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Quality Assurance Project Plan

Spokane River

PCBs and other Toxics

Long Term Monitoring at the Spokane Tribal Boundary

March 2015

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EAP: Environmental Assessment Program

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# 2.0 Abstract

The Spokane River is listed as water quality impaired for PCBs and dioxins/furans. PCBs are currently being addressed through the efforts of the Spokane River Regional Toxics Task Force (SRRTTF). There is a Total Maximum Daily Load (TMDL) or Water Clean-up Plan for cadmium, lead, and zinc. There is also a fish consumption advisory for PCBs and PBDEs in the Spokane River between Idaho and Long Lake Dam.

This plan describes establishment of a long-term monitoring station for polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), dioxins/furans and metals (cadmium, copper, lead and zinc) on the mainstem Spokane River upstream of the Spokane Tribal boundary. The planned station is downstream of all known sources of toxics and downstream of most of the current and ongoing toxics monitoring. The Spokane Tribal boundary represents an important compliance point for water quality standards, since the tribe has approved water quality standards. Monitoring toxics here over the long-term will help to indicate trends in the greater Spokane River over time and assess compliance with applicable water quality standards.

Ecology’s Environmental Assessment Program (EAP) will establish the long-term monitoring station. Surface water and suspended sediments will be monitored annually during the 3 major hydrologic regimes for the river: spring high flow, summer low flow, and winter moderate flow.

# Background

The Spokane River contains elevated levels of a number of toxic chemicals including polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), dioxins/furans and metals. These contaminants are prevalent in water, sediment, and fish tissue. Ecology first documented PCB contamination in the Spokane River in the early 1980s (Hopkins et al., 1985). Since that time, numerous studies and clean-up activities to address contamination have been conducted and are ongoing in the Spokane River watershed (Serdar et al., 2011).

The Spokane River is listed on the 303(d) List as water quality impaired for PCBs and dioxins/furans (see Appendix A for a table of all the 303(d) listings for toxics parameters in the Spokane River). PCBs are currently being addressed through the efforts of the Spokane River Regional Toxics Task Force (SRRTTF). There is a Total Maximum Daily Load (TMDL) or Water Clean-up Plan for cadmium, lead, and zinc. There are also fish consumption advisories for PCBs and PBDEs in the Spokane River between Idaho and Long Lake Dam.

The majority of the current and ongoing activities to address PCBs and other toxics have focused on the upstream portion of the Spokane River, where most of the known contamination exists. For the purposes of this document, upstream Spokane River refers to areas upstream of Lake Spokane. Downstream of Lake Spokane represents an important location in the river because it is the transition from water of the state to waters of the Spokane reservation The Spokane Tribal boundary is where tribal water quality standards apply and their criterion for total PCBs (1.3 pg/L) is far lower than the State Standard for total PCBs (170 pg/L). There is currently no routine monitoring for toxic chemicals occurring in this reach of the river to assess compliance with the state or tribal standards and evaluate trends.

With most of the known sources of toxics located upstream of Long Lake and because of its size and depth, Long Lake is a probable sink for many toxics moving downstream and getting deposited in lake sediments. Results from Ecology’s most recent fish tissue study conducted in 2012 (Seiders, et al., 2014) indicate that concentrations of PCBs and PBDEs are much lower in Little Falls Pool (the stretch of Spokane River between Long Lake Dam and Little Falls Dam) compared to all the other monitoring locations upstream.

Surface water concentrations for toxics in the Spokane River below Long Lake Dam are unknown, but expected to be lower than areas upstream.

## 3.1 Study area and surroundings

The Spokane River, shown in Figure 1, begins in Idaho at the outlet of Lake Coeur d’Alene and flows west 112 miles to the Columbia River. The Spokane River watershed encompasses over 6,000 square miles in Washington and Idaho (Serdar et. al., 2011). The river flows through the smaller cities of Post Falls and Coeur d’Alene in Idaho and large urban and industrial areas in Spokane Valley and Spokane in Washington. Other cities include Liberty Lake, Deer Park, and Medical Lake in Washington as well as Wallace and Kellogg Idaho upstream of Lake Coeur d’Alene. The Spokane Tribe of Indians reservation encompasses the north bank of the lower river from Chamokane Creek, below Long Lake Dam, downstream to the Columbia River.

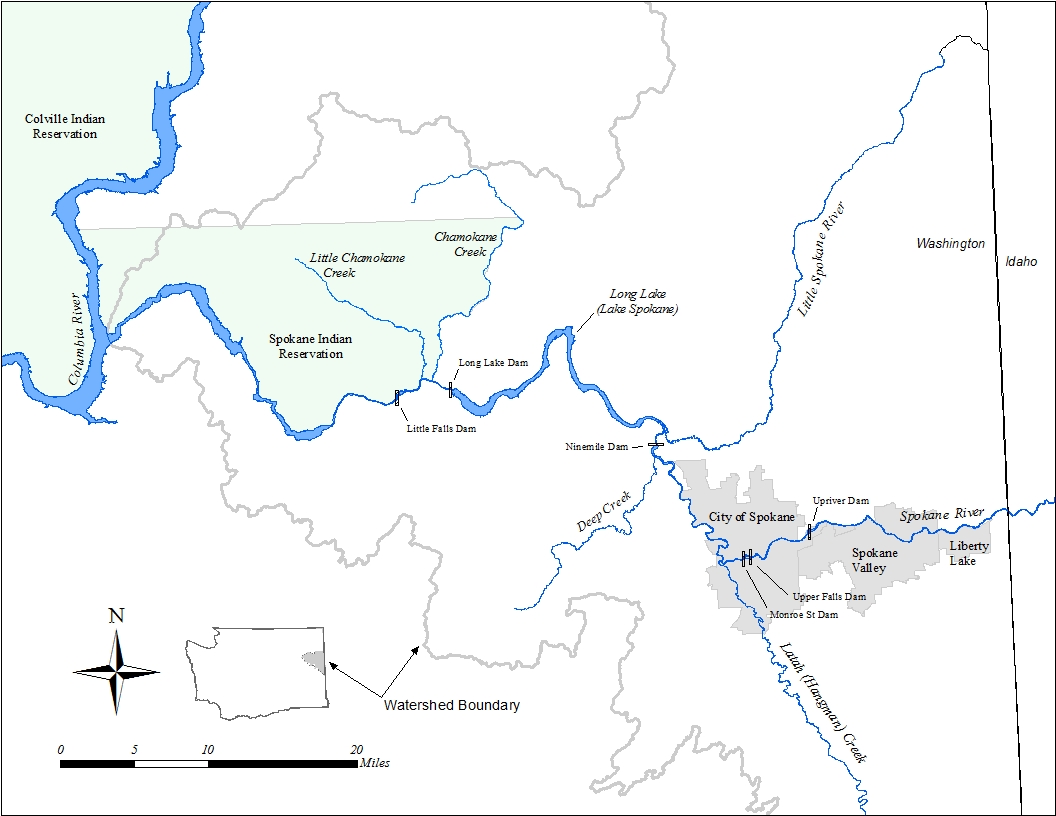


Figure 1. Spokane River Study Area.

The Spokane River sits atop the western portion of the Spokane Valley-Rathdrum Prairie Aquifer. There is significant interchange between the river and the aquifer. The river is the largest contributor to the aquifer (49% of aquifer inflow), but is also the largest recipient of aquifer water at about 58% of river outflow (MacInnis et. al., 2009).

The Spokane River is impacted by 7 major dams which create reservoirs behind them. From upstream to downstream they are: Post Falls Dam, Upriver Dam, Upper Falls Dam, Monroe Street Dam, Nine Mile Dam, Long Lake Dam and Little Falls Dam.

The Spokane River watershed is located in a transition area between the barren scablands of the Columbia Basin to the west, coniferous forests and mountainous regions to the north and east and prairie lands to the south. Spokane receives 16.5 inches of rain annually on average. Spring snow melt dominates flows in the Spokane River from April through June as shown in Figure 2.



Figure 2. Historical Average Annual Flow for the Spokane River.

### 3.1.1 Logistical problems

Water depth and current in the Spokane River below Long Lake Dam present potential logistical problems for the project. At least 10 feet of depth is required to deploy sediment traps so that they sit safely below the water’s surface. The depth of the water at the pool area downstream of the highway 231 bridge is estimated to be greater than 10 feet. Strong currents can also make retrieval of sediment traps difficult.

Ecology has permission to sample surface water at the two potential monitoring locations for the study: Avista Park (on the south bank just below Long Lake Dam) and at the Union Gospel Mission (on the north bank just upstream of Chamokane Creek). The planned surface water sampling will take up to 36 hours. As long as water levels don’t fluctuate more than a few inches during the <36 hour sampling period, sampling should not be effected. Reconnaissance of both locations will help determine which site will work best for surface water sampling. Depth of water will be a determining factor. Depths of least 2 feet will make deployment of CLAMs possible.

