

Spokane River Regional Toxics Task Force Evaluation of PCBs in Spokane River Artificial Bottom Fill Material

Prepared for:
Spokane River Regional Toxics
Task Force

~~June-July 1620~~, 2021
FINAL APPROVAL DRAFT

LimnoTech 
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TABLE OF CONTENTS

Executive Summary	1
1 Introduction	3
2 Sampling Activities	5
2.1 Sampling Locations	5
2.2 Monitoring Date.....	6
2.3 Field Sampling Activities.....	6
2.4 Quality Assurance	6
2.4.1 Data Quality Assessment.....	6
2.4.2 Blank Correction	7 ⁸
3 Analytical Results	9
3.1 Total PCBs	9
3.2 Homolog Distributions.....	10
4 Data Interpretation	15 ¹³
4.1 Recent Studies Containing PCB Concentration in Naturally Occurring Bottom Sediments	15 ¹³
4.2 Comparison to Fish Tissue ^{Sediment} PCB Concentrations from Prior Years.....	17 ¹⁵
5 References	21 ¹⁷
Appendix A: Synoptic Survey Results - PCBs by Homolog	A-1
Appendix B: Quality Assurance Project Plan	B-1
Appendix C: Laboratory Results	C-1



LIST OF FIGURES

Figure 1. Map of Sampling Area Locations.....	56
Figure 2. Spokane River Artificial Fill Total PCB Concentrations (pg/g).....	109
Figure 3. Average Blank-Corrected Homolog Concentrations for All Brick Samples.....	1140
Figure 4. Average Blank-Corrected Homolog Concentrations for All Concrete Samples.....	1240
Figure 5. Blank-Corrected Homolog Concentrations for the Asphalt Sample.....	1341
Figure 6. Ecology’s Urban Waters Program 2013 Sediment Sampling Locations (from Era-Miller, 2015).....	1644
Figure 7. Ecology’s Environmental Assessment Program 2018 Sediment Sampling Locations (from Era-Miller, 2020).....	1644
Figure 8. Spokane River Bottom Sediment PCB Concentrations from Different Sources and Dates.....	1845



LIST OF TABLES

Table 1. Sampling Area Descriptions and Locations.....	5
Table 2. Spokane River Artificial Fill Total PCB Concentrations (pg/g)	9



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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. To address these impairments, the Washington State 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.

Sampling conducted by the Ecology's Environmental Assessment Program in 2018 and 2019 showed elevated PCB concentrations in biofilm in the section of the Spokane River downstream of the Mission Avenue bridge (termed the Mission Reach) in Spokane. Initial forensic analyses conducted for the Task Force could not positively identify the source of PCBs causing these elevated biofilm concentrations. These forensic analyses did identify several potential categories of sources, with contaminated artificial bottom fill material (i.e., bricks and concrete that have been observed on the river bottom) being one of the candidate sources of PCBs. This project consisted of collecting samples and analyzing the PCB content of the artificial fill material observed in the Spokane River in the area of high biofilm PCB concentrations and comparing them to PCB concentrations previously measured in naturally occurring Spokane River bottom sediments. The PCB concentrations observed in the artificial fill samples were generally lower than PCB concentrations found in naturally occurring Spokane River bottom sediments. These results indicate that PCBs introduced to the river via artificial fill are likely not the primary causative source of elevated biofilm PCB concentrations in the Mission Reach.



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Introduction

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. 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. Ecology's Environmental Assessment Program conducted spatial surveys of the Spokane River using biofilms in August of 2018 and 2019 to assess possible suspected and unknown sources of PCBs to the river (Wong and Era-Miller 2019). The goals of the sampling were to collect and analyze PCB concentrations in biofilm, sediment, and macroinvertebrates in the river, and to assess the presence of unidentified sources of PCBs to the river. Both sampling events identified one segment of the river where biofilm PCB concentrations were particularly high, located between the Mission Avenue Bridge and the Spokane Falls Boulevard Bridge. This segment is commonly referred to as the Mission Reach.

