DEPARTMENT OF ECOLOGY
State of Washington

Addendum to Quality Assurance Project Plan

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

March 2020
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This Quality Assurance Project Plan Addendum is on the Department of Ecology's website at https://fortress.wa.gov/ecy/publications/SummaryPages/2003103.html. This is an addition to an original Quality Assurance Project Plan. It is not a correction (errata) to the original plan.

This QAPP addendum was approved to begin work in August 2019. It was finalized and approved for publication in March 2020.

Data for this project will be available on Ecology's Environmental Information Management (EIM) website at EIM Database. Search Study ID: SWON0001.

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Addendum to Quality Assurance Project Plan: Measuring PCBs in Biofilm, Sediment, and Invertebrates in the Spokane River: Screening Study

March 2020

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

1.0 Table of Contents

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Note: The numbered headings in this document correspond to the headings used in the original QAPP (Wong and Era-Miller 2019). Only modified sections are included. This is why some numbered headings are missing, and why, for instance, the text begins at 3.0.

3.0 Background

3.1 Introduction and problem statement

In August 2018, the Washington State Department of Ecology's (Ecology's) Environmental Assessment Program conducted a broad spatial survey of the Spokane River using biofilms to assess suspected and unknown sources of polychlorinated biphenyls (PCBs) to the river (Wong and Era-Miller 2019). The goals of the sampling were to collect and analyze PCB concentrations in biofilm, sediment, and macroinvertebrates in the river, and to assess the potential for unidentified sources of PCBs to the river. The study was initiated in collaboration with the Spokane River Regional Toxics Task Force (SRRTTF), which has been working to identify PCB sources in the Spokane River watershed since 2012.

The 2018 sampling identified locations of the river where biofilm PCB concentrations were particularly high (Section 3.2.2). This addendum to the original Quality Assurance Project Plan (QAPP) describes additional biofilm sampling for 2019 that focuses on these areas of the river. The main goal is to further delineate where PCBs are entering the river at these locations and to identify the possible sources. A secondary goal is to confirm the relative PCB concentrations and homolog patterns found at the 2018 sampling locations.

3.2.2 Summary of previous studies and existing data

The 2018 sampling for this study took place August 27 – 30, 2018. Biofilm samples were collected at 19 sites in the Spokane River between the Washington-Idaho state line (SL) and just below Nine Mile Dam (NMD; Figure 1). Sediment and macroinvertebrate samples were also collected at a small subset of the biofilm sites and analyzed for PCBs.

Total PCB concentrations in biofilms during the 2018 sampling ranged from about 90 – 630,000 pg/g, parts per trillion. The highest biofilm PCB concentrations were observed within the Spokane City limits, specifically between the Mission Bridge (MIB) and Spokane Gage (SG) sites (Figure 2).

The SR3A site (just upstream of the Trent Avenue bridge) had a biofilm PCB concentration that was over 100 times greater than the next highest concentration observed at the Spokane Gage site. The PCB congener pattern of the SR3A sample was most comparable to that of unweathered Aroclor 1260 (Figure 3).

