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Quality Assurance Project Plan

Measuring PCBs in Biofilm, Sediment, and Invertebrates in the Spokane River: Screening Study

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Author and Contact Information

Siana Wong and Brandee Era-Miller
P.O. Box 47600
Environmental Assessment Program
Washington State Department of Ecology
Olympia, WA 98504-7710

For more information contact:

Publications Coordinator
Environmental Assessment Program
P.O. Box 47600, Olympia, WA 98504-7600
Phone: (360) 407-6764

Washington State Department of Ecology – https://ecology.wa.gov

- Headquarters, Olympia 360-407-6000
- Northwest Regional Office, Bellevue 425-649-7000
- Southwest Regional Office, Olympia 360-407-6300
- Central Regional Office, Union Gap 509-575-2490
- Eastern Regional Office, Spokane 509-329-3400

Quality Assurance Project Plan

Measuring PCBs in Biofilm, Sediment, and Invertebrates in the Spokane River: Screening Study

March 2019

Approved by:

Signature:	Date:
Adriane Borgias, Client, WQP Program, Eastern Regional Office Signature:	Date:
Brook Beeler, Director, Eastern Regional Office Signature:	Date:
Brandee Era-Miller, Author / Project Manager, EAP Signature:	Date:
Siana Wong, Author / Principal Investigator, EAP Signature:	Date:
Debby Sargeant, Author's Unit Supervisor, EAP Signature:	Date:
Jessica Archer, Author's Section Manager, EAP Signature:	Date:
George Onwumere, Section Manager for Project Study Area, EAP Signature:	Date:
Alan Rue, Director, Manchester Environmental Laboratory Signature:	Date:
Arati Kaza, Quality Assurance Officer	

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

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2.0 Abstract

Sections of the Spokane River are currently listed as water quality impaired for polychlorinated biphenyls (PCBs) under Section 303(d) of the Clean Water Act. Listings are based on fish tissue concentrations that indicated exceedances of Washington's former human health criteria for PCBs (Federal Register, 1999).

The Spokane River Regional Toxics Task Force (SRRTTF) works to identify PCB sources. They use their findings to develop and implement strategies to reduce PCBs in the river as identified in their *Comprehensive Plan to Reduce Polychlorinated Biphenyls (PCBs) in the Spokane River*. However, unidentified sources remain, especially in areas influenced by groundwater discharge to the river.

In this study, Ecology will conduct a spatial survey of the Spokane River using biofilms, sediments, and invertebrates to assess additional PCB sources. The goals of this study are to:
(1) Characterize PCB concentrations in biofilm, sediment, and invertebrates in the Spokane River.
(2) Evaluate the use of biofilms for tracing PCB sources in the Spokane River.
(3) Evaluate the presence of previously unidentified sources of PCBs to the Spokane River.

Sampling locations will be coordinated with SRRTTF. These locations will include areas of unknown potential sources, known sources, and reference locations. Biofilm samples will be collected at 19 locations on the Spokane River between the Washington-Idaho border and just below Nine Mile Dam. Sediment and invertebrate samples will be collected at a subset of locations. Sampling will be conducted during the summer low-flow period in 2018. PCB concentrations in biofilms will be compared among potential, known, and reference locations. For all sample matrices, PCB concentrations and congener patterns will be explored and compared.

3.0 Background

3.1 Introduction and problem statement

Sections of the Spokane River are currently listed as water quality impaired for PCBs under Section 303(d) of the Clean Water Act. Listings are based on PCB concentrations in fish tissue that indicated exceedances of Washington's former human health criteria for PCBs (Federal Register, 1999). Because of high concentrations of PCBs and other contaminants in fish tissue, fish consumption advisories are in place for sections of the Spokane River[1].

The Spokane River Regional Toxics Task Force (SRRTTF) is a stakeholder group that was formed in 2012 to identify PCB sources and to develop and implement strategies to reduce PCBs in the river. This work was detailed in SRRTTF's *Comprehensive Plan to Reduce Polychlorinated Biphenyls (PCBs) in the Spokane River* (LimnoTech, 2016a). In the comprehensive plan, the following sources and transport mechanisms were identified and evaluated:

- Municipal and wastewater facilities
- Industrial facilities
- Stormwater
- Combined sewer outflows
- Groundwater discharges
- Surface water tributaries
- Upstream sources
- Fish hatcheries
- Atmospheric deposition

To assist SRRTTF in its goals of PCB source identification, the Environmental Assessment Program of the Washington State Department of Ecology (Ecology) will conduct a spatial survey of the Spokane River using biofilms to identify unknown potential source areas of PCBs to the river. In addition, PCB levels in sediments and invertebrates will be screened at a subset of biofilm sampling locations to characterize PCB concentrations and congener patterns at the lower trophic levels of the river food web.

In an aquatic environment, biofilms are complex assemblages of algae, microbes, and fine sediments growing as an attached layer on solid surfaces—typically large rocks. Biofilm can play an important ecological role, serving as the base of food webs in an aquatic trophic system. For example, biofilm can supply the organic material and nutrients to aquatic invertebrates, which then serve as the food items for fish. One of the benefits of using biofilm to measure organochlorine compounds like PCBs is that it serves as a natural passive sampler. PCBs in the river adhere to the organic matrices of biofilms, reflecting the local concentrations of PCBs in the water over a period of growth. Thus, PCB concentrations observed in biofilms typically represent an accumulation over time, rather than a snapshot from a single date and time.

[1] https://www.doh.wa.gov/CommunityandEnvironment/Food/Fish/Advisories

3.2 Study area and surroundings

The Spokane River watershed encompasses about 6,600 square miles and is situated in the Columbia Plateau ecoregion of eastern Washington. The watershed is located between the Cascades range to the west and the Northern Rockies to the north. On average, the Spokane area receives about 16.5 inches of rain and 48 inches of snow annually. Land use within city limits of the watershed includes a mixture of commercial, industrial, and residential areas. In surrounding areas, land use includes agriculture, rangeland, and forest (GeoEngineers et al., 2011). The Spokane River is widely used for recreational activities including fishing and swimming. It is also used for hydroelectric power generation, irrigation, and tribal ceremonial and cultural uses.

The Spokane River begins at Lake Coeur d'Alene in Idaho and flows west for 112 miles through Washington to the Columbia River (Figure 1). There are seven hydroelectric dams on the river and several cities including Coeur d'Alene and Post Falls in Idaho, and Spokane Valley and Spokane in Washington. The Spokane Indian Reservation encompasses the lower section of the river. The river is fed by two main tributaries: Latah (Hangman) Creek and the Little Spokane River. Deep and Coulee Creeks also feed into the river. Flows are typically low in the summer, increasing in the fall and winter with seasonal precipitation. High flows occur in the spring concurrent with snowmelt.

The Spokane River is heavily influenced by interactions with the Spokane Valley-Rathdrum Prairie Aquifer. The aquifer receives and discharges about one billion gallons of water per day. Roughly half of that flows into and out of the Spokane River (Molenaar, 1988). The Spokane River consistently loses streamflow to the aquifer in upstream reaches where groundwater levels are below the streambed (Hortness and Covert, 2005). Further downstream toward Spokane where groundwater levels intersect the streambed, the river mostly gains flow from the aquifer.

Much of the Spokane River lacks fine depositional sediments. Most of the finer sediments are situated behind the dams or are found as isolated deposits along the river and in interstitial spaces of the river bedrock (Serdar et al., 2011). Most of the river above Latah (Hangman) Creek is composed of coarse gravel, cobble, and boulders.

