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## **Quality Assurance Project Plan**

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# **Spokane River Regional Toxics Task Force 2020-2021 Water Column PCB Monitoring**

August 10, 2020

## Publication Information

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This study is being conducted by the Spokane River Regional Toxics Task Force (Task Force) with support from the Washington State Department of Ecology and must have an approved Quality Assurance Project Plan (QAPP). The plan describes the objectives of the study and the procedures to be followed to achieve those objectives. After completing the study, the Task Force will post the final report of the study to the Internet.

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

The final QAPP is available on the Task Force website at: <http://www.srrttf.org/>.

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A copy of the report is available upon request.

**Federal Clean Water Act 1996 303(d) Listings Addressed in this Study.** See Section 3.1.

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# Quality Assurance Project Plan

## Spokane River Regional Toxics Task Force 2020-2021 Water Column PCB Monitoring

by David Dilks, LimnoTech

August 10, 2020

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Signatures are not available on the Internet version.

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## 2.0 Abstract

The Washington State Department of Ecology (Ecology) has included language in the NPDES permits for the Spokane River dischargers in Washington that requires permittees to create and participate in the Spokane River Regional Toxics Task Force (Task Force) and to make measurable progress toward meeting applicable water quality criteria for polychlorinated biphenyls (PCBs). One metric used to assess whether measurable progress is occurring corresponds to outcomes, i.e. “Progress toward achievement of the applicable water quality criteria for PCBs in the Spokane River which could be demonstrated by achievement of the applicable water quality standards, health standards, and/or measured reductions of toxics to or in the Spokane River” (Ecology, 2014). Demonstration that this progress is occurring will require the establishment of a long-term monitoring program. The Task Force has authorized long term monitoring of PCBs in the water column and fish tissue in the Spokane River, to demonstrate that this progress is occurring.

This project consists of the initial year of water column PCB monitoring in support of the long term monitoring program. Semipermeable membrane devices (SPMDs) will be deployed to monitor PCB concentrations at four locations ranging from the WA/ID State Line to downstream of the majority of PCB loading sources from the Spokane area. SPMDs will be deployed for one month at a time, during each of the three primary seasonal flow regimes in the Spokane River: low summer flow, moderate winter flow and high spring flow. The data will be used to characterize annual average Spokane River water column PCB concentrations for the period Summer, 2020 through Spring, 2021, and serve as a reference point for comparison to monitoring data in future years.

## 3.0 Background

### 3.1 Introduction and problem statement

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 Washington State Department of Ecology has included language in the NPDES permits for the Spokane River dischargers in Washington that requires permittees to create and participate in the Spokane River Regional Toxics Task Force (Task Force). The Task Force was formed with the following vision statement:

The Regional Toxics Task Force will work collaboratively to characterize the sources of toxics in the Spokane River and identify and implement appropriate actions needed to make measurable progress towards meeting applicable water quality standards...

One metric used by Ecology to assess whether measurable progress is occurring corresponds to outcomes, i.e. “Progress toward achievement of the applicable water quality criteria for PCBs in the Spokane River which could be demonstrated by achievement of the applicable water quality standards, health standards, and/or measured reductions of toxics to or in the Spokane River” (Ecology, 2014). Demonstration that this progress is occurring will require the establishment of a long-term monitoring program.

The Task Force has authorized long term monitoring of PCBs in the water column and fish tissue in the Spokane River, to demonstrate that this progress is occurring. This project consists of the initial year of water column PCB monitoring in support of the long term monitoring program. The data collected under this study will be used to characterize annual average Spokane River water column PCB concentrations for the period Summer, 2020 through Spring, 2021, and serve as a reference point for comparison to monitoring data in future years.

### 3.2 Study area and surroundings

Ecology (Wong and Era-Miller, 2019) describes the relevant features of the Spokane River as follows:

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 Task force has focused its efforts on the portion of the Spokane River between its headwaters at the outlet of Lake Coeur d’Alene (RM 111) and the Ninemile Dam (RM 58.1) (Figure 1). This 53 mile segment of the river has been chosen to be the focus of the SRRTTF’s initial efforts for several reasons. In no particular order they are:



- Discharges from all of the major municipal and industrial sources in the watershed are located in this section.
- Virtually all urban area storm runoff in the watershed enters the river in this section
- This section of the river contains numerous river flow gauging stations, which allowed for the determination of in-stream loadings at multiple locations through mass balance calculations
- In this section of the river the vast majority of the aquifer/river interchange occurs, the impact of which has not been quantified by previous studies
- The likelihood of making near term source contribution reductions is greatest in this section of the river given the concentration of point source and storm runoff locations and the significant level of unidentified source contribution
- The ability to monitor and assess the effectiveness of PCB reductions is enhanced by the ability to track in-stream loadings with the infrastructure present (gauging stations) in this section of the river

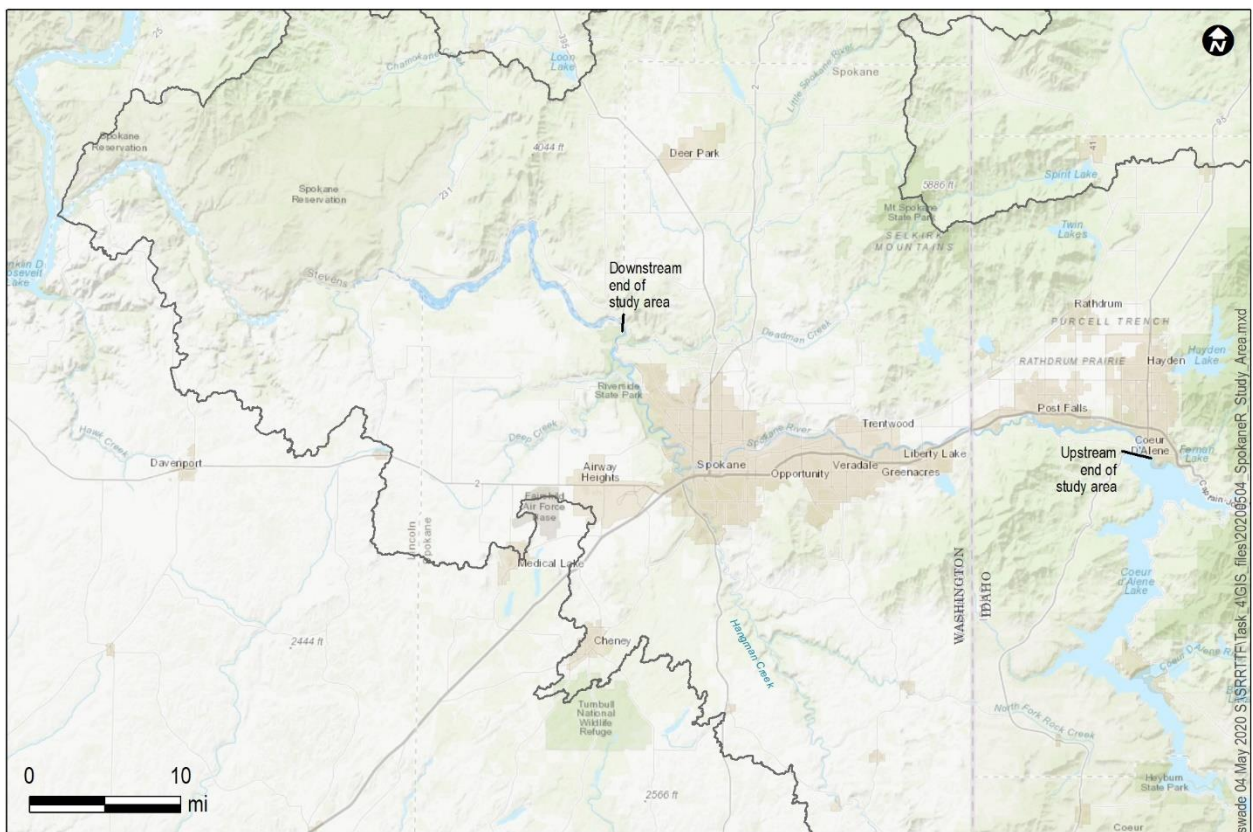


Figure 1. Map of larger study area.

