Spokane River Regional Toxics Task Force 2018 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

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Water Scientists Environment Engineers Blank Page





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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<sup>1</sup>. 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.

Prior technical activities of the Task Force included carrying out synoptic surveys to assess the presence of unmonitored dry weather sources of PCBs to the Spokane River. A synoptic survey conducted in August of 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, 2015). A follow-up survey was conducted in August of 2015, designed to confirm the findings of the 2014 survey and provide greater detail on the location of the unmonitored source (LimnoTech, 2016). This report documents a 2018 survey and associated analyses designed to address questions identified from analysis of the 2014 and 2015 sampling results. Survey activities were conducted in accordance with the Quality Assurance Project Plan (LimnoTech, 2018) developed for this phase of the project.

The following conclusions can be gathered from the data collected:

- Groundwater loading of PCBs upstream of Mirabeau Point was not observed during the synoptic survey. This does not rule out the possibility of groundwater PCB loading in this area during other times, as previous indications of loads have been intermittent, but does confirm that the frequency of such loads (if still occurring) is sporadic.
- Homolog-specific mass balance analyses for the reach downstream of Trent Avenue (Plante's Ferry) show similar results as prior surveys, with a net loss of lower chlorinated homologs and a net gain of moderately chlorinated homologs.
- Mass balance analyses for the portion of the river downstream of Greene St. indicate the potential for groundwater PCB loading, both between Greene St. and the USGS gage and between the USGS gage and Nine Mile Dam.

Two issues remain unresolved: 1) the reason for the loss of lower chlorinated homologs below Trent Avenue, and 2) the statistical significance of calculated loads for individual homologs. Further studies may be helpful in addressing these issues, although it is recommended that conduct of any such studies be postponed until results of Ecology's 2018 PCB sampling in biofilm, invertebrates, and sediments are available.

<sup>&</sup>lt;sup>1</sup> 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.



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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 (7 pg/l – based on a fish consumption rate of 175 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 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 80% 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 PCBs 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 Spokane River Regional Toxics Task Force (SRRTTF) has developed a comprehensive plan to reduce toxic pollutants in the Spokane River, specifically polychlorinated biphenyls (PCBs). The comprehensive plan is designed to identify specific management actions that can be undertaken to control pollutant loads such that water quality objectives can ultimately be attained. Comprehensive plans of this type require data capable of describing individual sources and site-specific processes that drive resulting concentrations. LimnoTech (2014) described the overall data collection strategy for a first year of monitoring, based on the work conducted to identify key gaps in the existing data set and issues addressed at a December 2013 monitoring workshop.

A Synoptic Survey was conducted in 2014 to identify potentially significant dry weather sources of PCBs to the Spokane River between Lake Coeur d'Alene and Nine Mile Dam. The results of this study showed the strong likelihood of a groundwater PCB source between Barker Road and the Trent Avenue Bridge, and the potential of an additional groundwater PCB source between the Trent Avenue Bridge and the Spokane USGS gage. No information on potential groundwater PCB sources between the Spokane USGS gage and Nine Mile Dam could be obtained, because fluctuations in river flow caused by maintenance activities at Nine Mile Dam violated the steady state assumption of the study design (LimnoTech, 2015a). The Task Force subsequently approved conducting a 2015 Synoptic Survey to confirm the findings of the 2014 Synoptic Survey over a narrower spatial scope. This work was conducted in August 2015 in accordance with the 2015 QAPP Addendum 1 (LimnoTech, 2015b). The results of the 2015 synoptic survey (LimnoTech, 2016) confirmed 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, with the location of where the load enters the river narrowed down to between upper Mirabeau Park/Sullivan Road and the Trent Avenue Bridge/Plante's Ferry.

In 2016, monthly water quality sampling was conducted to determine the seasonal variability in PCB concentrations in the Spokane River, to the extent that measured concentrations exceed laboratory blanks. Concurrent collection of flow data allowed for a semi-quantitative assessment of loading. The field monitoring program included six monthly sampling events. The results of the monthly sampling (LimnoTech, 2017) indicated that river PCB concentrations generally remain less than 40 pg/l during all months at the outlet of Lake Coeur d'Alene, with concentrations tending to increase downstream as the river passes through the Spokane metropolitan area. The amount of

increase varies seasonally in response to river flow, with lower river flows generally leading to larger increases in concentration.

In 2017, a homolog-specific mass balance analysis was conducted to provide additional insight into the presence of other PCB sources beyond that gained from the prior total PCB mass balance analyses. This analysis showed a loading source entering between Trent Avenue (Plante's Ferry) and Greene Street, although results were potentially confounded by the presence of a transition point between the losing and gaining sections of the river in this reach. It was recommended that future synoptic surveys include a sampling location at this transition point. QAPP Addendum 4 was prepared to document the procedural requirements of the 2017 analysis. The 2017 homolog specific mass balance analysis also showed a potential load of penta- and hexa-chloro homologs in the reach between Barker Road and Mirabeau Point, although the calculated load in this reach was driven solely by a single elevated PCB sample at Mirabeau Point. It is not clear whether this represents an anomalous measurement or the presence of an ephemeral groundwater loading source.

