Spokane River Regional Toxics Task Force 2015 Technical Activities Report: Continued Identification of Potential Unmonitored Dry Weather Sources of PCBs to the Spokane River

Prepared for:
Spokane River Regional Toxics Task Force

November 16, 2016

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EXECUTIVE SUMMARY

The Spokane River and Lake Spokane have been placed on the State of Washington's 303(d) list of impaired waters because of concentrations of polychlorinated biphenyls (PCBs) that exceed water quality standards[1]. To address these impairments, the Department of Ecology (Ecology) is pursuing a toxics reduction strategy that included the establishment of a Spokane River Regional Toxics Task Force (SRRTTF) to identify and reduce PCBs at their source in the watershed.

The Work Plan developed by the Task Force (SRRTTF, 2012) identified four distinct phases of work:

- Phase 1: Review of existing data and reports, and development of a data gaps assessment with recommendations for additional sampling
- Phase 2: Collection of additional data
- Phase 3: Analysis of data to characterize and quantify PCB sources
- Phase 4: Assessment of potential control actions and development of a Comprehensive Plan

Phase 2 technical activities have focused on carrying out synoptic surveys to assess the presence of unmonitored dry weather sources of PCBs to the Spokane River. A synoptic survey conducted from August 12 to 24, 2014 identified a potential unmonitored dry weather PCB source entering the Spokane River between Barker Rd. and the Trent Avenue Bridge/Plante's Ferry (LimnoTech, 2015a). This report documents a follow-up survey designed to confirm the findings of the 2014 survey and provide greater detail on the location of the unmonitored source. The follow-up survey was successfully conducted from August 18 to 22, 2015. Survey activities were conducted in accordance with the Quality Assurance Project Plan (LimnoTech, 2015b) developed for this phase of the project.

The following conclusions can be gathered from the data collected:

- The low concentrations of PCBs in the Spokane River (i.e. at magnitudes sometimes similar to those observed in blank samples) make precise calculations impossible and instead can best support semi-quantitative analyses.
- The presence of a large (i.e. as large as any other single dry weather source) incremental PCB load entering the Spokane River between Barker Road and the Trent Avenue Bridge was confirmed, with the location of where the load enters the river load narrowed down to between upper Mirabeau Park/Sullivan Road and the Trent Avenue Bridge/Plante's Ferry.

[1] PCB concentrations utilized to place the Spokane River and Lake Spokane on the 303(d) list were derived from fish tissue concentrations and a bioconcentration factor specified in the National Toxics Rule.

- Homolog-specific mass balance analyses indicate the potential presence of another groundwater loading source entering the river downstream of the Trent Avenue Bridge, although further study is needed to assess the nature of this source.

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1 INTRODUCTION

The Spokane River and Lake Spokane have been placed on [Category 5 of] the State of Washington's 303(d) list of impaired waters because of concentrations of polychlorinated biphenyls (PCBs) that exceed water quality standards. The Spokane River and Lake Spokane (also known as Long Lake, herein referred to as Lake Spokane) exceed the water quality standard (170 pg/l – based on a fish consumption rate of 6.5 g/day) for PCBs. Nineteen waterbody segments of the Spokane River and Lake Spokane and one segment of the Little Spokane River are on the 2008 2014 303(d) list for exceeding human health water quality criteria for PCBs. The Spokane Tribe of Indians have water quality standards for PCBs in the Spokane River below Lake Spokane (also known as the Spokane Arm of Lake Roosevelt) that are more than 95% lower than State standards (1.3 pg/l), based on a higher fish consumption rate (865 g/day) than the general population (Spokane Tribe of Indians, 2010). The Spokane River is not listed as impaired for PCB in Idaho. While PCB concentrations utilized to place the Spokane River and Lake Spokane on the 303(d) list were derived from fish tissue concentrations and a bioconcentration factor, historical monitoring of water column PCB concentrations has also been conducted (Serdar et al, 2011; Era-Miller, 2014). In Washington, the Spokane River and Lake Spokane were placed on the 303(d) list for PCBs in accordance with Department of Ecology's Water Quality Policy 1-11. Under this policy, Ecology compares concentrations of PCBs in fish with its Fish Tissue Equivalent Concentration (FTEC). The FTEC is an expression of the water quality standard that is derived from fish tissue concentrations and a bioconcentration factor.

To address these impairments, the Department of Ecology (Ecology) is pursuing a toxics reduction strategy that included the establishment of a Spokane River Regional Toxics Task Force (SRRTTF) to identify and reduce PCBs at their source in the watershed. The stated objective of the Task Force (SRRTTF, 2012) is "to work collaboratively to characterize the sources of toxics in the Spokane River and identify and implement appropriate actions needed to make measurable progress towards meeting applicable water quality standards." In order to take this approach, the SRRTTF has determined that it needs to develop a sufficient clearer understanding of in-stream loadings and source contribution to the Spokane River between its headwaters at the outlet of Lake Coeur d'Alene and the Nine Mile Dam. This 53 mile segment of the river has been chosen to be the focus of the SRRTTF's initial efforts for several reasons. In no particular order they are:

- Discharges from all of the major municipal and industrial sources in the watershed are located in this section of the river;
- Virtually all urban area storm runoff in the watershed enters the river in this section;

- This section of the river contains numerous river flow gaging stations, which will allow for the determination of in-stream loadings at multiple locations through semi-quantitative mass balance calculations;
- The vast majority of the aquifer/river interchange occurs In this section of the river, the impact of which has not been quantified by previous studies;
- The likelihood of making near term source contribution reductions is greatest in this section of the river given the concentration of point source and storm runoff locations and the significant level of unidentified source contribution; and
- The ability to monitor and assess the effectiveness of PCB reductions is enhanced by the ability to track in-stream loadings with the infrastructure present (gauging stations) in this section of the river

The Work Plan developed by the Task Force (SRRTTF, 2012) identified four distinct phases of work:

- Phase 1: Review of existing data and reports, development of a data gap assessment with recommendations for sampling, preparation of a Quality Assurance Project Plan for collection of additional data, and recommendation of analytical modeling tools to be used in Phase 3.
- Phase 2: Collection of additional data
- Phase 3: Analysis of data to characterize and quantify PCB sources
- Phase 4: Assessment of potential control actions and development of a Comprehensive Plan

The majority of Phase 1 activities were completed in 2013, and are documented separately in LimnoTech (2013a, 2013b, 2013c, and 2013d).

Phase 2 monitoring was initiated in 2014, with the intent to support a semi-quantitative mass balance assessment and be able to identify stream reaches where unmonitored loads (presumably from groundwater sources) lead to a significant increase in river concentrations. A synoptic survey conducted from August 12 to 24, 2014 identified a likely unmonitored dry weather PCB source entering the Spokane River between Barker Rd. and the Trent Ave. Bridge near Plante's Ferry. This survey also identified a potential unmonitored source upstream of Spokane USGS gaging station, although this finding was inconclusive (LimnoTech, 2015). The Task Force, in reviewing these findings, chose to initiate a follow-up synoptic survey in 2015 designed to confirm the 2014 findings and provide greater detail on the location of the unmonitored source.

This report documents the results of the above monitoring program and subsequent analyses. It is divided into sections of:

- Synoptic Survey
- Mass Balance Assessment

2 SYNOPTIC SURVEY

A dry weather synoptic survey was conducted between August 18 and 22, 2015. The intent of the survey was to measure PCBs in the river and external loading source, and to use these results to determine where unmonitored loads may be entering the river. Activities were conducted in accordance with the Quality Assurance Project Plan (LimnoTech, 2015b) developed for this project. Field activities are documented in Gravity (2016). Each of the above documents is included as an appendix to this report.

2.1 Monitoring Locations

Sampling locations (Figure 1) included five Spokane River stations, and three point source discharges. The Spokane River stations were at the following locations (with latitudes and longitudes specified):

- Spokane River at Barker Rd. Bridge, also referred to as Greenacres (-117.1534, 47.67835)
- Spokane River at Mirabeau Point, i.e. the upstream end of Mirabeau Park (-117.2137, 47.67918)
- Spokane River below Trent Ave. Bridge near Plante's Ferry (-117.2418, 47.69708)
- Spokane River below Greene St. Bridge (-117.3628, 47.67808)
- Spokane River at Spokane USGS Gage (117.4497, 47.65888)

The point source discharges consisted of:

- Kaiser Aluminum (-117.2219, 47.686603)
- Inland Empire Paper (-117.2782, 47.68867)
- Spokane County Regional Water Reclamation Facility

Samples from the Spokane County Regional Water Reclamation Facility were collected at the facility itself (-117.3532, 47.66705), while the location of the discharge to the river is north of the facility near Freya St. (-117.3469444, 47.675833).

