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ECOLOGY
State of Washington

Quality Assurance Project Plan

Survey of Phthalates in Washington State Waterbodies

May 2021

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Publication Information

Each study conducted by the Washington State Department of Ecology must have an approved Quality Assurance Project Plan (QAPP). 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.

This QAPP was approved to begin work in April 2021. It was finalized and approved for publication in May 2021.

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Quality Assurance Project Plan

Survey of Phthalates in Washington State Waterbodies

by Callie Mathieu

Published May 2021

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EAP: Environmental Assessment Program

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2.0 Abstract

The Washington State Department of Ecology (Ecology) will carry out a study in 2021 to evaluate current concentrations of phthalates and non-phthalate plasticizers in freshwater and marine environments throughout the state. Phthalate exposure is associated with human health concerns like endocrine disruption and neurodevelopmental impacts. While phthalate chemicals are not considered persistent or bioaccumulative, they are continuously released to the environment due to their abundance and widespread use in consumer products.

Ecology will collect (1) surface water and bottom sediment samples from 16 rivers and lakes during late spring and fall, and (2) suspended particulate matter from three of the rivers during the winter.

This study will also analyze phthalates and non-phthalate plasticizers in marine sediments previously collected by Ecology's Puget Sound Sediment Monitoring Program.

Several large studies have assessed the presence of six common phthalates in Puget Sound and its major tributaries. This study will expand our knowledge of phthalates in the environment by sampling a broader range of waterbodies throughout the state and by measuring previously untested phthalates and non-phthalate plasticizers.

3.0 Background

3.1 Introduction and problem statement

Phthalates are a group of chemicals that are used extensively in consumer products to make plastic more flexible. While phthalates are not considered persistent or bioaccumulative, they are continuously released to the environment and are widespread contaminants. They are considered 'pseudo-persistent' because of their constant and continuous release to waterbodies. Phthalates are a priority for Washington State due to their prevalent exposure to humans and the environment and their toxicity.

Phthalates are physically incorporated into plastic matrices, and not chemically bound. Therefore, phthalates can leach out of the product over time. They get released into the environment during the manufacture, use, and disposal of phthalate-containing products (Net et al., 2015). This includes releases from municipal waste and direct releases from products (EPA, 2012). Elevated concentrations of phthalates have been documented in urban areas, where atmospheric deposition from vehicle emissions and volatilization from building materials have been suggested as major sources (Wang et al., 2008). Stormwater runoff carries phthalates that originated from PVC, paints, buildings, and other plasticizer uses to waterbodies (Bergé et al., 2013).

Phthalates have been documented in river and marine waters, freshwater and marine sediments, biota, air, wastewater treatment plant effluents and sludge, and drinking water (Net et al., 2015). The largest contributor of phthalates to aquatic systems is thought to be through wastewater treatment plant effluent discharges (Gani and Kazmi, 2016). Atmospheric deposition has suggested as a major pathway of phthalates to waterbodies; however, the half-life of common

phthalates in the atmosphere is short – 0.3 to 15 days – and is of larger concern in urban areas (Bergé et al., 2013). Other studies have shown that particle-sorbed phthalates can be transported long distances, while in the vapor-phase they react rapidly with hydroxyl radicals in the atmosphere (ATSDR, 2019).

Washington's Sediment Phthalates Workgroup concluded that the primary pathway of phthalates to waterbodies in the urban environment is through off-gassing of polyvinyl chloride (PVC) products and stormwater carrying the redeposited phthalate-containing particulates to aquatic sediments (SPWG, 2007). This pathway appears to increase in areas with higher concentrations of fine particulates in the air, as the particulates draw more phthalates out of PVC products.

Animal studies suggest that exposure to di(2-ethylhexyl) phthalate (DEHP) can alter immune responses, cause developmental and reproductive effects, disrupt the endocrine system, and exhibit liver and kidney toxicity (ATSDR, 2019). People and animals are exposed to phthalates primarily through the diet, as well as through inhalation, dermal, and oral routes (ATSDR, 2019). DEHP and other phthalates bioconcentrate in aquatic organisms, but because they rapidly metabolize they do not biomagnify up food chains. Several low molecular weight phthalates have been found to have acute or chronic effects to algae, invertebrates, and fish (Staples et al., 1997). Higher molecular weight phthalates generally exhibit lower aquatic toxicity (Staples et al., 1997).

Ecology has addressed phthalates through the state's Safer Products for Washington program and the Children's Safe Products Act. Ecology, in consultation with the Washington State Department of Health (DOH), determined phthalates in vinyl flooring and personal care and beauty products as two of several priority chemical-product combinations (Ecology, 2020). Washington's Children's Safe Products Act restricts the use of six phthalates in children's products sold in the state (RCW 70A.430.020). Ecology is also currently developing a Phthalates Action Plan to synthesize what is known about phthalates in the state and make recommendations for state actions to reduce human and environmental exposure to them.

Ecology's Persistent, Bioaccumulative, and Toxics (PBT) Monitoring Program regularly conducts environmental monitoring studies to support agency toxics reduction efforts of priority contaminants. We monitor chemicals throughout the state to assess baseline concentrations and track progress over time. In 2021, the monitoring program will carry out a survey of current concentrations of phthalates throughout the state. This study will help to fill data gaps on waterbody types that haven't been tested for phthalates, like rivers and lakes outside of the Puget Sound area, as well as provide data on previously untested phthalates and non-phthalate plasticizers.

This study will have two components: (1) analysis of phthalates from multiple media collected from freshwater sites throughout the state, and (2) analysis of phthalates in marine sediments collected from throughout the Puget Sound. The analysis of marine sediments is being funded as part of a Puget Sound Partnership (PSP) near term action (NTA) grant to develop the Phthalate Action Plan.

3.2 Study area and surroundings

3.2.1 History of study area

Freshwater Study Locations

This study will collect surface water and bottom sediment samples from rivers, lakes, and reservoirs located throughout Washington State for analysis of a suite of phthalates and non-phthalate plasticizers. We will also collect suspended particulate matter (SPM) from a subset of three rivers. Figure 1 displays the freshwater study locations. Eight rivers and eight lakes/reservoirs will be sampled in 2021. Waterbodies selected for this study cover a range of physical and hydrological characteristics. Sites were selected based on the following criteria:

- Statewide distribution to represent varied regional, physical, and hydrological characteristics.
- A range of watershed land uses and phthalate contamination potential.
- Availability of historical data – either previous phthalates data or historical use of the site as an ambient toxics monitoring station.
- A range of flow conditions, lake surface areas, watershed areas, and elevations.
- Safe access to the site for sample collection.

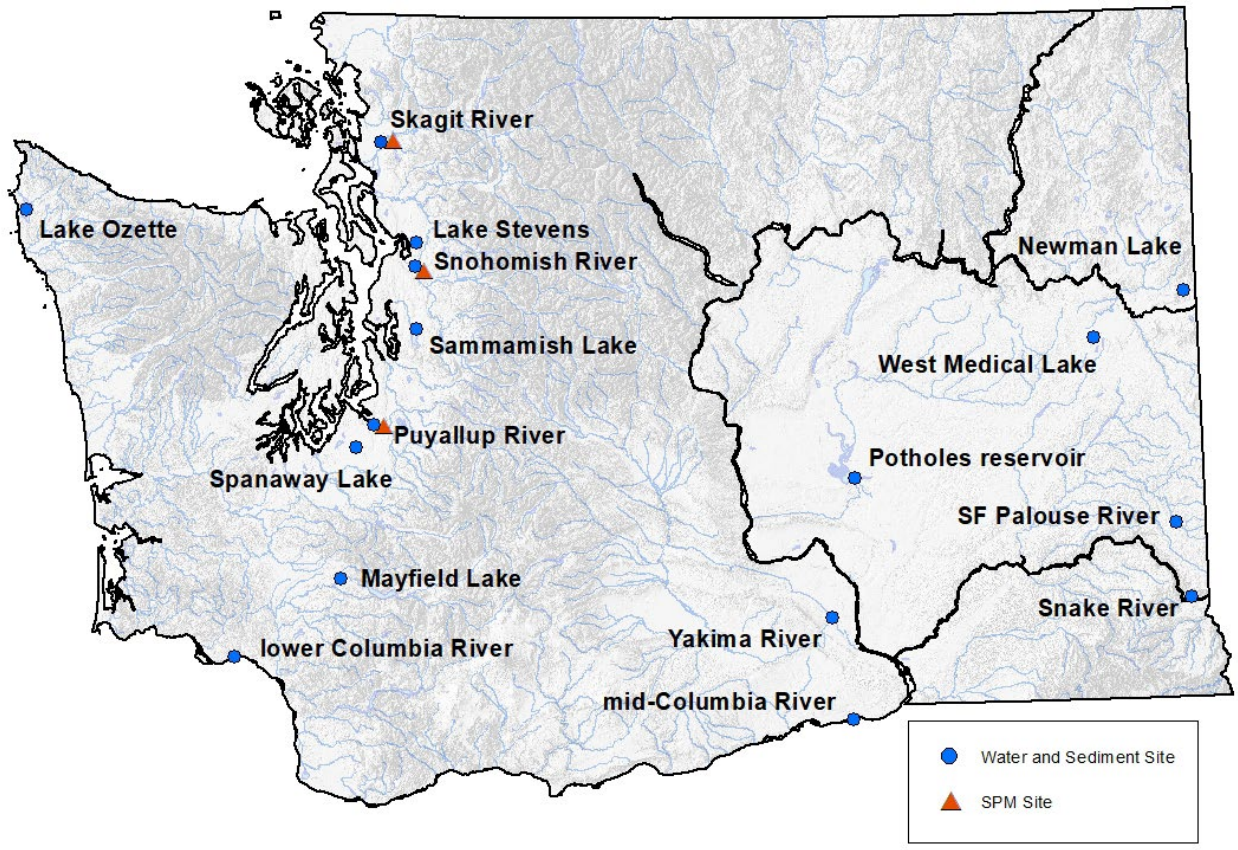

Figure 1. Map of Freshwater Study Locations in Washington State.

Table 1 provides physical descriptions of the freshwater study locations, dominant watershed land uses, and potential sources of phthalates to the waterbody based on the level of development in the watershed and potential inputs from stormwater and wastewater treatment plant (WWTP) discharges.

Table 1. Freshwater study location descriptions.

Study Location	Elevation	Max/Mean Depth (ft)	Lake Area (acre)	Watershed Area (sq mi)	Watershed Land Use	Contamination Potential	Potential Sources/ Pathways of Interest
Lakes/Reservoirs							
Lake Ozette	29	320/130	7,300	78	F	Low	Atm. Dep.
Lake Stevens	210	160/63	1,000	7	U/F	Medium	SW
Mayfield Lake	450	190	2,200	1400	F/R	Medium	WWTP
Newman Lake	2,124	30/19	1,200	28.6	F/R	Medium	Septic
Potholes Reservoir	1,046	140/18	28,000	3,920	A/S	Low	Ag. Sources
Sammamish Lake	26	105/58	4,900	98	U/F	Medium	SW
Spanaway Lake	320	28/16	280	17	U/F	High	SW
West Medical Lake	2,420	35/22	220	1.8	A/S	High	WWTP
Rivers							
Low-Columbia River	5	---	---	256,900	Mixed	Medium	WWTP, SW
Mid-Columbia River	343	---	---	104,000	Mixed	Medium	WWTP
Puyallup River	50	---	---	943	U/F	Medium	WWTP, SW
Skagit River	180	---	---	3,093	A/F/U	Medium	WWTP, SW
Snake River	760	---	---	107,500	A/S/U	Low	WWTP
Snohomish River	40	---	---	1,714	A/F/U	Medium	WWTP, SW
S.F. Palouse River	2,320	---	---	132	A/S/U	High	WWTP
Yakima River	900	---	---	3,479	A/S/U	Medium	Ag. Sources

F = forested; U = urban; A = agriculture; R = residential; S = shrubsteppe; Atm. Dep. = atmospheric deposition; SW = stormwater; WWTP = wastewater treatment plant effluent; Ag. = agriculture.