The 2018 monitoring described in this report was designed to provide supplemental information to address three gaps in understanding regarding groundwater PCB loading that exist from the prior studies:

- 1. The potential for groundwater loading sources between the Spokane USGS gage and Nine Mile Dam.
- 2. The specific nature of groundwater loading sources suspected between Trent Avenue (Plante's Ferry) and Greene Street.
- 3. The potential for groundwater loading sources between Barker Road and Mirabeau Point.

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

- Synoptic Survey
- Mass Balance Assessment

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# **2** SYNOPTIC SURVEY

A dry weather synoptic survey was conducted between August 4 and 8, 2018. The intent of the survey was to measure PCBs in the river and external loading sources, 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, 2018) developed for this project. Field activities are documented in Gravity (2018). Each of the above documents is included as an appendix to this report.

## **2.1 Monitoring Locations**

Sampling locations (Figure 1) included seven Spokane River stations, one station at the mouth of Hangman (Latah) Creek, and three point source discharges. The instream 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 Downriver of Upriver Dam (-117.334225, 47.680847)
- Spokane River below Greene St. Bridge (-117.3628, 47.67808)
- Spokane River at Spokane USGS Gage (117.4497, 47.65888)
- Spokane River below Nine Mile Dam (-117.5397324, 47.21437906)
- Latah (Hangman) Creek Gage Station (-117.44986, 47.6528668)

The point source discharges consisted of:

- Inland Empire Paper (-117.2782, 47.68867)
- Spokane County Regional Water Reclamation Facility
- City of Spokane Riverside Park Advanced WWTP (-117.471655, 47.693547)

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 4-8, 2015 Synoptic Survey



## 2.2 Field Sampling Activities

The field sampling activities as planned and implemented are detailed in the project QAPP (LimnoTech, 2018), and Gravity (2018) field report, both of which are included as appendices to this report. This section summarizes those activities. Environmental specialists from Gravity Consulting and LimnoTech conducted the sampling event. 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 4, 5, 6, 7 and 8 at the instream stations listed in Section 2.1. Point source effluents were sampled on August 4, 6, and 8.

## 2.3 Analytical Results

Field samples were shipped to SGS 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, 2018). 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, and dissolved organic carbon.

### 2.3.1 Data Quality Assessment - PCBs

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

The large majority of QC results complied with QAPP data quality indicators, with exceptions listed below:

- 49 Lab Control Sample Recovery results were under the QAPP criterion of 50% recovery. Sample results associated with the low recoveries were qualified as estimated using J/UJ data flags.
- 47 Sample and Method Blank Surrogate Recovery results were under the QAPP criterion of 25% recovery. Sample results associated with the low recoveries were qualified as estimated using J/UJ data flags.

• The relative percent differences (RPDs) for four congeners in one duplicate pair, and nine congeners in another duplicate pair, were above the QAPP-specified criteria (0-50% for congeners >10x EDL). Results for those congeners associated with the high RPDs were qualified as estimated using the J data flag.

There are no changes to the final PCB result values as originally reported by the laboratory.

All method blank concentrations were in compliance with the QAPP-specified criterion of total PCBs<180 pg/l. One sample batch, while compliant with QAPP criteria, showed elevated concentrations in the monochloro (66.3 pg/l) and dichloro (41.4 pg/l) homologs. Two samples in this batch, Hangman Creek on August 6 and Mirabeau Point on August 7, showed anomalously high concentrations in these homologs (526 pg/l monochloro and 312 pg/l dichloro at Hangman Creek, 219 pg/l monochloro and 126 pg/l dichloro at Mirabeau Point). These two samples were excluded from future analysis, because: 1) concentrations for these homologs were orders of magnitude higher than any others observed at these sites in other samples; 2) concentrations for all of the other homologs in these samples were at normal levels; and 3) the method blank for the batch containing these samples indicated that some degree of contamination existed for these homologs.

The QAPP has a completeness criterion for PCBs of 95%. 100% of the planned individual samples were collected and analyzed. Two samples were eliminated from further consideration due to suspected contamination in the mono- and di-chloro homologs as discussed above. Overall, 65 of 67 samples were successfully analyzed resulting in a completeness of 97%.

### 2.3.2 Data Quality Assessment – Conventional Pollutants

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.

### 2.3.3 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 homologs and 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.

### 2.3.4 Total PCB Concentrations

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 (and Hangman Creek) stations obtained using these quality assurance procedures are shown in Figure 2 and listed in Table 1. Observed point source effluent concentrations are listed in Table 2. Furthermore, a detailed listing of individual PCB homolog concentrations 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.

PCB concentrations are largely below 50 pg/l at Mirabeau Point and Barker Road. Moving downstream, concentrations are generally between 50 and 150 pg/l at the Trent Avenue Bridge, and between 50 and 100 pg/l at Greene St. and the Spokane USGS Gage. Concentrations at Nine Mile Dam are in the range of 50 to 150 pg/l. All of the samples downstream of Mirabeau Point exceed the Washington water quality standard of 7 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. As discussed above, two outlier samples are shown in Figure 2, corresponding to a total PCB concentration of 260 pg/l at Mirabeau Point and 1400 pg/l at Hangman Creek. These samples are considered anomalous and excluded from subsequent analyses.



