HUMBOLDT BAY HARBOR, RECREATION, AND CONSERVATION DISTRICT
NOTICE OF PUBLIC MEETING

NOTICE IS HEREBY GIVEN that the Humboldt Bay Harbor, Recreation and Conservation District will hold a public meeting on **October 4, 2018 from 3:00pm to 4:30pm** in the District Office Conference Room at the Woodley Island Marina, 601 Startare Drive, Eureka, CA 95501, to discuss the proposed Debris Pile Cleanup Project for Redwood Marine Terminal II, 1 TCF Drive, Samoa, CA. The Sampling and Analysis Plan and related documents for the Debris Cleanup Project may be reviewed at humboldtbay.org, or in the District Office. This project is being funded in part by a Brownfield Cleanup Grant awarded to the District from the US Environmental Protection Agency. Interested parties unable to attend the meeting are invited to submit in writing any comments relative to the proposed activity to the District office or bclueit@humboldtbay.org by October 4, 2018.

Sampling and Analysis Plan
Revision 2

Debris Cleanup Project
Redwood Marine Terminal II
1 TCF Drive
Samoa, California

Prepared for:

Humboldt Bay Harbor, Recreation & Conservation District

May 2018

016240.002

Reference: 016240.002

Sampling and Analysis Plan

Revision 2

Debris Cleanup Project

Redwood Marine Terminal II

1 TCF Drive

Samoa, California

Prepared for:

Humboldt Bay Harbor, Recreation & Conservation District

601 Startare Drive, Eureka, CA 95501

Prepared by:

812 W. Wabash Ave.
Eureka, CA 95501-2138
707-441-8855

May 2018

QA/QC:RMR

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Approval Page

Approved by: _____ 9·18·18
George Williamson, District Planner, HBHRCD — Date

Approved by: _____ 9/11/18
Mike Foget, Project Manager, SHN — Date

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for: Roland Rueber, Quality Assurance Officer, SHN — Date

Approved by: _____ _____
Eric Byous, Project Manager, EPA Region IX — Date

Approved by: _____ _____
Eugenia McNaughton, Quality Assurance Manager, EPA Region IX — Date

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George Williamson, District Planner, HBHRCD — Date

Approved by: _____ 9/11/18

Mike Foget, Project Manager, SHN — Date

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for: Roland Rueber, Quality Assurance Officer, SHN — Date

Approved by: _____ 9/12/18

Eric Byous, Project Manager, EPA Region IX — Date

Approved by: _____ 9/18/18

for Eugenia McNaughton, Quality Assurance Manager, EPA Region IX — Date

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List of Illustrations

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Acronyms and Abbreviations

---	not applicable/not found
˚C	degrees Celsius
mg/kg	milligrams per kilogram
ppm	parts per million
%R	percent recovery
A	measured concentration
AOI	area of interest
B	background concentration
BTEX	benzene, toluene, ethylbenzene, and total xylenes
CHHSL	California Human Health Screening Levels
COC	constituent of concern
DQO	data quality objectives
DTSC	Department of Toxic Substances Control
EPA	U.S. Environmental Protection Agency
FSP	field sampling plan
FTC	Freshwater Tissue Company
HBHRCD	Humboldt Bay Harbor, Conservation & Recreation District
IDW	investigation-derived waste
LCS	laboratory control sample
LP	Louisiana Pacific
LUFT	leaking underground fuel tank
MDL	method detection limit
MQO	measurement quality objective
MS/MSD	matrix spike and matrix spike duplicate
MTBE	methyl tertiary-butyl ether
MW-#	monitoring well-number
NA	not applicable
NCL	North Coast Laboratories, Ltd.
NR	no reference
PPE	personal protective equipment
QA	quality assurance
QA/QC	quality assurance/quality control
QAPP	quality assistance protection plan
QL	quantitation limit
R	recovery
RMTII	Redwood Marine Terminal II
RPD	relative percent difference
RSL	regional screening level
RWQCB	North Coast Regional Water Quality Control Board
S_1	sample
S_2	duplicate
SAP	sampling and analysis plan (an integrated FSP and QAPP)

Acronyms and Abbreviations, Continued

SiO_2	silicone dioxide
SOP	standard operating procedures
STLC	soluble threshold limit concentration
TCLP	toxicity characteristic leaching procedure
SVOC	semi-volatile organic compound
T	known true value of spike after spiking
TPHD	total petroleum hydrocarbons and diesel
TPHMO	total petroleum hydrocarbons and motor oil
VOA	volatile organic analysis (container)
VOC	volatile organic compound
XRF	x-ray fluorescence

1.0 Introduction

This sampling and analysis plan (SAP) has been prepared for Redwood Marine Terminal II (site) located in Samoa, Humboldt County, California. This SAP describes protocols and procedures that will be implemented for characterization of chemical impacts to debris from the demolition of infrastructure related to operations of the now defunct pulp mill (Figures 1 and 2). Demolition of site structures has resulted in generation of debris comprising various building materials, including reinforced and unreinforced concrete rubble, brick, tile, roofing materials, equipment parts (such as, pressure regulators, valves, etc.), and scrap metal. Laboratory analytical results reported for debris pile characterization sampling conducted in 2014 included detectable concentrations of leaking underground fuel tank (LUFT) metals cadmium, chromium, lead, nickel, and zinc, and petroleum hydrocarbons. Anticipated laboratory analyses for debris characterization include volatile organic compounds (VOCs) by Environmental Protection Agency (EPA) Method 8260B, petroleum hydrocarbons as motor oil (TPHMO) and as diesel (TPHD) by EPA Method 8015B, and trace elements (cadmium, chromium, nickel, lead, and zinc) by EPA 6010. Field screening of metals concentrations will be performed using a portable x-ray fluorescence (XRF) analyzer. Sampling and field characterization will be performed following segregation of debris pile materials by particle size. The date of sampling is undetermined, but is anticipated to occur in the second or third quarter of 2018.

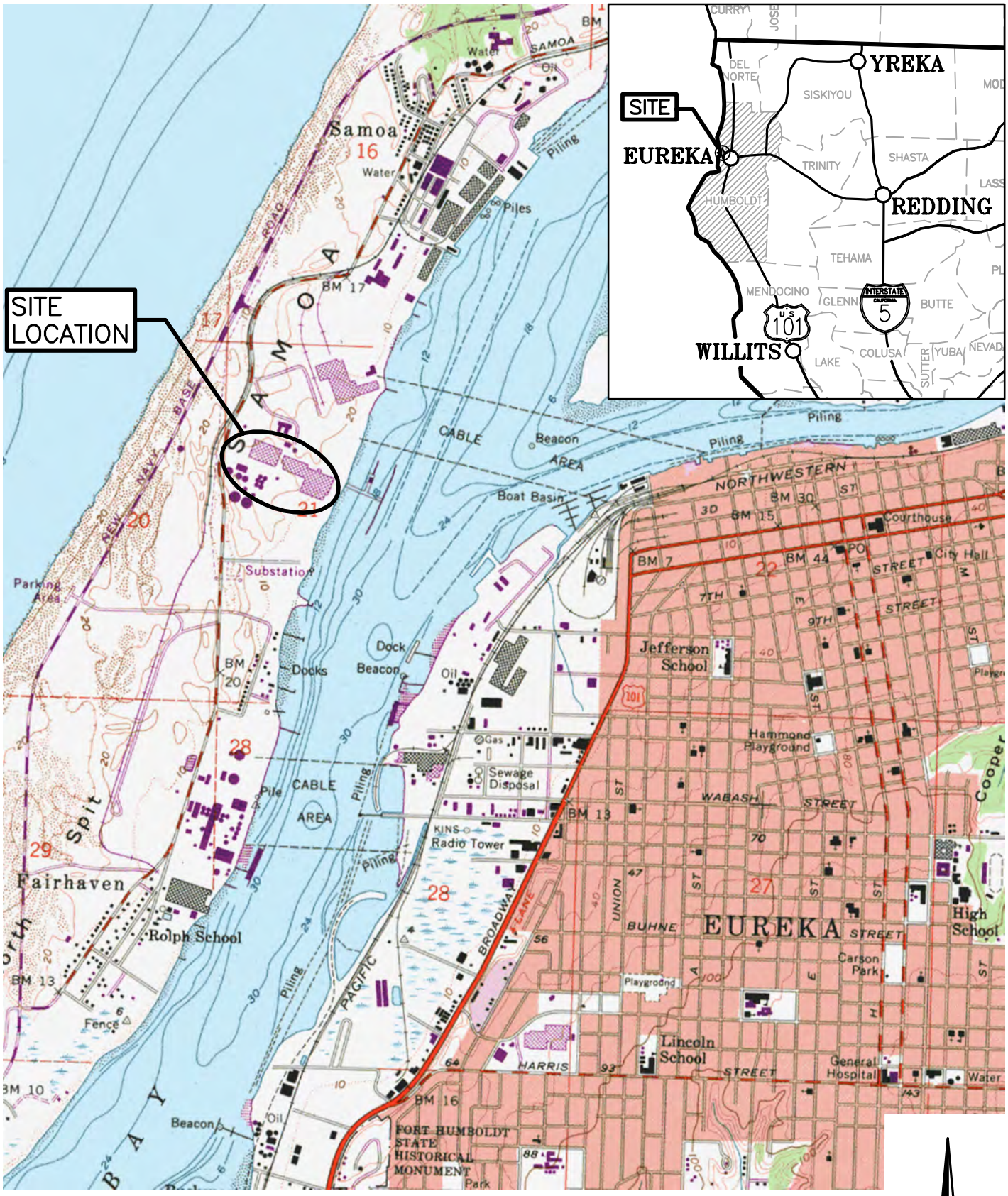
This SAP describes the sampling strategy and analytical program that will be used during site work. SHN staff will follow the SAP to ensure quality assurance/quality control (QA/QC) in the collection and reporting of data that are scientifically valid, representative of field conditions, and are legally defensible, if necessary. The work is being performed under site-specific Brownfields EPA Cleanup Program Grant #BF-99T55301-0 for cleanup of demolition debris impacted by elevated lead concentrations.

1.1 Site Name or Sampling Area

The site is locally referred to as the Samoa Pulp Mill, and has historically operated under several different corporate owners, the names of which were typically adopted during operation (such as, the Georgia Pacific Pulp Mill, Louisiana Pacific (LP) Pulp Mill, Evergreen Pulp, and Freshwater Tissue Company [FTC]). The current owner of the site, the Humboldt Bay Harbor, Recreation & Conservation District (HBHRCD), renamed the site Redwood Marine Terminal II (RMTII) following acquisition of the property in 2012. Historical and continuing characterization and remediation work at the site, performed under the guidance of the North Coast Regional Water Quality Control Board (RWQCB), has resulted in identification of Areas of Interest (AOI) 1 and 2, the location of the debris piles, and include the former process chemical recovery boilers number 1 and 2, and the former bleach plant, the sources of the debris pile materials.

1.2 Site Location

The site is located on the Samoa Peninsula, a narrow spit between the Pacific Ocean, approximately 800 yards to the west, and Humboldt Bay, adjoining the site to the east. Land use of the site and adjoining properties is industrial and commercial. No residences are in the immediate vicinity; however, the communities of Samoa and Fairhaven are located approximately 1.25 miles north and south of the site, respectively. The Samoa landfill (a closed Class III disposal site) is located to the west of the industrial facility, within the site property boundary. The approximately 86-acre site has an address of 1 TCF Drive, Samoa, California 95501, and is identified by Humboldt County Assessor's parcel number 401-112-021.



SOURCE: EUREKA USGS 7.5 MINUTE QUADRANGLE

LATITUDE: 40.8051198°
LONGITUDE: −124.194953°

N

1"=2000'±

SHN Consulting Engineers & Geologists, Inc.	Redwood Marine Terminal II Samoa, California	Site Location Map SHN 016240	
	December 2017	016240-LOCATION	Figure 1

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EXPLANATION

- MW–1 — MONITORING WELL LOCATION AND DESIGNATION (SHALLOW OR INTERMEDIATE WELLS)
- MW–5D — MONITORING WELL LOCATION AND DESIGNATION (DEEP WELLS)
- EX–1 — EXTRACTION WELL LOCATION AND DESIGNATION
- OBS–1 — OBSERVATION WELL LOCATION AND DESIGNATION
- AS–1 — SPARGE WELL LOCATION AND DESIGNATION
- DEBRIS PILE LOCATIONS

240' TO AOI–11 CHIP BLOWER/ FORMER UST

AOI–1 BLACK LIQUOR PROCESS AND RECOVERY AREA

AOI–2 BLEACH PLANT

AOI–3 RECAUSTICIZING AREA

AOI–4 HOT WATER HEATER/ FORMER DIESEL STORAGE TANK

AOI–5 PROCESS CHEMICAL STORAGE

AOI–6 LEACHFIELD

AOI–7 BONEYARD

AOI–8 VOC AREA SOUTHEAST

AOI–9 OFF–LOADING AREA

AOI–10 PETROLEUM HYDROCARBON STORAGE AREA

MANHOLE MH–5

MW–1, MW–2, MW–3, MW–4, MW–5, MW–5D, MW–6, MW–7, MW–8, MW–9, MW–9I, MW–10, MW–11, MW–11I, MW–11, MW–12, MW–13, MW–13I, MW–13D, MW–14, MW–15, MW–15D, MW–16, MW–16D, MW–17, MW–18, MW–19, MW–20, MW–20D, MW–21D, MW–22I, MW–23, MW–231, MW–24

ONE L P DRIVE

PAVED ACCESS ROAD

HUMBOLDT BAY

APPROXIMATE SHORELINE (HIGH TIDE)

APPROXIMATE SHORELINE (LOW TIDE)

PLAN DETAIL
1"=30'

0 200

1"=200'±

NOTE: ALL LOCATIONS ARE APPROXIMATE

SHN Consulting Engineers & Geologists, Inc.	Redwood Marine Terminal II Samoa, California	Site Plan SHN 016240
	December 2017 | 016240-SITE	Figure 2

1.3 Responsible Agency

SHN is a regional engineering and geology consulting firm with extensive local experience in environmental characterization and remediation activities. SHN has developed this SAP and will be providing project oversight, coordination, and sampling services. SHN has conducted multiple site environmental characterization efforts in conjunction with LP and the RWQCB, and has been involved in remediation at this site since 2009.

1.4 Project Organization

Table 1. Key Project Personnel Contact Information and Responsibilities

Title	Name	Phone Number Email Address	Responsibilities
EPA Project Manager	Eric Byous	(415) 972-3531 Byous.Eric@epa.gov	Project oversight
EPA Quality Assurance Officer (QAO)	Eugenia McNaughton, Ph.D.	(415) 972-3411 mcnaughton.eugenia@epa.gov	review and approve QA documents provide technical assistance
Grantee Project Manager	George Williamson, District Planner Humboldt Bay Harbor, Recreation and Conservation District	707-443-0801 districtplanner@humboldtbay.org	Planning and management of all aspects of project
Contractor Project Manager	Mike Foget, PE SHN	707-441-8855 mfoget@shn-engr.com	Oversight of project planning, implementation, budgeting, communication with client and funding entity
Contractor QAO	Roland Rueber, PG SHN	707-845-5909 rrueber@shn-engr.com	Oversight of planning and execution of approved work scope, assurance of attainment of approved data quality objectives
Contractor Field Team Leader	John Wellik, PG SHN	707-296-3660 jwellik@shn-engr.com	Oversight of field implementation of approved work scope, troubleshooting
Laboratory Quality Assurance Officer	Byran Furhmann North Coast Laboratories, INC.	707-822-4649 ext. 109 qa@northcoastlabs.com	All aspects of NCL quality assurance.

2.0 Background

Initial site development occurred in 1964 when a bleached Kraft pulp mill was constructed by Georgia Pacific. The pulp mill, in its original configuration, was in operation between 1965 and 1994, when it was converted to a chlorine-free process. Multiple owners including LP and Evergreen Pulp operated the mill from 1994 to 2008 (SHN, 2014). FTC purchased the site in 2009 and planned on reopening the mill; however, they abandoned these plans and began decommissioning equipment, demolishing various buildings, and liquidating assets. Historical buildings and land uses of the site included offices, pulp warehouses, a machine building, a sand blasting shop, petroleum products distribution and storage, a hazardous waste storage area, diesel aboveground storage tanks, a chemical storage tank farm, a water treatment plant, a "black liquor" processing area, a bleach plant, process chemical recovery boilers, and an electrical generation station. In August 2013, FTC transferred ownership of the site to HBHRCD. As of December 2017, cleanup of the hazardous waste storage area and demolition of a majority of the aboveground storage tanks, the bleach plant, and two recovery boilers, has been completed.

A draft *Analysis of Brownfields Cleanup Alternatives* was prepared in January 2014 describing debris pile characterization efforts conducted at that time, and presenting three alternatives for pile removal (LACO, 2014). Alternative #3 was identified as the recommended cleanup alternative, and includes characterizing and segregating debris pile materials based on hazard level and contamination type, with disposal of materials not cleared for reuse onsite at an appropriately classified landfill.

Demolition of recovery boilers #1 and #2 and bleach plant infrastructure has generated debris comprising various building materials, including reinforced and unreinforced concrete rubble, brick, tile, roofing materials, equipment parts (such as, pressure regulators, valves, etc.), and scrap metal. Demolition debris particle sizes range from boulders and cobble size materials, to gravel, sand and silt size materials. For the purposes of this SAP, debris pile materials the size of coarse gravel and smaller are defined as "sediment." The debris piles, located in a limited area in the central portion of the former industrial core of the mill site, referred to as AOI-1 and AOI-2 for RWQCB directed environmental assessment and remediation efforts, were previously characterized using a composite-based sampling strategy based on pre-disposal testing requirements for a proxy waste facility in Vacaville, California, which was selected to establish a defensible sampling methodology (LACO, 2014). Sample laboratory analytical results reported for the 2014 characterization effort included detectable concentrations of LUFT metals cadmium, chromium, lead, nickel, and zinc, and hydrocarbons.

As zoning for the site is Industrial-Coastal Dependent, future use of the site is not anticipated to be residential; therefore, California Human Health Screening Levels (CHHSLs) and EPA regional screening levels (RSLs) for commercial/industrial scenarios are used to evaluate potential constituents of concern (COCs).

Because of the range of particle sizes observed within the debris piles, samples collected during the 2014 characterization efforts were focused on coarse sand size and smaller materials, with larger particles (such as, large concrete or tile fragments) generally disregarded; therefore, the 2014 laboratory analytical results are interpreted to be representative of COC concentrations of coarse gravel and smaller particle sizes (hereafter referred to as sediment). Sediment samples comprised 4:1 composite ratios for each 250 cubic

yards of material; pile 1 of AOI-1 was a 20-point sample reduced to 5 composite samples, pile 2 of AOI-1 was analyzed as a singular 4-point composite sample, and pile 1 of AOI-2 was a 16-point sample reduced to 4 composite samples. Table 2 presents CHHSLs, RSLs, and reported peak concentrations for the noted COCs.

Table 2. Industrial/Commercial Screening Levels and 2014 Sediment Laboratory Results
Redwood Marine Terminal II, Samoa, California

COC[1]	Cadmium	Chromium	Lead	Nickel	Zinc	TPHMO[2]
CHHSL[3] (mg/kg)[4]	7.5	---[5]	320	16,000	100,000	---
RSL[6] (mg/kg)	---	180,000	800	1,100	35,000	3,300
Source Id						
AOI-1 Pile 1	6.9	740	90	490	1,000	2,200
AOI-1 Pile 2	0.75	100	29	72	2,100	300
AOI-2	2.7	110	**33,000**	85	840	500

1. COC: constituent of concern
2. TPHMO: total petroleum hydrocarbons as motor oil
3. CHHSLs: California Human Health Screening Levels
4. mg/kg: milligrams per kilogram
5. ---: not found
6. RSL: EPA regional screening level

Due to a lack of analytical data for the larger particle size materials, multiple larger pieces of concrete, brick and tile debris material, interpreted to be representative of the debris piles as a whole, were randomly selected, along with discreet sediment samples, in November 2017 for screening with a handheld Niton XLp 300 Series x-ray fluorescence analyzer (XRF). All XRF analyses were performed using the device's "standard bulk mode." XRF-derived metals concentration results for sediment samples were compared to the 2014 laboratory results for consistency and calibration of the XRF to laboratory results (Table 3). Because lead was the only metal constituent exceeding industrial/commercial CHHSL and RSL screening levels for reported laboratory data, the focus in Table 3 is on lead.

Table 3. Lead Concentration in Debris Sediment, XRF[1], Historical Laboratory Results, and Industrial/Commercial Screening Levels
Redwood Marine Terminal II, Samoa, California

Source Identification		Peak XRF Concentration (ppm)[2]	Peak Laboratory Result[3] (ppm)	CHHSLs[4]/RSLs[5] (ppm)
AOI-1 Pile 1	Sand (n[6]=5)	91	90	320/800
	Block (n=10)	56		
AOI-1 Pile 2	Sand (n=2)	33	29	
AOI-2 Pile 1	Sand (n=4)	**2,501**	**33,000**	320/800
	Block (n=10)	38[6]		

Table 3. Lead Concentration in Debris Sediment, XRF[1], Historical Laboratory Results, and Industrial/Commercial Screening Levels
Redwood Marine Terminal II, Samoa, California

Source Identification	Peak XRF Concentration (ppm)[2]	Peak Laboratory Result[3] (ppm)	CHHSLs[4]/RSLs[5] (ppm)

1. XRF: x-ray fluorescence
2. ppm: parts per million; equivalent to mg/kg
3. Materials submitted for laboratory analysis were limited to sand size particles or smaller
4. CHHSLs: California Human Health Screening Levels
5. RSLs: EPA regional screening level
6. n: number of samples analyzed
7. Elevated results were reported for sediment coated blocks scanned with a Niton XLp 300 XRF

As is recognizable in Table 3, XRF-derived concentrations are generally comparable to laboratory-derived results, save for the peak concentration reported for AOI-2 sand. The peak XRF lead concentration was recorded near 2,500 ppm, since the 2,500 ppm value exceeds the corresponding CHHSL by nearly one order of magnitude, field screening using a hand held XRF device will identify materials where metals concentrations exceed both CHHSLs and RSLs.

2.1 Site or Sampling Area Description

The sampling area occupies approximately 12,000 square feet in AOI-1 and AOI-2, a central location of an approximately 86 acre industrial site. The site is bordered on the north by industrial property owned by FTC, on the west by New Navy Base Road and the Pacific Ocean beyond that, on the south by a coastally dependent-zoned and currently vacant parcel, and on the east by Humboldt Bay (Figure 1). The specific location of the sampling area, in AOI-1 and AOI-2, is shown in Figure 2.

Historical buildings and land uses of the site included offices, pulp warehouses, a machine building, a sand blasting shop, petroleum products distribution and storage, a hazardous waste storage area, diesel aboveground storage tanks, a chemical storage tank farm, a water treatment plant, a “black liquor” processing area, a bleach plant, three process chemical recovery boilers, and an electrical generation station. To date, the petroleum products distribution and storage infrastructure, diesel aboveground storage tanks, the chemical storage tank farm, the black liquor processing area, the bleach plant, and two of three process chemical recovery boilers have been demolished.

2.2 Operational History

The sampling area spans portions of AOI-1 and AOI-2, locations of process chemical recovery and storage, and the former bleach plant, respectively. Process chemical recovery comprised removal of organic matter accumulated in the pulp bleaching process through combustion in recovery boilers 1, 2, and 3; the recovered chemicals were then available for reuse in the bleaching process. The bleaching process was performed to

remove tannins and lignins from wood chips prior to being introduced to the pulping process. GoogleEarth photographic evidence indicates that the structures from which the debris resulted were demolished between 2011 and 2012.

Chemical impacts to debris, including low concentrations of petroleum hydrocarbons and metals, likely result from operation and maintenance of machinery used in the bleaching and recovery process, from tooling and fittings used in the structures, and from paint. No work beyond basic grounds maintenance is currently being performed in AOI-1 or AOI-2.

2.3 Previous Investigations/Regulatory Involvement

A draft *Analysis of Brownfields Cleanup Alternatives* was prepared in January 2014 describing debris pile characterization efforts completed on December 23, 2013, and presenting three alternatives for pile removal (LACO, 2014). LACO personnel developed a debris pile sediment sampling methodology to conform to pre-disposal sampling requirements for a proxy-landfill. Fine-grained (coarse sand and smaller) debris pile sediments were collected and submitted to a state-licensed laboratory for analysis of asbestos by polarized light microscopy using EPA Method 600/R-93-116–Standard Building Materials; TPHD and TPHMO with silica gel cleanup by EPA 8105M; benzene, toluene, ethylbenzene, and total xylenes/methyl tertiary-butyl ether (BTEX/MTBE) by EPA 8260; pH by EPA 150.2; LUFT 5 metals by EPA 6010B; sulfide by EPA 300.0; and sulfate by SM 4500-S2 D in December 2013 (Table 4).

Table 4. Contaminants of Concern, Previous Investigations
Redwood Marine Terminal II, Samoa, California

Analytical Parameter (Contaminants of Concern)	Date of sampling	Sampling Contractor	Laboratory Analytical Results (mg/kg)	CHHSLs[1] (mg/kg)
Cadmium	12/23/2013	LACO Associates	0.75-6.9	7.5
Chromium			100-740	---[2]
Lead			29-**33,000**	320
Nickel			72-490	16,000
Zinc			840-2,100	100,000
TPHMO[3]			300-2,200	3,300[4]

1. CHHSLs: California Human Health Screening Levels
2. ---: not reported
3. TPHMO: total petroleum hydrocarbons as motor oil
3. RSL: regional screening levels (EPA)

The site has an extensive environmental assessment and remediation history that is impertinent to execution of the Brownfields Cleanup Grant scope of work, as grant funded work is focused on characterization and disposal of hazardous materials contained within the debris piles. Historical site characterization and remediation records are presented on the State of California Geotracker website (https://geotracker.waterboards.ca.gov/profile_report.asp?global_id=SL0602377769), and are on file with the RWQCB.

2.4 Scoping Meeting

An initial scoping meeting to develop the draft *Analysis of Brownfields Cleanup Alternatives* was conducted by the HBHRCD on November 25, 2013. The meeting covered the level of involvement by Humboldt County in the application and cleanup process, the scope of the grant, required documents to apply for the grant, time lines for submittal of an application and HBHRCD Board and Commission meeting dates during which the topic would be explored. The degree of community involvement was also a topic of discussion.

2.5 Geological/Meteorological Information

Not Applicable.

2.6 Impact on Human Health and/or the Environmental

Lead can affect multiple organs and systems. Children under the age of seven are most susceptible to the effects of lead. Even low levels of lead in the blood of children can result in behavior and learning problems, lower IQ and hyperactivity, slowed growth, hearing problems, and anemia. In rare cases, ingestion of lead can cause seizures, coma, and even death. Lead can accumulate in our bodies over time, where it is stored in bones along with calcium. During pregnancy, lead is released from bones as maternal calcium and is used to help form the bones of the fetus. This is particularly true if a woman does not have enough dietary calcium. Lead can also cross the placental barrier exposing the fetus the lead. This can result in serious effects to the mother and her developing fetus, including reduced growth of the fetus, and premature birth.

Lead is also harmful to adults. Adults exposed to lead can suffer from cardiovascular effects, increased blood pressure and incidence of hypertension, decreased kidney function, and reproductive problems.
Lead is a naturally occurring element found in small amounts in the earth's crust. Much of our exposure comes from human activities including the use of fossil fuels including past use of leaded gasoline, some types of industrial facilities, and past use of lead-based paint in homes.

The preceding discussion of potential health effects from exposure to lead was augmented with information viewed on: https://www.epa.gov/lead/learn-about-lead#effects.

3.0 Project and Data Quality Objectives

3.1 Project Task and Problem Definition

3.1.1 Debris Piles

The project involves segregation, characterization, and offsite disposal, or onsite reuse of debris pile materials, based on risk to human health and the environment posed by the materials based on laboratory analytical results. Historical laboratory concentration data indicates lead is the primary debris pile COC. Debris pile materials characterized as posing no risk to human health and the environment, based on state and federal industrial/commercial screening levels, will be retained for future use onsite. Debris pile materials characterized as impacted by lead concentrations exceeding industrial/commercial screening levels will be transported to an appropriate landfill facility.

3.1.2 Segregation of Debris

As described Section 2.0 above, AOI-1 and AOI-2 debris piles contain a variety of demolition-related materials and particle sizes. The relative degree of lead impact to materials is interpreted to be strongly correlated to particle size, with coarse gravel size and smaller particles tending to have higher lead concentrations than cobble and larger size materials. Due to this relation, classification of materials based upon particle size is proposed as the initial step in evaluation of material for reuse or disposal.

3.2 Site Activities

Procedures for XRF field screening classification, segregation and sediment sample collection to be followed in the field are described in this section. Sediment samples will be analyzed for COCs according to methods outlined in Section 4.0.

3.2.1 Debris Pile Classification and Segregation

Initial efforts include classification of materials in debris piles based on particle size. This initial step will substantially reduce the volume of material slated for disposal at landfills, and is anticipated to result in approximately 50 percent or greater reduction of volume of material to be disposed. We propose to classify materials by particle size using a track-mounted excavator equipped with a screening bucket (or equivalent); many screening buckets are capable of being fitted with a variety of screen mesh sizes, allowing for classification of materials to the desired particle size. Due to substantial differences in recorded COC concentrations between AOI-1 piles and the pile in AOI-2, fine materials from individual AOI stockpiles will be kept separate. Coarse materials from each AOI characterized with COC concentrations below action levels as determined using XRF field screening will be comingled into one stockpile.

Following classification by particle size, metal debris (such as, rebar, fittings, tubing, wiring, etc.), woody debris, and fiberglass (such as, roofing/siding, piping) will be removed by hand and stockpiled independently of concrete-type materials for subsequent disposal with similar materials currently stockpiled onsite.

Coarse gravel size and smaller materials will be stockpiled separately from cobble size and larger material; and the coarse gravel size and smaller stockpiled materials will be formed into a 3-foot thick pad at completion of segregation activities.

3.2.2 Chemical Characterization of Segregated Materials

Characterization of segregated materials for chemical impacts will be performed using different methods, based on particle size.

3.2.2.1 Coarse Material Characterization

Metals impacts to coarse materials will be characterized in the field using a hand-held Niton XLp 702A XRF. Coarse materials for XRF characterization will be randomly selected for analysis at a rate equivalent to 10 percent of the volume of each coarse-material stockpile. Records of concentrations of cadmium, chromium, lead, nickel, and zinc will be maintained, and XRF-screened blocky materials will be marked with paint for tracking purposes. Coarse material not passing chemical screening, as determined by XRF results exceeding the more conservative value of either State of California or EPA industrial/commercial screening levels, will be further evaluated for the presence of adhered sediment that may have resulted in higher concentration

detection than would have been recorded had the sediment size material have not been present on the coarse material. Adhered sediment may be removed and added to the fine material size particle debris pile; the coarse material may be subsequently re-evaluated using the XRF. Coarse material recorded with concentrations below screening levels will be stockpiled onsite for future use as needed.

3.2.2.2 Fine Material Characterization

Two stockpiles of coarse gravel and smaller particles, one pile each for AOI-1 and AOI-2, will be formed into rectangular prisms and stockpile volumes will be estimated. Sediment samples will comprise 4:1 composite ratios for each 250 cubic yards of stockpile material. Stockpiles will be divided into roughly equal area sample units based upon the number of samples determined from the volume estimate and composite ratio. Once stockpile volumes have been estimated and the number of samples has been determined, sediment samples will be collected from sample units using a stainless steel trowel. Sediment samples will be placed into clean, laboratory-supplied four ounce soil jars. Jars will be labeled with sample unit identification, date and time of collection, and sampler initials. Sample containers will be placed on ice in a cooler pending transportation to a state-certified laboratory under standard chain-of-custody protocols. The laboratory will composite and homogenize samples prior to analysis. Sediment sample collection, storage, labeling, and chain-of-custody documentation will be performed according to procedures specified in "Protocol A-1. Sediment Sampling for Chemical Analysis" (Appendix 1).

3.3 Data Quality Objectives (DQOs)

Quality assurance objectives for the soil and groundwater quality assessment at the site are intended to provide guidance for collecting and evaluating data that represent site conditions. Table 5 presents project goals for the above parameters.

The parameters used to evaluate data quality and their definitions are:

- Representativeness: The degree to which data is characteristic of environmental conditions through:
    - Precision: A measurement of the degree of agreement of replicate data, which is quantitatively assessed, based on the relative percent difference (RPD) or standard deviation.
    - Accuracy: The agreement of a measurement with an accepted reference or true value.
- Completeness: The amount of valid data obtained from a prescribed measurement system throughout the project as compared with that expected and required to meet the project goals.
- Comparability of data throughout the project will be attained by recording field and laboratory data in consistent units, as well as following the above protocols for collecting and analyzing samples.

Data collected will be used to determine if material is suitable for reuse or must be shipped to an appropriately classified landfill. HBHRCD plans to lease portions of the site for a variety of coastal dependent uses.

Table 5. Quality Assurance Goals For Field and Laboratory Analyses
Redwood Marine Terminal II, Samoa, California

Field Measurements	Precision Goal	Accuracy Goal (percent recovery of MS/MSDs, LCSs)[1,2]	Completeness (percent)
Metals Concentrations	20%	20%	90
Laboratory Measurements	**Soil**	**Soil**	**Completeness (percent)**
EPA Method 8260B	± 20-23	varies	90
EPA Method 8015B	± 37	varies	90
EPA Method 6010B	± 20	varies	90

1. Relative percent differences (RPD) are for matrix spikes and matrix-spike duplicates (MS/MSD) samples (soil, soil vapor, and water) or field duplicates (water only). Requirements for lab duplicates are presented in the quality assistance protective plan (QAPP) for each laboratory (Appendix 2). RPD goals are applicable only for samples with detected concentrations greater than five times the reporting limit.
2. Percent recovery behavior varies for each compound. Accuracy goals are laboratory specific internal goals that are updated periodically. The laboratories' goals are presented in Appendix 2 of this report; see EPA Publication SW-846 (a986: November 1990 update) for general goals for these methods.

The sediment samples will be submitted to the laboratory for analysis described in Section 5.0. The required laboratory sample containers, sample preservation, and sample hold times for each analytical method are also described in Section 5.0.

Sampling equipment will be decontaminated before and after collection of each sample according to the procedures specified in "Protocol 1-1: Sediment Sampling for Chemical Analysis."

3.4 Measurement Quality Objectives

Measurement quality objectives (MQOs) shall be maintained through data review and validation; data assessment, including precision, accuracy, and completeness; field and laboratory data management; and assessment oversight.

3.5 Data Review and Validation

The quality assurance manager will perform a Tier 1A level data validation. Such a review may include, but is not limited to, review of the data package for completeness; review of chain-of-custody forms (against laboratory reported information), for signatures, sample condition upon receipt by the laboratory, and sample preservation; review of holding times; review of QC summaries; review of blank results for possible field or laboratory contamination; random checks of reported results against raw data, and random checks of raw data for interference problems or system control problems (baseline anomalies, baseline drifts, etc.)

If comparison of data to previous measurements or known conditions at the site indicates anomalies, the laboratory will be instructed to review the submitted data while SHN reviews the methods used to collect and handle the samples. If anomalies remain, the laboratory might be asked to re-analyze selected samples. The quality assurance manuals for the analytical laboratories present the laboratory's procedures for reviewing data (Appendix 2). The methods for assessing and handling field and laboratory data are discussed below.

