

# 2020-2021 Evaluation of PCBs in the Spokane River via Semi Permeable Membrane Devices (SPMDs)

Prepared for:  
Spokane River Regional Toxics  
Task Force

~~December 8~~ February 15,  
~~2021~~ 2022

FINAL APPROVAL 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 because of concentrations of polychlorinated biphenyls (PCBs) ~~that exceed water quality standards in fish tissue~~. 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 (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.

This study describes the monitoring of water column PCB concentrations using semipermeable membrane devices (SPMDs). The results of this study are designed to provide ~~a baseline for long term trend~~ing assessment of PCB concentrations in the water column ~~and will 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 results of this study are not intended to be used for any regulatory purpose under the Clean Water Act. This study documents the challenges in using SPMDs to accurately and reliably measure water column PCBs for long-term trend assessment. Furthermore, test method 1668C used in this study is not an approved test method for use under the Clean Water Act in 40 CFR Part 136.

SPMDs were deployed at four locations in the Spokane River, corresponding to the Washington/Idaho State Line, downstream of Upriver Dam, at East Trent Avenue in Spokane and at Nine Mile Dam. Water column monitoring was conducted via three month-long deployments of SPMDs, corresponding to late summer 2020 low flow, winter 2021 moderate flow, and spring 2021 high flow conditions.

The following conclusions can be gathered from the data collected:

- The PCB concentration observed near Trent Avenue during low flow conditions was much higher than any recent water column measurement. This elevated concentration may not be representative of laterally-averaged water column concentrations, as the SPMD was placed in area where localized elevated biofilm concentrations had occurred in the past.
- PCB concentrations measured by SPMDs across multiple studies appear to be higher than those measured via analysis of grab samples at similar locations.
- The use of SPMDs to measure water column PCBs poses some challenges for long-term trend assessment, such as conversion of the freely dissolved phase PCB concentrations



measured by SPMDs into estimates of total PCB concentration. These challenges are balanced by the benefits of SPMDs relative to grab sampling, i.e., they are less affected by blank contamination than grabs (due to having a smaller proportion of the sample analytical result in the blanks) ~~are much less prone to blank contamination~~ and represent an integrated concentration over a month-long period.



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# 1

## Introduction

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Sections of 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 in fish tissue~~. 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 (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 effort 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 trending assessment of choice~~ after a review of other candidate methods (LimnoTech, 2020a). SPMDs were selected over other methods such as grab samples due to their superior performance with respect to blank contamination. This study describes the use of SPMDs at four different Spokane River locations for three separate month-long deployments. The results of this monitoring are intended to provide ~~a direct link to one means of assessing~~ the efficacy of control actions on Spokane River PCB concentrations.

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



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## 2

## Sampling Activities

The field monitoring program consisted of three separate month-long deployments of semi-permeable membrane devices at four locations in the Spokane River. 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 four 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. 2020-2021 SPMD Locations**

Description	Latitude	Longitude
WA/ID State Line	N 47° 41.666'	W 117° 00.597'
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 three separate approximately month-long periods, corresponding to late summer low flow, winter moderate flow, and spring high flow regimes (Table 2). Daily average river flows at the Spokane USGS gage ranged from 803 to 1300 cfs during the low flow deployment, 3390 to 4810 cfs during the moderate flow deployment and 6,930 to 13,500 cfs during the high flow deployment.

### 2.3 Field Sampling Activities

The field sampling activities as planned and implemented are detailed in the project QAPP (LimnoTech, 2020b). This section summarizes those activities. 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 steel canisters and spindle devices provided by Environmental Sampling Technologies (EST). 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 SGS AXYS Analytical Services, Ltd. in order to assess biofouling and the non-equilibrium uptake of the