### 3.2.1 History of study area

As described in Wong and Era-Miller (2019), the first report of elevated PCB concentrations in Spokane River was documented in fish tissue samples collected in 1980 (Hopkins et al., 1985; Johnson, 2001). Ecology and other groups have conducted numerous studies since then assessing PCB levels in fish tissue, surface water, effluent, groundwater, and sediment samples (see Section 3.2.2). LimnoTech (2016a) identified sources of PCBs and estimates their magnitudes. Strategies to clean up these known sources and reduce PCBs in the river have been assessed. Ongoing efforts

through the Task Force 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**

Wong and Era-Miller (2019) provide a detailed description 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 (2019) conducted additional synoptic dry weather water sampling in August 2018 and confirmed findings from the 2014 and 2015 surveys. Concentrations were again generally below 50 pg/L at Barker Road, and increased from Trent Bridge to Nine Mile Dam. This study also confirmed the presence of a large unknown source upstream of Trent Bridge at Plante's Ferry.

### **3.2.3 Parameters of interest and potential sources**

#### **PCBs**

The contaminant of interest is total polychlorinated biphenyls (PCBs), which the sum of 209 individual 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).

LimnoTech (2016a) identified the primary delivery mechanisms of PCBs to the Spokane River as:

- industrial and municipal wastewater treatment plants,
- contaminated groundwater,
- PCB entering from the outlet of Lake Couer d'Alene, and
- stormwater/combined sewer overflows.

#### **Ancillary Parameters**

Additional parameters will be collected and analyzed to allow PCB concentrations measured by the SPMDs (which represent only the dissolved phase) to be converted to total PCB concentrations. These ancillary parameters consist of total organic carbon (TOC), dissolved organic carbon (DOC) and total suspended solids (TSS).

### **3.2.4 Regulatory criteria or standards**

In this study, PCB concentrations are being used to support future temporal trend assessments. Results will not be compared to regulatory criteria or standards.

## 4.0 Project Description

The project goals and objectives described in this QAPP pertain to the initiation of long-term effectiveness monitoring to demonstrate that PCB control efforts being undertaken in the Spokane River basin will lead to decreases in PCB concentrations in the Spokane River. In this study, we will conduct a spatial survey of PCB concentrations in the Spokane River using semipermeable membrane devices (SPMDs). Hobbs (2018) used SPMDs to measure PCBs in the Wenatchee River as part of a PCBs source tracing study. This study will apply a similar methodology of SPMD sampling used in Hobbs (2018).

### 4.1 Project goals

The main goals of the study are to:

- (1) Characterize water column PCB concentrations within four reaches of interest in the Spokane River.
- (2) Provide a Year 2020-2021 baseline assessment of Spokane River PCB concentrations to support future long-term trend detection.

### 4.2 Project objectives

Project objectives are to:

- (1) Collect and analyze PCBs in water column SPMD samples at four locations during three different seasonal Spokane River flow regimes.
- (2) Collect and analyze ancillary parameters at the same Spokane River stations that will allow dissolved phase PCB concentrations to be converted to total PCB concentration.
- (3) Average the concentration across the three flow regimes to generate an annual average concentration at each location.

### 4.3 Information needed and sources

No further background data necessary.

### 4.4 Tasks required

Tasks required to achieve the study objectives are:

- Project planning meetings and discussion with the Task Force.
- Deployment and retrieval of passive water samplers.
- Analysis of samples for PCB congeners.
- Verification of data quality.
- Data analysis and report production.

### 4.5 Systematic planning process

This QAPP constitutes a suitable planning process.

## 5.0 Organization and Schedule

### 5.1 Key individuals and their responsibilities

**Table 1. Organization of project staff and responsibilities.**

Staff	Title	Responsibilities
<b>Robert Lindsay</b> President SRRTTF-ACE Phone: 509-477-7576	Task Force Client	Manage contracts: review and approve project specifications. Ensure project is completed in timely manner.
<b>David Dilks</b> LimnoTech Phone: 734-332-1200	Project Manager/ Principal Investigator	Prepare the QAPP. Review/approve all work products prior to delivery to SRRTTF-ACE. Ensure that work is done in accordance with QAPP. Review project with Laboratory Operations Directors prior to sampling. Provide oversight of field activities (variances, documentation, QA/QC). Arrange for system audits.
<b>Adriane Borgias</b> Water Quality Section Manager, Eastern Regional Office Phone: (509) 329-3515	Advisor	Review and approve QAPP.
<b>Karl Rains</b> Water Quality Planner, Eastern Regional Office Phone: (509) 329-3601	Contract Manager	Review and approve QAPP, manage SRRTTF contract.
<b>Robert Betz</b> LimnoTech Phone: 734-332-1200	Project Quality Assurance Officer	Performs systematic evaluation of data quality. Receives notices, initiates investigation, and documents nonconformance with DQOs. Manage the Project QA/QC file.
<b>Shea Hewage</b> SGS AXYS Analytical Services, Ltd. Phone: (250) 655-5800	Laboratory General Manager	Responsible for all aspects of the daily operation of the laboratory. Oversees laboratory operations including sample analysis and data reporting in accordance with defined procedures and client requirements. Oversees the completion of corrective actions to address any non-conformances.
<b>Sean Campbell</b> SGS AXYS Analytical Services, Ltd. Phone: (250) 655-5834	Laboratory Project Manager	Responsible for the execution of project-specific laboratory activities and interactions with the Task Force.
<b>Richard Grace</b> SGS AXYS Analytical Services, Ltd. Phone: 905-484-2314	Sales, Marketing, Service	Oversight of laboratory commercial terms. Serves as the main point of contact for laboratory for contract management or maintenance. Works closely with clients and laboratory management to develop project technical specifications.
<b>Dale Hoover</b> SGS AXYS Analytical Services, Ltd. Phone: 250-655-5800	Laboratory Technical Manager	Oversees laboratory technical offerings. Monitors laboratory and method performance and analytical results for conformance with established quality standards. Verifies the completion of corrective actions to address any non-conformances.