3.6 Data Assessment

As discussed in Section 3.4, the validity of data will be measured in terms of precision, accuracy, and completeness. The ways in which these three parameters will be evaluated for project data are described below.

3.6.1 Precision

For data generated by the laboratory, data precision will be estimated by comparing analytical results from duplicate samples and from matrix spikes and matrix spike duplicates. The comparison will be made by calculating the relative percent difference (RPD) given by:

$$RPD = \frac{2(S_1 - S_2)}{S_1+S_2} \times 100$$

Where: RPD: Relative Percent Difference
S_1: Sample
S_2: Duplicate

3.6.2 Accuracy

Data accuracy will be assessed for laboratory data only and is based on recoveries (R), expressed as the percentage of the true (known) concentration, from laboratory-spiked samples and QA/QC samples generated by the analytical laboratory. The equation for calculating recoveries is:

$$R = \frac{(A-B)}{T} \times 100$$

Where: R: Recoveries
A: Measured Concentration After Spiking
B: Background Concentration
T: Known True Value of Spike

This information will be reviewed periodically by the Project Manager or Project Quality Assurance (QA) Officer. The goals for the recovery of selected target analytes in a spiked or QA/QC sample are presented in Appendix 2. The objectives for accuracy for the primary compounds of potential concern are presented in Table 5. These objectives have been set at 40 percent of known or spiked values unless indicated otherwise in Appendix 2. Demonstration of consistent recoveries at ±20 percent allows the discrimination of a sample concentration at the method-reporting limit from the EPA's industrial preliminary remedial goals. These goals might need to be modified depending upon potential matrix interferences associated with Site

samples. Alteration or failure to meet these preliminary goals should not be construed to indicate that data collected should be invalidated because all of the data should be suitable for Site characterization and risk assessment as long as the uncertainty associated with the data is adequately characterized (EPA, 1992).

3.6.3 Completeness

Data generated during the debris characterization effort will be evaluated for completeness, that is, the amount of data meeting project QA/QC goals. If data generated during field operations or by means of analytical procedures appears to deviate significantly from observed trends, the Project Manager or Project QA Officer will review field or laboratory procedures with the appropriate personnel to evaluate the cause of such deviations. If data anomalies cannot be explained, resampling could be necessary. Goals for data completeness are presented in Table 3.

3.7 Data Management

XRF-derived concentrations of select metals will be read and recorded directly in the units of final use, as listed in Table 6.

Table 6. Measured Parameters
Redwood Marine Terminal II, Samoa, California

Parameter	Units
concentration, sediment	parts per million

Field task leaders are responsible for monitoring collection and reporting of field data. Field task leaders will also review field measurements at the time of measurement and will re-measure a parameter, as necessary. Monitoring of field data will be a continuous process for the field task leader; therefore, an audit in the field is not anticipated. Calibration of all field equipment will be conducted and documented on a daily basis.

Field data will be recorded on field data sheets (located in Appendix 1 Protocols) as they are collected and will be maintained in SHN's office project file. Upon delivery to SHN's office, appropriate field data will be entered into a computer database to expedite the validation and interpretation process. The Project Manager, Project QA Officer, or Task Leader will review field procedures and compare field data to previous measurements.

3.8 Management of Laboratory Data

Results of laboratory analyses will be reported as specified in the laboratory's QA manual. Analytical results will be reported in units of final use and will be downloaded and managed by the laboratory with a computerized acquisition system. Laboratory calculations will be performed as prescribed for each analytical method or in conformance with acceptable laboratory standards at the time the calculation is performed. Each laboratory will retain QA/QC records for at least six years. Copies of raw data will be available for review at the laboratory and can be requested as part of SHN's QA/QC review. Original laboratory reports will be stored in SHN's project files. SHN will enter laboratory data into a computerized database to expedite data reduction, interpretation, and reporting.

3.9 Assessment Oversight

The QA Manager shall review laboratory analytical results upon receipt of the reports, and prior to decision making regarding future disposition of the debris pile materials. Analytical data achieving QA/QC goals will be used in the decision making process, data falling outside of QA/QC goals will be re-evaluated for use in the decision making process, and resampling of the matrix may be performed to achieve QA/QC targets. Table 7 presents laboratory reporting or quantitation limits compared to CHHSLs and RSLs.

Table 7. Contaminants of Concern, Laboratory and Action Levels–Sediment

Analytical Parameter (Contaminants of Concern)	Laboratory Reporting or Quantitation Limits (mg/kg)[1]	Action Levels	
		DTSC[2] Industrial CHHSLs[3] (mg/kg)	EPA Industrial RSLs[4] (mg/kg)
Metals by Method 6010			
Cadmium	1.0	7.5	none
Chromium	2.0	none	180,000
Lead	1.0	320	800
Nickel	1.0	16,000	1,100
Zinc	1.0	100,000	35,000
Total Petroleum Hydrocarbons by Method 8015			
TPHMO[5]	10	none	3,300

1. mg/kg: milligrams per kilogram
2. Department of Toxic Substances Control
3. CHHSLs: California Human Health Screening Levels
4. RSLs: regional screening limits
5. TPHMO: total petroleum hydrocarbons as motor oil

4.0 Sampling Design and Rationale

This section presents field characterization efforts, the media to be sampled, the approach to sample collection, and analytical parameters to be evaluated.

4.1 Soil Sampling

Not Applicable.

4.2 Sediment Sampling

Characterization of segregated materials for chemical impacts will be performed using different methods based on material particle size.

4.2.1 Coarse Material Characterization

Chemical impacts to coarse materials will be characterized in the field using a hand-held Niton XLp 702A series XRF. Coarse materials for XRF characterization will be randomly selected for analysis at a rate equivalent to 10 percent of the volume of each coarse-material stockpile. Records of concentrations of

cadmium, chromium, lead, nickel, and zinc will be maintained, and XRF-screened blocky materials will be marked with paint for tracking purposes. Coarse material not passing chemical screening, as determined by XRF results exceeding the more conservative value of either State of California or EPA industrial/commercial screening levels, will be further evaluated for the presence of adhered sediment, which may have resulted in higher concentration detection than would have been recorded had the sediment size material not been present on the coarse material. Adhered sediment may be removed and added to the fine material stockpile; the coarse material may be subsequently re-evaluated using the XRF. Coarse material recorded with concentrations below screening levels will be stockpiled onsite for future use as needed.

4.2.2 Sediment Characterization

Two stockpiles of coarse gravel and smaller particles, one pile each for each AOI-1 and AOI-2, will be formed into rectangular prisms and stockpile volumes will be estimated. Sediment samples will comprise 4:1 composite ratios for each 250 cubic yards of stockpile material. Stockpiles will be divided into roughly equal area sample units based upon the number of samples determined from the volume estimate and composite ratio. Once stockpile volumes have been estimated and the number of samples has been determined, sediment samples will be collected from sample units using a trowel. Sediment samples will be placed into clean, laboratory-supplied four ounce soil jars and 40 milliliter (ml) volatile organic analysis (VOA) vials. Jars will be labeled with sample unit identification, date and time of collection, and sampler initials. Sample containers will be placed on ice in a cooler pending transportation to a state-certified laboratory under standard chain-of-custody protocols. The laboratory will composite and homogenize samples prior to analysis. Sediment sample collection, storage, labeling, and chain-of-custody documentation will be performed according to procedures specified in "Protocol A-1. Sediment Sampling for Chemical Analysis" (Appendix 1).

Table 8. Sampling Design and Rationale–Sediment

Sampling Location/ID Number	Depth (feet)	Analytical Parameter [1]	Rationale
AOI-1-1	0-3	LUFT[2] Metals, TPHMO[3], VOCs[4]	Composite samples to be analyzed for previously identified COCs[5]
AOI-1-2	0-3	LUFT Metals, TPHMO, VOCs	Composite samples to be analyzed for previously identified COCs
AOI-2	0-3	LUFT Metals, TPHMO, VOCs	Composite samples to be analyzed for previously identified COCs

1. Testing frequency per 250 cubic yards of material
2. LUFT: leaking underground fuel tank
3. TPHMO: total petroleum hydrocarbons as motor oil
4. VOCs: volatile organic compounds
5. COC: constituent of concern

4.3 Water Sampling

Not Applicable.

4.4 Other Sampling

Not Applicable.

5.0 Request for Analyses

5.1 Analyses Narrative

Sediment samples will be submitted to the laboratory for chemical analyses identified in Table 9. Sediment samples will be submitted to North Coast Laboratories (NCL) of Arcata, California, an accredited laboratory. Sample analysis will be performed on a standard turnaround time of two to three weeks because the work area will be stable and secure, and there will be no open excavation to present a threat to human health or the environment. NCL will analyze samples analyzed by EPA 8015B, EPA 8260B, and EPA 6010B.

Table 9. Sample Handling and Preservation Requirements
Redwood Marine Terminal II, Samoa, California

Parameter	Method	Containers	Preservation	Maximum Holding Time
TPHD[1] and TPHMO[2]	EPA 8015B	4-ounce jar	Cool to 0-6˚C[3]	14 days
Metals: Cadmium, Chromium, Nickel, Lead, and Zinc	EPA 6010B	4-ounce jar	Cool to 0-6˚C	6 months
Volatile Organic Compounds	EPA 8260B	EPA 5035 compliant sampler	Cool to 0-6˚C and methanol	14 days

1. TPHD: total petroleum hydrocarbons as diesel
2. TPHMO: total petroleum hydrocarbons as motor oil
3. ˚C: Celsius

5.2 Analytical Laboratory

The analytical laboratory that will perform project analytical services is NCL Arcata, California, an accredited laboratory. Table 10 presents proposed laboratory analyses for sediment samples.

Table 10. Analytical Services–Sediment

Sample Number	Sample Location	Depth (feet)	Special Designation	Analytical Methods[1]		
				EPA 8015B (TPHMO)[1]	EPA 6010B (metals)	EPA 8260B (volatiles)
AOI-1-1	AOI-1	0-3		X	X	X
AOI-1-2	AOI-1	0-3	Duplicate of AOI-1-1	X	X	X
AOI-2-1	AOI-2	0-3		X	X	X
AOI-2-2	AOI-2	0-3	Duplicate of AOI-2-1	X	X	X
Total number of sediment samples, excluding QC:				2	2	2
Total number of sediment samples, including QC:				4	4	4

1. Testing frequency per 250 cubic yards of material
2. TPHMO: total petroleum hydrocarbons as motor oil

Table 11 presents analytical methods, containers, preservation, and holding time requirements for sediment samples.

Table 11. Analytical Method, Containers, Preservation, and Holding Times Requirements–Sediment

Analytical Parameter and/or Field Measurements	Analytical Method Number	Containers (number, type, size/volume)	Preservation Requirements	Maximum Holding Times
Volatiles	Method 8260B	3 x 40-ml[1] VOA[2]	Methanol/distilled water	14 days
Metals	Method 6010B	4-ounce jar	none	80 days
TPHMO and TPHD[3]	Method 8015B	4-ounce jar	none	14 days

1. ml: milliliter
2. VOA: volatile organic analysis (container)
3. TPHMO: total petroleum hydrocarbons as motor oil; TPHD: total petroleum hydrocarbons as diesel

6.0 Field Methods and Procedures

Segregated debris pile contents will be characterized for chemical impacts by field screening and sample collection for laboratory analysis. Field screening of coarse materials will be performed with a hand held XRF, and finer-grained sediment samples will be collected as described in Section 4.2.2. Field personnel will wear appropriate personal protective equipment (PPE) when contacting debris materials; PPE for sampling activities will comprise durable outerwear (such as, long pants and a long-sleeved shirt, chemical resistant

steel-toed boots, disposable nitrile gloves, and a high visibility vest). Sediment samples will be collected and analyzed in conformance with methods and analyses presented in Section 4.0 of this SAP. Sample tracking and shipping will be performed in conformance with information presented in Section 7.0 of this SAP.

6.1 Field Equipment

6.1.1 List of Equipment Needed

Field screening will be performed using a Niton XLp 702A XRF analyzer. Sediment sampling will be performed using a stainless steel trowel. Sample containers will comprise clean laboratory-supplied four-ounce jars. Decontamination will be performed on the XRF unit in between sample analysis by wiping clean XRF unit surfaces that have come into direct contact with sample materials using a clean paper towel made damp with distilled water to remove adhered sediment, decontamination of the stainless steel trowel will be performed using Liquinox and distilled water. Containers for disposal of investigation derived waste (IDW) and decontamination materials will comprise 55-gallon Department of Transportation drums and plastic garbage bags as appropriate.

6.1.2 Calibration of Field Equipment

The Niton XLp 702A XRF is a self calibrating device that performs a calibration at the time the device is powered up. Evaluation of calibration is performed using standards provided by the manufacturer. Following start up and calibration of the XRF device, the supplied standards will be analyzed, and the results will be logged on the daily field sheet. If results of the standard analysis are 20 percent different from the noted standard value, the device will be rebooted and the calibration and assessment will be performed again. If results from the reboot also exceed a 20 percent difference, then manufacturer guidelines for adjusting calibration factors will be performed.

The stainless steel trowel is mechanical and does not require calibration.

6.2 Field Screening

Metals impacts to coarse materials will be characterized in the field using a hand-held Niton XLp 702A XRF. Coarse materials for XRF characterization will be randomly selected for analysis at a rate equivalent to 10 percent of the volume of each coarse-material stockpile. Exterior surfaces of coarse materials selected for field screening will be analyzed using the device's "standard bulk" mode, which includes analysis for 15 elements. Results of the analyses include identification of elements, element concentration, and a 2 sigma (95 percent) confidence interval. Relatively flat surfaces of coarse materials will be targeted for XRF field screening to minimize concentration error.

In order to confirm XRF field screening results, sediment samples will be analyzed using the hand held XRF, and results for select COCs will be recorded. XRF-analyzed sediment samples will be submitted to the laboratory for analysis by EPA 6010B, to which field screening results can be directly compared. This confirmation data will be used to screen coarse materials for reuse onsite, cleaning and reuse onsite, or disposal at an appropriate facility.

6.3 Soil Sampling

No soil samples will be collected.

6.3.1 Surface Soil Sampling

Not Applicable.

6.3.2 Subsurface Soil Sampling

Not Applicable.

6.4 Sediment Sampling

Two stockpiles of coarse gravel and smaller particles, one pile each for AOI-1 and AOI-2, will be formed into rectangular prisms and stockpile volumes will be estimated. Sediment samples will comprise 4:1 composite ratios for each 250 cubic yards of stockpile material. Stockpiles will be divided into roughly equal area sample units based upon the number of samples determined from the volume estimate and composite ratio. Once stockpile volumes have been estimated and the number of samples has been determined, sediment samples will be collected from sample units using a stainless steel trowel. Sediment samples will be placed into clean, laboratory-supplied four ounce soil jars. Jars will be labeled with sample unit identification, date and time of collection, and sampler initials. Sample containers will be placed on ice in a cooler pending transportation to a state-certified laboratory under standard chain-of-custody protocols. The laboratory will composite and homogenize samples prior to analysis. Sediment sample collection, storage, labeling, and chain-of-custody documentation will be performed according to procedures specified in "Protocol A-1. Sediment Sampling for Chemical Analysis" (Appendix 1).

Care will be taken to obtain as representative a sample as possible. Homogenization of the sample will be performed in by the analytical laboratory. Samples for analysis by EPA Method 8260B will be collected by laboratory personnel from the homogenized sample. Because gasoline-range materials have been recorded below standard detection limits for the *Draft Analysis of Brownfields Cleanup Alternatives* sampling effort, and the setting in which the debris piles have historically existed (unprotected and exposed to sun, wind and precipitation), it is our expectation that laboratory analytical results for VOC samples collected by the laboratory from laboratory-composited materials will be representative of debris pile conditions.

See Section 7.2 for preservation and shipping procedures.

6.5 Water Sampling

No water samples will be collected.

6.5.1 Surface Water Sampling

Not Applicable.

6.5.2 Groundwater Sampling

Not Applicable.

6.5.2.1 Water-Level Measurements
Not Applicable.

6.5.2.2 Purging
Not Applicable.

6.5.2.3 Well Sampling
Not Applicable.

6.6 Other Sampling
Not Applicable.

6.7 Decontamination Procedures
The stainless steel trowel used for sample collection will be decontaminated before and after filling one, four-ounce soil jar from each sampling unit, decontamination will be performed according to the procedures specified in "Protocol A-1. Sediment Sampling for Chemical Analysis."

Decontamination of the XRF unit will comprise wiping the unit's stainless steel base plate with a clean paper towel wetted with distilled water until the plate is visually clear of sediment, to be performed before and in between scanning of each individual debris block.

Decontamination of sampling equipment must be conducted consistently as to ensure the quality of samples collected. All equipment that contacts potentially contaminated materials will be decontaminated. Decontamination will occur prior to and after each use of a piece of equipment.

The following, to be carried out in sequence, is an EPA Region IX recommended procedure for the decontamination of sampling equipment.

1) Non-phosphate detergent and tap water wash, using a brush if necessary
2) Double distilled water rinse

Equipment will be decontaminated in a pre-designated area on plastic sheeting, and clean bulky equipment will be stored on plastic sheeting in uncontaminated areas. Cleaned small equipment will be stored in plastic bags. Materials to be stored more than a few hours will also be covered.

Table 12. Field and Sampling Equipment

Description of Equipment	Material	Dedicated
Excavator equipped with screening bucket	NA[1]	no
XRF[2]	NA	no
Trowel	Stainless steel	no
Sample jars	Glass with plastic lid	yes
40 ml VOAs[3,4]	Glass with plastic lid	yes
Decontamination equipment	Distilled water, Liquinox, bucket, scrubbing device (sponge/brush)	yes
Hand tools	Steel, wood, stainless steel	no

1. NA: not applicable
2. XRF: x-ray fluorescence
3. Ml: milliliter
4. VOA: volatile organic analysis (container)

Table 13. Field Equipment/Instrument Calibration, Maintenance, Testing, and Inspection

Analytical Parameter	Field Instrument	Calibration Activity	Frequency	Acceptance Criteria	Corrective Action
Metal concentra-tion	Niton XLp 702A X-ray fluorescence	Automatic calibration, instrument blank, calibration verification checks, confirmation sample collection	At device start up, every 20 samples, at end of day	Within 20 percent of the declared value of the standard analyzed	Perform device periodic maintenance according to manufacturer's recommendation,

7.0 Sample Containers, Preservation, Packaging and Shipping

The number and type of sample containers, volumes, and preservatives are listed in Table 11. The containers are new from the manufacturer and will not be rinsed prior to sample collection. Preservatives, if required, will be added by North Coast Laboratories during collection of subsamples for VOC analysis from homogenized samples.

7.1 Soil Samples

Not Applicable.

7.2 Sediment Samples

Sediment samples to be analyzed for VOCs using EPA Method 8260B will be placed into the appropriately preserved containers by the analytical laboratory following homogenization of the sample by the laboratory. Following homogenization of the sample by the laboratory, sample for VOC analysis will be collected by laboratory personnel using an EPA Method 5035-compliant sampling device, anticipated to be ESS Lock N' Load. Samples will be chilled to approximately 4°C immediately upon collection. If samples are preserved with either a methanol or a sodium bisulfate solution, the holding time is two weeks.

Sediment samples for analysis by EPA Method 8015B will be collected from the homogenized material and transferred from the sample-dedicated homogenization container into four-ounce glass jars using a trowel. The samples will be chilled to 4°C immediately upon collection.

Sediment samples that are to be analyzed for metals using the EPA Method 6010B will be homogenized and transferred from the sample-dedicated homogenization container into four-ounce glass jars. Samples will not be chilled.

7.3 Water Samples

Not Applicable.

7.4 Other Samples

Not Applicable.

7.5 Packaging and Shipping

All sample containers will be placed in a strong-outside shipping container. The following outlines the packaging procedures that will be followed for low concentration samples. Sample will be delivered by SHN personnel to NCL daily.

1. Use ice-filled plastic bottles to prevent leaking of water into the sample cooler.
2. Place custody seals on all sample container tops.
3. Label sample containers using indelible ink.
4. Double seal all sample containers in heavy duty plastic zip-lock bags. Write the sample numbers on the outside of the plastic bags with indelible ink.
5. Place samples in a sturdy cooler(s) lined with a large plastic trash bag. Enclose the appropriate chain-of custody forms in a zip-lock plastic bag affixed to the underside of the cooler lid.
6. Ice-filled plastic bottles may be used to cool samples, and will be placed on top and around the samples to chill them to the correct temperature.
7. Samples will be delivered by vehicle to NCL by SHN personnel.

8.0 Disposal of Residual Materials

In the process of collecting environmental, the sampling team will generate different types of potentially contaminated investigation derived waste (IDW) that include the following:

- Used PPE
- Disposable sampling equipment
- Decontamination fluids

The EPA's National Contingency Plan requires that management of IDW generated during sampling comply with all applicable or relevant and appropriate requirements to the extent practicable. The sampling plan will follow the *Office of Emergency and Remedial Response Directive 9345.3-02* (May 1991), which provides the guidance for the management of IDW. In addition, other legal and practical considerations that may affect the handling of IDW will be considered.

- Used PPE and disposable equipment will be double bagged and placed in a municipal refuse dumpster. These wastes are not considered hazardous and can be sent to a municipal landfill. Any PPE and disposable equipment that is to be disposed of that can still be reused will be rendered inoperable before disposal in the refuse dumpster.
- Decontamination fluids that will be generated in the sampling event will consist of deionized water, residual contaminants, and water with non-phosphate detergent. Decontamination fluids that will be generated in the sampling event will be transferred to SHN's Eureka office where it will be stored in an onsite treatment facility pending characterization. Following characterization, and assuming the decontamination fluids clear screening procedures, water will be disposed at the City of Eureka wastewater treatment plant under permit number 64.

9.0 Sample Documentation

9.1 Field Notes

This section presents the methods of documentation of field work, personnel involved with field efforts, site conditions, activities performed, and other field observations.

9.1.1 Daily Field Reports

Daily field reports (DFRs) will be completed by SHN field personnel daily during the performance of grant-funded work. At a minimum, the following information will be recorded during the collection of each sample:

- Sample location and description
- Stockpile map sketch showing sample location and measured distances
- Sampler name(s)
- Date and time of sample collection
- Designation of sample as composite
- Type of sample (debris)
- Sampling equipment used
- Field instrument readings and calibration
- Field observations and details related to analysis or integrity of samples (for example, weather conditions, noticeable odors, colors, etc.)
- Preliminary sample descriptions
- Sample preservation

In addition to the sampling information, the following specific information will also be recorded in the DFR for each day of sampling:

- Team members and their responsibilities
- Time of arrival/entry on site and time of site departure
- Other personnel on site
- Summary of any meetings or discussions with project-related personnel
- Deviations from sampling plans, site safety plans, and quality assistance protection plan (QAPP) procedures
- Changes in personnel and responsibilities with reasons for the changes
- Levels of safety protection
- Calibration readings for any equipment used and equipment model and serial number

9.1.2 Photographs

Photographs will be taken at the sampling locations. They will serve to verify information entered in the DFR. For each photograph taken, the following information will be written in the logbook or recorded in a separate field photography log:

- Time, date, location, and weather conditions
- Description of the subject photographed
- Name of person taking the photograph

9.2 Sample Labeling

All samples collected will be labeled in a clear and precise way for proper identification in the field and for tracking in the laboratory. A copy of the sample label is included in Appendix 3. The samples will have pre-assigned, identifiable, and unique numbers. At a minimum, the sample labels will contain the following information: station location, date of collection, analytical parameter(s), and method of preservation. Each composite sample will be assigned a unique sample number (Table 10).

9.3 Sample Chain-Of-Custody Forms and Custody Seals

All sample shipments for analyses will be accompanied by a chain-of-custody record. A copy of the form is found in Appendix 3. Form(s) will be completed and sent with the samples for each laboratory and each shipment (each day). If multiple coolers are sent to a single laboratory on a single day, form(s) will be completed and sent with the samples for each cooler.

The chain-of-custody form will identify the contents of each shipment and maintain the custodial integrity of the samples. Generally, a sample is considered to be in someone's custody if it is in someone's physical possession, in someone's view, locked up, or kept in a secured area that is restricted to authorized

personnel. Until the samples are shipped, the custody of the samples will be the responsibility of SHN field personnel. The sampling team leader or designee will sign the chain-of-custody form in the "relinquished by" box and note date, time, and air bill number.

A self-adhesive custody seal will be placed across the top of each sample container. A copy of the seal is found in Appendix 3. The shipping containers in which samples are stored (usually a sturdy picnic cooler or ice chest) will be sealed with self-adhesive custody seals any time they are not in someone's possession or view before shipping. All custody seals will be signed and dated.

10.0 Quality Control

10.1 Field Quality Control Samples

EPA recommendations include collection of field quality control samples at a rate of one quality control sample for every 20 samples collected. Because only four ISM composite samples will be collected, two of which will serve as field duplicates, the proposed approach will satisfy the recommended number of field quality control samples.

10.1.1 Assessment of Field Contamination

Assessment of field contamination will not be performed.

10.1.1.1 Equipment Blanks

The analysis of a field blank will be completed to test use of stainless steel trowels during the sampling program. Distilled water will be poured over clean trowels used in sample collection, then contained in a 250 ml plastic container preserved with nitric acid and analyzed for metals outlined in Table 9.

10.1.1.2 Field Blanks

The analysis of a methanol field blank will be completed due to VOC sample preservation method. A methanol field blank will be collected for analysis each day sampling for VOCs occurs.

10.1.1.3 Trip Blanks

Not Applicable; VOC samples will be collected in the laboratory environment from composited samples.

10.1.1.4 Temperature Blanks

For each cooler that is shipped or transported to an analytical laboratory a 40-milliliter volatile organic analysis (VOA) vial will be included that is marked "temperature blank." This blank will be used by the sample custodian to check the temperature of samples upon receipt.

10.1.2 Assessment of Field Variability

Duplicate sediment samples will be collected from each stockpile to verify COC concentrations and evaluate concentration variability in target materials for disposal at a landfill or reuse on site. Duplicate sediment samples to be analyzed for VOCs will be placed into appropriately preserved containers by the analytical laboratory following homogenization of the sample by the laboratory. Following homogenization of the sample by the laboratory, a sample for VOC analysis will be collected by laboratory personnel using an EPA

Method 5035-compliant sampling device, anticipated to be ESS Lock N' Load or an equivalent. Samples will be chilled to approximately 4°C immediately upon collection. If samples are preserved with either a methanol or a sodium bisulfate solution, the holding time is two weeks.
Duplicate sediment samples for analysis by EPA Method 8270B will be collected from the homogenized material and transferred from the sample-dedicated homogenization container into four ounce glass jars using a stainless steel trowel. The samples will be chilled to approximately 4°C immediately after collection.

Duplicate sediment samples that are to be analyzed for metals will be homogenized and transferred from the sample-dedicated homogenization container into four ounce glass jars.

Duplicate samples will be preserved, packaged, and sealed in the same manner as other samples of the same matrix. A separate sample number and station number will be assigned to each duplicate, and it will be submitted blind to the laboratory.

10.2 Background Samples

Not Applicable.

10.3 Field Screening, Including Confirmation Samples

Standard operating procedures (SOPs) for XRF field screening shall incorporate the following measures for QC:

1. Allow XRF device to warm up for a minimum of 15 minutes upon start up.
2. Perform device internal self-calibration.
3. Perform blank sample analysis before analyzing field samples, after the system has been turned off and restarted, and at the end of each day using manufacturer-supplied silicon dioxide standard. Blank sample analysis using the silicon dioxide blank provides baseline detection limits of the field screening device.
4. Perform calibration verification checks using a certified standard with concentrations similar to those found within the debris piles once per day. Relative standard deviation should not exceed 20 percent with the exception of chromium (not to exceed 30 percent). If results exceed a 20 percent difference, then manufacturer guidelines for adjusting calibration factors will be performed.

10.3.1 Field Screening Samples

Chemical impacts to coarse materials will be characterized in the field using a hand-held Niton XLp 702A XRF. Coarse materials for XRF characterization will be randomly selected for analysis at a rate equivalent to 10 percent of the volume of each coarse-material stockpile. The exterior surface of coarse materials selected for field screening will be analyzed using the device's "standard bulk" mode, which includes analysis for 15 elements. Results of the analyses include identification of elements, element concentration, and a 2 sigma (95percent) confidence interval.

10.3.2 Confirmation Samples (Field Screening)

In order to confirm XRF field screening results, sediment samples will be analyzed using the hand held XRF, and results for select COCs will be recorded. Sediment samples will then be submitted to the laboratory for analysis by EPA 6010B, to which field screening results can be directly compared. Because four sediment samples will be submitted for this confirmation data will be used to screen coarse materials for reuse onsite, cleaning and reuse onsite, or disposal at an appropriate facility.

10.4 Laboratory Quality Control Samples

Sediment sample volumes will comprise multiple four ounce jars from each sediment stockpile, the anticipated sample volume contains sufficient material for both routine sample analysis and additional laboratory QC analyses. Therefore, a separate soil sample for laboratory QC purposes will not be collected.

Sediment samples for VOC analyses for laboratory QC purposes will be obtained by collecting one duplicate sample from a single sample container in the same way as the original samples, and will be assigned a unique sample number.

Duplicate samples will be collected from each fine material debris stockpile; a total of four sediment samples are proposed for collection during the characterization effort of the two debris sediment stockpiles.

For this sampling event, samples collected at the following locations will be the designated laboratory QC samples:

- For sediment sample AOI-1-2

Sediment sample AOI-1-2 will be used for QA/QC purposes to confirm COC concentrations, because there is known detectable impacts by COCs in the AOI-1 debris pile, and historically reported concentrations are moderate in magnitude.

11.0 Field Variances

Because conditions in the field may vary, it may become necessary to implement minor modifications to sampling as presented in this plan. When appropriate, the QA Officer will be notified and a verbal approval will be obtained before implementing the changes. Modifications to the approved plan will be documented in the sampling project report.

12.0 Field Health and Safety Procedures

A site-specific safety plan has been developed for this project and is included as Appendix 4.

13.0 References Cited

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Protocols 1

Protocol 1-1. Sediment Sampling for Chemical Analysis

1.0 Introduction

This SHN Engineers & Geologists, Inc. (SHN) protocol describes procedures to be followed for collecting sediment samples and conducting field screening in conjunction with the collection of sediment samples from fine material debris pile surface locations. Selected sediment samples will be submitted to a designated laboratory for chemical analysis. The laboratory shall be certified by the California Department of Health Services, the Environmental Laboratory Accreditation Program or other appropriate agency for the analyses to be performed. The procedures presented herein are intended to be of general use. As work progresses, and if warranted, appropriate revisions will be made and approved by the SHN project manager.

2.0 Sample Collection

Sediment samples will be collected using a stainless steel trowel, and will be placed into clean, laboratory-supplied four ounce jars. Jars will be labeled with sample unit identification, date and time of collection, and sampler initials. Sample containers will be placed on ice in a cooler pending transportation to a state-certified laboratory under standard chain of custody protocols. Sample containers will be sealed with tape and placed in a zip top plastic bag. The sample container will be labeled and stored in an ice-filled chest until delivered to the laboratory.

2.1 Sample Containers and Preservation

Appropriate sample containers and preservatives for the analyses to be performed shall be obtained from the subcontracted analytical laboratory. Table 9 of the sampling and analysis plan lists analytical methods and the appropriate storage and handling requirements for site constituents of concern.

2.2 Sample Labeling

Sample containers shall be labeled with self-adhesive labels having the following information written in indelible ink:

- Project identification
- Sample number
- Date and time sample was collected
- Initials of sample collector
- Analysis Requested
- Preservative

3.0 Sediment Field Screening and XRF Calibration

A portable Niton XLp 702A series x-ray fluorescence analyzer (XRF) may be used to screen selected sediment samples. The purpose for the field screening of selected sediment samples is to evaluate the accuracy of the XRF. The XRF determines elemental concentrations present in samples in parts per million (ppm). XRF calibration occurs automatically upon startup of the device, after which the XRF measurements can be compared against manufacturer provided standards.

XRF screening of selected sediment samples consists of collection of sample aliquots from a sediment stockpile using a clean stainless steel trowel. One trowel scoop per sample unit will be placed into a common container at the same time as collection of samples for laboratory analysis. Upon collection of field screening samples from all sample units of a discreet debris pile, the samples will be homogenized by

thorough mixing with a trowel. The homogenized sample will be placed in a new one-gallon zip lock bag, and will be analyzed using the XRF bulk soil mode. XRF-derived elemental concentrations will be recorded on Daily Field Report (DFR) sheets. The XRF analyzed samples will be submitted to the laboratory for analysis for direct comparison of XRF-derived concentrations to laboratory derived concentrations. If consistent with laboratory results within 20%, XRF field screening of coarse materials will be used to decide the fate of materials for reuse onsite or disposal offsite at an appropriate facility.

4.0 Documentation

4.1 Daily Field Report

Details of field work, sediment sampling efforts, and XRF field screening efforts will be recorded on DFRs. Information recorded on the field sheets will include personnel onsite, weather conditions, site conditions, activities undertaken, a time log, and other information determined to be pertinent to project completion. Sampling maps of individual debris stockpiles will be developed. When sampling is completed, all original DFR sheets and a sampling map will be placed in the project file.

4.2 Chain-of-Custody Procedures

After samples have been collected and labeled, they will be maintained under chain-of-custody procedures. These procedures document the transfer of custody of samples from the field to the laboratory.

A Chain-of-Custody record will be completed for each sample sent to the laboratory for analysis. Information contained on the Chain-of-Custody form will include:

- Name of sampler
- Sample Identification.
- Date and time sampled
- Number of sample containers
- Sample Matrix
- Analyses requested
- Remarks, including any preservatives, special conditions, specific quality control measures, or electronic data requests
- Turnaround time and person to receive lab report
- Project number
- Signatures of all people assuming custody
- Signatures of field sampler

The field sampler will sign the Chain-of-Custody record and will record the time and the date at the time of transfer to the laboratory or an intermediate person. A set of signatures is required for each relinquished/received transfer, including transfer within SHN. The original imprint of the chain-of-custody record will accompany the sample containers. A duplicate copy will be placed in the SHN project file.

5.0 Equipment Cleaning

Decontamination of sampling equipment must be conducted consistently as to assure the quality of samples collected. All equipment that contacts potentially contaminated materials will be decontaminated. Decontamination will occur prior to and after each use of a piece of equipment.

The following, to be carried out in sequence, is an USEPA Region IX recommended procedure for the decontamination of sampling equipment.

- Non-phosphate detergent and tap water wash, using a brush if necessary
- Double distilled water rinse

Equipment will be decontaminated in a pre-designated area on plastic sheeting, and clean bulky equipment will be stored on plastic sheeting in uncontaminated areas. Cleaned small equipment will be stored in plastic bags.

Decontamination of the XRF unit will comprise wiping the unit's stainless steel base plate with a clean paper towel wetted with distilled water until the plate is visually clear of sediment, to be performed before and in between scanning of each individual debris block.

Water used in the decontamination of equipment and all well purge water will be contained in 50-gallon plastic drums or 5-gallon buckets. The water will be transported to the SHN purge water storage tanks to await proper disposal, if the constituents in the water are included in SHN's disposal permit with the City of Eureka. All decontamination water containing non-permitted constituents will be temporarily stored at the job site, until proper disposal arrangements are made.

