DEPARTMENT OF ECOLOGY
State of Washington

Quality Assurance Project Plan

Assessing Sources of Toxic Chemicals Impacting Juvenile Chinook Salmon

August 2019
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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 Quality Assurance Project Plan is available on Ecology's website at https://fortress.wa.gov/ecy/publications/SummaryPages/1903110.html

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Assessing Sources of Toxic Chemicals Impacting Juvenile Chinook Salmon

August 2019

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Signatures are not available on the Internet version.
EAP: Environmental Assessment Program

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2.0 Abstract

Approximately 30% of all juvenile Chinook salmon recently sampled by Washington State Department of Fish & Wildlife contained levels of toxic substances high enough to produce sublethal effects. Juvenile Chinook salmon accumulate toxicants from streams in urban and developing environments that receive stormwater and wastewater discharges. This can affect Chinook salmon's ability to survive in the marine environment due to increased risk of predation and disease. Chinook salmon are a major part of the southern resident Orca diet. Inadequate food supply has been identified as a key reason the resident Orca population is in decline.

This Quality Assurance Project Plan (QAPP) describes upcoming investigations to identify potential point and non-point sources of emerging and legacy toxicants previously measured and currently impacting juvenile Chinook outmigrating from their natal habitats. In order to find the sources of toxic contaminants, we will sample the freshwater river systems along the salmon's migratory pathway from the river mouth to upstream. We will use several monitoring techniques including:

- Surface water sampling (using passive samplers and solid phase extraction).
- Sediment sampling.
- Sampling of resident biota (for example, algae/biofilm, and aquatic macroinvertebrates).

The work will begin in the Snohomish River Basin where juvenile Chinook are potentially impacted by polybrominated diphenyl ethers (PBDEs)—flame retardants found in household products. The intent of this QAPP is to provide an adaptable approach to continued investigations in other Puget Sound and Columbia River watersheds.

3.0 Background

3.1 Introduction and problem statement

Returning and resident Chinook salmon (*Oncorhynchus tshawytscha*) are a vital food source for the endangered southern resident orca whales in the Puget Sound and offshore from the Columbia River Estuary (Krahn et al., 2007). Furthermore, Chinook have an important cultural role for Native Americans in Washington and are of commercial and recreational value. The early freshwater life stages of Chinook require passage through urbanized and developed landscapes and hydrologically-altered rivers. Habitat degradation has long been a focus of restoration efforts for declining Chinook populations, which are listed as threatened under the US Endangered Species Act (NMFS and NOAA, 2014). However, toxic contaminants from urban, residential, and agricultural landscapes can also degrade water quality and impact the freshwater food web on which the migrating juvenile Chinook depend.

In a recent survey by Washington Department of Fish & Wildlife (WDFW), approximately 30% of all juvenile Chinook salmon sampled contained levels of toxic substances high enough to produce sublethal effects (O'Neill et al., 2015). Previous work by others in both the Puget Sound

and Columbia River Basin also documented tissue burdens of toxics at concentrations high enough to suggest a possible impact to marine survival (Meador et al., 2010; Sloan et al., 2010; Johnson et al., 2013). The impairment of juvenile Chinook salmon's ability to survive in the marine environment, with a tissue burden of toxics above a certain threshold, is due to increased risk of predation and disease (Arkoosh et al., 2010; Meador et al., 2010). The implication of previous surveys is that juvenile Chinook are accumulating sublethal amounts of toxics from urbanized and developing watersheds. Though many of these watersheds have undergone habitat restoration efforts, receiving waters can be impacted by storm and wastewater containing toxic chemicals.

From their natal streams in the Puget Sound, juvenile Chinook either migrate directly to saltwater or spend up to several months rearing in freshwater (Quinn, 2005). Most juveniles enter the estuary in the spring and early summer. There are 29 stocks of Chinook in the Puget Sound region considered as one Puget Sound evolutionary significant unit (ESU), and the proportion supplemented by hatchery salmon varies from north to south (Duffy et al., 2011). Hatchery Chinook are held back to increase growth; they migrate directly to saltwater, whereas wild Chinook stocks tend to remain in the estuary for a few weeks (Quinn, 2005). Because of the different migratory habits, hatchery Chinook tend to have significantly lower contaminant burdens (Sloan et al., 2010).

Juvenile Chinook of the Columbia River Basin have much greater variability in early freshwater life stages, including run timing, geographic ranges, and length of freshwater and estuary residence (Fresh et al., 2005). A major life-history difference is based on emigration from freshwater, where yearlings spend their first year in freshwater tributaries and migrate the following spring (stream-type) and subyearlings migrate their first year and rear for up to several months in the Columbia River Estuary (ocean-type) (Johnson et al., 2013). Chinook in the Columbia River Basin can be grouped into 13 distinct ESUs. In general, the migratory and rearing habitat of juvenile Chinook in the Columbia Basin is more heavily influenced by forestry and agricultural land uses; however, this changes in the lower Columbia River and Willamette River where industrial and urban land uses are more prominent.

The presence (including rearing and spawning habitat) of Chinook salmon in Washington's rivers and streams can be divided by the timing of runs in the spring, summer, and fall (Figure 1). Many of the runs in the Columbia River Basin region are earlier spring runs, while the Puget Sound runs are predominately fall runs. Run timing is driven by migratory distance to natal spawning habitat. The damming of the Columbia River presents a number of anthropogenic obstacles that potentially impact the return and outward migration of Chinook smolts. Continued study and uncertainties surround the survival of adult and yearling salmon through hydrosystems (ISAB/ISRP, 2016).

The goal of this project is to identify contaminant sources along the salmon's migratory pathway, and develop a prioritized list of sources to control toxic effects on the early marine survival of juvenile Chinook salmon. This Quality Assurance Project Plan (QAPP) describes a broad approach to the source identification work that will take place in watersheds previously surveyed by WDFW. The work will begin in the Snohomish River Basin (WRIA 7) and is described in greater detail throughout this QAPP.

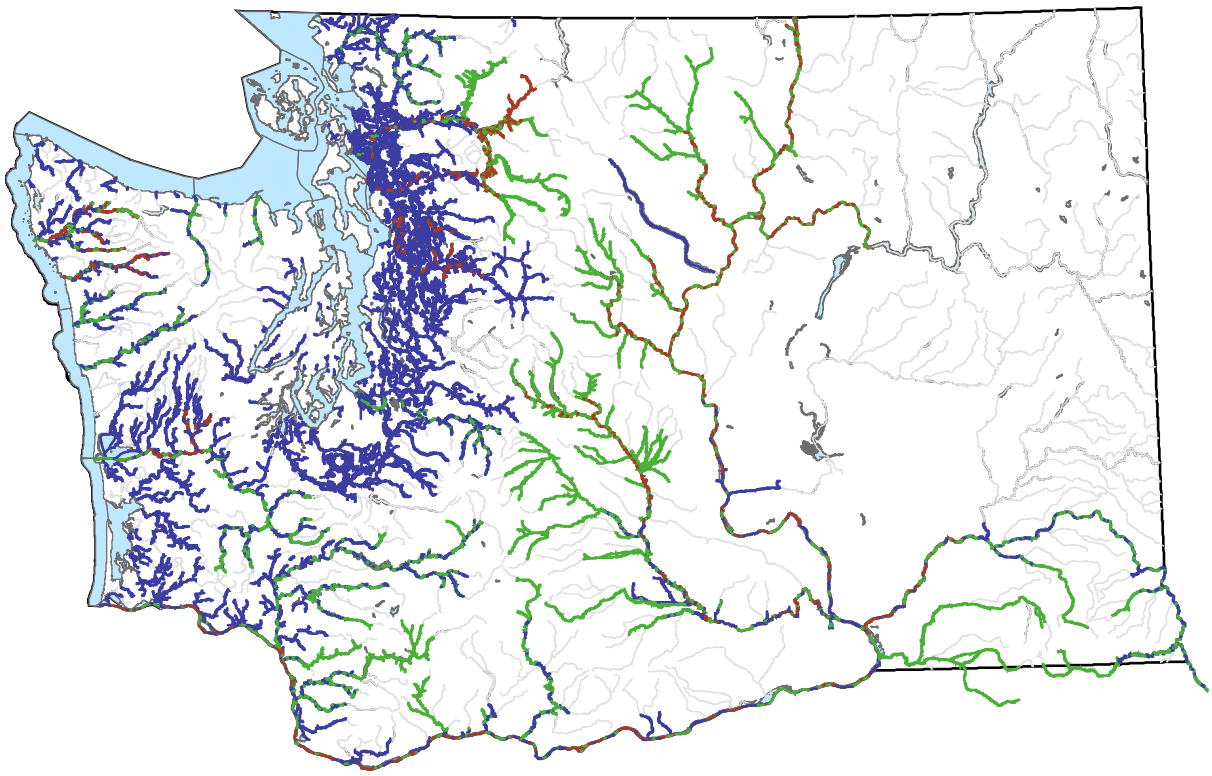

Figure 1. Geographic extent of the presence of Chinook salmon throughout Washington State (data courtesy WDFW).

Green lines are spring runs.
Red lines are summer runs.
Blue lines are fall runs.
Grey lines are rivers and streams with no documented Chinook presence.

3.2 Study area and surroundings

3.2.1 History of study area

The Snohomish River Basin is located in the Puget Sound drainage. The Snohomish is formed by the confluence of the Snoqualmie and Skykomish Rivers, which drain from headwaters in the Cascade Mountains. Approximately 75% of the 1,856 sq mile drainage basin is forested lands; in the lowland regions of the basin, agricultural and rural residential land uses become more prevalent. (Figure 2). There are a number of towns and smaller unincorporated, residential areas along the Snoqualmie and Skykomish Rivers within the urban growth area for the basin. The largest incorporated urban areas in the basin are the cities of Everett, Marysville, and Lake Stevens.

