

# **Quality Assurance Project Plan**

# **Dioxin in Surface Water Sources to Oakland Bay**

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#### **Publication Information**

Each study conducted by the Washington State Department of Ecology (Ecology) must have an approved Quality Assurance Project Plan. The plan describes the objectives of the study and the procedures to be followed to achieve those objectives. After completing the study, Ecology will post the final report of the study to the Internet.

The plan for this study is available on Ecology's website at www.ecy.wa.gov/biblio/1103118.html.

Data for this project will be available on Ecology's Environmental Information Management (EIM) website at <u>www.ecy.wa.gov/eim/index.htm</u>. Search User Study ID, RCOO0012.

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## **Quality Assurance Project Plan**

## Dioxin in Surface Water Sources to Oakland Bay

December 2011

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EAP: Environmental Assessment Program

EIM: Environmental Information Management database

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#### Abstract

In 2008 the Washington State Department of Ecology (Ecology) conducted a sediment study in Oakland Bay and reported dioxin and furans at relatively high concentrations across the study area (Herrera, 2010). Some historical sources have been identified but the major surface water inputs to the bay have never been evaluated.

Human health and environmental concerns have been raised because of the levels of dioxin and furans reported in Oakland Bay sediments and the highly productive shellfish growing areas in the bay. This study will determine if dioxin and furans are being discharged by surface water inputs to Oakland Bay from Shelton, Goldsborough, or Johns Creeks and whether current sources of dioxin and furans are entering the bay through creeks. It may also help identify historic sources.

During the fall of 2011, Ecology will collect sediment from four sites each on Shelton and Goldsborough Creeks, and two sites on Johns Creek. Results will be compared to available sediment quality guidelines and background levels. Downstream stations in each creek will be located as close as possible to discharge, while trying to avoid the marine influence. Remaining sites within each creek are positioned based on access and to isolate areas of each basin for possible follow-up. Two soil samples will also be collected from a mounded fill area adjacent to Shelton Creek's downstream site.

## Background

Oakland Bay has been identified by the Washington State Department of Ecology (Ecology) as a priority embayment under the Toxics Cleanup Program's Puget Sound Initiative. Under this plan seven Puget Sound bays were selected that would benefit most from toxics investigations to protect natural resources and human health.

Oakland Bay has a long history of industrial activity and is also one of the nation's most productive shellfish growing areas (Figure 1). Sediment contamination has been documented in previous investigations.

In 2008 the Toxic Cleanup Program directed a sediment investigation in Oakland Bay to support prioritization of cleanup and restoration. The study reported industrial contaminants of concern were found below screening levels of Ecology's Sediment Management Standards across the study area. Polychlorinated dibenzo-p-dioxins and dibenzofurans, also called dioxin and furans or dioxin were found at relatively high concentrations throughout the study area (Herrera, 2010). These compounds are not included in the Sediment Management Standards.

The sediment investigation reported that fifty surface sediment samples were collected from the study area. Samples are taken from within the top foot depth of sediment surface. Every site had detectable dioxin/furans ranging from 1 to 175 ng/Kg, Toxic Equivalents (TEQs). See discussion of TEQs in *Data Management Procedures* section. The highest concentrations were located along the western edge of Shelton Harbor. The mean total dioxin TEQ was higher in Shelton Harbor (198 ng/Kg, TEQ) than Oakland Bay (97.8 ng/Kg, TEQ).

Sources of dioxin and furans to Oakland Bay likely include surface and stormwater inputs, point source discharge (current and historical), and the atmospheric pool through wet and dry deposition. Shelton and Goldsborough Creeks are the largest surface water sources discharging within the urban/industrial area of Shelton Harbor. In addition, Johns Creek in upper Oakland Bay drains an area that includes an industrial park where wood treating facilities were located.

Identifying and reducing current inputs of dioxin and furans to Oakland Bay is important because of the relatively high levels of the chemicals found in the bay, and the need to eliminate sources of chemicals before sediment cleanup options can be considered. Levels of dioxin and furans have never been measured in streams discharging to Oakland Bay.