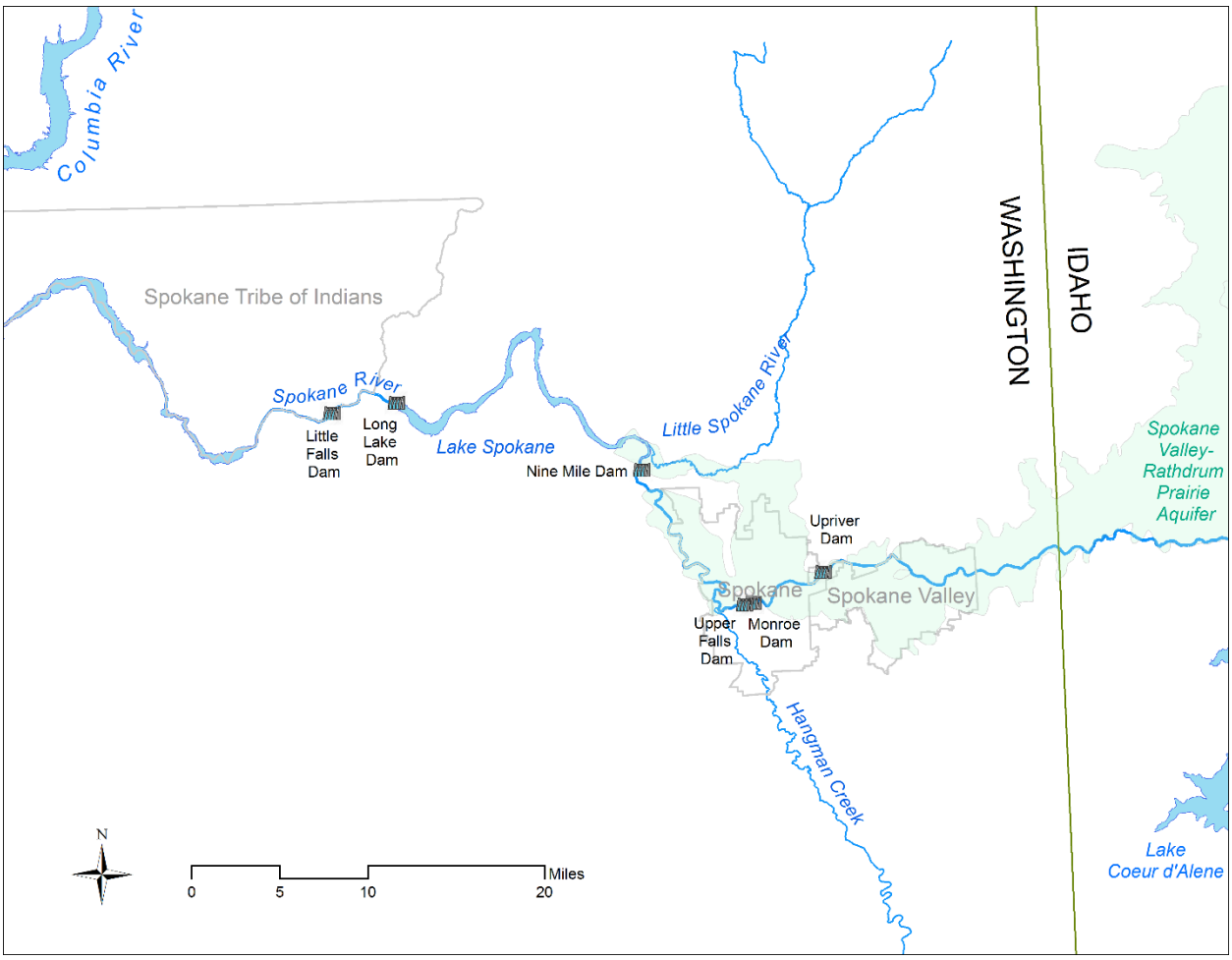

Figure 1. Map of larger study area.

3.2.1 History of study area

The first report of elevated PCB concentrations in Spokane River fish tissue was documented in samples collected in 1980 (Hopkins et al., 1985; Johnson, 2001). Since then, Ecology and other groups have conducted numerous studies assessing PCB levels in fish tissue, surface water, effluent, groundwater, and sediment samples (see Section 3.2.2). As summarized in LimnoTech (2016a), sources of PCBs have been identified and estimated. Strategies to clean up these known sources and reduce PCBs in the river have been assessed. Ongoing efforts through the SRRTTF include working with Ecology and others to fill data gaps to find previously unidentified source areas of PCBs to the river.

3.2.2 Summary of previous studies and existing data

There has been extensive monitoring and study of PCBs in the Spokane River watershed. This section of the report gives a brief overview of some of the work; however, a more detailed overview can be found in Serdar et al. (2011) and LimnoTech (2016a).

Earlier studies by Ecology have documented PCB concentrations in fish tissue from the Spokane River and tributaries (e.g., Johnson, 1994; EILS, 1995; Johnson, 1997; Johnson, 2000; Jack and Roose, 2002; Serdar and Johnson, 2006; Seiders et al., 2014; Friese and Coots, 2016). In general, high PCB concentrations in fish have been found to occur between upper Lake Spokane and above Upriver Dam, while moderate to low concentrations have been found closer to the Washington-Idaho state line and below Little Falls Dam (Johnson, 2001; Seiders et al., 2014).

A PCB source assessment was completed by Ecology to provide estimates of PCB concentrations and loads from various sources to the Spokane River (Serdar et al., 2011). The SRRTTF's comprehensive plan to address PCBs in the Spokane River was later developed. The plan compiled available and more recent PCB data and used these data to assess the range of sources, their pathways to the Spokane River, and their estimated magnitude (LimnoTech, 2016a).

Data gaps were also identified in the comprehensive plan. To address these, Ecology studies were implemented to assess PCB concentrations and loads from atmospheric deposition and from fish hatcheries. In the atmospheric deposition study, PCB concentrations and fluxes were estimated in bulk atmospheric deposition samples collected at urban and reference locations within the Spokane River watershed (Era-Miller and Wong, 2016). The study found atmospheric fluxes from urban-commercial and residential areas that were comparable to those from the Duwamish River watershed near Seattle. PCB congener patterns were unique in bulk deposition samples among the three monitoring locations, with the urban-commercial location containing more of the higher-chlorinated, heavier congeners compared to the other two locations. The study provided data and information on atmospheric deposition that was generally lacking for the Spokane River and eastern Washington.

In the fish hatchery study, PCB concentrations and loads from hatchery effluent, fish tissue, and fish feed were estimated (Wong, 2018). Of the total PCB load from fish hatchery operations (effluent discharges and fish stocking), the majority was represented by hatchery discharges to the Spokane River. PCBs were also detected in fish tissue from pre-released hatchery rainbow trout, presumably from contaminated feed. The higher PCB concentrations in post- versus pre-released fish suggested that most of the PCB body burden in post-released hatchery fish was accumulated after being released to the environment.

In 2014, a synoptic survey of the Spokane River was conducted by LimnoTech to identify potential dry weather sources of PCBs (LimnoTech, 2015). The study included water sampling for PCBs and other parameters at seven sites between Lake Coeur d'Alene and Nine Mile Dam. PCB concentrations in surface water samples were generally below 50 pg/L from Lake Coeur d'Alene to Barker Bridge, and 100–200 pg/L from Trent Bridge to Nine Mile Dam. One conclusion from the study, which was later confirmed in a 2015 follow-up survey (LimnoTech, 2016b), was that there could be a large unknown source leading to elevated PCB concentrations in the river between Barker Road and Trent Bridge (section of river within Spokane Valley city boundary), as well as between Greene Street and the Spokane Gage (section of river within Spokane city boundary).

LimnoTech will conduct additional synoptic dry weather water sampling in summer 2018 to further hone in on suspected PCB source areas based on 2014 and 2015 survey results (LimnoTech, 2018).

3.2.3 Parameters of interest and potential sources

PCBs
The contaminants of interest are the 209 PCB congeners. PCBs are synthetic organochlorine compounds consisting of two benzene rings with one to ten chlorine atoms attached. PCBs have hydrophobic and lipophilic properties. They are persistent in the environment, bioaccumulative, and toxic. PCBs can affect the immune, reproductive, nervous, and endocrine system, and are known to be carcinogenic (Davies, 2015).

The manufacture of PCBs began in 1929 and was banned in the U.S. in 1979 amid concerns about their effects on health and the environment. Current sources of PCBs include legacy contamination due to the persistence of the chemical in the environment, inadvertent production, and transport from other areas.

The primary delivery mechanisms of PCBs to the Spokane River include cumulative loading from wastewater and municipal treatment plants, contaminated groundwater, and stormwater/combined sewer operations (LimnoTech, 2016a). Based on previous monitoring, there may be PCB loads to the Spokane River coming from yet unidentified sources.

Ancillary Parameters
Additional parameters will be collected and analyzed to help explain variability in PCB concentrations among samples. These include lipid content for biofilm and invertebrate samples, and grain size and total organic carbon (TOC) for sediment samples.

Biofilm and invertebrate samples will also be analyzed for carbon (C) and nitrogen (N) composition and stable isotope ratios ($^{13}C/^{12}C$, $^{15}N/^{14}N$). These data will be useful in characterizing the general food web structure of the lower trophic levels in the Spokane River.

3.2.4 Regulatory criteria or standards

In this study, we will measure PCB concentrations in biofilms, surface sediments, and invertebrates. Results will be used to characterize PCB concentrations in lower trophic levels of the Spokane River, and to identify unknown potential sources. Results will not be compared to regulatory criteria or standards.

