SAMPLING AND ANALYSIS PLAN AMENDMENT:

SOUTH I STREET MILL REUSE PROJECT
ARCATA, CALIFORNIA
TARGETED BROWNFIELDS ASSESSMENT
PHASE II B

USACE Contract Number: DACA45-98-D-0004
Document Control Number: 20074.515.059

PREPARED FOR:
THE UNITED STATES ENVIRONMENTAL PROTECTION AGENCY REGION IX

AND

THE UNITED STATES ARMY CORPS OF ENGINEERS

PREPARED BY:

WESTON SOLUTIONS, INCORPORATED
SHERMAN OAKS, CALIFORNIA

REVISED
MARCH 2004

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1.0 INTRODUCTION

On September 12, 2003 the United States Environmental Protection Agency (EPA), through the United States Army Corps of Engineers (ACE), tasked Weston Solutions, Incorporated (Weston) to conduct a follow-up investigation at the Arcata Mill Site in Arcata, Humboldt County, California. Weston completed a Phase II Targeted Brownfields Assessment (Phase II TBA) of the site in December 2002 and prepared a draft final report. The TBA was conducted on behalf of the City of Arcata; the site history and details of that investigation are presented in the Phase II report. This Sampling and Analysis Plan Amendment (Phase II B) is an extension of the EPA-approved *South I Street Project Reuse Project, Arcata, California TBA Sampling and Analysis Plan* (Phase II SAP).

1.1 Project Organization

The project organization has not changed except for the following: The Weston Project Manager (PM) is Benjamin Castellana. Dr. Castellana is a Project Geoscientist in Weston's Sherman Oaks Office.

1.2 Distribution List

The distribution list for this Phase II SAP Amendment is:

Suzanne Perkins, US EPA Region IX Task Monitor
Gail Jones, US EPA Region IX Quality Assurance Office
Jennifer Gerhardt, US ACE Project Manager
Lisa Bernard, North Coast Regional Water Quality Control Board
Larry Oetker, City of Arcata

1.3 Statement of the Specific Problem

Based on the results of the Phase II TBA, the State of California, North Coast Regional Water Quality Control Board (NCRWQCB) deemed that several issues pertaining to the site need to be resolved before development at the site could proceed. Specifically, groundwater concentrations of total petroleum hydrocarbons (TPH), semi-volatile organic compounds (SVOCs) and metals measured from hydropunch samples exceeded the site-specific action levels outlined in the Phase II SAP. These contaminants were identified in soils at the site, but correlation with groundwater concentrations was not definitive. In addition, the SVOC compound pentachlorophenol (PCP) was identified in soil samples at the site; according to the NCRWQCB, this compound is commonly associated with dioxin contamination. Finally, the NCRWQCB deemed it necessary to determine whether the groundwater at the site might be considered a potable resource in order to identify the most appropriate remedial action for contaminants identified during the Phase II and Phase II B sampling events.

2.0 BACKGROUND

The background information has not changed, except for the following: based on the sampling conducted under the Phase II SAP, soils and groundwater at the site were found to be contaminated with TPH in the diesel and oil ranges, SVOCs, including PCP, and metals. Contaminants in groundwater do not correlate strongly with soil contamination, suggesting that they may not be entirely related (see Figure 2-1).

TPH as diesel range organic compounds (TPH diesel) was identified in 36 soil samples collected at the site (4.9 - 390 ppm), and detected above the Phase II action level of 100 parts per million (ppm) in eleven samples. TPH as motor oil range organic compounds (TPH oil) was detected in 36 soil samples collected at the site (5.5 - 850 ppm); no results were above the project action level of (1000 ppm). TPH as gasoline range organic compounds was not detected in any of the 15 site samples analyzed.

TPH diesel exceeded the action level in all nine groundwater samples collected at the site. Results ranged from 140 to 1,100 parts per billion (ppb). In general, the lower concentrations were detected along the western perimeter of the site; the highest TPH diesel results were detected along the eastern and southeastern perimeter of the site, which is bound by Jolly Giant Creek.

Cadmium and zinc were the only metals detected above background levels (0.40 and 620 ppm, respectively) in site soils during the Phase II TBA event. Cadmium concentrations ranged from background (0.21 - 0.25 ppm) to 6.9 ppm. Zinc concentrations ranged from background (118 - 168 ppm) to 664 ppm.

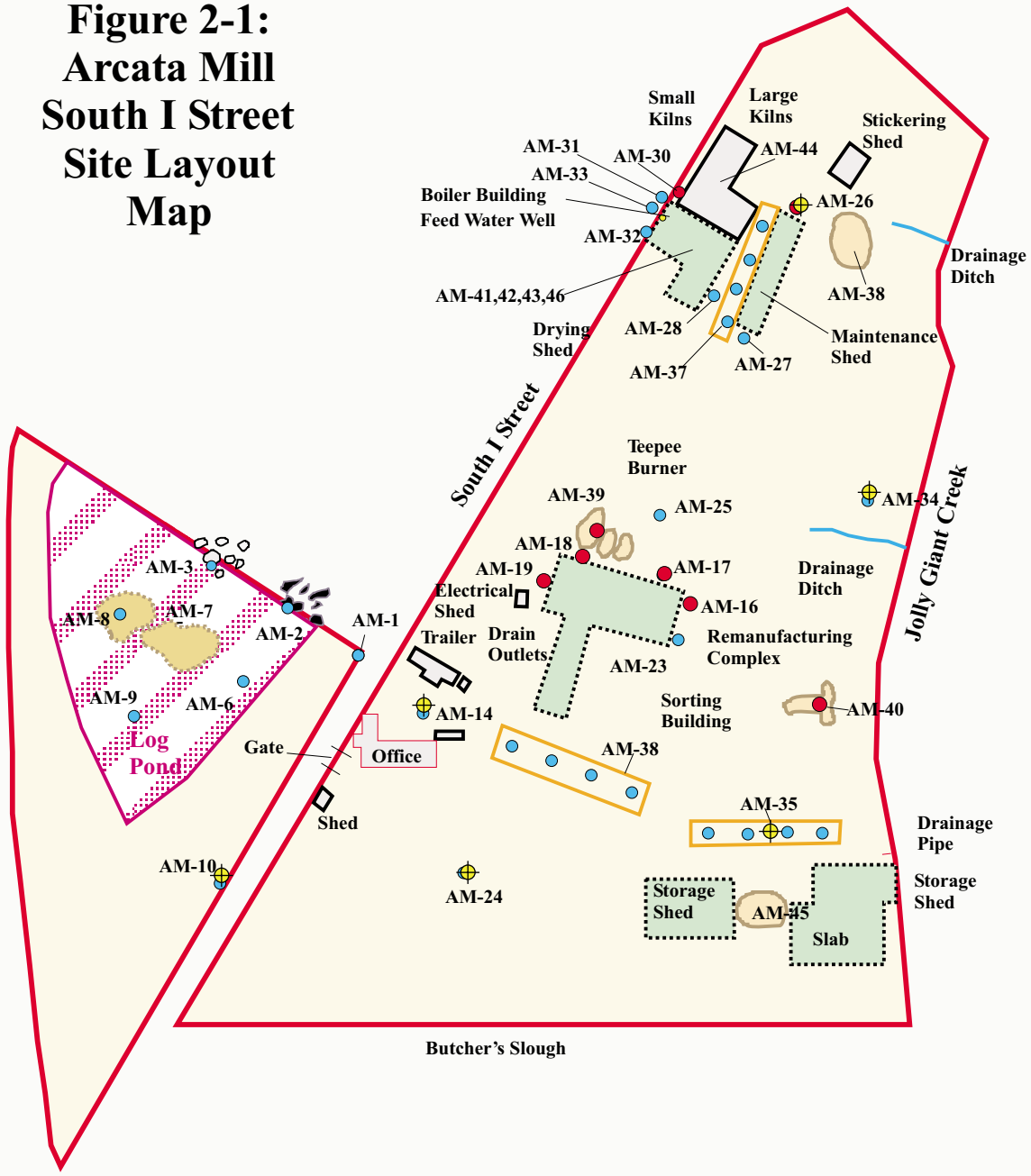
Arsenic, chromium, iron, and nickel were detected at concentrations above the established action levels in site soils; however, these concentrations were consistent with the background samples collected near the site. The site sediments have a mafic/ultramafic provenance that is typified by naturally elevated iron, nickel and chromium.

Arsenic, nickel, zinc, copper, iron, lead, chromium, thallium, and selenium were detected in groundwater at concentrations above the site action levels. The highest concentrations of all metals, with the exception of copper and zinc, were reported in the southeastern portion of the LLI property.

Benzene was the only VOC detected in soil above the action level. Benzene was detected at 0.009J ppm, which is above the action level of 0.002 ppm. In addition, acetone, 2-butanone, cis-dichloroethene, methyl acetate, toluene, and trichlorofluoromethane were detected in soils at the site below their respective action levels.

Only ethylbenzene was detected in groundwater at the site, a compound not detected in site soils. No chlorinated VOCs were detected.

Figure 2-1: Arcata Mill South I Street Site Layout Map



Legend

Structure
- Demolished
- Existing

Project Boundary

Soil Stockpile

Distressed Vegetation

Scattered Concrete

Scattered Metal Debris

Composite Sample Location

Sample Location

Sample Locations of Interest:

metals - AM-18, 19, 30, 33 37, 40

SVOCs - AM-40

Benzene - AM-17

PCP - AM-16, 18, 19, 39

Hydropunch groundwater sample location (co-located with surface sample)

Approximate Scale in Feet

0 190

Three SVOCs -benzo(a)pyrene, benzo(a)anthracene, and benzo(b)fluorane - were detected in excess of their action levels in one sample from a soil stockpile at concentrations of 0.110, 0.120, and 0.250 ppm, respectively. In addition, PCP was detected in four samples on the LLI property, ranging from non-detect to 0.190 ppm (action level is 0.0001 ppm). Naphthalene and caprolactam were detected in site soils below the site action level.

Of the SVOCs, naphthalene, diethylphthalate, phenol, and caprolactam were detected at concentrations less than 5 ppb in groundwater samples. Only phenol exceeded the site action level.

Two chlorinated pesticides, beta-benzene hexachloride and endrin aldehyde, were detected in one soil sample collected near the remanufacturing complex (0.006 and 0.006 ppm, respectively). DDT was detected at 0.032 ppm in soil near the maintenance shed. Only beta-benzene hexachloride exceeded the action level of 0.0001 ppm.

3.0 PROJECT OBJECTIVES

3.1 Project Task and Problem Definition

The EPA has tasked Weston to conduct soil and groundwater sampling at the site to determine the following:

1) Whether the contaminants in the soil are sufficiently leachable to pose a threat to groundwater;
2) Whether dioxins are present at the soil locations with the highest PCP concentrations, as identified in the Phase II TBA;
3) The nature of the groundwater flow under the site;
4) Whether the groundwater at the site can be considered a potable resource (in order to determine what action levels are appropriate);
5) The concentrations of contaminants in groundwater at a downgradient location, relative to an upgradient location (a determination of attribution of contamination to the site).
6) The inter-connectivity of groundwater and surface water.

3.2 Data Use Objective

Data collected during this phase of the investigation will be used to:
1) Determine the concentration of analytes of concern (AOCs) in site soils.
2) Determine the leachability of AOCs in site soils through California Waste Extraction Test (CalWET) analyses to be compared with total concentrations in order to establish the threat to groundwater posed by soil contamination.
3) Determine whether dioxin contamination may be an issue at the site by analyzing soils for dioxins at areas with the highest PCP contamination.
4) Determine the reportable concentrations of AOCs in groundwater across the site through the analysis of properly installed and developed groundwater wells.
5) Determine whether soil contamination threatens or contaminates a potable resource (groundwater) by establishing the total dissolved solids concentration of the groundwater and the upgradient concentrations of contaminants.
6) Determine whether groundwater and surface water are interconnected by comparing AOC concentrations and ratios between surface water samples and nearby groundwater samples.

3.3 Action levels

The AOC list, as well as pertinent action levels are presented as Table 3-1 in this Amendment. The AOC list includes SVOCs, VOCs, metals, TPH diesel and oil, and dioxin. Based on data from the Phase II TBA, TPH gasoline was deemed not to be important AOCs for further investigation. VOCs were present in groundwater at the site, but the analytes detected could not be attributed to site soils; VOCs are included in groundwater to determine whether an off-site source is possible. In addition, due to the unexpected presence of PCP suggesting the presence of treated wood products at the site, a limited number of dioxin analyses are added to the list.

The action levels for AOCs described in the Phase II SAP have not changed, except that the CA Waste Extraction Test (CalWET) will be used in lieu of the US EPA Soil Screening Levels (SSLs)

because the leach test is considered by the NCRWQCB to be a more accurate reflection of threat to groundwater from site soils than a generic model. Action levels for the Cal-WET will be the Maximum Contaminant Levels (MCL). The MCLs were used in this case because if the leachate exceeds the MCL than there is a likelihood of contaminating the shallow groundwater on site. However, if the limits listed in California Code of Regulations, Title 22 Part 66262.24 were below the MCL than the lower action level will be used by default. In addition, because the purpose of the limited number of dioxin samples is to establish whether this compound is an AOC, the action level for dioxin will be the detection limit. The dioxin detection limit should be sufficiently low as to detect concentrations below the Residential PRG (PRG_{res}), which is 0.0000039 ppm, or 3.9 parts per trillion (ppt).

3.4 Decision Rule

Results will be evaluated against the following decision rules:

1) If analysis of soil samples documents concentrations of AOCs to be greater than action levels, then the NCRWQCB may request the City to further characterize, remove, or remediate the impacted soil or proceed with a different redevelopment plan. If analysis of soil samples documents concentrations of AOCs to be less than action levels, then the NCRWQCB may request the City conduct further characterization or may allow the City to proceed with the current redevelopment plan.

2) If analysis of groundwater samples documents concentrations of AOCs to be greater than the action levels, then the NCRWQCB may request the City to further characterize, remove, or remediate the source of the contamination prior to site development or proceed with a different re-development plan. If analysis of groundwater samples documents concentrations of AOCs to be less than action levels, then the NCRWQCB may allow the City to proceed with the current redevelopment plan.

3) If the analysis of groundwater samples documents total dissolved solids in excess of potable water conditions (>3000 milligrams per liter; SWRCB, 88-63), then groundwater may not be considered a potable resource; the NCRWQCB may require the City to determine whether contaminants observed during this sampling event pose a threat to surface water via a groundwater to surface water pathway. If the analysis of groundwater samples for total dissolved solids determines potable groundwater conditions, then groundwater may be considered a potable resource; the NCRWQCB may require the City to determine whether contaminants at the site pose a threat to a drinking water resource.

Table 3-1: Action Levels			
Matrix	SOIL		WATER
	Total Concentration	Cal-WET	Total Concentration
Analyte	PRGres (mg/kg)	MCL (ug/L)	SSWQPL (ug/L)
Petroleum Products			
TPH - motor oil	-	1	1
TPH - diesel	-	56	56
Volatile Organic Compounds			
Benzene	-	-	0.35
Toluene	-	-	40
Ethylbenzene	-	-	30
Xylenes	-	-	20
Vinyl Chloride	-	-	0.02
Trichloroethene	-	-	0.8
c-1,2-Dichloroethene	-	-	6
t- 1,2-Dichloroethene	-	-	10
Methylene Chloride	-	-	0.13
Acetone	-	-	700
Tetrachloroethene	-	-	0.056
Semi-volatile Organic Compounds			
Acenaphthene	3700	-	420
Anthracene	22,000	-	2100
Benz(a)anthracene	0.62	-	0.04
Benzo(a)pyrene	0.062	0.2	0.0029
Fluoranthene	2300	-	280
Fluorene	2700	-	280
Naphthalene	56	-	14
Pyrene	2300	-	210
Pentachlorophenol	3	1	0.43

Table 3-1 (continued) Action Levels			
Matrix	SOIL		WATER
	Total Concentration	Cal-WET	Total Concentration
Analyte	PRGres (mg/kg)	MCL (ug/L)	SSWQPL (ug/L)
Inorganics			
Cadmium	1.7	1.0*	3.5
Total Chromium	210	5.0*	50
Lead	150	5.0*	2.0
Nickel	1600	-	100
Zinc	23,000	-	2100
Copper	3100	1300	170
Arsenic	0.39	5.0*	0.5
Iron	23,000	-	300
Miscellaneous			
Total Dissolved Solids	-	-	3000 mg/l
Dioxin	3.9×10^{-6}	-	2.7×10^{-7}
PRG res= Residential Preliminary Remediation Goal Cal-WET = California Waste Extraction Test SSWQPL = Site-Specific Water Quality Protection Level per NCRWQCB * = Title 22 California Code of Regulations		ug/L = micrograms per liter mg/kg = milligrams per kilogram - Not applicable	

4) If water quality parameters (contaminants and total dissolved solids) are comparable between surface water and nearby groundwater, then there is evidence for hydraulic communication between these water bodies. If water quality parameters are not comparable between surface water and nearby groundwater, then there may not be evidence for hydraulic communication between surface and ground water.

5) If the analysis of surface water samples documents contamination in upgradient samples, the NCRWQCB may extend its investigation to off-site sources. If the analysis of the surface water samples indicates that near-site, or downgradient surface water samples exceed upgradient concentrations, the NCRWQCB may request the City to further characterize, remove, or remediate the source of the contamination prior to site development or proceed with a different re-development plan.