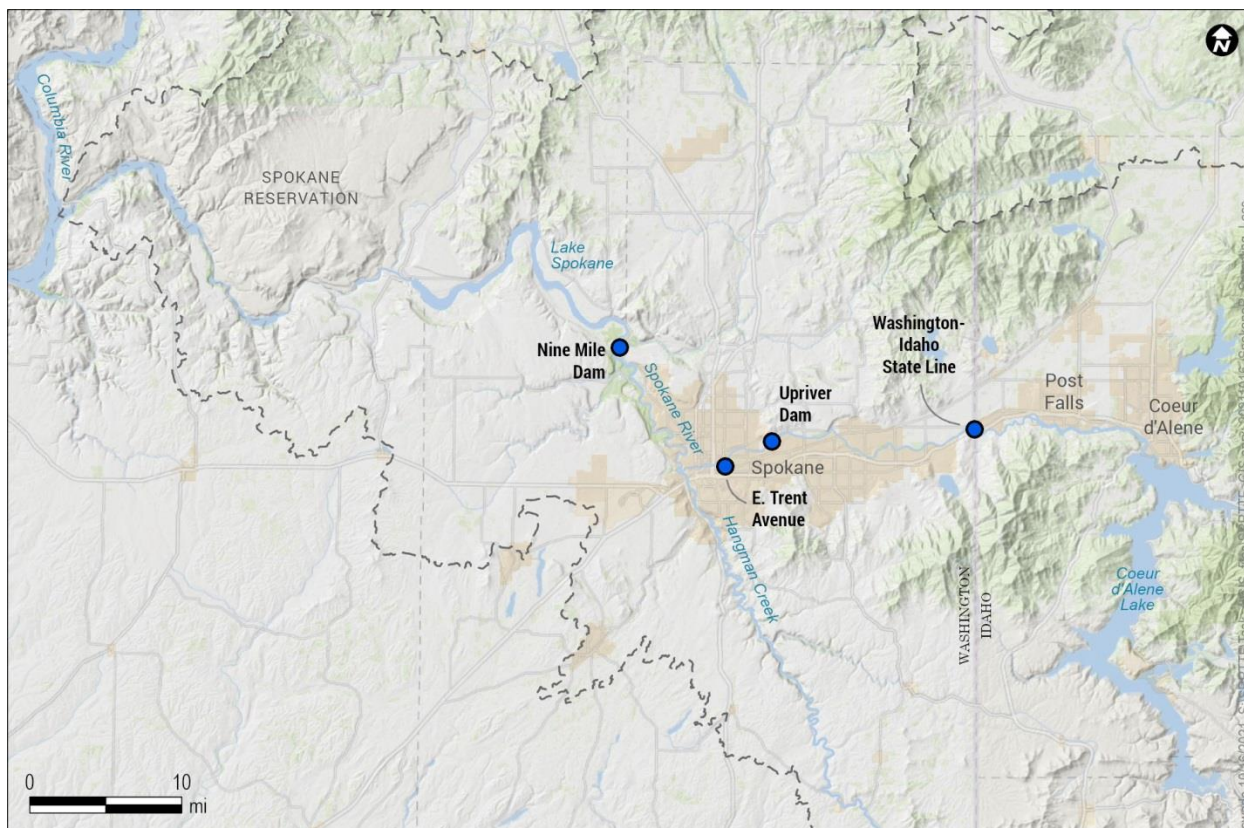


Figure 1. Locations for 2020-2021 SPMD Monitoring

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

Location	Date Deployed	Date of Mid-Deployment Check	Date Retrieved
<b>Late Summer Low Flow</b>			
WA/ID State Line to McMillan Rd.	8/25/2020	9/08/2020	9/22/2020
Downstream of Upriver Dam	8/26/2020	9/08/2020	9/22/2020
E. Trent Avenue Bridge	8/25/2020	9/08/2020	9/22/2020
Nine Mile Dam	8/26/2020	9/08/2020	9/22/2020
<b>Winter Moderate Flow</b>			
WA/ID State Line to McMillan Rd.	2/16/2021	3/4/2021	3/17/2021
Downstream of Upriver Dam	2/16/2021	3/4/2021	3/17/2021
E. Trent Avenue Bridge	2/16/2021	3/4/2021	3/17/2021
Nine Mile Dam	2/16/2021	3/4/2021	3/17/2021
<b>Spring High Flow</b>			
WA/ID State Line to McMillan Rd.	4/27/2021	5/11/2021	5/26/2021
Downstream of Upriver Dam	4/27/2021	5/11/2021	5/26/2021
E. Trent Avenue Bridge	4/27/2021	5/11/2021	5/26/2021
Nine Mile Dam	4/27/2021	5/11/2021	5/26/2021

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 total and dissolved organic carbon (TOC/DOC) and total suspended solids at each site during the time the SPMDs are exposed. Water grab samples were collected three times over the duration of each SPMD exposure to get an integrated measure of the conditions.

## 2.4 Quality Assurance

SPMDs 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:

- Select congeners and total PCB concentrations for two samples were flagged as failing the duplicate sample relative percent differences (RPDs).
- Select congeners for four samples were flagged as having high sample and method blank surrogate recovery.
- The percent recovery of performance reference compounds was outside of the desired range (20-80%) for ten samples, with an average percent recovery of 86% for the out-of-compliance samples. All individual congener results and total PCB concentrations for these samples will be flagged.
- There was a battery malfunction on the continuous temperature monitors at the Stateline and Trent stations during the first two weeks of the winter sampling event. New devices were deployed during the mid-period check and the SPMD cages appeared to be in the exact locations as deployed. All individual congener results and total PCB concentrations for these sample will be flagged.



- Due to shipping delays incurred between sample collection and delivery of samples to the laboratory, sample temperatures were 9.6 °C when they reached the laboratory. exceeded the target temperature of 4 °C. EPA method 1668C Section 8.3.2 states that solid samples should be “maintain[ed] ... at less than 6°C from the time of collection until receipt at the laboratory”. Consultation with SGS AXYS Laboratory Project Manager Sean Campbell indicated that, given the short duration and magnitude of the temperature exceedance and the stable nature of PCB congeners, the temperature exceedance should not materially affect laboratory results. Results were consequently not flagged, and a comment in the case narrative is providing noting the exceedance.

There are no changes to PCB result values due to this of this assessment, although data qualifiers were added to select results as described above.

#### 2.4.2 Blank ~~Correction~~Censoring

Total PCB concentrations were ~~corrected-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 ~~corrected-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% of the total SPMD concentration was above the LOD. At Nine Mile Dam, 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 24% of the total SPMD concentration were considered estimated values. The influence of field blank-derived LOQs was much smaller at the remaining stations. At Nine Mile Dam, for example, only 2% of the total SPMD concentration were considered estimated values.



## 3

## Analytical Results

This section summarizes the results of the 2020-2021 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 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 were 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,  $K_{OC,p}$ , 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	State Line	Upriver	Trent	Nine Mile
<b>Late Summer Low Flow</b>				
POC (mg/l)	0.24	0.04	0.12	0.39
DOC (mg/l)	1.62	1.36	1.27	1.23
<b>Winter Moderate Flow</b>				
POC (mg/l)	0.14	0.09	0.17	0.08
DOC (mg/l)	1.88	1.76	1.66	1.89
<b>Spring Hgh Flow</b>				
POC (mg/l)	0.01	0.05	0.01	0.07
DOC (mg/l)	1.94	1.87	1.69	1.75

### 3.2 PCB Concentrations

Freely dissolved and total PCB concentrations are shown below in Figures 2 and 3 and Table 4 for all SPMD monitoring locations and deployment periods. Dissolved and total PCB concentrations are consistently less than 100 pg/l at State Line, increasing to 150 to 370 pg/l at Upriver Dam. PCB concentrations near Trent Avenue are greater than 1000 pg/l during the low flow period and on the order of 200 pg/l during moderate and high flow. Dissolved PCB concentrations are approximately 200 pg/l at Nine Mile Dam for all flow regimes, with similar total PCB concentrations during periods of moderate and high flow. Total PCB concentrations were approximately 400 pg/l at Nine Mile Dam during the low flow period. Additional interpretation of these data is provided subsequently in Section 4 of this report.



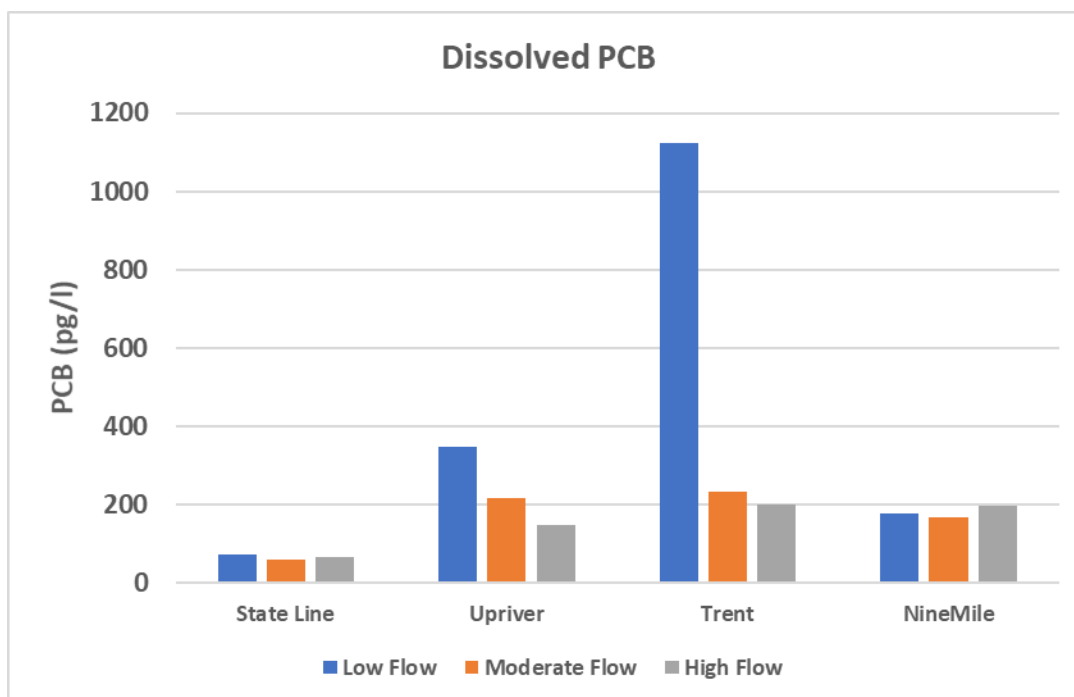


Figure 2. Spokane River Dissolved PCB Concentrations (pg/l) Measured during 2020-2021 SPMD Monitoring for Each Monitoring Location and River Flow Regime

