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Spokane River PCBs in Biofilm, Sediment, and Invertebrates, 2018 and 2019

Screening Study Results

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Cover photo: Spokane River facing upstream towards the Monroe Street bridge.
Photo taken by Siana Wong.

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Screening Study Results

by

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Abstract

In August 2018, the Washington State Department of Ecology (Ecology) measured PCBs in biofilm, sediment, and caddisflies in the Spokane River. In August 2019, Ecology sampled additional biofilm. A combination of comparing total PCB concentrations, as well as homologs and congener patterns, across monitoring locations allowed Ecology researchers to identify new source areas of PCBs and confirm suspected PCB source areas to the river. The highest levels of PCBs in biofilm were found in the Mission Reach, a 2.5-kilometer section of the Spokane River between East Mission Avenue Bridge and Gonzaga University. Homolog and congener patterns there suggest multiple sources of Aroclors in the Mission Reach, with Aroclors 1254 and 1260 dominating.

Five other source locations were much lower in PCBs compared to the Mission Reach but still elevated relative to background reference locations. From upstream moving downstream, these source areas are (1) Mirabeau Park, (2) Plantes Ferry, (3) near the General Electric clean-up site, (4) below Mission Avenue Bridge and (5) Hangman (Latah) Creek. Two other potential source locations were identified, but the PCB composition and concentrations were either not as clear or could not be confirmed with additional biofilm sampling. These locations are (1) below Upriver Dam and (2) at the Spokane flow gaging station upstream of Sandifer Bridge.

Sediments were collected at (1) Plantes Ferry, (2) near Gonzaga University (upstream of the Division Street Bridge), and (3) at the mouth of Hangman Creek. PCBs were highest near Gonzaga at the downstream end of the Mission Reach. PCB congener patterns in sediments and biofilm from Plantes Ferry closely matched indicating the strength of the Aroclor 1242/1248 signal in the river there.

Caddisflies and biofilm were collected at two locations. Comparison of the congener patterns and stable nitrogen isotope ^{15}N between the biofilm and caddisflies indicated that PCBs metabolize in caddisflies much more than in biofilm.

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Introduction

Background

The Spokane River does not meet Washington State water quality standards for polychlorinated biphenyls (PCBs), with sections of the river categorized as "impaired" under Section 303(d) of the federal Clean Water Act.[1] The listings are based on PCB concentrations in fish tissue that do not meet Washington's human health criteria. The Washington State Department of Health also issued fish consumption advisories for sections of the Spokane River where eating fish may be harmful to human health.[2]

In 2012, the Spokane River Regional Toxics Task Force (SRRTTF) was formed to address PCBs in the Spokane River. One of SRRTTF's goals is to identify the sources, amounts, and locations of PCBs in the Spokane River. This goal is being achieved through synthesis of existing data and information about PCBs in the watershed, as well as field collection and analyses of new PCB data to fill in data gaps. The Washington State Department of Ecology's (Ecology's) Environmental Assessment Program (EAP), Toxics Studies Unit (TSU), is providing technical assistance to help SRRTTF identify PCB sources.

Previous studies of PCBs in the Spokane River watershed include collection and analysis of:

- fish tissue
- river water
- industrial and municipal wastewater effluent
- stormwater
- sediments
- atmospheric deposition

A detailed summary of past studies addressing PCBs in the Spokane River is provided in the *Comprehensive Plan to Reduce Polychlorinated Biphenyls (PCBs) in the Spokane River* (LimnoTech, 2016a).

In August 2018, Ecology conducted a spatial survey of the Spokane River using biofilm as a method to address possible suspected and unknown sources of PCBs to the river. In addition to biofilm, several locations were sampled for sediments and invertebrates. The 2018 PCB results were used to identify hot spot areas to prioritize follow-up monitoring. In August 2019, Ecology conducted follow-up monitoring in areas displaying elevated PCB concentrations in biofilm during 2018.

Biofilm are complex assemblages of algae, microbes, detritus, and fine sediments attached to surfaces such as rocks, often having a brownish flocculent appearance. Biofilm can serve as the base of food webs in an aquatic trophic system, supplying nutrients to invertebrates and to organisms higher up in the food web. They can be used as natural passive samplers because of their ability to absorb and bind contaminants in surface water. The amount of PCBs in biofilm

[1] Current 303(d) listings for PCBs in the Spokane River can be found on the Washington State Water Quality Assessment website: https://apps.ecology.wa.gov/ApprovedWQA/ApprovedPages/ApprovedSearch.aspx

[2] Current fish consumption advisories for the Spokane River can be found on the Washington State Department of Health's website: https://www.doh.wa.gov/DataandStatisticalReports/HealthDataVisualization/fishadvisory

represent a localized, temporally-integrated sample over a period of growth, rather than a snapshot of conditions on a single date and time. Thus, biofilm can be used effectively to assess the spatial variation of contaminants in an aquatic system (Hobbs et al., 2019; Mahler et al., 2020).

Goals and Objectives

As stated in the introduction, this report serves as a synthesis of two seasons of sampling. The first season's (2018) goals were to identify suspected and unknown PCB source areas and to characterize PCBs in biofilm, sediment and macroinvertebrates (caddisfly larva). The second season's (2019) goals were to confirm and hone in on the suspected source areas identified in 2018 using biofilm only.

The main objectives of the project were to:

- Collect and analyze PCBs in biofilm samples from the Spokane River at:
  - 19 locations in 2018
  - 33 locations in 2019 (including most of the same locations as in 2018)
- Collect and analyze PCBs in sediment samples at three locations in the Spokane River.
- Collect and analyze PCBs in macroinvertebrate samples at two locations in the Spokane River.
- Compare PCB concentrations and patterns in biofilm among locations of unknown potential sources, known sources, and reference areas.

Methods

Study Area

The Spokane River begins at Lake Coeur d'Alene in Idaho, and flows west for about 112 miles, eventually emptying into the Columbia River in Washington (Figure 1). There are six hydroelectric dams in the Washington portion of the river. The watershed area covers about 6,600 square miles. The river is fed by two main tributaries: Hangman (Latah) Creek and the Little Spokane River. Other smaller tributaries include Deep and Coulee Creeks. River flows typically are lowest in the summer, increase during the fall and winter with seasonal precipitation, and are highest in the spring.

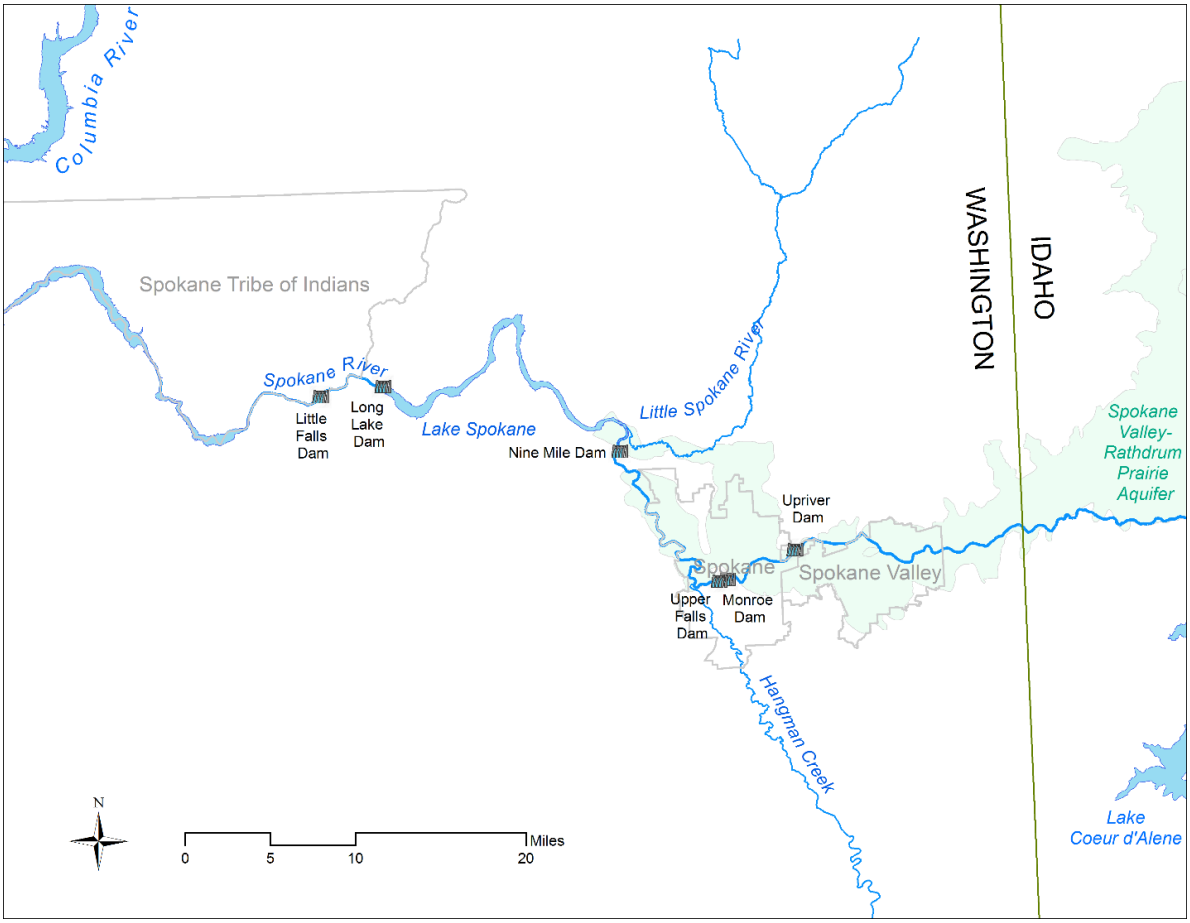

Figure 1. Spokane River Study Area.

Upstream of Lake Spokane, much of the Spokane River is underlain by the Spokane Valley Rathdrum Prairie Aquifer, an unconfined aquifer covering about 370 square miles in Idaho and Washington (Spokane County, 2015). Roughly half of the one billion gallons of groundwater per day that flows through the aquifer is discharged to the Spokane River, and roughly half is supplied to the aquifer by the river as aquifer recharge (Spokane County, 2015). In upstream reaches of the Spokane River, streamflow is mostly lost to the aquifer, while in downstream reaches toward the City of Spokane, streamflow is mostly gained from the aquifer (Hortness and Covert, 2005). Because of the coarseness of subsurface materials in the aquifer, the gains and losses in streamflow from interactions with the aquifer can be large—up to hundreds of cubic feet per second (Molenaar, 1988; Hortness and Covert, 2005).

For this project, our most upstream sampling site was near the Washington-Idaho border (Stateline). Our most downstream sampling site was just below Nine Mile Dam (Figure 2).

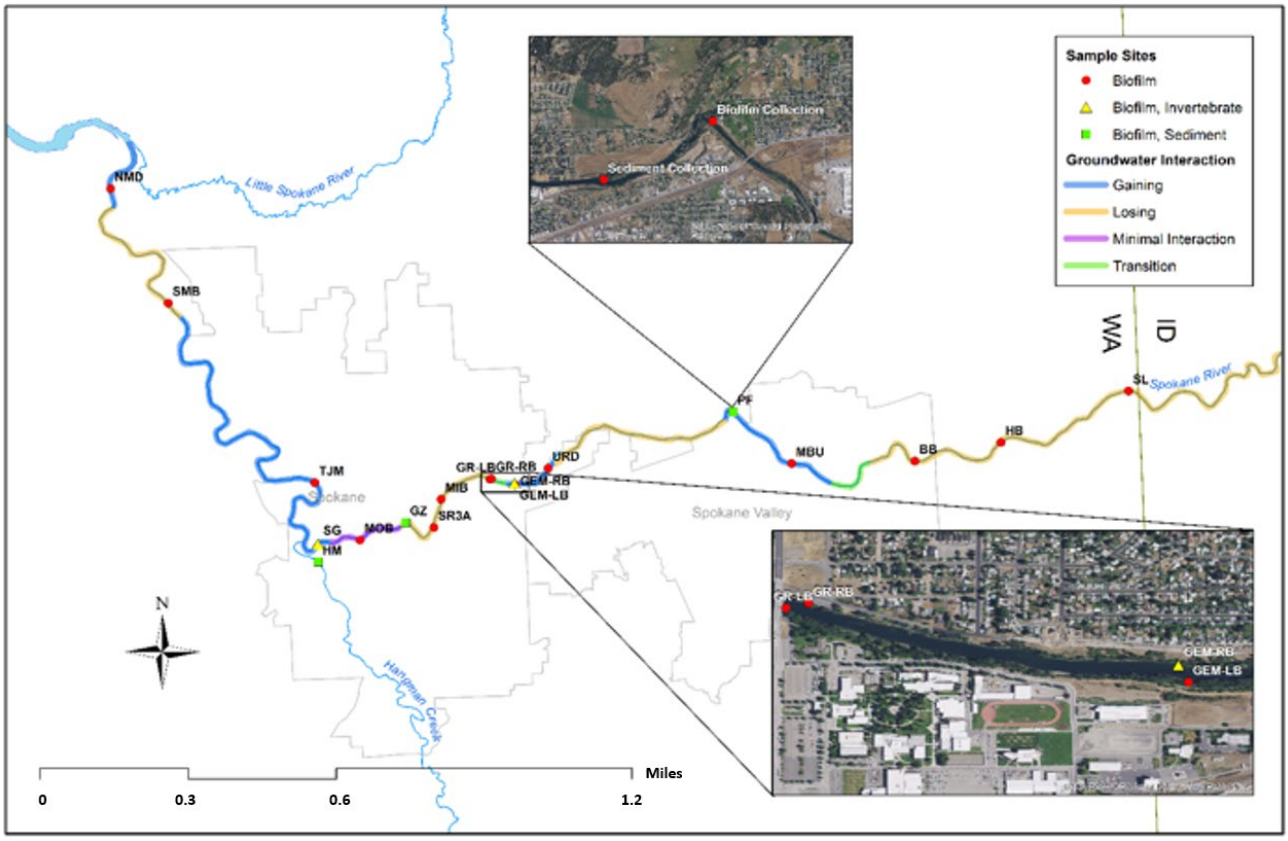

Figure 2. Monitoring Locations for Biofilm, Invertebrates, and Sediment, 2018.

Field Sampling

Field sampling for this project took place during August 27 – 30, 2018 and August 5 – 8, 2019, during the late summer low-flow period when biofilm are typically well established. Samples were collected following the procedures outlined in the Quality Assurance Project Plan (QAPP) for the 2018 sampling and the QAPP Addendum for the 2019 sampling (Wong and Era-Miller, 2019; Wong and Era-Miller, 2020).

Biofilm

Biofilm were collected on the Spokane River between the Washington and Idaho Stateline to just below Nine Mile Dam. In 2018, 19 sites were sampled, and in 2019, 33 sites were sampled for biofilm (Figure 2 and Figure 3). Monitoring sites were selected in coordination with SRRTTF. Site selection strategy included:

- three upstream reference sites (the most upstream sites: SL, HB, and BB)
- sites thought to represent unknown potential source areas
- sites thought to represent known source areas
- sites thought to be influenced by groundwater inputs

Appendix A, Table A-1 provides location details as well as the rationale for choosing each site.

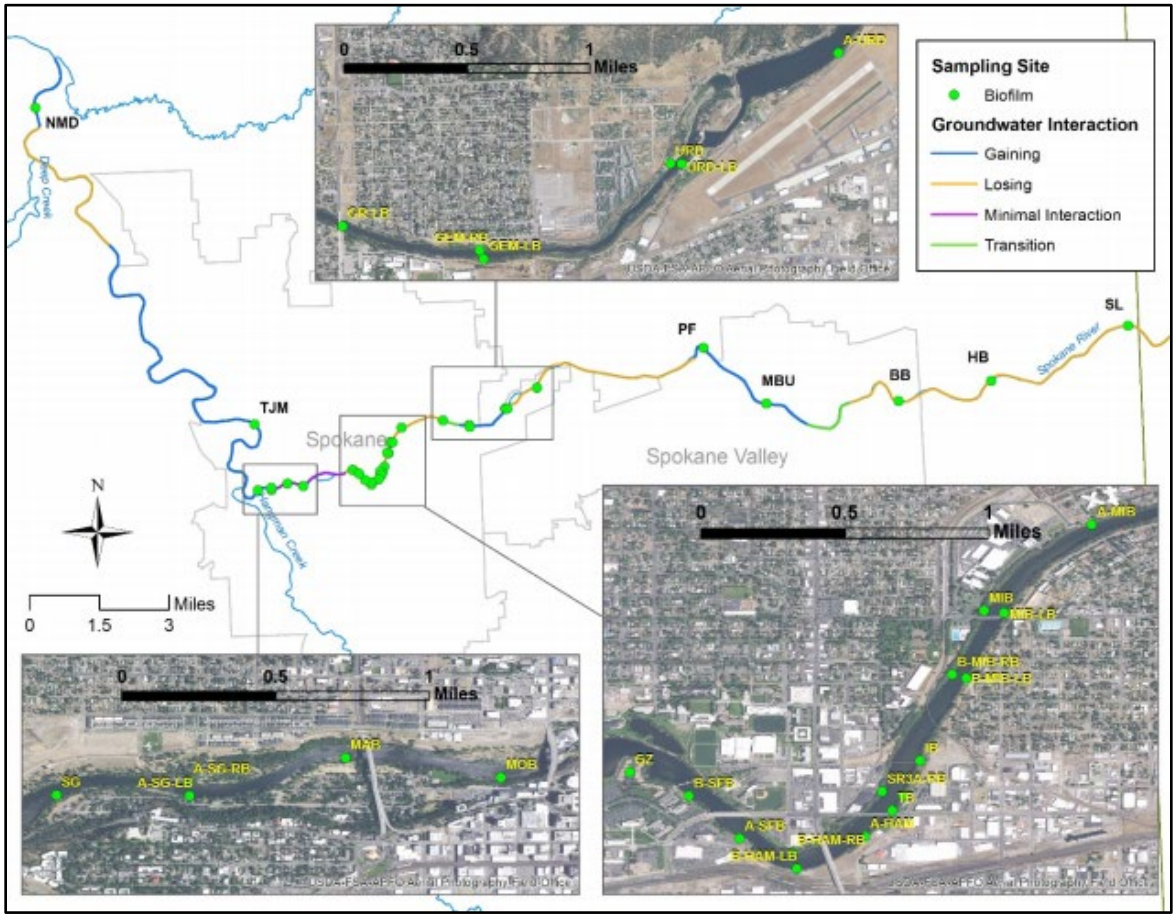

Figure 3. Monitoring Locations for Biofilm, 2019.

At each site, biofilm samples were collected for analyses of PCBs, lipids, carbon and nitrogen stable isotopes, biomass, and taxonomy. Rocks with visible biofilm growth (brown, flocculent appearance) were selected near the river's edge at water depths of several inches up to an arm's depth (~1.5 feet). Approximately 20-100 rocks were scraped to form a composite sample depending on the size of the rocks and the mass of the biofilm present at the site. The sampled area generally represented 30-40 feet of river bank length.

Biofilm from each rock was scraped into a decontaminated stainless steel bowl using a decontaminated (acetone and hexane-washed) blade/knife. Each biofilm sample was homogenized in the bowl using a decontaminated spoon, and then scooped into individual certified clean glass jars for analysis.

For this study, four field split duplicates (aliquots taken from one homogenized sample, and analyzed as separate samples) were collected to assess precision of PCB samples. Field splits were collected for all carbon and nitrogen isotope samples.

To get an estimate of biomass (biofilm mass/surface area), biofilm from about 5–10 rocks were scraped and scooped into a separate jar. The surface area of biofilm growth was approximated for each of these rocks using aluminum foil cutouts, which were later digitized using Image J software to estimate the total surface area.

Biofilm samples were stored in a cooler on ice in the field. Samples were then transferred to the chain-of-custody walk-in cooler at the Lacey Headquarters building until they were shipped on blue ice to the appropriate laboratories for analysis.

Sediment

Sediment was collected at three biofilm sites: Plants Ferry (PF), Gonzaga (GZ), and near the mouth of Hangman Creek (HM). Surface sediments were collected by using a decontaminated spoon to scoop approximately the top two centimeters of undisturbed sediment into a decontaminated stainless steel bowl. The sediment was then homogenized in the bowl, and scooped into separate certified clean sampling jars for PCB, total organic carbon (TOC), and grain size analyses. For this study, one field split for each of the PCB, TOC, and grain size samples was collected. Similar to biofilm, the sediment samples were stored in a cooler on ice in the field, transferred to the chain-of-custody walk-in cooler at the Lacey Headquarters building, and later shipped to the appropriate laboratories for analysis.

Invertebrates

Macroinvertebrate samples were collected at two biofilm sites: GE Mission – Right Bank (GEM-RB) and Gonzaga (GZ). The invertebrates were analyzed for PCBs, lipids, and carbon and nitrogen stable isotopes. Invertebrate samples consisted of the larval and pupal forms of caddisfly (*Hydropsychidae* and *Limnephilidae*). At each site, invertebrates were picked from rocks. Casings were removed, and the soft tissue was placed into certified clean sampling jars and stored on ice in the field. The samples were stored in the chain-of-custody walk-in cooler at the Lacey Headquarters building for later processing and homogenization. After homogenization, one field split was collected for PCB analysis, and two field splits were collected for carbon and nitrogen isotopic analyses. Samples were then shipped on blue ice to the appropriate laboratories for analysis.

Laboratory Methods

Before shipping to the laboratory for PCB analysis, biofilm and sediment samples were gravity settled and decanted back at Ecology Headquarters in Lacey, Washington. Invertebrate samples were homogenized with a decontaminated mortar and pestle. Biofilm, sediment, and invertebrate samples were analyzed for the 209 PCB congeners on a high resolution gas chromatography/high resolution mass spectrometer (EPA 1668C) by SGS AXYS Analytical Laboratories in British Columbia.

Sediment samples for TOC analyses were analyzed by Ecology's Manchester Environmental Laboratory (MEL) in Port Orchard, Washington (EPA 440.0). Sediment grain size was analyzed by Materials Testing & Consulting (PSEP 1986).

Biofilm and invertebrate samples for carbon and nitrogen isotopic analyses were freeze dried in a Labconco FreeZone 2.5 L freeze drier at Ecology Headquarters. Carbon and nitrogen isotopes in 2018 biofilm and invertebrate samples were analyzed by the University of Washington IsoLab on a ThermoFinnigan MAT 253 / Costech Elemental Analyzer for measurement of $\delta^{13}C$ and $\delta^{15}N$ in solid material. The University of California, Davis conducted the carbon and nitrogen isotope analysis for the 2019 biofilm samples.

Biofilm samples collected to estimate biomass were analyzed by MEL for percent solids (SM2540G), and ash free dry weight (SM10300C). Before shipping to MEL, the samples were weighed (wet weight) at Ecology Headquarters.

The algal compositions of biofilm samples were qualitatively assessed using a compound light microscope under 100x magnification at Ecology Headquarters.

Quality Assurance/Quality Control

PCB data were reviewed and received stage 4 data validation from a third party in accordance with the QAPP (Wong and Era-Miller, 2019), QA/QC requirements for EPA 1668C, and applicable criteria in EPA's National Functional Guidelines (EPA, 2016). The 2018 data were validated by Ginna Grepo-Grove at MEL. The 2019 data were validated by Carlton Environmental. All data used for the report and entered into Ecology's Environmental Information Management (EIM) database are useable as qualified by the data validators and as reviewed by the project manager.

Measurement quality objectives (MQOs) for PCBs, lipids, carbon and nitrogen isotopes, sediment grain size, and TOC data were defined in the QAPP for this project. This included collection of field splits for all sample matrices and parameters as well as analysis of laboratory duplicates, laboratory control standards, internal recovery standards, and laboratory method blanks for all PCB samples.

MQOs are shown in Appendix B, Table B-1. The percentage of PCB results meeting laboratory MQOs for recovery ranged from 95 – 100% for biofilm, sediment, and macroinvertebrates. The percentage of PCB results requiring qualification as non-detects due to method blank contamination was 1% for sediments, 5% for biofilm, and 9% for macroinvertebrates.

The relative percent difference (RPD) is the MQO used to measure sample replicate precision. Appendix B, Tables B-2 and B-3 give the RPDs for all three study matrices (biofilm, sediment, macroinvertebrates). The RPDs for the laboratory duplicate samples were generally much lower with less variability than the field split and field replicate samples. This is an expected outcome as laboratory duplicate analyses only account for the variability of the laboratory process, while field split samples and field replicate analyses account for the collective variability introduced from laboratory analyses, field collection processes, and the environment. The results generally met the RPD MQOs for precision (<20% RPD) with the exception of the 2018 biofilm and sediment samples at GZ (Gonzaga). Duplicate analysis was not conducted on the 2019 biofilm sample from Gonzaga. All 2018 results for the Gonzaga site should be considered estimates.

Data Reporting and Analysis

Biofilm Biomass

Biofilm biomass (g/cm2) was calculated by dividing the dry weight (g) of the biofilm samples by the area (cm^2) of the rocks that were scraped.

Treatment of Non-Detects for PCB Sums

Non-detected PCB congener results (those qualified as U, UJ, or NUJ) were excluded from PCB sums. For this project, PCB congener results less than three times the detected method blank result were qualified as non-detect. The "<3xMB" data censoring method falls in line with our study objective of PCB source identification, and with previous SRRTTF studies of PCBs in the Spokane River aimed at source identification.

Results

Biofilm

PCBs

Total PCBs in biofilm from 2018 and 2019 are shown in Figure 4. Total PCB results are also presented in Appendix C, Table C-1. Of the 19 locations sampled in 2018 and the 33 locations sampled in 2019, there was overlap at 16 locations. PCB concentrations were slightly higher in 2018 at 13 of 16 locations compared to 2019. The reason for this trend is unclear since samples were collected at the same locations during similar August low-flow conditions in the river. Though mean flows were similar in August of both years, water year 2018 had higher flows through much of the year compared to water year 2019 (Table 1). Overall the comparison and confirmation of the relative concentrations between sampling locations within each sampling year is more important to source identification than comparison between years.

Table 1. Mean Monthly Flow (CFS) at USGS Gage 12422500 for Water Year 2018 and 2019.

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
2017										2,729	3,792	5,723
2018	8,518	14,350	8,172	17,070	23,510	6,094	1,940	1,108	1,383	2,105	2,995	3,914
2019	3,797	4,024	3,897	16,610	11,780	4,684	1,580	1,016	1,344			

* Data from the United States Geological Survey (USGS) website for gaging station 1242250 Spokane River at Spokane, WA https://waterdata.usgs.gov/usa/nwis/uv?12422500.
CFS = cubic foot per second; a measure of river flow or discharge.

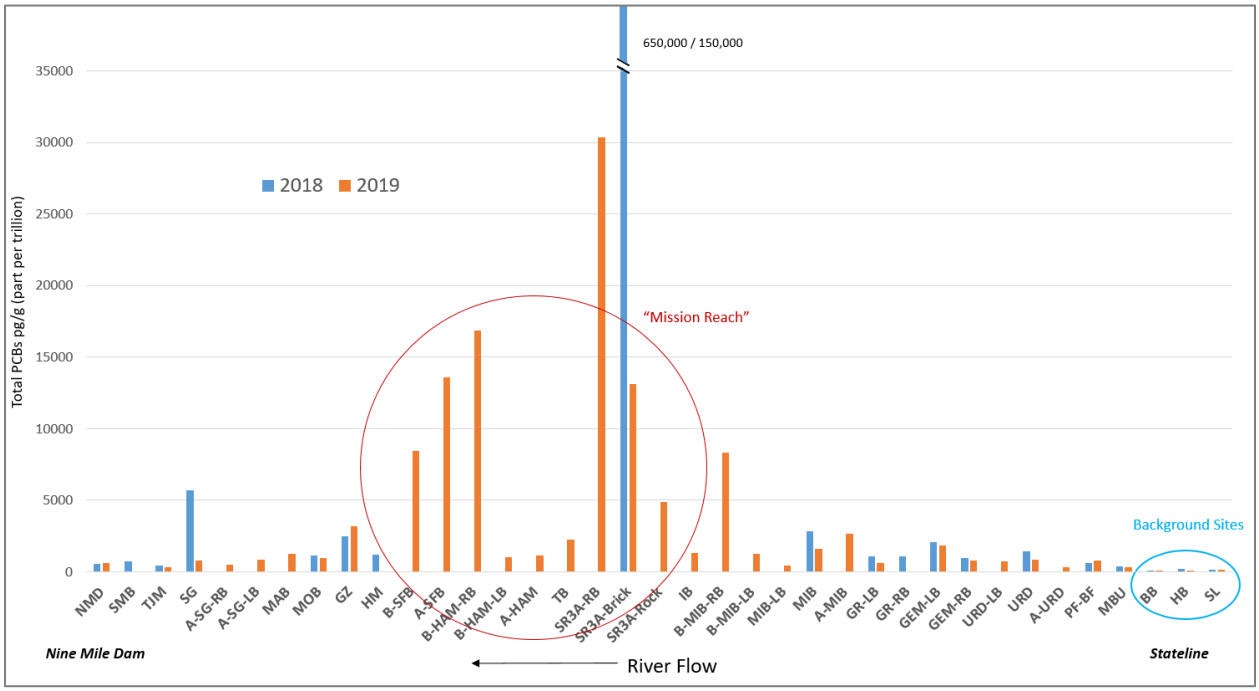

Figure 4. Total PCBs in Biofilm from the Spokane River, 2018 and 2019.

