

# SEDIMENT SAMPLING AND ANALYSIS PLAN

---

WASHINGTON STATE DEPARTMENT OF NATURAL RESOURCES  
AQUATIC LANDS LEASE NO. 22-A02150

*Prepared for*  
GRAYS HARBOR HISTORICAL SEAPORT AUTHORITY  
*September 12, 2013*  
*Project No. 0863.01.01*



*Prepared by*  
*Maul Foster & Alongi, Inc.*  
*911 Western Avenue, Suite 575, Seattle WA 98104*

SEDIMENT SAMPLING AND ANALYSIS PLAN  
WASHINGTON STATE DEPARTMENT OF NATURAL RESOURCES  
AQUATIC LANDS LEASE NO. 22-A02150

*The material and data in this plan were prepared  
under the supervision and direction of the undersigned.*

MAUL FOSTER & ALONGI, INC.



---

*Madi Novak*  
*Senior Environmental Scientist*



---

*Michael R. Murray*  
*Project Environmental Scientist*

# CONTENTS

TABLES AND ILLUSTRATIONS	V
ACRONYMS AND ABBREVIATIONS	VI
1 INTRODUCTION	1
1.1 INVESTIGATION OBJECTIVES	1
1.2 SITE SETTING	1
1.3 SITE BACKGROUND	2
1.4 EXISTING DATA	2
2 SAMPLING OBJECTIVES AND DESIGN	3
2.1 SAMPLING AND ANALYSIS APPROACH	3
2.2 CHEMICAL ANALYSIS	4
2.3 WOODWASTE SURVEY	4
3 FIELD SAMPLING METHODS	5
3.1 SAMPLE LOCATION	6
3.2 DECONTAMINATION PROCEDURES	6
3.3 SAMPLE PROCESSING	6
3.4 SAMPLE CONTAINERS AND LABELS	7
3.5 FIELD DOCUMENTATION	7
3.6 INVESTIGATION-DERIVED WASTE	8
3.7 COMPLIANCE WITH U.S. OCCUPATIONAL SAFETY AND HEALTH ADMINISTRATION REGULATIONS	8
3.8 UTILITY LOCATIONS	9
4 SAMPLE HANDLING PROCEDURES	9
4.1 FIELD QUALITY CONTROL SAMPLES	9
4.2 SAMPLE STORAGE	9
4.3 CHAIN-OF-CUSTODY PROCEDURES	9
4.4 DELIVERY OF SAMPLES TO ANALYTICAL LABORATORY	10
5 LABORATORY ANALYTICAL METHODS	10
5.1 CHEMICAL ANALYSES	10
5.2 SAMPLE QUANTITATION LIMITS	10
5.3 HOLDING TIMES	11
5.4 SAMPLE PRESERVATION	11
6 QUALITY ASSURANCE AND QUALITY CONTROL REQUIREMENTS	11
6.1 LABORATORY QUALITY ASSURANCE AND QUALITY CONTROL CHECKS	11
6.2 LABORATORY CALIBRATION AND PREVENTIVE MAINTENANCE	12
7 DATA ANALYSIS AND RECORDKEEPING	12
7.1 DATA REDUCTION, VALIDATION, AND REPORTING	12
8 REPORTING	14
LIMITATIONS	
REFERENCES	
TABLES	

## CONTENTS (CONTINUED)

---

FIGURE

APPENDIX

DIOXIN AND FURAN ANALYSIS, DATA VALIDATION AND TEQ CALCULATION RULES

# TABLES AND ILLUSTRATIONS

---

FOLLOWING PLAN:

## TABLES

- 1 PROPOSED SEDIMENT SAMPLE LOCATIONS AND ANALYTICAL TIERS
- 2 MARINE SEDIMENT ANALYTE LIST
- 3 SEDIMENT ANALYTICAL METHODS

## FIGURE

HISTORICAL AND PROPOSED SAMPLE LOCATIONS

## ACRONYMS AND ABBREVIATIONS

---

°C	degrees centigrade
ARI	Analytical Resources Incorporated
bml	below mudline
CFR	Code of Federal Regulations
cm	centimeter(s)
COC	chain of custody
CSL	cleanup screening level
DGPS	differential global positioning unit
DNR	Washington State Department of Natural Resources
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management
GHSA	Grays Harbor Historical Seaport Authority
Guide	DNR's Draft State Owned Aquatic Lands Sediment Sampling and Analysis Guide
HAZWOPER	Hazardous Waste Operations and Emergency Response
IDW	investigation-derived waste
LCS	laboratory control sample
leased property	tideland and in-water leased property
MFA	Maul Foster & Alongi, Inc.
MS/MSD	matrix spike and matrix spike duplicate
OSHA	U.S. Occupational Safety and Health Administration
pg/g	picograms per gram
QA	quality assurance
QC	quality control
RPM	revolutions per minute
SAIC	Science Applications International Corporation
SAP	sampling and analysis plan
site	leased property and upland property
SMS	Sediment Management Standards
SOAL	state-owned aquatic lands
TEQ	toxicity equivalent concentration
TOC	total organic carbon
USEPA	U.S. Environmental Protection Agency

# 1 INTRODUCTION

---

On behalf of Grays Harbor Historical Seaport Authority (GHHSA), Maul Foster & Alongi, Inc. (MFA) has prepared this sediment sampling and analysis plan (SAP) for the leased tideland and in-water property (the leased property) located at 500 North Custer Street in Aberdeen, Washington (see the attached figure). The leased property, on the Chehalis River in Grays Harbor County, is being leased from the Washington State Department of Natural Resources (DNR) by Weyerhaeuser under Lease No. 22-A02150. GHHSA will sublease the state-owned aquatic lands (SOAL) from Weyerhaeuser. As one of the conditions of consent to sublease the SOAL, DNR has requested that this SAP be prepared within three months of the effective date (March 29, 2013).

## 1.1 Investigation Objectives

The primary objective of this sediment SAP is to ensure quality control (QC) and consistency of the field aspects of sediment data collection. Typically, DNR requests “bookend” sediment sampling at the initiation and termination of an aquatic lease in order to differentiate baseline sediment conditions from impacts that occurred during the lease period, as well as to evaluate long-term trends in sediment conditions over the lease period.

On February 2, 2011, in correspondence with Weyerhaeuser, DNR requested sediment sampling and proposed a sampling approach. Floyd|Snider, consultant to Weyerhaeuser, proposed a modification to the DNR-requested sampling in a proposal letter prepared for Weyerhaeuser on March 15, 2012 (Floyd|Snider, 2012). On March 26, 2012, DNR modified the Floyd|Snider proposed sediment sampling plan (DNR, 2012) by expanding the analyte list for the three proposed surface sediment samples from the Chehalis River, and requesting three sediment core samples in the Former Mill Area, a portion of the property (see the figure). This SAP was prepared to satisfy DNR requirements stipulated in the March 26, 2012, response letter.

This sediment SAP has been prepared consistent with the requirements of DNR’s Draft State Owned Aquatic Lands Sediment Sampling and Analysis Guide (the Guide) (Integral, 2011).

## 1.2 Site Setting

The property leased from the DNR by Weyerhaeuser (and subleased by GHHSA) encompasses approximately 16.9 acres (see the figure). The leased property is located in the alluvial meander plain of the Chehalis River in the northwestern margins of the Willipa Hills physiographic region of southwest Washington.