Figure 2. Spokane River Total PCB Concentrations Measured during 2018 Synoptic Survey (Red Symbols Indicate Outliers)

#### Table 1. River Total PCB Concentrations (pg/l) Used in 2018 Mass Balance Assessment

	8/4	8/5	8/6	8/7	8/8
Barker Rd.	56.8/7.7*	6.1	7.6	61	5.1
Mirabeau Point	5.8	3.8/1.7*	22.3	-	4.7
Trent Ave.	79.6	87.0	88.7	86.6	101.6
Downriver of Upriver Dam	86.6	89.0	60.4	114.6/83.8*	129.1
Greene St.	54.7	75.5	37.5	53.9	63.1
Spokane Gage	82.5	62.8	79.4	67.0	82.8
Below Nine Mile Dam	96.1	88.8	63.8	82.2	118.3
Latah Creek	12.6	8.7	-	6.0	5.5/9.4*

\*Replicate sample

#### Table 2. Discharge Total PCB Concentrations (pg/l) Used in 2018 Mass Balance Assessment\*

	8/4	8/6	8/8
Inland Empire Paper	1937	1691	1122
Spokane County	234.5	240.9	221.6
City of Spokane	644.5	521.8	439.2

\*The original study design did not include a mass balance assessment for the Mirabeau Point to Trent Ave. reach. The decision was made subsequent to the monitoring to include this reach, so a Kaiser effluent value of 1537.2 pg/l was used, based on their routine August monitoring data.

# **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
- Application
- Conclusions and unresolved questions

### 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<sub>u</sub> and Q<sub>d</sub> represent the river flow at the upstream and downstream stations, respectively, while C<sub>u</sub> and C<sub>d</sub> represent the upstream and downstream PCB concentrations.



#### Figure 3. Simplified Description of Mass Balance Approach

The approach is described mathematically in Equation 1.

Unmonitored load = Downstream load – Upstream load

(1)

where:

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

Upstream load = Flow at Upstream location (Q<sub>u</sub>) x Concentration at upstream location (C<sub>u</sub>)

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.

Unmonitored load = Downstream load – Upstream load – Monitored Load (2)

### **3.2 Application**

Mass balance analyses were conducted on total PCBs and individual homologs. The data on flows are provided in Tables 3 and 4, which show individual daily flows as well as the average flow used for both of the mass balance assessments. Daily flow values generally remain with 2% of the average over the monitoring period, satisfying the requirement of the mass balance assessment that flows remain relatively steady.

Table 3. River Flows (cfs) Used in 2018 Mass Balance Assessment

	8/4	8/5	8/6	8/7	8/8	Average
Barker Rd.	244	220	238	235	245	236
Mirabeau Park	730	697	681	721	701	706
Trent Ave.	907	911	924	899	898	907
Downstream of Upriver Dam	851	906	870	811	857	859
Greene St.	1200	1210	1190	1180	1180	1192
Spokane Gage	1180	1190	1160	1150	1140	1160
Nine Mile	1480	1480	1510	1490	1430	1478

Table 4. Point Source Flows (cfs) Used in 2018 Mass Balance Assessment\*

	8/4	8/5	8/6	8/7	8/8	Average
Inland Empire Paper	11.4	11.4	11.2	11.7	11.9	11.5
Spokane County	11.9	12.3	12.5	12.2	12.4	12.3
City of Spokane	43.8	45.0	45.9	46.2	45	45.2

\*A flow of 13.7 cfs was specified for Kaiser based on their routine monitoring.

The remainder of this section applies the conceptual approach described above, first to total PCBs, then on a homolog-specific basis.

### 3.2.1 Total PCB Mass Balance Assessment

Results of the total PCB mass balance assessment are shown in Table 5 and Figure 5. There is small negative incremental load (-1.4 mg/day) of total PCBs in the Barker Road to Mirabeau Park reach. There is a larger negative incremental load (-33 mg/day) of total PCBs in the Trent Avenue to Downstream of Upriver Dam reach, with little incremental load observed in the reach between Downstream of Upriver Dam and Greene St. Incremental loads of 131.7, 36.1 and 66.1 mg/day are observed in the reaches from Mirabeau Point to Trent Ave., Greene St. to the Spokane USGS Gage, and from the Spokane USGS Gage to Nine Mile Dam, respectively. The groundwater load calculated for the Mirabeau Point to Trent Ave. reach is of similar magnitude to calculations of that load from 2014 and 2015.

River Reach	Incremental Load (mg/day)
Barker Road to Mirabeau Point	-1.4
Mirabeau Point to Trent Ave.	131.7
Trent Avenue to Downstream of Upriver Dam	-33.0
Downstream of Upriver Dam to Greene St.	-1.0
Greene St. to Spokane Gage	36.1
Spokane Gage to Nine Mile Dam	66.1





Figure 5. Results of Mass Balance for Total PCBs

#### **Homolog-Specific Mass Balance Assessment**

The mass balance assessment was also conducted on the individual homologs that comprise total PCB concentrations, with results summarized in Table 7. Figures 6 through 11 graph results on a reach-specific basis, and compare results to those from prior surveys when available.

