

Addendum to Quality Assurance Project Plan

Assessing Sources of Toxic Chemicals Impacting Juvenile Chinook Salmon

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by Alex D. Gipe

March 2023

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The numbered headings in this document correspond to the headings in the original QAPP. Only relevant sections are included here; therefore, some numbered headings may be missing.

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2.0 Abstract

The recovery of Puget Sound Chinook salmon populations is in part measured by the reduction of contaminant levels in juvenile Chinook. This key indicator of the health of the species population continues to not meet the goal of a declining trend in contaminant levels for 95% of juvenile Chinook sampled by 2030. During the last (2016) Puget Sound monitoring, juvenile Chinook from four of the 11 river estuaries continued to not meet recovery targets for tissue burdens of toxic chemicals (toxics).

Because juvenile Chinook from the White-Puyallup watershed did not meet target levels for PCBs and PBDEs, the state departments of Fish &Wildlife and Ecology are planning further monitoring to determine the sources of these contaminants.

The investigation of potential point and nonpoint sources of PCBs and PBDEs in the White-Puyallup watershed is needed to meet 2030 recovery targets through the reduction of toxic inputs into juvenile Chinook habitats. This document describes the up-coming study which will sample freshwater and estuarian environments in order to determine sources of toxics impacting juvenile Chinook along their migratory pathway from natal streams to the near-shore environment. We will use several monitoring techniques including:

- Integrated surface water sampling (passive samplers).
- Sediment sampling (benthic/suspended).
- Sampling of resident biota (aquatic macroinvertebrates).

This document is an addendum to the most recent Quality Assurance Project Plan (Hobbs, 2019) and provides updated information specific to sampling of the White-Puyallup watershed (WRIA 10). The goal of this study is to identify and prioritize sources of PCBs and PBDEs within the watershed that are impacting juvenile Chinook.

3.0 Background

3.1 Introduction and problem statement

Chinook salmon (*Oncorhynchus tshawytscha*) play an important role in the Puget Sound ecosystem. Returning and resident adult Chinook are a vital food source for endangered southern resident orca whales (Hanson et al., 2021; Ford et al., 2016), and juvenile Chinook are important prey for many avian species (Collis et al., 2011; Evans et al., 2016). Beyond their role in the ecosystem, Chinook are (1) culturally important to Native Americans in Washington and (2) of significant commercial and recreational value.

Chinook populations rely on freshwater habitats where juveniles spend their early life stages before migrating through estuaries to the Puget Sound. This migration requires passage through urbanized environments which are often hydrologically altered and contaminated with toxic chemicals (toxics) from stormwater runoff and wastewater discharges. While the restoration of threated Endangered Species Act (ESA)-listed Chinook populations often focuses on restoring degraded habitat, evidence suggests that impacts from toxics within the migratory pathway of juvenile Chinook also plays a role in this population decline.

A Washington Department of Fish and Wildlife (WDFW) survey of juvenile Chinook throughout the Puget Sound region found that polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) in fish tissues from urbanized river systems exceeded fish health thresholds (Figure 1; WDFW, 2016). Fish health threshold concentrations are a measure of the body burden of PCBs and PBDEs which, if exceeded, may reduce fish survival through increased disease susceptibility, reduced growth, and altered behavior (Arkoosh et al., 2010; Meador et al., 2010). Up to 45% of juvenile Chinook captured in the lower Puyallup River and estuary had levels of PCBs and PBDEs exceeding fish health thresholds (O'Neill et all. 2015). Juvenile Chinook migrating through Puget Sound estuaries contaminated with PCBs, PBDEs, and other toxics have been shown to have a 45% lower survival rate than Chinook migrating through uncontaminated estuaries (Meador 2014).



Figure 1. Concentrations of PCBs and PBDEs in juvenile Chinook tissue, 2016. Figure courtesy of Puget Sound Partnership's Puget Sound Vital Signs and WDFW

Toxics enter the migratory path of juvenile Chinook due to the urbanization and industrialization of the Puget Sound region. The development of watersheds near river and estuarian environments has led to greater discharges of stormwater and wastewater, both of which are pathways of PCBs and PBDEs into the environment (De Wit, 2002; Ecology, 2015). As juvenile Chinook move through river and estuarian environments during their migration to marine waters, they absorb toxics from the water column and contaminated prey (O'Neill et al., 2019; Johnson et al, 2007). The impacts of these toxics may affect the health of juveniles during the energy-

intense process of transitioning from freshwater to saltwater, limiting their growth and suppressing their immune system. The outcomes of these impacts limit the survival of juvenile Chinook and in turn may reduce the abundance of returning adult Chinook to Puget Sound.

A reduction in returning Chinook has been identified as a cause for the declining population of endangered southern resident orca whales (Southern Resident Orca Task Force, 2019). The Governor's Orca Task Force, convened in 2018 to address this population decline, has identified the need to assess sources of toxics in Chinook migratory river systems in order to reduce chemical contamination in Orca prey and bolster Chinook populations. The work outlined in this Quality Assurance Project Plan (QAPP) addendum directly addresses this need and supports further Puget Sound recovery work.

This assessment will build on the success of our previous source assessment studies in the Snohomish River watershed. Starting in 2019, the Washington State Department of Ecology (Ecology) conducted multi-year sampling focused on identifying sources of PBDEs impacting juvenile Chinook in the Snohomish, Snoqualmie, and Skykomish Rivers. This work included successfully identifying several areas of increased PBDE concentrations in water, sediment, and biota. These areas of concern are associated with localized discharges of treated wastewater. Through workgroups with local municipalities, wastewater treatment plant (WWTP) operators, and a non-governmental organization, we successfully brought together stakeholders within the watershed to address the issues identified through our sampling efforts.

The source assessment of PCBs and PBDEs in the White-Puyallup watershed is the next stage of our ongoing work to identify sources of toxics impacting juvenile Chinook salmon along their migratory pathway. The outcome of this work will be a prioritized list of sources of PCBs and PBDEs in the watershed. This list can ultimately be used to reduce toxics impacting juvenile Chinook and increase early marine survival. This addendum to the original QAPP (Hobbs, 2019), describes the approach to source identification work that will take place in the White-Puyallup watershed (WRIA 10).

3.2 Study area and surroundings

3.2.1 History of study area

The White-Puyallup watershed is located within the Puget Sound basin. The Puyallup River is formed by the confluence of the Puyallup, White, and Carbon Rivers. The Puyallup River drains from its headwaters at the glaciers of Mount Rainier National Park through the lowlands of the Puget Sound region to Commencement Bay. The White-Puyallup watershed drains an area of about 1,056 square miles through rivers and streams which total over 1,287 linear miles. The headwaters and upper reaches of the watershed are composed of forested lands; in the lowland regions of the basin, agricultural and rural residential land uses become more prevalent (Figure 2). Population density increases near the shores of Commencement Bay where the state's third largest city, Tacoma, is located.



Figure 2. Land use map for the White-Puyallup watershed.

The hydrology of the White-Puyallup watershed is rainfall and snowmelt dominated, with the highest river flows typically occurring from October through March (Figure 3). Annual precipitation ranges from 30-40 inches near Tacoma to over 120 inches in the Cascade Mountains. Low flow in the rivers occurs during summer months when precipitation is at its lowest and river flows are dominated by meltwater from snow and glaciers, along with groundwater.

There are three hydrologic control structures within the watershed: Mud Mountain dam and Buckley diversion dam on the White River and Electron diversion dam on the upper Puyallup. These structures provide a mechanism for flood control and power generation. In addition to these structures, the Puyallup River's natural course has been altered through levees and river straightening. There is limited tidal influence in the lower Puyallup River, with the saltwater wedge extending less than 2.5 miles upstream from the river mouth at Commencement Bay (Bell-McKinnon 2006).



Figure 3. Discharge of the Puyallup River from 2000-2022.

Red dots are the monthly harmonic means.

