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Memorandum

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To: SRRTTF

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Project: 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 laboratory 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 Lake Coeur d'Alene outlet, with samples being collected for both discrete and composite analyses. Replicate analyses are recommended for all samples.

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.

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.

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 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, and 2) natural variability of ambient concentrations. Because variance contributed from multiple sources is additive, this can be expressed mathematically as:

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

where

σ^2_{sample} = variance in sample measurement
σ^2_{lab} = variance in laboratory analysis
$\sigma^2_{ambient}$ = 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

σ^2_n = variance in average of n values
σ^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 samples composited be analysis:

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

where

σ^2_n = 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)
- Generate estimates of the confidence limits around the results to be obtained from the upcoming SRRTTF synoptic monitoring.

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 laboratory accuracy). The observed variability in results from replicate samples, along with results from laboratory QA procedures, will provide estimates of laboratory 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 σ^2_{lab} and $\sigma^2_{ambient}$ 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 on the Spokane River at the Lake Coeur d'Alene outlet. This location 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. If it is not feasible for Ecology to sample in Idaho, sampling could be conducted at any of the Spokane River locations where USGS gaging data are currently available.

Timing

Monitoring can begin immediately. For this information to be most useful in supporting the seasonally integrated analysis, it should be completed by mid-March.

Frequency

Five sampling events are recommended, each occurring on different days.

Sampling Method

For each event, samples should be collected to allow for:

- Analysis of concentration in a discrete grab sample
- Replicate analysis of a discrete grab sample
- A single subsequent composite analysis integrating samples from the five events.

An equipment blank should be collected during each sampling event.

Analytes

The samples will be analyzed for PCB using EPA Method 1668A, total suspended solids, total dissolved solids, total organic carbon and dissolved organic carbon.

Parameter	Confidence Testing Number of Samples Collected and Analyzed	Confidence Testing Number of Replicate Samples Collected & Analyzed	Confidence Testing Number of Equipment Blanks Collected & Analyzed	Confidence Testing Composite Sample
PCB	5	5	5	1
Dissolved Organic Carbon	5	5	5	1
Total Organic Carbon	5	5	5	1
Total Suspended Solids	5	5	5	1
Total Dissolved Solids	5	5	5	1
Temperature	5	0	0	0
Conductivity	5	0	0	0
pH	5	0	0	0
Dissolved Oxygen	5	0	0	0
Turbidity	5	0	0	0