly and low-viscosity LNAPLs flowing faster. Fluid viscosity is highly temperature dependent, with viscosity increasing as temperature decreases. Therefore, viscosity measurements must be made and reported at a known temperature. The viscosity of LNAPL was measured in 10 samples in October 2011and April 2012 and ranged from approximately 1.8 and 1.9 centipoise at a temperature of 34 °Fahrenheit (SCR – 2011; Barr 2012 and SCR – 2012 ARCADIS 2013a). For reference, the viscosity of water at 34 °F is approximately 1.7 centipoise, which means that site LNAPL, where mobile, would move slower than groundwater due to viscosity.

- *IFT.* When LNAPL comes in contact with groundwater, a sharp interface develops between the two fluids due to an imbalance of molecular forces within each fluid, and the intensity of this sharp interface is characterized by IFT. For example, water in contact with air forms a sharp, curved interface that is controlled by the IFT between air and water, also known as surface tension. The IFT of LNAPL and groundwater was measured in 10 samples in October 2011 and April 2012 and ranged from 16.8 to 22.7 dynes per centimeter (SCR – 2011 [Barr 2012]; and SCR – 2012 [ARCADIS 2013a]). Surface tension of LNAPL and groundwater controls the extent to which the LNAPL can invade pores of various sizes, and therefore exerts a dominant control on LNAPL mobility such that LNAPL in a water-wet soil is only able to invade the largest pores and is restricted from the smallest pores. Therefore, knowledge of the site-specific LNAPL-groundwater IFT can help understand mobility and recoverability of LNAPL.

12.2.5.2 Light Nonaqueous Phase Liquid Saturation

The degree of fluid saturation within soil pores controls the mobility of the fluid such that higher saturations result in greater fluid mobility and lower saturations result in lesser mobility. When fluid saturation has decreased to the point that the fluid exists as disconnected droplets and ganglia, the fluid is no longer mobile and is said to be at “residual saturation.”

Similar to water saturation, LNAPL saturation is the fraction of the pore space occupied by LNAPL, and LNAPL saturations in soil typically vary between approximately 5 and 20 percent, where the remainder of the pores is filled with some combination of water and air. The degree of LNAPL saturation controls LNAPL mobility, with higher LNAPL saturations resulting in greater mobility and lower saturations resulting in lesser mobility.

Residual LNAPL saturation occurs when LNAPL saturation decreases to the point at which the LNAPL exists as discontinuous droplets and ganglia and physically cannot flow. As defined by the ITRC, LNAPL saturations at or below the residual LNAPL saturation is not mobile (ITRC 2009a). Residual saturation depends on a combination of the properties of the LNAPL (e.g., IFT with water) and the hydraulic properties of the soil in which it resides and is, therefore, a highly site-specific property.

LNAPL saturations were measured in eight samples (ASB-01 through ASB-08) collected in October 2011 (Appendix O of the SCR – 2011; Barr 2012). The residual LNAPL ranged from 0.9 to 9.4 percent and the field LNAPL saturation ranged from nondetect to 9.4 percent.

12.2.5.3 Partitioning/Dissolution of Light Nonaqueous Phase Liquid into the Dissolved Phase

As discussed above, organic chemicals can exist in three phases. Partitioning is the degree to which a specific organic chemical is transferred into each of these phases. For example, dissolution will occur when petroleum LNAPL comes in contact with water and the water-soluble chemicals in the LNAPL will partition into the water phase. Similarly, when volatile chemicals partition from the LNAPL phase into the gaseous phase it is known as volatilization or evaporation. The extent to which COCs partition into various phases is an essential component of the CSM because partitioning controls the extent to which the COCs can be transported via various exposure pathways.

After an LNAPL has infiltrated the ground surface and migrated through the vadose zone, infiltrating precipitation can come into contact with and dissolve LNAPL compounds, forming an organic-compound-containing leachate that can continue to migrate downward and enter the water table. Similarly, if the LNAPL were to reach the water table, the LNAPL compounds can dissolve directly into groundwater.

Crude oils and refined petroleum products occur as LNAPL mixtures, consisting of hundreds of individual organic chemicals that are more or less soluble in water depending on the solubility limits of the individual chemicals. The solubility of an organic chemical is controlled by such factors as the molecular weight, molecular structure, molecular formula, and other factors. Organic compounds with higher solubility limits will dissolve into groundwater more readily than organic compounds with lower solubility limits. Accordingly, less soluble compounds will tend to remain in the LNAPL phase, while more soluble compounds tend to preferentially dissolve into water (API 2001). Benzene is an example of an organic chemical found in crude oil that has a relatively low molecular weight with a relatively simple molecular structure, and has a relatively high solubility limit. Thus, benzene is one of the more mobile compounds found in petroleum LNAPLs and is the focus of environmental investigations at many sites.

The composition of the dissolved chemical plume in groundwater and the remaining LNAPL will change through time due to the dissolution of different chemicals out of LNAPL and into infiltrating precipitation or groundwater at different rates due to variable aqueous solubility limits of those compounds. In time, as the lighter molecular weight compounds are preferentially leached out of the LNAPL, the composition of the remaining LNAPL will shift toward heavier-molecular weight compounds in a process known as “weathering,” which is discussed further below.

The key implications of partitioning and LNAPL compositional changes in the subsurface are:

- Hydrocarbon COCs will never achieve full solubility limits in groundwater when the source of COCs is dissolution from LNAPL mixtures due to the differential dissolution phenomenon.

- Dissolved-phase COCs can partition back into the LNAPL phase after dissolution has occurred.

- Differential dissolution of COCs into and out of LNAPLs in the subsurface can cause dissolved-phase COC concentrations measured in monitoring well samples to fluctuate through time.

- Over the long term, dissolved-phase COC concentrations measured in monitoring well samples will decrease through time as the more soluble COCs leach out of LNAPL faster.

- The remaining LNAPL will become gradually enriched in less soluble, heavier molecular weight hydrocarbons due to differential dissolution, which is another naturally occurring weathering process that immobilizes LNAPL.

- The ultimate fate of the LNAPL is to gradually dissolve into groundwater until it consists entirely of nonsoluble, heavier molecular weight compounds that are immobile.

- Some non-LNAPL compounds can also partition into and be stored in the LNAPL phase.

12.2.5.4 Sulfolane Partitioning into Light Nonaqueous Phase Liquid

Two LNAPL samples were collected onsite during fourth quarter 2010 and second quarter 2011 and analyzed for concentrations of sulfolane (Table 40 of the SCR – 2011; Barr 2012). Sulfolane was only detected in one LNAPL sample collected from well MW-138 during second quarter 2011 at a concentration of approximately 0.57 mg/kg. The other sample result was nondetect using an older test method with elevated detection limits.

Thirteen additional LNAPL samples were collected onsite in March and April 2013 and analyzed for sulfolane concentrations using liquid-liquid extraction with water and SPE. This extraction and analysis methodology was used to provide lower sulfolane detection limits and resolve uncertainty associated with elevated sulfolane detection limits in the 2010 and 2011 analyses. Wells sampled included MW-138-20, MW-176A-15, MW-186A-15, MW-334-15, O-19, O-27, R-32, S-21, S-22, and S-51. Sulfolane was detected in one sample and its duplicate, collected from well MW-176A-15, at concentrations of 37.2 J and 39.5 J µg/kg, respectively (Section 7.2.3.2, Table 7-5). These results demonstrate that subsurface LNAPL onsite is not a primary storage mechanism for sulfolane.

12.2.5.5 Light Nonaqueous Phase Liquid Weathering

Weathering of LNAPL, also known as NSZD, is a combination of natural processes that reduce the mass and mobility of LNAPL in the subsurface through time. These processes include primarily dissolution into groundwater and volatilization into soil vapor in the vadose zone. Different chemicals will be preferentially removed from the LNAPL through time and the composition of the remaining LNAPL will change because different chemicals in LNAPL have different solubility limits and different volatilization rates (i.e., vapor pressures). Lighter molecular weight COCs such as benzene and xylenes are more soluble in water and more volatile than heavier molecular weight COCs such as naphthalene and 1,3,5-TMB. Therefore, the weathering process naturally removes lighter molecular weight compounds faster, meaning that weathered LNAPL becomes enriched in heavier molecular weight compounds through time, which tends to increase LNAPL viscosity. Thus, LNAPL weathering also results in a reduction in LNAPL mobility and recoverability through time.

12.3 Role of the Capillary Zone in Constituent of Concern Fate and Transport

The capillary fringe is a zone of saturation above the water table located vertically between the vadose zone and the saturated zone below the water table. The fate and transport of COCs in the capillary fringe is different than in the vadose zone or below the water table and has unique characteristics that are relevant particularly at and near the onsite source areas because groundwater in the capillary fringe is above the water table and held there under tension forces, also known as soil suction.

The two main influences that the capillary fringe has on COC fate and transport are: how LNAPL behaves in the capillary fringe, and storage of dissolved COCs in the capillary fringe. These mechanisms are discussed in the following subsections.

12.3.1 Light Nonaqueous Phase Liguid in the Capillary Fringe

As the position of the water table fluctuates through time due to daily, monthly, seasonal, and annual temporal changes as discussed above, LNAPL in the capillary fringe will also fluctuate and form a smear zone, which is a zone of low-saturation LNAPL above the water table.

In time, water table fluctuations will drive LNAPL in the capillary fringe to residual saturation and effectively trap the LNAPL within the smear zone. The implications of this natural trapping mechanism are that:

- LNAPL in the capillary fringe will eventually become immobilized due to natural water table fluctuations as the LNAPL is driven to residual saturation.

- The rate of LNAPL dissolution in the capillary fringe can increase through time as LNAPL saturation decreases because lower LNAPL saturations result in greater surface area contact between LNAPL and groundwater.

- LNAPL and associated COCs can be stored in the capillary fringe for relatively long periods of time, where they function as a long-term source of dissolved-phase COCs.

As discussed above, stability, mobility, and recoverability of LNAPL in the onsite areas has been thoroughly investigated through a comprehensive, high-resolution sampling program (Section 7).

12.3.2 Storage of Dissolved Constituents of Concern in the Capillary Fringe

Researchers studying ethanol persistence at other sites found high concentrations of ethanol in soil pore water above the water table and within the capillary fringe despite the fact that ethanol is miscible (McDowell and Powers 2003, Freitas and Barker 2013) (Section 9.3). These studies, as well as the fact that sulfolane has similar physical characteristics to ethanol, influenced a high-resolution soil sampling program that was conducted at the SWA in 2013. This sampling program included the collection of data to assess the vertical distribution of soil sulfolane concentrations, organic content of the soil, soil moisture, and geotechnical properties of the unsaturated zone, capillary fringe, and saturated zone.

Results of the capillary fringe sampling program in the SWA area demonstrated that:

- High concentrations of sulfolane were found in vadose zone soil in the SWA more than a decade after the last suspected release of sulfolane-laden wash water in that area.

- High concentrations of sulfolane are present in capillary fringe soil that seasonally interact with the water table.

- Sulfolane concentrations in capillary fringe soil are strongly correlated with silt and clay-sized particle content.

These results indicate that fine-grained soil in the capillary fringe at the SWA have naturally occurring physical and hydraulic properties that trap and store substantial quantities of COCs for relatively long periods of time, and slowly release these COCs to the saturated zone below the water table. Given that soil in the SWA are similar to soil in most areas of the site because they were deposited in the same alluvial depositional environment, it can be concluded that fine-grained soil in the capillary fringe at other onsite source areas have naturally occurring physical and hydraulic properties that trap and store substantial quantities of COCs for relatively long periods of time, and slowly release these COCs to the saturated zone below the water table.

12.4 Transport Below the Water Table

Once dissolved-phase COCs reach the water table through the processes of precipitation, infiltration, and LNAPL dissolution, they may migrate in groundwater due to a combination of transport mechanisms including advection, dispersion, diffusion, hydrophobic sorption, and degradation.

12.4.1 Transport of Constituents of Concern via Groundwater Advection

Advection refers to the transport of COCs dissolved in groundwater by the bulk movement of flowing groundwater. Advection is the primary transport mechanism that controls the direction of COC migration in groundwater; it also controls the velocity of COC migration to some extent. Groundwater flow is controlled primarily by hydraulic gradients and variations in hydraulic conductivity in the subsurface, as described by Darcy’s Law. FHRA has devoted considerable resources to collecting detailed measurements of horizontal and vertical hydraulic gradients and hydraulic conductivity throughout the site. These measurements have been documented in the various site characterization reports that have been prepared for the site. The site hydraulic head and hydraulic conductivity information have also been used along with many other sources of information to develop a detailed numerical groundwater flow model for the site that simulates groundwater flow rates and directions. Thus, groundwater flow has been well characterized at the site and provides a solid basis for evaluating COC fate and transport via groundwater advection.

Hydraulic conductivity of onsite soil has been measured during six different site evaluations and found to vary between approximately 0.1 and 17,000 ft/day, with an average (geometric mean) of approximately 600 ft/day (Section 6). Hydraulic gradients have been measured at the onsite monitoring well network and have an average (arithmetic mean) of approximately 0.001 ft/ft (Appendix 6-B). Mobile porosity was estimated during three onsite tracer tests (Section 6). Mobile porosity represents the portion of total porosity that contributes to advective groundwater flow and transport. Mobile porosity was estimated to vary between approximately 2 and 21 percent, with an average of approximately 10 percent (Section 6).

The average linear groundwater velocity can be estimated using this information based on a form of Darcy’s Law, which states:

$$V = \frac{KI}{n_m}$$

Where:

V = average linear groundwater velocity
K = hydraulic conductivity
I = hydraulic gradient
n_m = mobile porosity

Based on this information, the estimated linear groundwater velocity varies between 0.1 and 30 feet per day, depending on the local soil characteristics. An average linear groundwater velocity of 1 foot per day was observed in a medium-grained sand layer during site tracer testing (Appendix 6-A of the Onsite Addendum). The upper end of the estimated groundwater velocity is for gravels at tracer test area 2. The transport velocity for contaminants is different than the average linear groundwater velocity, and is also dependent on the nature of the contaminant. For example, sulfolane has been transported a distance of almost 20,000 feet since the initial 1985 spills, resulting in an average sulfolane transport velocity of approximately 2 feet per day. The range of local linear groundwater velocities can be expected to vary from this average.

