2022-2023 Evaluation of PCBs in the Spokane River via Semi Permeable Membrane Devices (SPMDs)

Prepared for:
Spokane River Regional Toxics Task Force

June 21, 2023
PRELIMINARY DRAFT

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TTWG REDLINE REVIEW DRAFT

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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 due to elevated concentrations of polychlorinated biphenyls (PCBs) in fish tissue, as specified by Washington's Water Quality Assessment Listing Methodology to Meet Clean Water Act Requirements (Water Quality Program Policy 1-11)[1]. To address these impairments, the Department of Ecology (Ecology) has been pursuing a toxics reduction strategy that included the establishment of the Spokane River Regional Toxics Task Force (Task Force) to identify and reduce PCBs at their source in the watershed. One of the key missions of the Task Force is to make measurable progress toward meeting applicable water quality criteria for PCBs. Demonstrating that this progress is occurring requires a long-term monitoring program. The Task Force developed a long-term monitoring program consisting of parallel efforts monitoring PCB concentrations in the water column and fish tissue and began conducting monitoring in accordance with this program in 2020.

This study describes the continuation of monitoring of water column PCB concentrations using semipermeable membrane devices (SPMDs). The results of this study are designed to support a long-term trend assessment of PCB concentrations in the water column that may be used as one measure of the effectiveness of PCB control actions aimed at the reduction of PCBs in the Spokane River. The trend assessment was intended to analyze PCB concentrations in the Spokane River during three flow regimes (summer low flow, winter moderate flow, and spring high flow). Samples for summer 2022 low flow and winter 2022-2023 moderate flow have been collected and analyzed. Spring high flow samples have been collected but were not yet analyzed at the time of this report; therefore, this report includes the summer 2022 low flow and winter 2022-2023 moderate flow regimes but not the spring 2023 high flow regime. This study was also designed to assess whether time-integrated sampling indicates greater low-flow PCB concentrations at Mirabeau Point than those observed at the WA/ID State Line station, as an indication of the presence of unmonitored PCB loads entering the river upstream of Mirabeau Point.

SPMDs were deployed at five locations in the Spokane River. Four of the locations correspond to the long-term sampling stations established in 2020: Washington/Idaho State Line, downstream of Upriver Dam, at East Trent Avenue in Spokane, and Nine Mile Dam. Water column monitoring was conducted at these stations via a one-month-long deployment of SPMDs during late summer 2022 low flow and winter 2022-2023 moderate flow conditions. A fifth station was added downstream of Mirabeau Point independent of long-term monitoring; monitoring at this location consisted of a one-month-long deployment of a SPMD during late summer 2022 low flow conditions.

[1]Fish tissue PCB concentrations are considered as part of narrative water quality standards.

The following conclusions can be gathered from the data collected:

- The observed PCB concentration measured by SPMDs at the long-term trend stations, averaged across the low and moderate flow regimes, was greatest at East Trent Avenue (800 pg/l). The average PCB concentration was lowest at State Line (174 pg/l). Average concentrations at Upriver Dam and Nine Mile Dam were 475 pg/l and 359 pg/l, respectively.
- PCB concentrations in both this study and the original 2020-2021 study tend to be negatively correlated to Spokane River flow, with higher PCB concentrations occurring during lower river flows.
- It is premature to draw any conclusion about temporal trends in PCB concentrations from these data, as they represent only two of the three flow regimes intended to characterize annual average conditions. SPMDs have been deployed under a separate project to characterize PCB concentration from the third flow regime, but laboratory results from this monitoring will not be available prior to the sunsetting of the Task Force.
- The PCB concentrations measured by SPMDs continue to appear to be higher than those measured via analysis of grab samples at similar locations. Trend assessments on Spokane River PCB concentrations should be conducted separately between SPMD and grab sample results.
- PCB concentrations downstream of Mirabeau Point are not greater than those observed at the State Line stations, indicating that no significant unmonitored load was entering the river between those locations.

1 Introduction

Sections of the Spokane River and Lake Spokane have been placed on the State of Washington's 303(d) list of impaired waters due to elevated concentrations of polychlorinated biphenyls (PCBs) in fish tissue, as specified by Washington's Water Quality Assessment Listing Methodology to Meet Clean Water Act Requirements (Water Quality Program Policy 1-11)[2]. To address these impairments, the Department of Ecology (Ecology) is pursuing a toxics reduction strategy that included the establishment of the Spokane River Regional Toxics Task Force (Task Force) to identify and reduce PCBs at their source in the watershed. One of the key missions of the Task Force is to make measurable progress toward meeting applicable water quality criteria for PCBs. Demonstrating that this progress is occurring requires a long-term monitoring program, and development of such a program was identified as a priority activity as an outcome of a May 2019 Data Synthesis Workshop. The Task Force subsequently endorsed a long-term monitoring program consisting of parallel efforts monitoring PCB concentrations in the water column and fish tissue.

Semipermeable membrane devices (SPMDs) were selected as the preferred water column monitoring method for long-term trend assessment after a review of other candidate methods (LimnoTech, 2020). The Task Force conducted the first round of trend assessment monitoring in 2020-2021 (LimnoTech, 2022), consisting of three one-month-long deployments representing different seasonal flow regimes at four Spokane River locations, and concluded that trend assessments based on SPMD results should focus on dissolved phase PCBs. This study describes the beginning of the second round of sampling for this trend assessment. SPMDs were deployed at the same four Spokane River locations for two separate month-long deployments representing summer low flow and winter moderate flow. Samples for the third flow regime, spring high flow, have been collected under a separate project but will not have been analyzed prior to the sunsetting of the Task Force and, therefore, are not included in this report. The results of this monitoring are intended to provide one means of assessing the efficacy of control actions on Spokane River PCB concentrations.

SPMDs were also deployed at an additional location, downstream of Mirabeau Point during the late summer 2022 low flow data collection. Previous grab sampling conducted by the Task Force at Mirabeau Point showed occasional occurrences of elevated PCB concentrations, raising the question of whether these concentrations indicate the presence of an intermittent unmonitored loading source. SPMDs were deployed here during the summer low flow period to determine if time-averaged concentrations at Mirabeau Point were greater than those observed by SPMDs immediately upstream at the State Line.

[2]Fish tissue PCB concentrations are considered as part of narrative water quality standards.

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

- Sampling activities
- Analytical results
- Data interpretation

2 Sampling Activities

The field monitoring program for this project consisted of two[3] separate one-month-long deployments of semi-permeable membrane devices at four locations in the Spokane River with an additional fifth location downstream of Mirabeau Point during summer low flow. Sampling activities are described below, divided into sections corresponding to:

- Sampling locations
- Monitoring dates
- Field sampling activities
- Quality assurance

2.1 Sampling Locations

Sampling was conducted at five locations in the Spokane River between the Washington/Idaho State Line and Nine Mile Dam. Location descriptions and geographic coordinates are provided in Table 1 and mapped in Figure 1.

Table 1. 2022-2023 SPMD Locations

Description	Latitude	Longitude
WA/ID State Line	N 47° 41.666'	W 117° 00.597'
Downstream of Mirabeau Point	N 47° 41.315'	W 117° 13.715'
Downstream of Upriver Dam	N 47° 41.101'	W 117° 19.698'
Upstream of E. Trent Avenue	N 47° 39.769'	W 117° 23.608'
Nine Mile Dam	N 47° 46.477'	W 117° 32.700'

2.2 Monitoring Dates

Monitoring was conducted across two separate approximately month-long periods, corresponding to late summer 2022 low flow and winter 2022-2023 moderate flow (Table 2). Daily average river flows at the Spokane USGS gage ranged from 860 to 1,360 cfs during the low flow deployment and from 2,470 to 4,630 cfs during the moderate flow deployment.

2.3 Field Sampling Activities

The field sampling activities as planned and implemented are detailed in the project QAPP (LimnoTech, 2020b), which is provided as Appendix B to this report. This section summarizes those activities. SPMD sampling methods were based upon field SOPs provided in Hobbs (2020). SPMDs were deployed in secure areas to minimize vandalism and avoid strong currents, using stainless

[3] The Task Force subsequently authorized a separate project to deploy and retrieve SPMDs for the spring 2023 high flow regime. This sampling has been completed and the SPMDs delivered to Ecology for storage and future analysis.