Initial forensic analyses conducted by the Task Force could not positively identify the source of PCBs causing these elevated biofilm concentrations (LimnoTech, 2020). These forensic analyses did identify several potential categories of sources, with contaminated artificial bottom fill material (i.e., bricks and concrete that have been observed on the river bottom) being one of the candidate sources of PCBs. This project consisted of collecting samples and analyzing the PCB content of the artificial fill material observed in the Spokane River in the area of high biofilm PCB concentrations and comparing them to PCB concentrations previously measured in naturally occurring Spokane River bottom sediments.

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 a one-day sampling event at four Spokane River locations. Sampling activities are described below, divided into sections corresponding to:

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

2.1 Sampling Locations

Sampling locations consisted of four different areas within the Mission Reach, described in Table 1 and shown in Figure 1.

Table 1. Sampling Area Descriptions and Locations

Area Number	Location Descriptor	Latitude	Longitude
1	Behind Northern Lights Brewing	47.66286° N	-117.39339° W
2	Right bank halfway between Northern Lights Brewing and foot bridge	47.66378° N	-117.39315° W
3	Left bank near foot bridge	47.66448° N	-117.39138° W
4	Left bank across from Northern Lights Brewing	47.66344° N	-117.39193° W



Figure 1. Map of Sampling Area Locations



2.2 Monitoring Date

All sampling was conducted on March 17, 2021.

2.3 Field Sampling Activities

The field sampling activities as planned and implemented are detailed in the project QAPP (LimnoTech, 2021). This section summarizes those activities. Five samples (plus a replicate) were collected of brick substrate, with at least one brick substrate sample collected from each of the areas described in Table 1. Four samples were collected of concrete substrate, with one concrete substrate sample collected from each of the four areas. In addition, a single sample of asphalt substrate was collected from Area 3.

Sampling was performed by visually locating artificial fill on the stream bottom and manually removing the substrate. Substrate samples were taken to an onshore processing station. The processing station consisted of a table lined with aluminum foil. Periphyton growth, when present on the removed substrate, was wiped/washed off with a gloved hand in the river prior to processing. Samples were processed from shore following the SOP provided by EPA (2011). This consisted of drilling holes into the substrate to a depth of ½ inch and collecting the resulting powder. Multiple holes were drilled into the same piece of substrate as necessary to generate a minimum of 10 grams of sample material. The collected material for each sample was transferred to a certified clean glass jar w/Teflon lid and placed into an ice-filled cooler.

2.4 Quality Assurance

Field samples were shipped to AXYS Analytical Laboratories, Ltd. in Sidney, British Columbia for analysis of PCB concentrations (Method 1668), and percent moisture.

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. 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.

Other 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

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

- Two congeners exceeded the ion abundance limit check for the brick sample from Area 1.
- Seven congeners exceeded the ion abundance limit check for the concrete sample from Area 1.
- Three congeners exceeded the ion abundance limit check for the first brick sample from Area 2.
- Ten congeners exceeded the ion abundance limit check for the second brick sample from Area 2.
- Four congeners exceeded the ion abundance limit check for the concrete sample from Area 2.
- Four congeners exceeded the ion abundance limit check for the asphalt sample from Area 3.
- Six congeners exceeded the ion abundance limit check for the brick sample from Area 3.
- One congener exceeded the ion abundance limit check for the concrete sample from Area 3.
- Three congeners were outside of the control limits for ion abundance limit check for the brick sample for Area 4.
- Twelve congeners exceeded the ion abundance limit check for the concrete sample from Area 4.
- ~~One Eighteen~~ congener values ~~was were~~ flagged for failing the duplicate sample relative percent difference criterion for the brick duplicate sample.
- ~~ThirtyNinety-three-eight~~ congener values were flagged for failing the duplicate sample relative percent difference criterion for the concrete duplicate sample.
- Five congeners exceeded the ion abundance limit check for the replicate brick sample.
- Fourteen congeners exceeded the ion abundance limit check for the laboratory blank.
- ~~SixFive~~ congeners were outside of the control limits for sample and method blank surrogate %R evaluation.