During both 2018 and 2019, total PCB concentrations were lowest at the upstream background sites – Stateline (SL), Harvard Bridge (HB) and Barker Bridge (BB) – with concentrations ranging from 68-168 pg/g (part per trillion) (Figure 4). Total PCB concentrations more than doubled at the next downstream site, Mirabeau (MBU). After MBU, PCBs generally increased downstream until peaking at the SR3A site. Downstream of the peak at the SR3A sites, the trend in PCB concentrations tapered down.

The highest level of PCBs, 650,000 pg/g, was found at site SR3A in 2018 (Figure 4). This is two orders of magnitude above the next highest concentration found further downstream at Spokane Gage (SG) at 5,600 pg/g in 2018. Because the value at SR3A was vastly different from the rest of the data, it was decided to have an archive of the sample re-extracted and reanalyzed. The result of the reanalysis was four times lower, but still high at 150,000 pg/g. For the 2019 sampling, we chose to bracket the SR3A site with an increase in density of sampling points in order to hone in on the sources of PCBs in this reach, herein referred to as the "Mission Reach". Relative total PCB concentrations in the Mission Reach are displayed using Excel 3D Maps in Figure 5.

In 2019, the highest total PCB concentration was 30,000 pg/g at SR3A-Right Bank (SR3A-RB), located directly across the river from SR3A which is located on the left bank (Figure 4 and 5). The substrate at SR3A is mostly fill material containing bricks. Thus, bricks were scraped along with rocks to garner enough biofilm material for analysis in 2018. With the high concentration of PCBs found in this sample, there was concern that the bricks could contain PCBs. Therefore, rocks and bricks were sampled separately at SR3A in 2019 to test whether or not the bricks might be a source of PCBs to the biofilm. While some variation in total PCB concentrations (13,100 versus 4,900 pg/g) and homolog patterns was found between the brick and rock samples, it was not enough to be different from the variation among all the other Mission Reach samples. Data from the Mission Reach are examined further in the *Discussion* section of this report regarding *Confirmed and Suspected Sources of PCBs*.

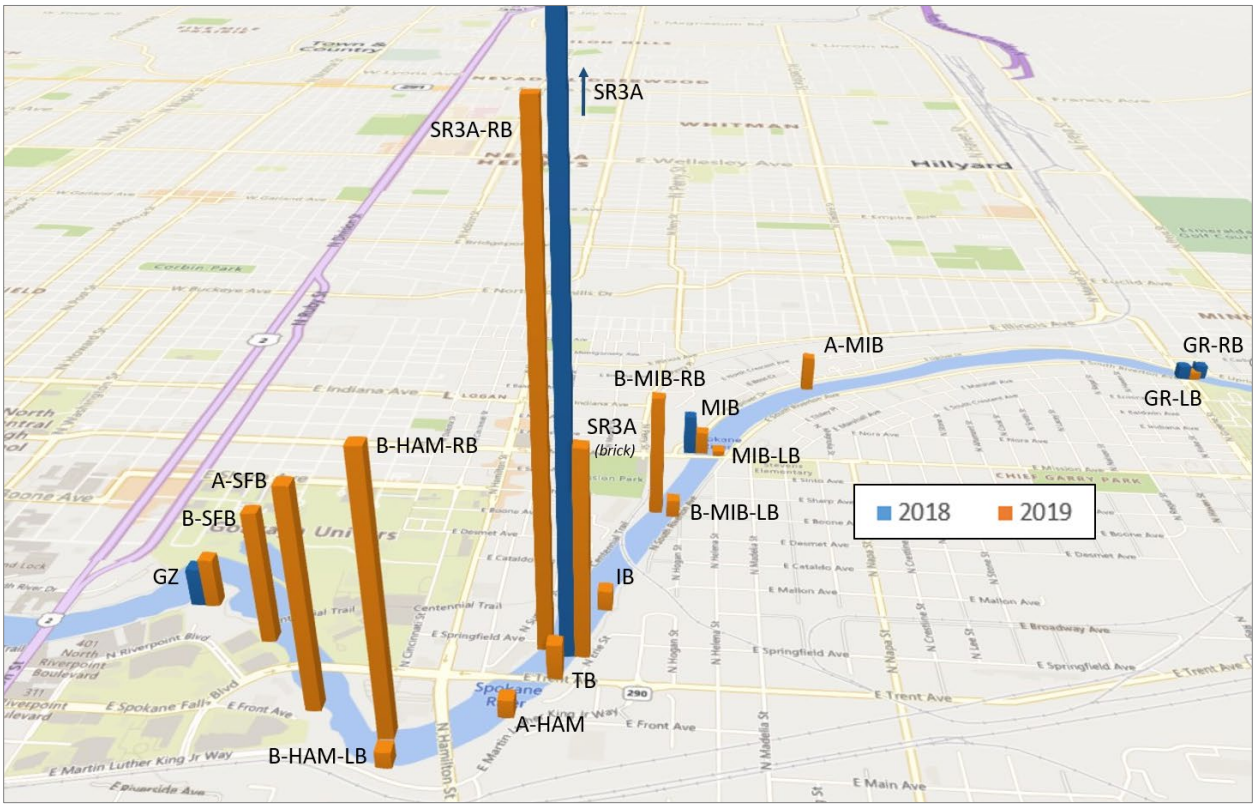

Figure 5. Total PCB Concentrations in the Mission Reach (*Bing Maps*).

In 2019, additional biofilm sampling locations were also added to several other areas of the Spokane River to hone in further on locations where the 2018 sampling identified slightly elevated PCB concentrations compared to the background sites. The additional locations were near Upriver Dam (URD), Mission Bridge (MIB), and the Spokane Gage (SG). These three areas are also discussed in the *Confirmed and Suspected Sources of PCBs* section of the report.

Homolog Patterns

PCB homolog distributions for the 2018 and 2019 biofilm samples, representing 19 and 33 sampling locations, are displayed separately in Figure 6 and Figure 7. Homolog totals are also presented in Appendix C, Table C-1. Figure 8 compares the homolog distributions at the 16 sites that overlapped between the 2018 and 2019 sampling events. Homolog patterns at these overlapping sites were generally similar between sampling years.

The three upstream background reference sites, Stateline (SL), Harvard Bridge (HB) and Barker Bridge (BB), had similar patterns within each sampling year, with the exception of Harvard Bridge (HB) having more of the lesser-chlorinated homologs: Di-, Tri-, and Tetra- during 2018. The more noticeable differences in homolog patterns for the rest of the sampling sites that indicate possible source areas are briefly described below and are further explored in the *Confirmed and Suspected Sources of PCBs* section of the report.

1. **Mirabeau (MBU)**
   Starting at the upstream site Stateline (SL) and moving downstream, the first clear homolog pattern change was at Mirabeau (MBU) where the higher-chlorinated

homologs, Hepta-, Octa- and Nona-, become more apparent. This pattern was seen in both 2018 and 2019 (Figures 6-8).

2. **Plantes Ferry (PF)**
   The pattern at the next site moving downstream from MBU, Plantes Ferry (PF), changed dramatically with more of the lighter to moderate chlorinated homologs, Tri-, Tetra- and Penta-. Tetra- made up almost 40% of the total homolog distribution in both 2018 and 2019 (Figures 6-8).

3. **GE-Mission Left Bank (GEM-LB)**
   GE-Mission Left Bank (GEM-LB) and GE-Mission Right Bank (GEM-RB) had different patterns from each other in both 2018 and 2019 even though they are along the same cross-section of river. Opposite banks were chosen for sampling to confirm if PCBs present in groundwater at the General Electric clean-up site located upgradient from the left bank could be reaching the river (Figures 6-8).

4. **Below Mission Bridge - Right Bank (B-MIB-RB)**
   In 2019, several locations were added to bracket the Mission Bridge (MB) location, which had the third highest total PCB concentration in 2018. In 2019, only one location from this reach, Below Mission Bridge-Right Bank (B-MIB-RB), exhibited a different pattern from the locations surrounding it with an increase in Penta- and Hexa- (Figure 7).

5. **SR3A (-rock and -brick) and SR3A-Right Bank (SR3A-RB)**
   The homolog pattern for SR3A was dramatically dissimilar from any other of the locations sampled in 2018 with an increase in Hepta- and Octa- and decrease in Tetra- and Penta- (Figure 6). In 2019, these homolog pattern changes were more subtle, but still present at SR3A. SR3A-RB, located a-cross the river on the right bank, also had a homolog pattern somewhat similar to the SR3A -rock and -brick samples, which were located along the left bank (Figure 7).

6. **Hangman Creek (HM)**
   Hangman Creek (HM) had a different homolog pattern from the nearby mainstem Spokane River locations Spokane Gage (SG) and TJ Meenach (TJM) in 2018 (Figure 6). HM had a lot more Tetra-. HM was not sampled in 2019.

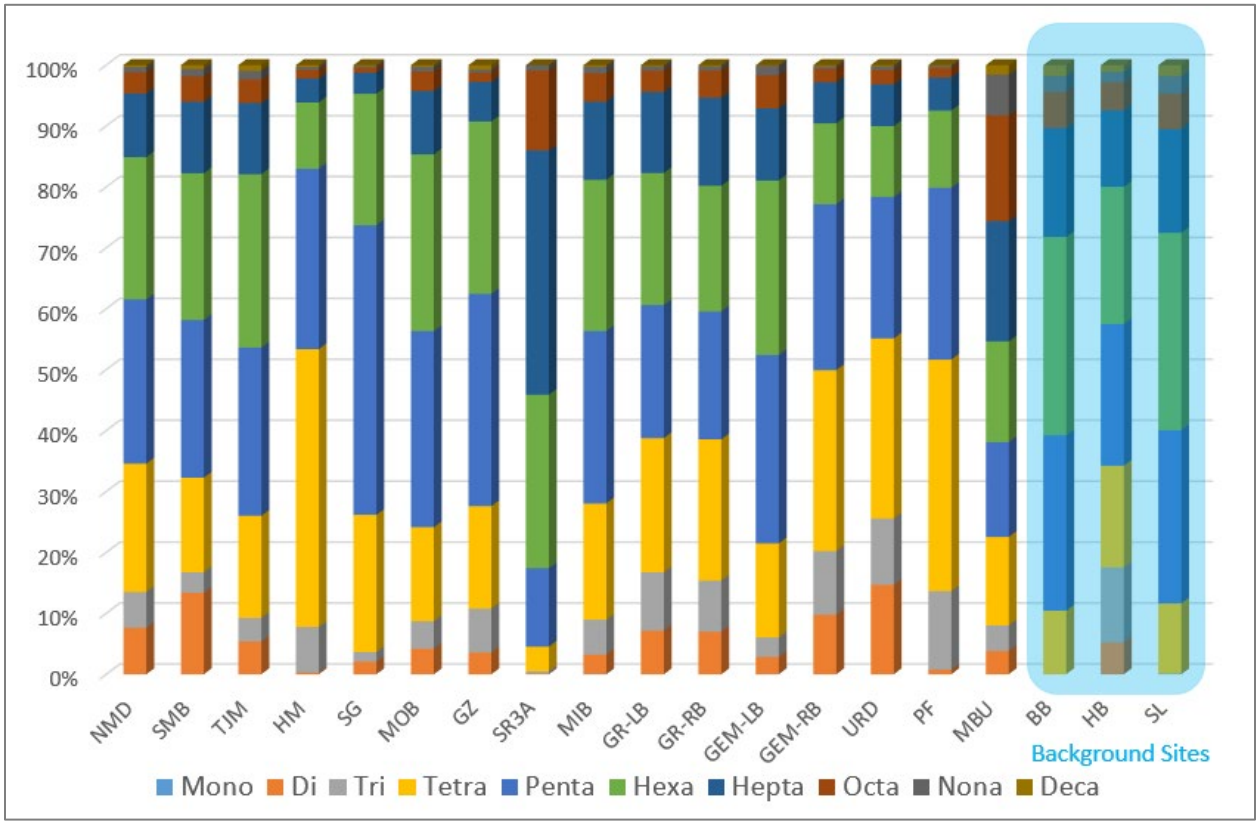

Figure 6. PCB Homolog Distributions in Spokane River Biofilm, 2018.

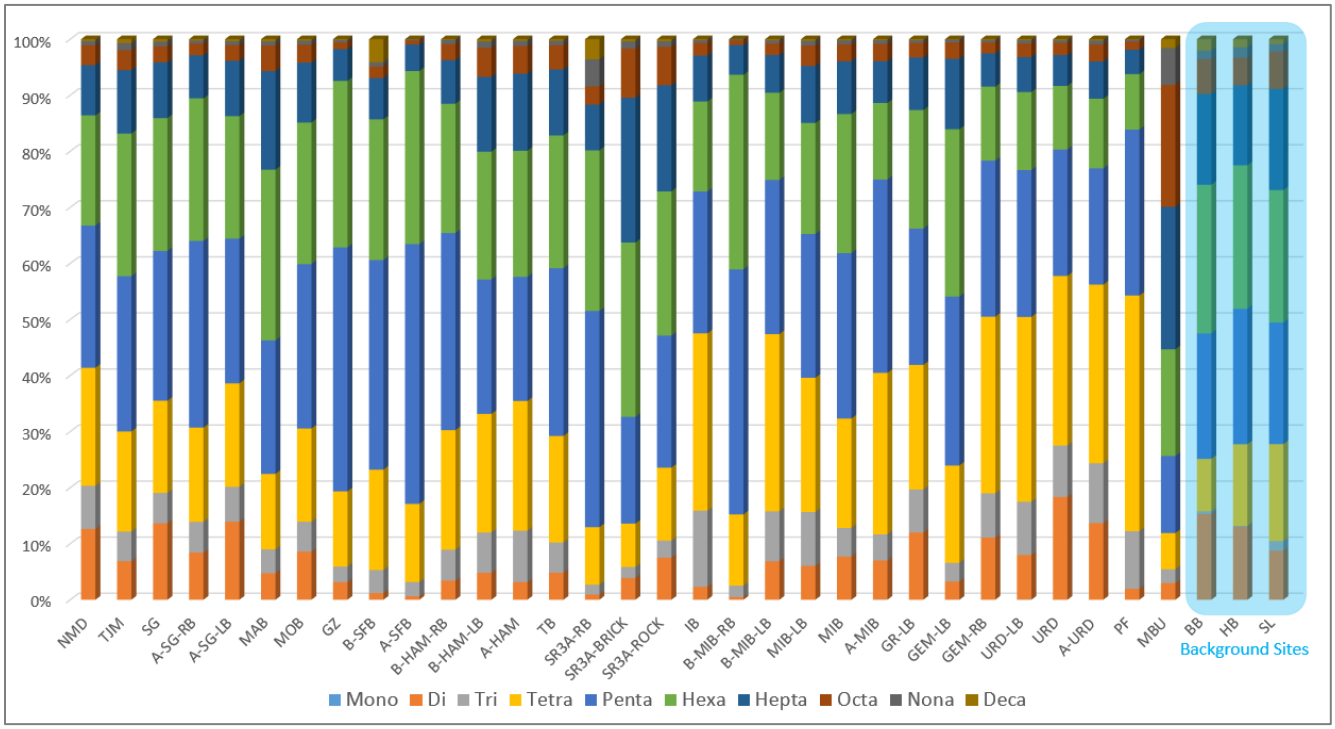

Figure 7. PCB Homolog Distributions in Spokane River Biofilm, 2019.

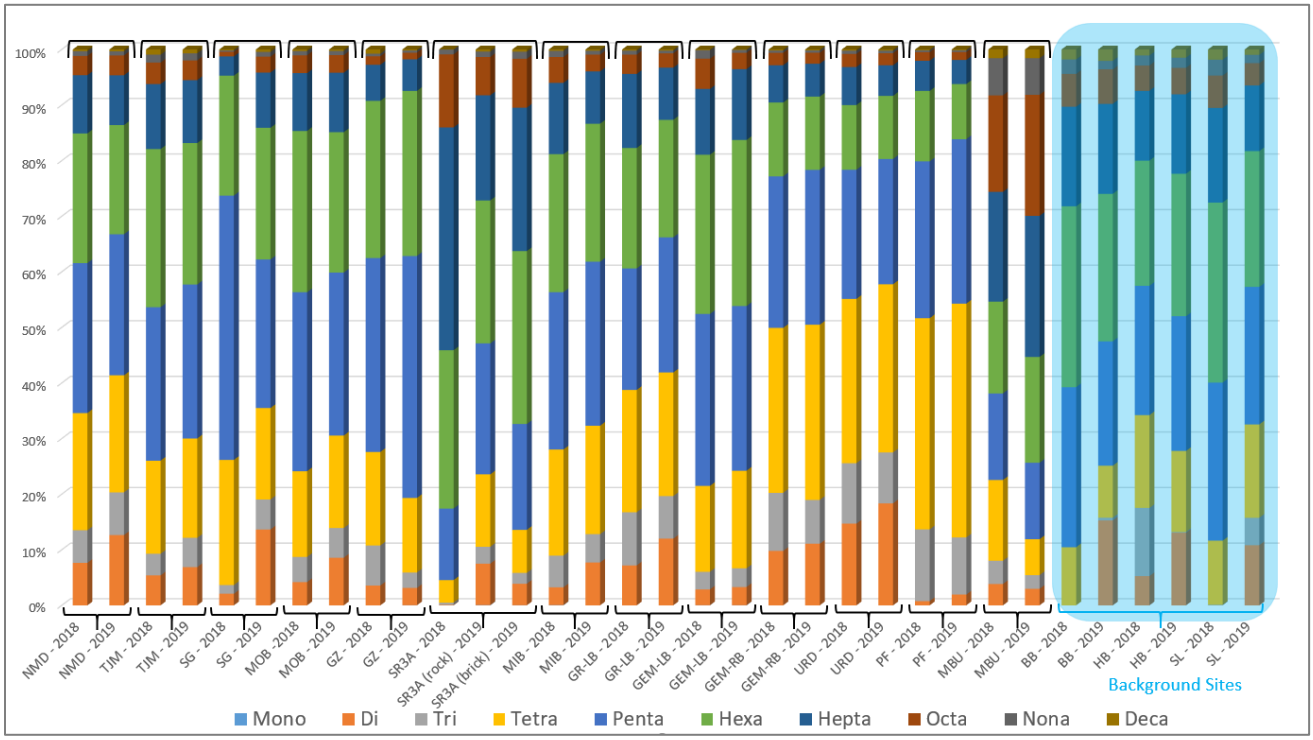

Figure 8. PCB Homologs in Biofilm at the Same Spokane River Locations, 2018 and 2019.

Conventional Parameters

Correlation analyses between biomass, lipids, organic carbon, and total PCB concentrations was performed on the 2018 and 2019 biofilm data to determine if any of the conventional parameters were related to PCB concentrations (Figures 9 and 10). None of the conventional parameters appeared to be strongly correlated with PCBs, and there was little consistency between years. For the 2018 biofilm data, only lipids were significantly correlated with PCBs ($r = 0.53$, $p = 0.03$). For the 2019 biofilm data, biomass ($r = 0.44$, $p = 0.0085$) and organic carbon ($r = -0.38$, $p = 0.034$) were significantly correlated. See Appendix C, Table C-2, for conventional data.

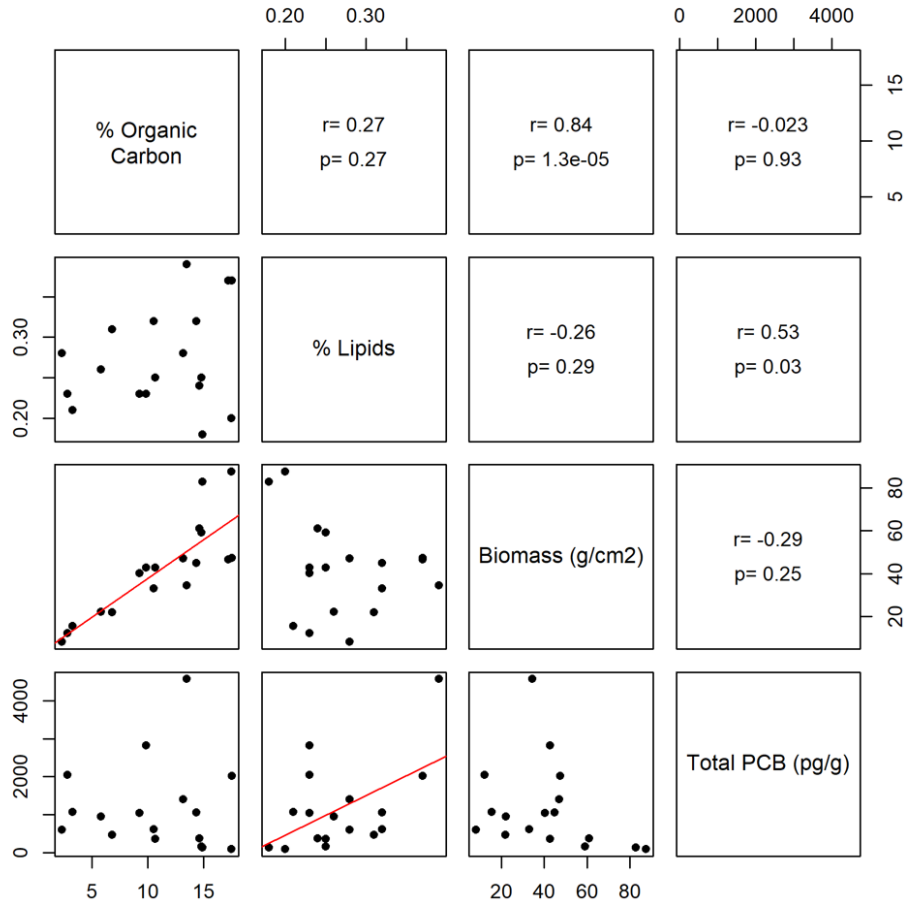

Figure 9. Correlation Analysis for Conventional Parameters and Total PCBs for the 2018 Biofilm samples.

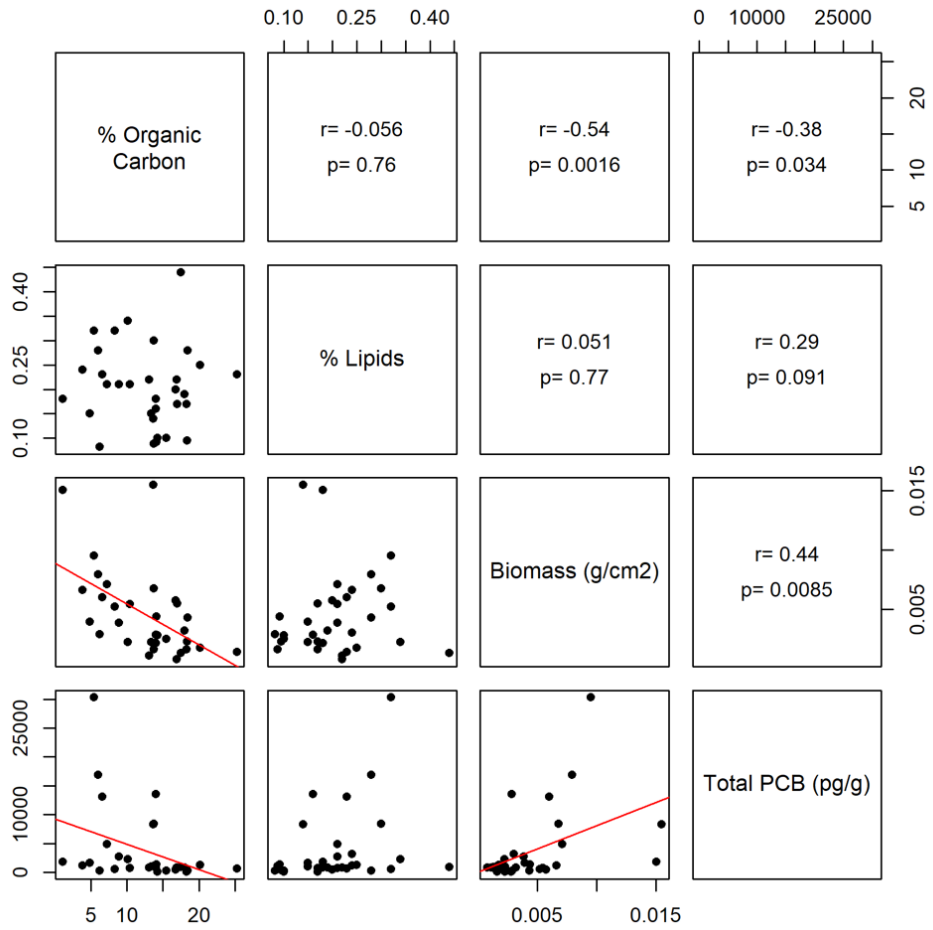

Figure 10. Correlation Analysis for Conventional Parameters and Total PCBs for the 2019 Biofilm samples.

C and N Isotopes

^{13}C and ^{15}N stable isotopes were analyzed in both biofilm and invertebrate samples to gain some information about the general structure of the food web in the Spokane River and to support future study of the Spokane River food web. ^{13}C and ^{15}N isotope data are shown in Appendix C, Table C-2. For this report, only nitrogen enrichment was examined in the *Discussion* section.

Taxonomy

The biofilm samples consisted mostly of diatoms with lesser amounts of green algae and other types of periphyton. Taxonomic identification of algae and diatoms in the biofilm samples was only conducted for the 2018 samples. A close-up photograph of algae and diatoms at one of the sampling locations is shown in Appendix C, Figure C-1. Qualitative relative abundance plots for each of the locations sampled in 2018 can be found in Figure C-2.

PBDEs in Biofilm

A subset of 13 archive Spokane River biofilm samples from 2019 were analyzed for Polybrominated Diphenyl Ethers (PBDEs). PBDEs and Per- and Polyfluoroalkyl chemicals (PFAS) were analyzed under an addendum (Wong, 2021a) to the QAPP for the current Spokane River PCB screening study as part of Ecology's ongoing research into using biofilm to assess contaminants in surface waters. The PFAS results are presented in a separate report (Wong, 2021b).

PBDEs are members of a broad class of brominated chemicals used as flame retardants. They resemble the structure of PCBs except they contain bromine instead of chlorine. The three main types of PBDEs used in consumer products are Penta-BDE, Octa-BDE and Deca-BDE (Ecology and DOH, 2006).

The 13 Spokane River archive samples collected in August 2019 were analyzed in January 2021 by MEL using method SW8270E-SIM. The data are available in EIM under Study ID: SWON0001. The results are shown in Figure 11. PBDEs were only detected in 3 out of 13 samples and only 4 PBDE congeners were detected: BDE-047, -099, -100 and -209. It appears that the detection limits for method SW8270E-SIM may not have been low enough to detect many of the PBDE congeners in the Spokane River biofilm samples. Ecology's recent research for PBDEs in biofilm from three western Washington rivers (Snohomish, Skykomish and Snoqualmie), using the higher resolution method EPA-1614, found total PBDEs levels in the 0.1-1.4 ug/kg (part per billion) range (personal comm., A. Gipe).