3.5 Data Quality Objectives

3.5.1 Data Quality Objective (DQO) Process

The DQO process, as set forth in the EPA document, *Guidance for the Data Quality Objectives Process*, EPA QA/G-4, was followed to establish the data quality objectives for this project. An outline of the process and the outputs for this project are included in Appendix A of this amendment.

3.5.2 DQO Data Categories

This investigation will involve the generation of definitive data for soil, groundwater, and surface water. The specific requirements for these data categories are detailed in Section 9. The data generated under this project will comply with the requirements for each data category as defined in *Data Quality Objective Process for Superfund*, EPA 540/G-93/71, September 1993. All definitive analytical methods employed for this project will be methods approved by the EPA.

3.5.3 Data Quality Indicators

Data quality indicator goals (DQIs) for this project were developed following guidelines in *EPA Guidance for Quality Assurance Project Plans*, EPA QA/G-5, February 1998. All sampling will be guided by procedures detailed in Section 6.2 to ensure representativeness of sample results. Table 3-2 and Appendix C document the DQIs for this project. As presented in Table 3-2 and Appendix C, the USEPA Contract Laboratory Program (CLP) Contract-Required Quantitation Limits were determined to be appropriate for this project. CLP methods or equivalent SW 846 and/or EPA Regional Laboratory methods are appropriate for this project.

3.6 Data Management

Data will be managed in accordance with Section 3.6 in the Phase II SAP.

3.7 Schedule of Sampling Activities

It is anticipated that field activities will begin the week of April 26, 2004**.** The date of the field sampling event is contingent on the project scoping team's ability to review the SAP Amendment and availability of drilling subcontractors. Field sampling is expected to last five days. Subsequent to the field sampling event, samples will be analyzed, data will be evaluated and validated, and a final report will be prepared. The target date for completion of the final report is July 19, 2004.

3.8 Special Training Requirements/Certifications

There are no additional special training requirements or certifications under this Amendment; the asbestos certification is not needed because there will be no asbestos-related work during this phase of activity.

Table 3-2: Data Quality Indicators						
Method Number (Method Name)	Matrix	Action Level (mg/kg soil) (ug/L water)	CRQL (mg/kg soil) (ug/L water)	Accuracy (% Recov. MS/MSD)	Precision (RPD for MS/MSD and duplicates)	Percent Complete
EPA Method 6010/7471 (Metals)	Soil	See Phase II SAP	See Phase II SAP	75 - 125%	<35%	90 - 100%
EPA CLPAS ILM05.2 (Metals)	Water	See Phase II SAP	See Phase II SAP	75 - 125%	<20%	90 - 100%
Cal/EPA modified Metals WET Test	Soil	See Appdx. B	See Appdx B	75 - 125%	<25%	90 - 100%
EPA CLPAS OLC03.2 (VOCs)	Water	See Phase II SAP	See Phase II SAP	65 - 135%	<35%	90 - 100%
EPA Method 8270 (SVOCs)	Soil	See Phase II SAP	See Phase II SAP	75 - 125%	<35%	90 - 100%
EPA CLPAS OLC03.2 (SVOCs)	Water	See Phase II SAP	See Phase II SAP	75 -125%	<35%	90 - 100%
Cal/EPA modified SVOC WET Test	Soil	See Appdx. B	See Appdx. B	75 - 125%	<35%	90 - 100%
EPA 8015 Mod-d,o (TPH as diesel and oil)	Soil	See Phase II SAP	See Phase II SAP	65 - 135%	<35%	90 - 100%
EPA 8015 Mod-d,o (TPH as diesel and oil)	Water	See Phase II SAP	See Phase II SAP	65 -135%	<35%	90 - 100%
Cal/EPA modified $TPH_{d,o}$ WET Test	Soil	See Appdx. B	See Appdx. B	65 - 135%	<35%	90 - 100%
EPA 160.1 Total Dissolved Solids	water	See Appdx. B	See Appdx B	75 - 125%	<35%	90 - 100%
EPA CLP DLM01.4 Dioxin	Soil	3.9×10^{-6}	1.0×10^{-6}	75 - 125%	<35%	90 - 100%

CLPAS = Contract Laboratory Program Analytical Services
CRQL = Contract Required Quantitation Limit
MS/MSD = Matrix Spike/Matrix Spike Duplicate
RPD = Relative Percent Difference
VOCs = Volatile Organic Compounds
bold = action level is less than the CRQL

USEPA = United Sates Environmental Protection Agency
PCBs = Polychlorinated Biphenyls
SVOCs = Semi-Volatile Organic Compounds
TPH - Total Petroleum Hydrocarbons
PQL = Practical Quantitation Limit

4.0 SAMPLING RATIONALE

4.1 Sampling Locations and Rationale

The objective of this phase of the investigation is to determine whether contaminated soils at the site are a threat to a potable water resource (groundwater). The Phase II TBA indicated soil and groundwater contamination at the site above action levels, which may dictate remedial action by the City. Proposed sampling locations are delineated in Figure 4-1

4.1.1 Soil Sampling

In order to determine whether contaminants in site soils threaten groundwater, a total of ten (10) soil samples will be collected from nine (9) locations. Six (6) surface soil samples will be collected at pre-determined locations for analysis for total AOCs and leachable AOCs. One (1) shallow subsurface sample will be collected at AM-101 location in order to confirm and duplicate the presence of AOCs found in the Phase II sampling event, as well as determine leachable AOCs. The sample locations are presented in Figure 4-1 and represent areas of highest concentrations of AOCs identified in the Phase II TBA. In addition, in order to determine whether dioxin is an issue at the site, two (2) surface soil samples will be collected for dioxin at the two locations with the highest PCP concentrations from the Phase II TBA. The field team will collect three (3) discretionary surface soil samples at locations to be determined in the field based on field evidence of staining, discoloration, or other field observations.

4.1.2 Groundwater Sampling

Five new groundwater wells will be installed at the site. The NCRWQCB believes that samples collected from properly installed groundwater wells will provide data that are much more representative of actual groundwater conditions than the previous hydropunch samples. In addition, new wells can be sampled by the City to reassess the impact to the environment as the redevelopment program at the site progresses. Three wells will be installed at predetermined locations (Figure 4-1) chosen for their proximity to soil contamination, as well as sufficiently distanced from each other in order to calculate a groundwater gradient across the site. The description of the well installation and sampling methodology is included in Section 6.2.2 of this amendment. Once these wells have been installed, they will be surveyed and checked for groundwater elevation. The resulting data will be used to field calculate the site groundwater gradient in order to locate the upgradient (MW-5 see Figure 4-1 for expected locations) and downgradient (MW-4) wells. Groundwater samples will be collected from five wells once the wells have been developed and purged. Data from all five wells will help to determine the disposition of contamination in groundwater across the site. In addition, total dissolved solids data will help determine whether water is potable. The EPA will only collect and analyze groundwater samples from these wells for this sampling event; the City and the NCRWQCB will negotiate a sampling strategy after the data from this investigation are reported.

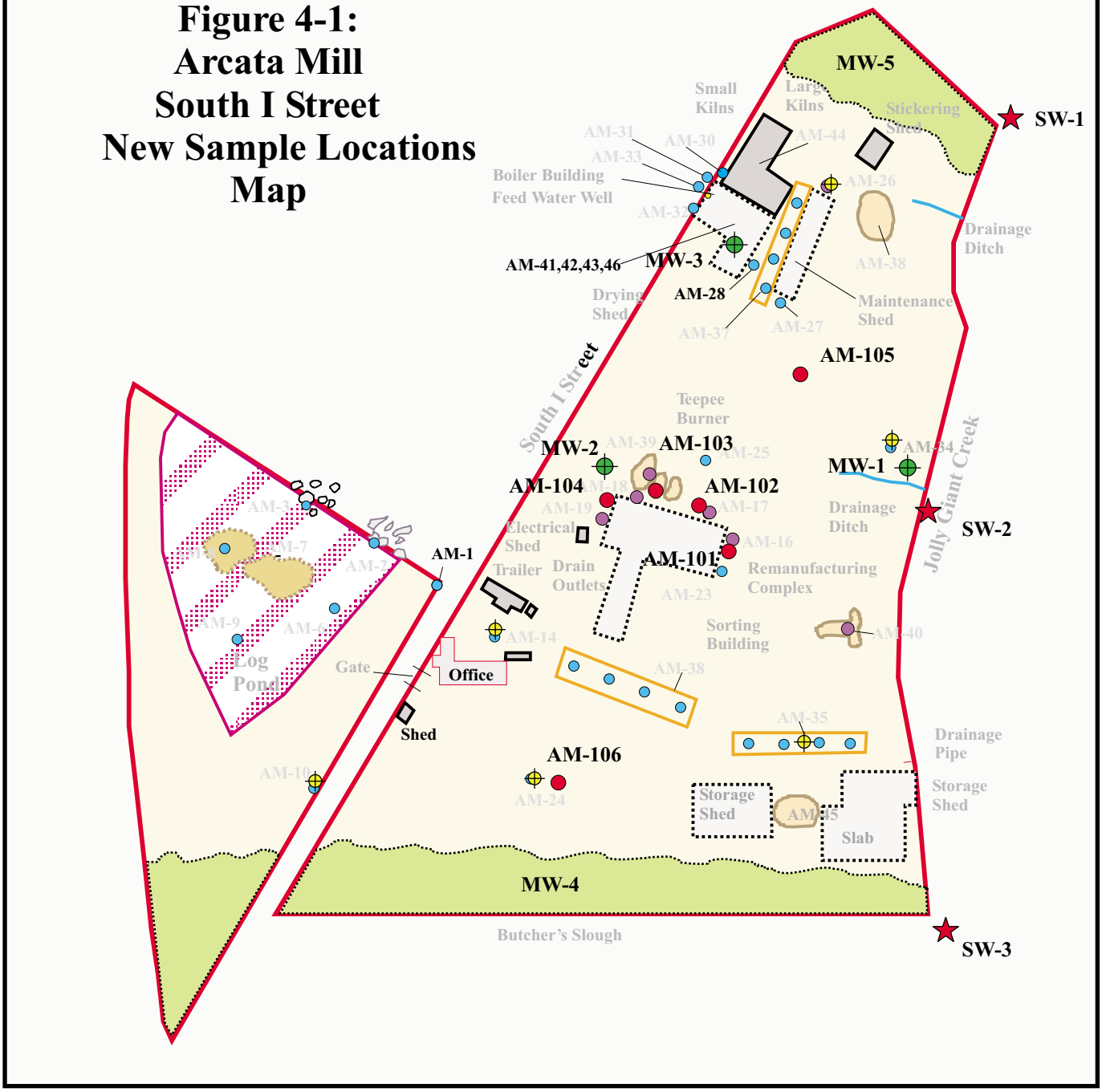
4.1.3 Surface Water Sampling

In order to determine the inter-connectivity of groundwater and surface water, three surface water samples will be collected and analyzed for the same parameters as groundwater for comparative analysis. Sample locations will be pre-determined based on the north to south flow of surface water in Jolly Giant Creek. An upstream sample will be collected in Jolly Giant Creek, just north of the site. A second sample will be collected just south of the southernmost drainage ditch (see Figure 4-1), and a downstream sample will be collected directly south of the site.

4.2 Analytes of Concern

Based on the data collected during the Phase II TBA, AOCs in surface soils include total concentrations of TPH diesel, TPH oil, SVOCs, metals, and dioxins, as well as California WET data for all of the above, except dioxins. The AOCs in water samples include TPH diesel, TPH oil, SVOCs, VOCs, metals, and total dissolved solids.

Figure 4-1: Arcata Mill South I Street New Sample Locations Map



Legend

Structure

- Demolished
- Existing
- Project Boundary
- Soil Stockpile
- Distressed Vegetation
- Scattered Concrete
- Scattered Metal Debris
- Composite Sample Location
- Phase II Sample Location
- Sample Locations of Interest:
  - metals - AM-18, 19, 30, 33 37, 40
  - SVOCs - AM-40
  - Benzene - AM-17
  - PCP - AM-16, 18, 19, 39
- Hydropunch groundwater sample location (co-located with surface sample)

Sample Locations for This Study

- Phase II B Surface soil sample locations
- Phase II B Groundwater monitoring well locations
- Phase II B Surface water sample location

Approximate Scale in Feet

0 — 190

- Expected area of upgradient, or downgradient monitoring well location

5.0 REQUEST FOR ANALYSIS

Laboratory services for total concentrations of dioxins in soil, and all AOCs in surface water and groundwater samples will be scheduled and arranged for by the EPA Region 9 Quality Assurance Office (QAO). Water samples will be analyzed for VOCs, SVOCs, TPH, total dissolved solids and metals through USEPA's Region 9 Laboratory. The USEPA Region 5 Laboratory will analyze dioxin soil samples. Weston will contract a commercial laboratory to conduct analysis of soil samples for TPH diesel, TPH oil, SVOCs, and metals. In addition, Weston will contract a commercial laboratory to conduct California WET analyses for TPH, SVOCs and metals. Sample containers, preservatives, holding times, and the estimated number of field and QC samples are summarized in Table 5-1 and Table 5-2.

Ten soil samples will be collected from nine locations and groundwater samples will be collected from five locations. Seven soil samples will be collected from pre-determined locations (see Figure 4-1) reflecting a minimum number of points for a statistically viable correlation between the total concentration and WET test data. Both a surface and a subsurface soil sample will be collected at location AM-101. In addition, three discretionary soil sample locations are included. As shown in Table 5-1 and Table 5-2, additional sample volume collected at one soil location and one groundwater location will be identified for use as a laboratory QC sample. Field duplicate samples will be collected at one soil and one groundwater location. Each soil and groundwater sample will be preserved immediately after collection and analyzed according to the methods listed in Tables 5-1 and 5-2.

To provide analytical quality control for the analytical program, the following measures will be utilized:

- All groundwater and soil sample analysis will be conducted by laboratories selected by the USEPA RSCC..
- Additional volume of sample will be collected for at least one sample per media per each analytical method, to be utilized for matrix spike/duplicate analysis (except for the asbestos sample).
- A CLP-type data package will be required from the laboratories for all soil and groundwater resultant data.

Table 5-1: Request for Analytical Services; Matrix - Soil						
Method Number & Analysis			**8015M TPH-d,o**	**6010/7471 Metals**	**8270 Low SVOCs**	**8290 Dioxin**
Preservatives			**Chill to 4°C**	**Chill to 4°C**	**Chill to 4°C**	**Chill to 4°C**
Analytical Holding Time			**14 days to extract, 40 days to analyze**	**6 months (28 day Hg)**	**14 days to extract, 40 days to analyze**	**30 days to extract, 45 days to analyze**
Sample Volume / Sample Container			**1 x 8 oz. Glass Jar w/ Teflon-lined lid**	**1 x 8 oz. Glass Jar**	**1 x 8 oz. Glass Jar w/ Teflon-lined lid**	**1 x 8 oz. Glass Jar w/ Teflon-lined lid**
Sample Information:						
Sample #	**Depth (ft bgs)**	**Desig.**	**8015M TPH-d,o**	**ILM05.2 Metals**	**OLM04.3 Low SVOCs**	**8290 Dioxin**
AM-101-0	**surface**	**MS/MSD**	**X**	**X**	**X**	**X**
AM-101-2	**2**		**X**	**X**	**X**	
AM-102-0	**surface**		**X**	**X**	**X**	**X**
AM-112-0	**surface**	**dup of AM-02-0**	**X**	**X**	**X**	**X**
AM-103-0	**surface**		**X**	**X**	**X**	
AM-104-0	**surface**		**X**	**X**	**X**	
AM-105-0	**surface**		**X**	**X**	**X**	
AM-106-0	**surface**		**X**	**X**	**X**	
AM-107-0	**discretionary**	**discretionary**	**X**	**X**	**X**	
AM-108-0	**discretionary**	**discretionary**	**X**	**X**	**X**	
AM-109-0	**discretionary**	**discretionary**	**X**	**X**	**X**	
Number of Field Samples:			**10**	**10**	**10**	**2**
Number of Field Duplicates:			**1**	**1**	**1**	**1**
Number of Samples as MS/MSDs			**1**	**1**	**1**	**1**
TOTAL NUMBER OF SAMPLES			**12**	**12**	**12**	**4**
TPH-d,o = Total Petroleum Hydrocarbons as Diesel, Oil **SVOCs = Semi-volatile Organic Compounds** **ft bgs = feet below ground surface** **Desig. = Special Designation**				**MS/MSD = Matrix Spike/ Matrix Spike Duplicate** **dup = Duplicate Sample**		