There are no changes to PCB result values as a result of this assessment, although data qualifiers were added to select samples subject to high relative percent difference, ~~ion abundance limit check~~, and sample and method blank surrogate %R evaluation as described above.

2.4.2 Blank Correction

Total PCB concentrations were corrected for method blank contamination following the procedures defined in the QAPP. Specifically, individual congeners found in the sample at a concentration less than three times the associated blank concentration were flagged and excluded from calculation of homolog and total PCB concentration. All total PCB and homolog results reported below are blank



corrected using the above method. 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.



3 Analytical Results

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

3.1 Total PCBs

Total PCB concentrations for each area and substrate type are provided in Table 2 and plotted in bar chart format in Figure 2. In addition, the single sample of asphalt substrate had an observed total PCB concentration of ~~13,700~~ pgug/kg.

Table 2. Spokane River Artificial Fill Total PCB Concentrations (pgug/kg)

Area	Substrate Type	
	Brick	Concrete
1	<u>0.438</u>	<u>0.465</u>
	<u>0.208</u>	
2	<u>0.553</u>	<u>0.204</u>
3	<u>2.283</u>	<u>0.087</u>
4	<u>0.541</u>	<u>1.084</u>



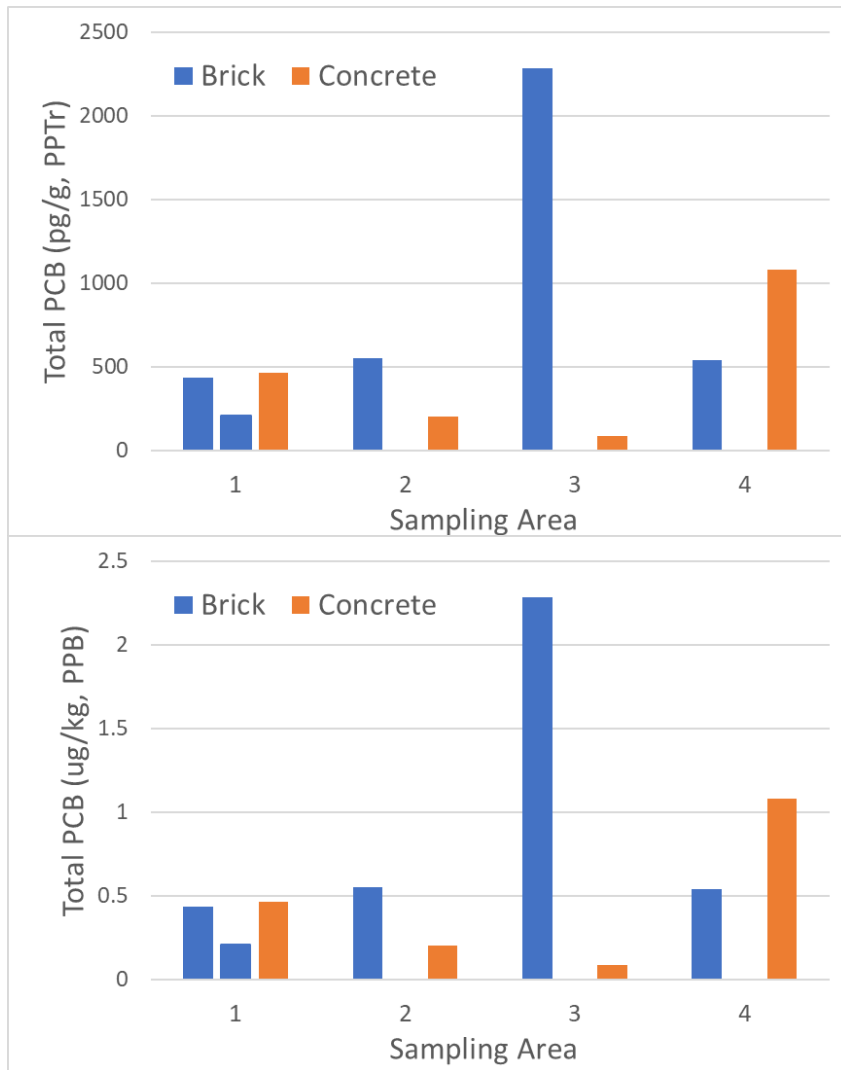


Figure 2. Spokane River Artificial Fill Total PCB Concentrations (pgug/kg)