### 3.1.2 History of study area

As stated in the *Background* section of this QA Project Plan, Ecology first documented PCB contamination in the Spokane River in the early 1980s (Hopkins et al., 1985). Since that time, numerous studies and clean-up activities to address contamination have been conducted and are ongoing in the Spokane River watershed (Serdar et al., 2011).

The Spokane River is a valuable resource to all the people who live in the watershed. The Spokane Valley – Rathdrum Prairie Aquifer, which interchanges substantially with the river, provides drinking water to more than 500,000 people (MacInnis et. al., 2009). Many people use the river for fishing, swimming and boating. Numerous Dams provide electricity and flood control.

The Spokane Tribe of Indians’ reservation borders the lower section of the river from Chamokane Creek down to the Columbia River (Figure 1). This river has been an important source of food and ceremony for the Spokane Tribe for centuries.

### 3.1.3 Parameters of interest

Parameters of interest for the project are presented in Table 1.

Table 1. Parameter of Interest for the Spokane River Long-term Monitoring Station.

|  |  |
| --- | --- |
| Parameter | Reason for Interest in Spokane River |
| PCBs | 303(d) listed, fish consumption advisory1, focus of Spokane River Regional Toxics Task Force (SRRTTF). |
| PBDEs | Fish consumption advisory1 |
| Dioxin/furans | 303(d) listed |
| Cadmium, Lead and Zinc | A TMDL2 for metals has been implemented |

1 DOH, 2009.

2 Butkus and Merrill, 1999.

### 3.1.4 Results of previous studies

Numerous datasets exist for toxics in the Spokane River (too many to list here). A few select studies including data from the 2012-2013 toxics sampling effort conducted by Ecology (Era-Miller, 2014) are discussed in this section.

Table 2 indicates what the total and dissolved organic carbon content (TOC and DOC) and total suspended solids (TSS) are like in surface water near the proposed monitoring site. Concentrations of these parameters are generally quite low and are usually measured near analytical reporting limits.

Table 2. Water Quality Results at the Chamokane Monitoring Site below Long Lake Dam.

|  |  |  |
| --- | --- | --- |
| Parameter | Result (mg/L) | |
| 10/24/12 – 10/25/12 | 5/23/13 – 5/24/13 |
| DOC | 1 U | 1.1 |
| TOC | 1 U | 1.2 |
| TSS | 1 U | 2 |

U = the analyte was not detected at or above the reported result

Data from Era-Miller, 2014

The Spokane Tribe records continuous dissolved oxygen, temperature and conductivity with a hydrolab from June through October at the Union Gospel Mission (UGM) site located on the north bank of the river just upstream of Chamokane Creek (Brian Crossley, personal communication).

Ecology’s Statewide River and Stream Ambient Monitoring Program has a station (54A070) located at the Highway 231 bridge (also known locally as Spring Creek Bridge). Relevant data collected here includes DOC, TOC, TSS, turbidity, conductivity, temperature, hardness, and flow. A search in Ecology’s EIM database shows that data for some of these parameters spans from 1959 – 2010.

Figures 3 shows total PCB congener results for CLAMs (Continuous Low-level Aqueous Monitoring device) deployed by Ecology at Upriver Dam and Nine Mile Dam in fall of 2012 compared to the water quality standards applicable to the Spokane River. The Day 2 results give an indication of the dissolved fraction of PCBs where CLAMs with and without prefilters (1.5 micron size) were compared. Figure 4 gives the results for PBDE congeners in CLAMs from the same deployments (Era-Miller, 2014)



Figure 3. PCB Congeners in CLAM Samplers Deployed in the Spokane River.



Figure 4. Total PBDEs (pg/L) in CLAM Samplers Deployed in the Spokane River.

Table 3. Shows PCB, PBDE, metals and dioxin TEQ (toxic equivalency) results for suspended sediments near Ninemile Dam and Upriver Dam where the CLAM data was collected in 2012 (Era-Miller, 2014).

Table 3. Toxics in Suspended Sediments from Sediment Traps Deployed in the Spokane River.



ND = not detected

J = result value in an estimate

TEQ = toxic equivalency

Perhaps the best indicator of what the concentrations of PCBs in suspended sediments from the proposed monitoring site will be like relative to other locations in the Spokane River is data from the 2003-2007 Spokane River Source Assessment (Serdar et al., 2011). Figure 5 indicates that surficial sediments (top 2 cm) from behind Little Falls Dam are comparatively lower in PCBs. Results in figure 5 are normalized to organic carbon.



Figure 5. Concentrations of Total PCBs in Surficial Sediments.

Another source of data that indirectly relates to, but may also be a good indicator for toxics levels in the Spokane River downstream of Long Lake Dam is the comprehensive fish tissue study conducted by Ecology in 2012 (Seiders, et al., 2014). Largescale suckers from Little Falls Pool (the river between Long Lake Dam and Little Falls Dam) were analyzed for PCBs and PBDEs. Concentrations were lower here compared to the 5 other sampling locations, which were all upstream, including the state line with Idaho.

### 3.1.5 Regulatory criteria or standards

The main objective for this study is to generate seasonal monitoring data that can be used to indicate trends for toxics in the Spokane River over time. Data may be compared to the standards in table 4.

Table 4. Applicable Water Quality and Freshwater Sediment Standards.

|  |  |  |  |
| --- | --- | --- | --- |
| Parameter | Matrix | WA State Standardsa,b | Spokane Tribal Standardsc |
| Total PCBs | Surface  Water | 170 pg/L | 1.3 pg/L |
| PBDEs | NA | NA |
| Copper | Hardness dependant | Hardness dependant |
| Cadmium |
| Lead |
| Zinc |
| Total PCBs1 | Sediments | 110 ug/Kg dw | NA |
| PBDEs | NA |
| Dioxins/furans | NA |
| Copper | 400 mg/Kg dw |
| Cadmium | 2.1 mg/Kg dw |
| Lead | 360 mg/Kg dw |
| Zinc | 3200 mg/Kg dw |

NA = Not applicable

a WAC 173-201A

b WAC 173-204

c Spokane Tribe of Indians, 2010

1based on total Aroclors

# Project Description

Ecology will establish a long-term monitoring station for PCBs, PBDEs, dioxins/furans and metals (cadmium, copper, lead and zinc) at the upper Spokane Tribal boundary on the lower portion of the Spokane River. The Spokane River is listed as water quality impaired for PCBs and dioxins/furans. PCBs are currently being addressed through the efforts of the Spokane River Regional Toxics Task Force (SRRTTF). There is a Total Maximum Daily Load (TMDL) or Water Clean-up Plan for cadmium, lead, and zinc. There is also a fish consumption advisory for PCBs and PBDEs in the Spokane River between Idaho and Long Lake Dam.

The planned long-term monitoring location is downstream of all known sources of toxics and downstream of most of the current and ongoing toxics monitoring. The Spokane Tribal boundary represents an important compliance point for water quality standards, since there is a transition from the WA state standards to the tribal standards. Monitoring toxics here over the long-term will help to evaluate compliance with applicable water quality standards and trends over time in the Spokane River.

Ecology’s Environmental Assessment Program (EAP) will establish the long-term monitoring station. Surface water and suspended sediments will be monitored annually during the 3 major hydrologic regimes in the river: spring high flow, summer low flow, and winter moderate flow.

The Spokane River long-term station will be included in a larger effort by EAP to assess the efficacy of various types of high volume techniques for collecting low-level organics in surface water. The QA project plan for the high volume study is currently in development. Because the Spokane River long-term station will be included in this larger effort, both CLAM (continuous low-level aqueous monitoring device) and 20 liter composite samples will be analyzed for PCBs and PBDEs for the first year of monitoring. In addition, a high number of field replicates and laboratory quality control samples will be taken during the first year of monitoring.

Specifics for a high-volume validation study for low-level organics and an SOP (standard operating procedure) for the use of CLAM will be laid out in a QA Project Plan to be authored by EAP in mid 2015.

## 4.1 Project goals

Goals for the project include:

* To establish a long-term monitoring station for toxics at the Spokane Tribal Boundary. Data from the first year of monitoring at the long-term station will be used to design a long-term trend program for the site.
* Characterize toxics in surface water and suspended sediments at the monitoring station during 3 hydrologic regimes for the river: spring high flow, summer low flow and winter moderate flow.
* In addition, data from the study will be used to support the development of standard operating procedures (SOP) for use of the CLAM collection device and the proposed validation study for various high volume surface water collection techniques for low-level organics. The goal of the proposed high volume study is to characterize the precision and accuracy of different high volume collection methods for use with low level analytical methods like the EPA 1600 series methods, with special focus on PCBs.

## 4.2 Project objectives

Objectives for the project include:

* Collect and characterize surface water samples for select toxics during 3 hydrologic regimes for the Spokane River: spring high flow, summer low flow and winter moderate flow at the Spokane Tribal boundary station to evaluate seasonal variability in concentrations of target parameters.
* Collect and characterize suspended sediments for select toxics on an annual basis by having sediment traps deployed continuously for one year. Traps will be set to collect for 4 months at a time with 3 deployments each year.
* Provide high quality data to support the development of standard operating procedures (SOP) for use of the CLAM collection device and the proposed validation study for high volume surface water collection techniques.