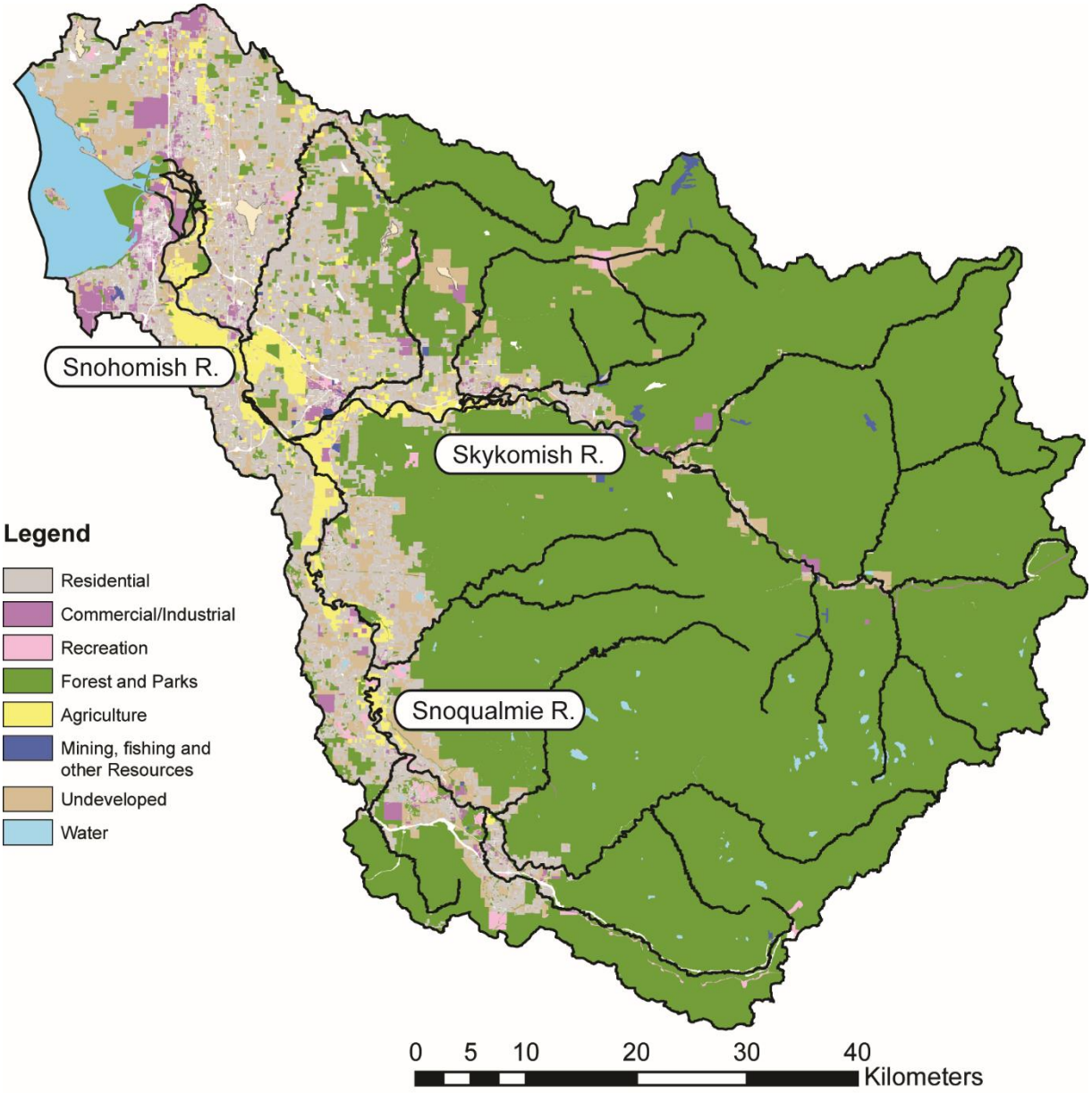

Figure 2. Land use map for the Snohomish River Basin.

The hydrology of the Snohomish River is both rainfall and snowmelt-dominated, and flow is typically highest from April through June (Figure 3). Low flow in the river occurs during August and September. There is considerable tidal influence in the lower Snohomish River, up to approximately river mile 20 where the Skykomish and Snoqualmie Rivers converge. Salt water wedges have been observed and modeled in the lower Snohomish during previous water quality studies by Ecology (Cusimano, 1997). The influence of saltwater in the lower Snohomish is dependent on the time of year, tidal cycles, and upstream freshwater flow.

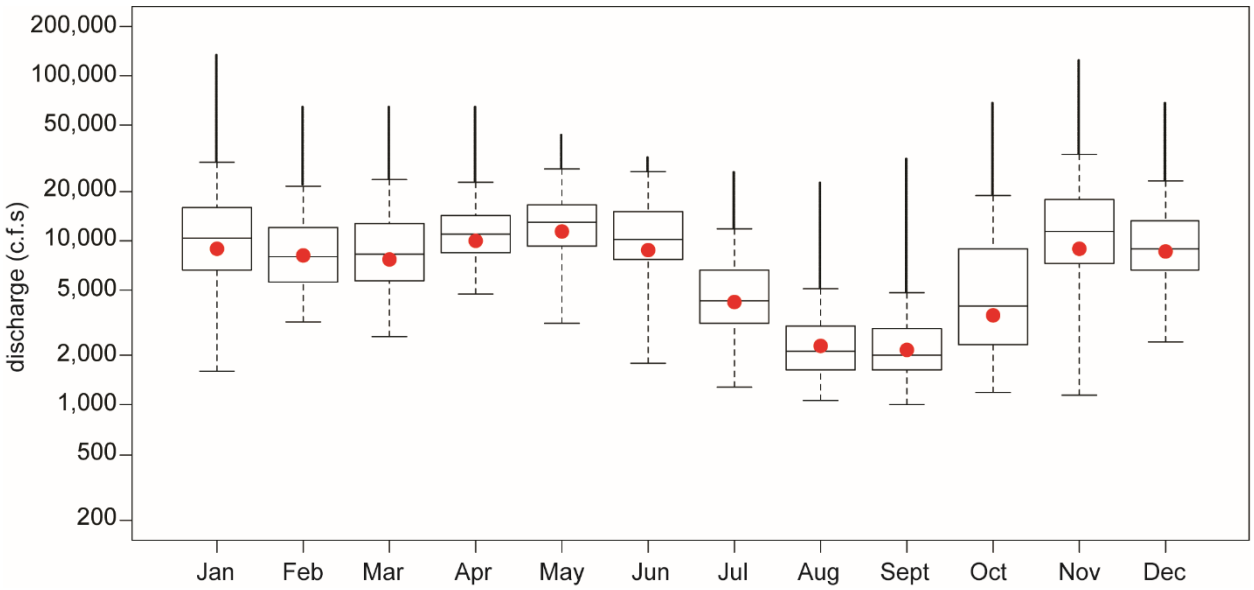

Figure 3. Discharge of the Snohomish River from 2000–2019.

Red dots are the monthly harmonic means.
Station is USGS 12150800—Snohomish River near Monroe.

Chinook (*Oncorhynchus tshawytscha*) use many of the major rivers and tributaries in the Snohomish Basin for migrating, rearing, and spawning (Figure 4). In addition to Chinook, there are a number of anadromous and non-anadromous salmonid species that utilize the basin: coho (*O. kisutch*), chum (*O. keta*), pink (*O. gorbuscha*), and sockeye salmon (*O. nerka*); steelhead and rainbow (*O. mykiss*), cutthroat (*O. clarki*), and bull trout (*Salvelinus confluentus*); and mountain whitefish (*Prosopium williamsoni*). Efforts to conserve and recover salmon stocks within the basin are ongoing (e.g., SBSRF, 2005). These efforts focus largely on habitat restoration and conventional water quality parameters such as temperature.

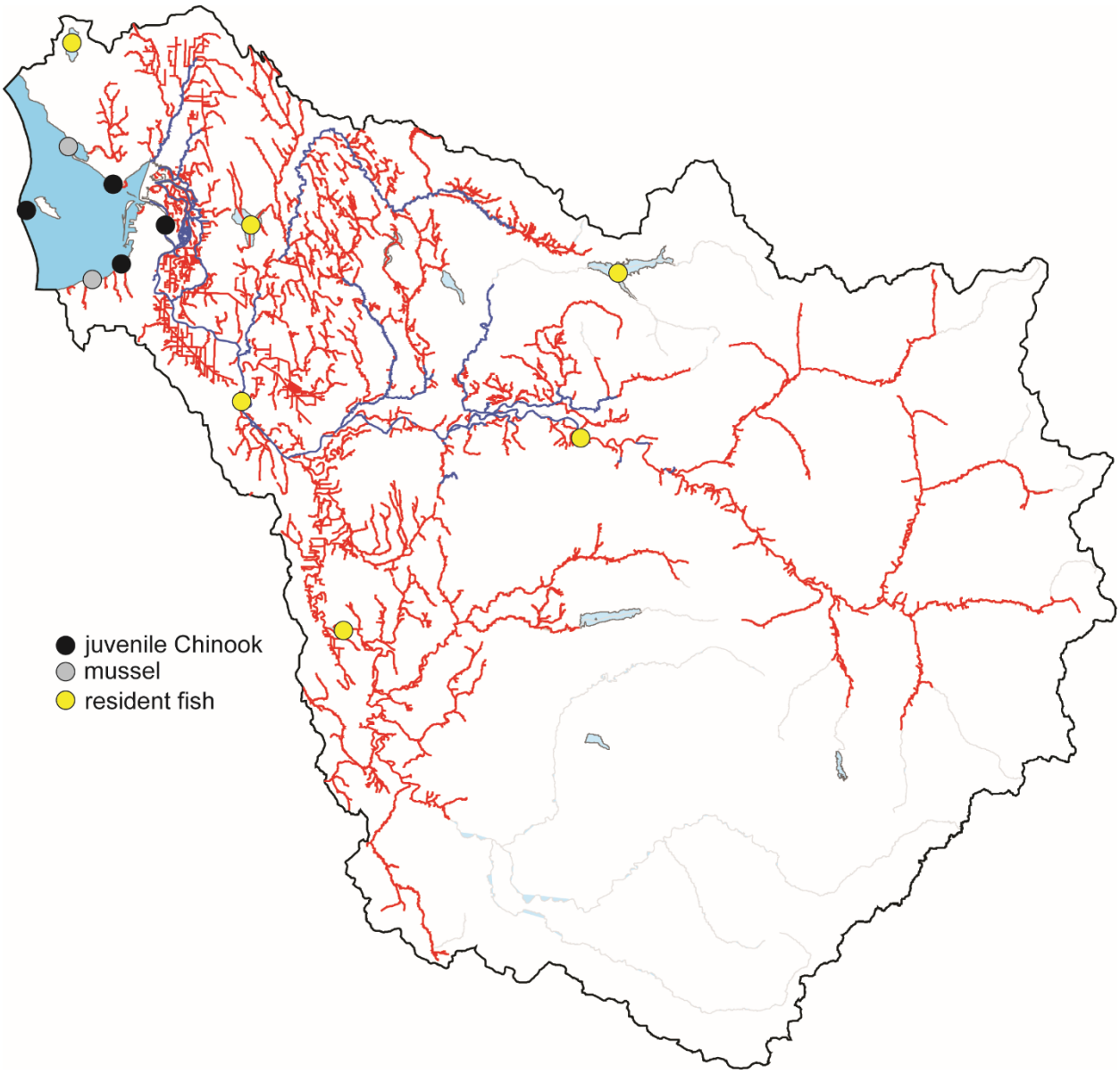

Figure 4. Extent of Chinook salmon in the Snohomish River Basin and previous fish and mussel monitoring locations.