COC migration rates vary due to the retarding influence of dual porosity mechanisms, operation of the onsite groundwater recovery system, and other attenuation mechanisms, discussed below. The fate and transport of COCs in onsite groundwater is controlled primarily by the site groundwater recovery system, which exerts a significant influence on the direction and magnitude of hydraulic gradients. The site groundwater recovery system creates significant inward and upward hydraulic gradients toward the extraction wells that captures onsite COCs and prevents them from migrating offsite (Section 15). Furthermore, the pumping levels within the groundwater recovery wells are maintained at elevations significantly lower than ambient groundwater elevations, which results in faster groundwater velocities and COC migration rates near and toward the wells. Therefore, transport of COCs in onsite groundwater due to groundwater advection will be influenced by the onsite groundwater recovery system.

12.4.2 Dispersion

Dispersion is a pore-scale COC fate-and-transport mechanism that results in mixing of groundwater with and without COCs in soil pores, and can cause spreading COCs both vertically and horizontally. The extent of COC dispersion may be enhanced by heterogeneities within aquifer materials.

Onsite dispersivity values have been estimated to vary between approximately 0.1 meter and 8.2 meters through the completion of onsite tracer tests (Section 6) and 10 and 50 meters through calibration of the site groundwater flow model (Geomega 2013b). Dispersivity is known to be scale dependent (Gelhar 1992) and increases with time and distance. The tracer tests were performed over a scale of approximately 10 to 50 feet, whereas the groundwater model considers transport over a scale of approximately 20,000 feet.

However, dispersion is considered to have a relatively negligible influence on onsite COC fate and transport because onsite COC fate and transport below the water table is dominated by the influence of the onsite groundwater recovery system.

12.4.3 Diffusion and Advection into and out of Low-Permeability Zones

Diffusion is a chemical process where COCs move from areas of high concentration to low concentration. In heterogeneous soil such as the soil found onsite, COCs may be transported into or out of the pore spaces of relatively low-permeability zones via diffusion at rates directly related to the concentration gradient and advection. These low-permeability pore spaces represent the immobile porosity of a soil mass. Soon after COCs reach the water table, COC concentrations will be higher in the pore spaces of higher permeability materials, referred to as mobile porosity, and will naturally diffuse into the immobile porosity of lower-permeability materials where COC concentrations are low. As the concentrations equilibrate between the mobile and immobile porosities, lower permeability zones may come to store a significant amount of COC mass depending, in part, on the nature of the soil heterogeneities. After the high concentrations of COCs have been reduced in the mobile porosity of higher permeability zones due to natural aquifer flushing or enhanced flushing due to the groundwater recovery system, the direction of diffusion reverses and COC mass diffuses from the immobile porosity zones back into the mobile porosity zones.

One implication of diffusion is that, in time, most of the COC mass will eventually be stored in the low-permeability zones. Because most of the advective and dispersive groundwater flow and COC transport occurs in 2 to 21 percent of the total pore space that represents the mobile porosity, the amount of COC mass stored in high-permeability zones will be relatively low. A second implication of the diffusion mechanism is that COC migration rates can be significantly retarded relative to the average linear groundwater velocity, because COC mass entering the mobile pore spaces will depend on contrast between the low- and high-permeability zones, and diffusion-derived retardation factors ranging between approximately 5 and 25 are possible. A third implication of the diffusion mechanism is that diffusion into and out of low-permeability zones can cause COC mass to be stored for relatively long periods of time in the subsurface and cause significant tailing of COC concentrations measured in groundwater monitoring and extraction wells. A fourth implication of the diffusion mechanism is that the reverse-diffusion process can cause rebound of COC concentrations in groundwater during and after remedial operations.

Diffusion and advection into and out of low-permeability zones onsite, and its control on COC migration in onsite groundwater, was demonstrated by the following site-specific datasets:

- Significant tailing of COC concentrations in COC-laden groundwater removed by the onsite groundwater recovery system (ARCADIS 2013a).
- There is a correlation between sulfolane concentrations detected in onsite soil samples and the median grain size of the soil sample, such that higher sulfolane concentrations are positively correlated with smaller soil grain sizes. This correlation demonstrates retention and storage of COC mass in lower-permeability soil zones because fine-grained soil has lower permeability than coarse-grained soil (Figure 12-1).
- Significant tailing of tracer concentrations was observed during performance of the three onsite tracer tests (Appendix I of the SCR – 2012 [ARCADIS 2013a] and Section 6 of this Onsite Addendum).

12.4.4 Hydrophobic Retardation

Some organic COCs can be sorbed into solid organic particles that are naturally present in soil due to the hydrophobicity of those COCs. This is another COC partitioning process and can result in retarding the velocity of COCs in groundwater relative to the average linear groundwater velocity. The extent to which hydrophobic sorption influences the fate and transport of COCs in groundwater depends on the amount of naturally occurring solid organic carbon in the soil and the chemical properties of the COCs. The range of TOC in 32 onsite soil samples collected in 2013 has been measured to vary between approximately 0.104 and 8.1 percent (Section 9-4 and Table 9-1e). The average was 0.767 percent.

The extent to which a specific COC is influenced by hydrophobic retardation may be evaluated through use of the COC-specific retardation factor, which can be estimated using the following equation (Freeze and Cherry 1979):

$$R_{coc} = 1 + \frac{K_{oc} f_{oc} \rho_b}{n}$$

Where:

R_{coc} = retardation factor for the COC
K_{oc} = COC-specific organic-carbon water partition coefficient
f_{oc} = fraction of organic carbon in the soil
n = total porosity
ρ_b = soil bulk density

Using this equation, retardation factors for the COCs are as follows:

COC	K_{oc} (L/kg)	R_{coc}
Sulfolane	0.08	1.0
Naphthalene	1230	47.7
Benzene	66	3.5
m-Xylene	204	8.8
0-Xylene	241	10.2
p-Xylene	313	12.9
1,3,5-TMB	973	38.0
PFOA	115	5.4
PFOS	727	28.6

Notes:

1. R_{coc} estimated using the equation above, average foc value of 0.767 percent derived from site-specific measurements, average porosity of 32.9 percent (refer to tracer appendix), and average bulk density of 1.63 g/cm^3 measured in the capillary fringe borings (Table 10-1).
2. L/kg = liters per kilogram

Retardation factors for the site COCs in onsite groundwater are estimated to vary between approximately 1 and 38. Notably, sulfolane is estimated to have a relatively low retardation factor because it does not readily sorb to organic matter.

12.4.5 Degradation

12.4.5.1 Sulfolane Degradation

Sulfolane is used at the NPR in the refining process, as detailed in the SCR – 2011 (Barr 2012). Sufficient scientific studies have been performed to prove that sulfolane is degradable under natural conditions. Aerobic biodegradation is a primary attenuation mechanism.

FHRA prepared an evaluation of the fate of sulfolane during the degradation process. The results of this work were submitted to ADEC in a memorandum that summarized methods, results, assumptions, and conclusions (ARCADIS 2013d). This evaluation demonstrated that potential sulfolane intermediate compounds are by nature unstable and transient, and would be difficult to measure if they were present. In most cases, chemical standards are not available and analytical methods to detect the compounds have not been developed. More importantly, there is no indication that intermediate compounds would persist or accumulate.

12.4.5.2 Benzene, Xylenes, and Hydrocarbon Degradation

Benzene and xylenes are readily degradable in groundwater under natural aerobic and anaerobic conditions. These processes have been proven to stabilize benzene and xylenes groundwater plumes and limit the plume length at most petroleum-impacted sites to less than 500 feet from the source. The benzene and xylenes plume at the NPR supports this generalization because the plume has remained relatively stable for more than a decade of monitoring, as illustrated by the contoured extent of the third quarter 2013 benzene plume, versus the benzene plume extent represented in the Site Characterization and Corrective Action Plan (SWI 2002).

12.4.6 Surface Water – Groundwater Interaction

In areas with shallow water tables, groundwater can interact with surface water features such as rivers, streams, and gravel pits. Groundwater-surface water interactions may influence groundwater flow rates and patterns as well as COC transport. Surface water features may be gaining when groundwater discharges to the surface water feature, or losing when surface water recharges groundwater. Surface water bodies may be gaining or losing at different locations along the surface water feature, and both gaining and losing at different times of the year depending on the hydraulic gradient between the surface water feature and groundwater. Variations in river stage through time are therefore believed to be the primary control on pressure gradients, and ultimately groundwater flow directions, in the aquifer between these rivers (Lilly et al. 1996, Nakanishi and Lilly 1998).

Groundwater-surface water interactions are important at the site because the site is near the Tanana River, Badger Slough, Chena River, Ditch C, gravel pits, and ponds; and numerous wetlands are present within the affected area. In terms of COC fate and transport, flow-through surface water features, such as the NGP and other gravel pits offsite, may collect and/or receive COCs from the groundwater, where they can be subject to biologic and abiotic processes unique to surface water features (e.g., volatilization to the atmosphere, biodegradation, abiotic degradation, sorption to sediment). Losing surface water features, such as the Tanana River during periods of higher stage, can create pressure gradients in the aquifer that control groundwater flow and COC transport and can function as important geochemical boundaries such as sources of oxygen and nutrient influx to aquifers.

12.5 Effects of Permafrost on Onsite Fate and Transport of Constituents of Concern

Permafrost will exert a strong control on groundwater flow and COC transport patterns because where it is present, it acts as an aquitard and does not transmit groundwater (Section 5). Permafrost has been observed in both onsite and offsite areas. It has been encountered during the installation of monitoring wells and has been noted in the logs of residential wells.

The extent and distribution of permafrost in the subsurface both onsite and offsite has been investigated through several site characterization activities completed during 2013, including monitoring well installation, geophysical surveys, and hand auger borings. Information regarding the depth and extent of permafrost is also present in numerous historical geologic logs and was used to delineate the extent of permafrost. Evaluation of hydrographs from the data logger program provided an additional line of evidence of the interaction of the suprapermafrost and subpermafrost aquifers in the vicinity of a thawed zone. Further, work completed by the UAF identified suprapermafrost and subpermafrost groundwater, which furthered the understanding of the permafrost extent. The methods, results, and conclusions of these evaluations are discussed in Section 5.

Results demonstrate that permafrost is largely absent under the developed portions of the site. Discontinuous permafrost is present in the northern portions of the site. Small discontinuous masses are present at the MW-154 nest, MW-179 nest, and along the VPT. An irregular, shallow mass is present in the wooded area south of Transfer Road (Section 5.3.3). The edge of a large, relatively continuous, permafrost mass is present near the site boundary; the mass extends to the north and west under the offsite plume. Because permafrost is largely absent onsite, it can be concluded that permafrost does not significantly influence the fate and transport of COCs in groundwater onsite, but plays a significant role in fate and transport of dissolved-phase sulfolane offsite.

13. Updated Source Information

Sulfolane sources to groundwater at the NPR were previously described in Appendix A, prepared by Geomega, to the SCR – 2012 (ARCADIS 2013a). The discussion in this section relies upon the source information presented in that Appendix A, and relates the 2012 and 2013 field data to the sources that it described. The soil and hydropunch sulfolane data collected during the 2012 and 2013 field seasons further confirm the contribution of sulfolane to groundwater from these source areas from operations that date back to the initial use of sulfolane at the refinery in 1985. Williams and its predecessors owned and operated the NPR from commencement of refinery operations in 1977 up until FHRA purchased the refinery on April 1, 2004. The land beneath the NPR was owned by the State of Alaska until it was transferred to Williams to complete the sale of the NPR to FHRA.

13.1 Primary Sources of Sulfolane to the Groundwater at the North Pole Refinery

There are six primary sources of sulfolane to groundwater at the NPR (Figure 9-1). The largest sources have been Lagoon B and the CU #2 EU. Other sources include the SWA, SGP, Sump 908, and CU #1 Wash Area.

13.1.1 Lagoon B

Lagoon B is a 220- x 240- x 6-foot-deep surface impoundment with a capacity of 2.28 million gallons constructed during refinery build-out, with a single, 30-mil PVC liner (Radian 1989). It was the only lagoon onsite until Lagoon A was built in October 1987 (MAPCO 1989) and was used for storage and sometimes treatment of wastewater from the refinery.

Almost immediately after sulfolane use at the refinery commenced (in September 1985) Lagoon B overflowed on October 2, 1985 into the adjacent gravel pit (MAPCO 1989) (Figure 13-1). Until the summer of 1986, wastewater from Lagoon B was also spread on roads for dust control (MAPCO 1989).

The integrity of the lagoon was suspect as early as 1987, when MAPCO reported in their environmental audit report to the USEPA (MAPCO 1987b) that "*the Stormwater Holding Pond may also be a source of contamination.*" In 1989, MAPCO reported to the USEPA that the lagoon had 45 holes that had been patched in 1986 (MAPCO 1989). Subsequently, the liner was reinstalled in Lagoon B in 1989 (USEPA n.d.) and again in 1991 (MAPCO 1991) to fix tears. It was reported that a Williams employee also shot at a large bubble in the liner during Williams' ownership (Britten 2012).

Lagoon B was used for storage of high concentration sulfolane wastewater until 2003 (ADEC 2003; Author unknown n.d. [FHR00083627]; Author unknown 1997; USEPA 2000; Guinn 2012; MAPCO 1987a, 1997a, 1997d; Mead 2012a; Northern Testing Laboratories Inc. 2002, 2003a, 2003b, 2004, 2005; Williams 1999b, 2000a, 2000b, 2000c, 2000d, 2001, 2002) based on analytical data which shows sulfolane decreasing from ~4,700 mg/L in 2000 to non-detect (less than 2 mg/L) in September 2003 (Figure 13-2).