Standard Operating Procedure
Bulk Sample Test Mode
Niton XLp 702A X-Ray Fluorescence Analyzer

This standard operating procedure (SOP) covers the steps necessary to gather Bulk Metal concentration data with the Niton XLp 702A x-ray fluorescence (XRF) analyzer. Review of this SOP prior to data collection is mandatory for all users.

WARNING: This device contains a radioactive source and uses radiation as part of its analysis. Any user must be trained in working with radioactive testing equipment and radiation safety. Anytime the lights are flashing, the analyzer is emitting radiation. For more detailed information, see the accompanying user's manual.

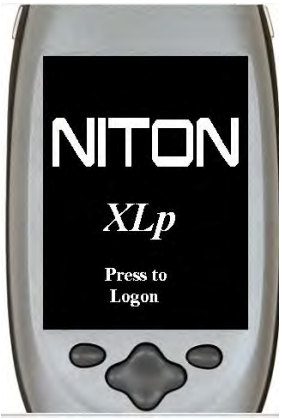
Storage and Transportation

1. The XRF Analyzer contains a 40 mCi Cadmium-109 radiation source. Special conditions in this SOP must be met when storing and transporting the XRF.

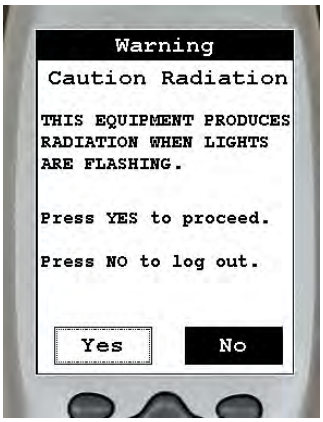
2. Storage:
    a. When stored, the device is kept under a minimum of three locks (Gate, Door, Chain/Lock, and Case Locks).
3. Transportation:
    a. The device is locked to the vehicle using chain/lock in addition to locks on the case.
    b. Current Bill of Lading papers must accompany the device while in transport.
    c. If the device is to be left unattended, it should meet the minimum "three locks requirement." To do this, you can 1) lock the device to the steering wheel using the chain and lock, 2) lock the doors to the vehicle, and 3) lock the case.

System Startup and Calibration

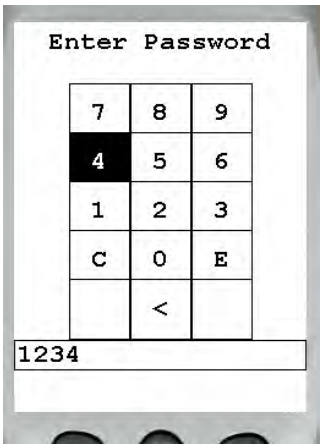
1. Power on device by holding power button.
2. The interface uses a touch screen; just tap to log in. There is a stylus pen located on the battery.



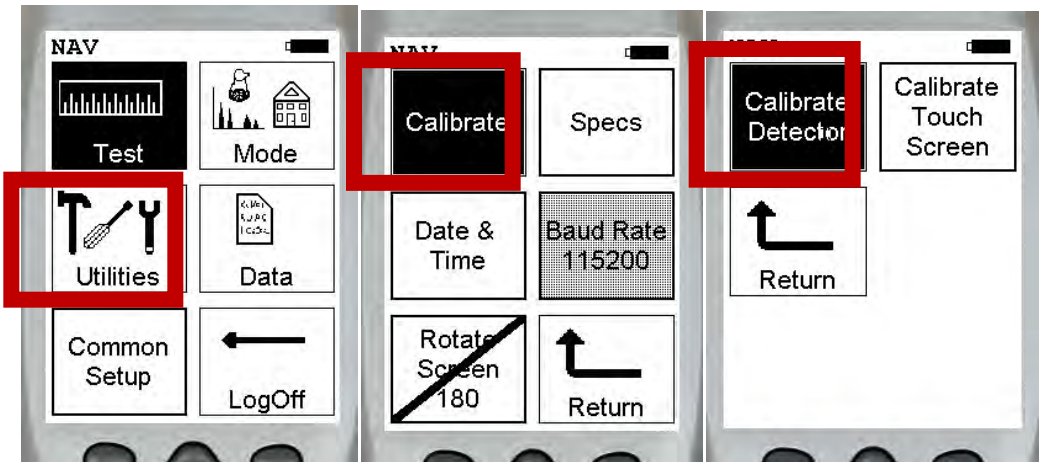
3. The next screen is the radiation warning. Read the warning and press yes to proceed.



4. Enter the password. The default password is 1234E

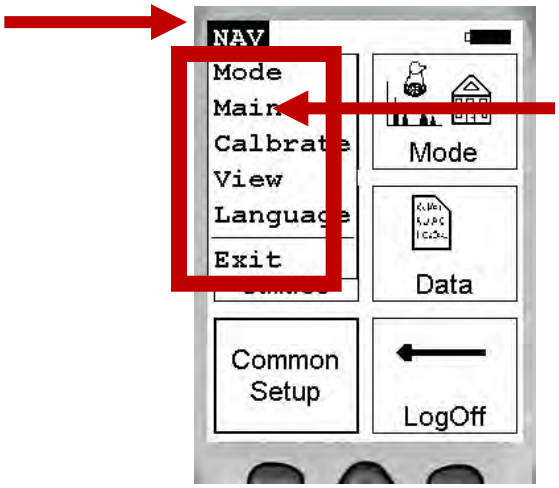


5. Allow device 15 minutes to warm up.
6. This is the navigation screen. **The device must be calibrated every time that it is turned on**. Click on the icons (denoted by the red boxes) to calibrate.



7. Following device calibration set the device for analysis using the Standard Bulk Mode to analyze manufacturer-supplied medium (CCRMP Till 4 pp) and high (RCRA pp) concentration standards, and record device measurements on calibration forms. Recordings exceeding, or below, 20% of the standard concentration for target analytes shall be rejected, and rebooting, or performing maintenance, of the device shall be conducted. Table A, presenting certified concentrations for manufacturer-supplied CCRMP Till 4 pp and RCRA pp concentration standards for comparison to XRF derived concentrations, is included as Attachment A of this SOP. Refer to the User's Guide "Adjusting Calibration Factors" (page 2-55) to adjust the device for consistently high or low results from the analyzer.

8. Once calibrated, return to the main menu. **To navigate at anytime, click on the NAV button**.

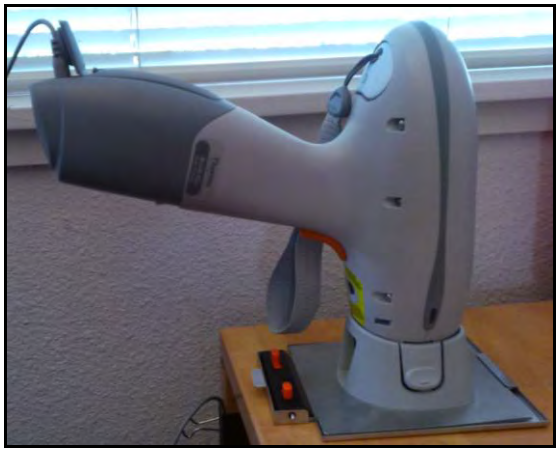


Calibration During Use

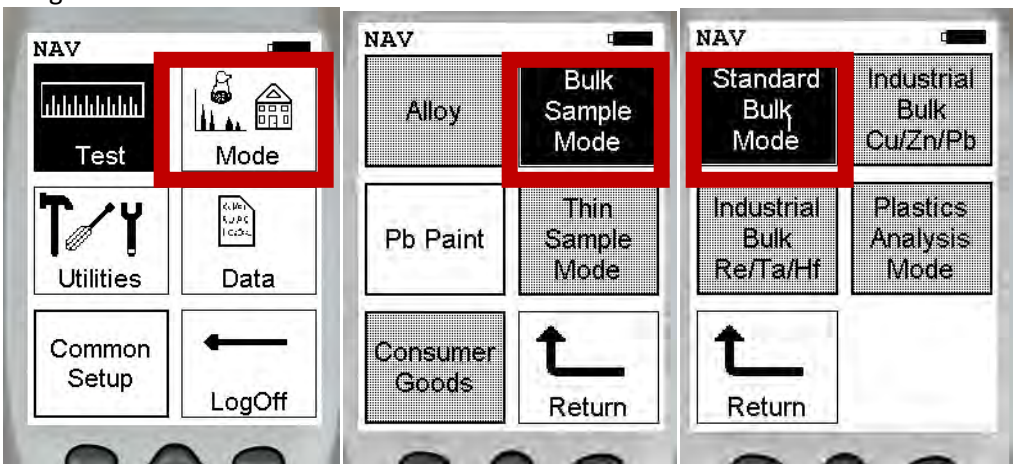
- Analyze the manufacturer-supplied SiO_2 blank every 20 samples analyzed.
- Relative Standard Deviation (Standard Deviation/Mean Concentration) x 100 must be less than 20 percent.

Bulk Sample Test Modes

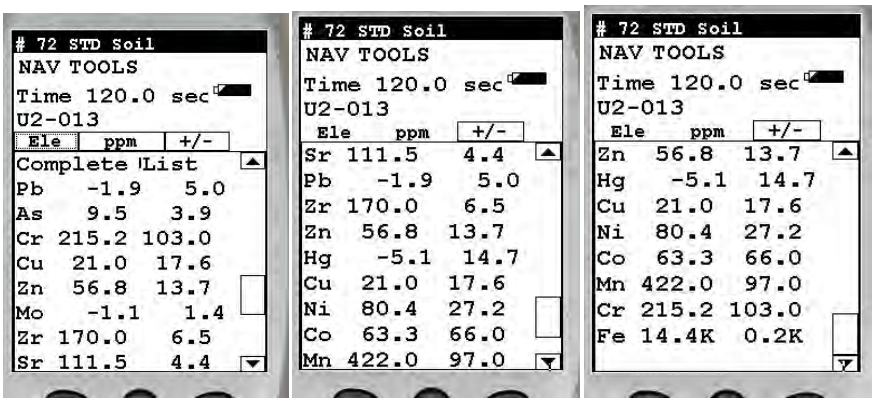
1. The Niton XLp 702 XRF Analyzer is programmed for multiple analysis modes (Alloy Testing, Lead Paint Mode, Thin Sample Test Modes and Bulk Sample Test Modes), with several analysis options within some of the mode options. Within the Bulk Sample Mode (XRF User's Guide Chapter 6, page 6-145), analysis options include a Standard Bulk Mode, and two Industrial Bulk Modes which scan for select metals based on site activities/constituents of concern. Select the mode that will best suit the needs of the study.
2. Analysis options include In Situ and Ex Situ analysis. Depending upon site conditions (time allowed for scan, soil/analyzed medium conditions, et cetera) a decision shall be made as to the most appropriate method of sample analysis. Methods of sample preparation are discussed beginning on page 6-159 of the User's Guide.
3. As scans using the Standard Bulk Mode, which analyses the sample medium for 15 element concentrations, typically last over a period of up to 10 minutes, attaching the base stand to the XRF unit may be appropriate.

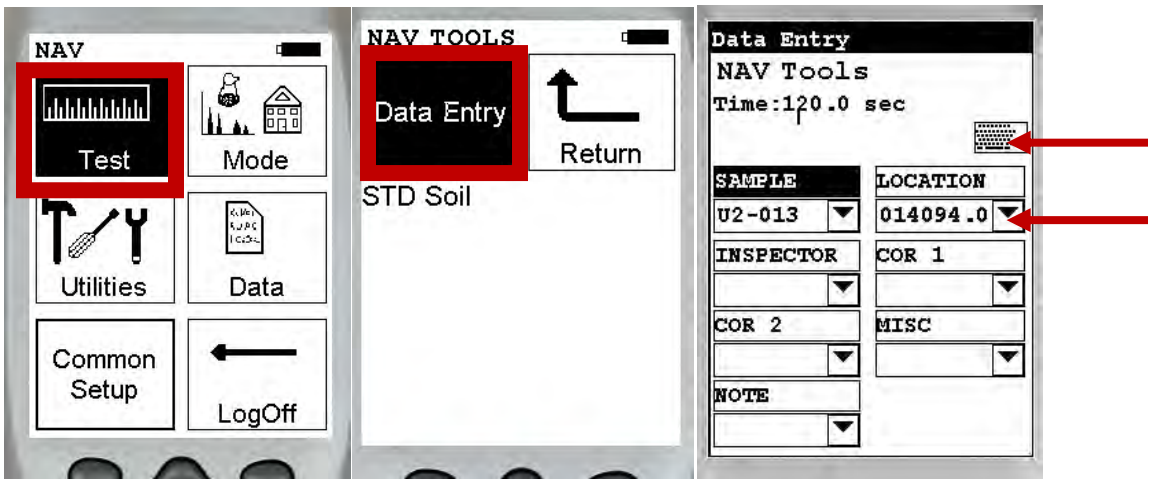
4. Select testing mode



5. Bulk Analysis has the capacity to analyze soils for 15 elements. The complete list is shown below:



6. Once the appropriate sampling mode has been selected, you are ready to begin analyzing samples. Depending on the site, number of locations for analysis, and number of contaminants of concern, you can scan and record results in the field, or the device will save the results of each scan by test number and data parameters. The data entry option enables users to add information in regard to each sample (see examples below). The first arrow is a keyboard so that users can customize entries. The second arrow is the location (which should be your Job #).

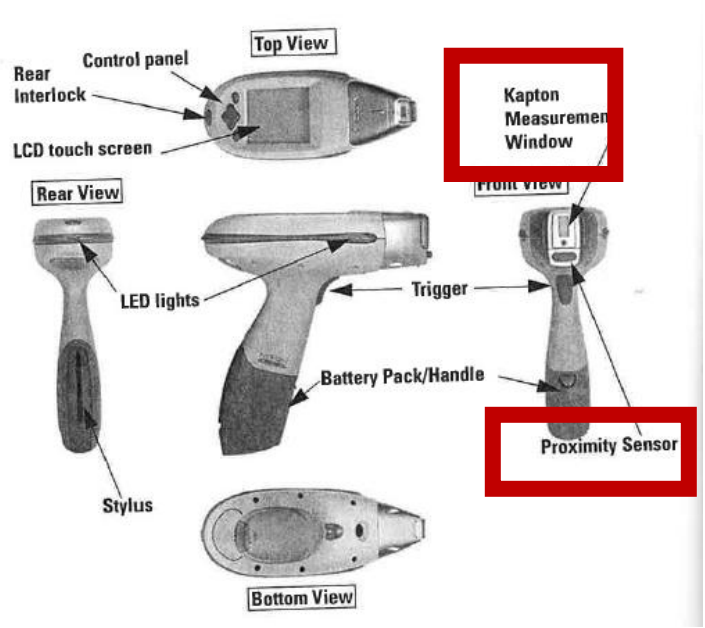


Once you entered your data you can begin analyzing.

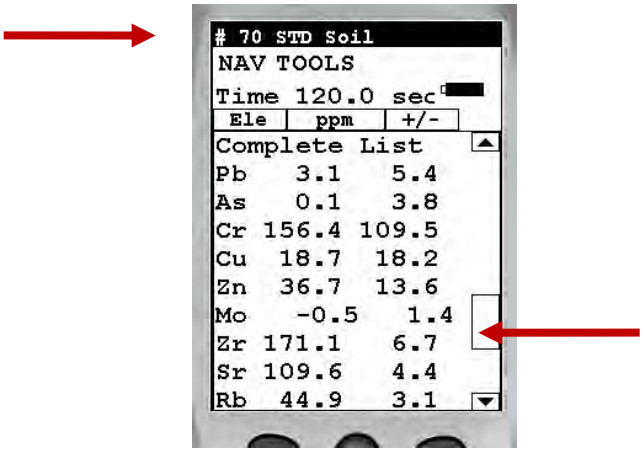
- For In Situ analysis, the XRF base stand will likely be useful. The base stand ensures the Kapton Window is not damaged, air space is minimized, and the Proximity Sensor button is depressed when the unit is placed on the surface to be analyzed; if during the course of an analysis the Proximity Sensor button is no longer depressed, the analysis will be terminated. Preparation of the analysis location is performed by creating a flat and nearly level surface the size of the base stand such that the air space is minimized and the device trigger is actuated, occasionally the device may need to be rotated within the flat surface so that the XRF device is balanced properly and the Proximity Sensor button remains depressed.
- Ex situ sample analysis includes collection of sufficient material for analysis so that the sample container has a lift of material a minimum of 0.4-inch (1 centimeter) thick when compressed beneath the XRF base stand. Ex Situ sample analysis can take several forms, and in general, the greater the homogenization and the drier the sample, the more accurate the results will be.

Descriptions of sample preparation for Ex Situ analysis are provided in the User's Guide starting on page 6-163. The User's Guide describes use of zip lock bags for sample containers through which the scan can be performed; cautionary notes regarding printed labels on the exterior of the bags, and the composition of the surface upon which the bag has been placed for analysis are presented as either may impart a signal in the results.

- **WARNING: The Kapton Window is sensitive and can be torn easily.**



7. While performing an analysis the device screen will display the following: the sample identification number, elapsed time, and element concentration (see below). Note that in the field, it is good to record the device sample number in relation to the field location of the analysis (providing a reference to the data on the device). This data does get cleared regularly (every few months based on number of samples), but can be retrieved if field recorded data is insufficient. You can navigate the samples using the scroll on the right.



Attachment A

Certified concentrations of manufacturer-supplied calibration standards CCRMP Till 4 pp and RCRA pp are presented in Table A. The values in Table A are to be compared to XRF-derived values for the standards for quality assurance purposes. Concentration variability +/- 20% of the certified concentration shall be rejected, and rebooting, or performing maintenance, of the device shall be conducted.

Table A. Certified Concentrations for CCRMP Till 4 pp and RCRA pp (parts per million)

Constituent	CCRMP Till 4 pp	+ 20% CCRMP Till 4 pp	- 20% CCRMP Till 4 pp	RCRA pp	+ 20% RCRA pp	- 20% RCRA pp
Chromium	53	63.6	42.4	500	600	400
Manganese	490	588	392	---	---	---
Cobalt	8	9.6	6.4	---	---	---
Nickel	17	20.4	13.6	---	---	---
Copper	237	284.4	189.6	---	---	---
Zinc	70	84	56	---	---	---
Arsenic	111	133.2	88.8	500	600	400
Selenium	---	---	---	500	600	400
Lead	50	60	40	500	600	400
Rubidium	161	193.2	128.8	---	---	---
Strontium	109	130.8	87.2	---	---	---
Zirconium	385	462	308	---	---	---
Molybdenum	16	19.2	12.8	---	---	---

--- : no concentration provided
63.6 : values presented in red represent the 20% variability threshold

Quality Assistance Protective Plan 2

North Coast Laboratories, Ltd.

MET	CODE	VERSION	COPY	EFFECTIVE DATE	WORDFILE
ME	247	02	L	10/25/06	G:\WPROC\ORGSOP\ME247v02.doc

	NAME	TITLE	DATE
REVISED BY:		CHEMIST II	10/25/06
APPROVED BY:	Colleen Blackstone	OL SUPERVISOR	10/25/06
APPROVED BY:		LAB MANAGER	10/25/06
REVIEWED BY:		QA OFFICER	10/25/06

1.0 **TITLE**

Volatile Organic Compounds and Gasoline in Water and Soil by Purge and Trap GC-MS, utilizing EPA 8260B.

2.0 **SCOPE**

This analytical method gives procedures required for the analysis of water and soil matrices for a wide range of volatile organic compounds, including chlorinated hydrocarbons, several gasoline oxygenate and lead scavenger additives, BTX&E compounds, and gasoline by GC-MS.

3.0 **DEFINITIONS**

LIMS – Laboratory Information Management System, Omega at the time of this version.
RL – Reporting Limit
CCVS – Continuing Calibration Verification Standard

4.0 **REFERENCES**

Test Methods for Evaluating Solid Waste Volume 1B: Laboratory Manual Physical/Chemical Methods, EPA Office of Solid Waste and Emergency Response, Washington, D.C., 20460, November 1986, SW-846 Third Edition, Revision 2, December 1996, Method 8260B.

5.0 **SUMMARY**

Water samples are purged with helium. The volatile analytes are trapped and then thermally desorbed into a gas chromatograph. The chromatographically separated analytes are detected by mass spectrometry. Soil samples are subjected to a gentle extraction procedure, using methanol. A portion of the methanol extract is then added to an aliquot of blank water and purged, trapped, desorbed, and determined as stated for water samples.

6.0 **REPORTING LIMITS**

See Exhibit A

7.0 **SAMPLE STORAGE AND HOLDING TIMES**

Aqueous samples are collected without headspace in three 40 mL glass screw-cap VOA vials with Teflon® lined silicone septa. The VOA vials are pre-preserved with two drops of 1:1 HCl:H2O. Soil samples are collected in brass tubes or wide mouth soil jars with a minimum of headspace.

All samples are stored at about 4°C in a location free from solvents. Samples are to be extracted and analyzed within 14 days of collection.

8.0 PREPARATION OF STANDARDS

8.1 Equipment, Glassware and Supplies

- 40 mL VOA vials
- various microliter syringes
- tall form 50 mL graduated cylinder(s)
- 2 mL volumetric flasks
- 2 mL reaction vials for standard storage, Supelco 33295
- 15 mm Mininert valves for standard vials, Supelco 33301
- Purge and trap grade methanol
- Purge and Trap (P&T) blank water. Check each new batch for contaminants. If interferents are found they MAY be removed by vigorous pre-purging with He for 15 or more minutes.
- 1:1 HCl in pre-purged P&T water
- 100 mL volumetric flasks

8.2 Standard preparation

8.2.1 General comments and precautions

- All the analytes in this method are very volatile. Consideration of this fact must be taken into account in every step.
- Transfers of standards and extracts should be made using the typical volatile analyte procedure of injecting aliquots under the surface of liquids.
- When water is used as the solvent it should be pre-chilled to about 4°C.
- Stock standards should be stored at <-15°C.
- Purge efficiencies are affected by matrix. It is, therefore, necessary to match the sample matrix in the production of instrument calibration solutions (ICS). For soil standards, add 500 µL of methanol to each ICS.
  NOTE: The component most affected by MeOH in the matrix is 1,2-DCA. When using the Supelco"J" trap, it is almost completely lost if 2 mL of MeOH is added to 40 mL of water. This doesn't appear to be as much of a problem using the "K" trap.

8.2.2 Suggested Sources for Stock Standards (Lot 1)

- Restek 502.2 Mega Mix, 54 components, 2000 PPM; Catalog #30431.
- Restek CA Oxygenates, 5 components, 2000 PPM (10,000 PPM T-Butyl Alcohol (TBA)); Catalog #30465.
- Restek TBA, 50,000PPM; Catalog #55335.
- Restek 502.2 Mix #1, 6 components, gasses, 2000 PPM; Catalog #30042.
- Gasoline: Restek unleaded composite, 2500 PPM; Catalog #30081.

8.2.3 Suggested Sources for Stock Standards (Lot 2)

- Supelco 502/524 Mix, 54 components, 2000 PPM; Catalog #502111.
- Accustandard Oxygenates, 5 components, 2000 PPM (10,000 PPM TBA); Catalog #OGAD-001.
- Chem Service TBA, Neat; Catalog #F2535.
- Supelco VOC Mix 6, 6 components, gasses, 2000 PPM; Catalog #48799-U
- Gasoline: Accustandard, 5000 PPM; Catalog #GA-001-10X.

8.2.4 Internal and Surrogate Standards

- CPI Internal/Surrogate combined, 2500 PPM (250 PPM BFB) catalog # 120265-03

8.2.5 Preparation of 50,000 PPM TBA Stock Standard for Lot 2

To prepare a 50,000 PPM standard, weigh a 10 mL volumetric flask to 4 significant figures on the analytical balance. Using a Pasteur pipette, drop in enough TBA to increase the weight by just over 0.5 g. Take care that the drops fall directly into the flask and do not hit the glass sides. Record the final weight. To calculate the amount of methanol needed to make a 50,000 PPM solution, use the following equation:

$$\text{Amount of methanol to add (mL)} = \frac{\text{weight (g)} \times \text{concentration of neat (µg/g)}}{50{,}000\ (\mu g/mL)}$$

This should be just over 10 mL. Fill the volumetric flask to the 10 mL mark and then add the required extra with a syringe.

8.2.6 Preparation of Mix Stock Standard for **Water and Soil**

The mix is used to prepare calibration and working standards and for preparing quality control samples. The mixed stock standard is prepared using the following table. The final volume is brought to 1.0 mL in an amber 1 mL vial with a mininert cap with Purge and Trap grade methanol. Store @ about -15°C.

Standard	Standard Concentration ng/µL (PPM)	Amount of Standard (µL)	Final Volume (mL)	Final Concentration ng/µL (PPM)
Restek Mega #30431	2,000	100	1.0	200
Restek Oxys #30465	2,000 (TBA10,000)	100	1.0	200 (TBA 1000)
Restek TBA #55335	50,000	60	1.0	3,000 (combined total TBA=4,000)
Restek Gasses #30042	2,000	100	0.9	200

The second source standard is made exactly the same way and has exactly the same concentrations of analytes.
It is recommended that the first three of these be combined to make a 200PPM standard (4000PPM TBA), and the permanent gasses standard be diluted separately to make a 200PPM permanent gasses standard. Then the working standards can be made by adding equal amounts of each of these to water. The reason for doing this is that the permanent gasses standard will go out of calibration quickly, in as little as one week, while the other components will remain stable for up to 6 months.

8.2.7 Preparation of Surrogate - Internal Standard Mix

Add 1.000 mL of 2,500 µg/mL 8260(250 µg/mL BFB) internal standard/surrogate mix below the surface of 9mL of P & T MeOH in a 12 mL vial. Cap and mix. Use this to fill the Varian Arcon autosampler surrogate

standard vial. The concentration of each component is 250 ug/ml (25 ug/ml BFB). The autosampler adds 1µl of this solution to each sample sent to the purge vessel. The concentration of each component (except BFB) in the sparged sample is:

$$\frac{.001\text{ml} \times 250\text{ug/ml}}{\text{sample volume in sparger (ml)}}$$

The concentration of BFB in the sparged sample is:

$$\frac{.001\text{ml} \times 25\text{ug/ml}}{\text{sample volume in sparger (ml)}}$$

This concentration is needed for calculations in section 10.4.2.4

8.3 Preparation of Working Standards, 8260 Water and Soil

8.3.1 **Chart for preparation of 8260 working standards for Water:**
Use this chart to make a set of working standards for calibrating the water method. The lower level standards are made by diluting levels 8, 9, and 10, as one would dilute a sample. For example, a 20×RL, Level 8 standard diluted 1:10 makes a 2×RL Level 5 standard.

Level in Method	Amount of Stock	Conc. of Stock	Final Volume (mL)	Standard Level
1	0.215 mL of 20×RL	Various	43	0.1×RL*
2	0.43 mL of 20×RL	Various	43	0.2×RL*
3	0.43 mL of 50×RL	Various	43	0.5×RL*
4	0.43 mL of 100×RL	Various	43	1×RL*
5	4.3 mL of 20×RL	Various	43	2×RL*
6	4.3 mL of 50×RL	Various	43	5×RL*
7	4.3 mL of 100×RL	Various	43	10×RL*
8#	10 µL	Various	100	20×RL * #
9	25 µL	Various	100	50×RL *
10	50 µL	Various	100	100×RL *

2 drops of 6N HCl are added to each "40" mL VOA. The vial is then filled with standard solution, and the opening is sealed with a septum cap. This is because samples are preserved with 2 drops of 6N HCl.

* For components with RL=1 PPB. See chart in 8.3.2 for ×RL for other components.

This is the mid-level standard used for CCVS's and the quality control sample fortification level for water analysis.

MET CODE VERSION
ME 247 002

The second source working standard is made exactly the same way and has exactly the same concentrations of analytes as the level 8 (20xRL) standard.

Example for analytes with a reporting limit of 1.0 PPB:

$$10\ \mu L \times \frac{200\ ng}{\mu L} = \frac{2000\ ng}{15\ mL^*} = \frac{133.33\ ng}{mL} \times 15\ mL^* = \frac{2000\ ng}{100\ mL^{**}} = \frac{20\ ng}{mL} = 20\ PPB$$

* The amount of sample sparged is 15 mL.
** The amount of standard prepared is 100 mL.

MET CODE VERSION
ME 247 002

CHART A: Water Working Standards

This chart gives the ×RL and working standard concentrations for the different analytes for the 10 levels of working standards made as described above. When calibrating the method, standard levels below 0.4×RL should not be used. For example, for the RL=1 PPB analytes, do not use levels 1 and 2.

Level in Method	RL=1 Analytes ×RL	RL=1 Analytes PPB	RL=2 Analytes ×RL	RL=2 Analytes PPB	RL=0.5 Analytes ×RL*	RL=0.5 Analytes PPB*	RL=10 TBA ×RL	RL=10 TBA PPB
10	100	100	50	100	200	100	200	2000
9	50	50	25	50	100	50	100	1000
8#	20	20	10	20	40	20	40	400
7	10	10	5	10	20	10	20	200
6	5	5	2.5	5	10	5	10	100
5	2	2	1	2	4	2	4	40
4	1	1	.5	1	2	1	2	20
3	.5	.5			1	.5	1	10
2					.4	.2	0.4	4
1					.2	.1		

This is the mid-level standard level and spike level for water.

* Multiply these by 2 for m and p-xylene, since these two compounds co-elute and are measured as one peak. Level 1 is needed only for m,p-xylene. Since the RL for m,p xylene is .5PPB, level 1 is needed because it is .2PPB for m-xylene and .2 PPB for p-xylene

To not use a level in the method, for a particular component:
When calibrating, the level number, concentration, and response (area counts) are automatically entered in that compound's calibration database. To not use a level, it is sufficient to just erase the concentration. The response number can remain.

8.3.2 **Chart for preparation of 8260 working standards for Soil:**
Use this chart to make a set of working standards for calibrating the soil method. The lower level standards are made by diluting levels 9, 10, and 11, as one would dilute a sample. For example, a 20×RL, Level 9 standard diluted 1:10 makes a 2×RL, Level 6 standard.

Level in Method	Amount of Stock	Conc. of Stock	Final Volume (mL)	Standard Level
1	.108 mL of 20×RL	Various	43	.05×RL*
2	.215 mL of 20×RL	Various	43	.1×RL*
3	.43 mL of 20×RL	Various	43	.2×RL*
4	.43 mL of 50×RL	Various	43	.5×RL*
5	.43 mL of 100×RL	Various	43	1×RL*
6	4.3 mL of 20×RL	Various	43	2×RL*
7	4.3 mL of 50×RL	Various	43	5×RL*
8	4.3 mL of 100×RL	Various	43	10×RL*
9#	4.67 µL	Various	100	20×RL* #
10	11.7 µL	Various	100	50×RL *
11	23.4 µL	Various	100	100×RL *

0.5 mL of purge and trap grade methanol are added to each "40" mL VOA. The vial is then filled with standard solution, and the opening is sealed with a septum cap. This is because samples are prepared by adding .5 mL methanol extract to water in a 43 mL VOA.

* For: TBA and components with RL=.02 PPM. See chart in 8.3.4 for ×RL for other components.

This is the mid-level standard used for CCVS's and the quality control sample fortification level for soil analysis.

The second source working standard is made exactly the same way and has exactly the same concentrations of analytes as the level 9 (20xRL) standard.

MET CODE VERSION
ME 247 002

8.3.3 **CHART B: Soil Working Standards**

This chart gives the × RL and working standard concentrations for the different analytes for the 11 levels of working standards made as described above. When calibrating the soil method, standard levels below 0.4×RL should not be used. For example, for the RL = 0.02 PPM analytes, erase in the method the entries for levels 1and 2 as they are below in the 0.5×RL for these analytes.
It is probably okay to let the standard curves extend to WS level #11 even though this gives × RL values of over 100 for some analytes. This will result in fewer dilutions of samples. If you do this, check that the presence of these high levels in the curve does not decrease accuracy at 1×RL by too much, particularly for m,p xylene.

Level in Method	RL=0.02 Analytes ×RL	PPM	RL=0.04 Analytes ×RL	PPM	RL=0.005 Analytes ×RL*	PPM*	RL=0.2 TBA ×RL	PPM
11	100	2.00	50	2.00	400	2.00	100	40
10	50	1.00	25	1.00	200	1.00	50	20
9#	20	.40	10	.40	80	.40	20	8
8	10	.20	5	.20	40	.20	10	4
7	5	.10	2.5	.10	20	.10	5	2
6	2	.040	1	.040	8	.040	2	.8
5	1	.020	.5	.020	4	.020	1	.4
4	.5	.010			2	.010	.5	.2
3					.8	.0040		
2					.4	.0020		
1					.2	.0010		

This is the mid-level standard level and spike level for soil.x
* Multiply these by 2 for m and p xylene, since these two compounds co-elute and are measured as one peak. Level 1 is needed only for m,p xylene. Since the RL for m,p xylene is .005PPB, level 1 is needed because it is .002PPB for m,p xylene.

To not use a level in the method, for a particular component:
When calibrating, the level number, concentration, and response (area counts) are automatically entered in that compound's calibration database. To not use a level, it is sufficient to just erase the concentration. The response number can remain.

MET CODE VERSION
ME 247 002

8.4 Preparation of Working Standards, Gasoline Water and Soil

8.4.1 **Chart for preparation of Gasoline working standards for Water:**
Use this chart to make a set of working standards for calibrating the water method. The lower level standards are made by diluting levels 6,7 and 8, as one would dilute a sample. For example, a 20xRL, Level 6 standard diluted 1:10 makes a 2xRL Level 3 standard.

Level in Method	Amount of Stock	Conc. of Stock (PPM)	Final Volume (mL)	Standard Level
1	0.43 mL of 50xRL	2.5	43	0.5 x RL
2	0.43 mL of 100xRL	5.0	43	1 x RL
3	4.3 mL of 20xRL	1.0	43	2 x RL
4	4.3 mL of 50xRL	2.5	43	5 x RL
5	4.3 mL of 100xRL	5.0	43	10 x RL
6#	40 µL	2500	100	20 x RL#
7	100 µL	2500	100	50 x RL
8	200 µL	2500	100	100 x RL

2 drops of 6N HCl are added to each "40" mL VOA. The vial is then filled with standard solution, and the opening is sealed with a septum cap. This is because samples are preserved with 2 drops of 6N HCl.

This is the mid-level standard level and spike level for water.

The second source working standard is made in the same way as the Level 6 standard.

8.4.2 **Chart for preparation of Gasoline working standards for Soil:**
Use this chart to make a set of working standards for calibrating the soil method. The lower level standards are made by diluting levels 6, 7 and 8, as one would dilute a sample. For example, a 20 xRL, Level 6 standard diluted 1:10 makes a 2 x RL, Level #3 standard.

Level in Method	Amount of Stock	Conc. of Stock (PPM)	Final Volume (mL)	Standard Level
1	0.43 mL of 50xRL	1.17	43	0.5xRL
2	0.43 mL of 100xRL	2.34	43	1xRL
3	4.3 mL of 20xRL	.468	43	2xRL
4	4.3 mL of 50xRL	1.17	43	5xRL
5	4.3 mL of 100xRL	2.34	43	10xRL
6#	18.7 µL	2500	100	20xRL #
7	46.7 µL	2500	100	50xRL
8	93.5 µL	2500	100	100xRL

0.5 mL of purge and trap grade methanol are added to each "40" mL VOA. The vial is then filled with standard solution, and the opening is sealed with a septum cap. This is because samples are prepared by adding 0.5 mL methanol extract to water in a 43 mL VOA.