Red lines show the presence of fall Chinook runs.
Blue lines show the presence of summer Chinook runs.
Circles are sample locations from previous studies (section 3.2.2).

3.2.2 Summary of previous studies and existing data

Previous sampling by Ecology and WDFW have suggested that resident and juvenile Chinook in the Snohomish River Basin are impacted by polybrominated diphenyl ethers (PBDEs), which are flame retardants found in products, such as plastics, furniture, upholstery, electrical equipment, and textiles. Sampling by Ecology in 2005, 2007, 2008, and 2014 all showed measurable concentrations of PBDEs in a variety of resident fish species from the Snohomish River Basin, including some lakes (Table A-1). Concentrations measured in the mountain whitefish tissues were generally the highest among species, and samples collected from the Snohomish River are

in the 90th percentile range among 460 samples taken in Washington State (Figure 5) (Johnson et al., 2006; Seiders et al., 2007; Mathieu and Wong, 2016). Total PBDEs in the tissue samples are dominated by congeners BDE-47 and BDE-99/100.

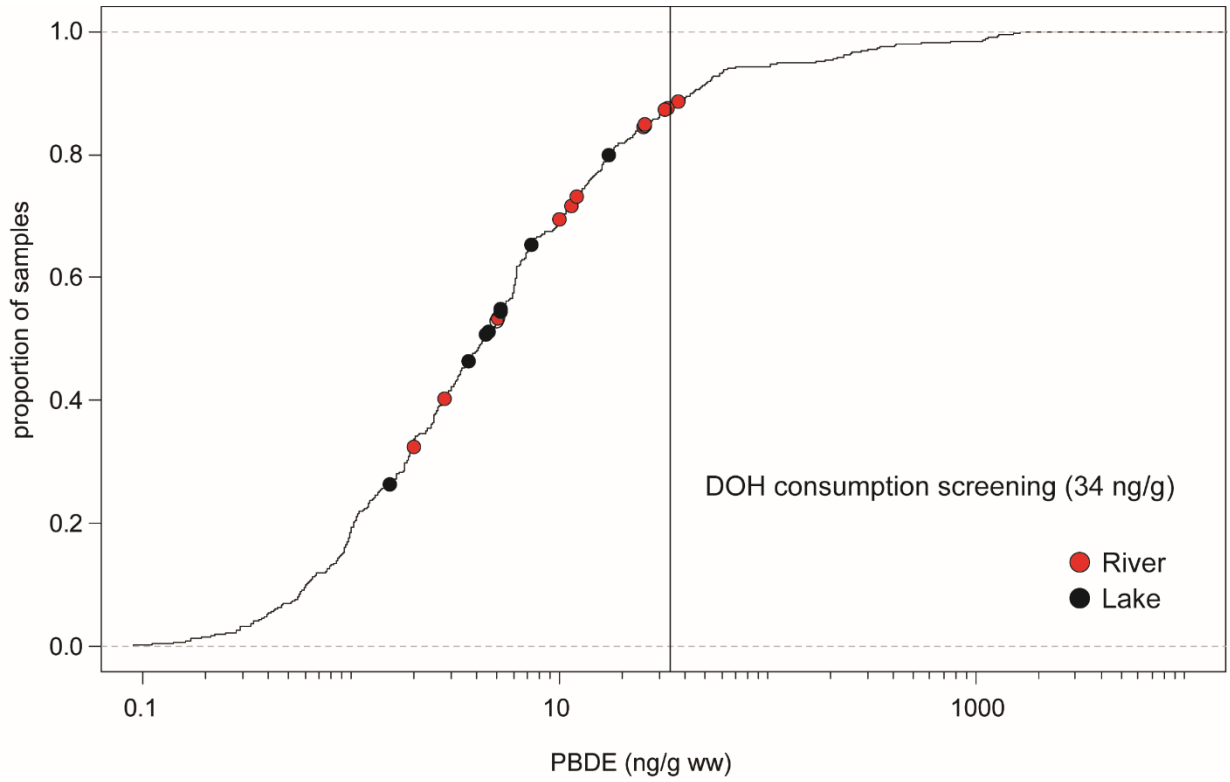

Figure 5. Empirical cumulative distribution function of PBDEs in Washington State fish tissues.

Samples collected from the Snohomish River Basin are shown as larger dots – river (red) and lakes (black).

Juvenile Chinook tissues from O'Neill et al., (2015) showed evidence of elevated PBDE concentrations in samples collected from the lower Snohomish River (Table A-1). Follow-up sampling (including wild and hatchery fish samples within the distributary channels of the estuary and the mainstem Snohomish River upstream from the estuary) have suggested that the juveniles are accumulating PBDEs in the lower Snohomish estuary (O'Neill unpublished data and personal communication). Furthermore, similar to previous work by Sloan et al., (2010) it appears that the hatchery individuals have much lower PBDE concentrations than the wild individuals.

There has been some previous sampling of PBDEs in wastewater effluent from major treatment plants in the Puget Sound, including the Everett facility in the Snohomish River Basin (Ecology and Herrera, 2010; Ecology and King County, 2011). In 2009, effluent samples were collected in winter and summer from 10 major WWTPs. The Everett WWTP's outfall 100, which discharges into Gardner Bay, contained the highest concentrations of total PBDEs (Table 1). In all of the WWTP effluent, three main congeners dominated the total-BDE concentrations: BDE-47, BDE-99 and BDE-209. Concentrations of PBDEs showed little evidence of seasonal differences.

Table 1. Previous samples of PBDE concentrations in WWTP effluent discharging to Puget Sound (Ecology and Herrera, 2010).

WWTP location	Date	Tetra-BDEs (pg/L)	Penta-BDEs (pg/L)	Deca-BDEs (pg/L)		Total-BDEs (pg/L)
Bellingham WWTP	2/12/2009	5453	5712	2000		14396
	7/16/2009	4083	3712	1390	U	8607
Bremerton WWTP	2/10/2009	5538	6328	3340		16829
	7/14/2009	5937	6030	750	UJ	13277
Burlington WWTP	2/10/2009	3565	2860	3060		10974
	7/14/2009	7697	7991	4460		22809
Chambers Cr WWTP	2/19/2009	8807	8623	2870		23838
	7/16/2009	7202	6058	250	U	15115
Everett WWTP (Outfall 100)	2/12/2009	34267	40280	35500		125387
	7/16/2009	44945	45920	22000		134737
Gig Harbor WWTP	2/10/2009	4960	5017	10700		22272
	7/14/2009	9980	10876	18800		45799
King Co West Pt	2/10/2009	6400	7094	2540		17894
	7/14/2009	7207	7824	2150		18273
Shelton WWTP	2/10/2009	15072	23132	10600		54393
	7/14/2009	6741	8178	5610		24478
Sumner WWTP	2/12/2009	3786	2732	1780		9096
	7/17/2009	7423	18316	250	UJ	30423
City of Tacoma (Central 1)	2/19/2009	15160	16954	6830		43492
	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 Snohomish River Basin, polybrominated diphenyl ethers (PBDEs) are the main group of organic chemicals that are of concern, due to the possible impairment of juvenile Chinook.

PBDEs—brominated flame-retardants—are a class of 209 congeners that resemble the structure of PCBs except they contain bromine instead of chlorine. They are manufactured as flame-retardants and used in a large variety of products (e.g., plastics, furniture, upholstery, electrical equipment, and textiles) (Hale et al., 2003). There are three main homologue groups of PBDEs: penta-, octa-, and deca-brominated diphenyl ethers (BDEs). 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 also largely phased out by the end of 2012. Like PCBs, PBDEs are bioaccumulative and bind to the fats 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 interfering with fetal development (Birnbaum and Staskal, 2003).

PBDEs are released and transported in the environment via atmospheric pathways and stormwater runoff pathways (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 wastewater (Song et al., 2006).

In addition to PBDEs there are several novel brominated flame retardants (NBFRs) that are of interest due to their use as replacement chemicals; they include: Pentabromoethylbenzene (PBEB), Hexabromobenzene (HBB), 1,2-Bis(2,4,6-tribromophenoxy)ethane (BTBPE), and Decabromodiphenylethane (DBDPE). These chemicals are halogenated and can have similar fate and transport characteristics (Zhang et al., 2016). They have similar sources in the urban environment to PBDEs and are measured using similar laboratory techniques.

3.2.4 Regulatory criteria or standards

There are no regulatory levels in Washington State for PBDEs. Previous work by WDFW has compared the tissue burden of PBDEs in juvenile Chinook to an effects threshold derived from laboratory studies at NOAA (Arkoosh et al., 2010; 2015). The work of Arkoosh et al. (2010; 2015) established a non-monotonic relationship between PBDE dose, tissue burden, and disease susceptibility, where an increased disease susceptibility was found at concentrations ≥ 470 ng PBDE / g lipid; however, this risk declines at concentrations ≥ 2,500 ng PBDE/ g lipid. O'Neill et al. (2015) relied on these tissue burdens in their assessment of juvenile Chinook throughout Puget Sound.