Station is USGS 1210500—Puyallup River at Puyallup, WA.

Both fall- and spring-run Chinook (*Oncorhynchus tshawytscha*) use many of the major rivers and tributaries in the White-Puyallup watershed for migrating, rearing, and spawning (Figure 4). In addition to Chinook, several anadromous and non-anadromous salmonid species inhabit the watershed: coho (*O. kisutch*), chum (*O. keta*), pink (*O. gorbuscha*) salmon, bull (*Salvelinus confluentus*), cutthroat (*O. clarki*), steelhead and rainbow (*O. mykiss*) trout; and mountain whitefish (*Prosopium williamsoni*). Work to conserve and recover salmon stocks within the basin is ongoing. These efforts focus largely on habitat restoration and conventional water quality parameters such as temperature.



Figure 4. Extent of Chinook salmon in the White-Puyallup watershed and previous juvenile Chinook monitoring locations.

Red lines show the distribution Chinook spawning and rearing. Circles are sample locations from previous WDFW juvenile Chinook survey.

3.2.2 Summary of previous studies and existing data

PBDEs and **PCBs** in biota

Previous sampling by WDFW and others suggests that resident fish species and juvenile Chinook in the White-Puyallup watershed are impacted by PBDEs and PCBs. WDFW sampling of juvenile Chinook tissues showed evidence of elevated PBDE and PCB concentrations in fish collected from the estuary and nearshore habitat of the Puyallup River. Juvenile Chinook whole body concentrations of PBDEs and PCBs exceeded fish health thresholds in about 18% and 45% of fish sampled, respectively (O'Neill et al., 2015). Fish health thresholds represent a body burden concentration of a toxic which, if exceeded, is expected to exhibit adverse sublethal effects. In the case of PBDEs and PCBs, the exceedance of these thresholds increases juvenile Chinook disease susceptibility by impairing growth and altering hormone and immune system activity (Meador et al., 2002, Arkoosh et al., 2013, Arkoosh et al., 2010).

Further sampling of juvenile Chinook stomach contents and livers from the Hylebos waterway, part of Commencement Bay, were found to contain PCBs at concentrations high enough to decrease growth rates and suppress immune function (Stehr et al., 2000). When juvenile Chinook from the Hylebos were compared to fish from reference sites within the Nisqually estuary, Hylebos Chinook had significantly higher levels of PCBs in both their liver and stomach contents.

Other tissue samples from Commencement Bay have led to portions of the waterbody being listed as impaired and included in EPA's 303(d) list. English sole, Dungeness crab, and mussel (*Mytilus trossulus*) tissue samples collected from 2006 to 2017 in the Thea Foss waterway all exceeded tissue exposure concentrations (TECs) for PCBs. Median tissue concentrations ranged from 0.0039 ppm in mussels to 0.070 ppm in English sole (EIM study IDs: C1200226, WDFW 11-1916, WDFW_TBiOS_EngSole). In addition to the Thea Foss, portions of Blair and Hylebos Waterways have both been listed as impaired based on PCB tissue concentrations in mussels. Median mussel tissue concentrations ranged from 0.024 to 0.061 ppm in Blair and Hylebos Waterways (EIM study ID: WDFW 11-1916).

PBDEs and PCBs in sediment and water

Sediments collected from Commencement Bay have also been shown to contain PCBs. Sediments dredged from Blair Waterway in 2000 contained PCBs concentrations ranging from 77.2 to 1050 ppb (EIM study ID: PCTEX158). Additionally, sediments sampled from the Thea Foss Waterway between 1989 and 1993 contained levels of PCBs ranging from 10 to 40 ppb (EIM study ID: PSAM_LT).

Previous sampling for PBDEs and PCBs in the White-Puyallup watershed determined daily instantaneous loads as well as concentrations of toxics in water and river sediments. Daily instantaneous loads in the Puyallup ranged from 0.063 to 0.65 mg/day and 0.015 to 0.11 mg/day for PBDEs and PCBs, respectively (Gries and Osterberg, 2011). Loadings were based on sampling of water and suspended particulate matter (SPM). Puyallup River PBDE and PCB water concentrations ranged from 10.9 to 265.2 pg/L and 2.6 to 40.2 pg/L, respectively. SPM concentrations for PBDEs and PCBs were 1032.9 ng/Kg dry and 145.4 ng/Kg dry, respectively.

In 2013, the USGS also analyzed White-Puyallup River sediments for PBDEs and PCBs. The study did not detect PCBs in sediments from the Puyallup River but detected PBDEs in riverbank sediments and suspended sediments (Takesue et al., 2013).

PBDEs and PCBs in WWTP effluent

There have also been sampling efforts for PBDEs and PCBs in effluent from major WWTPs in the Puget Sound basin, including the City of Tacoma Central facility within the White-Puyallup watershed (Ecology and Herrera, 2010; Ecology and King County, 2011). In 2009, effluent samples were collected in winter and summer from ten major WWTPs. The central Tacoma facility, which discharges to Commencement Bay, contained the third highest concentrations of PBDEs and second highest concentration of PCBs (Table 1). In all WWTP effluent samples, three main congeners dominated the total-BDE concentrations: BDE-47, BDE-99, and BDE-209. Concentrations of PBDEs showed little evidence of seasonal differences. These sampling efforts were part of a large-scale project led by Ecology to determine toxic loadings to Puget Sound.

 Table 1. Previous samples of PBDE and PCB concentrations (pg/L) in Wastewater Treatment

 Plant (WWTP) effluent discharging to Puget Sound (Ecology and Herrera, 2010).

WWTP Location	Date	Tetra- BDEs	Penta- BDEs	Deca BDE		Total- BDEs	Total- PCBs
Dellingtheme	2/12/2009	5453	5712	2000		14396	-
Bellingham	7/16/2009	4083	3712	1390	U	8607	-
Bremerton	2/10/2009	5538	6328	3340		16829	75
Diementon	7/14/2009	5937	6030	750	UJ	13277	-
Burlington	2/10/2009	3565	2860	3060		10974	-
Burlington	7/14/2009	7697	7991	4460		22809	-
Chambers	2/19/2009	8807	8623	2870		23838	572
Creek	7/16/2009	7202	6058	250	U	15115	-
Everett	2/12/2009	34267	40280	35500		125387	15598
(Outfall 100)	7/16/2009	44945	45920	22000		134737	-
Circularhan	2/10/2009	4960	5017	10700		22272	-
Gig Harbor	7/14/2009	9980	10876	18800		45799	-
King Co	2/10/2009	6400	7094	2540		17894	1856
West Pt	7/14/2009	7207	7824	2150		18273	-
Shelton	2/10/2009	15072	23132	10600		54393	197
Shellon	7/14/2009	6741	8178	5610		24478	-
Sumpor	2/12/2009	3786	2732	1780		9096	-
Sumner	7/17/2009	7423	18316	250	UJ	30423	-
City of Tacoma	2/19/2009	15160	16954	6830		43492	4729
(Central 1)	7/16/2009	15703	17848	8870		47070	

U = Analyte was not detected at or above the detection limits.

UJ = Analyte was not detected at or above the estimated reporting limit

3.2.3 Parameters of interest and potential sources

In the White-Puyallup watershed, PCBs and PBDEs are the main groups of organic chemical of concern, due to their potential for impairment of juvenile Chinook.

Polychlorinated biphenyls (PCBs)

PCBs are a class of man-made organic chemicals which are composed of two carbon rings surrounded by a varying number of chlorine atoms. There are 209 congeners which are differentiated by their number and location of chlorine atoms. PCBs were broadly manufactured and used from 1929 until they were banned in the U.S. in 1979. Industrial mixtures of PCB congeners were manufactured and are known by their trade name Aroclor. Due to the non-flammability, chemical stability, and electrical insulating properties, PCBs were used in industrial and commercial applications such as electrical equipment, transformers, plasticizers, caulks, and adhesives (Erickson & Kaley, 2011).