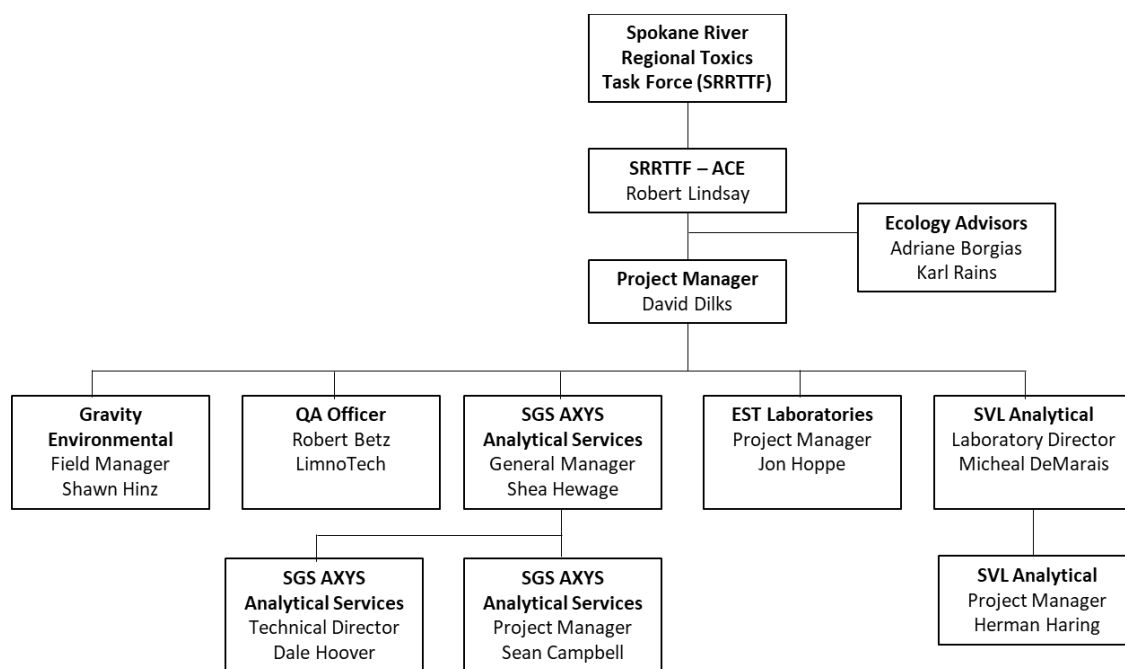
<b>Staff</b>	<b>Title</b>	<b>Responsibilities</b>
<b>Michael Desmarais</b> SVL Analytical, Inc. Phone: (208)784-1258	Laboratory Quality Manager	Manages laboratory QA activities. Responsible for accreditations and laboratory assessments. Addresses non-conformances and assesses corrective actions Provides training in aspects of laboratory operations, data integrity, and ethics.
<b>Herman Haring</b> SVL Analytical, Inc. Phone: (208)784-1258	Laboratory Project Manager	Responsible for the execution of project-specific laboratory activities and interactions with the Task Force.
<b>Shawn Hinz</b> Gravity Environmental Phone: (425)281-1471	Field Manager	Collects samples in accordance with QAPP and SAP. Prepares and follows the Invasive Species Plan. Prepares and administers Health and Safety Plan for employees. Maintains equipment logs, field records and data sheets. Transfers field data to Field Manager. Manages field equipment, conducts calibrations. Addresses nonconformance findings and responds to corrective actions.
<b>Jon Hoppe</b> EST Laboratories Phone: (816) 232-8860	Laboratory General Manager	Prepares SPMDs.
<b>Arati Kaza</b> Phone: 360-407-6964	Ecology Quality Assurance Officer	Reviews and approves the draft QAPP and the final QAPP.

## 5.2 Special training and certifications

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

## 5.3 Organization chart

The lines of reporting for the organizations in the project are shown in the organization chart (Figure 2).



**Figure 2. Project organization chart**

Each team member has responsibility for performance of assigned quality control duties in the course of accomplishing identified activities. The quality control duties include:

- Completing the assigned task on or before schedule and in a quality manner in accordance with established procedures; and
- Ascertaining that the work performed is technically correct and meets all aspects of the QAPP

## 5.4 Proposed project schedule

Start and end dates for key project activities are provided below in Table 2.

**Table 2. Proposed schedule for completing field and laboratory work and reports.**

Work type	Start Date	Due date	Lead staff
<b>Field and laboratory work</b>			
Summer low flow sampling	August, 2020	September, 2020	Shawn Hinz
Winter moderate flow sampling	February, 2021	March, 2021	Shawn Hinz
Spring high flow sampling	May, 2021	June, 2021	Shawn Hinz
Laboratory analyses	September, 2020	August, 2021	Sean Campbell
Laboratory data validation	August, 2021	October, 2021	Robert Betz
<b>Database</b>			
Database entry and review	August 2021	October, 2021	Amy Sumner
<b>Final report</b>			
Draft report to Task Force	October, 2021	December, 2021	David Dilks
Final report on web	March, 2022	March, 2022	David Dilks

## 5.5 Budget and funding

Funding for this work was provided by the Spokane River Regional Toxics Task Force, supported in part by funding allocated to the Task Force by the WA State legislature for fiscal years 2020 and 2021. See Table 3 for a budget overview and detailed laboratory budget.

**Table 3. Project budget and funding.**

Budget Overview					Total
Salary, benefits, and indirect/overhead					\$26,000.00
Equipment (SPMDs) <sup>1</sup>					\$10,060.78
Field Sampling <sup>1</sup>					\$67,314.00
Laboratory <sup>1</sup>					\$30,155.00
Parameter	Number of Samples	Number of QA Samples	Total Number of Samples	Cost Per Sample	Lab Subtotal
PCB Congeners	23	11	12	\$1,155	\$26,715.00 <sup>2</sup>
TOC/DOC/TSS	36	6	42	\$82	\$3,444.00
Lab Grand Total					\$30,155.00
<b>Project Grand Total</b>					<b>\$133,529.78</b>

<sup>1</sup> Contracts for SPMD devices, field sampling, and laboratory analyses will be written directly between the Task Force and respective consultants.

<sup>2</sup> Sub-total includes one-time charge of \$150 for preparation of Performance Reference Compounds



## 6.0 Quality Objectives

### 6.1 Data quality objectives

The main data quality objective (DQO) for this project is to collect passive water samples to characterize water column PCB concentrations during three seasonal flow regimes at four locations in the Spokane River. The analysis will use EPA methods with high-resolution gas chromatography-mass spectrometry to resolve the congener distribution present. Measurement quality objectives (MQOs) described in the subsequent section detail the targets for analytical precision, bias, and sensitivity.

### 6.2 Measurement quality objectives

The MQOs for laboratory analyses conducted for this study are detailed in Tables 4 and 5. There is also a precision objective for continuous temperature measurements of  $\pm 0.5$  °C assessed as part of an independent calibration check conducted during SPMD deployment, mid-point sampling, and retrieval

#### 6.2.1 Targets for precision, bias, and sensitivity

The MQOs for project results, expressed in terms of acceptable precision, bias, and sensitivity, are described in this section and summarized in Tables 4 and 5 below.

**Table 4. Measurement quality objectives for laboratory analyses of conventional water samples.**

MQO →	Precision		Bias			Sensitivity
Parameter	Duplicate Samples	Matrix Spike-Duplicates	Verification Standards (LCS,CRM,CCV)	Matrix Spikes	Surrogate Standards	MDL or Lowest Conc. of Interest
	Relative Percent Difference (% RPD)		Recovery Limits (%)			Concentration Units
Total Suspended Solids	± 20%	± 20%	80–120%	NA	NA	1.0 mg L <sup>-1</sup>
Total Organic Carbon	± 20%	± 20%	80–120%	75–125%	NA	1.0 mg L <sup>-1</sup>
Dissolved Organic Carbon	± 20%	± 20%	80–120%	75–125%	NA	0.5 mg L <sup>-1</sup>

MDL = method detection limit.