This is the mid-level standard level and spike level for soil.

The second source working standard is made in the same way as the Level 6 standard.

9.0 **EXTRACTION**

9.1 Equipment

-Water Extraction:

- None.

-Soil Extraction:

- Top loading balance capable of weighing to nearest 0.1 g.
- Centrifuge capable of swinging 40 mL VOAs at about 1800 rpm.

9.2 Glassware and Supplies

-Water Extraction:

- Various microliter syringes for fortifications.
- Pasteur pipets.
- 40 mL VOAs for making dilutions if required.
- Tall form 50 mL graduated cylinder.

-Soil Extraction:

- Various microliter syringes for fortifications and addition of methanol to standards.
- Pasteur pipets.

- 40 mL VOAs for performing extractions and diluting extracts.
- Tall form 50 mL graduated cylinder.

9.3 Reagents

-Water Extraction:

- 1:1 HCl for preservation of samples.
- P&T water for making dilutions if required.

-Soil Extraction:

- P&T methanol for sample extraction.
- P&T water for dilution of soil extracts.

9.4 Extraction Procedure (Water):

9.4.1 Retrieve samples for analysis according to SOP LA 003.

9.4.2 The water samples that are to be analyzed are loaded directly into the autosampler. If dilutions are necessary, the samples will be diluted prior to placing them in the autosampler.

9.4.3 Prepare the laboratory control sample(s) for gasoline and 8260 in the same manner as the 20×RL working standards using the primary source standard. Use the second lot standard for fortifying matrix spikes. Refer to Section 8.3. Prepare a method blank by filling a 40 mL VOA with blank water.

9.5 Extraction Procedure (Soil):

9.5.1 Weigh 10 g soil, or if preparing laboratory control sample(s) or method blanks(s), 10 g furnaced sand into a clean 40 mL VOA vial.

9.5.2 Using a calibrated pipetter attached to a 1 liter bottle of methanol, add 5.0 mL pre-tested P&T methanol to each vial containing the weighed sample immediately after weighing each sample into the vial. If addition of standard is not required, immediately cap the vial. If addition of standard is required for preparation of laboratory control samples (LCS) or fortifications (i.e. matrix spikes), add this immediately after addition of the methanol. Be sure to use the primary lot standards for fortifying LCSs. Use the second lot standard for fortifying matrix spikes. In this case, cap the vial immediately after addition of the standard aliquot. To fortify a laboratory control sample @ the 20×RL level, proceed as follows:

Gasoline:
Add 80 µL of 2500 ng/µL standard to the methanol and soil.

Example calculation for gasoline:

$$80\ \mu L \times \frac{2500\ ng}{\mu L} = \frac{200{,}000\ ng}{10\ g} = 20{,}000\ ng/g = 20\ \mu g/g$$

(1×RL = 1 µg/g for gasoline)

Individual Component Mix:
Add 20 µL of the stock mix standard to the methanol and soil for a final concentration of 20×RL (RL = 0.02 PPM components).
Example calculation for MTBE:

$$20\ \mu L \times \frac{200\ ng}{\mu L} = \frac{4000\ ng}{10\ g} = 400\ ng/g = 0.40\ \mu g/g$$

(1×RL= 0.02 µg/g for MTBE)
This is a 20×RL spike for MTBE

Example calculation for Toluene:

$$20\ \mu L \times \frac{200\ ng}{\mu L} = \frac{4000\ ng}{10\ g} = 400\ ng/g = 0.40\ \mu g/g$$

(1×RL= 0.005 µg/g for Toluene)
This is an 80×RL spike for Toluene.

NOTE: ERA and NSI soil samples for the above constituents are designed to use a 1:1 Soil:MeOH ratio. Our method uses a 2:1 Soil:MeOH ratio and our standards reflect this. It is therefore necessary to use a dilution factor (multiplier) of "2" for ERA/NSI results when following their directions. It is also possible to simply prepare EPA and NSI samples using 10 g of soil and 5 mL MeOH. This will require no dilution factors.
Also note that ERA/NSI **non-gasoline** constituents soil results are to be reported in "PPB" units, while our standards and reporting units are denominated in "PPM" units. This necessitates a multiplication factor of "1,000" to account for the difference. ERA/NSI soil gasoline results are reported in "PPM" units like ours are.

9.5.3 Place the extraction vials in a tube rack. Place a second rack over the top of the tubes. Gently invert the tubes for a total of 2 minutes. One inversion per second is about the correct speed.

9.5.4 Place the vials in a centrifuge and spin them at about 1,800 rpm for 2-5 minutes as required to settle particulates.

9.5.5 Place about 40 mL of pre-tested, pre-purged (if required) P&T water into clean 40 mL VOA vials.

9.5.6 Very carefully, in order to not re-suspend particulates, remove the tubes from the centrifuge and place them back in the rack.

9.5.7 Very carefully, use a 500 µL syringe to remove 500 µL of methanol supernatent from the extraction vial. Transfer it to the second VOA containing about 40 mL of pre-tested, P&T water. Carefully discharge the 500 µL aliquot of extract under the surface of the water. Fill the vial with P&T water, and cap. Slowly invert the vials about 5 times to mix the contents.

9.6 Special Precautions

The analytes under consideration in this analysis are very volatile. Extreme caution must be exercised to prevent evaporative losses. Stock standards must be stored at <-15°C. These stocks should be removed from the freezer and allowed to come to ambient temperature just before use (this is not necessary if "Mininert" valves are used). An alternate to warming the standards would be to use "Mininert" valves on the standard vials. When injecting stock standard into water for the preparation of instrument calibration standards, the water should be pre-chilled to about 4°C. Because of the high solubility of the analytes in methanol this precaution should not be necessary when injecting stock standard into methanol for fortification or making diluted standards. Purge efficiency is affected by the matrix. Caution must therefore be exercised to match the matrix of samples and standards. Water matrix standards must have two drops of 1:1 HCl added to each 40 mL aliquot, just as in the samples. Soil standards must contain 500 µL of methanol, just as in the samples.

10.0 ANALYSIS

NOTE: The parameters listed are suggested as guidelines and may be altered to reflect changes in the column, injector, and detector conditions as long as adequate sensitivity and separation is maintained.

10.1 Equipment

- Varian ARCON purge and trap autosampler(See Exhibit C for operating conditions)
- Tekmar 3100 purge and trap device (See Exhibit D for operating conditions)
- Hewlett Packard 6890 series gas chromatograph (See Exhibit E for operating conditions)
- Hewlett Packard 5973 MSD (See Exhibit E for operating conditions)
- Analytical column: Restek Rtx-VMS, 20M X 0.18 mm ID. Order # 49914
- Trap: Supelco "K" trap (Vocarb 3000)
- Injector liner: Restek Siltek # 20972-214.5 for a 5 pack.

10.2 Glassware/Supplies

NA

10.3 Reagents

NA

10.4 Procedure for Calibration, Procedure for Analysis

10.4.1 Initial tuning of MSD

10.4.1.1 Perform the H-P standard tune. Examine the tune results for acceptability as directed by the H-P/MSD instructions. Re-tune if results are not acceptable. If results are still not acceptable, contact the lab supervisor for guidance. Note the mass 219 abundance. It should be about ½ to 2/3 of the 69 abundance if all is going well. If the tune is successful proceed to the BFB tune.

10.4.1.2 Follow the procedures for the BFB tune in Exhibit F.

10.4.1.3 Alternate BFB tune procedure (to be used if procedure in Exhibit F does not work).

- Set the BFB tune limit for the filament current up from 35 to 49. This will assist in raising low mass abundances.
- Check to see that the mass 50 target abundance is raised from 1.0 to 1.1, that the 219 mass is lowered from 55 to 53, and that the 502 mass is lowered from 2% of mass 69 to 1%. These changes seem to give a tune which is more in the middle of the acceptable range for the troublesome masses of 50, 176, and 174.

10.4.1.4 Perform the BFB tune procedure on the H-P 5973 control-panel. To tune to the EPA BFB specifications from the H-P BFB auto tune follow the guidelines in 10.4.1.3 to 10.4.1.5.

10.4.1.5 After the tune is finished, adjust the EM voltage to give a mass 69 abundance of about 600,000. Note the mass 219 abundance. It should be about ½ to 2/3 of the 69 abundance if all is going well.

10.4.1.6 Note that the EM volts are often raised from the found tune setting by about 200 volts. This may not be necessary if these directions are followed and the EM is in good condition. Operate the EM at as low a voltage as possible to prolong its life.

10.4.1.7 Go into the dynamic lens setting table for your tune and multiply all the settings except 502 by 1.1000. Enter all 4 decimal places you find as a result into the table and let the computer do the rounding. This raises the abundance a little without significantly altering the BFB tune ion ratios.

10.4.1.8 Inject or purge about 5-50 ng of BFB into the MSD. Don't forget to allow for the high split ratio. For instance, 0.25 µL of a 1,000 ng/µL BFB standard purged or injected into a 100:1 split is 2.5 ng actually injected. If you are manually injecting, inject as little as possible to save the filament. Use only the "BFBTUNE" GC method for manual injections since this does not turn the filament current on for several minutes after injection. NEVER manually inject onto a purge method since the methanol won't be through the column before the filament comes on. Don't forget to save the BFB tune generated in 10.4.1.2 as a new tune file and use that file from this point on, and, when operating satisfactorily, for the 8260 method.

10.4.1.9 Average the 3 scans at the apex of the BFB peak and examine the ion abundance ratios for suitability according to the EPA tune criteria (Exhibit F). It is worth while to adjust the dynamic lens settings and/or the tune targets as required to achieve ion ratios as close to the middle of the acceptable range as possible. This will assure a long lasting tune. The smallest change in dynamic lens settings the instrument will accept is about 0.3 volts. These settings may be adjusted up or down a little to improve the tune. If the mass 50 is down towards 15% of mass 69 try raising the lens setting by a 0.3 volt unit. If this setting is raised too high the 50/69 ratio actually falls. The 174/69 ratio is ideally about 0.85. Try raising or lowering the 219 mass lens setting to adjust this ratio. When this setting is adjusted the 176/174 ratio may be thrown out of adjustment. The 414

mass lens setting seems to affect the 176/174 ratio. Try adjusting this a little. A 176/174 ratio of about 98% seems good. The dynamic lens ramping targets may also be adjusted as required. If these are adjusted properly, future tunes may be closer to the middle of the acceptable range without so much adjustment of the lens ramping settings. After each change of the tune TARGETS, a new BFB tune must be performed; this is time consuming since each tune takes from 10-15 minutes.

10.4.1.10 NOTE: There are no specific instrumental settings that will always give the most sensitive tune and still satisfy the BFB tuning criteria. Manual BFB tuning is a skill which must be developed through practice and experience. Altering one setting usually alters the "optimum" settings on other parameters. The appropriate settings for a successful tune must be "sneaked up on" by adjusting each parameter a little at a time, then adjusting the others to compensate for the change. As the instrument is used, the exact instrumental settings required to produce an acceptable tune will be altered. As more about this procedure is learned, this document will be revised.

- The HP-BFB tune seems to give a 50/69 ratio which is too low. This has been addressed by altering the tune target value from 1% to 1.1% for mass 50. The 176/69 ratio is often too high. This issue has been addressed by lowering the 219 tune target from 55% to 53%. The 176/174 ratio is also problematic. This ratio seems to go from too high to too low very quickly. This has been addressed by raising or lowering the 414/69 ratio as required. This seems to allow a finer adjustment of the 176/174 ratio without drastically affecting the 176/69 ratio. Lower the 502 target from 2% to 1% since this high a mass is of little concern to us in this application. All BFB ratios should be adjusted as close to the mid-point of their ranges as possible to lessen the frequency of re-tuning and hence re-standardization.

10.4.1.11 A satisfactory and long-lasting tune cannot be achieved if the repeller insulators and the lens insulators are not clean. These are in the MS Source. These cannot be cleaned, but must be replaced, typically at or after 6 months, depending on the amount of use. A symptom that they need replacing is that the BFB ion ratios will vary greatly between one run and the next. In particular, the isotopic ratios 173:174, 175:174, 176:174, and 177:176 will be erratic and will not stay within their limits. Also, dirty insulators will require a higher EM voltage for the electron multiplier tube, which will shorten its life. With a clean ion source a good tune should be easily achieved and should last for many months.

10.4.2 Initial Calibration procedure

10.4.2.1 Analyze and standardize the instrument on at least 7 levels of instrument calibration standards. Each reported analyte must be included in the standard list. By using at least 7 standards any analyte

may be calibrated using linear or quadratic regression. A typical concentration range of standards is one hundred fold. A calibration point at 0.5XRL should be used for each component, for accurate quantification at 1XRL.

10.4.2.2 For any concentration range of over twenty fold, use of one of the inverse weighting options available in the H-P data-system is suggested. This may give more accurate results at analyte concentrations near the lower end of the concentration range.

10.4.2.3 A correlation coefficient of 0.995 or greater must be obtained for a calibration curve to be acceptable.

10.4.2.4 System Performance Check Compound (SPCCs) –Initial Calibration
A system performance check must be made before the instrument calibration is used. Calculate the mean RF for each of the 5 SPCCs using the RF values calculated from the initial calibration. These must be greater than the minimums listed in the chart. If any are too low, the calibration can not be used.

SPCC	minimum mean response factor
Chloromethane	0.10
1,1-Dichloroethane	0.10
Bromoform	0.10
Chlorobenzene	0.30
1,1,2,2-Tetrachloroethane	0.30

The RF is calculated as follows:

$$RF = \frac{A \times C_{IS}}{A_{IS} \times C}$$

Where:
A = Peak area (or height) of the SPCC
A_{IS} = Peak area (or height) of the internal standard for the SPCC
C = Concentration of the SPCC in the purge vessel
C_{IS} = Concentration of the internal standard in the purge vessel

As an example: The in solution concentration of the internal standard is 0.0167 µg/mL for a 15 mL sample in the purge vessel. The in solution concentration each SPCC is 0.02 µg/mL (for the 20×RL Water standard) in the purge vessel. If A=1348910 and A_{IS}=2177431, RF calculates to 0.517.

10.4.2.5 BFB Tune Verification
Inject (or purge) from 5 to 50 ng of 4-bromofluorobenzene (BFB) onto the 6890 column (take into account the split ratio). BFB is introduced into all purged samples by the Arcon autosampler as BFB is a component of the Surrogate/Internal Std. Mix. Exhibit F shows the acceptable

ranges for the ion ratios. If the tune is not successful, retry with another run. If the tuning criteria are frequently or consistently not met, refer to the MS tuning procedures in section 10.4.1, or notify the laboratory supervisor for direction. If the criteria are met the calibration curve may be used.

10.4.2.6 Second source standard:

Analyze a second source standard at 20×RL (for most components) with each calibration curve. The standard should be within ± 25% of the nominal concentration.

10.4.3 Analytical Runs: Continuing calibration check procedures

10.4.3.1 Continuing calibration verification standards (CCVS) must be analyzed daily before sample analysis, at the end of the run, and once every 12 hours of analysis time. These are instrument calibration standards that are near the mid-range of the initial calibration set and include all reported analytes. For a typical standard range of 100 fold, a 20 x reporting limit (RL) standard is suggested. The general criteria of acceptability of CCV data for this method is a found concentration that is less than or equal to ±20% from the "true" or nominal concentration for the reported analytes. There may be exceptions to this acceptable range. Some compounds which are not listed in 8260B, such as t-butyl alcohol, may exhibit wider variation even when the system is functioning normally. As experience is gained, a normal acceptance range will be determined for these compound(s). Due to normal variation in instrument performance, up to 10% of the reported compounds may be allowed a variation of 20-40% (inclusive). If the above criteria are met, the instrument is considered to be in tune and in calibration for the duration of the analytical set for any analyte that meets the above conditions. Data for that analyte may be reported without qualification. Data generated for analytes which are outside the above criteria may be reported with qualification if the data meets the data quality objectives of the end user. The laboratory supervisor must be consulted in these instances to determine the appropriate course of action.

10.4.3.2 The first CCV must be analyzed before any other reported data file is generated. The final CCV must be analyzed after the last reported sample or QC data file is generated. If all reported analytes are within the acceptance limits, the instrument is considered to be acceptably calibrated for the duration of the analytical set. Any data for any analyte which was generated between two CCVs, either one of which showed unacceptable recovery for that analyte, shall be considered suspect. In the event that unacceptable CCV data is generated, the problem, most often a leak or the presence of active sites in the instrument(s), must be found and the instrument restored to proper operation. If the problem(s) cannot be corrected by other measures,

the instrument must be re-tuned and a new initial calibration curve is generated.

10.4.3.3 If the internal standard retention time in any CCV shifts by more than 30 seconds from the retention time found in the mid level standard of the most recent initial calibration curve the system is considered out of control. The problem(s) must be found and corrected before continuing analysis. Re-analysis of samples analyzed while the system was malfunctioning is required.

10.4.3.4 SPCCs: A system performance check must be made during every 12-hr. analytical shift. The CCVS must meet their minimum response factors. See section 10.4.2.4. If the minimum response factor is not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, column contamination, active sites in the column or chromatographic system.

10.4.3.5 Internal Standard Response: For a system to be considered in control, the response of the internal standard in any CCV should not vary by more than a factor of 2 (from -50% to +100%) from that of the corresponding mid level standard in the most recent initial calibration curve. The problem(s) must be found and corrected before continuing analysis. Re-analysis of samples analyzed while the system was malfunctioning is required. The most likely problem is that response will gradually become too low. This is most likely due to aging of the electron multiplier tube. An increase in EM Voltage will restore response.

10.4.3.6 Surrogate Standard Recovery: In general, surrogate recovery is expected to be within the range 80%-120%. As analysis of samples proceeds, surrogate recovery will be analyzed, and acceptability ranges adjusted to reflect actual laboratory generated data.

10.4.3.7 LCS and MS/MSD recoveries: In general, LCS, LCSD, MS and MSD recoveries are expected to be within the range of 70%-130%, with RSDs of duplicate pairs $\leq$ 20%. As analysis of samples proceeds, surrogate recovery will be analyzed, and acceptability ranges adjusted to reflect actual laboratory generated data

10.4.3.8 The Lot 1 stock standards should be used to make the CCVs and the LCS and LCSD. The Lot 2 stock standards should be used to make the MS and MSD.

10.4.3.9 A blank must be run during every 12-hr. analytical shift. The blank must be <RL for all reported analytes. If it is not, the system must be evaluated, and corrective action must be taken. Any samples run between the positive blank and the previous and subsequent blanks must be re-evaluated. The most common cause of a positive blank is carryover from a high sample. TBA is particularly prone to carryover, and may carry over even from a mid-level standard. Any sample positive for TBA, if it follows a standard or sample high in

TBA, should be suspected of carryover. In general, TBA is only found in samples high in MTBE. Experience will reveal the levels of other analytes that are likely to cause carryover.

10.4.4 Procedure for Analysis
- 10.4.4.1 Samples are retrieved from storage (see LA003).
- 10.4.4.2 Water samples are loaded directly into the autosampler.
- 10.4.4.3 Soil samples are prepared for analysis as directed in section 9.5 and the diluted extracts are loaded into the auto sampler.

10.5 Autosampler and P&T conditions
- 10.5.1 Autosampler and P&T conditions are listed in Exhibits C and D

10.6 Confirmation of Positive Samples
- 10.6.1 In general, the procedures for analyte identification recommended in section 7.6 of EPA method 8260B rev. 2 will be followed as closely as possible.
- 10.6.2 Several of the analytes do not exhibit two other ions that are greater than 30% intensity of the base ion.
- 10.6.3 Some of the analytes have ions that are over 30% of the abundance of the base ion but have co-eluting interferents overlapping the analyte peak at the m/z ratios of interest. These interferents may be significant at and near the RL of these analytes. Some sources of these interferents are Trap and analytical column bleed, and especially multiple, coeluting peaks from gasoline present in the samples.
- 10.6.4 For these reasons, qualifier ions must be chosen carefully. The most obvious ones are sometimes not the most practical ones. The skill and experience of the analyst must be relied upon for identification of analytes using ion ratios. In complex chromatograms with tentatively identified analytes at low levels, the analyst is advised to not rely entirely on the automated computer data system identification algorithms. The analyst should carefully examine the full spectrum of collected data and look for characteristic patterns of even minor ions as valuable clues to correct identification of analytes.

10.7 Special Precautions
- 10.7.1 The analytes listed in this method are very volatile. Extreme caution must be used to prevent significant analyte losses from both standard solutions and samples.
- 10.7.2 Identification of oxygenates, lead scavenger compounds and BTX&E constituents at low levels is difficult in samples which have co-eluting hydrocarbon peaks present.

11.0 CALCULATIONS

NONE: The calculations are performed by the H-P Chemstation software.

12.0 ACCEPTANCE LIMITS

See the most current limits in Omega. Until enough data is available to calculate limits, default limits of 70-130% recovery will be used.

13.0 REPORTING AND DOCUMENTATION

Extraction data will be documented as per SOP LA-003. Analytical data will be reported by Laboratory Information Management System (LIMS), see SOP LA-003.

14.0 WASTE DISPOSAL

Standards are deposited in the halogenated purge waste satellite accumulation storage container. The methanol from the soil extracts is poured into the non halogenated satellite accumulation storage container.

MET CODE VERSION
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EXHIBIT A

Reporting Limits

Parameter	Water (µg/L)	Soil (µg/g)
t-amyl methyl ether (TAME)	1.0	0.020
benzene	0.50	0.005
t-butyl alcohol	10.0	0.20
bromobenzene	1.0	0.020
bromochloromethane	1.0	0.020
bromodichloromethane	1.0	0.020
bromoform	1.0	0.020
bromomethane	1.0	0.020
n-butylbenzene	1.0	0.020
sec-butylbenzene	1.0	0.020
t-butylbenzene	1.0	0.020
carbon tetrachloride	1.0	0.020
chlorobenzene	1.0	0.020
chloroethane	1.0	0.020
chloroform	1.0	0.020
chloromethane	2.0	0.040
2-chlorotoluene	1.0	0.020
4-chlorotoluene	1.0	0.020
dibromochloromethane	1.0	0.020
1,2-dibromo-3-chloropropane	2.0	0.10
1,2-dibromoethane (EDB)	2.0	0.040
dibromomethane	1.0	0.020
1,2-dichlorobenzene	1.0	0.020
1,3-dichlorobenzene	1.0	0.020
1,4-dichlorobenzene	1.0	0.020
dichlorodifluoromethane	1.0	0.020
1,1-dichloroethane	1.0	0.020
1,2-dichloroethane	1.0	0.020
1,1-dichloroethene	1.0	0.020
cis-1,2-dichloroethene	1.0	0.020
trans-1,2-dichloroethene	1.0	0.020
1,2-dichloropropane	1.0	0.020
1,3-dichloropropane	1.0	0.020
2,2-dichloropropane	1.0	0.020
1,1-dichloropropene	1.0	0.020
cis-1,3-dichloropropene	1.0	0.020
trans-1,3-dichloropropene	1.0	0.020
ethylbenzene	0.5	0.005
ethyl t-butyl ether (ETBE)	1.0	0.020
hexachlorobutadiene	2.0	0.040
isopropylbenzene	1.0	0.020
di-isopropyl ether (DIPE)	1.0	0.020
p-isopropyltoluene	1.0	0.020

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methylene chloride	2.0	0.040
methyl t-butyl ether (MTBE)	1.0	0.020
naphthalene	2.0	0.040
n-propylbenzene	1.0	0.020
styrene	1.0	0.020
1,1,2,2,tetrachloroethane	1.0	0.020
1,1,1,2,tetrachloroethane	1.0	0.020
tetrachloroethene	1.0	0.020
toluene	0.5	0.005
1,2,3-trichlorobenzene	2.0	0.040
1,2,4-trichlorobenzene	2.0	0.040
1,1,2-trichloroethane	1.0	0.020
1,1,1-trichloroethane	1.0	0.020
trichloroethene	1.0	0.020
trichlorofluoromethane	1.0	0.020
1,2,3-trichloropropane	2.0	0.040
1,3,5-trimethylbenzene	1.0	0.020
1,2,4-trimethylbenzene	1.0	0.020
vinyl chloride	1.0	0.020
m,p-xylene	0.5	0.005
o-xylene	0.5	0.005
gasoline	50	1.0

8260 INTERNAL STANDARD
fluorobenzene
chlorobenzene-d5
1-bromo-4-fluorobenzene (BFB)

8260 SURROGATE STANDARDS
dibromofluoromethane
1,2-dichloroethane-d4
toluene-d8
1,4-dichlorobenzene-d4

GASOLINE INTERNAL STANDARDS
fluorobenzene
chlorobenzene-d5
1-bromo-4-fluorobenzene (BFB)
toluene-d8

GASOLINE SURROGATE STANDARDS

dibromofluoromethane
1,2-dichloroethane-d4
1,4-dichlorobenzene-d4

EXHIBIT B

FLOW CHART OF EXTRACTION FOR SOIL SAMPLES

Weigh 10 g of soil into a 40 mL VOA
↓
Add 5 mL P&T methanol
↓
Fortify appropriate quality control standard
↓
Cap VOAs securely
↓
Gently agitate VOAs 2 minutes to extract analytes into MeOH
↓
Centrifuge VOAs for 2-5 minutes as required to settle particulates
↓
Add 500 µL of methanol extract to a 40 mL VOA containing about 40 mL of P&T water
Fill the vial completely with P&T water
↓
Immediately cap the second VOA
Invert the vial about 5 times to mix the contents
↓
Place the VOA containing the diluted extract into the autosampler

MET CODE VERSION
ME 247 002

EXHIBIT C

Varian Arcon Purge & Trap Autosampler Operating Conditions

ORGCMS-2

- Method: 01 (water) used for both water and soil
- 1st vial___(Enter the number of the first vial to be sampled here)
- last vial___(Enter the number of the last vial to be sampled here)
- Sample volume: 15 mL
- Dilution factor: No
- Rinse volume: 15 mL
- #Rinses: 01
- Std 1: Yes (Internal-and Surrogate standards are contained in vial 1)
- Std 2: Yes (Methanol is kept in vial 2)
- Stir: No
- With stir timer(min): 0.0
- With settle time: 0.0
- Syringe flushes: 01
- Desorb time: 0.5 min. NOTE: This time must match the desorb time listed in the P&T method to keep the instruments in sync.
- Operation mode: Remote
- Cycle timer: 00.0
- Aux timer: 00.0
- Link to method: 0.0

ORGCMS-3

- Method: 01 (water) used for both water and soil
- 1st vial___(Enter the number of the first vial to be sampled here)
- last vial___(Enter the number of the last vial to be sampled here)
- Sample volume: 5 mL
- Dilution factor: No
- Rinse volume: 5 mL
- #Rinses: 01
- Std 1: Yes (Internal-and Surrogate standards are contained in vial 1)
- Std 2: Yes (Methanol is kept in vial 2)
- Stir: No
- With stir timer(min): 0.0
- With settle time: 0.0
- Syringe flushes: 01

MET CODE VERSION
ME 247 002

- Desorb time: 1.0 min. NOTE: This time must match the desorb time listed in the P&T method to keep the instruments in sync.
- Operation mode: Remote
- Cycle timer: 00.0
- Aux timer: 00.0
- Link to method: 0.0

MET CODE VERSION
ME 247 002

EXHIBIT D

Tekmar 3100 Purge & Trap Device ORGCMS-2
Operating Conditions

-	Method:	14
-	Line temp:	140°C
-	Valve temp:	140°C
-	Purge ready temp:	35°C
-	Purge temp:	0°C
-	Mount temp:	40°C
-	Turbo cool temp:	-20°C
-	MCS line temp:	40°C
-	Sample Heater:	On
-	Pre purge time:	0.00
-	Preheat time:	1.00
-	Sample temp:	40°C
-	Sample fill:	0.00
-	Purge time:	11.00
-	Dry purge time:	1.00
-	GC start:	DesStart
-	Cryo Focuser:	OFF
-	GC cycle time:	0.00
-	Cryo stby:	100
-	Cryofocus temp:	-150°C
-	Inject time:	1.00
-	Cryo inj temp:	180°C
-	Desorb preheat:	255
-	Desorb time:	1.5 min. NOTE: This time must match the Desorb time in the ARCON method for the two instruments to properly synchronize.
-	Desorb temp:	260°C
-	Sample drain:	On
-	Bake time:	9.00
-	Bake temp:	280°C
-	BGB off delay:	3.00
-	MCS Bake temp:	310°C

MET CODE VERSION
ME 247 002

EXHIBIT D

Velocity Purge and Trap Concentrator ORGCMS-3
Operating Conditions

-	Valve Oven Temp.	120°C
-	Transfer Line temp:	120°C
-	Sample Mount temp:	45°C
-	Purge ready temp:	40°C
-	DryFlow Standby temp:	150°C
-	Standby Flow:	10 mL/min.
-	Pre-Purge Time:	0.00 min.
-	Pre-Purge Flow:	40 mL/min.
-	Sample Heater:	On
-	Sample Preheat time:	0.50 min.
-	Preheat Temp:	30°C
-	Purge Time:	11.00 min.
-	Purge Temp:	0°C
-	Purge Flow:	40 mL/min.
-	Dry Purge Time:	1.00 min.
-	Dry Purge Temp:	40°C
-	Dry Purge Flow:	40 mL/min.
-	GC Start:	Start of Desorb
-	Desorb Preheat Temp:	250°C
-	Deborb Drain:	On
-	Desorb Time:	1.0 min.
-	Desorb Temp:	260°C
-	Desorb Flow:	100 mL/min.
-	Bake time:	6.00 min.
-	Bake temp:	300°C
-	Bake Flow:	350 mL/min.
-	Focus Temp.:	-150°C
-	Inject Time:	1.00 min.
-	Inject Temp.:	180°C

MET CODE VERSION
ME 247 002

EXHIBIT E

Hewlett Packard 6890 series Gas Chromatograph & Hewlett Packard 5973 MSD Operating Conditions

ORGCMS-2

Column:	Restek RTX-VMS .18mm ID, df 1 um, 20 Meter, catalog #49914
Inlet Sleeve:	Restek Gooseneck 2mm ID, Siltek coated, catalog #20795-214.1
Inlet Temp:	220C
Split Ratio:	50:1
Constant Flow:	0.5 ml/min
Oven Temp:	Initial Temp =40°C Hold 2 min Ramp 1: 3°C /min to 70°C, Hold 0 min. Ramp 2: 32°C /min to 220°C, Hold 2 min. Total time: 18.69 min.
MS data collection:	Scan
Start time:	1 min, ions collected 39-105, 1.69 scans/sec At 4.5 min, ions collected 49-134, 2.20 scans/sec At 10.5 min, ions collected 49-228, 2.09 scans/sec

ORGCMS-3

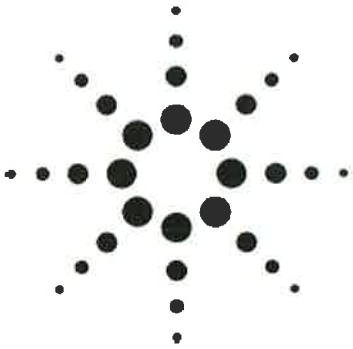
Column:	Restek RTX-VMS .18mm ID, df 1 um, 20 Meter, catalog #49914
Inlet Sleeve:	Restek Gooseneck 2mm ID, Siltek coated, catalog #20795-214.1
Inlet Temp:	220C
Split Ratio:	50:1
Constant Flow:	0.7 ml/min
Oven Temp:	Initial Temp =40°C Hold 2 min Ramp 1: 3°C /min to 70°C, Hold 0 min. Ramp 2: 32°C /min to 220°C, Hold 2 min. Total time: 18.69 min.
MS data collection:	Scan
Start time:	1 min, ions collected 49-105, 1.69 scans/sec At 3.93 min, ions collected 49-134, 2.20 scans/sec At 9.2 min, ions collected 49-230, 2.09 scans/sec

MET CODE VERSION
ME 247 002

EXHIBIT F
BFB TUNE PROCEDURE

BFB Tuning for Environmental Analysis: Three Ways to Succeed

Application



Environmental

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Abstract

The United States Environmental Protection Agency methods 524.2, 8260B, and Contract Laboratory Program Statement of Work employ purge and trap concentration of volatile compounds in water samples with analysis by gas chromatography/mass spectrometry. Each method requires the mass spectrometer to meet specific tuning criteria before proceeding to actual samples. This paper summarizes these tuning criteria, and shows three different ways that the Agilent Technologies 6890/5973 gas chromatograph/mass selective detector system can be tuned to meet them. A very simple and robust procedure is described in the Modified Autotune section. A quick reference guide for this procedure is given at the end of the paper under Modified Autotune Summary.

Introduction

If you are already familiar with 4-bromofluorobenzene (BFB) tuning and evaluation procedures, you may want to go directly to the section titled "Modified Autotune Summary" found at the end of this paper. It offers an alternative approach for tuning Agilent 6890/5973 GC/MSD systems that is routinely successful in this laboratory.

The United States Environmental Protection Agency (USEPA) has developed several methods for the analysis of volatile organic compounds (VOCs) in water samples. The three most widely used procedures all employ purge and trap (P&T) sample introduction followed by capillary column gas chromatography with mass spectral detection (P&T/GC/MS). USEPA Method 524.2 revision 4[1] is used for drinking water analysis while Method 8260B revision 2[2] is used for wastewater. The USEPA Contract Laboratory Program Statement of Work (CLP-SOW)[3] uses a similar P&T/GC/MS method for the analysis of hazardous waste.

There are many similarities among these three USEPA volatiles methods. One common requirement is that the GC/MS system must be tuned in such a way that 4-bromofluorobenzene (BFB) meets specific ion abundance criteria. This requirement helps to ensure that data are comparable between instruments of different design and

EXHIBIT F
BFB TUNE PROCEDURE, continued

Modified Autotune

With the convenience of automated tuning procedures available in the Agilent ChemStation software, most analysts have gladly given up the idea of manually tuning their 5973 MSDs. A combination of automated tuning with a slight manual modification has given excellent BFB results in this laboratory. The total process is easy and usually takes just a few extra minutes after the autotune is complete. The steps are described below and are summarized in a "quick reference" format in the next section.

1. From the Manual Tune portion of the software, perform an Autotune (select Tune/Autotune). This algorithm tunes the Agilent 5973 MSD for maximum sensitivity over the entire mass range and is widely used by methods that do not specify other tune criteria. This autotune emphasizes overall sensitivity by improving abundances for higher mass ions (for example, 502). As a result, the Autotune procedure typically gives an abundance for *m/z* 50 that is too low to meet 524.2 and 8260 criteria and an abundance of *m/z* 174 that may be too high, even for CLP-SOW tuning.
2. After completing the Autotune procedure, choose Edit MS Params (under the AdjParam menu item) which will display the screen shown in Figure 7.

Figure 7. The Edit Parameters screen found by selecting AdjParam/Edit MS Params in the main Manual Tune window.

3. Two changes are required in the default values used for adjusting parameters in this view. First, under the MoreParams menu, choose Ramp Params and change the "Stop" value for the ion focus to 140 as shown in Figure 8. Close this window and choose AcqParams under the MoreParams window and change Mass 3 from 502 to ion 50 as shown in Figure 9. Close this window and return to the main Edit Parameters screen (Figure 7).