Widespread use of PCBs in electrical equipment and other commercial applications led to their introduction into the environment as these products degrade or are improperly disposed of. PCBs also enter the environment from combustion, mainly from waste incineration, but also from steel smelting and combustion of coal and wood (Montano et al., 2022). Once in the environment, PCBs are persistent and bioaccumulative. Due to their lipophilic properties, they readily bind to sediments and accumulate in tissue of biota. PCBs have been shown to cause adverse health effects in humans and other animals. They are a known carcinogen and can affect immune, reproductive, and endocrine health (EPA, 2022).

Polybrominated diphenyl ethers (PBDEs)

PBDEs (brominated flame-retardants) are a class of 209 congeners that resemble the structure of PCBs except PBDEs contain bromine instead of chlorine. They are manufactured as flame-retardants and used in a wide variety of products (e.g., plastics, furniture, upholstery, electrical equipment, textiles) (Hale et al., 2003). Three major commercial mixtures of PBDEs were widely used in the U.S. starting in the 1970s. These mixtures are named for the PBDE homologue which is most prevalent in the mixture (penta-, octa-, and deca-brominated diphenyl ethers) but contain lesser amounts of other PBDE homologues.

The manufacturers of PBDEs voluntarily ceased production of penta- and octa- BDE formulations in 2004 following human health concerns (Ecology, 2006). The deca-BDE formulation was largely phased out by the end of 2012. PBDEs are bioaccumulative and bind to the fats/lipids of organisms. The fate and toxicity of PBDEs varies; the heavier congeners tend to bind more readily to dust and solids, and the lighter congeners are more volatile (Hale et al., 2003). Once in the body, PBDEs can inhibit the transport of thyroid hormones affecting metabolic functions and also interfering with fetal development (Birnbaum and Staskal, 2003).

PBDEs are released and transported in the environment via atmospheric deposition and stormwater runoff (Sutton et al., 2019). PBDEs are also contributed to the environment through household grey water that is treated and discharged via WWTPs. Current treatment technologies were not designed to remove PBDEs but appear to partially reduce PBDE mass in WWTP effluent (Song et al., 2006). Eight WWTPs discharge into waters of the White-Puyallup watershed. These facilities are potential discharge points of PBDEs into the White-Puyallup watershed.

Historical sources of PBDEs and PCBs

Additional potential sources of toxics to the watershed are areas of historical contamination in Commencement Bay due to industrial uses of the waterways and their surrounding shoreline. Several superfund sites have undergone cleanup work including locations within the Thea Foss, Wheeler-Osgood, and Hylebos waterways. Sediments within these locations contained unsafe levels of PCBs; therefore, efforts have been made to remove or cap contaminated sediments as part of the cleanup process. Fish and shellfish continue to be of concern for human consumption due to the bioaccumulation of PCBs (US EPA 2020). Though these sites have been remediated, there is still cause for concern that superfund sites may contribute to PCB contamination in the watershed.

In addition to contaminated sites within Commencement Bay, many sites within the watershed have been identified to contain PCBs and PBDEs at levels which could be potentially harmful to people and the environment. These sites are in varying stages of clean up, ranging from awaiting

clean up to ongoing monitoring of cleanup success. These sites are potential sources of PCBs and PBDEs in the watershed due to their proximity to the river system.

3.2.4 Regulatory criteria or standards

Washington State does not regulate concentrations of PBDEs in the environment. Laboratory studies by Arkoosh et al. (2010 & 2015) have determined sublethal effects thresholds from PBDE tissue burdens in juvenile Chinook. These two studies established a tissue burden threshold where increased disease susceptibility is found at concentrations \geq 470 ng PBDE / g lipid and \leq 2,500 ng PBDE/ g lipid. This relationship was determined based on PBDE dose, tissue burden, and measures of disease susceptibility. Previous WDFW studies throughout Puget Sound have relied on these tissue burdens to assess the health of juvenile Chinook (O'Neill et al., 2015; Carey et al., 2019)

While Washington State does not regulate environmental levels of PBDEs, guidance on environmentally relevant concentrations can be assessed from Federal Environmental Quality Guidelines (2013) from Environment Canada. The guidelines outline concentrations of PBDEs in water, sediment, and tissues which can be used in the assessment of environmental quality (Table 2). Water quality standards are designed to protect all forms of aquatic life from adverse effects of chronic exposure to PBDEs in the water column. Fish tissue and sediment PBDE guidelines are designed to protect fish and sediment dwellers from adverse outcomes due to bioaccumulation of PBDEs. Wildlife dietary guidelines are designed to protect mammalian and avian consumers of aquatic biota.

The Washington State Department of Health (DOH) has calculated a human health screening level for BDE-047 in fish tissues, based on neurobehavioral effects for high-consumer human populations (34 ng/g ww). This screening level is used by DOH in assessing waterbodies for fish consumption advisories, after considering risk management and risk communication.

Table 2. Environment Canada Federal Environmental Quality Guidelines for PBDEs
(Environment Canada, 2013).

Homologue ^[*]	Congener	Water (ng/L)	Fish Tissue (ng/g ww)	Sediment ^[**] (ng/g dw)	Wildlife Diet ^[1] (ng/g ww food source)
triBDE	total	46	120	44	-
tetraBDE	total	24	88	39	44
pentaBDE	total	0.2	1	0.4	3 (mammal) 13 (birds)
pentaBDE	BDE-99	4	1	0.4	3
pentaBDE	BDE-100	0.2	1	0.4	-
hexaBDE	total	120	420	440	4
heptaBDE	total	17 ^[3]	-	-	64
octaBDE	total	17 ^{[3], [4]}	-	5600 ^[4]	63 ^[4]
nonaBDE	total	_	-	-	78
decaBDE	total	_	_	19 ^{[4], [5]}	9

[*]Guidelines for triBDE (tribromodiphenyl ether), tetraBDE (tetrabromodiphenyl ether), hexaBDE (hexabromodiphenyl ether), heptaBDE (heptabromodiphenyl ether), nonaBDE (nonabromodiphenyl ether) and decaBDE (decabromodiphenyl ether) are based on data for the congeners: BDE-28, BDE-47, BDE-153, BDE-183, BDE-206, and BDE-209, respectively unless otherwise noted.

[**] Values normalized to 1% organic carbon.

[1] Applies to mammalian wildlife unless otherwise noted.

[2] Value based on the commercial PentaBDE formulation, DE-71, which contains mostly pentaBDE and some tetraBDE.

[3] Values based on commercial OctaBDE mixture DE-79, which is composed mainly of heptaBDE and octaBDE (octabromodiphenyl ether).

[4] Values adopted from Ecological Screening Assessment Report (Environment Canada 2006). Sediment guidelines for octaBDE and decaBDE were adapted from the SAR by being corrected for the sediment organic carbon in the actual tests, then normalized to 1% organic carbon instead of the 4% in the SAR.

[5] Values based on commercial decaBDE mixture, which is composed mainly of nonaBDE and decaBDE.

Washington State regulates PCBs in the environment to protect human health and aquatic life. Human health protection exists to limit toxic effects of PCBs when consuming fish (Table 3). The human health criteria for total PCBs in fish tissue is 0.00017 ppb. Surface water limits of PCBs exist to protect aquatic life from acute and chronic effects on survival, growth, and reproduction. Freshwater acute PCB exposure is limited to 2 ppb, and chronic exposure is limited to 0.014 ppb (Table 3).