## 4.3 Information needed and sources

River flow data from Avista, who own and operate Long Lake Dam, will be needed to calculate flux for sediment traps and useful to calculate loads for surface water toxics.

## 4.4 Target population

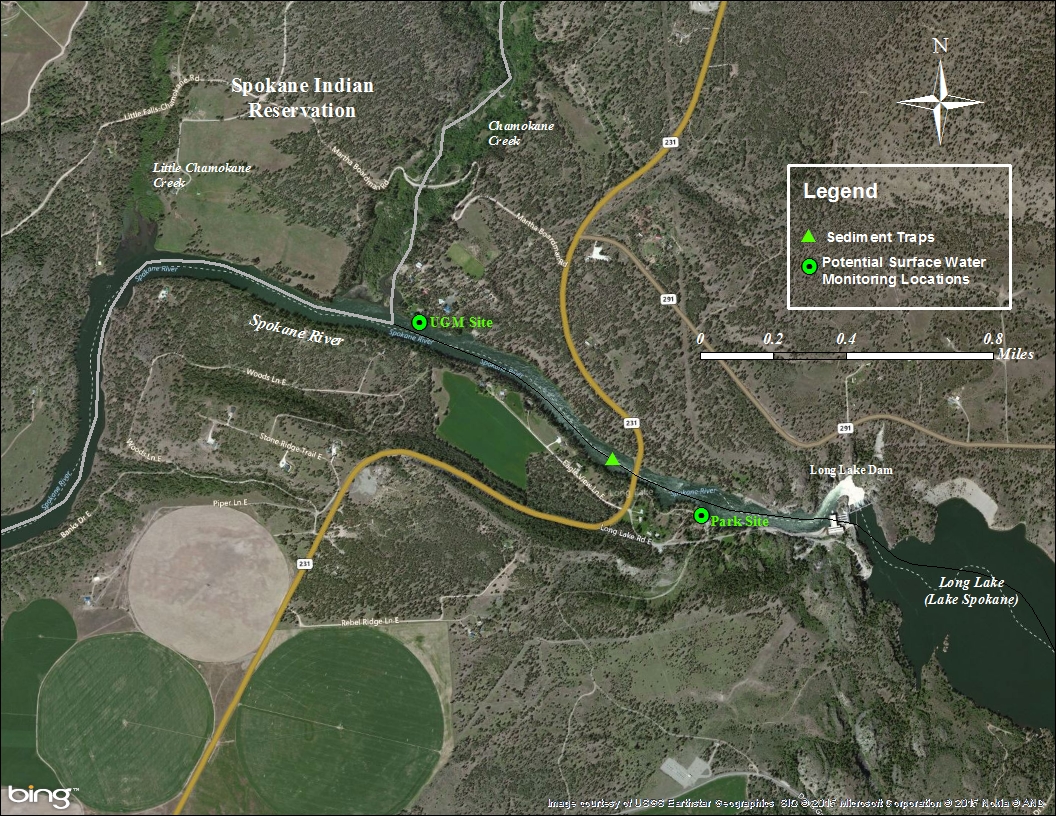
|  |  |  |
| --- | --- | --- |
| Parameter | Surface Water | Suspended Sediment |
| PCB congeners | X | X |
| PBDEs | X | X |
| Dioxin/furans |  | X |
| Metals† | X | X |

†Cadmium, copper, lead and zinc

## 4.5 Study boundaries

The study will characterize surface water conditions for select toxics in the lower Spokane River downstream of Long Lake Dam and upstream of the Spokane Tribal boundary and upstream of Chamokane Creek. See figure 1 for extent of the Spokane River Watershed boundary within Washington State and figure 6 for the proposed monitoring locations for the study.

Figure 6. Map showing boundary of project study area.



The Water Resource Inventory Area (WRIA) and 8-digit Hydrologic Unit Code (HUC) numbers for the study area are:

* WRIA 54
* HUC number 17010307

## 4.6 Tasks required

* Reconnaissance of the sampling area in late March or early April 2015 to decide whether the Park site or the UGM site will be better for surface water collection.
* Submit a bid solicitation by mid March 2015 for the toxics analyses to be conducted by contract laboratory.
* Work in tandem with other Ecology studies including the proposed validation study for high volume collection methods to maximize efficiencies with Quality Assurance/Quality Control (QA/QC) samples and purchasing of equipment.
* Purchase and acquire equipment needed for surface water and suspended sediment monitoring.
* Prepare all materials needed for sampling (e.g., special cleaning for low-level toxics, bottles, labels, and paperwork).

## 4.7 Practical constraints

Practical constraints for this project mostly revolve around high-flow/low-flow sampling issues for both surface water and suspended sediments. Reconnaissance of the sampling area in late March or early April 2015 and obtaining flow information from Long Lake Dam through Avista Utilities should help to better inform sampling and avoid potential problems.

## 4.8 Systematic planning process

Not Applicable

# Organization and Schedule

## 5.1 Key individuals and their responsibilities

Table 5. Organization of project staff and responsibilities.

| Staff  (all are 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  Toxics Studies Unit  Statewide Coordination Section  Phone: 360-407-6771 | Project Manager/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. |
| William Hobbs  Toxics Studies Unit  Statewide Coordination Section  Phone: 360-407-7512 | Field and Project Assistant – QAPP Peer Review | Reviews QAPP; Provides input on project use of high volume sample collection for low –level organics and will Help collect samples and record field information. |
| Melissa McCall  Toxics Studies Unit  Statewide Coordination Section  Phone: 360-407-7384 | Field Assistant | Helps collect samples and records field information. |
| Dale Norton  Toxics Studies Unit  Statewide Coordination Section  Phone: 360-407-6765 | Unit Supervisor for the Project Manager | Provides internal review of the QAPP, approves the budget, and approves the final QAPP. |
| Will Kendra  Statewide Coordination 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. |
| Thomas Mackie  Eastern Operations Section  Phone: 509-457-7136 | Section Manager for the Study Area | Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP. |
| Joel Bird  Manchester Environmental Laboratory  Phone: 360-871-8801 | Director | Reviews and approves the final QAPP. |
| Contract Laboratory | Project Manager | Reviews draft QAPP, coordinates with MEL QA Coordinator |
| William R. Kammin  Phone: 360-407-6964 | Ecology Quality Assurance  Officer | Reviews and approves the draft QAPP and the final QAPP. |

EAP: Environmental Assessment Program

EIM: Environmental Information Management database

QAPP: Quality Assurance Project Plan

## 5.2 Special training and certifications

The project lead, Brandee Era-Miller, has almost 15 years of experience conducting toxics studies and writing reports for Ecology’s EA Program Toxics Studies Unit.

## 5.3 Organization chart

Not Applicable

## 5.4 Project schedule

A schedule of field work for the project is shown in Table 6. The first surface water sampling (using both CLAM collection device and 20 liter composite samples) will occur in early May 2015 and again in August 2015 and January 2016. Sediment traps will be deployed continuously for collection of suspended sediments for a year. Traps will be retrieved, sampled, and collection cylinders re-placed every 4 months. The first deployment is slated for April 2015. The long term plan is for this schedule of sampling to occur on an annual basis.

Table 6. Schedule of Field Activities for the Project.



\*surface water sampling will occur over a 24-36 hour period

Table 7. 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 | March 2016 | Brandee Era-Miller |
| Laboratory analyses completed | June 2016 | |
| Environmental Information System (EIM) database | |  |
| EIM Study ID | BERA0012 | |
| Product | Due date | Lead staff |
| EIM data loaded | September 2016 | Brandee Era-Miller |
| EIM data entry review | October 2016 | Melissa McCall |
| EIM complete | November 2016 | Brandee Era-Miller |
| Final report | |  |
| Author lead / Support staff | Brandee Era-Miller | |
| Schedule | | |
| Draft due to supervisor | August 2016 | |
| Draft due to client/peer reviewer | September 2016 | |
| Draft due to external reviewer(s) | October 2016 | |
| Final (all reviews done) due to publications coordinator (Joan) | November 2016 | |
| Final report due on web | December 2016 | |

## 5.5 Limitations on schedule

Reserving sample collection equipment such as a Hydrolab, CLAM devices, sediment traps and a boat (for sediment trap deployment) will need to be considered for scheduling. Availability of field staff to assist in field work will also need to be considered.

All EAP staff, including the project manager, are current on their first Aid/CPR, defensive driving and EAP-specific safety training. The following sections from EAP’s Safety Manual (EAP, 2014) are relevant to this project and will be reviewed by staff prior to conducting field work:

* Chemical Use in EAP Specialized Rooms
* Working in Rivers and Streams
* Winter Safety/Hypothermia
* Preventing Heat-Related Injuries
* Towing Trailers
* EAP Boating Plan
* Operating 16’ Wooldridge Jet Boat

## 5.6 Budget and funding

The cost for the first year of toxics monitoring in the Spokane River at the Spokane Tribal Border is **$72,273** (table 8). The budget is further detailed in tables 9 – 10.

Table 8. Cost for Year 1 of Toxics Monitoring at the Spokane Tribal Border.