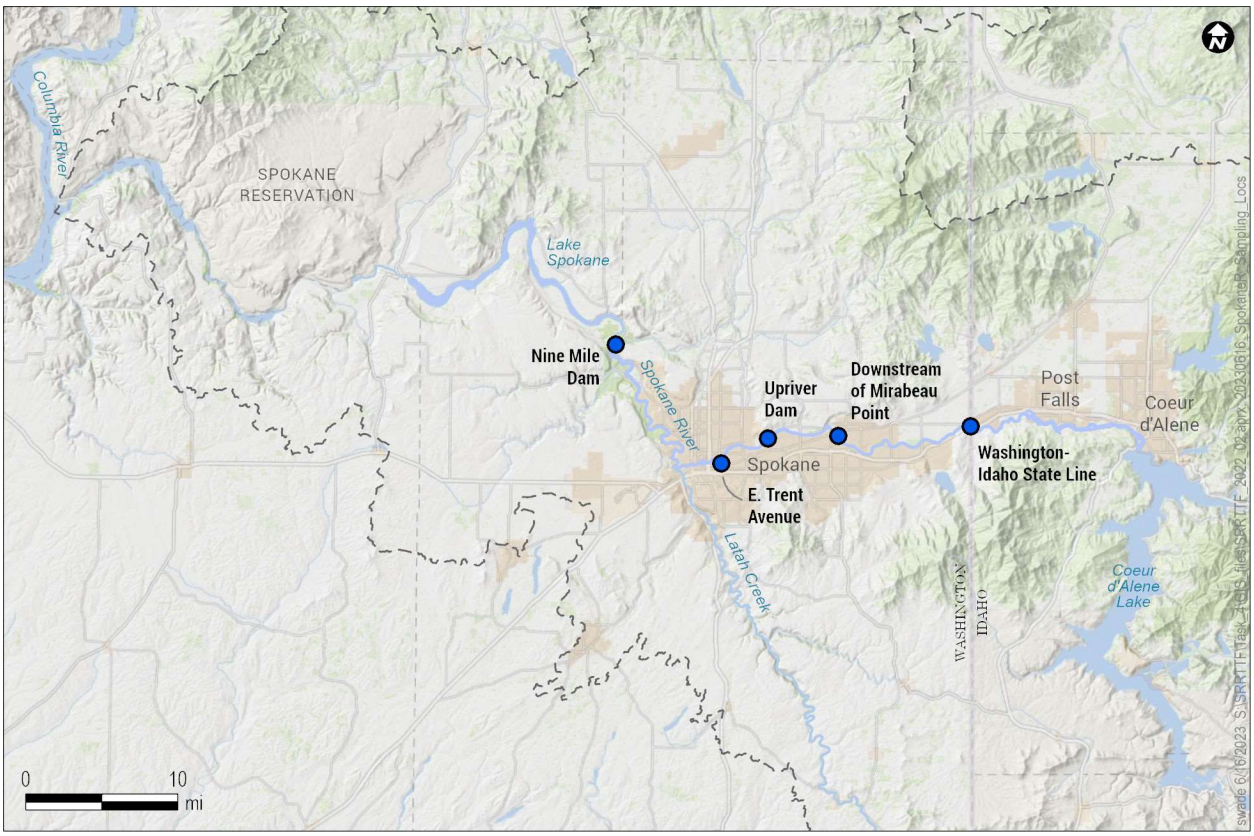

Figure 1. Locations for 2022-2023 SPMD Monitoring

Table 2. Dates of SPMD Deployment, Mid-Deployment Check, and Retrieval

Location	Date Deployed	Date of Mid-Deployment Check	Date Retrieved
Late Summer Low Flow			
WA/ID State Line to McMillan Rd.	8/31/2022	9/14/2022	9/29/2022
Downstream of Mirabeau Point	8/31/2022	9/14/2022	9/29/2022
Downstream of Upriver Dam	8/31/2022	9/14/2022	9/29/2022
E. Trent Avenue Bridge	8/31/2022	9/14/2022	9/29/2022
Nine Mile Dam	8/31/2022	9/14/2022	9/29/2022
Winter Moderate Flow			
WA/ID State Line to McMillan Rd.	12/19/2022	1/3/2023	1/17/2023
Downstream of Upriver Dam	12/19/2022	1/3/2023	1/17/2023
E. Trent Avenue Bridge	12/19/2022	1/3/2023	1/17/2023
Nine Mile Dam	12/19/2022	1/3/2023	1/17/2023

steel canisters and spindle devices provided by Environmental Sampling Technologies (EST). A suitable location could not be found for SPMD deployment in the direct vicinity of Mirabeau Point, so SPMDs were placed approximately 0.5 miles downstream of the originally intended location. Each site canister/SPMD contained five membranes preloaded onto spindles by EST and shipped in solvent-rinsed metal cans under argon gas. Prior to deployment, performance reference compounds (PRCs) were spiked into the membranes by EST in order to assess biofouling and the non-equilibrium uptake of the compounds of interest (Huckins et al., 2006). Continuous temperature loggers were deployed concurrent with the SPMDs to confirm that they remained submerged during the period of deployment.

Water grab samples were taken to measure the PCB, total and dissolved organic carbon (TOC/DOC), and total suspended solids concentrations at each site during the time the SPMDs were exposed. Water grab samples were collected three times across the duration of each SPMD exposure to get an integrated measure of the conditions. Grab samples were collected using Ecology standard operating procedures (Joy, 2019). Additional field parameters were measured in situ at the time of water sampling using a multiprobe sonde. Parameters included temperature, pH, dissolved oxygen, and conductivity.

2.4 Quality Assurance

SPMDs and PCB grab samples were shipped to SGS-AXYS Analytical Laboratories, Ltd. in Sidney, British Columbia for analysis of PCB concentrations using Method 1668. Water column grab samples were delivered to SVL Laboratories in Kellogg, Idaho for analysis of total organic carbon, dissolved organic carbon, and total suspended solids.

2.4.1 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)
- Completeness
- Recovery of performance reference compounds

All reviewed quality control (QC) results for PCBs comply with QAPP data quality indicators, with the following exceptions:

- The percent recovery of performance reference compounds was outside of the desired range (20-80%) for 28 out of 33 samples, with an average percent recovery of 86.1% for the out-of-compliance samples.

2.4.2 Blank Censoring

Total PCB concentrations were censored 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 laboratory blank concentration were flagged and excluded from calculation of homolog and total PCB concentration. All total PCB and homolog results reported below are blank censored using the above method.

In addition, field blanks were examined to estimate both the limit of detection (LOD) and limit of quantitation (LOQ) by congener. The LOD was calculated as the mean of the field blanks plus three standard deviations while the LOQ was calculated as the mean of the field blanks plus ten standard deviations as originally described by Keith (1991) and subsequently recommended in Ecology Standard Operating Procedures for SPMD data reduction (Seiders and Sandvik, 2020). Treating results that were at or below the LOD as non-detects had little effect on estimated total PCB concentrations. For example, at State Line (where the importance of blank contamination is greatest due to this station having lowest observed river concentrations) more than 98.5% of the total SPMD concentration was above the LOD. At Trent Avenue, where river concentrations are greatest, more than 99.7% of the total SPMD concentration was above the LOD.

Treating results that were at or below the LOQ as estimated values had a more noticeable effect at State Line, as 13% of the total SPMD concentration were considered estimated values. The influence of field blank-derived LOQs was much smaller at the remaining stations. At Trent Avenue, for example, only 2.5% of the total SPMD concentration were considered estimated values.

For purposes of calculating instream PCB concentrations from the SPMDs, congener values less than the LOD as described above were treated as zero. Congener values between the LOD and the LOQ were treated as the observed value.

2.4.1 Field Temperature Probes

Hobo temperature monitoring devices were deployed along with each SPMD canister. A separate temperature probe was placed in a tree near the Trent Ave. sample location to monitor air temperature. The purpose of these measurements was to identify whether SPMDs remained submersed in the water column throughout each 28-day sampling period. Meter malfunctioning occurred across all sites, starting on September 20 for the low flow deployment and on January 8 for the moderate flow deployment. However, there was no visual indication that any of the devices were tampered with or removed from the water, and the field crew believes that the SPMDs remained submerged throughout the deployment period.

3 Analytical Results

This section summarizes the results of the 2022-2023 monitoring, in terms of concentrations of total PCBs and individual homologs. Furthermore, a detailed listing of PCB homolog concentrations for each composite is provided in Appendix A, and full laboratory data sheets are provided in Appendix C.

3.1 Data Processing

The use of SPMDs requires processing of data on PCB concentrations in the SPMD to convert them into water column PCB concentrations. This processing was conducted in two steps:

- Conversion of PCB concentrations in the SPMD into water column freely dissolved phase PCB concentrations.
- Conversion of water column freely dissolved phase PCB concentrations into water column total PCB concentrations

Conversion of PCB concentrations in the SPMD into water column dissolved phase PCB concentrations was conducted using the USGS model (Alvarez, 2010) as provided by Ecology in their SPMD Data Management and Data Reduction template (Seiders and Sandvik, 2020).