4.0 Project Description

In this study, we will conduct a spatial survey of the Spokane River using biofilms as a method for identifying unknown potential sources of PCBs to the Spokane River. In 2016, Hobbs (2018) measured PCBs in water, biofilm, invertebrate, and fish tissue samples to trace the major sources of PCBs entering the Wenatchee River. This study will apply a similar methodology of biofilm sampling used in Hobbs (2018).

At a subset of biofilm sampling locations, we will also sample sediments and invertebrates. The data collected will be used to characterize PCB concentrations and congener patterns in lower trophic levels of the Spokane River food web, information that is generally lacking for the Spokane River.

4.1 Project goals

The main goals of the study are to:

(1) Characterize PCB concentrations in biofilm, sediment, and invertebrates within reaches of concern in the Spokane River.
(2) Evaluate the use of biofilms for tracing PCB sources in the Spokane River.
(3) Evaluate the presence of previously unidentified sources of PCBs to the Spokane River.

4.2 Project objectives

Project objectives are to:

(1) Collect and analyze PCBs in biofilm samples at 19 locations in the Spokane River.
(2) Collect and analyze PCBs in sediment samples at 3 locations in the Spokane River.
(3) Collect and analyze PCBs in invertebrate samples at 3 locations in the Spokane River.
(4) Compare PCBs in biofilms among locations of unknown potential sources, known sources, and reference areas.

4.3 Information needed and sources

This project will collect concentration data for the 209 PCB congeners in three types of samples. Relevant data, if found to be comparable, will be compiled from other reports and publications for purposes of comparison.

4.4 Tasks required

Field collection will occur as a one-time sampling event in August 2018 during the summer low-flow period. Tasks required include:

- Determining general sampling locations in coordination with SRRTTF.
- Scouting locations prior to field sampling to determine coordinates of sampling sites.
- Collecting biofilm, sediment, and invertebrate samples following QAPP guidelines.
- Reviewing and assessing laboratory data for data quality.
- Entering data into Ecology's Environmental Information Management System (EIM).
- Conducting data analysis and completing the final report.

4.5 Systematic planning process used

This QAPP serves as the systematic planning process.

5.0 Organization and Schedule

5.1 Key individuals and their responsibilities

Project staff and responsibilities are described in Table 1.

5.2 Special training and certifications

All Ecology staff involved in implementing this project have the relevant training and experience including Ecology's safety training and experience conducting the field work described in Sections 6 and 7 of this QAPP. No special certifications are required.

5.3 Organization chart

See Table 1 for Ecology staff responsibilities. Ecology staff will work in collaboration with SRRTTF to implement this project.

Table 1. Organization of project staff and responsibilities.

Staff (All EAP except client)	Title	Responsibilities
Adriane Borgias Water Quality Program Eastern Regional Office Phone: 509-329-3515	EAP Client	Clarifies scope of the project. Provides internal review of the QAPP and approves the final QAPP.
Brandee Era-Miller Toxic Studies Unit SCS Phone: 360-407-6771	Project Manager	Writes the QAPP. Oversees field sampling and transportation of samples to the laboratory. Conducts QA review of data, analyzes and interprets data, and enters data into EIM. Writes the draft report and final report.
Siana Wong Toxic Studies Unit SCS Phone: 360-407-6432	Principal Investigator	Writes the QAPP. Oversees field sampling and transportation of samples to the laboratory. Conducts QA review of data, analyzes and interprets data, and enters data into EIM. Writes the draft report and final report.
Debby Sargeant Toxic Studies Unit SCS Phone: 360-407-6775	Unit Supervisor for the Project Manager	Provides internal review of the QAPP, approves the budget, and approves the final QAPP.
Jessica Archer SCS Section Phone: 360-407-6698	Section Manager for the Project Manager	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
George Onwumere Eastern Operations Section Phone: (509) 454-4244	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	Director	Reviews and approves the final QAPP.
Arati Kaza Phone: 360-407-6964	Quality Assurance Officer	Reviews the draft QAPP and approves the final QAPP. May review and comment on the draft project report.

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

5.4 Proposed project schedule

Table 2 shows the proposed timeline for key project tasks.

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

Field and laboratory work	**Due date**	**Lead staff**
Field work completed	September 2018	Siana Wong
Laboratory analyses completed	April 2019	
Environmental Information Management (EIM) database		
EIM Study ID	SWON0001	
Product	Due date	Lead staff
EIM data loaded	September 2019	Siana Wong
EIM data entry review	October 2019	To Be Determined
EIM complete	November 2019	Siana Wong
Final report		
Author lead / Support staff	Siana Wong / Brandee Era-Miller	
Schedule		
Draft due to supervisor	May 2019	
Draft due to client/peer reviewer	June 2019	
Draft due to external reviewer(s)	July 2019	
Final (all reviews done) due to publications coordinator	September 2019	
Final report due on web	October 2019	

5.5 Budget and funding

The laboratory cost for this project is $35,675. Table 3 shows the budget broken down by sample matrix and number of samples.

Table 3. Project budget and funding.

	Number of Samples	Number of Field QC Samples	Total Number of Samples	Cost Per Sample	Contract Lab Subtotal
PCB Congeners					
Biofilm	19	2	21	$960	$20,160
Sediment	3	1	4	$885	$3,540
Invertebrate	3	1	4	$960	$3,840
Lipids[1]					
Biofilm	19	2	21	$ -	$ -
Invertebrate	3	1	4	$ -	$ -
Total Organic Carbon					
Sediment	3	1	4	$50	$200
Grain Size					
Sediment	3	1	4	$75	$300
C:N Stable Isotopes					
Biofilm	19	19	38	$15	$570
Invertebrate	3	3	6	$15	$90
				PCB Contract Lab Total:	$27,540
				PCB Contract Lab Fee Total (25%)[2]:	$6,885
				Grain Size Contract Lab Fee Total[2] (30%):	$90
				GRAND TOTAL:	**$35,675**

[1] Costs for lipids analyses are included in PCB congener analyses.
[2] Contract/data validation fee.

6.0 Quality Objectives

6.1 Data quality objectives

Our overall quality objective is to obtain results that are of known and documented accuracy (e.g., bias and precision) and represent the conditions at the sampling sites at the time of sample collection. Common indicators of data quality include the measurement quality objectives (MQOs) for precision, bias, and sensitivity described in the next section (Table 4).

6.2 Measurement quality objectives

6.2.1 Targets for precision, bias, and sensitivity

The MQOs for this study are shown in Table 4 and described in this section.

Table 4. Measurement quality objectives.

MQO →	Precision	Bias		Sensitivity
	Laboratory Duplicate/Field Split Samples	Lab Control Standard[1]	Internal Standard Recovery[2]	Lowest Concentrations of Interest
	Relative Percent Difference	Recovery Limits		Concentration Units
PCB Congeners				
Biofilm	± 20%	50 – 150%	50 – 150%	0.5 pg/g ww
Sediment	± 30%	50 – 150%	50 – 150%	0.5 pg/g dw
Invertebrate	± 20%	50 – 150%	50 – 150%	0.5 pg/g ww
Lipids				
Biofilm	± 20%	-	-	0.10% ww
Invertebrate	± 20%	-	-	0.10% ww
Total Organic Carbon				
Sediment	± 20%	75 – 125%	-	0.10% dw
Grain Size				
Sediment	± 20%	-	-	-
C:N Stable Isotopes				
Biofilm	± 20%	-	-	0.01‰ dw
Invertebrate	± 20%	-	-	0.01‰ dw

[1] Laboratory Control Standard is also referred to as Ongoing Precision and Recovery (OPR) Standard, in which a laboratory blank sample is spiked with known quantities of analyte.
[2] Internal Standard Recovery is also referred to as Surrogate or Labeled Compound Recovery, using $^{13}C_{12}$-labeled congeners.

6.2.1.1 Precision

Precision is a measure of the variability between results of replicate measurements due to random error. It can be assessed by calculating the relative percent difference (RPD) between the replicate measurements. Field splits are collected by taking two aliquots from one homogenized sample and analyzing them as separate samples. Precision of field splits is assessed in the same manner as field replicates.

For this project, field splits for each sample matrix (biofilm, sediment, and invertebrate) will be collected and analyzed. Field splits will be collected at about 10% of the total number of samples for each matrix. Laboratory duplicates will also be prepared and analyzed by the

laboratory. The targets for acceptable precision for each sample matrix are shown above in Table 4.