SWI (2006) concluded that the most reasonable explanation for the presence of high sulfolane concentrations in groundwater collected from MW-110 (immediately hydraulically downgradient of Lagoon B) is *"either leakage or spillage of stripper effluent from Lagoon B."*

Only one document has been identified indicating that wastewater was sent to Lagoon B during the FHRA era. A June 16, 2004 letter from Mr. A. Lasater to Mr. M. Lee of the USEPA indicates that water containing propylene glycol was put into the lagoon in April to June 2004 until the problem was resolved on June 11, 2004. That letter does not mention sulfolane. Lagoon B was completely drained and cleaned in 2006 (FHRA 2007) and in November 2006, FHRA began plans to abandon Lagoon B (Alaska Anvil 2006).

13.1.1.1 Supplemental Lagoon B Source Investigation Data

In 2012 and 2013, soil samples were collected to determine if there was residual sulfolane that could recharge to groundwater in the capillary/vadose zone below the liner (btl). These samples were designed to test the hypothesis that sulfolane is so soluble in water that it should have leached out of soil beneath Lagoon B between closure (2006) and the time of the investigation.

There were 32 soil samples collected from 2.5 to 3.8 feet btl and an additional four from 1.5 to 2 feet btl in 2012. In 2013, four additional samples were collected from 2 to 3.5 feet btl (Figure 9-9). Sulfolane ranged from non-detect (approximately 3.1 µg/kg) to 5,950 µg/kg (5.95 mg/kg) in samples collected from the middle of the lagoon (Figure 9-9). The elevation of the sulfolane in the soil profile compared to the mean depth to water demonstrates that the sulfolane is located primarily in the capillary zone and that even 7 years after closure, sulfolane is retained in the soil profile and remains a source to groundwater (Figure 13-3). The fact that sulfolane is not leached as readily as previously thought is probably due to secondary porosity and dead end pore space, combined with limited percolation of water through the vadose zone beneath the liner.

These findings are significant because Lagoon B has not contained sulfolane-laden wastewater since 2003, so the residual sulfolane in the soil beneath Lagoon B must be a legacy of the Williams' era operation.

13.1.2 Crude Unit #2 Extraction Unit

Sulfolane solvent is primarily handled and used at the refinery in the CU #2 EU. Due to the regular use of sulfolane in the EU since 1985, the use of a sump (02/04-02) as a collection point for spills and wastewater, and the use of holding tanks and underground drain lines within the unit, sulfolane may have been introduced to soil and groundwater throughout the EU footprint. Spills or other releases of sulfolane to the vadose zone in this area would have been exacerbated in the southern area of the present-day EU, which was unpaved until 1997.

13.1.2.1 Sump 02/04-02

This sump is located in the CU #2 EU and acts as a collection point for both units, connected to both by a drain system (Figure 9-16a). It was also used to collect residual drain-down and wash water during EU turnarounds. These turnarounds occurred more frequently and used different procedures during the Williams era than over the FHRA tenure (Table 13-1).

Due to the nature of work within the EU, the manner in which sulfolane-laden wastewater was handled within the EU during turnarounds and maintenance activities, as well as the inspection and repair history (Geomega 2013a), Sump 02/04-02 is probably the primary source of sulfolane to groundwater within the EU.

13.1.2.2 Sump 02/04-02 Inspection History

Sump 02/04-02 was found to have integrity issues during a 1997 inspection when it was noted that the upper sump walls had light general corrosion, the bottom 6 to 8 inches of the sump walls had severe corrosion around the entire circumference of the sump, and the sump floor was heavily pitted and corroded. Given the depth of the sump relative to the depth of groundwater, it is reasonable to conclude that the sump leaked and that the fluid observed entering the sump was groundwater (Mead 2012a, p. 141-142). Because of the substantial corrosion and failure of the sump found during the 1997 inspection, it is likely that this condition existed during previous turnarounds until its repair in 1997.

The actions recommended following the 1999 sump inspection were that the disbonded coating should be cut away and the sump should be recoated and reinspected during the summer of 2000 (Williams 1999a). However, there is no evidence that this repair was made and on May 18, 2009, it was discovered that there was no back weld placed around the nozzle and gasket when the steel lining was placed into the sump in 1997 (Acuren 2009). The coating of the sump was also found to have completely failed throughout the entire sump (Acuren 2009) indicating that the sump had leaked since 1997. In 2009, the sump was repaired and passed a leak test. FHRA used the sump during the 2010 turnaround after first determining that it had no leaks (Knowles 2011, pers. comm.).

13.1.2.3 Supplemental CU#2 EU Source Investigation Data

Soil and hydropunch samples collected and analyzed for sulfolane within the CU #2 EU illustrate that while low concentrations of sulfolane in the soil profile are pervasive across the CU #2 EU, there are some areas with higher concentrations, reflecting specific use histories in those areas (Figure 13-4). For example, SB13-39 is affiliated with the location of heat exchanger bundle extraction (2,020 JL µg/kg 0.5 to 1.7 feet bgs, 4,270 JL µg/kg 5 to 6 feet bgs 705 JL µg/kg 6.5 to 10 feet bgs, and 5,360 µg/L in water at 10 feet bgs). In addition, the sump near the fin fans (Sump 04-3) has a historical inspection record listing patches on the metal liner, which may explain the high concentrations in SB-175 (MAPCO 1999).

Sump 02/04-02 is has some of the highest sulfolane soil concentrations (SB13-26, SB13-25, and SB13-43; Figures 9-14a through 9-14d), which are attributed to the historical integrity problems previously described).

Section 9.1.7 provides a comprehensive evaluation of the data collected during the 2012 and 2013 field seasons in the CU #2 EU.

13.1.3 Southwest Former Wash Area

One of the former EU heat exchanger bundle cleaning areas is located in SWA, directly west of the FTA (Figure 9-1). This area is currently used for materials storage; however, one of its former uses was as a wash area where heat exchanger bundles from the EU were cleaned during turnarounds by Williams. FHRA never used this location as a wash area.

Aerial photographs of this former EU bundle cleaning area indicate that construction of the former wash pad began around April 1990 (Figure 13-5 tile a). Heat exchanger bundles removed from the extraction unit during turnarounds were washed at the pad (Figure 13-5 tile b), a practice continuing at least through 1999 (Figure 13-5 tile c). The former wash pad was replaced by a new wash pad with higher curbs and walls to contain the wash water by 2002 (Figure 13-5 tile d).

A former NPR employee in charge of wastewater confirmed that the materials storage area was used as a wash pad for the EU bundles during turnarounds (Mead 2012b, pers. comm.). He noted that overspray of the wash water onto adjacent soil was likely because there were only small, 6-inch curbs around the perimeter of the skid and no walls (at that time). A sample collected from the recirculation tank supplying the wastewater used to wash the bundles contained 97,000,000 µg/L (97,000 mg/L) sulfolane in April 2000.

13.1.3.1 Supplemental Southwest Former Wash Area Source Investigation Data

ADEC requested that FHRA characterize the sulfolane concentration in soil in the SWA in 2012 with follow-up data collection in 2013. The data set is discussed in its entirety in Section 9.1.3.

Spatially, the highest sulfolane soil concentrations were located directly adjacent to the east side entrance to the former EU exchanger bundle wash area between approximately 5 to 6.5 feet bgs (Figure 9-5b). The elevated concentrations of sulfolane in the SWA are especially notable as this location has not been used as a wash area since FHRA purchased the NPR.

In addition, these data support the hypothesis that flushing of sulfolane through the vadose zone is retarded by hydraulic properties of the soil matrix such as dead-end pore space and secondary porosity, combined with seasonal freezing of soil moisture and limited water percolation due to packed road surfaces and snow plowing. If the mobility of sulfolane was solely dictated by its water solubility, all sulfolane released to the soil surface from the washing operations would have drained down to the groundwater over the intervening 12+ years. The soil data from the SWA show this not to be the case.

13.1.4 South Gravel Pit

On October 2, 1985, there was an overflow of oily water from Lagoon B via a ditch into the SGP due to heavy rains (MAPCO 1985). An aerial photograph of the area taken on October 6, 1985 shows a sheen on the SGP similar to the one on Lagoon B (Figure 13-1 tile b). Since sulfolane use began onsite on September 1, 1985, and there was no treatment capacity onsite for sulfolane at that time, it is likely that discharge from the wastewater lagoon into the SGP would have contained sulfolane.

13.1.4.1 Supplemental South Gravel Pit Source Investigation Data

Since the former overflow ditch has been abandoned and filled in onsite, the coordinates of the former overflow ditch were determined using the 1978 and 1985 aerial photographs (Figure 13-1). Samples were collected along the axis of the ditch to test the hypothesis that the ditch may have been a source of sulfolane to groundwater (Figure 3-1 tile b). While surface soil was nondetect (as expected because the ditch has been filled in since the release in 1985), two of the three samples collected at approximately 5 feet bgs contained remnant sulfolane (SB13-06, 316 µg/kg and SB13-01, 39J µg/kg) demonstrating that sulfolane was released along this pathway during the Williams operational era. The data set is described in its entirety in Section 9.1.5.1.

13.1.5 Sump 908

Sump 908, located southwest of the current Gallery Pond, receives wastewater from the salt drier, which removes water from hydrocarbon products. Wastewater produced from this process contained 35,000 to 55,000 mg/L sulfolane in 2000 (Williams 2000c).

Sump 908 was found to have pitting and complete failure in the steel walls, base, and piping to the sump during an inspection in 1997 (MAPCO 1997b) after which it was lined with steel and coated with a polymer in October 1997 (MAPCO 1997c).

In September 26, 2006, the sump was again inspected. The floor of the sump was pitted and the polymer coating had deteriorated (Acuren 2006). However, there was no evidence of leakage.

The sump was inspected again on July 6, 2010, when complete coating failure throughout the sump was once again apparent. Heavy corrosion and pitting were identified during the visual inspection, which identified fully penetrating, pin-size holes in various areas on the floor and shell. Soon after the inspection, the shell and the floor were replaced with new plates (Acuren 2010).

Sulfolane concentrations in wastewater collected in Sump 908 would have been higher in the past, when sulfolane carryover was higher in gasoline (Figure 13-6).

13.1.5.1 Supplemental Sump 908 Source Investigation Data

SB-13-21 was located as close to Sump 908 as utilities would allow to evaluate if residual sulfolane was present in the soil as a result of sump leaks. Sulfolane was detected in this boring at 418JL µg/kg at 6.5 to 7 feet bgs (Figure 9-17), confirming minor releases from this sump. The soil data from Sump 908 is described in Section 9.1.8.

13.1.6 CU #1 Wash Area

The CU #1 Wash Area is identified in the Resource Conservation and Recovery Act (RCRA) Facility Assessment (RFA; Kearney and SAIC 1988) as solid waste management unit #11 and is referred to as the equipment cleaning area (Figure 9-1). The equipment cleaning area is reported to have been used for steam cleaning of drums, heat exchangers, and other equipment, and that spray or flow may have migrated beyond the edge of the paved area if large quantities of wash water were generated (Kearney and SAIC 1988).

Prior to development of the SWA, the only area available onsite for power washing of the EU heat exchanger bundles was the wash area in the CU #1 Wash Area, which includes slot drains to Sump 901 (Britten 2012). Inspection reports of Sump 901 showed no indication of leaks (MAPCO 1998, Williams 1999c and 2000e). Information about the integrity or inspections of the slot drain is unavailable. However, the RFA indicated that the slot drain had a steel liner (Kearney and SAIC 1988). Field notes attached to the RFA (Kearney and SAIC 1988) indicate that the trench was originally constructed with concrete, suggesting that the steel liner currently in place was a later improvement.

13.1.6.1 Supplemental CU #1 Wash Area Source Investigation Data

Soil bores were located north of the slot drains and Sumps 901 and 901.5 to evaluate this area (Figure 9-11). Soil samples SB13-16 (699 µg/kg), SB13-17 (354 µg/kg), SB13-18 (63.8 µg/kg), SB13-19 (11,700 JL µg/kg), and SB13-20 (661 JL µg/kg) collected in the 0- to 2-foot bgs range indicate that sulfolane has been released to soil, and therefore groundwater in the CU #1 Wash Area. A more detailed discussion of the soil samples collected in this area may be found in Section 9.1.6. The groundwater sample collected from boring SB13-16 located in the CU #1 Wash Area exceeded the ACL of 362 µg/L, with a concentration of 42,000 JL* µg/L. This result confirms that impacted soils in the CU #1 Wash Area serve as a long-term source of sulfolane to groundwater.

13.1.7 Light Nonaqueous Phase Liquid as a Potential Source of Sulfolane

Sulfolane was analyzed in 25 LNAPL samples collected from 16 wells over three sampling events in 2010, 2011, and 2013 (Figure 7-7). All nine LNAPL samples analyzed in 2010 were non-detect for sulfolane. Of the three LNAPL samples analyzed in 2011, only one (MW-138-20) contained sulfolane (573 µg/kg), just above the detection limit (500 µg/kg). However, a subsequent sample collected from this well in 2013 analyzed for sulfolane using the updated analytical method was non-detect (less than 80 µg/kg).

In 2013, of 13 LNAPL samples analyzed for sulfolane, only MW-176A and its duplicate contained sulfolane above the detection limit (37.2 J µg/kg and 39.5 J µg/kg) but below the limit of quantitation (37.2J µg/kg and 39.5 J µg/kg, respectively). Since sulfolane was only detected between the method detection limit and limit of quantitation (LOQ) in four samples, it has been determined that LNAPL is not a significant source (or sink) of sulfolane to groundwater at the NPR.

13.1.8 Spill History

Spill records reflect that there was a substantially greater volume of sulfolane-containing material spilled during Williams' operations. Spill records show that for documented spills of

100 gallons or more, 47,880 gallons of sulfolane-containing material were spilled prior to April 1, 2004, compared to 5,068 gallons spilled after that time.

The records reflect that FHRA recovered essentially all of the sulfolane-containing material that was spilled during its operations, but Williams' records indicate that a significant portion of its spills were not recovered. For FHRA, 5,053 of the 5,068 gallons spilled were recovered, leaving 15 gallons of sulfolane-containing material unrecovered. In contrast, Williams' records reflect that only 18,114 gallons were recovered from the 47,880 gallons of sulfolane-containing material spilled, leaving 29,766 gallons unrecovered (Figure 13-7).