This study will measure dioxin and furan levels in sediment within Shelton, Goldsborough, and Johns Creeks. Sediments are being sampled because dioxin and furans tend to be associated with particulates. Dioxin and furans may not be detectable in water so it makes sense to sample surface sediments to achieve study objectives.



Figure 1. Study area showing Shelton, Goldsborough, and Johns Creeks.

## **Project Description**

#### Description

Ecology's Environmental Assessment Program (EAP) will conduct the study and will collect sediment samples from Shelton, Goldsborough, and Johns Creeks during fall of 2011. Sampling will occur as close to discharge as possible, and at three upstream locations from Shelton and Goldsborough Creeks, and one upstream site on Johns Creek (Figure 2). Two surface soil samples will also be collected from a mounded fill of what appears to be a mix of ash and soil adjacent to the downstream sample site on Shelton Creek.

If deposits of fine sediment are not available at any site, instream sediment traps will be installed as an alternative. With traps deployed in low velocity areas of the stream, suspended sediment will be collected for between 1 and 2 months.

Sediment samples will be analyzed for the seventeen chlorinated dioxin/furan congeners of concern. Columbia Analytical Services of Houston, Texas, through a contract with Manchester Environmental Laboratories (MEL) will conduct this analysis using Method 1613B. This method uses high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). Reporting limits are expected to be in the low parts per trillion (ng/Kg). Total organic carbon (TOC) and grain size will also be analyzed by Puget Sound Estuary Program (PSEP) methods.

Data from this study will provide information on whether the major surface water sources to Oakland Bay associated with urban or industrial activities are currently discharging dioxin and furans. Study data will be compared to background data for determining if current sources are present. Upstream sample results will be compared to downstream for assessing the need of future source identification.

This Quality Assurance Project Plan follows guidance found in Lombard and Kirchmer (2004). A final report will be published describing study findings.

#### **Goal and Objectives**

The goal of the study is to identify whether there are current or historic sources of dioxin in the creeks discharging from industrial areas to the bay, so that Ecology's Toxic Cleanup Program can work toward reducing dioxin and furans to acceptable levels in Oakland Bay for the protection of human and environmental health. The objectives are to:

- Determine if dioxin and furans are currently being discharged to Oakland Bay via Shelton, Goldsborough, and Johns Creeks.
- Establish baseline conditions for future sediment evaluations.
- Recommend follow-up characterization as needed.

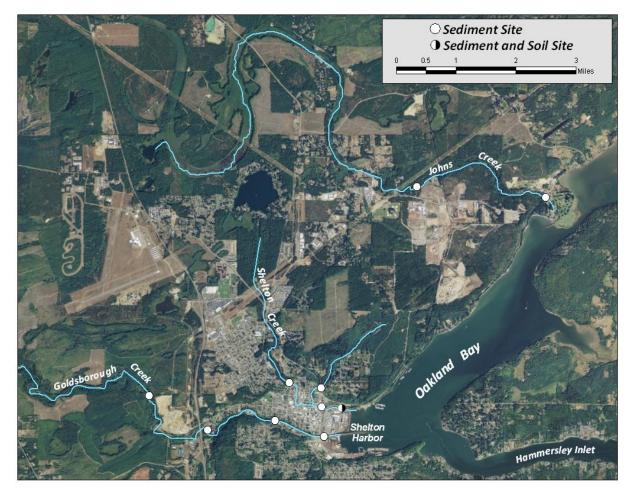


Figure 2. Shelton, Goldsborough, and Johns Creeks sampling locations.

## **Organization and Schedule**

Table 1 lists the people involved in this project. All are employees of the Washington State Department of Ecology. Table 2 presents the proposed schedule for this project.

Staff (all are EAP except client)	Title	Responsibilities
Joyce Mercuri Toxic Cleanup Program SWRO Phone: (360) 407-6260	EAP Client	Clarifies scopes of the project. Provides internal review of the QAPP and approves the final QAPP.
Randy Coots Toxics Studies Unit SCS Phone: (360) 407-6690	Project Manager	Writes the QAPP. Oversees field sampling and transportation of samples to the laboratory. Conducts QA review of data, analyzes and interprets data. Writes the draft report and final report.
Dale Norton Toxics Studies Unit SCS Phone: (360) 407-6765	Unit Supervisor for the Project Manager	Provides internal review of the QAPP, approves the budget, and approves the final QAPP.
Will Kendra SCS Phone: (360) 407-6698	Section Manager for the Project Manager	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Robert F. Cusimano Western Operations Section Phone: (360) 407-6596	Section Manager for the Study Area	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Stuart Magoon Manchester Environmental Laboratory Phone: (360) 871-8801	Director	Approves the final QAPP.
William R. Kammin Phone: (360) 407-6964	Ecology Quality Assurance Officer	Reviews the draft QAPP and approves the final QAPP.