Table 5. Measurement quality objectives for laboratory analyses of PCB samples.

Congener	Cong No. <sup>3</sup>	Test conc. ng/mL	CAL/VER (%)		IPR <sup>4</sup> (%)		OPR <sup>4</sup> (%)		Labelled compound <sup>4</sup> % recovery in samples	
			Warning limits	Acceptance limits	RSD	χ	Warning limits	Acceptance limits	Warning limits	Acceptance limits
2-MoCB	1	50	75-125	75-125	25	70-130	70-130	60-135	-	-
4-MoCB	3	50	75-125	75-125	25	70-130	70-130	60-135	-	-
2,2'-DiCB	4	50	75-125	75-125	25	70-130	70-130	60-135	-	-
4,4'-DiCB	15	50	75-125	75-125	25	70-130	70-130	60-135	-	-
2,2'6-TrCB	19	50	75-125	75-125	25	70-130	70-130	60-135	-	-
3,4,4'-TrCB	37	50	75-125	75-125	25	70-130	70-130	60-135	-	-
2,2'6,6'TeCB	54	50	75-125	75-125	25	70-130	70-130	60-135	-	-
3,3',4,4'-TeCB	77	50	75-125	75-125	25	70-130	70-130	60-135	-	-
3,4,4',5-TeCB	81	50	75-125	75-125	25	70-130	70-130	60-135	-	-
2,2',4,6,6'-PeCB	104	50	75-125	75-125	25	70-130	70-130	60-135	-	-
2,3,3',4,4'-PeCB	105	50	75-125	75-125	25	70-130	70-130	60-135	-	-
2,3,4,4',5-PeCB	114	50	75-125	75-125	25	70-130	70-130	60-135	-	-
2,3',4,4',5-PeCB	118	50	75-125	75-125	25	70-130	70-130	60-135	-	-
2',3,4,4',5-PeCB	123	50	75-125	75-125	25	70-130	70-130	60-135	-	-
3,3',4,4',5-PeCB	126	50	75-125	75-125	25	70-130	70-130	60-135	-	-
2,2',4,4',6,6'-HxCB	155	50	75-125	75-125	25	70-130	70-130	60-135	-	-
2,3,3',4,4',5-HxCB <sup>5</sup>	156	50	75-125	75-125	25	70-130	70-130	60-135	-	-
2,3,3',4,4',5'-HxCB <sup>5</sup>	157	50	75-125	75-125	25	70-130	70-130	60-135	-	-
2,3',4,4',5,5'-HxCB	167	50	75-125	75-125	25	70-130	70-130	60-135	-	-
3,3',4,4',5,5'-HxCB	169	50	75-125	75-125	25	70-130	70-130	60-135	-	-
2,2',3,4',5,6,6'-HpCB	188	50	75-125	75-125	25	70-130	70-130	60-135	-	-
2,3,3',4,4',5,5'-HpCB	189	50	75-125	75-125	25	70-130	70-130	60-135	-	-
2,2',3,3',5,5',6,6'-	202	50	75-125	75-125	25	70-130	70-130	60-135	-	-
2,3,3',4,4',5,5',6-	205	50	75-125	75-125	25	70-130	70-130	60-135	-	-
2,2',3,3',4,4',5,5',6-	206	50	75-125	75-125	25	70-130	70-130	60-135	-	-
2,2',3,3',4,4',5,5',6,6'-	208	50	75-125	75-125	25	70-130	70-130	60-135	-	-
DeCB	209	50	75-125	75-125	25	70-130	70-130	60-135	-	-
<b>Labeled Compounds</b>										
<sup>13</sup> C <sub>12</sub> -2-MoCB	1L	100	65-135	50-145	70	20-135	15-145	15-145	15-130	5-145
<sup>13</sup> C <sub>12</sub> -4-MoCB	3L	100	65-135	50-145	70	20-135	15-145	15-145	15-130	5-145
<sup>13</sup> C <sub>12</sub> -2,2'-DiCB	4L	100	65-135	50-145	70	20-135	15-145	15-145	25-130	5-145

<sup>3</sup> Suffix "L" indicates labelled compound.

<sup>4</sup> QC acceptance criteria for IPR, OPR, and samples based on a 20 µL extract final volume

<sup>5</sup> PCBs 156 and 157 are tested as the sum of two concentrations

Congener	Cong .No. <sup>3</sup>	Test conc. ng/mL	CAL/VER (%)		IPR <sup>4</sup> (%)		OPR <sup>4</sup> (%)		Labelled compound <sup>4</sup> % recovery in samples	
			Warning limits	Acceptance limits	RSD	X	Warning limits	Acceptance limits	Warning limits	Acceptance limits
<sup>13</sup> C <sub>12</sub> -4,4'-DiCB	15L	100	65-135	50-145	70	20-135	15-145	15-145	25-130	5-145
<sup>13</sup> C <sub>12</sub> -2,2',6'-TrCB	19L	100	65-135	50-145	70	20-135	15-145	15-145	30-130	5-145
<sup>13</sup> C <sub>12</sub> -3,4,4'-TrCB	37L	100	65-135	50-145	70	20-135	15-145	15-145	30-130	5-145
<sup>13</sup> C <sub>12</sub> -2,2',6,6'-TeCB	54L	100	65-135	50-145	70	20-135	15-145	15-145	30-130	5-145
<sup>13</sup> C <sub>12</sub> -3,3',4,4'-TCB	77L	100	65-135	50-145	50	45-135	40-145	40-145	30-130	10-145
<sup>13</sup> C <sub>12</sub> -3,4,4',5'-TeCB	81L	100	65-135	50-145	50	45-135	40-145	40-145	30-130	10-145
<sup>13</sup> C <sub>12</sub> -2,2',4,6,6'-PeCB	104	100	65-135	50-145	50	45-135	40-145	40-145	40-130	10-145
<sup>13</sup> C <sub>12</sub> -2,3,3',4,4'-PeCB	105	100	65-135	50-145	50	45-135	40-145	40-145	40-130	10-145
<sup>13</sup> C <sub>12</sub> -2,3,4,4',5'-PeCB	114	100	65-135	50-145	50	45-135	40-145	40-145	40-130	10-145
<sup>13</sup> C <sub>12</sub> -2,3',4,4',5'-PeCB	118	100	65-135	50-145	50	45-135	40-145	40-145	40-130	10-145
<sup>13</sup> C <sub>12</sub> -2',3,4,4',5'-PeCB	123	100	65-135	50-145	50	45-135	40-145	40-145	40-130	10-145
<sup>13</sup> C <sub>12</sub> -3,3',4,4',5'-PeCB	126	100	65-135	50-145	50	45-135	40-145	40-145	40-130	10-145
<sup>13</sup> C <sub>12</sub> -2,2',4,4',6,6'-HxCB	155	100	65-135	50-145	50	45-135	40-145	40-145	40-130	10-145
<sup>13</sup> C <sub>12</sub> -2,3,3',4,4',5'-HxCB <sup>5</sup>	156	100	65-135	50-145	50	45-135	40-145	40-145	40-130	10-145
<sup>13</sup> C <sub>12</sub> -2,3,3',4,4',5'-HxCB <sup>5</sup>	157	100	65-135	50-145	50	45-135	40-145	40-145	40-130	10-145
<sup>13</sup> C <sub>12</sub> -2,3',4,4',5,5'-HxCB	167	100	65-135	50-145	50	45-135	40-145	40-145	40-130	10-145
<sup>13</sup> C <sub>12</sub> -3,3',4,4',5,5'-HxCB	169	100	65-135	50-145	50	45-135	40-145	40-145	40-130	10-145
<sup>13</sup> C <sub>12</sub> -2,2',3,3',4,4',5'-HpCB	170	100	65-135	50-145	50	45-135	40-145	40-145	40-130	10-145
<sup>13</sup> C <sub>12</sub> -2,2',3,4,4',5,5'-HpCB	180	100	65-135	50-145	50	45-135	40-145	40-145	40-130	10-145
<sup>13</sup> C <sub>12</sub> -2,2',3,4',5,6,6'-HpCB	188	100	65-135	50-145	50	45-135	40-145	40-145	40-130	10-145
<sup>13</sup> C <sub>12</sub> -2,3,3',4,4',5,5'-HpCB	189	100	65-135	50-145	50	45-135	40-145	40-145	40-130	10-145
<sup>13</sup> C <sub>12</sub> -2,2',3,3',5,5',6,6'-	202	100	65-135	50-145	50	45-135	40-145	40-145	40-130	10-145
<sup>13</sup> C <sub>12</sub> -2,3,3',4,4',5,5',6-	205	100	65-135	50-145	50	45-135	40-145	40-145	40-130	10-145
<sup>13</sup> C <sub>12</sub> -2,2',3,3',4,4',5,5',6-	206	100	65-135	50-145	50	45-135	40-145	40-145	40-130	10-145
<sup>13</sup> C <sub>12</sub> -2,2',3,3',4,5,5',6,6'-	208	100	65-135	50-145	50	45-135	40-145	40-145	40-130	10-145
<sup>13</sup> C <sub>12</sub> -2,2',3,3',4,4',5,5',6,6'-	209	100	65-135	50-145	50	45-135	40-145	40-145	40-130	10-145
<b>Cleanup Standards</b>										
<sup>13</sup> C <sub>12</sub> -2,4,4'-TriCB	28L	100		65-135	70	20-135	15-145	15-145	40-130	5-145
<sup>13</sup> C <sub>12</sub> -2,3,3',5,5'-PeCB	111	100		75-125	50	45-135	40-145	40-145	40-130	10-145
<sup>13</sup> C <sub>12</sub> -2,2',3,3',5,5',6'-HpCB	178	100		75-125	50	45-135	40-145	40-145	40-130	10-145