Environment Canada has produced Federal Environmental Quality Guidelines (2013) for PBDEs in water, sediment, and tissue that can be used for assessment of environmental quality (Table 2). Water quality guidelines are benchmarks for aquatic ecosystems that are intended to protect all forms of aquatic life (vertebrates, invertebrates, and plants) from direct adverse effects for indefinite exposure periods via the water column. Fish tissue concentrations are intended to protect fish from potential adverse effects. Sediment guidelines for the protection of aquatic life are intended to protect sediment-dwelling animals as well as pelagic animals that bioaccumulate PBDEs from sediments. The wildlife dietary guidelines are intended to protect mammalian and avian consumers of aquatic biota.

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

3.3 Water quality impairment studies

There are no water quality impairments under CWA section 303(d) for PBDEs because there are no regulatory criteria for these contaminants. However, there are existing impairments in the Snohomish River basin for toxic chemicals. Table 3 details the current listings and contaminants.

Table 3. Water quality impairments in the Snohomish River Basin under section 303(d) of the Clean Water Act.

Waterbody Name	Listing ID	Medium	Parameter
Calligan Lake	43225	Tissue	Alpha-BHC
	43233	Tissue	2,3,7,8-TCDD (Dioxin)
	43251	Tissue	PCBs
Dorothy Lake	43094	Tissue	Dioxin
Goodwin Lake	75640	Tissue	Hexachlorobenzene
	77215	Tissue	Toxaphene
	78920	Tissue	PCBs
Powder Mill Creek	78305	Water	Copper
Skykomish River	78961	Tissue	PCBs
Snohomish River	51584	Tissue	2,3,7,8-TCDD (Dioxin)
	52699	Tissue	PCBs
Snoqualmie River	78966	Tissue	PCBs
	76547	Tissue	Toxaphene
Stevens Lake	75636	Tissue	Hexachlorobenzene
	76309	Tissue	Dieldrin
	76548	Tissue	Toxaphene
	78970	Tissue	PCBs
Unnamed Creek (tributary to Evans Creek)	79779	Water	Mercury
Unnamed Creek (tributary to Snohomish River)	79781	Water	Mercury

The chlorinated pesticides and PCBs listed for impairments in the Snohomish River were not found to be accumulating in tissues of juvenile Chinook at concentrations that would suggest sublethal effects (6,000 ng DDT / g lipid, Beckvar et al., 2005; 2,400 ng PCB / g lipid, Meador et al., 2002). Analytical budgets limit our ability to investigate the sources of additional toxic chemicals. In addition, the sources and pathways of PCBs and chlorinated pesticides could differ from PBDEs and would require a different sampling approach. We are therefore not investigating PCBs or chlorinated pesticides in the Snohomish Basin at this time.

4.0 Project Description

The project goals and objectives described in this QAPP pertain to the identification of sources of PBDEs in the Snohomish River Basin. This project is part of ongoing efforts that aim to identify potential point and non-point sources of emerging and legacy toxics previously measured and potentially impacting juvenile Chinook outmigrating from natal watersheds in the Puget Sound and Columbia River Basin. It is anticipated that QAPP addenda will follow in subsequent years as efforts move to focus on additional watersheds and toxic chemicals.

4.1 Project goals

The goal of the project in the Snohomish River basin is to assess and prioritize potential sources of polybrominated diphenyl ethers (PBDEs) to the Snohomish River that may be impacting outmigrating juvenile Chinook. This will involve an assessment of vectors, or pathways, to identify how the PBDEs are moving into and through environmental media and how the fish are obtaining PBDEs.

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 Snohomish River.
- Analyze samples for PBDEs.
- 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 Snohomish Basin.
- Field reconnaissance of suitable sample locations.
- Deployment and retrieval of passive water samplers.
- Sampling of relevant biotic media and estuary sediments.
- Analysis of samples for PBDE congeners.
- Verification of data quality.
- Data analysis and report production.
- Presentation of results to Ecology and Snohomish Basin stakeholders.

4.5 Systematic planning process

This QAPP constitutes a suitable planning process.

5.0 Organization and Schedule

5.1 Key individuals and their responsibilities

Table 4. Organization of project staff and responsibilities.

Staff	Title	Responsibilities
Jessica Archer EAP Headquarters Phone: 360-407-6698	Client and Section Manager for the Project Manager	Clarifies scope of the project. Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
William Hobbs Toxic Studies Unit, SCS Phone: 360-407-7512	Project Manager	Writes the QAPP. Oversees field sampling and transportation of samples to the laboratory. Conducts QA review of data, analyzes and interprets data. Writes the draft and final report.
Sandra O'Neill T-BioS Washington Department of Fish and Wildlife Phone: 360-902-2666	Project Scientist	Reviews QAPP. Assists with study development. Directs the use of WDFW resources when necessary. Collaborates with project scientists.
Patti Sandvik Toxic Studies Unit, SCS Phone: 360-407-7198	Field Assistant	Advises during sample site selection. Helps collect samples and records field information.
Siana Wong Toxic Studies Unit, SCS Phone: 360-407-6432	Field Assistant	Helps collect samples and records field information. Oversees data management in EIM.
Jim Medlen Toxic Studies Unit, SCS Phone: 360-407-6139	Acting Unit Supervisor for the Project Manager	Provides internal review of the QAPP, approves the budget, and approves the final QAPP.
Dale Norton WOS Phone: 360-407-6765	Section Manager for the Study Area	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Alan Rue Manchester Environmental Laboratory Phone: 360-871-8801	Manchester Lab 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 Quality Assurance Officer	Reviews and approves the draft and final QAPP.

EAP: Environmental Assessment Program
EIM: Environmental Information Management database
QAPP: Quality Assurance Project Plan
SCS: Statewide Coordination Section
WOS: Western Operations Section
T-BioS: Toxics-focused Biological Observing System for the Salish Sea

5.2 Special training and certifications

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

5.3 Organization chart

See Table 4.

5.4 Proposed project schedule

Table 5. 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	October 2019	William Hobbs
Synpotic Survey – high flow	May 2020	William Hobbs
Fieldwork completed	June 2020	William Hobbs
Laboratory analyses completed	August 2020	
Laboratory Data Validation complete	December 2020	
Environmental Information System (EIM) database		
EIM Study ID	WHOB010	
Product	Due date	Lead staff
EIM data loaded	January 2021	Siana Wong
EIM data entry review	February 2021	Siana Wong
EIM complete	February 2021	Siana Wong
Final report		
Author lead / Support staff	William Hobbs / Patti Sandvik and Siana Wong	
Schedule		
Draft due to supervisor	February 2021	
Draft due to client/peer reviewer	March 2021	
Draft due to external reviewer(s)	April 2021	
Final (all reviews done) due to publications coordinator	May 2021	
Final report due on web	July 2021	

5.5 Budget and funding

Funding for this work was received through the United States Environmental Protection Agency under assistance agreement 01J18101 (National Estuary Program Funds for Puget Sound). Additional funding for a broader geographic mandate was received under the Washington State Legislature, Model Toxics Control Operating Account. See Table 6 for a budget overview and detailed budget for the first two years of the project.

Table 6. Project budget and funding.

Budget Overview	Per fiscal year
Salary, benefits, and indirect/overhead	$135,000
Equipment	$1,000
Travel and goods and 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 Congeners and NBFRs					
SPMD/SPE	40	12	52	$1000	$52,000
Tissue/sediment	30	4	34	$800	$35,200
Conventionals (water)					
SSC	120	12	132	$20	$2,640
TOC/DOC	120	12	132	$75	$9,900
Conventionals (tissue/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*					**$30,810**
Lab contingency (PBDE analysis)					**$11,200**
Lab total (Year 1 and 2)					**$145,010**

NBFRs: novel brominated flame retardants
SSC: suspended sediment concentrations
TOC: total organic carbon
DOC: dissolved organic carbon
* Includes all PBDE analysis and contingency laboratory funds.

6.0 Quality Objectives

6.1 Data quality objectives

The main data quality objective (DQO) for this project is to collect sufficient samples of biota and passive water samples to characterize possible sources of PBDEs in the Snohomish River. The analysis will use EPA methods with high-resolution gas chromatography-mass spectrometry to resolve the congener distribution present in all sample media. Measurement quality objectives 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 7. The MQOs for the field parameters (pH, dissolved oxygen, temperature, and conductivity) are in Table 8.

6.2.1 Targets for precision, bias, and sensitivity

Table 7. Measurement quality objectives.

MQO →	Precision (% RPD)		Bias Recovery Limits (%)			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	± 20%	± 20%	80–120%	NA	NA	0.5 mg L^{-1}
Total Organic Carbon	± 20%	± 20%	80–120%	75–125%	NA	0.5 mg L^{-1}
Dissolved Organic Carbon	± 20%	± 20%	80–120%	75–125%	NA	0.5 mg L^{-1}
Passive water samplers (SPMDs) and In situ SPE media						
PBDE congeners	± 50%	NA	50–150%	NA	25–150%[a]	5.0–500.0 pg per sample**
NBFRs	± 50%	NA	50–150%	NA	25–150%	30–50,000 pg per sample
Tissue (invertebrate or biofilm)						
PBDE congeners	± 50%	NA	50–150%	NA	25–150%[a]	0.1–10.0 pg/g per cong**
NBFRs	± 50%	NA	50–150%	NA	25–150%	0.3–500 pg/g
C and N	± 20%	NA	80–120%	NA	NA	0.10%
Sediments						
PBDE congeners	± 50%	NA	50–150%	NA	25–150%[a]	0.1–100.0 pg/g per cong
NBFRs	± 50%	NA	50–150%	NA	25–150%	0.3–500 pg/g
Total organic carbon	± 20%	NA	80–120%	NA	NA	1%

*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%
SPE = *in situ* solid phase extraction media (C.L.A.M. device)
SPMD = semi-permeable membrane device

Table 8. Measurement quality objectives for multi-probe sonde calibration checks.