Table 1. Organization of project staff and responsibilities.	Table 1.	Organization	of project staff	and responsibilities.
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EAP: Environmental Assessment Program

SWRO: Southwest Regional Office

SCS: Statewide Coordination Section

EIM: Environmental Information Management database

QAPP: Quality Assurance Project Plan

Field and laboratory work	Due date	Lead staff	
Field work completed	December 2011 <sup>1</sup>	Randy Coots	
Laboratory analyses completed	February 2012		
Environmental Information System (EIM)	database		
EIM user study ID	RCOO0012		
Product	Due date	Lead staff	
EIM data loaded	July 2012	Tanya Roberts	
EIM quality assurance	August 2012	Tanya Roberts	
EIM complete	September 2012 Tanya Roberts		
Final report			
Author lead	Randy Coots		
Schedule			
Draft due to supervisor	May 2012		
Draft due to client/peer reviewer	June 2012		
Final (all reviews done) due to publications coordinator	August 2012		
Final report due on web	September 2012		

Table 2. Proposed schedule for completing field and laboratory work, data entry into EIM, and reports.

<sup>1</sup> If sediment traps are deployed, timelines will be extended an additional two months.

## **Quality Objectives**

Quality objectives for this study are to collect samples representative of sediments being discharged to Oakland Bay, and obtain analytical results of a quality that will minimize uncertainty and are comparable to past and future sediment sampling efforts in the Bay. Objectives will be achieved through careful planning and execution of sampling, analysis, and Quality control (QC) procedures presented in this plan.

MEL and their contractors are expected to meet quality control requirements of methods selected for the project. QC procedures used during laboratory analyses will provide data for determining the accuracy of the monitoring results.

Table 3 shows the measurement quality objectives (MQOs) for the methods selected for sample analysis. Table A1 in the Appendix includes achievable reporting limits for the 17 dioxin and furan congeners analyzed for the project, based on reporting limits achieved for other studies analyzing sediments by the contract laboratory.

Analytical precision and bias will be evaluated and controlled by use of laboratory check standards, duplicates, triplicates, and surrogate compounds analyzed along with study samples.

*Precision* is a measure of the ability to consistently reproduce results. Precision will be evaluated by analysis of check standards, duplicates, and spikes. Results of laboratory duplicate (split) analyses will be used to estimate laboratory precision.

*Bias* is the systematic error due to contamination, sample preparation, calibration, or the analytical process. Most sources of bias are minimized by adherence to established protocols for the collection, preservation, transportation, storage, and analysis of samples. Check standards (also known as laboratory control standards) contain a known amount of an analyte and indicate bias due to sample preparation or calibration.

Labeled congeners will be added to dioxin/furans samples prior to extraction. They have similar characteristics but do not interfere with resolution of target compounds. Their recovery is used to estimate the recovery of target compounds in samples.

The lowest concentrations of interest in Table 3 are the reporting limits MEL and their contractors have reported for analysis of similar sediment sample analysis from other studies.

Data outside MQOs will be evaluated for appropriate corrective action by Columbia Analytical Services and MEL. The project manager will be contacted by laboratory quality assurance personnel to discuss how to handle the data. The final decision to accept, to accept with qualification, or to re-analyze the samples in question will be the responsibility of the project manager.

Analyte	LCS or SRM <sup>1</sup> (% Recovery)	Duplicate/ Triplicate Samples	Surrogate Recoveries (% Recovery)	Lowest Concentration of Interest
Dioxin/Furans	Varies <sup>2</sup>	$\leq$ 50% RPD <sup>3</sup>	Labeled Congeners-	
TOC	75 – 125	≤ 20% RPD	NA	0.1 %
Grain Size	NA	$\leq 20\%$ RSD <sup>4</sup>	NA	NA

<sup>1</sup> Laboratory control sample or standard reference material.