Marine Sediment Sites

Ecology's Puget Sound Sediment Monitoring Program collects marine sediments throughout the Puget Sound every year, as well as from one rotating urban bay (Dutch et al., 2018). This study will analyze phthalates in marine sediments collected by their long-term monitoring program in 2021. The program will supply marine sediment samples from 20 of their Puget Sound long-term stations and 10 Elliott Bay stations, displayed in Figure 2. These locations provide a broad coverage of sites throughout Puget Sound and Elliott Bay.

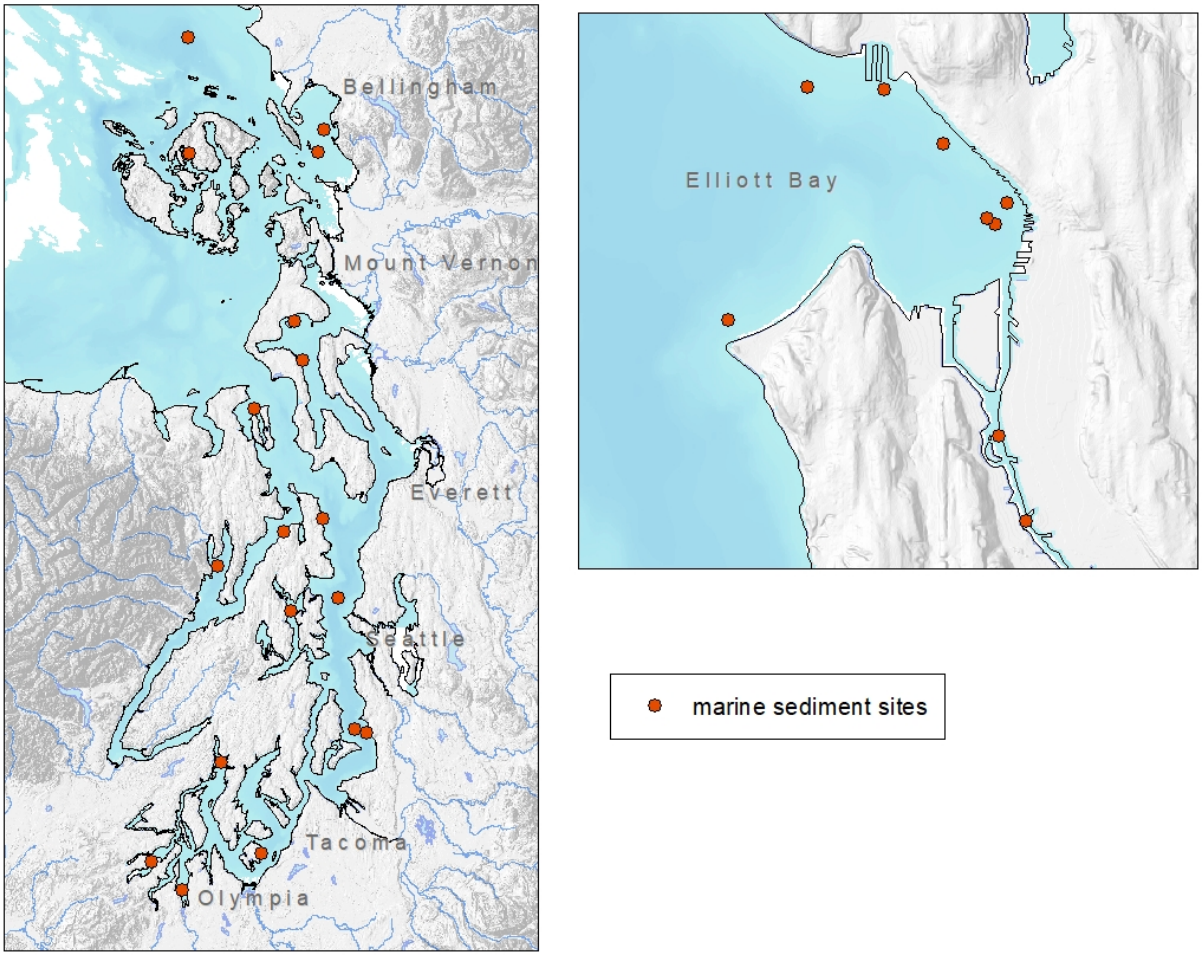

Figure 2. Map of Marine Sediment Locations in Puget Sound and Elliott Bay.

3.2.2 Summary of previous studies and existing data

Several studies have tested and reported on six common phthalates in Puget Sound and its immediate tributaries. Much of the existing data is focused on sediment clean-up site efforts. General environmental monitoring studies are discussed below and summarized in Tables 2 and 3.

1992 Washington Lakes Study

In 1992, Ecology analyzed a suite of contaminants in lakes throughout Washington, which included analysis of DEHP and diethyl phthalate (DEP) in sediment (Serdar et al., 1994). DEHP was detected at all five lakes sampled. DEP was only detected in one sediment sample, collected from Lake Spokane.

Control of Toxic Chemicals in Puget Sound Studies

Ecology and other agencies carried out a multi-phase project between 2006 and 2011 to evaluate sources of toxic chemicals entering Puget Sound. Results of the hazard evaluation based on the Puget Sound toxics loading studies identified several toxics to be found at concentrations where effects are documented or levels exceeded criteria used to protect aquatic organisms (Norton et al., 2011). DEHP was one of the toxics identified to present a hazard.

Gries and Osterberg (2011) included six phthalates in their study on toxics in Puget Sound and major rivers draining to the Sound. DEHP was detected in one surface and two deep water samples collected from the Puget Sound (0.01 – 0.06 µg/L), and in freshwater collected from the Puyallup River (0.07 µg/L). Di-n-octyl phthalate (DnOP) was also detected in a field replicate water sample from the Puyallup River (0.16 µg/L). DEHP was detected in all of the river SPM samples at concentrations ranging from 170 – 1,000 µg/kg dw. No other phthalates were detected in the SPM.

In a study on toxics loading to the Puget Sound, DEHP was frequently detected during storm events in commercial/industrial subbasin whole surface water samples (Herrera, 2011). The median concentration in the commercial/industrial storm event samples was 0.34 µg/L. In other land-use areas, DEHP was detected infrequently, though one sample collected from a residential area exceeded a human health criterion from the National Toxics Rule (40 CFR 131.36). Phthalates were rarely detected in the surface water samples collected during baseflow.

Stormwater Action Monitoring

Six phthalates were measured in the sediments of receiving waters as part of the Stormwater Action Monitoring study of contaminants in Puget Sound lowland streams in 2015 (DeGasperi et al., 2018). Of the phthalates analyzed in the study, DEHP was detected in the greatest frequency (46% of samples). Butyl benzyl phthalate (BBP) was detected in 7% of samples, DEP in 5%, and dibutyl phthalate (DBP) in 1% of samples. DnOP and dimethyl phthalate (DMP) were not detected in any samples. No sites exceeded Sediment Screening Levels (SSLs) above which adverse effects to benthic invertebrates may be expected (2,200 µg/kg dw). DEHP concentrations in sediments collected from two of the sites exceeded the no-effects threshold Sediment Cleanup Objective of 500 µg/kg dw.

A previous study assessed six phthalates in stormwater and stormwater sediments collected by Western Washington NPDES Phase 1 permittees (Hobbs et al., 2015). DEHP was the most frequently detected in both stormwater and stormwater sediments, with detection frequencies of 62% and 93%, respectively. Commercial land-use areas discharged greater concentrations of DEHP, BBP, and DBP in stormwater than other land use types, followed by industrial and high-density residential areas, and low-density residential areas contained the lowest. Land-use patterns were similar for stormwater sediments. DEHP and DnOP exceeded the Sediment Cleanup Objective (SCO) in 82% and 29% of samples, respectively.

Puget Sound Marine Sediment Monitoring

Ecology's Puget Sound Sediment Monitoring Program has analyzed 6 phthalates in Puget Sound bottom sediments since 1989 (Partridge et al., 2018). Between 1989 and 2016, DEHP was detected the most frequently, and at the highest concentrations of the phthalates analyzed, with BBP the second-most commonly detected phthalate. At the Thea Foss Waterway and Point Pully sentinel stations, DEHP was detected in 53% and 57% of samples between 1989 and 2016. At other stations throughout Puget Sound, DEHP detection frequency was generally in the 20-40% range. BBP was only detected in the Thea Foss Waterway, Point Pully, and Sinclair Inlet stations. It was detected in 24 – 39% of the samples from those stations.

Between 1989 and 2015, no trends in DEHP concentrations were found at most of the long-term stations (Partridge et al., 2018). The exception to this was the East Anderson Island sentinel station, where DEHP concentrations decreased, suggesting improvement.

Table 2. Historical phthalate data in water matrix.

Location	Sample Type	Collection Dates	n	BBP (min-max, µg/L)	DEHP (min-max, µg/L)	DBP (min-max, µg/L)	DEP (min-max, µg/L)	DMP (min-max, µg/L)	DnOP (min-max, µg/L)	Reference
Lake Whatcom watershed	Freshwater	1998	7-8	ND - 0.5	0.045 - 4.4	ND - 0.16	ND - 0.33	ND	ND	Serdar et al., 1999
Puget Sound tributaries	Freshwater	2009-2010	126	ND - 1.8	ND - 12	ND	ND - 0.17	ND - 0.17	ND - 0.35	Herrera, 2011
Puget Sound tributaries	Freshwater	2009-2010	15	ND	ND - 0.074	ND	ND	ND	ND	Gries and Osterberg, 2011
Thornton Creek	Freshwater	2003	36	ND - 0.91	ND - 16	ND - 2	ND - 0.79	ND - 0.07	ND - 0.57	Anderson et al., 2004
Indian Creek watershed	Groundwater	2013	3	ND	ND - 16.3	ND	ND	ND	ND	Marshall et al., 2014
Puget Sound	Marine Water	2009-2010	42	ND	ND - 0.059	ND	ND	ND	ND	Gries and Osterberg, 2011
Lake Whatcom watershed	Stormwater	1998	2	0.036 - 0.48	0.085 - 3.6	ND	ND	ND	ND - 0.58	Serdar et al., 1999
Lake Whatcom watershed	Stormwater	1998	2	ND	0.42 - 2.1	ND	ND	ND	ND	Serdar et al., 1999
Port Townsend, Seaview, Swantown	Stormwater	2006	4	0.03 - 2.1	ND - 15	0.16 - 4.3	0.05 - 1.2	0.22 - 13	ND	Johnson et al., 2006
Clark County commercial drainages	Stormwater	2017	13	ND (<0.2)	ND - 2.25	ND - 2.29	ND (<0.2)	ND - 0.48	ND (<0.2)	Medlen, 2018

Data accessed from EIM on 1/15/21.

Table 3. Historical phthalate data in sediment matrix.