Table 5-1: Request for Analytical Services; Matrix - Soil					
Method Number & Analysis			**8015M TPH-d,o WET**	**6010/7471 Metals WET**	**8270 SVOCs WET**
Preservatives			**Chill to 4ºC**	**Chill to 4ºC**	**Chill to 4ºC**
Analytical Holding Time			**14 days to extract soil, prepare extract ASAP, 40 days to analyze**	**6 months (28 day Hg) to analyze**	**14 days to extract, prepare extract ASAP, 40 days to analyze**
Sample Volume / Sample Container			**1 x 8 oz. Glass Jar w/ Teflon-lined lid**	**1 x 8 oz. Glass Jar**	**1 x 8 oz. Glass Jar w/ Teflon-lined lid**
Sample Information:					
Sample #	**Depth (ft bgs)**	**Desig.**	**8015M TPH-d,o WET**	**6010/7471 Metals WET**	**8270 SVOCs WET**
AM-101-0	**surface**	**MS/MSD**	**X**	**X**	**X**
AM-101-2	**2**		**X**	**X**	**X**
AM-102-0	**surface**		**X**	**X**	**X**
AM-112-0	**surface**	**dup of AM-02-0**	**X**	**X**	**X**
AM-103-0	**surface**		**X**	**X**	**X**
AM-104-0	**surface**		**X**	**X**	**X**
AM-105-0	**surface**		**X**	**X**	**X**
AM-106-0	**surface**		**X**	**X**	**X**
AM-107-0	**discretionary**	**discretionary**	**X**	**X**	**X**
AM-108-0	**discretionary**	**discretionary**	**X**	**X**	**X**
AM-109-0	**discretionary**	**discretionary**	**X**	**X**	**X**
Number of Field Samples:			**10**	**10**	**10**
Number of Field Duplicates:			**1**	**1**	**1**
Number of Samples as MS/MSDs			**1**	**1**	**1**
TOTAL NUMBER OF SAMPLES			**12**	**12**	**12**
TPH-d,o = Total Petroleum Hydrocarbons as Diesel, Oil **SVOCs = Semi-volatile Organic Compounds** **VOCs = Volatile Organic Compounds** **dup = Duplicate Sample**				**ft bgs = feet below ground surface** **Desig. = Special Designation** **MS/MSD = Matrix Spike/ Matrix Spike Duplicate**	

Table 5-2: Request for Analytical Services; Matrix - Water

Method Number & Analysis			8015M TPH-d,o	ILM05.2 Metals	OLC03.2 VOCs	160.1 TDS	OLC 03.2 SVOCs
Preservatives			HCl pH<2 & Chill to 4°C	HNO_3 pH<2 & Chill to 4°C	HCl pH<2 & Chill to 4°C	Chill to 4°C	Chill to 4°C
Analytical Holding Time			14 dy Ext 40 dy An	6 months 28 dy Hg	14 days	7 days	7 days to extract, 40 days to analyze
Sample Volume / Sample Container			1x 1 L Amber Glass w/ Teflon-lined cap	1 x 1 L Poly.	3 x 40 ml VOA with Teflon-lined septa	1x1 liter poly	2 x 1 L Amber Glass w/ Teflon-lined cap
Sample Information:							
Sample #	**Depth (ft bgs)**	**Desig.**	**8015M TPH-d,o**	**ILM05.2 Metals**	**OLC03.2 VOCs**	**160.1 TDS**	**OLC03.2 SVOCs**
MW-1	4		X	X	X	X	X
MW-2	4		X	X	X	X	X
MW-3	4		X	X	X	X	X
MW-4	4	BG	X	X	X	X	X
MW-5	4		X	X	X	X	X
MW-10	4	dup	X	X	X	x	X
SW-1	0	BG	X	X	X	x	X
SW-2	0		X	X	X	x	X
SW-3	0		X	X	X	x	X
Number of Field Samples:			9	9	9	5	9
Number of Field/Equip. Blanks			1	1	1	1	1
Number of Field Duplicates:			1	1	1	1	1
Number of Samples as MS/MSDs			1	1	1	1	1
TOTAL NUMBER OF SAMPLES			**12**	**12**	**12**	**12**	**12**

TPH-d,o = Total Petroleum Hydrocarbons as Diesel, Oil
SVOCs = Semi-volatile Organic Compounds
TDS = Total Dissolved Solids
ft bgs = feet below ground surface

Desig. = Special Designation
MS/MSD = Matrix Spike/ Matrix Spike Duplicate
BG = Background Sample
dup = Duplicate Sample

6.0 METHODS AND PROCEDURES

6.1 Field Equipment

6.1.1 Sampling Equipment

The following equipment will be used to obtain environmental soil, groundwater, and surface water samples:

Equipment	Fabrication	Dedicated
Direct Push MacroCore™ Sampler	**Hardened Steel**	**No**
Direct Push MacroCore™ Sampler Sleeves	**Acetate**	**Yes**
Geoprobe™ groundwater well casing and screen	**Stainless Steel**	**Yes**
Geoprobe™ Sampler Tubing	**Polyethylene**	**Yes**
Minibailer	**Stainless Steel**	**No**
Disposable Bailer	**Polyethylene**	**Yes**
Sample Buckets	**Paper**	**Yes**
Plastic Trowels	**Plastic**	**Yes**
Gloves	**Nitrile**	**Yes**

The planned equipment will be operated in accordance with USEPA Environmental Response Team (ERT) Standard Operating Procedures (SOPs) #2050 for GeoProbe® Operation, SOP #2012 for Soil and Groundwater Sampling. Copies of these SOPs are contained in Appendix D of the Phase II SAP.

6.1.2 Inspection/Acceptance Requirements for Supplies and Consumables

There are no changes to the Phase II SAP for this section.

6.1.3 Equipment Maintenance

There are no changes to the Phase II SAP for this section

6.2 Sampling Procedures

Both the number of samples and analytes have changed from the Phase II SAP. In addition, surface water samples have been added to the water matrix samples. The methods for collecting soil samples have not changed. The method for collecting groundwater samples has changed to reflect collection from an installed well, as opposed to a hydropunch.

6.2.1 Soil Sampling

Weston will collect soil samples from a combination of surface and subsurface (2 feet bgs) depths. All soil samples will be collected in accordance with ERT SOPs 2012 and 2050.

Weston will collect surface soil samples using dedicated plastic trowels. Surface samples to be analyzed for TPH-d,o, TPH wet test, SVOCs, SVOC wet test, inorganics, metals wet test, and dioxins will be collected from 0 to 2 inches bgs. Weston will collect subsurface soils samples using a combination of manual hand auguring and a direct-push rig with a MacroCore® sampler. Subsurface samples will be collected at 2 feet bgs unless groundwater is encountered at a shallower depth. If groundwater is encountered at less than 2 feet bgs, then the subsurface samples will be collected from the unsaturated soil immediately above the water line. Grab samples will be collected and transferred directly into a pre-labeled sample container (i.e. 8-ounce jars) using a dedicated plastic trowel. All sample containers will be closed as soon as they are filled, chilled immediately to 4^{o}C, and processed for shipment to the laboratory.

6.2.2 Groundwater Sampling

Weston will collect five groundwater samples following ERT SOPs #2012 and 2050. The groundwater samples will be collected from new groundwater monitoring wells installed for this sampling event. Monitoring wells will be installed under permit using a direct-push rig by installing a pre-packed Geoprobe® well screen and casing into the direct push bore tube. The bore tube will be extracted and the screened interval will be packed with an appropriate grade, clean sand. The remaining portion of the casing will be sealed and the well head will be installed with a locking, closed cover. The wells will be developed by purging up to five well volumes of water, or until turbidity, pH, and water temperatures (as read using a field water quality meter) have stabilized.

Water will be collected into a measured bucket to record the purge volume. Casing volumes will be calculated based on total well depth, standing water level, and casing diameter. One casing volume will be calculated as :

$V = pd^2h/77.01$

V =

where:

V is the volume of one well casing of water (1 ft^3 = 7.48 gallons);

d is the inner diameter of the well casing (in inches);
h is the total depth of water in the well (in feet).

It is most important to obtain a representative sample from the well. Stable water quality parameter (temperature, pH, and specific conductance) measurements indicate representative sampling is obtainable. Water quality is considered stable if for three consecutive readings:

temperature range is no more than ±1?C;
- pH varies by no more than 0.2 pH units;
- specific conductance readings are within 10% of the average.

The water from which measurements are taken will not be used to fill sample bottles.

If the well casing volume is known, measurements will be taken before the start of purging, in the middle of purging, and at the end of purging each casing volume. If the well casing volume is not known, measurements will be taken every 2.5 minutes after flow starts. If water quality parameters are not stable after 5 casing volumes or 30 minutes, purging will cease, which will be noted in the logbook, and groundwater samples will be collected. The depth to water, water quality measurements, and purge volumes will be entered in the logbook.

To minimize volatilization, VOC samples will be collected first by lowering a stainless-steel minibailer with a dedicated line down the well casing. The sample will be transferred directly into a pre-preserved volatile organic analysis (VOA) container. WESTON will check each VOA container to ensure no air bubbles exist. If air bubbles are found in the container, it will be discarded and the sample will be recollected. Groundwater samples to be analyzed for metals will be collected using a peristaltic pump with dedicated tubing and filtered in the field using a 0.45 micron filter if field turbidity readings exceed 5 NTU. WESTON will insert a dedicated 0.45 micron filter in-line, between the pump and the pre-preserved sample containers. Sample containers will be closed as soon as they are filled, chilled immediately to 4°C, and processed for shipment to the laboratory.

6.2.3 Surface water

If surface water is present, three surface water samples will be collected along Jolly Giant Creek where it borders the site. Surface watersamples will be collected and analyzed for VOCs, SVOCs, TPH and metals. Surface water samples will be collected by submerging the opening of the dedicated bottle at least two inches from the surface of the water. The bottles will be capped while submerged, if possible. The bottles will be wiped dry and placed into dedicated, re-sealable plastic bags in order to minimize cross contamination in the storage coolers. The samples will be immediately placed on ice awaiting transport to the laboratory.

6.3 Decontamination Procedures

The decontamination procedure has not changed from the Phase II SAP.

7.0 DISPOSAL OF INVESTIGATION-DERIVED WASTE (IDW)

The disposal of IDW has not changed from the Phase II SAP, except:

The purge water from the monitoring well development will be drummed on site pending analysis. Once analyses indicate the disposition of contaminants in the drums, the purge water will be disposed of in accordance with NCRWQCB guidance.

8.0 SAMPLE IDENTIFICATION, DOCUMENTATION, AND SHIPMENT

8.1 Field Notes

8.1.1 Field Logbooks

There are no changes from the Phase II SAP for this section.

8.1.2 Photographs

There are no changes from the Phase II SAP for this section.

8.2 Sample Nomenclature

As shown in Table 5-1 and Table 5-2, a unique, identifiable name will be assigned to each sample. The prefix "AM-" will be used to identify the soil samples, in keeping with the nomenclature outlined in the Phase II SAP; soil sample locations will begin with the number 101. Groundwater samples collected from monitoring wells will have the prefix "MW-," along with a number indicating the monitoring well location. Surface water samples will have the prefix "SW-," along with a number indicating the monitoring well location.

8.3 Container, Preservation, and Holding Time Requirements

There are no changes from the Phase II SAP for this section. Container, preservation, and technical holding time requirements are summarized in Table 5-1 and Table 5-2.

8.4 Sample Labeling, Packaging and Shipping

There are no changes from the Phase II SAP for this section.

8.5 Chain of Custody Forms and QA/QC Summary Forms

There are no changes from the Phase II SAP for this section.

9.0 QUALITY ASSURANCE AND CONTROL (QA/QC)

9.1 Field Quality Control Samples

The QA/QC samples described in the following subsections, which are also listed in Table 5-1 and Table 5-2, will be collected during this investigation.

9.1.1 Assessment of Field Contamination (Blanks)

9.1.1.1 Equipment Blanks

There are no changes from the Phase II SAP for this section. The equipment blanks will be analyzed according to Table 5-2 of this amendment.

9.1.1.2 Temperature Blanks

There are no changes from the Phase II SAP for this section.

9.1.2 Assessment of Sample Variability (Field Duplicate or Co-located Samples)

A duplicate soil sample will be collected at the location indicated in Table 5-1 of this amendment; this location has been selected because it is expected to have detectable concentrations of AOCs, based on the Phase II TBA. The duplicate groundwater sample will be collected at a location to be determined in the field based on 1) expected presence of AOCs (MWs 1, 2, or 3) and 2) groundwater production, as observed during the well development phase.
Duplicate samples will be labelled, preserved, packaged, and sealed in the same manner described in the Phase II SAP.

9.2 Background Samples

Background groundwater and surface water samples will be collected to differentiate between on-site and off-site contributions of AOCs. The background groundwater sample will be collected from a background monitoring well installed upgradient from the major points of contamination at the site; this location will be determined in the field based on triangulation of survey data from the first three wells installed on the site. The background surface water sample will be collected from Jolly Giant Creek, directly upstream of the site.

9.3 Laboratory Quality Control Samples

There are no changes from the Phase II SAP for this section; laboratory QC samples are delineated in Tables 5-1 and 5-2

9.4 Analytical and Data Package Requirements

It is required that all samples be analyzed according to Table 3-2 of this Amendment, and Appendix C of the Phase II SAP. The laboratory is required to supply documentation to demonstrate that their data meet the requirements specified in the methods.

There are no other changes from the Phase II SAP for this section.

9.5 Data Review and Validation

Validation of all analytical data generated during this sampling event, including those data generated by EPA Regional Laboratories, will be performed by WESTON in accordance with the *EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review and USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review*. A Tier 1B equivalent data validation will be conducted with approximately 95 percent of the data being validated. Upon completion of validation, data will be classified as one of the following: acceptable for use without qualifications, acceptable for use with qualifications, or unacceptable for use.

9.6 Field Variances

There are no changes from the Phase II SAP for this section.

9.7 Assessment of Project Activities

9.7.1 WESTON Assessment Activities

There are no changes from the Phase II SAP for this section.

9.7.2 USEPA Assessment Activities

There are no changes from the Phase II SAP for this section.

9.7.3 Project Status Reports to Management

There are no changes from the Phase II SAP for this section.

9.7.4 Reconciliation of Data with DQOs

There are no changes from the Phase II SAP for this section.

SAP AMENDMENT APPENDIX A:

AMENDED DATA QUALITY OBJECTIVES WORKSHEET

APPENDIX A

DATA QUALITY OBJECTIVE PROCESS WORKSHEET - ARCATA MILL

State the Problem - Summarize the contamination problem that will require new environmental data, and identify the resources available to resolve the problem.

Planning Team:
Suzanne Perkins, USEPA
Gail Jones, USEPA
Jennifer Gerhardt, USACE
Larry Oetker, City of Arcata
Lisa Bernard, NCRWQCB
Joe DeFao, Weston Solutions, Inc.
Ben Castellana, Weston Solutions, Inc.

Suzanne Perkins of the U. S. Environmental Protection Agency (EPA) is the primary decision maker of the scoping team.

Problem:

The Aracta Mill site is a 15 acre area composed of two adjacent properties located in Arcata, California. The first property, Little Lake Industries (LLI), was historically agricultural land, until 1948 when it was developed for lumber remanufacturing. Remanufacturing operations included drying, storing, and shipping lumber. Lumber remanufacturing remained the primary site operation until 1990, when LLI sold the property. Since 1990, no industrial activities are believed to have occurred on the site.

As part of remanufacturing operations hazardous materials such as fuels, oils, mineral spirits, kiln seal, boiler water chemicals, paint, paint thinners, lacquer, varnish, and insecticides were stored and used on site. Although lumber staining was reportedly not conducted at the site, an accidental release of iron oxide pigment occurred historically from drums being stored on the LLI property. Furthermore, Polychlorinated Biphenyls (PCBs) containing transformers may have also been present at the site. A clandestine methamphetamine laboratory was discovered in 2000 and small quantities of muriatic acid, iodine, red phosphorus, denatured alcohol, and caustic soda were removed. There is no indication that wood treatment or preservatives were applied on the site or that the lumber was treated prior to arrival.

The adjoining second property, called the Johnson Tract, was also used historically for agricultural purposes. After 1954, a plywood mill operated to the north and utilized a major portion of the Johnson Tract as a log pond. After 1981, the log pond became inactive and the land was re-vegetated. There is no information on whether wood was treated prior to arriving at the pond. No other mill operations are believed to be historically present on the Johnson Tract. The Johnson Tract shares its northern property boundary with the Johnson Industries Manufacturing Complex (JIMC). The JIMC has a history of hazardous materials violations along the shared property boundary. Hazardous materials kept at the JIMC may include oils, hydrocarbon solvents, fuels, zinc wastes, lead batteries, and mineral spirits.

The Arcata Community Development District (ACCD) is planning for the redevelopment of the site and has applied for assistance under the EPA Brownfield Program to evaluate

environmental concerns outlined in a Phase I Targeted Brownfield Assessment report (Phase I TBA). Currently, there is minimal sampling and analysis data to document site conditions. Further sampling and analysis is needed to evaluate redevelopment plans. The ACCD has not decided on a final use for the site, but the LLI property is tentatively projected to be of mixed industrial and residential use and the Johnson Tract is projected to be marshland.

Available Resources:

Current budget not to exceed approximately $80,000; use of EPA Contract Laboratory Program (CLP), Regional Laboratory, and Quality Assurance Office (QAO) data validation services; and WESTON personnel. A subcontract is required to install monitoring wells, survey the wells for location and elevations, and collect groundwater samples.

Identify the Decision - Identify the decision that requires new environmental data to address the contamination problem.

Principal Study Questions:

1) Are analytes of concern (AOCs) present in site soils?
1) Are AOCs in soils leachable (fail Cal-WET analysis)?
2) Are AOCs present in groundwater beneath the site?
3) What is the extent of groundwater contamination and migration pathway?
4) Is groundwater potable?
5) Are groundwater and surface water interconnected?

Define the alternative actions that could result from the resolution of the principal study question:

1) Further action may be required to address surface soil to minimize contact.
2) Further action may be required to address the soil to groundwater migration of contaminants.
3) Further action may be required to address the groundwater to surface water migration of contaminants.
4) Further action may be required to address existing contamination of groundwater or surface water.
5) There may be no further action necessary at the site.
6) Site data may be used to investigate an up-gradient source of contamination.