Water column dissolved phase PCB concentrations were converted into water column total PCB concentrations using equations 1 and 2:

$$f_d = 1 / (1 + K_{oc,p}[POC] + K_{oc,d}[DOC]) \quad (1)$$

$$C_t = C_d / f_d \quad (2)$$

where:

f_d = fraction of total PCB concentration in the freely dissolved phase
$K_{OC,p}$ = organic carbon partition coefficient to particulate organic carbon (l/mg)
[POC] = particulate organic carbon concentration (mg/l)
$K_{OC,d}$ = organic carbon partition coefficient to dissolved organic carbon (l/mg)
[DOC] = dissolved organic carbon concentration (mg/l)
C_t = water column total PCB concentration
C_d = water column dissolved phase PCB concentration

The organic carbon partition coefficient for particulate organic carbon, $K_{OC,p}$, was calculated on a congener-specific basis using values of K_{OC} reported by Hansen et al. (1993). The organic carbon partition coefficient for dissolved organic carbon, $K_{OC,d}$, was specified on a congener-specific basis as one tenth of $K_{OC,p}$, based upon the conclusion of Zarnadze and Rodenburg (2008) that "DOC is approximately an order of magnitude less effective at sorbing hydrophobic organic molecules (e.g., PCBs) compared with POC." Table 3 shows the average of the observed DOC and POC

concentrations at each station and deployment period used to convert freely dissolved PCB concentration into total PCBs.

Table 3. Dissolved Organic Carbon and Particulate Organic Carbon Concentrations Used to Convert Freely Dissolved PCB Concentration into Total PCBs

Location	Nine Mile	Trent	Upriver	D/S of Mirabeau	State Line
Late Summer Low Flow					
POC (mg/l)	0.07	0.13	0.19	0.4	0
DOC (mg/l)	1.15	1.11	1.95	0.9	1.72
Winter Moderate Flow					
POC (mg/l)	0.08	0.05	0.09	N/A	0.24
DOC (mg/l)	1.92	1.42	1.45	N/A	1.54

3.2 PCB Concentrations

3.2.1 SPMDs

Freely dissolved PCB concentrations are shown below in Figure 2 and Table 4 for all SPMD monitoring locations and deployment periods. PCB concentrations are less than 200 pg/l for both flow regimes at State Line, increasing to 460 to 490 pg/l at Upriver Dam. PCB concentrations near Trent Avenue are greater than 700 pg/l during both flow conditions. PCB concentrations are 450 pg/l at Nine Mile Dam during low flow and 268 pg/l during moderate flow. PCB concentrations downstream of Mirabeau Point were only measured during the low flow condition and were 74 pg/l. PCB concentrations were lower at moderate flow than low flow at three of the four stations. Additional interpretation of these data is provided subsequently in Section 4 of this report.

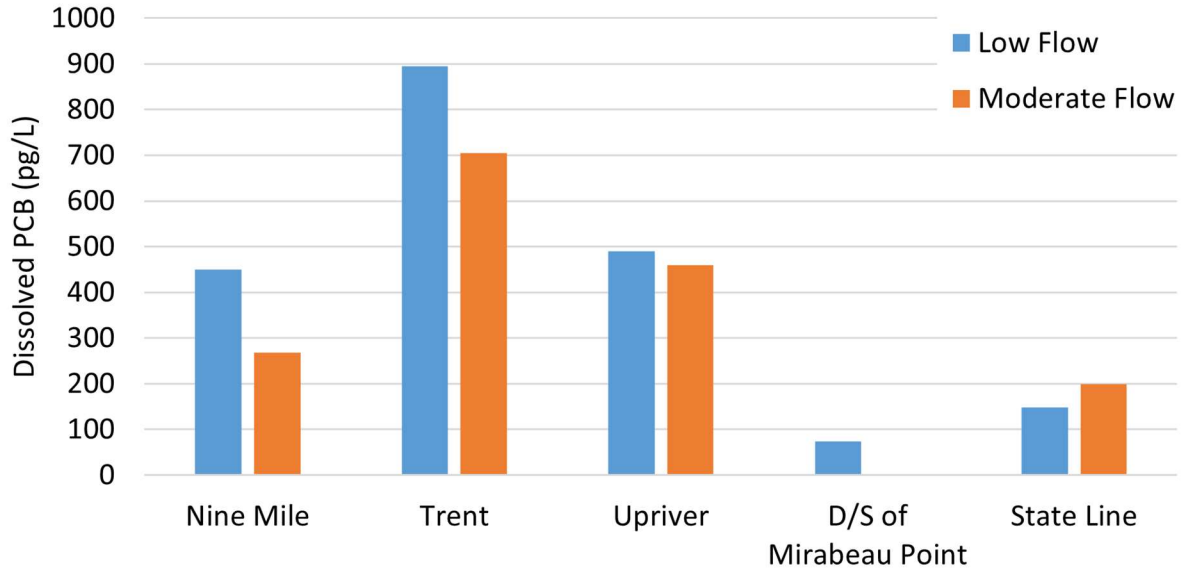

Figure 2. Spokane River Dissolved PCB Concentrations (pg/l) Measured during 2022-2023 SPMD Monitoring for Each Monitoring Location and River Flow Regime

Table 4. Spokane River Dissolved PCB Concentrations (pg/l) Measured by SPMD during 2022-2023 Monitoring

Location	Low Flow	Moderate Flow
State Line	148.5	198.7
Downstream of Mirabeau Point	74.2	N/A
Upriver	490.1	460
Trent	895.4	704.7
Nine Mile	450.1	268.1

3.2.2 Grab Samples

Grab sample total PCB concentrations are shown below in Figure 3 and Table 5 for all monitoring locations and deployment periods. Grab sample average concentrations during low flow exceed those during moderate flow for all stations. Average PCB concentrations are less than 10 pg/l at State Line for both flow conditions. At Upriver Dam, average PCB concentrations are 103 pg/l at low flow and less than 5 pg/l at moderate flow. PCB concentrations near Trent Avenue are greater than 250 pg/l during the low flow period and are 76 pg/l during moderate flow. Total PCB concentrations averaged 140 pg/l at Nine Mile Dam during the low flow period and less than 15 pg/l during moderate flow. Additional interpretation of these data is provided subsequently in Section 4 of this report.

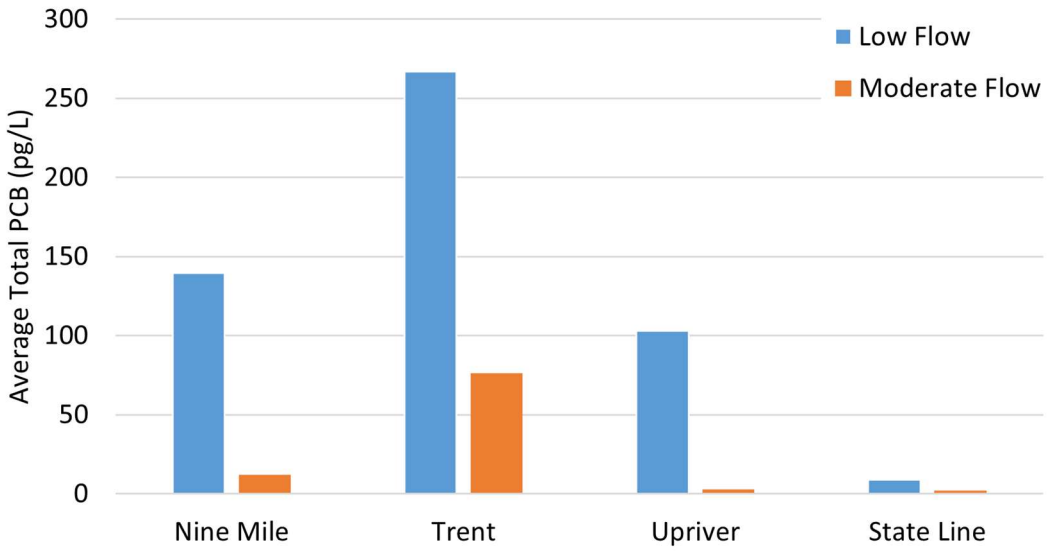

Figure 3. Spokane River Average Total PCB Concentrations (pg/l) Measured during 2022-2023 Grab Sample Monitoring for Each Monitoring Location and River Flow Regime

Table 5. Spokane River Total PCB Concentrations (pg/l) Measured during 2022-2023 Grab Sample Monitoring

	Low Flow			Moderate Flow		
Location	Deploy	MidPt	Retrieve	Deploy	MidPt	Retrieve
Stateline	18.032	4.287	3.87	2.638	1.98	1.294
Upriver	68.182	28.175	212.397	2.035	4.292	2.331
Trent	194.381	178.023	428.228	5.62	216.51	6.404
Nine Mile	52.281	57.669	309.115	5.406	22.692	8.421

3.3 Homolog Distributions

3.3.1 SPMDs

Homolog distributions for each station and sampling period are summarized for the SPMDs in Figures 4 and Figure 5, showing concentration by homolog for each location and flow regime. These data are provided in tabular format for each individual sample in Appendix A. The tetra-chlorinated homolog was the most prevalent and the tri-chloro homolog was the second most prevalent for all locations and flow regimes except for low flow at Trent Avenue, where the penta-chloro homolog was the most prevalent and the tetra-chloro homolog was the second most prevalent.