Location	Sample Type	Collection Dates	n	BBP (min-max, µg/kg)	DEHP (min-max, µg/kg)	DBP (min-max, µg/kg)	DEP (min-max, µg/kg)	DMP (min-max, µg/kg)	DnOP (min-max, µg/kg)	Reference
Budd Inlet, Chambers Creek, Puyallup	Biosolids	2008	3	ND - 631	ND - 43,900	ND	ND	ND	ND	Lubliner et al., 2010
Lake Whatcom watershed	Freshwater Sediment	1998-1999	7	ND - 590	ND - 10,500	ND - 16,640	ND - 39	ND	ND - 760	Serdar et al., 1999
Squalicum Creek	Freshwater Sediment	2002	1	ND	ND	ND	ND	ND	ND	Anderson and Roose, 2004
WA rivers and lakes	Freshwater Sediment	2008	27	ND	ND - 81	ND - 14	ND	ND	ND	Sloan and Blakley, 2009
Puget Sound tributaries	Freshwater Sediment	2015	85	ND - 69	ND - 640	ND - 910	ND - 45	ND	ND	DeGasperi et al., 2018
WA lakes	Freshwater Sediment	1992	10	---	ND - 920	---	ND - 190	---	---	Serdar et al., 1994
Puget Sound nearshore	Marine Sediment	2016	41	ND - 30	ND - 610	ND - 30	ND - 140	ND - 60	ND - 30	Black et al., 2018
Puget Sound, evenly distributed	Marine Sediment	1989 - 2019	1310	ND - 1,380	ND - 50,900	ND - 7,290	ND - 843	ND - 258	ND - 95	EIM, accessed 1/15/21
Puget Sound - urban bays	Marine Sediment	2007-2018	395	ND - 390	ND - 8,300	ND - 610	ND - 183	ND - 262	ND - 20	EIM, accessed 1/15/21
Port Townsend, Swantown, Seaview	Marine Sediment	2006	3	ND - 86	ND - 8,000	36 - 1,380	4 - 290	ND - 804	ND - 138	Johnson et al., 2006
Squalicum Creek	Stormwater Sediment	2002	4	ND - 584	ND - 15,100	ND - 188	ND	ND - 3110	ND - 1070	Anderson and Roose, 2004
Clark County commercial drainages	Stormwater Sediment	2017	30	ND - 1,460	ND - 21,800	ND	ND	ND - 718	ND - 923	Medlen, 2018
Lake Whatcom watershed	Stormwater Sediment	1998-1999	1	240	16,900	ND	ND	ND	ND	Serdar et al., 1999
Lake Whatcom watershed	Stormwater Sediment	1998-1999	1	ND	2,810 - 2,810	520 - 520	68 - 68	ND	ND	Serdar et al., 1999
Puget Sound Tributary Rivers	SPM	2009-2010	5	ND	170 - 1,000	ND	ND	ND	ND	Gries and Osterberg, 2011

Data accessed from EIM on 1/15/21.

3.2.3 Parameters of interest and potential sources

Phthalates are a large class of compounds used in many commercial and industrial products. The most common use of phthalates has been in polyvinyl chloride (PVC). DEHP was widely used as the main plasticizer for PVC, though heavier and more stable phthalates (diisononyl phthalate and diisodecyl phthalate) have recently been used as replacements, with the intention of lower releases to the environment (Bergé et al., 2013). Compounds with lower molecular weight, like DMP and DEP, have been incorporated into cosmetics, fragrances, and personal care products, while di-n-butyl phthalate (DnBP) is used in epoxy resins, cellulose esters, and adhesives (Bergé et al., 2013).

3.2.4 Regulatory criteria or standards

This study is not designed to assess compliance with regulatory criteria or standards. The final report will include a comparison of our results to adverse effects levels associated with potential ecological risks. Effects levels will be compiled from various resources, such as EPA's EcoTox database, peer-reviewed literature, and sediment management standards.

4.0 Project Description

4.1 Project goals

The goals of this study are to:

- Evaluate current levels of phthalates in freshwater and marine environments across a range of waterbody and land use types.
- Assess whether phthalates are present at exposure levels that could cause adverse effects.
- Gather data on previously un-tested phthalates and non-phthalate plasticizers in Washington State.

4.2 Project objectives

- Collect a total of 64 surface water and 32 sediment samples from 16 rivers and lakes throughout the state for analysis of phthalates during the spring and fall of 2021.
- Collect suspended particulate matter via centrifugation from three rivers (Puyallup, Skagit, Snohomish) during December 2021 for analysis of phthalates.
- Analyze phthalates in 20 marine sediment samples distributed throughout the Puget Sound and 10 marine sediment samples collected from Elliott Bay by Ecology's Puget Sound Sediment Monitoring Program.

4.3 Information needed and sources

This project will generate new environmental data. Previously reported values for phthalates in the environment will be used to provide general context for concentrations measured in this study. Previous studies are described in Section 3.2.2.

4.4 Tasks required

The following tasks will be carried out for this project:

- Conduct reconnaissance of sample locations.
- Prepare the centrifuge trailer and equipment for SPM collection.
- Collect samples during the planned sampling periods.
- Coordinate laboratory analysis of samples.
- Review data quality of analytical results and work with Manchester Environmental Laboratory (MEL) staff to resolve any issues.
- Review and assemble ecotoxicity thresholds for comparison in report.
- Analyze data and prepare written report summarizing findings. Route draft report following Environmental Assessment Program (EAP) publication review procedures and publish final report to Ecology's website.
- Load data into Ecology's EIM database following EAP review and finalization procedures.
- Load marine sediments phthalates data into EPA's WQX database.

4.5 Systematic planning process

This quality assurance project plan addresses the elements of a systemic planning process for this study.

5.0 Organization and Schedule

5.1 Key individuals and their responsibilities

Table 4 shows the responsibilities of those who will be involved in this project.

Table 4. Organization of project staff and responsibilities.

Staff (all EAP)	Title	Responsibilities
Jessica Archer SCS Phone: 360-407-6698	Client and SCS Manager	Clarifies scope of the project. Provides internal review of the QAPP and approves the final QAPP.
James Medlen Toxics Studies Unit, SCS Phone: 360-407-6194	Client and Supervisor for the Project Manager	Clarifies scope of the project. Provides internal review of the QAPP and final report. Approves the final QAPP. Manages budget and staffing needs.
Callie Mathieu Toxics Studies Unit, SCS Phone: 360-407-6965	Project Manager and Principal Investigator	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.
Jakub Bednarek Toxics Studies Unit, SCS Phone: 360-407-6765	Field Lead	Leads field collections, records field information, and sends samples to the laboratory. Enters data into EIM.
Alan Rue Manchester Environmental Laboratory Phone: 360-871-8801	Manchester Lab Director	Reviews and approves the final QAPP.
Britta Voss Phone: 360-407-6070	NEP Quality Coordinator	Reviews the draft QAPP and recommends the final QAPP for approval.
Arati Kaza Phone: 360-407-6964	Ecology Quality Assurance Officer	Reviews and approves the draft QAPP and the final QAPP.

EAP: Environmental Assessment Program
EIM: Environmental Information Management database
QAPP: Quality Assurance Project Plan
SCS: Statewide Coordination Section

5.2 Special training and certifications

All staff collecting field samples will be experienced and trained in the sample collection protocols outlined in the respective standard operating procedures (SOPs), as well as EAP's safety manual. Boat operators will follow EAP safety protocols outlined in the program's safety manual.

5.3 Organization chart

Not applicable – see Table 4.

5.4 Proposed project schedule

Tables 5 – 7 list key activities, due dates, and lead staff for this project.

Table 5. Schedule for completing field and laboratory work

Task	Due date	Lead staff
Field work - begins	05/2021	Jakub Bednarek
Field work - completed	12/2021	Jakub Bednarek
Laboratory analyses completed	02/2022	

Table 6. Schedule for data entry

Task	Due date	Lead staff
EIM data loaded	04/2022	Jakub Bednarek
EIM QA	05/2022	Callie Mathieu
EIM complete	06/2022	Jakub Bednarek

*EIM Project ID: CAME005
EIM: Environmental Information Management database

Task	Due date	Lead staff
WQX data loaded	04/2022	Jakub Bednarek
WQX QA	05/2022	Callie Mathieu
WQX data complete	06/2022	Jakub Bednarek

Table 7. Schedule for final report

Task	Due date	Lead staff
Draft to supervisor	05/2022	Callie Mathieu
Draft to client/ peer reviewer	06/2022	Callie Mathieu
Final draft to publications team	07/2022	Callie Mathieu
Final report due on web	09/2022	Callie Mathieu

5.5 Budget and funding

Tables 8 and 9 present the costs of the laboratory analyses for freshwater and marine samples, respectively. The number of laboratory quality control samples includes only those tests that are not included in the costs of analysis. Funding for laboratory costs associated with freshwater sampling outlined in Table 8 is provided by Ecology's PBT Monitoring Program. A one-time method development cost of $15,000 for sediments and $10,000 for water will be funded by the PBT Monitoring Program for MEL to add new analytes to their phthalates suite for this study. Laboratory analyses of marine sediments, outlined in Table 9, will be funded through a one-time PSP NTA grant.

Table 8. Laboratory budget details for freshwater samples.

Season	Analyte	Matrix	Total number of field samples	Number of field QC samples	Number of lab QC* samples	Total number of samples	Cost per sample	MEL Subtotal
Spring	Phthalates	water	32	8	4	44	$300	$13,200
Spring	SSC	water	32	6	---	38	$15	$570
Spring	DOC	water	32	6	---	38	$45	$1,710
Spring	TOC	water	32	6	---	38	$35	$1,330
Spring	Phthalates	sediment	16	2	2	20	$300	$6,000
Spring	TOC	sediment	16	2	---	18	$50	$900
Spring	Grain Size	sediment	16	2	---	18	$50	$900
							Spring total:	***$24,010***
Fall	Phthalates	water	32	8	4	44	$300	$13,200
Fall	SSC	water	32	6	---	38	$15	$570
Fall	DOC	water	32	6	---	38	$45	$1,710
Fall	TOC	water	32	6	---	38	$35	$1,330
Fall	Phthalates	sediment	16	2	2	20	$300	$6,000
Fall	TOC	sediment	16	2	---	18	$50	$900
Fall	Grain Size	sediment	16	2	---	18	$50	$900
Winter	Phthalates	sediment (SPM)	3	1	2	6	$300	$1,800
Winter	TOC	sediment (SPM)	3	1	---	4	$50	$200
Winter	LOI	sediment (SPM)	3	1	---	4	$50	$200
Winter	Phthalates	water**	3	---	2	5	$300	$1,500
							Fall/Winter total:	***$26,210***
							TOTAL:	**$50,220**

*Lab quality control (QC) samples refers to matrix spike and matrix spike duplicates. **equipment rinsate blank.
SSC = suspended sediment concentration; DOC = dissolved organic carbon; TOC = total organic carbon;
LOI = loss on ignition.

Table 9. Laboratory budget details for marine samples.

Season	Analyte	Matrix	Total number of field samples	Number of lab QC* samples	Number of field QC samples	Total number of samples	Cost per sample	MEL Subtotal
Spring - Puget Sound	phthalates	marine sediments	20	2	1	23	$300	$6,900
Spring - Elliott Bay	phthalates	marine sediments	10	2	1	13	$300	$3,900
							***TOTAL*:**	**$10,800**

*Lab QC samples refers to matrix spike and matrix spike duplicates.

6.0 Quality Objectives

6.1 Data quality objectives

The main data quality objective (DQO) for this project is to collect surface water samples and sediment samples representative of phthalate concentrations across a range of waterbodies and land use types throughout the state. The samples will be analyzed using standard methods to obtain phthalate concentration data that meet measurement quality objectives (MQOs) described below and that are comparable to previous study results.

6.2 Measurement quality objectives

The MQOs for analytical results, expressed in terms of acceptable precision, bias, and sensitivity, are described in this section and summarized in Table 10. For in-situ measurements, Table 11 provides acceptance criteria to be used during calibration and post-checks of the multi-parameter sonde.

6.2.1 Targets for precision, bias, and sensitivity

Table 10. Measurement quality objectives.