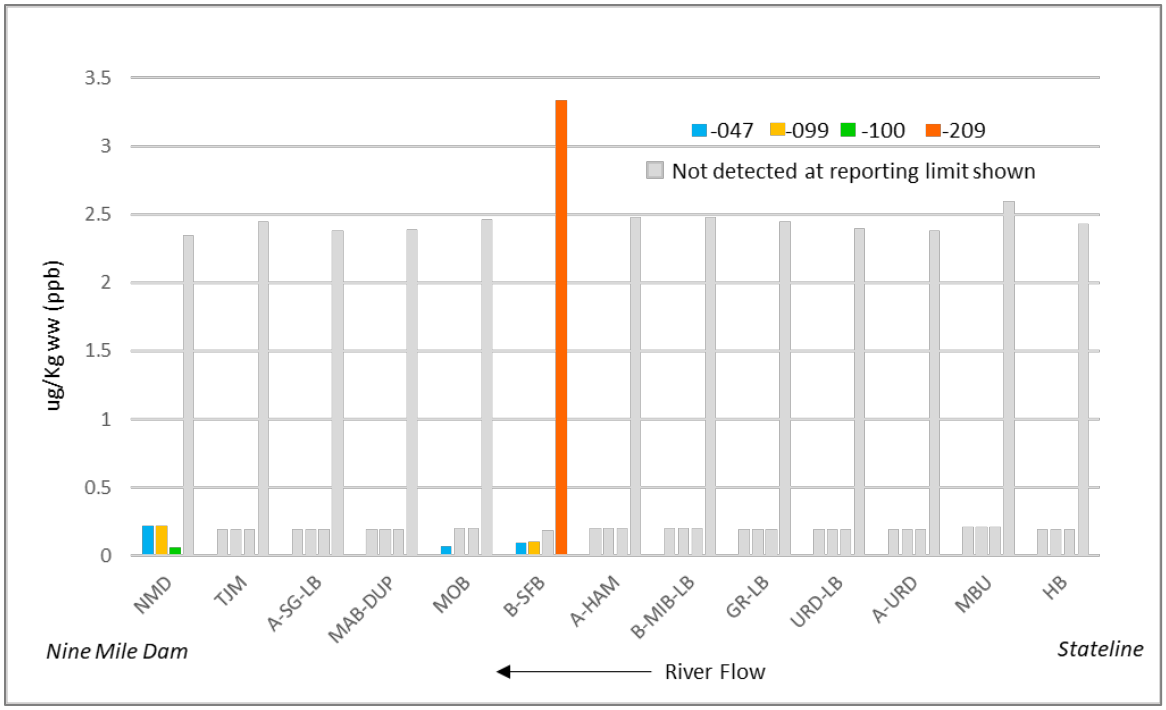

Figure 11. PBDEs in Biofilm Samples from Select 2019 Spokane River Monitoring Locations.

Sediment

Sediments can be difficult to collect in the Spokane River because the river is generally low in total suspended solids (TSS) and there are few depositional areas except in the reservoir areas behind the dams. Seasonal high flows in the river can also scour sediments from depositional areas. In 2018, sediment was collected at three locations: Plantes Ferry (PF-SED), Gonzaga (GZ-SED), and Hangman Creek (HM-SED). Sediments at GZ-SED and HM-SED were collected within 300 feet from the biofilm collection sites, whereas the PF-SED sediments were collected about 1.4 miles downstream from the PF biofilm site in a backwater area along the right bank (see Figure 2).

Total PCBs were 1-2 orders of magnitude higher at GZ-SED compared to PF-SED and HM-SED (Figure 12). GZ-SED is located at the tail end of the Mission Reach where biofilm samples contained elevated PCBs. Total Organic Carbon (TOC) and grain size are shown in Table 2. GZ-SED and GZ-SED-DUP came from the same sediment sample that was split for analysis. Based on split sample results for GZ, both total PCB concentration and TOC were variable, but grain size and homolog patterns were similar. Figure 13 displays the homolog patterns in the sediments. There are distinct homolog patterns for each of the 3 sediment locations.

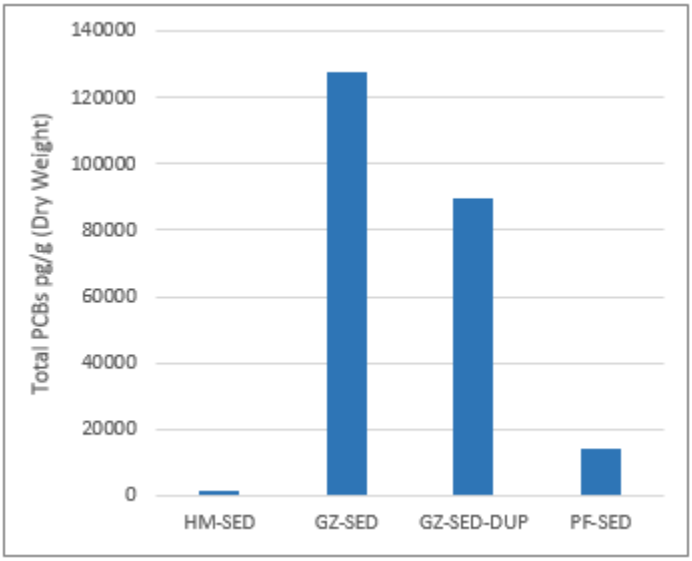

Figure 12. Total PCB Concentrations in Sediments.

Table 2. Sediment Total Organic Carbon (TOC) and Grain Size.

Location	Date	Sample No.	TOC (%)	Gravel (%)	Sand (%)	Silt (%)	Clay (%)
HM	8/29/18	1809040-22	3.78	22.6	48.4	22.2	6.8
GZ-SED	8/29/18	1809040-23	0.75	16	75.5	7.5	1
GZ-SED-DUP	8/29/18	1809040-25	1.54	21.8	70.3	6.8	1.1
PF-SED	8/30/18	1809040-24	0.86	0.9	91.6	6.2	1.3

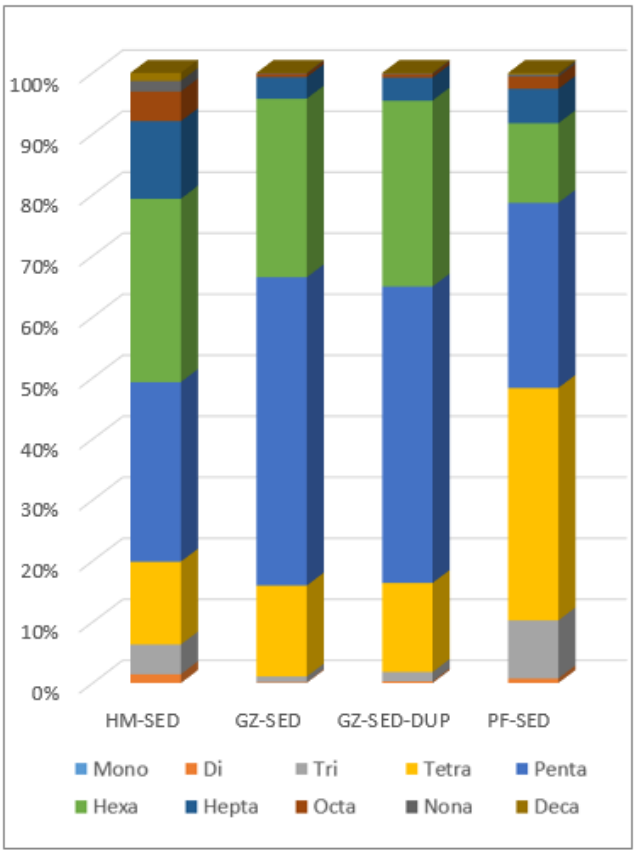

Figure 13. PCB Homolog Patterns in Sediments.

Invertebrates

In 2018, caddisflies were collected at two locations where biofilm were also collected: SG and GEM-RB. The caddisflies (order Trichoptera) consisted of family levels of *Hydropsychidae* and *Limnephilidae*. At the SG site, a mix of larval and pupal stage caddisflies were included in the composite sample, whereas at GEM-RB all the caddisflies were at the larval stage. The four major stages of caddisfly development are: egg, larval, pupal, and adult.

Total PCB concentrations were three times higher at SG compared to GEM-RB (Figure 14). PCB homolog patterns appeared to be very similar between the two locations (Figure 15). The SG-INVERT and SG-INVERT-DUP came from the same sample that was split for analysis.

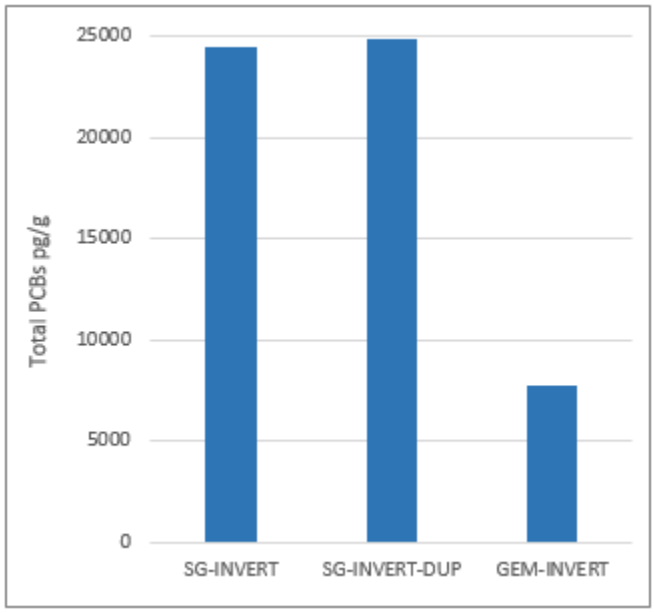

Figure 14. Total PCBs in Macroinvertebrates.

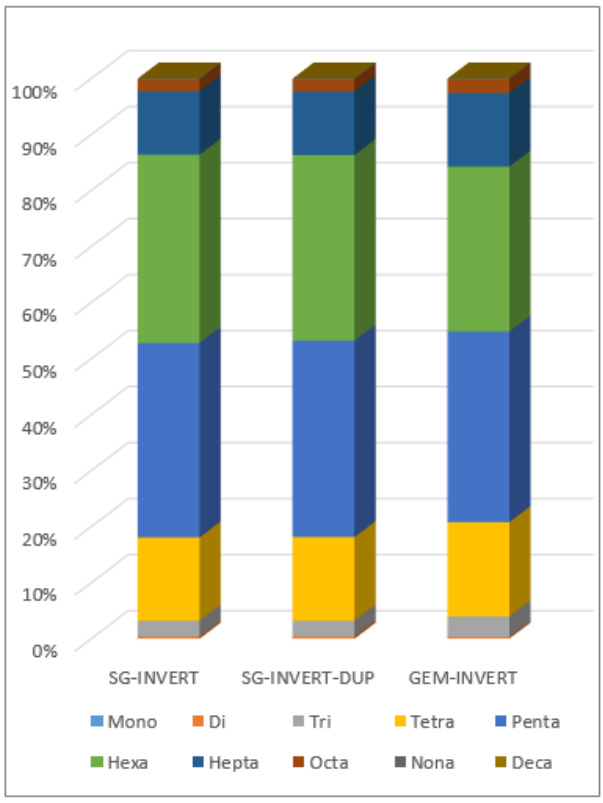

Figure 15. PCB Homolog Patterns in Macroinvertebrates.

Discussion

PCB Congener Patterns for the 2018 Data

A principle component analysis (PCA) was run for the 2018 biofilm, invertebrate, and sediment samples (Figure 16). The goal of PCA is to reduce the number of variables in a complex dataset without losing important information, thus making it easier to decipher patterns. The axes in the PCA for Figure 16 (PC1 and PC2) explain 48.8 % of the total variability for the 2018 samples. The different sample matrix types including laboratory method blanks are designated by both name and color in the PCA plot.

The closer samples group together in the PCA, the more similar their PCB congener patterns are. Alternatively, samples farther away from each other highlight the differences.

Some of the samples that grouped together were:

- Laboratory method blanks
- Background biofilm sites (SL, HB, and BB)
- Sediment and biofilm samples at Plantes Ferry (PF-BF and PF-SED)
- Two invertebrate samples, GEM-INVERT and SG-INVERT, as well as the replicate (split sample) for SG-INVERT
- Biofilm at the Green Street sites (GR-RB and GR-LB), located directly across the river from each other

Some of the samples that were spaced apart and indicated differences were:

- Biofilm GEM-LB and GEM-RB, though located directly across the river from each other
- SR3A stood alone as an outlier as did MBU
- Hangman Creek biofilm (HM-BF) and sediments (HM-SED)

The similarities and differences in PCB congener patterns among the biofilm, invertebrate, and sediment sample matrices in the PCA confirm the qualitative differences noted in the homolog patterns.

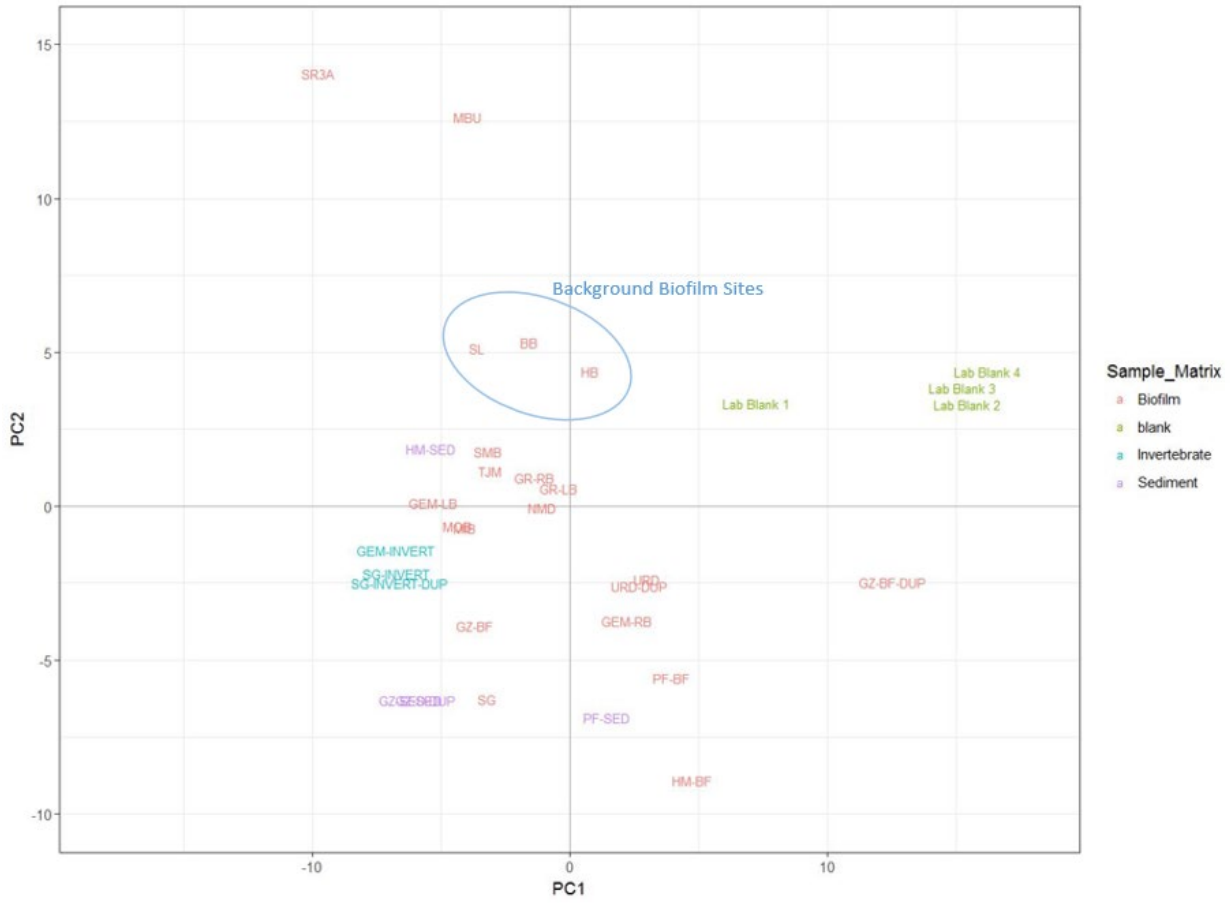

Figure 16. PCA of 2018 PCB Congener Data for Biofilm, Invertebrates, and Sediment.

PCB Congener Patterns for the 2019 Data

A PCA was conducted on the 2019 biofilm samples to look at congener pattern differences and similarities between sites (Figure 17). The axes in the PCA for Figure 17 (PC1 and PC2) explain 65.4 % of the total variability for the 2019 biofilm samples. The congener patterns for five common Aroclor mixtures (1242, 1248, 1254, 1260, and 1262) were also included in the analysis (Rushneck et al. 2004). The following was observed:

- Background sites (SL, HB, and BB) were grouped, but not as tightly as in 2018.
- The majority of the samples fall somewhere between the Aroclor quadrants suggesting that most sites may represent a mix of Aroclors.
- MBU is closest site to Aroclor 1262.
- PF-BF is right next to Aroclor 1242 and 1248, closest of all the biofilm sites to any of the Aroclors.
- URD-LB and URD (RB) are distanced from each other in the PCA though located directly across the river from each other geographically.
- As was observed in 2018, GEM-LB and GEM-RB still distanced from each other though located directly across the river.

- B-MIB-RB is spaced apart in the PCA from the other close by river sites: A-MIB, MIB, MIB-LB and B-MIB-LB, which is located directly across the river.
- SR3A-brick is closest to Aroclor 1260.
- A-SFB and B-MIB-RB are closest to Aroclor 1254.
- A-SG-LB and SG (also on the left bank, but further downstream) overlap in the PCA whereas A-SG-RB, located directly across the river from A-SG-LB is distanced away from A-SG-LB and SG.

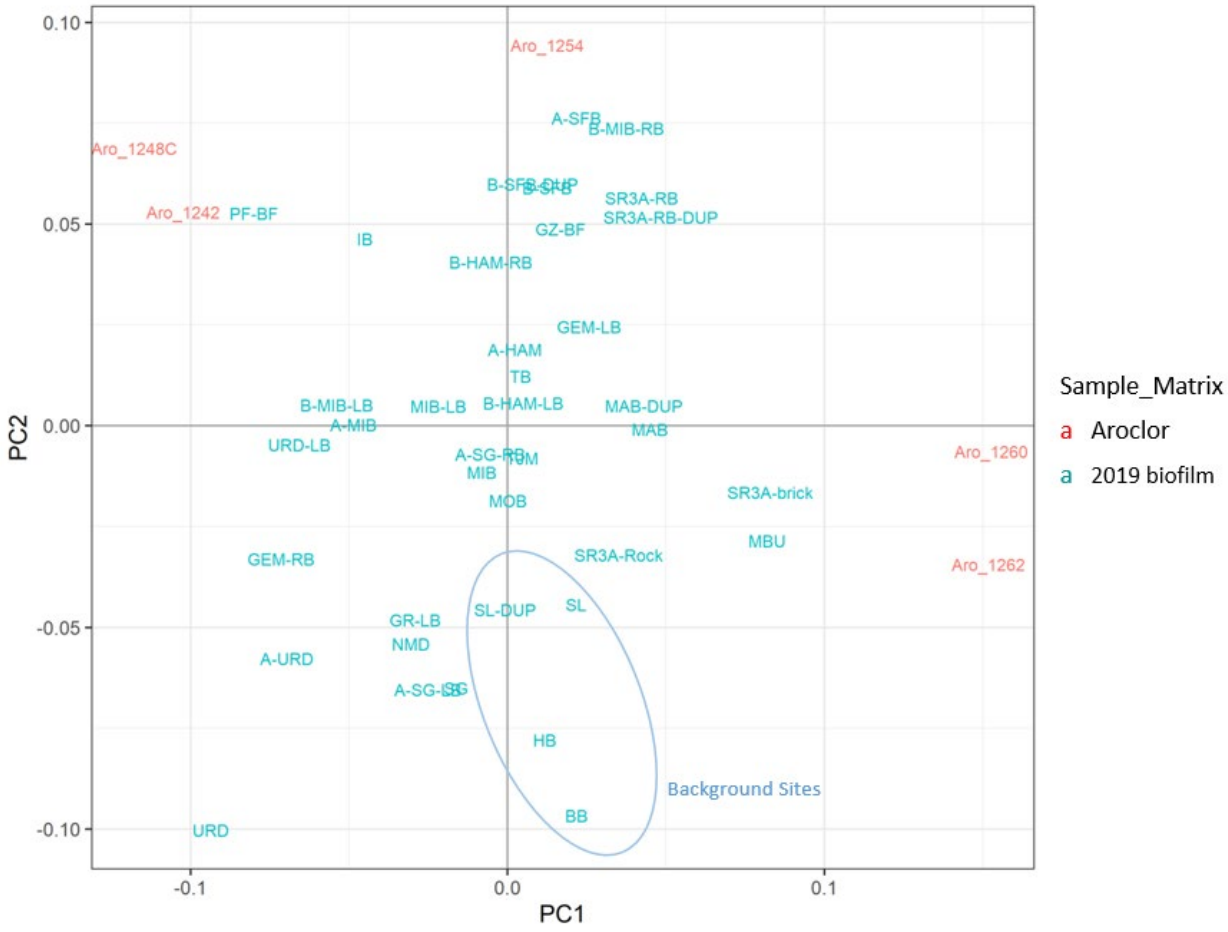

Figure 17. PCA Showing Similarities in Congener Patterns between 2019 Biofilm and Aroclors.

Confirmed and Suspected Sources of PCBs

The following discussion details each of the confirmed or suspected source areas for PCBs based on the results of the 2018 and 2019 screening study. The discussion starts at the Mirabeau source area and moves downstream. The focus is on each location having site-specific sources, but it is also important to recognize that (1) there is a continuum of contamination and (2) a particular site also reflects both what is coming from upstream and what is coming in directly to the site.

Mirabeau Source Area

Mirabeau (MBU) was a suspected PCB source area prior to the screening study and was confirmed by the results of the biofilm sampling in both 2018 and 2019. MBU is the first sampling location downstream of the background sites SL, HB, and BB. Total PCB concentrations at MBU were a factor of 2 – 4 times that of the background sites both sampling years (Figure 18). Homolog patterns in the MBU biofilm samples from both sampling years indicated a higher percentage of the heavier chlorinated homologs Hepta-, Octa-, and Nona-, compared to the background sites (Figure 8). The PCA also indicated that MBU was most similar to Aroclor 1262 (Figure 17).

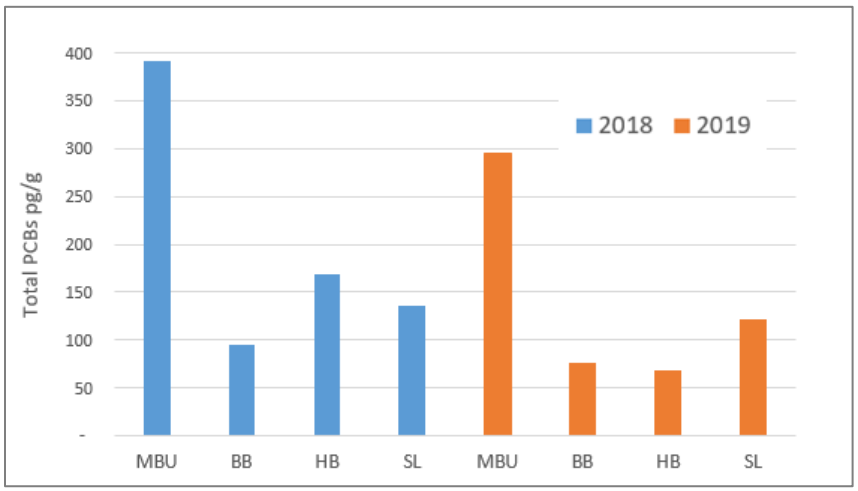

Figure 18. Total PCBs in Biofilm at Mirabeau and the Background Sites.

It is suspected that PCB-contaminated groundwater upgradient of the MBU site may be the source of the increase in higher-chlorinated PCBs in the biofilm samples there. This was confirmed by Tetra Tech, an EPA contractor (Tetra Tech 2021). Tetra Tech conducted an analysis using Ecology's 2018 biofilm data, Kaiser Trentwood's (Kaiser) upgradient groundwater well data and surface water data collected by LimnoTech. They found that the homolog patterns in the biofilm sample at MBU closely matched the groundwater homolog patterns in Kaiser's upgradient well. Previous research on water-biofilm bioconcentration factors for PCBs suggest that the congener distributions between co-located water and biofilm samples are very similar (Hobbs et al., 2019).

The PCBs in Kaiser's upgradient well could be coming from several potential sources in the Spokane Industrial Park. Further investigation is needed to pinpoint a source or sources in this area. Tetra Tech estimated that the average PCB load during the August low-flow time period to the Spokane River segment between Sullivan Road (downstream of the BB background biofilm

site) and Mirabeau was 12.0 mg/day. In contrast, Tetra Tech estimated the average PCB load during the August low-flow time period to the Spokane River at Plantes Ferry (downstream of the Kaiser PCB groundwater plume) to be 353 mg/day (Tetra Tech 2021).

Plantes Ferry Source Area

LimnoTech (2016) documented the PCB groundwater plume from Kaiser effecting the Spokane River prior to the 2018-2019 screening study. Sediment and biofilm from the Plantes Ferry sampling locations (PF-SED and PF-BF) confirmed that there is a clear signal that a PCB source is influencing this segment of the river during the August low-flow period.

Figure 19 shows that biofilm from Plantes Ferry (PF - 2018 and PF - 2019) have a different homolog signature with an increase of Tri-, Tetra- and Penta- compared to the closest upstream sites (MBU and BB). Tetra- made up almost 40% of the total homolog distribution in both the 2018 and 2019 biofilm. The sediment sample (PF - SED) had the same homolog pattern. Tri- and Tetra- homologs make up more than 70% of Aroclors 1242 and 1248 (Wischkaemper et al. 2013). Tri- and Tetra- are the main homologs found in the Kaiser groundwater plume (Tetra Tech 2021). Additionally, the PCA placed the PF biofilm congener results from 2019 directly adjacent to Aroclor 1242 and close to Aroclor 1248 (Figure 17).

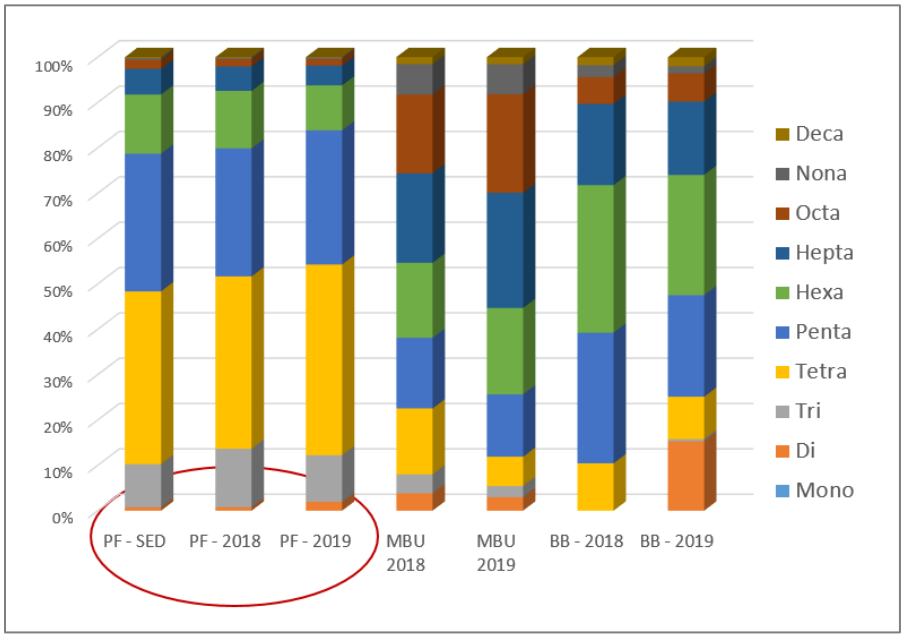

Figure 19. PCB Homolog Patterns at Plantes Ferry and other Upstream Sites.

Upriver Dam

The Upriver Dam (URD) sampling site, located just below Upriver Dam on the right bank, was originally chosen for sampling biofilm in 2018 because of previous PCB clean-up activities at the Dam and upstream of the Dam at Donkey Island. PCB-laden sediments behind the Dam were capped in 2006 and sediments at Donkey Island were excavated and backfilled in 2007 (Ecology 2007).

Results of the 2018 biofilm sampling indicated a moderate peak of total PCBs at URD. Total PCBs at URD were 1400 pg/g, slightly above the 2018 study median biofilm concentration of 1000 pg/g. The 2018 results also indicated a two-fold increase in total PCB concentrations compared to PF, the closest upstream biofilm site (Figure 20). Thus, two additional biofilm sites, A-URD and URD-LB, were added in 2019 to gain a better understanding of PCB concentrations in the Upriver area. A-URD is located about 0.8 km upstream of the Dam along the left bank of the river where it is ponded (Figure 3). URD-LB is located on the left bank of the river directly across the river from URD.