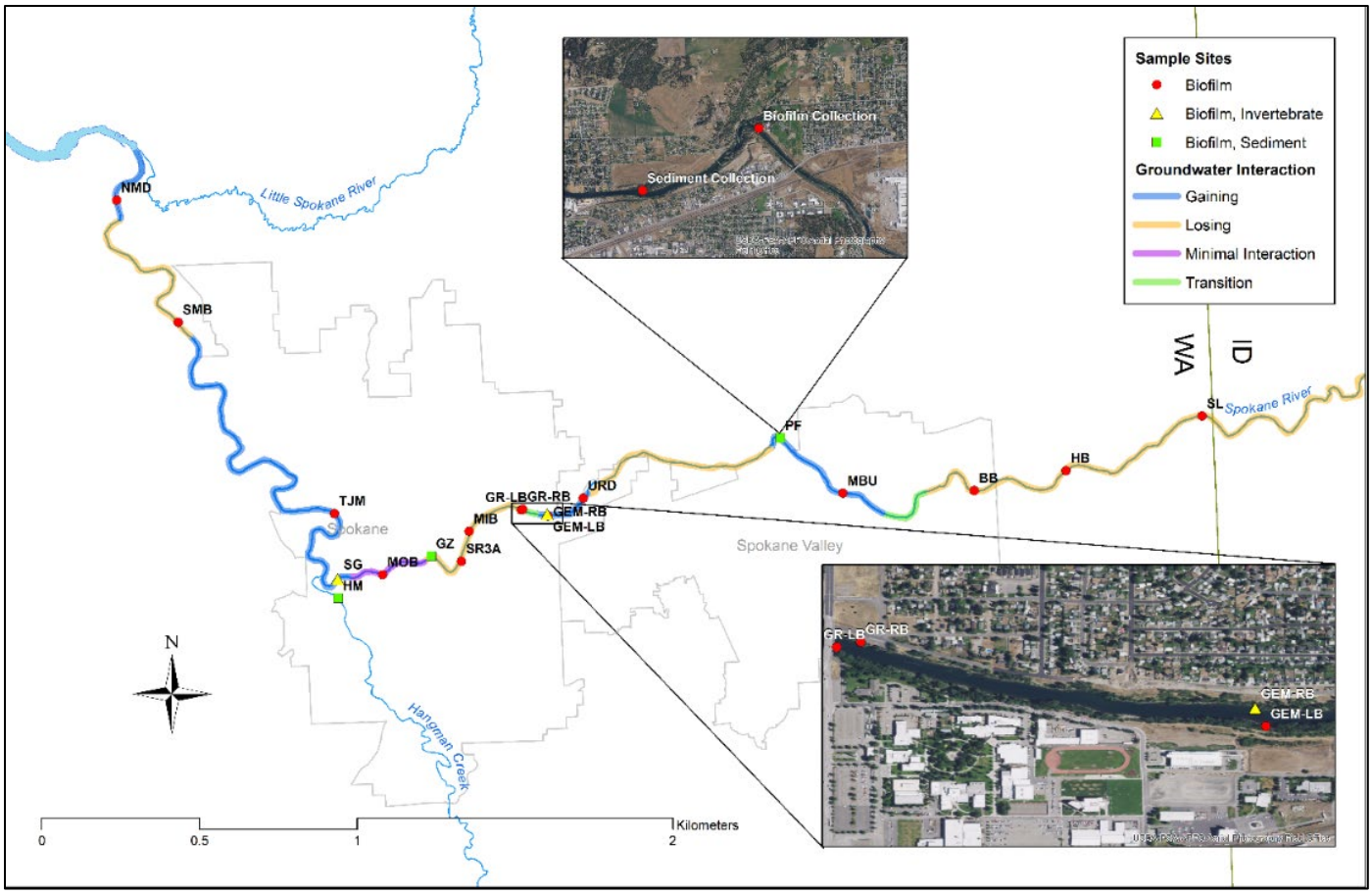

Figure 1. Map of the Spokane River showing sampling locations during the 2018 field study. Except for three sites (GR-RB, HM, SMB), the 2018 sampling sites will be resampled in 2019 (Figure 4, Table 7).