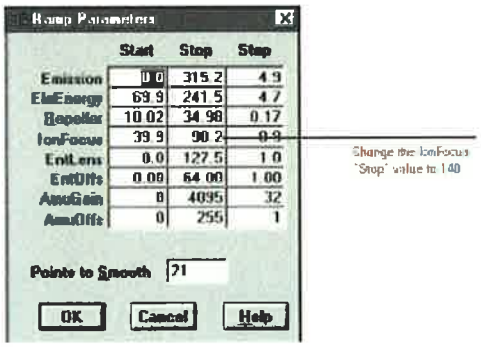

Figure 8. This window allows the user to set ranges for the various tuning parameters. The default ion focus "Stop" setpoint of 90 was set to 140.

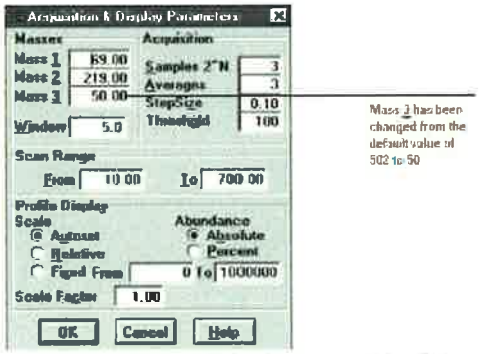

Figure 9. Acquisition and Display Parameters window. *M/z* values of 69, 219, and 50 have been chosen so that these responses can be ramped and their relative abundances displayed.

4. Highlight the IonFocus window with the cursor and then select Ramp. This gradually ramps the ion focus voltage over the specified range while monitoring the response of ions 69, 219, and 50. After about a minute, a plot of these ion responses vs. the ion focus voltage appears in the window (Figure 10).

EXHIBIT F
BFB TUNE PROCEDURE, continued

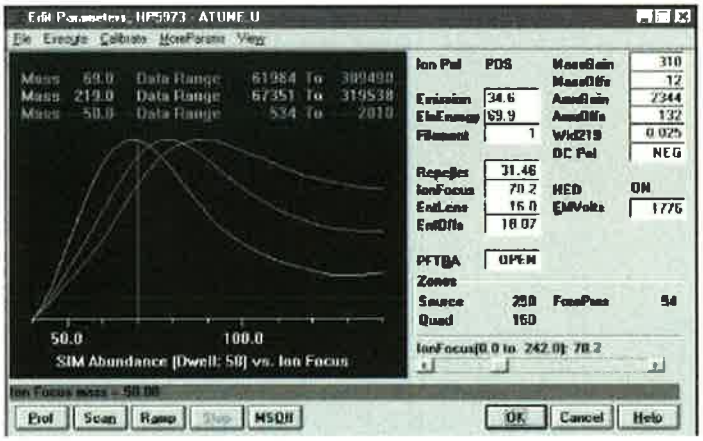

Figure 10. Abundances for ions 69, 219, and 50 while ramping the Ion Focus from 40 to 140.

5. Under the View dropdown menu item, choose Expand. This view shows the current Ion Focus setting, the abundance of *m/z* 69 and the relative abundances of ions 219 and 50 (Figure 11). From the plot, it is easy to see that an increase in the Ion Focus value should increase the 50:69 ratio while reducing the 219:69 ratio. These are exactly the changes that should enable the MSD to pass BFB tuning criteria.

Note that the ion focus ramping procedure can also be performed from the main Manual Tune screen by choosing Ramp/Ramp Ion Focus on the dropdown menu.

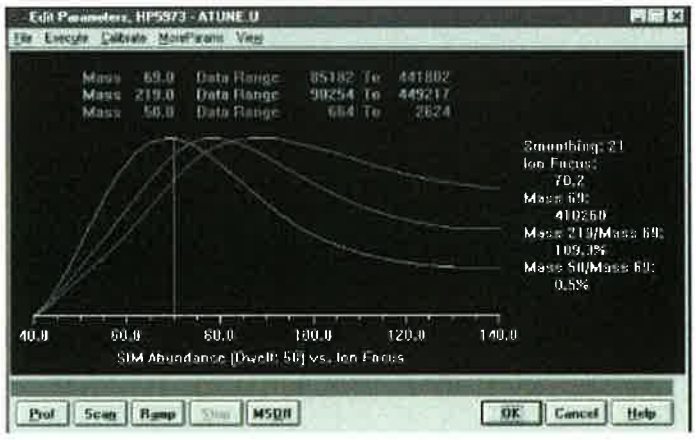

Figure 11. An expanded view of the SIM-Abundance-vs-Ion Focus plot obtained by selecting View/Expand. This view allows one to drag the vertical line to different setpoints while observing changes in the ion relative abundances.

EXHIBIT F
BFB TUNE PROCEDURE, continued

6. The vertical line indicates the current ion focus setpoint. Use the cursor to drag this setpoint line to the right while observing the change in the 219:69 and 50:69 ratios. Agilent laboratories have had good success by setting the Ion Focus to values between 100 and 135 V. This should result in a 219:69 ratio in the 60-80% range and a 50:69 ratio that is 0.8 or greater. If tuning to meet 524.2 requirements, the 219/69 ratio should be on the low side of this range.

   An alternative to the above procedure is to select Scan in the Edit Parameters window (Figure 7) while monitoring ions 69, 219, and 50. The 219:69 and 50:69 ratios are displayed under the Relative Abundance heading and are updated with each scan. Highlight the Ion Focus setting and adjust its value using the slider bar. The effect of different Ion Focus values will be seen almost immediately in the ion ratios. These ratios will bounce around somewhat, but trends can be seen over a few scans. A good choice for the 50:69 ratio would be about 0.85.

7. Click OK and return to the Manual Tune screen. Under the Calibrate menu item, choose Adjust Abundances, which will automatically reset the electron multiplier to get ion abundances in the optimum range. Save the tune, choosing a new name for the tune file (for example, BFB1.U). Return to Instrument Control (View/Instrument Control) and be sure to select this tune file for the method used to acquire the BFB checkout chromatogram. Inject or purge an appropriate amount of BFB and evaluate the tune using the software tools provided (Figures 2 through 4). Assuming that it passes, assign this tune to the P&T/GC/MS volatiles method in use.

Figure 12 shows the spectrum (average of the three scans across the apex with baseline subtraction) for a 1-µL syringe injection (50 ng/µL split 50:1) of BFB using an ion focus value of 115 V. All other parameters (except for the electron multiplier) were set by the Autotune algorithm. This spectrum passes any of the tuning criteria listed in Table I but has a higher 174/95 ratio than was achieved using the standard BFB tune.

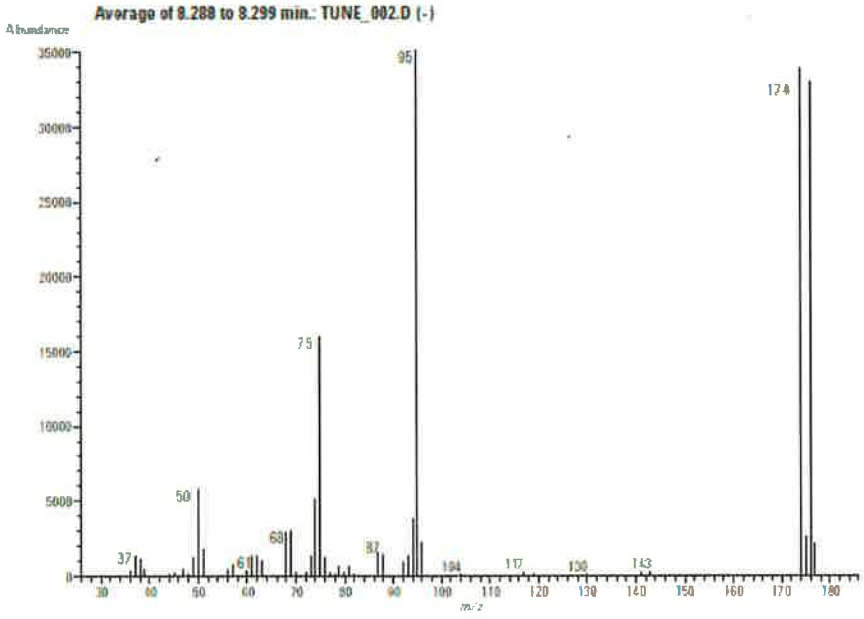

Figure 12. Average spectrum of BFB obtained after using the procedure described under Modified Autotune. After running a standard Autotune, the Ion Focus value was increased to 115 V.

EXHIBIT F
BFB TUNE PROCEDURE,continued

The true test of a successful BFB tune is whether it holds up during repetitive VOC analyses and through normal instrument maintenance procedures. In one extreme test, the same BFB tune easily passed CLP-SOW criteria during a period when two different MSD sources were installed and four different filaments were used. On one Agilent 6890/5973 GC/MS instrument this procedure did not work until the MSD source was cleaned.

Finally, a note of caution is appropriate. While these techniques have worked well for the Agilent 6890/5973A and N GC/MSD systems, this does not imply that the same procedures are appropriate for older Agilent MSDs. Tuning frequency is dictated by the nature of the samples, choice of column and other factors such as column bleed and source cleanliness. If the source becomes too dirty, it must be cleaned in order to pass BFB tuning criteria, no matter which approach is taken.

Modified Autotune Summary

These steps summarize the procedure for modifying the standard Agilent 5973 Autotune to pass BFB tuning criteria. It is provided here as a quick reference guide for those who are already familiar with tuning procedures.

1. In the Manual Tune portion of the Agilent GC/MS ChemStation software, perform a standard Autotune.
2. In the Ramp Parameters window, change the Ion Focus Stop value to 140.
3. In the Acquisition & Display Parameters window, change ion 502 to 50.
4. In the Edit Parameters window click on Ion Focus and then on Ramp.
5. Adjust the Ion Focus value so that the 50/69 ratio is 0.8 or larger. The 219/69 ratio usually falls in the 60 to 80% range. When this PFTBA ion ratio is under 70%, the 174/95 ratio of BFB is usually under 100%.
6. In the Manual Tune window under the Calibrate menu item, adjust ion abundances.
7. Save the tune file with a new name, assign it to the method and verify that the tune passes by injecting a BFB sample according to the method requirements.

Conclusions

There are several ways to tune the Agilent 6890/5973 GC/MSD system to meet any of the USEPA BFB tuning criteria. However, factors such as source cleanliness, choice of column, flow rates and instrument-to-instrument variability make each GC/MSD system unique. Automated BFB and target tuning procedures are normally successful but the 174/95-ion ratio may not be high enough to meet laboratory needs. In our experience, the most robust and long-lasting BFB tunes were generated by the procedure outlined above under Modified Autotune. The procedure takes just a few minutes to complete.

References

1. *Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry*, Method 524.2, revision 4.1, U.S. Environmental Protection Agency, Office of Research and Development, National Exposure Research Laboratory, Cincinnati, OH (1995).
2. *Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)*, Method 8260B, revision 2 (1996).
3. *USEPA Contract Laboratory Program Statement of Work for Organics Analysis, Multi-Media, Multi-Concentration, OLM04.2*, USEPA Contract Laboratory Program, Office of Emergency and Remedial Response.

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem.

MET CODE VERSION
ME 247 002

EXHIBIT G
BFB (4-BROMOFLUOROBENZENE) MASS INTENSITY CRITERIA

Ion ratio	Required intensity (relative abundance)
50:95	15-40%
75:95	30-60%
95:95	100%, Base Peak
96:95	5-9%
173:174	less than 2%
174:95	greater than 50%
175:174	5-9%
176:174	95-101%
177:176	5-9%

METHOD MODIFICATION FORM

MET, CODE, & VERSION: ME 247.02

EFFECTIVE DATE: 12/14/12

TITLE: Volatile Organic Compounds and Gasoline in Water and Soil by Purge and Trap GC-MS Utilizing EPA 8260B

PAGE(S): Various SECTION(S): 8.2.8, 8.3.2, 9.5.1,

MODIFICATION:

Section 8.0 PREPARATION OF STANDARDS

Section 8.2.8 (Added):

Stock Internal Standard for Soils prepared by methanol extraction

Supelco Internal Standard Mix, 5,000 µg/mL, catalog # 49113-U.

Working Internal Standard for soils prepared by methanol extraction

Take 500 µL of stock internal standard solution and dilute to 10 mL with purge and trap grade methanol. Final concentration is 250 µg/mL.

This solution is used to fill the second internal standard/surrogate vial on the Arcon autosampler.

Section 8.2.8 (Added):

Stock Surrogate Standard for soils prepared by methanol extraction

Supelco Surrogate Standard Mix High Concentration, 10,000 µg/mL, catalog # 49112-U.

Working Surrogate Standard for soils prepared by methanol extraction

Take 200 µL of stock internal standard solution and dilute to 10 mL with purge and trap grade methanol. Final concentration is 200 µg/mL.

Section 8.3.2 (Modified):

Chart for preparation of 8260 working standards for Soil:
Use this chart to make a set of working standards for calibrating the soil method. The lower level standards are made by diluting levels 9, 10, and 11, as one would dilute a sample. For example a 20xRL, Level 9 standard diluted 1:10 makes a 2xRL, Level 6 standard.

Level in Enviroquant Method	Standard Level	Amount of Stock/Surrogate	Final Volume (mL)	Final Concentration (mg/Kg, unless noted)				
				Standard Analytes	m- & p-Xylenes	Ketones	TBA	Surrogate
1	0.05×RL	108 µL of 20×RL	43	0.001	0.002	0.005	0.02	-
2	0.1×RL	215 µL of 20×RL	43	0.002	0.004	0.01	0.04	-
3	0.2×RL	430 µL of 20×RL	43	0.004	0.008	0.02	0.08	-
4	0.5×RL	430 µL of 50×RL	43	0.01	0.02	0.05	0.2	1.5 %
5	1×RL	430 µL of 100×RL	43	0.02	0.04	0.1	0.4	2 %
6	2×RL	4.3 mL of 20×RL	43	0.04	0.08	0.2	0.8	10 %
7	5×RL	4.3 mL of 50×RL	43	0.1	0.2	0.5	2.0	15 %
8	10×RL	4.3 mL of 100×RL	43	0.2	0.4	1.0	4.0	20 %
9	20×RL	5/9 µL	43	0.4	0.8	2.0	8.0	100 %
10	50×RL	12/14 µL	100	1.0	2.0	5.0	20	150 %
11	100×RL	23/19 µL	100	2.0	4.0	10	40	200 %

SECTION 9.0 EXTRACTION

Section 9.5.1.a (Insert):

Using a 50 µL syringe add 40 µL of working surrogate standard (Section 8.2.8) to each field sample and quality control sample; including method blank, laboratory control sample, laboratory control sample duplicate, matrix spike, and matrix spike duplicate. Spike directly onto the soil. Proceed immediately to Section 9.5.2 and the addition of methanol preservative.

APPROVALS/REVIEW:

SIGNATURE	TITLE	DATE
	CHEMIST II	12/14/12
	LAB MANAGER	12/13/12
	QA OFFICER	12/13/12

* SIGNATURES NOTE: MODIFICATIONS MUST BE SIGNED BY ALL PERSONS OF EQUIVALENT JOB TITLES TO THOSE WHO SIGNED THE ORIGINAL SOP.

NORTH COAST LABORATORIES, LTD.

MET	CODE	VERSION	COPY	EFFECTIVE DATE	MSW FILE
ME	322	01	D	06 / 21 / 2012	G:SOPS\ME322v.1

	NAME	TITLE	DATE
PREPARED BY:		CHEMIST II	06 / 21 / 12
APPROVED BY:		LAB SUPERVISOR	06 / 13 / 12
APPROVED BY:		LAB MANAGER	6 / 19 / 12
REVIEWED BY:		QA OFFICER	06 / 21 / 12

1.0 **TITLE**

EPA Method 6020 Trace Metal Analysis in Soils and Sludges Using the Perkin Elmer Elan 9000 ICP Mass Spectrometer

2.0 **SCOPE**

This Standard Operating Procedure describes the daily operation, tuning, optimization and analytical procedures for the analysis of samples according to EPA Method 6020 for the elements listed in Exhibit B. This method is applicable to soil, biosolids and solid waste matrices. Routine operation and maintenance procedures for the ELAN 9000 are described in the ELAN 9000 Hardware Manual. Detailed instructions on the operation of the ELAN software are found in the ELAN ICP-MS Software Manual.

3.0 **DEFINITIONS**

Calibration Blank – A volume of reagent water acidified with the same acid matrix as in the calibration standards. The calibration blank is a zero standard and used to calibrate the ICPMS instrument.

Calibration Standards – Solutions prepared from the dilution of stock standard solutions. These are used to calibrate the instrument response with respect to analyte concentrations.

CCB – Continuing Calibration Blank standard.

CCV – Continuing Calibration Verification standard.

DI – Laboratory-grade deionized water.

ICP – Inductively Coupled Plasma Spectrometer.

ICPMS – Inductively Coupled Plasma Mass Spectrometer.

ICV – Initial Calibration Verification standard, a second source standard used to verify the accuracy of the daily ICPMS calibration.

Instrument Detection Limit – The concentration equivalent to the analyte signal which is equal to three times the standard deviation of a series of 10 replicate measurements of the calibration blank signal at the selected analytical masses.

Internal Standards – Non-interfering analytes added to sample and standard solutions in known amounts and used to monitor and correct instrument drift and matrix effects.

Isobaric Interference – a positive interference that occurs when an isotope of one element is at the same nominal mass as an isotope of another element of interest (e.g. Mo 98 and Ru 98).

Laboratory Fortified Blank (LFB) – Equivalent to Laboratory Control Sample (LCS), a spiked blank solution that is put through the same preparation procedures as samples.

Laboratory Fortified Matrix (LFM) – Equivalent to Matrix Spike (MS), a spiked aliquot of sample that is put through the same preparation procedures as samples.

Laboratory Reagent Blank (LRB) – Equivalent to Method Blank (MB), an unfortified blank solution that is put through the same preparation procedures as samples.

Linear Dynamic Range – The concentration range over which the instrument response to an analyte is linear.

Molecular Interference – a polyatomic interference caused by molecular species formed in the plasma with plasma (argon) or matrix ions, resulting in molecules with the same nominal mass or mass/charge ratios as the isotope of interest.

Tuning Solution – A solution which is used to determine acceptable instrument performance prior to calibration and sample analyses.

4.0 REFERENCES

ELAN 9000 Hardware Manual, Perkin Elmer, 2003.

ELAN Version 3.0 Software Guide, Perkin Elmer, 2003.

EPA Method 6020, Inductively Coupled Plasma – Mass Spectrometry, Revision 0, 1992 in SW-846 Test Methods for Evaluating Solid Waste, Volume 1A.

EPA Method 3050B, Acid Digestion of Sediments, Sludges, and Soils, Revision 2, 1996 in SW-846 Test Methods for Evaluating Solid Waste, Volume 1A.

North Coast Laboratories, Ltd. SOP ME 155, version 05.

5.0 SUMMARY

Sample solutions are pneumatically nebulized into a radio frequency plasma where ionization and desolvation occurs. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated based on their mass-to-charge ratio and detected by a quadrupole mass spectrometer.

6.0 INTERFERENCES

6.1 Isobaric and molecular interferences are corrected for with the use of equations programmed into the ELAN software (see Exhibit B for list of correction equations). These interferences are mitigated mathematically by measuring the intensity present at another isotope and using

isotope ratios to calculate the amount of the interfering species (see ELAN Software Manual pp. 10-5 to 10-16 for a fuller discussion of correction equations).

6.2 Molecular or polyatomic interferences such as oxides and doubly charged ions can be further reduced by proper tuning and optimization procedures (Section 10.3) which reduce their relative abundance to 3 percent or less prior to sample analysis.

6.3 Matrix interferences and instrument drift are minimized by the use of internal standards in all sample and standard solutions.

7.0 EQUIPMENT AND SUPPLIES

7.1 Perkin-Elmer ELAN 9000 ICPMS system: includes the ELAN 9000 instrument with nickel cones, a pneumatic cross-flow nebulizer with a Scott-type spray chamber made of acid resistant Ryton plastic.

7.2 Perkin-Elmer AS-93Plus Autosampler with 16 mL and 50 mL polypropylene autosampler tubes.

7.3 PolyScience water recirculator

7.4 Pump windings:

Black-black 0.75mm i.d. (sample introduction)
Green-green 1.85mm i.d. (drain)
Red-red 1.14mm i.d (autosampler rinse)
Purple-white 2.79 i.d. (autosampler rinse)

7.5 Liquid argon (UHP grade)

7.6 Calibrated mechanical pipettes with metal-free tips:

10-100 µL
100-1000 µL
1000-5000 µL

7.7 100 mL polypropylene volumetric flasks for calibration standards

7.8 250, 500 and 1000 mL borosilicate glass volumetric flasks

8.0 REAGENTS AND STANDARDS

8.1 Note: Laboratory deionized water, trace metals grade nitric acid, and trace metals grade hydrochloric acid are used to prepare all standard solutions unless noted otherwise. Store solutions in polyethylene or Teflon bottles. Record the preparation of all standards in the Standards Preparation Logbook.

8.2 **Rinse Solution, Calibration Blank, CCB** – a 1% nitric acid/0.5% HCl solution. The Calibration blank and CCB are spiked with 200 µL Internal Standard Stock Solution (Section 8.3 below) per 100 mL.

8.3 **Internal Standard Stock Solution** – 100 mg/L Li6; 10mg/L Bi, Ho, In, Rh, Sc, Tb, Y; and 50 mg/L Ge in 1% nitric acid. Prepare by pipetting 12.5 mL of a 1000 ppm Germanium, 25mL of a 1000 ppm Lithium 6, solution and 2.5 mL each of 1000 ppm solutions of Bismuth, Yittrium, Rhodium, Indium Scandium, Holmium and Terbium into a 250 mL volumetric flask partially filled with DI. Add 2.5 mL concentrated nitric acid and bring to volume with DI. This solution may be prepared or purchased from an appropriate supplier.

8.4 **Tuning Solution** – 10 µg/L Ba, Be, Ce, Co, Cu, In, Pb, Mg, and Rh in 1% nitric acid. Prepare by pipetting 10 µL each of 1000 ppm stock solutions of Barium, Beryllium, Cerium, Cobalt, Copper, Indium, Lead, Magnesium and Rhodium into a 1000 mL

volumetric flask partially filled with DI. Add 10 mL nitric acid and bring to volume with DI. This solution may also be purchased.

8.5 **Auto Lens Solution** – 10 µg/L Be, Co and In in 1% nitric acid. Prepare by pipetting 10 µL each of 1000 ppm stock solutions of Beryllium, Cobalt and Indium into a 1000 mL volumetric flask partially filled with DI. Add 10 mL of nitric acid and bring to volume with DI.

8.6 **Dual Detector Cross-Calibration Solution** – 200 µg/L Mg, Cu, Rh, Cd, Pb and 2000 µg/L Be in 1% nitric acid. Prepare by pipetting 50 µL each of 1000 ppm stock solutions of Magnesium, Copper, Rhodium, Cadmium, Lead and 500 µL of Beryllium into a 250 mL volumetric flask partially filled with DI. Add 2.5 mL nitric acid and bring to volume with DI.

8.7 **Initial Calibration Verification Stock Solution** – Second source standard prepared for ICPMS analysis. 1000 µg/L Ag, Al, Ba, Be, Cd, Co, Cu, Cr, Mn, Mo, Ni, Pb, Sb, Se, Tl, V, Zn in 2% nitric acid. Prepared by pipetting 5.0 mL from each of two 100 ppm mixed standards (IV-7 and IV-19 from Inorganic Ventures) into a 500 mL volumetric flask partially filled with DI. Add 10 mL nitric acid and bring to volume.

8.8 **Initial Calibration Verification Standard** – 10 µg/L Ag, Al, Ba, Be, Cd, Co, Cu, Cr, Mn, Mo, Ni, Pb, Sb, Se, Tl, V, Zn in 2% nitric acid/0.5% hydrochloric acid. Prepared by pipetting 1.0 mL of ICV Stock Solution (Section 8.7) into a 100 mL volumetric flask partially filled by DI. Add 2 mL nitric acid, 0.5 mL hydrochloric acid, 200 µL Internal Standard Solution (Section 8.3) and bring up to volume. Note that this solution is not diluted in the same fashion as samples and therefore is read as 100 µg/L on the readout.

8.9 **Continuing Calibration Verification Standard** – The 100 ppb calibration standard (Section 8.11 below) is used as the CCV throughout sample analysis to verify the run is still in calibration.

8.10 **Multi-element Calibration Stock (MCS) Solution** – The multi-element stock standard is a 20 mg/L in 5% nitric acid (with trace tartaric acid) comprised of the following elements: Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Tl, Th, U, V, and Zn. It is Instrument Calibration Standard 1 manufactured by Spex CertiPrep, Inc. (Catalog # CL-CAL-1).

8.11 **Calibration Standards** – The following solutions are used.

Final Concentration	mL HNO3	mL HCl	µL Internal Standard	µL Multi-element Solution	Diluted with DI to final volume
0.0 ppm	1 mL	0.5 mL	200 µL	0 mL	100 mL
0.25 ppm	1 mL	0.5 mL	200 µL	0.25 mL of 100ppm cal std	100 mL
0.50 ppm	1 mL	0.5 mL	200 µL	0.50 mL of 100ppm cal std	100 mL
1.0 ppm	1 mL	0.5 mL	200 µL	1.0 mL of 100ppm cal std	100 mL
10.0 ppm	1 mL	0.5 mL	200 µL	50.0 µL of 20 ppm MCS	100 mL
50.0 ppm	1 mL	0.5 mL	200 µL	0.25 mL of 20 ppm MCS	100 mL
100.0 ppm	1 mL	0.5 mL	200 µL	0.50 mL of 20 ppm MCS	100 mL

8.12 **Interference Check Standard A –** a solution containing 10,000 µg/mL chloride, 2,000 µg/mL carbon, 1,000 µg/mL each Al, Ca, Fe, K, Mg, Na, P and S, 20 µg/mL each Mo and Ti. This is a certified solution purchased from Inorganic Ventures.

8.13 **Interference Check Standard B –** a solution containing 2.0µg/mL each Ag, As, Cd, Co, Cr, Mn, and Ni. This is a certified solution purchased from Inorganic Ventures

8.14 **Interference Check Solutions –** Interference check solution ICSA is prepared by adding 5.0 mL of interference check standard A (Section 8.12) and 1.0 mL trace metal nitric acid to a 50 mL volumetric flask. Bring to volume with deionized water. Make fresh weekly. Interference check solution ICSAB is prepared by adding 5.0 mL of interference check standard A, 5.0 mL of interference check standard B (Section 8.13) and 1.0 mL trace metal nitric acid to a 50 mL volumetric flask. Bring to volume with deionized water. Make fresh daily.

9.0 QUALITY CONTROL

9.1 Initial Demonstration of Laboratory Performance

9.1.1 Linear Dynamic Range

9.1.1.1 Calibrate the instrument (Section 10).

9.1.1.2 Run a series of increasing concentration standards close to the upper linear range of the instrument. The Upper Linear Dynamic Range limit is defined as the concentration above which the measured value deviates from the known value of the prepared standard by more than 10 percent.

9.1.1.3 Re-determine the Upper Linear Dynamic Range limit whenever a) the detector is changed, b) a new power tube is installed in the RF generator or c) a different type of sample introduction system is installed.

9.1.2 Instrument Detection Limits (IDLs) should be determined for all analytes.

9.1.3.1 Calibrate the instrument.

9.1.3.2 Run a blank (Section 8.11) as if it were a sample for a series of 10 sequential measurements.

9.1.3.3 Calculate the standard deviation of the 10 values and multiply the result by three to determine the IDL for each analyte.

9.1.3.4 IDLs should be calculated every three months, whenever a new analyst runs the instrument, whenever a significant change in sample preparation procedures occurs or whenever there is a significant change in the instrument (new detector, etc.).

9.1.4 Method Detection Limits (MDLs) should be determined for all analytes.

9.1.4.1 Fortify a reagent water blank with a concentration of each analyte that is two to five times the estimated detection limit (Remember that each solution used must include 200 µL Internal Standard Solution (Section 8.3) per 100 mL). The spike concentrations may be estimated from the IDL values or previous MDL studies.

9.1.4.2 Take seven replicate aliquots of this solution and process through the entire method including normal sample preparation steps. Calculate the standard deviation of the measured concentrations for the seven aliquots of each analyte. Multiply the standard deviation by 3.143 (student's t

value for n=7 and a 99% confidence level) to obtain the calculated MDL values (in concentration units).

9.1.4.3 MDLs should be determined when a new analyst operates the instrument, and when there is a major change to the method or to the instrument.

9.2 Mandatory Laboratory Performance Guidelines

9.2.1 Method Blank (MB) – A minimum of one MB must be run for every batch of 20 non-drinking water samples. MB values greater than ½ the reporting limit may indicate laboratory contamination or instrument malfunction. Check the calibration and run the blank calibration standard if necessary. If the method blank reads above the reporting limit either raise the reporting limit or redigest the appropriate samples and reanalyze.

9.2.2 Laboratory Control Sample (LCS) – One LCS must be analyzed with each batch of samples. The preparation of the MB, LCS and Matrix Spikes is described more thoroughly in the appropriate sample preparation SOPs (ME 094 – Drinking Waters, ME 118 – Nondrinking Waters, ME 145 – CAM Extractions, ME 083 – TCLP Extractions, ME 282 – Wastewaters). The percent recovery control limits for LCS samples is 80-120%. If the laboratory control sample recoveries for analytes of interest exceed the control limits, check the instrument calibration (and recalibrate if necessary) and reanalyze the standards as well as the samples for that batch. If the control samples are still out of range it may be necessary to redigest the sample batch. Consult with the lab supervisor. The percent recovery is calculated according to the following:

Percent Recovery = (LCS result – MB result)/spike value

9.2.3 Quality Control Sample Analysis – analysis of a second source multi-element standard that is carried out when beginning the use of this method and following daily calibrations. The results must be within ± 10% of the stated value. The Quality Control Sample is equivalent to the ICV (Section 8.8).

9.2.4 Matrix spikes (MS) – The laboratory must spike a known amount of analyte into a minimum 10% of all samples. Matrix spikes are normally in duplicate (i.e. two aliquots of sample are spiked). The spike levels are the same as LCS spike levels but originate from a separate lot or source. The percent recovery control limits for matrix spikes is 75-125%. If the spike recoveries for the analytes of interest exceed the limits, dilute the sample and reanalyze to lessen the matrix effect. If the results do not agree within 10% do not report the undiluted sample results. The percent recovery is computed as follows:

$$\text{Percent Recovery} = \frac{(C_{MS} - C_S)}{S} \times 100$$

Where: C_{MS} is the measured concentration in the matrix spike
C_S is the measured concentration in the sample
S is the amount of analyte added to the sample matrix

For duplicate samples a control limit of 20% RPD (relative percent difference) should not be exceeded for analyte values 100 times the instrument detection limit.

Note: Recovery calculations are not acceptable if the sample concentration exceeds ten times the spike concentration for the analyte(s) of interest.

9.2.5 Internal Standard Responses

Monitor the intensities of the internal standards during each run. The intensities of the internal standards in all samples, QC, and continuing calibration checks should be within 60-120% of the original internal standard responses in the calibration blank. If the intensities exceed these limits, flush the system with the rinse blank. If the intensities do not return to normal there may be a problem with the sample introduction system or the sample cones may be clogged. Do not accept results when the internal standard intensities exceed the control limits. In general the changes in internal standard intensity should not exceed 10% from one sample to the next unless the change is an attenuation due to a matrix effect or clogged line.

9.2.5 The Initial and Continuing Calibration Verification control limits are 90-110%. Following calibration, these standards must be analyzed at the beginning, every 10 samples or less and at the end of the analytical run. Sample results should be bracketed by CCVs that are within acceptance limits. (The exception would be samples with non-detectable levels of analyte(s) where the same analytes in the CCVs exceed the upper limit).

9.2.6 The interference check solutions (Section 8.14) should be analyzed at the beginning of every analysis after the calibration is complete. Analytes that are not present in ICSA should read below their respective detection limits. Analytes that are added to ICSAB should be recovered within 20% of their true values.

10.0 SAMPLE ANALYSIS PROCEDURE

10.1 Pre-start checks: Turn on the computer and load the ELAN NT software by double clicking on its icon. (See Exhibit C for the default instrument parameters and operating conditions). Check the following:

10.1.1 Vacuum pump oil – Open the front left door and examine the level and color of the pump oil in each pump. When the color of the vacuum pump oil is darker than that of iced tea it should be replaced. The oil in the smaller rotary pump should be changed at least once each six months because it is not exposed to oxygen and therefore does not darken readily. Particulates in the oil can lead to pump malfunction.

10.1.1 Vacuum pressure – Read the vacuum pressure from the "Instrument" window in the software. The torch should not be lit for analyses unless the pressure is less than $3x10^{-6}$.

10.1.2 Peristaltic pump winding – Check the tubing daily. Replace the tubing when it becomes flattened or when sample RSDs begin to increase.

10.1.3 Rinse solution – The rinse solution container should be at least one quarter full at the start of analysis.

10.1.4 Waste container – Empty and neutralize (per SOP WA 007) the acidic waste water when the container is over one half full.

10.1.5 Argon pressure – The argon supply pressure should be about 60 psi with the plasma on. Below 45 psi a safety interlock automatically shuts off the torch. Check the level of liquid argon in the dewar prior to analysis.

10.1.6 Interface cones – Periodically remove and inspect the outside of the sampling and skimming cones near the orifice. Deposits may be removed with a mild nitric acid solution and a cotton swab. Check the orifice of each cone with a magnifying glass. The orifice should be about 1 mm in diameter and round. Widened or corroded orifices will result in poor instrument performance.

10.1.7 Coolant – The cooling water pressure should be between 35 and 55 psi. A red light on the recirculator indicates the coolant level is low. Turn on the wall fan to facilitate the efficiency of the recirculator.

10.2 Torch Ignition and Warm-Up

10.2.1 Open the valve between the instrument and the liquid argon dewar.

10.2.2 Autosampler probe – send the autosampler probe to the rinse position using the *Sampling* screen of the *Method* window. Torch ignition – click on the *Instrument* icon to open the *Instrument* window, and then click on the Front Panel button to show the *ELAN Control Panel* screen. The system status indicator must say "Ready". Click on the Plasma Start button to initiate the ignition sequence

10.2.3 Peristaltic pump – ensure the flow is relatively smooth ("jerky" flow results in high RSDs and poor overall performance). Adjust the tubing as necessary by following the instructions in the ELAN 9000 Hardware Manual, page 3-23.

10.2.4 Warm-Up – allow instrument to warm-up for at least 30 minutes to ensure the torch and interface are at thermal equilibrium. During this time a series of blanks and 100 ppb standards can be run to warm up the detector and stabilize the blank intensities.

10.3 Tuning and Optimization Procedures

10.3.1 These procedures may be carried out during warm-up.

10.3.2 X-Y adjustments are necessary whenever the cones have been cleaned or replaced. Place the probe into the tuning solution (Section 8-4). Open **Tuning.wrk** and click on the analyze sample button. Monitor the Indium intensity while adjusting the X and Y knobs to achieve the optimal intensity. See page 3-42, ELAN Version 3.0 Software Guide.

10.3.3 Mass calibration. Place the probe into the tuning solution, open **Tuning.wrk** and click **Tune Mass Spec**. Repeat this procedure until all analytes are within $\pm$ 0.05 amu. Save the tuning file. See pp. 3-40 to 3-41 of the Software Guide.