6.2.1.2 Bias

Bias is the difference between the sample mean and the true value. For this project, bias will be measured as a percent recovery of laboratory blank spikes and percent recovery of labeled congener compounds. Targets for acceptable recoveries are shown in Table 4.

6.2.1.3 Sensitivity

Sensitivity measures the capability of an analytical method to detect a substance above background level, and is often described as a detection or reporting limit. The expected lowest concentrations of interest for PCB congeners are shown in Table 4, and are based on the estimated quantitation limit for PCB congeners.

6.2.2 Targets for comparability, representativeness, and completeness

6.2.2.1 Comparability

To ensure that data from this project are comparable to other studies, the following Ecology Standard Operating Procedures (SOPs) for field sample collection will be used:

- *Standard Operating Procedures for Decontaminating Field Equipment for Sampling Toxics in the Environment, Version 1.1.* SOP Number EAP090 (Friese, 2014).
- *Standard Operating Procedures for the Collection of Periphyton Samples for TMDL studies, version 1.1.* SOP Number EAP085 (Mathieu et al., 2013).
- *Standard Operating Procedure for Obtaining Freshwater Sediment Samples, Version 1.3*. SOP Number EAP040 (Blakely, 2008).

6.2.2.2 Representativeness

Field sampling will occur during the late summer low-flow period of the Spokane River, when biofilms are likely to be well-established due to longer growing period and relief from scouring during higher flows. Because biofilms act as natural passive samplers, the PCB concentrations observed represent an accumulation over time during the growing season, rather than a snapshot from a single date and time.

Biofilm samples will be collected at 19 sites between the Washington-Idaho state line and just below Ninemile Dam. We will sample various sections of the river thought to represent unknown potential sources, known sources, and reference locations. The number of biofilm samples planned is expected to be sufficient to capture a range of PCB concentrations across locations. Biofilm from multiple rocks at each site will be collected and composited to ensure representativeness of PCB concentrations in biofilms at a given sampling site.

Sediment and invertebrate samples will be collected at a subset of biofilm locations. Because of the low-sediment nature of the Spokane River, sediment samples will be collected opportunistically from known sediment accumulations areas. Invertebrate samples will be collected from known or potential source locations.

6.2.2.3 Completeness

This project will be considered complete if at least 95% of the planned samples were collected and analyzed successfully, and the data are deemed acceptable.

6.3 Acceptance criteria for quality of existing data

Not Applicable. We will collect new data for this project.

7.0 Study Design

7.1 Study boundaries

This project encompasses the portion of the Spokane River from the Washington-Idaho state line to above Lake Spokane (Figure 2, Table 5). The furthest downstream sampling location will be just below Nine Mile Dam. One biofilm and sediment sample will be collected near the mouth of Hangman Creek.

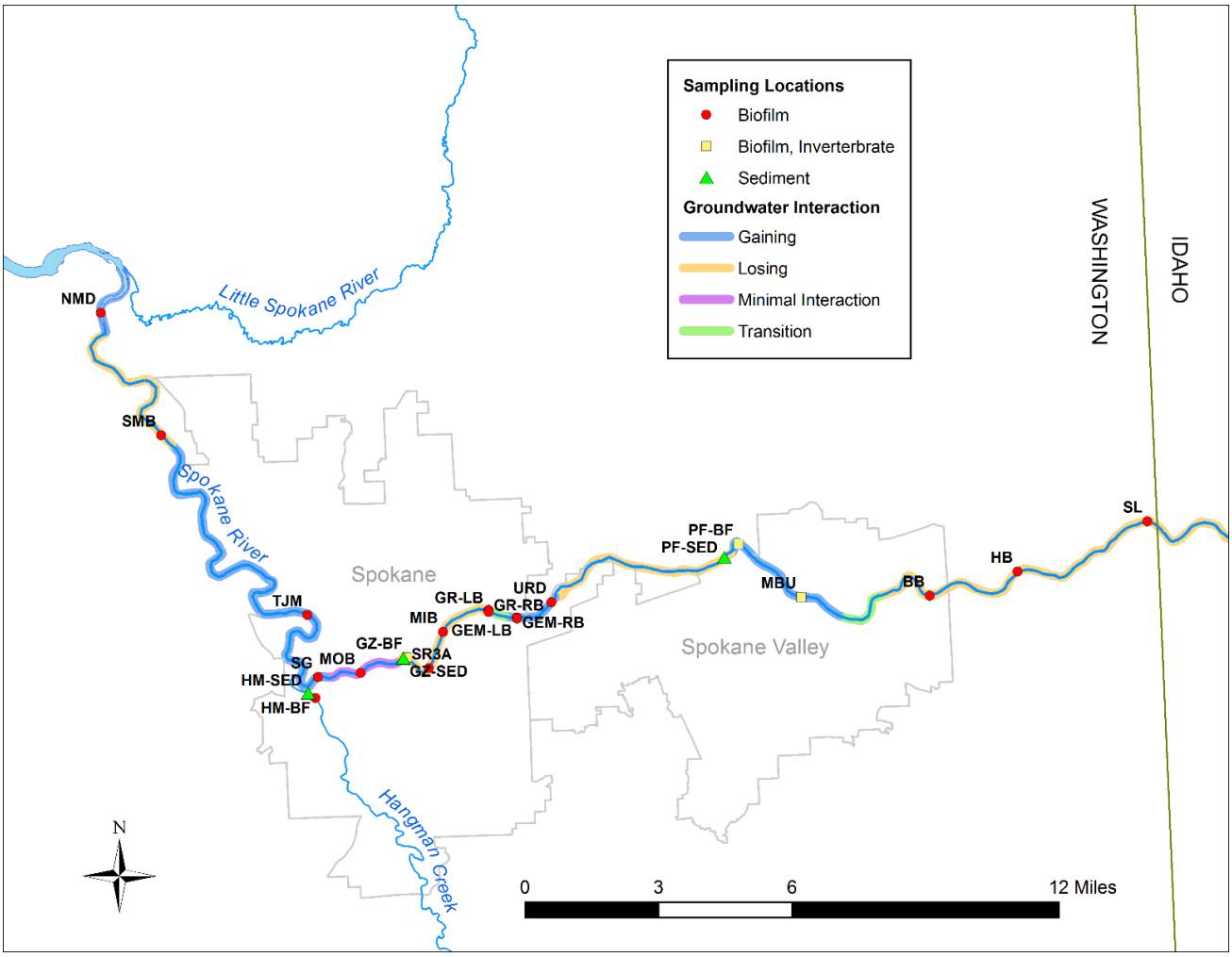

Figure 2. Proposed sampling locations.

Table 5. Sampling locations, sample types, and location descriptions. The coordinates shown are *generalized* locations of where samples will be collected.

Project Site Name	2018 Synoptic Survey Name	Sample Matrix	Latitude[1]	Longitude[1]	Groundwater Interaction	Rationale for Sampling
Below Nine Mile Dam (NMD)	**SR-1**	Biofilm	47.780474	-117.5459	Gaining	Location coincides with 2018 Synoptic Survey site: Spokane River-Nine Mile Dam Gage - 12426000.
Seven Mile Bridge (SMB)	-	Biofilm	47.74	-117.519111	Losing	Provides desired spatial resolution; downstream of Riverside WWTP.
TJ Meenach (TJM)	-	Biofilm	47.679739	-117.451908	Gaining	Provides desired spatial resolution.
Hangman-Biofilm (HM-BF)	**HC1**	Biofilm	47.652669	-117.4496579	-	Potential source area. Location coincides with 2018 Synoptic Survey site: Hangman Creek-Spokane River Confluence Gage - 12424000.
Spokane Gage (SG)	**SR-3**	Biofilm	47.659444	-117.448056	Gaining	Location coincides with 2018 Synoptic Survey site: Spokane River - Spokane Gage - 12422500.
Monroe Bridge (MOB)	-	Biofilm	47.660258	-117.427478	Minimal Interaction	Provides desired spatial resolution.
Gonzaga-Biofilm (GZ-BF)	-	Biofilm, Invertebrate	47.664732	-117.405038	Losing	Provides desired spatial resolution.
SR3A	-	Biofilm	47.66096	-117.394443	Losing	Downgradient of industrial area including City Parcel.
Mission Bridge (MIB)	-	Biofilm	47.672483	-117.387011	Losing	Provides desired spatial resolution.
Green St RB (GR-RB)	**SR-4**	Biofilm	47.6790594	-117.364657	Transition	Location coincides with 2018 Synoptic Survey site: Spokane River-Greene Street Gage - 12422000. **Right bank** – both riverbanks included to evaluate differences between each side.