In the Former Mill Area, there is an approximately 100-by-200-foot exposed area at low tide, and this area is inundated to an existing bulkhead wall at high tide. Immediately upstream of the Former Mill Area is the Filled Tidelands area, and immediately downstream is the Dock Area containing buildings and a dock structure. The leased property is proposed for future use as the homeport for

the Lady Washington and Hawaiian Chieftain tall ships and as part of a new maritime heritage facility called Seaport Landing.

### 1.3 Site Background

A sawmill has existed on the uplands property (directly south of the leased property) and the leased property (collectively herein referred to as the site) since before 1900. Weyerhaeuser acquired the site in 1955 and operated several sawmills and associated support facilities through January 2009, when the small log sawmill was permanently closed. There are no active wood products manufacturing operations at the site. When the facility was operational, raw logs were brought to the site in log rafts in the Chehalis River and tied up to pilings in the river in front of the Big Mill until the mid-1960s. After the mid-1960s, raw logs were brought to the site by truck and staged on log decks at various locations in and adjacent to the site. The Big Mill was originally configured to manufacture shingles and slats for housing construction. During World War II, the Big Mill was converted to manufacture ship keels for the war effort. The precursor to the small log mill was added in 1972. The last upgrade to the small log mill was in 2003. In 2006, the Big Mill and attached finger pier were closed; the associated structures were removed from the site between 2006 and 2008. This area is now known as the Former Mill Area. The site continued to operate a second mill, known as the small log mill, into early 2009. The operational history of the site is detailed in the Phase I assessment (PES, 2010). GHSA acquired the property on March 29, 2013.

### 1.4 Existing Data

Sediment data from the vicinity of the leased property, dating back to 1999, were made available to MFA and are summarized below:

In 1999, the Washington State Department of Ecology (Ecology) conducted a sediment quality investigation on the Chehalis River (Ecology, 1999). Two of the samples collected during this investigation were located in the leased property (see the figure for historical sample locations). Samples were analyzed for all Sediment Management Standards (SMS) compounds and for the presence of wood debris. There were no exceedances of the SMS, and no woodwaste accumulations were observed.

In April 2011, Science Applications International Corporation (SAIC) conducted a soil and sediment investigation at the leased property (SAIC, 2011). Eight surface sediment samples were collected in the dock area immediately downgradient of the Ecology samples collected in 1999 (see the figure). The surface sediment samples were analyzed for all SMS constituents and for the presence of wood debris and polychlorinated dibenzo-p-dioxins and -furans (referred to in this SAP as dioxins). Butylbenzyl phthalate was detected at a concentration slightly above the sediment quality standard screening level. No accumulation of wood debris was encountered in the area. Surface sediment dioxins) were detected at 5.4 picograms per gram (pg/g) in the Dock Area.

SAIC also collected surface and subsurface sediments in the Former Mill Area (see the figure). Fine wood debris was encountered in subsurface sediment at two of the three locations. Surface sediment from all three locations was composited for dioxin analysis, which resulted in a toxicity equivalent



concentration (TEQ) of 68 pg/g. Two of the sample locations had initial surface mercury detections in excess of the SMS cleanup screening level (CSL), but later averaging with split samples found that the surface mercury concentrations exceeded the sediment quality standard but were below the CSL. One of the locations had surface exceedances of the SMS CSL for bis(2-ethylhexyl) phthalate and 1,4-dichlorobenzene. There were several subsurface sediment exceedances of the CSL in the Former Mill Area; however, the surface sediments are the point of compliance for SMS (Ecology, 2008).

In order to identify existing available sediment analytical data in the vicinity of the leased property, MFA performed a search of Ecology's Environmental Information Management (EIM) Database. The EIM Database search identified 16 sediment samples with analytical data in the vicinity of the leased property. Samples were collected primarily by the U.S. Army Corps of Engineers in order to characterize dredge material. Analytical data for many of the SMS chemicals are available for these locations. Interpretation of these data will be included in the sediment sampling report.

## 2 SAMPLING OBJECTIVES AND DESIGN

---

DNR has requested that sediment sampling be completed as a condition of the SOAL lease renewal. In correspondence dated March 26, 2012, DNR modified the Floyd|Snider sediment sampling proposal by requesting an expanded analyte list for the three proposed surface sediment samples in the Chehalis River, and requested three sediment core samples in the Former Mill Area. This SAP was prepared to satisfy the surface and subsurface sampling requirements stipulated in the March 26, 2012, DNR response letter (DNR, 2012).

### 2.1 Sampling and Analysis Approach

Six proposed sediment sample locations are presented in the attached figure. Sample locations begin with the prefix "CR" to indicate that the sample originates in the Chehalis River. Surface sediment grab samples (uppermost 10 centimeters [cm] of sediment) will be collected at all six sample locations; subsurface samples will also be collected in the Former Mill Area.

All sediment samples will be evaluated in the field for woodwaste, as described in Section 2.3. A tiered approach will be used to trigger chemical analysis. Tier I samples will be submitted to the laboratory for analysis, while Tier II and Tier III samples will be held on archive at the analytical laboratory pending results.

Table 1 summarizes the proposed sediment sample locations and coordinates and analytical tiers. All six surface samples will be submitted for Tier I chemical analysis. Tier II and/or Tier III subsurface samples in the Former Mill Area will be analyzed if Tier I and/or Tier II sediment sample results exceed SMS criteria or, in the case of dioxins, are above background concentrations<sup>1</sup>. Additional

---

<sup>1</sup> Determination of background dioxin TEQs falls outside the scope of this document. Dioxin TEQs screening and/or cleanup levels should be developed in accordance with WAC 173-204-560 (regional background) and WAC 173-204-564 (bioaccumulation), both effective September 1, 2013.

samples collected will be archived and may be analyzed based on results of tiered sediment samples and in consultation with DNR.

Sediment cores will be collected in the Former Mill Area from 0 to 10 cm (surface), from 10 cm to 1 foot, 1 foot to 2.5 feet, 2.5 feet to 4 feet, and from 4 to 5 feet below mudline (bml), generally consistent with historical sampling in the area.

## 2.2 Chemical Analysis

### 2.2.1 Chehalis River Grab Samples

Surface sediment samples collected from the Chehalis River (CR-01, CR-02 and CR-03; see the figure) will be analyzed for all SMS constituents with marine criteria as listed in Table 2 of this document (also listed in Table A-1 in the Guidance [Integral, 2011]). Additionally, each of the three surface sediment samples will be analyzed for total organic carbon (TOC) and dioxins (DNR, 2012). Analytical data will be compared to both of the SMS marine screening levels presented in Table 2 to determine if one or more samples exceed the numerical criteria. Salinity in pore water will be analyzed to better understand the water conditions. Conventional parameters (TOC, total volatile solids, total solids, ammonia, total sulfides, pore water sulfides, and percent fines) will also be analyzed in any surface sediment sample location containing more than 25 percent woodwaste by volume (DNR, 2012; Integral, 2011) (see Section 2.3 below). As only surface grab samples will be collected in the Chehalis River, subsurface accumulations of wood waste will not be evaluated.