Analyte	Matrix	Precision			Bias		Sensitivity
		Field Replicates (RPD)	Lab Duplicates (RPD)	Matrix Spike Duplicates (RPD)	LCS (recovery)	Matrix Spike (recovery)	MDL or LLOQ
Phthalates	water	≤ 40%	≤ 40%	≤ 40%	50 - 150%	50 - 150%	0.5 – 2.5 µg/L
SSC	water	≤ 20%	≤ 20%	n/a	80 - 120%	n/a	0.5 mg/L
TOC	water	≤ 20%	≤ 20%	≤ 20%	80 - 120%	75 - 125%	0.5 mg/L
DOC	water	≤ 20%	≤ 20%	≤ 20%	80 - 120%	75 - 125%	0.5 mg/L
Phthalates	sediment	≤ 40%	≤ 40%	≤ 40%	50 - 150%	50 - 150%	12.5 - 25 µg/kg dw
TOC	sediment	≤ 20%	≤ 20%	n/a	80 - 120%	n/a	1% dw
Grain Size	sediment	n/a	< 25%	n/a	n/a	n/a	0.1%
LOI	suspended particulate matter	n/a	< 25%	n/a	n/a	n/a	---

RPD = relative percent difference; LCS = laboratory control samples; MDL = method detection limit; LLOQ = lower limit of quantitation; SSC = suspended sediment concentration; DOC = dissolved organic carbon; TOC = total organic carbon; LOI = loss on ignition; dw = dry weight.

Table 11. Acceptance criteria for in-situ measurement calibration and post-checks.

In-situ Parameter	Units	Accept	Qualify	Reject
pH	std. units	≤ +/- 0.3	≥ +/- 0.3 and ≤ +/- 1.0	≥ +/- 1.0
Conductivity	µS/cm	≤ +/- 10%	≥ +/- 10% and ≤ +/- 20%	≥ +/- 20%
Temperature	°C	≤ +/- 0.2	≥ +/- 0.2 and ≤ +/- 15%	≥ +/- 1.0
Dissolved oxygen	% saturation	≤ +/- 5%	≥ +/- 5% and ≤ +/- 15%	≥ +/- 15%
Dissolved oxygen	mg/L	≤ +/- 0.3	≥ +/- 0.3 and ≤ +/- 0.8	≥ +/- 0.8

6.2.1.1 Precision

Precision is a measure of variability among replicate measurements due to random error. Results from this project will be assessed for precision using replicate field measurements and analysis of laboratory duplicates and matrix spike duplicates. Precision for two replicate samples will be measured as the relative percent difference between the two results. For three or more replicate samples, precision will be measured by relative standard deviation. MQOs for precision are presented in Table 10.

Surface water and sediment sample field replicates will be collected for every 10% of samples during a sampling season and analyzed alongside the field samples. A field replicate sample will be collected immediately after the field sample using the same sampling technique.

6.2.1.2 Bias

Bias is the difference between the population mean and the true value. For this project, bias will be measured as acceptable percent recovery of laboratory control samples and matrix spikes. Measurement quality objectives for bias are shown in Table 10.

6.2.1.3 Sensitivity

Sensitivity is a measure of the capability of a method to detect a substance. Laboratory analysis sensitivity is defined for this project as the method detection limit or lower limit of quantitation (LLOQ). See Table 10 for detection limits and the lowest concentrations of interest.

6.2.2 Targets for comparability, representativeness, and completeness

6.2.2.1 Comparability

To facilitate comparability of the data generated by this project and other projects, field sampling will follow SOPs listed in Section 8.2. Comparability of SPM with previous centrifuged particulate studies will be achieved by following protocols described in QAPPs and reports for those studies, described in Section 8.2.

6.2.2.2 Representativeness

Surface water and bottom sediment samples will be collected during May-June to capture spring run-off, or high-flow, conditions and during September-October to represent baseflow conditions in rivers. Centrifuged SPM sampling will be conducted in December, 2021.

Sampling will adhere as close as possible to the target coordinates listed in this QAPP. In lakes and reservoirs, surface water and sediment samples will be collected from the deepest area of the lake, as identified through bathymetric maps, and far away from point sources near the shoreline. River surface water samples will be collected as close to the thalweg as possible, in flowing conditions, downstream of WWTP effluent mixing zones in order to represent ambient concentrations.

The freshwater study locations were non-randomly selected to represent various levels of contamination potential and a range of watershed land use types. The sites also cover a range of physical characteristics such as watershed areas, water surface areas, and elevations.

6.2.2.3 Completeness

The project manager will consider the study to have achieved completeness if 95% of the samples are collected and analyzed acceptably.

6.3 Acceptance criteria for quality of existing data

Any previously reported data used in comparison to or to support this study's results will have been collected under an approved QAPP, and findings documented in a final report. The laboratory methods, data quality, and sampling protocols for previously reported data will be assessed to ensure comparability to data provided by this study.

6.4 Model quality objectives

NA

7.0 Study Design

This study will collect surface water and sediment samples from 16 rivers and lakes during the spring and fall of 2021, and SPM from three rivers in the winter for analysis of phthalates and ancillary parameters. This study is designed to evaluate and assess current concentrations of phthalates from a wide range of waterbody types, hydrological conditions, and contamination potential (see Table 1). Most of the phthalates data available for Washington State is associated with sediment clean-up sites and the Puget Sound and its tributaries. This study will expand our knowledge base on the prevalence of phthalates in the environment to include lakes and reservoirs throughout the state, as well as rivers in eastern Washington that have not been previously sampled (Columbia River, Yakima River, Snake River, and South Fork Palouse River).

We will also analyze phthalates in marine sediment samples collected by EAP's Puget Sound Sediment Monitoring Program under their Quality Assurance Monitoring Plan (QAMP) (Dutch et al., 2018) and 2021 QAMP addendum (Dutch, 2021) as part of their ongoing monitoring of

Puget Sound sediments. The program currently analyzes six phthalates as part of their sediment chemistry suite. This study will extend that analysis to measure 10 additional phthalates and 3 non-phthalate plasticizers.

7.1 Study boundaries

The premise of this study is to evaluate phthalate concentrations in waterbodies throughout the state of Washington. Water resource inventory areas (WRIAs) and hydrologic unit codes (HUCs) for each of the freshwater study locations are presented in Table 12. The study boundaries for the marine sediment collections are the Puget Sound and Elliott Bay; more information is provided in the QAMP and QAMP Addendum for the marine sediment sampling (Dutch et al., 2018; Dutch, 2021). Geographic coordinates of individual sampling sites are given in Section 7.2.

Table 12. Study locations WRIA and HUC Numbers.

Study Location	County	WRIA	HUC
Lake Ozette	Clallam	20	17100101
Lake Stevens	Snohomish	7	17110011
Lower Columbia River	Cowlitz	25	17080003
Mayfield Lake	Cowlitz	26	17080005
Mid-Columbia River	Benton	31	17070101
Newman Lake	Spokane	57	17010305
Potholes reservoir	Grant	41	17020015
Puyallup River	Pierce	10	17110014
Sammamish Lake	King	8	17110012
Skagit River	Snohomish	5	17110008
Snake River	Whitman/Asotin	35	17060107
Snohomish River	Snohomish	7	17110011
South Fork Palouse River	Whitman	34	17060108
Spanaway Lake	Pierce	12	17110019
West Medical Lake	Spokane	43	17020013
Yakima River	Benton	37	17030003

WRIA = water resources inventory area; HUC = hydrologic unit code.

7.2 Field data collection

7.2.1 Sampling locations and frequency

Freshwater Sites

Table 13 presents the geographic coordinates and timing of sample collections for freshwater samples. Field crews will collect two surface water and one sediment sample at each site during the spring and again in the fall. Sampling will take place over a 2-3 week period in late May-June for the spring sampling event and in late September-October for the fall period.

All surface water samples, lake sediment samples, and SPM samples will be collected from the coordinates given in Table 13. River sediment samples will be collected from the closest depositional area to the coordinates, to be determined following desk and site reconnaissance. GPS locations will be collected in the field and recorded for all samples collected. Previous toxics studies have collected samples at all sampling coordinates outlined below. In lakes, these coordinates represent the deepest part of the basin to capture an integrated sample of fine depositional sediments and far from shoreline inputs. For rivers, these coordinates reflect sampling locations that are as close to the thalweg as possible and safely accessible by field staff.

Suspended particulate matter samples will be collected during winter baseflows in December from three of the rivers. The timing of the SPM sampling was selected to replicate historical SPM sampling of phthalates at those sites by Gries and Osterberg (2011). Suspended particulate matter samples will be collected over a 12-48 hour period.

Table 13. Sampling locations and timing for freshwater collections.

Waterbody	Latitude	Longitude	Sample Timing		
			Surface Water	Sediment	SPM
Lake Ozette	48.107	-124.651	S, F	S, F	
Lake Stevens	48.011	-122.093	S, F	S, F	
Lower Columbia River	46.173	-123.119	S, F	S, F	
Mayfield Lake	46.506	-122.579	S, F	S, F	
Mid-Columbia River	45.935	-119.286	S, F	S, F	
Potholes Reservoir	46.988	-119.267	S, F	S, F	
Puyallup River	47.214	-122.342	S, F	S, F	W
Newman Lake	47.773	-117.101	S, F	S, F	
Sammamish Lake	47.638	-122.084	S, F	S, F	
Skagit River	48.445	-122.335	S, F	S, F	W
Snake River	46.429	-117.153	S, F	S, F	
Snohomish River	47.911	-122.099	S, F	S, F	W
South Fork Palouse River	46.760	-117.225	S, F	S, F	
Spanaway Lake	47.113	-122.449	S, F	S, F	
West Medical Lake	47.579	-117.711	S, F	S, F	
Yakima River	46.380	-119.421	S, F	S, F	

SPM = suspended particulate matter; S = spring; F = fall; W = winter.

Marine Sediment Sites

Marine sediment samples will be collected by EAP's Puget Sound Sediment Monitoring Program under their Quality Assurance Monitoring Plan (QAMP) (Dutch et al., 2018) and 2021 QAMP addendum (Dutch, 2021). In 2021, their sampling will occur throughout the Puget Sound during April and within Elliott Bay during June. The Puget Sound stations are a part of the program's long-term monitoring stations distributed throughout the sound. The long-term stations represent a mix of non-random monitoring stations sampled since 1989, stations added in 2016, and randomly selected sites added in 2017 to increase the spatial extent of the study design.

The Puget Sound Sediment Monitoring Program collects sediment from urban bays on an annual rotation schedule of 6 years. In 2021, the program is collecting samples from Elliott Bay. The program samples 36 sites in the urban bays selected from a stratified random sampling design. Twenty of the Elliott Bay sites were non-randomly selected for this phthalates study, with an emphasis on equal distribution throughout the bay. None of the sites are located in close proximity of permitted outfalls, though many outfalls are present along the shoreline of this bay.

The Puget Sound Sediment Monitoring Program field crews will fill a separate sample jar for this phthalates project collected at the long-term and Elliott Bay stations outlined in Table 14.

Table 14. Sampling locations and timing for marine sediment collections.

Location and Site #	Latitude	Longitude	Sample Timing	
			April	June
Puget Sound #40025	48.624	-122.963	X	
Puget Sound #40034	48.094	-122.733	X	
Puget Sound #40021	48.279	-122.615	X	
Puget Sound #40022	47.672	-122.600	X	
Puget Sound #40025	48.625	-122.962	X	
Puget Sound #40026	47.762	-122.832	X	
Puget Sound #40027	47.866	-122.508	X	
Puget Sound #40028	47.136	-123.010	X	
Puget Sound #40029	48.637	-122.552	X	
Puget Sound #40030	47.545	122.651	X	
Puget Sound #40032	47.349	-122.806	X	
Puget Sound #3	48.870	-122.978	X	
Puget Sound #4	48.684	-122.538	X	
Puget Sound #13	47.838	-122.629	X	
Puget Sound #29	47.701	-122.454	X	
Puget Sound #38	47.428	-122.394	X	
Puget Sound #44	47.161	-122.674	X	
Puget Sound #49	47.080	-122.913	X	
Puget Sound #40036	47.420	-122.357	X	
Puget Sound #40037	48.200	-122.586	X	
Elliott Bay #174	47.625	-122.400		X
Elliott Bay #175	47.581	-122.420		X
Elliott Bay #180	47.625	-122.379		X
Elliott Bay #181	47.615	-122.362		X
Elliott Bay #182	47.604	-122.344		X
Elliott Bay #190	47.597	122.385		X
Elliott Bay #194	47.600	-122.347		X
Elliott Bay #196	47.601	-122.350		X
Elliott Bay #204	47.561	-122.345		X
Elliott Bay #205	47.545	-122.337		X

X = sample collected at station during that time frame.