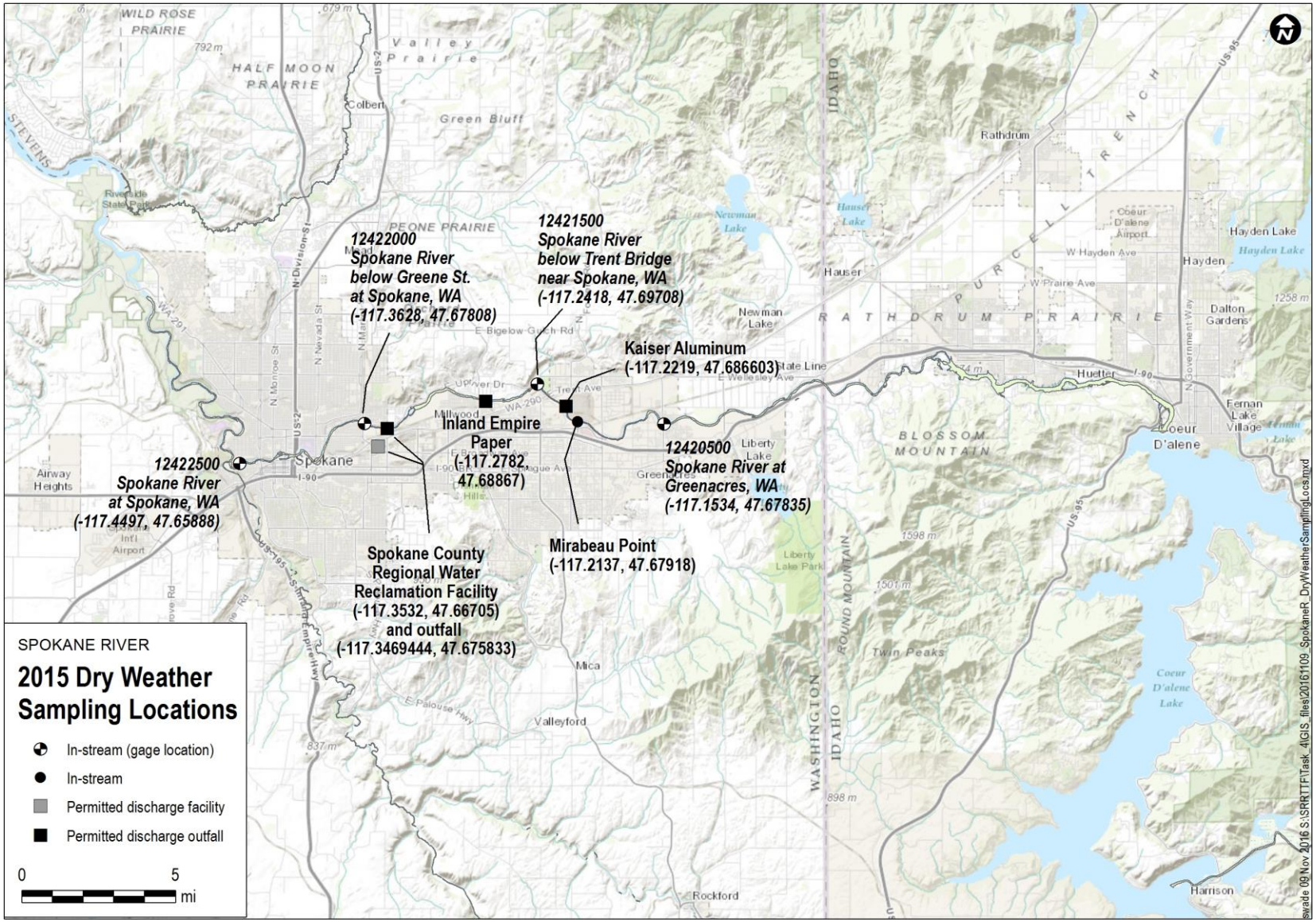

Figure 1. Sampling Locations for August 18-22, 2015 Synoptic Survey

2.2 Field Sampling Activities

The field sampling activities as planned and implemented are detailed in the project QAPP (LimnoTech, 2015b), and Gravity (2016) field report, both of which are included as appendices to this report. This section summarizes those activities. Environmental specialists from Gravity Consulting led the sampling event and collected samples along with representatives from LimnoTech and Washington State Department of Ecology. Grab samples were collected by hand using "clean hands" and "dirty hands" methodology combined with direct immersion techniques at most of the prescribed locations. These methods reduce the likelihood of any cross-contamination from direct (e.g., handling dirty equipment) or indirect (e.g., dust or air transport) sources. Samples were collected using a dip sampler at a few of the facilities due to safety concerns with access.

Surface water grab samples were collected on August 18, 19, 20, 21 and 22 at the stations listed in Section 2.1. Point source effluent was sampled on August 18, 20, and 22.

2.3 Analytical Results

Field samples were shipped to AXYS Analytical Laboratories, Ltd. in Sidney, British Columbia, for analysis of PCB concentrations. PCB concentrations for individual congeners were blank-corrected following the process defined in the QAPP (LimnoTech, 2015b). A separate set of samples were taken to SVL Analytical, Inc. in Coeur d'Alene, ID for analysis of total dissolved solids, total suspended solids, total organic carbon, dissolved organic carbon.

2.3.1 Data Quality Assessment

All data were reviewed for quality assurance in accordance with the project QAPP and as noted in the laboratory EDD-Excel files provided in the appendix. Data quality indicators evaluated for PCBs included the following:

- Daily Calibration Verification
- Lab Control Sample Recovery
- Sample and Method Blank Surrogate Recovery
- Matrix Spike Sample Recovery
- Duplicate sample relative percent differences (RPDs)
- Method blank concentrations
- Completeness

All reviewed QC results complied with QAPP data quality indicators with the exception of 33 surrogate recovery results and three duplicate sample relative percent differences. The out of control surrogate results are below the associated criteria range (25%-125%) for percent recovery specified in the QAPP. Sample results associated with the low surrogate recoveries were qualified as estimated using J/UJ data flags for positive/negative result values. The RPDs for the three out of control duplicate pairs were above the QAPP-specified criteria (0-50% for congeners >10x EDL). Duplicate pair results associated with the high RPDs are qualified as estimated using the J data flag. There are no changes to the final PCB result values as originally reported by the laboratory.

The QAPP has a completeness criterion for PCBs of 95%. 100% of the planned individual samples were collected and successfully analyzed, with one batch of samples requiring re-analysis of archive samples due to excessive blank contamination in the original analysis. Composite samples for each river station, representing a mixture of samples from each individual sampling date, were analyzed as part of the batch of samples that originally suffered from blank contamination. The available archive samples were used to re-analyze individual samples in the affected batch, such that the composite samples could not be reanalyzed. Factoring the composite samples into the completeness calculation, 88% of all samples were successfully analyzed. Because the composite samples were not intended for direct use in the mass balance assessment (their purpose was to provide as an independent check of the reasonableness of individual samples), failure to achieve the overall completeness criterion was not considered to compromise the project's quality objectives.

Data quality indicators evaluated for conventional parameters included the following:

- Bias (laboratory control samples, matrix spikes, and blanks)
- Precision (RPD of matrix spikes and replicate samples)
- Completeness

All reviewed QC results for conventional parameters complied with QAPP data quality indicators, with two minor exceptions described below.

- Holding Times and Sample Preservation: Eighteen samples were received at the laboratory either the morning after collection or the day of collection at a temperature of 7°C, which is outside of published EPA guidelines for preservation temperatures (0-6°C). Qualification of associated sample results was not considered necessary, due to the small discrepancy from the recommended guidelines.
- Matrix Spike Sample Recoveries: For one sample batch, the dissolved organic carbon matrix spike and matrix spike duplicate (MSD) percent recoveries (%R: 75.3 and 72.6) were below the QAPP %R limits (80-120); however, only the MSD %R was below the laboratory %R limits (75-125). Qualification of associated sample results was not necessary, due to the small discrepancy from the specified limits and the fact that the laboratory control sample recovery was acceptable.