10.3.4 Peak resolution. Place the probe into the tuning solution, open **Tuning.wrk.** Then open the **TUNETRY** method. Select **Peak Width Only** and click **Tune Mass Spec** to initiate scanning. The final resolution for each analyte must be less than or equal to 0.65 amu measured at 10% peak height (this is equivalent to 0.75 amu measured at 5% peak height – see Wolf, 2003). See pg. 3-41 of the Software Manual for the procedure to adjust peak resolution using DAC Resolution values. Save the tuning file.

10.3.5 Nebulizer Gas Flow. Open **Neb Lens Power Optimize.wrk**. In the Auto Optimize tab under Parameter Description highlight "Nebulizer Gas Flow". Select the Get Analyte List button and choose Rh as the analyte. Aspirate the

tuning solution. Select Maximum Intensity as the Optimization criterion. Press Optimize. Save the Optimization file when finished.

10.3.6 Lens Voltage. Open **Neb Lens Power Optimize.wrk**. In the Auto Optimize tab under Parameter Description highlight "Lens Voltage". Select the Get Analyte List button and choose Rh as the analyte. Aspirate the tuning solution. Select Maximum Intensity as the Optimization criterion. Press Optimize. Save the Optimization file when finished.

10.3.7 Auto Lens Voltage. Open **Auto Lens Calibration.wrk**. In the Auto Lens tab click "Clear Calibration". Then click the Get Analyte List. This will bring up a list containing Be, Co and In. Aspirate the Auto Lens Solution (Section 8.5). Click "Calibrate". Save the Optimization file.

10.3.8 Instrument Performance. Open **Daily Performance.wrk**. Aspirate the tuning solution. In the Sample window, click "Analyze Sample". The performance criteria are shown in Exhibit A. When optimized to satisfaction, make an extra copy of the Daily Performance Report and place it in the Daily Performance Logbook. (Note: Oxides and double charged levels can be reduced by slightly decreasing the nebulizer flow rate).

10.3.9 Optimizing the Detector. These procedures are only necessary when sensitivity cannot be recovered through the above optimization procedures or when the detector is replaced. Refer to pp. 3-48 to 3-51 of the Software Manual.

10.4 Running Samples

10.4.1 Create a new dataset.

10.4.2 Prepare calibration standards as per Section 8.11.

10.4.3 Open NCLSOIL method. Edit the Sample window for batch analysis with new sample information. [Note: Soil samples are routinely diluted 1:10: therefore, the "mL Aliquot" is 1. The Calibration action for the first sample must be "Analyze blank, standards, and sample". The calibration action for subsequent samples in the batch will be "Analyze Sample". Save Sample file.

10.4.4 Load the calibration blank, calibration standards, samples and QC samples into the autosampler positions specified in the autosampler page of the method.

10.4.5 Select the samples to be analyzed by highlighting the row numbers (click and drag the left mouse button). Select "Analyze Batch" to begin analysis.

10.4.6 Monitor the initial QC. Check the calibration blank Summary Report for signs of contamination and the rest of the calibration and initial QC Summary Reports for signs of problems. Periodically check the instrument to make sure it is operating smoothly. Monitor the internal standards (Section 9.2.4) for matrix effects, sample preparation errors or instrument malfunction.

10.4.7 Dilute and reanalyze samples when analytes exceed the linear dynamic range or matrix interferences are suspected.

10.4.8 Instrument Shutdown. When the plasma is turned off the peristaltic pump will automatically shut off. Loosen the tubing. Send the autosampler probe to the rinse station. Loosen the pump windings on the autosampler. Cap standards and any samples that require reanalysis.

10.4.9 Print data set. Open Report Option. Open NCLQUANT.CAL. Print Calibration file. Close Report Option. Save workspace.

10.4.10 Close ELAN program.

11.0 CALCULATIONS AND REPORTING

11.1 All calculations necessary to convert raw data (ion counts/second) are performed by the ELAN software.

11.2 All calculations performed in the ELAN software are based on the ratio of the analyte intensity (cps) to the internal standard intensity (cps). In all calculations the ration of the analyte intensity to internal standard intensity is taken before any other calculation is performed.

11.3 The ELAN report option for EPA method 6020 is nclreport.rop.

11.4 Benching data. Open ICPMS icon on the desktop. Choose appropriate test code. Choose samples to export to Omega. Save file.

12.0 CONTINGENCIES

12.1 When one or more analytes in the Quality Control samples are not within the acceptance limits described in Section 9.0 the data set may still be accepted if 1) they are not the analytes of interest or 2) the problem is related to the internal standard used and can be corrected by using a different internal standard and reprocessing the data.

12.2 Poor relative standard deviation (RSDs or precision) on standards and samples - Poor RSDs may be due to dirty or worn interface cones, improperly operating nebulizer or worn pump windings. Refer to the ELAN Hardware manual.

13.0 WASTE DISPOSAL

All sample digestates and nebulizer waste is acidic and should be treated and disposed of as per SOP WA 007.

14.0 SAFETY

Analysts should wear personal protective equipment such as nitrile gloves and safety glasses to prevent direct exposure to acid solutions. Preparation of solutions in Section 8.0 that require the addition of concentrated acids should be done in a fume hood or other well ventilated area.

MET CODE VERSION
ME 322 01

EXHIBIT A
ELAN 9000 PERFORMANCE CRITERIA

TEST	10 PPB RESPONSE
^{24}Magnesium Sensitivity	>100,000 cps
^{115}Indium Sensitivity	>400,000 cps
^{102} Rhodium Sensitivity	>300,000 cps
Precision	<3%
Ba^{2+}/Ba	<0.03
CeO/Ce	<0.03
Background Level (Mass 220)	<25 cps
Noise (Mass 220) Standard Deviation	<5

cps = counts per second

MET CODE VERSION
ME 322 01

EXHIBIT B

Table of Isotopes Monitored and Interference Correction Equations

Analyte	Symbol	Isotopes Monitored	Correction Equations
Aluminum	Al	27	
Antimony	Sb	121,**123**	Sb 123 = Sb 123 – 0.127189*Te 125
Arsenic	As	75	= As 75 – 3.127*[ArCl 77 – (0.815*Se 82)]
Barium	Ba	135,**137**	
Beryllium	Be	9	
Cadmium	Cd	**111**,114	Cd 111 = Cd 111 – 1.073*[MoO 108 – (0.712*Pd 106)] Cd 114 = Cd 114 – 0.026826*Sn 118
Chromium	Cr	**52**,53	
Cobalt	Co	59	
Copper	Cu	**63**,65	
Lead	Pb	206,207,**208**	Pb 208 = Pb 208 + Pb 206 + Pb 207
Manganese	Mn	55	
Molybdenum	Mo	98	= Mo 98 – 0.110588*Ru 101
Nickel	Ni	60	
Selenium	Se	77,**82**	Se 82 = Se 82 – 1.008696*Kr 83
Silver	Ag	107	
Thallium	Tl	205	
Vanadium	V	51	= V 51 – 3.127*[ClO 53 – (0.113*Cr 520]
Zinc	Zn	**66**,67,68	
Internal Standards			
Scandium	Sc	45	
Germanium	Ge	72	
Terbium	Tb	159	
Holmium	Ho	165	

MET CODE VERSION
ME 322 01

EXHIBIT C

ELAN 9000 ICPMS Operating Conditions

INSTRUMENT OPERATING CONDITIONS /METHOD PARAMETERS

Instrument manufacturer: PerkinElmer
Model number: SCIEX ELAN 9000 ICP-MS
Autosampler: PerkinElmer AS 93 Plus PE
Technique: Inductively Coupled Plasma Mass Spectrometry
Software Version: PerkinElmer ELAN software
RF Power: 1100 watts
Plasma Gas Flow: 15 L/min
Auxilliary Gas Flow: 1 L/min
Nebulizer Gas Flow: 0.88-0.96 L/min
Solution Pump Rate: 1.5 mL/min
Sample Introduction System: Cross-flow with Scott spray chamber
Rinse Time: 35 seconds @ 48 rpm
Sample uptake time: 25 seconds @ 48 rpm
Equilibration Time: 10 seconds @ 24 rpm
Analysis Time (total): 2:26 minutes
Detection Mode: Dual Mode
Lens: AutoLens Enabled
Sampler/Skimmer Cones: Nickel
Scanning Mode: Peak Hopping
Number of Points/Peak: 1
Dwell Time: 50 ms per point
Number of Sweeps/Reading 20
Number of Readings/Replicate: 1
Number of Replicates: 3
Total Acquisition Time: 4:17 minutes

North Coast Laboratories, Ltd.

Trace Metals in Solid and Aqueous Matrices, EPA 200.7 and 6010

Category	Code	Version	Effective Date	File Location
ME	330	01	03/14/2017	G:\SOPs

Prepared	Name:	Bob Stuart	Title:	Inorganic Lab Supervisor
	Signature:		Date:	3/14/17
Technical Review	Name:	Greg Jordan	Title:	Laboratory Manager
	Signature:	Greg Jordan	Date:	3-13-17
QA Approval	Name:	Jeff Schindler	Title:	QA Officer
	Signature:		Date:	03/14/2017

1.0 SCOPE AND APPLICATION

This SOP provides the analytical method to analyze solid and aqueous matrices for select metals by inductively coupled argon plasma, utilizing EPA method 6010B and 200.7. The analytes are listed in Section 8.0 Reporting Limits.

2.0 SUMMARY

Sample digestates are introduced into argon plasma where analyte-specific emission spectra are produced. The intensities are monitored and measured at specific wavelengths.

3.0 DEFINITIONS

Calibration Blank - A reagent blank that is prepared as a working standard without the addition of analyte(s) to autozero an instrument prior to the analysis of the calibration standard(s)

Continuing Calibration Verification Standard "CCV" - A mid-level standard used to verify instrument performance during analysis

Laboratory Control Spike "LCS" - A matrix blank spiked with a verified amount of analyte(s) to determine accuracy and precision

Matrix Spike "MS" - A sample spiked with a verified amount of analyte(s) to determine accuracy, precision, and matrix interference

Method Blank "MB" - A matrix blank similar to the batch being run to determine interference and contamination

4.0 RESPONSIBILITIES

4.1 Users

4.1.1 Follow the SOP

4.1.2 Alert Supervisor or QAU if this SOP needs to be updated

4.2 Laboratory Supervisor

4.2.1 Enforce the use of this SOP

4.2.2 Review results

4.3 Quality Assurance Unit

4.3.1 Review SOP

5.0 SAFETY

5.1 The toxicity and carcinogenicity of each reagent used in this method has not been precisely defined. All of the chemicals used in this method should be treated as a potential health hazard. Relevant safety data sheets should be reviewed prior to starting this analysis.

5.2 Use appropriate personal protective gear (safety glasses or goggles, lab coat, and nitrile gloves) when preparing reagents, samples, and standards.

5.3 Although the Agilent 720 has a shielded torch window it is recommended that the analyst also wear UVEX safety glasses that are compliant with ANSI Z87.1-2003

6.0 INTERFERENCES

6.1 Spectral Interferences

Emission lines from other analytes may overlap with the analyte of interest leading to false positives or inaccurate test results. The best way to avoid this interference is to select wavelengths that are free of spectral overlap. The Interferent Check Standard (Section 10.14) is helpful in identifying interferences from overlapping peaks.

6.2 Chemical Interferences

If the metal analyte is not atomized in the plasma, but instead forms some other chemical species, the emitted wavelength will not be the same wavelength as the one emitted by the atom and the results will be low. Because of the high temperature of the plasma the only significant chemical interferences are ionization interferences for the alkali metals, especially sodium and potassium. Ionization interferences are managed by adding an ionization suppressant, such as a cesium solution (Section 10.2), which will be preferentially ionized instead of the analytes. Alternatively dilute samples that read high for sodium (>70 ppm) and/or potassium (>50 ppm).

6.3 Physical Interferences

These are dissolved solutes or samples with viscosities different from the calibration standards (saltwater or high acid samples, for instance). This type of interference is minimized by the appropriate dilution of the sample.

6.4 Background Correction

The The Agilent 720 ICP Expert software offers an automated correction technique called Point Sum, which is available in two forms: Fitted or Off Peak. The Fitted background correction works well for both simple and complex matrices and applies peak-shaping functions to the analyte peak to create a model of the measured spectrum. Once the model has been fitted, the analyte peak component will be removed from the equation to leave a model of the background, which is then automatically corrected. This program corrects for interfering peaks within the spectrum window that do not directly overlap with the analyte peak. For wavelengths less than 250 nm choose 2 to 3 Fitted points for the lowest detection limits. For wavelengths above 250 nm 1 point per peak is recommended. Off Peak background correction can be used when the background is simple and linear in nature. See 'Selecting Background Correction' in the Help menu in the ICP Expert II software for a fuller discussion.

7.0 SAMPLE COLLECTION AND PRESERVATION

7.1 Aqueous Samples

7.1.1 Use plastic sample containers. Do not reuse sample containers

7.1.2 Preserve with 1+1 metals grade nitric acid to a pH <2

7.2 Non-Aqueous Samples

7.2.1 Use glass sample containers. Do not reuse sample containers

7.3 Store samples in the walk-in refrigerator at ~4°C until analyzed

7.4 Samples must be analyzed within 6 months of collection

7.5 Dissolved Metals

7.5.1 Filter samples through a 0.45 micron membrane filter

7.5.2 Samples must be filtered at the time of collection or as soon as practically possible. The official hold time is 15 minutes from the time of collection.

8.0 REPORTING LIMITS

Analyte	Acid Digested Aqueous Matrices (ppb)		Acid Digested Soil Matrices (ppm)		Acid Preserved Aqueous Matrices (ppb)	
	MDL	PQL	MDL	PQL	MDL	PQL
Aluminum, Al	1.7	20	0.58	2	1.5	20
Antimony, Sb	6.7	10	0.82	2	N/A	N/A
Arsenic, As	4	10	0.83	2	N/A	N/A
Barium, Ba	0.28	1	0.016	1	0.14	1
Beryllium, Be	0.29	1	0.012	0.5	0.1	1
Boron, B	3.3	10	0.38	1	1.2	5

Analyte	Acid Digested Aqueous Matrices (ppb)		Acid Digested Soil Matrices (ppm)		Acid Preserved Aqueous Matrices (ppb)	
	MDL	PQL	MDL	PQL	MDL	PQL
Cadmium, Cd	0.61	5	0.012	1	0.1	1
Calcium, Ca	9.8	20	0.19	5	4.3	20
Chromium, Cr	1.7	5	1.3	2	0.14	5
Cobalt, Co	2.2	5	0.21	1	0.69	5
Copper, Cu	0.85	2	0.13	1	0.82	2
Iron, Fe	0.21	15	0.14	5	1.1	15
Lead, Pb	4.5	5	0.38	1	N/A	N/A
Magnesium, Mg	2.4	20	0.3	2	2.3	20
Manganese, Mn	0.17	1	0.014	1	0.1	1
Molybdenum, Mo	5.5	10	0.2	1	2.1	5
Nickel, Ni	0.75	5	0.14	1	1.1	5
Potassium, K	3.2	10	0.18	5	1.3	20
Selenium, Se	8.3	20	0.98	2	N/A	N/A
Silver, Ag	2.9	10	0.27	1	0.54	5
Sodium, Na	3.8	20	0.45	5	4.1	20
Strontium, Sr	0.024	1	N/A	N/A	N/A	N/A
Thallium, Tl	3	10	0.53	2	N/A	N/A
Vanadium, V	0.65	1	0.039	1	0.55	1
Zinc, Zn	0.93	5	0.15	1	0.32	10

9.0 QUALITY CONTROL

9.1 The analyst must make an initial demonstration of capability "IDOC" establishing the ability to generate acceptable accuracy and precision using this method

9.2 The following QC samples should be prepared and analyzed at the same time as the unknown samples

9.2.1 MB – 1 per batch

9.2.2 LCS and LCSD – 1 each per batch

9.2.3 MS and MSD – 1 each per batch

NOTE: The batch size limit for drinking waters is 10 samples. The batch size limit for other matrices is 20 samples

9.3 MDL Requirements – A valid MDL study should be on file

10.0 STANDARD PREPARATION

10.1 Apparatus and Materials

- Balance, analytical capable of weighing 0.0001 g
- Wash Bottle, LDPE 1 L (for metals use only)
- Acid resistant 1 L dispenser for concentrated nitric acid
- Graduated cylinders, various
- Syringes, 10 mL, plastic (B-D) for 25 mm 0.45 micron PES syringe filters
- Volumetric flasks, various, polypropylene
- Volumetric pipettes, various
- Autosampler tubes, 14 mL round bottom, 16 x 100 mm, polypropylene

10.2 Reagents and Chemicals

- Nitric acid "HNO_3", trace metal grade
- Deionized water "DI", laboratory grade Class II
- 2% nitric acid rinse water "2% HNO_3"– Add 20 mL of nitric acid to a wash bottle containing ~500 mL DI. Add DI to 1 L
- Triton-X 100 wash solution (2% nitric acid, 0.1% Triton-X 100) – Add 20 mL nitric acid and 1 mL Triton-X 100 to a 1 L volumetric flask containing ~500 mL DI. Add DI to 1 L
- Cesium chloride "CsCl", 99.99%, trace metal grade
- 1% CsCl solution (ionization suppressant solution) – Dissolve 1.0 g CsCl per 100 mL DI

10.3 Wavelength Calibration Solution

10.3.1 Order neat standard from Agilent (6610030000) or an equivalent supplier

10.3.2 Prepare a 50 ppm K and 5 ppm each Al, As, Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Se, Mo, Sr, and Zn by making a 1:10 dilution of the neat standard with 2% HNO_3

10.4 Torch Alignment Solution

10.4.1 Order neat standard

- This solution contains 5 ppm Mn

10.4.2 Prepare in-house

10.4.2.1 Wash a 200 mL polypropylene vol flask with 2% HNO_3 and rinse with DI

10.4.2.2 Add ~100 mL DI, 4 mL HNO_3, and 1.0 mL 1000 ppm Mn standard

10.4.2.3 Bring to 200 mL with DI and mix thoroughly

10.5 Calibration Stock Solution "CSS" – Order neat standard from Inorganic Ventures (IV-28) or an equivalent supplier

- This solution contains 100 ppm each Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Li, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sr, Ti, Tl, V, and Zn; 1000 ppm K; 50 ppm Si

10.6 Initial Calibration Verification "ICV" Stock Solution – Same as Calibration Stock Solution but from a separate lot or source

10.7 CLP Interferents A Solution – Order from CPI (4400-INTA1-100) or equivalent

- This solution contains 5000 ppm each Al, Ca, and Mg; 2000 ppm Fe

10.8 CLP Analytes B Solution - Order from CPI (4400-INTB1-100) or equivalent

- This solution contains 50 ppm each Ba, Be, Co, Cr, Cu, Mn, and V; 100 ppm each Ag, Cd, Ni, Pb, and Zn

10.9 CLP Alternate Analytes B Solution - Order from CPI (4400-INTB2-100) or equivalent

- This solution contains 10 ppm each Ca, Fe, Mg and Si; 100 ppm each Al, Sb, As, B, Mo, Se, Na, and Tl

10.10 Calibration/Rinse Blank – Prepared daily

10.10.1 Wash a 1000 mL Nalgene with 2% HNO_3 and rinse with DI

10.10.2 Add ~900 mL of DI to the Nalgene, then add 20 mL of HNO_3

10.10.3 Bring to 1000 mL with DI and mix thoroughly

10.11 Calibration Standard – Prepare whatever levels are needed for the run

NOTE: For all calibration standards the stated concentration applies to all analytes except potassium, which is 10X higher, and silica, which is 0.5X lower

10.11.1 Wash a 100 mL polypropylene volumetric flask with 2% HNO_3 and rinse with DI

10.11.2 Add ~50 mL DI and 2 mL HNO_3

10.11.3 Add the amount of Calibration Stock Solution determined from the following equation:

$$\text{CSS volume (mL)} = \frac{\text{Calibration Standard conc. (ppb) x Final volume (mL)}}{\text{CSS concentration (ppb)}}$$

Example:

$$\text{CSS volume} = \frac{25{,}000 \text{ ppb x } 100 \text{ mL}}{100{,}000 \text{ ppb}} = 25.0 \text{ mL}$$

10.11.4 Bring to 100 mL with DI and mix thoroughly

10.12 ICV Standard, 1000 ppb – Prepare as needed

10.12.1 Use ICV Stock Solution and prepare as shown in Section 10.11. If 200 mL of ICV Standard are needed, double the recipe

10.13 Continuing Calibration Verification "CCV" Standard, 1000 ppb – Prepare as needed

10.13.1 Wash a 500 mL polypropylene volumetric flask with 2% HNO_3 and rinse with DI

10.13.2 Add ~300 mL of DI, 10 mL HNO_3, and 5.0 mL CSS

10.13.3 Bring to 500 mL with DI and mix thoroughly

10.14 Interference Check Standard "ICS" – Prepare as needed

10.14.1 Wash a 200 mL polypropylene volumetric flask with 2% HNO_3 and rinse with DI

10.14.2 Add the following:
~100 mL DI
4 mL HNO_3
10 mL Interferents A Solution
2 mL CLP Analytes B Solution
2 mL CLP Alternate Analytes B Solution

10.14.3 Bring to 200 mL with DI and mix thoroughly

10.15 Tuning Solution

- Dilute the Wavelength Calibration Stock Solution 1:10 with 2% HNO_3

11.0 INSTRUMENT SET UP AND OPTIMIZATION – AGILENT 720

NOTE: Instrument optimization procedures should only be carried out when the plasma has been ignited for at least 30 minutes and has stabilized. Power and Nebulizer flow rates are variable and often change during the optimization procedures

11.1 Torch Alignment

11.1.1 Perform when the torch is replaced or moved. It consists of a horizontal and a vertical scan of a single line, 257.610 nm Mn

11.1.2 In the instrument menu, select "Instrument Setup," then "Torch Align"

11.1.3 Aspirate the Torch Alignment solution for at least 30 seconds

11.1.4 Select "Torch Scan" to perform the horizontal scan. After the scan is complete, select "Store Results"

11.1.5 Select "Torch Scan" to perform the vertical scan. After the scan is complete, select "Store Results"

NOTE: This moves the pre-optics to the optimal position for viewing the plasma

11.2 Wavelength Calibration

11.2.1 Monthly performance recommended. This is an automated correlation between selected wavelengths and the detector pixels

11.2.2 In the instrument menu, select "Instrument Setup," then select "W/L Cal"

11.2.3 Aspirate the rinse solution during the Dark Current Scan

11.2.4 Select "Dark Current Scan." After the scan is complete, select "Store Dark Current"

11.2.5 Fill an autosampler tube with Wavelength Calibration solution and begin aspirating the solution. Select "Calibrate" to perform the Wavelength Calibration

NOTE: This takes several minutes and the tube may need to be refilled during the calibration

11.2.6 After the calibration is complete, select "Calibrate Drift"

11.3 AutoMax

NOTE: The routine optimizes the element measurement results by varying the nebulizer flow rate and/or the RF power. If the RF power selected by "AutoMax" is less than 1.2 kW, there is a tendency for calibration drift over the course of long runs. Unless a method is being developed for a specific analyte it is advised to select all wavelengths in the analysis.

11.3.1 In the Tools menu of the Method Editor, select "AutoMax"

11.3.2 Set the RF parameter at 1.0 – 1.3 kW and the nebulizer flow parameter to 0.55 – 1.00 L/min

11.3.3 After stabilization, aspirate a solution containing all the chosen analytes, typically a low level calibration standard

11.3.4 Select "Signal to Background Ratio," or the best optimization criterion, and select "Start"

11.3.5 After AutoMax is complete, select "Save"

11.4 Operating Conditions

NOTE: * Values vary with each optimization

Instrument Conditions	
Parameter	**Setting**
Power	1.30 kW*
Plasma Gas Flow	15.0 L/min
Auxiliary Gas Flow	1.5 L/min
Nebulizer Type	SeaSpray Glass Concentric
Nebulizer Gas Flow	1.0 L/min*
Pump Speed	15 rpm
Sample Tubing	Two stop White/White
Ionization Suppressant Tubing	Two stop Orange/Red
Sample Uptake Delay	30 sec
Maximum Rinse Time	120 sec
Replicate Time	10 sec
Stabilization Time	15 sec
Replicates	3
Background Correction	Point Sum – Fitted
Autosampler	Agilent SPS-5

12.0 ANALYSIS

12.1 Apparatus and Materials

- Agilent 720 ICP-OES (Axial Viewed), with autosampler
- Lytron Cooling System
- Overhead Exhaust System
- Filtration apparatus for 47 mm 0.45 micron membrane filters
- Pump windings
  - White-White 2-stop 1.02 mm ID for sample stream
  - Blue-Blue 2-stop 1.65 mm ID for plasma waste stream
  - Grey-Grey 3-stop 1.30 mm ID for autosampler rinse
  - Orange-Red 2-stop 0.19 mm ID for ionization suppression solution
- Y-adaptor and capillary tubing
- Wash Bottle, LDPE 1 L (for metals use only)

- Acid resistant 1 L dispenser for concentrated nitric acid
- Graduated cylinders, various
- Syringes, 10 mL, plastic (B-D) for 25 mm 0.45 micron PES syringe filters
- Volumetric flasks, various, polypropylene
- Volumetric pipettes, various
- Autosampler tubes, 14 mL round bottom, 16 x 100 mm, polypropylene
- Dewar liquid argon

12.2 Reagents and Chemicals

- Nitric acid "HNO_3", trace metal grade
- Deionized water "DI", laboratory grade Class II
- 2% nitric acid rinse water "2% HNO_3"– Add 20 mL of nitric acid to a wash bottle containing ~500 mL DI. Add DI to 1 L

12.3 Analysis

12.3.1 Prepare the instrument

12.3.1.1 Turn on argon gas supply. Open the ICP Expert II software to monitor the purge. After purging for 20 minutes, the instrument will be ready for plasma ignition

12.3.1.2 Turn on the autosampler, chiller, and exhaust fan. Engage the pump tubings on the instrumental peristaltic pump and the pump windings on the autosampler

12.3.1.3 Fill the water reservoir with 2% HNO_3

12.3.1.4 Select the plasma torch icon to initiate the plasma ignition sequence. Samples can be analyzed after the torch is stabilized, at least 30 minutes after the torch is ignited

12.3.2 Create a new worksheet, using the most recent previous worksheet as a template. Copy the method (but not the calibration or sequence) and save it using the current date as the file name:

Example: A worksheet called 063014S would be a soils analysis conducted on June 30, 2014

12.3.3 Select "Sequence" to build an analytical sequence. Typically as follows:

- Instrument calibration standard, followed by 3 rinses
- Quality Control standards
  - ICV standard
  - Initial Calibration Blank standard "ICB"

- ICS, followed by a rinse
- CCV standard
- Continuing Calibration Blank standard "CCB"

- The sample digests (10 or fewer) including digested QC samples and periodic QC standards (CCV/CCB)

Continue running samples in groups of 10 or fewer until complete

12.3.4 Dispense the standards and samples listed in Step 12.3.3 into autosampler tubes, and arrange them in the positions assigned in the sequence table. Tubes should be at least half full. Load rack(s) onto the autosampler

12.3.5 In the Analysis tab, select the samples to be analyzed. Select the green arrow to begin analysis

12.3.6 During the course of the run it is advised to monitor the following:

- ICB – Examine wavelength for contamination. Refresh and reanalyze if necessary
- CCVs / CCBs – If many wavelengths fail, stop the run and determine the cause
- Carryover – Examine wavelengths for memory effects. Reanalyze samples suspected of carryover. Place rinses after high level samples

12.3.7 When the analytical run is complete, carefully review the results before turning the plasma off in case any samples need to be reanalyzed

12.3.7.1 Dilute and reanalyze any analyte of interest is above 90% of its Linear Dynamic Range

12.3.7.2 Check for interferences, using alternate wavelengths if necessary. Interferences are often manifested by substantial test results between wavelengths of the same element and atypical wavelength chromatograms

12.3.8 Shut down the instrument

12.3.8.1 Flush system with rinse water for at least 10 minutes

12.3.8.2 In the autosampler tab in Instrument Setup, move the sipper into the "Park" position

12.3.8.3 Allow the system to drain of residual liquid

12.3.8.4 Turn off the plasma, disengage the pump windings, then turn off the chiller, the gas, and the ventilation fan

12.3.9 Select the accepted data by highlighting the elemental "Mean" columns and export to Omega

13.0 INSTRUMENT – ROUTINE MAINTENANCE

13.1 Pump Windings

- Inspect the pump winding, especially the sample pump tubing (white-white), for flat spots or wear before operating the instrument
- Stretch new tubing gently 2-3 times before installing
- When pump is not in use, release the pressure plate and tubing to prevent damage

13.2 Air Filter (on top of instrument) – Clean or replace as necessary

13.3 Lytron Chiller

- Add coolant (propylene glycol/water) as needed to keep float within recommended limits
- Drain and replace with fresh coolant annually
- The coolant is not hazardous and can be sewered

13.4 Torch

- When deposits build up on the end of the torch, remove and soak in aqua regia overnight
- Rinse with DI and dry before putting it into operation. Do not scrub
- Dispose of aqua regia into the Metals Acid Waste carboy
- Replace the torch if it shows signs of cracks, devitrifying, or melting
- It is recommended to keep a spare torch on hand
- Always conduct a torch alignment whenever a torch is replaced or moved in any way, see Section 11.1

13.5 Nebulizer and Spray Chamber

13.5.1 Check for clogs and/or deposits before each use

13.5.2 Clean by soaking the glassware in Triton-X 100 wash solution and sonicating

13.5.3 Rinse will with DI and allow to dry

- At the end of an analytical run, let the instrument rinse for ~15 minutes to ensure there is complete removal of sample residue from the capillary tubing and glassware

13.6 Capillary and other tubing

- Remove tubing that is crimped or shows signs of deposits
- Replace as needed

14.0 CALCULATIONS

14.1 Reported values must fall within the instrument's calibration range. Any result response or concentration of the highest standard must be diluted and reanalyzed to bring the response into the mid-range of the calibration curve.

15.0 ACCEPTANCE RANGES

15.1 See the most current data in Omega

	200.7 (% recovery)	6010B (% recovery)
ICV	95 – 110	90 – 110
ICS	90 – 110	80 – 120
CCV	90 – 110	90 – 110
LCS	85 – 115	85 – 115
MS	70 – 130	75 – 125
Duplicate	<20% RPD	<20% RPD

16.0 REPORTING AND DOCUMENTATION

16.1 Record instrument maintenance in the Maintenance Log ICP2

16.2 Record the preparation of standards in the ICP/ICPMS Standards Log

16.3 Record the preparation of reagents in the Wet Lab Reagents Log

16.4 File copies of all analytical runs in the Agilent 720 Run Log

16.5 File and archive data per NCL SOP AR 005

16.6 Disposition raw data and reports per AR 005

16.7 Data will be documented per NCL SOP LA 003

16.8 Analytical data will be reported by the LIMS

17.0 WASTE DISPOSAL

17.1 Sample digestates, calibration standards, quality control standards and analytical waste are considered Metal Acid Waste. The proper treatment and disposal of Metals Acid Waste is discussed in NCL SOP WA 007

18.0 CONTINGENCIES

18.1 If personnel encounter problems using this SOP, consult the Laboratory Supervisor

19.0 REVISION HISTORY

Version 01 – New SOP. See Section 2.0 for information contained in this SOP

20.0 REFERENCES

U.S. Environmental Protection Agency. 1994. *Determination of Metals and Trace Elements in Water and Wastes by inductively Coupled Plasma-Atomic Emission Spectrometry, Method 200.7, Revision 4.4*. Office of Research and Development, Cincinnati, OH

U.S. Environmental Protection Agency. December 1996. *Inductively Coupled Plasma-Atomic Emission Spectrometry, Method 6010B, Revision 2*. EPA Office of Solid Waste and Emergency Response, Washington, D.C.

21.0 ATTACHMENTS

N/A

NORTH COAST LABORATORIES, LTD.

MET	CODE	VERSION	COPY	EFFECTIVE DATE	WORDFILE
ME	291	03	F	6/1/07	G:WPROC\ORGSOP\ME291v03.doc

	Name	Title	Date
REVISED BY:	Cherie Thomas	CHEMIST I	6/1/07
APPROVED BY:	Ellen Blackstone	LAB SUPERVISOR	5/31/07
APPROVED BY:		LAB MANAGER	5/31/07
REVIEWED BY:	T Shem	QA OFFICER	6/1/07

1.0 TITLE

Analytical Methodology for the Analysis of Diesel Fuel in Soil – Micro Extraction Method Plus Silica Gel Cleanup

2.0 SCOPE

To provide detailed documentation of analytical methodology for analysis and silica gel cleanup for diesel fuel in soil.

3.0 DEFINITIONS

LIMS – Laboratory Information Management System, Omega at the time of this revision.

PES – Post Extraction Surrogate

4.0 REFERENCE(S)

Leaking Underground Fuel Tank Field Manual: Guidelines for Site Assessment, Cleanup, and Underground Storage Tank Closure. October 1989. State of California Leaking Underground Fuel Task Force.

Test Methods For Evaluating Solid Waste Volume 1B:Laboratory Manual Physical/Chemical Methods, SW-846 Third Edition, Revision 2, Method 3550B. December 1996. EPA Office of Solid Waste and Emergency Response, Washington D.C., 20460.

5.0 SUMMARY

A soil sample is dried with sodium sulfate and then extracted by shaking and sonicating with hexane. Particulates are settled by centrifugation. The extract is analyzed by GC-FID with "Optic" Programmable Injector. If required, a silica gel removal of polar organics may be included.

6.0 REPORTING LIMITS

The reporting limit for Diesel fuel in soil is 1.0µg/g (PPM).

7.0 STORAGE OF SAMPLES AND HOLDING TIMES

Samples are stored in the cold room at ~4° C until they are extracted. The samples must be extracted within 14 days of sampling.

8.0 STANDARD PREPARATION - TPH-DIESEL ANALYSIS

8.1 Equipment

- analytical balance capable of weighing 0.0001 g

8.2 Glassware and Supplies

- 12mL amber vials and Teflon lined lids
- 1.8mL vials with Teflon lined septum in the lids
- various syringes
- volumetric flasks and volumetric pipettes

8.3 Reagents

- hexane, pesticide grade
- MTBE (methyl tert-butyl ether) pesticide grade

8.4 Preparation of TPH-Diesel Standard

Neat diesel fuel is obtained from a commercial gas station.

To prepare a 5000 µg/mL (PPM) standard weigh ~ 0.050 g of neat diesel fuel into a 12mL amber vial and record the weight to four decimal places. Add the appropriate amount of MTBE to make a 5000 PPM standard. To calculate the amount of MTBE necessary, use the following equation:

$$\text{amount of solvent (mL)} = \frac{\text{weight (g)} \times \text{concentration of neat (µg/g)}}{\text{final concentration (PPM)}}$$

To prepare a 1000 PPM standard combine 1.0 mL of the 5000 PPM standard with 4.0 mL of MTBE in a 12mL amber vial.

8.5 Preparation of Undecane (C-11) Stock Standards:

Preparation of Undecane (C-11) 5,000 PPM stock

To prepare a 5000 PPM standard weigh ~0.050 g of neat n-undecane into a 12 mL amber vial and record the weight to four sig. figs. Add the appropriate amount of hexane to make a 5000 PPM standard using the equation in 8.4.