7.2.2 Field parameters and laboratory analytes to be measured

Table 15 lists the analytes to be measured by the laboratory for this study. The phthalates listed in the table will be analyzed in both sediments and water. Three non-phthalate plasticizers are also being analyzed as part of the "phthalate" suite and are included in the mention of phthalates throughout this QAPP.

Ancillary parameters to help support the results of the study will also be analyzed, including suspended sediment concentration (SSC), total organic carbon (TOC), and dissolved organic carbon (DOC) in surface water and TOC and grain size in sediments. Field crews will also measure temperature, pH, conductivity, and dissolved oxygen in-situ at the site of surface water collections with a multi-parameter probe. These ancillary parameters will be measured in order to examine relationships with phthalate concentrations among sites.

For SPM samples, the amount of material collected may be limited. Loss on ignition (LOI) will be analyzed in the SPM samples instead of grain size due to sample size limitations. The priority for analysis of the SPM samples is: phthalates > TOC > LOI > archive.

Table 15. Phthalates to be analyzed for this project.

Name	Abbreviation	CAS
bis(2-butoxyethyl) phthalate	DBEP	117-83-9
butyl benzyl phthalate	BBP	85-68-7
di(2-ethylhexyl) phthalate	DEHP	117-81-7
di(2-methoxyethyl) phthalate	DMEP	117-82-8
diallyl phthalate	DAP	131-1-9
dicyclohexyl phthalate	DcHP	84-61-7
diethyl phthalate	DEP	84-66-2
diheptyl phthalate	DHpP	3648-21-3
dihexyl phthalate	DHP	84-75-3
diisobutyl phthalate	DiBP	84-69-5
dimethyl phthalate	DMP	131-11-3
dipentyl phthalate	DPP	131-18-0
dibutyl phthalate	DBP	84-74-2
diisononyl phthalate	DINP	28553-12-0
diisodecyl phthalate	DIDP	26761-40-0
di(2-ethylhexyl) adipate *	DEHA	103-23-1
di(2-ethylhexyl) azelate*	DEHAz	103-24-2
tris(2-ethylhexyl) trimellitate *	TOTM	3319-31-1

*non-phthalate plasticizer

7.3 Modeling and analysis design

NA

7.4 Assumptions underlying design

This study design makes the assumption that the number of samples and targeted selection of sites will provide sufficient data to evaluate environmental concentrations of phthalates across a range of contamination potential in Washington state. Another assumption is that analytical reporting limits will be low enough to detect phthalates in the matrices collected.

7.5 Possible challenges and contingencies

7.5.1 Logistical problems

All sites selected for this study have been accessed in the past by Ecology staff conducting sampling. However, logistical problems could arise if current access is limited due to boat launch closures, impediments to shoreline based access, or field crew safety considerations. To mitigate these potential access issues, desk reconnaissance will be carried out to determine current status of access points. Field-based reconnaissance may also be conducted if necessary.

7.5.2 Practical constraints

Practical constraints include resource issues that may arise from uncertainties with the COVID-19 pandemic and associated field work restrictions. Field and laboratory staff will follow agency-provided protocols to reduce the risk of exposure or transmission of COVID-19.

7.5.3 Schedule limitations

Impacts to the project schedule could occur due to the challenges outlined above, or from changes in staff capacity to carry out the work. Delays in sampling, laboratory analysis, or staff resources to write the final report may result in a change to the project schedule. Internal forms and tracking of project schedules will be updated to reflect changes in deadlines.

8.0 Field Procedures

8.1 Invasive species evaluation

Field staff will follow the Environmental Assessment Program (EAP) standard operating procedure (SOP) EAP070 – Minimizing the Spread of Invasive Species (Parsons et al., 2018). Desk reconnaissance will identify sampling locations in areas of moderate or extreme concern for invasive species and follow the appropriate decontamination procedures. Several sites in the Puget Sound and Columbia River watersheds will require decontamination planning.

8.2 Measurement and sampling procedures

Field staff will collect samples and record measurements following EAP SOPs. The field sampling procedures are described below, based on the following SOPs:

- EAP015 – Manually Obtaining Surface Water Samples (Joy, 2019)
- EAP033 – Hydrolab® DataSonde®, MiniSonde®, and HL4 Multiprobes (Anderson, 2020)
- EAP040 – Obtaining Freshwater Sediment Samples (Wong, 2020)

For all sampling, field staff will wear clean nitrile gloves and follow a clean hands – dirty hands procedure. All equipment will be decontaminated before sample collection following SOPs (Friese, 2021) and Section 8.4 of this QAPP.

Surface Water Sampling

Field crews will collect two surface water samples from each study location following the EAP SOP listed above. At each site, two surface water samples will be collected during each visit: a near surface grab collected about 1 meter below water surface, and a second lower surface water sample collected about 1 meter above the sediment (bottom) surface. The near surface grab is being collected for comparability to other studies. The bottom grab is being collected to assess concentrations of phthalates near sediments and in the anoxic zone.

In lakes and large rivers or reservoirs, field staff will deploy a stainless steel Kemmerer for collection of water samples. For some river locations, the flow may be too strong for the Kemmerer to deploy correctly. In that case, field crews may use a weighted stainless steel bridge sampler or extension pole and collect a single sample from a well-mixed portion of the river as close as possible to the thalweg.

Field crews will measure depth profiles of temperature, conductivity, pH, and dissolved oxygen with a multi-parameter YSI probe at the sampling site for lake and reservoirs. Depth profile measurements will begin just below the water surface and measurements recorded every 1.0 m until 0.5 m above the sediment bottom. For sampling sites with a water depth of over 20 meters, measurements will be taken every 2.0 meters or more, depending on depth. The metalimnion will be defined as an observed change of ≥ 1° C per meter depth and noted on the field sheets. For river sites, field crews will take a single measurement of pH, conductivity, temperature, and dissolved oxygen just below the water surface.

Surface water samples will be placed inside the laboratory-provided plastic bag and stored in a cooler on ice until return to Ecology headquarters. At headquarters, surface water samples will

be placed in a temperature-controlled, walk-in cooler and then shipped to the laboratory. To accommodate MEL's organics extraction schedule, sampling for this project will occur on Tuesdays – Fridays over several weeks, and samples will be shipped to MEL on the Monday following sampling.

Bottom Sediment Sampling

Bottom sediments from each study location will be collected using either a standard ponar, petite ponar, or Ekman dredge, depending on the characteristics of the waterbody and sediments. Field crews collecting the sediments will follow the SOP listed above (Wong, 2020). Sediment samples will consist of a composite of three grabs from each site, within a 10 meter radius. Each grab will be inspected to ensure the sampler did not overfill, that the sediment/water interface is intact and clear (not overly turbid), and that the grab achieved at least 5 cm sediment depth. Overlying water will be siphoned off prior to collection of sediment.

Field reconnaissance is needed to identify suitable depositional sediment sampling sites at the Skagit, Snohomish, and Puyallup Rivers. If boat access is accessible and river conditions are safe, a ponar may be deployed from a boat to retrieve the river sediment samples. If boat access is not possible, sediments may be collected with stainless steel scoops under low tide and low flow conditions or using a bipod boom from the shoreline to extend the petite ponar out toward the thalweg of the river.

The top 2 cm of sediment not touching the side of the sampler will be collected with a stainless steel spoon and transferred to a large stainless steel mixing bowl. Once three successful sediment grabs are collected at a site, the material in the stainless steel mixing bowl will be well-mixed into a uniform consistency and color. Well-mixed sediment will then be subsampled into the appropriate containers for phthalates, TOC, and grain size. Sample jars will be placed on ice in coolers in the field, then brought to Ecology Headquarters chain-of custody room. At Ecology Headquarters, the sediment samples for phthalates analysis will be centrifuged and overlying water decanted. Samples will be stored inside a temperature-controlled walk-in cooler (grain size) and walk-in freezer (phthalates and TOC) at Ecology headquarters before being shipped to the laboratory.

Centrifuged SPM Sampling

Suspended particulate matter samples will be collected with Ecology's centrifuge trailer unit used in previous Ecology studies (Hobbs et al., 2019; Gries and Osterberg, 2011; Gries and Sloan, 2008). Sampling procedures will follow descriptions given in Quality Assurance Project Plans written by Hobbs and McCall (2016), Coots and Osterberg (2009), and Gries and Sloan (2008). A detailed operations checklist compiled by Hobbs and McCall (2016) will also be used for this project (Appendix A).

River water will be pumped into two continuous flow-through centrifuges to collect enough SPM for analysis of phthalates and ancillary parameters. A pump (Model SP4, Gundfos Inc.) will be used to draw river water from the thalweg of the river at about 6/10 depth to the centrifuge trailer unit. The position of the river water intake line may be adjusted based on field conditions, but will remain focused on obtaining a representative sample of average SPM loads in the river. River water will be pumped through Teflon-lined tubing into two flow-through centrifuges (Alfa-Laval Corporate AB, MAB 103B) where the SPM will be separated and concentrated.

About 30% of the flow from the intake tubing will enter the centrifuge unit. The other 70% is routed back to the river downstream of the intake line. Flow will be regulated inside the centrifuge unit to maintain a rate of 3 L/min to each of the two centrifuges to maximize solids removal efficiency (Gries and Sloan, 2008). In-line optical flow meters will determine flow rates to each of the centrifuges and the total volume of water sampled by each centrifuge. Field crews will continue running the centrifuge unit until the minimum amount of SPM is collected for target analyses and archive (about 200 g). Gries and Osterberg (2011) reported pump times of 17, 16, and 20 hours to collect sufficient sample sizes for organic contaminant analyses from the Skagit, Snohomish, and Puyallup Rivers, respectively, in December of 2009.

Centrifuged SPM will be collected into a stainless steel bowl and well-mixed with a stainless steel spoon. Once a uniform color and consistency are obtained, the SPM will be subsampled into separate jars for analysis of phthalates, TOC, and LOI. The remaining mass will be archived. Sample containers will be placed on ice in coolers immediately after subsampling and transported to Ecology's Headquarters chain-of-custody room where they will be stored in the walk-in refrigerator (TOC only) and walk-in freezer (all other analytes) until shipment to the laboratory.

Several months prior to using the centrifuge unit to collect samples, an equipment blank of laboratory-provided reagent water will be circulated through the entire system and sent to MEL for analysis of phthalates to assess potential contamination in the unit. Decontamination of the centrifuge unit is discussed in Section 8.4.

During sampling events in December, an equipment rinse blank will be collected using laboratory-provided reagent water prior to sample collection at each site. Field crews will also collect a SSC sample of the influent and effluent twice during the period of sampling to assess efficiency of the centrifuge unit.

Marine Sediment Sampling

Ecology's Puget Sound Sediment Monitoring Program will collect the marine sediments following methods outlined in their QAMP (Dutch et al., 2018) and QAMP Addendum (Dutch, 2021). At each station coordinate, field crews will deploy a double 0.1 m^2 stainless steel modified van Veen grab sampler for collection of sediment. After inspection for suitability of the grab (i.e., lacking fine-grained particles, over- or under-penetration of surface), one side of the double van Veen will be sampled for several chemistry analyses.