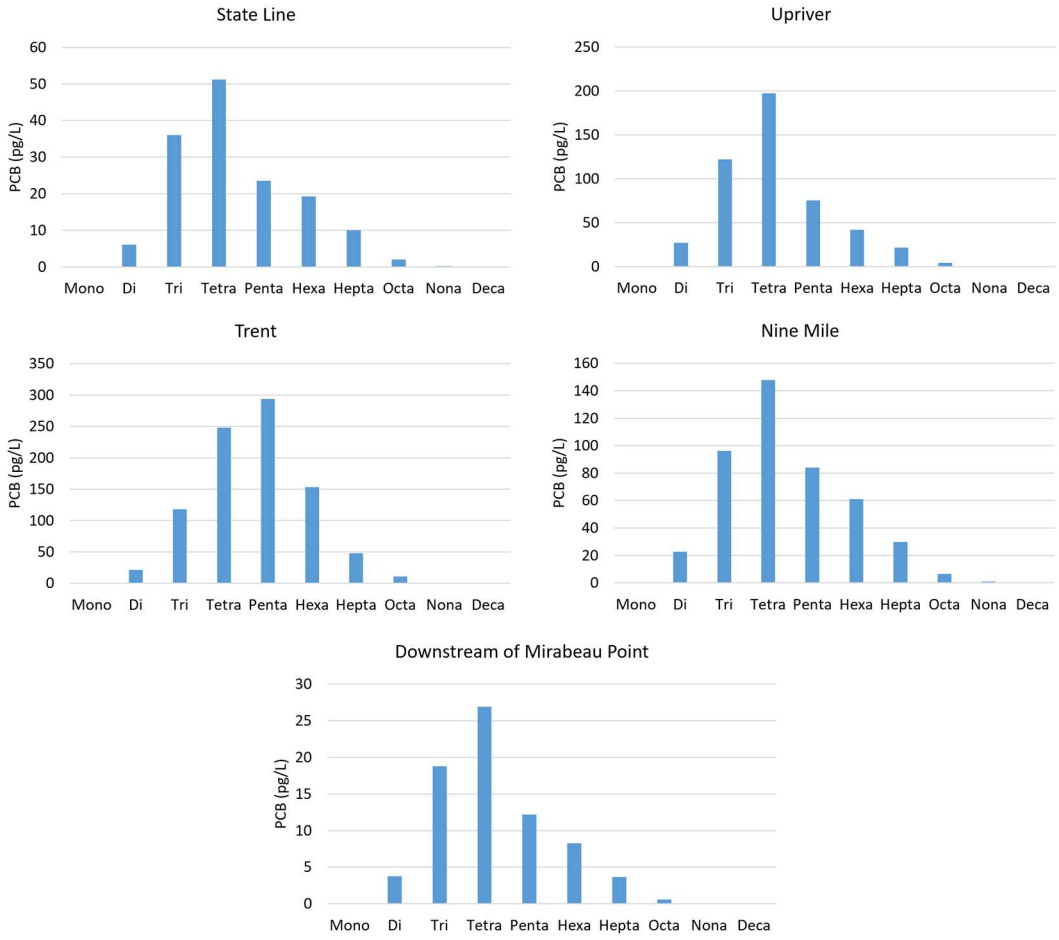

Figure 4. Field Blank-Corrected SPMD Dissolved Homolog Concentrations during Low Flow Deployment.

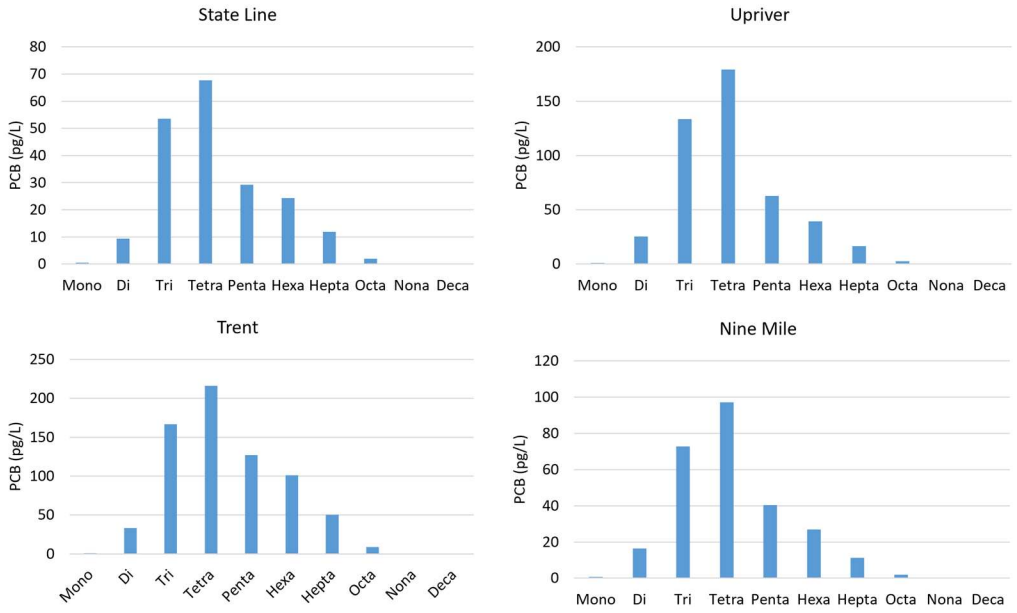

Figure 5. Field Blank-Corrected Dissolved Homolog Concentrations during Moderate Flow Deployment.

3.3.2 Grab Samples

Homolog distributions for each station and grab sample are provided in Figure 6 and Figure 7 and in tabular format in Appendix A. The observed distributions tended to be more dominated by the heavier homologs than the SPMD modeled distributions with the exception of Upriver Dam during low flow. The low flow grab samples were dominated by the hexa-chloro homolog at all stations except Upriver Dam which was dominated by the tetra-chloro homolog. The penta-chloro homolog was frequently the second most prevalent homolog. The moderate flow grab samples at State Line, Upriver Dam, and Nine Mile Dam were dominated by the hepta-chloro homolog whereas the hexa-chloro homolog dominated at Trent Avenue.

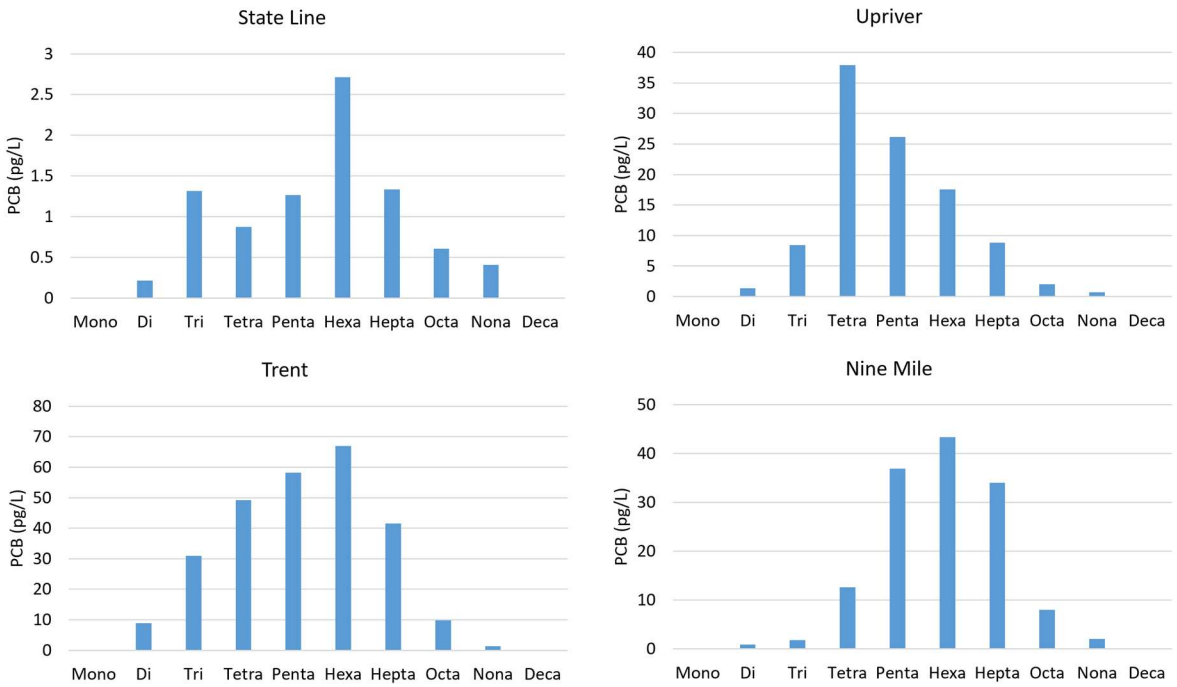

Figure 6. Lab Blank Corrected Homolog Concentrations during Low Flow.