2.3.2 Blank Correction

Total PCB concentrations were corrected for method blank contamination following the procedures defined in the QAPP. Specifically, individual congeners found in the sample at a concentration less than three times the associated blank concentration were flagged, and excluded from calculation of total PCB. It should be noted that there is no standard blank correction method, and numerous approaches are utilized, both nationally and within the Spokane River Basin. The selection of the most appropriate blank correction methodology must consider factors such as study objectives, sample matrix, sampling methodology, expected range of results, and tolerance for biased results.

No blank corrections were conducted on conventional parameters, as all blank samples for all conventional parameters were below the relevant detection limit.

2.3.3 Total PCB Concentrations in Spokane River

The Task Force collected effluent and surface water samples using quality assurance procedures consistent with supporting a semi-quantitative loading assessment. Total PCB concentrations for the river stations obtained using these quality assurance procedures are shown in Figure 4. Concentrations are largely below 50 pg/l at Mirabeau Point and Barker Road, with the exception of two outlier values (indicated in red). Concentrations are generally between 100 and 200 pg/l from the Trent Avenue Bridge downstream to the Spokane Gage. Approximately one third of all samples exceed the Washington water quality standard of 170 pg/l, while all of the samples exceed the downstream Spokane Tribe of Indians' water quality standard of 1.3 pg/l. As noted above, the quality assurance procedures used to process this data are designed to supporting a semi-quantitative loading assessment and are not intended to determine compliance with applicable water quality standards. These data, along with the tributary and point source data and outliers, are discussed in the following section. Furthermore, a detailed listing of PCB concentrations (total PCBs, plus individual homologs) and conventional parameters for each date at each sampling location is provided in Appendix A, and full laboratory data sheets are provided in Appendix D.

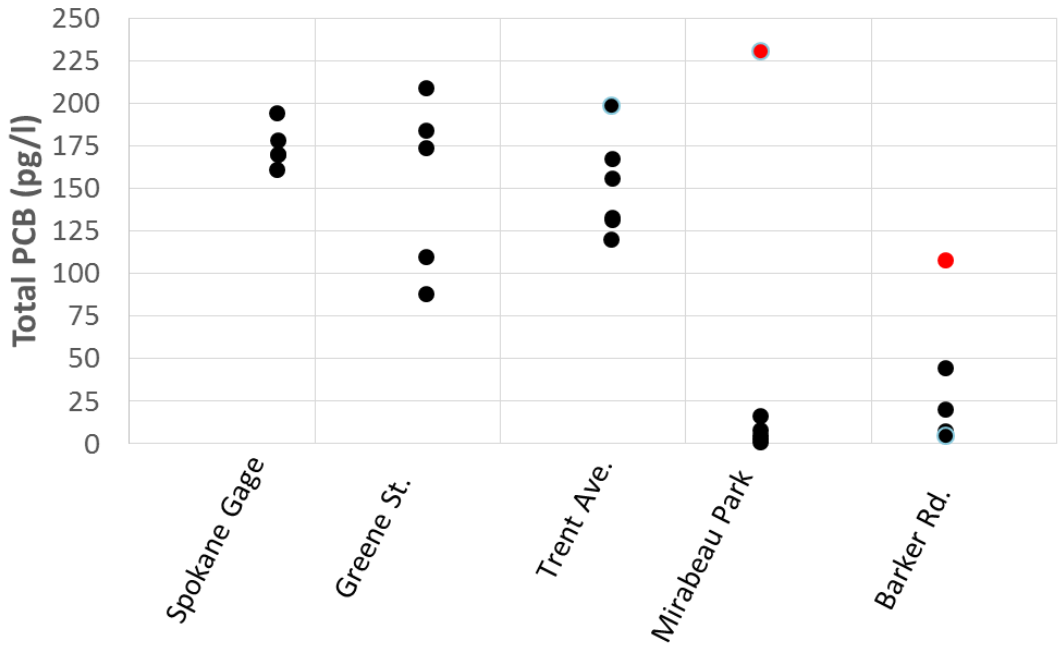

Figure 2. Spokane River Total PCB Concentrations Measured during 2015 Synoptic Survey (Outliers in Red)

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3 MASS BALANCE ASSESSMENT

The objective of the mass balance assessment is to use the results of the synoptic survey to identify stream reaches where incremental loads lead to a significant increase in river concentrations. This section describes the application of the mass balance assessment, and is divided into subsections of:

- Conceptual approach
- Initial application
- Revisions to initial application

3.1 Conceptual approach

The general conceptual approach of the mass balance assessment is to determine the presence of unmonitored loads (presumably from groundwater sources) by comparing the amount of mass passing through the Spokane River at two locations where flow and concentration measurements are available. The magnitude of the unmonitored load can be determined as the difference in monitored load at the downstream and upstream locations, as depicted below in Figure 3 and Equation 1. Q_u and Q_d represent the river flow at the upstream and downstream stations, respectively, while C_u and C_d represent the upstream and downstream PCB concentrations.

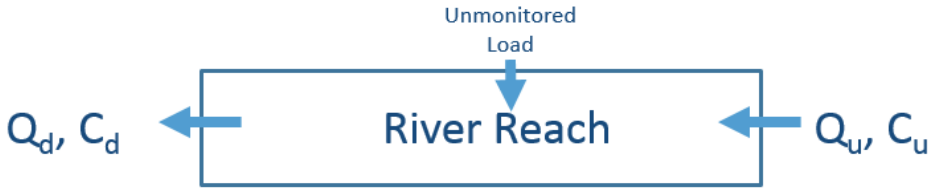

Figure 3. Simplified Description of Mass Balance Approach

The approach is described mathematically in Equation 1.

$$\text{Unmonitored load} = \text{Downstream load} - \text{Upstream load} \quad (1)$$

where:

Downstream load = Flow at downstream location (Q_d) x
Concentration at downstream location (C_d)

Upstream load = Flow at Upstream location (Q_u) x
Concentration at upstream location (C_u)

Equation 1 is based upon the assumption that environmental loss processes affecting PCBs are relatively insignificant between the two monitoring locations. This assumption was verified using

low-flow hydraulic results from model of the Spokane River, observed data on suspended solids concentrations, and literature values for coefficients related to solids partitioning and volatilization.

The concept can be extended to address situations where a monitored load (e.g. wastewater treatment plant discharge) enters the reach between the upstream and downstream monitoring locations, as shown in Figure 4.

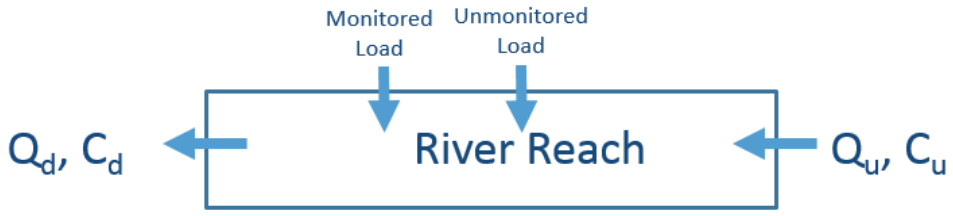

Figure 4. Mass Balance Approach in the Presence of a Monitored Load

In this situation, the mass balance equation is expanded to consider the monitored load as shown in Equation 2.

$$\text{Unmonitored load} = \text{Downstream load} - \text{Upstream load} - \text{Monitored Load} \quad (2)$$

3.2 Application

The data on flows and concentrations used in the mass balance assessment are provided in Tables 1 through 4. These data are blank-corrected using the methods described in the QAPP. Results for laboratory method blanks, trip blanks, and transfer blanks are provided in Table 5.

Table 1. River Flows (cfs) Used in 2015 Mass Balance Assessment

	8/18	8/19	8/20	8/21	8/22
Barker Rd.	110	110	120	120	120
Mirabeau Park	500	490	470	460	450
Trent Ave.	620	630	600	620	610
Greene St.	810	810	810	810	800
Spokane Gage	700	700	700	700	690

Table 2. Point Source Flows (cfs) Used in 2015 Mass Balance Assessment

	8/18	8/19	8/20	8/21	8/22
Kaiser Aluminum	13	13	13	13	13
Inland Empire Paper	11	11	11	11	11
Spokane County	12	12	12	12	12

Table 3. River Total PCB Concentrations (pg/l) Used in 2015 Mass Balance Assessment

	8/18	8/19	8/20	8/21	8/22
Barker Rd.	4.6	6.6	20	110	7.4/ 45*
Mirabeau Park	230	17	5.0	8.4/ 1.4*	3.0
Trent Ave.	200	170/ 130*	110	120	160
Greene St.	180	210	110	170	88
Spokane Gage	190	160	180	170	170

*Replicate sample

Table 4. Discharge Total PCB Concentrations (pg/l) Used in 2015 Mass Balance Assessment

	8/18	8/20	8/22
Kaiser Aluminum	2200	2800/ 2600*	3200
Inland Empire Paper	2800	4400	3100
Spokane County	290	470	320

*Replicate sample.