Surface water sampling conducted in May of 2015 will be covered by funds from fiscal year 2015 (FY15) as shown in table 9. The rest of the project work will be covered from funds in fiscal year 2016, which starts July 1, 2015 (tables 10 – 11).

Table 9. Budget for Surface Water Sampling in May 2015.



The budget for surface water samples collected in August 2015 and January 2016 is shown in Table 10. The items highlighted in yellow will be covered by the Spokane River Long-Term Monitoring Station project and the gray highlighted items will be covered by the high volume validation study for low-level organics (QA project plan in draft).

Table 11 gives the annual (3 deployments of 4 months each) budget for analysis of the suspended sediment samples collected with sediment traps.

Table 10. Budget for Surface Water Sampling in August 2015 and January 2016.



Table 11. Budget for Analysis of Suspended Sediments.



# Quality Objectives

## 6.1 Decision Quality Objectives (DQOs)

Quality objectives for this project are to obtain data of sufficient quality to minimize uncertainty. For monitoring using continuous low-level aquatic monitoring (CLAM) samplers and 20 liter surface water samples, the objective is to produce enough field duplicate data and laboratory quality assurance and quality control (QA/QC) data to assist in efforts to evaluate the precision and accuracy of these collection methods and analytical methods. This will be a major objective of the proposed high volume validation study for which the 1st year of monitoring data from the Spokane Tribal boundary site will be included. Precision and accuracy information will be used to inform the development of a long-term monitoring program to evaluate trends in select toxics at the Spokane Tribal boundary site.

Ecology’s Manchester Environmental Laboratory (MEL) and laboratories contracted by MEL for analysis of project samples are expected to meet the measurement quality objectives (MQOs) selected for the project. The MQOs that will be used for the project are shown in table 12.

## 6.2 Measurement Quality Objectives

Table 12. Measurement Quality Objectives for the Study.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Parameter | Analytical Method | Lab Control Samples  (% Recovery) | Duplicate Samples (RPD) | Matrix  Spike  (% Recovery) | Matrix Spike Duplicates (RPD) | Surrogate Recoveries  (% Recovery) |
| *Surface Water (20 Liter, 1 gallon and grabs)* | | | | | | |
| TOC & DOC | SM 5310B | 80 – 120 | ≤20% | 75 – 125 | ≤20% | NA |
| TSS | SM 2540D | 80 – 120 | ≤20% | NA | NA | NA |
| TNVSS | SM 2540B/E | 80 – 120 | ≤20% | NA | NA | NA |
| Hardness\* | SM 2340B | 85 – 115 | ≤20% | 75 – 125 | ≤20% | NA |
| Cd, Cu, Pb, & Zn\* | EPA 200.8 | 85 – 115 | ≤20% | 75 – 125 | ≤20% | NA |
| PCBs | EPA 1668c | 50 – 150† | ≤50% | NA | NA | 25 – 150a |
| PBDEs | EPA 1614 | 50 – 150† | ≤50% | NA | NA | 25 – 150a,b |
| *Surface Water (CLAM)* | | | | | | |
| PCBs | EPA 1668c | 50 – 150† | ≤50% | NA | NA | 25 – 150a |
| PBDEs | EPA 1614 | 50 – 150† | ≤50% | NA | NA | 25 – 150a,b |
| *Suspended Sediments* | | | | | | |
| % Solids | SM 2540G | NA | ≤20% | NA | NA | NA |
| TOC | PSEP – TOC | 80 – 120 | ≤20% | NA | NA | NA |
| Cd, Cu, Pb, & Zn | EPA 200.7 | 85 – 115 | ≤20% | 75 – 125 | ≤20% | NA |
| PCBs | EPA 1668c | 50 – 150† | ≤50% | NA | NA | 25 – 150a |
| PBDEs | EPA 1614 | 50 – 150† | ≤50% | NA | NA | 25 – 150a,b |
| Dioxins/furans | EPA 1613 | 25 – 150† | ≤50% | NA | NA | 25 – 150a |

\* hardness and metals collected as single grab samples

† Per Method for Ongoing Precision and Recovery (OPR), internal standards, and labeled compounds

a labeled congeners

b PBDE 209 recovery of 20 – 200%

CLAM: Continuous Low-Level Aquatic Monitoring device

EPA: the Environmental Protection Agency

SM: Standard Methods

PSEP: Puget Sound Estuary Protocols

RPD: relative percent difference

TOC: total organic carbon

TSS: total suspended solids

TNVSS: total non-volatile suspended solids

DOC: dissolved organic carbon

Cd: cadmium; Cu: copper; Pb: lead; and Zn: zinc

### 6.2.1 Targets for Precision, Bias, and Sensitivity

#### 6.2.1.1 Precision

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

Measurement quality objectives for the precision of laboratory duplicate samples and matrix spike duplicate samples are shown in table 12. PCBs and PBDEs in both the 20 liter and CLAM surface water samples will be analyzed as field triplicates during the May 2015 sampling. Acceptance limits for field precision of these samples is ≤20 RSD. CLAMs deployed in triplicate in the Spokane River in 2012 were 11% and 14% for total PCBs and 9% and 19% for total PBDEs (Era-Miller, 2014).

#### 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 control samples (LCS), matrix spikes and surrogates are shown in table 12. Calibration of field instruments will also reduce the bias of field measurements.

#### 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. The laboratory reporting limits (RLs) for the project are described in Section 9.2.

### 6.2.2 Targets for Comparability, Representativeness, and Completeness

#### 6.2.2.1 Comparability

Section 8.1 lists the standardized operating procedures (SOPs) to be followed for field sampling. Appendix B gives a summary of the field and laboratory procedures used by EAP for sample collection using CLAMs. All analytical methods used for the project are approved methods commonly used by Ecology and other entities in the Spokane River watershed for monitoring of toxics.

#### 6.2.2.2 Representativeness

Surface water and suspended sediment samples will be collected during the 3 major flow regimes of the Spokane River: spring high flow, summer low flow and winter moderate flow. Surface water samples will cover a 24 – 36 hour period giving a better temporal average than with a single grab sampling event. Sediment traps will be deployed, retrieved and analyzed during each of the 3 flow regimes, but will be present in the river year round such that results can be averaged to represent annual conditions.

#### 6.2.2.3 Completeness

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

# Sampling Process Design (Experimental Design)

## 7.1 Study Design

PCBs, PBDEs, dioxins/furans and metals are contaminants of concern (COCs) for the Spokane River. Clean-up activities and monitoring for these COCs is ongoing, but has mostly been focused to areas upstream of the Lake Spokane Dam. This project will focus on establishing a long-term monitoring station for COCs downstream of Lake Spokane near the upper Spokane Tribal boundary.

Ecology’s Environmental Assessment Program (EAP) will establish the long-term monitoring station. Surface water and suspended sediments will be monitored for COCs during the 3 major hydrologic regimes annually for the river: spring high flow, summer low flow, and winter moderate flow. The monitoring schedule is shown in table 6 and discussed in Section 5.4.

The first year of monitoring for the Spokane River long-term station will be included in a larger effort by EAP to assess the precision and accuracy of various types of high volume techniques for collecting low-level organics in surface water with a special focus on PCBs. The QA project plan for the high volume collection techniques study is currently under development. Because the Spokane River long-term station will be included in this larger effort, both CLAM (continuous low-level aqueous monitoring device) and 20 liter composite samples will be used to measure for PCBs and PBDEs for the first year of monitoring. In subsequent years, surface water monitoring at the long-term station will likely focus on a single high volume collection method such as the CLAM that can be used to evaluate trends in the Spokane River.

A higher number of field replicate samples and laboratory quality assurance/quality control (QA/QC) samples will be analyzed during the first year of monitoring, especially for PCBs. Fewer QA/QC samples should be needed for all COCs in subsequent years because questions around the precision and accuracy of the chosen high volume collection technique will have been addressed through the efforts of both the first year of monitoring for the long-term station as well as through the high volume collection methods validation study.

High resolution methods will be used to analyze for PCBs (EPA 1668c), PBDEs (EPA 1614) in surface water and suspended sediments. Suspended sediments will also be analyzed for dioxins and furans (EPA 1613b). These high resolution methods allow for the lowest detection limits available as well as providing detection for as many of the 209 congeners as possible for both PCBs and PBDEs. Having full congener data gives more information and allows for future “finger-printing” and source tracing efforts. Much of the recent monitoring conducted by The SRRTTF and others in the Spokane River watershed includes the use of EPA 1668c for measuring PCBs.

### 7.1.1 Field measurements

Surface water measurements will be taken at the same time as surface water samples. A MiniSonde hydrolab will be used to collect the following parameters:

* Temperature
* pH
* Conductivity
* Dissolved Oxygen

The starting and ending flow rates for the CLAM samplers will be recorded. These volumetric measurements are used to estimate the total volume of water sampled by the CLAMs. A totalizer from the CLAM manufacturer will also used to get a more accurate recording of the total volume sampled. More information on the use of CLAMs in the field is available in Appendix B.