3.2 Homolog Distributions

Homolog distributions are provided in Figures 3 through 5, showing average concentration by homolog across all samples for each substrate type. These data are provided in tabular format for each individual sample in Appendix A. Concentrations in brick and asphalt are dominated by the



hexa-chloro homolog, while concentrations in concrete are dominated by the penta-chloro homolog.

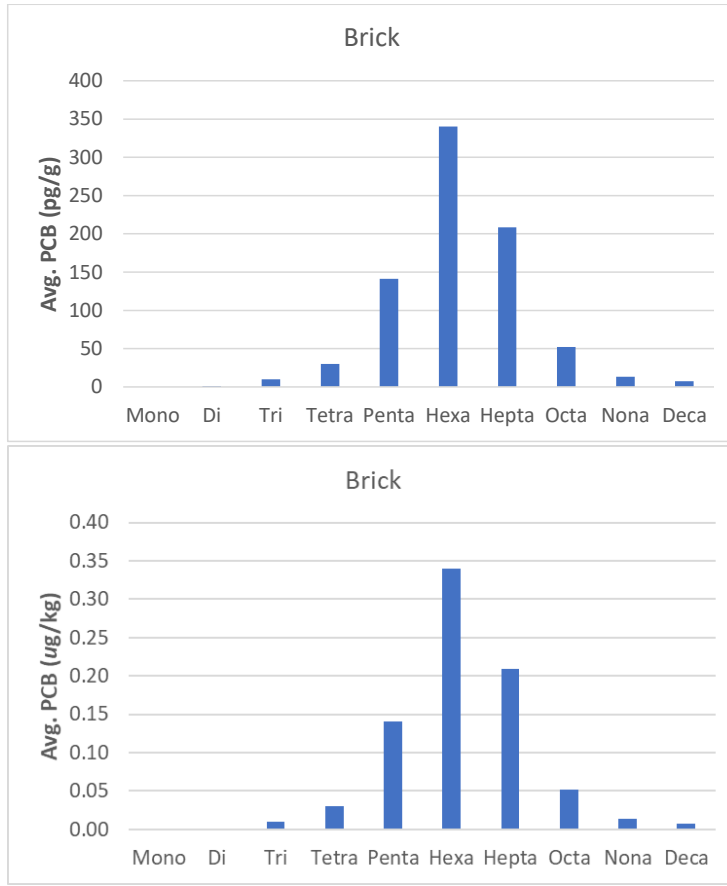


Figure 3. Average Blank-Corrected Homolog Concentrations for All Brick Samples.



