

DEPARTMENT OF  
**ECOLOGY**  
State of Washington

## **Addendum to Quality Assurance Monitoring Plan**

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### **Statewide River and Stream Ambient Water Quality Monitoring**

*Selected Toxics in the  
Upper Green River Watershed*

February 2023

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## Publication Information

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This Quality Assurance Monitoring Plan Addendum is on the Department of Ecology's website at <https://apps.ecology.wa.gov/publications/SummaryPages/2303101.html>. This is an addition to an original Quality Assurance Monitoring Plan (QAMP). It is not a correction to the original plan.

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**Addendum to**  
**Quality Assurance Monitoring Plan**  

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**Statewide River and Stream**  
**Ambient Water Quality Monitoring**  
*Selected Toxics in the Upper Green River Watershed*

by  
Brandee Era-Miller, Cleo Neculae, and Meghan Rosewood-Thurman

February 2023

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EAP: Environmental Assessment Program

NWRO: Northwest Regional Office

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## 2.0 Abstract

The Department of Ecology's (Ecology's) *Statewide River and Stream Ambient Water Quality Monitoring Program* has been collecting monthly water quality samples at over 60 freshwater monitoring locations since the 1950s. Ecology's Freshwater Monitoring Unit (FMU) leads the program. Parameters monitored monthly include temperature, pH, dissolved oxygen, streamflow, bacteria, and nutrients. In addition, FMU collects metals data and water hardness data every other month at a subset of select stations.

During water year 2023 (Oct 2022 – Sept 2023), FMU staff were asked to collect additional samples of toxic chemicals (toxics) at one location: long-term monitoring station 09A190, located on the Green River above Kanaskat-Palmer State Park, about 6.5 miles downstream of Howard Hanson Dam.

The seven toxics parameters are as follows:

- *Three metals*: Arsenic, copper, zinc
- Hardness
- Carcinogenic polycyclic aromatic hydrocarbons (cPAHs)
- Di [2-ethylhexyl] Phthalate (DEHP)
- Polychlorinated biphenyls (PCBs)

As one of the select metals monitoring stations for water year 2023, FMU will already collect samples every other month for metals (including arsenic, copper, and zinc) and hardness at station 09A190. FMU has been asked to collect samples for arsenic, copper, zinc, and hardness during the months when they would not usually collect metals samples.

The monthly sampling for metals (arsenic, copper, zinc), hardness, and organic pollutants (cPAHs, DEHP, PCBs) is needed to support pollutant-modeling efforts in the Green/Duwamish River watershed.

This Quality Assurance Monitoring Plan (QAMP) addendum to the *Statewide River and Stream Ambient Water Quality Program* QAMP describes the additional elements needed for the collection of the proposed toxics.

## 3.0 Background

### 3.1 Introduction and problem statement

The Green/Duwamish watershed has 303(d) listings for over 50 parameters, including toxic chemicals (toxics) and conventional parameters. Segments of the lower Duwamish River are in various stages of sediment cleanup under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) or Superfund Act, and the Washington State Model Toxics Control Act (MTCA).

The Green/Duwamish Pollutant Loading Assessment (PLA) is a study that addresses seven of these parameters: arsenic, copper, zinc, water hardness, polychlorinated biphenyls (PCBs), carcinogenic polycyclic aromatic hydrocarbons (cPAHs), and di [2-ethylhexyl] Phthalate (DEHP).

The primary goals of the PLA are as follows:

- Model the impact of point and nonpoint sources to understand what level of effort is necessary to control these sources,
- Prevent the recontamination of sediment cleanup, and
- Attain water quality standards.