The top 2-3 cm of sediment will be collected with a stainless steel spoon and placed in a stainless steel bucket with a covered lid. Grabs will be taken until enough sediment is collected to fill all sample containers for the station. Field crews will then mix the composited sediment in the bucket with a stainless steel spoon or paint mixer until a well-mixed texture and color are achieved. A separate jar will be filled from the composite bucket for the phthalates analysis for this project. The jars filled for this project will use separate work order and lab sample IDs, provided for this project.

The marine sediment field crews will off-load the sediment samples from the research vessel every 1-3 days and transport them to Ecology's Operations Center. Sediments will be stored at the Operations Center in either the walk-in refrigerator or freezer under the appropriate holding temperature until transport to MEL for analysis. The field lead will then transport the sediment

samples to Ecology headquarters to be centrifuged and overlying water decanted. Samples will be stored inside a temperature-controlled walk-in freezer at Ecology headquarters before being shipped to the laboratory.

8.3 Containers, preservation methods, holding times

Table 16. Sample containers, preservation, and holding times.

Parameter	Matrix	Minimum Quantity Required	Container	Preservation	Holding Time
Phthalates	water	1 L	1 liter amber glass bottle certified organic free w/ Teflon lid	Cool to ≤ 6° C	7 days
SSC	water	2 L	2 L HDPE container	Cool to ≤ 6° C	7 days
DOC	water	60 mL	125 mL preacidified poly bottle	Field-filter w/ 0.45 µm pore size; 1:1 HCl to pH <2; Cool to 6° C	28 days
TOC	water	60 mL	125 mL preacidified poly bottle	1:1 HCl to pH <2; Cool to 6° C	28 days
Phthalates	Sediment (freshwater and marine)/SPM	100 g ww	8 oz certified organic-free wide-mouth glass jar w/ Teflon lid	Freeze at -18° C	1 year frozen
TOC	Sediment/SPM	20 g ww	2 oz clear glass jar w/ Teflon lid	Cool to ≤ 6° C	14 days; 6 months if frozen
Grain Size	sediment	100 g ww	8 oz plastic jar	Cool to ≤ 6° C	6 months
LOI	SPM	25 g ww	4 oz glass jar	Cool to ≤ 6° C; Freeze at -18° C	6 months

SSC = suspended sediment concentration; DOC = dissolved organic carbon; TOC = total organic carbon;
SPM = suspended particulate matter; LOI = loss on ignition; ww = wet weight.

8.4 Equipment decontamination

All sampling equipment will be decontaminated prior to use with the following procedure: hand washed with Liquinox soap and hot tap water, deionized water rinse, acetone rinse, and a final hexane rinse. After equipment is completely dry, it will be wrapped with aluminum foil (dull side in) for transport to the field. All aspects of decontamination will follow Ecology's SOP for Decontamination of Sampling Equipment for Use in Collecting Toxic Chemical Samples (Friese, 2020).

All centrifuge unit parts coming in contact with the river water and SPM samples will be decontaminated with the following procedure prior to the first river sampling event, following Gries and Osterberg (2011):

- The stainless steel pump will soak for 48 hours in deionized water.
- Tubing and centrifuge parts will be cleaned with Liquinox and deionized water, followed by acetone and hexane rinses. Methanol will be used to rinse the tubing and flow meters inside the trailer.
- Between river sampling events, centrifuge parts will be cleaned with Liquinox and deionized water. River water from each site will be pumped through the tubing for at least 15 minutes before collecting SPM.

8.5 Sample ID

Laboratory sample IDs will be assigned using a MEL work order number followed by consecutive numbers starting with -01.

8.6 Chain of custody

Chain of custody will be maintained for all samples throughout this project. Samples will be stored in a cooler or freezer in Ecology's locked headquarters chain of custody room or locked Operations Center cooler. Ecology staff will use MEL's chain of custody form for shipment to the laboratory.

8.7 Field log requirements

Field data will be recorded in a bound, waterproof notebook on Rite-in-the-Rain paper. Corrections will be made with single line strikethroughs, initials, and date. The following will be filled out at each sampling location:

- Name and location of project
- Field personnel
- Sequence of events
- Any changes or deviations from the QAPP
- Environmental conditions
- Date, time, location, ID, and description of each sample
- Water depth at location of sampling and depths at which samples were collected
- Field instrument calibration procedures
- Field measurement results
- Identity of quality control (QC) samples collected
- Stage height at nearby USGS gaging station (for rivers)
- Unusual circumstances that might affect interpretation of results

8.8 Other activities

For the marine sediment sample analysis, the project manager will coordinate with the NEP grant lead to provide appropriate progress reports. Final results of the marine sediments analysis will be incorporated in the final report for this study.

The field lead for this project is also researching methods to obtain time-integrated samples (2-3 months) of SPM from large rivers. Several in-situ samplers are being considered for fabrication and deployment in the fall of 2021. If prototypes provide a suitable quantity and quality of material for analysis of phthalates, a QAPP addendum will be written to include this sample collection in the fall.

9.0 Laboratory Procedures

9.1 Lab procedures table

Manchester Environmental Laboratory (MEL) will carry out all analyses presented in Tables 17 and 18, with the exception of grain size. A contract laboratory will be used for grain size analysis.

Table 17. Laboratory analysis procedures for freshwater samples.

Parameter	Matrix	Number of spring samples / Arrival date	Number of fall samples / Arrival date	Number of winter samples / Arrival date	Expected range of results	Sample Prep/Clean-up Method	Analytical Method
Phthalates	water	40 / May-Jun	40 / Sept-Oct	---	<0.1 - 20 µg/L	EPA 3535/EPA 3620C florisil*	EPA 8270E (GC/MS)
SSC	water	38 / May-Jun	38 / Sept-Oct	---	1-300 mg/L	n/a	D3977B
DOC	water	38 / May-Jun	38 / Sept-Oct	---	<1-20 mg/L	---	SM5310B
TOC	water	38 / May-Jun	38 / Sept-Oct	---	<1-20 mg/L	---	SM5310B
Phthalates	sediment	20 / May-Jun	20 / Sept-Oct	---	ND - 1,000 µg/kg	EPA 3541/EPA 3620C florisil	EPA 8270E (GC/MS)
TOC	sediment	18 / May-Jun	18 / Sept-Oct	---	<0.1-40%	---	EPA 440.0
Grain Size	sediment	18 / May-Jun	18 / Sept-Oct	---	1-100%	---	PSEP 1986
Phthalates	sediment (SPM)	---	---	4 / Dec 2021	ND - 1,000 µg/kg	EPA 3541/EPA 3620C florisil	EPA 8270E (GC/MS)
TOC	sediment (SPM)	---	---	4 / Dec 2021	<0.1-40%	---	EPA 440.0
LOI	sediment (SPM)	---	---	4 / Dec 2021	0.1 – 20% of dw	ASTM D2584	Muffle furnace
SSC	water	---	---	8 / Dec 2021	1-300 mg/L	n/a	D3977B
Phthalates	water (SPM blank)	---	---	4 / Dec 2021	<0.1 - 20 µg/L	EPA 3535/EPA 3620C florisil	EPA 8270E (GC/MS)

SSC = suspended sediment concentration; DOC = dissolved organic carbon; TOC = total organic carbon; ND = non-detect; LOI = loss on ignition. *Water samples may not require clean-up.

Table 18. Laboratory analysis procedures for marine samples.

Parameter	Matrix	Number of Puget Sound samples / Arrival date	Number of Elliott Bay samples / Arrival date	Expected range of results	Sample Prep/Clean-up Method	Analytical Method
Phthalates	marine sediment	20 / April 2020	10 / June 2021	ND - 1,000 µg/kg	EPA 3541/EPA 3620C florisil	EPA 8270E (GC/MS)

ND = non-detect.

9.2 Sample preparation method(s)

Sample preparation methods are presented in Tables 17 and 18.

9.3 Special method requirements

All analyses will follow EPA, Standard Methods, and Puget Sound Estuary Partnership (PSEP) methods. Five of the compounds in the phthalate suite have never been analyzed by MEL before and require special method development. Further development will also be needed for eight of the analytes that MEL currently analyzes in consumer products, but not in environmental samples. MEL will need to develop a lower reporting limit for these analytes than what is achieved for consumer products. MEL is responsible for carrying out this method development prior to analyzing the samples.

MEL will conduct the following tasks during their method development for new analytes, prior to analyzing extracts from the first round of samples in May 2021:

- Run calibrations for the method with the new analyte standards and evaluate background contamination.
- Complete initial demonstration of capability (IDC) in aqueous and solid matrices.
- Complete lower limit of quantitation (LLOQ) in aqueous and solid matrices and provide these limits to the project officer.

Results of the method development (calibrations, method blank contamination, IDCs, and LLOQs) will be shared with the project officer and Ecology's Quality Assurance Officer before sample analysis.

9.4 Laboratories accredited for methods

All analyses will be conducted by MEL for methods that the laboratory is accredited for, or by a contract laboratory accredited to carry out the analysis. MEL will seek a waiver for accreditation of new analytes being developed for this study. No laboratories were identified during development of this QAPP to hold accreditation for all phthalate analytes requested. MEL was chosen as the laboratory for these analyses because they could develop the method for the additional analytes in time for this study. An accreditation waiver will also be requested for analysis of DOC in water and LOI in suspended particulate matter, as MEL currently does not hold accreditation for those analyses.

10.0 Quality Control Procedures

10.1 Table of field and laboratory quality control

Table 19. Quality control samples, types, and frequency.

Parameter	Matrix	Field blank	Field replicate	LCS	Method blanks	Matrix spikes	Matrix spike duplicates	Laboratory duplicates
Phthalates	water	10% of samples	10% of samples	1/batch	1/batch	1/batch	1/batch	1/batch
SSC	water	---	10% of samples	1/batch	1/batch	---	---	1/batch
DOC	water	---	10% of samples	1/batch	1/batch	1/batch	1/batch	1/batch
TOC	water	---	10% of samples	1/batch	1/batch	1/batch	1/batch	1/batch
Phthalates	Sediment (freshwater and marine)	---	10% of samples	1/batch	1/batch	1/batch	1/batch	1/batch
TOC	sediment	---	10% of samples	1/batch	1/batch	---	---	1/batch
Grain Size	sediment	---	10% of samples	1/batch	1/batch	---	---	1/batch
Phthalates	sediment (SPM)	---	10% of samples	1/batch	1/batch	1/batch	1/batch	1/batch
TOC	sediment (SPM)	---	10% of samples	1/batch	1/batch	---	---	1/batch
LOI	sediment (SPM)	---	10% of samples	1/batch	1/batch	---	---	1/batch
Phthalates	water (SPM equipment blanks)	10% of samples	---	1/batch	1/batch	1/batch	1/batch	1/batch

SSC = suspended sediment concentration; DOC = dissolved organic carbon; TOC = total organic carbon; SPM = suspended particulate matter; LOI = loss on ignition. Batch = a laboratory batch of 20 or fewer samples.

10.2 Corrective action processes

MEL and contract laboratories will be expected to follow corrective action processes outlined in the methods listed in Table 17. The project manager will work with MEL staff to examine data that fall outside of QC criteria stated in this QAPP. The project manager will determine whether data should be re-analyzed, rejected, or used with appropriate qualification. These decisions will be documented in the final report, along with any other deviations from the QAPP.

11.0 Data Management Procedures

11.1 Data recording and reporting requirements

All field data and observations will be recorded on waterproof paper kept in field notebooks. Staff will transfer information contained in field notebooks to Excel spreadsheets after they return from the field. This manual transfer of field data to electronic spreadsheets will be reviewed by the project manager for accuracy and any errors will be addressed.