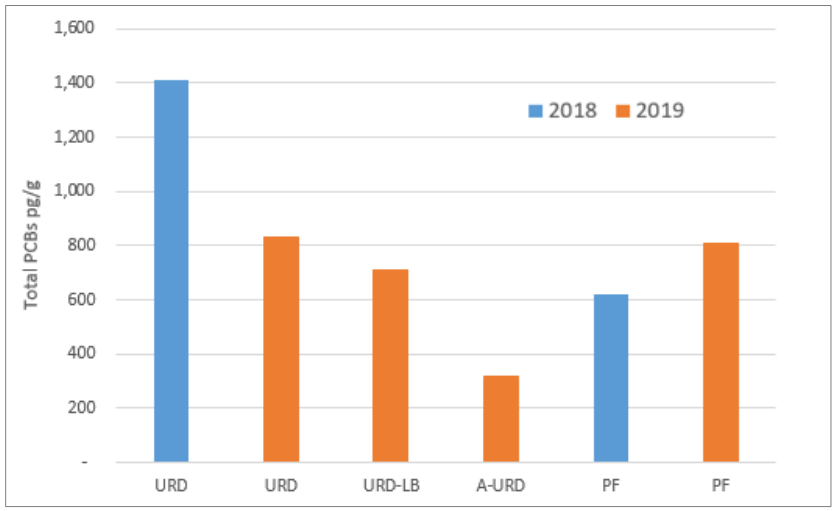

Figure 20. Total PCBs in Biofilm at the Upriver Dam and Plantes Ferry Sites.

The 2019 biofilm results showed that total PCB concentrations were roughly the same at both URD and PF (~800 pg/g) unlike the 2018 biofilm samples (Figure 20). Differences in homolog patterns at all 3 Upriver Dam locations were not very distinguishable (see Figure 7), but were all distanced from each other in the congener PCA (Figure 17).

GE-Mission Source Area

Biofilm results at GE-Mission Left Bank (GEM-LB) and GE-Mission Right Bank (GEM-RB) revealed that the two sites had both differing total PCB concentrations and homolog patterns from each other even though they are located on the same river transect. This pattern was clear in both 2018 and 2019. It was suspected that the GE clean-up site (Facility Site ID 630) could be a source of PCBs to GEM-LB via groundwater entering from the left bank of the river. A review of the groundwater well data from the clean-up site confirmed that the GE clean-up site is a likely source of PCBs to GEM-LB.

Figure 21 indicates the general groundwater flow direction along with the GE clean-up site monitoring wells (dark blue circles) and the biofilm collection sites (green pins). Total PCB concentrations were twice as high in biofilm along the left bank where groundwater enters the river. Homolog patterns were consistently different though the biofilm sites were along the same cross-sectional area of the river. The PCA analyses also confirmed that the two sites had different congener patterns (Figures 16 and 17).

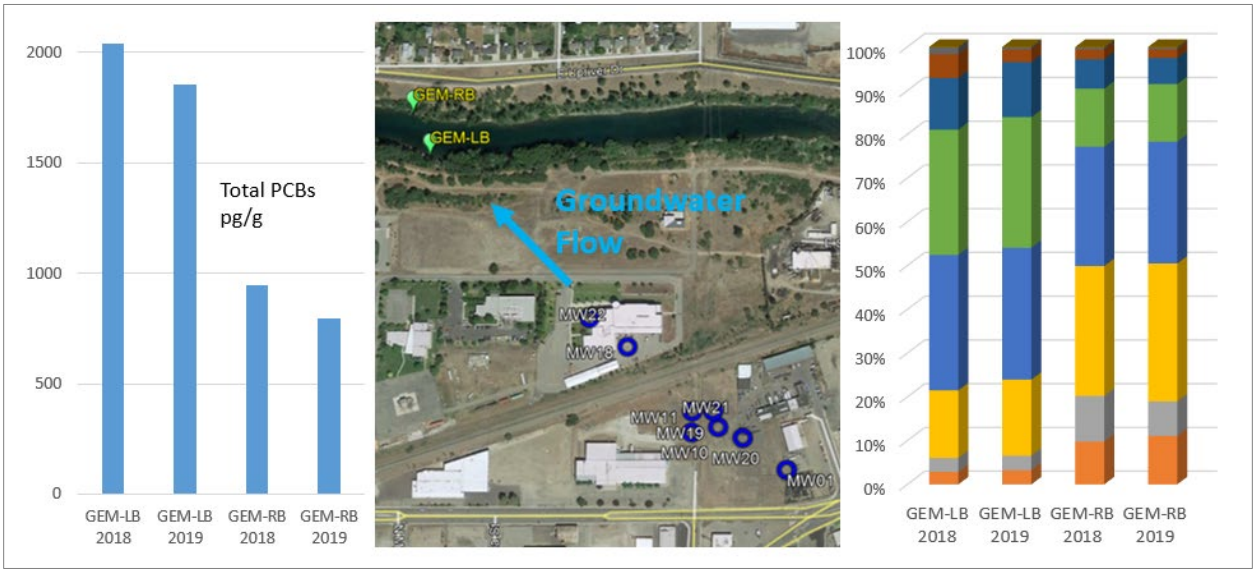

Figure 21. GEM-LB and GEM-RB PCB Biofilm Results with Map Showing GE Cleanup-Site Monitoring Wells and General Groundwater Flow Direction.

Further evidence that PCB contamination from groundwater at the GE cleanup-site is influencing the river is shown in Figure 22. PCBs have been routinely detected at GE site monitoring well MW-18, and homolog patterns show that the PCBs in the groundwater there are dominated by Aroclor 1260. Biofilm site GEM-LB homolog patterns do not look much like MW-18; however, when we averaged the results of GEM-RB data (representing PCBs present in surface water from upstream) with MW-18 groundwater data, the result is a homolog pattern that looks similar to GEM-LB.

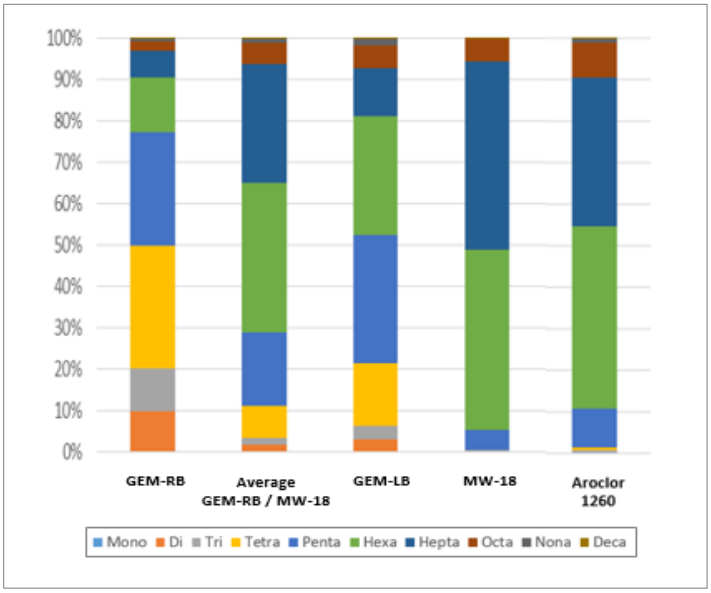

Figure 22. Homolog Patterns at GEM Biofilm Sites Compared to GE Groundwater and Aroclors.

Below East Mission Avenue Bridge

The Mission Bridge site (MIB) was originally chosen for sampling in 2018 as a potential source area. Total PCB concentrations were the third highest at this site in the 2018 biofilm, thus four additional sites were added in 2019 to bracket MIB (Figure 5). The 2019 results indicated that the samples located along the right bank (A-MIB, MIB, and B-MIB-RB) tended to have higher total PCBs compared to the left bank samples (MIB-LB and B-MIB-LB). Total PCBs at B-MIB-RB were higher than the other sampling locations in this reach by a factor of 3 to 20 (Figure 23). Homolog patterns also appeared different at B-MIB-RB with an increase in Penta- and Hexa-. Additionally, the PCA also showed B-MIB-RB spaced apart from the other nearby sampling locations (Figure 17). These differences are especially notable when B-MIB-RB is compared to B-MIB-LB which is located directly across river. B-MIB-RB fell close to Aroclor 1254 in the PCA, suggesting that there could be a source of Aroclor 1254 somewhere near B-MIB-RB.

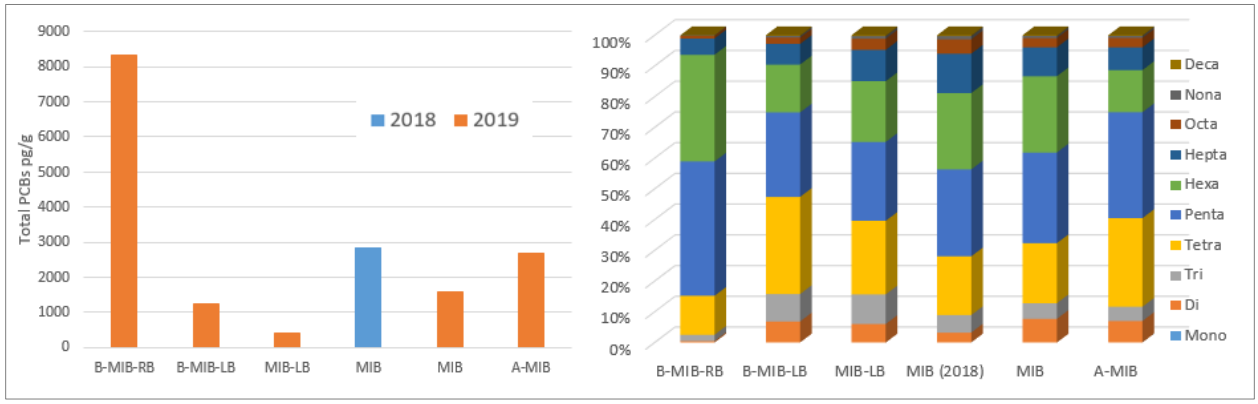

Figure 23. PCB Totals and Homologs at the Near Mission Bridge.

Mission Reach Source Area

The SR3A sampling site was originally chosen for biofilm sampling in 2018 due to its proximity to the City Parcel clean-up site (Facility Site ID 650). SR3A is located along the left bank of the Spokane River about 100 m upstream of East Trent Ave Bridge. The exceptionally high concentration of PCBs found in the 2018 biofilm at SR3A prompted the addition of eight additional sampling locations in 2019. The additional sites from upstream moving downstream include: IB, SR3A-RB (across the river from SR3A on the right bank), TB, A-HAM, B-HAM-RB, B-HAM-LB, A-SFB and B-SFB (Figure 5). This area is referred to as the "Mission Reach" for the screening study.

In 2019, the highest total PCB concentration found was not at SR3A, but rather at SR3A-RB located directly across the river from SR3A (Figure 5). Rocks and bricks were scraped separately at SR3A (LB) and were formed into separate biofilm samples (SR3A-Rock and SR3A-Brick) in 2019 to test whether scraped bricks in 2018 could help explain the elevated PCBs in biofilm found there. There was some variation with total PCB concentrations (13,100 versus 4,900 pg/g) and homolog patterns between the brick and rock samples, but not enough to be different from the variation among all the other Mission Reach samples in 2019 (Figures 4 and 24).

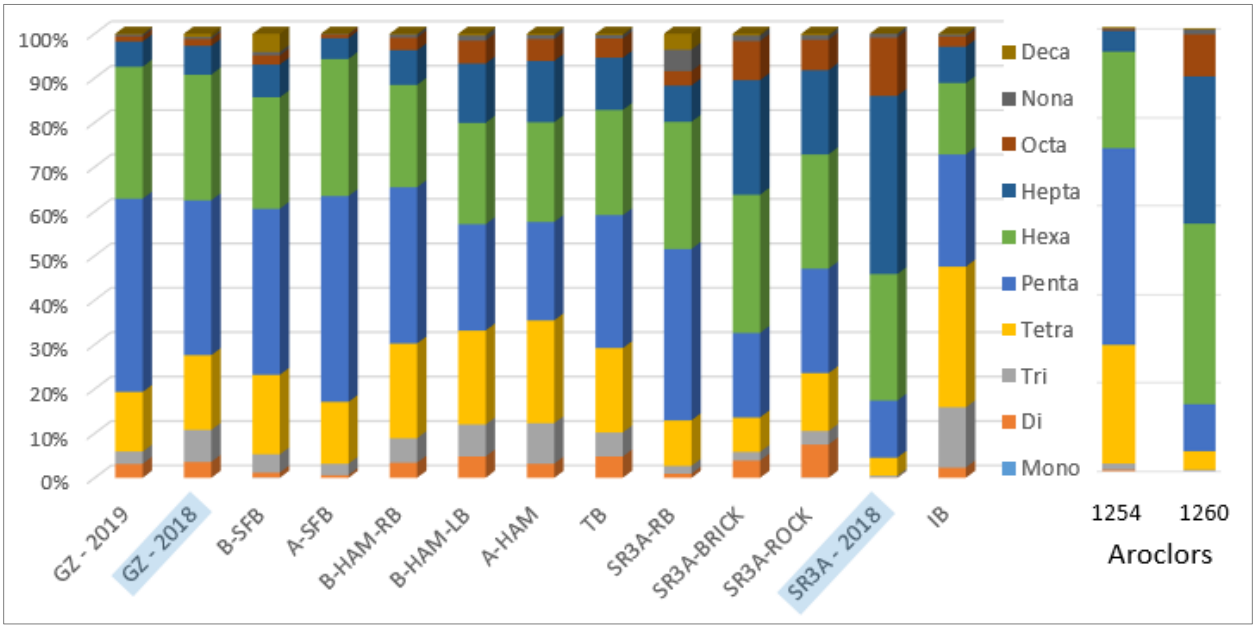

Figure 24. PCB Homologs in Mission Reach Biofilm Samples (*2018 samples shaded blue*) Compared to Aroclors 1254 and 1260.

The homolog pattern for SR3A was dissimilar from any of the other sites sampled in 2018 and looked similar to Aroclor 1260 (Figure 24). In 2019, the homolog patterns at SR3A-Brick and SR3A-Rock looked more like SR3A in 2018 and Aroclor 1260 than any of the other Mission Reach sites with more Hepta- and Octa- and less penta-. PCA congener analysis for the 2019 samples also showed that SR3A-Brick and SR3A-Rock plotted near Aroclor 1260 (Figure 17).

SR3A-RB had a homolog pattern that looked most like Aroclor 1254, but also had more of the heavier homologs Nona- and Deca- compared to SR3A (2018) and SR3A-Brick and SR3A-Rock (Figure 24). Nona- and Deca- are found in Aroclor 1268. SR3A-RB, A-SFB, B-SFB, and GZ all plot closest to Aroclor 1254 in the congener PCA for the 2019 biofilm samples (Figure 17).

The Mission Reach has historically had some of the highest PCB concentrations in fish tissue and sediments in the Spokane River (Seiders et al. 2014 and Serdar et al. 2011). Biofilm results suggest that there may be multiple sources of Aroclors in this reach with a source of Aroclor 1260 possibly originating near SR3A-left bank and Aroclor 1254 at SR3A-right bank and some of the other sites downstream. Aroclor 1268 or some other source of heavier congeners may also be contributing to the Mission Reach.

Hangman Creek

Biofilm and sediment (HM-BF and HM-SED) were collected in 2018 at the same location in Hangman Creek where PCBs have been sampled for surface water as part of the synoptic surveys funded by SRRTTF (LimnoTech 2016). LimnoTech found Hangman Creek to be a source of PCBs to the Spokane River with estimated loads ranging from near zero to 215 mg/day (LimnoTech 2016). Ecology did not sample HM-BF in 2019.

Total PCB concentrations at HM-BF were 1200 pg/g, slightly above the 2018 study median biofilm concentration of 1000 pg/g, demonstrating that the creek does contribute PCBs to the

Spokane River. HM-BF also had a different homolog signature compared to SG, indicating that PCB sources are different between the two waterbodies.

Unlike the Plantes Ferry sediment and biofilm, the homolog patterns between the sediments and biofilm in Hangman Creek were quite different (Figure 25).

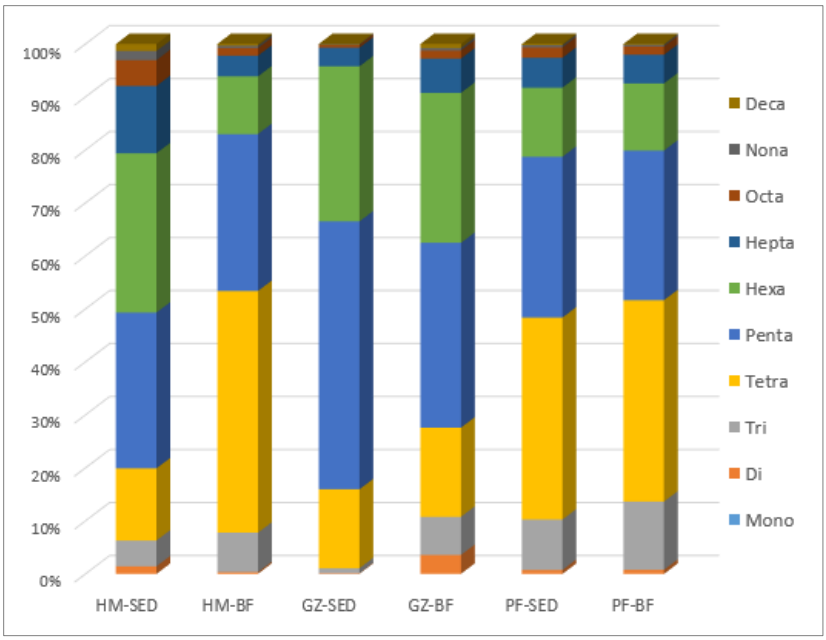

Figure 25. Homolog Patterns at Sites with both Sediments and Biofilm.

Spokane Gage Area

Biofilm at the Spokane Gage (SG) were collected at the same location where PCBs have been sampled for surface water as part of the SRRTTF synoptic surveys (LimnoTech 2016). The second highest concentration of PCBs in biofilm (5,600 pg/g) was found here in 2018. Several sampling locations were added in 2019 to hone in on a possible source near SG. A-SG-RB and A-SG-LB were added 0.5 km upstream of SG on the right and left banks, directly across the river from each other (Figure 3). MAB was added even further upstream (1.1 km) from SG along the left bank and just downstream of Maple Street Bridge by Peaceful Valley Park.

Both total PCB concentrations and homolog patterns in biofilm were quite different at the SG sampling site between 2018 and 2019 (Figure 26). The 2019 biofilm data showed that total PCB concentrations and homolog patterns were somewhat similar at all four sampling sites in this reach: MAB, A-SG-LB, A-SG-RB and SG. The PCA was able to determine a few subtler patterns with SG and A-SG-LB overlapping, indicating nearly identical congener patterns, while MAB and A-SG-RB were somewhat dissimilar (Figure 17).

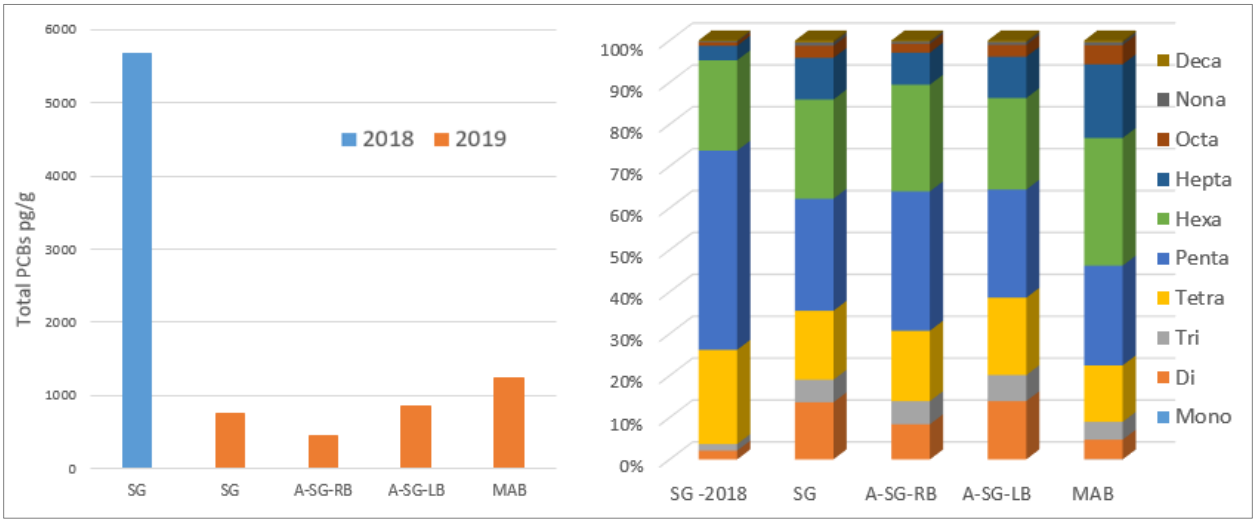

Figure 26. PCB Totals and Homologs at the Spokane Gage Sampling Sites.

Carbon and Nitrogen Isotopes

Stable isotopes of carbon (^{13}C) and nitrogen (^{15}N) were analyzed in the biofilm and macroinvertebrate samples. Only the ^{15}N results are discussed for the current report, but data for both isotopes can be used to support future efforts in understanding the aquatic food webs of the Spokane River.

The stable isotopes of nitrogen are ^{14}N and ^{15}N. More than 99% of naturally occurring nitrogen is ^{14}N with the remainder being ^{15}N. The basis for using the N stable isotope ratio ($\delta^{15}N$) as a measurement of trophic level is the enrichment of organisms with the heavier isotope (^{15}N) when moving up the food chain. Trophic enrichment is typically on the order of 3.4‰ (Post 2002); at the SG site, we saw an enrichment of $\delta^{15}N$ of about 2.6‰ between biofilm and caddisfly larvae, and an enrichment of 3.2‰ at the GEM site. This stable isotope data may be useful in future efforts to understand and model the food web in sections of the Spokane River.

Changes in $\delta^{15}N$ can also be used to assess differences in the nutrient sources to organisms such as biofilm (Pastor et al. 2013). Hobbs and Friese (2016) suggested that a trend of $\delta^{15}N$ enrichment in the lower Wenatchee River could be due to inorganic nitrogen (nitrate; NO3 and ammonium; NH4) inputs from fertilized lands and wastewater treatment plants.

Figure 27 shows fluctuations of $\delta^{15}N$ in the biofilm from the Spokane River in 2018 and 2019. Many of these fluctuations are likely due to changes in nitrogen sources. For example, $\delta^{15}N$ levels drop dramatically at the MBU site compared to the background biofilm sites (SL, HB, and BB). This is probably because upstream of MBU the river shifts from surface water mainly coming from Lake Coeur d'Alene to groundwater from the aquifer. Hangman Creek (HM-BF) had a much higher level of ^{15}N in 2018 (it was not sampled in 2019) compared to the Spokane River both above (SG) and below (TJM) the creek's confluence with the Spokane River. HM-BF is at the downstream end of the Hangman Creek watershed, a watershed that is dominated by farming and agriculture (Andrew et al. 2017).

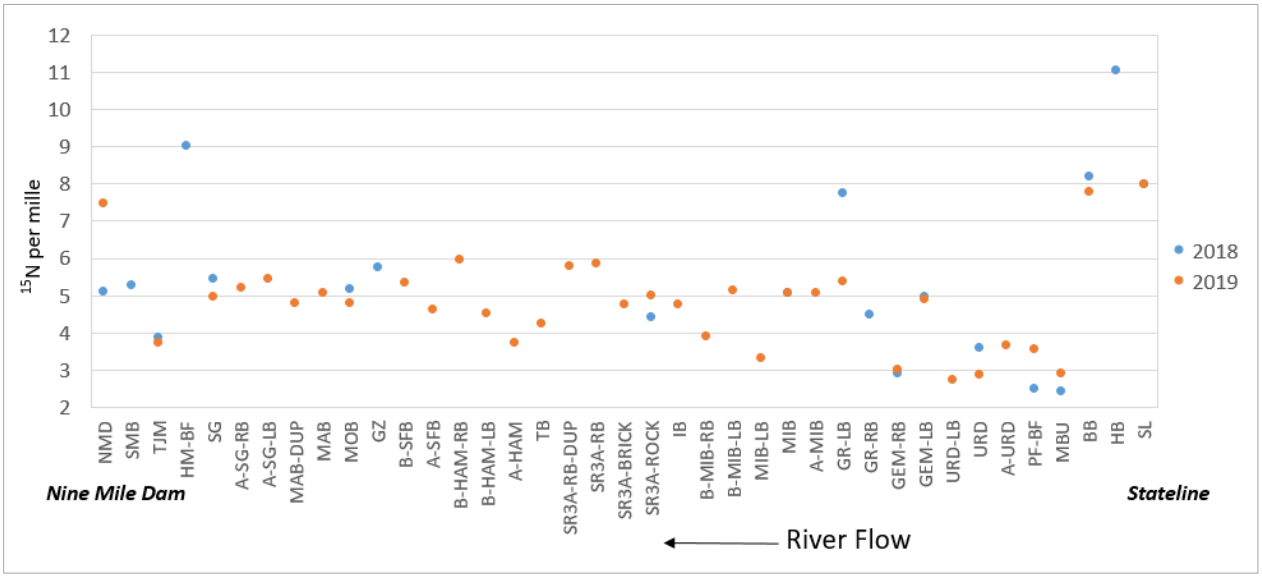

Figure 27. ^{15}Nitrogen Concentrations in Biofilm Samples.

Bioaccumulation of PCBs in Macroinvertebrates

Macroinvertebrates (caddisflies) were analyzed for PCBs in 2018 at the GEM-RB and SG sampling locations where biofilm were also sampled. A side-by-side comparison of the homolog patterns between the caddisflies and biofilm at these sites indicate that the caddisflies are metabolizing PCBs (Figure 28). The homolog patterns are visibly different between the biofilm samples and also varied between the biofilm and the caddisflies at each site, while the caddisfly samples are very similar between both sites. During metabolism of PCBs some congeners are transformed and excreted from an organism while other congeners are stored in the organism (Grimm et al. 2015; Katagi and Tanaka 2016). Thus, many of the same congeners will bioaccumulate in an organism while others do not, giving specific species similar congener and homolog patterns.

Rodenburg and Delistraty (2019) found that PCB fingerprints in co-located sediment and benthic biota at the Portland Harbor Superfund Site and the ratio between the coeluting congener pairs 147+149 and 153+168 was a good indication of PCB metabolism. For sediments the ratio of 147+149/153+168 was close to 1.0 and for benthic biota it was around 0.5 depending on the specific organism. On a bar graph, a ratio of 1.0 looks like twin columns of the same height and a ratio of 0.5 looks lopsided with the 153+168 tower twice the height of the 147+149 tower.

For the two Spokane River locations where both biofilm and macroinvertebrates were collected in 2018 (SG and GEM-RB), the congener ratios were compared (Figure 29). Though too small of a dataset (n=2) to be certain, the ratios indicate that there is metabolism happening in the caddisfly samples and little to no metabolism in the biofilm.

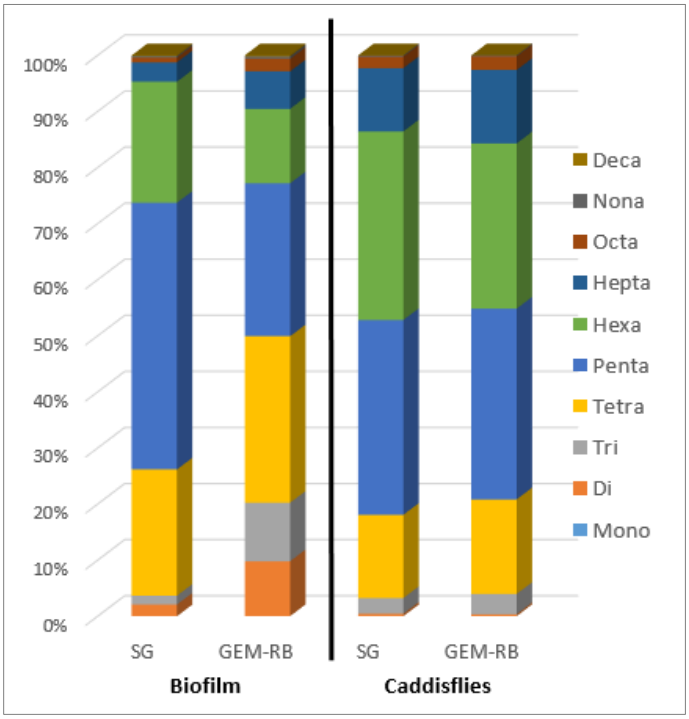

Figure 28. Homolog Patterns in Biofilm and Macroinvertebrates.