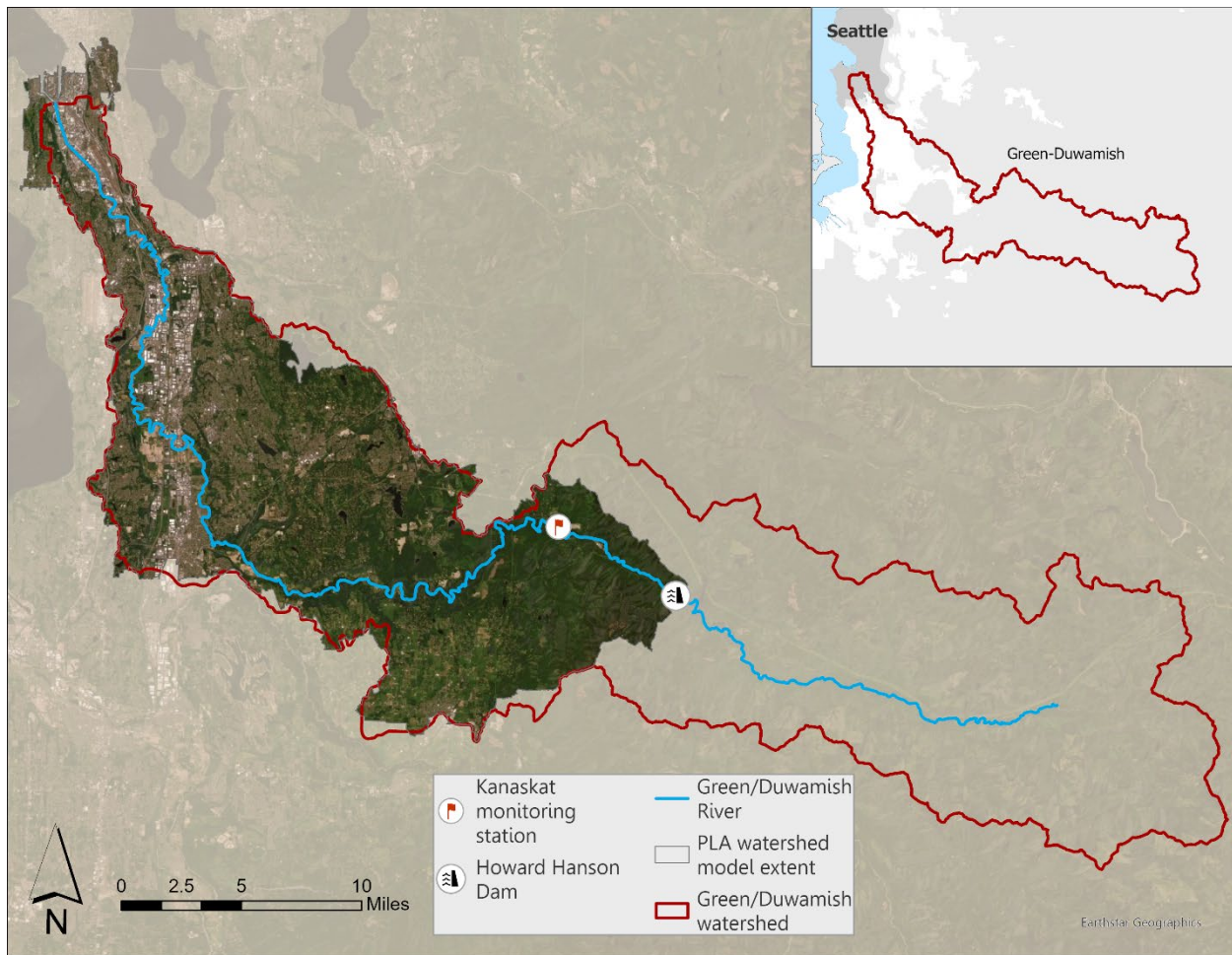
The PLA models several pathways, including stormwater, groundwater, interflow, and air deposition, within the entire Green/Duwamish watershed downstream of Howard Hanson Dam (HHD).

While extensive studies have produced significant amounts of data for the Lower Duwamish watershed, the data is sparse further upstream, toward the HHD, which makes up the upper boundary condition for the PLA's watershed model.

This Quality Assurance Monitoring Plan (QAMP) addendum outlines the study design to collect data for metals (arsenic, copper, zinc), water hardness, and organic pollutants (PCBs, cPAHs, phthalates) at the water quality monitoring station 09A190 on the Green River above Kanaskat-Palmer State Park. The newly collected data will be used to validate our calibrated model, show how concentrations of these toxics change under varying weather and environmental conditions, and determine whether there are any relationships among the toxic's concentrations.

### 3.2 Study area and surroundings

The PLA's watershed model describes processes and pathways for metals, PCBs, cPAHs, and phthalates for about 260 square miles of the Green/Duwamish watershed, about half of the entire watershed area. The model's upper boundary is set at HHD, about 6.5 river miles upstream of Ecology's Environmental Assessment Program (EAP) long-term monitoring station 09A190, located on the Green River above Kanaskat-Palmer State Park (Figure 1).



**Figure 1. Map of the Green/Duwamish watershed and PLA watershed model extent.**

Since most of the land upstream of the monitoring station is undeveloped, sampling for these organics and metals parameters upstream of Kanaskat-Palmer State Park will help us to better understand the contribution of the baseline pollution, such as air deposition, to the watershed. This is separate from the contribution of point sources and other nonpoint sources.

## 4.0 Project Description

### 4.1 Project goals

- Collect monthly samples for metals (arsenic, copper, and zinc), hardness, carcinogenic polycyclic aromatic hydrocarbons (cPAHs), di [2-ethylhexyl] Phthalate (DEHP) and PCB congeners at the long-term monitoring station 09A190, located on the Green River above Kanaskat-Palmer State Park. These samples will be collected in addition to the regular ambient monitoring conducted by EAP's Freshwater Monitoring Unit (FMU) staff.
- Provide high quality toxics data to Ecology's Northwest Regional Office Water Quality Program (NWRO-WQP) to support the PLA.