Decision Statement:

Determine the extent of groundwater contamination at the site. Determine whether the groundwater at the site is a potable resource. Determine whether contaminants are present in groundwater above action levels. Determine whether concentrations/leachabilities of contaminants in the site soils account for groundwater contamination at the site. Determine whether contaminants may have migrated from an off-site source.

Identify Inputs to the Decision - Identify the information needed to support the decision, and specify which inputs require new environmental data.

Information required to resolve the decision statement: Definitive laboratory analyses analysis of all AOCs in groundwater from strategically located wells are necessary. Additional soil sample total concentration and leachability data from specific locations are necessary to determine whether site soils have contributed to the groundwater contamination problem.

Surface water samples are necessary to determine interconnectivity of surface water and groundwater, as well as establish possible contributions to surface water contamination from the site.

Source(s) for information:

Suspected locations of contamination are outlined in the Phase I TBA. The Phase I TBA also highlights information and analytical results drawn from several Underground Storage Tank (UST) investigations and cleanups at the site and two Phase I Environmental Site Assessments from 1989 and 1998, respectively. The City of Arcada released results from a surface and subsurface sampling event in September 2002. This report documents TPH and BTEX results from surface and subsurface samples collected on the eastern and southern boundary of the LLI property along Jolly Creek.

The Arcata Phase II report identifies areas of concern for both groundwater and soil contamination. Data gaps in the Phase II report include: 1) metals concentrations in site soils may not be elevated enough to attribute to metals contamination in groundwater; leachability data are required to determine whether contaminants are mobile through vadose water migration. 2) There is a poor correlation between the TPH diesel contamination in groundwater and potential sources in the on-site soils; further TPH characterization is necessary, especially the amount of TPH that is mobile through vadose migration.

Information needed to establish action levels:

Groundwater: action levels will be California-modified drinking water standards (MCLs).

Soil: For total concentrations of AOCs, the Residential Preliminary Remediation Goals will be used. For California WET analyses, the MCL will be used because groundwater is deemed close enough to the surface soils that an attenuation model may underestimate the degree of contaminant concentration released to groundwater by site soils.

Confirm that measurement methods exist to provide data:

US EPA CLPAS ILM04.1 (metals water).
US EPA Method 6010/7471 (metals soil)
US EPA Method 8270 (Organics Soil)
US EPA CLPAS OLC03.2 (Organics Low Level Water)
US EPA Method 8015B Mod- Oil, Diesel
US EPA Method 160.1 total dissolved solids (water)
US EPA CLPA DLM01.4 dioxin (soil)
US EPA modified WET test for extractable metals (soil)
US EPA modified WET test for extractable TPH (soil)
US EPA modified WET test for extractable SVOCs (soil)

Define the Study Boundaries - Specify the spatial and temporal aspects of the environmental media that the data must represent to support the decision.

Specific characteristics that define population being studied: Concentrations of the metals, VOCs, TPH-d,o, in soil and groundwater, and total dissolved solids in groundwater.

Spatial boundary of decision statement: The assessment boundary will be limited to the

legal site boundary with the possible exception of one background monitoring well to be installed at a location on public lands to be determined based on the well survey data. The vertical boundary of the assessment will be limited by the depth to groundwater (<4 feet bgs). Sample locations will be biased to areas of concern stipulated in the Phase II TBA. Three of the monitoring well locations will be chosen on the basis of groundwater grab data from the Phase II TBA; the upgradient and downgradient monitoring wells will be chosen on the basis of survey data and groundwater elevations from the previous three well installations.

Temporal boundary of decision statement: The LLI property soil data from this event will be used to establish whether contaminants identified at the site pose a risk to groundwater. Locations will be chosen on the basis of worst-case contamination identified in the Arcata Phase II event.

In addition, soil data will be used to identify the presence of additional contaminants of concern, including dioxins in site soils; these sample locations will be chosen based on the two locations with the highest PCP concentrations.

Groundwater samples will be collected from five temporary wells installed on the LLI property. Groundwater data will be used to establish: 1) whether upgradient groundwater is potable, 2) the concentrations of contaminants found in groundwater, and 3) the likelihood of the contribution to groundwater of contaminants from site soils, as opposed to an off-site source.

When to collect samples: A field team is tentatively scheduled to mobilize to the site in either late October or early November.

Practical constraints on data collection: Data collection at the LLI property is subject to accessability to proposed sample locations. Accessability may be limited due to current construction work and past demolition work at the site. Data collection at the Johnson Tract property may be limited by site access due to heavy vegetation. The vertical extent of the contamination may be limited due drilling refusal.

Develop a Decision Rule - Develop logical "if...then" statements that define the conditions that would cause the decision maker to choose among alternative actions.

Statistical parameter that characterizes a population: Each analytical result, not statistical parameter, will be evaluated against the action levels.

Specify the action level(s) for the study:

a) Soil action levels for the site will be based on several criteria: 1) Total concentration data will be initially compared to residential PRGs (PRG_{res}) for health issues pertaining to direct contact with site soils; 2) WET analyses data will be compared to MCLs to determine the likely impact to groundwater. In addition, a statistical regression (sum of squares) method will be used to compare leach test data with the higher volume of total concentration data to evaluate the threat to groundwater.

b) Total Petroleum Hydrocarbons (TPH) - D,O will be evaluated against California Regional

Water Quality Control Board Soil Screening Levels (May 1996) for protection of groundwater.

d) Groundwater action levels will be set out US EPA Maximum Contaminant Levels (MCLs) for protection of human health if groundwater is found to be potable; groundwater action levels will be set by NOAA SQuIRTS if groundwater is found to be non-potable.

Decision Rules:

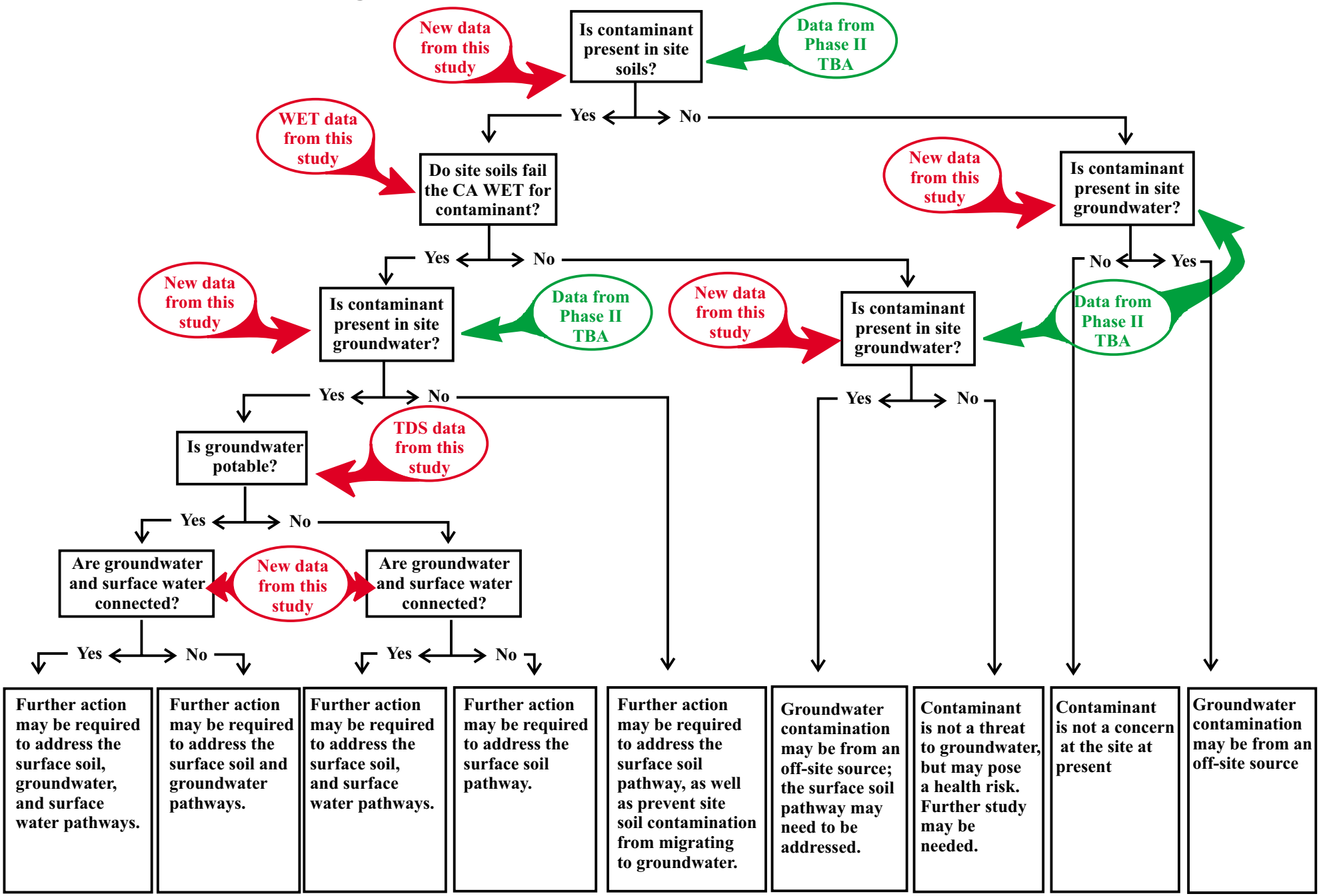
The VOC analyses in groundwater are meant to definitively characterize groundwater at the site, based on tentative hydropunch data in the Phase II TBA study. The dioxin analysis of site soil is meant to answer the question "is dioxin a concern at the site." In each case, these are judgemental sample locations, and the determination of further action is based on the presence of these contaminants above the site action levels outlined in Table 3-1.

Due to the number of parameters measured in this study, a DQO Flow Sheet is presented to direct the possible outcomes of the SVOC, metals, and TPH (both total concentration and WET) analyses and the decisions to be made based on those outcomes (see Figure A-1). For all AOCs, with the exception of dioxin and VOCs, determination of action is based on a nested series of binary logic steps. the logic steps begin with "Is contaminant present in site soils?", progress to "Do the site soils fail the CA WET for contaminant" to determine leachability, then to "Is the contaminant present in groundwater?" The final two determining factors for contaminants present in site soils, exceeding the WET action level, and present in groundwater involve the questions "Is groundwater potable?" and "Are groundwater and surface water connected?"

"Is contaminant present in site soils?"

If the AOC is present in site soils above the detection limit, the result is that the sample result fails the null hypothesis for this decision parameter, and the decision path will proceed along the "Yes" pathway. The presence of the contaminant in site soils indicates that the risk exists for leachability to groundwater, regardless of the Residential PRG. The Residential PRG will only be used to evaluate health risk due to contact with site soils, not risk to groundwater.

Figure A-1: Arcata Phase II B DQO Flow Sheet



"Do site soils fail the CA WET for contaminant?"

If the AOC can be leached from site soils at concentrations above the MCL, then the decision path will proceed along the "Yes" pathway. The leachability, as determined by the CA WET analysis, is an indication that AOCs are capable of threatening groundwater at regulatory thresholds.

"Is contaminant present in groundwater?"

If the AOC is present in site groundwater above the detection limit, the result is that the sample result fails the null hypothesis for this decision parameter, and the decision path will proceed along the "Yes" pathway. the presence of the contaminant in groundwater is an indication of groundwater pollution, but not necessarily an indication that the pollution originated at the site.

"Is grounwater potable?"

If the total dissolved solids analysis of the groundwater exceeds 3000 milligrams per liter for water under the site, then the sample result passes the null hypothesis for this decision parameter, and the decision path will proceed along the "No" pathway.

"Are groundwater and surface water connected?"

Establishing hydrologic connectivity between groundwater and surface water will be based on the following criteria: 1) Examination of site drilling logs by a geologist to determine whether site soils in the water-bearing zone are continuously conductive across the site to the intersection of groundwater and surface water at Jolly Giant Creek. 2) Comparative analyses of total dissolved solids and contaminants between the surface waters of Jolly Giant Creek and groundwater adjacent to the creek.

The results of each step provide a unique possible action, as shown in Figure A-1.

Specify the Limits on Decision Errors - Specify the decision maker's acceptable limits on decision errors, which are used to establish performance goals for limiting uncertainty in the data.

Use of biased sampling points precludes statistical determination of limits on decision errors. Measurement error, rather than sampling error, is deemed to be the primary factor affecting any decision error. Validated, definitive data will be required to evaluate measurement error. Sampling error will be limited to the extent practicable by following approved US EPA methods and applicable standard operating procedures (SOPs). Sampling error and tolerable limits cannot be quantified.

The primary error for any sample location and analyte is the analytical error. The probability of a decision error when the reported result is significantly higher, or lower than the action level is low (significantly higher or lower defines the situation where the range of analytical error does not overlap the action level). The probability of a decision error increases as the analytical error overlaps the action level. If the result erroneously indicates that the site action level has been exceeded, then a Type I error has been committed; in this case, action may be taken to remediate where it is not necessary. If the result erroneously indicates that the site

action level has not been exceeded, then a Type II error has been committed; in this case, remedial action may not be taken where it is warranted. The Type II error is considered to be the more egregious error for this site, as residential housing may be part of the redevelopment plan. The decision team will scrutinize analytical data where the results are below, but within analytical error, of the action level to determine whether the action level has been exceeded.

Optimize the Design for Obtaining Data - Identify the most resource-effective sampling and analysis design for generating data that are expected to satisfy the data quality objectives (DQOs).

The goals of the sampling event are to determine whether soil and groundwater at the site have been impacted above agreed upon action levels from historic site uses. To accomplish these objectives Weston will conduct biased surface soil sampling based on the areas of environmental concern outlined in the Phase I and II TBA. Groundwater sampling will be conducted by installing three initial groundwater wells at locations chosen on the basis of previously identified groundwater contamination and proximity to establish a site groundwater gradient. Wells will be installed using a direct push rig to minimize drill cuttings. Once the three initial wells are installed, a subcontracted surveyor will establish elevations and locations for the wells. With the survey data and groundwater elevations, Weston will calculate the groundwater gradient at the site. The groundwater gradient will be used to identify the optimal upgradient and downgradient well locations for this study.

SAP AMENDMENT ATTACHMENT B:

AMENDED ANALYTICAL METHODS

METHOD #: 160.1	Approved for NPDES (Issued 1971)
TITLE:	Residue, Filterable (Gravimetric, Dried at 180°C)
ANALYTE:	Residue, Filterable
INSTRUMENTATION:	Drying Oven
STORET No.	70300

1.0 Scope and Application

1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
1.2 The practical range of the determination is 10 mg/L to 20,000 mg/L

2.0 Summary of Method

2.1 A well-mixed sample is filtered through a standard glass fiber filter. The filtrate is evaporated and dried to constant weight at 180°C.
2.2 If Residue, Non-Filterable is being determined, the filtrate from that method may be used for Residue, Filterable.

3.0 Definitions

3.1 Filterable residue is defined as those solids capable of passing through a glass fiber filter and dried to constant weight at 180°C.

4.0 Sample Handling and Preservation

4.1 Preservation of the sample is not practical; analysis should begin as possible. Refrigeration or icing to 4°C, to minimize micro-biological decomposition of solids, is recommended.

5.0 Interferences

5.1 Highly mineralized waters containing significant concentrations of calcium, magnesium, chloride and/or sulfate may be hygroscopic and will require prolonged drying, desiccation and rapid weighing.
5.2 Samples containing high concentrations of bicarbonate will require careful and possibly prolonged drying at 180°C to insure that all the bicarbonate is converted to carbonate.
5.3 Too much residue in the evaporating dish will crust over and entrap water that will not be driven off during drying. Total residue should be limited to about 200 mg.

6.0 Apparatus

6.1 Glass fiber filter discs, 4.7 cm or 2.1 cm, without organic binder, Reeve Angel type 934-AH, Gelman type A/E, or equivalent
6.2 Filter holder, membrane filter funnel or Gooch crucible adapter
6.3 Suction flask, 500 mL
6.4 Gooch crucibles, 25 mL (if 2.1 cm filter is used)
6.5 Evaporating dishes, porcelain, 100 mL volume. (Vycor or platinum dishes may be substituted)
6.6 Steam bath
6.7 Drying oven, 180°C ± 2°C
6.8 Desiccator
6.9 Analytical balance, capable of weighing to 0.1 mg

7.0 Procedure

7.1 Preparation of glass fiber filter disc: Place the disc on the membrane filter apparatus or insert into bottom of a suitable Gooch crucible. While vacuum is applied, wash the disc with three successive 20 mL volumes of distilled water. Remove all traces of water by continuing to apply vacuum after water has passed through. Discard washings.
7.2 Preparation of evaporating dishes: If Volatile Residue is also to be measured heat the clean dish to 550 ± 50°C for one hour in a muffle furnace. If only Filterable Residue is to be measured heat the clean dish to 180 ± 2°C for one hour. Cool in desiccator and store until needed. Weigh immediately before use.
7.3 Assemble the filtering apparatus and begin suction. Shake the sample vigorously and rapidly transfer 100 mL to the funnel by means of a 100 mL graduated cylinder. If total filterable residue is low, a larger volume may be filtered.
7.4 Filter the sample through the glass fiber filter, rinse with three 10 mL portions of distilled water and continue to apply vacuum for about 3 minutes after filtration is complete to remove as much water as possible.
7.5 Transfer 100 mL (or a larger volume) of the filtrate to a weighed evaporating dish and evaporate to dryness on a steam bath.
7.6 Dry the evaporated sample for at least one hour at 180 plus or minus 2°C. Cool in a desiccator and weigh. Repeat the drying cycle until a constant weight is obtained or until weight loss is less than 0.5 mg.