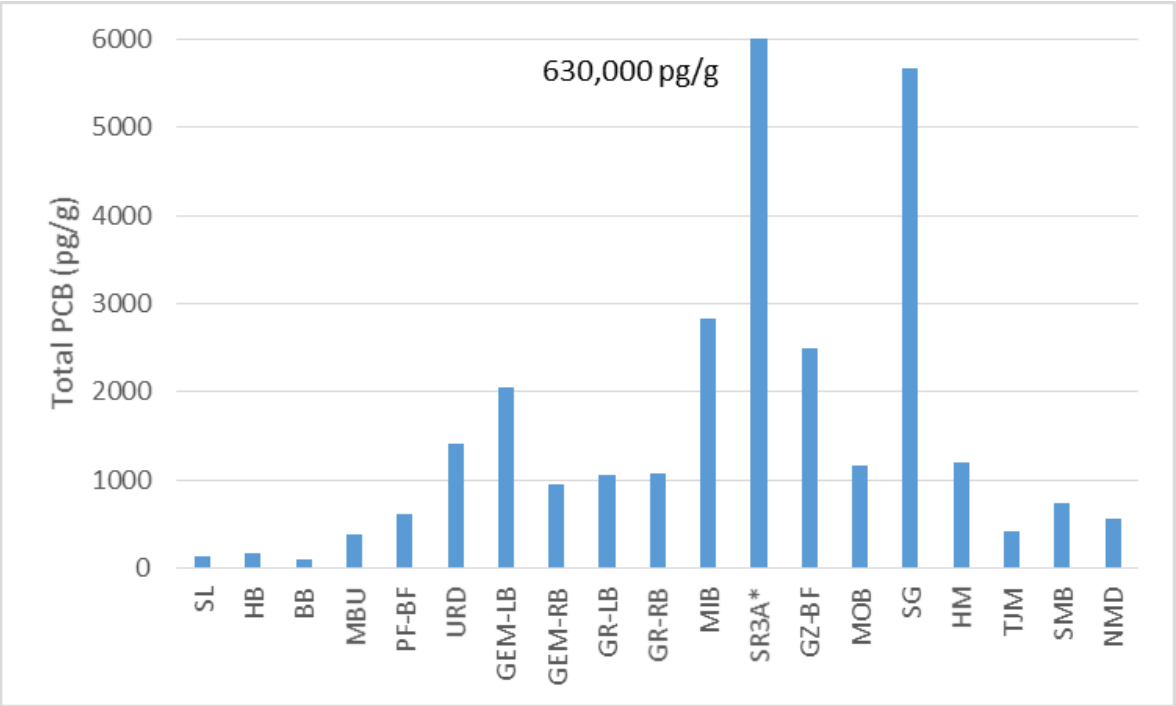

Figure 2. Total PCB concentrations measured in biofilms collected at sites in the Spokane River in 2018. Sites are ordered from upstream (left) to downstream (right). *Site SR3A had a concentration of 630,000 pg/g and is off the scale of this plot.