## 5.0 Organization and Schedule

### 5.1 Key individuals and their responsibilities

Ecology staff involved in this project are listed in Table 1.

**Table 1. Project Personnel and Responsibilities.**

Staff	Title	Responsibilities
<b>Cleo Neculae</b> NWRO-WQP TMDL Lead Phone: (425) 389-2685	Client	Co-writes QAMP addendum; provides periodic check-in on the project.
<b>Yi Xiong</b> NWRO-ISU Data Modeler Phone: (425) 516-4104	Client	Recipient of final data packages for use in PLA Model.
<b>Meghan Rosewood-Thurman</b> Toxics Studies Unit, EAP Phone: (360) 819-3566	Project Manager	Coordinates with MEL staff on review and validation of monthly data packages; provides final data to client; enters data into EIM at end of study.
<b>Brandee Era-Miller</b> Toxics Studies Unit, EAP Phone: (360) 764-3559	Project Assistance	Co-writes QAMP addendum and assists Project Manager with data review.
<b>Welles Bretherton</b> Freshwater Monitoring Unit, EAP Phone: (360) 407-6770	Field Lead	Collects monthly toxics samples and sends to MEL.
<b>Brad Hopkins</b> Freshwater Monitoring Unit, EAP Phone: (360) 701-6686	Unit Supervisor for Field Lead	Reviews and approves draft and final QAMP addendums.
<b>James Medlen</b> Toxics Studies Unit, EAP Phone: (360) 480-6175	Unit Supervisor for Project Manager	Reviews the project scope and budget; tracks progress; reviews and approves the draft and final QAMP addendums.
<b>Jessica Archer</b> Statewide Coordination Section, EAP Phone: (360) 890-2721	Section Manager for Project Manager	Reviews the project scope and budget; reviews and approves the draft and final QAMP addendums.
<b>Nancy Rosenbower</b> MEL, EAP Phone: (306) 871-8800	MEL Project Manager and Sample Coordinator	Coordinates with project manager, field staff, and contract laboratories on sample chain-of-custody.
<b>John Weakland</b> MEL, EAP Phone: (360) 480-7515	Data Validator	Provides data validation on data packages from the contract laboratories.
<b>Christina Frans</b> MEL, EAP Phone: (360) 995-2473	MEL Quality Assurance Coordinator	Reviews and approves draft statement of work for lab analysis and data validation services. Reviews lab data package and data validation package to verify the statement of work requirements are met.
<b>Dean Momohara</b> MEL, EAP Phone: (360) 871-8801	Acting Director	Reviews and approves the final QAMP addendum.
<b>Arati Kaza</b> Phone: (360) 407-6964	Ecology Quality Assurance Officer	Reviews and approves the draft and final QAMP addendums.

EAP = Environmental Assessment Program

EIM = Environmental Information Management database

MEL = Manchester Environmental Laboratory

NWRO = Northwest Regional Office

PLA = Pollutant Loading Assessment

TMDL = Total Maximum Daily Load (water clean-up plan)

WQP = Water Quality Program



## 5.4 Proposed project schedule

Monthly sampling will take place during water year 2023 (Oct 2022 through Sept 2023). If NWRO-WQP staff decide they need additional sample data after September 2023, they may request an extension of sample collection into the following water year if resources are available.

### Organic Parameters

Due to the 7-day holding time, analysis of cPAHs and DEHP will occur monthly such that there will be separate data packages generated for each monitoring event (12 data packages in total). The holding time for PCB congeners is one year. EAP’s Manchester Environmental Laboratory (MEL) will store the PCB samples for six months and send them off for analysis by the contract lab (CL) twice a year. Thus, there will be two analytical batches/data packages generated for PCBs over the course of the yearlong study.

The CLs will provide Level 4 data packages to MEL within 60 days of sample receipt. MEL will conduct Stage 4 data validation on the data on a quarterly basis for cPAHs and DEHP and twice a year (biannually) for PCBs. The proposed schedule for the project is shown in Table 2.

### Metals

As part of the *Statewide River and Stream Ambient Water Quality Monitoring Program*, FMU staff will collect their typical suite of metals during “even” months starting October 2022. For example, January is an odd month (1<sup>st</sup>), and February is an even month (2<sup>nd</sup>). Also, they will collect three metals, arsenic, copper, and zinc, during the “odd” months starting November 2022. Hardness is analyzed along with metals. MEL will analyze all samples.