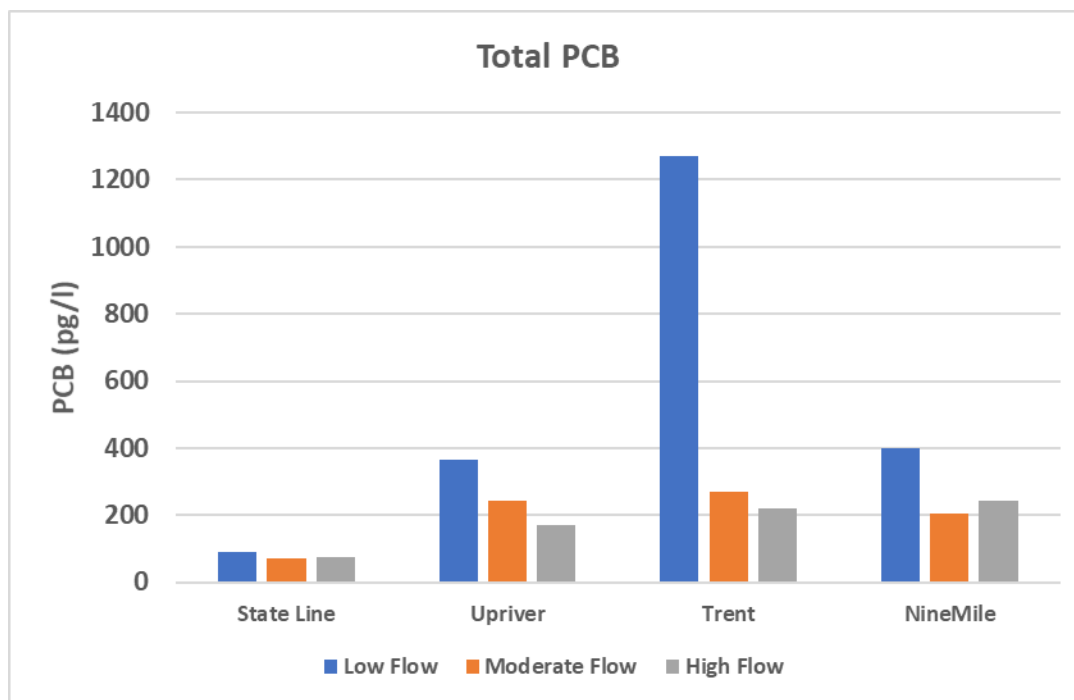


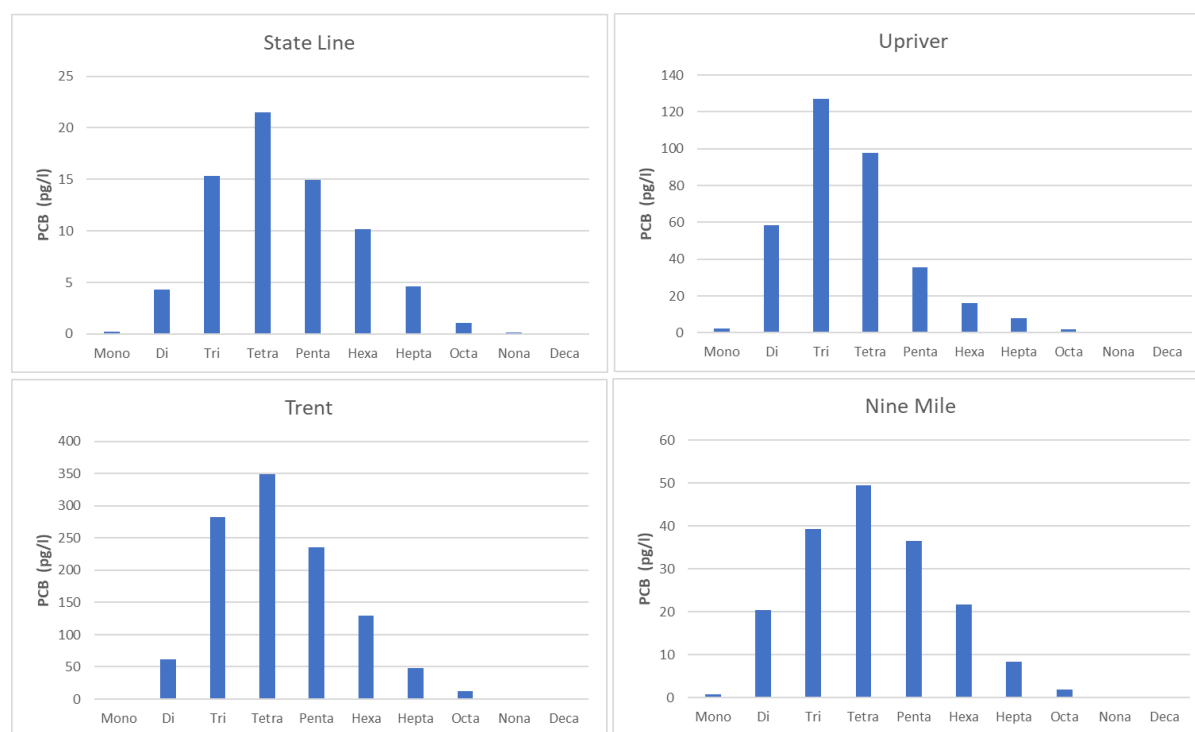
Figure 3. Spokane River Total PCB Concentrations (pg/l) Measured during 2020-2021 SPMD Monitoring