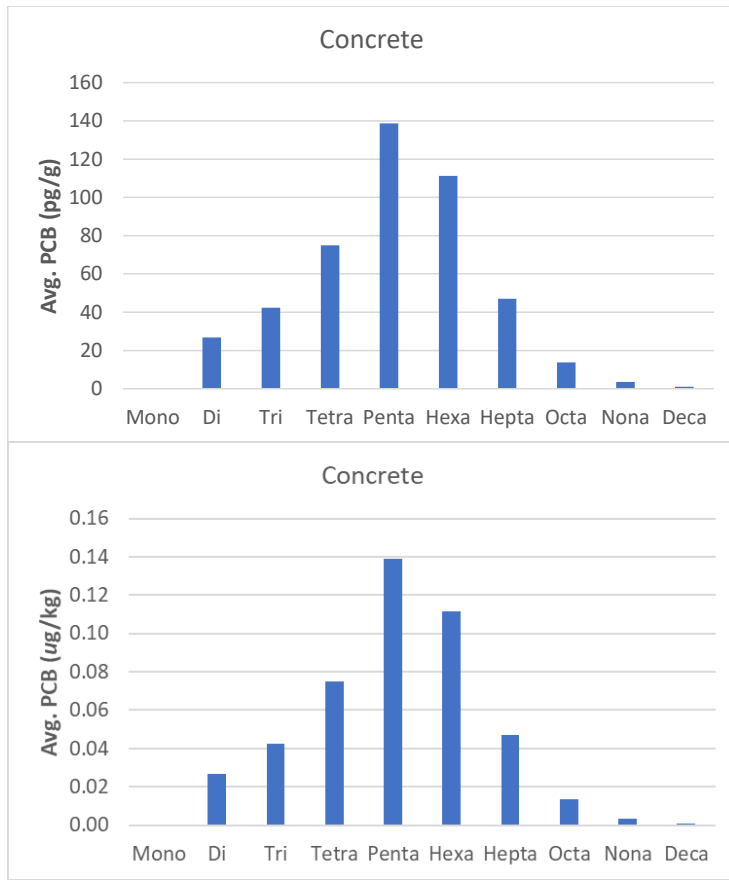


Figure 4. Average Blank-Corrected Homolog Concentrations for All Concrete Samples.



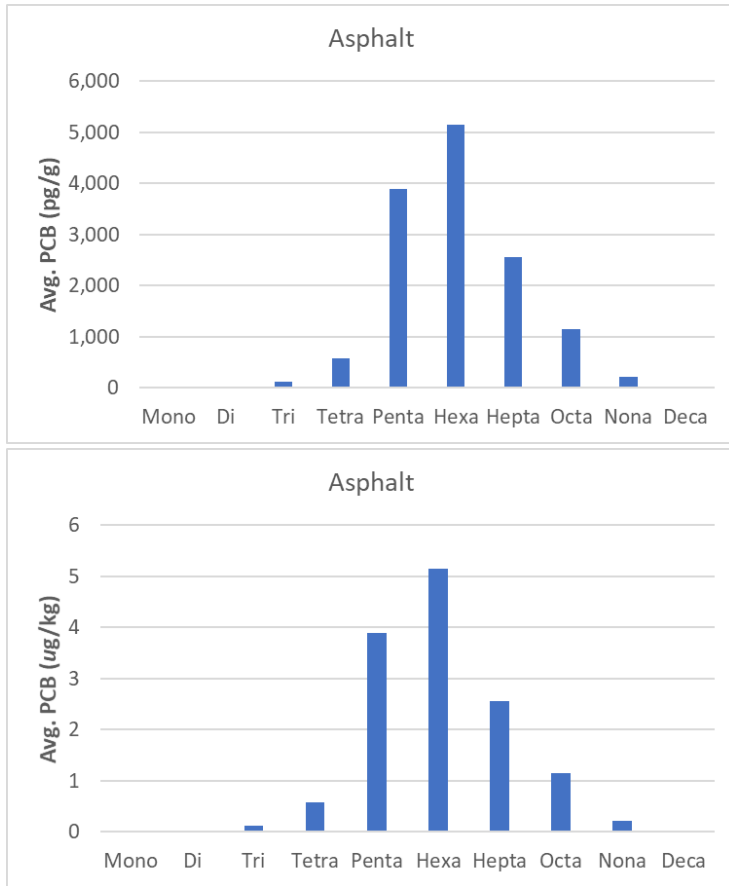


Figure 5. Blank-Corrected Homolog Concentrations for the Asphalt Sample.



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Data Interpretation

The objective of this sampling is to compare PCB concentrations from artificial fill material in Mission Reach to PCB concentrations from naturally occurring bottom sediments in the Spokane River. If PCB concentrations in artificial fill are significantly greater than in naturally occurring bottom sediments, that would serve as an indication that PCBs introduced to the river from artificial fill are a causative source of the Mission Reach hot spot. This section provides an interpretation of the PCB results provided in Section 3 in term of comparison to previously measured bottom sediment concentrations.