**Table 2. Proposed schedule for completing field and laboratory work, sending final data deliverables to client, and data entry into EIM.**

Field and laboratory work	Due date	Lead staff
Field work completed	Monthly/September 2023*	Welles Bretherton
Laboratory analyses completed	Monthly/Biannual for PCBs	Contract Labs and MEL
Data validation	Quarterly/ Biannual for PCBs	MEL
Electronic data deliverable	Quarterly/February 2024*	Meghan Rosewood-Thurman
Environmental Information System (EIM) database		
EIM Study ID	PLAGreenToxics	
Product	Due date	Lead staff
EIM data loaded	February 2024	Meghan Rosewood-Thurman
EIM Quality Assurance	March 2024	Brandee Era-Miller
EIM complete	April 2024	Meghan Rosewood-Thurman

EIM = Environmental Management System database

MEL = Manchester Environmental Laboratory

\*Monthly sampling will take place during water year 2023 (Oct 2022 – Sept 2023).

Due dates represent completion of 12 months of sample collection, with the last collection in Sept 2023.

## 5.5 Budget

The budget for the project is shown in Table 3. The *Statewide River and Stream Ambient Water Quality Monitoring Program* will pay for metals analysis during “even” sampling months starting in October 2022. Ecology’s NWRO-WQP will pay for metals analysis for the “odd” months (starting in November), as well as the additional toxics listed in Table 3.

**Table 3. Toxics and Metals Budget Analysis for Monthly Sampling.**

Parameter	Laboratory	No. of Samples	No. of QA Samples*	Total No. of Samples	Cost Per Sample	Subtotal
DEHP and cPAHs	Eurofins	12	5	17	\$157	\$2,669
PCB Congeners	SGS-AXYS	12	3	15	\$905	\$13,575
<b>Subtotal</b>						\$16,244
MEL Fee (30%) <sup>†</sup>						\$4,873
Metals - <i>total</i> <sup>‡</sup>	MEL	6	0	6	\$82	\$492
Metals - <i>dissolved</i> <sup>‡</sup>	MEL	6	0	6	\$78	\$468
<b>Total</b>						<b>\$22,077</b>

cPAHs = carcinogenic polycyclic aromatic hydrocarbons

DEHP = di (2-ethylhexyl) Phthalate

PCBs = Polychlorinated biphenyls

Metal, total = arsenic, copper, zinc, and hardness

Metals, dissolved = arsenic, copper, and zinc

MEL = Manchester Environmental Laboratory

\*Includes two field replicate samples and one field blank for all analytes. Includes one matrix spike and one matrix spike duplicate analysis for DEHP and cPAHs. QA samples for metals will be collected by the *Statewide River and Stream Ambient Water Quality Monitoring Program* during even sampling months starting in October 2022.

<sup>†</sup> MEL charges a fee of 30% for contracting of analysis and data validation services.

<sup>‡</sup> Metals includes arsenic, copper, zinc, and hardness only.

## 6.0 Quality Objectives

### 6.1 Data quality objectives

The main data quality objective (DQO) for this project is to collect monthly data for arsenic, copper, zinc, hardness, cPAHs, DEHP, and PCB congeners at FMU’s long-term monitoring station 09A190, located on the Green River above Kanaskat-Palmer State Park. This will be during water year 2023 (Oct 2022 – Sept 2023) to support the Green/Duwamish PLA. This DQO will be met by (1) following the original QAMP and this QAMP addendum and (2) meeting the specific Measurement Quality Objectives (MQOs) for the toxics’ parameters described below.

### 6.2 Measurement quality objectives

MQOs are defined here as the precision, bias, and accuracy guidelines against which field and laboratory quality control (QC) results are compared.

## 6.2.1 Targets for precision, bias, and sensitivity

### 6.2.1.1 Precision

Precision is a measure of the variability in the results of replicate measurements due to random error. Precision will be measured as the relative percent difference (RPD) for replicate samples. RPDs for lab duplicates and matrix spike duplicates are shown in [Table 4](#).

### 6.2.1.2 Bias

Bias is the difference between the population mean and the true value and will be measured as acceptable percent recovery. 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, LCS), matrix spikes, and labeled surrogates contain a known amount of an analyte and indicate bias due to sample preparation or calibration. Acceptance limits for LCS and matrix spike recoveries are provided in [Table 4](#).

### 6.2.1.3 Sensitivity

Sensitivity is a measure of the capability of a method to isolate the concentration of a substance from the analytical method's background noise. Sensitivity is commonly described as reporting limit, or detection limit. Lab reporting limits are shown in [Table 4](#). Method capabilities and lab procedures are discussed in more detail in [Section 9](#).