### 6.2.1.1 Precision

Field replicate samples will be collected at a frequency of 1 in 10. The defined relative percent difference for water and passive samplers is  $\pm 50\%$ . Replicates are collected either simultaneously or as close together as possible.

Field trip blanks will be conducted for the SPMDs. The field blank SPMD is taken into the field and opened for the same duration of time that the sample SPMD is exposed to the air during deployment. The blank is sealed, transported cold back to Gravity offices, and stored frozen. The blank is then taken back into the field and exposed to air for the same duration as the sample SPMD during retrieval. Two field blanks will be used.

### 6.2.1.2 Bias

Bias is the difference between the population mean and the true value. For this project, bias is measured as acceptable % recovery. Acceptance limits for laboratory verification standards, matrix spikes, and surrogate standards are shown in Tables 4 and 5.

### 6.2.1.3 Sensitivity

Sensitivity is a measure of the capability of a method to detect a substance above the background noise of the analytical system. Sensitivity for each parameter is expressed in Table 4 as a method detection limit (MDL)<sup>6</sup> For the high-resolution methods being used in this study, each congener is assessed for sensitivity and qualified or censored if the sample is not above three times the laboratory blank. The laboratory reporting limits (RLs) for the project are described in Section 9.1.

## 6.2.2 Targets for comparability, representativeness, and completeness

### 6.2.2.1 Comparability

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

### 6.2.2.2 Representativeness

Representativeness is a measure of whether the sample media reflects reality. We will ensure proper representatives by adhering to the approved SOPs and sampling protocols. Samples will be preserved and stored in a way that ensures holding conditions and lab holding times are met. Samples will be collected during the three primary seasonal flow regimes, and will capture the range of flow-related impacts on concentration. In addition, SPMDs will be deployed continuously for a month at a time, minimizing the chance that measured concentrations reflect non-representative short term fluctuations.

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<sup>6</sup> The lowest quantity of a physical or chemical parameter that is detectable (above background noise) by each field instrument or laboratory method.

#### 6.2.2.3 Completeness

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

### **6.3 Acceptance criteria for quality of existing data**

All data used to support the findings of this project will meet project DQOs. To the extent that any previous data are used, they will also be evaluated for compliance with current DQOs.

### **6.4 Model quality objectives**

N/A

# 7.0 Study Design

## 7.1 Study boundaries

This study will focus on measuring PCB concentrations in the Middle and Lower Spokane River Basin (WRIAs 57 and 54, respectively). The area of study specifically corresponds to the portion of the Spokane River between the Washington/Idaho border and Nine Mile Dam (Figure 3).