4.1 Recent Studies Containing PCB Concentration in Naturally Occurring Bottom Sediments

The Washington State Department of Ecology measured sediment PCB concentrations within the past ten years as part of the following studies:

- Samples collected by Ecology's Urban Waters Program in 2013 (Era-Miller, 2015).
- Samples collected by Ecology's Environmental Assessment Program as part of the 2018 biofilm study (Era-Miller, 2020).

Ecology's Urban Waters Program sampled PCB content in Spokane River bottom sediments at eight locations in August 2013 (Figure 6). Seven of the stations were located upstream of the peak observed biofilm PCB concentrations, with the eighth location (named PostTerm2) located within the Mission Reach hot spot area.

Ecology's Environmental Assessment Program conducted a screening study measuring PCBs in biofilm, sediment, and invertebrates in the Spokane River in August 2018 that collected Spokane River sediment samples at Plantes Ferry (PF) and Gonzaga (GZ) plus a third sediment location from Latah (Hangman, HM) Creek (Figure 7).





Figure 6. Ecology's Urban Waters Program 2013 Sediment Sampling Locations (from Era-Miller, 2015)

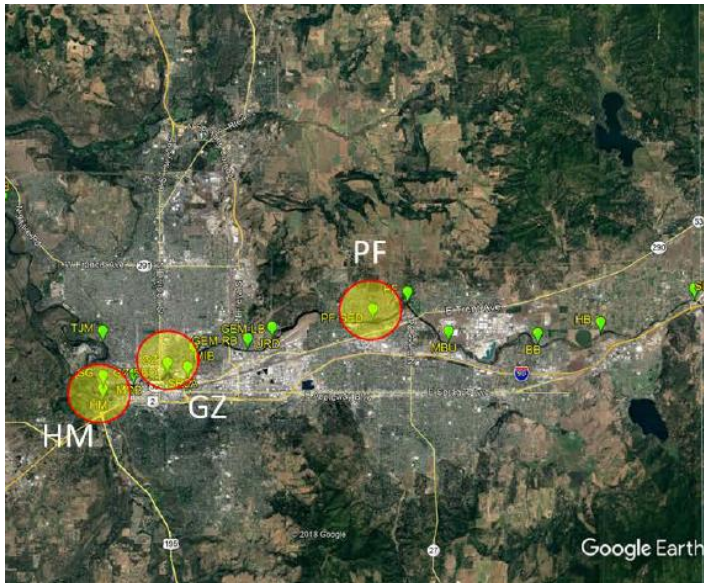


Figure 7. Ecology's Environmental Assessment Program 2018 Sediment Sampling Locations (from Era-Miller, 2020)



4.2 Comparison to ~~Fish Tissue~~Sediment PCB Concentrations from Prior Years

Figure 8 shows a comparison of PCB concentrations in Mission Reach artificial bottom fill samples compared to those observed previously in naturally occurring Spokane River bottom sediments. PCB concentrations in both the brick and concrete artificial fill samples are lower than concentrations observed in any of the naturally occurring sediments. The asphalt sample collected in 2021 has PCB concentrations greater than the brick and concrete samples, but still at a level equivalent to the median concentration of the naturally occurring bottom sediments.