### 2.2.2 Former Mill Area Sediment Cores

Both DNR and Ecology have requested further sampling in the Former Mill Area to delineate historical elevated concentrations of butyl benzyl phthalate, pentachlorophenol, mercury and dioxins (DNR, 2012). Three sediment cores were recommended by DNR and will be collected from the locations shown on the attached figure (CR-04, CR-05, and CR-06). Sediment cores from the Former Mill Area will be analyzed using the tiered approach described above and summarized in Table 1. The surface 0- to 10-cm bml of each sediment core will be analyzed for mercury and dioxins. Tier II (10 cm to 2.5 feet bml) and Tier III (2.5 to 5 feet bml) sediment stored on archive can be analyzed at a later date, pending the results of the Tier I analysis. Conventional parameters (TOC, total volatile solids, total solids, ammonia, total sulfides, pore water sulfides, and percent fines) will also be analyzed in any sediment sample increment containing more than 25 percent woodwaste by volume (DNR, 2012; Integral, 2011) (see Section 2.3 below). Cores will be physically examined to delineate the depth of woodwaste.

## 2.3 Woodwaste Survey

Because of current and past leased-property uses, a woodwaste survey will be performed during surface and subsurface sediment sampling. There is potential for woodwaste deposition on aquatic lands during log-handling operations. Woodwaste may include bark; branches; submerged logs; sawdust; wood chips; and woody, fibrous materials. Woodwastes are commonly found in surface

deposits that range from thin to thick and are considered a deleterious substance as defined in Washington Administrative Code 173-204-200(17) (Integral, 2011).

All sediment samples will be evaluated in the field to determine the amount of woodwaste present, which will be reported as a percentage and documented. Sediment samples found to contain more than 25 percent woodwaste will be submitted for analysis of conventional parameters (TOC, total volatile solids, total solids, ammonia, total sulfides, pore water sulfides, and percent fines) (DNR, 2012; Integral, 2011). Sediment retained for conventional analysis will not be homogenized.

## 3 FIELD SAMPLING METHODS

---

Both surface and subsurface sediment samples will be collected at proposed locations in the leased property as requested by the DNR (2012). Proposed sample locations are presented on the attached figure. Surface sediment will be collected from the 0- to 10-cm biologically active zone. Subsurface sediment cores will be collected at three locations in the Former Mill Area to a depth of 5 feet bml. Samples will be collected by staff trained and certified in handling potentially contaminated materials (see Section 3.6).

A manually deployed Ponar<sup>®</sup> grab sampling device (i.e., modified Van Veen) with a 10-cm penetration capacity will be used to collect surface sediment samples in the Chehalis River (i.e., CR-01, CR-02, and CR-03). Sampling locations will be approached at slow boat speeds with minimal wake to minimize disturbance of bottom sediments before sampling. Sediment samples will be handled carefully to minimize disturbance during collection and transportation to the laboratory. The grab sampler will be lowered over the side of the boat from a cable wire at an approximate speed of 0.3 feet per second. When the sampler reaches the mudline, the cable will be drawn taut and differential global positioning unit (DGPS) location measurements recorded. Each surface grab sample will be retrieved aboard the vessel and evaluated for the following acceptance criteria:

- Adequate penetration depth is achieved.
- Sampler is not overfilled.
- Sediment surface is undisturbed.
- There are no signs of winnowing or leaking from sampling device.

Grab samples not meeting these criteria will be rejected near the location of sample collection, and the process will be repeated until acceptance criteria have been met. Deployments will be repeated within a 20-foot radius of the proposed sample location. If adequate penetration is not achieved after multiple attempts, less volume will be accepted, and this will be noted in the field notebook. Once the samples have been accepted, the Ponar device will be emptied into a decontaminated stainless steel bowl and the samples will be homogenized.

Sediment cores will be manually advanced in the Former Mill Area at low tide. A decontaminated stainless steel sediment sampling device or hand auger will be used to retrieve sediment from the

surface to 5 feet bml or to refusal. Sediment from each core location will be transferred to decontaminated stainless steel bowls for homogenization.

The reusable stainless steel sampling devices will be decontaminated between stations, as described in Section 3.2.

### 3.1 Sample Location

The horizontal locations of all sample locations will be surveyed using a Trimble™ DGPS capable of subfoot accuracy, depending on satellite coverage. The target coordinates are shown in Table 1. The horizontal datum will be North American Datum 83, Washington State Plane South, reported in feet. The vertical elevation of each sediment station will be measured using a lead line.

### 3.2 Decontamination Procedures

Sample containers, instruments, working surfaces, technician protective gear, and other items that may come into contact with sediment sample material must meet high standards of cleanliness. All equipment that comes into direct contact with the sediment collected for analysis will be made of stainless steel and will be cleaned prior to use at each sampling location. Decontamination of all items will follow Puget Sound Estuary Program protocols. The decontamination procedure is:

1. Prewash rinse with tap water.
2. Wash with solution of tap water and Alconox soap (brush).
3. Rinse with tap water.
4. First rinse with distilled water.
5. Rinse three more times with distilled water.
6. Cover (no contact) all decontaminated items with aluminum foil.
7. Store in clean, closed container for next use.

Liquid generated by decontamination will be properly handled, according to procedures described in Section 3.6.

### 3.3 Sample Processing

The 10 cm of surface sediment collected in the Ponar sampler will be transferred to a large, decontaminated stainless steel bowl, using a decontaminated stainless steel spoon. Sediment from each sediment core location in the Former Mill Area will be transferred to three individual decontaminated stainless steel bowls, one for each sediment core tier (i.e., 0 to 10 cm, 10 cm to 2.5 feet, and 2.5 to 5 feet bml), and homogenized.

Before homogenization, sediment will be evaluated for the presence of woody debris, and the sediment will be physically described. The quantity of woody debris will be recorded in the field notebook. Sediment will then be homogenized and spooned immediately into appropriate precleaned, prelabeled sample containers, placed in coolers filled with ice, and maintained at approximately 4 degrees centigrade (°C). Sample holding times and preservation methods are

presented in Table 3. Debris and materials more than 2 inches in diameter will be omitted from sample containers. If woodwaste is present in excess of 25 percent, additional non-homogenized sample volume will be collected for the required conventional parameter analysis.

### 3.4 Sample Containers and Labels

Sample containers and preservatives will be provided by the analytical laboratory. The analytical laboratory will maintain documentation certifying the cleanliness of the sample containers and the purity of preservatives provided. Specific container requirements will be determined by the analytical laboratory.

Each sample will have an adhesive plastic or waterproof paper label affixed to the container and will be labeled at the time of collection. The following information will be recorded on the container label at the time of collection:

- Project name
- Sample identification
- Date and time of sample collection
- Preservative type (if applicable)

Samples will be uniquely identified with a sample identification that, at a minimum, specifies sample number and sample location.

### 3.5 Field Documentation

After sample collection, the following information will be recorded in the project field notebook:

- The date, the time, and the name of person logging sample
- Weather conditions
- Sample location number
- Percentage of woody debris
- Depth of water at the location
- Sediment penetration and depth

Each sample will be photographed. Sediment will be described in the field, using the visual-manual description procedure (Method ASTM [American Society for Testing and Materials] D-2488 modified). This information will also be recorded in the field notebook. Visual-manual characterization includes the following:

- Grain size distribution
- Density/consistency
- Plasticity
- Color and moisture content

- Biological structures (e.g., shells, tubes, macrophytes, bioturbation)
- Presence of debris and quantitative estimate (e.g., wood chips or fibers, paint chips, concrete, sandblast grit, metal debris)
- Presence of oily sheen
- Odor (e.g., hydrogen sulfide)

### 3.6 Investigation-Derived Waste

Investigation-derived waste (IDW) will consist of decontamination fluids only. IDW will be stored in a designated area on the upland property, in a 55-gallon drum approved by the Washington State Department of Transportation.