<sup>2</sup> The NIST-SRM #1944 (www-naweb.iaea.org/nahu/nmrm/nmrm2003/material/ni1944.htm) will be analyzed for the project.

<sup>3</sup> Relative percent difference (difference between two samples divided by their mean, times 100).

<sup>4</sup> Relative standard deviation (standard deviation of three or more samples divided by the mean, times 100).

#### Comparability

We will ensure comparability of study results by using standard operating procedures and adhering to established data quality criteria consistent with previous Oakland Bay studies analyzing dioxin and furans in sediment. Detection limits will be equal to or better than other sediment investigations conducted in the basin.

#### Representativeness

The sampling design was developed to obtain representative data on dioxin and furans being discharged to Oakland Bay from study streams. We will ensure representativeness by using appropriate sampling and sample handling procedures, using composite samples, and using a sampling network that defines areas for needed follow-up.

#### **Completeness**

Completeness can be defined as the need to collect enough valid data to allow decisions to be made for which the study was designed. The goal of completeness is to collect and analyze 100% of the samples described in the sampling plan.

## **Sampling Design**

This study will generate baseline data for dioxin and furans that may be discharged to Oakland Bay from Shelton, Goldsborough, and Johns Creeks. The data are needed to (1) determine if these major surface water sources are likely to be discharging dioxin and furans to the bay, (2) assist with identifying locations of potential upstream sources, (3) establish baseline conditions for comparisons to future sediment evaluations, and (4) recommend needed follow-up activities.

Concentrations of dioxin and furans are expected to be below detection levels in whole water samples. Sediments were chosen to quantify the contaminants because they are typically detected at higher concentrations, not requiring specialized sample techniques. Sediment also represents a chronology of contaminant discharge over a longer period than a single point or grab sample from water. Sample sites were selected to correspond to stream access, availability of fine sediment, isolation of areas, and changes in land use.

In addition to sediment, soils samples will be collected from the mounded fill adjacent to the downstream Shelton Creek site (Figure 2). The fill appears to be made largely from ash. The ash mound has little vegetative cover and washes directly into Shelton Creek.

Samples for TOC and grain size will be collected to evaluate predictable relationships with dioxin and furans. They will also allow normalization of dioxin and furan results for site to site comparisons.

Samples will be collected once at each site, during fall of 2011. Areas with accumulations of fine sediment will be targeted for sampling. If accumulations of fine sediment cannot be located at a site, sediment traps will be deployed for between one and two months.

Sample time was selected to represent lower flows to allow access to sediment following the summer dry period. Sample sites are shown on Figure 2. Table B-1 in Appendix B presents latitude, longitude, and general description information for each site.

Downstream sample locations within study creeks will be as close to discharge as possible, avoiding marine influence if possible. Sampling will occur during low tide for downstream sites, avoiding any possible upstream movement of marine particulates.

## **Sampling Procedures**

To the extent possible, sediment sampling methods will follow PSEP (1996) protocols. All persons processing samples will also be familiar with standard operating procedures (SOPs) for field sampling as outlined in Ecology SOPs EAP040 (Blakley, 2008) and EAP013 (Janisch, 2006).

Surface sediment samples will be collected by use of a stainless steel 0.05 m<sup>2</sup> Ponar grab or stainless steel spoon depending on depth of the overlying water at each site. Soil samples will be collected using dedicated stainless steel spoons. The latitude and longitude of sediment and soil stations will be located by a global positioning system (GPS) and recorded in field logs. Station position relative to significant land structure will also be recorded. Other parameters also recorded in field logs include site name, sampler names, date, time, weather conditions, sample identification, and any other pertinent comments about the sample or site.

Following collection of each sediment grab, an evaluation of acceptability will be made. Information about each grab will be recorded in field logs. A Ponar grab will be considered acceptable if it is not overfilled, overlying water is present but not overly turbid, and the sediment surface appears intact.