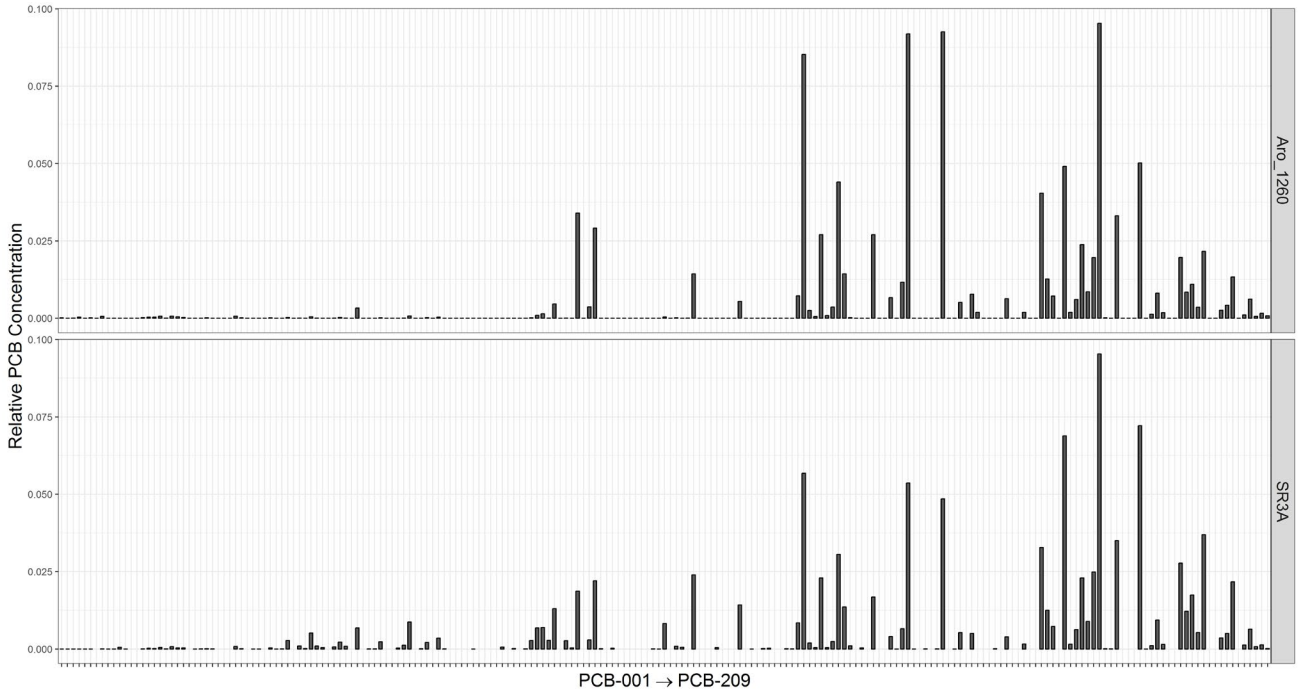

Figure 3. Relative PCB congener concentrations (PCB Congener/Total PCB) for unweathered Aroclor 1260 (top) compared to biofilm collected at site SR3A (bottom). The bars represent each PCB congener, ordered from PCB-001 (left) to PCB-209 (right).

4.0 Project Description

4.1 Project goals

The goals of this project addendum are to:

(1) Verify biofilm PCB concentrations observed in 2018 in the Spokane River from the state line (SL) site to the Nine Mile Dam (NMD) site.
(2) Further delineate possible PCB sources between the Upriver Dam (URD) and Spokane Gage (SG) site where the highest biofilm concentrations were observed.

4.2 Project objectives

Objectives of the follow-up sampling are to:

(1) Collect and analyze PCBs in biofilm samples at 33 sites in the Spokane River.
(2) Compare biofilm PCB concentrations and congener patterns among sites.

4.4 Tasks required

Tasks required include:

- Collaborate with SRRTTF in the final selection of biofilm sampling locations.
- Conduct site reconnaissance prior to sampling.
- Coordinate with laboratories in preparation for biofilm analyses.
- Collect biofilm samples during the low-flow period in late summer 2019.
- Review and assess laboratory data quality.
- Enter data into Ecology's Environmental Information Management System (EIM).
- Conduct data analysis, and complete final report.

5.0 Organization and Schedule

5.3 Organization chart

Table 1. Organization of project and staff responsibilities.

Staff (All EAP except client)	Title	Responsibilities
Karl Rains 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.
Siana Wong Toxic Studies Unit SCS Phone: 360-407-6432	Project Manager	Primary author of 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. Primary author of the draft report and final report.
Brandee Era-Miller Toxic Studies Unit SCS Phone: 360-407-6771	Principal Investigator	Assists with writing the QAPP. Oversees field sampling and transportation of samples to the laboratory. Provides technical assistance. Conducts QA review of data, analyzes and interprets data. Assists with writing the draft report and final report.
James Medlen Toxic Studies Unit SCS Phone: 360-407-6194	Acting Unit Supervisor for the Project Manager	Provides internal review of the QAPP, approves the budget, and approves the final QAPP. Provides review of draft report and final approval.
Jessica Archer SCS 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.
Ginna Grepo-Grove Manchester Environmental Laboratory Phone: 360-871-8829	Quality Assurance Coordinator	Develops the scope of work for contract laboratory. Validates contract laboratory data.
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. Schedule for completing field and laboratory work

Task	Due date	Lead staff
Field work	Sept. 2019	Siana Wong
Laboratory analyses	Jan. 2020	Siana Wong
Contract lab data validation	April 2020	Siana Wong

