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Memorandum

From: Dave Dilks, Cathy Whiting

Date: July 16, 2014

Project: SRRTTF

To: SRRTTF

CC:

SUBJECT: **DRAFT: Confidence Testing Results from Spokane River PCB Sampling**

Summary

Washington Department of Ecology (Ecology) conducted monitoring of Spokane River PCBs at two locations during May 13-21, 2014, to support the design of upcoming monitoring to be conducted for the Spokane River Regional Toxics Task Force (SRRTTF). The magnitude and variability of these monitoring data were assessed in terms of whether the proposed Sampling and Analysis Plan (SAP) will provide data sufficient to satisfy the data quality objectives provided in the Quality Assurance Project Plan (QAPP).

Sampling results and associated recommendations can be summarized as follows:

- PCBs concentrations were very low at both stations, with lab blank-corrected concentrations ranging from 7.7 to 54 pg/l at the Lake Coeur d'Alene Outlet and 6.2 to 80 pg/l at Mirabeau Park. Concentrations observed in trip blanks and laboratory blanks were at similar levels to those observed in field samples, making it difficult to distinguish an environmental signal from the noise in laboratory measurement.
- PCB concentrations are expected to be significantly higher during the SRRTTF August sampling than they were during the May sampling, due to much lower river flows and consequently lower dilution of weather-independent external PCB sources.
- The variability in measured August concentrations is expected to be so large as to be unlikely to satisfy original data quality objectives; however, no other monitoring approach is immediately available to supply data that will meet the original objectives. It is recommended that the data quality objectives be revised to read as follows:
    - The data shall be sufficient to support a semi-quantitative mass balance assessment, and be able to identify stream reaches where incremental loads lead to a significant increase in river concentrations.
    - The data shall be sufficient to support an adaptive management approach, where grab sample results can be directly compared to results from other sampling methodologies to allow determination of an improved monitoring approach for future phases of this work.

Description of Sampling

Sampling events were conducted by Ecology on the Spokane River at two locations (Figure 1):

1. The State Park Parcel at River Mile 87, located between Mirabeau and Sullivan Parks (referred to as the Mirabeau Park site), and
2. The outlet of Lake Coeur d'Alene.