MEL will provide data electronically in EIM format via the Laboratory Information System (LIMS). Field and laboratory data for the project will be entered into Ecology's EIM system and the EIM data entry will be independently verified for accuracy by another member of the project team following standardized EAP procedures for QC of data entry.

In addition to EIM, all phthalates data from the marine sediment samples will be uploaded to EPA's Water Quality eXchange (WQX) database to satisfy requirements of the NEP grant.

11.2 Laboratory data package requirements

MEL will provide the electronic data deliverable described above, which will include results of samples and QC tests. The laboratory will also provide a case narrative documenting the condition of samples upon receipt, sample preparation, methods of analysis, instrument calibration, and results of QC tests. Narratives will address any problems encountered with analyses, corrective actions taken, changes to the referenced method, and explanations of data qualifiers. The MEL sample coordinator will send the project manager the case narrative via email, as well as copies of signed chain of custody forms.

11.3 Electronic transfer requirements

MEL staff will enter laboratory data generated by MEL into their Laboratory Information Management System (LIMS). The LIMS electronically transfers the data in an EIM deliverable format to the Project Manager. The format of data deliverables is typically a comma separated values (CSV) table. Comma Separated Value format is generally readable by most common data analysis and management tools such as Excel.

11.4 EIM/WQX data upload procedures

MEL must provide all of their analytical results in an EDD format that meets Ecology requirements for loading to Ecology's EIM database. Analytical data for the project will be entered into Ecology's EIM database following internal Environmental Assessment Program (EAP) protocols and business rules. An independent reviewer will conduct a QC review of this data upload, following internal EAP protocols.

Data submittal to WQX will be done using EPA's standard web-based application and Excel spreadsheets. EPA procedures for uploading to WQX will be followed.

11.5 Model information management

NA

12.0 Audits and Reports

12.1 Field, laboratory, and other audits

MEL and contracted laboratories must participate in performance and system audits of their routine procedures. No audits are planned specifically for this project.

12.2 Responsible personnel

NA

12.3 Frequency and distribution of reports

A draft and final report of the study findings will be developed according to the schedule in Table 7. The report will include, at a minimum, the following:

- Map showing all sampling locations and any other pertinent features of the study area.
- Description of field and laboratory methods.
- Discussion of data quality and the significance of any problems encountered.
- Final results of phthalate concentrations measured in the samples.
- Analyte concentrations relative to other studies in the state and U.S.
- Recommendations for follow-up actions, based on study results.

12.4 Responsibility for reports

The project manager will have lead responsibility for the draft and final report. The field lead will assist with report development.

13.0 Data Verification

Data verification is the process of evaluating the completeness, correctness, and conformance/compliance of a specific data set against the method, procedural, or contractual requirements. Data verification will take place after each field collection event before leaving the site. Laboratory generated data will be verified by MEL staff when data are entered into LIMS. Data will also be verified during the data archival step where data are loaded to EIM. The verification steps will establish a quality level that meets credibility requirements needed for informing decisions.

13.1 Field data verification, requirements, and responsibilities

The project manager will verify that all field data were recorded without error or omission.

13.2 Laboratory data verification

MEL staff will conduct verification of laboratory data before entering results into the LIMS. Verification will include examining the data for errors, omissions, and compliance with QC acceptance criteria and the method. MEL will include a case narrative that discusses whether (1) MQOs were met, (2) proper analytical methods and protocols were followed, (3) calibrations and controls were within limits, and (4) data were consistent, correct, and complete, without errors or omissions. The case narrative will also define qualifiers and the reason for their use and will be released to the project manager. Laboratory staff may be consulted in order to review QC data that are normally retained by MEL.

The project manager is responsible for the final acceptance of the project data. 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. Accuracy of data entered into EIM will be verified by someone other than the data engineer per the Environmental Assessment Program's EIM data entry business rules.

13.3 Validation requirements, if necessary

Independent validation will not be required for this project.

13.4 Model quality assessment

NA

14.0 Data Quality (Usability) Assessment

14.1 Process for determining project objectives were met

The project manager will determine data usability by assessing whether data meet the MQOs outlined in Section 6 and Table 10. Data will either be accepted, accepted with qualification, or rejected and re-analysis considered. Results of usability assessment will be included in the final report of study findings.

14.2 Treatment of non-detects

Non-detect samples will be qualified "U" or "UJ" at the lower limit of quantitation. Results below the lower limit of quantitation will be reported if qualitative criteria are met and the analyte is not present in the method blank. These values will be qualified "J" as an estimate. Summed values will include only detected concentrations. Results qualified "NJ" (the analyte is tentatively identified and the result is an estimate) will not be included in summed values. Statistical analysis requiring treatment of non-detects will not be included in the final report.

14.3 Data analysis and presentation methods

Data will be presented in the form of summary tables, graphs, and spatial maps for the final report. See Section 12.3 for more information on how the data will be presented in the final report.

14.4 Sampling design evaluation

The number and type of samples collected is expected to be sufficient to meet the objectives of this project.

14.5 Documentation of assessment

Documentation of assessment will occur in the final report.

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16.0 Appendices

Appendix A. Details for operating flow-through centrifuge unit

This checklist was used by Hobbs and McCall (2016), as compiled through their personal communication with Brandi Lubliner.

Pre-Use Checklists

- Check tire pressure.
- Check gas level for the generator – fill with unleaded gasoline without ethanol because ethanol gums up small engines such as generators.
- Start generator to see if it is running well.
- Clean centrifuge parts to study quality needs. This takes a whole day.

Centrifuge Generator Set-up

- At the back of the generator, turn yellow knob to vertical position to open up the gas flow to the generator engine.
- At the back of the generator, toggle the switch toward the "external fuel tank" writing. It will make a click when orientation is good (roughly 2 o'clock position).
- At the toe of the big red fuel tank by the generator, turn the white knob all the way open to allow gas flow to the generator.
- On the generator itself:
    - Pull the choke knob out.
    - Turn the start switch to turn it on.
    - Flip the toggle switch on the side of the generator that says "Fuel pump on."
    - Push choke back in after about 20 seconds.
    - Don't turn circuit breaker switch yet.

Power from the Circuit Breaker to the Trailer

- Plug in the large black plug (4-prong) into the plug below the circuit breaker box. Note: large black power cord coming out of the circuit breaker itself is just for extra power if needed to run instruments (3-prong one).
- Plug 4-prong plug into the face of the generator and flip the circuit breaker switch on face of generator.
- In the circuit breaker box, flip "main circuit breaker" switch to power the inside of the trailer.
- Inside the centrifuge trailer, flip all the circuits up to power the lights and outlets.
- Light switch is on the wall (gray toggle).

Centrifuge bowl assembly

- Match numbers from the centrifuge spindle bases to the bowls.
- Put some of the Vaseline on the spindle.
- Brakes should be backed off to allow bowl to slide down the spindle, spin to make sure the bowl is seated (no sounds of catching) and that the bowl spins true and is not wobbly.
- Lock brakes by screwing pins (both in place).

- Put cone assembly in bowls and match the notches.
- Set the lid in next, match the notches, and place the o-ring in place.
- Screw the nut at the top of post to keep the bowls in place.
- Use crescent wrench to get it slightly snugger than "finger tight". Don't wrench it down.
- Unlock the brakes and spin bowl. Listen and look for spinning trueness.
- Relock the brakes.
- Put large locking ring on hand tight (reverse threaded), then grab large red locking ring wrench and rubber mallet.
- Align the two markings that look like this by hitting the wrench with the mallet. They must be within a ¼ inch of alignment.
- Next set the small cone hood and small locking ring in place. It is reverse threaded also.
- Use the small red locking ring wrench (there is a small notch to grab the ring), and hand/body to tighten. Get it as tight as possible, but don't hammer.
- Unlock the brakes and spin bowl. Listen and look for spinning trueness.
- The hood manifold is next. They're interchangeable and don't need to match the numbers on the bowls. Line up the outlet tube to the hose to catch the exit water.
- Hook up the lines to plumb hoods to the incoming water. The compression fittings are fairly soft Teflon thread, so tighten carefully to not cross thread.
- Screw lug-nuts to hold down the manifold once the plumbing is connected. Hand tight is fine. You may need to check after several hours of operation to see if they've loosened.

Powering up the Centrifuges

- Once the bowls have been assembled, the centrifuge can be turned on. Plug the power cable into the outlet. Power up one bowl at a time to minimize the power draw on the generator. It takes about 3 minutes for the centrifuge to reach full power. Then turn second centrifuge on.
- Once the centrifuges are running, the oil globe will be opaque with frothy oil.
- Turn on the water source. Ideal sampling flow rate for the centrifuges is 6 liters per minute to the trailer when running both centrifuges (3L/min each).

While centrifuges are sampling

- Keep constantly aware of clogging on the plumbing board. The small diameter fittings clog easily on stormwater or highly turbid water. Flick all joints and turn on and off flow toggles to dislodge sediment. It is also a good idea to measure exit water flow rates at regular intervals or after disruptions.

Shutting down the Centrifuge

- Shut off the water source and wait until the bowls' exit water dries out.
- Pull the power plug. It takes about 5 minutes for the centrifuge to slow down.
- There is a breaking button, but just let the bowls slow down naturally.
- Unscrew all locking rings and spindle.
- Siphon off water into centrifuge jars or waste it, depending on how much sample you think you need.
- Use the "puller" to lift the bowls off the spindle.

Appendix B. Glossaries, acronyms, and abbreviations

Glossary of General Terms

Ambient: Background or away from point sources of contamination. Surrounding environmental condition.

Baseflow: The component of total streamflow that originates from direct groundwater discharges to a stream.

Conductivity: A measure of water's ability to conduct an electrical current. Conductivity is related to the concentration and charge of dissolved ions in water.

Effluent: An outflowing of water from a natural body of water or from a human-made structure. For example, the treated outflow from a wastewater treatment plant.

Nonpoint source: Pollution that enters any waters of the state from any dispersed land-based or water-based activities, including but not limited to atmospheric deposition, surface-water runoff from agricultural lands, urban areas, or forest lands, subsurface or underground sources, or discharges from boats or marine vessels not otherwise regulated under the NPDES program. Generally, any unconfined and diffuse source of contamination. Legally, any source of water pollution that does not meet the legal definition of "point source" in section 502(14) of the Clean Water Act.

pH: A measure of the acidity or alkalinity of water. A low pH value (0 to 7) indicates that an acidic condition is present, while a high pH (7 to 14) indicates a basic or alkaline condition. A pH of 7 is considered to be neutral. Since the pH scale is logarithmic, a water sample with a pH of 8 is ten times more basic than one with a pH of 7.

Point source: Source of pollution that discharges at a specific location from pipes, outfalls, and conveyance channels to a surface water. Examples of point source discharges include municipal wastewater treatment plants, municipal stormwater systems, industrial waste treatment facilities, and construction sites where more than 5 acres of land have been cleared.

Sediment: Soil and organic matter that is covered with water (for example, river or lake bottom).

Stormwater: The portion of precipitation that does not naturally percolate into the ground or evaporate but instead runs off roads, pavement, and roofs during rainfall or snow melt. Stormwater can also come from hard or saturated grass surfaces such as lawns, pastures, playfields, and from gravel roads and parking lots.

Streamflow: Discharge of water in a surface stream (river or creek).

Suspended particulate matter: Inorganic and organic particles transported in suspension within a river.

Thalweg: The deepest and fastest moving portion of a stream.

Watershed: A drainage area or basin in which all land and water areas drain or flow toward a central collector such as a stream, river, or lake at a lower elevation.