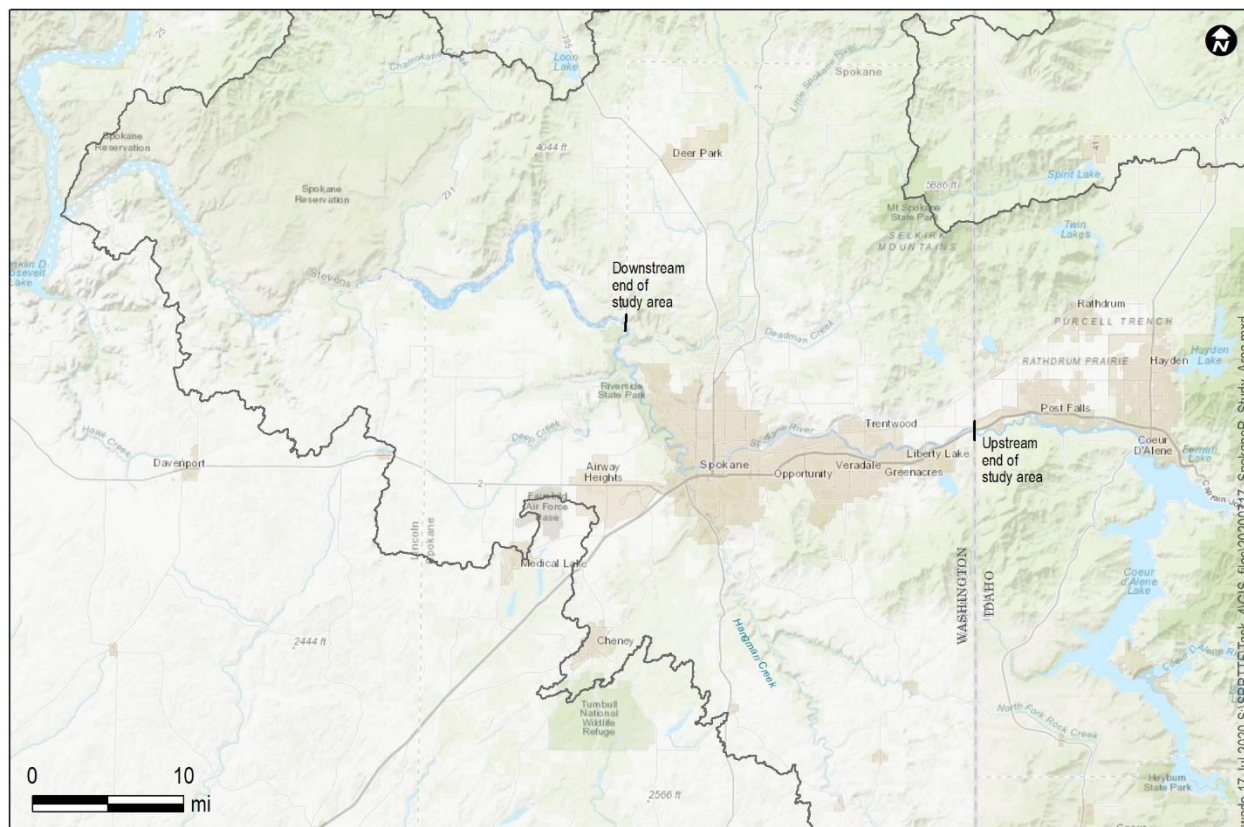


Figure 3. Map showing boundary of project study area.

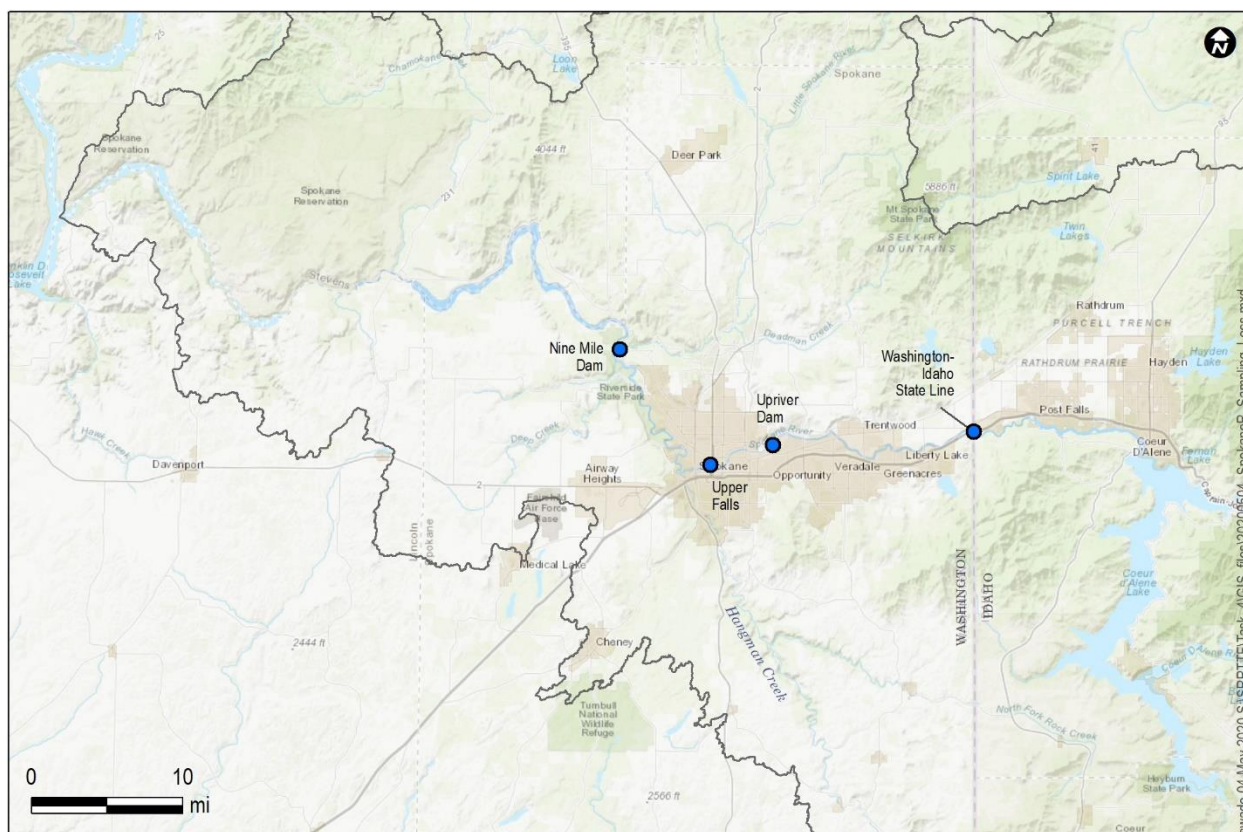
## 7.2 Field data collection

### 7.2.1 Sampling locations and frequency

Sampling will encompass locations ranging from the WA/ID State Line to downstream to Nine Mile Dam of the majority of PCB loading sources from the Spokane area.

SPMD samplers will be deployed at four locations (Figure 4):

- WA/ID State Line
- Upriver Dam
- Near Upper Falls
- Nine Mile Dam



**Figure 4. Map showing sampling locations**

The overall objective of this work is to serve as the first step in a long term monitoring program to demonstrate that PCB control actions being implemented by the Task Force are resulting in a decrease in Spokane River PCB concentrations. These specific sampling locations have been selected to help isolate the effect of load reductions from different source areas. Long term sampling at the State Line will (ultimately) indicate whether PCB loads from Idaho sources are changing over time. Sampling at Upriver Dam will indicate the effect of load reductions at two industrial wastewater treatment plants as well as groundwater PCB remediation at the Kaiser Trentwood facility. Sampling near Upper Falls will indicate whether loading from suspected contamination in Mission Park area is changing over time. Sampling at Nine Mile Dam will indicate the effect of load reductions from City of Spokane sources (wastewater treatment plant, storm water runoff, combined sewer overflows) and will also reflect the cumulative reduction of loading from all Spokane-area sources.

SPMD samplers will be deployed one month at a time during the three major seasonal flow regimes in the Spokane River: high spring flow, low summer flow, and moderate winter flow. This sampling frequency is designed to explicitly consider seasonal variability in PCB concentrations, and provide an estimate of annual average concentrations. The ancillary parameters of organic carbon and suspended solids will be collected via grab sample at the beginning, midpoint, and end of each SPMD deployment, resulting in six SPMD measurements and nine ancillary parameter measurements at each of the four stations.

## **7.2.2 Field parameters and laboratory analytes to be measured**

The complete parameter list was provided previously in Section 6.2 Measurement Quality Objectives.

## **7.3 Modeling and analysis design**

N/A.

## **7.4 Assumptions underlying design**

The assumptions associated with the study design are that we will be able to accurately measure PCBs in the water column and at an appropriate temporal scale to capture the effects of the entire range of seasonally-dependent loading sources. Additionally, the study design assumes that the average concentration across three month-long deployments is a reasonable representation of average PCB concentrations at each location over the course of the year.

## **7.5 Possible challenges and contingencies**

### **7.5.1 Logistical problems**

The challenges impacting the study design are limited to the logistics of SPMD deployment and retrieval over the course of the study period. To alleviate this issue, adequate time for reconnaissance of field sites and confirmation of safe deployment and retrieval throughout the year and range of flow conditions will take place well in advance of any sampling.