	Aquatic Life Criteria - Freshwater		Aquatic Life Criteria - Marine Water		Human Health Criteria for Consumption of:	
Compound	Acute	Chronic	Acute	Chronic	Water & Organism	Organism only
PCBs	2.0	0.014	10	0.03	0.00017	0.00017

 Table 3. Washington State PCB Water Quality Criteria (Chapter 173-201A WAC)

Criteria concentration units = ppb

Chapter 173-201A WAC- Water Quality Standards for Surface Waters of the State of Washington

Previous work by WDFW has compared the tissue burden of PCBs in juvenile Chinook to an effects threshold derived from laboratory studies assessed by NOAA Northwest Fisheries Science Center. Meador et al. (2002) assessed 15 ecotoxicological studies to determine a residue effect threshold in wild juvenile Chinook above which adverse sublethal effects would be expected. The value of 2400 ng PCB/ g lipid was established as the effect threshold, and it was used in subsequent WDFW studies to characterize potential impacts of PCBs on out-migrating juvenile Chinook (O'Neill et al., 2015)

3.3 Water quality impairment studies

Under the federal Clean Water Act (CWA) section 303(d), there are several water quality impairments for PCBs in the White-Puyallup watershed. Table 4 details the current listings and contaminants. There are no water quality impairments under CWA section 303(d) for PBDEs because there are no regulatory criteria for these contaminants.

Table 4. Water quality impairments in the White-Puyallup watershedunder section 303(d) of the Clean Water Act.

Waterbody Name	Listing IDs	Medium	Parameter
Hylebos Waterway	8671 86636 97871 36178	Tissue	PCBs
Thea Foss Waterway	35738	Tissue	PCBs
Blair Waterway	86635	Tissue	PCBs
Commencement Bay	35739	Tissue	PCBs
Dalco Passage and East Passage	35740 35741 35743	Tissue	PCBs

4.0 Project Description

The project goals and objectives described in this QAPP addendum pertain to the identification of sources of PBDEs and PCBs in the White-Puyallup watershed. This project is part of ongoing efforts to identify potential point and nonpoint sources of emerging and legacy toxics previously measured and potentially impacting juvenile Chinook out-migrating from natal watersheds in the Puget Sound and Columbia River basins.

4.1 Project goals

The goal of the project in the White-Puyallup watershed is to assess and prioritize potential sources of PBDEs and PCBs to the Puyallup, White, and Carbon Rivers that may be impacting out-migrating juvenile Chinook. This will involve an assessment of vectors, or pathways, to identify how PBDEs and PCBs are moving into and through environmental media (e.g., water, sediment, algae) and how fish are obtaining these toxics.

4.2 Project objectives

The objectives of this project are to:

- Sample water, sediment, and biota during the low- and high-flow periods for the Puyallup, White, and Carbon Rivers.
- Analyze samples for PBDEs and PCBs.
- Report and disseminate findings.

4.3 Information needed and sources

No further background data necessary.

4.4 Tasks required

Tasks required to achieve the study objectives are:

- Project planning meetings and discussion with stakeholders in the White-Puyallup watershed.
- Field reconnaissance of suitable sample locations.
- Deployment and retrieval of passive water samplers.
- Sampling of relevant biotic media and sediments (benthic/suspended).
- Analysis of samples for PBDE and PCB congeners.
- Verification of data quality.
- Data analysis and report production.
- Presentation of results to Ecology and White-Puyallup watershed stakeholders.

4.5 Systematic planning process

This QAPP addendum constitutes a suitable planning process.

5.0 Organization and Schedule

5.1 Key individuals and their responsibilities

Table 5. Organization of project staff and responsibilities.

Staff	Title	Responsibilities
Jessica Archer SCS Phone: 360-407-6698	Section Manager for the Project Manager	Conducts annual planning to assess client/program needs and scope, reviews deliverables and products, provides upper management support.
Jim Medlen Toxic Studies Unit, SCS Phone: 360-407-6139	Unit Supervisor for the Project Manager	Reviews the project scope and budget, tracks progress, reviews the draft and final QAPP, reviews draft and final project reports, helps resolve work issues with client and management.
Alex Gipe Toxic Studies Unit, SCS Phone: 360-584-4447	Project Manager	Oversees all aspects of the project. Writes the draft and final QAPP and draft and final study report. Oversees field sampling and transportation of samples to the laboratory. Conducts QA review of data, analyzes and interprets data. Tracks budget and communicates with client and management to resolve issues.
Will Hobbs Toxic Studies Unit, SCS Phone: 360-995-3369	Project Scientist	Reviews QAPP. Assists with study development, helps with field work, advises site selection, Collaborates with project scientists
Sandra O'Neill T-BioS, WDFW Phone: 360-902-2666	Project Scientist	Reviews QAPP. Assists with study development. Directs the use of WDFW resources when necessary. Collaborates with project scientists.
TSU Staff Toxic Studies Unit, SCS	Field Assistant	Advises during sample site selection. Helps collect samples and records field information.
TSU Staff Toxic Studies Unit, SCS	Field Assistant	Helps collect samples and records field information. Oversees data management in EIM.
Dean Momohara MEL Phone: 360-871-8801	Acting Director	Reviews and approves the final QAPP.
Contract Laboratory, TBD	Project Manager	Reviews draft QAPP, coordinates with MEL QA Coordinator
Arati Kaza Phone: 360-407-6964	Ecology QA Officer	Reviews and approves the draft and final QAPP.

EAP: Environmental Assessment Program

EIM: Environmental Information Management database

MEL: Manchester Environmental Laboratory

QAPP: Quality Assurance Project Plan

SCS: Statewide Coordination Section

WDFW: Washington Department of Fish and Wildlife

WOS: Western Operations Section

T-BioS: Toxics-focused Biological Observing System for the Salish Sea

5.2 Special training and certifications

No special training needed. Experience with passive samplers and boats is relevant.

5.3 Organization chart

See Table 5.

5.4 Proposed project schedule

Table 6. Proposed schedule for completing field and laboratory work, data entry into EIM, and reports.

Field and laboratory work	Due date	Lead staff	
Synoptic Survey – low flow	Aug/Sept 2023/2024	Alex Gipe	
Synoptic Survey – high flow	Apr/May 2023/2024	Alex Gipe	
Fieldwork completed	Oct 2024	Alex Gipe	
Lab analyses completed	Jan 2025		
Lab Data Validation complete	Apr 2025		
Environmental Information System	em (EIM) database		
EIM Study ID	AGIP0001		
EIM data loaded	Apr 2025	Alex Gipe	
EIM data entry review	Jun 2025	Jakub Bednarek	
EIM complete	Jun 2025	Alex Gipe	
Final report			
Author lead / Support staff	Alex Gipe / Will Hobbs		
Schedule			
Draft due to supervisor	Oct 2025		
Draft due to client/peer reviewer	Nov 2025		
Draft due to external reviewer(s)) Dec 2025		
Final (all reviews done) due to publications team	Jan 2026		
Final report due on web	Mar 2026		

5.5 Budget and funding

Funding for the Toxics Impacting Juvenile Chinook Program was received under the Washington State Legislature, Model Toxics Control Operating Account. See Table 7 for a budget overview.

Budget Overview	Per Fiscal Year				
Salary, benefits, and	\$135,000				
Equipment					\$1,000
Travel and goods an	d services				\$7,000
Contracts (WDFW)					\$30,000
Laboratory					\$72,500
Parameter	Number of Samples	Number of QA Samples	Total Number of Samples	Cost Per Sample	Lab Subtotal (per Biennium)
PBDE & PCB Conge	eners				
PBDEs in SPMD	30	8	38	\$940	\$35,720
PBDEs in Tissue/sediment	10	2	12	\$940	\$11,280
PCBs in SPMD	30	8	38	\$895	\$34,010
PCBs in Tissue/sediment	10	2	12	\$895	\$10,740
Conventionals (wat	er)	1	1		
SSC	90	9	99	\$20	\$1,980
TOC/DOC	90	9	99	\$75	\$7,425
Conventionals (tiss	ue/sediment)				
C and N (TOC, TN, and isotopes)	30	30	60	\$15	\$900
Grain size	20	2	22	\$100	\$2,200
Data validation (Manchester Environmental Lab) – 30% surcharge on contract					\$27,525
Lab contingency					\$13,220
Lab total (Year 1 and 2)					\$145,000

Table 7. Project budget and funding.