Homolog	Barker Road to Mirabeau Point	Mirabeau Point to Trent Ave.	Trent Avenue to Upriver	Upriver to Greene	Greene St. to Spokane Gage	Spokane Gage to Nine Mile Dam
Mono-	-0.3	0.0	-0.6	-0.1	0.0	0.0
Di-	0.2	0.5	-9.1	-2.4	8.7	21.1
Tri-	-0.3	52.3	-21.7	-9.3	-11.8	-9.9
Tetra-	0.4	85.2	-28.7	3.5	-5.0	23.9
Penta-	-0.3	-1.7	11.6	-3.4	31.7	20.6
Hexa-	-0.7	-0.6	10.1	7.9	11.6	5.3
Hepta-	-1.1	-1.3	3.7	3.4	0.0	3.6
Octa-	0.4	-0.6	0.8	0.3	0.3	1.6
Nona-	0.5	-0.6	0.5	-0.6	0.7	0.0
Deca-	-0.1	0.0	0.3	-0.3	0.0	0.0

Table 6. Incremental Loads (mg/day) Estimated by Homolog-Specific Mass Balance Assessment for 2018 (Greenshading indicates an increase in PCB Load; Red shading indicates a decrease in PCB Load.)

Figure 6 plots homolog-specific results for the Barker to Mirabeau reach, and compares results from 2018 to those observed from the 2015 synoptic survey. The incremental loading is small (i.e. less than 1 mg/day) in 2018 across all homologs. This is in contrast to 2015, where loadings greater than 5 mg/day were observed for the penta- through hepta-chlorinated homologs. These results indicate that little to no groundwater load was occurring in this reach during the 2018 synoptic survey. It is noted that groundwater loading in this area up-gradient of Kaiser has appeared to be very sporadic in nature. The incremental load calculated for 2015 was based upon a single river sample with elevated concentrations. Similarly, total PCB concentrations in background wells are generally very low, with occasionally high concentrations. The absence of observed incremental loading in 2018 does not rule out the possibility of groundwater PCB loading in this area during other times, but does indicate that the frequency of such loads (if still occurring) is sporadic.



Figure 6. Homolog-Specific Mass Balance Results for Barker to Mirabeau Reach

Figure 7 plots homolog-specific results for the Mirabeau Point to Trent Avenue reach in 2018. The majority of the load comes in the form of tetra-chloro homologs, with the remainder in the form of tri-chloro homologs. Loads of all other homologs were negligible. Figure 8 plots homolog-specific results for the Barker Rd. to Trent Avenue reach in 2014, 2015, and 2018, to provide comparison to other years. The results for 2018 are very similar to 2014 and 2015, with all three years showing most of the load coming from tetra-chloro homologs and a secondary contribution from tri-chloro homologs. The primary difference between 2018 and the earlier years is the absence of a penta-chloro homolog signal, which was present (albeit relatively small) in the two earlier years.



Figure 7. Homolog-Specific Mass Balance Results for Mirabeau to Trent Avenue Reach



Figure 8. Homolog-Specific Mass Balance Results for Barker to Trent Avenue Reach

Figure 9 plots homolog-specific results for the Trent Avenue to Upriver reach. There is a net loss (i.e. negative incremental load) in the mono- to tetra-chlorinated homologs, and an increase in the penta- and higher chlorinated homologs. Figure 10 plots homolog-specific results for the Upriver to Greene St. reach. None of the incremental loads for any homolog are greater than 10 mg/day in a positive or negative direction.



Figure 9. Homolog-Specific Mass Balance Results for Trent Avenue to Upriver Reach



Figure 10. Homolog-Specific Mass Balance Results for Upriver to Greene St. Reach

Figure 11 merges data from the Trent to Upriver and Upriver to Greene St. reaches to allow the calculations from 2018 to be compared to those from prior synoptic surveys that did not contain a station near Upriver Dam. All three years show a very similar qualitative pattern, with losses of lower chlorinated homologs and gains of higher chlorinated homologs. The magnitude of these incremental loads is somewhat lower in 2018 than in 2014 and 2015, both in a positive and negative direction.



#### Figure 11. Homolog-Specific Mass Balance Results for Trent Avenue to Greene St. Reach

Figure 12 plots homolog-specific results for the Greene St. to Spokane USGS Gage reach, and compares results from 2018 to those observed from the 2014 and 2015 synoptic survey. The only

incremental loading observed consistently across years corresponds to the pentachloro homologs, which is calculated to be above 20 mg/day for all three years.





Figure 13 plots homolog-specific results for the Spokane USGS Gage to Nine Mile Dam reach. Incremental loads are on the order of 20 mg/day for the di-, tetra-, and penta-chlorinated homologs, with loadings for all other homologs being 5 mg/day or less.





## **3.3 Conclusions and Unresolved Questions**

### 3.3.1 Conclusions

The following conclusions can be gathered from the mass balance assessment:

- Groundwater loading of PCBs upstream of Mirabeau Point was not observed during the synoptic survey. This does not rule out the possibility of groundwater PCB loading in this area during other times, as previous indications of loads have been intermittent, but does confirm that the frequency of such loads (if still occurring) is sporadic.
- Homolog-specific mass balance analyses for the reach between Trent Avenue (Plante's Ferry) and Greene St. show similar results as prior surveys, with a net loss of lower chlorinated homologs and a net gain of moderately chlorinated homologs.
- Mass balance analyses for the portion of the river downstream of Greene St. indicate the potential for groundwater PCB loading, both between Greene St. and the USGS gage and between the USGS gage and Nine Mile Dam.