8.0 Calculation

8.1 Calculate filterable residue as follows:

$$\text{Filterable residue, mg/L} = \frac{(A - B) \times 1{,}000}{C}$$

where:

A = weight of dried residue + dish in mg
B = weight of dish in mg
C = volume of sample used in mL

9.0 Precision and Accuracy

9.1 Precision and accuracy are not available at this time.

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1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 92, Method 208B, (1975).

METHOD 3050B

ACID DIGESTION OF SEDIMENTS, SLUDGES, AND SOILS

1.0 SCOPE AND APPLICATION

1.1 This method has been written to provide two separate digestion procedures, one for the preparation of sediments, sludges, and soil samples for analysis by flame atomic absorption spectrometry (FLAA) or inductively coupled plasma atomic emission spectrometry (ICP-AES) and one for the preparation of sediments, sludges, and soil samples for analysis of samples by Graphite Furnace AA (GFAA) or inductively coupled plasma mass spectrometry (ICP-MS). The extracts from these two procedures are not interchangeable and should only be used with the analytical determinations outlined in this section. Samples prepared by this method may be analyzed by ICP-AES or GFAA for all the listed metals as long as the detecion limits are adequate for the required end-use of the data. Alternative determinative techniques may be used if they are scientifically valid and the QC criteria of the method, including those dealing with interferences, can be achieved. Other elements and matrices may be analyzed by this method if performance is demonstrated for the analytes of interest, in the matrices of interest, at the concentration levels of interest (See Section 8.0). The recommended determinative techniques for each element are listed below:

FLAA/ICP-AES		GFAA/ICP-MS
Aluminum	Magnesium	Arsenic
Antimony	Manganese	Beryllium
Barium	Molybdenum	Cadmium
Beryllium	Nickel	Chromium
Cadmium	Potassium	Cobalt
Calcium	Silver	Iron
Chromium	Sodium	Lead
Cobalt	Thallium	Molybdenum
Copper	Vanadium	Selenium
Iron	Zinc	Thallium
Lead		
Vanadium		

1.2 This method is not a total digestion technique for most samples. It is a very strong acid digestion that will dissolve almost all elements that could become “environmentally available.” By design, elements bound in silicate structures are not normally dissolved by this procedure as they are not usually mobile in the environment. If absolute total digestion is required use Method 3052.

2.0 SUMMARY OF METHOD

2.1 For the digestion of samples, a representative 1-2 gram (wet weight) or 1 gram (dry weight) sample is digested with repeated additions of nitric acid (HNO_3) and hydrogen peroxide (H_2O_2).

2.2 For GFAA or ICP-MS analysis, the resultant digestate is reduced in volume while heating and then diluted to a final volume of 100 mL.

2.3 For ICP-AES or FLAA analyses, hydrochloric acid (HCl) is added to the initial digestate and the sample is refluxed. In an optional step to increase the solubility of some metals (see Section 7.3.1: NOTE), this digestate is filtered and the filter paper and residues are rinsed, first

with hot HCl and then hot reagent water. Filter paper and residue are returned to the digestion flask, refluxed with additional HCl and then filtered again. The digestate is then diluted to a final volume of 100 mL.

2.4 If required, a separate sample aliquot shall be dried for a total percent solids determination.

3.0 INTERFERENCES

3.1 Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed in accordance with the quality control requirements given in Sec. 8.0 to aid in determining whether Method 3050B is applicable to a given waste.

4.0 APPARATUS AND MATERIALS

4.1 Digestion Vessels - 250-mL.

4.2 Vapor recovery device (e.g., ribbed watch glasses, appropriate refluxing device, appropriate solvent handling system).

4.3 Drying ovens - able to maintain 30°C $\pm$ 4°C.

4.4 Temperature measurement device capable of measuring to at least 125°C with suitable precision and accuracy (e.g., thermometer, IR sensor, thermocouple, thermister, etc.)

4.5 Filter paper - Whatman No. 41 or equivalent.

4.6 Centrifuge and centrifuge tubes.

4.7 Analytical balance - capable of accurate weighings to 0.01 g.

4.8 Heating source - Adjustable and able to maintain a temperature of 90-95°C. (e.g., hot plate, block digestor, microwave, etc.)

4.9 Funnel or equivalent.

4.10 Graduated cylinder or equivalent volume measuring device.

4.11 Volumetric Flasks - 100-mL.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is questionable, analyze the reagent to determine the level of impurities. The reagent blank must be less than the MDL in order to be used.

5.2 Reagent Water. Reagent water will be interference free. All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

5.3 Nitric acid (concentrated), HNO_3. Acid should be analyzed to determine level of impurities. If method blank is < MDL, the acid can be used.

5.4 Hydrochloric acid (concentrated), HCl. Acid should be analyzed to determine level of impurities. If method blank is < MDL, the acid can be used.

5.5 Hydrogen peroxide (30%), H_2O_2. Oxidant should be analyzed to determine level of impurities. If method blank is < MDL, the peroxide can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be demonstrated to be free of contamination at or below the reporting limit. Plastic and glass containers are both suitable. See Chapter Three, Section 3.1.3, for further information.

6.3 Nonaqueous samples should be refrigerated upon receipt and analyzed as soon as possible.

6.4 It can be difficult to obtain a representative sample with wet or damp materials. Wet samples may be dried, crushed, and ground to reduce subsample variability as long as drying does not affect the extraction of the analytes of interest in the sample.

7.0 PROCEDURE

7.1 Mix the sample thoroughly to achieve homogeneity and sieve, if appropriate and necessary, using a USS #10 sieve. All equipment used for homogenization should be cleaned according to the guidance in Sec. 6.0 to minimize the potential of cross-contamination. For each digestion procedure, weigh to the nearest 0.01 g and transfer a 1-2 g sample (wet weight) or 1 g sample (dry weight) to a digestion vessel. For samples with high liquid content, a larger sample size may be used as long as digestion is completed.

> NOTE: All steps requiring the use of acids should be conducted under a fume hood by properly trained personnel using appropriate laboratory safety equipment. The use of an acid vapor scrubber system for waste minimization is encouraged.

7.2 For the digestion of samples for analysis by GFAA or ICP-MS, add 10 mL of 1:1 HNO_3, mix the slurry, and cover with a watch glass or vapor recovery device. Heat the sample to 95°C ± 5°C and reflux for 10 to 15 minutes without boiling. Allow the sample to cool, add 5 mL of concentrated HNO_3, replace the cover, and reflux for 30 minutes. If brown fumes are generated, indicating oxidation of the sample by HNO_3, repeat this step (addition of 5 mL of conc. HNO_3) over and over until no brown fumes are given off by the sample indicating the complete reaction with HNO_3. Using a ribbed watch glass or vapor recovery system, either allow the solution to evaporate to approximately 5 mL without boiling or heat at 95°C ± 5°C without boiling for two hours. Maintain a covering of solution over the bottom of the vessel at all times.

NOTE: Alternatively, for direct energy coupling devices, such as a microwave, digest samples for analysis by GFAA or ICP-MS by adding 10 mL of 1:1 HNO_3, mixing the slurry and then covering with a vapor recovery device. Heat the sample to 95°C ± 5°C and reflux for 5 minutes at 95°C ± 5°C without boiling. Allow the sample to cool for 5 minutes, add 5 mL of concentrated HNO_3, heat the sample to 95°C ± 5°C and reflux for 5 minutes at 95°C ± 5°C. If brown fumes are generated, indicating oxidation of the sample by HNO_3, repeat this step (addition of 5 mL concentrated HNO_3) until no brown fumes are given off by the sample indicating the complete reaction with HNO_3. Using a vapor recovery system, heat the sample to 95°C ± 5°C and reflux for 10 minutes at 95°C ± 5°C without boiling.

7.2.1 After the step in Section 7.2 has been completed and the sample has cooled, add 2 mL of water and 3 mL of 30% H_2O_2. Cover the vessel with a watch glass or vapor recovery device and return the covered vessel to the heat source for warming and to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides and cool the vessel.

NOTE: Alternatively, for direct energy coupled devices: After the Sec. 7.2 "NOTE" step has been completed and the sample has cooled for 5 minutes, add slowly 10 mL of 30% H_2O_2. Care must be taken to ensure that losses do not occur due to excessive vigorous effervesence. Go to Section 7.2.3.

7.2.2 Continue to add 30% H_2O_2 in 1-mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged.

NOTE: Do not add more than a total of 10 mL 30% H_2O_2.

7.2.3 Cover the sample with a ribbed watch glass or vapor recovery device and continue heating the acid-peroxide digestate until the volume has been reduced to approximately 5 mL or heat at 95°C ± 5°C without boiling for two hours. Maintain a covering of solution over the bottom of the vessel at all times.

NOTE: Alternatively, for direct energy coupled devices: Heat the acid-peroxide digestate to 95°C ± 5°C in 6 minutes and remain at 95°C ± 5°C without boiling for 10 minutes.

7.2.4 After cooling, dilute to 100 mL with water. Particulates in the digestate should then be removed by filtration, by centrifugation, or by allowing the sample to settle. The sample is now ready for analysis by GFAA or ICP-MS.

7.2.4.1 Filtration - Filter through Whatman No. 41 filter paper (or equivalent).

7.2.4.2 Centrifugation - Centrifugation at 2,000-3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

7.2.4.3 The diluted digestate solution contains approximately 5% (v/v) HNO_3. For analysis, withdraw aliquots of appropriate volume and add any required reagent or matrix modifier.

7.3 For the analysis of samples for FLAA or ICP-AES, add 10 mL conc. HCl to the sample digest from 7.2.3 and cover with a watch glass or vapor recovery device. Place the sample on/in the heating source and reflux at 95°C ± 5°C for 15 minutes.

NOTE: Alternatively, for direct energy coupling devices, such as a microwave, digest samples for analysis by FLAA and ICP-AES by adding 5 mL HCl and 10 mL H_2O to the sample digest from 7.2.3 and heat the sample to 95°C ± 5°C, Reflux at 95°C ± 5°C without boiling for 5 minutes.

7.4 Filter the digestate through Whatman No. 41 filter paper (or equivalent) and collect filtrate in a 100-mL volumetric flask. Make to volume and analyze by FLAA or ICP-AES.

NOTE: Section 7.5 may be used to improve the solubilities and recoveries of antimony, barium, lead, and silver when necessary. These steps are optional and are not required on a routine basis.

7.5 Add 2.5 mL conc. HNO_3 and 10 mL conc. HCl to a 1-2 g sample (wet weight) or 1 g sample (dry weight) and cover with a watchglass or vapor recovery device. Place the sample on/in the heating source and reflux for 15 minutes.

7.5.1 Filter the digestate through Whatman No. 41 filter paper (or equivalent) and collect filtrate in a 100-mL volumetric flask. Wash the filter paper, while still in the funnel, with no more than 5 mL of hot (~95°C) HCl, then with 20 mL of hot (~95°C) reagent water. Collect washings in the same 100-mL volumetric flask.

7.5.2 Remove the filter and residue from the funnel, and place them back in the vessel. Add 5 mL of conc. HCl, place the vessel back on the heating source, and heat at 95°C ± 5°C until the filter paper dissolves. Remove the vessel from the heating source and wash the cover and sides with reagent water. Filter the residue and collect the filtrate in the same 100-mL volumetric flask. Allow filtrate to cool, then dilute to volume.

NOTE: High concentrations of metal salts with temperature-sensitive solubilities can result in the formation of precipitates upon cooling of primary and/or secondary filtrates. If precipitation occurs in the flask upon cooling, do not dilute to volume.

7.5.3 If a precipitate forms on the bottom of a flask, add up to 10 mL of concentrated HCl to dissolve the precipitate. After precipitate is dissolved, dilute to volume with reagent water. Analyze by FLAA or ICP-AES.

7.6 Calculations

7.6.1 The concentrations determined are to be reported on the basis of the actual weight of the sample. If a dry weight analysis is desired, then the percent solids of the sample must also be provided.

7.6.2 If percent solids is desired, a separate determination of percent solids must be performed on a homogeneous aliquot of the sample.

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

8.2 For each batch of samples processed, a method blank should be carried throughout the entire sample preparation and analytical process according to the frequency described in Chapter One. These blanks will be useful in determining if samples are being contaminated. Refer to Chapter One for the proper protocol when analyzing method blanks.

8.3 Spiked duplicate samples should be processed on a routine basis and whenever a new sample matrix is being analyzed. Spiked duplicate samples will be used to determine precision and bias. The criteria of the determinative method will dictate frequency, but 5% (one per batch) is recommended or whenever a new sample matrix is being analyzed. Refer to Chapter One for the proper protocol when analyzing spiked replicates.

8.4 Limitations for the FLAA and ICP-AES optional digestion procedure. Analysts should be aware that the upper linear range for silver, barium, lead, and antimony may be exceeded with some samples. If there is a reasonable possibility that this range may be exceeded, or if a sample's analytical result exceeds this upper limit, a smaller sample size should be taken through the entire procedure and re-analyzed to determine if the linear range has been exceeded. The approximate linear upper ranges for a 2 gram sample size:

Ag	2,000 mg/kg
As	1,000,000 mg/kg
Ba	2,500 mg/kg
Be	1,000,000 mg/kg
Cd	1,000,000 mg/kg
Co	1,000,000 mg/kg
Cr	1,000,000 mg/kg
Cu	1,000,000 mg/kg
Mo	1,000,000 mg/kg
Ni	1,000,000 mg/kg
Pb	200,000 mg/kg
Sb	200,000 mg/kg
Se	1,000,000 mg/kg
Tl	1,000,000 mg/kg
V	1,000,000 mg/kg
Zn	1,000,000 mg/kg

NOTE: These ranges will vary with sample matrix, molecular form, and size.

9.0 METHOD PERFORMANCE

9.1 In a single laboratory, the recoveries of the three matrices presented in Table 2 were obtained using the digestion procedure outlined for samples prior to analysis by FLAA and ICP-AES. The spiked samples were analyzed in duplicate. Tables 3-5 represents results of analysis of NIST Standard Reference Materials that were obtained using both atmospheric pressure microwave digestion techniques and hot-plate digestion procedures.

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TABLE 1

STANDARD RECOVERY (%) COMPARISON FOR
METHODS 3050A AND 3050B[a]

Analyte	METHOD 3050A[a]	METHOD 3050B w/option[a]
Ag	9.5	98
As	86	102
Ba	97	103
Be	96	102
Cd	101	99
Co	99	105
Cr	98	94
Cu	87	94
Mo	97	96
Ni	98	92
Pb	97	95
Sb	87	88
Se	94	91
Tl	96	96
V	93	103
Zn	99	95

[a] All values are percent recovery. Samples: 4 mL of 100 mg/mL multistandard; n = 3.

TABLE 2

PERCENT RECOVERY COMPARISON FOR METHODS 3050A AND 3050B

Analyte	Percent Recovery[a,c]							
	Sample 4435		Sample 4766		Sample HJ		Average	
	3050A	3050B	3050A	3050B	3050A	3050B	3050A	3050B
Ag	9.8	103	15	89	56	93	27	95
As	70	102	80	95	83	102	77	100
Ba	85	94	78	95	b	b	81	94
Be	94	102	108	98	99	94	99	97
Cd	92	88	91	95	95	97	93	94
Co	90	94	87	95	89	93	89	94
Cr	90	95	89	94	72	101	83	97
Cu	81	88	85	87	70	106	77	94
Mo	79	92	83	98	87	103	83	98
Ni	88	93	93	100	87	101	92	98
Pb	82	92	80	91	77	91	81	91
Sb	28	84	23	77	46	76	32	79
Se	84	89	81	96	99	96	85	94
Tl	88	87	69	95	66	67	74	83
V	84	97	86	96	90	88	87	93
Zn	96	106	78	75	b	b	87	99

a - Samples: 4 mL of 100 mg/mL multi-standard in 2 g of sample. Each value is percent recovery and is the average of duplicate spikes.

b - Unable to accurately quantitate due to high background values.

c - Method 3050B using optional section.