SSC: suspended sediment concentrations TOC: total organic carbon DOC: dissolved organic carbon C: carbon N: nitrogen TN: total nitrogen

6.0 Quality Objectives

6.1 Data quality objective

The main DQO for this project is to collect sufficient samples of biota and passive water samples to characterize possible sources of PBDEs and PCBs in the Puyallup, White, and Carbon Rivers. The analysis of PBDEs and PCBs will use EPA methods 1614 and 1668C, with high-resolution gas chromatography-mass spectrometry to resolve the congener distribution present in all sample media. Measurement quality objectives (MQOs) described in the subsequent section detail the targets for analytical precision, bias, and sensitivity.

6.2 Measurement quality objectives

The MQOs for this study are detailed in Table 8. The MQOs for the field parameters (pH, dissolved oxygen, temperature, and conductivity) are in Table 9.

6.2.1 Targets for precision, bias, and sensitivity

$\text{MQO} \rightarrow$		cision RPD)	Bias Re	covery Limit (%)	S	Sensitivity Concentration Units
Parameter	Duplicate Samples	Matrix Spike- Duplicates	Verification Standards (LCS,CRM,CCV)	Matrix Spikes	Surrogate Standards*	MDL or Lowest Conc. of Interest
Water	•					
Suspended Sediment Concentration	NA	NA	80–120%	NA	NA	0.5 mg L ⁻¹
Total Organic Carbon	± 20%	NA	80–120%	75–125%	NA	0.5 mg L ⁻¹
Dissolved Organic Carbon	± 20%	NA	80–120%	75–125%	NA	0.5 mg L ⁻¹
Passive water sa	amplers (SPM	Ds)				
PBDE congeners	± 50%	NA	50–150%	NA	25–150%ª	5.0–500.0 pg per sample**
PCB Congeners	± 50%	NA	50–145%	NA	5–145%	0.7–4.7 pg per sample
Tissue (inverteb	rate or biofilm	ı)				
PBDE congeners	± 50%	NA	50–150%	NA	25–150%ª	0.1–10.0 pg/g per cong**
PCB Congeners	± 50%	NA	50–145%	NA	5-145%	0.4-4.7 pg/g per cong**
C and N	± 20%	NA	80–120%	NA	NA	0.10%
Sediments		1				
PBDE congeners	± 50%	NA	50–150%	NA	25–150%ª	0.1–100.0 pg/g per cong
PCB Congeners	± 50%	NA	50–145%	NA	5-145%	0.7-4.7 pg/g per cong
Total organic carbon	± 20%	NA	80–120%	NA	NA	1%

Table 8. Measurement quality objectives.

See Notes on next page

Notes for Table 8

*Surrogate recoveries are compound specific.

**MDLs will vary among congeners. Deca and nona-BDEs have substantially higher MDLs.

LCS = laboratory control sample

CRM = certified reference materials

CCV = continuing calibration verification standards

RPD = relative percent difference

^a PBDE 209 recovery of 20-200%

SPMD = semi-permeable membrane device

Table 9. Measurement	quality o	bjectives	for multi-	probe sonde	calibration checks.
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Parameter	Units	Accept	Qualify	Reject
рН	std. units	< or = <u>+</u> 0.2	> <u>+</u> 0.2 and < or = <u>+</u> 0.8	> <u>+</u> 0.8
Conductivity*	uS/cm	< or = <u>+</u> 5	> <u>+</u> 5 and < or = <u>+</u> 15	> <u>+</u> 15
Temperature	°C	< or = <u>+</u> 0.2	> <u>+</u> 0.2 and < or = <u>+</u> 0.8	> <u>+</u> 0.8
Dissolved Oxygen	% saturation	< or = <u>+</u> 5%	> <u>+</u> 5% and < or = <u>+</u> 15%	> <u>+</u> 15%
Dissolved Oxygen	mg/L	< or = <u>+</u> 0.3	> <u>+</u> 0.3 and < or = <u>+</u> 0.8	> <u>+</u> 0.8

* Criteria expressed as a percentage of readings. For example:

Buffer = 100.2 uS/cm and Hydrolab = 98.7 uS/cm; (100.2-98.7)/100.2 = 1.49% variation, which would fall into the acceptable data criteria of less than 5%.

7.0 Study Design

7.1 Study boundaries

This study will focus on identifying sources and environmental pathways of PBDEs and PCBs in the White-Puyallup watershed (WRIA 10). PBDEs and PCBs are released into the environment as products containing these chemicals breakdown over their life span. PCBs can also be released during their manufacture and disposal as well as from accidental spills. Due to these chemicals' hydrophobicity, they tend to bind to dust, soils, and lipid-rich substances. For this reason, these chemicals can accumulate in particulate matter and be transported by domestic wastewater or stormwater to surface waters. PBDEs and PCBs are released into the environment from domestic (or municipal) wastewater (Song et al., 2006; Ecology, 2006), which is treated and discharged through WWTPs under NPDES permits (Figure 5). Current WWTP technologies are not designed to remove PBDEs or PCBs.

Additionally, these contaminants can enter surface waters from stormwater catchment systems. The major path of PCB loading to Puget Sound is from surface runoff. The White-Puyallup watershed also contains many legacy sources of PCBs, including superfund sites within Commencement Bay and contaminated sites throughout the watershed. This study will assess the relative importance of potential transport pathways of PBDEs and PCBs in the watershed.

This study will begin with an assessment of the watershed during the spring when wet-weather conditions prevail. This sampling will assess the potential pathways from stormwater runoff and higher groundwater table discharges to the White-Puyallup watershed. Stormwater inputs to the river system and Commencement Bay are vast; therefore, the scope of this study will not account for all potential inputs of contaminants from these sources. It is instead the goal of this work to identify toxic hotspots within the watershed that are impacting the rearing of juvenile Chinook.

During the late summer and early fall, low-flow conditions will be assessed to determine ambient exposure concentrations. Low-flow conditions are intended to represent the following known and potential transport pathways: domestic wastewater, aerial deposition to the surface of the waterbodies, baseflow contributions from groundwater, and sediment flux. Throughout the investigation, this study will assess (1) the spatial prevalence of PBDEs and PCBs and (2) the potential food-web based transport mechanisms to juvenile Chinook.



Figure 5. White-Puyallup watershed showing potential sample sites.

7.2 Field data collection

7.2.1 Sampling locations and frequency

Sample locations for the initial synoptic survey will be situated near WWTP outfalls and industrial NPDES outfalls within the watershed. Exact locations will depend on site access, security, and access permissions. Final sampling sites will be determined following site reconnaissance. The tentative locations of 19 sites are detailed in Table 10 and mapped in Figure 5. Following the initial synoptic survey at high flow, some of the sites may change, and additional sites may be added to cover areas of interest.