**Table 4. Spokane River PCB Concentrations (pg/l) Measured during 2020-2021 SPMD Monitoring**

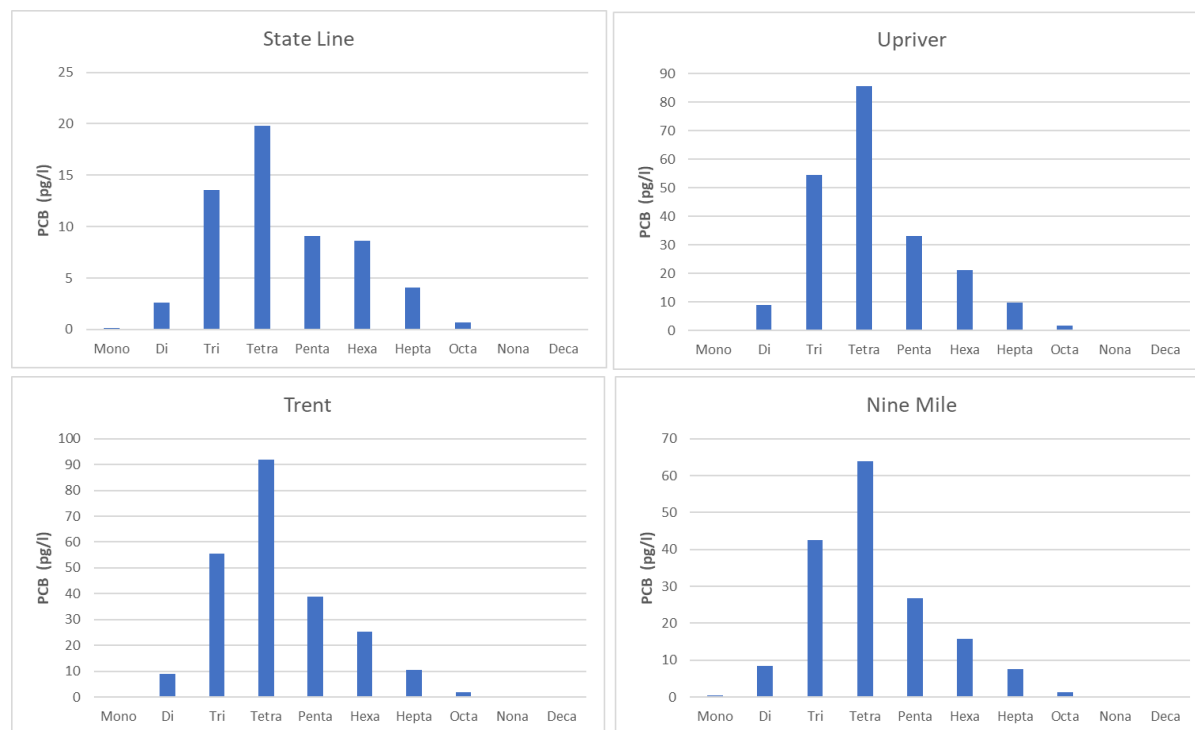
Location	Low Flow		Moderate Flow		High Flow	
	Dissolved	Total	Dissolved	Total	Dissolved	Total
Stateline	72.4	91.7	58.7	69.9	67.3	76.8
Upriver	347.2	367.1	216.2	243.8	149.8	169.1
Trent	1122.9	1272.1	234.0	271.0	201.4	220.2
Nine Mile	179.1	397.8	167.2	205.7	196.3	241.7

### 3.3 Homolog Distributions

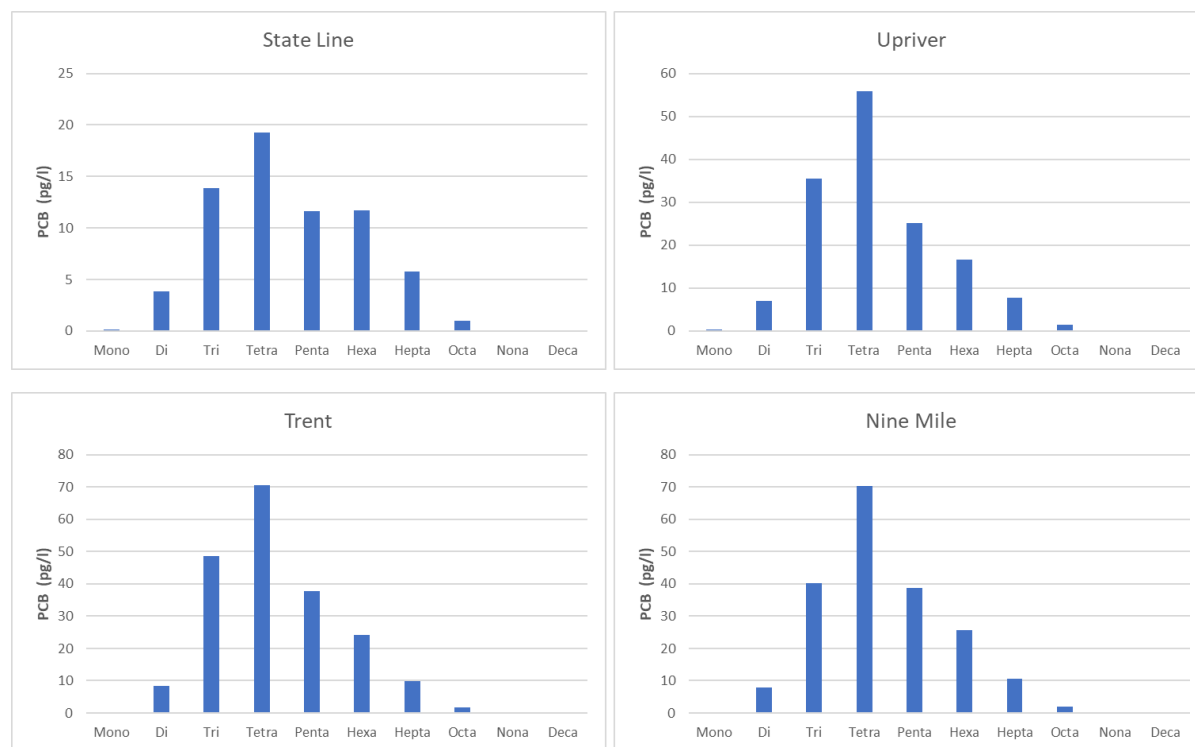
Homolog distributions for each station and sampling period are summarized in Figures 4 through 9, showing average concentration by homolog across all samples within a given reach. These data are provided in tabular format for each individual sample in Appendix A. Figures 4 through 6 show dissolved phase homolog concentrations. The tetra-chlorinated homolog was the most prevalent and tri-chloro homolog was the second most prevalent for all locations and flow regimes except for low flow at Upriver, where the tri-chloro homolog was the most prevalent and the tetra-chlorinated homolog was the most second prevalent.