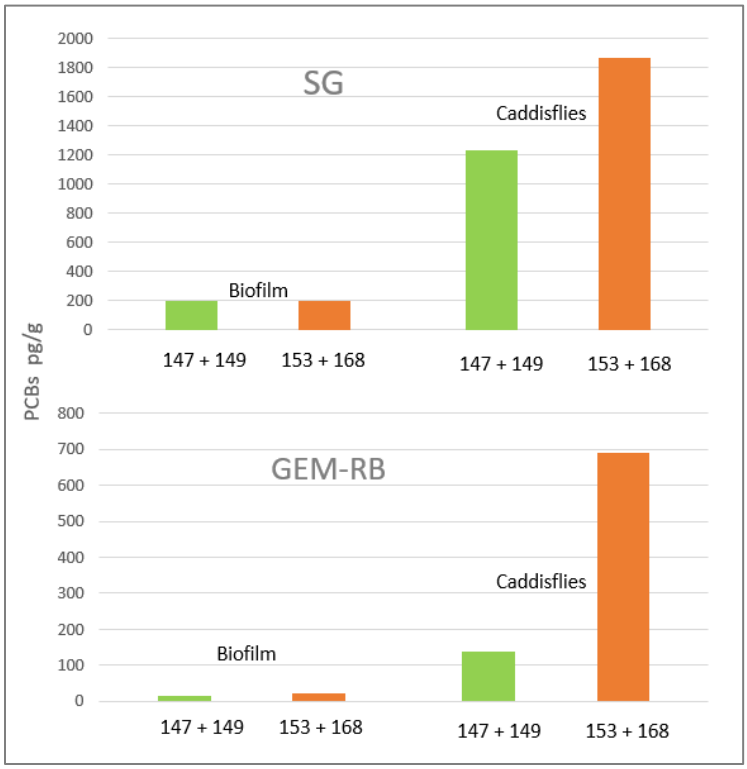

Figure 29. Comparison of PCB Congener Metabolism in Biofilm and Macroinvertebrates.

Conclusions

Results of this 2018-2019 study support the following conclusions:

- Biofilm were a useful tool for both confirming suspected source areas of PCBs and for identifying new source areas of PCBs to the Spokane River for the study area (between the state line with Idaho and Nine Mile Dam). A combination of comparing the total PCB concentrations as well as homolog and congener patterns between monitoring locations allowed for the identification of specific source areas.
- The highest levels of PCBs in biofilm were found in the Mission Reach, a 2.5 km section of the Spokane River from East Mission Avenue Bridge downstream to Gonzaga University. In 2018, total PCBs at monitoring site SR3A, just upstream of East Trent Avenue Bridge along the *left river bank*, were orders of magnitude higher than the rest of the monitoring sites. In 2019, the highest concentration was found at SR3A-RB along the *right bank* directly across the river from SR3A. Homolog and congener patterns suggest that there may be multiple sources of Aroclors in the Mission Reach with a source of Aroclor 1260 possibly originating near SR3A (*left river bank*) and Aroclor 1254 at SR3A-RB (*right river bank*) and some of the other Mission Reach sites further downstream. Aroclor 1268 or another source of heavier congeners may also be contributing to the Mission Reach.
- Other identified source locations were much lower in PCBs compared to the Mission Reach but still elevated relative to background reference locations. From upstream moving downstream, these other source areas include:
  - **MBU** (near Mirabeau Park) – probable source: Spokane Industrial Park
  - **PF** (Plantes Ferry) – known source: Kaiser Clean-up site
  - **GEM-LB** (GE Mission, left bank) – known source: GE Clean-up site
  - **B-MIB-RB** (below East Mission Avenue Bridge, right bank) – source unknown
  - **HM** (Hangman Creek near confluence with the Spokane River) – source unknown
- Two other *Potential* source locations were also identified, but the PCB signal was either not as clear or could not be confirmed with additional biofilm sampling:
  - **URD** (below Upriver Dam, right bank)
  - **SG** (near the USGS flow gage upstream of the Sandifer Bridge, left bank)
- Due to the difficulty of locating fine sediments in the study area, sediments were collected at only three locations: PF (Plantes Ferry), GZ (Gonzaga), and HM (Hangman Creek). Total PCB concentrations were highest near Gonzaga at the downstream end of the Mission Reach. PCB congener patterns in sediments and biofilm from Plantes Ferry closely matched indicating the strength of the Aroclor 1242/1248 signal in the river there. Sediments from Gonzaga and Hangman Creek were more varied compared to their biofilm counterparts.
- Caddisflies and biofilm were collected at 2 locations: GEM-RB (GE Mission, right bank) and SG (Spokane Gage). Comparison of the congener patterns and stable nitrogen isotope ratios between the biofilm and caddisflies showed predictable patterns of bioaccumulation and indicated that PCBs were being metabolized in the caddisflies much more than the biofilm.

Recommendations

Results of this 2018-2019 study support the following recommendations:

- Follow-up research in the Mission Reach of the Spokane River should be conducted to identify specific source(s) of PCBs, focusing on the SR3A and SR3A-RB locations. Sampling should be conducted during summer/dry season, low-flow conditions. The following actions have either already taken place or are planned for the Mission Reach, based on the findings of this 2018-2019 Spokane River biofilm study:
  - In September 2020, Ecology scientists floated the Mission Reach and recorded continuous temperature and conductivity at the surface and bottom of the right and left river banks to look for potential areas of groundwater flow in to the river (Stuart 2021). The results of the survey did not identify any significant areas of groundwater inflow into the Mission Reach. This corroborates the general understanding that the Mission Reach is a "losing stretch" where surface water generally flows into the aquifer. While this is true on a coarse scale, there is some sporadic well data and river elevation data from monitoring wells near Hamilton Street that indicate groundwater can enter the Mission Reach during select periods (Spokane County 2021).
  - In March 2021, LimnoTech (SRRTTF consultant) analyzed samples of submersed artificial fill material near the riverbanks at sites SR3A and SR3A-RB. They found that brick, concrete, and asphalt in the Mission Reach were likely not the primary causative source of elevated biofilm PCB concentrations in the Mission Reach (LimnoTech 2021a).
  - From August through September 2021, LimnoTech conducted a set of activities to help identify sources of PCBs in the Mission Reach (LimnoTech 2021b). The results will inform next steps for in the Mission Reach. LimnoTech's summer 2021 activities included:
    - Water column and sediment sampling
    - Sampling of an artesian well at the downstream end of Mission Reach
    - Sub-bottom object detection survey for items such as buried drums
    - Survey of the riverbank areas by a PCB detection dog
    - Scoping analysis of drive point piezometers for future groundwater study
  - In order to gain a better understanding of groundwater and surface water interactions in the Mission Reach, the Spokane County Water Resources Department is planning monthly collection of groundwater elevation data at five existing wells on the south side of the river near Hamilton Street Bridge (Spokane County 2021). The sampling will take place during October 2021 – April 2023.
- Additional biofilm sampling should be conducted at shorter intervals to help pinpoint PCB sources in the Mission Reach. LimnoTech conducted a geostatistical analysis of Ecology's biofilm samples and found that sampling distances of 100 – 125 feet in the direction of river flow are likely needed to locate a PCB source in the Mission Reach (LimnoTech 2020). In 2019, Ecology's closest monitoring distance in the Mission Reach was about 300 feet between sites SR3A and TB (Trent Bridge), and other distances between sampling sites in the Mission Reach were from 600 to 1,000 feet.

- Follow-up sampling and research could also be conducted for the other identified and potential PCB source areas in the Spokane River study area. These locations are listed below in order of recommended importance, along with suggested follow-up work:
  - **B-MIB-RB**: Higher density biofilm monitoring could be conducted near this site to identify where PCBs may be coming from. The 100 – 125-foot distance between sampling locations is recommend here since it is at the upstream boundary of the Mission Reach.
  - **GEM-LB**: While the GE Clean-up site has been determined to be the likely source of PCBs to the Spokane River at this site via contaminated groundwater, the overall load of the source is unknown. A groundwater load assessment using piezometers would help determine if the groundwater load was large enough to justify additional clean-up at the site or if natural attenuation is a practical course of action.
  - **MBU**: Groundwater from the Spokane Industrial Park is the likely source of PCBs at this site. The groundwater loading here appears small (12 mg/day) relative to the groundwater load at Plantes Ferry (353 mg/day). Follow-up actions for this site should be considered and prioritized compared to other source areas.
  - **URD**: There appears to be a weak PCB signal near URD (below Upriver Dam along the right bank). Higher density biofilm monitoring at this site could be conducted to isolate possible PCB sources. The river above the Dam is ponded and there are few areas with substrate suitable for biofilm collection except at A-URD where boulders have slid down into the river from a build-out of a primitive road along the steep bank.
  - **HM**: Hangman Creek is a variable source of PCBs to the Spokane River that has its own unique homolog and congener patterns. PCB loading from this site has been estimated to range from near zero to 215 mg/day (LimnoTech 2016). Research by Ecology's Urban Waters Program in Spokane suggests that stormwater may be the likely source of PCBs in Hangman Creek (Ross 2018). Biofilm could be used as a source-tracing tool in Hangman Creek during summer low-flow periods. However, biofilm may not be the best tool for identifying suspected PCB sources if PCBs are associated with stormwater runoff events that are more likely to occur during late fall through spring.
  - **SG**: In 2018, the second highest concentration of PCBs in biofilm was found at Spokane Gage, but that was not the case in 2019. The 2019 data suggest a possible weak PCB signal at this site. Higher density biofilm monitoring could be conducted near this site along with desk research into possible sources such as stormwater. Any follow-up work near this site should be a lower priority compared to other recommended follow-up actions in other sections of the river already mentioned.
  - **PF**: No additional work is recommended for the Plantes Ferry reach at this time since clean-up actions at the Kaiser Facility, the major known source of PCBs, are currently underway.
- The Spokane River is a complex riverine system. There are multiple dams, which create ponded reservoirs. In addition, there are river sections completely dominated by surface water from Lake Coeur d'Alene and other sections dominated by groundwater due to the large and active aquifer underneath. All of this complexity creates a diversity of habitats and thus a diversity of aquatic food webs. Additional study of food webs in the Spokane River

would help explain PCB concentrations in fish tissue; however, the food webs should be studied on a reach-by-reach basis beginning with the Mission Reach.

- Biofilm have proven to be an effective tool for PCB source identification. It is important to consider their strengths and weaknesses as a tool for future source assessment and contaminant characterization in waterbodies. Because biofilm are collected near riverbanks in shallow water, they can represent localized inputs from groundwater and upland sources in addition to ambient river conditions. Biofilm may not represent a homogenized mix of the entire river cross-section, especially in large river systems. An example of localized representation is the differences seen in PCB homolog patterns at the left bank (GEM-LB) and right bank (GEM-RB) of the monitoring sites near the GE cleanup site during this 2018-2019 study.

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Appendices

Appendix A. Sampling Location Information

Table A-1. Sampling Locations and Rationale for Sampling.

Site ID	Site Name	Year	Sample Matrix	Bank	Latitude*	Longitude*	Groundwater Interaction	Rationale for Sampling
SL	Stateline	2018	Biofilm	Left	49.69861	-117.04626	Losing	Reference Location
SL	Stateline	2019	Biofilm	"	"	"	"	"
HB	Above Harvard Bridge	2018	Biofilm	Right	47.68336	-117.11036	Losing	Reference Location
HB	Above Harvard Bridge	2019	Biofilm	"	"	"	"	"
BB	Above Barker Bridge	2018	Biofilm	Right	47.67835	-117.1533	Losing	Reference Location. Site coincides with SRRTTF Synoptic Survey site SR-9.
BB	Above Barker Bridge	2019	Biofilm	"	"	"	"	"
MBU	Mirabeau	2018	Biofilm	Right	47.67928	-117.21422	Gaining	Known source. Location coincides with SRRTTF Synoptic Survey site SR-8a.
MBU	Mirabeau	2019	Biofilm	"	"	"	"	Confirm 2018 results
PF	Plantes Ferry	2018	Biofilm, Sediment	Right	47.69734 (Biofilm) 47.693056 (Sediment)	-117.24207 (Biofilm) - 117.25027 (Sediment)	Gaining	Known source. Biofilm location coincides with SRRTTF Synoptic Survey site SR-7: Spokane River - Trent Bridge Gage (Plantes Ferry Park) - 12421500
PF	Plantes Ferry	2019	Biofilm	"	"	"	"	Confirm 2018 results
A-URD	Above Upriver Dam	2019	Biofilm	Left	47.6871582	-117.319545	Losing	Bracket URD
URD	Below Upriver Dam	2018	Biofilm	Right	47.68106	-117.33459	Gaining	Known source. Location coincides with SRRTTF Synoptic Survey site SR-5a. Right bank.
URD	Below Upriver Dam	2019	Biofilm	Right	"	"	"	Possible source area based on 2018 sampling
URD-LB	Below Upriver Dam-Left Bank	2019	Biofilm	Left	47.6810248	-117.333622	Gaining	Bracket URD. Left bank across from URD.

Site ID	Site Name	Year	Sample Matrix	Bank	Latitude*	Longitude*	Groundwater Interaction	Rationale for Sampling
GEM-LB	GE Mission-Left Bank	2018	Biofilm	Left	47.6759	-117.35124	Gaining	Potential groundwater source area from GE - Left bank
GEM-LB	GE Mission-Left Bank	2019	Biofilm	Left	"	"	"	Confirm 2018 results
GEM-RB	GE Mission-Right Bank	2018	Biofilm, Inverte-brates	Right	47.67641	-117.35155	Gaining	Potential groundwater source area from GE - Right bank
GEM-RB	GE Mission-Right Bank	2019	Biofilm	Right	"	"	"	Confirm 2018 results
GR-LB	Green Street-Left Bank	2018	Biofilm	Left	47.67815	-117.36348	Transition	Potential source area. Location coincides with SRRTTF Synoptic Survey site SR-4: Spokane River-Greene Street Gage - 12422000
GR-LB	Green Street-Left Bank	2019	Biofilm	"	"	"	"	Confirm 2018 results
GR-RB	Green Street-Right Bank	2018	Biofilm	Right	47.6783	-117.36279	Transition	Potential source area. Location coincides with SRRTTF Synoptic Survey site SR-4: Spokane River-Greene Street Gage - 12422000
A-MIB	Above Mission Bridge	2019	Biofilm	Right	47.6764298	-117.382663	Losing	Bracket MIB
MIB	Mission Bridge	2018	Biofilm	Right	47.67211	-117.3881	Losing	Potential source area
MIB	Mission Bridge	2019	Biofilm	"	"	"	"	Possible source area based on 2018 sampling
MIB-LB	Mission Bridge-Left Bank	2019	Biofilm	Left	47.6719968	-117.387084	Losing	Bracket MIB
B-MIB-LB	Below Mission Bridge-Left Bank	2019	Biofilm	Left	47.6687158	-117.388992	Losing	Bracket MIB
B-MIB-RB	Below Mission Bridge-Right Bank	2019	Biofilm	Right	47.6688918	-117.389697	Losing	Bracket MIB
IB	Iron Bridge	2019	Biofilm	Left	47.6645768	-117.39131	Losing	Bracket SR3A
SR3A	SR3A	2018	Biofilm	Left	47.66285	-117.39217	Losing	Potential source from City Parcel. Left bank.

Site ID	Site Name	Year	Sample Matrix	Bank	Latitude*	Longitude*	Groundwater Interaction	Rationale for Sampling
SR3A	SR3A	2019	Biofilm	"	"	"	"	Confirm 2018 results. Separate collections from rocks (SR3A-rock) and bricks (SR3A-brick)
SR3A-RB	SR3A-Right Bank	2019	Biofilm	Right	47.6630278	-117.393229	Losing	Bracket SR3A
TB	Trent Bridge	2019	Biofilm	Left	47.6620728	-117.39273	Losing	Bracket SR3A
A-HAM	Above Hamilton Bridge	2019	Biofilm	Left	47.6607808	-117.394099	Losing	Bracket SR3A
B-HAM-LB	Below Hamilton Bridge-Left Bank	2019	Biofilm	Left	47.6591588	-117.397535	Losing	Bracket SR3A
B-HAM-RB	Below Hamilton Bridge-Right Bank	2019	Biofilm	Right	47.6599668	-117.397757	Losing	Bracket SR3A
A-SFB	Above Spokane Falls Blvd	2019	Biofilm	Left	47.6606598	-117.400419	Losing	Bracket SR3A and GZ
B-SFB	Below Spokane Falls Blvd	2019	Biofilm	Left	47.6628088	-117.40298	Losing	Bracket SR3A and GZ
GZ	Gonzaga	2018	Biofilm, Sediment	Left	47.664	-117.40595	Losing	Potential source area
GZ	Gonzaga	2019	Biofilm	"	"	"	"	Confirm 2018 results
MOB	Monroe Bridge	2018	Biofilm	Left	47.65962	-117.42886	Minimal Interaction	Potential source area
MOB	Monroe Bridge	2019	Biofilm	"	"	"	"	Confirm 2018 results
MAB	Maple Bridge	2019	Biofilm	Left	47.6605428	-117.436184	Minimal Interaction	Bracket SG
A-SG-LB	Above Spokane Gage-Left Bank	2019	Biofilm	Left	47.6587578	-117.443548	Minimal Interaction	Bracket SG
A-SG-RB	Above Spokane Gage-Right Bank	2019	Biofilm	Right	47.6594198	-117.443605	Minimal Interaction	Bracket SG
SG	Spokane Gage	2018	Biofilm, Inverte-brates	Left	47.65879	-117.44981	Gaining	Location coincides with SRRTTF Synoptic Survey site SR-3: Spokane River - Spokane Gage - 12422500

Site ID	Site Name	Year	Sample Matrix	Bank	Latitude*	Longitude*	Groundwater Interaction	Rationale for Sampling
SG	Spokane Gage	2019	Biofilm	"	"	"	"	Possible source area based on 2018 sampling
HM	Hangman Creek	2018	Biofilm, Sediment	Left	47.65284	-117.44991	Gaining	Known source. Location coincides with SRRTTF Synoptic Survey site HC-1: Hangman Creek-Spokane River Confluence Gage - 12424000
TJM	TJ Meenach	2018	Biofilm	Right	47.67931	-117.45013	Gaining	Potential source
TJM	TJ Meenach	2019	Biofilm	"	"	"	"	Confirm 2018 results
SMB	Seven Mile Bridge	2018	Biofilm	Right	47.74098	-117.51913	Losing	Location bridging distance between NMD and TJM sampling sites and downstream of Riverside Wastewater Treatment Plant
NMD	Below Nine Mile Dam	2018	Biofilm	Right	47.77985	-117.54559	Gaining	Location coincides with SRRTTF Synoptic Survey site SR-1: Spokane River-Nine Mile Dam Gage - 12426000
NMD	Below Nine Mile Dam	2019	Biofilm	"	"	"	"	Confirm 2018 results

*Coordinates established using NAD83
SRRTTF = Spokane River Regional Toxics Task Force

Appendix B. Data Quality Tables

Table B-1. Measurement Quality Objectives (MQO) Evaluation.

Matrix	Analyte	Continuing Calibration Verification		Laboratory Control Standard/Blank Spike		Laboratory Control Standard Duplicate		Field Split		Method Blank Contamination (% PCB Congener Results Qualified)
		MQO (% Recovery)	Results Meeting MQO (%)	MQO (% Recovery)	Results Meeting MQO (%)	MQO (% Recovery)	Results Meeting MQO (%)	MQO (%)	Range [Median] (RPD)	
Biofilm	PCBs	50 - 150	99	50 - 150	99	50 - 150	95	<20	1-95 [21]	5
	Lipids	-	-	-	-	-	-	<20	0-21 [10]	-
	^{13}C	-	-	-	-	-	-	<20	0-13 [2]	-
	^{15}N	-	-	-	-	-	-	<20	0-64 [6]	-
Sediment	PCBs	50 - 150	97	50 - 150	100	50 - 150	98	<20	35	1
	TOC	-	-	75 - 125	100	-	-	<20	69	-
	Grain Size	-	-	-	-	-	-	<20	7-31 [10]	-
Invertebrates	PCBs	50 - 150	97	50 - 150	99	50 - 150	95	<20	2	9
	Lipids	-	-	-	-	-	-	<20	1	-
	^{13}C	-	-	-	-	-	-	<30	0-1 [1]	-
	^{15}N	-	-	-	-	-	-	<20	0-15 [8]	-

C = Carbon; N = Nitrogen
RPD = relative percent difference

Table B-2. Replicate Precision for Sediments.

Site	Date	Matrix	Replicate Type	Sample ID	Total PCBs	TOC	Gravel	Sand	Silt	Clay	Fines
					pg/g	%	%	%	%	%	%
GZ-SED	8/29/18	Sediment	Field Split	1809040-23	127382	0.75	16	75.5	7.5	1	8.5
				1809040-25	89770	1.54	21.8	70.3	6.8	1.1	7.9
				RPD	35%	69%	31%	7%	10%	10%	7%

RPD = relative percent difference
Fines = Silt + Clay fractions

Table B-3. Replicate Precision for Biofilm and Invertebrates.

Site	Date	Matrix	Replicate Type	Sample ID	Total PCBs	Lipids	^{13}C	^{15}N
					pg/g	%	per mille	per mille
URD	8/28/18	Biofilm	Field Split	1809040-06	1411	0.28	--	--
				1809040-20	1107	0.26	--	--
				RPD	**24%**	**7%**	--	--
GZ-BF	8/29/18	Biofilm	Field Split	1809040-13	2490	0.37	--	--
				1809040-21	7022	0.37	--	--
				RPD	**95%**	**0%**	--	--
SL	8/5/19	Biofilm	Lab Dup.	1908046-01	129	0.17	--	--
				1908046-01	114	0.16	--	--
				RPD	**12%**	**6%**	--	--
SR3A-*Rock*	8/7/19	Biofilm	Field Rep.	1908046-18	4878	0.21	--	--
SR3A-*Brick*				1908046-34	13106	0.23	--	--
				RPD	**92%**	**9%**	--	--
SR3A-RB	8/7/19	Biofilm	Field Split	1908046-19	33033	0.32	-20.35	5.86
				1908046-35	27627	0.26	-20.83	5.77
				RPD	**18%**	**21%**	**2%**	**2%**
B-SFB	8/7/19	Biofilm	Lab Dup.	1908046-25	8804	0.3	--	--
				1908046-25	8072	0.27	--	--
				RPD	**9%**	**11%**	--	--
MAB	8/8/19	Biofilm	Field Split	1908046-28	1253	0.25	-18.55	5.05
				1908046-36	1240	0.22	-19.05	4.80
				RPD	**1%**	**13%**	**3%**	**5%**
SG	8/30/18	Invert.	Field Split	1809040-28	24428	7.48	--	--
				1809040-30	24813	7.59	--	--
				RPD	**2%**	**1%**	--	--

-- Not Analyzed For; RPD = relative percent difference; Dup. = duplicate; Invert. = macroinvertebrates (caddisflies)

Appendix C. Data Tables and Qualitative Information

Table C-1. Total PCBs and Total Homolog Data

Site ID	Sample ID*	Matrix	Homolog Group										Total PCBs
			Mono	Di	Tri	Tetra	Penta	Hexa	Hepta	Octa	Nona	Deca	
SL	1809040-01	BF	-	-	0.1	16	39	44	23	8	4	3	136
HB	1809040-02	BF	-	9	21	28	39	38	21	8	3	2	168
BB	1809040-03	BF	-	-	-	10	27	31	17	6	2	2	95
MBU	1809040-04	BF	-	15	16	57	61	65	77	68	26	6	391
PF-BF	1809040-05	BF	-	5	80	235	174	78	34	10	2	0.8	618
URD	1809040-06	BF	-	207	153	417	328	164	97	33	8	3	1,411
URD-DUP	1809040-20	BF	-	174	119	308	256	142	69	30	7	2	1,107
GEM-LB	1809040-07	BF	0.3	58	65	316	632	585	242	111	32	2	2,042
GEM-RB	1809040-08	BF	-	93	99	281	258	126	64	21	4	2	948
GR-LB	1809040-09	BF	-	76	101	233	231	229	141	37	8	2	1,057
GR-RB	1809040-10	BF	-	75	90	248	225	221	155	48	8	2	1,070
MIB	1809040-11	BF	1	90	161	539	799	701	363	131	31	7	2,824
SR3A	1809040-12	BF	8	426	2,614	25,611	81,053	179,559	252,737	82,838	5,403	119	630,368
SR3A	1809040-12 (rex)	BF	1	399	1,686	10,622	25,211	47,970	50,097	13,154	1,044	165	150,350
GZ-BF	1809040-13	BF	-	89	180	419	868	704	162	38	12	19	2,490
GZ-BF-DUP	1809040-21	BF	-	216	2,924	1,840	1,072	728	176	49	13	5	7,022
MOB	1809040-14	BF	-	48	52	178	373	336	120	37	9	3	1,157
SG	1809040-15	BF	-	119	89	1,277	2,697	1,224	196	47	15	9	5,672
HM-BF	1809040-16	BF	-	4	90	548	356	131	47	17	5	4	1,201
TJM	1809040-17	BF	-	22	16	69	114	117	48	16	6	4	412
SMB	1809040-18	BF	-	100	25	115	193	179	87	31	9	5	744
NMD	1809040-19	BF	-	43	33	120	153	132	59	20	5	2	567
HM-SED	1809040-22	Sediment	-	19	65	180	390	398	168	64	23	17	1,325
GZ-SED	1809040-23	Sediment	5	156	1,205	18,982	64,377	37,269	4,515	663	148	62	127,382
GZ-SED-DUP	1809040-25	Sediment	7	241	1,377	13,086	43,617	27,363	3,401	484	131	63	89,770
PF-SED	1809040-24	Sediment	-	107	1,363	5,450	4,342	1,865	810	281	58	32	14,308
SG-INVERT	1809040-28	Inverts	1	106	685	3,624	8,483	8,213	2,760	495	52	8	24,428
SG-INVERT-DUP	1809040-30	Inverts	1	110	691	3,700	8,699	8,223	2,815	511	55	7	24,813
GEM-INVERT	1809040-29	Inverts	-	26	280	1,303	2,633	2,278	1,013	187	14	1	7,735
SL	1908046-01	BF	-	11	2	22	28	30	23	9	2	1	129
SL	1908046-01 (dup)	BF	-	12	6	19	28	28	13	5	2	1	114
HB	1908046-02	BF	-	9	0.1	10	16	17	10	3	1	1	68
BB	1908046-03	BF	-	12	0.4	7	17	20	12	5	1	2	76
MBU	1908046-04	BF	-	9	7	19	41	56	75	64	19	5	295
PF	1908046-05	BF	-	16	83	339	238	80	35	11	3	1	806

Site ID	Sample ID*	Matrix	Homolog Group										Total PCBs
			Mono	Di	Tri	Tetra	Penta	Hexa	Hepta	Octa	Nona	Deca	
A-URD	1908046-06	BF	-	44	34	102	66	40	21	10	2	0.8	320
URD	1908046-07	BF	-	153	76	252	188	95	46	18	4	2	833
URD-LB	1908046-08	BF	0.3	56	67	234	186	99	44	17	4	1	710
GEM-RB	1908046-09	BF	-	88	63	251	222	105	47	16	3	1	796
GEM-LB	1908046-10	BF	0.4	60	61	322	558	554	233	54	10	2	1,854
GR-LB	1908046-11	BF	-	74	48	138	151	131	58	16	3	1	619
A-MIB	1908046-12	BF	0.3	187	124	771	922	366	199	82	18	5	2,674
MIB	1908046-13	BF	-	123	82	312	472	397	151	48	11	4	1,599
MIB-LB	1908046-14	BF	-	24	39	97	103	80	41	15	3	1	403
B-MIB-LB	1908046-15	BF	-	84	109	386	336	190	82	25	7	3	1,222
B-MIB-RB	1908046-16	BF	0.3	39	169	1,058	3,638	2,889	442	72	13	3	8,324
IB	1908046-17	BF	0.3	30	180	419	335	213	109	30	6	2	1,326
SR3A-ROCK	1908046-18	BF	2	364	148	635	1,149	1,254	923	335	48	18	4,878
SR3A-BRICK	1908046-34	BF	1	509	256	1,015	2,495	4,077	3,382	1,153	167	52	13,106
SR3A-RB	1908046-19	BF	2	302	580	3,390	12,746	9,459	2,702	1,071	1,592	1,190	33,033
SR3A-RB-DUP	1908046-35	BF	2	285	557	2,977	10,635	8,095	3,305	1,430	301	41	27,627
TB	1908046-20	BF	0.2	108	121	427	672	532	264	98	18	7	2,247
A-HAM	1908046-21	BF	-	36	103	261	250	254	155	56	10	3	1,129
B-HAM-LB	1908046-22	BF	-	49	73	214	243	231	135	52	12	4	1,012
B-HAM-RB	1908046-23	BF	4	572	927	3,595	5,926	3,886	1,314	481	121	27	16,854
A-SFB	1908046-24	BF	0.2	83	345	1,893	6,286	4,189	640	103	22	7	13,567
B-SFB	1908046-25	BF	3	101	362	1,576	3,291	2,211	648	182	67	362	8,804
B-SFB	1908046-25 (dup)	BF	2	102	331	1,568	3,103	2,106	565	170	56	69	8,072
GZ	1908046-26	BF	0.2	99	88	425	1,379	941	180	38	13	6	3,169
MOB	1908046-27	BF	-	80	50	156	275	237	100	30	7	2	938
MAB	1908046-28	BF	0.2	59	53	169	298	381	220	57	9	5	1,253
MAB-DUP	1908046-36	BF	-	54	47	154	328	358	203	55	24	17	1,240
A-SG-LB	1908046-29	BF	-	119	53	158	221	187	85	24	6	3	856
A-SG-RB	1908046-30	BF	-	39	25	77	153	117	35	10	2	1	460
SG	1908046-31	BF	-	103	41	124	201	179	75	22	6	3	754
TJM	1908046-32	BF	-	21	16	54	83	77	34	11	4	2	301
NMD	1908046-33	BF	-	73	44	122	147	114	52	21	4	2	579

*The first two numbers of the Sample ID represent the year the data were collected (2018 or 2019)
BF = biofilm
Inverts = macroinvertebrates (caddisflies)
-DUP = split sample
(rex) = re-extracted and reanalyzed sample
(dup) = laboratory duplicate
- = no detected congeners in homolog total (only with Mono, Di and Tri)

Table C-2. Conventional Data and Carbon and Nitrogen Isotopes for Biofilm and Invertebrates.