Any overlying water will be siphoned off prior to sub-sampling. Equal volumes of sediment will be removed from three separate grabs per site when available. Dedicated stainless steel spoons and bowls will be used for sub-sampling and to homogenize sediments or soil from each station to a uniform color and consistency. Debris on the sediment surface or materials contacting the sides of the Ponar grab will not be retained for analysis.

Dioxin can be broken down by sunlight (photolysis) and free radicals in the atmosphere (USDOH, 1998). For soil samples the top 10 centimeters (cm) of surface soil will be removed and discarded. The soil below the top 10 cm will be collected and retained for analysis.

If adequate amounts of fine sediment cannot be located at a site, sediment traps will be deployed to collect suspended sediment. Each sediment trap will consist of a 4-inch diameter Plexiglas cylinder, mounted vertically on a concrete block and anchored by lanyard and stake. Traps will be deployed in low velocity areas of streams collecting sediment over a one to two month period. Following retrieval, sediment will be allowed to settle. Overlying water will be siphoned off and remaining sediment will be placed in sample containers. Figure C1 in Appendix C shows a typical sediment trap design, proposed as an alternative to grab sampling when fine sediment is not available. Additional information on design and use of the sediment traps can be found in Johnson et al. (2011).

Homogenized sediment or soil from each station will be placed in 8-oz. glass jars with Teflon-lined lids for analysis of dioxin and furans. Sample containers will be cleaned to EPA (1992) QA/QC specifications and certified for trace organic analyses. Additionally, 2-oz. glass jars will be filled with homogenate for total organic carbon analysis, while 8-oz. plastic jars will be filled for determination of grain size.

All equipment used to collect sediment or soil samples will be washed thoroughly with tap water and Liquinox detergent, followed by sequential rinses of hot tap water, de-ionized water, and pesticide-grade acetone. Sampling equipment will be air dried between each cleaning step under a fume hood. Following the last rinse, the air-dried equipment will be wrapped in aluminum foil, dull side contacting equipment, until used in the field. The same cleaning procedure will be used on the grab sampler and sediment trap cylinders prior to going into the field. To avoid crosscontamination between sample stations, the grab will be thoroughly brushed down with on-site water at each of the next sample locations.

Immediately following collection, sediment and soil samples will be placed in coolers on ice at 4°C and transported to MEL within 48 hours. MEL will ship the samples in coolers to the contract laboratory.

Requirements for containers, preservation, and holding times are listed in Table 4. Chain-of-custody procedures will be maintained throughout the sampling and analysis process.

Parameter	arameter Container <sup>1</sup> Preservative		Holding Time	
Dioxin/Furans	Certified 8-oz Amber Glass w/ Teflon Lid Liner	Store: Freeze, -18°C. Transport ( <i>protect from</i> <i>light</i> ): Cool to 4°C.	1 Year Extraction 1 Year Analysis	
Grain Size	8-oz Glass or Poly	Cool to 4°C.	6 Months	
TOC <sup>2</sup> Certified 2-oz Glass w/ Teflon Lid Liner		Cool to 4° C.	14 Days; 6 months frozen	

Table 4. Containers, preservation, and holding times for study samples.

<sup>1</sup> Sample containers provide by Manchester Environmental Laboratory or their contract laboratory.

<sup>2</sup> Total organic carbon.

#### **Measurement Procedures**

#### Laboratory

The analytical parameters, sample numbers, expected range of results, reporting limits, and analytical methods to be used for the study are presented below in Table 5. Method selection is based on detection limits and what is achievable for analysis of dioxin and furans in sediment.

All project samples will be analyzed at MEL or through a contractor selected by MEL. Laboratories contracted by MEL must be on the Ecology list of accredited laboratories (<u>www.ecy.wa.gov/programs/eap/labs/lab-accreditation.html</u>). Additionally, when available, laboratories conducting analysis for Ecology studies must be on the General Administration master contract. MEL and contract laboratories may use other appropriate methods following consultation with the project lead.

Analytical methods were selected to achieve reporting limits equal to or better than the lowest concentration of interest. Dioxin/furan analysis of sediment will be contracted out by MEL. The samples will be analyzed by HRGC/HRMS using EPA 1613B methods.