### 7.1.2 Sampling location and frequency

Surface water sampling will occur at either the Avista Park site on the south bank of the river or the UGM site on the north side of the river upstream of the Chamokane River confluence with the Spokane River (figure 6). The UGM site is the first choice for sampling due to its location just upstream of the upper Spokane Tribal border, because it’s the location where the Spokane Tribe takes water measurements with their hydrolab and it may have better security than at the Park site. Sediment traps will be deployed in the slack water area downstream of the highway 231 bridge (figure 6).

The flow regime for the Spokane River falls into 3 major hydrologic regimes: 1) spring high flow, 2) summer base or low flow and 3) winter moderate flow. Figure 2 shows the historical flow regime for the river. Surface water and suspended sediment sampling will occur during each of the 3 major river conditions.

The sampling schedule for the project is shown in table 6. The first surface water sampling (using both CLAM collection device and 20 liter composite samples) will occur in early May 2015 and again in August 2015 and January 2016. Sediment traps for collection suspended sediment will be deployed 3 times a year for 4 months at a time. The first deployment is slated for late April 2015. The long term plan is for this schedule of sampling to occur on an annual basis.

### 7.1.3 Parameters to be determined

* Surface Water
  + DOC
  + TOC
  + TNVSS
  + TSS
  + Hardness
  + Cadmium, copper, lead and zinc (low-level)
  + PCB congeners
  + PBDEs
* SuspendedSediments
  + Percent solids
  + TOC
  + Cadmium, copper, lead and zinc
  + PCB congeners
  + PBDEs
  + Dioxins and furans

## 7.2 Maps or diagram

A map of the Washington portion of the Spokane River Watershed is shown in Figure 1. A map with the proposed sampling locations is shown in Figure 6. Surface water sampling will occur at either the Avista Park site on south bank of the river or the UGM site on the north side of the river above the Chamokane River confluence with the Spokane River.

## 7.3 Assumptions underlying design

There is an assumption that with using high-volume collection methods and low-level analyses, that PCBs and PBDEs will be detected at the required reporting limits for the project = 1.0 (for PCBs) and 10 – 100 (for PBDEs) pg absolute per extract of 20 or more liters of surface water.

There is also an assumption that sediment traps will work in the section of Spokane River between Long Lake Dam and the Spokane Tribal border. Depth and current are major factors for successful deployment and retrieval of sediment traps.

## 7.4 Relation to objectives and site characteristics

Not applicable

## 7.5 Characteristics of existing data

There is a lack of surface water and sediment data for toxics for the section of river to be monitored in this study. Recent fish tissue data (2012) suggests that concentrations of PCBs, PBDEs and dioxins and furans near the study site are low compared to areas sampled upstream (Seiders, et al., 2014).

# Sampling Procedures

**Surface Water Monitoring**

CLAMs will be deployed for 24-36 hours at the long-term station. Including replicates, there will be 4 CLAMs deployed during each sampling event. At deployment and again at retrieval, half the amount of surface water for the 20 liter samples (~10 liters) will be collected and transferred into clean 20 liter carboys in order to complete a composite sample for the PCBs and PBDEs. For the DOC, TOC, TSS, and TNVSS samples, water will be composited into a clean 1 gallon jar for later transfer into the appropriate sample bottles. The hardness and metals samples will be conducted as grab samples and will be collected once at deployment and then sampled a second time at retrieval. See table 13.

Table 13. Surface Water Collection Methods.



As described in the SOP EAP003 – *Sampling of Pesticides in Surface Waters, Version 2.1* (Anderson, 2012), clean jars will be used for compositing into the 20 liter and 1 gallon jars. Compositing jars will be acquired from the laboratories. Proof of cleanliness of the compositing jars and 20 liter carboys for analysis of PCBs and PBDEs will be required by the contract laboratory.

Figure 6 shows the types and numbers of prefilters and SPE disks to be used for CLAM and 20 liter samples. There will be 2 CLAM replicates with a prefilter disk designed to capture solids ≥1.5 microns followed by 1 SPE disk. Prefilters will not be analyzed for PCBs and PBDEs. In addition, there will 2 CLAM replicates with 2 SPE disks each that will be analyzed for PCBs and PBDEs. The first SPE disk in this series will be spiked with a field spiking solution and the second disk will not have the field spiking solution. Analysis of both of these SPE disks in the CLAM will allow for an assessment of breakthrough or wash-off of the field spiked labeled compounds and the native PCBs and PBDEs. The field spiking solution will consist of the following labeled compounds: 13C-PCB-31, 13C-PCB-95, 13C-PCB-153 and 13C12-2,2’,3,4,4’,6-HxBDE.

The 20 liter samples will be filtered and extracted at the contract laboratory using the same SPE disks as with the CLAM samples. These SPEs will also be spiked with the field spiking solution.

Deployment and retrieval methods for the CLAM are described in detail in Appendix B.



Figure 7. CLAM Deployment Set-up.

**Sediment Traps**

Sediment traps will be deployed in duplicate at the long-term monitoring station. Each trap holds 2 collection cylinders, for a total of 4 cylinders in each reservoir. Deploying 2 traps has several benefits:

* With low sediment rates, more cylinders means more material can be collected.
* There is a back-up sampler in case something happens to one of the traps.
* Coverage in 2 locations can be more representative as hydrology can vary even in short distances.

The sediment trap cylinders will be swapped out after 4 months of deployment. New cylinders will then be deployed for another 4 months. This will allow for sedimentation rates to be calculated for 3 separate 4-month deployment periods and characterized on an annual basis.

The EAP’s standard sediment trap deployment method for reservoirs and deep water is to suspend a trap in the middle of the water column with an anchor, snag line, and hardball float. This method is described in detail in Norton (1996) and a schematic of the sediment trap design and deployment configuration is displayed in Figure 7. The hardball float sits 6 feet below the water surface so that it can stay taut with fluctuating water levels and so it’s not disturbed by vessel traffic or floating debris. The trap is then retrieved by dragging a hook to grab the snag line underwater.

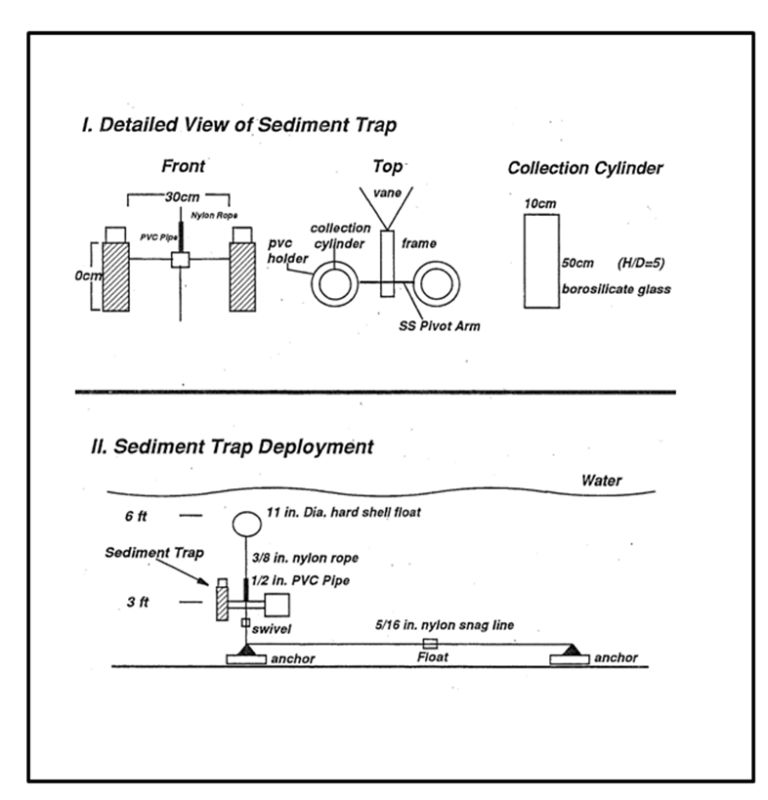


Figure 8. Schematic of Sediment Trap Design and Deployment Configuration (Norton, 1996).

Each sediment trap holds two glass collection cylinders each with a collection area of 78.5 cm2 and a height-to-width ratio of 5. This same type of trap was successfully used in the Spokane River at Upriver Dam and Ninemile Dam in the fall of 2012 (Era-Miller, 2014).

Before deployment, cylinders will be cleaned with Liquinox soap and hot water, followed by 10% nitric acid, and then rinsed with deionized water. Cylinders will then be rinsed with pesticide-grade acetone and finally hexane. This procedure is covered in more detail in SOP EAP090 – *Decontaminating Field Equipment for Sampling Toxics in the Environment* (Friese, 2014). During transport to the field, the tops of each cylinder will be covered with clean aluminum foil.

At deployment, the cylinders are filled partway with high salinity water (4% sodium chloride – NaCl), which contains mercuric chloride (HgCl) as a preservative to reduce microbial degradation of the samples.