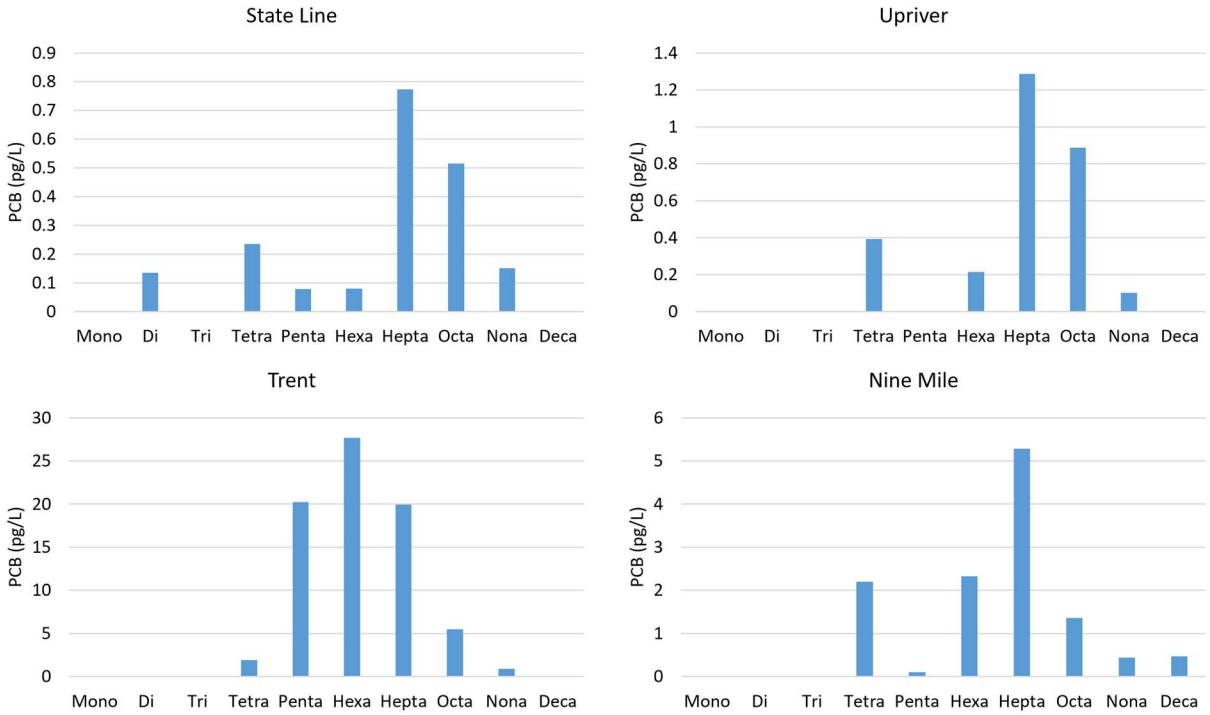

Figure 7. Lab Blank Corrected Homolog Concentrations during Moderate Flow

4 Data Interpretation

The primary objective of this sampling is to provide for long term trend assessment of PCB concentrations in the water column that may be used as one measure of the effectiveness of PCB control actions aimed at the reduction of PCBs in the Spokane River. The secondary objective is to identify whether unmonitored PCB loads are entering the river upstream of Mirabeau Point. This section provides some interpretation of the PCB results provided in Section 3 in terms of long-term trend assessment and evaluation of PCB loading upstream of Mirabeau Point. It is divided into sections of:

- Conversion of freely dissolved phase to total PCB concentration
- Comparison to SPMD-estimated water column PCB concentrations from prior years
- Comparison of contemporaneous SPMD-estimated and grab sample PCB concentrations
- Assessment of unmonitored loads upstream of Mirabeau Point

4.1 Conversion of Dissolved Phase to Total PCB Concentration

SPMDs measure the concentration of freely dissolved PCB in the water column. These freely dissolved PCB concentrations require a conversion step, described above in Section 3.1, to generate estimates of total PCB concentrations. Table 6 provides a summary of calculated total PCB concentrations converted from the SPMD dissolved phase results (and measured DOC and POC).

Table 6. Comparison of Total and Dissolved Phase PCB Concentration (pg/l) Estimated from SPMDs

	Low Flow		Moderate Flow	
Location	Total	Dissolved	Total	Dissolved
State Line	164	148.5	240.5	198.7
Downstream of Mirabeau	92.9	74.2	NA	NA
Upriver	577.2	490.1	503.7	460
Trent	1,047.6	895.4	790.8	704.7
Nine Mile	506	450.1	300.9	268.1

Total PCB concentrations observed from SPMDs were only marginally higher than dissolved phased PCB concentrations. This finding is consistent with conclusions from previous studies which found that the large majority of PCBs in the Spokane River are in the dissolved form.

As discussed in the report from the initial phase of this monitoring (LimnoTech, 2022), the conversion of dissolved phase PCB concentration into predicted total PCB concentrations introduces uncertainty due to two causes: 1) temporal variability in observed POC and TOC concentrations, and 2) uncertainty in dissolved organic carbon partition coefficients. For this reason, the Task Force has decided to focus its temporal trend analysis on SPMD results for dissolved phase PCB rather than total PCB concentrations.

4.2 Comparison to SPMD-Estimated Water Column PCB Concentrations from Prior Years

The objective of the Task Force's SPMD monitoring is to support a long-term trend assessment via implementation of a consistent monitoring program over time. It is premature at this time to conduct a trend assessment with the 2022-2023 data because: 1) trends are to be calculated using annual average concentrations calculated over three different flow regimes and 2) results from the third flow regime for the second year are not available. Absent a formal trend assessment, this section qualitatively compares water column PCBs measured by SPMDs during 2022-2023 to prior water column measurements determined by SPMDs. The Task Force conducted water column PCB monitoring by SPMDs of the Spokane River in 2020-2021 (LimnoTech, 2022). Additionally, Ecology has conducted prior water column assessment of PCB concentrations using SPMDs in 2003-2004 (Serdar et al, 2011) and 2010-2011 (Sandvik and Seiders, 2012). The comparison is summarized in Figure 8Figure 8, which shows average concentrations at four locations across four sampling programs.

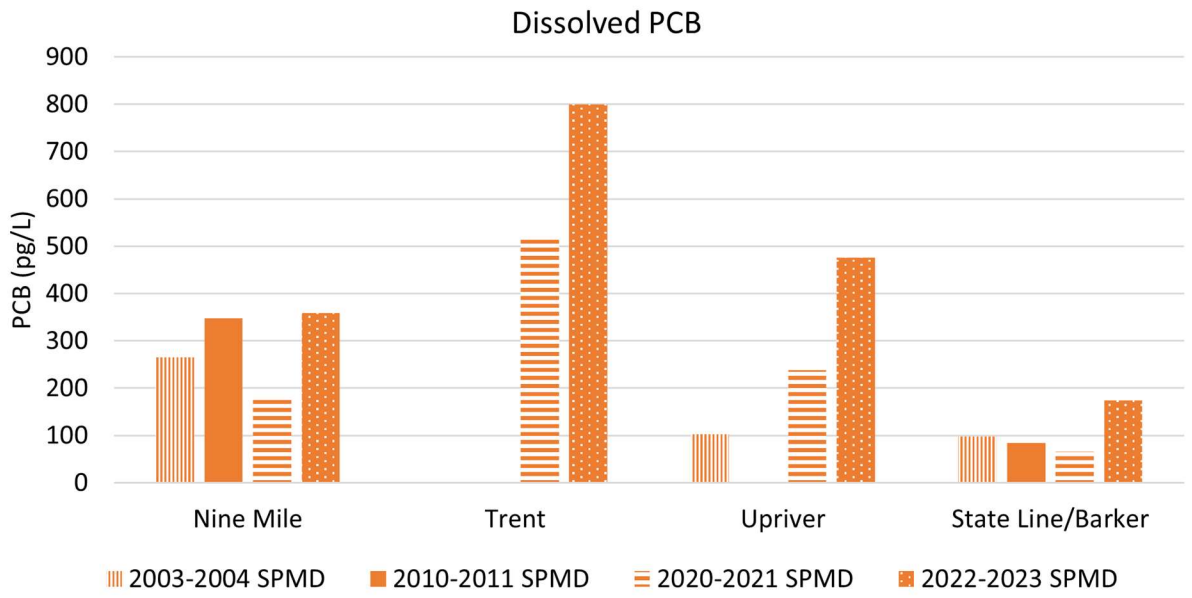

Figure 8. Dissolved PCB Concentrations Measured by SPMD across Four Monitoring Programs[4]