Site ID	Site name	Waterbody	Latitude	Longitude	Justification
10TheaFossW	Thea Foss waterway	Commencement Bay	47.258986	-122.434474	Industrial NPDES outfalls
10BlairW	Blair Waterway	Commencement Bay	47.270998	-122.40173	Industrial NPDES outfalls
10HylebosW	Hylebos waterway	Commencement Bay	47.271238	-122.377403	Industrial NPDES outfalls
10MiddleW	Middle Waterway	Commencement Bay	47.267536	-122.39087	WDFW Juvenile Chinook Survey
10MilwaW	Milwaukee Waterway	Commencement Bay	47.269201	-122.422565	WDFW Juvenile Chinook Survey
10PUY0.6	Puyallup RM0.6	Puyallup River	47.260012	-122.418554	Industrial NPDES outfalls
10PUY6.5	Puyallup RM6.5	Puyallup River	47.20877	-122.326959	Puyallup USGS Gauge Station
10PUY31.1	Puyallup RM31.1	Puyallup River	46.993046	-122.1771	Puyallup River Background
10WHIT0.0	White RM0.0	White River	47.199982	-122.257436	Downstream of Sumner WWTP Outfall
10WHIT3.9	White RM3.9	White River	47.24296	-122.234903	Industrial NPDES outfalls/salmon survey
10WHIT22.1	White RM22.2	White River	47.170818	-122.042558	Downstream of Buckley WWTP Outfall
10WHIT23.0	White RM23.0	White River	47.174183	-122.025593	Downstream of Eatonville WWTP Outfall
10WHIT44.0	White RM44.0	White River	47.095091	-121.594069	White River Background
10CARB1.6	Carbon RM01.3	Carbon River	47.112073	-122.215961	Downstream of Orting WWTP Outfall
10CARB11.3	Carbon RM11.3	Carbon River	47.077619	-122.062975	Downstream of Carbonado WWTP Outfall
10CARB22.5	Carbon RM22.5	Carbon River	46.993007	-121.926999	Carbon River Background
10WILKCK	Wilkeson CK	Wilkeson Creek	47.110537	-122.053325	Downstream of Wilkeson WWTP Outfall
10SPRAIRIE	South Prairie CK	South Prairie Creek	47.140815	-122.098359	Downstream of South Prairie WWTP Outfall
10WAPCK	Wapato CK	Wapato Creek	47.225887	-122.320427	Downstream of Cherry- wood Mobile Home Pk

Table 10. Proposed sample locations and rationale.

NPDES: National Pollutant Discharge Elimination System WWTP: Wastewater Treatment Plant

The rates at which each WWTP discharged into the receiving waters during 2021 in the months proposed for sampling in this project (April and August) are found in Table 11. The amount discharged is generally proportional to the population served and the capacity of the WWTP. The highest discharges are to Commencement Bay and Dumas Bay in central Puget Sound.

WWTP	Mean	Standard Deviation	Median	Minimum	Maximum
April 2021					
Tacoma Central	17.18	0.67	17.10	16.30	18.90
Lakota	4.69	0.14	4.65	4.54	5.11
Sumner	2.14	0.07	2.12	2.01	2.37
Enumclaw	1.27	0.18	1.29	1.03	1.87
Orting	0.59	0.08	0.60	0.46	0.74
Buckley	0.49	0.07	0.49	0.38	0.66
Wilkeson	0.03	0.01	0.03	0.01	0.05
Carbonado	0.02	0.004	0.02	0.02	0.03
South Prairie	0.02	0.003	0.02	0.01	0.03
Cherrywood Mobile Home Park	0.012	0.004	0.011	0.005	0.022
August 2021					
Tacoma Central	14.70	0.42	14.70	13.40	15.60
Lakota	4.59	0.07	4.57	4.45	4.75
Sumner	1.95	0.07	1.94	1.83	2.10
Enumclaw	0.85	0.03	0.85	0.80	0.91
Orting	0.47	0.03	0.46	0.37	0.53
Buckley	0.36	0.03	0.36	0.32	0.46
Wilkeson	0.02	0.01	0.03	0.01	0.04
Carbonado	0.02	0.002	0.02	0.02	0.03
South Prairie	0.02	0.002	0.02	0.01	0.02
Cherrywood Mobile Home Park	0.006	0.001	0.006	0.003	0.009

Table 11. WWTP discharge rates (MG/day) in the White-Puyallup watershed.

Discharge rates accessed through Discharge Monitoring Reports in Ecology's Water Quality Permitting and Reporting Information System (PARIS). WWTPs are ordered by highest mean discharge.

*Flow measurements for Cherrywood Mobile Home Park were reported as Influent flow.

7.4 Assumptions underlying design

The study design assumes that the spatial scale and media sampled (e.g., water, sediment, algae, invertebrates) will provide an accurate measure of the sources and pathways of PCBs and PBDEs in the watershed. Further investigation may be necessary to resolve sources and pathways of these contaminants if initial surveys do not provide the information needed to do so. The study also assumes that it will be possible to collect sample media from planned sites during the study period, 2023 to 2025. Also, the study design assumes that seasonal comparisons of contaminant levels within surface waters and sediments will provide sufficient evidence to conclude the different potential pathways of PCBs and PBDEs: wastewater, stormwater, aerial depositions, and sediment deposition.

7.5 Possible challenges and contingencies

7.5.1 Logistical problems

The White-Puyallup watershed is a large, complex river system with dynamic flows and complex river braids. This type of environment can be logistically challenging to sample due to determining suitable sampling sites and dealing with the variability of the river system. The complexity of the river system makes it difficult to collect comparable sample media (e.g., water, sediment, algae, invertebrates) throughout the river basin. The watershed is also urbanized which can pose difficulties when selecting protected sampling sites which will not be disturbed during sampling deployments. To combat these logistical issues, field site reconnaissance will focus on determining appropriate sites which can be sampled during both dry- and wet-weather conditions and have comparable sample media.

7.5.3 Schedule limitations

The possible logistical issues in capturing representative samples in such a large, complex watershed may require additional sampling. This would cause a delay in completing this project. Schedule limitations may also occur during the analysis of samples, data validation, and report production. Current scheduling is based on recent estimates of the time required under staff workloads.

8.0 Field Procedures

8.1 Invasive species evaluation

Field staff for this project are required to follow the procedures described in SOP EAP070 (Parsons et al., 2018), *Minimizing the Spread of Invasive Species*.

8.2 Measurement and sampling procedures

Several types of sample media (e.g., water, sediment, algae, invertebrates) will be collected under this project. Sampling methods for this study have been employed in other source identification studies for toxics (Johnson et al., 2010; Hobbs, 2018). Five field SOPs will be followed during this study:

- SOP EAP001 (Seiders et al., 2022) Standard Operating Procedure for Conducting Studies Using SPMDs.
- SOP EAP079 (Seiders et al., 2019) Standard Operating Procedure for Semipermeable Membrane Devices (SPMD) Data Management and Data Reduction.
- SOP EAP040 (Blakley, 2019) Standard Operating Procedure for Obtaining Freshwater Sediment Samples.
- SOP WQP003 (Lubliner, 2018) Standard Operating Procedure for Collection of Stormwater Solids Using In-line Traps, version 2.0.
- SOP EAP033 (Anderson, 2019) Standard Operating Procedure for Hydrolab® DataSonde® and MiniSonde® Multiprobes.

Semi-permeable membrane devices (SPMDs)

The initial synoptic survey of the basin for PBDEs and PCBs in water will rely heavily on passive samplers, SPMDs. SPMDs are composed of a thin-walled, layflat polyethylene tube (91.4 cm x 2.5 cm x 70–95 um thickness) filled with 1 ml of triolein, a neutral lipid compound (Figure 6). The SPMDs emulate natural biological uptake by allowing chemicals to diffuse through the membrane and concentrate over time (typically a 28-day deployment). After deployment, the membranes are removed, extracted, and analyzed for the contaminant of interest.

In this study, field staff will deploy SPMDs in secure areas to minimize vandalism and avoid strong currents. They will use stainless steel canisters and spindle devices provided by Environmental Sampling Technologies (EST). In areas where security may be an issue, two canisters/SPMDs will be placed at each site, but only one will be analyzed for the presence of PBDEs and PCBs. The second (backup) canister/SPMD would be analyzed only if the other canister at the site is lost. Each site canister/SPMD will contain five membranes preloaded onto spindles by EST and shipped in solvent-rinsed metal cans under argon gas.

Prior to deployment, performance reference compounds (PRCs) will be spiked into the membranes to assess biofouling and the non-equilibrium uptake of the compounds of interest (Huckins et al., 2006). The use of PRCs is essentially an *in situ*, site-specific calibration technique based on the observation that the rate of analyte loss is proportional to the rate of analyte uptake. A labeled congener (BDE-138L) and two native congeners (BDE-10 and BDE-38) will be used as PRCs for PBDEs. PRCs for PCBs will include one native congener (PCB-14)

and three labeled congeners (PCB-31L, PCB-95L, PCB-153L). PRCs will be added at a concentration of 2.5 ng per SPMD.