Analysis	Number of Samples <sup>1</sup>	Expected Range of Results	Reporting Limit	Sample Preparation Method	Analytical Method
Dioxins/Furans	15	0.01 – 50 ng/Kg, dry	0.05 ng/Kg, dry	Silica-gel if needed	EPA 1613B
TOC	14	1.0 - 20.0%	0.1%	Combustion/NDIR	PSEP-TOC <sup>2</sup>
Grain Size <sup>3</sup>	14	NA	0.1%	Sieve and pipette	PSEP, 1996

Table 5. Analytical methods for analysis of sediment samples.

<sup>1</sup> Includes quality control samples-one field replicate and one standard reference material (SRM) for dioxin/furans. <sup>2</sup> From MEL, 2008

<sup>3</sup> Four fractions – gravel/sand/silt/clay

NA: Not applicable

MEL will contract out the analysis of sediment collected for dioxin/furans to Columbia Analytical Services, Houston, Texas. Grain size will be contracted to Analytical Resources Incorporated, in Tukwila, Washington. MEL will analyze the total organic carbon samples.

Analytical cost for the project is estimated to be \$10,766 (Table 6). The estimate includes a 50% cost discount for analysis conducted by the MEL. There is also a 25% surcharge included for MEL's contracting services and data quality review for results from contract laboratories.

The cost estimate assumes analysis of sediment collected on one occasion from Shelton, Goldsborough, and Johns Creeks totaling 12 sites, with one additional field duplicate sample. If during sample collection more samples are needed to characterize an area or inputs to streams, the project budget can allow for collection of up to five additional sample sets.

Analysis	Number of Samples	Number of QA Samples	Sample Total	Cost Per Sample	Subtotal
Dioxin/Furans	12	3	15	\$465	\$6,975
TOC	12	2	14	\$42	\$588
Grain Size	12	2	14	\$90	\$1,260
Contracting Services:					\$2,058
			C	rand Total:	\$10,766

 Table 6. Cost of sediment sample analysis (includes contract services).

## **Quality Control Procedures**

#### Field

Field quality control (QC) samples provide an estimate of the total variability of study results for field and laboratory. For this study, field QC will involve collection and analysis of duplicate samples. Field duplicates will consist of three discrete grab samples collected from a sample site, placed in a stainless steel bowl previously cleaned to analyte specific requirements, homogenized to a consistent color and texture, and placed in two appropriate sample containers at the same time and location for each analysis. Table 7 lists the number and type of field QC samples to be analyzed for the project.

Analysis	Duplicates <sup>1</sup>
Dioxin/Furans	2/study
Total Organic Carbon (TOC)	2/study
Grain Size	2/study <sup>2</sup>

Table 7. Field quality control samples.

<sup>1</sup> Two samples taken at the same time and place from a single homogenized batch of three grab samples.

<sup>2</sup> Triplicates are required by PSEP methods for grain size.

Sampling will be conducted to avoid cross-contamination. Samplers will wear non-talc nitrile gloves during collection. Immediately following collection, samples will be tagged with appropriate identification information and stored in iced coolers, until delivered to MEL.

To help minimize field variability from sample collection, field samplers will be familiar with and follow methods described in standard operating procedures SOP EAP040 developed for collection of freshwater sediments (Blakley, 2008), SOP EAP013 for acquiring geographic coordinates (Janisch, 2006) and PSEP (1996) protocols for sample collection. All sampling equipment will be cleaned prior to going into the field according to protocols (see *Field Procedures* section). Pre-cleaned sampling equipment will be wrapped in aluminum foil until used.

#### Laboratory

MEL routinely runs laboratory control samples for total organic carbon which will be satisfactory for the purposes of this project. MEL will follow SOPs as described in the *Manchester Environmental Laboratory Quality Assurance Manual* (MEL, 2006). Laboratory QC samples for this project are presented in Table 8.

Analysis	Method Blank	Check Standard	Duplicate <sup>1</sup> Analysis	Labeled Compounds	OPR Standards	Standard Reference Material
Dioxins/Furans	1/batch	1/batch		All samples	Each batch	1/batch
TOC	1/batch	1/batch	1/batch			
Grain Size			2/batch			

Table 8. Laboratory quality control samples for sediments.