### **7.5.2 Practical constraints**

The one known practical constraint corresponds to potential travel and enterprise restrictions related to COVID-19. We will monitor applicable guidelines and adjust our activities accordingly.

### **7.5.3 Schedule limitations**

Should COVID-19 restriction prevent implementation of the Summer 2020 low flow sampling event, summer low flow sampling would be moved to 2021. This would require a three month extension to the proposed study schedule.



## 8.0 Field Procedures

### 8.1 Invasive species evaluation

Field personnel for this project are required to be familiar with and follow the procedures described in SOP EAP070 (Parsons et al., 2018), Minimizing the Spread of Invasive Species.

### 8.2 Measurement and sampling procedures

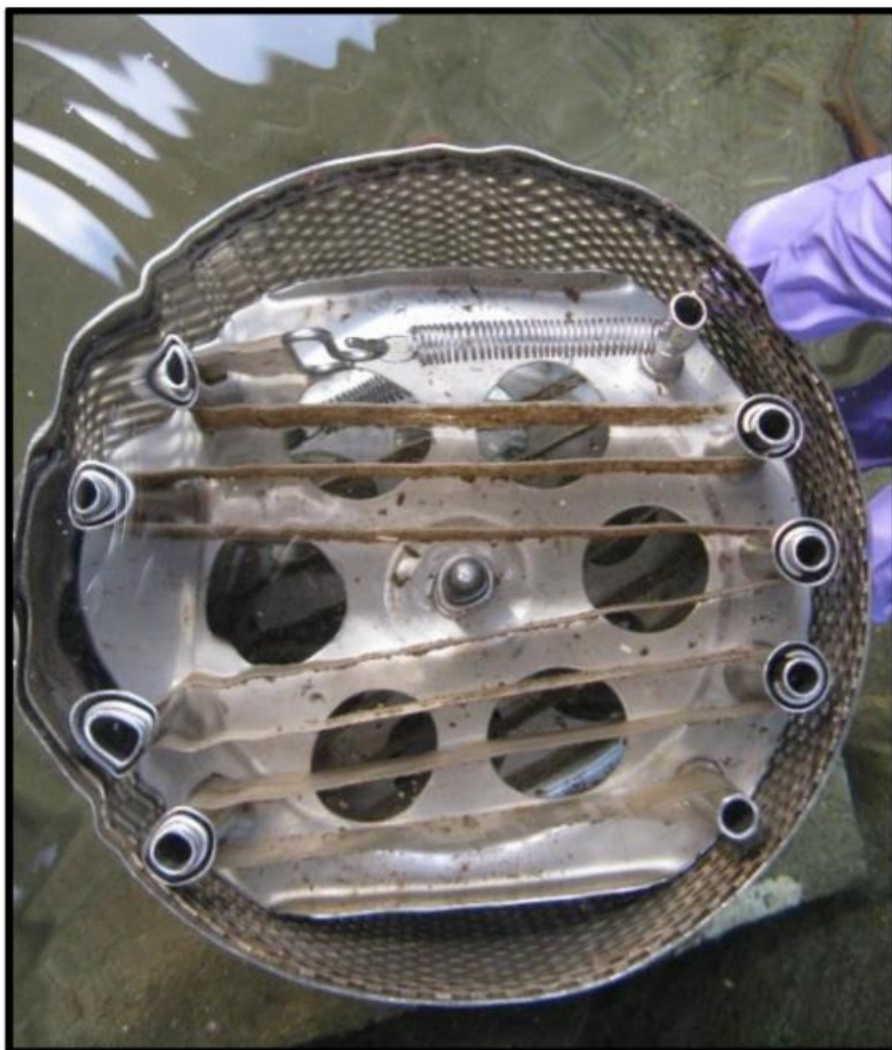
Sampling methods for this study have been employed in other studies for toxics (Johnson et al., 2010; Hobbs, 2018), and the procedures described here draw extensively from existing QAPPs (Ecology, 2019; Hobbs, 2014). Two field SOPs will be followed during the study:

- Hobbs (2020) — Standard Operating Procedure EAP001, Version 4.1. Standard Operating Procedure for Conducting Studies Using SPMDs.
- Seiders et al. (2020) — Standard Operating Procedure for Semipermeable Membrane Devices (SPMD) Data Management and Data Reduction

#### Semi-permeable membrane devices

The measurement of PCBs in the Spokane River water column water will depend upon passive samplers called semi-permeable membrane devices (SPMDs). SPMDs are composed of a thin-walled, layflat polyethylene tube (91.4 cm x 2.5 cm x 70–95 um thickness) filled with 1 ml of triolein, a neutral lipid compound (Figure 5). The goal of SPMDs is to allow chemicals to diffuse through the membrane and concentrate over time (typically a 28- day deployment). After deployment, the membranes are removed, extracted, and analyzed for the contaminant of interest (Ecology, 2019).

In this study, SPMDs will be deployed in secure areas (i.e., to minimize vandalism and avoid strong currents), using stainless steel canisters and spindle devices provided by Environmental Sampling Technologies (EST). Each site canister/SPMD will contain five membranes preloaded onto spindles by EST, and shipped in solvent-rinsed metal cans under argon gas. Prior to deployment, performance reference compounds (PRCs) will be spiked into the membranes in order to assess biofouling and the non-equilibrium uptake of the compounds of interest (Huckins et al., 2006). The use of PRCs is essentially an in situ, site-specific calibration technique based on the observation that the rate of analyte loss is proportional to the rate of analyte uptake. We will use isotopically labeled (<sup>13</sup>C) PCB congeners PCB-31, -95, and -153 as PRCs, in addition to PCB-14, - which is not labeled but commonly used. The labeled congeners are not present in significant amounts in the environment and have shown appropriate rates of loss (20-80%). The spiking level will be 2 ng of each PRC congener per membrane. The PRCs are added to the triolein oil before the manufacture of the SPMD membranes. The contract lab will order, prepare, and validate the PCB standard and will provide the PRC spiking solution to EST. Temperature loggers will be deployed concurrent with the SPMDs to confirm that they remained submerged during the period of deployment.



**Figure 5. An SPMD canister showing the upper membrane (from Ecology, 2019).**

### **Surface water grab samples**

Water grab samples will be taken to measure the total and dissolved organic carbon (TOC/DOC) and total suspended solids (TSS) suspended sediment concentrations (SSC) at each site during the time the SPMDs are exposed. These parameters will be used as ancillary data to help understand relationships between suspended matter and the PCB contaminants. Water grab samples will be collected three times over the duration of the SPMD exposure to get an integrated measure of the conditions. Grab samples will be collected using Ecology standard operating procedures (Joy, 2006). Additional field parameters will be measured in situ at the time of water sampling using a multiprobe sonde (Swanson, 2007). Parameters include: temperature, pH, dissolved oxygen, and conductivity.

## 8.3 Containers, preservation methods, holding times

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

Parameter	Matrix	Minimum Quantity Required	Container	Preservative	Holding Time
PCB congeners	SPMD	5 SPMDs	Stainless steel carrier	Freeze to < -7°C	One year after extraction
DOC/TOC	Surface water	60 ml	125 mL pre-acidified poly bottle	1:1 HCl to pH<2; Cool to 6°C	28 days
TSS		2 L	2L HDPE container	Cool to 6°C	7 days

## 8.4 Equipment decontamination

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

## 8.5 Sample ID

Laboratory sample IDs will be assigned by SVL and SGS AXYS.