The drum (tops and sides) will be labeled with its contents, the volume of material, the date of collection, and the origin of the material. The waste drum will be sealed, secured, and transferred to a designated, secured area on the upland property at the end of field sampling activities. The waste will be stored in the designated holding area until it has been characterized. Hazardous-waste and/or risk labels will be placed on the drum after characterization, if necessary.

An aliquot of the fluid drum may be submitted to the analytical laboratory to characterize the waste fluids if this determination cannot be made from the sediment analytical data. After the work is complete and analytical results are received, IDW will be characterized and disposed of appropriately.

### 3.7 Compliance with U.S. Occupational Safety and Health Administration Regulations

In accordance with Code of Federal Regulations (CFR) 1910.120, the following safety programs will be incorporated during the sediment sampling event:

- A site-specific health and safety plan shall be developed to the standards presented in CFR 1910.120 before field activities begin.
- All field staff participating in sediment sampling activities will be U.S. Occupational Safety and Health Administration (OSHA) 40-hour Hazardous Waste Operations and Emergency Response (HAZWOPER) trained, with subsequent OSHA 8-hour HAZWOPER refresher courses completed as appropriate.

Further, in order to protect personnel working over water, an overwater workers insurance policy will be in place during the field sampling activities.

### 3.8 Utility Locations

Buried underground utilities present a unique hazard for subsurface sampling. Private and public utility location services will be utilized to identify locatable utilities in the subsurface sampling area before field sampling activities begin.

## 4 SAMPLE HANDLING PROCEDURES

---

In order to maintain sample integrity between the field collection and the laboratory analysis, the storage, handling, and shipping of sediment samples will follow the procedures described in this section.

### 4.1 Field Quality Control Samples

Field QC samples will be collected to improve the reliability of the data. DNR recommends collecting field duplicate samples, although this is not required. MFA will collect one each of the following samples:

- **Field Duplicate:** collected to assess the homogeneity of the samples and the precision of the sampling process
- **Rinsate Blank:** used to help identify possible contamination from the sampling environment and/or from decontaminated sampling equipment
- **Temperature Blank:** used to verify that adequate sample storage temperature was maintained

In addition, extra volume for matrix spike and matrix spike duplicate (MS/MSD) analysis will be collected. The rinsate blank and field duplicate QC sample will be analyzed for all sediment chemistry analytes (see Section 5).

### 4.2 Sample Storage

In order to maintain sample integrity, sample containers will be placed in coolers filled with ice or equivalent immediately after being filled with sediment. Samples will be maintained at approximately 4°C.

### 4.3 Chain-of-Custody Procedures

Samples in the custodian's possession, in a secured location (under lock) with restricted access or in a container that is secured with official seals such that the sample cannot be reached without breaking the seals, are considered to be under custody. Chain-of-custody (COC) procedures will be followed for all samples throughout the collection, handling, and analysis process. The principal

document used to track possession and transfer of samples is the COC form supplied by the analytical laboratory. Each sample will be represented on the COC form. All data entries will be made with an ink pen.

#### 4.4 Delivery of Samples to Analytical Laboratory

All samples will be shipped under COC procedures to the analytical laboratory no later than the day after collection. If samples are collected on Friday, they may be held until the following Monday for shipment, provided that this does not adversely impact holding time requirements. Sample containers will be placed in a sealable plastic bag, packed to prevent breakage, and transported in a sealed ice chest containing ice or equivalent.

Upon transfer of sample possession to the analytical laboratory, the persons transferring custody of the sample container will sign the COC form. Upon receipt of samples at the laboratory, the shipping container seal will be broken and the receiver will record the condition of the samples on a sample receipt form. COC forms will be used internally in the lab to track sample handling and final disposition.

## 5 LABORATORY ANALYTICAL METHODS

---

### 5.1 Chemical Analyses

The specific chemical analytes described in Section 2 are summarized, along with the numerical screening criteria and chemical-specific limits of quantitation, in Table 1. Table 3 presents a summary of the proposed analytical methods, preservation methods, and holding times. MFA proposes submitting samples to the Analytical Resources Incorporated (ARI) laboratory in Tukwila, Washington.

Pore water samples will be obtained from sediment by ARI in the laboratory. Wet sediment will be placed in a centrifuge for 30 minutes at 3,000 revolutions per minute (RPM). This initial water will be decanted off and the sediment removed. The decanted water is then returned to the centrifuge for an additional 30 minutes at 7,000 RPM. Water will be decanted off again and retained for porewater analysis.

### 5.2 Sample Quantitation Limits

Effort will be made to ensure that sample quantitation limits will be below the screening levels presented in Table 1. Unforeseen matrix interference could cause elevated quantitation limits for some compounds. All reasonable means, including additional cleanup steps and method modifications, will be used to bring sample quantitation limits below the screening levels. In addition, an extra aliquot (8 ounces) of each sediment sample will be archived and preserved at -18°C for followup analysis, if necessary.



### 5.3 Holding Times

Samples will be maintained at the analytical laboratory and will be analyzed within the holding times shown in Table 3.

### 5.4 Sample Preservation

Chemical preservatives are required only for total sulfides (see Table 3). All samples will be preserved by storage at 4°C.

## 6 QUALITY ASSURANCE AND QUALITY CONTROL REQUIREMENTS

---

### 6.1 Laboratory Quality Assurance and Quality Control Checks

U.S. Environmental Protection Agency (USEPA) methods include specific instructions for the analysis of QC samples and the completion of QC procedures during sample analysis. These QC samples and procedures verify that the instrument is calibrated properly and remains in calibration throughout the analytical sequence, and that the sample preparation procedures have been effective and have not introduced contaminants into the samples. Additional QC samples are used to identify and quantify positive or negative interference caused by the sample matrix. The following laboratory QC procedures are required for most analytical procedures:

- **Calibration Verification**—Initial calibration of instruments will be performed at the start of the project or sample run, as required, and when any ongoing calibration does not meet control criteria. The number of points used in the initial calibration is defined in the analytical method. Continuing calibration will be performed as specified in the analytical method to track instrument performance. If a continuing calibration does not meet control limits, analysis of project samples will be suspended until the source of the control failure is either eliminated or reduced to within control specifications. Any project samples analyzed while the instrument was outside of control limits will be reanalyzed.
- **Method Blanks**—Method blanks are used to assess possible laboratory contamination of samples associated with all stages of preparation and analysis of samples and extracts. The laboratory will not apply blank corrections to the original data. A minimum of one method blank will be analyzed for every sample extraction group, or one for every 20 samples, whichever is more frequent.
- **MS/MSD Samples**—MS samples are analyzed to assess the matrix effects on the accuracy of analytical measurements. A minimum of one MS will be analyzed for each sample delivery group, or one for every 20 samples, whichever is more frequent. Because

the spike is a duplicate sample, it measures the quality of laboratory preparatory techniques and the heterogeneity of the sample.

- **Surrogate Spike Compounds**—Surrogate spikes are used to evaluate the recovery of an analyte from individual samples. All project samples to be analyzed for organic compounds will be spiked with appropriate surrogate compounds as defined in the analysis method. Recoveries determined using these surrogate compounds will be reported by the laboratory; however, the laboratory will not correct sample results using these recoveries.
- **Laboratory Control Samples (LCSs)**—Analyses of LCSs will be performed by the lab at a frequency that satisfies the analytical methods' requirements.