Preparation of Undecane (C-11) 200 PPM stock.

To prepare a 200 PPM standard, add 1.0 mL of the 5000 PPM standard to a 25mL volumetric flask. Add sufficient hexane to bring the volume to 25mL. Transfer the 200 PPM standard to a 40mL VOA.

Preparation of Undecane (C-11) 320 PPM stock.
To prepare a 320 PPM standard, add 1,600 uL of the 5000 PPM standard to a 25mL volumetric flask. Add sufficient hexane to bring the volume to 25mL. Transfer the 320 PPM standard to a 40mL VOA.

8.6 Preparation of Tricosane - C23 (Surrogate Standard)
To prepare a 5000 PPM standard weigh ~0.050 g of neat tricosane into a 12 mL amber vial and record the weight to four sig. figs. Add the appropriate amount of MTBE to make a 5000 PPM standard using the equation in 8.4.

Prepare a 200 PPM standard by adding 1.0 mL of the 5000 PPM tricosane standard to a 25 mL volumetric flask and add enough MTBE to bring volume to 25 mL mark.

8.7 Preparation of Working Standards for silica gel cleaned samples

For 10 mL of 10 X RL Working Standard: Use a 10 mL volumetric flask. Add 40 µL of 5000-PPM diesel and 100 µL of 200-PPM n-tricosane and 320 uL of 200 PPM undecane. Adjust the volume to 10 mL with hexane.

Calculations:
40 µL X 5000 ng/uL = (200,000 ng)(1/5 g) = 40,000 ng/g X (0.5 mL/2.0 mL) = 10,000 ng/g (PPB) or 10 ug/g (PPM). This is 10 X LOQ.

The factor of 0.5 mL/2.0 mL is included the calculation to account for the 2.0 mL volume added to the silica gel column and the final volume of 0.5 mL for the cleaned extract.

The lot 2 working standard is prepared in the same manner as the 10 X RL working standard. The diesel used is from a different source than that used for fortifying the laboratory control samples or preparation of the calibration curve.

For 1.0 mL of 20 X RL Working Standard: Add 908 uL of hexane to a 1.8 mL autosampler vial. Add 8 µL of 5000 PPM diesel and 20 µL of 200 PPM n-tricosane. Finally, add 64 uL of 200 PPM undecane.

For 1.0 mL of a 0.8 x RL Working Standard: Dilute the 10 X RL Working Standard 1:12.5 (e.g. 80 uL 0f 10 X RL standard plus 920 uL of hexane.

For 1.0 mL of 1 X RL Working Standard: Dilute the 10 X RL Working Standard 1:10 (e.g. 100 µL of 10 X RL standard plus 900 µL of hexane).

For 1.0 mL of 200 X RL Working Standard: Combine 80 µL of 5000 PPM diesel with 920 µL of hexane.

For 1.0 mL of 100 X RL Working Standard: Dilute the 200 X RL Working Standard, 1:2 (e.g. 400 µL of 200 X RL standard plus 400 µL hexane).

Neither PES nor surrogate is added to the 100 X RL and 200 X RL working standards.

8.8 Preparation of Working Standards for **NON** silica gel cleaned samples

For 10 mL of 10 X RL Working Standard: Use a 10 mL volumetric flask. Add 10 µL of 5000-PPM diesel and 25 µL of 200-PPM n-tricosane and 80 uL of undecane. Adjust the volume to 10 mL

Calculations:
10 µL X 5000 ng/uL = (50,000 ng)(1/5 g) = 10,000 ng/g = 10 ug/g (PPM). This is 10 x RL.

The lot 2 working standard is prepared the same as the 10 X RL working standard. The diesel used is from a different source than that used for fortifying the laboratory control samples or preparation of the calibration curve.

For 1.0 mL of 20 X RL Working Standard: Add 977 uL of hexane to a 1.8 mL autosampler vial. Add 2 µL of 5000 PPM Diesel and 5.0 µL of 200 PPM n-tricosane. Finally, add 16 uL of 200 PPM undecane.

For 1.0 mL of a 0.8 x RL Working Standard: Dilute the 10 x RL Working Standard 1:12.5 e.g. 80 uL of 10 X RL standard plus 920 uL hexane.

For 1.0 mL of 1 X RL Working Standard: Dilute the 10 X RL Working Standard 1:10 (e.g. 100 µL of 20 X RL standard plus 900 µL of hexane).

For 1.0 mL of 200 X RL Working Standard: Combine 20 µL of 5000 PPM diesel with 980 µL of hexane.

For 1.0 mL of 100 X RL Working Standard: Dilute the 200 X RL Working Standard, 1:2 e.g. 400 µL of 200 X RL standard plus 400 µL hexane.

Neither PES nor surrogate is added to the 100 X RL and 200 X RL working standards.

9.0 EXTRACTION - TPH-DIESEL FROM SOIL

9.1 Equipment

- top loading balance capable of weighing to 0.1 g
- clean "spoonulas"

9.2 Glassware and Supplies

- Pasteur pipettes and rubber bulbs
- various syringes
- automatic pipette
- 40 mL VOAs
- 1.8mL autosampler vials
- Champagne columns, Supelco # 58099
- Glass wool, Soxleted in $MeCl_2$ for approximately 16 hours

9.3 Reagents

- Hexane, pesticide grade
- 3:2 hexane:$MeCl_2$. Add 40 mL $MeCl_2$ to a 100 mL graduated cylinder. Bring to the 100-mL mark with interference free hexane. Mix thoroughly and store in airtight container.
- Methylene chloride($MeCl_2$), pesticide grade
- Sodium chloride (furnaced at 400 °C X 4hrs)
- Sodium sulfate:(furnaced at 400 °C X 4hrs)
- Davidson grade 923, 100-200 mesh silica gel. Sigma-Aldrich # 214477. Heat @ 135-140°C for at least 16 hours. Cool to near room temperature and store in tightly closed jars sealed with parafilm in dessicator until use.

9.4 Special Precautions - Sample Preparation and Extraction

- The diesel test is extremely sensitive to contamination in the lab. All glassware must be free of all soap residue and rinsed with methylene chloride. Use no plastic pipet tips or other plasticware. Interferents have been found in the autosampler and storage vials. Rinse autosampler and other extract storage vials with 3 rinsings of clean hexane and allow the glassware to dry before use. Rinse KD vials and glass silicagel columns with 3 $MeCl_2$ rinsings before each use. Interferents have been caused by the septa in the 9 mm blue caps (Fisher #03-391-14). These septa must be replaced with 8 mm red or cream PTFE/Silicon Seal (CRS # 308515 or 908915). The septa in the caps that come with 1.8 mL clear screw top standard mouth vials (CRS # 123225) appear not to produce interferents and therefore, may be used.
- It is extremely important to transfer only the hexane phase to the autosampler vial. The presence of water in the extract could ruin the gas chromatograph. If necessary, centrifuge the VOAs at no more than 1100 rpm to aid phase separation. Consult the lab supervisor if you are unsure of how to handle a particular sample.

9.5 Extraction Procedure

9.5.1 Retrieve sample from storage (see SOP LA 003)

9.5.2 Prepare all glassware by rinsing with methylene chloride.

9.5.3 Homogenize the sample and measure 5.0 g of soil (or Ottawa sand for blank and laboratory control samples) into a 40 mL VOA.

9.5.4 Add at least 5g of furnaced sodium sulfate and mix thoroughly. Continue adding sodium sulfate and stirring until the mixture is free flowing and friable.

9.5.5 Prepare spike and laboratory control samples by adding 50 µL of 1000 PPM diesel to the mixture of sodium sulfate and matrix or sodium sulfate and Ottawa sand. Use the primary lot standard to fortify the laboratory control samples and the second lot to fortify the matrix spikes. The spike concentration will be 10.0 µg/g (PPM) with respect to a 5.0 g sample as demonstrated in the following equation:

$$(50\ \mu L)\left(\frac{1{,}000\ ng}{uL}\right) = (50{,}000\ ng.)/(5.0\ g).= 10{,}000\ ng/g = 10\ \mu g/g\ (PPM)$$

9.5.6 Add 25 µL of 200 PPM n-tricosane to each sample, blank and Quality Control sample. The concentration will be 1 µg/g with respect to a 5.0 g sample as demonstrated in the following equation:

$$(25\ \mu L)\left(\frac{200\ ng}{uL}\right) = \frac{5{,}000\ ng}{5.0g} = \frac{1{,}000\ ng}{g} = 1.0\ \mu g/g\ (PPM)$$

9.5.7 Add 10.0 mL of hexane and shake as vigorously as possible for 2 minutes. Sonicate for 15 minutes.

9.5.8 Allow phases to separate, centrifuge @ 1100 RPM for about 5 minutes if required for complete phase separation. If the hexane level is not above the surface of the soils add about 5.0 mL of deionized water (DI) and tap lightly on the counter to settle the water or re-centrifuge. The hexane will rise to the surface.

9.5.9 Transfer ~ 4 mL of hexane phase to an 8 mL storage vial. **Note:** It is extremely important to transfer only the hexane phase to the autosampler vial. The presence of water in the extract could ruin the gas chromatograph. Add 40µL of 320 PPM n-undecane(PES) and store in the freezer.

9.5.10 NOTE: This fraction of the extract will be used for both diesel screening and the silica gel cleanup (if required). If no silica gel cleanup is required, the fraction will be used for the final analysis.

9.5.11 Prior to analysis, transfer ~ 1 mL of the hexane phase to an autosampler vial, or ~ 200 µL to an autosampler vial containing a 0.3 mL target polyspring insert. The vial and the insert must be pre-rinsed with $MeCl_2$

NOTE: It is also acceptable to store the extraction vial containing the 9 remaining milliliters of extract in a freezer until the extract is required for the silica gel cleanup. At this time carefully withdraw 2.0 mL of the extract and transfer it to the prepared silica gel column.

9.6 Micro silica gel cleanup.

9.6.1 Place a small wad of soxleted glass wool in the tip of a Supelco Champagne column that has been previously rinsed with $MeCl_2$

9.6.2 Add 1.0 g activated Davidson grade 923 silica gel to a 10 mL beaker.

9.6.3 Add about 10 mL $MeCl_2$ to the beaker and stir to release air bubbles.

9.6.4 Using a Pasteur pipet, transfer the silica gel to the Champagne column in about 1 mL increments. Do not allow the liquid level to go below the silica gel in the column.

9.6.5 Allow the $MeCl_2$ to percolate through the column to waste. As the liquid in the column approaches the top of the silica gel add about 10 mL of 3:2 hexane:$MeCl_2$ to the reservoir without disturbing the bed and allow this to percolate to waste. As this rinse approaches the top of the column bed add about 5 mL of hexane to the reservoir and allow to percolate through the column to waste. The column is now ready for use.

9.6.6 Place the tip of the column in a 10 mL KD vial that has a calibrated graduation mark at the 0.5 mL level.

9.6.7 Add the 2.0 mL of hexane phase that was stored for this purpose at the time of initial extraction to the column and collect the column effluent.

9.6.8 Rinse the storage vessel into the column with 1.0 mL hexane (or, if the extract was transferred directly from the extraction vessel, add 1 mL of hexane directly to the column.) and allow to reach the top of the column bed.

9.6.9 Using a pre-rinsed pipet add 3.0 mL 3:2 hexane:$MeCl_2$ to the column without disturbing the bed and allow to percolate through the column under the influence of gravity.

9.6.10 There should be approximately 6 mL of liquid collected in the KD vial at this point.

9.6.11 Reduce the volume to between 490- 400 µL @ 40°C under a moderate stream of N_2 on a 24 position N-Evap. All 24 valves on the N-Evap should be open about 1 turn with the flow set at about 4 LPM. The needle tips should be set at about 3-5 mm above the liquid surface. All needles should be pre-rinsed with $MeCl_2$ before use. The progress of the volume reduction should be checked periodically. The needle tips may be moved down as the liquid level decreases. Once the liquid level reaches the 1 mL KD vial tip, monitor the progress of the volume reduction very carefully. It may go astonishingly quickly and recovery will suffer if the liquid goes below about 300 µL.

9.6.12 Adjust volume to 500 µL mark with hexane.

9.6.13 Transfer the extract to an autosampler vial pre-rinsed with $MeCl_2$

9.6.14 Prior to analysis, visually compare the volume of extract in the autosampler vial with

the volume in an autosampler vial containing 500 µL of hexane measured by syringe; adjust the volume of the extract as needed with hexane dropwise from a glass Pasteur pipet. Transfer ~ 200 µL of the extract to an autosampler vial containing a 0.3 mL target polyspring insert pre-rinsed with $MeCl_2$.

10.0 ANALYSIS - TPH-DIESEL IN SOIL

10.1 Special Precautions - Analysis

If the samples do not contain the typical pattern of the fresh diesel standard report the amount of material in the diesel range. An appropriate note to describe the pattern of the chromatogram and how it compares or differs from that of a fresh diesel standard is included with the data sheets. See Exhibit B for a list of the common notes.

10.2 Equipment

- gas chromatograph with FID and "Optic" Programmable Injector.

10.3 Glassware and Supplies

- 100 µL syringe
- 1.8 mL storage vials (for dilutions)
- assorted syringes (for dilutions)

10.4 Reagents

- hexane, pesticide grade

10.5 Procedure for Calibration

Two calibration curves are run, a 4-point "Low Level" curve and a 6-point "High Level" curve. The 4-point curve consists of the 0.8 X RL 1 X RL, 10 X RL, and the 20XRL diesel working standards. The 6-point curve consists of the same standards as the 4-point curve with the addition of the 100 X RL and the 200 X RL diesel working standards. Linear fits are used when possible; quadratic fit is used otherwise. The r^2 value, correlation coefficient, should be ≥ 0.995 for acceptance. When a curve is not run, a 10XRL diesel working standard is run as a continuing calibration verification (CCV) standard. Acceptance limits for CCV standards are $\pm$ 15% of the true value.

10.6 Procedure for Analysis

NOTE: The parameters listed are suggested as guidelines and may be altered to reflect changes in the column, injector, and detector conditions as long as proper sensitivity is maintained.

Instrument conditions:

Instrument:	OR-GC-5 or OR-GC-7, equipped with "Optic" programmable injector.

MET CODE VERSION
ME 291 03

Method Name:	NCLNT1\TCSupport \GC5 \.....
Data File:	NCLNT1\TCData\GC5\(month)\(week)\.....__ (Add sequential letters in the blank space to differentiate analytical runs.)
Channel:	A
Run Time:	13.2
Flow Rate:	20 mL/min
Oven Temp Program:	55° C hold 2.5 min, to 110° C at 50° C/min hold 0.1 min, to 200° C at 50° C/min hold 1.5 min. to 310° C at 50° C hold 4.00 minutes
Inj Program (Atas):	Program name: TPHTESTS Initial temp = 45° C Vent time = 35 sec Ramp rate = 15° C/sec Final Temperature = 310°C End Time = 13.34 min Split Open Time = 1 min Purge press. = 7.0 PSI Transfer press. = 21.0 PSI Transfer time = 1.00 min. Initial press. = 21.0 PSI Final press. = 21.0 PSI Solvent threshold = 0
Det Temp:	350° C
Column Type:	Rtx-5(or similar phase), 15 m, 0.54mm ID, 1.5 µm film thickness
Amount Inj for silica gel cleaned ext:	10 µL
Amount Inj for **NON** silica gel cleaned ext:	40 µL
Detector:	FID - Range 12

Instrument: **GC14 Varian CP-3800 Gas Chromatograph**

Sample Delivery:

Injection Mode: User
Sample Penetration Depth: 80%
Solvent Penetration Depth: 90%
Prep Ahead Delay: 0

MET CODE VERSION
ME 291 03
Air Plug After Sample: 1 uL
Sample Air Gap: No
Fill Strokes: 3
Fill Volume for Fill Strokes: 50 uL
Viscosity Delay: 1 sec
Plunger Speed During fill: 20 uL/sec
Plunger Speed During Injection: 50 uL/sec
Pre-Injection Delay: 0
Post-Injection Delay: 0
Injection Volume for silica gel extract: 10 uL
Injection Volume for **NON** silica gel extract: 40 uL

Injector:

	Temp (°C)	Rate (°C/min)	Hold (min)
Initial	25		0.5
1	300	180	2.0
2	300	180	9.25

Coolant: On
Enable Coolant: 250 °C
Coolant Timeout: 10 min

Injector (con'd):

Time	Split State	Split Ratio
Initial	On	15
0.5	Off	Off
2.0	On	30
13	On	15

Flow Pressure:

	Pres (psi)	Rate (°C/min)	Hold (min)
Initial	21		5
1	26	2	0
2	36	2	1.5

Constant Flow Mode: No

MET CODE VERSION
ME 291 03
Column Flow Rate: 10 mL/min

Column Oven:

	Temp (°C)	Rate (°C/min)	Hold (min)
Initial	45		2.5
1	100	40	0
2	200	50	0
3	203	5	.5

Stabilization time: 1.5

Detector:

325 °C
Electronics: On
Front FID Range 12
Autozero: Yes

Column Type:

Varian Select Mineral Oil LVI Stationary Phase, 15 m, 0.32 mm ID, 0.25 um film thickness

10.7 Confirmation of Positive Samples
Positive diesel samples do not need to be confirmed.

11.0 **CALCULATIONS**
None

12.0 **ACCEPTANCE RANGES**
See the most current data in Omega.

13.0 **REPORTING AND DOCUMENTATION**
Extraction data will be documented as per SOP LA-003. Analytical data will be reported by Laboratory Information Management System (LIMS).

14.0 **WASTE DISPOSAL**

14.1 Extraction and Analysis
All sample extracts, stock standards, and working standards are deposited in the diesel satellite accumulation storage container.

Spikes/Laboratory Control Samples:
For the laboratory control samples add 50 µL of the 1000 PPM diesel standard to 5.0 g of

MET CODE VERSION
ME 291 03

Ottawa sand. For the matrix spikes add 50 uL of the 1000 PPM second lot standard to 5.0 g of sample. The concentration of the spikes and laboratory control samples will be 10.0 PPM with respect to a 5.0 g soil sample.

(50 µL) (1,000 ng) = (50,000 ng.)/(5.0 g).= 10,000 ng/g= 10 µg/g (PPM)

Surrogate:

Add 25 µL of the 200 PPM n-tricosane to each sample, blank, and QC sample. The concentration of the surrogate will be 1 PPM with respect to a 5.0 g soil sample.

$$(25\ \mu L)\left(\frac{200\ ng}{\mu L}\right) = \frac{5{,}000\ ng}{5.0\ g} = \frac{1{,}000\ ng}{g} = 1.0\ \mu g/g\ (PPM)$$

PES:

Add 40 µL of the 320 PPM n-undecane to each ~ 4 mL sample, blank, and QC sample extract. The concentration of the n-undecane will be set to 1.0 rather than an actual concentration.

MET CODE VERSION
ME 291 03

Exhibit B

NOTES FOR HYDROCARBON RESULTS

REPORT COMMENTS

Diesel:

Sample __ contains some material of lighter molecular weight than diesel.

Sample __ contains some material lighter than diesel. However, some of this material extends into the diesel range of molecular weights.

Sample __ contains material similar to degraded or weathered diesel oil.

Sample __ contains material in the diesel range of molecular weights, but the material does not exhibit the peak pattern typical of diesel oil.

Sample __ contains material in the diesel range of molecular weights and beyond. This suggests the presence of an oil heavier than diesel.

Sample __ contains material in the diesel range of molecular weights and beyond. It also exhibits the peaks typical of diesel. This indicates the presence of diesel plus an oil heavier than diesel.

The surrogate for sample __ could not be quantified due to a sample dilution.

Sample __ contains material beyond the diesel range. This suggests the presence of an oil heavier than diesel. The amount of this material is not included in the result reported.

The low surrogate receovery for sample __ may be due to the formation of an emultion during the sample extraction.

All diesel results reported represent the amount of material in the diesel range of molecular weights only.

Motor Oil:

Sample __ does not have the typical pattern of fresh motor oil The material is lighter/heavier than motor oil. However, the result reported represents the amount of material in the motor oil range.

A surrogate is not added to the diesel/motor oil samples because the surrogate elutes in he motor oil range.

EXTRA COMMENTS:

Sample Forms 3

CONSULTING ENGINEERS & GEOLOGISTS, INC.
812 W. Wabash • Eureka, CA 95501-2138 • 707/441-8855 • FAX: 707/441-8877 • info@shn-eureka.com

Soil Sampling Data Sheet

Project Name:		Date/Time:		
Project No.:		Sampler Name:		
Location:		Sample Type:	Soil	
Sample #:		Weather		

	Time	Depth (ft BGS)	Soil Type	Color	Odor	Moisture	Comments
1							
2							
3							
4							
5							
6							
7							
8							
9							
10							

Laboratory Information				
Sample ID	**# & Type of Containers**	**Preservative / Type**	**Laboratory**	**Analyses**

Sampler Signature/Date:

Reviewer Signature/Date:

NAME:
SAMPLE ID:
DATE/TIME:
TEST(S):

NORTH COAST LABORATORIES LTD.

CUSTODY SEAL

Date _____

Signature _____

Nalge Nunc International

I-CHEM™ Brand Products

90009

CUSTODY SEAL

Date _____

Signature _____

Nalge Nunc International

I-CHEM™ Brand Products

90009

CUSTODY SEAL

Date _____

Signature _____

Nalge Nunc International

I-CHEM™ Brand Products

90009

CUSTODY SEAL

Date _____

Signature _____

Nalge Nunc International

I-CHEM™ Brand Products

90009

CUSTODY SEAL

Date _____

Signature _____

Nalge Nunc International

I-CHEM™ Brand Products

90009

NORTH COAST
LABORATORIES LTD.
5680 West End Road • Arcata • CA 95521-9202
707-822-4649 Fax 707-822-6831

Chain of Custody

LABORATORY NUMBER:

Attention: _____
Results & Invoice to: _____
Address: _____
_____
Phone: _____
Copies of Report to: _____
_____
Sampler (Sign & Print): _____

TAT: ☐ STD (2-3 Wk) ☐ Other:
PRIOR AUTHORIZATION IS REQUIRED FOR RUSH SAMPLES.

REPORTING REQUIREMENTS:
☐ State Forms
☐ Geotracker ☐ SWAMP ☐ Other EDD:
☐ Final Report PDF ☐ FAX By:

CONTAINER CODES: 1—½ gal. pl; 2—250 ml pl; 3—500 ml pl; 4—1 L Nalgene; 5—250 ml BG; 6—500 ml BG; 7—1 L BG; 8—40 ml VOA; 9—60 ml VOA; 10—125 ml VOA; 11—4 oz glass jar; 12—8 oz glass jar; 13—brass tube; 14—other
PRESERVATIVE CODES: a—HNO_3; b—HCl; c—H_2SO_4; d—$Na_2S_2O_3$; e—NaOH; f—$C_2H_3O_2Cl$; g—other

PROJECT INFORMATION

Project Number: _____
Project Name: _____
Purchase Order Number: _____

LAB ID	SAMPLE ID	DATE	TIME	MATRIX*	PRESERVATIVE	CONTAINER	ANALYSIS

SAMPLE CONDITION/SPECIAL INSTRUCTIONS

RELINQUISHED BY (Sign & Print)	DATE/TIME	RECEIVED BY (Sign)	DATE/TIME

SAMPLE DISPOSAL
☐ NCL Disposal of Non-Contaminated
☐ Return ☐ Pickup

CHAIN OF CUSTODY SEALS Y/N/NA
SHIPPED VIA: UPS Fed-Ex Hand

***MATRIX:** DW=Drinking Water; Eff=Effluent; Inf=Influent; SW=Surface Water; GW=Ground Water; WW=Waste Water; S=Soil; O=Other.

ALL CONTAMINATED NON-AQUEOUS SAMPLES WILL BE RETURNED TO CLIENT

XRF Field Screening Data Sheet
RMT II Debris Pile Characterization
1 TCF Drive, Samoa, CA

Date: Technician:

Page ____ of ____	Target Constituent		
	Lead (ppm)	**Chromium (ppm)**	**Notes**
CCRMP Till 4 pp Standard			scan at start up daily
RCRA pp Standard			scan at start up daily

Screened Material Description and Source Identification

s: sediment sources: AOI-1, AOI-2
b: block

Site Safety Plan 4

Site Safety Plan

Redwood Marine Terminal II
Samoa, California
EPA Grant ID No. BF-99T55301-0

Prepared for:

Humboldt Bay Harbor, Recreation & Conservation District

SHN
Engineers & Geologists

January 2018

016240.002

Reference: 016240.002

Site Safety Plan

Redwood Marine Terminal II

Samoa, California
EPA Grant ID No. BF-99T55301-0

Prepared for:
Humboldt Bay Harbor, Recreation & Conservation District

Prepared by:

Engineers & Geologists
812 W. Wabash Ave.
Eureka, CA 95501-2138
707-441-8855

January 2018

QA/QC:KBV___

Table of Contents

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List of Illustrations

Acronyms and Abbreviations

mg/kg	milligrams per kilogram
mg/m^3	milligrams per cubic meter
ppm	parts per million
µg/dl	micrograms per deciliter
ACGIH	American Conference of Governmental Industrial Hygienists
AIHA	American Industrial Hygiene Association
AL	action level
AOI	area of interest
APR	air purifying respirator
BLL	blood lead level
Cal-OSHA	California Occupational Health and Safety Administration
CCR	California Code of Regulations
CFR	Code of Federal Regulations
EL	exposure limit
FTC	Freshwater Tissue Company
HEPA	high-efficiency particulate absorbing
IDLH	immediately dangerous to life or health
IIPP	injury and illness prevention program
NIOSH	National Institute For Occupational Safety And Health
nr	no reference
OSHA	United States Occupational Safety and Health Administration
PEL	permissible exposure limit
PID	photoionization detector
PPE	personal protective equipment
RWQCB	North Coast Regional Water Quality Control Board
SHN	SHN Engineers & Geologists
SSP	site safety plan
SSS	Site Safety Supervisor
TWA	time-weighted average
USA	Underground Service Alert
ZPP	zinc protoporphyrin

General Information

Project:	Redwood Marine Terminal II	Site Address:	**1 TCF Drive, Samoa, CA**
RWQCB Case #:	1NHU892	Date:	December 2017
Site Phone:	Mobile Phone: John Wellik, 707-296-3660	Client:	Humboldt Bay Harbor, Recreation & Conservation District
Plan Prepared By:	John Wellik/Kaila Benton-Vitz		

Key Personnel and Responsibilities

Title	Name	Office Telephone Number	Mobile Phone Number
Project Manager:	Mike Foget	707-441-8855	707-845-3040
Site Safety Supervisor (SSS):	John Wellik	707-441-8855	707-296-3660
Project Industrial Hygienist	Kaila Benton-Vitz	916-213-8473	916-213-8473

1.0 Introduction

This site safety plan (SSP) was prepared by SHN Engineers & Geologists (SHN), for the Redwood Marine Terminal II, in Samoa, Humboldt County, California. This SSP is designed to provide health and safety guidelines for the protection of SHN employees that are involved with hazardous materials operations at the project site. The primary goal of this SSP is to establish general site safety requirements in order to limit personal exposure to potentially hazardous materials.

the project site under analysis in this cleanup proposal consists of two areas of interest (AOIs); AOI 1 contains two debris piles, and AOI 2 contains one debris pile. Collectively, the area containing the three debris piles totals approximately 9,250 square feet. These piles have been found to contain heavy metals and boiler smelt, which is primarily sodium sulfide and sodium carbonate.

The preferred cleanup alternative involves the removal of hazardous waste from the three debris piles within the boundaries of the site, and retention of non-hazardous waste on site for future industrial fill uses. All hazardous waste would be removed by a qualified contractor, and transported and disposed of at a permitted Class I waste facility. All non-hazardous solid waste would undergo additional testing with x-ray spectroscopy at the cubic yard level of discretion to support an evaluation of its reuse on the subject property for industrial fill material, following site analysis and development of industrial controls and under a waste discharge permit from the North Coast Regional Water Quality Control Board (RWQCB). Prior to the use of the retained non-hazardous material for industrial fill, the material would be covered with durable

sheeting and fenced off to prevent access. The non-hazardous waste would need to be stored properly on the site, which may entail the application of best management practices to prevent release of pollutants into stormwater runoff and associated water quality impacts.

There is a potential for encountering soils below the debris piles with elevated concentrations of petroleum hydrocarbons, metals (cadmium, chromium, nickel, lead, and zinc), volatile organic compounds, and semi-volatile organic compounds. It is pertinent that all site personnel and visitors read and understand the SSP prior to entering the operational areas.

General United States Occupational Safety and Health Administration (OSHA) requirements pertaining to the operation of equipment, including loaders and excavators, will be followed at the project site at all times. This SSP provides limited specific safety guidelines for general construction activities or heavy equipment operations.

2.0 Subcontractors

All subcontractors will operate under their own OSHA-required injury and illness prevention program (IIPP). SHN subcontractors must meet the requirements of the SHN SSP and may also become responsible for preparing an SSP as applicable to their specialized scope of work. Their SSP must be relative to their scope of work and provide for the means and methods ensuring the health and safety of the subcontractor's employees and property. SHN does not assume the responsibility for the safe work practices of a subcontractor's employees. Further, SHN is not responsible for hazardous substances brought onto the project site by a contractor or subcontractor.

Site workers will typically report to the SHN project manager listed in the SSP and shall also follow the direction of the SSP identified Site Safety Supervisor (SSS), or other SHN field personnel if the SSS is not present on site**. If SHN staff members are not present on site, and unsafe or hazardous conditions are discovered, the site workers (Subcontractor) are to notify the SHN project manager and/or other listed key personnel by phone, immediately.**

3.0 Hazard Analysis

___	Serious	___	Impoundment	___	Active
X	Moderate	___	Landfill	X	Inactive
___	Low	___	Open,	___	Unknown
___	None	X	Other Former pulp mill		

___	Gas	X	Toxic	X	Dust
___	Groundwater	___	Corrosive	___	Liquid
___	Sludge	___	Ignitable	___	Fumes
X	Solid, sediment	___	Volatile	___	Vapors
___	Unknown	___	Radioactive	X	Contact
___	Other	___	Reactive	X	Respiratory
		X	Unknown, (pending investigation)	X	Particulates
		___	Other	___	IDLH[1]

4.0 Background

The subject facility is located at 1 TCF Drive, Samoa, Humboldt County, California. Initial site development occurred in 1964 when a bleached Kraft pulp mill was constructed by Georgia Pacific. The pulp mill was in operation between 1965 and 1994, at which time it was converted to a chlorine-free process. Multiple owners including LP and Evergreen Pulp operated the mill from 1994 to 2008 (SHN, 2014). Freshwater Tissue Company (FTC) purchased the site in 2009 and planned on reopening the mill; however, the plans were abandoned, and site decommissioning, including demolishing structures and liquidating assets, was initiated. Buildings and land uses of the site included offices, pulp warehouses, a machine building, a sand blasting shop, petroleum products distribution and storage, a hazardous waste storage area, diesel aboveground storage tanks, a chemical storage tank farm, a water treatment plant, a "black liquor" processing area, a bleach plant, process chemical recovery boilers, and an electrical generation station. In August 2013, FTC transferred ownership of the site to Humboldt Bay Harbor Recreation and Conservation District. As of November 2017, remediation and cleanup of the hazardous waste storage area, and demolition of a majority of the aboveground storage tanks, the bleach plant, and two of the recovery boiler facilities, had occurred.

A draft analysis of Brownfields cleanup alternatives was prepared in January 2014 describing debris pile characterization efforts, and presenting three alternatives for pile removal (LACO, 2014). Alternative #3 was identified as the recommended cleanup alternative; it includes characterizing and segregating the debris pile materials based on hazard level and contamination type, with disposal of materials at an appropriately classified landfill for those materials not cleared for onsite reuse.

IDLH: immediately dangerous to life and health

Currently, the site houses several service and light industrial businesses, including: a mariculture operation, an electrician, a package delivery company, a salt manufacturer, and a wholesale butane distributor. Active remediation of soil and groundwater impacts related to historical site operations is being performed by Louisiana Pacific under the purview of the RWQCB.

5.0 Hazard Assessment: Contaminant of Concern

The project site consists of two areas of interest (AOIs); AOI 1 contains two debris piles and AOI 2 contains one debris pile. Historical laboratory data provides evidence of potential for encountering sediment with elevated concentrations of petroleum hydrocarbons, metals (cadmium, chromium, nickel, lead, and zinc); additional potential contaminants of concern include volatile organic compounds, and semi-volatile organic compounds.

Based on concentration data, exposure routes, and permissible exposure limits, the primary contaminant of concern is lead in soil/contaminated materials in AOI 2. Other contaminants of concern are VOCs.

6.0 Activity Description and Compliance Achievement

Work activities with potential for lead and VOC exposure to employees includes:

- Sorting debris piles
- Handling/separating hazardous materials from non-hazardous materials inside AOIs.

Exposure potential for lead is greater when performing these activities on AOI 2 than when performing these activities on AOI 1.

7.0 Dust Exposure Calculations

Using data from the debris pile characterizations (LACO, 2014), SHN modeled the air concentration of total dust at which the California-OSHA (Cal-OSHA) permissible exposure limit (PEL) for the contaminants of concern may be exceeded (Marlowe, 1999).

$$EL_{mix} = \frac{10^6 \text{ mg/kg}}{[\sum(conc_n/EL_n)](\text{Safety Factor})}$$

Where:

EL_{mix}:	air concentration of total dust at which the contaminants of concern (cadmium, chromium, lead, nickel, and zinc) would be at its established exposure limit
EL:	PEL exposure limit, in mg/m^3 (milligrams per cubic meter)
10^6:	conversion factor
Conc:	soil concentration of the contaminant of concern, in mg/kg (milligrams per kilogram)
Safety Factor:	4

A safety factor of 4 was chosen based on SHN's judgment of how the following items apply:

- The concentration of the contaminant in the airborne dust is the same as the concentration in the soil.
- The soil concentration data depicts a representative or worst case.
- The laboratory analysis and soil sample collection was properly performed.

The EL_{mix} are reported in Tables 1 and 2 using the average soil concentrations of the contaminants of concern.

Table 1. Exposure Limit Modeling, Area of Interest 1

Area	Average[1] Soil Concentration (mg/kg)[2]	Maximum EL_{mix}[3] (mg/m^3)[4]
Cadmium	4.9	25
Chromium	332	
Lead	64	
Nickel	310	
Zinc	790	
Cal-OSHA PELs[5] for Contaminants of Concern Cadmium: 0.005 mg/m^3 Chromium: 0.05 mg/m^3 Lead: 0.05 mg/m^3 Nickel: 0.5 mg/m^3 Zinc: 5.0 mg/m^3 Dust (total): 10 mg/m^3		

1. Average: an average of the soil sample results expressed as a concentration of the hazardous material as reported in LACO, 2014.
2. mg/kg: milligram per kilogram
3. EL_{mix}: the air concentration of total dust at which the contaminant of concern would be at its established exposure limit.
4. mg/m^3: milligram per cubic meter
5. Cal-OSHA PEL: California permissible exposure limit (PEL) given by the California Occupational Safety and Health Administration

Table 2 Exposure Limit Modeling, Area of Interest 2

Area	Average[1] Soil Concentration (mg/kg)[2]	Maximum EL_{mix}[3] (mg/m^3)[4]
Cadmium	2	1.25
Chromium	95	
Lead	9925	
Nickel	73	
Zinc	663	
Cal-OSHA PELs[5] for Contaminants of Concern Cadmium: 0.005 mg/m^3 Chromium: 0.05 mg/m^3 Lead: 0.05 mg/m^3 Nickel: 0.5 mg/m^3 Zinc: 5.0 mg/m^3 Dust (total): 10 mg/m^3		

1. Average: an average of the soil sample results expressed as a concentration of the hazardous material as reported in LACO, 2014.
2. mg/kg: milligram per kilogram
3. EL_{mix}: the air concentration of total dust at which the contaminant of concern would be at its established exposure limit.
4. mg/m^3: milligram per cubic meter
5. Cal-OSHA PEL: California permissible exposure limit (PEL) given by the California Occupational Safety and Health Administration

7.1 Area of Interest 1:

The model output shows that given a safety factor of 4 and the highest (maximum) given concentrations of the contaminants of concern, it is not possible for the concentration of these contaminants to reach their PEL if the Cal-OSHA PEL for total dust (10 mg/m^3) is maintained. At 25 mg/m^3 of dust, over an 8-hour period and given a worst-case scenario, the PEL for the highest risk contaminant (in this case, chromium) may be reached.