Table 3
Results of Analysis of Nist Standard Reference Material 2704
"River Sediment" Using Method 3050B (µg/g ± SD)

Element	Atm. Pressure Microwave Assisted Method with Power Control	Atm. Pressure Microwave Assisted Method with Temperature Control (gas-bulb)	Atm. Pressure Microwave Assisted Method with Temperature Control (IR-sensor)	Hot-Plate	NIST Certified Values for Total Digestion (µg/g ±95% CI)
Cu	101 ± 7	89 ± 1	98 ± 1.4	100 ± 2	98.6 ± 5.0
Pb	160 ± 2	145 ± 6	145 ± 7	146 ± 1	161 ± 17
Zn	427 ± 2	411 ± 3	405 ± 14	427 ± 5	438 ± 12
Cd	NA	3.5 ± 0.66	3.7 ± 0.9	NA	3.45 ± 0.22
Cr	82 ± 3	79 ± 2	85 ± 4	89 ± 1	135 ± 5
Ni	42 ± 1	36 ± 1	38 ± 4	44 ± 2	44.1 ± 3.0

NA - Not Available

Table 4
Results of Analysis of NIST Standard Reference Material 2710
"Montana Soil (Highly Elevated Trace Element Concentrations)" Using Method 3050B
(µg/g ± SD)

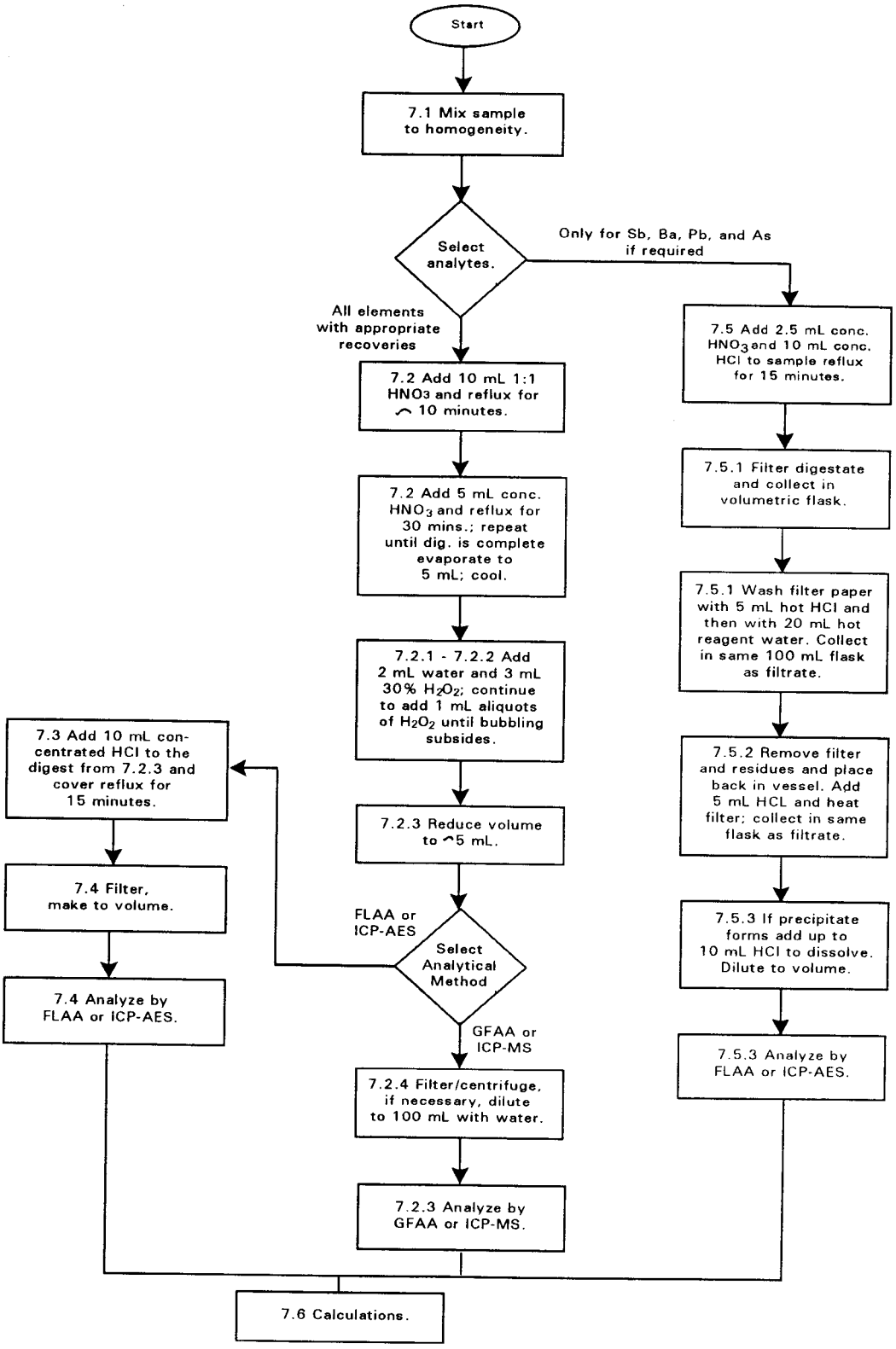
Element	Atm. Pressure Microwave Assisted Method with Power Control	Atm. Pressure Microwave Assisted Method with Temperature Control (gas-bulb)	Atm. Pressure Microwave Assisted Method with Temperature Control (IR-sensor)	Hot-Plate	NIST Leachable Concentrations Using Method 3050	NIST Certified Values for Total Digestion (µg/g ±95% CI)
Cu	2640 ± 60	2790 ± 41	2480 ± 33	2910 ± 59	2700	2950 ± 130
Pb	5640 ± 117	5430 ± 72	5170 ± 34	5720 ± 280	5100	5532 ± 80
Zn	6410 ± 74	5810 ± 34	6130 ± 27	6230 ± 115	5900	6952 ± 91
Cd	NA	20.3 ± 1.4	20.2 ± 0.4	NA	20	21.8 ± 0.2
Cr	20 ± 1.6	19 ± 2	18 ± 2.4	23 ± 0.5	19	39*
Ni	7.8 ± 0.29	10 ± 1	9.1 ± 1.1	7 ± 0.44	10.1	14.3 ± 1.0

NA - Not Available * Non-certified values, for information only.

Table 5
Results of Analysis of NIST Standard Reference Material 2711
"Montana Soil (Moderately Elevated Trace Element Concentrations)" Using Method 3050B
(µg/g ± SD)

Element	Atm. Pressure Microwave Assisted Method with Power Control	Atm. Pressure Microwave Assisted Method with Temperature Control (gas-bulb)	Atm. Pressure Microwave Assisted Method with Temperature Control (IR-sensor)	Hot-Plate	NIST Leachable Concentrations Using Method 3050	NIST Certified Values for Total Digestion (µg/g ±95% CI)
Cu	107 ± 4.6	98 ± 5	98 ± 3.8	111 ± 6.4	100	114 ± 2
Pb	1240 ± 68	1130 ± 20	1120 ± 29	1240 ± 38	1100	1162 ± 31
Zn	330 ± 17	312 ± 2	307 ± 12	340 ± 13	310	350.4 ± 4.8
Cd	NA	39.6 ± 3.9	40.9 ± 1.9	NA	40	41.7 ± 0.25
Cr	22 ± 0.35	21 ± 1	15 ± 1.1	23 ± 0.9	20	47*
Ni	15 ± 0.2	17 ± 2	15 ± 1.6	16 ± 0.4	16	20.6 ± 1.1

NA - Not Available
* Non-certified values, for information only.


Start
7.1 Mix sample to homogeneity.
Select analytes.
Only for Sb, Ba, Pb, and As if required
All elements with appropriate recoveries
7.2 Add 10 mL 1:1 HNO3 and reflux for ~ 10 minutes.
7.2 Add 5 mL conc. HNO3 and reflux for 30 mins.; repeat until dig. is complete evaporate to 5 mL; cool.
7.2.1 - 7.2.2 Add 2 mL water and 3 mL 30% H2O2; continue to add 1 mL aliquots of H2O2 until bubbling subsides.
7.2.3 Reduce volume to ~5 mL.
FLAA or ICP-AES
Select Analytical Method
GFAA or ICP-MS
7.2.4 Filter/centrifuge, if necessary, dilute to 100 mL with water.
7.2.3 Analyze by GFAA or ICP-MS.
7.3 Add 10 mL concentrated HCl to the digest from 7.2.3 and cover reflux for 15 minutes.
7.4 Filter, make to volume.
7.4 Analyze by FLAA or ICP-AES.
7.5 Add 2.5 mL conc. HNO3 and 10 mL conc. HCl to sample reflux for 15 minutes.
7.5.1 Filter digestate and collect in volumetric flask.
7.5.1 Wash filter paper with 5 mL hot HCl and then with 20 mL hot reagent water. Collect in same 100 mL flask as filtrate.
7.5.2 Remove filter and residues and place back in vessel. Add 5 mL HCL and heat filter; collect in same flask as filtrate.
7.5.3 If precipitate forms add up to 10 mL HCl to dissolve. Dilute to volume.
7.5.3 Analyze by FLAA or ICP-AES.
7.6 Calculations.

METHOD 3500B

ORGANIC EXTRACTION AND SAMPLE PREPARATION

1.0 SCOPE AND APPLICATION

1.1 Method 3500 provides general guidance on the selection of methods used in the quantitative extraction (or dilution) of samples for analysis by one of the semivolatile or nonvolatile determinative methods. Cleanup and/or analysis of the resultant extracts are described in Chapter Two as well as in Method 3600 (Cleanup) and Method 8000 (Analysis).

1.2 The following table lists the extraction methods, the matrix and the analyte category.

SAMPLE EXTRACTION METHODS FOR SEMIVOLATILES AND NONVOLATILES

Method #	Matrix	Extraction Type	Analytes
3510	Aqueous	Separatory Funnel Liquid-Liquid Extraction	Semivolatile & Nonvolatile Organics
3520	Aqueous	Continuous Liquid-Liquid Extraction	Semivolatile & Nonvolatile Organics
3535	Aqueous	Solid-Phase Extraction (SPE)	Semivolatile & Nonvolatile Organics
3540	Solids	Soxhlet Extraction	Semivolatile & Nonvolatile Organics
3541	Solids	Automated Soxhlet Extraction	Semivolatiles & Nonvolatile Organics
3542	Air Sampling Train	Separatory Funnel & Soxhlet Extraction	Semivolatile Organics
3545	Solids	Pressurized Fluid Extraction (ASE) (Heat & Pressure)	Semivolatile & Nonvolatile Organics
3550	Solids	Ultrasonic Extraction	Semivolatile & Nonvolatile Organics
3560/ 3561	Solids	Supercritical Fluid Extraction (SFE)	Semivolatile Petroleum Hydrocarbons & Polynuclear Aromatic Hydrocarbons
3580	Non-aqueous Solvent Soluble Waste	Solvent Dilution	Semivolatile & Nonvolatile Organics

1.3 Method 3580 may be used for the solvent dilution of non-aqueous semivolatile and nonvolatile organic samples prior to cleanup and/or analysis.

1.4 Methods 3545, 3560, and 3561 are techniques that utilize pressurized solvent extraction to reduce the amount of solvent needed to extract target analytes and reduce the extraction time when compared to more traditional techniques such as Soxhlet extraction.

1.5 Prior to employing this method, analysts are advised to consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the allowed flexibility in the choice of apparatus, reagents, and supplies. In addition, unless specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in this procedure is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to meet the data quality objectives or needs for the intended use of the data.

2.0 SUMMARY OF METHOD

2.1 A sample of a known volume or weight is extracted with solvent or diluted with solvent. Method choices for aqueous samples include liquid-liquid extraction by separatory funnel or by continuous extractor and solid-phase extraction (SPE). Method choices for soil/sediment and solid waste samples include standard solvent extraction methods utilizing either Soxhlet, automated Soxhlet, or ultrasonic extraction. Solids may also be extracted using pressurized extraction techniques such as supercritical fluid extraction or heated pressurized fluid extraction.

2.2 The resultant extract is dried and concentrated in a Kuderna-Danish (K-D) apparatus. Other concentration devices or techniques may be used in place of the Kuderna-Danish concentrator if the quality control requirements of the determinative methods are met (Method 8000, Sec. 8.0).

NOTE: Solvent recovery apparatus is recommended for use in methods that require the use of Kuderna-Danish evaporative concentrators. EPA recommends the incorporation of this type of reclamation system as a method to implement an emissions reduction program.

2.3 See Sec. 7.0 for additional guidance to assist in selection of the appropriate method.

3.0 INTERFERENCES

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method for specific guidance on quality control procedures and to Chapter Four for guidance on the cleaning of glassware.

3.2 Interferences coextracted from the samples will vary considerably from source to source. If analysis of an extracted sample is prevented due to interferences, further cleanup of the sample extract may be necessary. Refer to Method 3600 for guidance on cleanup procedures.

3.3 Phthalate esters contaminate many types of products commonly found in the laboratory. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Serious phthalate contamination may result at any time if consistent quality control is not practiced.

3.4 Soap residue (e.g. sodium dodecyl sulfate), which results in a basic pH on glassware surfaces, may cause degradation of certain analytes. Specifically, Aldrin, Heptachlor, and most organophosphorus pesticides will degrade in this situation. This problem is especially pronounced with glassware that may be difficult to rinse (e.g., 500-mL K-D flask). These items should be hand-rinsed very carefully to avoid this problem.

4.0 APPARATUS AND MATERIALS

4.1 Refer to the specific method of interest for a description of the apparatus and materials needed.

4.2 Solvent recovery apparatus is recommended for use in methods that require the use of Kuderna-Danish evaporative concentrators. Incorporation of this apparatus may be required by State or local municipality regulations that govern air emissions of volatile organics. EPA recommends the incorporation of this type of reclamation system as a method to implement an emissions reduction program. Solvent recovery is a means to conform with waste minimization and pollution prevention initiatives.

5.0 REAGENTS

5.1 Refer to the specific method of interest for a description of the solvents needed.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water as defined in Chapter One.

5.3 Stock standards for spiking solutions - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. The stock solutions used for the calibration standards are acceptable (dilutions must be made in a water miscible solvent) except for the quality control check sample stock concentrate which must be prepared independently to serve as a check on the accuracy of the calibration solution.

5.3.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure compound. Dissolve the compound in a water miscible solvent (i.e., methanol, acetone, 2-propanol, etc.) and dilute to volume in a 10-mL volumetric flask. If compound purity is 96 percent or greater, the weight can be used without correction to calculate the concentration of the stock standard solution. Commercially-prepared stock standard solutions can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.3.2 Stock standard solutions should be stored in polytetrafluoroethylene (PTFE)-sealed containers at 4°C or below. The solutions should be checked frequently for stability. Refer to the determinative method for holding times of the stock solutions.

5.4 Surrogate standards - A surrogate (i.e., a compound that is chemically similar to the analyte group but is not expected to occur in an environmental sample) should be added to each sample, blank, laboratory control sample (LCS), and matrix spike sample just prior to extraction or processing. The recovery of the surrogate standard is used to monitor for unusual matrix effects, gross sample processing errors, etc. Surrogate recovery is evaluated for acceptance by determining whether the measured concentration falls within the acceptance limits.

5.4.1 Recommended surrogates for certain analyte groups are listed in Table 1. For methods where no recommended surrogates are listed, the lab is free to select compounds that fall within the definition provided above. Even compounds that are on the method target analyte list may be used as a surrogate as long as historical data are available to ensure their absence at a given site. Normally one or more standards are added for each analyte group.

5.4.2 Prepare a surrogate spiking concentrate by mixing stock standards prepared above and diluting with a water miscible solvent. Commercially prepared spiking solutions are acceptable. The concentration for semivolatile/nonvolatile organic and pesticide analyses should be such that a 1-mL aliquot into 1000 mL of a sample provides a concentration of 10 times the quantitation limit or near the mid-point of the calibration curve. Where volumes of less than 1000 mL are extracted, adjust the volume of surrogate standard proportionately. For matrices other than water, 1 mL of surrogate standard is still the normal spiking volume. However, if gel permeation chromatography will be used for sample cleanup, 2 mL should be added to the sample. See Table 1 for recommended surrogates. The spiking volumes are normally listed in each extraction method. Where concentrations are not listed in a method, a concentration of 10 times the quantitation limit is recommended. If the surrogate quantitation limit is unknown, the average quantitation limit of method target analytes may be utilized to estimate a surrogate quantitation limit. As necessary or appropriate to meet project objectives, the surrogates listed in Table 1 may be modified by the laboratory. The concentration of the surrogate in the sample (or sample extract) should either be near the middle of the calibration range or approximately ten times the quantitation limit.

5.5 Matrix spike standards - The following are recommended matrix spike standard mixtures for a few analyte groups. Prepare a matrix spike concentrate by mixing stock standards prepared above and diluting with a water miscible solvent. Commercially-prepared spiking solutions are acceptable. The matrix spike standards should be independent of the calibration standard. A few methods provide guidance on concentrations and the selection of compounds for matrix spikes (see Table 2).

5.5.1 Base/neutral and acid matrix spiking solution - Prepare a spiking solution in methanol that contains each of the following base/neutral compounds at 100 mg/L and the acid compounds at 200 mg/L for water and sediment/soil samples. The concentration of these compounds should be five times higher for waste samples.

Base/neutrals	Acids
1,2,4-Trichlorobenzene	Pentachlorophenol
Acenaphthene	Phenol
2,4-Dinitrotoluene	2-Chlorophenol
Pyrene	4-Chloro-3-methylphenol
N-Nitroso-di-n-propylamine	4-Nitrophenol
1,4-Dichlorobenzene	

5.5.2 Organochlorine pesticide matrix spiking solution - Prepare a spiking solution in acetone or methanol that contains the following pesticides in the concentrations listed for water and sediment/soil. The concentration should be five times higher for waste samples.

Pesticide	Concentration (mg/L)
Lindane	0.2
Heptachlor	0.2
Aldrin	0.2
Dieldrin	0.5
Endrin	0.5
4,4'-DDT	0.5

5.5.3 For methods with no guidance, select five or more analytes (select all analytes for methods with five or less) from each analyte group for use in a spiking solution. Where matrix spike concentrations in the sample are not listed it should be at or below the regulatory concentration or action level, or 1 to 5 times higher than the background concentration, whichever, concentration would be larger.