Parameter	Units	Accept	Qualify	Reject
pH	std. units	< or = ± 0.2	> ± 0.2 and < or = ± 0.8	> ± 0.8
Conductivity*	uS/cm	< or = ± 5	> ± 5 and < or = ± 15	> ± 15
Temperature	° C	< or = ± 0.2	> ± 0.2 and < or = ± 0.8	> ± 0.8
Dissolved Oxygen	% saturation	< or = ± 5%	> ± 5% and < or = ± 15%	> ± 15%
Dissolved Oxygen	mg/L	< or = ± 0.3	> ± 0.3 and < or = ± 0.8	> ± 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%.

6.2.1.1 Precision

Precision is a measure of the variability in the results of replicate measurements due to random error. Precision for two replicate samples is measured as the relative percent difference (RPD) between the two results. If there are more than two replicate samples, then precision is measured as the relative standard deviation (RSD).

Measurement quality objectives for the precision of laboratory duplicate samples and matrix spike duplicate samples are shown in Table 7.

6.2.1.2 Bias

Bias is the difference between the population mean and the true value. For this project, bias is measured as acceptable % recovery. Acceptance limits for laboratory verification standards, matrix spikes, and surrogate standards are shown in Table 7.

6.2.1.3 Sensitivity

Sensitivity is a measure of the capability of a method to detect a substance above the background noise of the analytical system. For the high-resolution methods being used in this study, each congener is assessed for sensitivity and qualified or censored if the sample is not above five times the laboratory blank. The laboratory reporting limits (RLs) for the project are described in Section 9.2.

6.2.2 Targets for comparability, representativeness, and completeness

6.2.2.1 Comparability

Section 8.2 lists the standard operating procedures (SOPs) to be followed for field sampling. All analytical methods used for the project are approved methods commonly used by Ecology for monitoring of toxic chemicals.

6.2.2.2 Representativeness

Representativeness is a measure of whether the sample media reflects reality. We will ensure proper representatives by adhering to the approved SOPs and sampling protocols. Samples will be preserved and stored in a way that ensures holding conditions and lab holding times are met. Samples will be collected to represent high-flow and low-flow conditions in one river. Additional samples will be collected to represent high-flow conditions in a second river.

6.2.2.3 Completeness

The data for this project will be considered complete if 95% of the planned samples were collected and analyzed acceptably.

6.3 Acceptance criteria for quality of existing data

All data used to support the findings of this project will meet project DQOs. Any previous data used will also be evaluated for compliance with current DQOs.

6.4 Model quality objectives

NA

7.0 Study Design

7.1 Study boundaries

This study will focus on identifying sources and environmental pathways of PBDEs in the Snohomish River Basin (WRIA 7). PBDEs are released to the environment via air, enabling atmospheric transport and stormwater runoff pathways. PBDEs also accumulate in indoor dust from PBDE-containing consumer products, adhering to fabrics and surfaces and are then washed and transported to domestic wastewater. The PBDEs are then released into the environment from domestic (or municipal) wastewater (Song et al., 2006; Ecology, 2006), which is treated and discharged through wastewater treatment plants (WWTPs) under NPDES permits (Figure 6). Current wastewater treatment technologies are not designed to remove PBDEs. This study will assess the relative importance of potential transport pathways in the Snohomish River basin.

This study will begin with an assessment of the basin during low-flow conditions to assess ambient exposure concentrations. Low-flow conditions are intended to represent the following known and potential PBDE transport pathways: domestic wastewater, aerial deposition to the surface of the waterbodies, and sediment flux.

During the spring when wet weather conditions prevail, this study will assess the potential pathways from stormwater runoff, combined sewer overflows, and higher groundwater table discharges to the Snohomish River. Throughout the investigation, this study will assess both the spatial prevalence of PBDEs and the potential food-web based transport mechanisms to juvenile Chinook.

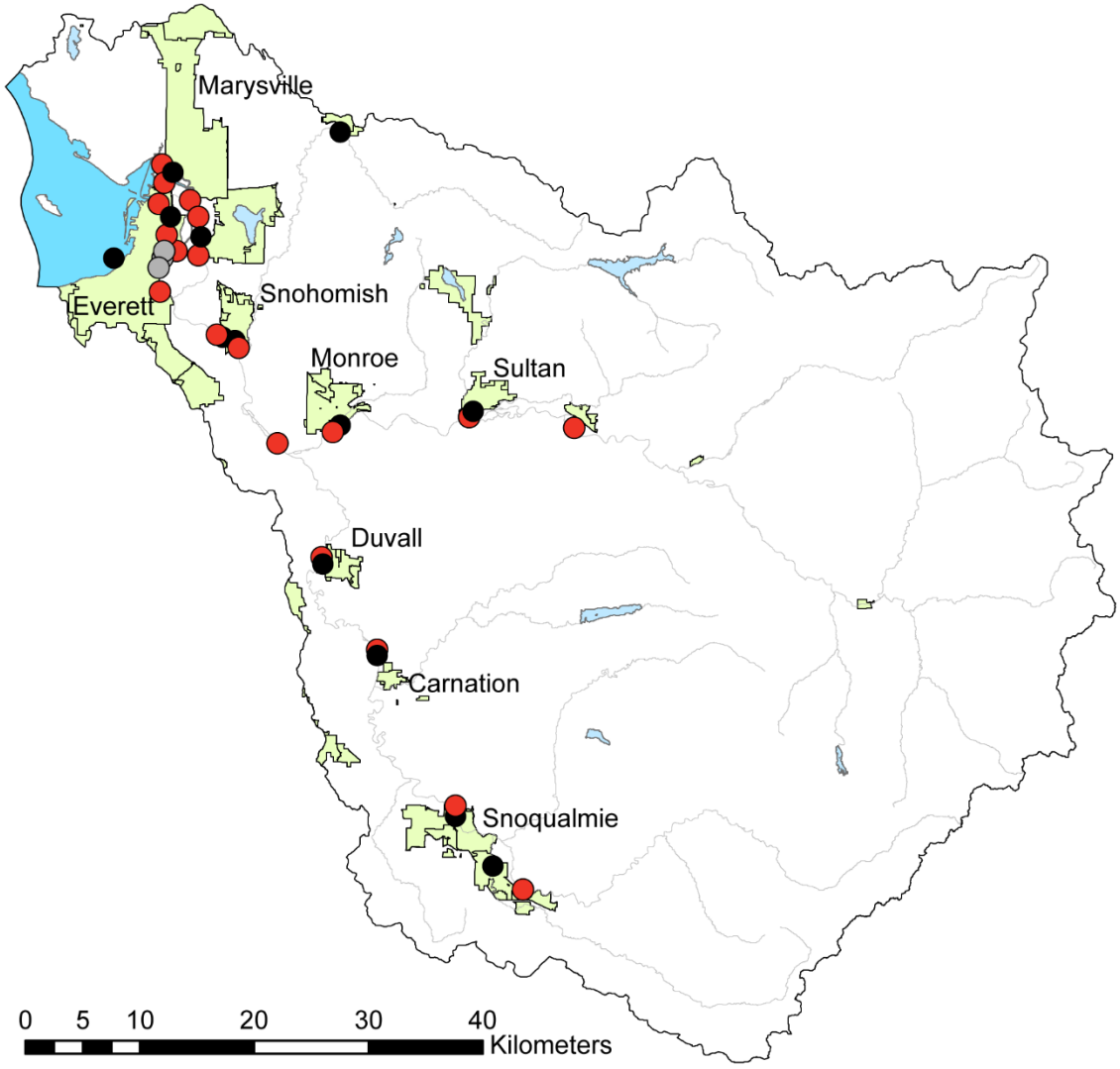

Figure 6. Snohomish River Basin showing potential sample sites.

Red circles are potential sample sites.
Black circles are WWTP outfalls.
Grey circles are WWTP CSOs.

7.2 Field data collection

7.2.1 Sampling locations and frequency

Sample locations for the initial synoptic survey will be situated near the WWTP outfalls and throughout the lower Snohomish River estuary. Exact locations will be dependent on site access, security, and access permissions. Final site locations will be decided following site reconnaissance. The tentative locations of 19 sample sites are detailed in Table 9 and Figure 6.

Following the initial synoptic survey at low flow, some of the sample locations may change and additional sites may be added to cover areas of interest.

Table 9. Proposed sample locations and rationale.

Site ID	River/Slough	River mile	Latitude	Longitude	Rationale
07Snoh01.1	Snohomish R	1.1	48.01656514	-122.1890627	Lower Snohomish estuary
07Snoh02.9	Snohomish R	2.9	47.99698637	-122.179482	Everett WWTP
07SS0.0	Steamboat Slough	0	48.03513088	-122.1845032	Entry into Gardner Bay
07ES0.0	Ebey Slough	0	48.04674016	-122.1871142	Entry into Gardner Bay
07SS01.7	Steamboat Slough	1.7	48.01972672	-122.1527195	Lower Snohomish estuary
07ES04.3	Ebey Slough	4.3	48.00660307	-122.1436357	Snohomish estuary and vicinity of Lk Stevens WWTP
07ES06.2	Ebey Slough	6.2	47.97818072	-122.1447771	Snohomish estuary and vicinity of Lk Stevens WWTP
07Snoh03.9	Snohomish R	3.9	47.9845138	-122.1676062	Upgradient of Everett WWTP
07Snoh07.1	Snohomish R	7.1	47.94724464	-122.1849027	Upgradient of Lower Snohomish estuary
07Snoh12.0	Snohomish R	12	47.9125194	-122.114229	Downgradient Snohomish CSO & WWTP
07Snoh13.0	Snohomish R	13	47.90840121	-122.0927792	Upgradient Snohomish CSO & WWTP
07Snoh20.0	Snohomish R	20	47.83078458	-122.047795	Skykomish- Snoqualmie confluence
07Sky24.5	Skykomish R	24.5	47.84237729	-121.9781917	Monroe WWTP
07Sky34.4	Skykomish R	34.4	47.85888908	-121.8213547	Sultan WWTP
07Sky41.5	Skykomish R	41.5	47.84401534	-121.6933215	Background Skykomish
07Snoq10.0	Snoqualmie R	10	47.73937133	-121.991276	Duvall WWTP
07Snoq23.0	Snoqualmie R	23	47.66620345	-121.9245416	Carnation WWTP
07Snoq40.7	Snoqualmie R	40.7	47.53920446	-121.8328771	Snoqualmie WWTP
07Snoq47.8	Snoqualmie R	47.8	47.48698192	-121.7584099	Background Snoqualmie (middle Fork)

The rates at which each WWTP discharged into the receiving waters during 2018 in the months proposed for sampling in this project (August and April) are found in Table 10. The amount discharged is generally proportional to the population served and the capacity of the WWTP. The highest discharges are to the Snohomish estuary and Gardner Bay in the Lower Snohomish Basin.