14. Pilot Tests and Remedial Investigations

Pilot testing and remedial investigation activities were completed at the site to support feasibility study technology screening. This section summarizes the activities completed during 2013.

14.1 Air Sparge Pilot Test

Based on the monitoring results at the Gallery Pond and bench-scale testing, which indicated sulfolane removal associated with aeration, FHRA commenced an AS pilot test in 2012 to evaluate if aeration will create conditions for sulfolane removal in situ. A technical memorandum describing the pilot test startup, monitoring results, and data evaluation is included as Appendix 14-A.

The AS pilot system continued operation until July 10, 2013, when it was shut down after 70 weeks of operation. Following shutdown, monitoring was continued to evaluate the persistence of DO in groundwater in the aquifer and potential rebound in sulfolane concentration.

In 2013, AS pilot test monitoring data collected prior to shutdown continued to demonstrate remediation of sulfolane by the AS system to non-detect, except for AS-MW-1and AS-MW-8. As shown on Figure 14-1, AS-MW-1 is located on the perimeter of the AS pilot test area and AS-MW-8 is upgradient. Post-shutdown monitoring shows persistent DO in groundwater within the pilot test area and corresponding relatively low or non-detectable sulfolane concentrations in pilot test monitoring wells. At wells AS-MW-5 and AS-MW-2, which are located directly downgradient from the AS points, sulfolane has not been detected in any of the post-shutdown sampling events through 14 weeks post-shutdown.

14.2 North Gravel Pit Investigation

14.2.1 Bathymetric Survey

On July 22, 2013, FHRA conducted a bathymetric survey at the NGP to measure the depth and to map the bottom of the NGP and support an evaluation of the remedial effects of the NGP on shallow groundwater.

14.2.1.1 Bathymetric Survey Methods

Design Alaska, Inc. installed two GPS base stations near the NGP to collect static depth data over control points near the NGP. A GPS receiver and echosounder were mounted in a canoe that was pulled across the water surface in a grid pattern by personnel on each side of the NGP. Using sonar technology, an echosounder measured the depth to the bottom of the NGP. Depth readings were collected at pre-established intervals as the canoe was pulled across the water surface. The depth data were processed with readings from the GPS base stations and were used to develop a topographic map of the bottom of the NGP, also known as a “bathymetric map.” Surveyors working around the perimeter of the NGP collected additional terrestrial topographic data, including land surface elevations at points along the edge of the water and top of the bank.

The volume of the NGP was calculated using 3-D analysis within ArcMap 10.1. A Triangular Irregular Network (TIN) was created using nearest neighbor interpolation based on the bathymetric contours and elevations. The TIN surface was used to calculate the 3-D area of the NGP floor surface and the volume of water present at the time of the survey. The Surface Volume Tool was used to calculate the volume between the interpolated TIN and the reference plane of 485.5 feet above MSL.

14.2.1.2 Bathymetric Survey Results

The surface water level in the NGP was approximately 485.5 feet above MSL at the time of the bathymetric survey. Historical surface water levels in the NGP have varied between approximately 484.6 and 485.8 feet above MSL based on eight measurements collected since February 2012. The July 2013 NGP surface water level is consistent with past water levels collected since July 2012. The average surface water level in the NGP since gauging began was found to be approximately 484.55 feet above MSL.

As shown in Table 14-1, the bottom of the NGP has the following characteristics:

- Maximum depth: 41.9 feet below water surface (i.e., the lowest elevation in the NGP was 443.6 feet above MSL)
- Average depth: 18 feet below water surface (i.e., an elevation of 467.5 feet above MSL)
- Surface area: 22.6 acres
- Volume: 252 acre feet

The NGP bathymetric contour lines are shown on Figure 14-2. As shown, the NGP appears to have three sub-basins that extend below an elevation of approximately 470 feet above MSL and are separated by topographic ridges. For example, the bottom of the southeastern portion of the NGP rises to a northwest-southeast-oriented ridge at an elevation of approximately 480 feet above MSL. This ridge separates the eastern and southern sub-basins of the NGP. Accordingly, the western sub-basin of the NGP occupies the northwestern portion.

14.3 Remedial Effects Investigation

On August 26, 2013, FHRA submitted the Work Plan for Additional Site Monitoring Activities During Construction Dewatering (CD Support Work Plan; ARCADIS 2013i) to ADEC. Construction is planned to replace the transfer line from the SGP to the NGP, which is a below grade pipe that currently has constrictions limiting flow from the SGP to the NGP. The objective of the CD Support Work Plan (ARCADIS 2013i) was to collect data necessary to evaluate the potential influence of upcoming construction dewatering activities associated with the transfer line replacement activities on the distribution of sulfolane, if any, in groundwater and to address concerns expressed by ADEC.

The Work Plan for Additional Site Characterization Activities and Remedial Evaluation at the North Gravel Pit (NGP Work Plan; ARCADIS 2013k) was submitted to ADEC with the primary objective of collecting data to support a remedial effects evaluation of the NGP. The two mechanisms identified that would remediate sulfolane in groundwater are degradation and dilution; the objectives to evaluate these two mechanisms are presented below:

- Evaluate groundwater/surface water interactions at the NGP.
- Estimate the extent of sulfolane attenuation that may be occurring in the NGP and in the groundwater zone near the NGP.
- Evaluate the availability of DO within the NGP and the potential for oxygenated surface water in the NGP to recharge groundwater.
- Evaluate the feasibility of using the NGP, and possibly additional gravel pits at other locations at the site, as part of a long-term groundwater remedy.

To evaluate the potential for sulfolane degradation in the NGP, sulfolane, DO, and nutrient (nitrate, phosphorus, and potassium) data were also collected.

Due to weather constraints, the transfer line replacement project was delayed until 2014. Because of this delay, the remaining scope of work proposed in the NGP Work Plan (ARCADIS 2013k) is currently anticipated to be performed in 2014 in conjunction with the transfer line replacement project.

14.3.1 Temporary Piezometer Installation

As proposed in the CD Support Work Plan and the NGP Work Plan (ARCADIS 2013i and 2013k), 14 temporary piezometers were installed using a HSA drill rig. Three piezometers (PZ-1-15, PZ-2-15, and PZ-3-15) were installed per the CD Support Work Plan (ARCADIS 2013i) for the proposed monitoring activities. Eleven additional piezometers (PZ-1-20, PZ-1-40 and PZ-1-66, PZ-4-10, PZ-4-20, PZ-4-45, PZ-4-66, PZ-5-13, PZ-5-20, PZ-5-45, and PZ-5-65) were installed as part of the NGP Work Plan (ARCADIS 2013k).

The piezometers were installed around the NGP and near the SGP, as shown on Figure 14-2. Each piezometer was constructed of 2-inch Schedule 40 PVC risers with 0.010-inch machine-slotted screen set at the intervals summarized in Table 3-1. Each piezometer borehole was logged and soil was classified according to the RSAP. Soil observed in these borings is consistent with other site borings; the boring logs are included in Appendix 14-B.

Final piezometer locations will be surveyed to a common datum for spatial coordinates and elevation. Each location will be developed in accordance with the RSAP prior to initiating the next phase of investigation at the gravel pits. After development, single-well pumping tests will be performed in conjunction with initial groundwater monitoring at each piezometer. Upon completion of the gravel pit evaluation, each location will be properly decommissioned.

14.3.2 North Gravel Pit Surface Water Sampling and Analysis

On October 25 and 26, 2013, 26 surface water samples were collected from the NGP at five of seven sub-basin sampling locations along two transects (Figure 14-2, Table 14-1). FHRA completed sampling at four of the seven proposed sampling locations (NGP-4 through NGP-7) in accordance with the NGP Work Plan (ARCADIS 2013k). A portion of the proposed work was initiated at a fifth location (NGP-3), but work was not completed at NGP-1, NGP-2, or NGP-3 due to weather conditions and excessive ice buildup. At the completed locations, water samples were collected at regular vertical intervals starting at the top of the water column based on the bathymetric survey discussed in Section 14.2.1. A Yellow Springs Instruments (YSI) multiparameter probe was used at four of the five sample locations to record both temperature and DO throughout the water column (Figure 14-3). Sampling locations were recorded using a handheld GPS unit.

The proposed sampling method was modified to allow collection of data relative to the top of the surface water instead of relative to the bottom of the NGP. This allowed data collection at consistent depths below the surface of the water. The YSI and submersible pump were attached to a weighted line, staged by boat, and slowly lowered through the water column. The monitoring apparatus was periodically held steady at specific depths to collect field measurements and water samples until the weight, placed approximately 2 feet below the YSI, contacted the bottom. The weighted line was then kept taut to keep the YSI and submersible pump from breaching the pit bottom. At each monitoring depth, DO and temperature measurements were recorded manually after the YSI stabilized. Continuous logging of DO and temperature was also conducted.

At predetermined sampling depths, the submersible pump was activated, with tubing purged to minimize water column disruption and sample collection. During sampling, the presence of ice on the water surface held the boat in place, minimizing boat drift. Continuous DO and temperature data were correlated to depth and averaged for each interval for plotting purposes, respective of the bathymetric survey (Figure 14-3).

Surface water samples were submitted to SGS for sulfolane, nitrate and nitrite, total Kjeldahl nitrogen (TKN), total phosphorus, and potassium analysis in accordance with the RSAP. Greene et al. (1998) studied the effect of stimulating laboratory soil microcosms and cultures by amending with nitrogen and phosphate. Amendment with nitrogen appeared to have the greatest effect, while amendment with phosphate had a lesser effect, but still increased microbial activity compared to sulfolane. Results of nutrient sampling in the NGP are discussed below and summarized in Table 14-1. Analytical laboratory reports are includes as Appendix 14-C.

14.3.3 North Gravel Pit Surface Water Sampling Results

Sulfolane was not detected in any sample from any depth within the NGP. FHRA collected 26 surface water samples and submitted the samples to SGS for laboratory analysis of sulfolane and nutrients. Results of the nutrient evaluation showed that nitrate and nitrite were detected in three of the samples at 0.057 J mg/L. Each of these samples was collected from at least 15 feet below the top of surface water. This relatively low concentration is consistent with groundwater at the site. TKN was not detected in any of the samples, which is also consistent with historical groundwater monitoring data. Total phosphorous was detected in 17 of the 26 samples. Finally, potassium concentrations were generally consistent, ranging from 3.01 to 3.7 µg/L (Table 14-1).

Temperature ranged from 2.71 to 3.94 °C within the NGP. Temperature increased approximately 0.5 °C within the first 5 feet of the water column, with a continued minimal warming trend with depth at all locations except NGP-4, which showed a relatively consistent temperature to depth. There was no evidence of a thermocline (a distinct layer of water in a thermally stratified body of water) present within the NGP at the time of sampling.

DO concentrations ranged from 11.4 to 14.7 mg/L throughout the NGP sampling locations. DO saturation values at the observed NGP temperature range are from 13.1 to 13.8 mg/L (for water in contact with atmospheric air), suggesting that the elevated DO concentrations within the NGP are at or near saturation. DO concentrations did not exhibit any significant changes or trends throughout the water column, barring a slight increase of 2 mg/L (from 11.8 to 13.8 mg/L) at location NGP-4 between 460 and 455 feet above MSL (Figure 14-3).

14.3.4 North Gravel Pit Sediment Sampling and Analysis

On October 26, 2013, sediment samples were collected by dredge from the NGP at three of seven sub-basin sampling locations (NGP-4, NGP-5, and NGP-6). Sample locations are shown on Figure 14-2 and in Table 14-2. Sampling at the four remaining locations (NGP-1 through NGP-4) was not completed due to weather and excessive ice buildup on the surface of the NGP.

Sediment samples were submitted to SGS for analysis of biological oxygen demand (BOD) and TOC. BOD concentrations detected greater than the detection limit suggest that the sediment exerts some oxygen demand. TOC concentrations ranged from 0.779 to 1.15 percent and are within the range of TOC concentrations previously detected in onsite soil samples. BOD and TOC data are discussed below and summarized in Table 14-2.

14.4 Preliminary Conclusions

The following conclusions are based on a review of the NGP remedial investigation data:

- The NGP is well oxygenated. DO concentrations were near saturation, ranging from 11.4 to 14.6 mg/L. Little variation was observed with increasing depth from the water surface, with no evidence of a thermocline present during sampling.

- Sulfolane was not detected in any of the surface water samples, at any depth. These data, combined with the elevated DO, suggest that attenuation of sulfolane would occur if sulfolane were to enter the pit. In addition, the pit may serve as a method to attenuate sulfolane discharging to the pit and as a DO source for groundwater discharging out of the pit.

- The low TOC present in the sediment suggests that TOC in the sediment will not serve as a large sink for DO. However, the BOD evaluation indicates that a low-level BOD is exerted by the sediment. Together these data suggest that the sediment will not significantly impede the infiltration of high DO surface water into the aquifer.

Due to freezing of the NGP during data collection, it was not possible to complete sampling from all surface water or sediment locations. Of the seven proposed water column sampling locations, three water column locations were fully sampled and one was partially sampled.

Three of the seven proposed sediment samples were collected. Due to the lack of detections of sulfolane in the surface water samples, which were located along the eastern portion of the NGP and thus closest to the known dissolved-phase sulfolane plume, additional sampling of the NGP is not planned.

The data collected to date show DO concentrations in the NGP at or near saturation. It is likely that the DO supports aerobic degradation of sulfolane. This observation is consistent with the removal of sulfolane across the groundwater recovery system air stripper and Gallery Pond, and within the AS pilot system area. Nutrient data collected from the NGP are consistent with concentrations observed in the groundwater aquifer.

Due to the postponement of the transfer line replacement project and the associated water balance study of the NGP, both the evaluation of the mass flux of sulfolane and the hydraulic connection between the NGP and groundwater (gaining or losing) have not been completed. It is currently anticipated that these scopes of work will be completed in 2014, as detailed in the NGP Work Plan (ARCADIS 2013k).

14.5 Soil Vapor Extraction and In-Situ Respiration Pilot Testing

SVE and in-situ respiration (bioventing pilot) testing were proposed by FHRA in the Soil Vapor Extraction and In-Situ Respiration Pilot Study Work Plan (ARCADIS 2013j). The pilot testing was proposed to support the evaluation of SVE and bioventing as potential remedial alternatives in the upcoming Draft Onsite Feasibility Study.