Site	Sample Number	% Solids	Biomass g/cm^2 dry	% Organic Carbon†	% Lipids	^{13}C per mil	^{15}N per mil
SL	1809040-01	4	0.002251	14.89	0.18	-15.69	7.961
HB	1809040-02	1.9	0.000851	14.79	0.25	-15.55	11.03
BB	1809040-03	2.4	0.003696	17.51	0.2	-14.19	8.182
MBU	1809040-04	2.9	0.002704	10.67	0.25	-26.19	2.432
PF-BF	1809040-05	2.4	0.001274	10.55	0.32	-21.28	2.470
URD	1809040-06	2.2	0.001525	13.16	0.28	-21.84	3.580
URD-DUP	1809040-20	--	--	--	0.26	--	--
GEM-LB	1809040-07	4.4	0.002566	2.809	0.23	-18.68	4.953
GEM-RB	1809040-08	2.8	0.004729	5.790	0.26	-20.89	2.900
GEM-INVERT	1809040-29	NA	NA	NA	6.16	-27.86	6.143
GR-LB	1809040-09	2.6	0.003297	14.35	0.32	-21.28	7.721
GR-RB	1809040-10	1.1	0.001953	3.276	0.21	-21.49	4.463
MIB	1809040-11	2.3	0.001013	9.829	0.23	-24.64	5.075
SR3A	1809040-12	8	0.008937	6.585	0.32	-20.79	4.416
GZ-BF	1809040-13	3.4	0.003192	17.53	0.37	-17.11	5.738
GZ-BF-DUP	1809040-21	--	--	--	0.37	--	--
MOB	1809040-14	2.4	0.003826	17.22	0.37	-21.87	5.156
SG	1809040-15	5.1	0.005591	13.48	0.39	-18.20	5.429
SG-INVERT	1809040-28	NA	NA	NA	7.48	-26.77	7.957
SG-INVERT-DUP	1809040-30	NA	NA	NA	7.59	--	--
HM-BF	1809040-16	14.8	0.039128	9.267	0.23	-21.29	9.018
TJM	1809040-17	1.7	0.003048	14.63	0.24	-27.73	3.862
SMB	1809040-18	18.6	0.015028	2.285	0.28	-16.07	5.248
NMD	1809040-19	4.2	0.005021	6.820	0.31	-18.45	5.102
SL	1908046-01	4.8	0.001629	18.29	0.17	-14.11	7.984
HB	1908046-02	3.6	0.002307	--	0.17	--	--
BB	1908046-03	4.3	0.002804	14.27	0.1	-15.24	7.770
MBU	1908046-04	5.8	0.002530	15.46	0.1	-29.07	2.885
PF-BF	1908046-05	5.7	0.000797	16.89	0.22	-17.30	3.548
A-URD	1908046-06	5.1	0.004330	18.45	0.28	-16.42	3.660
URD-LB	1908046-08	3.6	0.005459	10.40	0.21	-25.90	2.873
URD	1908046-07	4.9	0.001133	13.07	0.22	-22.88	2.721
GEM-LB	1908046-10	22.3	0.015045	1.096	0.18	-21.85	4.888
GEM-RB	1908046-09	5	0.002170	14.05	0.18	-19.03	3.001
GR-LB	1908046-11	10.2	0.001421	25.27	0.23	-17.39	5.375
A-MIB	1908046-12	7.4	0.003860	8.940	0.21	-17.06	5.066
MIB	1908046-13	6.1	0.003946	4.880	0.15	-22.69	5.048

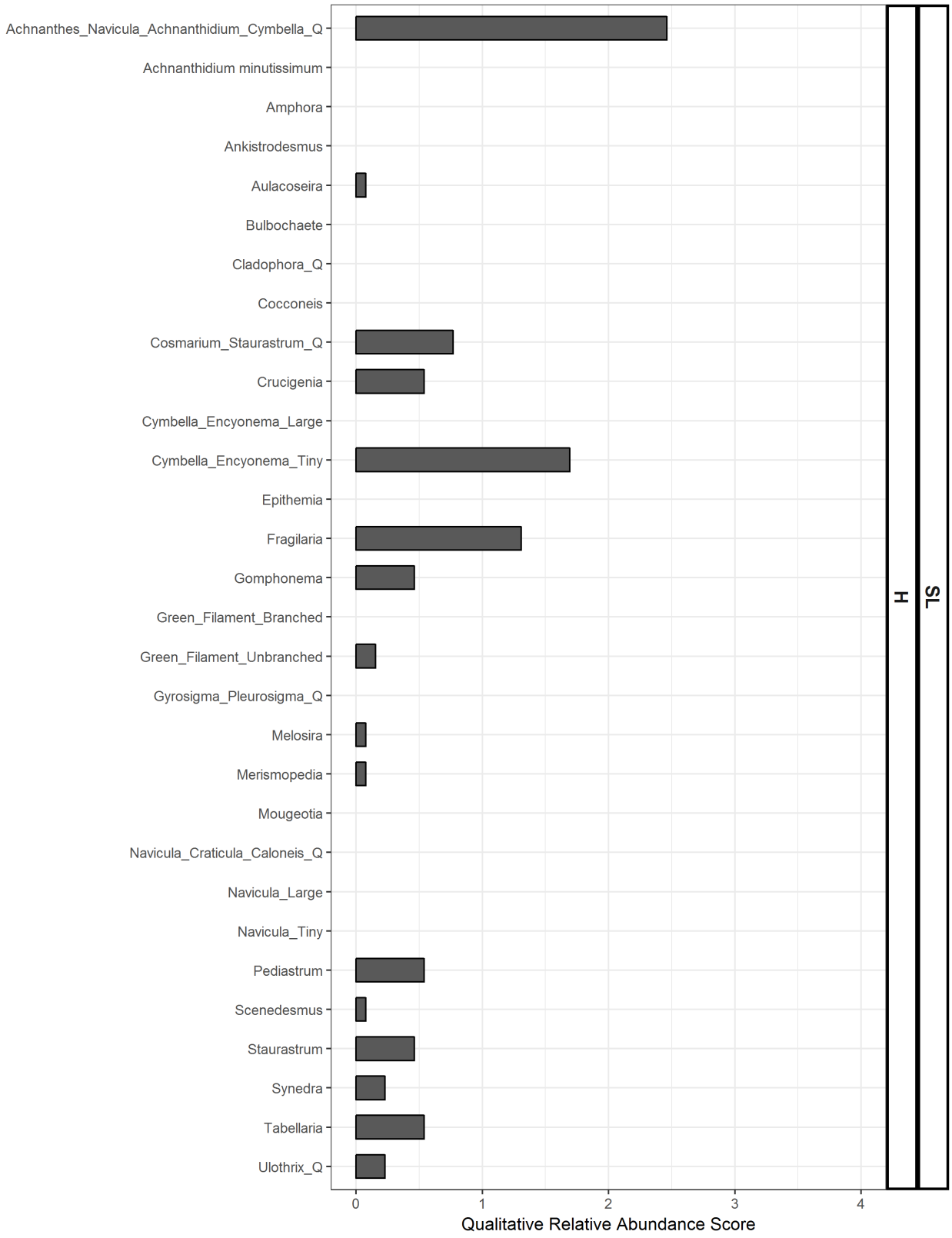
Site	Sample Number	% Solids	Biomass g/cm^2 dry	% Organic Carbon†	% Lipids	^{13}C per mil	^{15}N per mil
MIB-LB	1908046-14	10.1	0.002290	18.33	0.095	-29.64	3.309
B-MIB-LB	1908046-15	12.6	0.006636	3.847	0.24	-21.22	5.121
B-MIB-RB	1908046-16	41.6	0.015493	13.69	0.14	-23.35	3.877
IB	1908046-17	8.2	0.004385	14.10	0.092	-27.96	4.734
SR3A-Rock	1908046-18	12	0.007121	7.273	0.21	-20.73	4.976
SR3A-Brick	1908046-34	10.7	0.006038	6.580	0.23	-21.36	4.751
SR3A-RB	1908046-19	18.7	0.009530	5.476	0.32	-20.35	5.856
SR3A-RB-DUP	1908046-35	--	--	6.83	0.26	-20.83	5.765
TB	1908046-20	6.8	0.002262	10.12	0.34	-23.87	4.237
A-HAM	1908046-21	2.5	0.001625	13.72	0.088	-26.04	3.729
B-HAM-LB	1908046-22	4.1	0.002275	13.35	0.15	-22.44	4.510
B-HAM-RB	1908046-23	13.1	0.007944	6.003	0.28	-22.25	5.936
A-SFB	1908046-24	5.5	0.002851	14.03	0.16	-20.80	4.610
B-SFB	1908046-25	15.2	0.006788	13.71	0.3	-19.84	5.347
GZ-BF	1908046-26	4.4	0.003028	--	0.24	--	--
MOB	1908046-27	4	0.001338	17.50	0.44	-21.63	4.781
MAB	1908046-28	3.9	0.001783	20.12	0.25	-18.55	5.047
MAB-DUP	1908046-36	--	--	20.37	0.22	-19.05	4.800
A-SG-LB	1908046-29	5.4	0.003211	18.01	0.19	-18.07	5.428
A-SG-RB	1908046-30	5.1	0.005764	16.77	0.2	-18.38	5.192
SG	1908046-31	5.4	0.005507	17.00	0.17	-19.24	4.949
TJM	1908046-32	7.3	0.002916	6.242	0.082	-25.17	3.720
NMD	1908046-33	12.5	0.005213	8.339	0.32	-18.49	7.455

† = 2018 analysis by WA Isolab and 2019 by UC Davis
NA = Not Applicable
-- Not Analyzed For

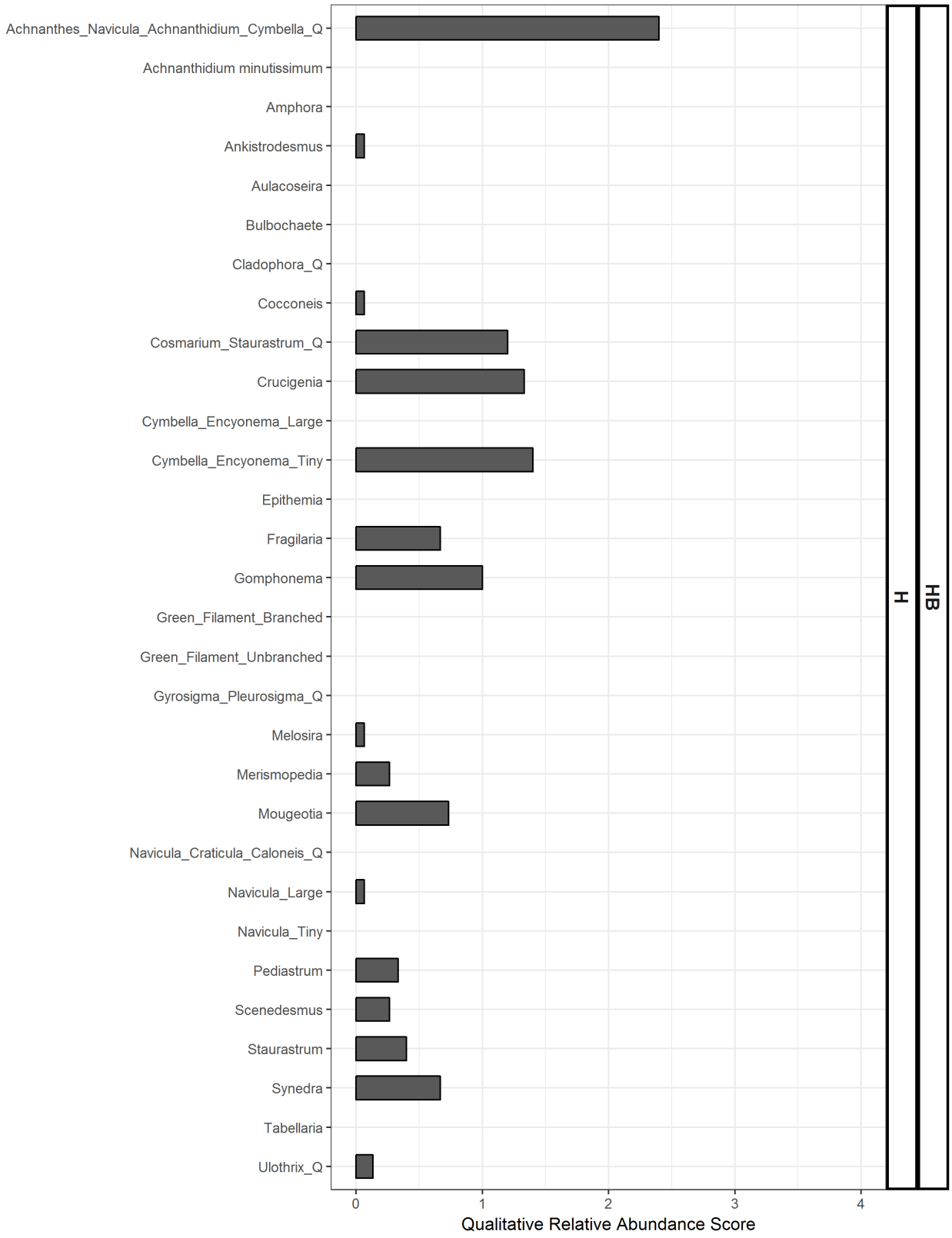
Figure C-1. Photograph of Diatoms and Algae in Spokane River Biofilm.

Figure C-2 is shown on the following pages.

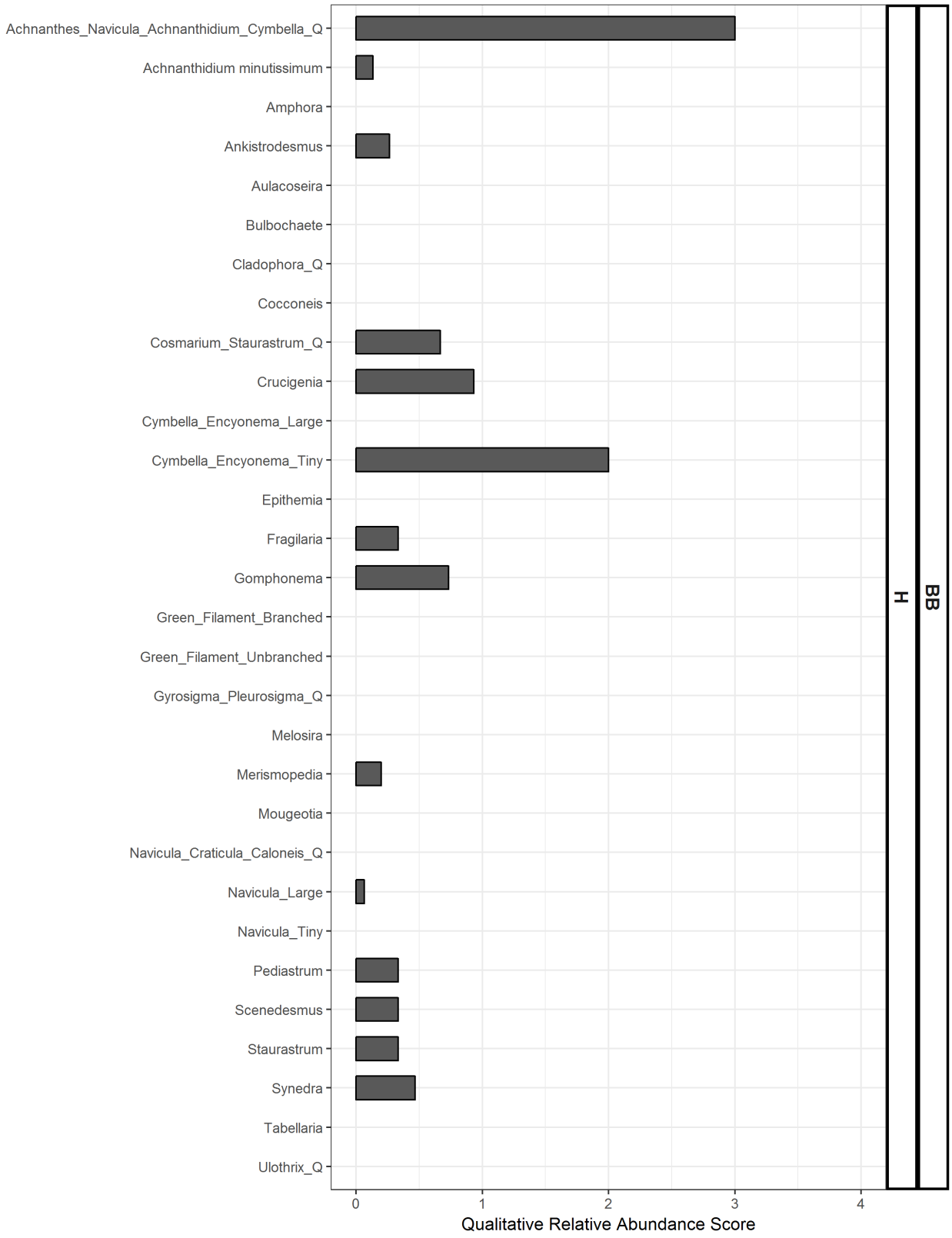
Figure C-2. Qualitative Relative Abundance Plots.



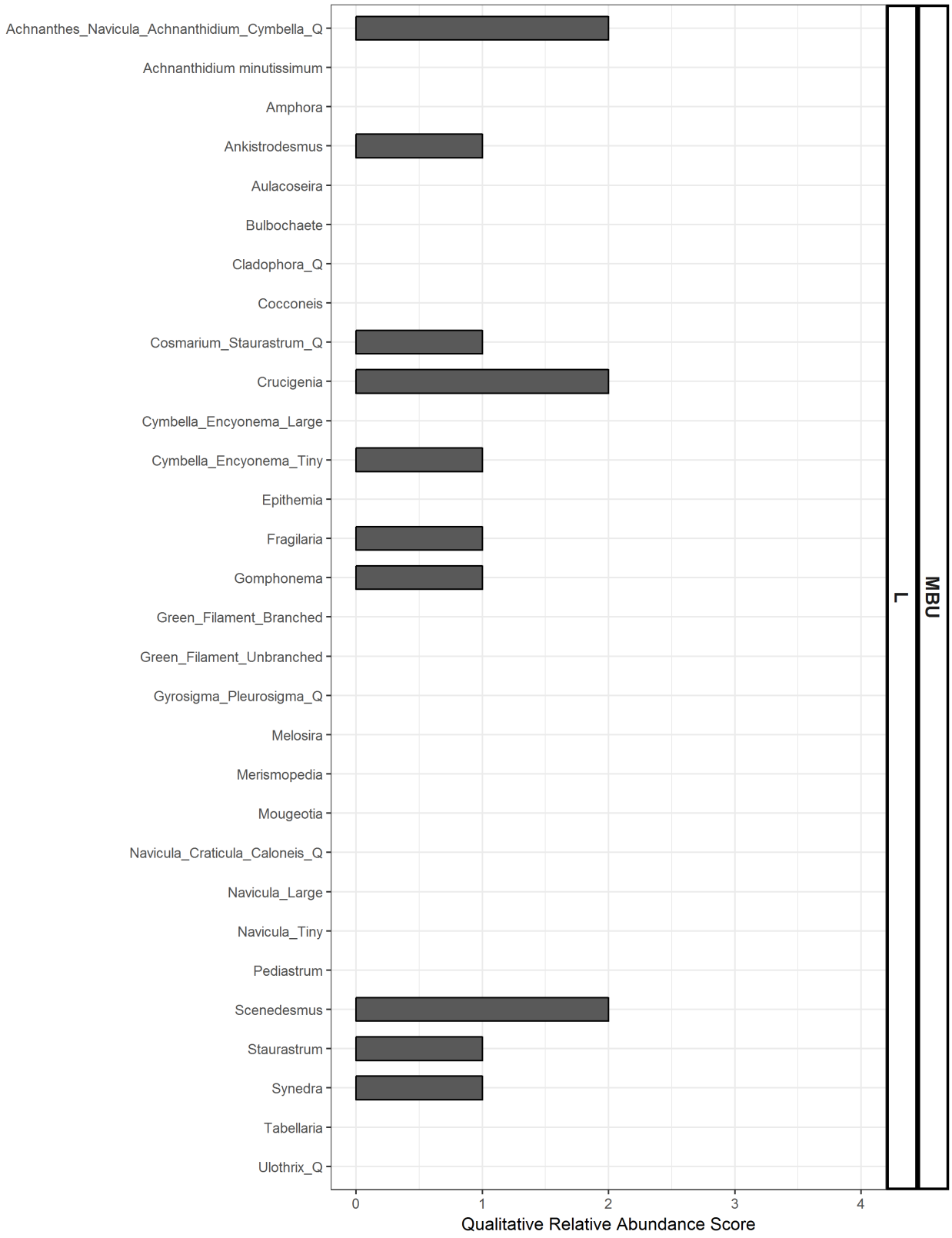
Stateline (SL)



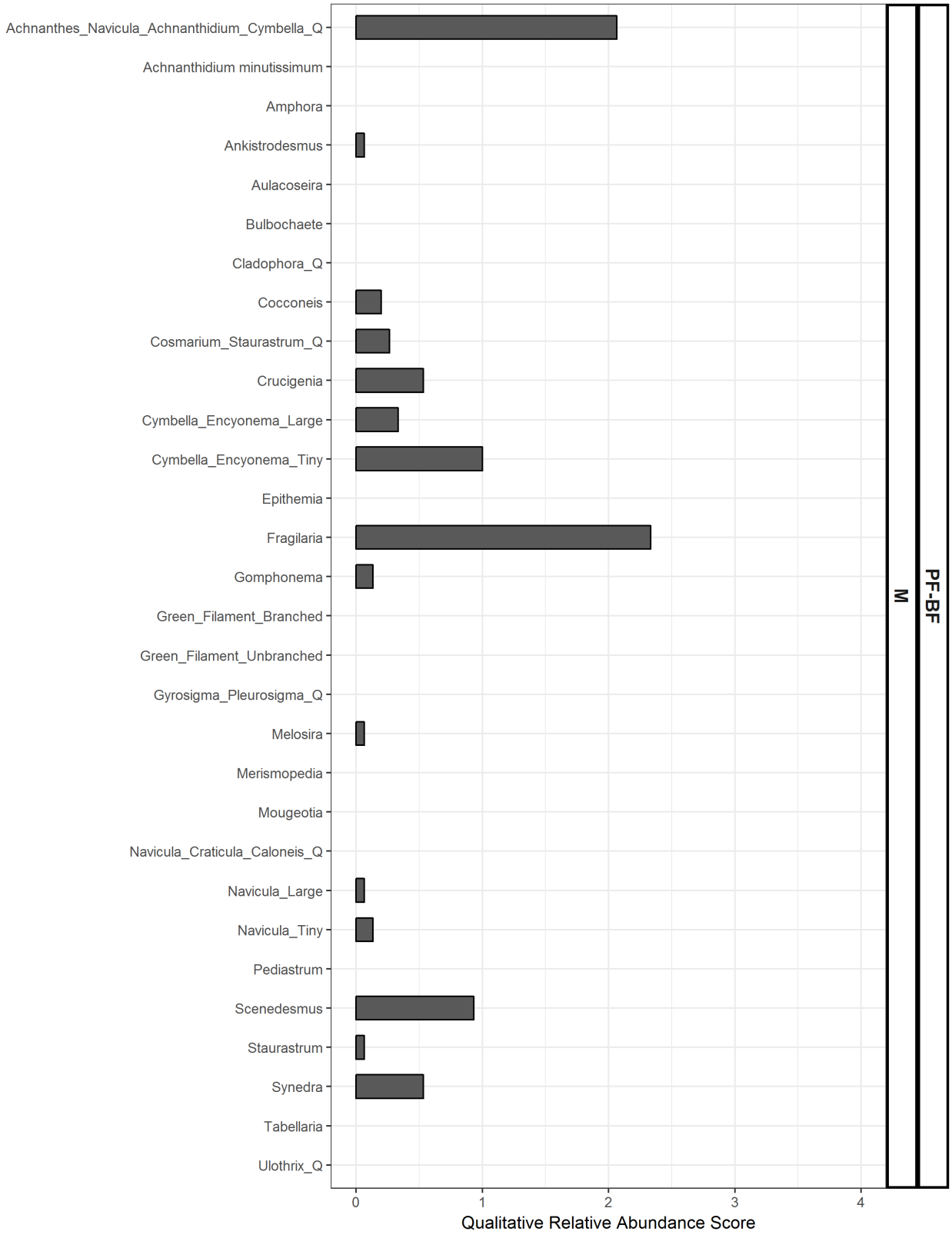
Harvard Bridge (HB)