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



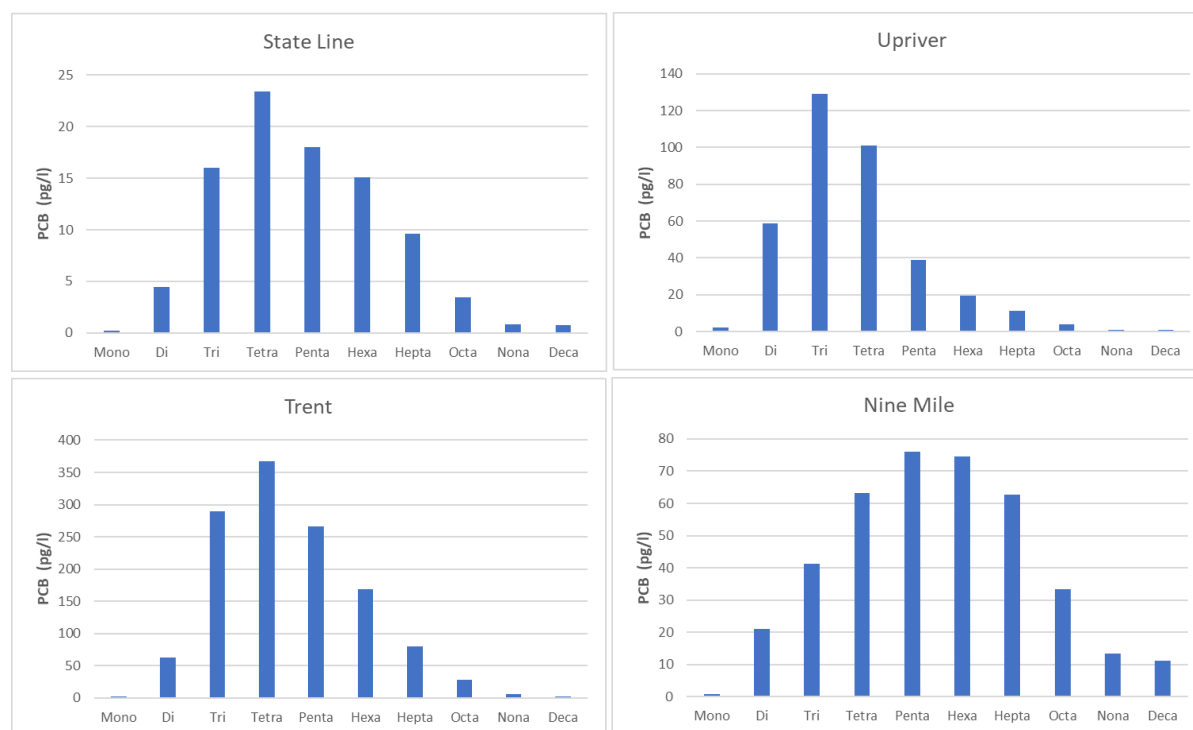
**Figure 5. Blank-Corrected Dissolved Homolog Concentrations during Moderate Flow Deployment.**



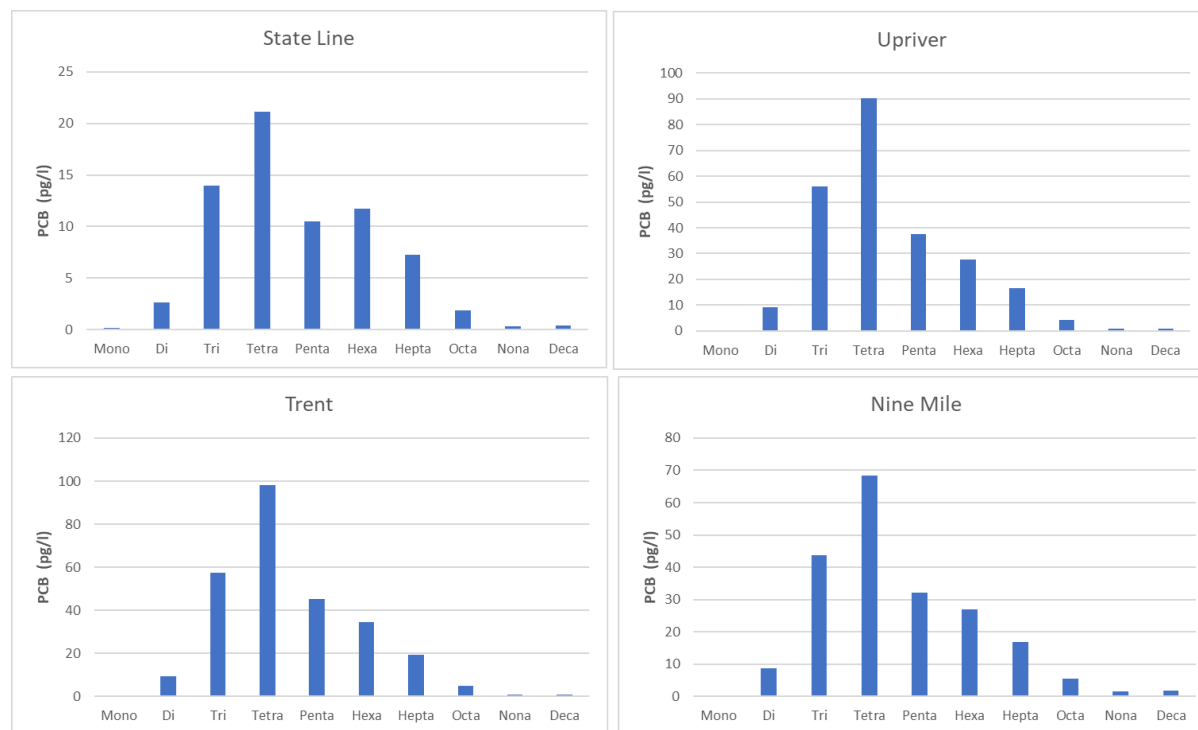
**Figure 6. Blank-Corrected Dissolved Homolog Concentrations during High Flow Deployment.**



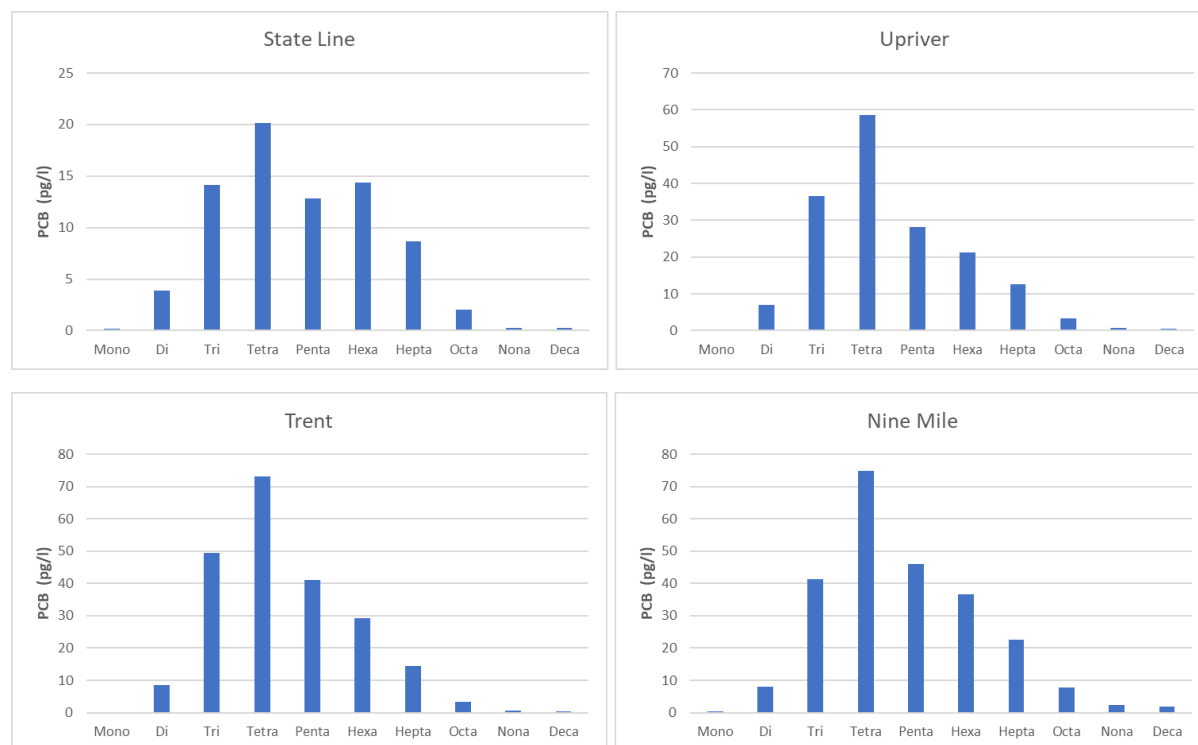
Figures 7 through 9 show the distribution for total homolog concentrations. The distribution among total homologs is similar as to what was observed for dissolved homologs (e.g., tetra-chlorinated homolog was the most prevalent) and shifted slightly towards the higher chlorinated homologs, reflecting the greater affinity of the higher chlorinated homologs to sorb to particulate organic material. The low flow sample at Nine Mile was the one exception to similarity of distribution between patterns for dissolved and total homologs. The total homolog distribution was greatly shifted towards the higher chlorinated homologs, with penta- and hexa-chlorinated homologs being the most prevalent, due to the high concentration of particulate organic carbon observed at Nine Mile during low flow.