## 6.2 Laboratory Calibration and Preventive Maintenance

The laboratory calibration ranges specified in SW-846 (USEPA, 1986) will be followed.

Preventive maintenance of laboratory equipment will be the responsibility of the laboratory personnel and analysts. This maintenance includes routine care and cleaning of instruments and inspection and monitoring of carrier gases, solvents, and glassware used in analyses. The preventive maintenance approach for specific equipment will follow the manufacturers' specifications and good laboratory practices.

Precision and accuracy data will be examined for trends and excursions beyond control limits to determine evidence of instrument malfunction. Maintenance will be performed when an instrument begins to change, as indicated by the degradation of peak resolution, shift in calibration curves, decrease in sensitivity, or failure to meet any of the QC criteria.

# 7 DATA ANALYSIS AND RECORDKEEPING

---

## 7.1 Data Reduction, Validation, and Reporting

The analytical laboratory will submit an electronic data deliverable, which will be incorporated into MFA's EQIS database. Analytical data will also be made available in pdf format and/or hard copy if requested. The analytical data package will include laboratory quality assurance (QA)/QC results to permit independent and conclusive determination of data quality. Only compounds presented in Table 1 will be reported by the analytical laboratory. Data quality will be determined by MFA, using the data evaluation procedures described in this section. The results of the MFA evaluation will be used to determine if the project data quality objectives are being met, and will be presented in a data validation memorandum as an appendix to the final report.

An internal memorandum prepared by MFA chemists provides an approach for dioxin data validation and TEQ calculation and is included as an appendix to this SAP.

## 7.1.1 Laboratory Evaluation

Initial data reduction, evaluation, and reporting at the analytical laboratory will be carried out as described in USEPA SW-846 manuals for organic analyses (USEPA, 1986), as appropriate. Additional laboratory data qualifiers may be defined and reported to further explain the laboratory's QC concerns about a particular sample result. All additional data qualifiers will be defined in the laboratory's narrative reports associated with each case.

## 7.1.2 Data Deliverables

Laboratory data deliverables are listed below. Electronic deliverables will contain the same data presented in the hard-copy report.

- Transmittal cover letter
- Case narrative
- Analytical results
- COC
- Surrogate recoveries
- Method blank results
- MS/MSD results
- Laboratory duplicate results

## 7.1.3 Data Quality Assurance and Quality Control Review

MFA will evaluate the laboratory data for precision, completeness, accuracy, and compliance with the analytical method. MFA will perform a Tier II validation, consistent with the USEPA's Superfund risk assessment guide (USEPA, 1989), and will assign data qualifiers to sample results, following applicable sections of the USEPA procedures for data review (USEPA, 1986, 2008, 2010).

Data qualifiers, as defined by the USEPA, are used to classify sample data according to their conformance to QC requirements. The most common qualifiers are listed below:

- J—Estimate, qualitatively correct but quantitatively suspect.
- R—Reject, data not suitable for any purpose.
- U—Not detected at a specified reporting limit.

Poor surrogate recovery, blank contamination, or calibration problems, among other things, can cause the sample data to be qualified. Whenever sample data are qualified, the reasons for the qualification will be stated in the data evaluation report.

QC criteria not defined in the guidelines for evaluating analytical data are adopted, where appropriate, from the analytical method.

The following information will be reviewed during data evaluation, as applicable:

- Sampling locations and blind sample numbers
- Sampling dates
- Requested analysis
- COC documentation
- Sample preservation
- Holding times
- Method blanks
- Surrogate recoveries
- MS/MSD results
- Laboratory duplicates (if analyzed)
- Field duplicates
- Field blanks
- LCSs
- Method reporting limits above requested levels
- Any additional comments or difficulties reported by the laboratory
- Overall assessment

The results of the data evaluation review will be summarized for the data package. Data qualifiers will be assigned to sample results on the basis of USEPA guidelines, as applicable.

#### 7.1.4 Data Management and Reduction

MFA uses EQuIS to manage all laboratory data. The laboratory will provide the analytical results in electronic EQuIS-deliverable format. Following data evaluation, data qualifiers will be entered into the EQuIS database.

Data may be reduced to summarize particular data sets and to aid interpretation of the results. Statistical analyses may also be applied to results. Data reduction QC checks will be performed on all hand-entered data, any calculations, and any data graphically displayed. Data may be further reduced and managed using one or more of the following computer software applications:

- Microsoft Excel (spreadsheet)
- EQuIS (database)
- AutoCad and/or Arc GIS (graphics)
- USEPA ProUCL (statistical software)

---

## 8 REPORTING

After the data are received, MFA will prepare a letter report documenting all activities associated with collection, compositing, transportation, and chemical analysis of samples. The laboratory

reports will be included as appendices. At a minimum, the following will be included in the final letter report:

- Protocols used during sampling and testing and an explanation of any deviations from the sampling plan protocols.
- Descriptions of each sample, recorded on a field sampling data sheet.
- Locations where the sediment samples were collected and a plan view of the project, showing actual sample locations. Any sample with numerical exceedances of the screening criteria will be displayed on the figure (Integral, 2011).
- QA/QC data validation memorandums describing the usability of the analytical results.
- Results of the chemical and physical data analysis, with comparisons to the CSL values presented in Table A-1 of the Guide and a description of woody debris, if any. Separate tables will be prepared for dry-weight and TOC normalized concentrations (Integral, 2011). Locations with woodwaste of more than 25 percent will be scored according to Table A-3 of the Guide.
- Data interpretation.
- Recommendations.

MFA will also submit the analytical data electronically to the EIM Database.

After completion of data collection, evaluation, and reduction, the data will be incorporated into reports. Copies of the reports will be kept in MFA's main project files, submitted to the client for review, and then submitted to DNR.

## LIMITATIONS

---

The services undertaken in completing this plan were performed consistent with generally accepted professional consulting principles and practices. No other warranty, express or implied, is made. These services were performed consistent with our agreement with our client. This plan is solely for the use and information of our client unless otherwise noted. Any reliance on this plan by a third party is at such party's sole risk.

Opinions and recommendations contained in this plan apply to conditions existing when services were performed and are intended only for the client, purposes, locations, time frames, and project parameters indicated. We are not responsible for the impacts of any changes in environmental standards, practices, or regulations subsequent to performance of services. We do not warrant the accuracy of information supplied by others, or the use of segregated portions of this plan.

## REFERENCES

---

DNR. 2012. Letter (re: Aberdeen former large log mill site sampling recommendations) to K. Johnson, Weyerhaeuser Company, Federal Way, Washington, from E. Shaffer, Washington State Department of Natural Resources, Aquatic Resources Division, Olympia, Washington. March 26.

Ecology. 1999. Grays Harbor estuary sediment evaluation, chemical screening and station cluster analysis of selected locations. Publication No. 99-300. Washington State Department of Ecology Environmental Assessments Programs, Watershed Ecology Section, Olympia, Washington. January.

Ecology. 2008. Sediment sampling and analysis plan appendix, guidance on the development of sediment sampling and analysis plans meeting the requirements of the sediment management standards (Chapter 173-204 WAC). Publication No. 03-09-043. Washington State Department of Ecology Toxics Cleanup Program. Olympia, Washington. February.

Floyd|Snider. 2012. Letter (re: proposed sediment investigation in the Weyerhaeuser Aberdeen aquatic lands lease area) to K. Johnson and R. Laishley, Weyerhaeuser, from S. Bentsen, PE, and T. Floyd, PhD, Floyd|Snider, Seattle, Washington. March 15.