**Table 4. Measurement quality objectives for laboratory analyses.**

QC Measure	Bias	Precision	Bias	Precision	Bias	Sensitivity
Parameter	LCS % Recovery Limits	Lab Duplicates (% RPD)	Matrix Spikes % Recovery Limits	Matrix Spike Duplicates (% RPD)	Surrogate % Recovery Limits	Lab Reporting Limits
cPAHs	15-130*	40	42-110*	40	50-150*	0.05 - 0.1 <sup>†</sup> ug/L
DEHP	80-130	40	35-130	40	30 -150	0.2 ug/L
PCB congeners	50-150	50	NA	NA	25-150	Varies by congener
Arsenic, Copper & Zinc (Total) <sup>‡</sup>	85-115	20	75-125	20	NA	0.1, 0.4, 5 ug/L
Arsenic, Copper & Zinc (Dissolved) <sup>‡</sup>	85-115	20	75-125	20	NA	0.1, 0.1, 1 ug/L
Hardness <sup>‡</sup>	85-115	20	75-125	20	NA	1 mg/L

cPAHs = carcinogenic polycyclic aromatic hydrocarbons

DEHP = di (2-ethylhexyl) Phthalate

PCBs = Polychlorinated biphenyls

\* Recovery limits for PAHs vary by parameter. Recovery limits for Benzo(a)pyrene shown in table.

<sup>†</sup> Reporting limits for PAHs vary by parameter. The reporting limit for Benzo(a)pyrene is 0.1 ug/L.

<sup>‡</sup> Information obtained from the *Statewide River and Stream Ambient Water Quality Monitoring QAMP* (Von Prause, 2021).

NA = not applicable, matrix spikes are not performed for PCB congener method 1668C.

LCS = laboratory control standard

RPD = relative percent difference

# 7.0 Study Design

## 7.2 Field data collection

### 7.2.1 Sampling locations and frequency

Monthly sampling will occur at the long-term monitoring station 09A190, located on the Green River above Kanaskat-Palmer State Park. Carcinogenic PAHs, DEHP, and PCB congeners will be added to the regular set of parameters collected monthly as part of the *Statewide River and Stream Ambient Water Quality Monitoring Program*. Arsenic, copper, zinc, and hardness sampling will be added to the odd-numbered months (starting in November 2022) when metals are not usually collected by FMU, such that monthly sampling can occur for these metals of concern.

### 7.2.2 Laboratory analytes to be measured

#### 7.2.2.1 Metals

Arsenic, copper, and zinc are common inorganic contaminants found in polluted water. More information on these metals can be found at the following links:

- Arsenic: [Arsenic | Toxicological Profile | ATSDR \(cdc.gov\)](https://www.cdc.gov/TSP/ToxProfiles/ToxProfiles.aspx?id=22&tid=3)<sup>1</sup>
- Copper: [Copper | Toxicological Profile | ATSDR \(cdc.gov\)](https://www.cdc.gov/TSP/ToxProfiles/ToxProfiles.aspx?id=206&tid=37)<sup>2</sup>
- Zinc: [Zinc | Toxicological Profile | ATSDR \(cdc.gov\)](https://www.cdc.gov/TSP/ToxProfiles/ToxProfiles.aspx?id=302&tid=54)<sup>3</sup>

#### 7.2.2.2 Hardness

An increase of dissolved minerals (largely calcium and magnesium) results in hard water. Hardness creates mineral or scale deposits on industrial and domestic equipment. More information on hardness can be found on the [USGS website](https://www.usgs.gov/special-topics/water-science-school/science/hardness-water)<sup>4</sup> It also affects the bioavailability of metals and thus the toxicity to aquatic organisms. Acute and chronic freshwater aquatic life criteria for metals uses hardness values in the calculations. For more information, see [WAC 173-201A-240 Water Quality Standards for Surface Waters in the State of Washington](https://apps.leg.wa.gov/WAC/default.aspx?cite=173-201A)<sup>5</sup>

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<sup>1</sup> <https://www.cdc.gov/TSP/ToxProfiles/ToxProfiles.aspx?id=22&tid=3>

<sup>2</sup> <https://www.cdc.gov/TSP/ToxProfiles/ToxProfiles.aspx?id=206&tid=37>

<sup>3</sup> <https://www.cdc.gov/TSP/ToxProfiles/ToxProfiles.aspx?id=302&tid=54>

<sup>4</sup> <https://www.usgs.gov/special-topics/water-science-school/science/hardness-water>

<sup>5</sup> <https://apps.leg.wa.gov/WAC/default.aspx?cite=173-201A>

### 7.2.2.3 Organic Pollutants

Three organic toxic analytes/analyte groups will be measured for this project in support of the Green/Duwamish River PLA. The analytes include cPAHs, DEHP, and PCB congeners.