Table 5. Reported Blanks (Total PCBs, pg/L)

Laboratory Blank	Trip Blank	Field Blank
50.9	71.2	110
60.4	81.1	71.3
77.5		

Two of the observed PCB concentrations were considered outliers (i.e. defined as an observation that is distant from other observations), as they were much higher than other concentrations observed at the same site. These outlier values correspond to river concentrations of 110 pg/l measured at Barker Road, and 230 pg/l measured at Mirabeau Park. Because the mass balance analysis assumes steady-state conditions, the presence of concentrations un-representative of steady conditions provide the potential of biasing model results. For this reason, the mass balance analysis was conducted twice, once using all data values and once excluding outliers. The analysis will be considered robust to the extent that the same conclusions are drawn using each of the above approaches for handling outliers.

Results of the analysis are shown in Table 6 and graphed in Figure 7. The primary finding is the confirmation of the LimnoTech (2015a) findings of a relative large unmonitored PCB source in the river reach between Barker Road and Trent Avenue. This conclusion holds regardless of whether the outlier values are included or excluded from the analysis. This analysis provides additional refinement of the location of where that load enters, as the large bulk of that load is estimated to enter between Mirabeau Park and the Trent Avenue Bridge.

Table 6. Results of 2015 Mass Balance Assessment on Total PCBs

River Reach	Incremental Load (mg/day)	
	All Data	Outliers Excluded
Barker Road to Mirabeau Park	42	3.2
Mirabeau Park to Trent Avenue	88	130
Trent Avenue to Greene St.	-22	-22
Greene St. to Spokane Gage	-4.0	-4.0

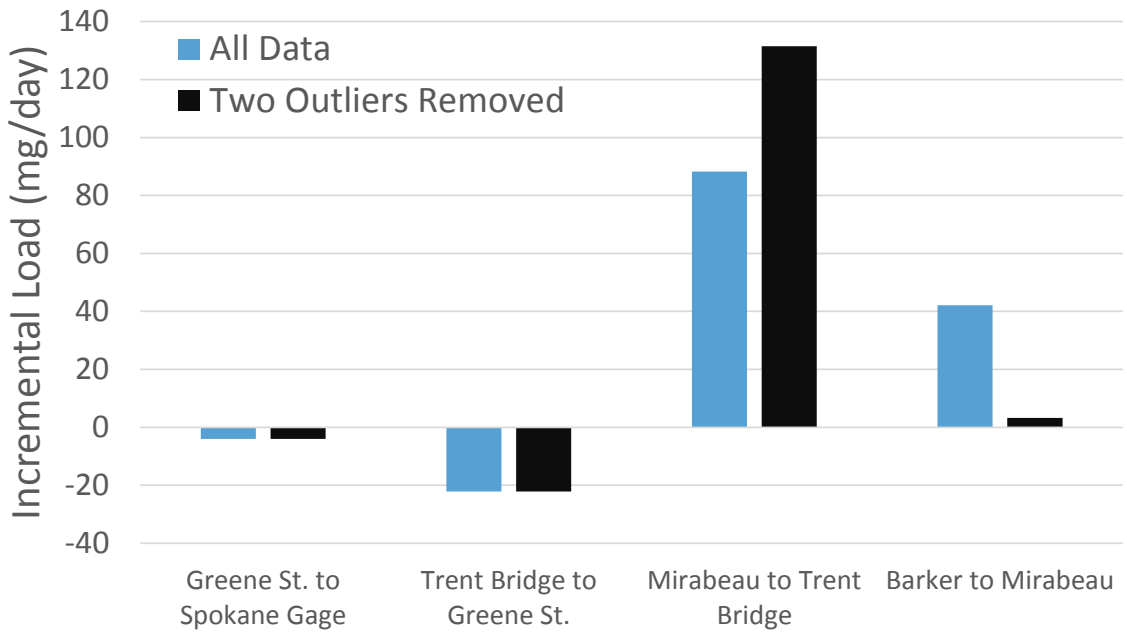

Figure 5. Results of Mass Balance Assessment on Total PCBs

3.3 Uncertainty Assessment

The results of the mass balance assessment have the potential to be highly uncertain, due to ambient PCB concentrations being very close to the level of blank contamination, as well as due to the day to day variability in observed concentrations and flows. In recognition of this fact, an assessment was conducted to attempt to quantify the uncertainty in the mass balance assessment.

The uncertainty assessment was conducted via Monte Carlo analysis, where each input to the mass balance assessment was characterized as a statistical frequency distribution instead of a single value. Statistical distributions for river flow were based upon the observed day-to-day variability in flows observed over the survey period, and are displayed in Table 6 for river flows and Table 7 for discharge flows. In addition to a mean and standard deviation, a serial correlation coefficient was also specified to account for the fact that daily variation in river flows was correlated between gages, e.g. a higher than average flow on a given day at one gage was typically associated with higher than average flows that day at the other gages.

Table 7. Characterization of Uncertainty in River Flows Used in 2015 Mass Balance Assessment

	Mean (cfs)	Std. Dev. (cfs)	Distribution	Serial Correlation
Barker Rd.	120	7.1	Normal	1.0
Mirabeau Park	470	20	Normal	-0.93
Trent Ave.	620	11	Normal	0.48
Greene St.	810	5.3	Normal	0.19
Spokane	700	4.3	Normal	0.86

Table 8. Characterization of Uncertainty in Discharge Flows Used in 2015 Mass Balance Assessment

	Mean (cfs)	Std. Dev. (cfs)	Distribution
Kaiser Aluminum	13	0.05	Normal
Inland Empire Paper	11	0.21	Normal
Spokane County	12	0.20	Normal

The uncertainty in measured PCB concentrations was characterized by the summation of two components: 1) The observed day-to-day variability in measured concentration, and 2) The uncertainty caused by measurements at levels close to that of blank contamination. The input distributions used to represent these components are displayed in Table 8 for river concentrations and Table 9 for discharge concentrations. The influence of the one outlier river PCB concentration of 230 pg/l at Mirabeau Park is seen in Table 8, as the variability in concentrations at that station (i.e. standard deviation of 92 pg/l) is much greater than at any other station.

Table 9. Characterization of Uncertainty in River Concentrations Used in 2015 Mass Balance Assessment

	Variability			Measurement Uncertainty		
	Mean (pg/l)	Std. Dev. (pg/l)	Distribution	Mean (pg/l)	Std. Dev. (pg/l)	Distribution
Barker Rd.	32	40	Normal	0	15	Normal
Mirabeau Park	44	92	Normal	0	15	Normal
Trent Ave.	150	33	Normal	0	15	Normal
Greene St.	150	52	Normal	0	15	Normal
Spokane	170	12	Normal	0	15	Normal

Table 10. Characterization of Uncertainty in Discharge Concentrations Used in 2015 Mass Balance Assessment

	Variability			Measurement Uncertainty		
	Mean (pg/l)	Std. Dev. (pg/l)	Distribution	Mean (pg/l)	Std. Dev. (pg/l)	Distribution
Kaiser Aluminum	2700	400	Lognormal	0	15	Normal
Inland Empire Paper	3500	850	Lognormal	0	15	Normal
Spokane County	360	91	Lognormal	0	15	Normal

A Monte Carlo analysis was conducted for the mass balance assessment, whereby the mass balance calculations were repeated thousands of times, with the inputs for each simulation randomly selected from the statistical frequency distributions defined in Tables 6 through 9. The results of each simulation were stored, and then compiled to characterize the uncertainty in predicted unknown loads. The resulting frequency distributions are shown in Figures 8 through 12. Although the resulting uncertainty in estimated loads is relatively high, the large majority of estimated loads for the Mirabeau Park to Trent Ave section are greater than zero, indicating high confidence that an unmonitored PCB load is entering the river in this segment. The distribution of loads around the remaining reaches are centered around zero, showing no conclusive evidence of incremental load. The influence of the outlier data point of 230 pg/l at Mirabeau Park is seen in both Figures 6 and 7. Figure 6 shows a long "tail" to the right of the most commonly occurring results, reflecting the possibility of high concentrations at Mirabeau Park. This same phenomenon in seen in mirror image in Figure 7, with a long "tail" to the left of the most commonly occurring results for the Mirabeau Park to Trent Avenue reach. These two tails are directly correlated; the individual simulations that used a high Mirabeau Park concentration result in a larger calculated load in the Barker Rd. to Mirabeau Park reach, but also directly lead to calculation of a smaller calculated load in the Mirabeau Park to Greene St. reach. The overall conclusion is that there is a large load entering between Barker Rd. and Trent Ave.; the one high concentration value observed at Mirabeau Park (if representative) indicates that some of this load may be entering the river upstream of Mirabeau Park.