**Figure 7. Blank-Corrected Total Homolog Concentrations during Low Flow Deployment.**



**Figure 8. Blank-Corrected Total Homolog Concentrations during Moderate Flow Deployment.**



**Figure 9. Blank-Corrected Total Homolog Concentrations during High Flow Deployment.**

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# 4

## Data Interpretation

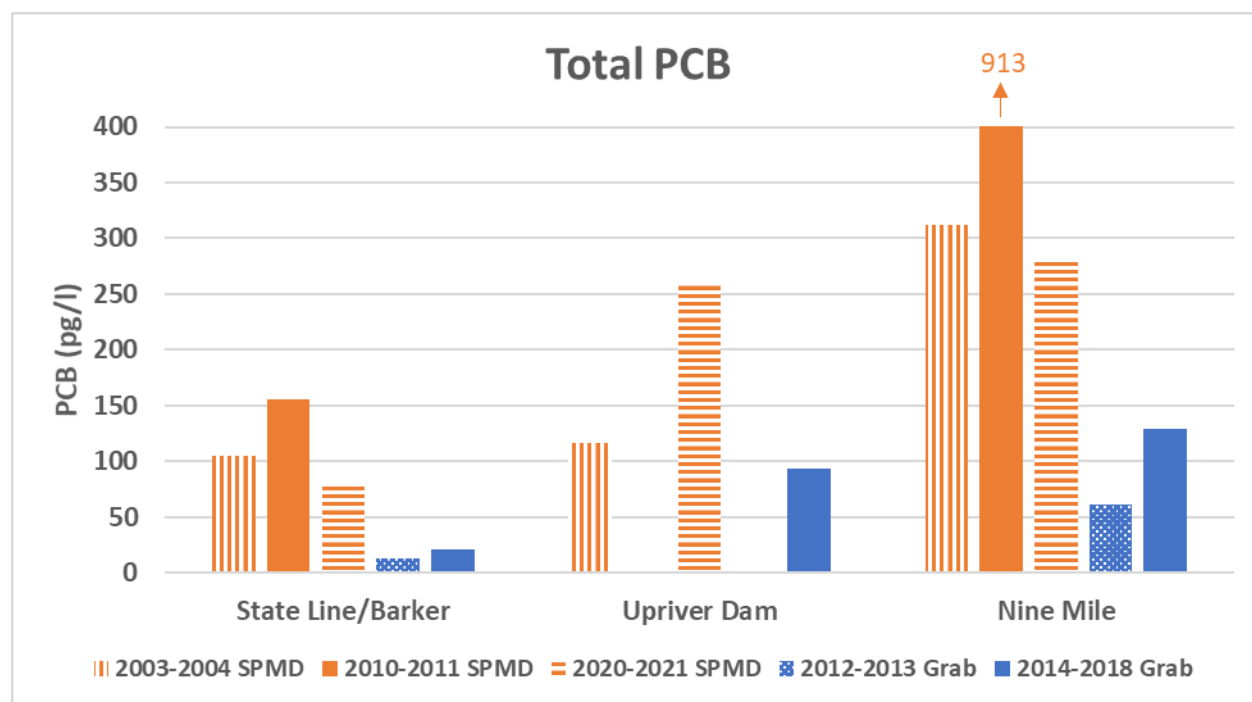
The objective of this sampling is to provide for long term trending assessment of PCB concentrations in the water column that may be used as one measure of the effectiveness of PCB control actions aimed at the reduction of PCBs in the Spokane River. ~~present-day baseline water column concentrations against which future concentrations can be compared to evaluate whether PCB control efforts are resulting in decreased concentrations.~~ This section provides some interpretation of the PCB results provided in Section 3 in term of suitability to support long-term trend assessment. It is divided into sections of:

- Comparison to water column PCB concentrations from prior years
- Conversion of freely dissolved phase to total PCB concentration
- Utility of SPMD data to support long-term trend assessment

### 4.1 Comparison to Water Column PCB Concentrations from Prior Years

This section compares water column PCBs measured by SPMDs during 2020-2021 to prior water column measurements determined by SPMDs and grab sampling at similar sampling locations. The Spokane River Regional Toxics Task Force conducted water column PCB monitoring of the Spokane River in 2014, 2015, 2016, and 2018 (SRRTTF, 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 comparison is summarized in Figure 10, which shows average concentrations at two locations across five sampling programs.





**Figure 10. Total PCB Concentrations Measured by SPMD and Grab Samples across Five Monitoring Programs**

The left-hand side of Figure 10 compares SPMD samples at Barker Rd. and the State Line to grab samples at the same locations. While the Barker Road location is downstream from the State Line, PCB concentrations are not expected to vary significantly between sites. Total PCB concentrations from SPMD monitoring at the State Line during 2003-2004 averaged 105 pg/l, while a single SPMD concentration at the State Line during 2010 was 156 pg/l. PCB concentrations at the State Line during this study averaged 79 pg/l. Both Ecology grab samples in 2012-2013 were 13 pg/l. The average PCB concentration measured at Barker Rd. via SRRTTF grab sampling was 21 pg/l.

The middle of Figure 10 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 measured during this study average 260 pg/l. The average PCB concentration measured just downstream of Upriver Dam via Task Force grab sampling was 94 pg/l.