Project Site Name	2018 Synoptic Survey Name	Sample Matrix	Latitude[1]	Longitude[1]	Groundwater Interaction	Rationale for Sampling
Green St LB (GR-LB)	**SR-4**	Biofilm	47.678465	-117.364747	Transition	Location coincides with 2018 Synoptic Survey site: Spokane River-Greene Street Gage - 12422000. **Left bank** – both riverbanks included to evaluate differences between each side.
GE Mission RB (GEM-RB)	-	Biofilm	47.676303	-117.351192	Gaining	Potential groundwater source area from GE site. **Right bank** – both riverbanks included to evaluate differences between each side.
GE Mission LB (GEM-LB)	-	Biofilm	47.675925	-117.351189	Gaining	Potential groundwater source area from GE site. **Left bank** – both riverbanks included to evaluate differences between each side.
Below Upriver Dam (URD)	**SR-5a**	Biofilm	47.680847	-117.334225	Gaining	Provides desired spatial resolution. Location coincides with 2018 Synoptic Survey site: SR-5a.
Plantes Ferry-Biofilm (PF-BF)	**SR-7**	Biofilm, Invertebrate	47.697222	-117.243056	Gaining	Downstream of known source area. Location coincides with 2018 Synoptic Survey site: Spokane River - Trent Bridge Gage (Plantes Ferry Park) - 12421500.
Mirabeau (MBU)	**SR-8a**	Biofilm, Invertebrate	47.679141	-117.21407	Gaining	Potential groundwater source area from sources upgradient of Kaiser. Location coincides with 2018 Synoptic Survey site: SR-8a.
Above Barker Bridge (BB)	**SR9**	Biofilm	47.677783	-117.152227	Losing	Reference location. Location coincides with 2018 Synoptic Survey site: Spokane River - Greenacres Gage (Barker Road) - 12420500.
Above Harvard Bridge (HB)	-	Biofilm	47.684487	-117.109387	Losing	Reference location.
Stateline (SL)	-	Biofilm	47.698908	-117.045864	Losing	Reference location.

Project Site Name	2018 Synoptic Survey Name	Sample Matrix	Latitude[1]	Longitude[1]	Groundwater Interaction	Rationale for Sampling
Hangman-Sediment (HM-SED)	-	Sediment	47.654278	-117.452983	-	Known source area. Possible area of sediment deposition.
Gonzaga-Sediment (GZ-SED)	-	Sediment	47.664453	-117.406708	Losing	Known area of sediment deposition.
Plantes Ferry-Sediment (PF-SED)	-	Sediment	47.693056	-117.25027	Gaining	Possible area of sediment deposition.

[1]World Geodetic System 1984 (WGS84).

7.2 Field data collection

7.2.1 Sampling locations and frequency

Biofilm
Biofilm samples will be collected at 19 sites along the Spokane River and analyzed for PCB congeners (Figure 2). Sampling for this project will occur as a one-time sampling event during the dry season, low-flow period in August 2018, ideally before Labor Day. After Labor Day (September 3, 2018), flows will increase due to a slow water release from the reservoirs. Sampling will coincide with the timing and locations of the synoptic survey as much as possible.

The general sampling locations were selected in collaboration with SRRTTF and include unknown potential sources, known sources, and reference locations (Table 5). The reference locations have no known upstream PCB sources and were included to obtain background levels of PCB concentrations in biofilms in the Spokane River.

The main focus of the site selection is to evaluate potentially contaminated groundwater discharging to the Spokane River as sources of PCBs. As such, some of the biofilm collection sites will be explicitly located in gaining reaches of the river.

In July and August, prior to field sampling, the proposed locations will be scouted. Exact sampling sites within the general locations will be determined based on access and availability of substrate for biofilm growth.

Sediment
Sediment samples will be collected at three of the general biofilm locations where isolated areas of sediment accumulation are known to occur (Table 5). Because of the nature of the different sample types, it may not be possible to collect sediments at the exact site coordinates as biofilm. For example, ideal biofilm sites will have coarse substrates for scraping biofilms from large rocks. Ideal sediment collection sites will contain substrate composed of fine depositional sediments. For this reason, sediment locations are listed as separate from the corresponding biofilm locations. The sediment locations shown in Table 5 and Figure 2 are approximations of where sediment deposition near the proposed biofilm locations is known to occur based on earlier studies.

Invertebrates
Invertebrates will be collected at three of the known or unknown potential source biofilm sampling locations (Table 5). At two of the locations (Plantes Ferry and Gonzaga), all three sample types will be collected (biofilm, sediment, and invertebrate).

7.2.2 Field parameters and laboratory analytes to be measured

All field samples will be analyzed for the 209 PCB congeners. Biofilm and invertebrate samples will also be measured for lipid content, C and N composition, and stable isotopes. TOC and grain size analyses will be included for sediment samples.

7.3 Modeling and analysis design

Not Applicable.

7.4 Assumptions in relation to objectives and study area

This study will use the measurement of PCBs in biofilms as a method for identifying and evaluating potential PCB sources in the Spokane River. Although measurement of organochlorine contaminants in periphyton has been demonstrated in other studies (e.g., Hill and Napolitano, 1997; Berglund, 2003; Hobbs, 2018), it is not known to have been applied in the Spokane River watershed. An underlying assumption of the study design is that differences in PCB concentrations in biofilms among reference, known, and potential source locations can be related to differences in the magnitude of sources at those locations.

7.5 Possible challenges and contingencies

7.5.1 Logistical problems

Optimal conditions for biofilm sampling include access to proposed locations, availability of substrate, and adequate biofilm growth for sample collection. Collections of sediment and invertebrates also depend on substrate availability. If sites cannot be sampled within a general sample location because of limited access or availability of sample matrix, Ecology will coordinate with SRRTTF to select alternative sampling sites.

7.5.2 Practical constraints

Field sampling is expected to occur as a one-time event within one to two weeks. We anticipate no practical constraints for this project.

7.5.3 Schedule limitations

The field sampling schedule will primarily depend on environmental conditions. The optimal time for sampling is during the low-flow period in August. Sampling will also occur before water is released from the reservoirs, which typically occurs after Labor Day. We do not anticipate the QAPP review and approval process to inhibit the proposed field sampling schedule.

8.0 Field Procedures

8.1 Invasive species evaluation

This project will involve sampling different reaches of the Spokane River above Lake Spokane and near the mouth of Hangman Creek. Field staff for this project are required to follow procedures in Ecology's SOP for minimizing the impact of invasive species (Parsons et al., 2018).

8.2 Measurement and sampling procedures

Field sampling will follow the SOPs listed in Section 6.2.2.1. The procedures that will be used for collecting biofilm, sediment, and invertebrate samples are summarized below.

Biofilms

At each biofilm site, rocks with visible biofilm attached to the surface will be collected. Desirable rocks are cobblestones with an abundant layer of biofilm growing on an approximately flat surface. Along the Spokane River from the state line to below Nine Mile Dam, biofilm composition and abundance likely varies due to gradients in riverine habitat and nutrient availability. Biofilms that are dominated by an organic-rich growth of diatoms tend to have a brown color and flocculent appearance; these biofilms will be collected for this project. Rocks with large green or brown filamentous periphyton will be avoided. Prior to collecting the biofilm, any loose silt or debris on the rock will be gently shaken off underwater, taking care not to slough off the biofilm. The biofilm will be scraped off each rock into a decontaminated (acetone and hexane-washed) stainless steel bowl using a decontaminated blade or knife. The biofilm sample will be homogenized in the bowl using a decontaminated spoon, then scooped into a certified clean glass sampling jar. Samples will be stored in a cooler on ice until further processing.

To get an estimate of biomass, the surface area of biofilm growth for each rock will be measured. Aluminum foil cutouts can be used to approximate the surface area of each rock. The cutouts can be digitized, and Image J software can be used to estimate the total biofilm surface area (Mathieu et al., 2013).

If necessary, samples will be decanted back at Ecology Headquarters to remove excess water prior to shipping to the laboratory for analysis.

A small subsample of each biofilm sample (~5mg) will be collected for C:N isotopic analysis. Samples will be freeze-dried prior to shipping to the University of Washington IsoLab.

Sediment

Surface sediment samples will be collected using a decontaminated ponar dredge. A watercraft will be used to access the site to collect the ponar grab sample. Any excess water from the ponar grab will be siphoned off. The top two centimeters of sediment from the ponar will be scooped into a decontaminated stainless steel bowl using a decontaminated

spoon, homogenized, then scooped into separate certified clean sampling jars for PCB, TOC, and grain size analyses. Samples will be stored in a cooler on ice until further processing.