Table 3. Schedule for data entry

Task	Due date	Lead staff
Environmental Information Management (EIM) data loaded*	May 2020	Siana Wong
EIM QA	June 2020	To be determined
EIM complete	July 2020	Siana Wong

*EIM Project ID: SWON0001

Table 4. Schedule for final report

Task	Due date	Lead staff
Draft to supervisor	May 2020	Brandee Era-Miller
Draft to client/ peer reviewer	June 2020	Brandee Era-Miller
Draft to external reviewers	July 2020	Brandee Era-Miller
Reviewed draft to publications	Sept. 2020	Brandee Era-Miller
Published	Oct. 2020	Brandee Era-Miller

5.5 Budget and funding

The laboratory cost for this addendum is estimated to be $47,124. Table 5 shows the budget broken down by sample type and number of samples. Ecology will cover the costs of analyses for 21 samples and 2 quality control (QC) samples per analyte ($30,107). In agreement with SRRTTF, SRRTTF will supplement the project by covering the costs of 12 samples and 1 QC sample per analyte ($17,017).

Table 5. Project budget and funding for 2019 biofilm sampling.

Analyte	Number of Samples	Number of Field QC Samples	Total Number of Samples	Cost Per Sample	Contract Lab Subtotal
PCB Congeners	33	3	36	$960	$34,560
Lipids[1]	33	3	36	$	$
C & N Stable Isotopes	33	3	36	$21	$756
Ash Free Dry Weight	33	3	36	$40	$1,440
				PCB Contract Lab Fee Total (30%)[2]:	$10,368
				GRAND TOTAL:	**$47,124**

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

6.0 Quality Objectives

6.2 Measurement quality objectives

Measurement quality objectives (MQOs) for this addendum are shown in Table 6. MQOs for biofilm samples are the same as the original QAPP and are repeated in Table 6. Ash-free dry weight is included.

Table 6. Measurement quality objectives.

Parameter	Laboratory Duplicate (%RPD)	Field Duplicate (%RPD)	Matrix Spike Duplicate (%RPD)	Lab Control Standard (%Recovery)	Matrix Spike (% Recovery)	Internal Standard Recovery (% Recovery)	Lowest Concentrations of Interest
PCB Congeners	± 20%	± 40%	± 40%	50 - 150%	50 - 150%	50 - 150%	0.5 pg/g ww
Lipids	± 20%	± 20%	-	-	-	-	0.10% ww
C & N Stable Isotopes	± 20%	± 20%	-	80 - 120%	-	-	0.01‰ dw
Ash-Free Dry Weight	± 20%	± 20%	± 20%	-	-	-	± 1% dw

7.0 Study Design

7.1 Study boundaries

The 2019 biofilm sampling locations range from the Washington-Idaho state line (SL) to just below Nine Mile Dam (NMD). Figure 4 and Table 7 show the tentative sampling sites for 2019. Sampling sites may be refined based on collaborative inputs from SRRTTF members and site reconnaissance.