Figure 6. An SPMD canister showing the upper membrane. Note that some biofouling on the membrane is evident.

A Hobo Pendant MX TM temperature logger will be attached to each canister to continuously monitor the water temperature during deployment. A second data logger will be attached nearby to monitor air temperature. The data collected from the temperature loggers will be used to confirm that the SPMD remained submerged during the deployment period.

SPMDs will be exposed to ambient air for no more than 45 seconds at each site during deployment and retrieval. Staff will always wear Nitrile gloves when handling monitoring equipment and samples. SPMDs will be deployed for about 28 days during each deployment. The same laboratory-supplied shipping cans will be used during retrieval. The cans will be properly sealed, cooled, and kept near freezing until arrival at the contract lab for the extraction of the membranes (dialysis). Analysis of PBDEs and PCBs will be performed by EPA Method 1614 and 1668, respectively.

Surface water grab samples

Water grab samples will be collected to measure total and dissolved organic carbon (TOC/DOC) as well as suspended sediment concentrations (SSC) at each site during the time the SPMDs are exposed. These parameters will be used as ancillary data to help us understand relationships between suspended matter and the PBDE and PCB contaminants. Water grab samples will be collected three times over the duration of the SPMD exposure to get an integrated measure of the conditions. Grab samples will be collected using procedures detailed in SOP EAP015 (Joy, 2019).

At the time of water sampling, additional field parameters (temperature, pH, dissolved oxygen, and conductivity) will be measured *in situ* using a multi-probe sonde following deployment and calibration procedures described in SOP EAP033 (Anderson, 2019). All sensors will be calibrated before each field deployment and checked daily during deployments..

Collection and analyses of biofilm

Biofilm refers to the mixture of periphyton, microbial biomass, and fine sediments. Periphyton is algae attached to the river bottom, rocks, or debris in the river (Figure 7). Standard protocols for collecting attached algae will be followed (Stevenson and Bahls, 1999; Larson and Collyard, 2022). Biofilm will be scraped from rocks and collected in a stainless-steel bowl for weighing in the field to confirm that sufficient biomass is retrieved (~10 g ww). Samples will be transferred from the bowl to a cleaned glass jar.



Figure 7. Example of a biofilm being scraped from a rock.

Biofilms will be analyzed for PBDEs, PCBs, carbon (C) and nitrogen (N) abundance, and stable isotope ratios. Analyzing for stable isotopes will help detect changes in nutrient and wastewater inputs within the White-Puyallup watershed study area.

Invertebrate tissues

The analysis of invertebrates may also be used to more effectively measure PBDE and PCB concentrations and potential bioaccumulation of these toxics in the food source of juvenile Chinook. Chinook go through ontogenetic changes during their migration (Duffy et al., 2011), causing their diet to shift as they mature. They generally feed on aquatic insects in freshwater and then calanoid copepods, crab larvae, polychaetes, and gammarids in the estuary and nearshore environments. The limiting factor in collections of invertebrate tissues for the analysis of contaminants is the mass required (~ 10g wet weight). Therefore, sampling of invertebrate biomass will need to be assessed as the project progresses. Possible sampling approaches include:

- Picking invertebrates from rocks or debris in the freshwater environment.
- Sorting sediment dredge samples for sediment-dwelling invertebrates.
- Establishing drift nets to capture invertebrates drifting downstream at night.
- Carrying out plankton tows in the estuary.

Sediment sampling

Sediments will be sampled throughout the White-Puyallup watershed but will likely focus on the lower Puyallup River and Commencement Bay where finer sediments are likely to accumulate. Verification of the presence and approximate grain size will be characterized during site reconnaissance. Sediment collection will follow procedures outlined in SOP EAP040 (Blakley, 2019) and rely on composite samples from a ponar sampler. Because organic chemicals tend to bind to finer sediments with higher organic content, all sediments will be sieved to less than 2 mm and total organic content and grain size assessed at each site. If possible, the <63 μ m fraction will also be isolated in the field for analysis. Sediment grain size and organic carbon content are particularly important for the binding of PBDEs and PCBs to sediments and uptake by the benthos (Dinn et al., 2012; Frouin et al., 2017).

Suspend sediments will be collected throughout the river system (watershed) to determine if toxics are transported by suspended sediments. A modified bottle-type trap will be used to collect suspend sediments over a 30-day period. The sampling device consists of four 1 liter precleaned amber glass jars deployed to depth by a telescoping PVC pole (Figure 8) which can be attached to structures within the river system. Bottle-type traps will be deployed following procedures modified from SOP WQP003 (Lubliner, 2018). Traps will be deployed in-line with river flow, capturing suspended sediments passively over the deployment period. Bottle-type traps have been used to successfully collect suspended sediments from stormwater systems during toxics investigations (Norton, 1998; Wilson and Norton, 1996). Once collected, sediments will be centrifuged to remove excess water. Suspended sediments will be analyzed for PBDEs, PCBs, percent solids, and total carbon and nitrogen.



Figure 8. Suspended Sediment Bottle Trap.

8.3 Containers, preservation methods, and holding times

Table 12. Sample containers, preservation, and holding times.

Parameter	Matrix	Minimum Quantity Required	Container	Preservative	Holding Time
PBDE	SPMD	5 SPMDs	Stainless steel carrier and can	cool to 4°C	1 year
and PCB congeners	Biofilms/ invertebrates/ sediment	10 g ww	8 oz glass jar w/ teflon lid	cool to 4°C	1 year
C and N (TOC, TN, and isotopes)	Biofilms/ invertebrates/ sediment	0.5 g	2 oz clear glass jar w/ teflon lid	cool to 4°C	14 days
Grain size	Sediment	100 g	8 oz plastic jar	cool to 4°C	6 months
DOC/TOC	Surface water	60 ml	125 mL pre- acidified poly bottle	1:1 HCl to pH<2; cool to 6°C	28 days
SSC		2 L	2L HDPE container	cool to 6°C	7 days

9.0 Laboratory Procedures

9.1 Lab procedures table

Table 13. Measurement methods (laboratory).

Analy- tical Lab	Analyte	Sample Matrix	Samples (Number)	Expected Range of Results	Detection or Reporting Limit	Sample Prep Method	Analytical (Instrumental) Method	
Water sa	Water samples							
MEL	Suspended sediment concentrations (mg / L)	Surface water	100	0.5–50	0.5	N/A	ASTM D3977 B	
MEL	Total Organic Carbon (mg / L)	Surface water	100	1–20	1	N/A	SM 5310B	
MEL	Dissolved Organic Carbon (mg / L)	Surface water	100	0.5–20	0.5	N/A	SM 5310B	
CL	PBDE congeners (pg / sample ⁾	SPMD	38	5–10,000 per cong	10–100	EPA 1614	EPA 1614	
CL	PCB (pg / sample)	SPMD	38	5–10,000	10–100	EPA 1668	EPA1668C	
Sedimer	nt and Tissue sample	es						
CL	PBDE congeners (ng / Kg)	Sediments/ tissue	12	0.5–25000 per cong	10–100	EPA 1614	EPA 1614	
CL	PCBs (pg / g)	Sediments/ tissue	12	5-10,000	10-100	EPA 1668	EPA 1668C	
MEL	Total organic carbon (%)	Sediments	60	1–15%	0.1%	PSEP TOC	PSEP TOC	
NOAA- NFSC	C and N isotopes	Sediments/ tissue	60	0.1–2.0 (%N); 1.0– 15 (%C)	0.10%	lyophilization	≠ stable isotopes of N and C	
CL	Grain size	Sediment	22	1–15%	0.1%	N/A	PSEP	

MEL = Manchester Environmental Laboratory

CL = Contract Lab

NOAA-NFSC = National Oceanic and Atmospheric Administration-Northwest Fisheries Science Center ‡ Costech Elemental Analyzer, Conflo III, MAT253

9.2 Sample preparation methods

Laboratory sample preparation methods are found in Table 13.