Integral. 2011. Draft state owned aquatic lands sediment sampling and analysis guide. Prepared for Washington State Department of Natural Resources, Olympia, Washington, by Integral Consulting, Olympia, Washington. June.

PES. Level I Environmental Site Assessment. PES Environmental, Eugene, Oregon. August 13.

SAIC. 2011. Weyerhaeuser aquatic lands lease confirmatory sampling, data report final. Submitted to Washington State Department of Natural Resources. Science Applications International Corporation, Bothell, Washington. August 12.

USEPA. 1986. Test methods for evaluating solid waste: physical/chemical methods. EPA-530/SW-846. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. September (revision 6, February 2007).

USEPA. 1989. Risk assessment guide for Superfund. Vol. I, human health evaluation manual (Part A). Interim final. EPA/540/1A89/002. U.S. Environmental Protection Agency, Office of Emergency and Remedial Response. December.

USEPA. 2008. USEPA contract laboratory program, national functional guidelines for organics data review. EPA 540/R-08/01. U.S. Environmental Protection Agency, Office of Emergency and Remedial Response. June.

USEPA. 2010. USEPA contract laboratory program, national functional guidelines for inorganics data review. EPA 540/R-94/013. U.S. Environmental Protection Agency, Office of Superfund Remediation and Technology Innovation. January.

# TABLES





**Table 1**  
**Proposed Sediment Sample Locations and Analytical Tiers**  
**Grays Harbor Historical Seaport Authority**  
**Aberdeen, Washington**

Sample Name	Sample Location	Sample Type	Sample Depth	Sample Coordinates		Analytical Tier	Proposed Analysis
CR-01	Chehalis River	Surface Grab (Ponar)	0-10 cm bml	817108.6634	615592.2936	Tier I	SMS constituents with marine criteria, dioxins/furans, salinity in pore water, and TOC. If woodwaste > 25%, then add Conventionals.
CR-02	Chehalis River	Surface Grab (Ponar)	0-10 cm bml	817677.5240	615747.8208	Tier I	SMS constituents with marine criteria, dioxins/furans, salinity in pore water, and TOC. If woodwaste > 25%, then add Conventionals.
CR-03	Chehalis River	Surface Grab (Ponar)	0-10 cm bml	818247.8576	615977.6148	Tier I	SMS constituents with marine criteria, dioxins/furans, salinity in pore water, and TOC. If woodwaste > 25%, then add Conventionals.
CR-04	Former Mill Area	Sediment Core	0-10 cm bml	816947.2280	615369.5003	Tier I	Butyl benzyl phthalate, pentachlorophenol, mercury, dioxin/furans. If woodwaste > 25%, then add Conventionals.
			10cm - 2.5 feet bml			Tier II	Archive at analytical laboratory. Followup analysis to be determined based on Tier I results.
			2.5-5 feet bml			Tier III	Archive at analytical laboratory. Followup analysis to be determined based on Tier II results.
CR-05	Former Mill Area	Sediment Core	0-10 cm bml	816990.4379	615478.2966	Tier I	Butyl benzyl phthalate, pentachlorophenol, mercury, dioxin/furans. If woodwaste > 25%, then add Conventionals.
			10 cm - 2.5 feet bml			Tier II	Archive at analytical laboratory. Followup analysis to be determined based on Tier I results.
			2.5-5 feet bml			Tier III	Archive at analytical laboratory. Followup analysis to be determined based on Tier II results.
CR-06	Former Mill Area	Sediment Core	0-10 cm bml	817048.6941	615391.8769	Tier I	Butyl benzyl phthalate, pentachlorophenol, mercury, dioxin/furans. If woodwaste > 25%, then add Conventionals.
			10 cm - 2.5 feet bml			Tier II	Archive at analytical laboratory. Followup analysis to be determined based on Tier I results.
			2.5-5 feet bml			Tier III	Archive at analytical laboratory. Followup analysis to be determined based on Tier II results.
<p>NOTES:</p> <p>Samples collected at 1 and 4 feet bml may be analyzed upon review of sample results and in consultation with Washington Department of Natural Resources.</p> <p>cm = centimeters.</p> <p>bml = below mudline.</p> <p>Conventionals = total organic carbon, total volatile solids, total solids, ammonia, total sulfides, pore water sulfides, and percent fines.</p> <p>SMS = Sediment Management Standards.</p> <p>TOC = total organic carbon.</p>							

**Table 2**  
**Marine Sediment Analyte List**  
**Grays Harbor Historical Seaport Authority**  
**Aberdeen, Washington**

Chemical Parameter	SQS	SIZ <sub>max</sub> , CSL, MCUL	LOQ
<b>Metals (mg/kg, dry weight)</b>			
Arsenic	57	93	5.0
Cadmium	5.1	6.7	0.2
Chromium	260	270	0.5
Copper	390	390	0.2
Lead	450	530	2.0
Mercury	0.41	0.59	0.025
Silver	6.1	6.1	0.3
Zinc	410	960	1.0
<b>Organic Chemicals (mg/kg organic carbon)</b>			
Total LPAH	370	780	NA
Naphthalene	99	170	0.02
Acenaphthylene	66	66	0.02
Acenaphthene	16	57	0.02
Fluorene	23	79	0.02
Phenanthrene	100	480	0.02
Anthracene	220	1,200	0.02
2-methylnaphthalene	38	64	0.02
Total HPAH	960	5,300	NA
Fluoranthene	160	1,200	0.02
Pyrene	1,000	1,400	0.02
Benz(a)anthracene	110	270	0.02
Chrysene	110	460	0.02
Total benzofluoranthenes	230	450	0.04
Benzo(a)pyrene	99	210	0.02
Indeno (1,2,3-c,d)pyrene	34	88	0.02
Dibenzo(a,h)anthracene	12	33	0.02
Dibenzo(g,h,i)perylene	31	78	0.02
1,2-dichlorobenzene	2.3	2.3	0.02
1,4-dichlorobenzene	3.1	9	0.02
1,2,4-trichlorobenzene	0.81	1.8	0.02
Hexachlorobenzene	0.38	2.3	0.02
Dimethyl phthalate	53	53	0.02
Diethyl phthalate	61	110	0.02
Di-n-butyl phthalate	220	1,700	0.02
Butyl-benzyl phthalate	4.9	6.4	0.02
bis(2-ethylhexyl)phthalate	47	78	0.02
Di-n-octyl phthalate	58	4,500	0.02
Dibenzofuran	15	58	0.02
Hexachlorobutadiene	3.9	6.2	0.02
n-Nitrosodiphenylamine	11	11	0.02
Total PCBs	12	65	0.231

**Table 2**  
**Marine Sediment Analyte List**  
**Grays Harbor Historical Seaport Authority**  
**Aberdeen, Washington**