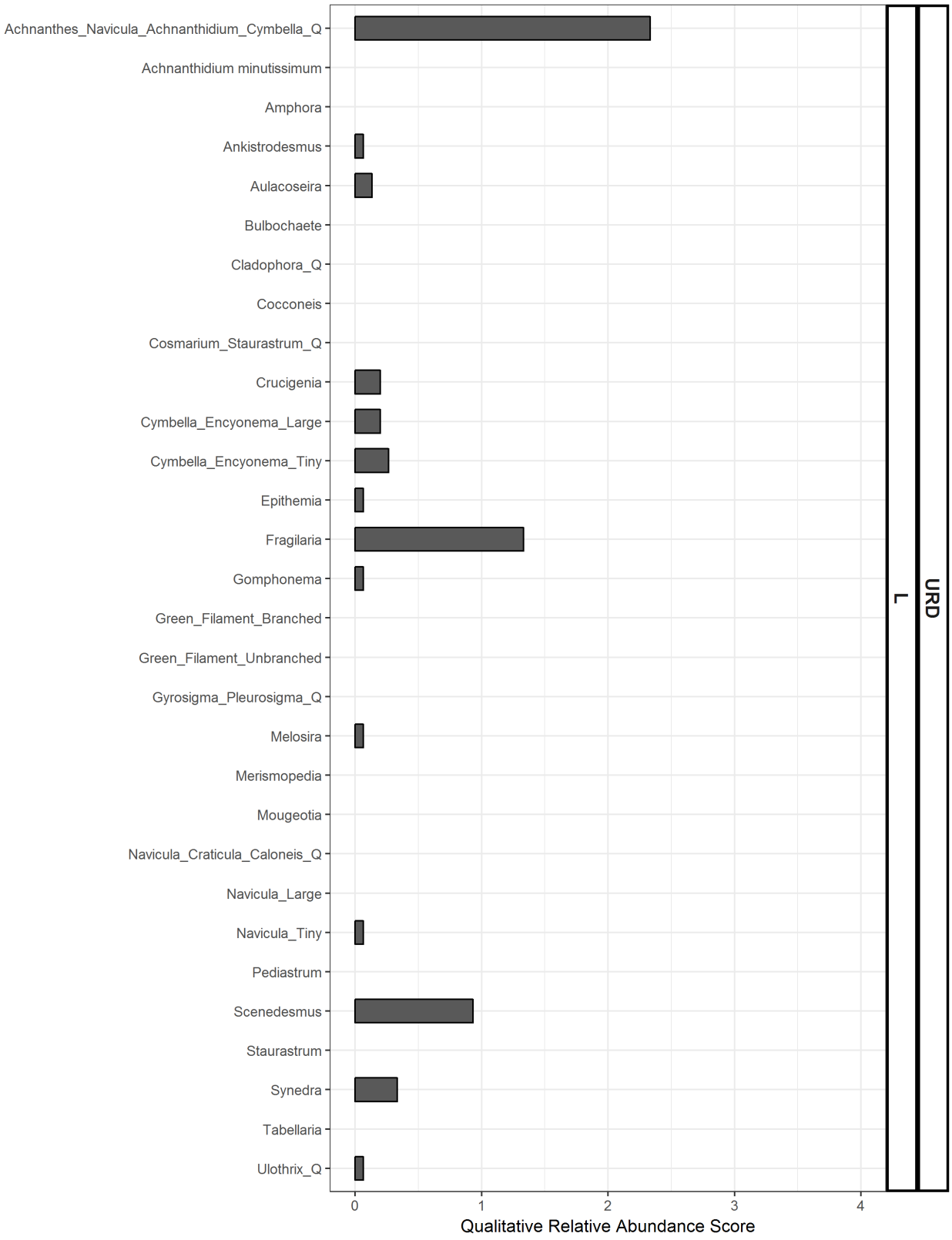
Barker Bridge (BB)



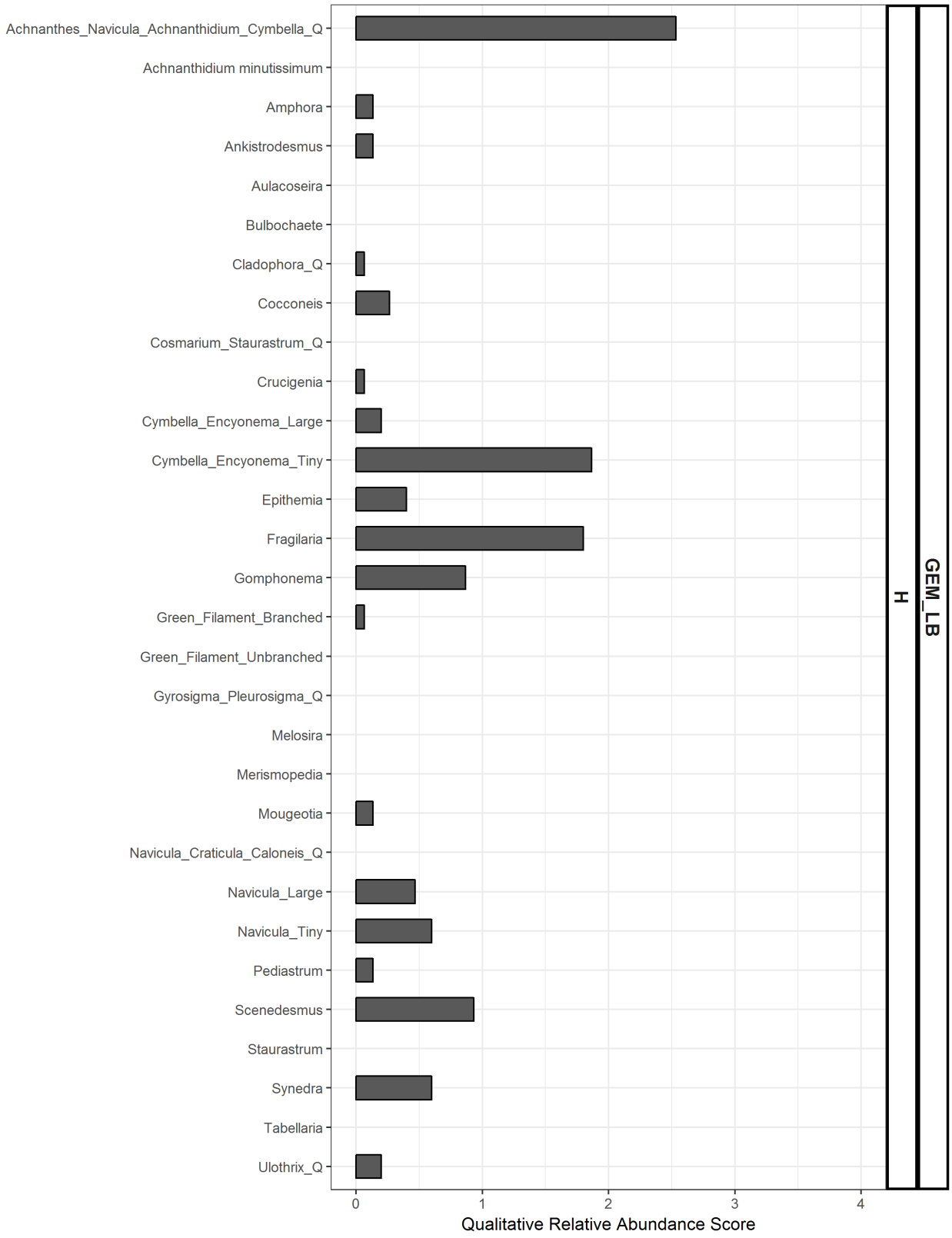
Mirabeau (MBU)



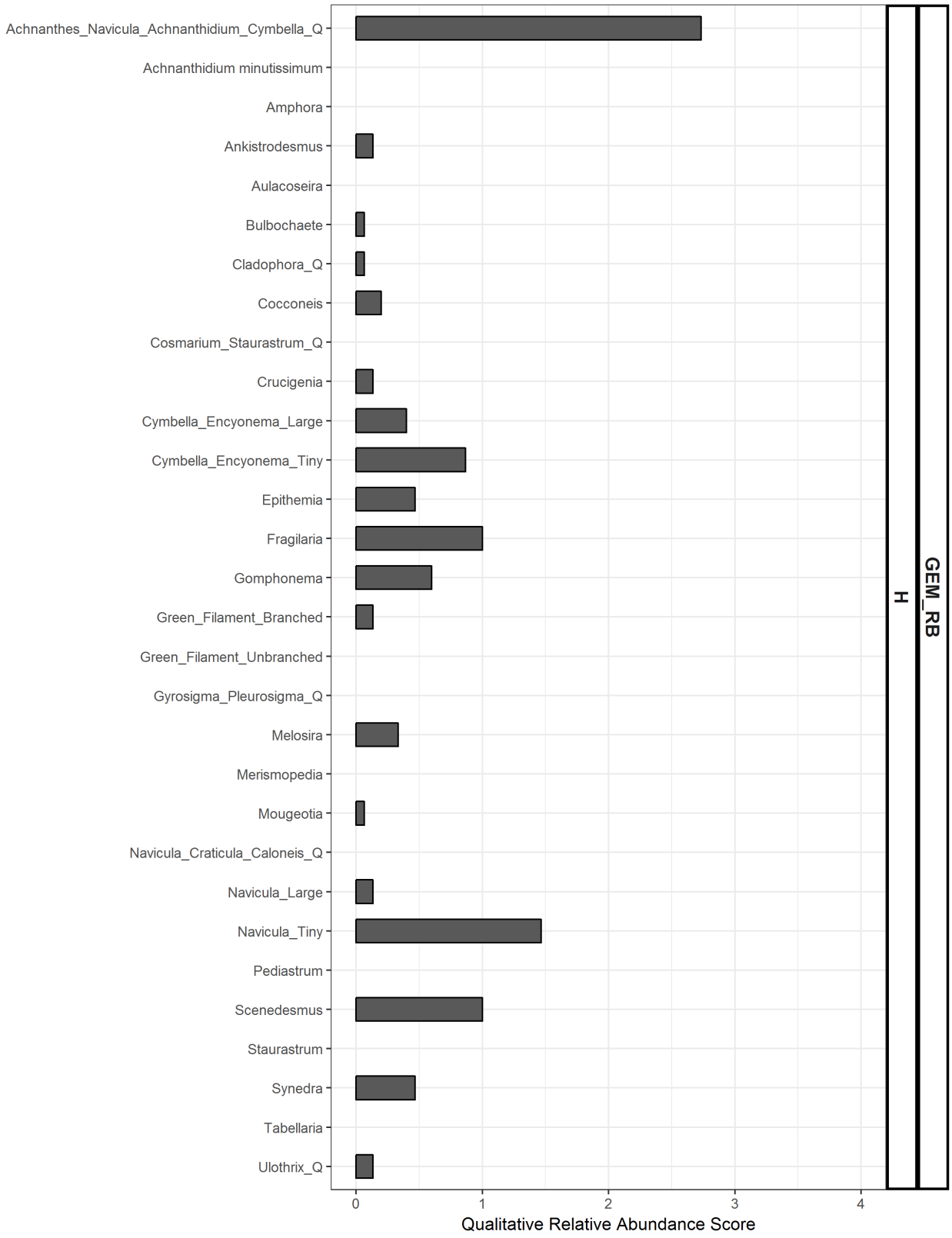
Plantes Ferry (PF)



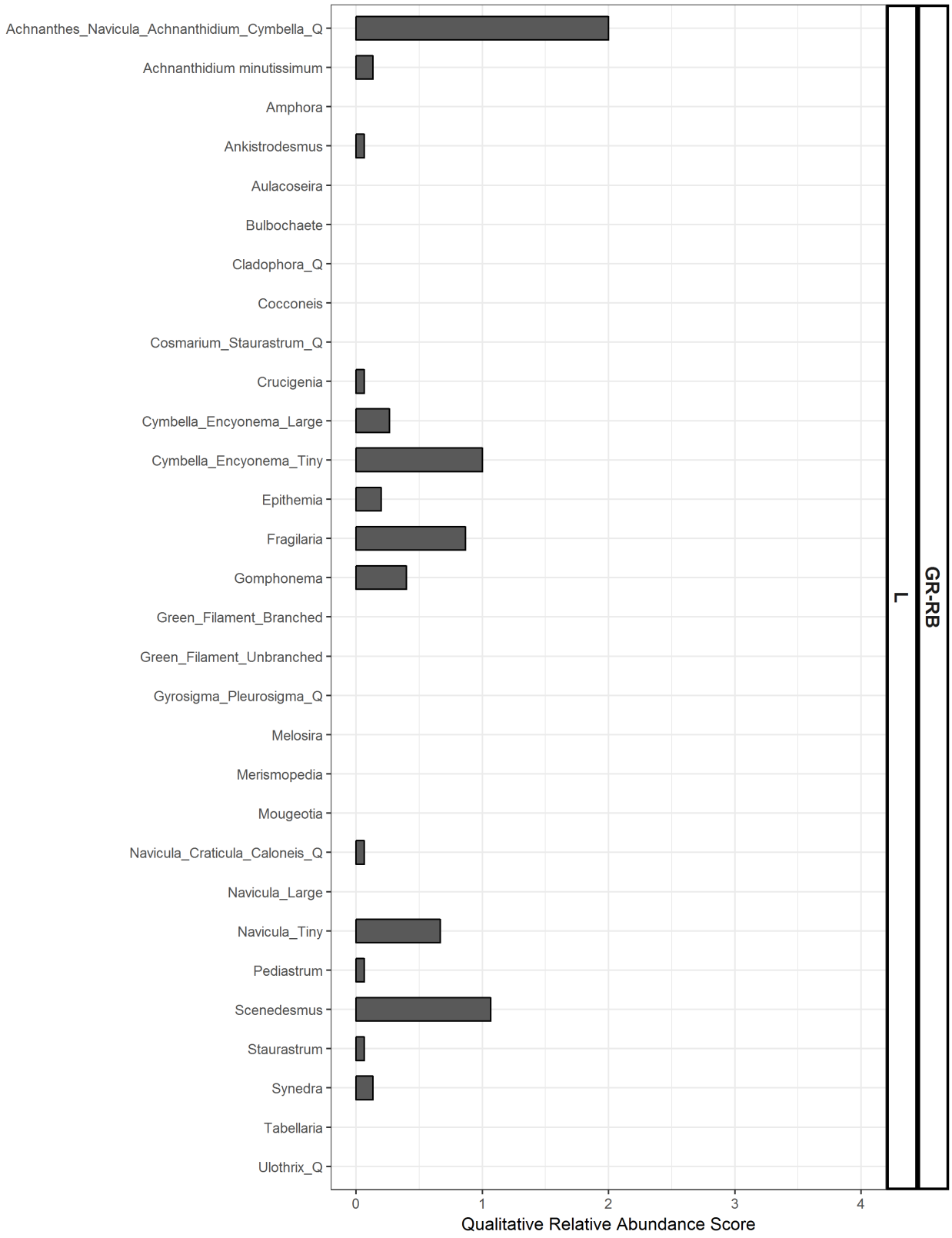
Upriver Dam (URD)



GE Mission - Left Bank (GEM-LB)



GE Mission - Right Bank (GEM-RB)



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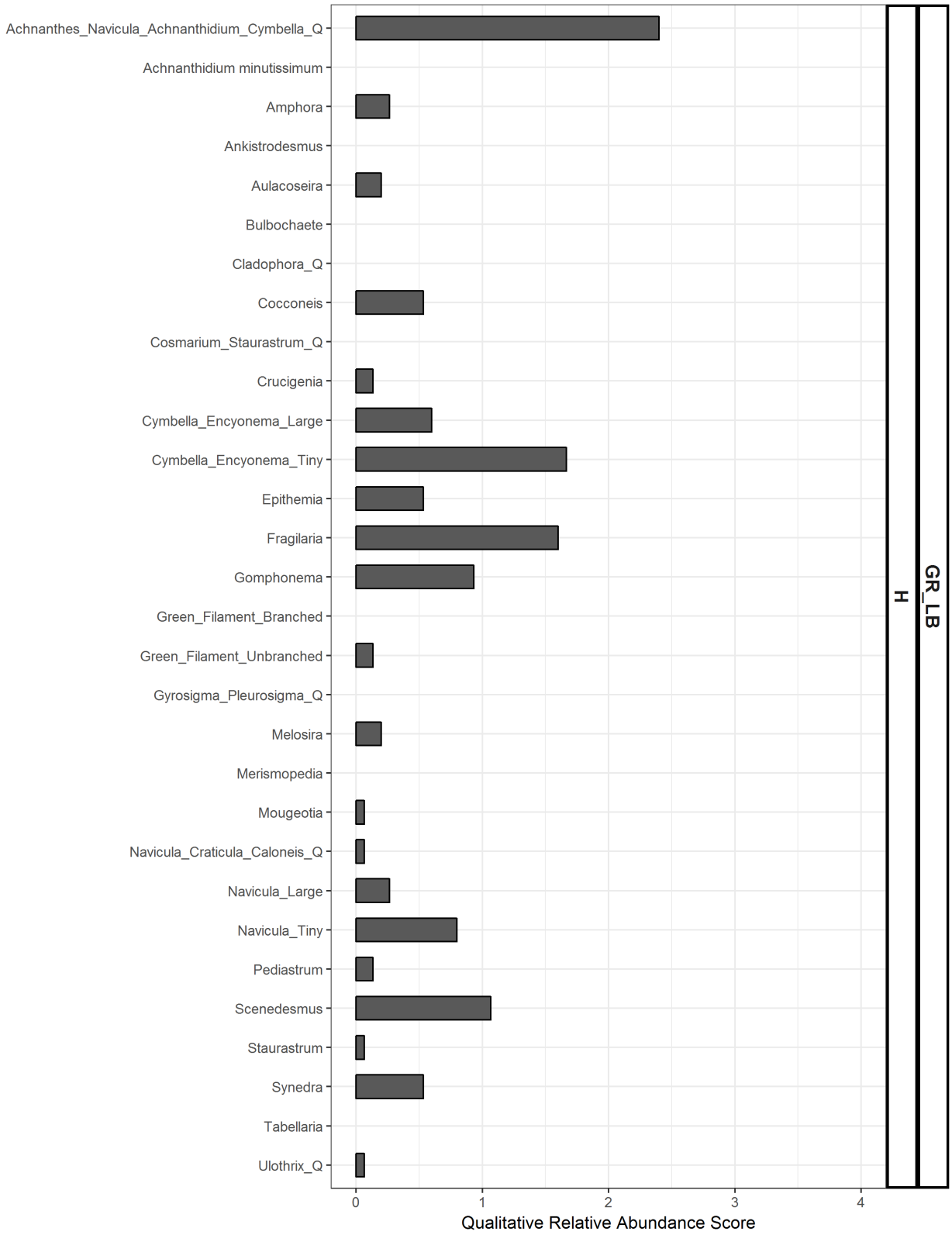

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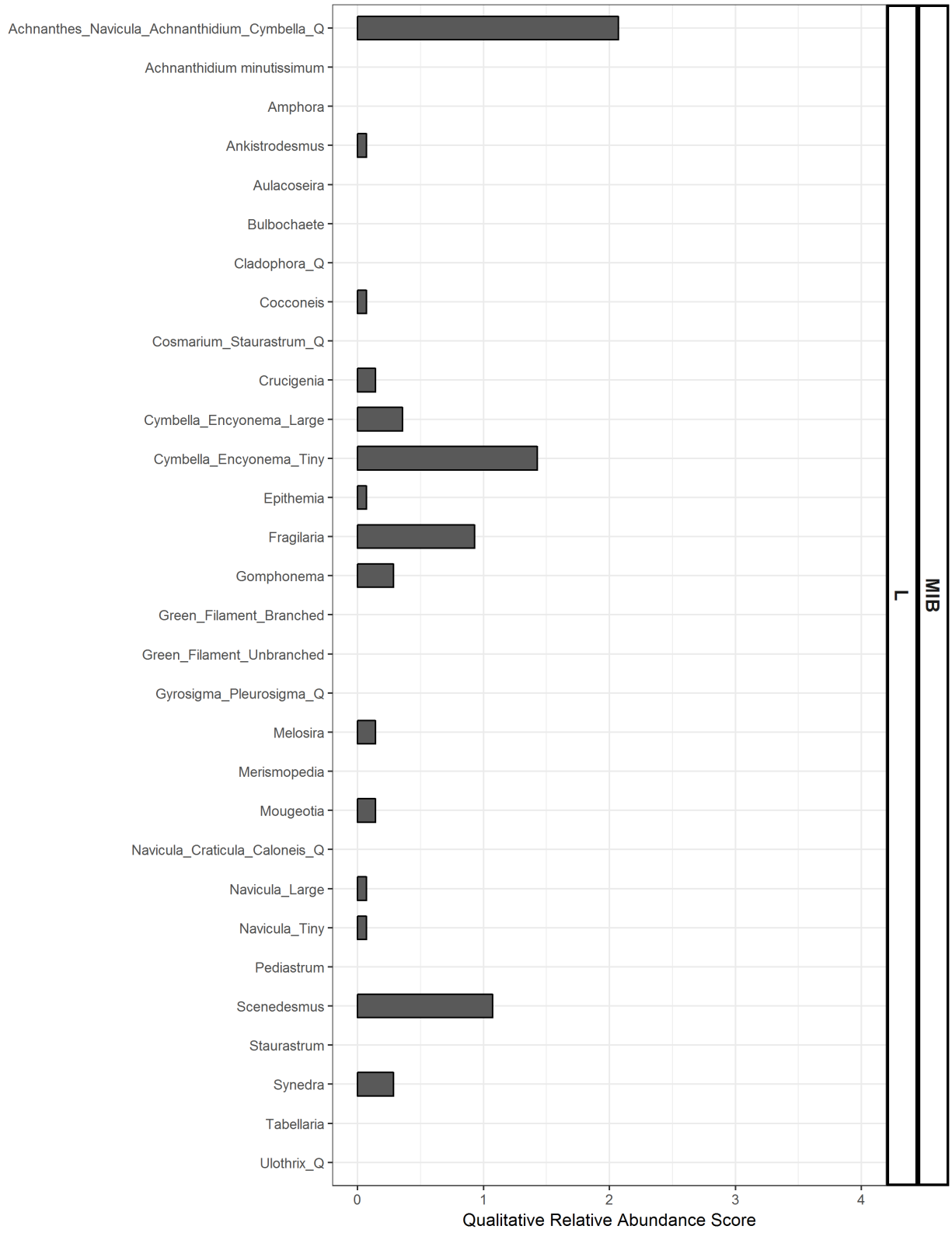
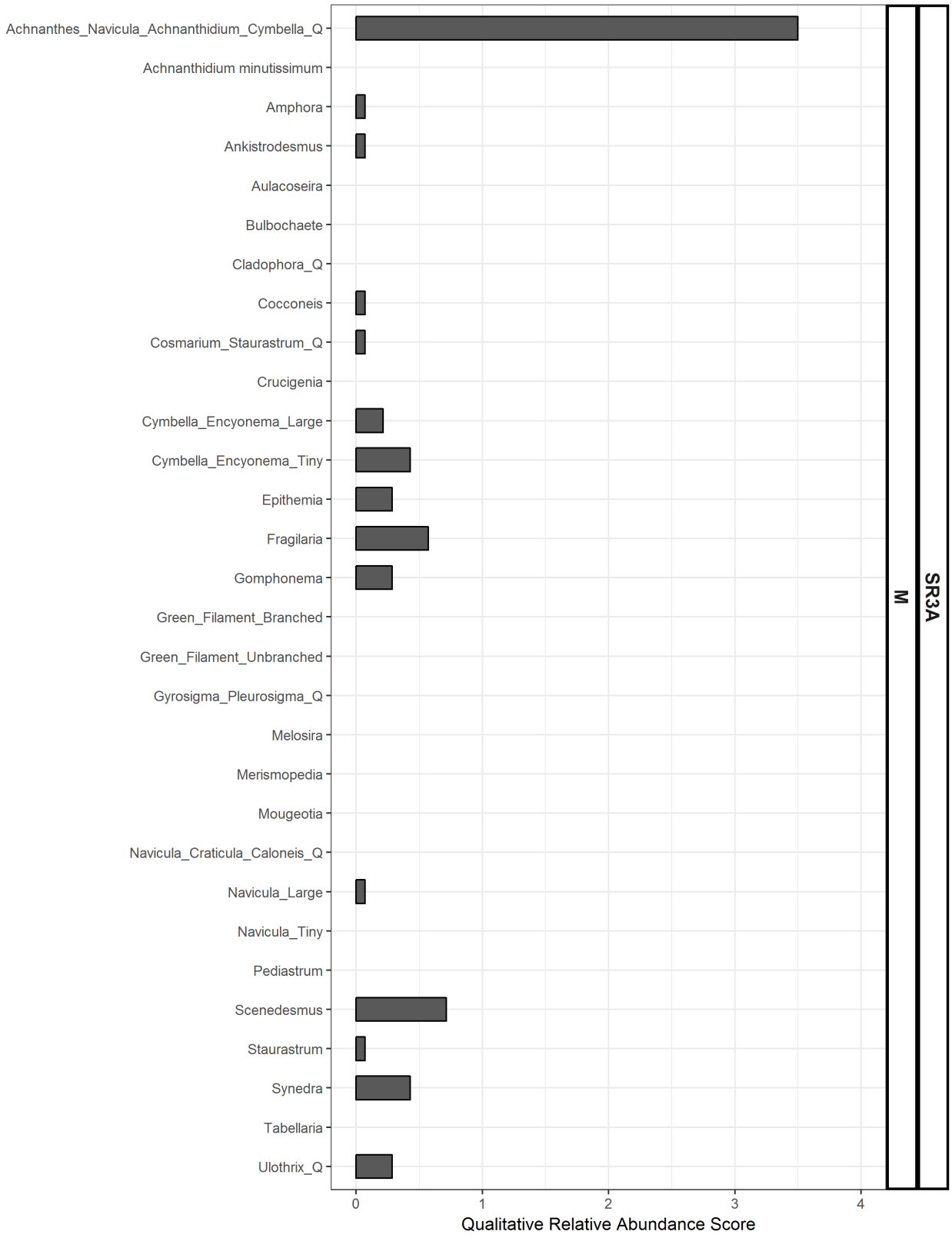


Mission Bridge (MIB)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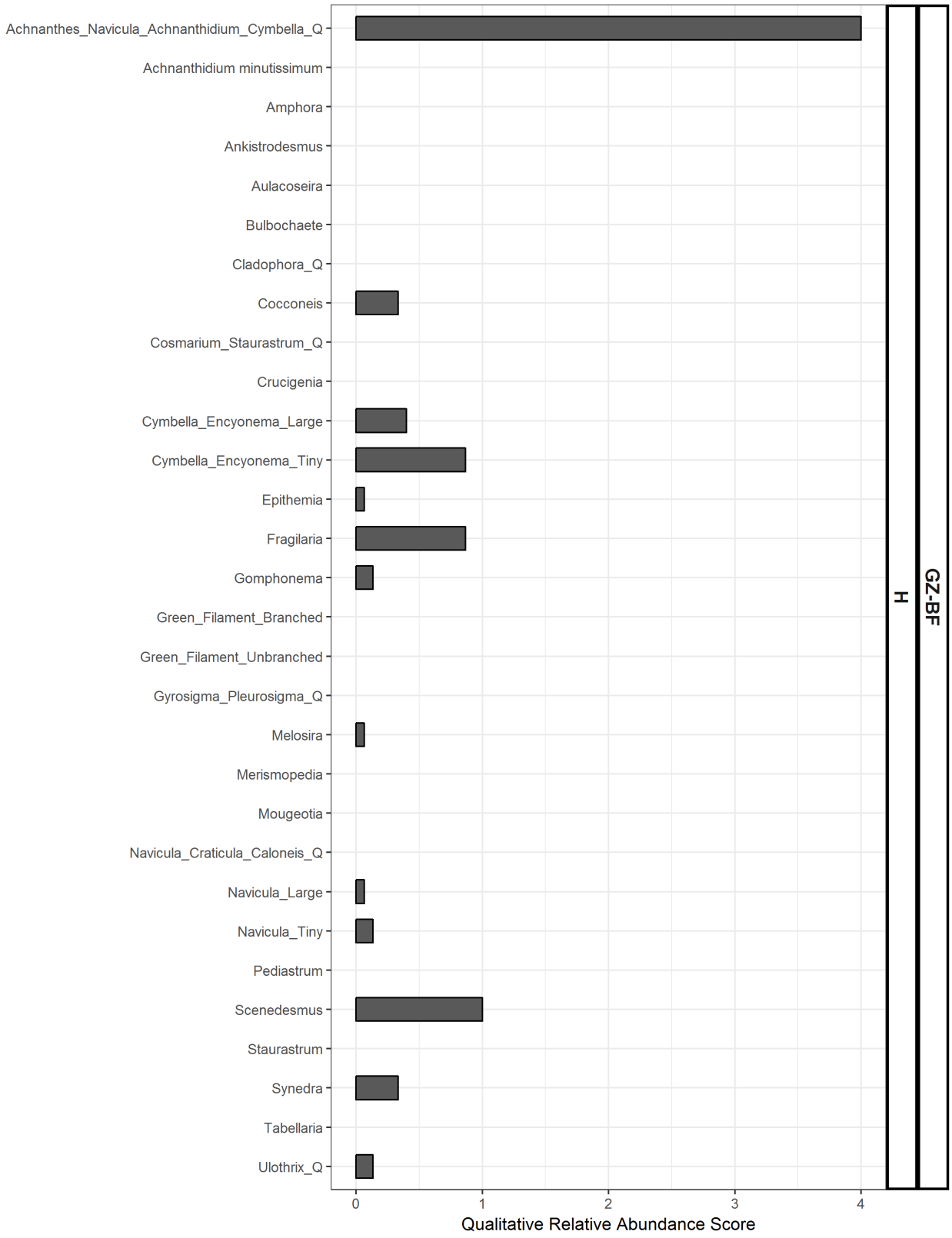
Amphora
Ankistrodesmus
Aulacoseira
Bulbochaete
Cladophora_Q
Cocconeis
Cosmarium_Staurastrum_Q
Crucigenia
Cymbella_Encyonema_Large
Cymbella_Encyonema_Tiny
Epithemia
Fragilaria
Gomphonema
Green_Filament_Branched
Green_Filament_Unbranched
Gyrosigma_Pleurosigma_Q
Melosira
Merismopedia
Mougeotia
Navicula_Craticula_Caloneis_Q
Navicula_Large
Navicula_Tiny
Pediastrum
Scenedesmus
Staurastrum
Synedra
Tabellaria
Ulothrix_Q
0
1
2
3
4
Qualitative Relative Abundance Score
M
SR3A