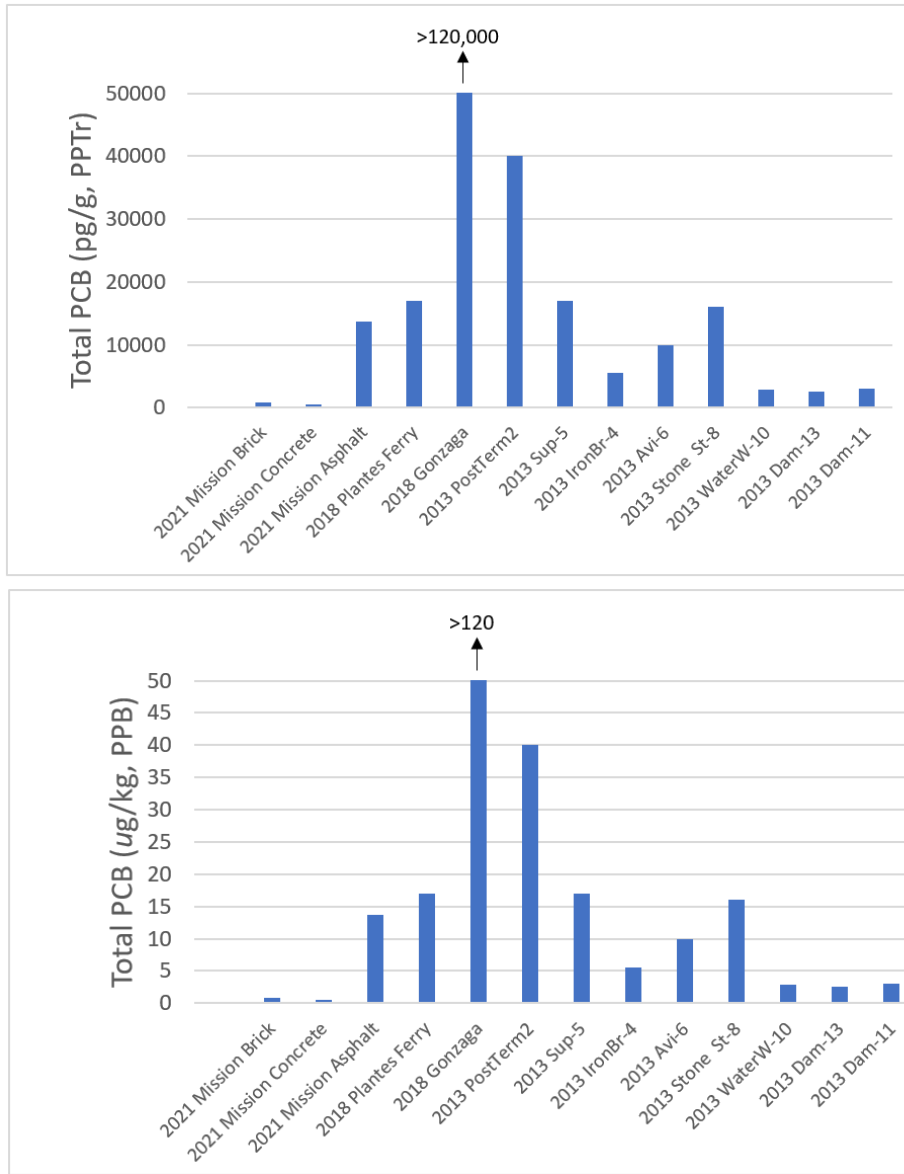


Figure 8. Spokane River Bottom Sediment PCB Concentrations from Different Sources and Dates

The fact that PCB concentrations in the artificial bottom fill samples are not noticeably greater than (and in most cases are noticeably less than) PCB concentrations in naturally occurring bottom



sediments indicate that PCBs introduced to the river via artificial fill are likely not the primary causative source of elevated biofilm PCB concentrations in the Mission Reach. The possibility still exists that a small percentage of the total amount of artificial fill present in the Mission Reach is highly contaminated, and that the number of samples collected during this monitoring event were not sufficient to detect infrequently occurring contamination. Nonetheless, the data collected during this study provide no evidence that artificial fill is the source of the Mission Reach contamination.