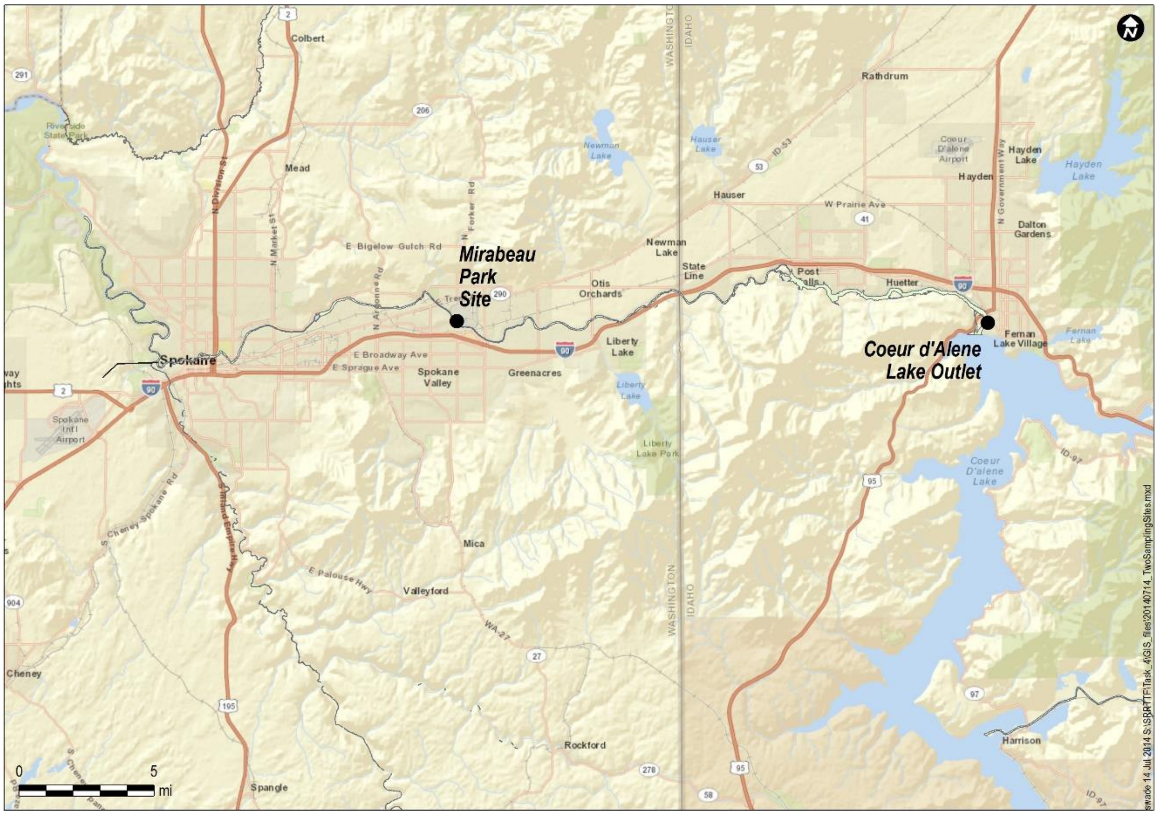

Figure 1. Sampling Locations

Samples were collected in 2.375/l glass bottles, and subsequently concentrated at the laboratory for analysis. Samples at the Mirabeau Park site were collected on May 13, 15, 17, 19, and 21 of 2014. Three sampling events were conducted at the Lake Coeur d'Alene outlet, on May 13, 15, and 17. Samples were collected for both discrete and composite analyses at Mirabeau Park, while only discrete samples were collected at the Lake Coeur d'Alene outlet. Trip blanks were prepared at the lab and accompanied the sample bottles to the field during each sampling trip and back to the lab unopened. Moisture was noted in some of the plastic bags that contained the trip blanks. Three laboratory blank assessments were conducted, corresponding to the date when individual sample batches were analyzed. River flows over the period of sampling ranged from 18,000 to 18,900 cfs at the Post Falls USGS gage.

Sampling Results

Sampling results for total PCB are provided in Table 1. Results are reported in two forms:

1. Lab Reported Total PCB: Total PCB concentration reported by laboratory, with no correction for blank contamination, and
2. Blank Corrected Total PCB: Estimated total PCB concentration after correcting for blank contamination in each individual congener using the method described in the QAPP (i.e. analytes found in the sample at a concentration less than three times the associated blank concentration are B flagged, and the B flagged data are not used in congener summations for total PCB.)

PCB concentrations were very low at both sites, with lab blank-corrected concentrations ranging from 7.7 to 54 pg/l at the Lake Coeur d'Alene Outlet and 6.2 to 80 pg/l at Mirabeau Park. Concentrations observed in trip blanks and laboratory blanks were at similar levels to those observed in field samples, making it difficult to distinguish an environmental signal from the noise in laboratory measurement. The relative percent difference (RPD) in replicate samples ranged from 9 to 130%. Assessment of results is further complicated by the fact that the variability of the Coeur d' Alene Lake outlet samples and the replicate samples is less than the variability of the field blanks and the laboratory blanks.

Interpretation

One objective of the confidence testing monitoring as described in the May 1, 2014 draft QAPP and the July 13, 2014 memorandum "Sampling Recommendations for Spokane River PCB Confidence Testing" (documents available at http://srrttf.org/?page_id=1632) was to generate site-specific information on the sources of variability in PCB measurements, describing temporal day-to-day variability in ambient concentrations as well as laboratory variability. This objective was only partially satisfied by the confidence testing results, because the small environmental signal relative to analytical noise makes it infeasible to parse out temporal variation in ambient concentration. Even though temporal variability cannot be defined from the confidence testing data, the understanding of laboratory variability provided from the replicate data is still of value, as discussed below.