Table 10. WWTP discharge rates (MG/day) in the Snohomish basin.

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.

	Mean	Standard deviation	Median**	Minimum**	Maximum
April 2018					
Everett Outfall 100*	13.23	8.40	14.60	0.00	27.10
Everett Outfall 015	8.54	7.55	8.00	0.00	21.10
Marysville Outfall 001	5.57	3.98	7.69	0.00	9.68
Lake Stevens	3.52	0.71	3.31	2.54	5.27
Marysville Outfall 100*	2.45	3.49	0.00	0.00	8.33
Snohomish	2.45	1.40	2.09	1.35	6.47
Monroe	2.09	0.40	1.98	1.53	3.27
Snoqualmie	1.30	0.32	1.21	1.02	2.10
North Bend	1.01	0.38	0.83	0.66	2.02
Duvall	0.78	0.21	0.72	0.52	1.41
Sultan	0.58	0.20	0.53	0.34	1.17
Granite	0.44	0.09	0.42	0.32	0.69
Carnation	0.10	0.01	0.10	0.08	0.11
August 2018					
Everett Outfall 100*	6.31	4.65	5.60	0.00	16.30
Marysville Outfall 100*	3.77	0.57	3.88	1.28	4.35
Everett Outfall 015	3.11	2.37	5.00	0.00	5.10
Lake Stevens	2.15	0.09	2.16	2.02	2.37
Monroe	1.43	0.07	1.43	1.31	1.69
Snohomish	0.62	0.31	0.76	0.00	0.86
Duvall	0.42	0.03	0.41	0.36	0.48
North Bend	0.39	0.01	0.39	0.36	0.42
Sultan	0.31	0.03	0.31	0.24	0.36
Granite	0.22	0.01	0.22	0.21	0.25
Snoqualmie	0.04	0.11	0.00	0.00	0.52
Marysville Outfall 001	0.02	0.08	0.00	0.00	0.47
Carnation	0.00	0.00	0.00	0.00	0.00

* Outfall 100 for the Everett and Marysville WWTP discharges into Gardner Bay.
** Discharges of 0.00 MG/day are recorded in Ecology's PARIS database when flow is directed to an alternate outfall or discharge is to ground (e.g., Carnation WWTP in August).

7.2.2 Field parameters and laboratory analytes to be measured

The complete parameter list has been discussed in section 6.2 Measurement Quality Objectives.

7.3 Modeling and analysis design

NA

7.4 Assumptions underlying design

Assumptions associated with the study design are that we will be able to accurately measure PBDEs in the relevant environmental media and at an appropriate spatial scale to resolve possible transport pathways and identify any outlier sources for further investigation. It may be necessary to alter the timing or repeat some of the sampling if the environmental media chosen do not provide the necessary data.

Additionally, the study design assumes that a comparison of dry-weather and wet-weather sample results, coupled with surface sediment samples, will allow conclusions as to the relative importance of different PBDE pathways: domestic wastewater, aerial deposition, stormwater runoff, and sediment deposition.

7.5 Possible challenges and contingencies

7.5.1 Logistical problems

The challenges impacting the study design are limited to the logistics of suitable field sampling sites. The Snohomish River is a large, high-energy river above the tidally influenced reaches, which drains into a complex estuarine environment. There is therefore a large gradient in salinity and material (sediment) flow and deposition along the river. This variability in the conditions poses a challenge to the availability of comparable sample media throughout the river basin. To alleviate this issue, adequate time for reconnaissance of field sites and confirmation of sample media will take place well in advance of any sampling.

7.5.2 Practical constraints

Practical constraints on the field aspect of this project are having adequate personnel support for sampling. Regional collaborators may be brought in to assist in the field.

7.5.3 Schedule limitations

The possible logistical issues in capturing representative samples in such a large, complex river basin may require an additional sampling event. Contingency laboratory funding has been built in to the budget for this project. This would cause a delay in the completion of the project. Additional schedule limitations may occur during external data validation and QAPP and report production. Current scheduling is based on recent estimates of the time required under current workloads.

8.0 Field Procedures

8.1 Invasive species evaluation

Field personnel for this project are required to be familiar with and follow the procedures described in SOP EAP070 (Parsons et al., 2018), *Minimizing the Spread of Invasive Species*. The Union Slough in the Snohomish River estuary is designated as an area of extreme concern due to New Zealand mudsnail. Should any samples be taken in this area of the lower Snohomish, they will be taken last and decontamination protocols will be followed throughout the basin.

8.2 Measurement and sampling procedures

A number of sample media 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). A number of field SOPs will be followed during the study, including:

- Seiders et al. (2012a) — Standard Operating Procedure for Conducting Studies Using SPMDs.
- Seiders et al. (2012b) — Standard Operating Procedure for Semipermeable Membrane Devices (SPMD) Data Management and Data Reduction.
- Wong (2019) — Standard Operating Procedure for Sampling Trace Contaminants using Continuous Low-Level Monitoring Devices (CLAMs).
- Blakely (2008) — Standard Operating Procedure for Obtaining Freshwater Sediment Samples.

Semi-permeable membrane devices

The initial synoptic survey of the basin for PBDEs in water will rely heavily on passive samplers, semi-permeable membrane devices (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 7). The goal of SPMDs is to 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.

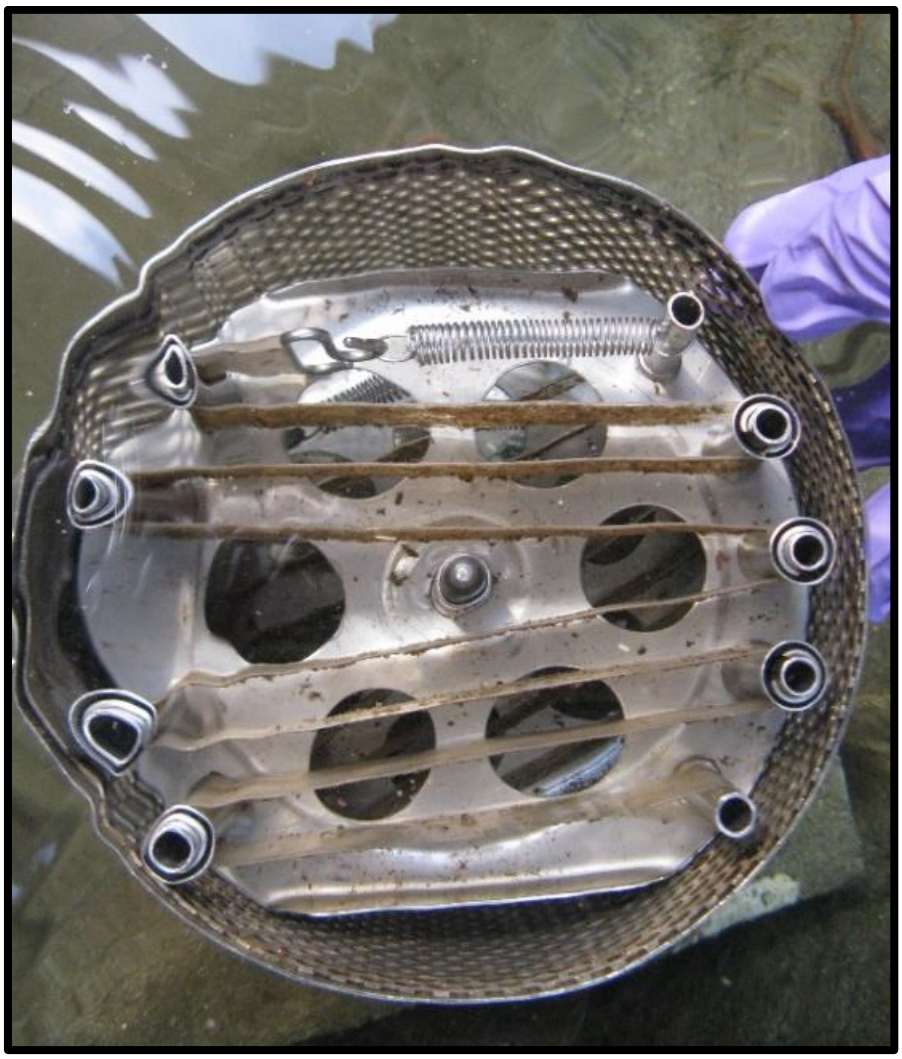

Figure 7. An SPMD canister showing the upper membrane.

Note: some biofouling on the membrane is evident.

In this study, SPMDs will be deployed in secure areas (i.e., to minimize vandalism and avoid strong currents), using 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, however, only one will be analyzed for the presence of PBDEs. The second canister/SPMDs are backups that would only be analyzed if the other canister/SPMD 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 in order 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. PRCs will be added at a concentration of 2.5 ng per SPMD.

A StowAway® TidbiT™ 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 sampling period and incorporated into the uptake rates for PBDEs.

SPMDs will be exposed to ambient air for no more than 45 seconds at each site during deployment and retrieval. Nitrile gloves will be used at all times. SPMDs will be deployed for approximately 28 days in the late summer (i.e., August to September), when water flows are low. The same laboratory-supplied shipping cans will be used during retrieval. They will be properly sealed, cooled, and kept near freezing until arrival at the contract lab for the extraction of the membranes (dialysis). PBDE analysis will be performed via EPA Method 1614.