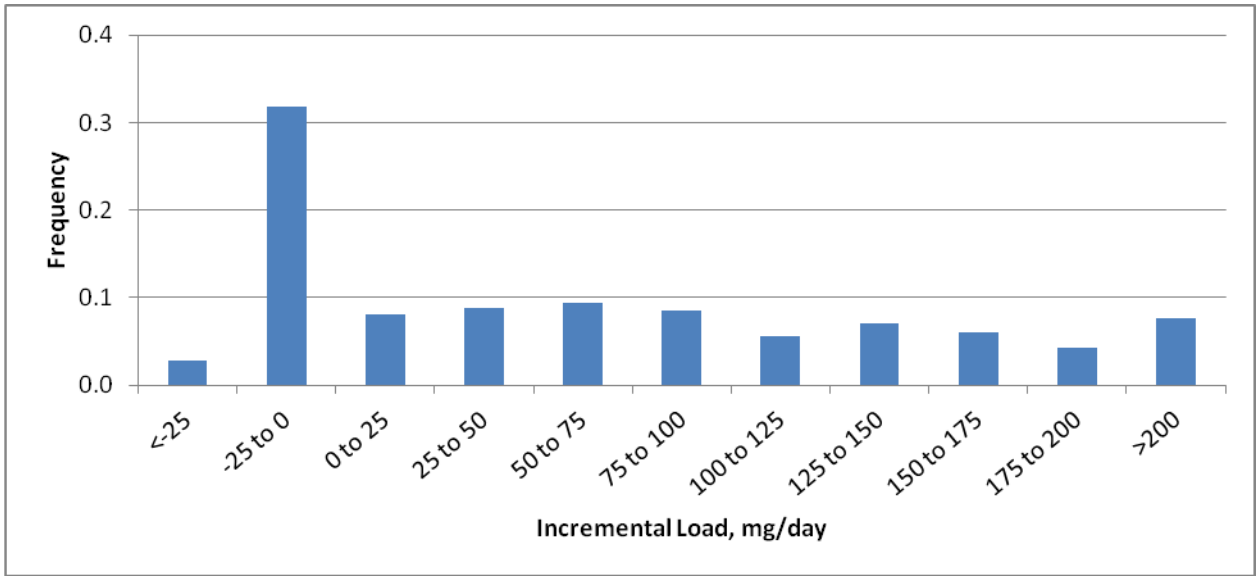

Figure 6. Uncertainty Distribution for Unknown Load - Barker Rd. to Mirabeau Park

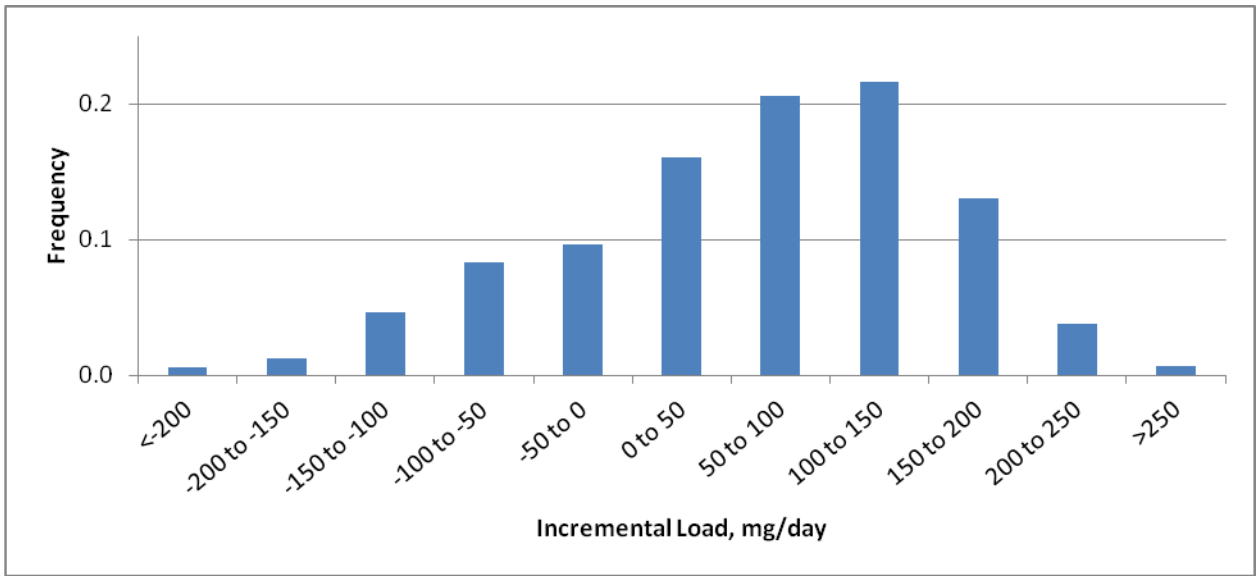

Figure 7. Uncertainty Distribution for Unknown Load - Mirabeau Park to Trent Ave.

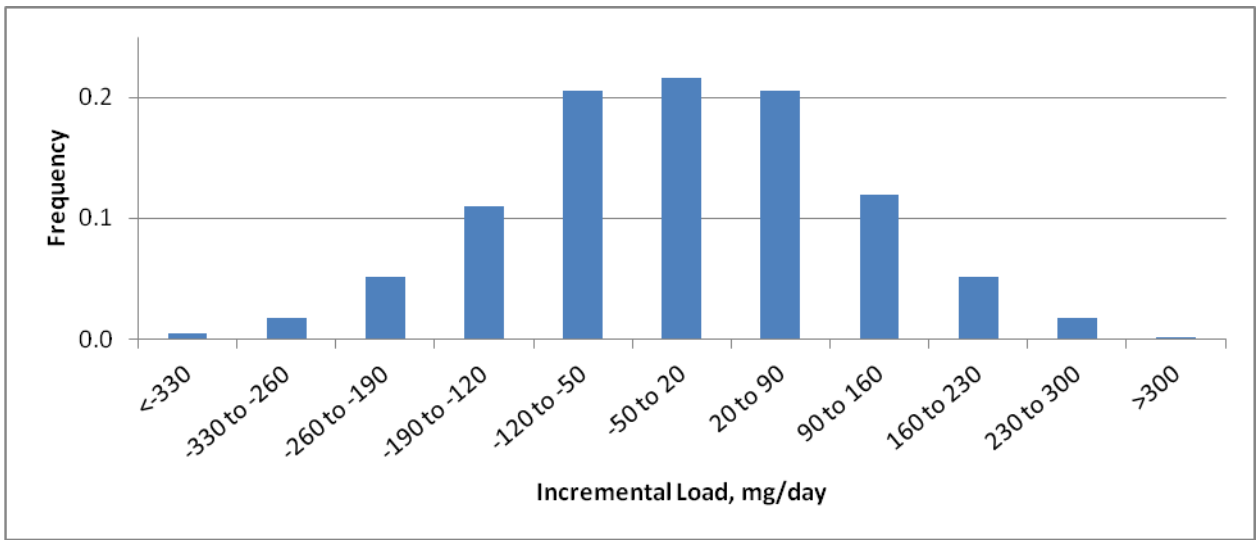

Figure 8. Uncertainty Distribution for Unknown Load - Trent Ave. to Greene St.