If necessary, sediment samples will be decanted back at Ecology Headquarters to remove excess water prior to shipping to the laboratory for analysis.

Invertebrates

The target invertebrate species will be the prey of rainbow trout. Rainbow trout likely feed on caddis and mayfly larvae, which are represented in the grazers/scrapers or shredders functional feeding groups. Should these invertebrate species be selected, only the soft tissue of the invertebrates will be collected (casings will be removed). The appropriate invertebrate species to collect will be confirmed with Washington State Department of Fish & Wildlife (WDFW) staff. Specimens will be picked from sample site rocks. A portable field scale (Ohaus CL201, ±0.1 g) will be used to ensure that enough biomass has been collected for laboratory analyses. Samples will be scooped into a certified clean glass sampling jar, and then stored in a cooler on ice until further processing. Invertebrate samples will be homogenized prior to shipping to the laboratory.

A small subsample of each invertebrate sample (~5mg) will be collected for C:N isotopic analysis. Samples will be freeze-dried prior to shipping to the University of Washington IsoLab.

8.3 Containers, preservation methods, holding times

Sample containers, preservation, and holding times for each parameter and sample matrix are shown in Table 6.

Table 6. Sample containers, preservation, and holding times.

Parameter	Matrix	Minimum Quantity	Container	Preservative	Holding Time
PCB Congeners	Biofilm	10 g ww	8 oz certified clean glass jar w/Teflon lid	Cool to < 4°C; store at < -10°C	1 year if frozen
	Sediment	10 g dw	8 oz certified clean glass jar w/Teflon lid	Cool to < 4°C; store at < -10°C	1 year if frozen
	Invertebrate	10 g ww	8 oz certified clean glass jar w/Teflon lid	Cool to < 4°; store at < -10°C	1 year if frozen
Lipids	Biofilm	2 g ww	8 oz certified clean glass jar w/Teflon lid	Cool to < 4°; store at < -10°C	14 days
	Invertebrate	2 g ww	8 oz certified clean glass jar w/Teflon lid	Cool to < 4°; store at < -10°C	14 days
Total Organic Carbon	Sediment	25 g dw	2 oz certified clean glass jar w/ Teflon lid	Cool to < 4°	14 days; 6 months if frozen
Grain Size	Sediment	100 g dw	8 oz plastic jar	Cool to < 4°	6 months
C:N Stable Isotopes	Biofilm	5 mg dw	5x9 mm or 3.5x5 mm tin capsules	Freeze dry	6 months if freeze dried
	Invertebrate	5 mg dw	5x9 mm or 3.5x5 mm tin capsules	Freeze dry	6 months if freeze dried

8.4 Equipment decontamination

Prior to sampling, equipment will be decontaminated following procedures in Friese (2014). Upon return to Ecology Headquarters, field equipment will be washed before storing. Watercraft used for sediment sampling will be washed following Ecology's SOP for minimizing the spread of invasive species (Parsons et al., 2018).

8.5 Sample ID

A laboratory work order will be assigned prior to field collection. Field IDs and sample numbers will be assigned by the project manager. Field splits will be identified as such in their field IDs, and will be assigned unique sample numbers.

8.6 Chain of custody

We will follow chain of custody procedures as outlined in the document, *Manchester Environmental Laboratory Lab User's Manual* (MEL, 2016), as well as the contract laboratory's specific procedures.

8.7 Field log requirements

Field notes will be recorded in a bound, waterproof notebook on Rite in the Rain paper. Any corrections to field sheets will be made with a single line strikethrough with initials and date. An example field sheet template for this project is included in Appendix A.

Information to be recorded include:

- Project name and location.
- Field personnel.
- Sequence of events.
- Any changes or deviations from the QAPP.
- Environmental conditions.
- Date, time, site name, site coordinates, sample ID, and description of each sample.
- Identity of quality control (QC) samples collected.
- Unusual circumstances that might affect interpretation of results.

8.8 Other activities

All activities have been described in the prior sections.

9.0 Laboratory Procedures

9.1 Lab procedures table

Table 7 summarizes the number of samples, sample matrices, expected range of results, reporting limits, and analytical methods for collection and analysis of PCB congeners.

Table 7. Measurement methods (laboratory).

Analyte	Sample Matrix	Samples	Expected Range of Results	Detection or Reporting Limit	Analytical (Instrumental) Method
PCB Congeners	Biofilm	19	0.5 – 200 pg/g ww	0.5 pg/g ww per congener	EPA 1668C
	Sediment	3	0.5 – 1,000 pg/g dw	0.5 pg/g dw per congener	EPA 1668C
	Invertebrate	3	0.5 – 30,000 pg/g ww	0.5 pg/g ww per congener	EPA 1668C
Lipids	Biofilm	19	0.5 – 2.0% ww	-	EPA 1668C
	Invertebrate	3	0.5 – 5.0% ww	-	EPA 1668C
Total Organic Carbon	Sediment	3	0.10 – 10% dw	0.10% dw	EPA 440.0
Grain Size	Sediment	3	Unknown	0.10%	PSEP 1986 Combust/Grav
C:N Stable Isotopes	Biofilm	3	-2.0 – 7.0 ‰ (N) and -35.0 – -20.0‰ (C)	0.01‰ dw	Costech ECS 4010 Elemental Analyzer
	Invertebrate	3	2.0 – 9.0 ‰ (N) and -25.0 – -10.0‰ (C)	0.01‰ dw	Costech ECS 4010 Elemental Analyzer

9.2 Sample preparation method(s)

The preparation and extraction method used for analysis of PCBs is documented in EPA Method 1668C (*Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS*) and Method 3540C (*Soxhlet Extraction*).

9.3 Special method requirements

Not Applicable. Methods have been described in previous sections.

9.4 Laboratories accredited for methods

An Ecology-accredited laboratory will analyze all PCB samples. Sediment grain size samples will also be analyzed by an accredited laboratory. Sediment samples for TOC will be analyzed by Manchester Environmental Laboratory (MEL) in Port Orchard, WA. C and N stable isotopes will be analyzed by the University of Washington IsoLab upon completion and approval of Ecology Form ECY 070-152 (*Request to Waive Required Use of Accredited Lab*).

10.0 Quality Control Procedures

10.1 Table of field and laboratory quality control

The number and type of QC samples to be collected in the field and analyzed in the lab is summarized in Table 8.

Table 8. Quality control samples, types, and frequency.

	Field	Laboratory		
	Splits	**Lab Control Standard[1]**	**Method Blanks**	**Internal Standard Recovery[2]**
PCB Congeners				
Biofilm	2/batch[3]	1/batch	1/batch	All samples
Sediment	1/batch	1/batch	1/batch	All samples
Invertebrates	1/batch	1/batch	1/batch	All samples
Lipids				
Biofilm	1/batch	-	-	-
Invertebrates	1/batch	-	-	-
Total Organic Carbon				
Sediment	1/batch	1/batch	1/batch	-
Grain Size				
Sediment	1/batch	-	-	-
C:N Stable Isotopes				
Biofilm	Each sample	3/batch	3/batch	-
Invertebrate	Each sample	3/batch	3/batch	-

[1] Laboratory Control Standard is also referred to as Ongoing Precision and Recovery (OPR) Standard, in which a laboratory blank sample is spiked with known quantities of analyte.
[2] Internal Standard Recovery is also referred to as Surrogate or Labeled Compound Recovery, using $^{13}C_{12}$-labeled congeners.
[3] A batch is a group of samples (typically of the same matrix) processed and analyzed in the laboratory together as a unit.

10.2 Corrective action processes

Any field activities in departure of this QAPP will be documented in the field log and in the final report for this project. Deviations from the stated laboratory methods, or cases in which data results do not meet MQOs will be documented by the laboratory analyst as part of the laboratory data package. These cases will be described in the final report. The project manager will discuss appropriate corrective actions, which may include re-analyzing samples with the laboratory.

11.0 Data Management Procedures

11.1 Data recording and reporting requirements

Field notes will be scanned electronically and entered into the appropriate EIM data entry templates. Final quality-checked laboratory data (excluding laboratory QC samples) will also be entered into the same EIM data entry template.

11.2 Laboratory data package requirements

The laboratories will provide data packages that include a case narrative and final laboratory results. The case narrative will provide QC results, discuss any problems encountered during the analyses, and discuss corrective actions made. This information will be used to help evaluate data quality and determine whether MQOs for this project were met.