The right-hand side of Figure 8 shows results for Barker Rd. and the State Line. While the Barker Road location is downstream from the State Line, PCB concentrations are not expected to vary significantly between sites. Dissolved phase PCB concentrations at the State Line during 2003-2004 averaged 97 pg/l, while the single SPMD concentration measured at the State Line during 2010 was 83.5 pg/l. PCB concentrations at the State Line during the 2020-2021 study averaged 66 pg/l. PCB concentrations at the State Line during this study averaged 174 pg/l.

[4] The 2020-2021 SPMD represents an average concentration over all three flow regimes (summer low flow, winter moderate flow, and spring high flow) while the 2022-2023 SPMD does not include spring 2023 high flow scenario.

The right/middle of Figure 8 compares results in the vicinity of Upriver Dam. Dissolved PCB concentrations upstream of Upriver Dam measured by SPMD during 2003-2004 averaged 103 pg/l, while concentrations just downstream of Upriver Dam measured during the 2020-2021 study averaged 238 pg/l. Concentrations for the current study average 475 pg/l just downstream of Upriver Dam.

The left/middle of Figure 8 compares results in the vicinity of Trent Avenue. Dissolved PCB concentrations at this station measured during the 2020-2021 study averaged 519 pg/l. Concentrations for the current study average 800 pg/l. The Trent Avenue sampling location was selected primarily to identify the presence of PCB sources contributing to elevated biofilm PCB concentrations in the Mission Reach. The sampling site was specifically located in an area where localized biofilm contamination had been observed. PCB concentrations observed via SPMD sampling at this site may reflect a localized source rather than laterally-averaged river concentrations. The interpretation of data from Trent Avenue as part of the trend assessment should recognize that future concentrations changes at this site may be more reflective of changes in the localized source rather than changes in overall PCB loads from all upstream sources. The Upriver Dam monitoring location will be sufficient for assessing trends in overall loads near the geographic mid-point of the study area.

The left-hand side of Figure 8 compares results in the vicinity of Nine Mile Dam. PCB concentrations at the Nine Mile Dam during this study averaged 359 pg/l. PCB concentrations from SPMD monitoring at Nine Mile Dam averaged 265 pg/l during 2003-2004, 348 pg/l during 2010-2011, and 181 pg/l during 2020-2021.

4.3 Comparison of Contemporaneous SPMD-Estimated and Grab Sample PCB Concentrations

LimnoTech (2022) found that PCB concentrations estimated from SPMDs tended to be greater than those observed from grab samples taken at similar times and locations; this observation remains true in the 2022-2023 sampling. This section extends that assessment to include the most recently collected data. Figure 9 compares water column total PCB concentrations measured by SPMDs and grabs during 2022-2023 to prior water column measurements determined by SPMDs and grab sampling at similar sampling locations. The Task Force conducted water column PCB monitoring of the Spokane River in 2014, 2015, 2016, and 2018 (LimnoTech, 2019). Additionally, Ecology has conducted prior water column assessment of PCB concentrations using SPMDs in 2003-2004 (Serdar et al, 2011) and 2010-2011 (Sandvik and Seiders, 2012), and grab sampling in 2012-2013 (Era-Miller, 2014).

The right-hand side of Figure 9 compares SPMD samples at Barker Rd. and the State Line to grab samples at the same locations. Total PCB concentrations from SPMD monitoring at the State Line during 2003-2004 averaged 105 pg/l, while the single SPMD concentration measured at the State Line during 2010 was 156 pg/l. PCB concentrations at the State Line during the 2020-2021 Task Force SPMD study averaged 79 pg/l. The PCB concentration at the State Line during this SPMD study averaged 202 pg/l. Both Ecology grab samples in 2012-2013 were 13 pg/l. The average PCB concentration measured at Barker Rd. via the 2014 Task Force grab sampling was 21 pg/l, and the

average PCB concentration measured at the State Line in the 2022-2023 Task Force grab sampling was 5 pg/l.

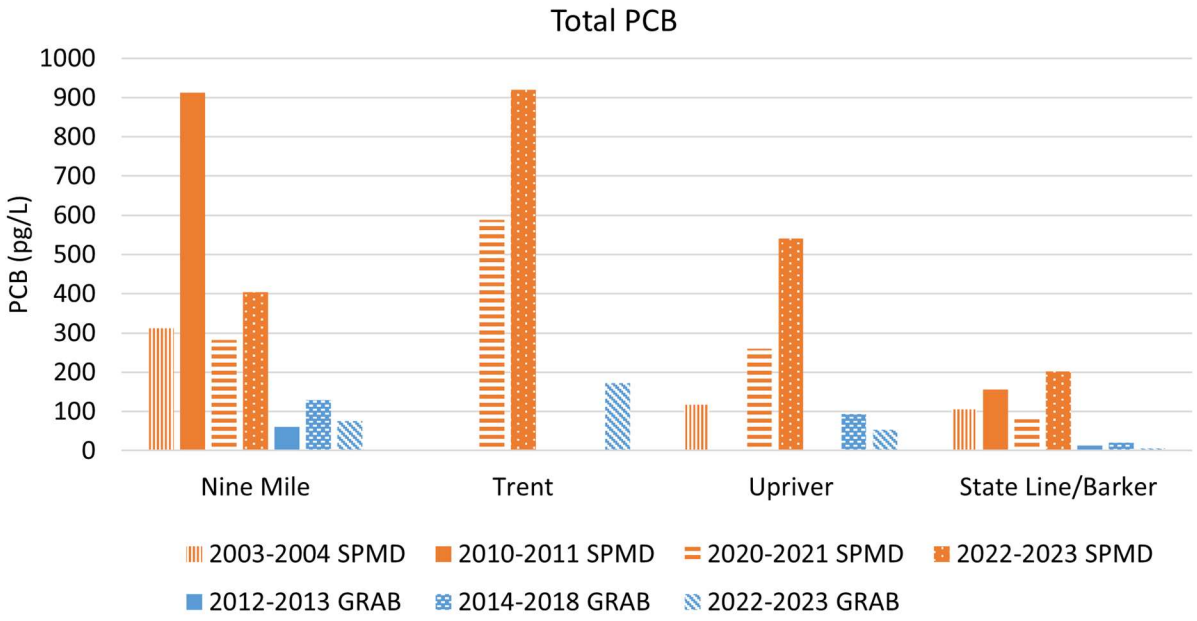

Figure 9. Total PCB Concentrations Measured by SPMD and Grab Samples across Six Monitoring Programs[5]

The right/middle of Figure 9 compares SPMD samples to grab samples in the vicinity of Upriver Dam. Total PCB concentrations upstream of Upriver Dam measured by SPMD during 2003-2004 averaged 117 pg/l, while concentrations just downstream of Upriver Dam were 260 pg/l during the 2020-2021 Task Force study and 540 pg/l during the 2022-2023 Task Force study. The average PCB concentration measured just downstream of Upriver Dam via Task Force grab sampling in 2015-2018 was 94 pg/l, while the average grab sample concentration for this study was 53 pg/l.

The left/middle of Figure 9 compares SPMD samples to grab samples in the vicinity of Trent Avenue. Total PCB concentrations from SPMDs near Trent Avenue during 2020-2021 sampling averaged 588 pg/l while total PCB concentrations near Trent Avenue during this SPMD sampling averaged 919 pg/l. The average grab sample concentration for this study was 172 pg/l.