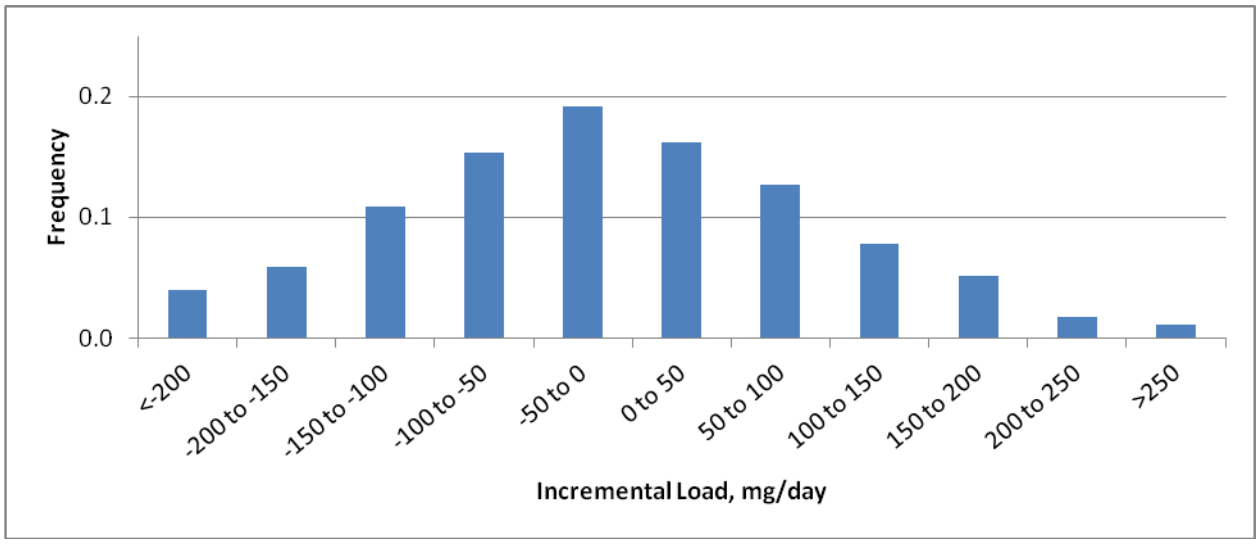

Figure 9. Uncertainty Distribution for Unknown Load – Greene St. to Spokane Gage

3.4 Homolog-Specific Mass Balance Assessment

While the mass balance assessment conducted by the Task Force focused solely on total PCBs, Spokane County conducted a similar mass balance assessment on the individual homologs that comprise total PCB concentrations. Results for the homolog-specific analysis were generally consistent with those found for total PCBs (i.e. no significant incremental loading sources identified other than the one upstream of Trent Avenue Bridge), except for the section of river downstream of Trent Avenue Bridge. The results of the homolog-specific mass balance assessment for the reaches upstream and downstream of Trent Avenue are summarized in Table 10 for the 2014 synoptic survey and Table 11 for the 2015 synoptic survey. Results for 2014 are presented for the River Reach Trent to Spokane Gage, because no flow gaging station was available at Greene St. in 2014.

Table 11. Incremental Loads (mg/day) Estimated by Homolog-Specific Mass Balance Assessment for 2014 (Green shading indicates an increase in PCB Load; Red shading indicates a decrease in PCB Load.)

Homolog	River Reach	
	Barker to Trent	Trent to Spokane Gage
Monochloro	-1	-1
Dichloro	-3	28
Trichloro	43	-42
Tetrachloro	123	-85
Pentachloro	26	45
Hexachloro	2	44
Heptachloro	0	14
Octachloro	1	2
Nonachloro	0	0
Decachloro	0	0
Sum	190	7

Table 12. Incremental Loads (mg/day) Estimated by Homolog-Specific Mass Balance Assessment for 2015. (Green shading indicates an increase in PCB Load; Red shading indicates a decrease in PCB Load.)

Homolog	River Reach	
	Mirabeau to Trent	Trent to Greene
Monochloro	*0*	*-1*
Dichloro	*-1*	*-20*
Trichloro	*36*	*-65*
Tetrachloro	*81*	*-45*
Pentachloro	*19*	*31*
Hexachloro	*-1*	*50*
Heptachloro	*0*	*17*
Octachloro	*0*	*4*
Nonachloro	*0*	*4*
Decachloro	*0*	*0*
Sum	*130*	*-26*

These results confirm the earlier finding of a large incremental load entering the river upstream of Trent Avenue for both years of the synoptic survey, and shows that these loads are in the tri-, tetra-, and penta-chloro forms. Interesting results are observed downstream of Trent Avenue for both years when examining the mass balance assessment on a homolog-specific basis. While the incremental load of total PCBs below Trent Avenue is small for both synoptic surveys, both surveys show a significant loading of the penta- through hepta-chloro forms, and a significant negative load in the tri- and tetra-chloro forms. The cause of these results are currently unknown, and could potentially indicate:

- An additional unmonitored incremental loading source of the penta-chloro through hepta-chloro forms, and/or
- Confounding effects of groundwater exchange mechanisms which are more complex than assumed in the mass balance assessment.

The potential for confounding groundwater interactions is depicted in Figure 10, which indicates that the river alternates between stretches where water is lost from the river to the aquifer (i.e. losing reaches) and stretches where water is delivered to the river from the aquifer (i.e. gaining reaches.) The modeled reach between Trent Ave. and Greene St. contains a combination of gaining and losing reaches. As discussed in the assessment report for the 2014 survey, mass balance results for the reach downstream of Trent can be very sensitive to the assumptions made regarding the nature of groundwater flow. The mass balance assessment as currently structured implicitly assumes that PCBs lost from the river in the losing stretch between Trent and Greene all re-enter the river prior to Greene St. This may not be a reasonable assumption if the groundwater that enters the river just upstream of Greene St. is comprised of a different source of water than what left the river immediately upstream. Should the river water that was lost in this segment not immediately return to the river, that would explain the apparent negative incremental load observed in the homolog-specific assessment.