## 8.1 Field measurement and field sampling SOPs

The following Ecology Standard Operating Procedures (SOPs) will be used for this project:

* EAP003 – *Sampling of Pesticides in Surface Waters, Version 2.1* (Anderson, 2012).
* EAP015 – *Manually Obtaining Surface Water Samples, Version1.2* (Joy, 2013).
* EAP029 – *Collection and Field Processing of Metals Samples, Version 1.5* (Ward, 2015).
* EAP033 – *Hydrolab® DataSonde® and MiniSonde® Multiprobes, Version 1.0* (Swanson, 2007).
* EAP070 – *Minimizing the Spread of Invasive Species* (Parsons et al., 2012).
* EAP090 – *Decontaminating Field Equipment for Sampling Toxics in the Environment* (Friese, 2014).

## 8.2 Containers, preservation methods, holding times

Sampling containers, preservation, and holding times are shown in table 14. Information for analyses being conducted at MEL was adapted from the Manchester Laboratory User’s Manual and through conversations with MEL and the contract laboratories (MEL, 2008).

Table 14. Sample Containers, Preservation, and Holding Times.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Parameter** | **Matrix** | **Container** | **Preservation** | **Holding Time** |
| DOC | Surface Water  (20 L, 1 gallon and grabs) | 60 mL poly bottle;  0.45 um pore size filters | Filter in field with 0.45um pore size filter; 1:1 HCl to pH<2;Cool to 6°C | 28 days |
| TOC | 60 mL poly bottle | 1:1 HCl to pH<2; Cool to 6°C |
| TNVSS | 1 L poly bottle | Cool to 6°C | 7 days |
| Hardness\* | taken from the total metals sample bottle | HNO3 to pH<2 by the lab within 24 hours of collection | 6 months after  preservation |
| Metals: Cu, Cd, Pb & Zn\* | 500 mL  HDPE bottle | Field filter for dissolved; HNO3 to pH<2 by the lab within 14 days of collection | 6 months after  preservation |
| PCB congeners | 20 L carboy or canister | Cool to 6°C | 1 year |
| PBDEs |
| PCB congeners | Surface Water (CLAM) | The self-contained C-18 SPE disks are placed in amber plastic bags provided by the manufacturer | Cool to 6°C | 14 days |
| PBDEs |
| Percent Solids | Suspended Sediments | From same jar as particulate organics (4-oz jar) | Cool to 6°C | 7 days or 6 months frozen |
| TOC | Certified 2-oz amber glass w/ Teflon lid liner | 14 days or 6 months frozen |
| Cu, Cd, Pb & Zn | Certified 4-oz amber glass w/ Teflon lid liner | Transport at 6°C; can store frozen at -18°C | 6 months or 2 years frozen |
| PCB congeners | 1 year extraction; 1 year analysis |
| PBDEs |
| Dioxins/furans |

\* Hardness and metals collected as grab samples

## 8.3 Invasive species evaluation

Field personnel for this project are required to be familiar with and follow the procedures described in SOP EAP070, *Minimizing the Spread of Invasive Species*.

The Spokane River Watershed is considered to be an area of moderate concern. Because all monitoring for the project will occur in the same stream segment, chances of carrying aquatic invasive Species (AIS) from one part of the basin to another will be greatly reduced.

## 8.4 Equipment decontamination

Glass cylinders used in the sediment traps will be cleaned according to Ecology’s SOP EAP090, *Decontamination of Sampling Equipment for Use in Collecting Toxic Chemical Samples*. Before deployment, cylinders will be cleaned with Liquinox soap and hot water, followed by 10% nitric acid, and then rinsed with deionized water. Cylinders will then be rinsed with pesticide-grade acetone and finally hexane. During transport to the field, the tops of each cylinder will be covered with clean aluminum foil.

Proof of cleanliness of the compositing jars and 20 liter carboys for analysis of PCBs and PBDEs will be required by the contract laboratory.

CLAMs are clean and ready for use when they arrive from the contractor. Surface water is filtered through single-use SPE disks that are specifically cleaned as part of the conditioning process by the contract laboratory.

## 8.5 Sample ID

Sample numbers will be assigned by MEL by way of a work order number for each monitoring event. Sample numbers will follow chronologically after the work order number (e.g., 1501027 -1, 1501027 -2, etc.). Sample IDs will be assigned by the project manager for each sampling event prior to collection.

## 8.6 Chain-of-custody, if required

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

Not Applicable. Necessary activities are detailed in other sections of this QA Project Plan.

# Measurement Methods

## 9.1 Field procedures table/field analysis table

Field data will be measured using a MiniSonde® multi-meter following guidance in SOP EAP033 – Hydrolab® DataSonde® and MiniSonde® Multiprobes, Version 1.0 (Swanson, 2007).

Field parameters for the project include:

* Temperature
* pH
* Conductivity
* Dissolved Oxygen

## 9.2 Lab procedures table

Table 15. Laboratory Methods and Sample Information.



†reporting limit for BDE 209 is 200 pg per sample

\* based on a 10 gram sample

UOM = unit of measurement

PSEP = Puget Sound Estuary Program

SM = Standard Methods

### 9.2.1 Analyte

* DOC
* TOC
* Hardness
* TNVSS
* TSS
* Percent Solids
* Metals (cadmium, copper, lead and zinc)
* PCB congeners
* PBDEs
* Dioxin and furans

### Matrix

* Surface water
  + collected via 20 liter or 1 gallon compositing
  + collected via CLAM
  + collected as single grab samples (metals only)
* Suspended sediments

### 9.2.3 Number of samples

See table 15.

### 9.2.4 Expected range of results

See table 15.

### 9.2.5 Analytical method

See table 15.

### 9.2.6 Sensitivity/Method Detection Limit (MDL)

For the EPA 1600 series methods for PCBs, PBDEs and dioxin/furans, the reporting limits shown in Table 15, are the estimated detection limits (EDLs). The reporting limits shown for the rest of parameters are the MDLs as reported by MEL.

## 9.3 Sample preparation method(s)

For the EPA 1600 series methods for PCBs, PBDEs and dioxin/furans, the preparation and extraction methods are described in the analytical methods, however, for the CLAM and 20 liter surface water samples, the same type of SPE disk will be used during extraction. More information on the specifics of CLAM SPE extraction can be found in Appendix B.

## 9.4 Special method requirements

The use of CLAM and 20 liters for surface water sample collection for low-level analysis will require special coordination with the contract laboratory. The project manager, Karin Fedderson from MEL, who manages and reviews contracts with the contract laboratories, and Brent Hepner (from C.I.Agent – the CLAM manufacturer) will have a conference call with contract laboratory conducting the high resolution methods for the CLAM and 20 liter water samples shortly after the bid for the laboratory analysis is awarded. The purpose of the meeting will be to discuss specific methods for SPE disk conditioning, field spiking and eluting as well logistics for collection and transport of the 20 liter samples.

## 9.5 Lab(s) accredited for method(s)

All laboratories for the project will be accredited and all the analyses will be standard published methods.

# Quality Control (QC) Procedures

## 10.1 Table of field and lab QC required

Table 16. Field and Laboratory QC Samples.

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Parameter | Lab Control Sample | Method Blank | Surrogate Recoveries | OPR Standards | MS/  MSD | Lab Duplicate Analysis | Field Duplicate Analysis | Filter Blank | Travel Blank | Field Transfer Blank |
| *20 Liter, 1 gallon and grabs* | | | | | | | | | | |
| DOC & TOC | 1/batch | 1/batch | **--** | **--** | 1/batch | 1/batch | 1/batch | **--** | **--** | 1/batch |
| TSS & TNVSS | 1/batch | 1/batch | **--** | **--** | **--** | 1/batch | 1/batch | **--** | **--** | 1/batch |
| Hardness | 1/batch | 1/batch | **--** | **--** | 1/batch | 1/batch | 1/batch | **--** | **--** | 1/batch |
| Metals† | 1/batch | 1/batch | **--** | **--** | 1/batch | 2/batch | 1/batch | 1/batch | **--** | 1/batch |
| PCBs | 1/batch | 1/batch | all samples | all samples | **--** | **--** | 1/batch | 1/batch\* | 1/batch | 1/batch |
| PBDEs | 1/batch | 1/batch | all samples | all samples | **--** | **--** | 1/batch | 1/batch\* | 1/batch | 1/batch |
| *CLAM* | | | | | | | | | | |
| PCBs | 1/batch | 1/batch | all samples | all samples | **--** | **--** | 1/batch | 1/batch\* | **--** | 1/batch |
| PBDEs | 1/batch | 1/batch | all samples | all samples | **--** | **--** | 1/batch | 1/batch\* | **--** | 1/batch |
| *Suspended Sediments* | | | | | | | | | | |
| TOC | 1/batch | 1/batch | **--** | **--** | 1/batch | 1/batch | 1/batch | **--** | **--** | **--** |
| Metals | 1/batch | 1/batch | **--** | **--** | 1/batch | 1/batch | 1/batch | **--** | **--** | **--** |
| PCBs | 1/batch | 1/batch | all samples | all samples | **--** | 1/batch | 1/batch | **--** | **--** | **--** |
| PBDEs | 1/batch | 1/batch | all samples | all samples | **--** | 1/batch | 1/batch | **--** | **--** | **--** |
| Dioxins/furans | 1/batch | 1/batch | all samples | all samples | **--** | 1/batch | 1/batch | **--** | **--** | **--** |

Batch: One sampling event (3/yr)

OPR: Ongoing Precision and Recovery

MS/MSD: Matrix Spike and Matrix Spike Recovery

† Field duplicate and transfer blank will be conducted on the total sample; filter blank conducted on the dissolved sample; and the laboratory duplicate analysis will be conducted on both.