### **3.3.2 Unresolved Questions**

The objective of this project was to help identify the presence of groundwater sources of PCBs to the Spokane River, as part of the larger Task Force objective of reducing PCB loads to the river. The results of the work conducted here raise two key questions which limit the identification of groundwater sources to be remediated. Those questions are:

- 1. Why is there a consistent loss of lower chlorinated homologs in the section of the river downstream of Trent Avenue Bridge at Plante's Ferry?
- 2. What degree of confidence can be placed in incremental loading estimates for individual homologs?

As shown in Figure 9, mass balance results for all three years of synoptic surveys consistently show a loss of lower chlorinated hydrocarbons in the section of the river downstream of Trent Avenue Bridge at Plante's Ferry. Several theories have been proposed as a potential explanation for this loss. Those theories include: 1) loss of these homologs to the atmosphere via volatilization, 2) preferential loss of lower chlorinated homologs to groundwater, and 3) groundwater exchange patterns which are more complex than those assumed by the current mass balance model framework. A better understanding of why these losses are occurring would be helpful in supporting the Task Force's objective of identifying groundwater sources of PCBs. If, for example, the process causing a loss in lower chlorinate homologs also causes a decrease in other homologs, gross loading of PCBs from groundwater sources may be higher than the net loading being calculated from the mass balance assessment.

The second question pertains to the degree of confidence that can be placed in incremental loading estimates for individual homologs. Previous mass balances on total PCB concentration contained uncertainty analyses, which expressed the incremental loads as probability distributions rather than a single number. A similar type of uncertainty analysis on the homolog-specific mass balance

analysis would provide insight into whether the calculated incremental loads represent actual conditions or are the result of measurement variability.

Future studies to address the above questions could facilitate identification of groundwater sources to be remediated. It is recommended to delay implementation of such studies until the results of the biofilm, sediment, and invertebrate PCB Monitoring conducted by Ecology (Wong and Era-Miller, 2018) are available. Joint consideration of the results of that study and the one described here will allow development of future studies to conducted on an integrated basis.

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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 / 4	8 / 5	8 / 6	8 / 7	8 / 8	8 / 4-R			
Total PCBs (pg/I)	56.8	6.1	7.6	61.0	5.1	7.7			
Total Monochloro Biphenyls (pg/l)	3.6	1.8	0.0	0.0	0.0	0.0			
Total Dichloro Biphenyls (pg/l)	5.8	0.3	0.0	0.0	0.3	3.5			
Total Trichloro Biphenyls (pg/l)	5.9	1.6	0.0	0.0	0.0	1.6			
Total Tetrachloro Biphenyls (pg/l)	3.4	0.0	0.0	0.3	1.0	1.2			
Total Pentachloro Biphenyls (pg/l)	1.3	1.9	1.4	10.5	1.0	0.0			
Total Hexachloro Biphenyls (pg/l)	10.4	0.2	3.1	24.9	1.6	1.1			
Total Heptachloro Biphenyls	20.4	0.3	1.9	17.5	0.6	0.2			
Total Octachloro Biphenyls (pg/l)	5.6	0.0	0.8	5.5	0.2	0.0			
Total Nonachloro Biphenyls (pg/l)	0.4	0.0	0.4	1.2	0.3	0.0			
Total Decachloro Biphenyls (pg/l)	0.0	0.0	0.0	1.2	0.0	0.0			
Total Dissolved Solids (mg/l)	50	23	55	38	41	44.0			
Total Suspended Solids (mg/l)	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0			
Total Organic Carbon (mg/l)	1.93	1.88	1.90	1.87	2.09	1.81			
Dissolved Organic Carbon (mg/l)	1.82	1.73	1.80	1.81	1.81	1.81			

Table A-2: Blank-Corrected Analytical Results for Spokane River at Mirabeau Park								
Station SR8a	8 / 4	8 / 5	8 / 6	8 / 7*	8 / 8	8 / 5-R		
Total PCBs (pg/l)	5.8	3.8	22.3	259.4	4.7	1.7		
Total Monochloro Biphenyls (pg/l)	0.0	0.0	0.0	101.6	0.0	0.0		
Total Dichloro Biphenyls (pg/l)	2.1	0.6	0.0	99.7	0.0	0.9		
Total Trichloro Biphenyls (pg/l)	0.3	0.6	0.0	4.8	0.2	0.0		
Total Tetrachloro Biphenyls (pg/l)	1.2	0.8	0.3	7.0	1.1	0.2		
Total Pentachloro Biphenyls (pg/l)	0.0	0.3	1.5	12.7	0.8	0.0		
Total Hexachloro Biphenyls (pg/l)	1.1	1.4	6.9	16.4	1.6	0.2		
Total Heptachloro Biphenyls (pg/l)	0.4	0.0	7.7	12.2	0.2	0.0		
Total Octachloro Biphenyls (pg/l)	0.6	0.2	4.2	3.8	0.2	0.4		
Total Nonachloro Biphenyls (pg/l)	0.0	0.0	1.8	1.2	0.5	0.0		
Total Decachloro Biphenyls (pg/l)	0.0	0.0	0.0	0.0	0.0	0.0		
Total Dissolved Solids (mg/l)	158	152	153	140	135	135		
Total Suspended Solids (mg/l)	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0		
Total Organic Carbon (mg/l)	1.58	<1.00	<1.00	<1.00	<1.00	1.04		
Dissolved Organic Carbon (mg/l)	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00		

\*PCB results for 8/7 rejected as anomalous due to elevated mono-chloro and di-chloro homolg concentrations in the sample and associated laboratory blank.