The completed scope of work includes:

- Installation of nested vadose zone observation points SG-07 through SG-12 to serve as monitoring points during SVE pilot testing. These boring logs are included in Appendix 14-B.

- Installation of an SVE well (SVE-1) for pilot testing. This boring log will be provided in a future submittal.

- Collection of soil analytical data from SG-07 through SG-12 and SVE-1. These analytical data are included in Appendix 9-B and the data were included in the soil data evaluation presented in Section 9.1.

- Completion of one in-situ respiration test on soil gas point SG-05. Data were successfully collected during the test; however, a high-pressure front moved into the area and disturbed the test due to extreme cold weather conditions during and after the test, additional testing could not be completed to verify the results. A comprehensive summary of this test is included in Appendix 14-D.

Only testing on SG-05 was completed in 2013 due to weather conditions. The remaining testing is currently anticipated to be completed when weather conditions are warmer.

15. Ongoing Corrective Actions

As required in AAC 75.335 (c) (5), a site characterization report will propose cleanup techniques for the site. Corrective actions for sulfolane began at the site in 1985 or 1986 and substantially increased in scope beginning in 2009 as FHRA responded to the identification of sulfolane impacts in groundwater beyond the site boundary. As described in this section, FHRA has implemented an alternative water supply (AWS) program and an enhanced groundwater extraction and treatment system to exert hydraulic control over the source areas on the NPR.

15.1 Alternative Water Solutions

Alternative Water Solutions

Upon detection of sulfolane in an offsite monitoring well in October 2009, FHRA immediately began sampling private wells of residents and businesses near the NPR and providing AWSs to those with impacted wells (Barr 2012). As of September 20, 2013 and since monitoring began, 800 private wells have been sampled and 354 have contained detectable concentrations of sulfolane.

To address potential drinking water risks associated with offsite dissolved-phase sulfolane impacts, the following mitigation activities have been completed:

- Replaced the city’s existing municipal wells

- Provided AWSs to residences and businesses with wells exhibiting detections of sulfolane

As described in the Final Alternative Water Solutions Program – Management Plan (Barr 2013c), three long-term AWS options are currently available to homeowners within the plume boundary:

1. An in-home water treatment system that uses the existing well water and treats for sulfolane before water is distributed throughout the residence (point of entry [POE] treatment system).

2. A bulk water tank option where water would be delivered by a water delivery company from another site to the tank, and that water would be distributed throughout the residence.

3. Long-term bottled water delivery, consisting of 3- or 5-gallon bottles of water, for drinking and cooking, delivered to the residence on a weekly basis.

In addition, FHRA has offered homeowners a garden tank specifically for watering home gardens. These tanks are filled by FHRA twice per growing season.

Through 2013, 158 POE treatment systems and 113 bulk water tanks have been installed, 32 properties have chosen ongoing bottled water service as their permanent solution, and 48 garden tanks have been installed for properties outside the city's water main system. Some properties required more than one alternative solution because of multiple dwellings on one property. Long-term AWSs have been provided or offered to all properties where sulfolane has been detected in groundwater. Additionally, properties within or near the known sulfolane plume boundary area but without a detection of sulfolane have been provided an AWS on a case by case basis in response to specific concerns or circumstances. As described in the Final Alternative Water Solutions Program – Management Plan (Barr 2013b), FHRA also established a buffer zone around the known sulfolane plume where private wells have been sampled and bottled water is being provided as a precautionary measure to prevent exposure to sulfolane.

15.2 Current Onsite Remedial Operations

FHRA is currently remediating groundwater by extracting and treating groundwater onsite, as summarized in the Third Quarter 2013 Groundwater Monitoring Report (ARCADIS 2013l). The layout of the current groundwater extraction and recovery well network is shown on Figure 15-1.

Extraction operations have undergone continued optimization since 2009. Groundwater recovery is currently ongoing at seven recovery wells (R-21, R-35R, R-42, R-43, R-44, R-45, and R-46).

FHRA is currently completing the design and permitting necessary to complete the implementation of the interim corrective actions described in the Interim Remedial Action Plan (IRAP; Barr 2010a), SCR – 2011 (Barr 2012), and Revised IRAP Addendum (Revised IRAP Addendum; ARCADIS 2013h), including an expansion of the groundwater recovery and treatment system to the west of the current layout. This includes installation of new treatment infrastructure and two additional wells: R-47 and R-48. These corrective actions expand and optimize the existing groundwater extraction and treatment remediation system to address remaining sulfolane source areas that were identified through the completion of the site characterization process and provide full capture and treatment of the sulfolane across the transect of recovery wells.

15.3 Updated Hydraulic Containment and Capture Evaluation

As proposed in the Revised IRAP Addendum (ARCADIS 2013h), performance monitoring of the recovery system is ongoing to confirm the continued efficacy of the system. Currently, performance monitoring is completed monthly.

Evaluations were previously reported for the June 6, 2013 (Barr 2013a), August 1, 2013 (Barr 2013a; ARCADIS 2013l), and September 30, 2013 (ARCADIS 2013l) monitoring events. The next monthly event was completed on October 22, 2013 and the estimated extent of the capture zone is shown on Figure 15-4.

The capture zone measured on October 22, 2013 encompasses the extent of the dissolved-phase benzene, total xylenes, and sulfolane plumes on the east side of the NPR. The western portion of the capture zone encompasses the dissolved-phase benzene and xylenes plume extents; however, it does not extend the full width of the detectable dissolved-phase sulfolane plume. The estimated capture zone extends vertically to depths as great as 80 feet bgs.

15.4 Potential Cleanup Techniques

FHRA believes that the site characterization data presented this document and the companion reports, in conjunction with the Revised Draft Final HHRA (ARCADIS 2012), are sufficient to support a risk-based evaluation of appropriate remedial alternatives for the site. The interim remedial actions, including the AWS program and the existing groundwater extraction and treatment systems are considered applicable cleanup techniques for the site.

There are other potential remedial techniques that may also warrant further consideration in the development of a final cleanup plan for the offsite affected area, however, further consideration of those alternatives will be reserved until approval of this document is received from ADEC along with ADEC’s acknowledgement that the Site Characterization requirements under AAC 75.335 have been met.

16. 2013 Site Characterization Data Quality

QA/QC procedures assist in producing data of acceptable quality and reliability. Analytical results for laboratory QC samples were reviewed and a QA assessment of the data was conducted as the data were generated. The QA review procedures provided documentation of the accuracy and precision of the analytical data and confirmed that the analyses were sufficiently sensitive to detect analytes at levels below suggested action levels or regulatory standards, where such standards exist.

The laboratory reports for each of the samples for this Onsite Addendum, including case narratives describing laboratory QA results and completed ADEC data review checklists, are included in Appendices 16-A and 16-B, respectively. SWI conducted QA/QC reviews of the data for this reporting period; ESI conducted an additional review of select Level IV data packages if new preparatory methods were used or interferences were noted. ESI's data validation reports are presented in Appendix 16-C. Data qualifiers (flags) applied to the analytical results are summarized along with the data in the respective tables.

16.1 Soil and Groundwater Data from SGS Laboratories

This section summarizes the data that were reviewed for this reporting period, including onsite Phase 8 well installation soil and initial water samples, soil boring samples (including samples from capillary fringe soil borings and SVE well borings), hydropunch water samples, and NGP surface water and sediment samples. ADEC data review checklists for each work order (WO) are included in Appendix 16-A.

Phase 8 well installation soil samples were submitted to SGS for analysis of sulfolane, BTEX, GRO, DRO, PAH, and/or TOC, depending on location. The SGS WOs reviewed for the Phase 8 soil samples are listed in the table below.

Phase 8 Soil				
1135694	1138052	1138251	1138328	1138344
1138381	1138395	1138401	1138421	1138461
1138473	1138481	1138486	1138495	1138500
1138501	1138523	1138525	1138539	1138553
1138558	1138579	1138596	1138597	1138611
1138612	1138666	1138673	1138682	1138688
1138708	1138710	1138715	1138725	1138728

Phase 8 initial water samples (Q2, Q3, and Q4) were submitted for analysis of sulfolane and/or BTEX, depending on location. The SGS WOs reviewed for the Phase 8 initial water samples are listed in the table below.

Phase I Initial Water				
1138414	1137658	1138672	1138593	1138177
1138671	1138287	1138603	1138681	1138675
1138718	1138721	1138707	1138727	1138714
1138735	1138557	1138592	1138595	1138178

Soil boring samples were submitted for analysis of sulfolane and/or BTEX, depending on location. The SGS WOs reviewed for the soil boring samples are listed in the table below.

Soil Borings				
1135153	1138279	1138360	1138365	1138369
1138371	1138374	1138399	1138400	1138422
1138429	1138437	1138439	1138457	1138474
1138494	1138510	1138526	1138535	1138544
1138554	1138566	1138571	1138599	1138605
1138613	1138624	1138630	1138649	1138703

Capillary fringe soil boring samples were submitted for analysis of sulfolane or TOC, depending on location. The SGS WOs reviewed for the capillary fringe soil boring samples are listed in the table below.

Capillary Fringe Soil Borings					
1138295	1138304	1138308	1138320	1138340	1138343

SVE well soil boring samples were submitted for analysis of GRO, DRO, BTEX, 1,3,5-TMB, and naphthalene. The SGS WOs reviewed for the SVE soil boring samples are listed in the table below.

SVE Soil Borings			
1138729	1138680	1138732	1138694

Hydropunch water samples (including hand-driven wellpoint samples from select soil borings) were submitted for analysis of sulfolane and/or BTEX, depending on location. The SGS WOs reviewed for the hydropunch water samples are listed in the table below.

Hydropunch Water							
1138273	1138280	1138289	1138298	1138297	1138296	1138317	1134718
1138322	1138339	1138338	1138346	1138475	1138509	1138527	1138543
1138573	1138600	1138614	1138606	1138536	1138623	1135219	1138650

NGP surface water samples were submitted for analysis of sulfolane, nitrate and nitrite, TKN, total phosphorus, and potassium. NGP sediment samples were submitted for analysis of BOD and TOC. WO 1138652 was reviewed for the water samples; WO 1138653 was reviewed for the sediment samples

Results of the QA/QC review are discussed below. Only those issues that affected data quality (i.e., resulted in applying data qualifiers) are summarized; for additional details regarding QA/QC for each WO, refer to the data review checklists (Appendix 16-A).

16.1.1 Sample Handling and Holding Times

Samples were hand delivered to the SGS (Fairbanks, Alaska) receiving office and then shipped overnight via Lynden Transport or Alaska Airlines Goldstreak to SGS in Anchorage, Alaska to perform the requested analyses, using the methods specified in the chain of custody records.

Sample receipt forms were reviewed for each WO for both SGS Alaska locations and checked to verify that samples were received in good condition and within the acceptable temperature range. ADEC data review checklists (Appendix 16-A) contain details regarding this review. ADEC considers samples received between 0 and 6 °C acceptable in the absence of ice, as specified by USEPA Method SW-846. Therefore, for this Onsite Addendum, temperatures between 0 and 6°C are considered acceptable.

Samples were received within the acceptable temperature range upon arrival at each location during the reporting period, and were received properly preserved and in good condition, with one exception (soil boring WO 1138510). The BTEX sample jar for sample SB13-40 (0.7-1.2) was determined to have leaked methanol between the time the sample was collected and the time it was received at the laboratory. BTEX results for this sample, where detected, were considered estimated, biased high, and flagged ‘JH.’

For soil samples, SWI checked that the results were reported on a dry-weight basis. This was generally the case, but five soil boring samples submitted for BTEX analysis did not have additional soil to determine percent solids; those results were reported on a wet-weight basis. For those samples, BTEX results are considered estimated, biased low, with detections flagged 'JL' and nondetect analyte results were flagged 'UJ' at the LOD. The following table lists the work order and sample name of the affected samples.

WO	Sample Name
1138374	HP13-67 (9.0-10.0)
1138437	SB13-01 (2.9-3.2)
1138429	SB13-06 (2.5-3.3)
1138703	SB13-20a(10.0-11.0)
1138703	SD13-20a(10.0-11.0)

Chain of custody records for each WO were also reviewed to confirm that information was complete, custody was not breached, and samples were analyzed within the acceptable holding time. COC records were complete and correct, except for several minor naming or sample time discrepancies that did not affect data quality or usability (see QC checklists in Appendix 16-A for details).

Each sample was extracted and analyzed within the relevant method-specific holding time limits. Several samples were re-extracted outside the sulfolane holding time (7 days for water, 14 days for soil) due to the need to use an alternate sample cleanup method or high-level sulfolane method. In each case, the results were considered estimated and biased low, with detections flagged 'JL' and nondetects flagged 'UJ' at the LOD. Table 16-1 presents details regarding the applied flags including WO, sample name, and event name for samples that exceeded the sulfolane holding times specified by the analytical method.

Analytes other than sulfolane were extracted and analyzed within holding times, with one exception. For NGP sediment WO 1138653, BOD was analyzed outside the holding time for samples NGP-5 (27.2-27.5), NGP-6 (20.2-20.5), and NGP-7 (29.8-30.1). These results are considered estimated and biased low, and were flagged 'JL.'

Other sample handling anomalies were not identified during the reporting period that would adversely affect data quality or usability.

16.1.2 Analytical Sensitivity and Blanks

Reported LODs for regulated analytes were generally below ADEC cleanup levels or interim action levels during the reporting period, for analytes not detected. Exceptions are identified in Tables 16-1 and 16-2 and in the QC checklists provided in Appendix 16-A.

Laboratory method blanks were analyzed in association with samples collected for this project to check for contributions to the analytical results possibly attributable to laboratory-based contamination. Equipment blanks were collected to assess the possibility of cross-contamination from sampling equipment (for Phase 8 initial water sampling only). For samples that were analyzed for volatile analytes, a trip blank was carried and shipped with the samples to check for cross-contamination between samples or contamination from an outside source.