The PAHs of interest for this project are the analytes considered by the U.S. Environmental Protection Agency (EPA) to be carcinogenic. These carcinogenic PAHs include:

- Benz(a)anthracene
- **Benzo(a)pyrene**
- Benzo(b)fluoranthene
- Benzo(k)fluoranthene
- Chrysene
- Dibenz(a,h)anthracene
- Indeno(1,2,3-cd)pyrene

Benzo(a)pyrene is the PAH of highest interest for Green/Duwamish River PLA project due to its toxicity. [More information on carcinogenic PAHs can be found on the EPAs website<sup>6</sup>](#)

The cPAHs will also be converted to cPAH total equivalent concentrations (cPAH TEQs) for modeling use.

Many different types of phthalates are present in the environment. DEHP is the main phthalate of interest for the Green/Duwamish River PLA project.

[More information on DEHP can be found on CDC's website.<sup>7</sup>](#)

PCB congeners are analyzed as a suite of 209 possible congeners ranging in chlorination level from one chlorine to ten chlorine atoms.

[More information on PCBs can be found on EPA's website<sup>8</sup>.](#)

## 8.0 Field Procedures

### 8.2 Measurement and sampling procedures

Staff will follow EAP's Standard Operating Procedure (SOP) [EAP029, Version 1.6: Collection and Field Processing of Metals Samples \(Ward and Hoselton, 2018\) for collection of metals<sup>9</sup>](#) and [SOP EAP015, Version 1.4: Manually Obtaining Surface Water Samples \(Joy, 2019\)<sup>10</sup>](#) for the collection of cPAHs, DEHP and PCBs. Samples will be collected with an extension pole. Care will be taken to minimize exposure of the water sample to the air by quickly capping the sample after collection.

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<sup>6</sup> <https://www.epa.gov/risk/other-carcinogenic-polycyclic-aromatic-hydrocarbons>

<sup>7</sup> <https://wwwn.cdc.gov/TSPS/ToxFAQs/ToxFAQsDetails.aspx?faqid=377&toxid=65>

<sup>8</sup> <https://www.epa.gov/pcbs>

<sup>9</sup> <chrome-extension://efaidnbmnnnibpcajpegglefindmkaj/https://apps.ecology.wa.gov/publications/documents/1803204.pdf>

<sup>10</sup> <chrome-extension://efaidnbmnnnibpcajpegglefindmkaj/https://apps.ecology.wa.gov/publications/documents/2103208.pdf>

## 8.3 Containers, preservation methods, and holding times

**Table 5. Containers, preservation methods, and holding times.**

Parameter	Recommended Quantity*	Container	Holding Time	Preservation
cPAHs and DEHP	1 liter	1-liter amber glass bottle	7 days	Cool to $\leq 6^{\circ}\text{C}$
PCB Congeners	1 - 4 liters	1-liter amber glass bottle	1 year	Cool to $\leq 6^{\circ}\text{C}$
Arsenic, Copper & Zinc (Total) <sup>†</sup>	350 mL	500 mL HDPE bottle	6 months	HNO <sub>3</sub> to pH < 2
Arsenic, Copper & Zinc (Dissolved) <sup>†</sup>	350 mL	500 mL HDPE bottle	6 months	Filter within 15 minutes of collection; then add HNO <sub>3</sub> to pH < 2, Cool to $\leq 6^{\circ}\text{C}$ until preservation
Hardness <sup>†</sup>	100 mL	125 mL w/m poly bottle	6 months	H <sub>2</sub> SO <sub>4</sub> to pH < 2, Cool to $\leq 6^{\circ}\text{C}$ until preservation

cPAHs = carcinogenic polycyclic aromatic hydrocarbons

DEHP = di (2-ethylhexyl) Phthalate

PCBs = Polychlorinated biphenyls

\*An extra 1-liter bottle should be collected for both laboratories in case of breakage or need for reanalysis.

<sup>†</sup> Information from the *Statewide River and Stream Ambient Water Quality Monitoring QAMP* (Von Prause, 2021).

## 9.0 Laboratory Procedures

### 9.1 Lab procedures table

After a competitive bid process, Eurofins Environment Testing Northwest, LLC (Eurofins) was selected for analysis of cPAHs and DEHP. Ecology has a contract with SGS-AXYS for analysis of PCB congeners through the state Department of Enterprise Services (DES). Both labs are accredited for the methods needed for this project. MEL will analyze metals and hardness data. Reporting limits, method detection limits, and analytical methods are shown in Table 6.