\*Filter blanks for 20 liter and CLAM samples will consist of analysis of a clean SPE disks in the laboratory.

The QC samples shown in table 16 have MQOs associated with them as described in Section 6.2. These criteria must be met to obtain fully usable data.

## 10.2 Corrective action processes

The laboratory analysts will document whether or not 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 and also in the final report for the project.

In order to not split the surface water sample extracts and raise reporting limits, archive samples will not be saved for the May 2015 sampling event. If a significant number of analytical results fall outside established MQOs then the laboratory analyst and the project manager will decide what changes will need to occur for the surface water sampling events in August and January so that QC criteria are met. Sediment samples will be archived in the event that re-analysis is needed.

# Data Management Procedures

## 11.1 Data recording/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 for creating data tables and figures and for basic statistical analysis.

## 11.2 Laboratory data package requirements

MEL’s standard data deliverable package will be adequate for this project and the data deliverables required by the contract laboratory will be detailed in the bid solicitation for the contract laboratory work.

## 11.3 Electronic transfer requirements

MEL has an EDD (electronic data deliverable) that is compatible with EIM data requirements and that will meet the requirements of this project. The contract laboratory will also have an EDD that meets the requirements of this project. These requirements will be detailed in the bid solicitation for the contract laboratory work.

## 11.4 Acceptance criteria for existing data

All existing data is stored in EIM and as such is acceptable for use as described under the data quality descriptions in EIM.

## 11.5 EIM/STORET data upload procedures

All completed project data will be entered into Ecology’s Environmental Information Management (EIM) database for availability to the public and interested parties, with the exception of the surface water data generated using CLAM. CLAM is still in the developmental phase and until standard operating procedures have been approved for the CLAM, data will not be entered into EIM.

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

EIM can be accessed on Ecology’s Internet homepage at www.ecy.wa.gov. The project will be searchable under Study ID BERA0012.

# Audits and Reports

## 12.1 Number, frequency, type, and schedule of audits

MEL participates in performance and system audits of their routine procedures. The results of these audits are available on request. The contract laboratories are also routinely audited as part of their internal procedures and as part of their accreditation.

## 12.2 Responsible personnel

MEL chemists and the project manager will be responsible for review of the data packages. The quality assurance officer for MEL, Karin Feddersen, will carry out the review of the contract laboratory data packages.

## 12.3 Frequency and distribution of report

A stand-alone report will be written after the first year of data is collected and analyzed for this project. However, it is anticipated that monitoring will continue in subsequent years to evaluate long-term trends.

After the client for the project, Ecology Eastern Regional Office Water Quality Program (ERO WQP) has reviewed the draft report, it will go out for review by the Spokane River Regional Toxics Task Force (SRRTTF) and Spokane Tribe of Indians.

## 12.4 Responsibility for reports

Brandee Era-Miller, project manager and principal investigator, will write a final stand-alone report for the first year of monitoring at the Spokane River long-term station. Data from the first year of monitoring at the long-term station will also be included in a larger report assessing various high-volume surface water collection techniques for low-level organics. This report will be written by William Hobbs from EAP and published in 2017. In addition, data from the first year of monitoring at the long-term station will be used to help develop a standard operating procedure (SOP) for use of CLAM samplers by EAP. Michael Friese from EAP will write the SOP.

# Data Verification

## 13.1 Field data verification, requirements, and responsibilities

Data verification for all field generated data will be conducted by the project manager.

## 13.2 Lab data verification

Data verification for all laboratory data will be conducted by the project manager. Karin Fedderson, the quality assurance officer at MEL, will review and verify data from the contract laboratories.

## 13.3 Validation requirements, if necessary

Third party data validation will not be required for this project.

# Data Quality (Usability) Assessment

## 14.1 Process for determining whether project objectives have been met

The project manager will determine if the project data is useable by assessing whether or not the data has met the MQOs outlined in table 12. Based on this assessment, the data will either be accepted, accepted with appropriate qualifications, or rejected and re-analysis considered.

## 14.2 Data analysis and presentation methods

Not applicable.

## 14.3 Treatment of non-detects

Non-detected data (data with a “U” or “UJ” flag designated by the lab) will not be used for summation of total results, homologue groups or for calculation of Toxic Equivalencies (TEQs) for dioxins and furans.

For summing of totals, non-detected results will be assigned a value of zero. If only non-detected results comprise a total value, then the final total result was simply reported as “ND” for not detected. Sample totals will be assigned a qualifier of “J” (estimated) if more than 10% of the result concentrations are composed of results containing “J” qualifiers.

*Data Qualifier Definitions:*

U The analyte was not detected at or above the reported sample quantitation limit.

UJ The analyte was not detected at or above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately measure the analyte in the sample.

J The analyte was positively identified; the associated numerical value is the approximate

concentration of the analyte in the sample.

NJ The analyte has been “tentatively identified” and the associated numerical value represents its approximate concentration.

ND Not Detected.

### Censoring for Method Blank Contamination

For high resolution methods (EPA 1600 series for PCBs, PBDEs and dioxins/furans), individual congener results will be considered non-detects (“U” or “UJ”) if the concentrations are less than 3 times the concentration of the associated laboratory method blanks. The result values (qualified as non-detects) will then be reported at the estimated quantitation limit (EQL) or at the level of detection, whichever is higher.

### Censoring for Tentatively Identified Analytes

Results for the high resolution methods that do not meet the isotopic abundance ratio and retention time criteria for positive identification will be qualified by MEL with an “NJ” and considered to be tentatively identified. For reporting purposes, the project manager will censor all “NJ” qualified data by assigning a qualifier of “UJ” and using a result value at the estimated quantitation limit (EQL) or at the level of detection, whichever is higher.

## 14.4 Sampling design evaluation

Sampling and collection methods for the project are designed to be time integrated such that seasonal averages will be possible to determine. If the project as currently designed yields acceptable data then it can be used to characterize 1 year of seasonal toxics data for the monitoring site. Several more years of data will be needed to accurately determine long-term trends at the monitoring site.

## 14.5 Documentation of assessment

This will occur in the final report.

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# Figures

The figures in this QAPP are inserted after they’re first mentioned in the text.

# Tables

The tables in this QAPP are inserted after they’re first mentioned in the text.

# Appendices

## Appendix A. 303(d) Listings for Toxics in the Spokane River

Table A-1 shows all the water quality impairments and waters of concern for toxics parameters in the mainstem Spokane River including Lake Spokane. Not shown in table A-1 are the listings for category 1 (meets tested criteria) and category 3 (insufficient data). Table A-2 gives the definitions for all the categories (1–5).

Table A-1. 303(d) Listings for Toxic Parameters in the Spokane River.



\*Proposed category is draft and subject to change. The proposed listings are currently undergoing public review and will require EPA approval before finalization.

Table A-2. State Water Quality Assessment Categories (Ecology, 2012)

|  |  |
| --- | --- |
| Not impaired, or not known to be impaired | |
| Category 1. Meets Tested Criteria | EPA approval and TMDL not required |
| Category 2. Water of Concern |
| Category 3. Insufficient Data |
| Impaired | |
| Category 4. Impaired But Does Not Require a TMDL because  4a. Has a TMDL approved by EPA  4b. Has a Pollution Control Plan  4c. Impaired by a Non-Pollutant | EPA approval and TMDL not required |
| Category 5. The 303(d) List | EPA approval and TMDL required |

## Appendix B. Continuous low-level aquatic monitoring

*This information was taken from the Pine Creek Toxaphene Source Assessment Quality Assurance Project Plan (Hobbs, 2014).*

The continuous low-level aquatic monitoring (CLAMTM) sampling device is a submersible, low-flow sampler that continuously and actively draws water through filtration and solid-phase extraction (SPE) media. The main supplier of the devices and the SPE disks used in this study is C.I.Agent (<http://www.ciagent-stormwater.com>). The pumps were commercially introduced in 2007, but the technology for SPE disks has been in laboratory use for the last 15 years under established EPA protocols (EPA3535A). Recent work by Coes et al. (2014) has documented the efficacy of CLAMTM devices when compared to both grab samples and passive samplers. Ecology has also begun using CLAMTM samplers on a more regular basis (Anderson and Sargeant, 2009; Coots, 2014; Hobbs, 2014); however, there is no established SOP and therefore the technique is still in trial.