11.3 Electronic transfer requirements

Laboratory data will be delivered in the form of an Electronic Data Deliverable that meets MEL's formatting requirements.

11.4 EIM/STORET data upload procedures

Data for this project will be loaded into EIM using EIM data entry templates. Following EAP protocols, data loaded into EIM will be reviewed by a second EAP staff member, and any errors will be noted by the reviewer and then corrected. The project manager will conduct a final review of the data.

11.5 Model information management

Not Applicable.

12.0 Audits and Reports

12.1 Field, laboratory, and other audits

Audits are conducted as a regular part of laboratory operating procedures. Upon request, results of the audits will be made available. No field audits are planned for this project.

12.2 Responsible personnel

The laboratory's quality assurance manager is responsible for any routine laboratory audits.

12.3 Frequency and distribution of reports

After all data have been received, reviewed, and analyzed, the results of this project will be presented in the form of a draft final report. The draft will be distributed to the client, Eastern Operations Section Manager, and SRRTTF for review.

12.4 Responsibility for reports

The project manager and principal investigator will author the final report.

13.0 Data Verification

13.1 Field data verification, requirements, and responsibilities

The project manager will review all field notes and metadata to ensure that information is accurate.

13.2 Laboratory data verification

The laboratory conducting the analyses will review laboratory results prior to submitting the data package. The MEL Quality Assurance Coordinator will serve as an independent third party validator, and will review the complete PCB congener data package submitted by the external lab following EPA guidelines (EPA, 2016), this QAPP, and QC requirements of EPA Method 1668C. The MEL Quality Assurance Coordinator will prepare a report of the Level 4 data validation, which includes an overall assessment of data quality, usability, and whether project MQOs were met.

13.3 Validation requirements, if necessary

Not Applicable.

13.4 Model quality assessment

Not Applicable.

14.0 Data Quality (Usability) Assessment

14.1 Process for determining project objectives were met

After data have been independently validated, the project manager will review the data and assess whether project MQOs were met. The data will either be accepted, accepted with qualification, or rejected. If MQOs were not met, the project manager will discuss whether any samples should be re-analyzed, or if any other corrective actions should be taken with the laboratory.

14.2 Treatment of non-detects

All PCB congener results including non-detects will be loaded into EIM. Non-detected congener results (those qualified as U, UJ, or NUJ) will not be included in calculations of total PCBs. Results qualified as "NJ" (evidence that the analyte is present; result is an estimate) will be included in total PCB calculations.

EPA Method 1668C allows for low-level detection of PCB congeners. However, PCB congeners may be present in laboratory method blanks at higher concentrations than the detection limit. Different censoring methods can be used to censor results due to method blank contamination. The choice of method depends on study objectives. For example, censoring at <10 times the detected method blank concentration provides the most numerically conservative approach to quantification. It provides the greatest assurance that the analyte present in the sample represents actual sampling site conditions; however, it may lead to the censoring of true positive results. Censoring at <3 times the detected method blank concentration is a useful approach that helps in the ability to detect trends. Therefore, it is commonly used in source identification.

For this project, congener results that are less than three times the detected method blank concentration will be qualified as non-detect. Application of this qualification rule aligns with this study's main objective of identifying sources, and with previous and ongoing work conducted by the SRRTTF.

14.3 Data analysis and presentation methods

Total PCBs will be calculated from PCB congener results. Data results for each sample matrix will be presented as summary statistics (e.g., median, minimum, maximum) in the form of tables and simple scatter or bar plots. A map of the Spokane River depicting PCB concentrations in biofilms will be created using Geographic Information Systems. PCB concentrations among potential source, known source, and reference locations will be compared. PCB concentrations in biofilms can be normalized using lipid or organic carbon content data to help identify trends.

The expectation is that biofilms collected from known source areas will measure in the upper range of biofilm PCB concentrations, and biofilms collected from reference locations will measure in the lower range of biofilm PCB concentrations (background levels). For this project, we will use the upper 95th confidence interval of total PCB concentrations at reference locations as a threshold for background levels of PCBs in biofilms in the Spokane River.

Homolog groups will also be calculated and PCB congener profiles will be explored. Data analysis and presentation methods will include examination of bar plots for each location, and Principal Components Analysis to explore congener distribution patterns among sample matrices and locations.

Sediment grain size and TOC results will be used to help explain variability in PCB concentrations in sediments among samples.

Isotopic ratios of C and N in biofilms and invertebrates will be explored to characterize the general food web structure of the lower trophic levels in the Spokane River. These data may also be useful in interpretation of PCB concentration and congener patterns found in biofilms and invertebrates.

14.4 Sampling design evaluation

This project is designed to be a spatial survey of the Spokane River. The main goal of the data analysis is to identify and evaluate unknown potential sources of PCBs using biofilms as a sampling media. The number and type of biofilm sample locations is expected to be adequate to draw conclusions from the study. In collaborative efforts to provide overall evaluation of potential ongoing PCB sources to the Spokane River, data obtained from this project should be interpreted in conjunction with data collected from other studies assessing water column and mass balance data.

14.5 Documentation of assessment

Data results and discussion will be documented in the final report.

15.0 References

Berglund, O. 2003. Periphyton density influences organochlorine accumulation in rivers. Limnology and Oceanography 48:2106–2116. https://aslopubs.onlinelibrary.wiley.com/doi/epdf/10.4319/lo.2003.48.6.2106

Blakely, N. 2008. Standard Operating Procedure EAP040, Version 1.3: Obtaining Freshwater Sediment Samples. Revised by J. Medlen. Recertified December 2016. Washington State Department of Ecology, Olympia.

Davies, H. 2015. PCB Chemical Action Plan. Publication No. 15-07-002. Washington State Department of Ecology, Olympia. https://fortress.wa.gov/ecy/publications/documents/1507002.pdf

EILS. 1995. Department of Ecology 1993-94 Investigation of PCBs in the Spokane River. Environmental Investigations and Laboratory Services Program. Publication No. 95-310. Washington State Department of Ecology, Olympia.

EPA. 2016. National Functional Guidelines for High Resolution Superfund Methods Data Review. EPA Report Number 542-B-16-001. United States Environmental Protection Agency, Washington D.C. https://www.epa.gov/sites/production/files/2016-05/documents/hrsm_nfg.pdf

Era-Miller, B. and S. Wong. 2016. Quality Assurance Project Plan: Spokane River Atmospheric Deposition Study for PCBs. Publication No. 16-03-112. Washington State Department of Ecology, Olympia. https://fortress.wa.gov/ecy/publications/SummaryPages/1603112.html

Federal Register. 1999. Water Quality Standards; Establishment of Numeric Criteria for Priority Toxic Pollutants; States' Compliance – Revision of Polychlorinated Biphenyls (PCBs) Criteria; Final Rule. Volume 64. No. 216. Tuesday November 9, 1999. Pages 61182-61196.

Friese, M. 2014. Standard Operating Procedure EAP090, Version 1.1: Decontaminating Field Equipment for Sampling Toxics in the Environment. Revised by J. Medlen. Recertified February 2017. Washington State Department of Ecology, Olympia.

Friese, M. and R. Coots. 2016. Little Spokane River PCBs Screening Survey of Water, Sediment, and Fish Tissue. Publication No. 16-03-001. Washington State Department of Ecology, Olympia. https://fortress.wa.gov/ecy/publications/SummaryPages/1603001.html

GeoEngineers, Hubbard Ray Consulting, Inc., and HDR Engineering, Inc. 2011. Spokane River Watershed Nonpoint Source Phosphorus Reduction Plan. http://www.spokanecounty.org/DocumentCenter/View/4189/Final-Nonpoint-Source-Phosphorus-Reduction-Plan-PDF

Hill, W. R. and G. E. Napolitano. 1997. PCB Congener Accumulation by Periphyton, Herbivores, and Omnivores. Archives of Environmental Contamination and Toxicology 32: 449–455. https://link.springer.com/content/pdf/10.1007%2Fs002449900212.pdf

Hobbs, W. 2018. Wenatchee River PCB Source Assessment: 2016 and 2017. Publication No. 18-03-010. Washington State Department of Ecology, Olympia. https://fortress.wa.gov/ecy/publications/documents/1803010.pdf

Hopkins, B., D. Clark, M. Schlender, and M. Stinson. 1985. Basic Water Monitoring Program, Fish Tissue and Sediment Sampling for 1984. Publication No. 85-7. Washington State Department of Ecology, Olympia. https://fortress.wa.gov/ecy/publications/documents/857.pdf