5.5.4 Sec. 8.3.3 provides guidance on determining the concentration of the matrix spike compounds in the sample. As necessary or appropriate to meet project objectives, the matrix spiking compounds listed in Secs. 5.5.1, 5.5.2, and/or the concentrations listed in the spiking solutions may be modified by the laboratory. When the concentration of an analyte is not being checked against a regulatory limit or action level (see Sec. 8.3.3.3) the concentration of the matrix spike compound in the sample (or sample extract) should be near the middle of the calibration range or approximately ten times the quantitation limit.

5.6 Laboratory control spike standard - Use the matrix spike standard prepared in Sec. 5.5 as the spike standard for the laboratory control sample (LCS). The LCS should be spiked at the same concentration as the matrix spike.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See Chapters Two and Four for guidance on sample collection.

7.0 PROCEDURE

7.1 Water, soil/sediment, sludge, and waste samples requiring analysis for semivolatile and nonvolatile organic compounds (within this broad category are special subsets of analytes, i.e., the different groups of pesticides, explosives, PCBs etc.), must undergo solvent extraction prior to analysis. This manual contains method choices that are dependent on the matrix, the physical properties of the analytes, the sophistication and cost of equipment available to a given laboratory, and the turn-around time required for sample preparation.

7.1.1 The laboratory should be responsible for ensuring that the method chosen for sample extraction will provide acceptable extraction efficiency for the target analytes in a given matrix. There are several approaches that may be employed to ensure the appropriateness of the extraction method.

7.1.1.1 Prior to employing any extraction procedure on samples submitted for regulatory compliance monitoring purposes, the laboratory should complete the initial demonstration of proficiency described in Sec. 8.2. This demonstration applies to all SW-846 extraction methods, including those for which specific performance data are provided in a determinative method.

7.1.1.2 In addition, when a new or different extraction technique is to be applied to samples, the laboratory should also demonstrate that their application of the technique provides acceptable performance in the matrix of interest for the analytes of interest. One approach to demonstrating extraction method performance is to make a direct comparison between the chosen method and either Method 3520 (continuous liquid-liquid extraction of aqueous samples) or Method 3540 (Soxhlet extraction of solid samples), as these methods have the broadest applicability to environmental matrices.

When direct comparisons are performed, they should be conducted using either standard reference materials derived from real-world matrices or samples from a given site that can be reasonably expected to contain the analytes of interest. Because of concerns with the incorporation of spiking materials into samples, the use of samples spiked by the laboratory is generally a less useful comparison relative to either real-world contaminated samples or standard reference materials, and thus should generally only be employed when neither of these latter materials are available. Analyze at least four portions of a well homogenized sample by the extraction method of interest and either Method 3520 or Method 3540, depending on the matrix.

7.1.1.3 When direct comparisons between methods are conducted, the laboratory may use statistical tests such as an F-test to determine if the results are comparable between the methods. The laboratory may employ the method of interest provided that the demonstrated performance can be shown to be either as good or better than that of the "reference" method, or adequate for project needs, that is, meeting the requirements of the QA Project Plan for a specific project.

7.1.1.4 Whatever approaches are taken to ensure the adequacy of the extraction procedure for the matrix of interest, it is the responsibility of the laboratory to document the results and maintain records of such demonstrations.

7.1.2 Each method has QC requirements that normally include the addition of surrogates to each analytical sample and QC sample as well as the inclusion of a matrix spike/matrix spike duplicate (or matrix spike and duplicate sample), a laboratory control sample, and a method blank in each sample extraction batch. As defined in Chapter One, a "batch" consists of up to 20 environmental samples processed as a unit. In the case of samples that must undergo extraction prior to analysis, each group of 20 samples extracted together by the same method constitutes an extraction batch.

The decision of whether to prepare and analyze a matrix spike/matrix spike duplicate pair or a matrix spike and a duplicate sample should be based on knowledge of the samples in the extraction batch. If the samples are expected to contain the analytes of interest, then the analysis of a duplicate sample may yield data on the precision of the analytical process and the analysis of the matrix spike will yield data on the accuracy of the process. In contrast, when the samples are not known or expected to contain the analytes of interest, then the batch should include a matrix spike/matrix spike duplicate pair to ensure that both accuracy and precision data will be generated within the extraction batch.

7.2 Method 3510 - Applicable to the extraction and concentration of water-insoluble and slightly water-soluble organics from aqueous samples. A measured volume of sample is solvent extracted using a separatory funnel. The extract is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis. Separatory funnel extraction utilizes relatively inexpensive glassware and is fairly rapid (three, 2-minute extractions followed by filtration) but is labor intensive, uses fairly large volumes of solvent and is subject to emulsion problems. Method

3520 should be used if an emulsion forms between the solvent-sample phases, which cannot be broken by mechanical techniques.

7.3 Method 3520 - Applicable to the extraction and concentration of water-insoluble and slightly water-soluble organics from aqueous samples. A measured volume of sample is extracted with an organic solvent in a continuous liquid-liquid extractor. The solvent must have a density greater than that of the sample. The extract is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis. Continuous extractors are excellent for samples with particulates (of up to 1% solids) that cause emulsions, provide more efficient extraction of analytes that are more difficult to extract and once loaded, require no hands-on manipulation. However, they require more expensive glassware, use fairly large volumes of solvent and extraction time is rather lengthy (6 to 24 hours).

7.4 Method 3535 - Applicable to the extraction and concentration of water-insoluble and slightly water-soluble organics from aqueous samples. A measured volume of water is pumped through an appropriate medium (e.g., disk or cartridge) containing a solid phase that effects the extraction of organics from water. A small volume of extraction solvent is passed through the medium to elute the compounds of interest. The eluant is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis. Appropriate solid-phase extraction media allow extraction of water containing particulates, are relatively fast and use small volumes of solvent. However, they do require some specialized pieces of equipment.

7.5 Method 3540 - This method is applicable to the extraction of nonvolatile and semivolatile organic compounds from solids such as soils, relatively dry sludges, and solid wastes. A solid sample is mixed with anhydrous sodium sulfate, placed into an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in a Soxhlet extractor. The extract is concentrated and, if necessary, exchanged into a solvent compatible with further analysis. Soxhlet extraction uses relatively inexpensive glassware, once loaded requires no hands-on manipulation, provides efficient extraction, but is rather lengthy (16 to 24 hours) and uses fairly large volumes of solvent. It is considered a rugged extraction method because there are very few variables that can adversely affect extraction efficiency.

7.6 Method 3541 - This method utilizes a modified Soxhlet extractor and is applicable to the extraction of semivolatile/nonvolatile organic compounds from solids such as soils, relatively dry sludges, and solid wastes. A solid sample is mixed with anhydrous sodium sulfate, placed into an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in an automated Soxhlet extractor. This device allows the extraction thimble to be lowered into the boiling liquid for the first hour and then extracted in the normal thimble position for one additional hour. The automated Soxhlet allows equivalent extraction efficiency in 2 hours, combines the concentration step within the same device but requires a rather expensive device.

7.7 Method 3542 - This method is applicable to the extraction of semivolatile organic compounds from the Method 0010 air sampling train. The solid trapping material (i.e., glass or quartz fiber filter and porous polymeric adsorbent resin) are extracted using Soxhlet extraction and the condensate and impinger fluid are extracted using separatory funnel extraction.

7.8 Method 3545 - This method is applicable to the extraction of nonvolatile/semivolatile organic compounds from solids such as soils, relatively dry sludges, and solid wastes. A solid sample is mixed with anhydrous sodium sulfate, placed into an extraction cell and extracted under pressure with small volumes of solvent. The extract is concentrated and, if necessary, exchanged into a solvent compatible with further analysis. The method is rapid and efficient, in that it uses small volumes of solvent, but does require the use of an expensive extraction device.

7.9 Method 3550 - This method is applicable to the extraction of nonvolatile and semivolatile organic compounds from solids such as soils, sludges, and wastes using the technique of ultrasonic extraction. Two procedures are detailed depending upon the expected concentration of organics in the sample; a low concentration and a high concentration method. In both, a known weight of sample is mixed with anhydrous sodium sulfate and solvent extracted using ultrasonic extraction. The extract is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis. Ultrasonic extraction is fairly rapid (three, 3-minute extractions followed by filtration) but uses relatively large volumes of solvent, requires a somewhat expensive device and requires following the details of the method very closely to achieve acceptable extraction efficiency (proper tuning of the ultrasonic device is very critical). This technique is much less efficient than the other extraction techniques described in this section. This is most evident with very non-polar organic compounds (e.g., PCBs, etc.) that are normally strongly adsorbed to the soil matrix. EPA has not validated Method 3550 for the extraction of organophosphorus compounds from solid matrices. In addition, there are concerns that the ultrasonic energy may lead to breakdown of some organophosphorus compounds (see Reference 1). As a result, this extraction technique should not be used for organophosphorous compounds without extensive validation on real-world samples. Such studies should assess the precision, accuracy, ruggedness, and sensitivity of the technique relative to the appropriate regulatory limits or project-specific concentrations of interest.

7.10 Methods 3560 and 3561 - These methods are applicable to the extraction of total recoverable petroleum hydrocarbons and PAHs from solids such as soils, sludges, and wastes using the technique of supercritical fluid extraction (SFE). SFE normally uses CO_2 (which may contain very small volumes of solvent modifiers). Therefore, there is no solvent waste for disposal, may be automated, provides relatively rapid extraction, but, is currently limited to total recoverable petroleum hydrocarbons and PAHs. It also requires a rather expensive device and sample size is more limited. Research on SFE is currently focusing on optimizing supercritical fluid conditions to allow efficient extraction of a broader range of RCRA analytes in a broad range of environmental matrices.

7.11 Method 3580 - This method describes the technique of solvent dilution of non-aqueous waste samples. It is designed for wastes that may contain organic chemicals at a level greater than 20,000 mg/kg and that are soluble in the dilution solvent. When using this method, the analyst must use caution in the addition of surrogate compounds, so as not to dilute out the surrogate response when diluting the sample.

7.12 Sample analysis - Following preparation of a sample by one of the methods described above, the sample is ready for further analysis. Samples prepared for semivolatile/nonvolatile analysis may, if necessary, undergo cleanup (See Method 3600) prior to application of a specific determinative method.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific guidance on quality control procedures. Each laboratory using SW-846 methods should maintain a formal quality assurance program. Each extraction batch of 20 or less samples should contain: a method blank; either a matrix spike/matrix spike duplicate or a matrix spike and duplicate samples; and a laboratory control sample, unless the determinative method provides other guidance.

8.2 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean reference matrix. This will include a combination of the sample extraction method (usually a 3500 series method for extractable

organics) and the determinative method (an 8000 series method). The laboratory should also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made.

8.2.1 The reference samples are prepared from a spiking solution containing each analyte of interest. The reference sample concentrate (spiking solution) may be prepared from pure standard materials, or purchased as certified solutions. If prepared by the laboratory, the reference sample concentrate should be made using stock standards prepared independently from those used for calibration.

8.2.2 The procedure for preparation of the reference sample concentrate is dependent upon the method being evaluated. Guidance for reference sample concentrations for certain methods are listed below. In other cases, the determinative methods contain guidance on preparing the reference sample concentrate and the reference sample. If no guidance is provided, prepare a reference sample concentrate in methanol (or other water miscible solvent). Spike the reference sample at the concentration on which the method performance data are based. The spiking volume added to water should not exceed 1 mL/L so that the spiking solvent will not decrease extraction efficiency. If the method lacks performance data, prepare a reference standard concentrate at such a concentration that the spike will provide a concentration in the clean matrix that is 10 - 50 times the MDL for each analyte in that matrix.

The concentration of target analytes in the reference sample may be adjusted to more accurately reflect the concentrations that will be analyzed by the laboratory. If the concentration of an analyte is being evaluated relative to a regulatory limit or action level, see Sec. 8.3.1 for information on selecting an appropriate spiking level.

8.2.3 To evaluate the performance of the total analytical process, the reference samples must be handled in exactly the same manner as actual samples. Therefore, 1 mL (unless the method specifies a different volume) of the reference sample concentrate is spiked into each of four (minimum number of replicates) 1-L aliquots of organic-free reagent water (now called the reference sample), extracted as per the method. For matrices other than water or for determinative methods that specify a different volume of water, add 1.0 mL of the reference sample concentrate to at least four replicates of the volume or weight of sample specified in the method. Use a clean matrix for spiking purposes (one that does not have any target or interference compounds) e.g., organic-free reagent water for the water matrix or sand or soil (free of organic interferences) for the solid matrix.

8.2.4 Preparation of reference samples

The following sections provide guidance on the QC reference sample concentrates for many SW-846 determinative methods. The concentration of the target analytes in the QC reference sample for the methods listed below may need to be adjusted to more accurately reflect the concentrations of interest in different samples or projects. If the concentration of an analyte is being evaluated relative to a regulatory limit or action level, see Sec. 8.3.3 for information on selecting an appropriate spiking level. In addition, the analyst may vary the concentration of the spiking solution and the volume of solution spiked into the sample. However, because of concerns about the effects of the spiking solution solvent on the sample, the total volume spiked into a sample should generally be held to no more than 1 mL.

8.2.4.1 Method 8041 - Phenols: The QC reference sample concentrate should contain each analyte at 100 mg/L in 2-propanol.

8.2.4.2 Method 8061 - Phthalate esters: The QC reference sample concentrate should contain the following analytes at the following concentrations in acetone: butyl benzyl phthalate, 10 mg/L; bis(2-ethylhexyl)phthalate, 50 mg/L; di-n-octyl phthalate, 50 mg/L; and any other phthalate at 25 mg/L.

8.2.4.3 Method 8070 - Nitrosamines: The QC reference sample concentrate should contain each analyte at 20 mg/L in isooctane.

8.2.4.4 Method 8081 - Organochlorine pesticides: The QC reference sample concentrate should contain each single-component analyte at the following concentrations in acetone: 4,4'-DDD, 10 mg/L; 4,4'-DDT, 10 mg/L; endosulfan II, 10 mg/L; endosulfan sulfate, 10 mg/L; and any other single-component pesticide at 2 mg/L. If the method is only to be used to analyze chlordane or toxaphene, the QC reference sample concentrate should contain the most representative multicomponent parameter at a concentration of 50 mg/L in acetone.

8.2.4.5 Method 8082 - PCBs: The QC reference sample concentrate should contain the most representative multicomponent parameter at a concentration of 50 mg/L in acetone.

8.2.4.6 Method 8091 - Nitroaromatics and cyclic ketones: The QC reference sample concentrate should contain each analyte at the following concentrations in acetone: each dinitrotoluene at 20 mg/L; and isophorone and nitrobenzene at 100 mg/L.

8.2.4.7 Method 8100 - Polynuclear aromatic hydrocarbons: The QC reference sample concentrate should contain each analyte at the following concentrations in acetonitrile: naphthalene, 100 mg/L; acenaphthylene, 100 mg/L; acenaphthene, 100 mg/L; fluorene, 100 mg/L; phenanthrene, 100 mg/L; anthracene, 100 mg/L; benzo(k)fluoranthene 5 mg/L; and any other PAH at 10 mg/L.

8.2.4.8 Method 8111 - Haloethers: The QC reference sample concentrate should contain each analyte at a concentration of 20 mg/L in isooctane.

8.2.4.9 Method 8121 - Chlorinated hydrocarbons: The QC reference sample concentrate should contain each analyte at the following concentrations in acetone: hexachloro-substituted hydrocarbons, 10 mg/L; and any other chlorinated hydrocarbon, 100 mg/L.

8.2.4.10 Method 8131 - Aniline and selected derivatives: The QC reference sample concentrate should contain each analyte at the following concentrations in acetone at a concentration 1,000 times more concentrated than the selected spike concentration.

8.2.4.11 Method 8141 - Organophosphorus compounds: The QC reference sample concentrate should contain each analyte in acetone at a concentration 1,000 times more concentrated than the selected spike concentration.

8.2.4.12 Method 8151 - Chlorinated herbicides: The QC reference sample concentrate should contain each analyte in acetone at a concentration 1,000 times more concentrated than the selected spike concentration.

8.2.4.13 Method 8260 - Volatile organics: The QC reference sample concentrate should contain each analyte in methanol at a concentration of 10 mg/L. This concentrate is spiked into 100 mL of organic-free reagent water, producing enough reference sample for four aliquots of up to 25 mL each.

8.2.4.14 Method 8270 - Semivolatile organics: The QC reference sample concentrate should contain each analyte in acetone at a concentration of 100 mg/L.

8.2.4.15 Method 8310 - Polynuclear aromatic hydrocarbons: The QC reference sample concentrate should contain each analyte at the following concentrations in acetonitrile: naphthalene, 100 mg/L; acenaphthylene, 100 mg/L; acenaphthene, 100 mg/L; fluorene, 100 mg/L; phenanthrene, 100 mg/L; anthracene, 100 mg/L; benzo(k)fluoranthene, 5 mg/L; and any other PAH at 10 mg/L.

8.2.5 Analyze at least four replicate aliquots of the well-mixed reference samples by the same procedures used to analyze actual samples (Sec. 7.0 of each of the methods). This will include a combination of the sample preparation method (usually a 3500 series method for extractable organics) and the determinative method (an 8000 series method). Follow the guidance on data calculation and interpretation presented in Method 8000, Sec. 8.0.

8.2.6 The following methods contain specific extraction and sample preparation requirements applicable only to that method. Refer to these individual methods for extraction and preparation procedures required prior to instrumental analysis, and for information on the preparation of QC reference samples.