The second objective of the monitoring was to generate estimates of the confidence limits around the results to be obtained from the upcoming SRRTTF synoptic monitoring, in order to determine whether the upcoming monitoring will satisfy data quality objectives. This can be partially accomplished by assessing the extent to which laboratory variability contributes to expected confidence limits. The coefficient of variation (i.e. standard deviation divided by the mean) was calculated for all of the replicate samples reported in Table 1, for both sampling sites. Similar variability was seen between sites, so a pooled coefficient of variation of 0.48 was used to represent the entire data set. The uncertainty caused by this variability can be reduced in future monitoring by analyzing multiple samples, because the standard error of the mean of multiple samples decreases in proportion to the square root of the number of samples analyzed. Because the synoptic sampling is designed to collect seven samples at each river monitoring station, the coefficient of variation of the average of seven samples due to laboratory variability will be reduced from 0.48 to 0.18 (i.e. $0.48/\sqrt{7}$) – assuming that the future coefficient of variation remains at 0.48.

Table 1. Summary of Results of 2014 Confidence Testing Monitoring

				Total PCB		
Sample ID	Location	Date	Sample Type	Lab Reported (pg/L)	Blank Corrected (pg/L)	RPD %
SR8A-051314-1410	Mirabeau Park	5/13	Primary	57.4	9.68	-
Replicate 2	Mirabeau Park	5/13	Field Replicate	26	16.2	50
SR8A-051314-1420	Mirabeau Park	5/13	Trip Blank	33.2	13.6	-
SR8A-051514-1145	Mirabeau Park	5/15	Primary	59	38.1	-
Replicate 4	Mirabeau Park	5/15	Field Replicate	107	16.7	78
SR8A-051514-1200	Mirabeau Park	5/15	Trip Blank	14.9	6.16	-
SR8A-051714-1010	Mirabeau Park	5/17	Primary	47.2	35.9	-
Replicate 6	Mirabeau Park	5/17	Field Replicate	68.1	65.1	58
SR8A-051714-1020	Mirabeau Park	5/17	Trip Blank	47.2	36.6	-
SR8A-051914-1220	Mirabeau Park	5/19	Primary	38.4*	49.1	-
Replicate 7	Mirabeau Park	5/19	Field Replicate	64.4	53.8	9
SR8A-051914-1235	Mirabeau Park	5/19	Trip Blank	42.9	33.0	-
SR8A-052114-0840	Mirabeau Park	5/21	Primary	50.5	39.8	-
Replicate 8	Mirabeau Park	5/21	Field Replicate	59.8	8.4	130
SR8A-062114-0850	Mirabeau Park	5/21	Trip Blank	38.4	27.2	-
COMPOSITE	Mirabeau Park	---	Composite	91.2	80.3	-
SR15-051314-1000	Lake Coeur d'Alene Outlet	5/13	Primary	15.1	7.76	-
Replicate 1	Lake Coeur d'Alene Outlet	5/13	Field Replicate	21.3	12.8	49
SR15-051314-1030	Lake Coeur d'Alene Outlet	5/13	Trip Blank	70.8	39.6	-
SR15-051514-0845	Lake Coeur d'Alene Outlet	5/15	Primary	53.6	15.3	-
Replicate 3	Lake Coeur d'Alene Outlet	5/15	Field Replicate	32.4	21.7	35
SR15-051514-0900	Lake Coeur d'Alene Outlet	5/15	Trip Blank	22.1	11.4	-
SR15-051714-0845	Lake Coeur d'Alene Outlet	5/17	Primary	46.3	31.7	-
Replicate 5	Lake Coeur d'Alene Outlet	5/17	Field Replicate	59.3	48.0	94
SR15-051714-0900	Lake Coeur d'Alene Outlet	5/17	Trip Blank	48.8	36.8	-
Lab Blank	---	6/5	Lab Blank	7.67	7.67	-
Lab Blank	---	6/16	Lab Blank	44.2	48.3	-
Lab Blank	---	6/3	Lab Blank	54.4	53.9	-

* Total reported is incorrect - should be 58.8

This information can be used to estimate the expected uncertainty in future measured concentrations due to laboratory variability. Frequency distributions can be generated to assess the uncertainty in measured river concentration, as well as the uncertainty in estimated differences in concentration between river monitoring stations. The uncertainty in estimated differences in concentration is of particular interest to this study, due to the study's original objective of back-calculating incremental loads to the river by performing a mass balance analysis between concentrations at upstream/downstream locations.