If analytes were detected in blank samples, corresponding sample results were evaluated. In general, if the affected analyte was not detected, or was detected at greater than five times the concentration in the blank, the results were not considered affected.

Several method blank and trip blank detections affected data quality, for several analytes. In each case, if a sample result was affected by blank contamination, it was considered not detected and flagged ‘UB’ at the LOQ or the concentration detected in the sample, whichever was higher.

The following table lists the WO, sample name, event name, and analyte affected by method blank detections, as well as details regarding the applied flags and final reporting value.

WO	Sample Name	Event Name	Analyte
1138652	NGP-3-01	North Gravel Pit Water	Total phosphorus
1138652	NGP-5-05	North Gravel Pit Water	Total phosphorus
1138652	NGP-5-25	North Gravel Pit Water	Total phosphorus
1138652	NGP-5-15	North Gravel Pit Water	Total phosphorus
1138652	NGP-5-20	North Gravel Pit Water	Total phosphorus
1138421	R-32R (1.5-2.0)	2013 Well Installation Soil	GRO
1138558	S-41R (7.5-9.0)	2013 Well Installation Soil	Naphthalene
1138558	S-41R (15.0-16.5)	2013 Well Installation Soil	GRO
1138558	S-41R (5.0-6.5)	2013 Well Installation Soil	GRO
1138558	S-41R (0.0-1.5)	2013 Well Installation Soil	GRO

1138523	MW-355-55(5.0-6.5)	2013 Well Installation Soil	GRO
1138523	MW-355-55(0-1.5)	2013 Well Installation Soil	1-Methylnaphthalene
1138523	MW-355-55(0-1.5)	2013 Well Installation Soil	GRO
1138381	O-31 (0.6-1.2)	2013 Well Installation Soil	GRO
1138381	O-31 (0.6-1.2)	2013 Well Installation Soil	Toluene
1138579	MW-334-85 (0.0-1.5)	2013 Well Installation Soil	Naphthalene
1138579	MW-434-85 (6.5-8.0)	2013 Well Installation Soil	Naphthalene
1138395	O-32(17.2-17.8)	2013 Well Installation Soil	GRO
1138395	O-32(9.5-9.8)	2013 Well Installation Soil	GRO
1138553	MW-336-15(0.5-2.0)	2013 Well Installation Soil	Naphthalene
1138553	MW-336-15(0.5-2.0)	2013 Well Installation Soil	GRO
1138553	MW-336-15(0.5-2.0)	2013 Well Installation Soil	1-Methylnaphthalene
1138553	MW-336-15(0.5-2.0)	2013 Well Installation Soil	2-Methylnaphthalene
1138344	MW-110-65 (5.5-6.0)	2013 Well Installation Soil	GRO
1138344	MW-110-65 (0.0-1.0)	2013 Well Installation Soil	GRO
1138344	MW-110-65 (16.0-16.5)	2013 Well Installation Soil	GRO
1138539	MW-336-20 (15.0-16.5)	2013 Well Installation Soil	GRO
1138539	MW-336-20 (0.5-2.0)	2013 Well Installation Soil	Sulfolane
1138539	MW-336-20 (0.5-2.0)	2013 Well Installation Soil	GRO
1138535	SB13-28 (6-6.6)	2013 Soil Borings	Sulfolane
1138535	SB13-25 (3-4)	2013 Soil Borings	Sulfolane
1138535	SB13-25 (6-6.6)	2013 Soil Borings	Sulfolane
1138571	SB13-26 (1.0-1.5)	2013 Soil Borings	Naphthalene

The following table lists the WO, sample name, event name, and analyte affected by trip blank detections.

WO	Sample Name	Event Name	Analyte
1138328	O-24-65 (11.0-11.5)	2013 Well Installation Soil	GRO
1138328	O-26-65 (0.5-1.5)	2013 Well Installation Soil	GRO
1138579	MW-334-85 (0.0-1.5)	2013 Well Installation Soil	GRO
1138579	MW-434-85 (6.5-8.0)	2013 Well Installation Soil	GRO
1138553	MW-336-15(0.5-2.0)	2013 Well Installation Soil	Toluene

1138539	MW-336-20 (0.5-2.0)	2013 Well Installation Soil	o-Xylene
1138539	MW-336-20 (0.5-2.0)	2013 Well Installation Soil	P & M -xylene
1138539	MW-336-20 (0.5-2.0)	2013 Well Installation Soil	Total xylenes
1138510	SB13-40 (0.7-1.2)	2013 Soil Borings	Toluene
1138510	SB13-42 (17-18)	2013 Soil Borings	Toluene
1138510	SB13-29 (17-18.5)	2013 Soil Borings	Toluene
1138510	SB13-42 (1-2)	2013 Soil Borings	Toluene
1138510	SB13-42 (5-6)	2013 Soil Borings	Toluene
1138510	SB13-29 (5-6)	2013 Soil Borings	Toluene
1138510	SB13-40 (17-17.8)	2013 Soil Borings	Toluene
1138510	SB13-29 (15-17)	2013 Soil Borings	Toluene
1138535	SB13-25 (3-4)	2013 Soil Borings	Toluene
1138571	SB13-26 (1.0-1.5)	2013 Soil Borings	Benzene
1138571	SB13-26 (1.0-1.5)	2013 Soil Borings	P & M -xylene
1138571	SB13-26 (1.0-1.5)	2013 Soil Borings	Toluene
1138571	SB13-44 (1-2)	2013 Soil Borings	Benzene
1138571	SB13-44 (1-2)	2013 Soil Borings	Toluene
1138571	SB13-26 (3.0-3.5)	2013 Soil Borings	Toluene
1138571	SB13-26 (3.0-3.5)	2013 Soil Borings	Benzene

16.1.3 Accuracy

Laboratory analytical accuracy may be assessed by evaluating the analyte recoveries from continuing calibration verification (CCV), laboratory control sample (LCS), and LCS duplicate (LCSD) analyses. LCS/LCSD samples assess the accuracy of analytical procedures by checking the ability to recover analytes added to clean aqueous or solid matrices. In some cases, the laboratory spiked project samples as matrix spike (MS) and MS duplicate (MSD) to assess their ability to recover analytes from a matrix similar to that of project samples. Accuracy was also assessed for organic analyses by evaluating the recovery of analyte surrogates added to project samples. For sulfolane results, recovery of the internal standard (sulfolane-d8) was evaluated.

There were no CCV failures affecting data quality for samples obtained during the reporting period, based on information provided in analytical laboratory report case narratives. Recovery information was reviewed for all surrogates, LCS/LCSDs, and MS/MSDs associated with project samples.

LCS and LCSD recoveries were within laboratory control limits for each preparatory batch. In general, MS/MSD recoveries were within laboratory control limits, the sample spiked for the MS/MSD was not in the sample set, or the spiking concentration was small compared to the native concentration of the analyte. However, several MS/MSD recovery failures affected data quality. Generally, samples affected by high MS/MSD recovery were considered estimated and biased high, and were flagged 'JH'; samples affected by low MS/MSD recovery were considered estimated and biased low, and were flagged 'JL.' The following table lists the WO, sample name, event name, and analyte affected by MS/MSD recovery failures.

WO	Sample Name	Event Name	Analyte
1138474	SB13-19(0.0-2.0)	2013 Soil Borings	Sulfolane
1138304	CF13-4B(11.9-12.0)	2013 Cap-Fringe Soil Borings	TOC
1138344	MW-110-65 (62.7-63.2)	2013 Well Installation Soil	TOC
1138682	MW-359-60(31.5-31.7)	2013 Well Installation Soil	TOC
1138052	O-5-65(36.5-37.0)	2013 Well Installation Soil	TOC
1138553	MW-336-15(5.0-6.5)	2013 Well Installation Soil	Benzo(a)anthracene
1138612	MW-337-20(16-17)	2013 Well Installation Soil	2-Methylnaphthalene
1138612	MW-337-20(16-17)	2013 Well Installation Soil	1-Methylnaphthalene
1138381	O-31 (15.5-16.0)	2013 Well Installation Soil	2-Methylnaphthalene
1138381	O-31 (15.5-16.0)	2013 Well Installation Soil	1-Methylnaphthalene
1138395	O-32(9.5-9.8)	2013 Well Installation Soil	Naphthalene
1138571	SB13-26 (5.0-5.5)	2013 Soil Borings	Sulfolane
1138381	O-31 (15.5-16.0)	2013 Well Installation Soil	Naphthalene

Sample SB13-19(0.0-2.0) was affected by low MS recovery and exceeded the sulfolane holding time (see Section 16.2), implying additional low bias. Remaining MS/MSD recoveries were within laboratory control limits.

Several surrogate recovery failures occurred for GRO, BTEX, and PAHs. In general, surrogate recovery failures attributed to matrix interference were considered to affect data quality; surrogate failures due to dilution were not considered to affect data quality. Samples affected by high surrogate recovery were considered estimated and biased high, and were flagged 'JH'; samples affected by low surrogate recovery were considered estimated and biased low, and were flagged 'JL.' Table 16-2 presents details regarding the applied flags including the WO, sample name, event name, and analyte affected by surrogate recovery failures.

Recovery failures did not occur for sulfolane-d8 during the reporting period. Laboratory CCV, LCS/LCSD, MS/MSD, and surrogate recovery information indicate that the analytical results were accurate, except for the results listed above.

16.1.4 Precision

Generally, duplicate samples were collected at a frequency of 10 percent of the overall number of samples collected to evaluate the precision of analytical measurements, as well as the reproducibility of the sampling technique. The relative percent difference (RPD [difference between the sample and its field duplicate divided by the mean of the two]) was calculated to evaluate the precision of the data. An RPD was evaluated only if the results of the analyses for both duplicates were detected quantitatively (above the LOQ).

During the reporting period, the following duplicate samples were collected:

- Four duplicates for Phase 8 soil samples (125 samples total)
- Six duplicates for Phase 8 initial groundwater samples (47 samples total)
- Twenty-seven duplicates for soil boring samples (247 samples total)
- Seventeen duplicates for hydropunch water samples (143 samples total)

Field duplicate samples were not collected from the capillary fringe soil borings, due to limited sample quantity from the high-resolution sampling technique. In addition, field duplicate samples were not collected from SVE soil borings or the NGP. Phase 8 duplicate collection frequency was lower than the targeted 10 percent due in part to the low recovery of soil in split-spoon samples at depth. Phase 8 well installation is ongoing; therefore, additional field duplicate samples are currently being collected.

Results of RPD calculations for each of the duplicate samples were within the data quality objective of 30 percent for water data and 50 percent for soil data, where calculable, except for the field duplicate pairs presented in Table 16-3.

Laboratory analytical precision can also be evaluated by laboratory RPD calculations using the LCS/LCSD and MS/MSD, or laboratory duplicate sample results. RPDs above laboratory control limits that affected data quality did not occur during the reporting period, with one exception. For soil boring WO 1138279, the laboratory duplicate RPD for sulfolane was above the laboratory control limit for sample SB13-37 (17.6-17.9). The result was considered estimated and was flagged ‘J’ for imprecision.

Based on a review of the data, the results associated with the reporting period are considered precise, with the exceptions noted above.

16.1.5 Hydrocarbon Interference and Level IV Review

In addition to the standard QA review, additional review of select WOs was conducted if the laboratory noted interference issues (such as ion ratios outside QC criteria). ESI conducted an additional review of these WOs, and where warranted, produced a Level IV validation report; these reports are included in Appendix 16-C. ESI and SGS also reviewed the entire soil dataset for the reporting period to identify any sulfolane results below the LOQ where ion ratios were outside criteria (not originally identified in the case narratives); these results were considered tentative identifications and were flagged 'JN.' The following table lists the WO, sample name, and event name of affected results. A Reanalysis of Soil Samples from Flint Hills Resources Alaska, LLC North Pole Refinery Site Due to High Concentrations of Sulfolane Memorandum is included as Appendix 16-B.

WO	Sample Name	Event Name
1138481	MW-354-15 (5.0-7.0)	2013 Well Installation Soil
1138481	MW-354-60 (0.0-1.5)	2013 Well Installation Soil
1138481	MW-354-60 (5.0-6.5)	2013 Well Installation Soil
1138481	MW-454-60 (5.0-6.5)	2013 Well Installation Soil
1138536	SB13-28-09	2013 Hydropunch Water
1138457	SB13-10 (0.0-1.3)	2013 Soil Borings
1138571	SB13-33 (1.5-1.8)	2013 Soil Borings
1138535	SB13-25 (0-2)	2013 Soil Borings
1138554	SB13-12 (2.5-3.5)	2013 Soil Borings
1138566	SB13-30 (3.2-3.8)	2013 Soil Borings
1138571	SB13-26 (1.0-1.5)	2013 Soil Borings
1138630	SB13-24(6.0-6.6)	2013 Soil Borings

For the samples in WO 1138481, results were further affected by a holding time exceedance; however, the 'JN' flag was retained as the final and more conservative flag. In addition to the samples listed above, one additional sample was affected by compounded QC issues. For Phase 8 Soil WO 1138539_rev1, the revised WO notes that sulfolane results for sample MW-336-20 (0.5-2.0) were below the LOQ with ion ratios outside of QC criteria. Typically, the sulfolane result for this sample would be considered a tentative identification at an estimated concentration ('JN' flag); however, the result is flagged 'UB' (considered the more conservative flag) and considered not detected due to a method blank detection. Section 16.3 provides additional information regarding this result.

In addition to the low-level sulfolane detections affected by interference, some higher levels of interference prevented the laboratory from identifying sulfolane, and one instance occurred of ion ratios out of QC criteria without interference present, as summarized below:

- *Phase 8 Soil WO 1138251*. Sulfolane and sulfolane-d8 could not be quantified in samples MW-348-65 (8.0-8.3) and MW-348-15 (6.9-7.3) due to hydrocarbon interference in the original extraction. A sufficient sample amount was not available to re-extract using the sample cleanup method. Sulfolane results are considered rejected for these samples and were flagged ‘R.’

- *Phase 8 Initial Water WO 1138557*. Sulfolane and sulfolane-d8 could not be quantified in sample O-31 due to hydrocarbon interference in the original extraction. Limited sample volume and laboratory error prevented re-extraction using the sample cleanup method. Sulfolane results were considered rejected for these samples, and were flagged ‘R.’