The right-hand side of Figure 10 compares grab samples to SPMD samples at Nine Mile Dam. Total PCB concentrations at the Nine Mile Dam during this study averaged 282 pg/l while PCB concentrations from SPMD monitoring at Nine Mile Dam during 2003-2004 averaged 312 pg/l. PCB concentrations from SPMD monitoring at Nine Mile Dam during 2010-2011 ranged from non-detect to 1600 pg/l, averaging 913 pg/l. The average PCB concentration measured at Nine Mile Dam via Task Force grab sampling was 129 pg/l, while Ecology grab samples in 2012-2013 at Nine Mile Dam averaged 61 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 7 indicate that PCB concentrations measured by SPMDs were always 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. ~~This incomparability with grab samples further supports that SPMDs should not be used in assessing water quality concentrations for any regulatory purpose under the Clean Water Act.~~

## 4.2 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. This conversion introduces uncertainty into concentration estimates due to two causes: 1) temporal variability in observed POC and TOC concentrations, and 2) uncertainty in dissolved organic partition coefficients.

### 4.2.1 Temporal Variability in Observed POC and DOC Concentrations

The first factor causing uncertainty in the conversion of dissolved phase to total PCB concentration corresponds to the temporal variability in observed POC and DOC concentrations and how this variability affects estimated total PCB concentrations. This issue is illustrated via examination of organic carbon at Nine Mile Dam during low flow conditions. POC and DOC were measured at three points in time over the deployment period, with observed concentrations shown in Table 5. POC concentrations were elevated during the September 8 mid-point sampling, with a concentration more than four times greater than measured during deployment and removal. The average POC concentration over the period of deployment, which is used to convert freely dissolved PCB to total PCB, varies by more than a factor of two (0.39 mg/l vs. 0.14 mg/l) depending upon whether the mid-point sample was considered.

**Table 5. Observed POC and DOC Concentrations at Nine Mile Dam during low flow conditions**

	<b>Deployment 8/26/2020</b>	<b>Mid-Point 9/08/2020</b>	<b>Retrieval 9/22/2020</b>	<b>Average</b>	<b>Average without Mid-Point Sample</b>
POC (mg/l)	0.08	0.89	0.2	0.39	0.14
DOC (mg/l)	1.27	1.29	1.14	1.23	1.21

This variability in POC concentration has a major impact on the estimate of total PCB concentration. The calculated total PCB concentration during low flow at Nine Mile Dam using all three organic carbon samples was 398 pg/l. The estimated PCB total concentration using only the organic carbon measured at deployment and retrieval, is 258 pg/l (Figure 8). The presence of the mid-point sample changes the predicted total PCB concentration by approximately 140 pg/l.



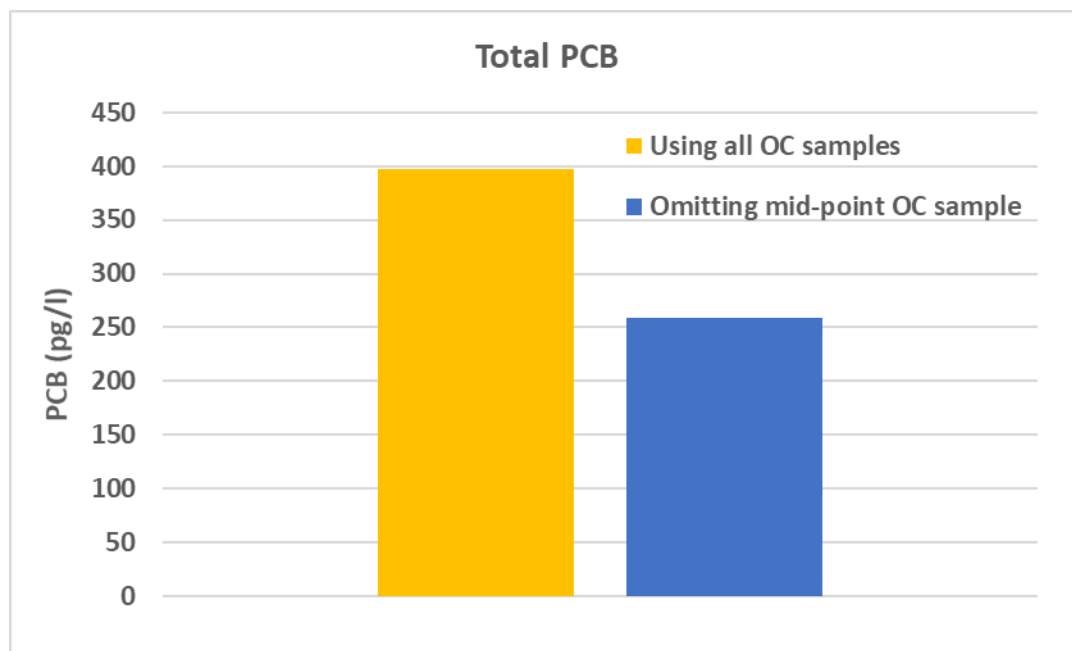


Figure 11. Sensitivity of Estimated Total PCB Concentration at Nine Mile Dam during Low Flow to Inclusion of Mid-Point Organic Carbon Sample

#### 4.2.2 Uncertainty In Dissolved Organic Partition Coefficients

The second issue causing uncertainty in the conversion of dissolved phase to total PCB concentration corresponds to uncertainty in dissolved organic partition coefficients. The conversion used in this study assumes that DOC is one tenth as effective at sorbing PCBs compared with POC, based upon the conclusion of Zarnadze and Rodenburg (2008). While the scientific literature supports the assumption that DOC is less effective at sorbing PCBs, the effectiveness of DOC on a site-specific basis is poorly understood. Burkhard (2000) found that the 95% confidence limit on the sorbing efficiency of DOC varied by a factor of 10 or more, due to the variability in structure and composition of dissolved organic carbon. The majority of organic carbon in the Spokane River is in dissolved form, such that uncertainty in the ability of DOC to sorb PCBs directly correlated into uncertainty in estimates of total PCB concentration. Using representative values for  $K_{OC,p}$  ( $10^6$  l/kg), POC (0.1 mg/l) and DOC (1.6 mg/l) in Equation 1, a three-fold uncertainty in the sorbing efficiency of DOC results in a range of calculated fraction dissolved of 63% to 87%. This translates to a large uncertainty in estimated total PCB concentration (115% vs 158% of the dissolved concentration) when applied in Equation 2.

#### 4.3 Considerations for Long-Term Trend Assessment

The objective of this sampling is to provide [for long term trending 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.](#) ~~present-day baseline concentration against which future concentrations can be compared to evaluate whether PCB control efforts are resulting in decreased water column concentrations.~~ This section provides some considerations regarding future SPMD monitoring to support trend assessment, consisting of:

- Use freely dissolved concentrations to conduct trend assessment
- Recognize that Trent Avenue sample reflects localized sources
- Refine performance reference compounds
- Continue use of grab sampling

#### 4.3.1 Use Freely Dissolved Concentrations to Conduct Trend Assessment

The sensitivity analyses conducted above in Section 4.2 demonstrated that a large amount of uncertainty is introduced when converting dissolved phase PCB concentrations into total PCB concentrations. This uncertainty could be eliminated from the trend assessment by conducting the assessment using the measured freely dissolved concentrations and not converting them to total PCB concentrations.