<sup>1</sup>PSEP methods require a triplicate analysis for grain size.

#### **Data Management Procedures**

All field data and observations will be recorded in notebooks on waterproof paper. The information contained in field notebooks will be transferred to Excel spreadsheets after return from the field. Data entries will be independently verified for accuracy by another member of the project team.

Case narratives, included in the data package from MEL, will discuss any problems encountered with the analyses, corrective action taken, changes to the requested analytical method, and a glossary for data qualifiers. Laboratory QC results will also be included in the data package. This will include results for surrogate recoveries, laboratory duplicates, matrix spikes, and laboratory blanks. The information will be used to evaluate data quality, determine if the MQOs were met, and act as acceptance criteria for project data.

Field and laboratory data for the project will be entered into Ecology's EIM system. Laboratory data will be downloaded directly into EIM from MEL's data management system. Data from contract laboratories will be submitted in electronic format for inclusion into the EIM system.

#### **TEQs and Non-detects**

The toxicity of dioxin and furan congeners can range over orders of magnitude. A TEQ system was developed by the World Health Organization (WHO, 2005) for human risk assessment based on the seventeen chlorinated dioxin and furan congeners of concern, and applied by measuring them in relation to 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), the most toxic form of dioxin.

Each of the 17 dioxin and furan congeners is assigned a Toxic Equivalency Factor (TEF) as a decimal fraction of that compound's toxicity relative to TCDD, which has a TEF of 1. Congeners detected in a sample are multiplied by their respective TEFs and results are summed. The summed values are the TEQ. The TEQ can then be compared to the NTR human health water quality criterion for TCDD.

Often in dioxin and furan analysis not all of the 17 congeners in a sample are above reporting limits. A number of possible options exist for censored data from not using non-detected data to using  $\frac{1}{4}$ ,  $\frac{1}{2}$ , or the full detection limit for the purpose of calculating TEQs. For this study if a congener is not detected in a sample it will not be included in the TEQ estimates.

## **Audits and Reports**

MEL participates in performance and system audits of their routine procedures. Results of these audits are available upon request.

A draft report of the study findings will be completed by the principal investigator in May 2012 and a final report in September 2012. The report will include, at a minimum, the following:

- Map showing all sampling locations and any other pertinent features of the study area.
- Coordinates of each sampling site.
- Description of field and laboratory methods.
- Discussion of data quality and the significance of any problems encountered.
- Summary tables of the chemical and physical data including dioxin TEQs.
- Results of the dioxin and furans related to available sediment quality guidelines and background data.
- Complete set of chemical and physical data and MEL quality assurance review in the Appendix.

Upon study completion, all project data will be entered into Ecology's EIM system. Public access to electronic data and the final report for the study will be available through Ecology's Internet homepage (www.ecy.wa.gov).

### **Data Verification**

Data verification is a process conducted by people producing data. Verification of laboratory data is normally performed by a MEL unit supervisor or an analyst experienced with the method. It involves a detailed examination of the data package using professional judgment to determine whether the measurement quality objectives (MQOs) have been met.

Final acceptance of the project data is the responsibility of the principal investigator. The complete data package, along with MEL's written report, will be assessed for completeness and reasonableness. Based on these assessments, the data will either be accepted, accepted with qualifications, or rejected and re-analysis considered.

Data verification involves examining the data for errors, omissions, and compliance with QC acceptance criteria. MEL's SOPs for data reduction, review, and reporting will meet the needs of the project. Data packages, including QC results for analyses conducted by MEL, will be assessed by Ecology's QA Coordinator using the EPA Functional Guidelines for Organic Data Review.

MEL staff will provide a written report of their data review which will include a discussion of whether (1) MQOs were met; (2) proper analytical methods and protocols, including storage conditions and holding times, were followed; (3) calibrations and controls were within limits; and (4) data were consistent, correct, and complete, without errors or omissions.

## Data Quality (Usability) Assessment

After the project data have been reviewed and verified, the principal investigator will determine if the data are of sufficient quality to make determinations and decisions for which the study was conducted. The data from the laboratory's QC procedures, as well as results from field and laboratory duplicates, will provide information to determine if MQOs (Table 3) have been met. Laboratory and quality assurance staff familiar with assessment of data quality may be consulted. The project final report will discuss data quality and whether the project objectives were met. If limitations in the data are identified, they will be noted.