8.2.6.1 Method 8275 - Thermal Extraction/Gas Chromatography/Mass Spectrometry (TE/GC/MS) for Semivolatile Organic Compounds.

8.2.6.2 Method 8280 - Polychlorinated Dibenzo-*p*-dioxins and Polychlorinated Dibenzofurans.

8.2.6.3 Method 8290 - Polychlorinated Dibenzo-*p*-dioxins and Polychlorinated Dibenzofurans.

8.2.6.4 Method 8318 - N-Methylcarbamates by High Performance Liquid Chromatography (HPLC).

8.2.6.5 Method 8321 - Solvent Extractable Nonvolatile Compounds by High Performance Liquid Chromatography/Thermospray/Mass Spectrometry (HPLC/TS/MS) or Ultraviolet (UV) Detection.

8.2.6.6 Method 8325 - Solvent Extractable Nonvolatiles by High Performance Liquid Chromatography/Particle Beam/Mass Spectrometry (HPLC/PB/MS).

8.2.6.7 Method 8330 - Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC).

8.2.6.8 Method 8331 - Tetrazene by Reverse Phase High Performance Liquid Chromatography (HPLC).

8.2.6.9 Method 8332 - Nitroglycerine by High Performance Liquid Chromatography (HPLC) or Thin-Layer Chromatography (TLC).

8.2.6.10 Method 8410 - Gas Chromatography/Fourier Transform Infrared (GC/FT-IR) Spectrometry for Semivolatile Organics.

8.2.6.11 Method 8430 - Bis(2-chloroethyl) ether and Hydrolysis Products by GC/FT-IR.

8.2.6.12 Method 8440 - Total Recoverable Petroleum Hydrocarbons (TRPH) by Infrared (IR) Spectrophotometry.

8.3 Sample Quality Control for Preparation and Analysis

8.3.1 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair per analytical batch. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, the laboratories should use a matrix spike and matrix spike duplicate pair. See Sec. 5.5 for additional guidance on matrix spike preparation. Sec. 8.3.3 provides guidance on establishing the concentration of the matrix spike compounds in the sample chosen for spiking. The choice of analytes to be spiked should reflect the analytes of interest for the specific project. Thus, if only a subset of the list of target analytes provided in a determinative method are of interest (e.g., Method 8270 is used for the analysis of only PAHs), then these would be the analytes of interest for the project. In the absence of project-specific analytes of interest, it is suggested that the laboratory periodically change the analytes that are spiked with the goal of obtaining matrix spike data for most, if not all, of the analytes in a given determinative method.

8.3.2 A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume: e.g., organic-free reagent water for the water matrix or sand or soil (free of organic interferences) for the solid matrix. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

8.3.3 The concentration of the matrix spike sample and/or the LCS should be determined as described in the following sections.

8.3.3.1 If, as in compliance monitoring, the concentration of a specific analyte in the sample is being checked against a regulatory limit or action level, the spike should be at or below the regulatory limit or action level, or 1 - 5 times the background concentration (if historical data are available), whichever concentration is higher.

8.3.3.2 If historical data are not available, it is suggested that an uncontaminated sample of the same matrix from the site be submitted for matrix spiking purposes to ensure that high concentrations of target analytes and/or interferences will not prevent calculation of recoveries.

8.3.3.3 If the concentration of a specific analyte in a sample is not being checked against a limit specific to that analyte, then the spike should be at the same concentration as the reference sample (Sec. 8.2.4) or 20 times the quantitation limit in

the matrix of interest. It is again suggested that a background sample of the same matrix from the site be submitted as a sample for matrix spiking purposes.

8.3.4 Analyze these QC samples (the LCS and the matrix spikes or the optional matrix duplicates) following the procedure (Sec. 7.0) of the selected determinative method. Calculate and evaluate the QC data as outlined in Sec. 8.0 of Method 8000.

8.3.5 Blanks - Use of method blanks and other blanks are necessary to track contamination of samples during the sampling and analysis processes. Refer to Chapter One for specific quality control procedures.

8.3.6 Surrogates - A surrogate is a compound that is chemically similar to the analyte group but not expected to occur in an environmental sample. Surrogate should be added to all samples when specified in the appropriate determinative method (See Table 1). See Sec. 5.4 for additional guidance on surrogates.

8.4 The laboratory must have procedures in place for documenting and charting the effect of the matrix on method performance. Refer to Chapter One and Method 8000 for specific guidance on developing method performance data.

9.0 METHOD PERFORMANCE

9.1 The recovery of surrogates is used to monitor unusual matrix effects, sample processing problems, etc. The recovery of matrix spiking compounds, when compared to laboratory control sample (LCS) recoveries, indicates the presence or absence of unusual matrix effects.

9.2 The performance of each 3500 method will be dictated by the overall performance of the sample preparation in combination with the cleanup method and/or the analytical determinative method.

10.0 REFERENCES

None required.

TABLE 1

SURROGATES FOR SW-846 CHROMATOGRAPHIC METHODS
FOR SEMIVOLATILE AND NONVOLATILE COMPOUNDS

Method Number	Technique	Suggested Surrogates*
8041	Phenols by GC	2-Fluorophenol, and 2,4,6-Tribromophenol
8061	Phthalate Esters by GC	Diphenyl phthalate, Diphenyl isophthalate, and Dibenzyl phthalate
8070	Nitrosamines by GC	None listed**
8081	Organochlorine Pesticides by GC	2,4,5,6-Tetrachloro-m-xylene, and Decachlorobiphenyl
8082	Polychlorinated Biphenyls by GC	Decachlorobiphenyl
8091	Nitroaromatics by GC	2-Fluorobiphenyl
8100	PAHs by GC	2-Fluorobiphenyl, and 1-Fluoronaphthalene
8111	Haloethers by GC	None listed**
8121	Chlorinated Hydrocarbons by GC	α,2,6-Trichlorotoluene, 2,3,4,5,6-Pentachlorotoluene, and 1,4-Dichloronaphthalene
8131	Anilines by GC	None listed**
8141	Organophosphorus Pesticides by GC	None listed**
8151	Acid Herbicides by GC	2,4-Dichlorophenylacetic acid
8270	Semivolatiles by GC/MS	Phenol-d_6, 2-Fluorophenol, 2,4,6-Tribromophenol, Nitro-benzene-d_5, 2-Fluorobiphenyl, and p-Terphenyl-d_{14}
8275	Semivolatiles by TE/GC/MS	Not listed**
8280	PCDDs and PCDFs by HRGC/LRMS	Internal standards added at time of extraction. No surrogates.
8290	PCDDs and PCDFs by HRGC/HRMS	Internal standards added at time of extraction. No surrogates.
8310	PAHs by HPLC	Decafluorobiphenyl
8318	Carbamates by HPLC	None listed**
8321	Nonvolatiles by HPLC/TS/MS or UV Detection	None listed**

Table 1 (continued)

Method Number	Technique	Suggested Surrogates*
8325	Nonvolatiles by HPLC/PB/MS or UV/Vis	Benzidine-d_8, Caffeine-$^{15}N_2$, 3,3'-Dichlorobenzidine-d_6, Bis-(perfluorophenyl)-phenylphosphine oxide
8330	Explosives by HPLC	None listed**
8331	Tetrazene by HPLC	None listed**
8332	Nitroglycerine by HPLC or TLC	None listed**
8410	GC/FT-IR for Semivolatiles	None listed**
8430	Bis(2-chloroethyl) ether and Hydrolysis Products by GC/FT-IR	None listed**
8440	Total Recoverable Petroleum Hydrocarbons by IR	None listed**

* Suggested water concentration = 10 times the quantitation limit or near the mid-point of the calibration curve. See Sec. 5.4.2.

** Surrogate compounds selected should be similar in analytical behavior to the analytes of interest, but which are not expected to be present in the sample matrix or extract.

GC = Gas Chromatography
HR = High Resolution
LR = Low Resolution
IR = Infrared
TS = Thermospray
PB = Particle Beam
MS = Mass Spectrometry
HPLC = High Performance Liquid Chromatography
PCDD = Polychlorinated Dibenzo-*p*-dioxins
PCDF = Polychlorinated Dibenzofurans
FT-IR = Fourier Transform Infrared Detector
UV = Ultraviolet
TLC = Thin-Layer Chromatography
TE = Thermal Extraction

United States Environmental Protection Agency | Office of Solid Waste and Emergency Response | OSWER Document 9240.1-38FS
EPA Publication 540-F-02-007
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Multi-Media Dioxin and Furan Analytical Service for Superfund (DLM01.4)

Office of Emergency and Remedial Response
Analytical Operations/Data Quality Center (5204G)

Quick Reference Fact Sheet

Under the legislative authority granted to the U.S. Environmental Protection Agency (EPA) under the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) and the Superfund Amendments and Reauthorization Act of 1986 (SARA), EPA develops standardized analytical methods for the measurement of various pollutants in environmental samples from known or suspected hazardous waste sites. Among the pollutants that are of concern to the EPA at such sites are a series of chlorinated dibenzo-p-dioxins (CDDs) and dibenzofurans (CDFs) that are analyzed using High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS). The Analytical Operations/Data Quality Center (AOC) of EPA's Office of Emergency and Remedial Response (OERR) offers an analytical service that provides data from the analysis of water, soil, sediment, sludge, tissue (not human tissue), ash, oil, and oily matrices for use in the Superfund decision-making process. Through a series of standardized procedures and a strict chain-of-custody, the dioxin analytical service produces data of known and documented quality.

DESCRIPTION OF SERVICES

The dioxin/furan non-routine analytical service provides a flexible contractual framework for laboratories to apply EPA analytical methods for the isolation, detection, and quantitative measurement of 17 2,3,7,8-substituted tetra- through octa-chlorinated dibenzo-p-dioxins (CDDs) and dibenzofurans (CDFs) in water, soil, sediment, sludge, tissue (no human tissue), ash, oil, and oily matrices. EPA AOC has prequalified laboratories that use the Dioxin/Furan Statement of Work (SOW) DLM01.4 to provide this service. Data evaluation can be performed by the data requestor using National Functional Guidelines provided by EPA AOC. The standard data Turn-around Time (TAT) for this service is 35 days after laboratory receipt of the last sample in the Sample Delivery Group (SDG). This TAT can be changed to meet project-specific requirements.

REQUESTING THIS FLEXIBLE SERVICE

This service can be requested by EPA Regions and other interested parties by submitting a Task Order to EPA AOC. These Task Orders can modify the SOW to meet project-specific requirements (e.g., changes in TAT, detection limits, analyte lists, etc.). The SOW and National Functional Guidelines can be accessed at www.epa.gov/superfund/programs/clp/dlm1.htm.

DATA USES

This analytical service provides data that EPA uses for a variety of purposes such as: determining the nature and extent of contamination at a hazardous waste site; assessing priorities for response based on risks to human health and the environment; determining appropriate clean-up actions; and determining when remedial actions are complete. The data may be used in all stages in the investigation of hazardous waste sites, including: site inspections; Hazard Ranking System (HRS) scoring; remedial investigation/feasibility studies; remedial design; treatability studies; and removal actions. In addition, this service provides data that are available for use in Superfund enforcement/litigation activities.

TARGET COMPOUNDS

The compounds and quantitation limits for which this service is applicable are listed in **Table 1**. For water samples, the lowest reportable quantitation limit is 10 pg/L. For solid samples, the lowest reportable quantitation limit is 1.0 ng/Kg. The specific quantitation limits are highly matrix-dependent. The quantitation limits listed herein are provided for guidance and may not always be achievable.

METHODS AND INSTRUMENTATION

For water samples, the stable isotopically labeled analogs of 15 of the 2,3,7,8-substituted CDDs/CDFs are spiked into a 1 L sample. Samples with no visible particles are extracted with methylene chloride in a separatory funnel or vacuum-filtered through a glass-fiber filter on top of a solid-phase extraction disk.

Table 1. Target Compound List and Contract Required Quantitation Limits (CRQLs)

CDD/CDF	Water (pg/L)	Solids (ng/Kg)
2378-TCDD	10	1.0
12378-PeCDD	50	5.0
123678-HxCDD	50	5.0
123478-HxCDD	50	5.0
123789-HxCDD	50	5.0
1234678-HpCDD	50	5.0
OCDD	100	10
2378-TCDF	10	1.0
12378-PeCDF	50	5.0
23478-PeCDF	50	5.0
123678-HxCDF	50	5.0
123789-HxCDF	50	5.0
123478-HxCDF	50	5.0
234678-HxCDF	50	5.0
1234678-HpCDF	50	5.0
1234789-HpCDF	50	5.0
OCDF	100	10

Samples containing visible particles are vacuum-filtered through a glass-fiber filter, the filter is extracted in a Soxhlet/Dean-Stark (SDS) extractor, and the filtrate is extracted with methylene chloride in a separatory funnel.

For soil/sediment samples, the labeled compounds are spiked into a sample containing 10 g (dry weight) of soil/sediments. The soil/sediments are then extracted in an SDS extractor.

For fish and other tissue, a 20 g aliquot of frozen or non-frozen sample is homogenized and a 10 g aliquot is spiked with the labeled compounds. The frozen sample is mixed with sodium sulfate, allowed to dry overnight, and extracted for 12 to 24 hours using methylene chloride:hexane in a Soxhlet extractor. The non-frozen sample is allowed to equilibrate, then hydrochloric acid and methylene chloride:hexane are added and the bottle is agitated for 12 to 24 hours. In both cases, the extract is evaporated to dryness and the lipid content is determined.

For all samples, the extracts are cleaned and injected with two internal standards to determine percent recoveries of the CDD/CDF congeners. An aliquot of the extract is injected into the High Resolution Gas Chromatograph (HRGC), the analytes are separated by the HRGC and detected by a High Resolution Mass Spectrometer (HRMS). **Table 2** summarizes the methods and instruments used in this analytical service.

DATA DELIVERABLES

Data deliverables for this service include the hardcopy data reporting forms and supporting raw data. Electronic (diskette) deliverables are specified in the Task Order. The laboratory must submit data to EPA within 35 days after laboratory receipt of the last sample in the SDG, or as stated in the Task Order. The EPA Regions then review the data based on project-specific requirements and the National Functional Guidelines.

QUALITY ASSURANCE

The Quality Assurance (QA) process consists of management review and oversight at the planning, implementation, and completion stages of the environmental data collection activity. This process ensures that the data provided are of the quality required.

During the planning of the data collection program, QA activities focus on defining data and designing a Quality Control (QC) system to measure the quality of data being collected. During the implementation of the data collection effort, QA activities ensure that the QC system is functioning effectively, and the deficiencies uncovered by the QC system are corrected.

After environmental data are collected, QA activities focus on assessing the quality of data to determine its suitability to support enforcement or remedial decisions.

Each contract laboratory prepares a Quality Assurance Plan (QAP) with the objective of providing sound analytical chemical measurements. The QAP must specify the policies, organization, objectives, and functional guidelines, as well as the QA/QC activities designed to achieve the data quality requirements for this analytical service.

Table 2. Methods and Instruments

Fraction	Preparation Method	Analytical Instrument
Water - no visible particles	Solid-phase extraction or extraction with methylene chloride in a separatory funnel.	HRGC/HRMS analysis
Water - visible particles	Solid-phase extraction or vacuum filtration/ filter extraction in an SDS extractor. Filtrate extraction with methylene chloride in a separatory funnel.	HRGC/HRMS analysis
Soil/Sediment	Extraction in an SDS extractor.	HRGC/HRMS analysis
Fish and other tissue	Mixed with sodium sulfate, extraction with methylene chloride:hexane in Soxhlet extractor or mixed with hydrochloric acid and methylene chloride:hexane, agitation for 12-24 hours.	HRGC/HRMS analysis

Table 3. Quality Control

QC Operation	Frequency
Initial Calibration	Upon contract award, initial setup of each instrument used, and each time continuing calibration fails to meet the acceptance criteria.
Continuing Calibration Verification	Every 12 hours for each instrument used for analysis and at end of a run.
Internal Standards	Added to all extracts prior to analysis.
Performance Evaluation (PE) Samples	Prepared and analyzed (if provided) with each set of 20 field samples.
Laboratory Control Sample (LCS)	Prepared and analyzed with each group of 20 field samples of a similar matrix in an SDG.
Method Blank	Prepared with each group of 20 field samples or less, or each time samples are extracted.
Window Defining Mixture	Every 12 hours for each instrument used for analysis; precedes Initial and Continuing Calibration.
HRMS System Tune	Every 12 hours.
Isomer Specificity Check	Every 12 hours; may be combined with Window Defining Mixture.
Clean-up Standard	Added to all extracts prior to cleanup.
Gel Permeation Chromatography (GPC) Calibration (optional)	Upon initial setup of instruments, when GC column changed, when channeling occurs, and once every 7 days when samples are cleaned using GPC.

QUALITY CONTROL

The QC process includes those activities required during analytical data collection to produce data of known and documented quality. The analytical data acquired from QC procedures are used to estimate and evaluate the analytical results and to determine the necessity for, or the effect of, corrective action procedures. The QC procedures required for this analysis are shown in **Table 3**. A number of optional cleanup procedures are available for this SOW.

PERFORMANCE MONITORING ACTIVITIES

Laboratory performance monitoring activities are provided primarily by AOC and the Regions to ensure that contract laboratories are producing data of the appropriate quality. EPA performs on-site laboratory audits, data package audits, HRGC/HRMS tape audits, and evaluates laboratory performance through the use of blind performance evaluation samples.

For more information, or to submit suggestions to improve this analytical service, please contact:

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