In Situ solid-phase extraction disks

Solid-phase extraction (SPE) disks may be used during the project to actively sample the waters of the Snohomish River. SPE disks will be deployed in continuous low-flow sampling devices (C.L.A.M.s) and deployed for a period of 24 to 36 hours, following Wong (2019). Briefly, the SPE media is mounted in front of a small pump (C.L.A.M.) that pulls water through the disk. Organic contaminants are bound to the SPE media. The media is removed from the disk housing and shipped to the contract lab for extraction and analysis. C.L.A.M.s will be suspended in the water column or mounted to concrete blocks on the riverbed. All water pumped through the device will be collected to measure the precise volume pumped, in order to calculate a PBDE concentration.

Stainless steel housings for the SPE media will be used in this project, similar to Hobbs et al. (2018) (Figure 8). Prior to the first sampling event, the housing and SPE media will be tested for blank contamination by the contract lab. We will assess the retention of the analytes bound to the SPE media using the same performance reference compounds as the SPMDs, injected into the SPE media by the contract lab prior to deployment. The contract lab will be responsible for cleaning the disk housing, conditioning the SPE media, and shipping the disk ready for deployment into the field.

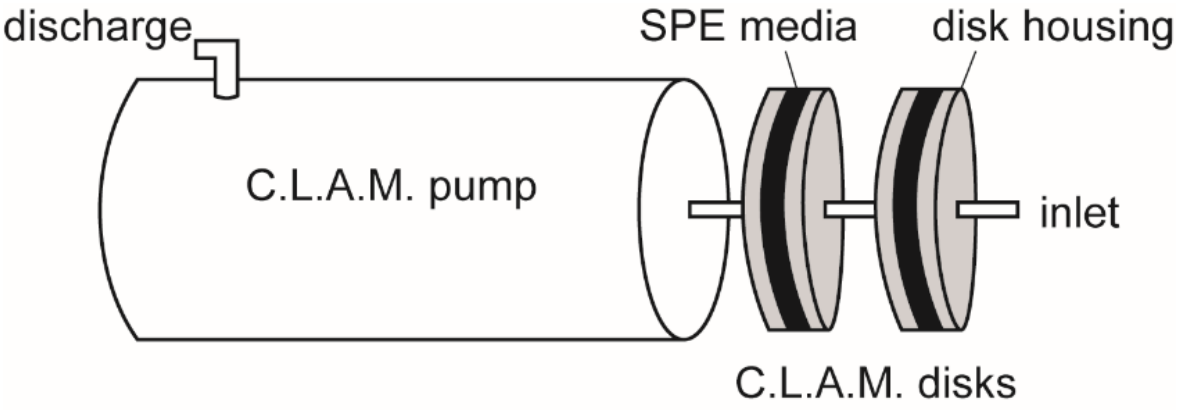

Figure 8. Schematic of the C.L.A.M. sampler with SPE media in a disk housing.

Surface water grab samples

Water grab samples will be taken to measure the total and dissolved organic carbon (TOC/DOC) and suspended sediment concentrations (SSC) at each site during the time the SPMDs are exposed. These parameters will be used as ancillary data to help understand relationships between suspended matter and the PBDE 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 Ecology standard operating procedures (Joy, 2006).

Additional field parameters will be measured *in situ* at the time of water sampling using a multi-probe sonde (Swanson, 2007). Parameters include: temperature, pH, dissolved oxygen, and conductivity.

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 9). Standard protocols for sampling attached algae will be followed to collect biofilm samples (Stevenson and Bahls, 1999; Larson and Collyard, 2019). Biofilm will be scraped from rocks and collected in a stainless 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. A sample to assess areal biomass (g dry weight / cm^2) will be collected separately; each rock scraped for biofilm will be measured by cutting a piece of aluminum foil tracing the sample area. The aluminum foil is then measured at Ecology using software.

Figure 9. Example of a biofilm being scraped from a rock.

Biofilms will be analyzed for PBDEs, ash-free dry weight (areal biomass), and carbon (C) and nitrogen (N) abundance and stable isotope ratios. Stable isotopes of the biofilms will assist in detecting changes in nutrient and wastewater inputs over the study area.

Invertebrate tissues

In order to measure the PBDE concentrations and potential bioaccumulation of PBDEs from the food source of the juvenile Chinook, we may include the analysis of invertebrates in the sampling. Chinook will go through ontogenetic changes during their migration (Duffy et al., 2010), however they generally feed on aquatic insects in the 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 basin, but will likely focus on the lower Snohomish River estuary 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 Blakely (2008) 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 2mm and total organic content and grain size assessed at each site. If possible, the <63µm 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 to sediments and uptake by the benthos (Dinn et al., 2012; Frouin et al., 2017).

The Marine Monitoring Unit of EAP will be conducting an intensive study of the offshore and nearshore sediments in Gardner Bay/Everett Harbor during the summer of 2019 (Dutch et al., 2018). This coincident sampling may provide an opportunity to collect additional sediment samples in the nearshore areas just downstream of the Snohomish River estuary. These opportunities will be explored as this project proceeds. All sampling methods and quality assurance for the MMU are detailed in the approved Quality Assurance Monitoring Plan (QAMP) (Dutch et al., 2018).

8.3 Containers, preservation methods, holding times

Table 11. Sample containers, preservation, and holding times.

Parameter	Matrix	Minimum Quantity Required	Container	Preservative	Holding Time
PBDE congeners and NBFRs	SPMD	3 SPMDs	Stainless steel carrier and can	cool to 4°C	14 days
	SPE	20L of water processed	HDPE filter case; CLAM sampler	cool to 4°C	14 days
	Biofilms/ invertebrates/ sediment	10g ww	8 oz glass jar w/ teflon lid	cool to 4°C	14 days
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	60ml	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

8.4 Equipment decontamination

Decontamination of equipment will follow Friese (2014). Field blanks and manufacturing blanks of the SPMDs will be analyzed as part of the QA program for this project. No decontamination in the field (between sample sites) is necessary for this project.

8.5 Sample ID

Laboratory sample IDs will be assigned by MEL and the contract lab.

8.6 Chain of custody

Chain of custody will be maintained for all samples throughout the project.

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 information will be recorded in the project field log:

- 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
- Field instrument calibration procedures
- Field measurement results
- Identity of QC samples collected
- Unusual circumstances that might affect interpretation of results

8.8 Other activities

No additional activities require description.

9.0 Laboratory Procedures

9.1 Lab procedures table

Table 12. Measurement methods (laboratory).

Analytical Lab	Analyte	Sample Matrix	Samples (Number)	Expected Range of Results	Detection or Reporting Limit	Sample Prep Method	Analytical (Instrumental) Method
Water Samples							
MEL	Suspended sediment concentrations (mg / L)	Surface water	120	0.5–50	0.5	N/A	ASTM D3977 B
MEL	Total Organic Carbon (mg / L)	Surface water	120	1–20	1	N/A	SM 5310B
MEL	Dissolved Organic Carbon (mg / L)	Surface water	120	0.5–20	0.5	N/A	SM 5310B
CL	PBDE congeners (pg / sample)	SPMD and SPE extract	40	5–10,000 per cong	10–100	EPA 1614	EPA 1614
CL	NBFRs (pg / sample)	SPMD and SPE extract	40	30–10,000	30–50000	EPA 1614	Amended EPA 1614
Sediment and Tissue Samples							
CL	PBDE congeners (ng / Kg)	Sediments/tissue	40	0.5–25000 per cong	10–100	EPA 1614	EPA 1614
CL	NBFRs (pg / g)	Sediments/tissue	40	0.3–5000	0.3–500	EPA 1614	Amended EPA 1614
MEL	Total organic carbon (%)	Sediments	30	1–15%	0.1%	PSEP TOC	PSEP TOC
UW	C and N isotopes	Sediments/tissue	60	0.1–2.0 (%N); 1.0–15 (%C)	0.10%	lyophilization	ǂ stable isotopes of N and C
CL	Grain size	Sediment	20	1–15%	0.1%	N/A	PSEP

MEL = Manchester Environmental Lab
CL = contract Lab
UW = University of Washington IsoLab
ǂ Costech Elemental Analyzer, Conflo III, MAT253

9.2 Sample preparation method(s)

Laboratory sample preparation methods are found in Table 12.

9.3 Special method requirements

There are no special method requirements.

9.4 Laboratories accredited for methods

A summary of lab responsibilities can be found in Table 12. A contract laboratory will be sought for the PBDE analysis on all environmental media. A laboratory waiver will be sought for the C and N stable isotope analysis on tissues. The UW IsoLab will be used for this analysis.

10.0 Quality Control Procedures

10.1 Table of field and laboratory quality control

Table 13. Quality control samples, types, and frequency.

Parameter	Field		Laboratory				
	Blanks	Replicates	Check Standards	Method Blanks	Analytical Duplicates	Matrix Spikes	OPR Standards
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 congeners and NBFRs	3/sample collection	10% of samples	1/batch	1/batch	1/batch	1/batch	1/sample collection
Sediment and Tissue Samples							
PBDE congeners and NBFRs		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		

10.2 Corrective action processes

The laboratory analysts will document whether project data meets method QC criteria. Any departures from normal analytical methods will be documented by the laboratory and described in the data package from the laboratories as well as in the final report for the project. If any samples do not meet QC criteria, the project manager will determine whether data should be re-analyzed, rejected, or used with appropriate qualification.

Field instruments will be checked and calibrated prior to the fieldwork. The post-field check of the instrument should be within the MQOs defined in Table 8. The appropriate qualification or rejection threshold is detailed in the MQOs.

11.0 Data Management Procedures

11.1 Data recording and reporting 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. Data will be transferred to Microsoft Excel templates for creating data tables and entry into EIM. Data will be entered into EIM by the project data steward. Once entered into EIM, the project manager will verify the sample locations and project description. An R script will be used to verify each entry with the original laboratory data EDD and data tables.

11.2 Laboratory data package requirements

The laboratory data package will be generated or overseen by MEL. MEL will provide a project data package that will include: a narrative discussing any problems encountered in the analyses, corrective actions taken, changes to the referenced method, and an explanation of data qualifiers. Quality control results will be evaluated by MEL (discussed below in *Section 13.0 Data Verification*). A level 4 data package will be required from the contract lab.