Table A-3: Blank-Corrected Analytical Results for Spokane River Below Trent Bridge									
Station SR7	8 / 4	8 / 5	8/6	8 / 7	8 / 8	8/6-R			
Total PCBs (pg/l)	79.6	87.0	88.7	86.6	101.6				
Total Monochloro Biphenyls (pg/l)	0.0	0.0	0.0	0.0	0.0				
Total Dichloro Biphenyls (pg/l)	2.8	4.1	0.0	0.0	2.4				
Total Trichloro Biphenyls (pg/l)	26.2	29.0	29.5	29.5	35.6				
Total Tetrachloro Biphenyls (pg/l)	48.7	47.9	54.9	53.1	55.9				
Total Pentachloro Biphenyls (pg/l)	0.0	4.4	2.7	2.4	2.3				
Total Hexachloro Biphenyls (pg/l)	1.5	0.9	0.9	0.3	3.5				
Total Heptachloro Biphenyls (pg/l)	0.2	0.0	0.5	0.7	1.9				
Total Octachloro Biphenyls (pg/l)	0.3	0.7	0.2	0.6	0.0				
Total Nonachloro Biphenyls (pg/l)	0.0	0.0	0.0	0.0	0.0				
Total Decachloro Biphenyls (pg/l)	0.0	0.0	0.0	0.0	0.0				
Total Dissolved Solids (mg/l)	136	136	151	140	141	159			
Total Suspended Solids (mg/l)	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0			
Total Organic Carbon (mg/l)	1.17	<1.00	<1.00	<1.00	1.10	<1.00			
Dissolved Organic Carbon (mg/l)	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00			

Table A-4: Blank-Corrected Analytical Results for Inland Empire Paper					
Station SR6	8 / 4	8/6	8 / 8		
Total PCBs (pg/l)	1938	1692	1122		
Total Monochloro Biphenyls (pg/l)	42.1	0.0	16.6		
Total Dichloro Biphenyls (pg/l)	550.9	398.6	283.6		
Total Trichloro Biphenyls (pg/l)	798.6	763.6	515.1		
Total Tetrachloro Biphenyls (pg/l)	425.3	362.9	250.5		
Total Pentachloro Biphenyls (pg/l)	88.0	87.9	47.3		
Total Hexachloro Biphenyls (pg/l)	26.4	38.4	6.3		
Total Heptachloro Biphenyls (pg/l)	4.0	29.5	1.1		
Total Octachloro Biphenyls (pg/l)	2.3	9.3	0.4		
Total Nonachloro Biphenyls (pg/l)	0.4	1.3	0.6		
Total Decachloro Biphenyls (pg/l)	0.0	0.0	0.0		
Total Dissolved Solids (mg/l)	754	610	443		
Total Suspended Solids (mg/l)	<5.0	<5.0	<5.0		
Total Organic Carbon (mg/l)	57.6	39.3	29.4		
Dissolved Organic Carbon (mg/l)	54.2	39.8	29.2		

Table A-5: Blank-Corrected Analytical Results for Spokane River Below Upriver Dam						
Station SR-5a	8 / 4	8 / 5	8 / 6	8 / 7	8 / 8	8 / 7-R
Total PCBs (pg/l)	86.6	89.0	60.4	114.6	129.1	83.8
Total Monochloro Biphenyls (pg/l)	0.0	0.0	0.0	0.0	0.0	0.0
Total Dichloro Biphenyls (pg/l)	5.1	4.4	0.0	0.0	2.6	2.4
Total Trichloro Biphenyls (pg/l)	31.2	36.3	22.0	21.4	28.8	30.1
Total Tetrachloro Biphenyls (pg/l)	47.3	45.8	29.0	42.9	47.0	43.5
Total Pentachloro Biphenyls (pg/l)	0.5	0.3	5.7	16.5	27.6	5.1
Total Hexachloro Biphenyls (pg/l)	1.6	1.5	1.3	17.0	20.2	1.6
Total Heptachloro Biphenyls (pg/l)	0.6	0.3	1.5	11.0	2.3	0.7
Total Octachloro Biphenyls (pg/l)	0.2	0.4	0.7	3.9	0.0	0.0
Total Nonachloro Biphenyls (pg/l)	0.0	0.0	0.2	0.9	0.5	0.4
Total Decachloro Biphenyls (pg/l)	0.0	0.0	0.0	1.1	0.0	0.0
Total Dissolved Solids (mg/l)	150	130	145	135	128	139
Total Suspended Solids (mg/l)	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Total Organic Carbon (mg/l)	1.44	1.98	1.44	1.33	1.45	1.36
Dissolved Organic Carbon (mg/l)	1.44	1.76	1.22	1.25	1.26	1.24