**Table 6. Measurement methods.**

Analyte	Expected Concentration	Reporting Limit	Method Detection Limit	Prep/Analytical Method	Analytical Laboratory
cPAHs	<0.2 ug/L	0.05 – 0.1 <sup>†</sup> ug/L	0.012 – 0.037 ug/L	8270E-SIM	Eurofins
DEHP	<0.06 – 1* ug/L	0.2 ug/L	0.087 ug/L	8270E-SIM	Eurofins
PCB Congeners	5 – 500 <sup>‡</sup> pg/L total PCBs	Varies by congener	Varies by congener	1668C	SGS-AXYS
Arsenic, Copper & Zinc (Total) <sup>‡</sup>	0.25 – 0.55, <0.4, <5 ug/L	0.1, 0.4, 5 ug/L	0.0364, 0.124, 1.664 ug/L	EPA 200.8	MEL
Arsenic, Copper & Zinc (Dissolved) <sup>‡</sup>	0.23 – 0.50, 0.13 – 0.19, <1 ug/L	0.1, 0.1, 1 ug/L	0.0126, 0.052, 0.25 ug/L	EPA 200.8	MEL
Hardness <sup>‡</sup>	14.2 -18.1 mg/L	1 mg/L	0.067 mg/L	EPA 200.7/ SM 2340B	MEL

cPAHs = carcinogenic polycyclic aromatic hydrocarbons

DEHP = di (2-ethylhexyl) Phthalate

PCBs = Polychlorinated biphenyls

Eurofins = Eurofins Environment Testing Northwest, LLC – Tacoma, WA

\* Based on data from Ecology's EIM database via Method EPA-8270.

<sup>†</sup> Reporting limits for PAHs vary by parameters. The reporting limit for Benzo(a)pyrene is 0.1 ug/L.

<sup>‡</sup> Based on data from the 2009-2010 Puget Sound Toxics Loading Analysis (Ecology and King County, 2011).

Concentrations ranged from 10 – 500 pg/L total PCBs in surface water from residential watersheds (n=12 samples).

Concentrations were 5-500 pg/L for all land use types (n=69).

<sup>‡</sup> Information on reporting limits and method detection limits from the *Statewide River and Stream Ambient Water Quality Monitoring QAMP* (Von Prause, 2021). Expected concentrations from an EIM search on station 09A190, accessed 10/26/22.



# 10.0 Quality Control Procedures

## 10.1 Table of field and laboratory quality control

Table 7. Quality control samples, types, and frequency.

	Field	Field	Lab	Lab	Lab	Lab	Lab
Parameter	Field Replicates	Field Blanks	Method Blanks	Analytical Duplicates	MS and MS Duplicate	LCS	Labeled Surrogates
cPAHs	2 per Project	1 per Project	1 per Batch	2 per Project	1 set per Project	1 per Batch	NA
DEHP	2 per Project	1 per Project	1 per Batch	2 per Project	1 set per Project	1 per Batch	NA
PCBs	2 per Project	1 per Project	1 per Batch	2 per Project	NA	1 per Batch	Each Sample
Arsenic, Copper & Zinc (Total) <sup>†</sup>	1 per Project	1 per Project	1 per Batch	1 per Project	1 per Batch	1 per Batch	NA
Arsenic, Copper & Zinc (Dissolved) <sup>†</sup>	1 per Project	1 per Project	1 per Batch	1 per Project	1 per Batch	1 per Batch	NA
Hardness <sup>†</sup>	1 per Project	1 per Project	1 per Batch	1 per Project	1 per Batch	1 per Batch	NA

cPAHs = carcinogenic polycyclic aromatic hydrocarbons

DEHP = di (2-ethylhexyl) Phthalate

PCBs = Polychlorinated biphenyls

MS = Matrix Spike

NA = Not Applicable

LCS = Laboratory control standard

<sup>†</sup> Information from the *Statewide River and Stream Ambient Water Quality Monitoring QAMP* (Von Prause, 2021).

Batch = defined for the project as an analytical batch. A year of monthly sampling should equal about 12 analytical batches for arsenic, copper, zinc, hardness, cPAHs and DEHP. PCB congener samples will be refrigerated at MEL for 3 months and then sent to SGS-AXYS for analysis as quarterly batches.

## 10.2 Corrective action processes

The contract labs must follow the corrective actions that are a part of the analytical methods. Deviations from accredited laboratory methods will be documented by the lab analyst and communicated to the data validator at MEL. The project manager will discuss the best course of action with MEL and the analytical laboratory; this may include having archive samples reanalyzed by the lab, qualifying the data, or rejecting the data.

# 11.0 Data Management Procedures

The U.S. Environmental Protection Agency (EPA) Level 4 data packages will be provided to MEL from the contract labs. MEL will then perform Stage 4 validation of the PCB congener data from SGS-AXYS and Stage 2B validation for the cPAHs and DEHP data from Eurofins (EPA, 2009 and 2016). MEL will then provide the validated data packages to EAP's project manager.