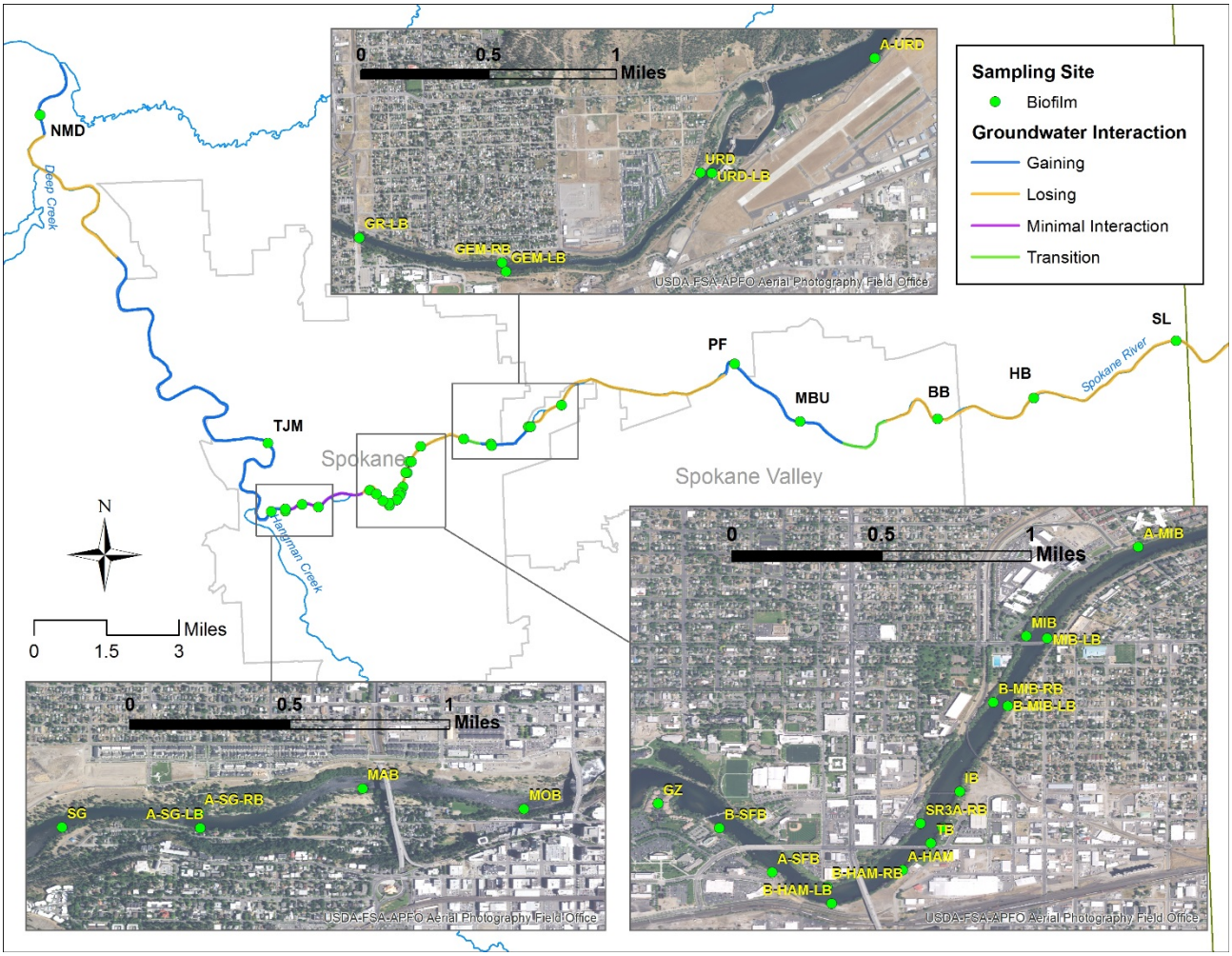

Figure 4. Map of biofilm sampling sites planned for 2019.

7.2 Field data collection

7.2.1 Sampling locations and frequency

Biofilm samples will be collected at 33 sites on the Spokane River. The sampling will occur as a one-time event during the dry, low-flow season in August 2019.

The majority of sites will be located between the Upriver Dam (URD) and Spokane Gage (SG) sites to further delineate where PCBs may be entering the river.

As in 2018, three upstream sites (SL, BB, and HB) will serve as reference locations to assess background levels of PCBs in biofilm in the river.

7.2.2 Field parameters and laboratory analytes to be measured

All biofilm samples will be analyzed for 209 PCB congeners. Ancillary parameters will also be analyzed by the laboratory for each sample to help assess sample variability. These include lipid content, biomass, and carbon (C) and nitrogen (N) isotopes. At each site, periphyton samples for microscopic identification will also be collected, and conductivity and temperature of the water will be measured using a calibrated DiST Hanna EC/TDS handheld meter.