Chemical Parameter	SQS	SIZ <sub>max</sub> , CSL, MCUL	LOQ
<b>Ionizable Organic Compounds (µg/kg dry weight)</b>			
Phenol	420	1,200	20
2-methylphenol	63	63	20
4-methylphenol	670	670	20
2,4-dimethylphenol	29	29	20
Pentachlorophenol	360	690	200
Benzyl Alcohol	57	73	20
Benzoic Acid	650	650	400
<p>NOTES:</p> <p>CSL = cleanup screening level.</p> <p>HPAH = high molecular weight polycyclic aromatic hydrocarbon.</p> <p>LOQ = limit of quantitation.</p> <p>LPAH = low molecular weight polycyclic aromatic hydrocarbon.</p> <p>MCUL = minimum cleanup level.</p> <p>mg/kg = milligrams per kilogram.</p> <p>µg/kg = micrograms per kilogram.</p> <p>NA=not applicable.</p> <p>PCB = polychlorinated biphenyl.</p> <p>SIZ<sub>max</sub> = Sediment Impact Zone maximum allowable concentration (WAC 173-204-420).</p> <p>SQS = Sediment Quality Standards (WAC 173-294-320).</p> <p>WAC = Washington Administrative Code.</p>			

**Table 3**  
**Sediment Analytical Methods**  
**Grays Harbor Historical Seaport Authority**  
**Aberdeen, Washington**

Sample Type	Hold Time (4°C)	Preservative	Method Description
SVOAs	14 days	None	USEPA 8270
PCBs	14 days	None	USEPA 8082
Metals except mercury	6 months	None	USEPA 6010
Mercury	28 days	None	USEPA 7471
Dioxins/Furans	1 year	None	USEPA 1613
TOC	14 days	None	Plumb
Ammonia	7 days	None	USEPA 350.3
Total Sulfides	7 days	Zinc Acetate	PSEP
TVS	6 months	None	PSEP
Total Sulfides (pore water)	7 days	None	SM4500S
Salinity (pore water)	28 days	None	SM2520
Grain Size	6 months	None	PSEP
Total Solids	14 days	None	PSEP
Archiving	14 days	None	Frozen upon receipt at laboratory
NOTES: °C = degrees centigrade. PCB = polychlorinated biphenyl. PSEP = Puget Sound Estuary Program. SVOA = semivolatile analytes. TOC = total organic carbon. TVS = total volatile solids. USEPA = U.S. Environmental Protection Agency Method.			

FIGURE









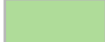




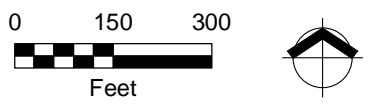
Path: X:\IP0863.01.01\Projects\Figure 1\_SampleFeaturesUpdate.mxd  
Project: P0863.01.01  
Produced By: cmikes  
Approved By: M.Murray  
Print Date: 6/25/2013



**Figure  
Historical and Proposed  
Sample Locations**  
Grays Harbor Historical  
Seaport Authority  
Aberdeen, Washington

**Legend**

-  Downstream Composite Sediment Sample Location
-  Dock Front Composite Sediment Location
-  Upstream Composite Sediment Location
-  Upland Soil Boring Location
-  2011 Sediment Core Location
-  1999 Sediment Sample Locations
-  Proposed Sediment Sample Location
-  Dock Area
-  Filled Tidelands
-  Former Mill Area
-  DNR Lease Area Boundaries



Source: Aerial photograph (2013) obtained from Esri ArcGIS Online

 MAUL FOSTER ALONGI  
p. 971 544 2139 | www.maulfoster.com

This product is for informational purposes and may not have been prepared for, or be suitable for legal, engineering, or surveying purposes. Users of this information should review or consult the primary data and information sources to ascertain the usability of the information.

# APPENDIX

## DIOXIN AND FURAN ANALYSIS, DATA VALIDATION AND TEQ CALCULATION RULES





## MEMORANDUM

To: File

Date: June 27, 2013

From: Erik Naylor

A handwritten signature in blue ink, appearing to read "Erik Naylor", is written over a horizontal line.

RE: Dioxin and Furan Analysis, Data Validation, and TEQ Calculation Rules

---

The term “dioxin” is used to refer to a family of toxic chemicals that share a similar chemical structure and a common mechanism of toxic action. While there are 210 dioxin congeners, typically only the 17 most toxic congeners are reported by laboratories. The reported concentrations of the 17 dioxin congeners typically are validated to assess usability and then a toxicity equivalent concentration (TEQ) is calculated from the reported results to evaluate the toxicity of these compounds as a whole. The purpose of this memo is to provide an approach for dioxin data validation and TEQ calculation. Further, analytical method recommendations and requirements for laboratory deliverables are provided to enable consistent data validation and TEQ calculation using data from a variety of laboratories.

Critical to consistent data use is consistent use of terminology. Terms used in this memorandum are defined below.

- **Method Detection Limit (MDL)**—The minimum concentration of a compound that can be measured and reported with 99 percent confidence that the value is greater than zero according to the Washington State Department of Ecology’s (Ecology) Model Toxics Control Act (MTCA) (Ecology, 2007).
- **Estimated Detection Limit (EDL)**—The sample- and analyte-specific EDL is an estimate made by the laboratory of the concentration of a given analyte that would have to be present to produce a signal with a peak height of at least 2.5 times the background noise signal level (U.S. Environmental Protection Agency [USEPA], 2005).
- **Practical Quantitation Limit (PQL)**—The lowest concentration that can be reliably measured within specified limits of precision, accuracy, representativeness, completeness, and comparability during routine laboratory operating conditions, using Ecology-approved methods (Ecology, 2007). This value is usually the lowest concentration used to calibrate the instrument after being adjusted for sample volume, sample extract volume, cleanups performed, and injection volume. PQLs should be no greater than 10 times the MDL (Ecology, 2007) and no greater than limits established by the USEPA in 40 Code of Federal Regulations (CFR) 136, 40 CFR 141-143, or 40 CFR 260-270.



- Estimated Maximum Potential Concentration (EMPC)—An EMPC is a value calculated for a reported analyte when the signal-to-noise ratio is at least 2.5:1 for both quantitation ions, but the ion abundance ratio criteria used for analyte confirmation are not met (USEPA, 2005). An EMPC value represents the maximum possible result of an analyte that could not be positively identified. The inability to positively identify the analyte could be a result of matrix interference, a coeluting compound, or low response.
- Toxic Equivalency Factor (TEF)—The factor by which each congener is multiplied in order to calculate its toxicity relative to 2,3,7,8-TCDD (Ecology, 2007). These values are summed to calculate the TEQ. TEFs depend on the endpoint that is being examined (i.e., birds, fish, mammals).
- TEQs—Concentrations of each congener are adjusted and summed to reflect their potency relative to 2,3,7,8-TCDD, one of the most toxic congeners. The TEQ is the sum of congener results multiplied by their specific TEF (Ecology, 2007).

## **ANALYTICAL METHODS**

Dioxins are analyzed generally by USEPA Method 1613B or 8290, using a high-resolution gas chromatograph paired with a high-resolution mass spectrometer. A laboratory's PQL is usually the same for both methods. While the methods are very similar, Method 1613B is preferred, as it requires more rigorous quality assurance and quality control (QA/QC) through the use of six more internal standards than Method 8290. Because analytical technology and methodology have advanced rapidly since the methods were written, many laboratories combine elements of both methods to obtain the best results possible (Hoffman and Fox, 2010). Often the preparation and analyses are run using Method 1613B (for the additional QA/QC), while the calculations are performed by Method 8290 (in order to obtain the sample- and analyte-specific EDLs). Method 1613B with calculated EDLs is the preferred method.