The uncertainty in the difference in concentration between two stations can be estimated, as long as the uncertainty distribution for each individual station is known (or accurately assumed). While the sample size resulting from this study is too small to confidently define the underlying distribution of the data, it is informative to roughly assess the magnitude of the uncertainty for the case where the data are assumed to be normally distributed. For the assumed coefficient of variation of 0.18, Figure 2 shows the frequency distribution for the estimated difference between concentrations for an example case where the actual concentration at the upstream station is 72 pg/l and the actual concentration at the downstream station is 100 pg/l. Figure 2 indicates that the most likely estimate for the difference in concentration between stations to result from sampling would be 28 pg/l. This is as expected, as it corresponds to the difference between the true upstream and downstream concentrations. The figure also demonstrates that there is significant uncertainty around this estimated difference, with a non-zero probability that the data could indicate a negative concentration difference, i.e. that downstream concentrations are lower than upstream concentrations.

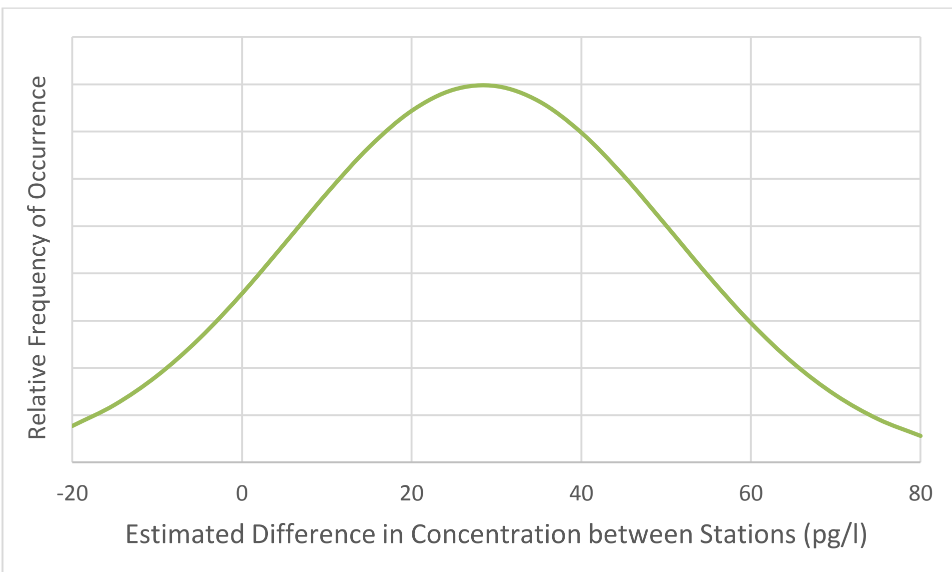

Figure 2. Frequency Distribution for Estimated Difference in Concentration between Stations for the Example where True Upstream Concentration is 72 pg/l and Downstream Concentration is 100 pg/l

The probability of the data indicating a negative concentration change can be determined by converting the frequency distribution as shown in Figure 2 into a cumulative probability distribution as in Figure 3. Figure 3 shows the probability of the data indicating a concentration difference less than or equal to the value on the x-axis for the same example case used above. For this example, the probability of the data indicating a difference in concentrations of 28 ug/l or less between stations is 50%. The probability of the data indicating a difference in concentrations between stations of zero or less is 10%. This means that, for a case where the downstream concentration is 28 ug/l less than the upstream concentration, there will still be a 10% probability that the sampling will not indicate any increase in concentrations between the upstream and downstream stations.