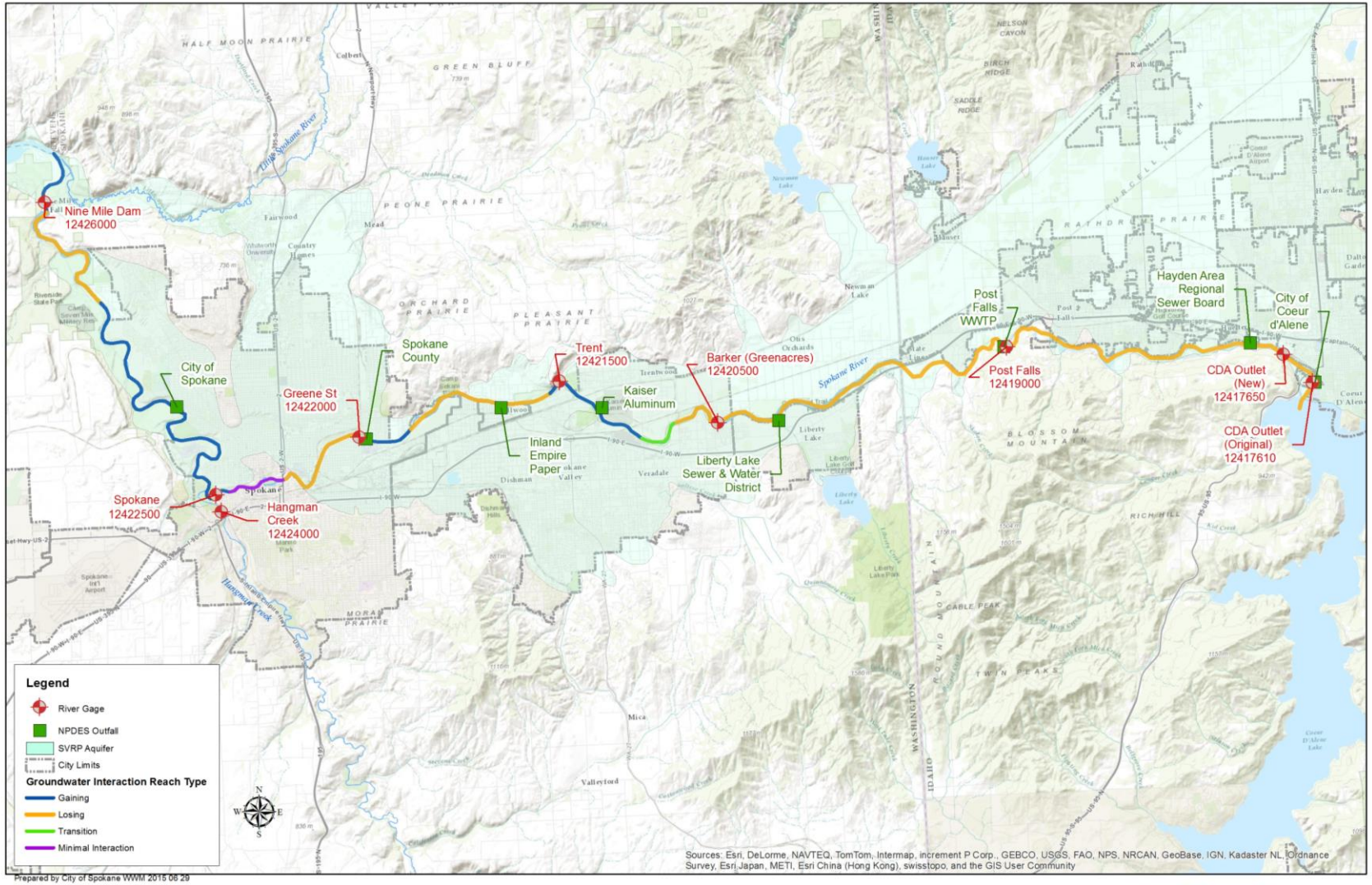

Figure 10. Map of Groundwater Interactions throughout Study Area

3.5 Summary of Mass Balance Assessment

The results of the semi-quantitative mass balance assessment for total PCBs are shown in Figure 11, with error bars representing the inter-quartile range (i.e. 25th to 75th percentile) determined from the uncertainty analysis. The unknown load between Barker Road and the Trent Avenue Bridge near Plante's Ferry is seen to be the largest load. The next largest loads are the point source discharges from Inland Empire Paper and Kaiser Aluminum. All remaining sources are relatively small, contributing 5% or less to the overall load. The large uncertainty in the loads entering the river between: 1) Mirabeau Point and Trent, and 2) Barker and Mirabeau Point, are caused by consideration of the one previously noted outlier concentration observed at Mirabeau Point. As discussed above, the predicted loads between these reaches are directly and negatively correlated to the assumed concentration at Mirabeau Point. The situations that result in a small incremental load being predicted between Mirabeau and Trent always correspond to a large load between Barker and Mirabeau, and vice versa. This indicates that there is little uncertainty in the presence of a load between Barker and Trent, whatever uncertainty exists corresponds to whether the load enters upstream or downstream of Mirabeau Point.

The uncertainty in the load between Trent Ave. and Greene Street is also noteworthy; although the best estimate for this load is relatively small, the homolog-specific analysis indicates that the presence of an additional load in this reach cannot be ruled out.

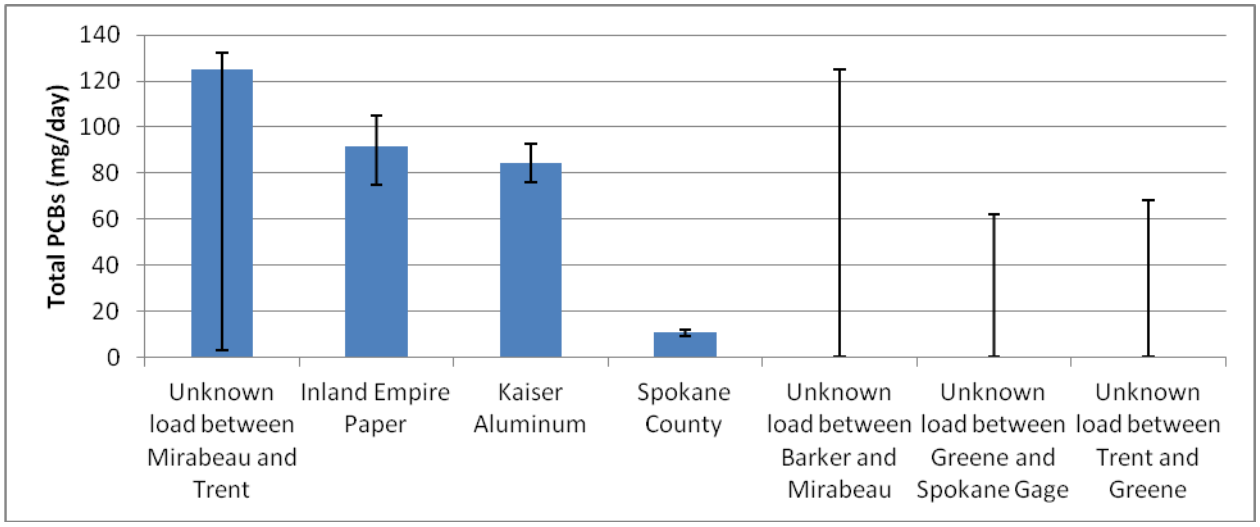

Figure 11. Summary of Mass Balance Estimates (mg/day)

The following conclusions and can be gathered from the mass balance analysis:

- The low concentrations of PCBs in the Spokane River (i.e. at magnitudes sometimes similar to those observed in blank samples) make precise calculations impossible and instead can best support semi-quantitative decisions.
- The presence of a large (i.e. as large as any other single dry weather source) incremental PCB load entering the Spokane River between Barker Road and the Trent Avenue Bridge

was confirmed, with the location of the load very likely narrowed down to between Mirabeau Park and the Trent Avenue Bridge.

- Homolog-specific mass balance analyses indicate the potential presence of another groundwater loading source downstream of the Trent Avenue Bridge, although further study is needed to assess the nature of this source.

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Appendix A:
Synoptic Survey Results by Homolog

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Table A-1: Blank-Corrected Analytical Results for Spokane River at Barker Road Bridge						
Station SR9	8 / 18	8 / 19	8 / 20	8 / 21	8 / 22	8 / 22-R
Total PCBs (pg/l)	4.598	6.613	20.464	108.139	7.382	44.529
Total Monochloro Biphenyls (pg/l)	0	0	0	0	0	0
Total Dichloro Biphenyls (pg/l)	0	1.76	4.868	0.486	0.938	0.413
Total Trichloro Biphenyls (pg/l)	0.254	0.614	5.19	0.201	1.407	0.272
Total Tetrachloro Biphenyls (pg/l)	1.188	0.449	4.22	6.1	0.711	6.596
Total Pentachloro Biphenyls (pg/l)	1.881	0.49	0.539	62.288	0.644	31.192
Total Hexachloro Biphenyls (pg/l)	0.856	1.359	2.781	37.388	1.388	4.521
Total Heptachloro Biphenyls	0	1.456	1.925	1.144	1.365	1.093
Total Octachloro Biphenyls (pg/l)	0.419	0.485	0.941	0.532	0.929	0.442
Total Nonachloro Biphenyls (pg/l)	0	0	0	0	0	0
Total Decachloro Biphenyls (pg/l)	0	0	0	0	0	0
Total Dissolved Solids (mg/l)	44	42	37	63	86	86
Total Suspended Solids (mg/l)	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Total Organic Carbon (mg/l)	1.84	1.81	1.73	1.8	1.71	1.71
Dissolved Organic Carbon (mg/l)	1.66	1.66	1.59	1.55	1.56	1.56

Table A-2: Blank-Corrected Analytical Results for Spokane River at Mirabeau Park						
Station SR8a	8 / 18	8 / 19	8 / 20	8 / 21	8 / 21-R	8 / 22
Total PCBs (pg/l)	230.708	16.648	5.011	8.385	1.417	2.96
Total Monochloro Biphenyls (pg/l)	0	0	0	0	0	0
Total Dichloro Biphenyls (pg/l)	0.541	1.194	1.022	0	0.834	0
Total Trichloro Biphenyls (pg/l)	0.266	0.51	0.229	0.188	0	0.402
Total Tetrachloro Biphenyls (pg/l)	8.943	0.92	0.23	0.748	0.201	0.469
Total Pentachloro Biphenyls (pg/l)	73.097	5.688	0.632	6.69	0	0.76
Total Hexachloro Biphenyls (pg/l)	112.675	6.415	1.11	0.489	0.199	1.005
Total Heptachloro Biphenyls (pg/l)	29.604	1.921	1.55	0.27	0.183	0.324
Total Octachloro Biphenyls (pg/l)	4.2	0	0.238	0	0	0
Total Nonachloro Biphenyls (pg/l)	1.382	0	0	0	0	0
Total Decachloro Biphenyls (pg/l)	0	0	0	0	0	0
Total Dissolved Solids (mg/l)	129	142	130	162	162	159
Total Suspended Solids (mg/l)	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Total Organic Carbon (mg/l)	<1	<1	<1	<1	<1	<1
Dissolved Organic Carbon (mg/l)	<1	<1	<1	<1	<1	<1