Hortness, J. E. and J. J. Covert. 2005. Streamflow Trends in the Spokane River and Tributaries, Spokane Valley/Rathdrum Prairie, Idaho and Washington. U.S. Geologic Survey Scientific Investigations Report 2005–5005. https://ecology.wa.gov/DOE/files/d8/d8b93e31-020f-45da-8264-1dc19cd931d8.pdf

Jack, R. and M. Roose. 2002. Analysis of Fish Tissue from Long Lake (Spokane River) for PCBs and Selected Metals. Publication No. 02-03-049. Washington State Department of Ecology, Olympia. https://fortress.wa.gov/ecy/publications/summarypages/0203049.html

Johnson, A. 1994. Planar PCBs in Spokane River Fish. Memorandum to C. Nuechterlein. Publication No. 94-e23. Washington State Department of Ecology, Olympia. https://fortress.wa.gov/ecy/publications/summarypages/94e23.html

Johnson, A. 1997. 1996 Results on PCBs in Upper Spokane River Fish. Memorandum to C. Nuechterlein and D. Knight. Publication No. 97-e04. Washington State Department of Ecology, Olympia. https://test-fortress.wa.gov/ecy/publications/SummaryPages/97e04.html

Johnson, A. 2000. Results from Analyzing PCBs in 1999 Spokane River Fish and Crayfish Samples. Memorandum to J. Roland. Publication No. 00-03-040. Washington State Department of Ecology, Olympia. https://fortress.wa.gov/ecy/publications/summarypages/0003040.html

Johnson, A. 2001. An Ecological Hazard Assessment for PCBs in the Spokane River. Publication No. 00-03-040. Washington State Department of Ecology, Olympia. https://fortress.wa.gov/ecy/publications/documents/0103015.pdf

LimnoTech. 2015. Spokane River Regional Toxics Task Force Phase 2 Technical Activities Report: Identification of Potential Unmonitored Dry Weather Sources of PCBs to the Spokane River. Prepared for the Spokane River Regional Toxics Task Force.

LimnoTech. 2016a. 2016 Comprehensive Plan to Reduce Polychlorinated Biphenyls (PCBs) in the Spokane River. Prepared for the Spokane River Regional Toxics Task Force. http://srrttf.org/wp-content/uploads/2016/04/2016_Comp_Plan_Final_Approved.pdf

LimnoTech. 2016b. Spokane River Regional Toxics Task Force 2015 Technical Activities Report: Continued Identification of Potential Unmonitored Dry Weather Sources of PCBs to the Spokane River. Prepared for the Spokane River Regional Toxics Task Force.

LimnoTech. 2018. Quality Assurance Project Plan, Addendum 5 – Spokane River Toxics Reduction Strategy Study. Prepared for the Spokane River Toxics Task Force. June 12, 2018.

Mathieu, N., S. Collyard, and T. Mohamedali. 2013. Standard Operating Procedure EAP085, Version 1.1: Collection of Periphyton Samples for TMDL studies. Washington State Department of Ecology, Olympia.

MEL. 2016. Manchester Environmental Laboratory *Lab Users Manual*, Ninth Edition. Manchester Environmental Laboratory, Washington State Department of Ecology, Manchester.

Molenaar, D. 1988. The Spokane Aquifer, Washington: Its Geologic Origin and Water-Bearing and Water Quality Characteristics. U.S. Geological Survey Water-Supply Paper 2265. https://pubs.usgs.gov/wsp/2265/report.pdf

Parsons, J., D. Hallock, K. Seiders, B. Ward, C. Coffin, E. Newell, C. Deligeannis, and K. Welch. 2018. Standard Operating Procedure EAP070, Version 2.2: Minimize the Spread of Invasive Species. Washington State Department of Ecology, Olympia. https://fortress.wa.gov/ecy/publications/documents/1803201.pdf

Seiders, K., C. Deligeannis, P. Sandvik, and M. McCall. 2014. Freshwater Fish Contaminant Monitoring Program – 2012 Results. Publication No. 04-03-020. Washington State Department of Ecology, Olympia. https://fortress.wa.gov/ecy/publications/SummaryPages/1403020.html

Serdar, D. and A. Johnson. 2006. PCBs, PBDEs, and Selected Metals in Spokane River Fish, 2005. Publication No. 06-03-025. Washington State Department of Ecology, Olympia. https://fortress.wa.gov/ecy/publications/summarypages/0603025.html

Serdar, D., B. Lubliner, A. Johnson, and D. Norton. 2011. Spokane River PCB Source Assessment, 2003–2007. Publication No. 11-03-013. Washington State Department of Ecology, Olympia. https://fortress.wa.gov/ecy/publications/summarypages/1103013.html

Wong, S. 2018. Evaluation of Fish Hatcheries as Sources of PCBs to the Spokane River. Publication No. 18-03-014. Washington State Department of Ecology, Olympia. https://fortress.wa.gov/ecy/publications/documents/1803014.pdf

16.0 Appendices

Appendix A. Field Sheet Example Template

Spokane River Biofilm | Aug/Sep 2018

Created 07.03.2018 SW

Date: _____ Time: _____ Staff: _____

Site Name: _____

Lat: _____ Lon:_____ WGS-84 | NAD83 | NAD27

Site Conditions: _____

_____

_____

_____

Samples Collected: BIOFILM | SEDIMENT | INVERTEBRATE

Sample ID: _____

_____

QA Samples Collected: BIOFILM | SEDIMENT | INVERTEBRATE

QA Sample ID: _____

_____

Biofilm

# of Rocks Scraped for Biomass: _____

Sediment

Description of Sediment: _____

Water Depth: _____

Invertebrates:

Type (e.g., Caddisfly, Mayfly, Stonefly, Chironomid): _____

Collection Method: _____

Sample Weight: _____

Other Notes: _____

_____

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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(d) of the Clean Water Act establishes the TMDL program.

Designated uses: Those uses specified in Chapter 173-201A WAC (Water Quality Standards for Surface Waters of the State of Washington) for each water body or segment, regardless of whether or not the uses are currently attained.

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.

Municipal separate storm sewer systems (MS4): A conveyance or system of conveyances (including roads with drainage systems, municipal streets, catch basins, curbs, gutters, ditches, manmade channels, or storm drains): (1) owned or operated by a state, city, town, borough, county, parish, district, association, or other public body having jurisdiction over disposal of wastes, stormwater, or other wastes and (2) designed or used for collecting or conveying stormwater; (3) which is not a combined sewer; and (4) which is not part of a Publicly Owned Treatment Works (POTW) as defined in the Code of Federal Regulations at 40 CFR 122.2.

Nutrient: Substance such as carbon, nitrogen, and phosphorus used by organisms to live and grow. Too many nutrients in the water can promote algal blooms and rob the water of oxygen vital to aquatic organisms.

Reach: A specific portion or segment of a stream.

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

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

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.g.	For example
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
et al.	And others
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective
NTR	National Toxics Rule
PCB	polychlorinated biphenyls
QC	Quality control
RM	River mile
RPD	Relative percent difference
SOP	Standard operating procedures
USGS	United States Geological Survey
WAC	Washington Administrative Code
WDFW	Washington Department of Fish and Wildlife
WQA	Water Quality Assessment
WRIA	Water Resource Inventory Area
WWTP	Wastewater treatment plant

Units of Measurement

°C	degrees centigrade
dw	dry weight
g	gram, a unit of mass
mg	milligram
‰	per mil (one per mil is equal to 1/1000)
pg/g	picograms per gram (parts per trillion)
pg/L	picograms per liter (parts per quadrillion)
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

Ecology. 2004. Guidance for the Preparation of Quality Assurance Project Plans for Environmental Studies. Publication No. 04-03-030. Washington State Department of Ecology, Olympia. https://fortress.wa.gov/ecy/publications/SummaryPages/0403030.html

Kammin, B. 2010. Definition developed or extensively edited by William Kammin, 2010. Washington State Department of Ecology, Olympia.

USEPA. 1997. Glossary of Quality Assurance Terms and Related Acronyms. U.S. Environmental Protection Agency.

USEPA. 2006. Guidance on Systematic Planning Using the Data Quality Objectives Process EPA QA/G-4. http://www.epa.gov/quality/qs-docs/g4-final.pdf

USGS. 1998. Principles and Practices for Quality Assurance and Quality Control. Open-File Report 98-636. U.S. Geological Survey. http://ma.water.usgs.gov/fhwa/products/ofr98-636.pdf