7.4 Assumptions in relation to objectives and study area

Hobbs (2018) demonstrated that biofilms could be useful for identifying potential sources of PCBs in the Wenatchee River. The same methods used in Hobbs (2018) were applied to the Spokane River during the 2018 biofilm sampling. The method assumes that large differences in the concentrations and congener patterns of PCBs in biofilms among sites in the river may be indicative of differences in their sources. Based on this assumption, results from the 2018 biofilm sampling seemed to show potential for the use of biofilms as a suitable tool for source identification in the Spokane River.

Biofilm sampling in 2019 will include revisiting many of the 2018 sampling sites to confirm results. The 2018 sampling also showed that right and left bank sampling may be useful for distinguishing among PCB sources; this will be further tested in the Spokane River during the follow-up sampling.

Table 7. List of biofilm sampling sites planned for 2019 (on next page).

Site ID	Site Name	Bank	Latitude (NAD83)	Longitude (NAD83)	2018 Sampling Site	Ground-water Interaction	Rationale for Sampling
SL	Stateline	Left	47.69861	-117.04626	X	Losing	Reference location
HB	Harvard Bridge	Right	47.68336	-117.11036	X	Losing	Reference location
BB	Barker Bridge	Right	47.67835	-117.1533	X	Losing	Reference location
MBU	Mirabeau	Right	47.67928	-117.21422	X	Gaining	Confirm 2018 results
PF	Plantes Ferry	Right	47.69734	-117.24207	X	Gaining	Confirm 2018 results
A-URD	Above Upriver Dam	Left	47.6871582	-117.319545		Losing	Bracket URD
URD	Upriver Dam	Right	47.68106	-117.33459	X	Gaining	Possible source area based on 2018 sampling
URD-LB	Upriver Dam-Left Bank	Left	47.6810248	-117.333622		Gaining	Bracket URD
GEM-LB	GE Mission-Left Bank	Left	47.6759	-117.35124	X	Gaining	Confirm 2018 results
GEM-RB	GE Mission-Right Bank	Right	47.67641	-117.35155	X	Gaining	Confirm 2018 results
GR-LB	Green Street-Left Bank	Left	47.67815	-117.36348	X	Transition	Confirm 2018 results
A-MIB	Above Mission Bridge	Right	47.6764298	-117.382663		Losing	Bracket MIB
MIB	Mission Bridge	Right	47.67211	-117.3881	X	Losing	Possible source area based on 2018 sampling
MIB-LB	Mission Bridge-Left Bank	Left	47.6719968	-117.387084		Losing	Bracket MIB
B-MIB-LB	Below Mission Bridge-Left Bank	Left	47.6687158	-117.388992		Losing	Bracket MIB
B-MIB-RB	Below Mission Bridge-Right Bank	Right	47.6688918	-117.389697		Losing	Bracket MIB
IB	Iron Bridge	Left	47.6645768	-117.39131		Losing	Bracket SR3A
SR3A	SR3A (Upstream of Trent Ave Bridge)	Left	47.66285	-117.39217	X	Losing	Possible source area based on 2018 sampling
SR3A-RB	SR3A-Right Bank	Right	47.6630278	-117.393229		Losing	Bracket SR3A
TB	Trent Bridge	Left	47.6620728	-117.39273		Losing	Bracket SR3A
A-HAM	Above Hamilton Bridge	Left	47.6607808	-117.394099		Losing	Bracket SR3A