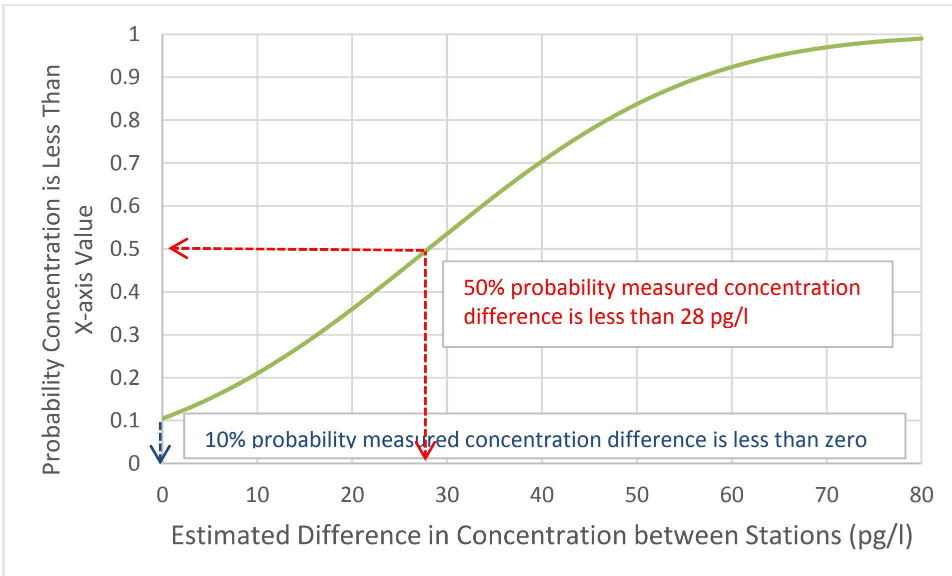

Figure 3. Cumulative Frequency Distribution for Estimated Difference in Concentration between Stations for the Example where True Upstream Concentration is 72 pg/l and Downstream Concentration is 100 pg/l

Recommendations

The results of the confidence testing indicate that the existing synoptic monitoring program as described in the SAP will not provide data sufficient to satisfy data quality objectives nor to support regulatory assessments. The primary objective of the synoptic monitoring as defined in the May 1, 2014 draft QAPP is to collect the necessary data to conduct a PCB mass balance assessment of the Spokane River. The confidence testing results show two key limitations in terms of meeting that objective:

- Observed PCB concentrations from the river were of a similar magnitude to the concentrations observed in trip blank samples and the laboratory blank samples.
- The variability in laboratory measurements of replicate samples is so large that there is a 10% probability that differences in concentrations between stations of approximately 30 pg/l will not be detected strictly due to laboratory variability.

Alternative sampling methodologies (e.g. CLAM sampler, Gravity high volume sampler) were investigated to determine whether their use could satisfy existing data quality objectives. While each method shows promise to eventually satisfy project requirements, neither has been developed/ demonstrated to the extent that they are currently a viable replacement to grab sampling.

The inability of the current SAP to meet existing data quality objectives does not mean that there is no merit to continuing with the sampling plan, for the following three reasons:

1. **It is expected that the August sampling will see environmental concentrations that rise above the noise in laboratory measurement.** Many sources of PCBs to the Spokane River are independent of flow. As river flows decrease, these sources will receive less dilution and river PCB concentrations will increase. Projected river flows for the August synoptic survey are less than 10% of the flows that occurred during the May confidence testing.
2. **Synoptic survey results may still provide valuable qualitative/semi-quantitative information:** While the above analysis demonstrates that the planned monitoring may not distinguish differences in concentration between stations of up to 28 pg/l, the monitoring may be sufficient to identify incremental changes in concentration larger than that amount. Being able to identify the existence of larger (e.g. more than 30 pg/l) increases in concentration will help support project objectives of identifying major PCB sources.
3. **Grab sampling, conducted in conjunction with testing of other monitoring methods, will support an adaptive management approach towards future monitoring:** No single sampling method is currently suited to satisfy existing data quality objectives. Both the CLAM sampler and Gravity high volume sampler show potential for ultimately meeting these objectives, as these methods may be better suited to measuring concentrations at low levels where grab sample results are obscured by blank contamination. Modification of the QAPP and SAP to include monitoring activities with the above methods will allow an assessment of the viability of each method (and the comparability of results between methods), and will support an adaptive management approach to allow determination of an improved monitoring approach for future phases of this work. Future phases of this work should consider a wider range of alternate sampling methods, and be prepared to test the most viable methods during upcoming wet weather monitoring.

Given the above factors and the absence of suitable alternatives for meeting existing data quality objectives, it is recommended that the synoptic monitoring be conducted as planned and data quality objectives be revised to read as follows:

a. The data shall be sufficient to support a semi-quantitative mass balance assessment, and be able to identify stream reaches where incremental loads lead to a significant increase in river concentrations.
b. The data shall be sufficient to support an adaptive management approach, where grab sample results can be directly compared to results from other sampling methodologies to allow determination of an improved monitoring approach for future phases of this work.