

## Memorandum

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**Project:** SRRTTF

**To:** SRRTTF

**CC:**

**SUBJECT: DRAFT: Sampling Recommendations for Spokane River PCB Confidence Testing**

### Summary

This memorandum provides recommendations to the Washington Department of Ecology (Ecology) for immediate-term monitoring of Spokane River PCBs, with the objective of informing upcoming monitoring to be conducted for the Spokane River Regional Toxics Task Force (SRRTTF). These monitoring recommendations are designed to generate information both on the temporal variability of PCB concentrations, as well as estimates of measurement uncertainty for the low PCB concentrations occurring in the Spokane River.

Five sampling events are recommended to be conducted as soon as possible on the Spokane River at the State Park Parcel at River Mile 87, located between Mirabeau and Sullivan Parks (referred to as the Mirabeau Park site) and three sampling events at the Lake Coeur d'Alene outlet. Samples will be collected for both discrete and composite analyses at Mirabeau Park, while discrete samples will be collected at the Lake Coeur d'Alene outlet. This information will be used to satisfy two objectives:

1. Generate site-specific information on the sources of variability in PCB measurements (i.e. laboratory vs. variability in ambient concentrations)
2. Generate estimates of the confidence limits around the results to be obtained from the upcoming SRRTTF synoptic monitoring.
3. Determine if the proposed sampling methodology will provide data that can be distinguished from the lab blank.

If the expected confidence limits turn out to be too large to meet SRRTTF objectives, the upcoming sampling plan could be modified to adjust the sample volume, specified number of composite samples and/or laboratory analyses to generate results expected to comply with desired confidence limits. Furthermore, if blank contamination is determined to be an issue, the upcoming sampling methodology will be adjusted to incorporate sampling of larger volumes of water.

### Justification

The upcoming year of the Spokane River monitoring program includes a synoptic survey at low river flow designed to support a mass balance assessment of PCB loads in the Spokane River. PCB samples will be collected at eight instream stations where flow gaging information is available, allowing calculation of the total mass of PCBs passing through each location. PCB concentrations and discharge flow volumes will also be monitored from the eight primary point source discharges during this same period. Information on point source PCB loading rates to the river, in conjunction with PCB mass measured in the river, will allow an implicit estimation of the net PCB load from all other sources between any two river monitoring locations. The large majority of the

incremental load is expected to be attributable to groundwater, because: 1) Wet weather-driven sources should be minimal during dry weather, 2) Screening-level calculations conducted by LimnoTech as part of this project show that environmental fate processes (volatilization, settling) have a small effect on instream concentrations.

Because groundwater loading will be calculated as the difference between measured instream loads, the estimate of its magnitude can be extremely sensitive to uncertainty/variability in the measured stream load. For example, consider the case where there is a 10% uncertainty in the measured instream load such that the downstream load is 110(±11) and the upstream load is 100 (±10). The estimated groundwater load in this case could range from -11 (i.e. using lower bound downstream load of 99 and upper bound upstream load of 110) to 31 (i.e. using upper bound downstream load of 121 and lower bound upstream load of 90) . For this reason, we want to better understand the relationship between the number of samples collected and the uncertainty in our estimate of the instream loads, to help constrain the uncertainty in groundwater loading estimates.

We recognize that uncertainty in the loading estimate can arise from: 1) accuracy of the measurement, including blank contamination, and 2) natural variability of ambient concentrations. Because variance contributed from multiple sources is additive, this can be expressed mathematically as:

$$\sigma^2_{\text{total}} = \sigma^2_{\text{lab}} + \sigma^2_{\text{ambient}} \quad (1)$$

where

- $\sigma^2_{\text{total}}$  = total variance in concentration
- $\sigma^2_{\text{lab}}$  = variance in measurement, including that caused by blank contamination
- $\sigma^2_{\text{ambient}}$  = natural day-to-day variance in ambient concentration

We also know that the variance of the mean of n samples is related to the individual variance as follows

$$\sigma^2_n = \sigma^2_1/n \quad (2)$$

where

- $\sigma^2_n$  = variance in average of n values
- $\sigma^2_1$  = variance in individual values

Equations 1 and 2 can be combined to estimate the variance in estimated average concentration, based on a given number of laboratory analyses and number of individual field samples composited for analysis:

$$\sigma^2_{\text{mean}} = \sigma^2_{\text{lab}}/n_l + \sigma^2_{\text{ambient}}/n_c \quad (3)$$

where

- $\sigma^2_{\text{mean}}$  = variance in estimated mean concentration
- $n_l$  = number of laboratory samples analyzed
- $n_c$  = number of composited samples in a laboratory analysis

Depending on the relative magnitude of the various individual sources of variance, the variance in the estimated mean concentration can be reduced by either analyzing a large number of samples compositing multiple samples from several different time periods prior to laboratory analysis.

The Confidence Limit testing proposed here will be used to satisfy two objectives:



- Generate site-specific information on the sources of variability in PCB measurements (i.e. laboratory vs. variability in ambient concentrations). Although laboratories have historically reported variability in results, these may not be directly transferable to the low concentrations observed in the Spokane River.
- Generate estimates of the confidence limits around the results to be obtained from the upcoming SRRTTF synoptic monitoring. These estimates will be admittedly rough, as they will not reflect seasonal differences, but will still be an improvement over what is currently known.