The PCB data will be evaluated and qualified according to High Resolution National Functional Guidelines (EPA, 2020) and MEL SOPs. The semi-volatiles data will be evaluated and qualified according to Organics National Functional Guidelines (EPA, 2020). Method blank contamination will be addressed by censoring sample result values when they are less than five times the detected value in the associated method blank. The data validator will ensure that there are two columns with final validated data, one with 5x censoring and one with no censoring.

The arsenic, copper, zinc, and hardness data will be evaluated and qualified by MEL according to the Inorganic National Functional Guidelines (EPA, 2020).

EAP's project manager will review the data and check for completeness. If any issues are found, the project manager will work with the MEL data validator to correct them. Once the data is considered final, the electronic data will be sent to the client. See *Section 5.4* for the schedule on data deliverables.

At the end of the yearlong project, after all the data packages have been validated, reviewed, and finalized, the project manager will enter the data into the EIM database (*see Section 11.2*).

## 11.1 Lab data package requirements

The data packages from the analytical labs should include a case narrative in PDF format. The case narrative will include:

- Whether specific project MQOs were met.
- Whether proper analytical procedures were followed.
- Problems encountered during sample analysis and corrective actions taken.
- Explanation of data qualifiers.

The data package will include all raw data for samples, field blanks and duplicates, batch QC, and instrument QC to facilitate recalculation of reported calculations.

Data will be qualified according to EPA's National Functional Guidelines and MEL's SOPs. The qualifiers will be used in accordance with the method reporting limits such that:

- For non-detect values, the estimated detection limit (EDL) is recorded in the "Result Reported Value" column and a "UJ" in the "Result Data Qualifier" column.
- No results are reported below the EDL.
- The only results reported are for those congeners that have a value at least FIVE times the signal-to-noise ratio, and that meet ion abundance ratios required by the method.
- Detected values that are below the quantitation limits (QL) are reported and qualified as estimates ("J").

- Results that do not meet ion abundance ratio criteria are reported with “NJ.” If an Estimated Maximum Possible Concentration (EMPC) value is calculated and reported, the calculation is explained in the narrative, and an example calculation used for this value is provided.
- Results that contain interference from polychlorinated diphenyl ethers (PCDEs) are qualified with “NJ.”

## 11.2 EIM data upload procedures

At the end of the yearlong project, once all the data packages have been validated, reviewed and finalized, EAP’s project manager will enter it into the EIM database, which can be accessed on Ecology’s [EIM web page](#)<sup>11</sup>.

Validated lab data results will be entered into the EIM results template and uploaded into the EIM database under the Study ID *PLAGreenToxics*. The data include:

- Monthly PCB congener data from SGS-AXYS
- Monthly cPAH and DEHP data from Eurofins
- Arsenic, copper, zinc, and hardness data from MEL for the six odd months (November, January, etc.)

A second EAP staff member will review the data uploaded into EIM and document any errors. The final corrected data will be reviewed by the project manager, and re-uploaded into EIM, if necessary.

The full suite of metals data sampled on the six even months (October, December, etc.), which includes arsenic, copper, zinc, and hardness will be entered into the EIM database under AMS001. This is the EIM Study ID for the *Statewide River and Stream Ambient Water Quality Monitoring Program*. As such, staff from that program are responsible for data review of the uploaded data.

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<sup>11</sup> <https://ecology.wa.gov/Research-Data/Data-resources/Environmental-Information-Management-database>

## **12.0 Audits and Reports**

None needed for this study.

## **13.0 Data Verification**

### **13.1 Field data verification, requirements, and responsibilities**

EAP's Freshwater Monitoring Unit (FMU) staff have a thorough field data verification process that is described in their QAMP. The project manager for EAP's Toxics Studies Unit (TSU) will be responsible for the toxics data: cPAHs, DEHP, PCB congeners, metals (arsenic, copper, zinc), and hardness for the odd sampling months. TSU staff will enter the toxics data into EIM following EAP's data entry and review protocol.

### **13.2 Laboratory data verification**

The labs conducting the analyses will review lab results according to their established protocols. MEL will perform data verification to ensure the labs submit a complete data package.

### **13.3 Validation requirements**

MEL will perform Stage 4 data validation on the PCB congener data following EPA's National Functional Guidelines for Organics and National Functional Guidelines for High Resolution (EPA, 2016) and project MQOs. MEL will perform a Stage 2B validation for the cPAHs and DEHP data from Eurofins following the Organics National Functional Guidelines (EPA, 2017) and project MQOs. There will be no data validation of MEL's inorganic data.

## **14.0 Data Quality (Usability) Assessment**

Not needed for this study.

## 15. References

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