7.2 Area of Interest 2:

The model output shows that given a safety factor of 4 and the highest (maximum) given concentrations of the contaminants of concern, it is possible for the concentration of these contaminants to reach their PEL at a total dust level of 1.2 mg/m^3. At 1.25 mg/m^3 of dust, over an 8-hour period and given a worst-case scenario, the PEL for the highest risk contaminant (in this case, lead) may be reached.

Given this, the following project action levels have been set**:**

Area of Interest 1: **5 mg/m^3**, or one half of the Cal-OSHA PEL for total dust.

Area of Interest 2: **1.25 mg/m^3**, or one quarter of the Cal-OSHA PEL for total dust *until a personal exposure assessment has been performed to assess worker exposure to lead.* If the personal exposure assessment yields lead exposure within allowable limits, a project action level of 5 mg/m^3 may commence.

Based on the output of the model, dust at AOI 1 is *not* expected to have lead in concentrations harmful to workers. Dust at AOI 2 is possible, therefore a personal exposure assessment for lead is required.

SHN recommends dust suppression control techniques be followed to maintain compliance with the Cal-OSHA PEL for total dust. As a rule of thumb, total airborne dusts are often visible at concentrations of 2 mg/m^3; thus, visible dusts should be suppressed. Air monitoring, as described in Section 8, below, will be conducted to ensure that concentrations of dust do not exceed the project action level for total dust.

Note: Soil sample results taken from AOI 2 included one sample with an anomalous lead level result (33,000 mg/kg) that has skewed the modeling results. This sample may have contained a material (such as, a lead paint chip) that resulted in high soil sample results, but would be unlikely to aerosolize and cause worker exposure.

8.0 Dust Suppression and Air Monitoring for Dust

8.1 Area of Interest 1:

Although the existing concentration of the contaminants of concern in project soils may pose a hazard to employees if proper hygiene practices are not followed, the inhalation potential is low, given that dust suppression is adequate. As such, either a qualitative or a quantitative approach to air monitoring may be selected:

Air Monitoring Qualitative Approach: Control dust to maintain no airborne dust emissions (concentration approximately 2 mg/m^3), as monitored visually continuously by site personnel.

Air Monitoring Quantitative Approach: Control dust to maintain concentrations less than the project action level for total dust (5 mg/m^3), as measured with a real-time instrument.

With either approach, soil dust control is a project requirement. If, during the course of handling debris pile materials, visible dust is emitted, work shall cease and effective dust suppression techniques shall be immediately implemented. It is important to note that dust disturbed by vibrations from power tools, discharged air from pneumatic equipment, or during cleanup and handling waste may contain lead.

Quantitative air monitoring may be conducted in real-time for airborne dust concentrations using an aerosol monitor, such as a DUSTTRAK™ Aerosol Monitor Model 8520, or equivalent to assess the concentration of

suspended particulate matter in the air. If used, the monitor shall be calibrated according to the manufacturer's specifications. At no point during the course of the project should suspended particulate matter in the air exceed 5 mg/m^3.

If the airborne concentration of dust is visible (qualitative air monitoring method) or exceeds a project action level of 5 mg/m^3 (quantitative air monitoring method) the project personnel with appropriate responsibility and authority shall stop work until dust concentrations are reduced beneath the project action level. Real time measurements or visual observations for suspended particulate matter shall be recorded on the data form in Appendix 1.

8.2 Area of Interest 2:

A personal exposure assessment for worker exposure to lead shall be conducted to determine employee exposure to lead during a worst case exposure representative of enough operations to determine the range of exposure. Data from the exposure assessment will be used to adjust the project action level and determine if a respiratory hazard exists above a level that would trigger the need for respirator use.

Until such time that a personal exposure assessment is conducted, at no point during the course of the project should suspended particulate matter in the air exceed 1.25 mg/m^3. Real time measurements or visual observations for suspended particulate matter shall be recorded on the data form in Appendix 1.

9.0 Monitoring for Volatile Organic Compounds

Real time measurements will be taken in the breathing zones of the personnel in the work area. A photoionization detector (PID) shall be used on a daily or periodic basis to monitor site air and soil for potential exposure to volatile organic compounds.

An action level of 100 parts per million (ppm) has been chosen for this site. If the PID reads 100 ppm of total organic vapors, work shall cease and the area shall be secured. The SSS must notify the SHN project manager and the SHN industrial hygienist.

10.0 Personal Protective Equipment

Level of Protection: A _____ B _____ C X D X

Level C, Modified

- Full-face or half-face air purifying respirator (APR) equipped with National Institute For Occupational Safety And Health (NIOSH)-approved combination organic vapor and dust/mist filter cartridges (based on contaminant of concern)
- Chemically-resistant gloves (nitrile)
- Steel toe boots
- Safety vest, for traffic and heavy equipment safety
- Tyvek® suits, with built in shoe covers to protect from potentially contaminated soils

- Safety glasses
- Hard hat

Level D work includes any work performed at this site. If the action levels are reached, upgrade to a full or half-face APR with organic vapor and dust/mist filter cartridges.

Level D, Modified

- Steel toe boots
- Chemically-resistant gloves (nitrile)
- Safety glasses
- Hard hat
- Safety vest, for traffic and heavy equipment safety
- Tyvek® suits, as needed to protect from potentially contaminated soils

Respirators may be removed in areas where it is determined to be safe by the SSS, or acting SHN representative.

Respirators will be used, if warranted by site conditions, in order to minimize inhalational exposure to volatile and/or ambient air organic chemicals or other contaminants within dust. A full-face respirator also provides a higher level of protection than a half-face respirator. Organic vapor/dust and mist cartridges will be used, and new cartridges will be installed daily at a minimum, or as exposure and hours of usage warrant. To prevent exposure to particulates (dust, mists, or fumes), and to extend the usability of the organic vapor cartridges, dust and mist filters will be used, if warranted by site conditions. All respirators, cartridges, and filters will be NIOSH-approved.

Boots, gloves, and protective clothing will be used to prevent direct contact with potential contaminants in the piles and ambient air, and to provide a simple method of personal decontamination after fieldwork has been completed.

All employees of SHN and the project subcontractors will meet the minimum level of personal protective equipment (PPE) specific to the job task when entering or working in an area of known contamination. If the level of contamination is unknown, the maximum level of PPE will be donned prior to entering the suspected contamination zone. Once appropriate site monitoring has been conducted to determine the level of contamination present, the level of PPE may be reduced, as appropriate. If known or suspected conditions require an increase in the level of PPE in the contamination zones or newly-designated contamination zones, all field activities will immediately cease until the appropriate changes in PPE are made.

11.0 Occupational Exposure to Lead, Area of Interest 2

Lead enters the body primarily by oral and inhalation routes. Lead is a systemic poison with acute and chronic health effects. Acute and chronic exposures to airborne lead fumes or dust can cause central and peripheral nervous system damage, and gastrointestinal tract symptoms, including diarrhea, constipation,

and lead colic. Furthermore, lead can cause interference with hemoglobin synthesis and blood anemia, male and female reproductive system abnormalities, birth defects, kidney and liver damage, and replacement of calcium in bones leading to osteoporosis.

11.1 Employee Training

It is the responsibility of all contractors and subcontractors to be current in the training required by Cal-OSHA's Hazard Communication Standard (Title 8 California Code of Regulations [CCR] 5194). As with many other hazards associated with construction, the contractors are required to provide health and safety hazard training for the work being performed. Providing employees with this SSP will assist to meet the requirements for hazard communication for lead-related work. Training topics to be covered should include:

- Lead Health Hazards
- Applicable Hazard Reduction Controls
- Contents of this SSP
- Required Personal Hygiene Practices
- Safe Use of Hazardous Materials or Products
- Safe Use of Personal Protective Equipment including Respiratory Protection

Given the nature of the work and the work practices that will be implemented according to this SSP, airborne lead concentrations are not expected to exceed the Cal-OSHA PEL (0.05 mg/m^3) or Cal-OSHA action level (AL) (0.03 mg/m^3) as 8-hour time-weighted average exposures (TWA).

11.2 Housekeeping and Hygiene Facilities

Work practices, as described in this SSP, will be used for worker protection. Exposure routes for lead are through inhalation and ingestion. Table 3 provides lead exposure routes and symptoms.

Table 3. Lead Exposure Routes and Symptoms, Area of Interest 2

Substance	Exposure	Range of Symptoms
Lead (as Pb)	Inhalation and Ingestion	**Acute Exposure:** colic, muscle aches, weakness, memory disorders, permanent kidney or brain damage, seizures from extremely high exposures **Chronic Exposure:** anemia causing skin pallor, dark gray-blue line along gumline, visual-motor and intellectual impairment, lead colic, wrist drop, triad of gout, hypertension, and chronic progressive renal failure, clinical depression, probable teratogen

In accordance with Title 8 CCR, 1532.1 (h) and application of that regulation to this project, housekeeping practices shall include the following:

- Maintain surfaces free of accumulations of dust or material containing lead.
    - Such surfaces include the inside and outside of vehicles, tools, and personal protective equipment.
    - Surfaces may be cleaned by washing, wet wiping, vacuuming, or other methods that minimize the likelihood of lead becoming airborne.
- Vacuums shall be equipped with high efficiency particulate absorbing (HEPA) filters and used in a manner that minimizes reentry of lead onto the work surfaces or onto personal work clothing or surfaces.
- Any wastes shall be immediately contained.
- Compressed air shall not be used to remove dust from any surface.
- Decontamination hand wash facilities will be set up on site.
- Hand to mouth contact (ingestion exposure) will be prevented by prohibiting smoking, eating, and drinking on site.
- Employees must wash their hands and faces prior to eating, drinking, using tobacco products, or applying cosmetics.
- Lead hazard signage will be posted at the work area entry that reads as follows:

WARNING
LEAD WORK AREA
POISON
NO SMOKING OR EATING

- Change areas shall be available on site.
- Dispose of lead-contaminated wash water in accordance with applicable local, state, or federal regulations.
- Employees shall remove all PPE prior to leaving the workplace.

11.3 Blood Lead Levels and Medical Surveillance

Blood lead levels of workers exposed to lead in construction activities is regulated under the Cal-OSHA Lead in Construction Standard (Title 8 CCR 1532.1 [j]). Biological monitoring as indicated for workers in the following situations:

- Initial blood lead levels (BLL) and zinc protoporphyrin (ZPP) are required for all new employees working with unknown airborne lead levels or exposed above the AL for at least one day.

- Employees exposed at or above the AL for more than 30 days in any 12 consecutive months must participate in a medical surveillance program including BLL and ZPP testing at least every two months for the first six months and every six months thereafter.
- Any employee with BLL at or above 40-micrograms of lead per deciliter (µg/dL) of blood shall have BLL and ZPP testing every two months until two consecutive samples show BLL less than 40 µg/dL.
- Any employee with BLL above 50 µg/dL shall receive follow-up BLL testing within two weeks after the first test.
- The employer shall remove employees from work having exposure at or above the AL when the BLL and a follow-up BLL test are at or above 50 µg/dL. Employees who have been removed due to an elevated BLL can return to the job after having two consecutive BLL tests at or below 40 µg/dL.
- The employer shall notify all employees in writing of their BLL and ZPP test results within five working days after receipt of the results.

In addition to blood lead tests, all employees who may work with lead will receive an annual physical examination and be included in the contractor's medical monitoring program. The examination will be completed before the employee is exposed to lead-containing residues or soils.

- Workers will receive a baseline medical examination by a licensed occupational physician including:
  - medical and occupational health history,
  - BLL and ZPP testing before and after the project,
  - pulmonary function testing,
  - determination by the physician if the employee is medically qualified to wear a negative pressure respirator, and
  - basic physical examination.
- The examining physician should be provided with the following information:
  - Title 8 CCR §5144—Respiratory Protection,
  - Title 8 CCR §1532.1—Lead in Construction Standard, and this SSP.

12.0 Physical Hazards

The physical hazards that are associated with the project site include field activities, excess noise, proximity to the operation of heavy equipment, and the use of heavy equipment. Personnel should exercise caution and use proper lifting techniques, material handling techniques, and pay attention to tight quarters. During heavy equipment operations, proper care should be exercised in the physical placement and location of site personnel. All clothing articles that are worn by site personnel should be reasonably close fitting and have no loose or hanging items attached.

Potential hazards exist from falling objects, uneven working surface, stored energy, as well as from hearing impairment and communication difficulties that are associated with the operation of heavy equipment. An effective method of communication should be established prior to commencement of field activities.

If any SHN subcontractor does not know how to control these hazards, contact the SHN representative PRIOR TO INITIATING WORK AT THE SITE.

13.0 Heavy Equipment Safety

SHN will minimize hazards associated with heavy equipment operation by working with heavy equipment operators to implement the following work practices.

- Safety vests will be worn by all personnel.
- All site visitors will be advised of site hazards associated with heavy equipment operations.
- Site workers will stay out of the reach of heavy equipment operations.
- Employees shall not place any part of their bodies outside the running lines of equipment/trucks or other parts of the equipment where shear or crushing hazards exist.
- Site workers will communicate with equipment operators to let them know the locations of any potential hazards and personnel.
- Equipment shall not be operated in areas that expose the operator to the hazard of collision with overhead obstructions.
- Drivers/operators shall inspect the equipment at the start of each shift to ensure its safe operation and functioning systems.
- No equipment shall be operated with a leak in its fuel system.
- Only drivers authorized by the employer and trained in the safe operations of heavy equipment or trucks shall be permitted to operate such equipment.
- Drivers shall look in the direction of travel and shall not move a vehicle until certain that all persons are in the clear.
- Equipment/vehicles shall not be driven up to anyone standing in front of a fixed object of such size that the person could be caught between the equipment/vehicle and the object.

14.0 Housekeeping, Area of Interest 1 and 2

The site shall be kept clean. SHN and the subcontractor(s) shall make coordinated efforts to keep the site clean of debris and used equipment that may create a safety hazard. The following procedures shall apply:

- Ample lighting shall be provided if working in low light.
- All work areas will be kept free of tripping hazards to the degree possible.
- Means of access and egress will be kept clear.

15.0 Electrical Safety

SHN shall communicate with contractors that electrical wiring or extension cords shall be placed in non-traffic and/or non-heavy equipment operating areas. If wiring must be routed through such areas, it shall be installed with a clearance of not less than 16 feet to allow the safe passage of vehicles and heavy equipment. Wiring shall not be placed in decontamination areas or other areas where water may pose the risk of electric conductivity on wetted ground or other shock hazards.

16.0 Fire Response Equipment

Fire extinguishing equipment meeting the requirements of 29 Code of Federal Regulations (CFR) 1910 Subpart L will be on hand and ready to use to control incipient fires. All SHN vehicles used on a project site will be equipped with a portable fire extinguisher.

Portable fire extinguishers will meet the requirements of 29 CFR 1910.157 with particular attention paid to ensure that it is:

- appropriate to the potential fire hazard at the site;
- operable and fully charged;
- regularly inspected, maintained, and tested; and
- visible, identifiable, and accessible (within 50 feet of an employee, and unobstructed at the work site).

In making a selection from available incipient fire control resources, the classification of the potential fire hazard will direct the appropriate choice. Portable fire extinguishers may be appropriate for a single class of fires or a combination of classes of fires.

17.0 Heat Stress Illness

Heat stress can be a potential hazard when field activities are conducted during periods of warm weather. In addition, heat stress can be accentuated when chemical protective clothing and equipment are worn by site personnel. If not prevented, heat stress can result in illness.

17.1 General Prevention of Heat Stress Illnesses

- Rest in shaded areas
- Stay hydrated
- Avoid vigorous physical activities in hot and humid weather
- At work, if you must perform physical activities in hot weather:
  - Drink plenty of fluids.
  - Avoid alcohol, coffee, and tea which may lead to dehydration.
  - Take frequent mini-breaks to hydrate yourself.

17.2 Provision of Water

Employees are encouraged to drink water frequently. Water shall be "fresh, pure, suitably cool, and provided to employees free of charge." The water shall be located as close as practicable to the areas where employees are working and be readily available.

- Site Safety Supervisors are responsible to ensure employees have an adequate supply of drinking water.
- Site Safety Supervisors shall encourage the frequent consumption of small quantities of water, up to 4 cups per hour, when the work environment is hot and employees are likely to be sweating more than usual in the performance of their duties.
- Drinking water will be provided in sufficient quantities to provide one quart per employee per hour for the entire shift (at least 2 gallons per employee for an 8-hour shift).
- If there are effective procedures for replenishing the water supply during the shift, a minimum of 2 quarts of water per employee may be provided at the beginning of the shift.

17.3 Shade and Rest

A shaded area will be provided when the temperature exceeds 80 degrees Fahrenheit. The amount of shade present shall be at least enough to accommodate the number of employees on recovery or rest periods, so that they can sit in a normal posture fully in the shade without having to be in physical contact with each other. The shade shall be located as close as practicable to the areas where employees are working. Subject to the same specifications, the amount of shade present during meal periods shall be at least enough to accommodate the number of employees on the meal period who remain on site. The shaded area shall be open to the air or ventilated and cooled and access shall be permitted at all times. Canopies, umbrellas, or other temporary structures may be used to provide shade, provided they block direct sunlight.

Site Safety Supervisors are responsible for the following tasks:

- Ensuring that employees have access to shaded or air conditioned areas (such as a break room) to prevent or recover from heat illness symptoms or to take rest breaks
- Emphasizing the importance of taking recovery or rest periods

In the event an employee feels discomfort from the heat, accommodating a preventative cool-down rest to allow the employee to cool down and prevent the onset of heat illness.

An individual employee who takes a preventative cool-down rest shall:

- be monitored and asked if he or she is experiencing symptoms of heat illness;
- be encouraged to remain in the shade; and
- not be ordered back to work until any signs or symptoms of heat illness have abated, but in no event less than 5 minutes in addition to the time needed to access the shade.

17.4 High-Heat Procedures

High heat procedures (when temperatures exceed 95 degrees Fahrenheit) are not expected to be required at this project site.

17.5 Responding to Heat Illness Emergencies Employee Procedures

Any employee who recognizes the symptoms or signs of heat illness in themselves or in co- workers should immediately report this condition to the Site Safety Supervisor. When you recognize signs of heat illness in yourself or in a co-worker:

- Move them to a shaded area for a recovery period of at least 5 minutes
- If the condition appears to be severe or the employee does not recover, then emergency medical care is needed.
- Immediately report to your supervisor any symptoms or signs of your heat illness you may be experiencing or observing in a co-worker.
- Call 911 if supervisor is not readily available.

17.5.1 Site Safety Supervisor Procedures

Site Safety Supervisors shall:

- Carry cell phones, radios, or other means of communication ensuring emergency services can be called and verifying the radios or other means of communication are functional prior to each shift.
- Know the exact work locations and have clearly written and precise directions to the work site for emergency responders.
- Conduct pre-shift meetings before the commencement of work to review the high heat procedures, encourage employees to drink plenty of water, and remind employees of their right to take a cool-down rest when necessary.

17.5.2 Emergency Contact Procedures

- Call 911.
- Be ready to provide emergency response personnel with directions to work location.
- When working at remote locations, you must be able to provide concise directions to emergency response personnel.

Further emergency response guidance for supervisors is provided in Section 9.

17.6 Response to Heat Stroke Symptoms

- Victims of heat stroke must receive immediate treatment to avoid permanent organ damage.
- Always notify emergency services (911) immediately. If their arrival is delayed, they can give you further instructions for treatment of the victim.
- If possible, get the victim to a shady area to rest.
- Remove heavy or change to lightweight clothing.
- Cool the victim; effective cooling measures include:
    - Administering cool, non-alcoholic beverages
    - Applying cool or tepid water to the skin (for example you may spray the victim with cool water from a garden hose)
    - Providing a cool shower or sponge bath
    - Moving victim to an air-conditioned environment or fanning the victim to promote evaporation
    - Placing ice packs under armpits and groin
    - Monitoring body temperature with a thermometer and continuing cooling efforts until the body temperature drops to 101-102 degrees

18.0 Site Control

To the extent feasible, personnel, equipment, and the decontamination station shall be located upwind of any suspected or known sources of contamination. During field activities, the project site will be divided into three basic areas: a contamination zone, a contamination reduction zone, and an uncontaminated zone. The uncontaminated zone will include all area(s) of the project site that can be documented as not containing any detectable levels of contamination by the selected methods of site monitoring that are presented in this SSP. At the project site, the contamination reduction zone and uncontaminated zone may be the same location, but must first be determined based on the site monitoring program.

No staff shall be allowed in an area that is designated as a contamination zone, or a contamination reduction zone (that is not also an uncontaminated zone), unless authorized by the SSS or acting SHN representative. Workers entering areas other than uncontaminated zones must comply with the PPE provisions of this plan, and satisfy all the requirements as specified in 29 CFR 1910.120. The SSS or acting SHN representative may, and will cease activities if the site control portions of this SSP are not properly followed.

19.0 Decontamination Procedures

19.1 Decontamination Areas

The decontamination areas of the project site will be established prior to the commencement of any operations in the contamination reduction zone(s) or uncontaminated zone(s). Decontamination areas may be reestablished by the SSS or SHN representative, in response to changes that occur in environmental conditions, or as site activities warrant.

19.2 Equipment Decontamination

All equipment will be appropriately decontaminated between each sampling event, and before it is transported away from the project site. All non-disposable PPE will also be appropriately decontaminated before it is removed from the site. Water generated from decontamination of equipment will be temporarily stored in containers and, subsequent to sample collection and analyses, properly disposed. Decontamination of personnel will be accomplished by removing any contaminated clothing and gear, washing all exposed skin with a solution of deionized water and Liquinox®, and rinsing with deionized water. All rinse water will be temporarily stored in containers, and disposed of properly.

19.3 Emergency Decontamination

The decision whether or not to decontaminate a worker is based on the contaminant type and severity of the resulting injury or illness. For some emergency victims, immediate decontamination may be an essential part of life-saving first aid. For others, decontamination may aggravate the injury or delay life-saving treatment. If decontamination does not interfere with essential treatment, it shall be performed.

- **If decontamination can be performed:**

  All protective clothing and equipment will be removed, cut off, or rinsed.

- **If decontamination cannot be performed:**

  The worker will be wrapped in blankets, plastic, or rubber in order to reduce the potential of contaminating other site personnel. The appropriate emergency medical personnel will be alerted to any potential contamination that is present, and instructed about specific decontamination procedures, if necessary. Site personnel that have specific knowledge of the incident will be sent along with emergency medical staff to an appropriate care facility.

  If immediate medical treatment is required to save a life, decontamination procedures should be delayed until the worker is stabilized. If decontamination can be performed without interfering with essential life-saving techniques or first aid, or if a worker has been contaminated with an extremely toxic or corrosive material that could cause severe injury or loss of life, decontamination must be performed immediately.

  If an emergency attributable to a heat-related illness develops, protective clothing should be removed from the worker as soon as possible, in order to reduce heat stress.

20.0 General Safety Requirements

The following general safety procedures shall be followed by all persons entering and/or working in the immediate area of project activities:

1. No SHN or subcontractor personnel will be allowed on site without the prior knowledge and consent of the SSS.
2. There will be no field activities conducted without sufficient backup personnel. At a minimum, two persons who currently satisfy the health and safety requirements as specified in 29 CFR 1910.120 (e) must be present at the site while field activities are in progress.
3. All personnel involved with the project shall bring to the attention of the SSS or SHN project representative, any unsafe condition or practice associated with site activities.
4. Site personnel must avoid unnecessary contamination, such as, walking through known or suspected "hot" zones or contaminated puddles, kneeling or sitting on the ground, and/or leaning against potentially contaminated equipment.
5. Respiratory devices may not be worn by staff with beards, or under any other conditions that may prevent a proper seal or fit.
6. Respiratory devices may not be worn with contact lenses.
7. No entry of any excavation or test pit that is greater than 5 feet in depth will be allowed without the proper installation of trench shoring, or other approved means of excavation security designed and installed in conformance with current California Occupational Health and Safety Administration (Cal-OSHA)/OSHA regulations.
8. Smoking will only be allowed in designated areas of the project site.
9. Hard hats will be worn within 10 feet of any heavy equipment that is operating.
10. Proper hearing protection will be worn at all times at the project site, in conformance with current Cal-OSHA/OSHA regulations.
11. Proper eye protection will be worn at the project site, in order to protect the eyes from liquid splashes, flying debris, or other potential hazards.

21.0 Emergency Response Plan

The SSS or SHN representative shall be immediately notified of any injury or accident that occurs at the project site. Listed below are emergency telephone numbers and the locations of nearby medical care facilities in the event that a job site injury requires off-site medical aid. Written directions to Saint Joseph's Hospital are provided in Table 4 (on the next page). Figure 1 shows the location of the hospital.

Table 4. Saint Joseph's Hospital Driving Directions
Redwood Marine Terminal II
Samoa, California

Mileage (mi.)	Directions	Distance (mi.)
0	TCF Drive to Vance Avenue	0.1
0.3	Vance Avenue to right on New Navy Base Road	0.1
0.8	New Navy Base Road to right on CA-255	1.6
1.0	CA-255 to Myrtle Avenue	2.1
6.3	Myrtle Avenue to right on Harrison Avenue	1.0
7.3	Harrison Avenue to right on Saint Joseph Lane	0.5

Figure 1: Map of Driving Directions to Saint Joseph's Hospital.

21.1 Emergency Contacts

In the event of an emergency, the following agencies and persons shall be appropriately notified immediately following the necessary emergency response contacts:

Medical Facility	Ph#
Emergency Medical Facilities:	911 or 707-445-8121
Saint Joseph Hospital: 2700 Dolbeer Street, Eureka CA	
Ambulance	911
Fire Department	911
Police Dept	911
Poison Control Hotline	800-523-2222

21.2 Government Contacts

In the event of an unauthorized release of potentially hazardous materials, the following agencies will be notified:

Contact	Phone #
North Coast Regional Water Quality Control Board	707-576-2220
State Office of Emergency Services	800-852-7550
Humboldt County Division of Environmental Health	707-445-6215

22.0 Implementation Schedule

Before fieldwork begins, the following activities must be completed:

- Site personnel must read and acknowledge this SSP by signing the "Daily Record, Site Safety Meeting Attendance" form presented in Appendix 2.
    - The Site Safety Supervisor is responsible for ensuring that all site personnel, including subcontractors, read and acknowledge this SSP.
- Workers must be trained on the hazards of lead and the potential for exposure prior to beginning work (Hazard Communication/Lead Awareness Training).
- Under the supervision of a licensed physician, workers must be medically qualified to work at the site. Initial blood sampling and analysis for BLL and ZPP are required.
- Hand washing facilities must be in place at the work site and ready to use prior to fieldwork.

During lead-related work, the following activities are required:

- Dust suppression techniques such that no visible dust is emitted.
- Area of Interest 1: Air monitoring (qualitative or quantitative approach) shall be conducted to ensure that airborne dust concentrations do not exceed the project action level:
    - Quantitative approach: 5 mg/m^3
    - Qualitative approach: visible airborne dust emissions (approximately 2mg/m^3)

- Area of Interest 2: Air monitoring shall be conducted to ensure that airborne dust concentrations do not exceed the project action level:
    - Quantitative approach: 1.25 mg/m^3
    - A personal exposure assessment must be performed to assess worker exposure to lead. If the personal exposure assessment yields lead exposure within allowable limits, a project action level of 5 mg/m^3 may commence.
- The SSS will ensure that housekeeping practices and debris waste handling instructions are followed.
- The SSS will ensure that dust suppression techniques are used when handling earth materials containing lead and during removal and reconstruction of roadway.

23.0 Onsite Documentation

Compliance with this SSP will be documented by execution of the "Daily Record, Site Safety Meeting Attendance" form presented in Appendix 2. By signing these sheets, each person to be involved in the project field activities acknowledges willingness to comply with this SSP throughout the period of the current field activities. Safety meetings will be scheduled at the beginning of field operations, and will be held at the start of each day. Field monitoring results will be recorded and stored at SHN. Cal-OSHA regulation, 8 CCR § 1532.1 requires the employer to communicate information concerning hazards to employees according to the Hazard Communication Standard, 8 CCR § 5194. Documentation of SHN employee medical surveillance, training, and respirator fit test records is maintained at the corporate office located at 812 West Wabash Avenue in Eureka, California. Copies of these records are provided to each SHN employee. SHN subcontractors are responsible for maintaining their own safety training records.

24.0 Hazardous Site Operations Employee Training

All SHN personnel who work at hazardous materials sites have received the mandated OSHA 40-hour Hazardous Site Operations Training and subsequent annual 8-hour recertification, as specified in CFR Title 29 §1910.120.

25.0 Medical Surveillance

All employees are required to have a complete physical examination prior to their assignment at a hazardous materials project site. Comprehensive physical examinations provide not only baseline health and monitoring information, but also include a level of assurance that the employee is capable of wearing the required protective equipment and performing potentially strenuous work. Refer to Section 11.3 for additional medical surveillance requirements.

26.0 References Cited

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California Occupational Safety and Health Administration. (NR). "1532.1 Title 8, CCR Lead." Sacramento, CA:Cal-OSHA.

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Marlowe, Christopher. (1999). "Safety Now: Controlling Chemical Exposures at Hazardous Waste Sites with Real-Time Measurements." Fairfax, VA: AIHA Press.

SHN Consulting Engineers & Geologists, Inc. (2014). Site Investigation Report of Findings for the Eastern Half of the Former Louisiana-Pacific Pulp Mill, One TCF Drive, Samoa, California; Case No. 1NHU892

1 Suspended Particle Matter Monitoring

Suspended Particle Matter Monitoring
Redwood Marine Terminal II
Samoa, California

Project Number:

Work Area/Activities:

Date: **Monitored By:**

Area of Interest 1

Instructions: If using qualitative method, observe project for dust emissions and note presence/absence. If using quantitative method, use aerosol monitor in accordance with manufacturer's instructions. Ensure that background samples are collected when debris pile disturbances are not taking place.

Project Action Levels	Quantitative: 5 mg/m^3 or Qualitative: visible airborne dust emissions

Time of Day	Site Location/Activity	Total Dust Concentration[1]

Time of Day	Site Location/Activity	Total Dust Concentration[1]

1. Total Dust Concentration:
   Quantitative Method: mg/m^3 – measured in milligrams per cubic meter with a real-time instrument
   Qualitative Method: visible emissions observed (presence/absence)

Suspended Particle Matter Monitoring
Redwood Marine Terminal II
Samoa, California

Project Number:

Work Area/Activities:

Date: **Monitored By:**

Area of Interest 2

Instructions: Quantitative method—use aerosol monitor in accordance with manufacturer's instructions. Ensure that background samples are collected when debris pile disturbances are not taking place.

Project Action Levels	Quantitative: 1.25 mg/m^3 or 5.0 mg/m^3 after results are received documenting a negative worker exposure assessment for lead

Time of Day	Site Location/Activity	Total Dust Concentration[1]

Time of Day	Site Location/Activity	Total Dust Concentration[1]

1. Total Dust Concentration:
   Quantitative Method: mg/m^3 – measured in milligrams per cubic meter with a real-time instrument

VOC Monitoring Results
Total Organic Vapor
Redwood Marine Terminal II
Samoa, California

Project Number:

Work Area/Activities:

Date: **Monitored By:**

Instructions: If using qualitative method, observe project for dust emissions and note presence/absence. If using quantitative method, use aerosol monitor in accordance with manufacturer's instructions. Ensure that background samples are collected when earth-moving activities are not taking place.

Project Action Levels	100 ppm total organic vapor
Instrument	Photoionization detector

Time of Day	Sample Reading	Volatile Organic Compound Concentration[1]	Exceeds Project Action Level? Y/N	Action Taken or Comments

Time of Day	Sample Reading	Volatile Organic Compound Concentration[1]	Exceeds Project Action Level? Y/N	Action Taken or Comments
1. Volatile Organic Compound Concentration: ppm – measured in parts per million with a real-time instrument (photoionization detector, PID)				

Site Safety Forms 2

Hazardous Materials Site Operations
Site Safety Meeting Attendance
Redwood Marine Terminal II
Samoa, California

Job Name: **Activity:** **Job #:**

Given By: **Signature:** **Date:** **Time:**

Company/Agency	Name	Operation/ Function	Signature	Read SSP	29CFR1910.120(e)	
					40 hr	24 hr
				Y / N	Y / N	Y / N
				Y / N	Y / N	Y / N
				Y / N	Y / N	Y / N
				Y / N	Y / N	Y / N
				Y / N	Y / N	Y / N
				Y / N	Y / N	Y / N
				Y / N	Y / N	Y / N
				Y / N	Y / N	Y / N
				Y / N	Y / N	Y / N

Job Hazard Analysis

Action Level Monitoring Results
Total Organic Vapor
Redwood Marine Terminal II
Samoa, California

Job Name: **Activity:** **Job #:**

Sampled By: **Signature:** **Date:** **Time:**

Time	Instrument	Sample Reading	Upgrade To?	Comments

Job Hazard Analysis

Activity:	**Date:**
	Project:
Description of the work:	**Site Supervisor:**
	Site Safety Officer:
	Review for latest use: Before the job is performed.

Work Activity Sequence (Identify the principal steps involved and the sequence of work activities)	**Potential Health and Safety Hazards** (Analyze each principal step for potential hazards)	**Hazard Controls** (Develop specific controls for each potential hazard)
	1.	1.
	2.	2.
	3.	3.
	4.	4.
	5.	5.

Job Hazard Analysis

Work Activity Sequence (Identify the principal steps involved and the sequence of work activities)	**Potential Health and Safety Hazards** (Analyze each principal step for potential hazards)	**Hazard Controls** (Develop specific controls for each potential hazard)
	1.	1.
	2.	2.
	3.	3.
	4.	4.
	5.	5.
	6.	6.
	7.	7.
	8.	8.

Job Hazard Analysis

Equipment to be used (List equipment to be used in the work activity)	**Inspection Requirements** (List inspection requirements for the work activity)	**Training Requirements** (List training requirements including hazard communication)

Job Hazard Analysis

	PRINT NAME	SIGNATURE	
Supervisor Name:			**Date/Time:**
Safety Officer Name:			**Date/Time:**
Employee Name(s):			**Date/Time:**
			Date/Time:
			Date/Time:
			Date/Time:
			Date/Time:
			Date/Time:
			Date/Time:

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