- *Hydropunch Water WO 1138317*. Sulfolane ion ratios were outside QC criteria for sample HP13-70-49, although a hydrocarbon interference was not present and the sample was not re-extracted or reanalyzed. The sulfolane result was conservatively flagged ‘J’ as estimated.

16.1.6 Data Quality Summary

Based on the methods outlined in the RSAP, the samples collected are considered to be representative of site conditions at the locations and times they were obtained. Based on the QA review, three sample results were rejected as unusable due to QC failures. In general, the quality of the analytical data for this reporting period does not appear to have been compromised by analytical irregularities, and results affected by QC anomalies are usable as qualified with the appropriate data flags.

16.2 Soil and Groundwater Samples Data Quality for Polychlorinated Biphenyls, Polyfluorinated Hydrocarbons, and Perfluorinated Compounds

This section summarizes the results of the QA/QC review of groundwater samples data for this reporting period. Groundwater samples were submitted to the TestAmerica, for analysis of PCBs by USEPA Method 8082A, PFCs, and FOSA.

ADEC data review checklists are included in Appendix 16-B. The WOs reviewed for this reporting period are listed in the table below.

Groundwater Samples	
WO #	**Method/Parameters**
280-46485	8082/PCBs, SOP LC-0012/PFCs and FOSA
280-46199	8082/PCBs, SOP LC-0012/PFCs

16.2.1 Sample Handling

Samples were shipped overnight via Federal Express to Test America. Chain of custody forms were reviewed and checked to verify that samples were received in good condition and within the acceptable temperature indicated on the ADEC data review checklist (4 ± 2 °C). The ADEC data review checklist (Appendix 16-A) contains details regarding this review. ADEC considers temperatures received between 0 and 6 °C acceptable in the absence of ice, as specified by USEPA Method SW-846. Therefore, for this Onsite Addendum, temperatures between 0 and 6°C are considered acceptable. The chain of custody records were also reviewed to confirm that information was complete, custody was not breached, and samples were analyzed within the acceptable holding time.

Samples were received in good condition, within the acceptable temperature range upon arrival at the laboratory, and analyzed within an acceptable holding time.

16.2.2 Analytical Sensitivity

Reported LODs for regulated analytes were below ADEC cleanup levels or interim action levels during the reporting period.

Laboratory method blanks were analyzed in association with samples collected for this project to check for contributions to the analytical results, possibly attributable to laboratory-based contamination. An equipment rinsate blank was also collected as part of the sampling event. There were no blank detections affecting data quality for the reporting period, with one exception. For WO 280-46485, the laboratory method blank analyzed for PFCs had detections of PFHxA (0.00431 µg/L) and PFOS (0.0436 µg/L). The associated sample results were greater than 10 times the method blank concentrations; therefore, data qualification was not required.

For PFCs and FOSA analyses, the ratio between quantifying and qualifying ions was also evaluated. The acceptance criteria for the ion ratio is less than 30 percent of the ratio in the mid-point calibration standard. The ion ratios were within criteria with the following exceptions:

- *WO 280-46199*. The PFBS results for samples PFC13-01(1.2-1.6), PFC13-08(1.5-2.0), PFC13-04(1.2-1.6), and PFC13-05(1.2-1.6) were qualified “J” due to out-of-criteria ratios.

- *WO 280-46199*. The PFHxS result for sample PFC13-02(1.5-2.0) was qualified “J” due to out-of-criteria ratio.

- *WO 280-46199*. The PFDS results for samples PFC13-01(1.2-1.6), PFC13-02(1.5-2.0), PFC13-08(1.5-2.0), PFC13-02(1.5-2.0), PFC13-03(1.4-1.8), PFC13-04(1.2-1.6), PFC13-05(1.2-1.6), PFC13-06(1.2-1.6), and PFC13-07(1.2-1.6) were qualified “J” due to out-of-criteria ratio.

- *WO 280-46485*. The PFOS result for sample MW-321-15 was qualified “J” due to out-of-criteria ratio.

16.2.3 Accuracy

Laboratory analytical accuracy may be assessed by evaluating the analyte recoveries from surrogate, CCV, LCS, LCSD recoveries, MS, and MSD recoveries. LCS/LCSD samples assess the accuracy of analytical procedures by checking the ability to recover analytes added to clean aqueous matrices. MS/MSD samples are used to assess accuracy, considering matrix influences. Accuracy was also assessed for organic analyses by evaluating the recovery of surrogates (decachlorobiphenyl and tetrachloro-m-xylene for PCBs, and $^{13}C_8$ PFOA and $^{13}C_8$ PFOS for PFCs) added to project samples. CCV recoveries were assessed to evaluate instrument accuracy. Internal standard recoveries were also evaluated for PFC and FOSA analyses. Surrogate, CCV, LCS/LCSD, and MS/MSD recoveries were within laboratory control limits for each preparatory batch, with the following exceptions:

- *WOs 280-46199.* Surrogate recoveries for PCB analyses were outside of laboratory acceptance limits for samples PFC13-03(1.4-1.8), PFC13-05(1.2-1.6), and PFC13-06(1.2-1.6). PCB results for these samples were qualified “UJ” to indicate a potential low bias.

- *WOs 280-46199.* Surrogate recoveries for PFC analyses were outside of laboratory acceptance limits for samples PFC13-07(1.2-1.6), PFC13-05(1.2-1.6), and PFC13-06(1.2-1.6). PCB results for these samples were qualified “UJ” to indicate a potential bias.

- *WOs 280-46199.* Sample PFC13-07(1.2-1.6) had internal standard recoveries outside of acceptance limits for $^{18}O_2$ PFHxS, $^{13}C_4$ PFOA, $^{13}C_4$ PFOS, $^{13}C_5$ PFNA, $^{13}C_2$ PFDA,

$^{13}C_2$ PFUnA, and $^{13}C_8$ FOSA. PFC results for sample PFC13-07(1.2-1.6) were qualified "J" for detects to indicate a potential bias.

- *WOs 280-46485.* Sample MW-321-15 had internal standard recoveries outside of acceptance limits for $^{13}C_4$ PFOS, $^{13}C_5$ PFNA, $^{13}C_2$ PFDA, and $^{13}C_8$ FOSA. PFC results for sample MW-321-15 were qualified "J" for detects to indicate a potential bias.

16.2.4 Precision

Field duplicate samples were collected at a frequency of at least 10 percent of the overall number of samples collected to evaluate the precision of analytical measurements, as well as the reproducibility of the sampling technique. The RPD (difference between the sample and its field duplicate divided by the mean of the two) was calculated to evaluate the precision of the data. An RPD can be evaluated only if the results of the analyses for both duplicates are detected quantitatively (above the LOQ).

During the reporting period, one field duplicate was collected: PFC13-08(1.5-2.0) is the field duplicate of PFC13-02-(1.3-2.0). The field duplicate RPDs were within acceptable range.

Laboratory analytical precision can also be evaluated by laboratory RPD calculations using the LCS/LCSD and MS/MSD results. There were no RPDs above laboratory control limits that affected data quality during the reporting period.

Based on a review of the data, the soil and groundwater sample results associated with the reporting period are considered precise, with the exceptions described above.

16.3 Air Sample Data Quality for United States Environmental Protection Agency Methods TO-17 and TO-15, and ASTM International D-1946

This section summarizes the results of the QA/QC review of air sample data for this reporting period. Air samples were collected in either sorbent tubes, 1-liter Summa canisters, or 1-liter Tedlar bags and submitted to Eurofins Air Toxics for analysis of naphthalene by modified USEPA Method TO-17, VOCs (benzene, toluene, ethylbenzene, m&p-xylenes, o-xylene, 1,3,5-TMB, and naphthalene) and aliphatic hydrocarbons (APHs) by modified USEPA Method TO-15, and methane and fixed gases (oxygen, nitrogen, carbon dioxide, and helium) by method ASTM D1946.

ADEC data review checklists are included in Appendix 16-A. The WOs reviewed for this reporting period are listed in the table below.

Air Samples	
WO #	**Method/Parameters**
1309480	Mod TO-17/naphthalene
1309492A	Mod TO-15/VOCs
1309492B	Mod TO-15/APHs
1309492C	ASTM D1946/methane and fixed gases
1309517A	Mod TO-15/VOCs
1309517B	Mod TO-15/APHs
1309517C	ASTM D1946/methane and fixed gases

Results of the QA/QC analysis are discussed below. Only those issues that affected data quality (i.e., resulted in applying data qualifiers) are summarized; additional details regarding QA/QC for each laboratory report are presented in the data review checklists (Appendix 16-A).

16.3.1 Sample Handling

Samples were shipped overnight via Federal Express to the Eurofins Air Toxics laboratory in Folsom, California. Chain of custody forms were reviewed and checked to verify that samples were received in good condition and within the acceptable temperature indicated on the ADEC data review checklist (4 ± 2 °C). The ADEC data review checklist (Appendix D) contains details regarding this review. ADEC considers temperatures received between 0 and 6 °C acceptable in the absence of ice, as specified by USEPA Method SW-846. Therefore, for this Onsite Addendum, temperatures between 0 and 6°C are considered acceptable. Summa canisters and Tedlar bags are not required to be chilled. The chain of custody records were also reviewed to confirm that information was complete, custody was not breached, and samples were analyzed within the acceptable holding time.

Samples were received in good condition and within the acceptable temperature range upon arrival at the laboratory with the following exceptions. For WOs 1309492A, 10309492B, and 1309492C, samples were not relinquished properly. A signature and date were not recorded on the chain of custody form by the field sampler. This discrepancy did not require data qualification.

No other sample handling anomalies were identified during the reporting period that would adversely affect data quality.

16.3.2 Analytical Sensitivity

Reported limits of detection for regulated analytes were below ADEC cleanup levels or interim action levels during the reporting period.

Laboratory method blanks were analyzed in association with samples collected for this project to check for contributions to the analytical results, possibly attributable to laboratory-based contamination. A field blank and equipment blank were also collected as part of the sampling event. There were no blank detections affecting data quality for the reporting period, with one exception. For WO 1309492C, the equipment blank analyzed by method ASTM D1946 had detections of oxygen (2.9 percent) and nitrogen (97 percent). These detections did not result in any qualified data.

16.3.3 Accuracy

Laboratory analytical accuracy may be assessed by evaluating the analyte recoveries from surrogate, CCV, LCS, and LCSD recoveries. LCS/LCSD samples assess the accuracy of analytical procedures by checking the ability to recover analytes added to clean aqueous matrices. Accuracy was also assessed for organic analyses by evaluating the recovery of surrogates (1,2-dichloroethane-d4, toluene-d8, naphthalene-d8 for VOCs) added to project samples. CCV recoveries were assessed to evaluate instrument accuracy. Surrogate, CCV, LCS, and LCSD recoveries were within laboratory control limits for each preparatory batch, with the following exceptions:

- *WOs 1309480.* Recovery of 1,2-dichloroethane-d4 and toluene-s8 for the field blank were below laboratory control limits. Surrogate recoveries for the samples associated with the field blank were within an acceptable range; therefore, data qualification was not required.

- *WOs 1309492A.* 1,2-Dichloroethane-d4 recoveries were above laboratory control limits for samples SG-03-3.5 and SG-04-4. The detected results for SG-04-4 were qualified “J” to indicate a potential high bias. Sample SG-03-3.5 results were not detected, and data qualification was not required.

- *WOs 1309492 and 1309517.* LCS/LCSD recoveries for naphthalene were below laboratory control limits. Associated samples (SGC-05-8, SG-03-03.5, SG-03-6.5, SG-04-4, SG-02-3.5, SG-02-6.5, and BD-3) were qualified “UJ” to indicate a potential low bias.

Laboratory CCV, LCS/LCSD, and surrogate recovery information indicate that the analytical results were accurate, with the exceptions noted above.

16.3.4 Precision

Field duplicate samples were collected at a frequency of at least 10 percent of the overall number of samples collected to evaluate the precision of analytical measurements, as well as the reproducibility of the sampling technique. The RPD was calculated to evaluate the precision of the data. An RPD can be evaluated only if the results of the analyses for both duplicates are detected quantitatively (above the LOQ).

During the reporting period, three field duplicates were collected: SG-02-6.5/BD-2, SG-05-8/BD-1, and SG-02-6.5/BD3. The field duplicate RPDs were within acceptable range with one exception. Sample SG-05-8 and its associated field duplicate BD-1 had an RPD value for >C10-C12 aliphatic hydrocarbons of 62.1 percent. The >C10-C12 aliphatic hydrocarbon results for these samples were qualified “J” to indicate an estimated value.

Laboratory analytical precision can also be evaluated by laboratory RPD calculations using the LCS/LCSD results. There were no RPDs above laboratory control limits that affected data quality for the reporting period.

Based on a review of the data, the air sample results associated with the reporting period are considered precise, with the exceptions described above.

16.4 Soil Samples Data Quality for Method 8290

This section summarizes the results of the QA/QC review of soil data for this reporting period. Soil samples were submitted to SGS laboratory for analysis of dioxins/furans by USEPA Method 8290.

ADEC data review checklists are included in Appendix 16-A. The WO reviewed for this reporting period is listed in the table below.

Soil Samples	
WO #	**Method/Parameters**
1134810	USEPA Method 8290/Dioxins and Furans

16.4.1 Sample Handling

Samples were delivered to SGS in Fairbanks, Alaska, shipped overnight via Lynden Transport to SGS in Anchorage, Alaska, and then shipped overnight to SGS in Wilmington, North Carolina. Chain of custody forms were reviewed and checked to verify that samples were received in good condition and within the acceptable temperature indicated on the ADEC data review checklist (4 ± 2 °C). The ADEC data review checklist (Appendix 16-A) contains details regarding this review. ADEC considers temperatures received between 0 and 6 °C acceptable in the absence of ice, as specified by USEPA Method SW-846. Therefore, for this Onsite Addendum, temperatures between 0 and 6°C are considered acceptable. The chain of custody records were also reviewed to confirm that information was complete, custody was not breached, and samples were analyzed within the acceptable holding time.