Table A-6: Blank-Corrected Analytical Results for Spokane County Regional Water Reclamation Facility					
Station SR5	8/4	8 / 6	8 / 8		
Total PCBs (pg/l)	234.5	240.9	221.6		
Total Monochloro Biphenyls (pg/l)	4.4	0.0	7.2		
Total Dichloro Biphenyls (pg/l)	62.8	49.0	61.2		
Total Trichloro Biphenyls (pg/l)	72.6	93.0	67.9		
Total Tetrachloro Biphenyls (pg/l)	59.1	64.7	55.9		
Total Pentachloro Biphenyls (pg/l)	30.3	30.2	26.5		
Total Hexachloro Biphenyls (pg/l)	2.4	3.9	2.6		
Total Heptachloro Biphenyls (pg/l)	0.2	0.3	0.3		
Total Octachloro Biphenyls (pg/l)	1.0	0.0	0.0		
Total Nonachloro Biphenyls (pg/l)	1.7	0.0	0.0		
Total Decachloro Biphenyls (pg/l)	0.0	0.0	0.0		
Total Dissolved Solids (mg/l)	546	554	453		
Total Suspended Solids (mg/l)	<5.0	<5.0	<5.0		
Total Organic Carbon (mg/l)	5.72	6.63	5.21		
Dissolved Organic Carbon (mg/l)	5.65	5.83	5.00		

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Table A-7: Blank-Corrected Analytical Results for Spokane River at Greene Street Bridge					
Station SR4	8 / 4	8 / 5	8/6	8 / 7	8 / 8
Total PCBs (pg/l)	54.7	75.5	37.5	53.9	63.1
Total Monochloro Biphenyls (pg/l)	0.0	0.0	0.0	0.0	0.0
Total Dichloro Biphenyls (pg/l)	3.9	4.2	0.0	0.0	0.8
Total Trichloro Biphenyls (pg/l)	21.0	25.8	4.2	16.6	18.6
Total Tetrachloro Biphenyls (pg/l)	26.4	38.6	22.7	30.2	34.4
Total Pentachloro Biphenyls (pg/l)	0.3	0.5	2.0	1.6	2.2
Total Hexachloro Biphenyls (pg/l)	2.0	4.5	5.1	4.4	5.2
Total Heptachloro Biphenyls (pg/l)	1.0	1.3	2.9	1.1	1.7
Total Octachloro Biphenyls (pg/l)	0.2	0.6	0.7	0.0	0.2
Total Nonachloro Biphenyls (pg/l)	0.0	0.0	0.0	0.0	0.0
Total Decachloro Biphenyls (pg/l)	0.0	0.0	0.0	0.0	0.0
Total Dissolved Solids (mg/l)	146	134	151	143	132
Total Suspended Solids (mg/l)	<5.0	<5.0	<5.0	<5.0	<5.0
Total Organic Carbon (mg/l)	1.70	1.25	1.40	1.24	1.12
Dissolved Organic Carbon (mg/l)	1.17	1.08	1.18	<1.00	1.03

Table A-8: Blank-Corrected Analytical Results for Spokane River at Spokane Gage						
Station SR3	8 / 4	8 / 5	8 / 6	8 / 7	8 / 8	
Total PCBs (pg/l)	82.5	62.8	79.4	67.0	82.8	
Total Monochloro Biphenyls (pg/l)	0.0	0.0	0.0	0.0	0.0	
Total Dichloro Biphenyls (pg/l)	2.6	0.0	0.0	0.9	11.0	
Total Trichloro Biphenyls (pg/l)	18.4	0.4	8.9	16.7	16.6	
Total Tetrachloro Biphenyls (pg/l)	34.8	23.3	29.4	30.2	31.0	
Total Pentachloro Biphenyls (pg/l)	13.8	19.9	20.5	9.2	12.6	
Total Hexachloro Biphenyls (pg/l)	10.0	14.2	14.2	8.1	7.8	
Total Heptachloro Biphenyls (pg/l)	2.2	3.8	5.4	1.5	3.0	
Total Octachloro Biphenyls (pg/l)	0.7	0.8	0.8	0.3	0.2	
Total Nonachloro Biphenyls (pg/l)	0.0	0.4	0.3	0.0	0.5	
Total Decachloro Biphenyls (pg/l)	0.0	0.0	0.0	0.0	0.0	
Total Dissolved Solids (mg/l)	141	131	152	138	133	
Total Suspended Solids (mg/l)	<5.0	<5.0	<5.0	<5.0	<5.0	
Total Organic Carbon (mg/l)	1.63	1.20	1.29	1.16	1.51	
Dissolved Organic Carbon (mg/l)	1.07	1.07	1.03	1.08	1.06	