Acronyms and Abbreviations

BBP	Butyl benzel phthalate
DAP	Diallyl phthalate
DBEP	Bis(2-butoxyethyl) phthalate
DBP	Dibutyl phthalate
DcHP	Dicyclohexyl phthalate
DEHA	Di(2-ethylhexyl) adipate
DEHAz	Di(2-ethylhexyl) azelate
DEHP	Di(2-ethylhexyl) phthalate
DEP	Diethyl phthalate
DHP	Dihexyl phthalate
DHpP	Diheptyl phthalate
DiBP	Diisobutyl phthalate
DIDP	Diisodecyl phthalate
DINP	Diisononyl phthalate
DMEP	Di(2-methoxyethyl) phthalate
DMP	Dimethyl phthalate
DnOP	Di-n-octyl phthalate
DOC	Dissolved organic carbon
DPP	Dipentyl phthalate
e.g.	For example
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
et al.	And others
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective
PBT	Persistent, bioaccumulative, and toxic substance
QA	Quality assurance
QC	Quality control
RM	River mile
RPD	Relative percent difference
RSD	Relative standard deviation
SOP	Standard operating procedures
SPM	Suspended particulate matter
SSC	suspended sediment concentration
TOC	Total organic carbon
TOTM	Tris(2-ethylhexyl) trimellitate
WRIA	Water Resource Inventory Area
WWTP	Wastewater treatment plant

Units of Measurement

°C	degrees centigrade
Dw	dry weight
Ft	feet
G	gram, a unit of mass

mg/L	milligram per liter (parts per million)
s.u.	standard units
µg/kg	micrograms per kilogram (parts per billion)
µg/L	micrograms per liter (parts per billion)
µS/cm	microsiemens per centimeter, a unit of conductivity
ww	wet weight

Quality Assurance Glossary

Accreditation: A certification process for laboratories, designed to evaluate and document a lab's ability to perform analytical methods and produce acceptable data. For Ecology, it is "Formal recognition by (Ecology)…that an environmental laboratory is capable of producing accurate analytical data." [WAC 173-50-040] (Kammin, 2010)

Accuracy: The degree to which a measured value agrees with the true value of the measured property. USEPA recommends that this term not be used, and that the terms *precision* and *bias* be used to convey the information associated with the term *accuracy* (USGS, 1998).

Analyte: An element, ion, compound, or chemical moiety (pH, alkalinity) which is to be determined. The definition can be expanded to include organisms, e.g., fecal coliform, Klebsiella (Kammin, 2010).

Bias: The difference between the sample mean and the true value. Bias usually describes a systematic difference reproducible over time and is characteristic of both the measurement system and the analyte(s) being measured. Bias is a commonly used data quality indicator (DQI) (Kammin, 2010; Ecology, 2004).

Blank: A synthetic sample, free of the analyte(s) of interest. For example, in water analysis, pure water is used for the blank. In chemical analysis, a blank is used to estimate the analytical response to all factors other than the analyte in the sample. In general, blanks are used to assess possible contamination or inadvertent introduction of analyte during various stages of the sampling and analytical process (USGS, 1998).

Calibration: The process of establishing the relationship between the response of a measurement system and the concentration of the parameter being measured (Ecology, 2004).

Check standard: A substance or reference material obtained from a source independent from the source of the calibration standard; used to assess bias for an analytical method. This is an obsolete term, and its use is highly discouraged. See Calibration Verification Standards, Lab Control Samples (LCS), Certified Reference Materials (CRM), and/or spiked blanks. These are all check standards but should be referred to by their actual designator, e.g., CRM, LCS (Kammin, 2010; Ecology, 2004).

Comparability: The degree to which different methods, data sets and/or decisions agree or can be represented as similar; a data quality indicator (USEPA, 1997).

Completeness: The amount of valid data obtained from a project compared to the planned amount. Usually expressed as a percentage. A data quality indicator (USEPA, 1997).

Continuing Calibration Verification Standard (CCV): A quality control (QC) sample analyzed with samples to check for acceptable bias in the measurement system. The CCV is usually a midpoint calibration standard that is re-run at an established frequency during the course of an analytical run (Kammin, 2010).

Control chart: A graphical representation of quality control results demonstrating the performance of an aspect of a measurement system (Kammin, 2010; Ecology 2004).

Control limits: Statistical warning and action limits calculated based on control charts. Warning limits are generally set at +/- 2 standard deviations from the mean, action limits at +/- 3 standard deviations from the mean (Kammin, 2010).

Data integrity: A qualitative DQI that evaluates the extent to which a data set contains data that is misrepresented, falsified, or deliberately misleading (Kammin, 2010).

Data quality indicators (DQI): Commonly used measures of acceptability for environmental data. The principal DQIs are precision, bias, representativeness, comparability, completeness, sensitivity, and integrity (USEPA, 2006).

Data quality objectives (DQO): Qualitative and quantitative statements derived from systematic planning processes that clarify study objectives, define the appropriate type of data, and specify tolerable levels of potential decision errors that will be used as the basis for establishing the quality and quantity of data needed to support decisions (USEPA, 2006).

Data set: A grouping of samples organized by date, time, analyte, etc. (Kammin, 2010).

Data validation: An analyte-specific and sample-specific process that extends the evaluation of data beyond data verification to determine the usability of a specific data set. It involves a detailed examination of the data package, using both professional judgment and objective criteria, to determine whether the MQOs for precision, bias, and sensitivity have been met. It may also include an assessment of completeness, representativeness, comparability, and integrity, as these criteria relate to the usability of the data set. Ecology considers four key criteria to determine if data validation has actually occurred. These are:

- Use of raw or instrument data for evaluation.
- Use of third-party assessors.
- Data set is complex.
- Use of EPA Functional Guidelines or equivalent for review.

Examples of data types commonly validated would be:

- Gas Chromatography (GC).
- Gas Chromatography-Mass Spectrometry (GC-MS).
- Inductively Coupled Plasma (ICP).

The end result of a formal validation process is a determination of usability that assigns qualifiers to indicate usability status for every measurement result. These qualifiers include:

- No qualifier – data are usable for intended purposes.
- J (or a J variant) – data are estimated, may be usable, may be biased high or low.

- REJ – data are rejected, cannot be used for intended purposes.
  (Kammin, 2010; Ecology, 2004).

Data verification: Examination of a data set for errors or omissions, and assessment of the Data Quality Indicators related to that data set for compliance with acceptance criteria (MQOs). Verification is a detailed quality review of a data set (Ecology, 2004).

Detection limit (limit of detection)**:** The concentration or amount of an analyte which can be determined to a specified level of certainty to be greater than zero (Ecology, 2004).

Duplicate samples: Two samples taken from and representative of the same population, and carried through and steps of the sampling and analytical procedures in an identical manner. Duplicate samples are used to assess variability of all method activities including sampling and analysis (USEPA, 1997).

Field blank: A blank used to obtain information on contamination introduced during sample collection, storage, and transport (Ecology, 2004).

Initial Calibration Verification Standard (ICV): A QC sample prepared independently of calibration standards and analyzed along with the samples to check for acceptable bias in the measurement system. The ICV is analyzed prior to the analysis of any samples (Kammin, 2010).

Laboratory Control Sample (LCS): A sample of known composition prepared using contaminant-free water or an inert solid that is spiked with analytes of interest at the midpoint of the calibration curve or at the level of concern. It is prepared and analyzed in the same batch of regular samples using the same sample preparation method, reagents, and analytical methods employed for regular samples (USEPA, 1997).

Matrix spike: A QC sample prepared by adding a known amount of the target analyte(s) to an aliquot of a sample to check for bias due to interference or matrix effects (Ecology, 2004).

Measurement Quality Objectives (MQOs)**:** Performance or acceptance criteria for individual data quality indicators, usually including precision, bias, sensitivity, completeness, comparability, and representativeness (USEPA, 2006).

Measurement result: A value obtained by performing the procedure described in a method (Ecology, 2004).

Method: A formalized group of procedures and techniques for performing an activity (e.g., sampling, chemical analysis, data analysis), systematically presented in the order in which they are to be executed (EPA, 1997).

Method blank: A blank prepared to represent the sample matrix, prepared and analyzed with a batch of samples. A method blank will contain all reagents used in the preparation of a sample, and the same preparation process is used for the method blank and samples (Ecology, 2004; Kammin, 2010).

Method Detection Limit (MDL): This definition for detection was first formally advanced in 40CFR 136, October 26, 1984 edition. MDL is defined there as the minimum concentration of an analyte that, in a given matrix and with a specific method, has a 99% probability of being identified, and reported to be greater than zero (Federal Register, October 26, 1984).

Percent Relative Standard Deviation (%RSD): A statistic used to evaluate precision in environmental analysis. It is determined in the following manner:

$$\%RSD = (100 * s)/x$$

where s is the sample standard deviation and x is the mean of results from more than two replicate samples (Kammin, 2010).

Parameter: A specified characteristic of a population or sample. Also, an analyte or grouping of analytes. Benzene and nitrate + nitrite are all parameters (Kammin, 2010; Ecology, 2004).

Population: The hypothetical set of all possible observations of the type being investigated (Ecology, 2004).

Precision: The extent of random variability among replicate measurements of the same property; a data quality indicator (USGS, 1998).

Quality assurance (QA): A set of activities designed to establish and document the reliability and usability of measurement data (Kammin, 2010).

Quality Assurance Project Plan (QAPP): A document that describes the objectives of a project, and the processes and activities necessary to develop data that will support those objectives (Kammin, 2010; Ecology, 2004).

Quality control (QC): The routine application of measurement and statistical procedures to assess the accuracy of measurement data (Ecology, 2004).

Relative Percent Difference (RPD): RPD is commonly used to evaluate precision. The following formula is used:

$$[Abs(a-b)/((a + b)/2)] * 100$$

where "Abs()" is absolute value and a and b are results for the two replicate samples. RPD can be used only with 2 values. Percent Relative Standard Deviation is (%RSD) is used if there are results for more than 2 replicate samples (Ecology, 2004).

Replicate samples: Two or more samples taken from the environment at the same time and place, using the same protocols. Replicates are used to estimate the random variability of the material sampled (USGS, 1998).

Representativeness: The degree to which a sample reflects the population from which it is taken; a data quality indicator (USGS, 1998).

Sample (field): A portion of a population (environmental entity) that is measured and assumed to represent the entire population (USGS, 1998).

Sample (statistical): A finite part or subset of a statistical population (USEPA, 1997).

Sensitivity: In general, denotes the rate at which the analytical response (e.g., absorbance, volume, meter reading) varies with the concentration of the parameter being determined. In a specialized sense, it has the same meaning as the detection limit (Ecology, 2004).

Spiked blank: A specified amount of reagent blank fortified with a known mass of the target analyte(s); usually used to assess the recovery efficiency of the method (USEPA, 1997).

Spiked sample: A sample prepared by adding a known mass of target analyte(s) to a specified amount of matrix sample for which an independent estimate of target analyte(s) concentration is available. Spiked samples can be used to determine the effect of the matrix on a method's recovery efficiency (USEPA, 1997).

Split sample: A discrete sample subdivided into portions, usually duplicates (Kammin, 2010).

Standard Operating Procedure (SOP): A document which describes in detail a reproducible and repeatable organized activity (Kammin, 2010).

Surrogate: For environmental chemistry, a surrogate is a substance with properties similar to those of the target analyte(s). Surrogates are unlikely to be native to environmental samples. They are added to environmental samples for quality control purposes, to track extraction efficiency and/or measure analyte recovery. Deuterated organic compounds are examples of surrogates commonly used in organic compound analysis (Kammin, 2010).

Systematic planning: A step-wise process which develops a clear description of the goals and objectives of a project, and produces decisions on the type, quantity, and quality of data that will be needed to meet those goals and objectives. The DQO process is a specialized type of systematic planning (USEPA, 2006).

References for QA Glossary

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