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5 References

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Appendix A: Synoptic Survey Results - PCBs by Homolog



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Table A-1: Blank-Corrected Homolog Results for Brick Samples					
	Area 1	Area 1, Sample 2	Area 2	Area 3	Area 4
Total PCBs (pg/gug/kg)	0.438	0.208	0.553	2.283	0.541
Total Monochloro Biphenyls (pg/gug/kg)	0.0000-0	0.0000-0	0.0000-0	0.0000-0	0.000
Total Dichloro Biphenyls (pg/gug/kg)	0.0032-6	0.0000-0	0.0011-0	0.0011-0	0.002
Total Trichloro Biphenyls (pg/gug/kg)	0.02322-7	0.0010-6	0.0077-2	0.0066-4	0.014
Total Tetrachloro Biphenyls (pg/gug/kg)	0.04545-2	0.0065-5	0.02727-0	0.04241-9	0.030
Total Pentachloro Biphenyls (pg/gug/kg)	0.07676-3	0.02828-3	0.10410-4	0.41241-1	0.085
Total Hexachloro Biphenyls (pg/gug/kg)	0.145145-1	0.08181-3	0.20620-6	1.0941-9	0.174
Total Heptachloro Biphenyls (pg/gug/kg)	0.108107-8	0.06766-9	0.14314-2	0.56256-2	0.163
Total Octachloro Biphenyls (pg/gug/kg)	0.03131-3	0.01919-3	0.04948-7	0.10510-4	0.057
Total Nonachloro Biphenyls (pg/gug/kg)	0.0065-6	0.0044-2	0.01211-6	0.03232-5	0.013
Total Decachloro Biphenyls (pg/gug/kg)	0.0021-9	0.0022-0	0.0043-8	0.02827-5	0.002

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Table A-2: Blank-Corrected Homolog Results for Concrete Samples				
	Area 1	Area 2	Area 3	Area 4
Total PCBs (pg/gug/kg)	0.465	0.204	0.087	1.084
Total Monochloro Biphenyls (pg/gug/kg)	0.0000-0	0.0000-0	0.0000-0	0.0021-7
Total Dichloro Biphenyls (pg/gug/kg)	0.08383-4	0.0055-0	0.0000-4	0.01818-3
Total Trichloro Biphenyls (pg/gug/kg)	0.103102-9	0.0055-4	0.0044-1	0.05756-9
Total Tetrachloro Biphenyls (pg/gug/kg)	0.128127-9	0.02423-7	0.01111-1	0.13713-7
Total Pentachloro Biphenyls (pg/gug/kg)	0.07776-7	0.06363-3	0.02423-9	0.39139-1
Total Hexachloro Biphenyls (pg/gug/kg)	0.04949-1	0.06362-8	0.02323-4	0.31030-8
Total Heptachloro Biphenyls (pg/gug/kg)	0.01919-5	0.03030-3	0.01313-2	0.12512-5

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Table A-2: Blank-Corrected Homolog Results for Concrete Samples				
	Area 1	Area 2	Area 3	Area 4
Total Octachloro Biphenyls (pg/pgug/kg)	0.0044 5	0.0109 6	0.0077	0.0343 4
Total Nonachloro Biphenyls (pg/pgug/kg)	0.0010 6	0.0033 2	0.0033	0.0077
Total Decachloro Biphenyls (pg/pgug/kg)	0.0000 0	0.0014 0	0.0014	0.0022

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Table A-3: Blank-Corrected Homolog Results for Asphalt Sample	
	Area 3
Total PCBs (pg/pgug/kg)	76.14 13.74
Total Monochloro Biphenyls (pg/pgug/kg)	0.0030 00
Total Dichloro Biphenyls (pg/pgug/kg)	0.0290 17
Total Trichloro Biphenyls (pg/pgug/kg)	0.1322 87
Total Tetrachloro Biphenyls (pg/pgug/kg)	0.5824 1.99
Total Pentachloro Biphenyls (pg/pgug/kg)	3.8922 4.72
Total Hexachloro Biphenyls (pg/pgug/kg)	5.1532 5.58
Total Heptachloro Biphenyls (pg/pgug/kg)	2.5598 6.64
Total Octachloro Biphenyls (pg/pgug/kg)	1.1574 80
Total Nonachloro Biphenyls (pg/pgug/kg)	0.2150 33
Total Decachloro Biphenyls (pg/pgug/kg)	0.0200 0.04

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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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