Samples were received in good conditions and within the acceptable temperature range upon arrival at the laboratory, with one exception. For WO 1134810, samples were extracted 5 and 7 days outside of the required holding time (30 days from collection to extraction). Results were qualified “J” for detects and “UJ” for nondetects to indicate a potential low bias.

No other sample handling anomalies were identified during the reporting period that would adversely affect data quality.

16.4.2 Analytical Sensitivity

Reported LODs for regulated analytes were below ADEC cleanup levels or interim action levels during the reporting period.

Laboratory method blanks were analyzed in association with samples collected for this project to check for contributions to the analytical results, possibly attributable to laboratory-based contamination. There were no blank detections affecting data quality for the reporting period, with the following exceptions:

- *WO 11134810*. The laboratory method blank contained a total TCDD detection of 0.222 picograms per gram. The total TCDD results from the following samples were qualified “UB”: PFC13-01(1.2-1.6), PFC13-08(1.5-2.0), PFC13-03(1.4-1.8), PFC13-04(1.2-1.6), and PFC13-05(1.2-1.6).

- *WO 11134810*. Results that were reported as estimated maximum possible concentration were qualified “UX” to indicate an estimated concentration based on the potential compound identification and quantitation interference.

16.4.3 Accuracy

Laboratory analytical accuracy may be assessed by evaluating the dioxin/furan ongoing precision and recovery sample recoveries, as well as recoveries of spiked isotopically

($^{13}C_{12}$) labeled standards. The recoveries were all within acceptance limits, indicating that the analytical results were accurate, with the exceptions noted above.

16.4.4 Precision

There were no field duplicate samples collected for dioxins/furans for this sampling event.

16.4.5 Data Quality Summary

Based on the methods outlined in the RSAP, the samples collected are considered to be representative of site conditions at the locations and times they were obtained. Based on the QA review, no samples were rejected as unusable due to QC failures. In general, the quality of the analytical data for this reporting period does not appear to have been compromised by analytical irregularities and results affected by QC anomalies are qualified with the appropriate data flags.

17. Conclusions

This Onsite Addendum is the last in a series of site characterization reports that collectively present a large body of information that has been gathered to ascertain the physical characteristics of the site, define the sources of contamination, and determine the nature and extent of contamination present at the site.

FHRA completed the following onsite site characterization activities in 2013:

- Installation of Phase 8 monitoring, observation, and LNAPL recovery wells and well nests for further characterization and delineation.
- Collection of soil samples for sulfolane and BTEX analytical data for additional delineation of source areas.
- Collection of soil samples to evaluate grain size distribution, verify visual observations of soil types recorded during borehole drilling, assess aquifer heterogeneity, and estimate hydraulic conductivity.
- Collection of soil samples at a high resolution to evaluate storage of sulfolane in the vadose zone, capillary fringe, and shallow groundwater table.
- Collection of BTEX groundwater analytical data from monitoring wells screened below the groundwater table zone.
- Collection of groundwater samples for sulfolane and BTEX analytical data from monitoring wells, hydropunch borings, and hand-driven sampling points.
- LNAPL assessment, including LNAPL transmissivity testing, LNAPL composition analysis, and analysis of LNAPL recovery data.
- Collection of soil gas samples for laboratory analysis and diffusivity testing data to evaluate bioventing, explosion risk, NSZD, and volatile hydrocarbon distribution.
- Phase III PFC investigation including sampling of groundwater and FTA soil (including additional analytes).
- Measurement of water levels using automated and manual methods.
- Capture zone analysis and vertical gradient data collection in conjunction with surveying for the expanded recovery system (hydrologic studies).

- Implementation of an aquifer pumping test at the onsite recovery wells.

- Execution of two tracer tests onsite, including installation of nearby monitoring wells, conduct of single-well pumping tests, and high-frequency collection of water level and tracer samples.

- Collection of subsurface data using geophysical field surveys that included airborne, ground-based, and down-hole methods to characterize permafrost.

- In-situ respiration testing.

- Collection of data from an onsite AS pilot test.

- Collection of bathymetric, water, and sediment data for remedial evaluation of the NGP.

17.1 Geology

Geological information collected from soil borings advanced in 2013 was consistent with historical observations. Additional understanding was gleaned about the widespread presence of peat/high organic soil and plastic silt in 2013 because of their importance in influencing COC transport. Soils in the vadose and shallow groundwater zone at the site are heterogeneous mixtures of silt, sand, gravel, peat/high organics soil, and clay-sized particles. Studies related to the heterogeneous nature of the geology validated previously posed hypotheses on how sulfolane is retained in the subsurface environment . The GSA data collected in 2013 validate field observations of higher silt content in the shallower (0 to 20 feet bgs) zone. The GSA data also verify that field soil identification of sand and gravel in the saturated zone are accurate.

17.2 Permafrost

Permafrost is largely absent under the developed portions of the site as indicated by observations made during well installations and the geophysical surveys conducted in 2013. Discontinuous permafrost is present in the northern portions of the site. In particular, small discontinuous masses are present at the MW-154 and MW-179 clusters and along the VPT. An irregular, massive, shallow permafrost body is present in the undeveloped area south of Transfer Road. The edge of a large, relatively continuous permafrost mass is present near the NPB. This permafrost mass extends to the north and northwest under the offsite suprapermafrost plume, exhibiting a high variability in thickness and trending shallower in many areas to the northwest.

17.3 Hydrogeology

Groundwater flow and transport at the site is dynamic and complex due to a combination of factors including heterogeneously distributed soil types, discontinuous permafrost, seasonal fluctuations in surface water elevations at the Tanana and Chena rivers causing fluctuations in flow direction, and annual freeze-thaw cycles that extend well below ground.

Multiple phases of site investigations have been performed that have focused on characterizing groundwater flow and the fate and transport of site-related COCs. These hydrogeologic investigations have resulted in the completion of 227 onsite soil borings, installation of 339 onsite groundwater monitoring wells, collection and analysis of 1,032 soil samples, and collection and analysis of 2,737 groundwater samples onsite. Hydrogeologic investigations onsite have also included measuring hydraulic conductivity at more than 50 well locations; performing three large-scale pumping tests using the groundwater recovery wells, three tracer tests, and several geophysical surveys; collecting many years' worth of high-resolution water-level monitoring data; and constructing and calibrating a 3-D numerical groundwater flow and transport model.

Results of these investigations have enabled the creation of a detailed hydrogeologic conceptual model that addresses the complexities encountered at the site and rationally accounts for the fate and transport of site-related COCs. The hydrogeologic and fate and transport conceptual site models are within a reasonable degree of accuracy necessary to evaluate potential risks associated with groundwater COC transport and remediation alternatives. The CSM will support development of the final cleanup plan for the site.

17.4 Constituent of Concern Distribution in Soil

Soil samples were collected from multiple locations across the site in 2013 including Lagoon B, SGP, CU #1 Wash Area, CU #2 EU, and Sump 908. Additionally, high-density vertical soil sampling was conducted in the SWA. Significant findings of the 2013 soil investigation are:

- Sulfolane concentrations in soil exceeding the calculated ACL (999 µg/kg) are generally confined to identified source areas (SWA, CU #1 Wash Area, and CU #2 EU). The confirmation of elevated soil sulfolane concentrations and storage in soil in these locations is consistent with the observed plume concentrations beneath and downgradient from historical source areas.

- Petroleum hydrocarbon impacts in soil, including the COCs of interest (benzene, total xylenes, 1,3,5-TMB, and naphthalene) are confined within the site boundaries. The highest concentrations of COCs are consistently found at the capillary fringe.

- Retention of sulfolane in the unsaturated zone and capillary fringe was investigated in the SWA. Sulfolane concentrations in soil were correlated with fine-grained soil and, in particular, the percent of silt and clay-sized particles in the soil matrix. Sulfolane concentrations in pore water within the unsaturated zone in the SWA exceed current groundwater concentrations in that area verifying that site soil conditions are such that legacy sulfolane releases are a key source of sulfolane detections in groundwater.

17.5 Constituent of Concern Distribution in Groundwater

Current sulfolane concentrations in groundwater exceeding the ACL of 362 µg/L are largely in groundwater upgradient of the groundwater recovery system capture zone. Sulfolane concentrations exceeding the ACL do not extend to the VPT.

Sulfolane concentrations are either stable or decreasing in onsite monitoring wells downgradient from the remediation system. These decreasing trends are largely due to the expansion and optimization of the groundwater recovery system at the site, which was implemented in the second quarter 2013.

Benzene concentrations exceeding the 590 µg/L ACL are limited to the operational area of the site, and are consistent with the presence of LNAPL. The highest concentrations are present at the water table, but some concentrations exceeding the ACL are present below the water table in the area of the CU #2 EU. Exceedances of total xylenes are generally consistent with the exceedances of dissolved-phase benzene. Detectable concentrations of benzene and total xylenes are delineated above 55 feet bgs.

Naphthalene concentrations exceeding the ACL were also generally consistent with the presence of benzene at the water table. However, naphthalene has not been detected in samples collected below the water table. 1,3,5-TMB detections are limited to site process areas and areas where LNAPL has been observed. 1,3,5-TMB was only detected at concentrations exceeding the ACL in three wells sampled between 2001 and 2012, and has not been detected in samples collected below the water table.

17.6 Light Nonaqueous Phase Liquid

The nature and extent of LNAPL has been thoroughly characterized through 26 years of data collection of petroleum impacts at the site. These data were bolstered by efforts to assess LNAPL composition, mobility, and recoverability in the past 3 years. As a result, it can be stated that the extent of LNAPL impacts is known, LNAPL is not a significant source of sulfolane to groundwater, the LNAPL plume is stable, LNAPL is readily recoverable in some areas of the site, and natural processes are depleting the LNAPL at a significant rate.

The large body of data for LNAPL characterization is comprehensive and informs preparation of a feasibility study for the site.

17.7 Soil Gas

The soil gas investigation characterized soil gas quality in LNAPL-affected areas onsite. The findings of the soil gas investigation include:

- Methane was detected at one deep soil gas sample above 100 percent LEL. However, natural attenuation of methane vertically through the soil column is evident and the NPR has vapor intrusion mitigation measures in place.

- Bioventing or other oxygenation technologies may be applicable potential remedies to be considered in future remedial alternative evaluations for some portions of the site depending on the remedial action objectives.

- Site-specific soil diffusion coefficients were determined from tracer gas injection tests that were used in conjunction with the soil gas data to update the 2012 NSZD evaluation (Section 8).

The distribution of VPH in soil gas is consistent with the reported LNAPL types at the site. In general, the highest concentrations of TVH in soil gas were measured in the area with naptha-dominated LNAPL (SG-04).

17.8 Fire Training Area Investigation

PFCs are adequately characterized in groundwater at the site. The detections are limited in area as determined during the Phase I and Phase II investigations (ARCADIS 2013b). PFCs exceeding the site-specific ACLs for PFOS and PFOA in groundwater do not extend downgradient from these two locations. The levels of PFOS and PFOA reported in the initial October 2012 groundwater sample from MW-321-15 have not been observed during follow-up sampling events and are attributed to matrix interference noted by the laboratory during the October 2012 analysis. Accordingly, further groundwater investigation for PFCs is not warranted.

The soil investigation identified PFC concentrations in soil located above the FTA liner. However, because of the presence of a liner, an ACL based on direct contact is the appropriate comparison. In the absence of ADEC-derived ACLs for direct contact, the soil results were compared to USEPA RSL calculator developed screening levels. The detected soil concentrations did not exceed these values.

One soil sample collected above the FTA liner exceeded the ADEC ingestion CUL for DRO and, while PCDD and PCDF concentrations were detected, their cumulative risk did not exceed the ADEC direct-contact CUL for the reference compound TCDD. Consistent with ADEC guidance, risk calculations were prepared to evaluate PCDD and PCDF risk at the site. The calculations, which are consistent with USEPA guidance (USEPA 2000), show that these compounds do not present an unacceptable risk through direct contact. Therefore these compounds are not identified as COCs for the site.

17.9 Updated Source Information

The results of the 2013 source area investigation updated information previously presented that documented the spill history. Additional sources were not identified. There are six primary sources of sulfolane to groundwater at the NPR (Figure 9-1). The largest sources have been identified as Lagoon B and the CU #2 EU. Other sources include the SWA, SGP, Sump 908, and CU #1 Wash Area. The site investigation data validates the spill records and history that led to the identification of the source areas.

17.10 Pilot Test and Remedial Investigations

NGP investigations including a bathymetric survey of the NGP and a remedial investigation consisting of water and sediment sampling from the NGP were completed. Initial results indicate that sulfolane is not present in the NGP and DO concentrations near saturation are nearly ubiquitous throughout the water column.

17.11 Ongoing Corrective Actions

FHRA continues to implement remedial actions to address sulfolane and petroleum impacts. These response actions include:

- Continuation of the AWS Program for residences and businesses with wells exhibiting detections of sulfolane.
- Continued optimization and operation of the groundwater recovery system onsite. Since 2010, FHRA has initiated several phases of optimization and expansion of the groundwater recovery system to improve capture and treatment of sulfolane-impacted groundwater. These efforts have resulted in establishment of a capture zone that fully captures sulfolane concentrations exceeding the ACL of 362 µg/L and nearly spans the lateral and vertical extent of the detected plume characterized along the recovery well transect.

- Continued operation of onsite LNAPL recovery systems. The cone of depression created by the groundwater extraction system increases the effectiveness of the LNAPL recovery systems.

17.12 Conceptual Site Model

The CSM summarizes how chemicals were historically released to the environment at the NPR, how the released chemicals move through the environment, how those chemicals affect people and other living things, and ongoing efforts to protect people from being exposed to those chemicals. The CSM is based on extensive environmental assessment activities that have been conducted at the NPR during the past 26 years, with the majority of activities occurring since 2009. The assessment included a thorough review of historical chemical use at the NPR, collection of water and soil samples from the surface and subsurface and numerically modeled predictions of the movement of contamination in the subsurface. The extensive LNAPL, soil, groundwater, and soil gas data collected to date and the CSM are sufficient to support a risk-based evaluation of appropriate remedial alternatives for the onsite area.

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