The first objective of the monitoring is to generate site-specific information on the sources of variability in PCB measurements. The variability in measured concentrations across sampling events will provide information on total uncertainty (temporal variability plus measurement accuracy). The observed variability in results from replicate samples, along with results from laboratory QA procedures, will provide estimates of measurement uncertainty. Temporal variability can be estimated from the difference between total uncertainty and measurement uncertainty, i.e. by rearranging Equation 1.

The second objective of the monitoring is to generate estimates of the confidence limits around the results to be obtained from the upcoming SRRTTF synoptic monitoring. Information on  $\sigma^2_{\text{lab}}$  and  $\sigma^2_{\text{ambient}}$  gained above will be input into Equation 2, along with the planned number of laboratory analyses and composites. If the expected confidence limits turn out to be too large to meet SRRTTF objectives, the upcoming sampling plan could be modified to adjust the specified number of composite samples and/or laboratory analyses to generate results expected to comply with desired confidence limits.

## Recommended Sampling Plan

Ecology may have resources available to conduct some PCB monitoring in the near future to support the needs described above. This section provides a sampling plan that would provide information to better inform the generation of confidence limits associated with upcoming SRRTTF sampling. All aspects of the project QAPP and SAPP (reference) related to the Seasonally Integrated Sampling apply to the Confidence Testing sampling event, with the exception of the specific details described below.

### *Location*

If possible, monitoring should be conducted at two locations on the Spokane River. The first is the Lake Coeur d'Alene outlet, which is desirable in that PCB concentration data collected here will directly support the seasonally integrated analysis to be conducted by the SRRTTF at this location. Concentrations may be so low at this location, however, that the signal of environmental concentrations may be obscured by blank contamination. Samples will therefore also be collected at the Mirabeau Park site, where PCB concentrations are expected to be higher than at the lake outlet.

### *Timing*

Monitoring can begin immediately. For this information to be most useful in supporting the seasonally integrated analysis, it should be completed as soon as possible.



### **Frequency**

The samples will be collected with the following frequency:

- Lake Coeur d'Alene outlet: 3 samples collected on separate days (two days apart)
- Mirabeau Park site: 5 samples collected on separate days (two days apart)

In the event of a rainfall event during the sampling period the following changes will be made to the sampling frequency:

- Lake Coeur d'Alene outlet: Samples should be collected within two days of the rainfall event, to get samples before runoff-driven conditions appear. If necessary, samples can be collected on the same day.
- Mirabeau Park site: Samples should be collected two days after the rainfall event, to allow urban stormwater loads to pass downstream.

Day 0: Rain

Days 1-2: Three samples at lake outlet

Days 3-5: Five samples at Mirabeau Park

### **QC Samples**

At the Lake Coeur d'Alene outlet the following QC samples will be collected for all parameters:

- Replicate samples will be collected during each sampling round for analysis at the laboratory.
- Trip blanks will be collected during each sampling round. The trip blank will consist of filling a clean sample bottle with laboratory provided deionized water.

At Mirabeau Park the following QC samples will be collected:

- Replicate samples will be collected during each sampling round for analysis at the laboratory.
- Trip blanks will be collected during each sampling round.
- A separate sample will be collected during each sampling round for the purpose of compositing. The five samples for compositing will be submitted to the laboratory to be composited.

### **Sampling Method**

PCB samples will consist of 2.36 liters of water collected in a 2.36 liter amber sample bottles. An extra 2.36 liter bottle will be collected during each round to provide extra volume in case of sample breakage. The samples will be collected in accordance with the methods presented in the SAP/QAPP.

It is understood that river flows are variable and river access can be difficult. The safety of the sampling personnel is the highest priority.

The samples collected at the lake outlet will be collected by wading into the channel where the water is at least three feet deep and the direction of the current is from the open lake. Sample bottles will be filled by direct immersion. If wading is prohibited because the velocity and/or



depth of water do not allow for a sample free from shoreline influence at the time of the sampling event, the samples will be collected using a boat.

The samples collected at Mirabeau Park will be collected by wading into the main channel flow, if possible. The best effort will be made without jeopardizing the safety of the sampling crew. The sample bottles will be filled by direct immersion.

An attempt will be made to collect field measurements as near to the sampling location as possible.

### **Analytes**

The samples will be analyzed for PCB (using EPA Method 1668C), total suspended solids, total dissolved solids, total organic carbon and dissolved organic carbon, in accordance with the SAP/QAPP.

EPA Method 1668C QC criteria will be followed with the following exception:

- The more stringent EPA Method 1668A Sample and MB Standard Recovery range will be used: 25-150%.

Prior to collecting the surface water grab samples, in-situ measurements of temperature, dissolved oxygen, pH, conductivity and turbidity will be made by lowering a YSI 600 OMS or equivalent below the water surface.

Parameter	Confidence Testing Number of Samples	Confidence Testing Number of Replicate Samples	Confidence Testing Field Blanks	Confidence Testing Composite Sample	Total
<b>PCB</b>	8	8	8	1	25
<b>Dissolved Organic Carbon</b>	8	8	8	1	25
<b>Total Organic Carbon</b>	8	8	8	1	25
<b>Total Suspended Solids</b>	8	8	8	1	25
<b>Total Dissolved Solids</b>	8	8	8	1	25
<b>Temperature</b>	8	0	0	0	8
<b>Conductivity</b>	8	0	0	0	8
<b>pH</b>	8	0	0	0	8
<b>Dissolved Oxygen</b>	8	0	0	0	8
<b>Turbidity</b>	8	0	0	0	8