The following data qualifiers will be used:

- "J" – The analyte was positively identified. The associated numerical result is an estimate.
- "UJ" – The analyte was not detected at or above the estimated reporting limit.
- "NJ" – The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical value represents its approximate concentration.

The qualifiers will be used in accordance with the method reporting limits such that:

- For non-detect values, the estimated detection limit (EDL) is recorded in the "Result Reported Value" column and a "UJ" in the "Result Data Qualifier" column.
- No results are reported below the EDL.
- Only results reported are for those congeners that have a value at least FIVE times the signal-to-noise ratio, and that meet ion abundance ratios required by the method.
- Detected values that are below the quantitation limits (QL) are reported and qualified as estimates ("J").
- Results that do not meet ion abundance ratio criteria are reported with "NJ." If an Estimated Maximum Possible Concentration (EMPC) value is calculated and reported, the calculation is explained in the narrative, and an example calculation used for this value is provided.
- Results that contain interference from polychlorinated diphenyl ethers (PCDEs) are qualified with "NJ."

11.3 Electronic transfer requirements

All laboratory data will be accessed and downloaded from MEL's Laboratory Information Management System (LIMS) into Excel spreadsheets. The contract lab will provide an electronic data deliverable (EDD) that meets the format defined by MEL.

11.4 EIM/STORET data upload procedures

All completed project data will be entered into Ecology's Environmental Information Management (EIM) database for availability to the public and interested parties, with the exception of the surface water data generated using SPMDs. Concentrations of PBDEs 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 www.ecology.wa.gov. The project will be searchable under Study ID WHOB010.

11.5 Model information management

NA

12.0 Audits and Reports

12.1 Field, laboratory, and other audits

No defined audit exists for the fieldwork in this project.

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

12.2 Responsible personnel

The project manager will be responsible for all reporting.

12.3 Frequency and distribution of reports

One final report will be written at the end of the project summarizing the study and describing the assessment of PBDE pathways and potential sources in the Snohomish River Basin.

12.4 Responsibility for reports

The report will be authored by William Hobbs.

13.0 Data Verification

13.1 Field data verification, requirements, and responsibilities

The field assistant will review field notes once they are entered into Excel spreadsheets. Oversight will be provided by the project manager.

13.2 Laboratory data verification

As previously described, MEL will oversee the review and verification of all laboratory data packages. All data generated by the contract lab must be included in the final data package, including but not limited to:

- A text narrative.
- Analytical result reports.
- Analytical sequence (run) logs.
- Chromatograms.
- Spectra for all standards.
- Environmental samples.
- Batch QC samples.
- Preparation benchsheets.

All of the necessary QA/QC documentation must be provided, including results from matrix spikes, replicates, and blanks.

13.3 Validation requirements, if necessary

A level 2B data validation will be requested for this project, but will include the conversion of contract laboratory flags to MEL-amended qualifiers. Data validation will be carried out by the MEL QA Coordinator. A level 4 data package will be required from the contract lab, should a level 4 data validation be necessary in the future.

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 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 and 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 congeners. Non-detect 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, then 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."

14.3 Data analysis and presentation methods

No specific numerical analyses are necessary for this project. The data analysis will follow the approach of Hobbs (2018). Time-integrated samples (SPMDs and biofilms) do alleviate some of the replication necessary for instantaneous grab samples because they represent average exposure concentrations. However, if possible, the sample collections will be of sufficient size (minimum three) to statistically compare different sections of the river, including regional background samples. In order to determine whether there are true differences between upstream and downstream samples, efforts will be made to constrain the local variability of the sample media (through replication) and use this as a confidence interval when comparing sample concentrations.

14.4 Sampling design evaluation

The sampling design of this project will undergo evaluation between sampling events. The effectiveness of the sample media, the spatial resolution of the samples, and our ability to access the necessary sample sites will undergo revision if necessary.

14.5 Documentation of assessment

The final report will present the findings, interpretations, and recommendations from this study

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16.0 Appendices

Appendix A. Results of Previous Fish Tissue Studies

Table A-1. Results of PBDE concentrations in fish tissues from previous studies in the Snohomish River Basin.

All samples are composites of muscle tissue, concentrations are in wet weight.

Waterbody	Year	Study ID	Species	Lat	Long	t-PBDEs (ppb)	% lipids
Snohomish R	2014	EAP 16-03-012	MWF	47.8754	-122.087	5.03	3.2
Snohomish R	2014	EAP 16-03-012	MWF	47.8754	-122.087	36.97	2.5
Snohomish R	2014	EAP 16-03-012	PEA	47.8754	-122.087	1.99	1.8
Snohomish R	2014	EAP 16-03-012	PEA	47.8754	-122.087	2.78	1.7
Snohomish R	2005	EAP 06-03-027	LSS	47.8754	-122.087	11.37	2.4
Snohomish R	2005	EAP 06-03-027	MWF	47.8754	-122.087	33.20	4.1
Snohomish R	2005	EAP 06-03-027	CTT	47.8754	-122.087	25.18	3.6
Snohomish R	2005	EAP 06-03-027	NPM	47.8754	-122.087	12.07	2.5
Skykomish R	2008	WSTMP08	MWF	47.8436	-121.695	10.00	3.2
Snoqualmie R	2008	WSTMP08	MWF	47.6921	-121.966	25.80	4.2
Lake Stevens	2014	EAP 16-03-012	BBH	48.005	-122.082	4.56	3.8
Lake Stevens	2014	EAP 16-03-012	BBH	48.005	-122.082	5.23	3.0
Lake Stevens	2014	EAP 16-03-012	LMB	48.005	-122.082	3.63	1.2
Lake Stevens	2014	EAP 16-03-012	LMB	48.005	-122.082	4.40	1.8
Lake Stevens	2008	WSTMP08	RBT	48.005	-122.082	4.90	0.7
Lake Stevens	2008	WSTMP08	KOK	48.005	-122.082	17.20	2.0
Goodwin Lake	2008	WSTMP08	LMB	48.1462	-122.295	5.20	0.7
Goodwin Lake	2008	WSTMP08	RBT	48.1462	-122.295	7.30	1.9
Goodwin Lake	2008	WSTMP08	SMB	48.1462	-122.295	5.20	0.6
Spada Lake	2007	WSTMP07	CTT	47.97	-121.65	1.52	0.4
Port Gardner Bay	2013	13WB_EHN-MXW01	Mussel	47.9721	-122.232	3.35	unk
Port Gardner Bay	2013	13WB_EH-MTW01	Mussel	47.9721	-122.232	1.64	unk
Tulalip Bay	2013	13WB_HP-MTW01	Mussel	48.06175	-122.293	0.99	unk

Waterbody	Year	Study ID	Species	Lat	Long	t-PBDEs (ppb)	% lipids
Tulalip Bay	2013	13WB_HPN-MXW01	Mussel	48.06175	-122.293	2.13	unk
Port Gardner Bay	2013	13SNME01-TW01	Juv Chin	48.03284	-122.244	3.84	unk
Port Gardner Bay	2013	13SNME01-TW02	Juv Chin	48.03284	-122.244	3.01	unk
Port Gardner Bay	2013	13SNME01-TW03	Juv Chin	48.03284	-122.244	3.98	unk
Port Gardner Bay	2013	13SNME01-TW04	Juv Chin	48.03284	-122.244	4.41	unk
Port Gardner Bay	2013	13SNME01-TW05	Juv Chin	48.03284	-122.244	3.58	unk
Port Gardner Bay	2013	13SNME02-TW01	Juv Chin	47.95964	-122.264	3.37	unk
Port Gardner Bay	2013	13SNME02-TW02	Juv Chin	47.95964	-122.264	4.42	unk
Port Gardner Bay	2013	13SNME02-TW03	Juv Chin	47.95964	-122.264	5.58	unk
Port Gardner Bay	2013	13SNME02-TW04	Juv Chin	47.95964	-122.264	18.98	unk
Port Gardner Bay	2013	13SNME02-TW05	Juv Chin	47.95964	-122.264	7.61	unk
Port Gardner Bay	2013	13WB-TW01A	Juv Chin	48.01221	-122.343	4.33	unk
Snohomish R	2013	13SNMR-TW01	Juv Chin	48.00422	-122.178	31.57	unk
Snohomish R	2013	13SNMR-TW02	Juv Chin	48.00422	-122.178	16.69	unk
Snohomish R	2013	13SNMR-TW03	Juv Chin	48.00422	-122.178	38.88	unk
Snohomish R	2013	13SNMR-TW04	Juv Chin	48.00422	-122.178	34.16	unk

MWF – mountain whitefish (*Prosopium williamsoni*)
PEA – peamouth chub (*Mylocheilus caurinus*)
LSS – largescale sucker (*Catostomus macrocheilus*)
NPM – northern pikeminnow (*Ptychocheilus oregonensis*)
BBH – black bullhead (*Ameiurus melas*)
LMB – largemouth bass (*Micropterus salmoides*)
SMB – smallmouth bass (*Micropterus dolomieu*)
CTT – cutthroat trout (*Oncorhynchus clarkia*)
RBT – rainbow trout (*Oncorhynchus mykiss*)
Juv Chin – juvenile Chinook salmon (*Oncorhynchus tshawytscha*)
KOK – kokanee salmon (*Oncorhynchus nerka*)
Mussel – nearshore bay mussel, *Mytilus trossulus*

Appendix B. Glossaries, Acronyms, and Abbreviations

Glossary of General Terms

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.

Total suspended solids (TSS): Portion of solids retained by a filter.

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

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
NBFR	Novel Brominated Flame Retardant
NPDES	(See Glossary above)
PBDE	polybrominated diphenyl ethers
PCB	polychlorinated biphenyls
QA	Quality assurance
QC	Quality control
RM	River mile
RPD	Relative percent difference
SOP	Standard operating procedures
SSC	Suspended Sediment Concentrations
TOC	Total organic carbon
TSS	(See Glossary above)
WAC	Washington Administrative Code
WDFW	Washington Department of Fish and Wildlife
WRIA	Water Resource Inventory Area
WWTP	Wastewater treatment plant

Units of Measurement

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)
µg/L	micrograms per liter (parts per billion)
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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