The left-hand side of Figure 9 compares grab samples to SPMD samples at Nine Mile Dam. Total PCB concentrations from SPMDs at the Nine Mile Dam during this study averaged 403 pg/l. Total PCB concentrations from SPMDs at Nine Mile Dam during the 2020-2021 Task Force sampling averaged 282 pg/l. PCB concentrations from SPMD monitoring at Nine Mile Dam during 2010-2011 ranged from non-detect to 1,600 pg/l, averaging 913 pg/l while PCB concentrations from SPMD monitoring at Nine Mile Dam during 2003-2004 sampling averaged 312 pg/l. The average PCB concentration measured at Nine Mile Dam via Task Force grab sampling in 2014-2018 was 129 pg/l, while

[5] The 2020-2021 SPMD represents an average concentration over all three flow regimes (summer low flow, winter moderate flow, and spring high flow) while the 2022-2023 SPMD does not include spring 2023 high flow scenario.

Ecology grab samples in 2012-2013 at Nine Mile Dam averaged 61 pg/l. The average grab sample concentration at Nine Mile Dam for this study was 76 pg/l.

While the limited number of samples and difference in times between monitoring efforts prevents a rigorous statistical assessment, the results shown in Figure 9 continue to indicate that PCB concentrations measured by SPMDs are higher than PCB concentrations measured by grab samples at the same or similar location. While no broad conclusions can be drawn, the potential for incomparability of results between sampling methods should be considered prior to any pooling of data between methods for future trend assessments.

4.4 Assessment of Unmonitored Loads Upstream of Mirabeau Point

The final objective of this study was to compare SPMD concentrations from the low flow period between the State Line and Mirabeau Point stations, to assess whether an unmonitored load of PCBs was entering the river between those stations. The PCB concentration observed downstream of Mirabeau Point was 74.2 pg/l and less than the concentration of 148.5 pg/l that was measured at the State Line. Therefore, the SPMD results show no indication of unmonitored PCB loads entering the river between the State Line and Mirabeau Point stations. There was potential concern that the revised Mirabeau Point monitoring location could reflect PCB loading from Kaiser, but the low observed PCB concentration (in both the primary SPMD sample and field replicate) indicate no influence from Kaiser PCB loads.

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5 Conclusions

This report assesses the available 2022-2023 SPMD data in the context of the Spokane River water column long-term trend assessment. Laboratory analysis of the spring high flow SPMDs was not complete at the time of this report, therefore, this report includes the late summer 2022 and winter 2022-2023 flow regimes and not spring high flow. SPMD results were compared across flow regimes, across years, and across sampling technique (SPMD vs. grab sampling) as well as analyzing the homolog distribution at each site. The key conclusions of this analysis include:

- The observed PCB concentration measured by SPMDs at the long-term trend stations, averaged across the low and moderate flow regimes, was greatest at East Trent Avenue (800 pg/l). The average PCB concentration was lowest at State Line (174 pg/l). Average concentrations at Upriver Dam and Nine Mile Dam were 475 pg/l and 359 pg/l, respectively.
- PCB concentrations in both this study and the original 2020-2021 deployment tend to be negatively correlated to Spokane River flow, with higher PCB concentrations occurring during lower river flows.
- It is premature to draw any conclusion about temporal trends in PCB concentrations from these data, as they represent only two of the three flow regimes intended to characterize annual average conditions. SPMDs have been deployed under a separate project to characterize PCB concentration from the third flow regime, but laboratory results from this monitoring will not be available prior to the sunsetting of the Task Force.
- The PCB concentrations measured by SPMDs continue to appear to be higher than those measured via analysis of grab samples at similar locations. Trend assessments on Spokane River PCB concentrations should be conducted separately between SPMD and grab sample results.
- PCB concentrations downstream of Mirabeau Point are not greater than those observed at the State Line station, indicating that no significant unmonitored load was entering the river between those locations.

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6 Next Steps

This 2022-2023 study contributes to a larger trend assessment of PCB concentrations in the Spokane River. The work documented in this report only covers monitoring results for two of the three seasonal flow periods. The Task Force deployed SPMDs for the third flow regime and delivered them to Ecology for subsequent analysis. The most important next step is to complete all required analyses for the 2022-2023 sampling year. Specific steps in this regard consist of:

- Conduct laboratory PCB analysis on the SPMDs deployed during the high flow regime of Spring 2023;
- Convert PCB concentrations measured in the SPMDs into estimated water column concentrations; and
- Compute an annual average PCB concentration at all trend stations by merging the results from the high flow regime with the results from the low and moderate flow regimes provided in this report.

Future studies should continue to sample at the four primary locations (State Line, Upriver Dam, Trent Avenue, and Nine Mile Dam) across the three flow regimes (low, moderate, and high) to inform a comprehensive trend assessment. These future studies should maintain the practice of collecting contemporaneous grab samples of PCBs, because grab samples have been used to support prior trend assessments (Rains, 2022) and will likely remain an important component of future trend assessments in Spokane.

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7 References

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Appendix A:
Synoptic Survey Results - PCBs by Homolog

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Table A-1: Blank-Corrected Analytical Results for SPMD Dissolved and Total PCB: State Line						
	Low Flow		Moderate Flow		High Flow	
	Diss.	Total	Diss.	Total	Diss.	Total
Total PCBs (pg/l)	148.53	163.99	198.65	240.53		
Total Monochloro Biphenyls (pg/l)	0	0	0.572	0.580		
Total Dichloro Biphenyls (pg/l)	6.079	6.154	9.334	9.579		
Total Trichloro Biphenyls (pg/l)	36.072	36.742	53.537	55.847		
Total Tetrachloro Biphenyls (pg/l)	51.243	53.135	67.643	73.486		
Total Pentachloro Biphenyls (pg/l)	23.558	25.604	29.265	35.038		
Total Hexachloro Biphenyls (pg/l)	19.259	23.171	24.320	35.316		
Total Heptachloro Biphenyls (pg/l)	10.051	14.525	11.841	23.517		
Total Octachloro Biphenyls (pg/l)	2.049	4.013	1.951	6.134		
Total Nonachloro Biphenyls (pg/l)	0.221	0.642	0.189	1.034		
Total Decachloro Biphenyls (pg/l)	0	0	0	0		

Table A-2: Blank-Corrected Analytical Results for SPMD Dissolved and Total PCB: Downstream of Mirabeau Point						
	Low Flow		Moderate Flow		High Flow	
	Diss.	Total	Diss.	Total	Diss.	Total
Total PCBs (pg/l)	74.17	92.90				
Total Monochloro Biphenyls (pg/l)	0	0				
Total Dichloro Biphenyls (pg/l)	3.733	3.866				
Total Trichloro Biphenyls (pg/l)	18.799	19.826				
Total Tetrachloro Biphenyls (pg/l)	26.890	29.728				
Total Pentachloro Biphenyls (pg/l)	12.183	15.230				
Total Hexachloro Biphenyls (pg/l)	8.266	13.168				
Total Heptachloro Biphenyls (pg/l)	3.665	8.490				
Total Octachloro Biphenyls (pg/l)	0.568	2.173				
Total Nonachloro Biphenyls (pg/l)	0.064	0.420				
Total Decachloro Biphenyls (pg/l)	0	0				

Table A-3: Blank-Corrected Analytical Results for SPMD Dissolved and Total PCB (pg/l): Upriver						
	Low Flow		Moderate Flow		High Flow	
	Diss.	Total	Diss.	Total	Diss.	Total
Total PCBs (pg/l)	490.05	577.17	459.97	503.69		
Total Monochloro Biphenyls (pg/l)	0.695	0.704	0.967	0.975		
Total Dichloro Biphenyls (pg/l)	26.878	27.525	25.266	25.618		
Total Trichloro Biphenyls (pg/l)	122.01	127.04	133.44	136.80		
Total Tetrachloro Biphenyls (pg/l)	197.28	213.46	179.17	188.19		
Total Pentachloro Biphenyls (pg/l)	75.279	89.814	62.780	70.079		
Total Hexachloro Biphenyls (pg/l)	41.850	60.522	39.220	49.564		
Total Heptachloro Biphenyls (pg/l)	21.445	42.688	16.367	25.903		
Total Octachloro Biphenyls (pg/l)	4.159	12.998	2.525	5.720		
Total Nonachloro Biphenyls (pg/l)	0.453	2.413	0.228	0.830		
Total Decachloro Biphenyls (pg/l)	0	0	0	0		

Table A-4: Blank-Corrected Analytical Results for SPMD Dissolved and Total PCB (pg/l): Trent						
	Low Flow		Moderate Flow		High Flow	
	Diss.	Total	Diss.	Total	Diss.	Total
Total PCBs (pg/l)	895.45	1047.63	704.67	790.80		
Total Monochloro Biphenyls (pg/l)	0.447	0.451	1.134	1.141		
Total Dichloro Biphenyls (pg/l)	21.264	21.591	33.200	33.590		
Total Trichloro Biphenyls (pg/l)	118.16	121.27	166.55	170.05		
Total Tetrachloro Biphenyls (pg/l)	248.32	261.18	216.00	225.13		
Total Pentachloro Biphenyls (pg/l)	293.87	330.92	126.74	139.25		
Total Hexachloro Biphenyls (pg/l)	153.25	199.67	101.22	124.39		
Total Heptachloro Biphenyls (pg/l)	47.867	79.970	50.473	76.511		
Total Octachloro Biphenyls (pg/l)	10.746	26.233	8.686	18.501		
Total Nonachloro Biphenyls (pg/l)	1.276	4.952	0.678	2.240		
Total Decachloro Biphenyls (pg/l)	0.251	1.391	0	0		