## **LABORATORY DELIVERABLES**

It is important to work closely with the laboratory performing the dioxin analyses because different laboratories report data in different ways. The following items should be requested to ensure that the analytical report and electronic data deliverable (EDD) will contain all of the requisite information to validate the data and calculate TEQs:

- EDLs<sup>1</sup> and PQLs should be included in the final analytical report. EDLs, MDLs, and PQLs should all be included in the EDD.
- Results should be reported to the sample- and analyte-specific EDL. Results below the PQL but above the EDL will be qualified as estimates (J).

---

<sup>1</sup> Note that USEPA Method 1613B does not provide for the calculation of EDLs; therefore, the laboratory must use the calculation approach provided in Method 8290 to report the required limits.

- EMPC results should be reported at the EMPC value (EMPC values will be assigned a “U” qualifier [the analyte was not detected at or above the concentration qualified] at the time of validation).

TEQ concentrations will not be requested from the laboratory. If the laboratory provides TEQ concentrations, they will not be used because the data have not been validated. TEQs should be calculated only after the data are validated.

## VALIDATION

Dioxin data are validated much like other organic data, but there are a few issues that do not typically arise in other organic data sets. In addition to standard validation procedures (USEPA, 2005), the following scenarios should be addressed in the fashion described below, consistent with other Ecology sites (Ecology and Environment and G. L. Glass, 2011):

- EMPC reported values should be assigned a U qualifier at the reported EMPC value.
- EMPC values that appear to be significantly elevated should be investigated further with the laboratory and may be assigned an R qualifier (unusable) when applicable.
- Non-detected results should be assigned a U qualifier and reported at the EDL value.

Further dioxin validation guidelines can be found in the National Functional Guidelines for Chlorinated Dibenzo-p-Dioxins (CDDs) and Chlorinated Dibenzofurans (CDFs) Data Review (USEPA, 2005). Data must be validated before TEQs are calculated.

## TEQS

To express the overall toxicity of the 17 reported dioxins, the concentration of each congener is adjusted based on its toxicity relative to the most toxic congener, 2,3,7,8-TCDD, and then all 17 are added together. The adjustment factors, the TEFs, are provided by the 2005 World Health Organization. TEQs are commonly calculated by one of the following two methods:

- Non-detected values (U) are set as one half of the EDL. Values that are detected, even as estimates (J), should be used at face value. Multiply congener values by their corresponding TEF and then sum all of the products.
- Non-detected values (U) are set as 0. Values that are detected, even as estimates (J), should be used at face value. Multiply congener values by their corresponding TEF and then sum all of the products.

These methods result in two different TEQ values that can be shown as TEQ (U=1/2) and TEQ (U=0). TEQs should not be calculated to more significant figures than the original data. The table below illustrates these methods:

Dioxin	Result (ng/kg)	TEC <sup>1</sup> (U=1/2) (ng/kg)	TEC <sup>1</sup> (U=0) (ng/kg)	TEF Mammals
1,2,3,4,6,7,8,9-Octachlorodibenzofuran (OCDF)	44	44	44	0.0003
1,2,3,4,6,7,8,9-Octachlorodibenzo-p-dioxin (OCDD)	3000 J	3000	3000	0.0003
1,2,3,4,6,7,8-Heptachlorodibenzofuran (HpCDF)	41	41	41	0.01
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin (HpCDD)	510	510	510	0.01
1,2,3,4,7,8,9-Heptachlorodibenzofuran (HpCDF)	2.9 U	1.45	0	0.01
1,2,3,4,7,8-Hexachlorodibenzofuran (HxCDF)	6.9 U	3.45	0	0.1
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin (HxCDD)	7.4	7.4	7.4	0.1
1,2,3,6,7,8-Hexachlorodibenzofuran (HxCDF)	5.2 U	2.6	0	0.1
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin (HxCDD)	27	27	27	0.1
1,2,3,7,8,9-Hexachlorodibenzofuran (HxCDF)	0.5 U	0.25	0	0.1
1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin (HxCDD)	22	22	22	0.1
1,2,3,7,8-Pentachlorodibenzofuran (PeCDF)	3.4 U	1.7	0	0.03
1,2,3,7,8-Pentachlorodibenzo-p-dioxin (PeCDD)	3.2 U	1.6	0	1
2,3,4,6,7,8-Hexachlorodibenzofuran (HxCDF)	2.4	2.4	2.4	0.1
2,3,4,7,8-Pentachlorodibenzofuran (PeCDF)	3 U	1.5	0	0.3
2,3,7,8-Tetrachlorodibenzofuran (TCDF)	1.4 U	0.7	0	0.1
2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)	0.23 U	0.115	0	1
Total Heptachlorodibenzofuran (HpCDF)	99	99	99	--
Total Heptachlorodibenzo-p-dioxin (HpCDD)	1,100	1100	1100	--
Total Hexachlorodibenzofuran (HxCDF)	97 J	97	97	--
Total Hexachlorodibenzo-p-dioxin (HxCDD)	250	250	250	--
Total Pentachlorodibenzofuran (PeCDF)	44	44	44	--
Total Pentachlorodibenzo-p-dioxin (PeCDD)	32 J	32	32	--
Total Tetrachlorodibenzofuran (TCDF)	19	19	19	--
Total Tetrachlorodibenzo-p-dioxin (TCDD)	8.2	8.2	8.2	--
<b>TEQ (U=1/2)</b>	<b>15.2</b>	--	--	--
<b>TEQ (U=0)</b>	<b>12.3</b>	--	--	--
NOTES: -- = no value. ng/kg = nanograms per kilogram. <sup>1</sup> TEC is analyte-specific TEF adjusted concentration.				

The difference between TEQ (U=1/2) and TEQ (U=0) values gives data reviewers an idea of how much the EDL substitution affects the TEQ summation (Hoffman and Fox, 2010). While MTCA

does not specify using the TEQ (U=1/2) method, it is the method that historically has been used at the Port of Ridgefield and that will continue to be used.

## SUMMARY

- USEPA Method 1613B is recommended for dioxin analysis (with Method 8290 EDL calculations).
- The laboratory must include in the final analytical report a PQL and EDL for each sample and each congener, and provide in the EDD a PQL, EDL, and MDL for each sample and each congener.
- Results should be reported to the sample- and analyte-specific EDL. Results below the PQL but above the EDL will be qualified as estimates (J).
- EMPC results should be reported at the EMPC value (EMPC values will be assigned a “U” qualifier at the time of validation). However, if the EMPC is significantly elevated, additional qualification may be appropriate.
- Non-detected results should be assigned a U qualifier and reported at the EDL value.
- Laboratory data must be validated before a TEQ is calculated.
- TEQs should be calculated as follows: non-detected values (U) are set as one half of the EDL. Values that are detected, even as estimates (J), should be used at face value. Multiply congener values by their corresponding TEF and then sum all of the products.

## REFERENCES

Ecology. 2007. Model Toxics Control Act statute and regulation. Publication No. 94-06. Washington State Department of Ecology. November.

Ecology and Environment Inc. and Gregory L. Glass. 2011. Rayonier Mill off-property soil dioxin study. June.

Hoffman, E., and D. Fox. 2010. Polychlorinated dioxins and furans (PCDD/F): revisions to the supplemental quality assurance project plan (SQAPP). U.S. Environmental Protection Agency. November.

USEPA. 2005. USEPA contract laboratory program national functional guidelines for chlorinated dibenzo-p-dioxins (CDDs) and chlorinated dibenzofurans (CDFs) data review. EPA 540-R-05-001. U.S. Environmental Protection Agency, Office of Superfund Remediation and Technology Innovation. September.