Site ID	Site Name	Bank	Latitude (NAD83)	Longitude (NAD83)	2018 Sampling Site	Ground-water Interaction	Rationale for Sampling
B-HAM-LB	Below Hamilton Bridge-Left Bank	Left	47.6591588	-117.397535		Losing	Bracket SR3A
B-HAM-RB	Below Hamilton Bridge-Right Bank	Right	47.6599668	-117.397757		Losing	Bracket SR3A
A-SFB	Above Spokane Falls Blvd	Left	47.6606598	-117.400419		Losing	Bracket SR3A/GZ
B-SFB	Below Spokane Falls Blvd	Left	47.6628088	-117.40298		Losing	Bracket SR3A/GZ
GZ	Gonzaga	Left	47.664	-117.40595	X	Losing	Confirm 2018 results
MOB	Monroe Bridge	Left	47.65962	-117.42886	X	Minimal Interaction	Confirm 2018 results
MAB	Maple Bridge	Left	47.6605428	-117.436184		Minimal Interaction	Bracket SG
A-SG-LB	Above Spokane Gage-Left Bank	Left	47.6587578	-117.443548		Minimal Interaction	Bracket SG
A-SG-RB	Above Spokane Gage-Right Bank	Right	47.6594198	-117.443605		Gaining	Bracket SG
SG	Spokane Gage	Left	47.65879	-117.44981	X	Gaining	Possible source area based on 2018 sampling
TJM	TJ Meenach	Right	47.67931	-117.45013	X	Gaining	Confirm 2018 results
NMD	Nine Mile Dam	Right	47.77985	-117.54559	X	Gaining	Confirm 2018 results

8.0 Field Procedures

8.3 Containers, preservation methods, holding times

Sample containers, preservation, and holding times for PCB congeners, lipids, and C and N isotopes are the same as in the original QAPP. Ash-free dry weight is included in Table 8.

Table 8. Sample containers, preservation, and holding time for ash-free dry weight samples.

Parameter	Matrix	Minimum Quantity Required	Container	Preservative	Holding Time
Ash-Free Dry Weight	Biofilm	2 g ww	2 oz clear glass jar w/ closed Teflon lid	Cool to <4°	14 days

9.0 Laboratory Procedures

9.1 Lab procedures table

Laboratory measurement methods for PCB congeners, lipids, and C and N isotopes are the same as in the original QAPP. Ash-free dry weight is included in Table 9.

Table 9. Laboratory measurement method for ash-free dry weight.

Analyte	Sample Matrix	Samples	Expected Range of Results	Detection or Reporting Limit	Analytical (Instrumental) Method
Ash-Free Dry Weight	Biofilm	28	1 - 50,000 mg/kg	1.00 mg/kg	SM10300C

9.4 Laboratories accredited for methods

An Ecology-accredited contract laboratory will analyze all samples for PCBs and lipids. C and N isotopes will be analyzed by the University of California-Davis Stable Isotope Facility. Ash-free dry weight will be analyzed by Manchester Environmental Laboratory in Port Orchard, WA.

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 by the laboratory are summarized in Table 10.

Table 10. Quality control samples, types, and frequency for biofilm.

Biofilm Analyte	Field Splits/ Duplicates	Lab Control Standard[1]	Laboratory Method Blanks	Internal Standard Recovery[2]
PCB Congeners	10%	1/batch[3]	1/batch	All samples
Lipids	10%	-	-	-
C & N Isotopes	10%	1/batch	1/batch	-
Ash-Free Dry Weight	10%	-	1/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.

14.0 Data Quality (Usability) Assessment

14.3 Data analysis and presentation methods

Data collected as part of this addendum will be analyzed and presented as described in the original QAPP, including calculations and graphic analyses of total PCBs and homologs. We will also compare biofilm results from 2019 to results from 2018.

14.4 Sampling design evaluation

This project is designed to verify 2018 results and to further delineate the river by bracketing areas where high biofilm PCB concentrations were observed in 2018. The sampling strategy and number of biofilm samples is expected to be adequate to draw conclusions from the study.

15.0 References

Hobbs, W. 2018. Wenatchee River PCB Source Assessment: 2016 and 2017. Publication 18-03-010. Washington State Department of Ecology, Olympia. https://fortress.wa.gov/ecy/publications/SummaryPages/1803010.html.

Wong, S. and B. Era-Miller. 2019. Quality Assurance Project Plan: Measuring PCBs in Biofilm, Sediment, and Invertebrates in the Spokane River: Screening Study. Publication 19-03-103. Washington State Department of Ecology, Olympia. https://fortress.wa.gov/ecy/publications/SummaryPages/1903103.html.