Solid-Phase Extraction (SPE) Disks

The CLAM device is simply a vessel for the SPE disk, which binds organic contaminants as water is pumped through. The pore size of the disks is 1.5 micrometers. The SPE media is specific to the contaminant of interest. C-18 extraction media is composed of a bonded silica filter with an octadecyl functional group that binds semi-volatile and non-volatile organic compounds (e.g., organochlorine pesticides, PCBs, and PAHs). The hydrophilic/lipophilic balanced (HLB) media uses a modified styrene polymer to effectively bind polar and non-polar compounds. The HLB disk has been used to sample many different pesticides, pharmaceuticals, and emerging contaminants.

The manufacturer of the CLAM device has conducted a retention and depletion bench study of the pump and the SPE disks for non-polar compounds. They found that there was excellent retention of spiked PAH and pesticide compounds in the disks following 100L of flushing with de-ionized water (DI) (Aqualytical, 2014; available at <http://www.ciagent-stormwater.com/documents/watermonitoring/RetentionandDepletionofIntegratedAnalytesintheCLAM.pdf>). The manufacturers of the SPE media and the lab suppliers have also conducted many retention studies for a variety of compounds.

The disks themselves are not directly handled by the lab or the field personnel. Disks are ordered and come contained in a sealed HDPE filter case with lure-locks at either end. Before deployment, the disks require conditioning with solvent, which rids the disk of any possible residual contamination. A complete step-by-step procedure is outlined in the manufacturer’s laboratory application notes available online (<http://www.ciagent-stormwater.com/new-water-monitoring/>). Briefly, the disks are cleaned with 50ml of dichloromethane (DCM), conditioned with 50ml of methanol, and rinsed with 50ml of reagent quality DI water. Residual DI water is left in the disk to maintain the pore space in the glass pre-filter that has been established by the conditioning rinse. The disks are capped and placed back in the foil pouch for shipment to the field. Conditioned disks can be kept refrigerated for up to 30 days; unconditioned disks are stable for up to a year.

Deployment

The CLAM devices can be secured to suit the sample site. During deployment, the device must be carefully situated so that it does not obstruct the intake port. Typically in small streams the CLAM is positioned with the intake facing downstream and the device is suspended at 2/3 the channel depth. In a shallow stream (such as Pine Creek) U-shaped rebar can be hammered into the stream bed and the device suspended horizontally. In a deeper stream or lake, a concrete block with a float attached by cable and positioned just below the water surface can be used as line to attach the CLAM to (Anderson and Sargeant, 2009).

Before deployment, the flow rate of the device must be measured. Protocols describing a step-by-step method can be found at the manufacturer’s website (http://www.ciagent-stormwater.com/new-water-monitoring/). The device is assembled and the battery pack is hooked up; this starts the internal pump. The device and extraction media are not compromised if the pump runs out of the water during set-up. A stainless steel bucket is filled with water from the site and the CLAM is placed in the bucket. Air is purged from the filter and then flow rate can be measured. A syringe is attached to the discharge port of the CLAM, with tubing, and the collected water volume is measured in the syringe and timed with a stopwatch. This procedure is repeated until the flow rate is consistent. The device can now be deployed and time of deployment recorded.

Retrieval

The typical time of deployment for the CLAM is 12 to 36 hours. The device’s battery pack limits the maximum time of deployment, and the water turbidity limits the minimum time of deployment. Suspended solids can slow flow rate by clogging the filter, ultimately stopping flow; this could result in a lost sample. Therefore, in turbid waters field personnel need to either return to the pump periodically to verify the pump is still running or deploy the pump for less time. There are no experimentally derived guidelines for time of deployment in turbid waters, since times vary dramatically with particle size and streamflow.

Before removing the device, personnel should take notes on its condition and exact time of retrieval. The flow rate of the CLAM is then measured as per the deployment. Currently, the user must then assume that the flow rate between the time of deployment and retrieval is linear. This flow rate is then used to calculate the total volume of water extracted over the period of deployment.

The following example illustrates this process. The CLAM is deployed at 1500 on March 3 and retrieved at 1200 March 4. The flow rate at deployment was 50 ml min-1 and at retrieval had decreased to 20 ml min-1. The mean flow is therefore 35 ml min-1 and the total time of deployment is 21 hours. The total volume of water extracted is 44.1 L.

The CLAM is pulled from the water and disassembled at the site. The SPE disk is removed and placed back in the foil shipping pouch. The disks are placed in a cooler on ice until shipped directly to the lab. Refrigerated SPE disks have a holding time of 14 days.

Analysis

SPE disks are shipped directly to the lab, accompanied by a standard chain of custody form. SPE disks are generally considered “other” as a matrix description and not water samples. While there is not an established SOP for the CLAM deployed SPEs, the contract lab should have an SOP for large volume extraction in the lab using similar or the same media. Established preparatory procedures should be in place from previous projects using CLAM samplers (J. Weakland, personal communication).

To analyze the total contaminant concentration bound to the SPE media, the lab must completely elute the deployed disks into separatory funnels. The disks are first rinsed with acetone to remove any water from the disk and then rinsed with dichloromethane to elute the disk. Before the DCM is added, the disk is spiked with a surrogate for laboratory QC of the separatory funnel extraction. The sample is concentrated using micro-Kuderna-Danish distillation under an N2 atmosphere. The final extract volume is 1.0 mL. The extract is then run according to the methods pertaining to the contaminant of concern (e.g., GC/ECD in the case of toxaphene).

Data Calculations and Reporting

The final quantified concentration is derived from the mass of the compound per milliliter of extract. The concentration of the compound in the sampled water is then calculated, using the total volume of water pumped through the CLAM.

The following example illustrates this process. If the concentration of toxaphene in the extract is 5.05 ng ml-1, and the final volume of extract was 2.0 ml, there is 10.1 ng of toxaphene in the sample. If 44.1 L of water were sampled, as described earlier, the concentration is therefore 0.23 ng L-1.

Given that we are assuming the flow rate of the device is linear from deployment to retrieval, we can only consider the total water volume sampled to be an estimate. Therefore, the derived water concentration is an estimate and should be qualified as such.

C.I.Agent is currently developing a “totalizer” that will accurately measure the volume of water sampled with each CLAM. If proven successful as an effective volume measurement tool, analyte concentrations from the CLAM can be considered as accurate as any sample volume analyzed by the laboratory.

## Appendix C. Glossaries, Acronyms, and Abbreviations

Glossary of General Terms

**Ambient:** Background or away from point sources of contamination. Surrounding environmental condition.

**Baseflow:** The component of total streamflow that originates from direct groundwater discharges to a stream.

**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.

**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.

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

**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.

**Pollution:** Contamination or other alteration of the physical, chemical, or biological properties of any waters of the state. This includes change in temperature, taste, color, turbidity, or odor of the waters. It also includes discharge of any liquid, gaseous, solid, radioactive, or other substance into any waters of the state. This definition assumes that these changes will,   
or are likely to, create a nuisance or render such waters harmful, detrimental, or injurious to   
(1) public health, safety, or welfare, or (2) domestic, commercial, industrial, agricultural, recreational, or other legitimate beneficial uses, or (3) livestock, wild animals, birds, fish, or other aquatic life.

**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.

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

**Surface waters of the state:**  Lakes, rivers, ponds, streams, inland waters, salt waters, wetlands and all other surface waters and water courses within the jurisdiction of Washington State.

**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

Following are acronyms and abbreviations used frequently in this report.

DOC Dissolved organic carbon

Ecology Washington State Department of Ecology

e.g. For example

EIM Environmental Information Management database

EPA U.S. Environmental Protection Agency

et al. And others

i.e. In other words

MEL Manchester Environmental Laboratory

MQO Measurement quality objective

NTR National Toxics Rule

PBDE polybrominated diphenyl ethers

PCB polychlorinated biphenyls

QA Quality assurance

RPD Relative percent difference

RSD Relative standard deviation

SOP Standard operating procedures

TMDL (See Glossary above)

TOC Total organic carbon

TSS (See Glossary above)

USGS United States Geological Survey

WRIA Water Resource Inventory Area

WSTMP Washington State Toxics Monitoring Program

*Units of Measurement*

°C degrees centigrade

cfs cubic feet per second

dw dry weight

ft feet

g gram, a unit of mass

kg kilograms, a unit of mass equal to 1,000 grams

m meter

mm millimeter

mg milligram

mg/Kg milligrams per kilogram (parts per million)

mg/L milligrams per liter (parts per million)

mL milliliter

ng/g nanograms per gram (parts per billion)

ng/Kg nanograms per kilogram (parts per trillion)

ng/L nanograms per liter (parts per trillion)

NTU nephelometric turbidity units

pg/g picograms per gram (parts per trillion)

pg/L picograms per liter (parts per quadrillion)

s.u. standard units

ug/g micrograms per gram (parts per million)

ug/Kg micrograms per kilogram (parts per billion)

ug/L micrograms per liter (parts per billion)

um micrometer

umhos/cm micromhos per centimeter

uS/cm microsiemens per centimeter, a unit of conductivity

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 population 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 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 is usable for intended purposes.
* J (or a J variant), data is estimated, may be usable, may be biased high or low.
* REJ, data is 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:** The term split sample denotes when a discrete sample is further 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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