## 8.6 Chain of custody

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

## 8.7 Field log requirements

Field data will be recorded in a bound, waterproof notebook on Rite in the Rain paper. Corrections will be made with single line strikethroughs, initials, and date.

The following information will be recorded in the project field log:

- Name and location of project
- Field personnel
- Sequence of events
- Any changes or deviations from the QAPP
- Environmental conditions
- Date, time, location, ID, and description of each sample
- Field instrument calibration procedures
- Field measurement results
- Identity of QC samples collected
- Unusual circumstances that might affect interpretation of results

## **8.8 Other activities**

No additional activities require description.

## 9.0 Laboratory Procedures

### 9.1 Lab procedures table

Table 7. Measurement methods (laboratory).

Analyte	Sample Matrix	Samples (Number/ Arrival Date)	Expected Range of Results	Detection or Reporting Limit	Sample Prep Method	Analytical (Instrumental) Method
<b>Analytical Lab: SVL</b>						
Total Suspended Solids (mg / L)	Surface water	42 ( 15: September, 2020; 12: February, 2021; 15: May, 2021)	0.5-20	1.0	N/A	SM 2540D
Total Organic Carbon (mg / L)	Surface water	42 ( 15: September, 2020; 12: February, 2021; 5: May, 2021)	1-10	1.0	N/A	SM 5310B
Dissolved Organic Carbon (mg / L)	Surface water	42 ( 15: September, 2020; 12: February, 2021; 15: May, 2021)	0.5-5	0.5	N/A	SM 5310B
<b>Analytical Lab: SGS AXYS</b>						
PCBs Congeners	SPMD extract	23 ( 8: September, 2020; 7: February, 2021; 8: May, 2021)	100 - 200 ng (t-PCBs)	0.5 pg per congener	dialysis; EPA 1668C	EPA 1668C

### 9.2 Sample preparation method(s)

Laboratory sample preparation methods are found in Table 7.

### 9.3 Special method requirements

There are no special method requirements.

### 9.4 Laboratories accredited for methods

A summary of lab responsibilities is shown in Table 7.

## 10.0 Quality Control Procedures

### 10.1 Table of field and laboratory quality control

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

Parameter	Field		Laboratory				OPR Standards
	Blanks	Replicates	Check Standards	Method Blanks	Analytical Duplicates	Matrix Spikes	
Total Suspended Solids	-	10% of samples	1/batch	1/batch	1/batch	-	-
TOC/DOC	-	10% of samples	1/batch	1/batch	1/batch	1/batch	-
PCB congeners	2/sample collection	10% of samples	1/batch Initial cal. ver. and ongoing cal. ver. if needed (12 hour frequency)	1/batch	2 field duplicates per batch	1/batch	1/batch

### 10.2 Corrective action processes

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

## **11.0 Data Management Procedures**

### **11.1 Data recording and reporting requirements**

Field data will be recorded in a bound, waterproof notebook on Rite in the Rain paper. Corrections will be made with single line strikethroughs, initials, and date. Data will be transferred to Microsoft Excel templates for creating data tables and subsequent entry into the Task Force database.

### **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 LimnoTech's formatting requirements.

### **11.4 EIM/STORET data upload procedures**

Data for this project will be loaded into the Task Force data base and EIM.

### **11.5 Model information management**

N/A

## **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 summarizing the study and describing the assessment of current PCB concentrations in the Spokane River study area. The draft will be distributed to the Task Force and Ecology for review, and revised in response to comments.

### **12.4 Responsibility for reports**

The report will be authored by David Dilks.



## **13.0 Data Verification**

### **13.1 Field data verification, requirements, and responsibilities**

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

### **13.2 Laboratory data verification**

The laboratory conducting the analyses will review laboratory results prior to submitting the data package. The LimnoTech 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 LimnoTech 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**

It is expected that external data validation will not be necessary for this project.

### **13.4 Model quality assessment**

NA.

## **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 outlined in Tables 4 and 5 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 the project data base. 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.

For this project, congener results that are <3 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 trends, and with previous and ongoing work conducted by the Task Force.

### **14.3 Data analysis and presentation methods**

As these data are designed to define baseline conditions for future trend assessments, no specific numerical analyses are necessary for this project beyond calculation of water column PCB concentrations from the mass of PCBs in the SPMD. This calculation will be conducted using the equations developed in Huckins et al (2006) and implemented in the spreadsheet “SPMD Water Concentration Estimator v5-2” ([https://www.usgs.gov/centers/cerc/science/passive-sampling-using-spm-ds-and-pocis?qt-science\\_center\\_objects=0#qt-science\\_center\\_objects](https://www.usgs.gov/centers/cerc/science/passive-sampling-using-spm-ds-and-pocis?qt-science_center_objects=0#qt-science_center_objects)). Annual average PCB concentrations at each of the four stations will be calculated as the arithmetic average of the observed concentrations of the three seasonal exposures, and presented in tabular form.

### **14.4 Sampling design evaluation**

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

## **14.5 Documentation of assessment**

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

## 15.0 References

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## 16.0 Appendices

## Appendix A. Glossaries, Acronyms, and Abbreviations

### Glossary of General Terms

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

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

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

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

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

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

**Point source:** Source of pollution that discharges at a specific location from pipes, outfalls, and conveyance channels to a surface water. Examples of point source discharges include domestic wastewater treatment plants, industrial wastewater treatment facilities, and stormwater from certain municipal systems and industrial and construction activities.

**Reach:** A specific portion or segment of a stream.

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

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

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



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

**Total Maximum Daily Load (TMDL):** A distribution of a substance in a water body designed to protect it from not meeting (exceeding) water quality standards. A TMDL is equal to the sum of all of the following: (1) individual wasteload allocations for point sources, (2) the load allocations for nonpoint sources, (3) the contribution of natural sources, and (4) a margin of safety to allow for uncertainty in the wasteload determination. A reserve for future growth is also generally provided.

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

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

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

## Acronyms and Abbreviations

DOC	Dissolved organic carbon
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
GIS	Geographic Information System software
i.e.	In other words
MQO	Measurement quality objective
NPDES	(See Glossary above)
PCB	Polychlorinated biphenyls
QA	Quality assurance
QC	Quality control
RM	River mile
RPD	Relative percent difference
RSD	Relative standard deviation
SOP	Standard operating procedures
SRRTTF	Spokane River Regional Toxics Task Force
TMDL	(see Glossary above)
TOC	Total organic carbon
TSS	(see Glossary above)
USGS	United States Geological Survey
WAC	Washington Administrative Code
WRIA	Water Resource Inventory Area
WWTP	Wastewater treatment plant

## Units of Measurement

°C	degrees centigrade
Cfs	cubic feet per second
Cms	cubic meters per second, a unit of flow
Ft	feet
G	gram, a unit of mass
km	kilometer, a unit of length equal to 1,000 meters
m	meter
mg	milligram
mgd	million gallons per day
mg/d	milligrams per day
mg/L	milligrams per liter (parts per million)
mL	milliliter
ng/L	nanograms per liter (parts per trillion)
pg/L	picograms per liter (parts per quadrillion)
s.u.	standard units
µg/L	micrograms per liter (parts per billion)

## 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:

$$[\text{Abs}(a-b)/((a + b)/2)] * 100$$

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

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

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

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

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

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

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

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

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

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

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

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

## References for QA Glossary

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