#### 4.3.2 Recognize that Trent Avenue Sample Reflects Localized Sources

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 ~~the~~ 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 monitoring location will be sufficient for assessing trends in overall loads near the geographic mid-point of the study area.

#### 4.3.3 Refine Performance Reference Compounds

Many of the SPMD samples had recovery of performance reference compounds outside of the desired range, resulting in concentrations being reported at estimated values. Other performance reference compounds exist that may improve the likelihood of obtaining acceptable recovery percentages. The use of alternate performance reference compounds, specifically lower weight PCBs, should be investigated for future iterations of the trend monitoring.

#### 4.3.4 Continue Use of Grab Sampling

SPMDs performed as expected in terms of ~~being less affected by blank contamination than grabs due to having a smaller proportion of the sample analytical result in the blanks providing superior performance over grab samples in reducing the influence of blank contamination.~~ That said, SPMDs pose other challenges (e.g., uncertain conversion to total PCB, recovery of performance reference compounds) relative to grab samples. The benefit of SPMDs ~~will~~may increase in the future when PCB concentrations decrease to the level where blank contamination from grab sampling becomes are a larger percentage of the ambient concentration. In the immediate term, however, consideration should be given to continued use of grab sampling to support near-term ~~implementation of the~~ trend assessment.



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## Appendix A: Synoptic Survey Results - PCBs by Homolog

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Table A-1: Blank-Corrected Analytical Results for Dissolved and Total PCB: State Line						
	Low Flow		Moderate Flow		High Flow	
	Diss.	Total	Diss.	Total	Diss.	Total
Total PCBs (pg/l)	72.44	91.74	58.66	69.87	67.27	76.75
Total Monochloro Biphenyls (pg/l)	0.21	0.21	0.14	0.14	0.17	0.17
Total Dichloro Biphenyls (pg/l)	4.34	4.45	2.58	2.63	3.82	3.86
Total Trichloro Biphenyls (pg/l)	15.33	16.00	13.53	14.00	13.84	14.14
Total Tetrachloro Biphenyls (pg/l)	21.51	23.40	19.81	21.15	19.28	20.13
Total Pentachloro Biphenyls (pg/l)	14.94	18.02	9.08	10.48	11.62	12.80
Total Hexachloro Biphenyls (pg/l)	10.18	15.08	8.61	11.70	11.68	14.40
Total Heptachloro Biphenyls (pg/l)	4.63	9.58	4.09	7.25	5.74	8.64
Total Octachloro Biphenyls (pg/l)	1.05	3.41	0.68	1.83	0.96	2.04
Total Nonachloro Biphenyls (pg/l)	0.14	0.81	0.07	0.30	0.09	0.30
Total Decachloro Biphenyls (pg/l)	0.09	0.78	0.06	0.39	0.06	0.26

Table A-2: Blank-Corrected Analytical Results for Dissolved and Total PCB (pg/l): Upriver						
	Low Flow		Moderate Flow		High Flow	
	Diss.	Total	Diss.	Total	Diss.	Total
Total PCBs (pg/l)	347.19	367.13	216.20	243.75	149.83	169.10
Total Monochloro Biphenyls (pg/l)	2.18	2.19	0.36	0.37	0.27	0.28
Total Dichloro Biphenyls (pg/l)	58.38	58.89	9.10	9.24	6.95	7.05
Total Trichloro Biphenyls (pg/l)	127.08	129.26	54.46	55.97	35.55	36.46
Total Tetrachloro Biphenyls (pg/l)	97.54	101.25	85.66	90.39	55.79	58.65
Total Pentachloro Biphenyls (pg/l)	35.53	38.80	33.22	37.54	25.15	28.22
Total Hexachloro Biphenyls (pg/l)	16.23	19.68	21.23	27.60	16.63	21.30
Total Heptachloro Biphenyls (pg/l)	7.73	11.30	9.98	16.48	7.82	12.67
Total Octachloro Biphenyls (pg/l)	2.00	3.99	1.81	4.34	1.39	3.27
Total Nonachloro Biphenyls (pg/l)	0.33	1.02	0.24	0.94	0.17	0.63
Total Decachloro Biphenyls (pg/l)	0.17	0.75	0.15	0.87	0.10	0.56



Table A-3: Blank-Corrected Analytical Results for Dissolved and Total PCB (pg/l): Trent						
	Low Flow		Moderate Flow		High Flow	
	Diss.	Total	Diss.	Total	Diss.	Total
Total PCBs (pg/l)	1122.86	1272.08	234.04	271.03	201.44	220.18
Total Monochloro Biphenyls (pg/l)	1.82	1.83	0.39	0.40	0.25	0.25
Total Dichloro Biphenyls (pg/l)	61.34	62.16	9.08	9.26	8.32	8.41
Total Trichloro Biphenyls (pg/l)	282.67	289.97	55.60	57.51	48.56	49.47
Total Tetrachloro Biphenyls (pg/l)	348.76	367.19	91.90	98.10	70.48	73.12
Total Pentachloro Biphenyls (pg/l)	235.92	265.60	38.90	45.12	37.74	41.12
Total Hexachloro Biphenyls (pg/l)	130.03	168.47	25.42	34.69	24.26	29.23
Total Heptachloro Biphenyls (pg/l)	48.45	79.96	10.62	19.21	9.91	14.41
Total Octachloro Biphenyls (pg/l)	11.90	28.66	1.78	4.89	1.64	3.27
Total Nonachloro Biphenyls (pg/l)	1.59	6.22	0.22	1.03	0.19	0.58
Total Decachloro Biphenyls (pg/l)	0.37	2.02	0.12	0.82	0.07	0.31

Table A-4: 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)	179.09	397.81	167.22	205.66	196.28	241.69
Total Monochloro Biphenyls (pg/l)	0.89	0.90	0.40	0.41	0.28	0.28
Total Dichloro Biphenyls (pg/l)	20.35	20.93	8.48	8.62	7.95	8.07
Total Trichloro Biphenyls (pg/l)	39.33	41.37	42.51	43.69	40.24	41.29
Total Tetrachloro Biphenyls (pg/l)	49.48	63.32	63.96	68.37	70.40	74.88
Total Pentachloro Biphenyls (pg/l)	36.45	76.09	26.81	32.12	38.74	45.93
Total Hexachloro Biphenyls (pg/l)	21.75	74.52	15.83	26.85	25.66	36.63
Total Heptachloro Biphenyls (pg/l)	8.47	62.71	7.62	16.90	10.60	22.59
Total Octachloro Biphenyls (pg/l)	1.85	33.40	1.29	5.44	1.96	7.86
Total Nonachloro Biphenyls (pg/l)	0.32	13.45	0.17	1.48	0.28	2.28
Total Decachloro Biphenyls (pg/l)	0.19	11.11	0.14	1.78	0.16	1.89



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## Appendix B: Quality Assurance Project Plan

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## Appendix C: Laboratory Results

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