Some analytes may be reported near the detection capability of the selected methods. MQOs are difficult to achieve for these results. MEL's SOP for data qualification and best professional judgment will be used in the final determination of whether to accept, reject, or accept the results with qualification. The assessment will be based on a review of field duplicates, along with laboratory QC results. This will include assessment of laboratory precision, accuracy, matrix interferences, and the success of laboratory QC samples meeting control limits.

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# Appendices

#### Appendix A. Dioxin and Furans Achievable Reporting Limits

Dioxin/Furan Congener	CAS No.	$EDL^1$	MRL <sup>2</sup>
<b>Dioxin</b> (ng/Kg, dry)			
2,3,7,8-TCDD	1746-01-6	0.066	0.2
1,2,3,7,8-PeCDD	40321-76-4	0.066	1
1,2,3,4,7,8-HxCDD	57653-85-7	0.050	1
1,2,3,6,7,8-HxCDD	39227-28-6	0.062	1
1,2,3,7,8,9-HxCDD	19408-74-3	0.053	1
1,2,3,4,6,7,8-HpCDD	35822-46-9	0.054	1
OCDD	3268-87-9	0.099	2
<b>Furans</b> (ng/Kg, dry)			
2,3,7,8-TCDF	51207-31-9	0.073	0.2
1,2,3,7,8-PeCDF	57117-41-6	0.050	1
2,3,4,7,8-PeCDF	57117-31-4	0.044	1
1,2,3,4,7,8-HxCDF	57117-44-9	0.049	1
1,2,3,6,7,8-HxCDF	72918-21-9	0.052	1
1,2,3,7,8,9-HxCDF	70648-26-9	0.069	1
2,3,4,6,7,8-HxCDF	60851-34-5	0.049	1
1,2,3,4,6,7,8-HpCDF	67562-39-4	0.048	1
1,2,3,4,7,8,9-HpCDF	55673-89-7	0.056	1
OCDF	39001-02-0	0.078	2

Table A-1. Expected quantitation limits for dioxin and furan analysis.

<sup>1</sup> Estimated detection limit <sup>2</sup> Method reporting limit

Note: Increasing the amount of sample material for extraction may lower the estimated quantitation limits.

#### Appendix B. Sample Site Descriptions

Waterbody	Latitude	Longitude	Location
Shelton Creek (Shel 1)	47.2139	-123.0951	100 m from discharge
Shelton Creek (Shel 2)	47.2139	-123.0983	At Front Street
Shelton Creek (Shel 3)	47.2172	-123.0994	Base of Capitol Hill
Shelton Creek (Shel 4)	47.2179	-123.1068	Sediment Pond at Laurel St
Shelton Creek (Soil 1)	47.2140	-123.0950	At Shel 1 site
Shelton Creek (Soil 2)	47.2139	-123.0949	At Shel 1 site
Goldsborough Creek (Gold 1)	47.2093	-123.0968	200 m from discharge
Goldsborough Creek (Gold 2)	47.2115	-123.1079	At 7 <sup>th</sup> Street bridge
Goldsborough Creek (Gold 3)	47.2094	-123.1250	Shelton-Matlock Rd bridge
Goldsborough Creek (Gold 4)	47.2109	-123.1394	At fish weirs above Miles Sand
Johns Creek (John 1)	47.2483	-123.0458	At Highway 3 bridge
Johns Creek (John 2)	47.2502	-123.0749	Just above PUD complex

Table B-1. Sample sites, coordinates, and location.

Datum: NAD 83 HARN

### Appendix C. Sediment Trap Design



Figure C1. Typical sediment trap design for collection of suspended sediments.

## Appendix D. Abbreviations

Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency
GPS	Global Positioning System
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective
NTR	National Toxics Rule
QA	Quality assurance
RPD	Relative percent difference
RSD	Relative standard deviation
SOP	Standard operating procedures
TEF	Toxic equivalency factor
TEQ	Toxic equivalents
TOC	Total organic carbon
TSS	Total suspended solids