Table A-3: Blank-Corrected Analytical Results for Kaiser Aluminum				
Station SR8	8 / 18	8 / 20	8 / 20-R	8 / 22
Total PCBs (pg/l)	2226.452	2789.61	2645.791	3178.628
Total Monochloro Biphenyls (pg/l)	0	0	0	0
Total Dichloro Biphenyls (pg/l)	120.05	164.18	158.96	150.178
Total Trichloro Biphenyls (pg/l)	602.126	1117.625	1011.411	1169.813
Total Tetrachloro Biphenyls (pg/l)	1228.568	1231.701	1250.748	1543.444
Total Pentachloro Biphenyls (pg/l)	234.598	222.133	222.637	281.621
Total Hexachloro Biphenyls (pg/l)	38.992	36.921	1.785	27.483
Total Heptachloro Biphenyls (pg/l)	0.783	12.641	0.25	4.712
Total Octachloro Biphenyls (pg/l)	1.335	4.409	0	1.377
Total Nonachloro Biphenyls (pg/l)	0	0	0	0
Total Decachloro Biphenyls (pg/l)	0	0	0	0
Total Dissolved Solids (mg/l)	183	173	173	215
Total Suspended Solids (mg/l)	<5.0	<5.0	<5.0	<5.0
Total Organic Carbon (mg/l)	1.4	1.29	1.29	2.05
Dissolved Organic Carbon (mg/l)	1.13	26.8	26.8	1.44

Table A-4: Blank-Corrected Analytical Results for Spokane River Below Trent Bridge						
Station SR7	8 / 18	8 / 19	8 / 19-R	8 / 20	8 / 21	8 / 22
Total PCBs (pg/l)	199.359	167.575	132.322	113.012	119.714	155.927
Total Monochloro Biphenyls (pg/l)	0	0	0	0	0	0
Total Dichloro Biphenyls (pg/l)	0.88	8.461	2.002	1.395	0.822	0.63
Total Trichloro Biphenyls (pg/l)	53.518	43.044	44.993	39.718	38.266	45.953
Total Tetrachloro Biphenyls (pg/l)	99.448	77.693	72.854	64.22	73.027	92.484
Total Pentachloro Biphenyls (pg/l)	43.483	29.259	9.665	5.744	6.804	16.24
Total Hexachloro Biphenyls (pg/l)	1.762	7.347	1.366	0.628	0.269	0.394
Total Heptachloro Biphenyls (pg/l)	0	1.771	1.028	1.065	0.236	0.226
Total Octachloro Biphenyls (pg/l)	0.268	0	0.414	0.242	0.29	0
Total Nonachloro Biphenyls (pg/l)	0	0	0	0	0	0
Total Decachloro Biphenyls (pg/l)	0	0	0	0	0	0
Total Dissolved Solids (mg/l)	133	144	144	144	171	143
Total Suspended Solids (mg/l)	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Total Organic Carbon (mg/l)	<1	<1	<1	<1	<1	<1
Dissolved Organic Carbon (mg/l)	<1	<1	<1	<1	<1	<1

Table A-5: Blank-Corrected Analytical Results for Inland Empire Paper				
Station SR6	8 / 18	8 / 18-R	8 / 20	8 / 22
Total PCBs (pg/l)	2824.355	na	4449.304	3101.042
Total Monochloro Biphenyls (pg/l)	0	na	78.5	62.6
Total Dichloro Biphenyls (pg/l)	397.61	na	879.97	732.47
Total Trichloro Biphenyls (pg/l)	1164.11	na	1762.501	1244.79
Total Tetrachloro Biphenyls (pg/l)	930.275	na	1288.138	822.212
Total Pentachloro Biphenyls (pg/l)	246.497	na	333.259	187.602
Total Hexachloro Biphenyls (pg/l)	65.579	na	77.636	43.453
Total Heptachloro Biphenyls (pg/l)	13.963	na	22.064	6.707
Total Octachloro Biphenyls (pg/l)	4.649	na	6.452	1.208
Total Nonachloro Biphenyls (pg/l)	1.672	na	0.784	0
Total Decachloro Biphenyls (pg/l)	0	na	0	0
Total Dissolved Solids (mg/l)	561	561	598	955
Total Suspended Solids (mg/l)	<5.0	<5.0	<5.0	<5.0
Total Organic Carbon (mg/l)	47.8	47.8	47	62.7
Dissolved Organic Carbon (mg/l)	44.1	44.1	42	63.4

Table A-6: Blank-Corrected Analytical Results for Spokane County Regional Water Reclamation Facility			
Station SR5	8 / 18	8 / 20	8 / 22
Total PCBs (pg/l)	292.029	465.948	322.823
Total Monochloro Biphenyls (pg/l)	0	0	0
Total Dichloro Biphenyls (pg/l)	81.58	106.826	81.536
Total Trichloro Biphenyls (pg/l)	81.718	141.489	88.988
Total Tetrachloro Biphenyls (pg/l)	76.8	125.875	81.576
Total Pentachloro Biphenyls (pg/l)	49.283	70.047	61.803
Total Hexachloro Biphenyls (pg/l)	1.964	19.671	8.622
Total Heptachloro Biphenyls (pg/l)	0	2.04	0.298
Total Octachloro Biphenyls (pg/l)	0.684	0	0
Total Nonachloro Biphenyls (pg/l)	0	0	0
Total Decachloro Biphenyls (pg/l)	0	0	0
Total Dissolved Solids (mg/l)	526	497	533
Total Suspended Solids (mg/l)	<5.0	<5.0	<5.0
Total Organic Carbon (mg/l)	4.62	4.04	4.13
Dissolved Organic Carbon (mg/l)	4.51	3.98	22.2

Table A-7: Blank-Corrected Analytical Results for Spokane River at Greene Street Bridge					
Station SR4	8 / 18	8 / 19	8 / 20	8 / 21	8 / 22
Total PCBs (pg/l)	184.25	209.292	109.781	173.835	88.156
Total Monochloro Biphenyls (pg/l)	0	0	0	0	0
Total Dichloro Biphenyls (pg/l)	3.994	0.378	1.307	2.582	0.939
Total Trichloro Biphenyls (pg/l)	13.634	9.372	33.367	46.263	0.938
Total Tetrachloro Biphenyls (pg/l)	83.819	49.648	50.363	61.458	26.287
Total Pentachloro Biphenyls (pg/l)	65.619	48.367	9.556	29.015	24.457
Total Hexachloro Biphenyls (pg/l)	15.153	73.741	9.14	23.212	16.439
Total Heptachloro Biphenyls (pg/l)	1.557	25.162	3.919	10.184	5.22
Total Octachloro Biphenyls (pg/l)	0.474	2.624	1.248	1.121	4.313
Total Nonachloro Biphenyls (pg/l)	0	0	0.881	0	8.695
Total Decachloro Biphenyls (pg/l)	0	0	0	0	0.868
Total Dissolved Solids (mg/l)	142	142	144	175	183
Total Suspended Solids (mg/l)	<5.0	<5.0	<5.0	<5.0	<5.0
Total Organic Carbon (mg/l)	1.21	1.06	1.08	<1	<1
Dissolved Organic Carbon (mg/l)	1.15	<1	<1	<1	<1

Table A-8: Blank-Corrected Analytical Results for Spokane River at Spokane Gage					
Station SR3	**8 / 18**	**8 / 19**	**8 / 20**	**8 / 21**	**8 / 22**
Total PCBs (pg/l)	194.061	161.416	178.515	170.28	170.341
Total Monochloro Biphenyls (pg/l)	0	10.98	0	0	0
Total Dichloro Biphenyls (pg/l)	0.65	1.715	1.448	1.795	2.13
Total Trichloro Biphenyls (pg/l)	13.75	10.733	42.402	36.147	40.309
Total Tetrachloro Biphenyls (pg/l)	75.326	54.561	57.036	56.756	68.723
Total Pentachloro Biphenyls (pg/l)	82.309	52.28	35.35	37.488	39.109
Total Hexachloro Biphenyls (pg/l)	19.571	24.62	29.412	27.227	13.625
Total Heptachloro Biphenyls (pg/l)	1.873	5.333	11.291	9.819	6.101
Total Octachloro Biphenyls (pg/l)	0.582	1.194	1.576	1.048	0.344
Total Nonachloro Biphenyls (pg/l)	0	0	0	0	0
Total Decachloro Biphenyls (pg/l)	0	0	0	0	0
Total Dissolved Solids (mg/l)	143	143	146	196	174
Total Suspended Solids (mg/l)	<5.0	<5.0	<5.0	<5.0	<5.0
Total Organic Carbon (mg/l)	1.21	1.16	1.05	1.09	1.05
Dissolved Organic Carbon (mg/l)	1.03	1.09	<1	<1	1.02

Appendix B: Gravity Report

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Appendix C:
Quality Assurance Project Plan

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Appendix D: Laboratory Results

Provided separately as electronic spreadsheets

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