Table A-9: Blank-Corrected Analytical Results for Hangman Creek						
Station HC1	8 / 4	8 / 5	8 / 6*	8 / 7	8 / 8	8 / 8-R
Total PCBs (pg/l)	12.6	8.7	1043	6.0	5.5	9.4
Total Monochloro Biphenyls (pg/l)	0.0	0.0	525.6	0.0	0.0	0.0
Total Dichloro Biphenyls (pg/l)	3.2	0.0	307.0	0.4	0.6	0.6
Total Trichloro Biphenyls (pg/l)	0.6	0.0	15.1	0.0	0.0	0.2
Total Tetrachloro Biphenyls (pg/l)	2.0	0.3	8.7	1.0	1.0	1.5
Total Pentachloro Biphenyls (pg/l)	0.4	1.4	73.0	1.0	0.9	1.1
Total Hexachloro Biphenyls (pg/l)	1.9	3.4	67.4	1.8	1.6	2.6
Total Heptachloro Biphenyls (pg/l)	2.4	2.3	33.2	0.8	0.6	1.8
Total Octachloro Biphenyls (pg/l)	1.8	0.9	9.8	0.2	0.4	0.8
Total Nonachloro Biphenyls (pg/l)	0.2	0.3	2.0	0.8	0.3	0.8
Total Decachloro Biphenyls (pg/l)	0.0	0.0	1.6	0.0	0.0	0.0
Total Dissolved Solids (mg/l)	276	267	300	295	278	282
Total Suspended Solids (mg/l)	5.0	6.0	6.0	<5.0	<5.0	<5.0
Total Organic Carbon (mg/l)	3.12	3.00	3.03	2.97	2.96	2.99
Dissolved Organic Carbon (mg/l)	2.74	2.71	2.74	2.71	2.74	2.71

\*PCB results for 8/6 rejected as anomalous due to elevated mono-chloro and di-chloro homolog concentrations in the sample and associated laboratory blank.

Table A-10: Blank-Corrected Analytical Results for City of Spokane Riverside Park						
Advanced WWTP						
Station SR2	8 / 4	8 / 6	8 / 8			
Total PCBs (pg/l)	644.5	521.8	439.2			
Total Monochloro Biphenyls (pg/l)	0.0	0.0	0.0			
Total Dichloro Biphenyls (pg/l)	58.9	33.8	53.7			
Total Trichloro Biphenyls (pg/l)	86.3	79.0	69.9			
Total Tetrachloro Biphenyls (pg/l)	132.3	107.2	93.2			
Total Pentachloro Biphenyls (pg/l)	171.9	156.7	109.3			
Total Hexachloro Biphenyls (pg/l)	126.0	99.7	76.2			
Total Heptachloro Biphenyls (pg/l)	49.4	34.0	27.9			
Total Octachloro Biphenyls (pg/l)	15.8	9.2	6.8			
Total Nonachloro Biphenyls (pg/l)	4.0	2.2	2.2			
Total Decachloro Biphenyls (pg/l)	0.0	0.0	0.0			
Total Dissolved Solids (mg/l)	451	447	436			
Total Suspended Solids (mg/l)	8.0	9.0	7.0			
Total Organic Carbon (mg/l)	5.03	5.15	5.50			
Dissolved Organic Carbon (mg/l)	4.46	4.61	4.65			

Table A-11: Blank-Corrected Analytical Results for Spokane River at Nine Mile Dam					
Station SR1	8 / 4	8 / 5	8 / 6	8 / 7	8 / 8
Total PCBs (pg/l)	96.1	88.8	63.8	82.2	118.3
Total Monochloro Biphenyls (pg/l)	0.0	0.0	0.0	0.0	0.0
Total Dichloro Biphenyls (pg/l)	19.1	0.0	0.0	11.8	16.6
Total Trichloro Biphenyls (pg/l)	13.3	5.5	0.2	13.1	19.0
Total Tetrachloro Biphenyls (pg/l)	32.9	42.4	22.0	31.6	35.0
Total Pentachloro Biphenyls (pg/l)	21.6	22.4	21.6	14.0	21.5
Total Hexachloro Biphenyls (pg/l)	6.7	13.8	13.5	7.4	18.2
Total Heptachloro Biphenyls (pg/l)	1.8	3.3	5.5	3.4	5.5
Total Octachloro Biphenyls (pg/l)	0.7	1.0	0.6	0.6	2.0
Total Nonachloro Biphenyls (pg/l)	0.0	0.4	0.3	0.3	0.5
Total Decachloro Biphenyls (pg/l)	0.0	0.0	0.0	0.0	0.0
Total Dissolved Solids (mg/l)	161	153	181	165	163
Total Suspended Solids (mg/l)	<5.0	<5.0	<5.0	<5.0	<5.0
Total Organic Carbon (mg/l)	1.25	2.65	1.75	1.31	1.64
Dissolved Organic Carbon (mg/l)	1.18	1.19	1.08	1.13	1.25

Table A-12: Blank-Corrected Analytical Results for Kaiser Effluent				
Total PCBs (pg/l)	1537.2			
Total Monochloro Biphenyls (pg/l)	0			
Total Dichloro Biphenyls (pg/l)	59.27			
Total Trichloro Biphenyls (pg/l)	424.31			
Total Tetrachloro Biphenyls (pg/l)	856.43			
Total Pentachloro Biphenyls (pg/l)	182.83			
Total Hexachloro Biphenyls (pg/l)	11.262			
Total Heptachloro Biphenyls (pg/l)	2.306			
Total Octachloro Biphenyls (pg/l)	0.76			
Total Nonachloro Biphenyls (pg/l)	0			
Total Decachloro Biphenyls (pg/l)	0			

## Appendix B: Gravity Report

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# Appendix C: Quality Assurance Project Plan

Provided separately as an electronic document

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# Appendix D: Laboratory Results

Provided separately as electronic spreadsheets

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