Table A-5: Blank-Corrected Analytical Results for Dissolved and Total PCB (pg/l): Nine Mile						
	Low Flow		Moderate Flow		High Flow	
	Diss.	Total	Diss.	Total	Diss.	Total
Total PCBs (pg/l)	450.09	505.95	268.06	300.87		
Total Monochloro Biphenyls (pg/l)	0.544	0.547	0.827	0.834		
Total Dichloro Biphenyls (pg/l)	22.590	22.868	16.484	16.749		
Total Trichloro Biphenyls (pg/l)	96.271	98.203	72.793	74.896		
Total Tetrachloro Biphenyls (pg/l)	147.69	153.63	97.117	102.77		
Total Pentachloro Biphenyls (pg/l)	84.150	92.249	40.491	45.957		
Total Hexachloro Biphenyls (pg/l)	60.917	74.589	26.952	35.226		
Total Heptachloro Biphenyls (pg/l)	29.860	44.873	11.290	18.867		
Total Octachloro Biphenyls (pg/l)	6.646	13.810	1.865	4.623		
Total Nonachloro Biphenyls (pg/l)	0.909	2.881	0.239	0.947		
Total Decachloro Biphenyls (pg/l)	0.512	2.302	0	0		

Table A-6: Blank-Corrected Analytical Grab Results for Spokane River at State Line								
	8 / 31	9 / 14	9 / 29	12 / 19	1/3	1/17		
Total PCBs (pg/l)	18.032	4.287	3.87	2.638	1.98	1.294		
Total Monochloro Biphenyls (pg/l)	0	0	0	0	0	0		
Total Dichloro Biphenyls (pg/l)	0	0.644	0	0	0	0.407		
Total Trichloro Biphenyls (pg/l)	3.942	0	0	0	0	0		
Total Tetrachloro Biphenyls (pg/l)	2.35	0.268	0	0.24	0.23	0.238		
Total Pentachloro Biphenyls (pg/l)	3.515	0.284	0	0	0.234	0		
Total Hexachloro Biphenyls (pg/l)	4.175	2.137	1.825	0	0.241	0		
Total Heptachloro Biphenyls (pg/l)	2.532	0.681	0.785	1.389	0.565	0.367		
Total Octachloro Biphenyls (pg/l)	1.132	0	0.691	0.751	0.513	0.282		
Total Nonachloro Biphenyls (pg/l)	0.386	0.273	0.569	0.258	0.197	0		
Total Decachloro Biphenyls (pg/l)	0	0	0	0	0	0		
Dissolved Organic Carbon (mg/l)	1.94	1.57	1.64	1.52	1.39	1.71		
Total Organic Carbon (mg/l)	1.73	1.53	1.73	1.49	1.54	2.31		
Total Suspended Solids (mg/l)	<1.0	<1.0	1.5	1.0	1.2	4.0		

Table A-7: Blank-Corrected Analytical Grab Results for Spokane River Downstream of Mirabeau Point								
	8 / 30	9 / 14	9 / 29					
Dissolved Organic Carbon (mg/l)	0.61	0.95	1.14					
Total Organic Carbon (mg/l)	<1.00	<1.00	1.91					
Total Suspended Solids (mg/l)	<1.0	<1.0	2.1					

Table A-8: Blank-Corrected Analytical Grab Results for Spokane River at Upriver Dam								
	8 / 31	9 / 14	9 / 29	12 / 19	1/3	1/17		
Total PCBs (pg/l)	68.182	28.175	212.397	2.035	4.292	2.331		
Total Monochloro Biphenyls (pg/l)	0	0	0	0	0	0		
Total Dichloro Biphenyls (pg/l)	1.962	0	2.04	0	0	0		
Total Trichloro Biphenyls (pg/l)	18.283	3.277	3.702	0	0	0		
Total Tetrachloro Biphenyls (pg/l)	40.062	19.97	53.665	0.259	0.49	0.43		
Total Pentachloro Biphenyls (pg/l)	4.743	0	73.648	0	0	0		
Total Hexachloro Biphenyls (pg/l)	1.67	2.895	48.078	0.222	0.216	0.208		
Total Heptachloro Biphenyls (pg/l)	1.148	0.698	24.58	0.872	1.945	1.046		
Total Octachloro Biphenyls (pg/l)	0.314	0.785	5.034	0.682	1.336	0.647		
Total Nonachloro Biphenyls (pg/l)	0	0.55	1.65	0	0.305	0		
Total Decachloro Biphenyls (pg/l)	0	0	0	0	0	0		
Dissolved Organic Carbon (mg/l)	2.68	1.37	1.81	1.25	1.48	1.71		
Total Organic Carbon (mg/l)	2.98	1.24	2.20	1.34	1.51	2.31		
Total Suspended Solids (mg/l)	<1.0	<1.0	2.8	<1.0	1.0	1.8		

Table A-9: Blank-Corrected Analytical Grab Results for Spokane River above Trent Avenue						
	8 / 31	9 / 14	9 / 29	12 / 19	1/3	1/17
Total PCBs (pg/l)	194.381	178.023	428.228	5.62	216.51	6.404
Total Monochloro Biphenyls (pg/l)	0	0	0	0	0	0
Total Dichloro Biphenyls (pg/l)	19.36	2.45	4.96	0	0	0
Total Trichloro Biphenyls (pg/l)	19.403	11.664	61.986	0	0	0
Total Tetrachloro Biphenyls (pg/l)	39.986	13.743	93.794	0.257	5.219	0.264
Total Pentachloro Biphenyls (pg/l)	51.166	31.738	91.602	0	60.512	0.204
Total Hexachloro Biphenyls (pg/l)	43.784	56.364	100.529	0.486	82.357	0.251
Total Heptachloro Biphenyls (pg/l)	16.196	49.265	59.182	4.231	51.035	4.542
Total Octachloro Biphenyls (pg/l)	3.871	11.626	13.99	0.646	14.952	0.883
Total Nonachloro Biphenyls (pg/l)	0.615	1.173	2.185	0	2.435	0.26
Total Decachloro Biphenyls (pg/l)	0	0	0	0	0	0
Dissolved Organic Carbon (mg/l)	1.16	1.08	1.09	1.14	1.55	1.57
Total Organic Carbon (mg/l)	1.10	1.18	1.45	1.30	1.60	1.52
Total Suspended Solids (mg/l)	1.6	1.2	1.7	1.0	1.6	2.6

Table A-10: Blank-Corrected Analytical Grab Results for Spokane River at Nine Mile Dam						
	8 / 31	9 / 14	9 / 29	12 / 19	1/3	1/17
Total PCBs (pg/l)	52.281	57.669	309.115	5.406	22.692	8.421
Total Monochloro Biphenyls (pg/l)	0	0	0	0	0	0
Total Dichloro Biphenyls (pg/l)	2.679	0	0	0	0	0
Total Trichloro Biphenyls (pg/l)	1.37	1.563	2.45	0	0	0
Total Tetrachloro Biphenyls (pg/l)	20.751	7.137	10.014	0.299	6.03	0.265
Total Pentachloro Biphenyls (pg/l)	14.59	11.65	84.413	0	0.293	0
Total Hexachloro Biphenyls (pg/l)	8.337	22.324	99.536	0.291	5.348	1.324
Total Heptachloro Biphenyls (pg/l)	3.593	12.138	86.411	3.95	6.953	4.96
Total Octachloro Biphenyls (pg/l)	0.666	2.14	21.231	0.663	1.894	1.516
Total Nonachloro Biphenyls (pg/l)	0.295	0.717	5.06	0.203	0.754	0.356
Total Decachloro Biphenyls (pg/l)	0	0	0	0	1.42	0
Dissolved Organic Carbon (mg/l)	1.22	1.12	1.10	1.19	2.27	2.29
Total Organic Carbon (mg/l)	1.26	1.09	1.31	1.24	2.40	2.34
Total Suspended Solids (mg/l)	7.8	1.37	3.4	1.2	34.2	20.2

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Appendix B:
Quality Assurance Project Plan

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Appendix C: Laboratory Results

Provided separately as electronic spreadsheets

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