9.4 Laboratories accredited for methods

A summary of lab responsibilities can be found in Table 13. A contract lab will be sought for the PBDE and PCB analyses on all environmental media. A lab waiver will be sought for the Carbon and Nitrogen stable isotope analysis on tissues. The NOAA Northwest Fisheries Science Center will conduct this analysis.

10.0 Quality Control Procedures

10.1 Table of field and laboratory quality control

	Fi	Field		Laboratory			
Parameter	Blanks	Replicates	Check Standards	Method Blanks	Analytical Duplicates	Matrix Spikes	OPR Standards
Water or SPMD sa	Water or SPMD samples						
Suspended sediment concentrations		10% of samples	1/batch	1/batch	1/batch		
TOC/DOC		10% of samples	1/batch	1/batch	1/batch	1/batch	
PBDE and PCB congeners	3/sample collection	10% of samples	1/batch	1/batch	1/batch	1/batch	1/sample collection
Sediment and Tis	sue samples						
PBDE and PCB congeners		10% of samples	1/batch	1/batch	1/batch	All samples	
Total organic carbon		10% of samples	1/batch	1/batch	1/batch		
C and N isotopes		10% of samples	1/batch	1/batch			
Grain size		10% of samples	1/batch		1/batch		

 Table 14. Quality control samples, types, and frequency.

11.0 Data Management Procedures

11.1 Data recording and reporting requirements

See original QAPP for details (Hobbs, 2019)

11.2 Laboratory data package requirements

See original QAPP for details (Hobbs, 2019)

11.3 Electronic transfer requirements

See original QAPP for details (Hobbs, 2019)

11.4 EIM data upload procedures

All completed project data, excluding surface water data generated using SPMDs, will be entered into Ecology's Environmental Information Management (EIM) database for availability to the public. Concentrations of PBDEs and PCBs generated using SPMDs are considered estimates by Ecology and are not entered into EIM.

Data entered into EIM follow a formal data review process where data are reviewed by the project manager, the person entering the data, and an independent reviewer.

EIM can be accessed on Ecology's Internet homepage at <u>www.ecology.wa.gov</u>. The project will be searchable under Study ID AGIP0001.

12.0 Audits and Reports

12.1 Field, laboratory, and other audits

No defined audit exists for the fieldwork in this project.

Ecology's Environmental Laboratory Accreditation Program (ELAP) evaluates a lab's quality system, staff, facilities and equipment, test methods, records, and reports. It also establishes that the lab is capable of providing accurate, defensible data. All ELAP assessments, including Manchester Environmental Lab's (MEL's) internal performance and audits, are available from Ecology upon request.

12.2 Responsible personnel

The project manager will be responsible for all reporting.

12.3 Frequency and distribution of reports

At the end of the project, one final report will be written summarizing the study and describing the assessment of PBDE and PCB pathways and potential sources in the White-Puyallup watershed. The report will be published by January 2026.

12.4 Responsibility for reports

The final report will be authored by Alex Gipe.

13.0 Data Verification

See original QAPP for details (Hobbs, 2019)

14.0 Data Quality (Usability) Assessment

14.1 Process for determining if project objectives were met

The project manager will determine if the project data are useable by assessing whether the data have met the MQOs outlined in Tables 7 and 8. Based on this assessment, the data will either be accepted, accepted with appropriate qualifications, or rejected (with re-analysis considered).

14.2 Treatment of non-detects and data qualifiers

The handling of non-detects will be relevant to the summing of PBDE and PCB congeners. Nondetect values (U, UJ) are assigned a value of zero for the summing process when the group of analytes being summed has both detected and non-detected results. Alternatively, for results with large numbers of non-detects, the Kaplan-Meier method can be used to compute the mean concentration that is then multiplied by the number of analytes (Helsel, 2012).

If qualified data comprise more than 10% of the total summed concentration, the total concentration should be qualified. If qualified data make up less than 10% of the total summed concentration, the total should not be qualified. Data sums will be qualified with:

- "J" if that is the only qualifier used.
- "NJ" if that is the only qualifier used.
- "J" if there is a mix of "J" and "NJ" qualifiers.

When all values for individual analytes in the group are reported as non-detects and the reporting limits are different, the highest value present is assigned as the "total" value. The sum "total" will be qualified with:

- "U" if that is the only qualifier used.
- "UJ" if that is the only qualifier used.
- "U" if there is a mix of both "U" and "UJ."

All samples will be screened against the method blanks associated with each analysis batch. Sample results that are less than or equal to 5x the method blank concentration will be qualified as non-detect due to background levels of the target chemical.

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16.0 Appendix. Glossary, Acronyms, and Abbreviations

Glossary

Clean Water Act: A federal act passed in 1972 that contains provisions to restore and maintain the quality of the nation's waters. Section 303(c) requires the adoption of water quality standards. Section 303(d) of the Clean Water Act establishes the TMDL program. Section 304(a) establishes the publication of federally recommended water quality criteria. Section 402 establishes the National Pollutant Discharge Elimination System (NPDES).

Dissolved oxygen (DO): A measure of the amount of oxygen dissolved 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.

National Pollutant Discharge Elimination System (NPDES): National program for issuing, modifying, revoking and reissuing, terminating, monitoring, and enforcing permits, and imposing and enforcing pretreatment requirements under the Clean Water Act. The NPDES program regulates discharges from wastewater treatment plants, large factories, and other facilities that use, process, and discharge water back into lakes, streams, rivers, bays, and oceans.

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 domestic wastewater treatment plants, industrial wastewater treatment facilities, and stormwater from certain municipal systems and industrial and construction activities.

Salmonid: Fish that belong to the family Salmonidae. Species of salmon, trout, or char.

Sediment: Settled particulate matter located in the biologically active aquatic zone, or exposed to the water column (for example, river or lake bottom). Refer to WAC 173-204-200(24).

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.

Synoptic survey: Data collected simultaneously or over a short period of time.

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.

303(d) list: Section 303(d) of the federal Clean Water Act, requiring Washington State to periodically prepare a list of all surface waters in the state for which beneficial uses of the water – such as for drinking, recreation, aquatic habitat, and industrial use – are impaired by pollutants. These are water quality-limited estuaries, lakes, and streams that fall short of state surface water quality standards and are not expected to improve within the next two years.

Acronyms and Abbreviations

e	
С	Carbon
CWA	Clean Water Act
DO	(see Glossary above)
DOC	Dissolved organic carbon
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
et al.	And others
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective
Ν	Nitrogen
NFSC	Northwest Fisheries Science Center
NOAA	National Oceanic and Atmospheric Administration
NPDES	(See Glossary above)
PBDE	polybrominated diphenyl ethers
PCB	polychlorinated biphenyls
QA	Quality assurance
QAPP	Quality Assurance Project Plan
QC	Quality control
RM	River mile
RPD	Relative percent difference
SOP	Standard operating procedures
SSC	Suspended Sediment Concentrations
TOC	Total organic carbon
WAC	Washington Administrative Code
WDFW	Washington Department of Fish and Wildlife
WRIA	Water Resource Inventory Area
WWTP	Wastewater treatment plant
Units of Mea	surement
cfs	cubic feet per second
MG/day	millions of gallons per day
mg/L	milligrams per liter (parts per million)

ng/kg	nanograms per kilogram (parts per trillion)

- pg/g picograms per gram (parts per trillion)
- pg/L picograms per liter (parts per quadrillion)
- μg/kg micrograms per kilogram (parts per billion)
- $\mu g/L$ micrograms per liter (parts per billion)
- ww wet weight