SR3A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Achnanthidium minutissimum
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Cocconeis
Cosmarium_Staurastrum_Q
Crucigenia
Cymbella_Encyonema_Large
Cymbella_Encyonema_Tiny
Epithemia
Fragilaria
Gomphonema
Green_Filament_Branched
Green_Filament_Unbranched
Gyrosigma_Pleurosigma_Q
Melosira
Merismopedia
Mougeotia
Navicula_Craticula_Caloneis_Q
Navicula_Large
Navicula_Tiny
Pediastrum
Scenedesmus
Staurastrum
Synedra
Tabellaria
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0
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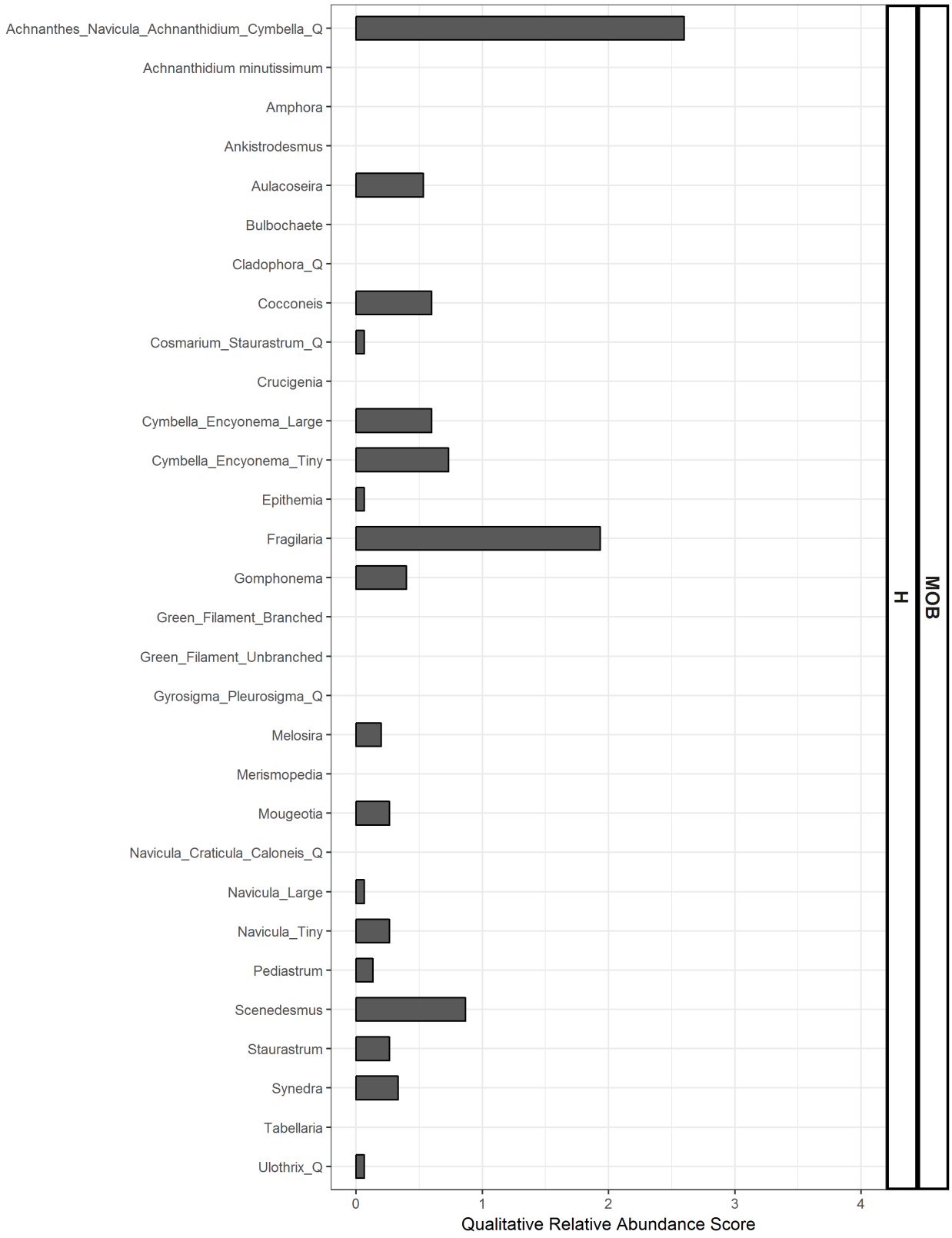
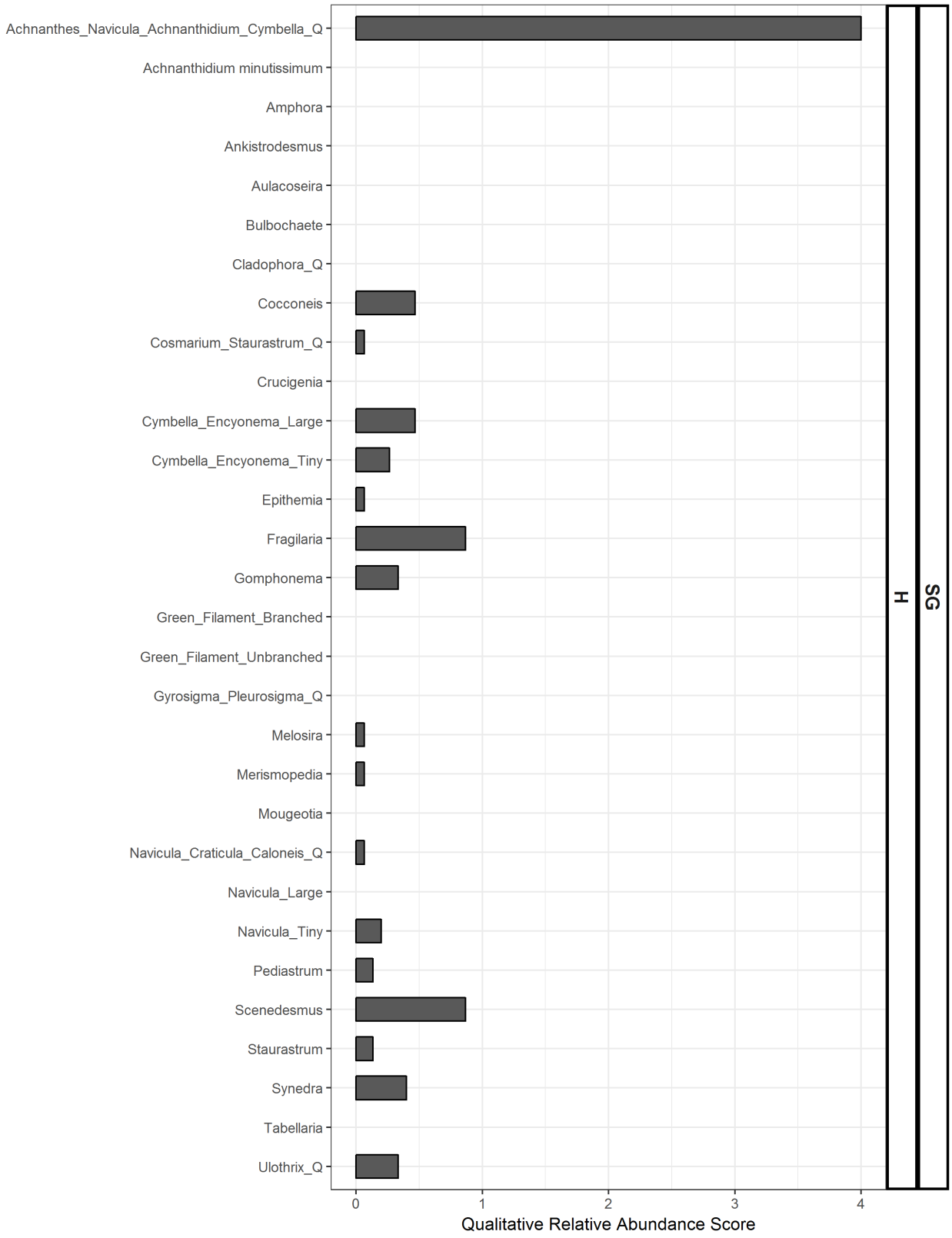
2
3
4
Qualitative Relative Abundance Score
H
GZ-BF

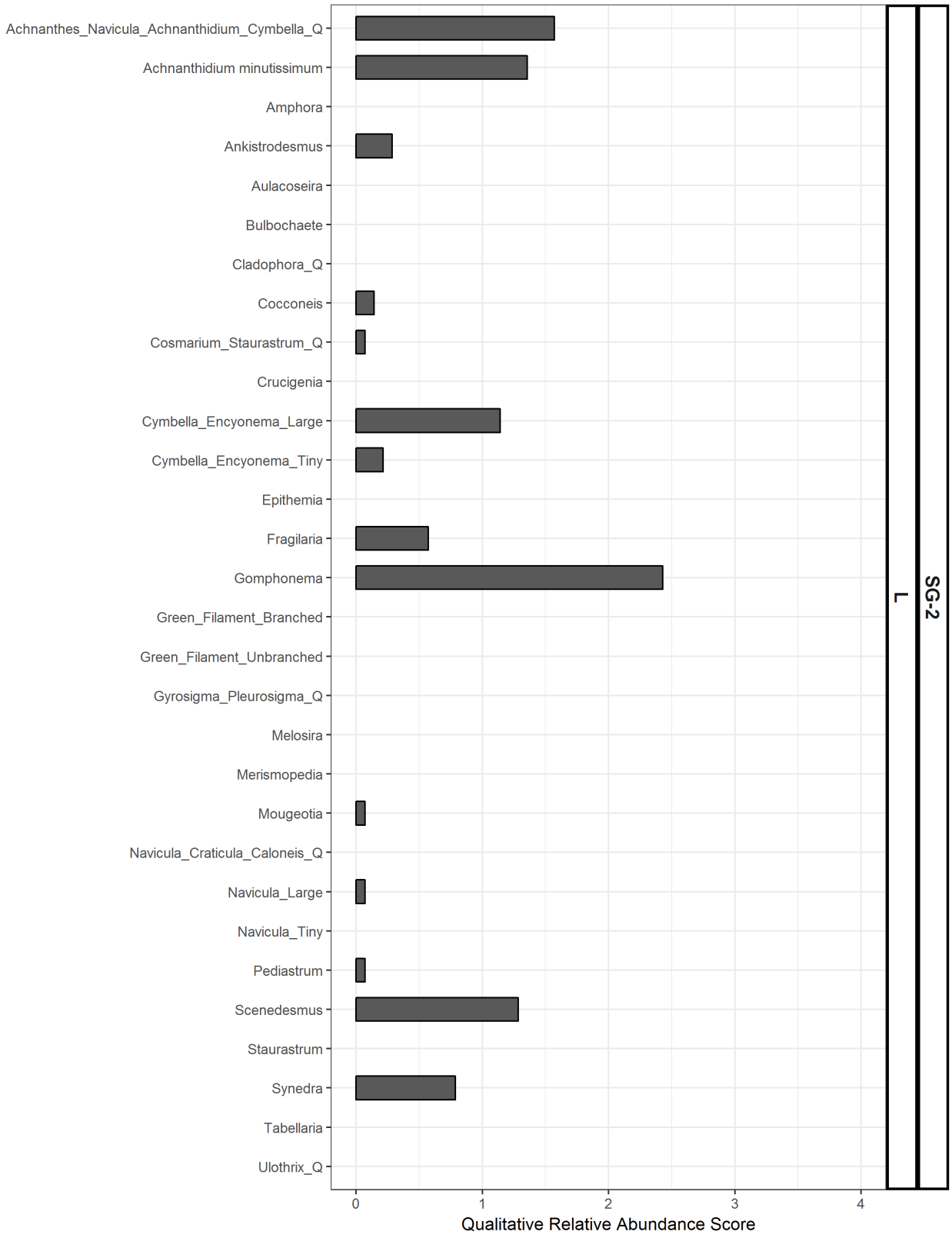
Gonzaga (GZ)



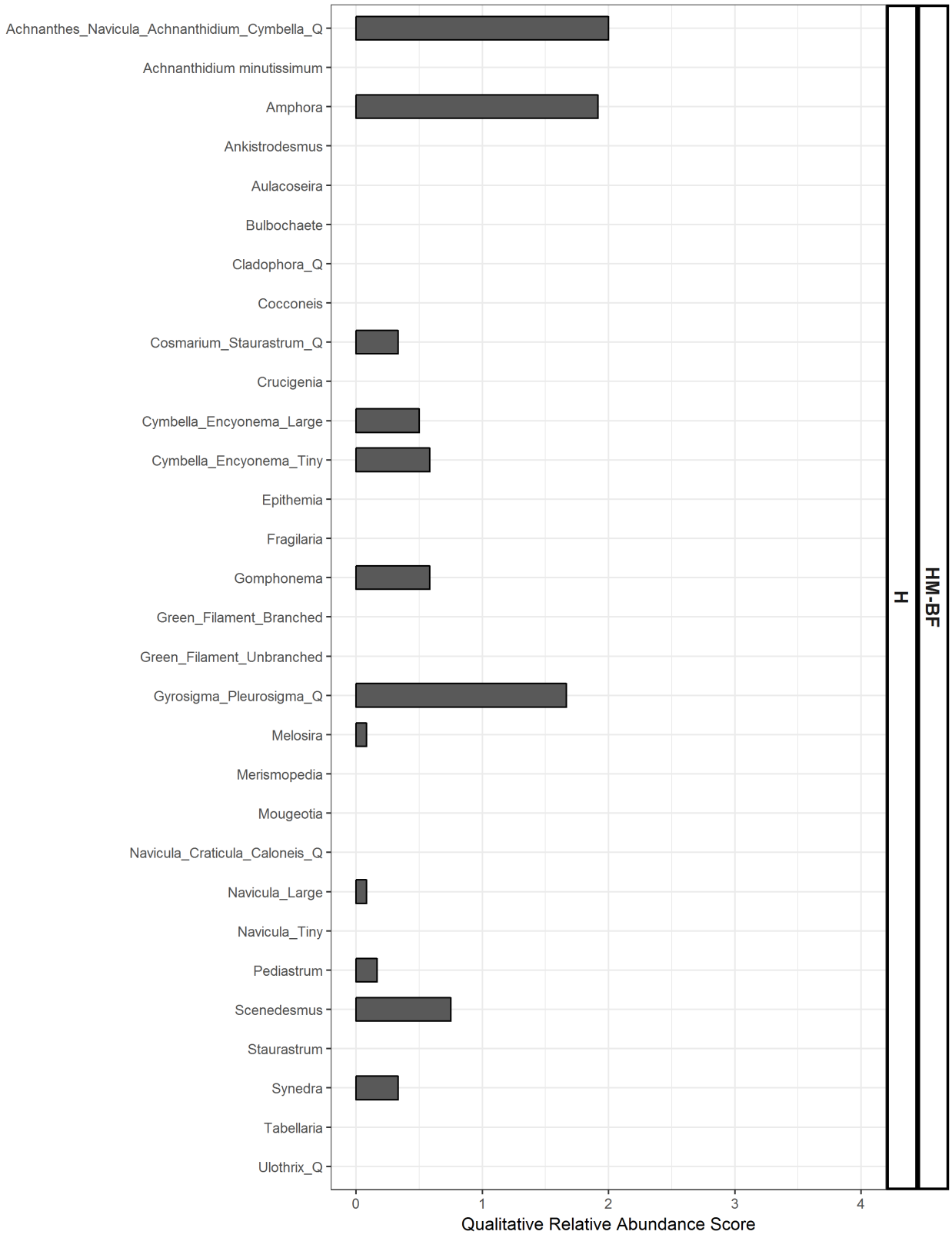
Monroe Bridge (MOB)



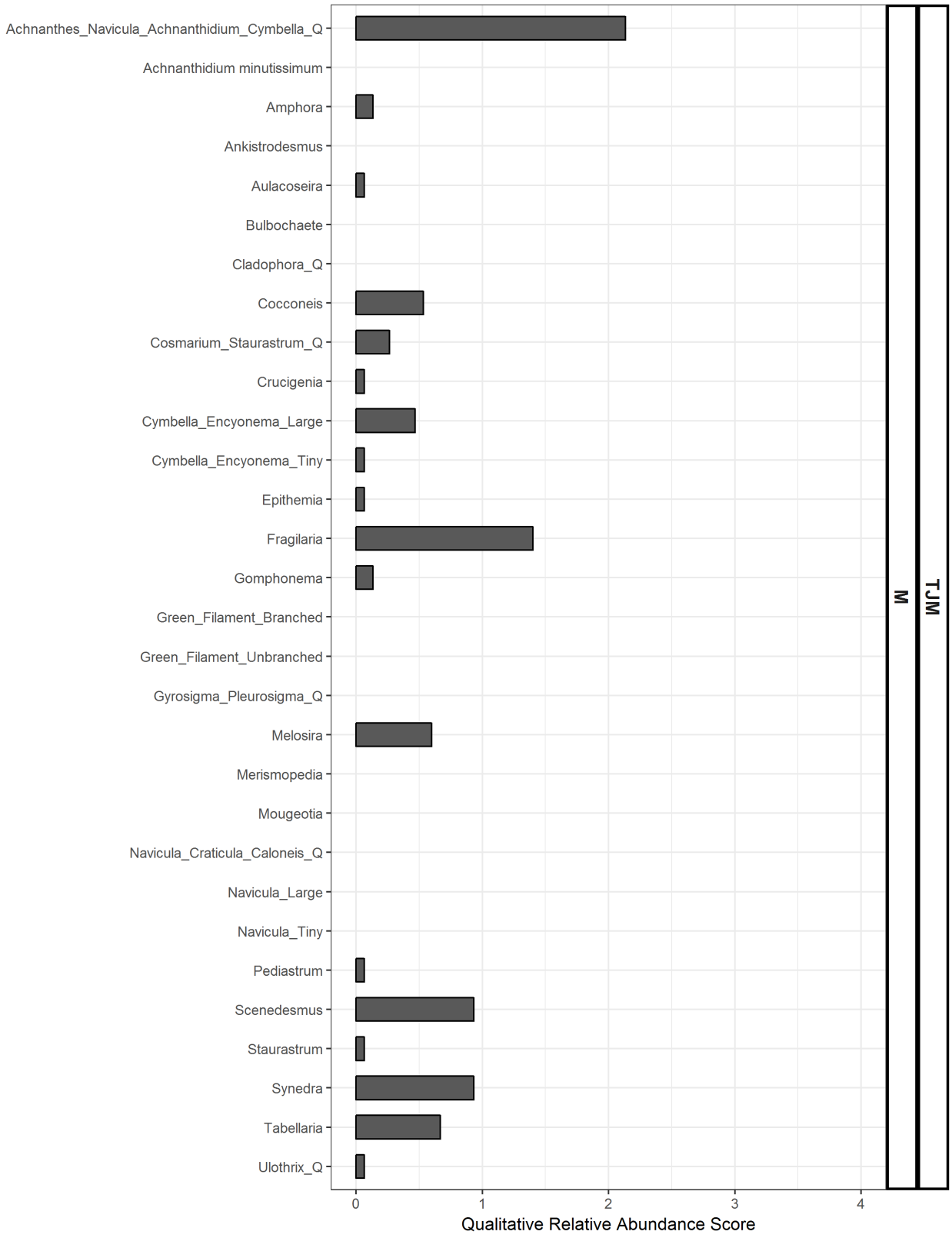
Spokane Gage (SG)



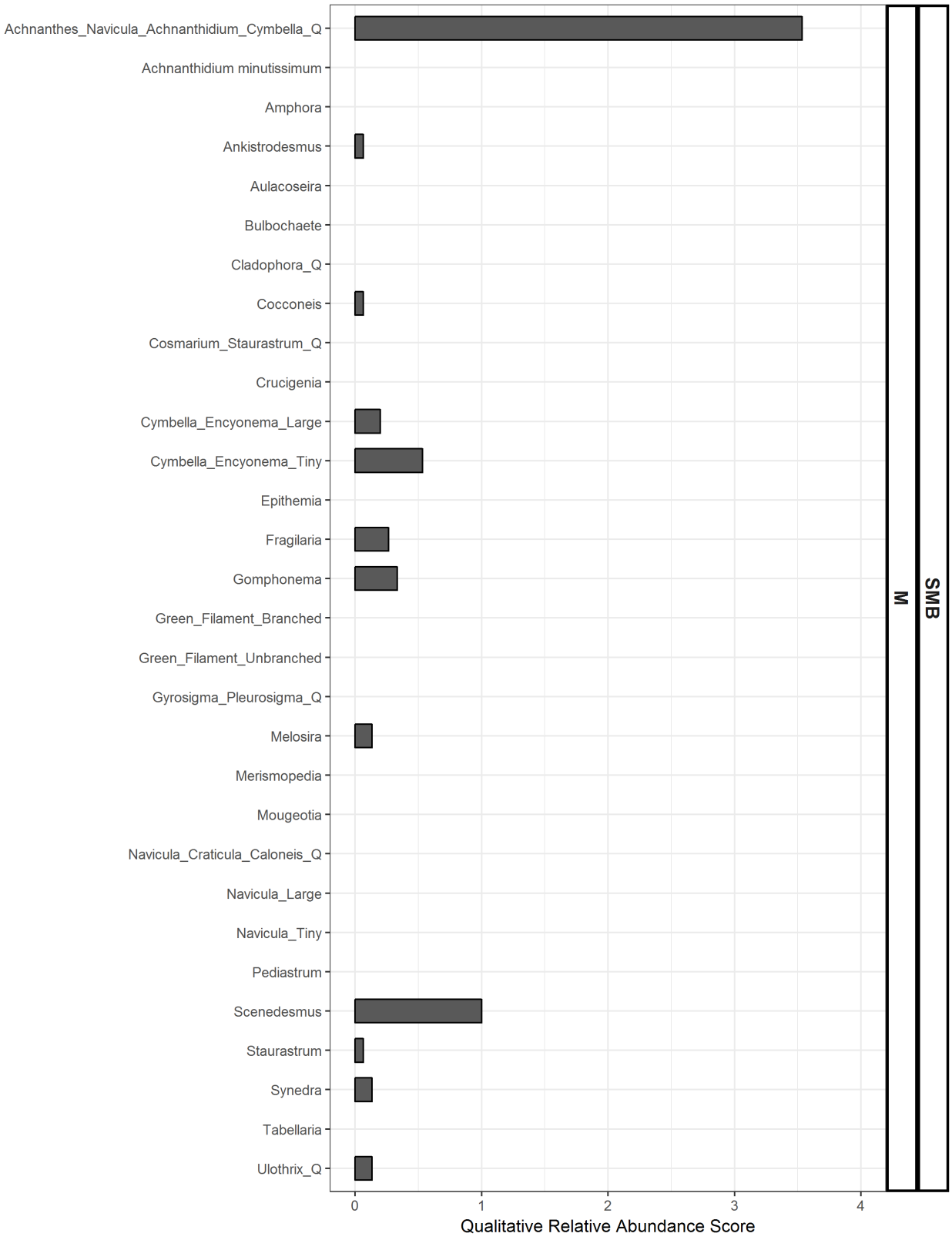
Spokane Gage (SG) – Duplicate



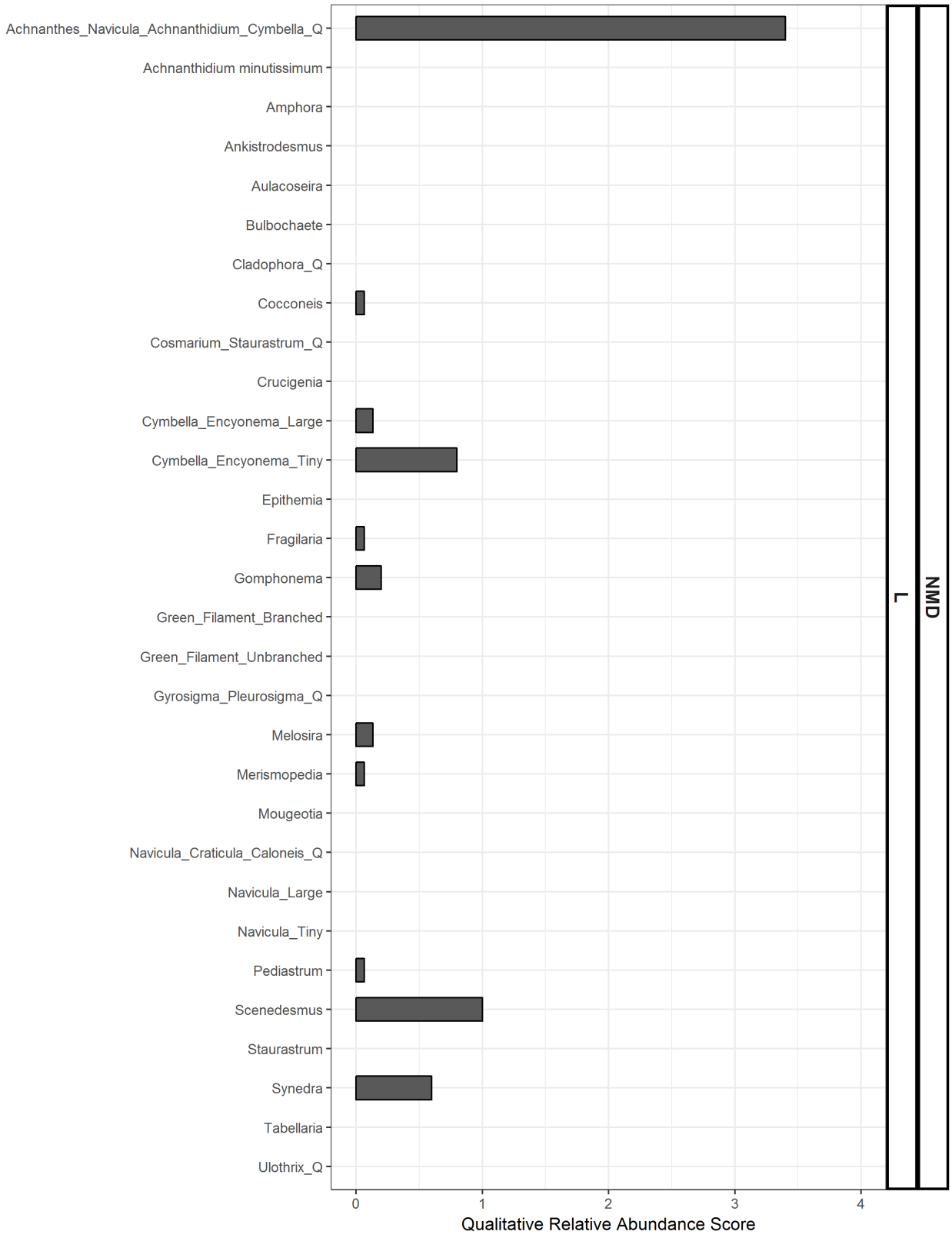
Hangman Creek (HM)



TJ Meenach (TJM)



Seven-Mile Bridge (SMB)



Nine Mile Dam (NMD)

Appendix D. Glossary, Acronyms, and Abbreviations

Glossary

Aroclor: Aroclor is a PCB mixture produced from approximately 1930 to 1979. It is one of the most commonly known trade names for PCB mixtures.

Clean Water Act: A federal act passed in 1972 that contains provisions to restore and maintain the quality of the nation's waters. Section 303(d) of the Clean Water Act establishes the TMDL program.

Effluent: An outflowing of water from a natural body of water or from a man-made structure. For example, the treated outflow from a wastewater treatment plant.

Parameter: Water quality constituent being measured (analyte). A physical, chemical, or biological property whose values determine environmental characteristics or behavior.

PCB Congener: A PCB congener is a single unique PCB chemical. There are 209 possible congeners. They are numbered in sequential order from -001, -002…-208, -209.

PCB Homolog: A set of PCB congeners grouped by the number of chlorine atoms they have.

Principle component analysis: PCA is a type of eigenvector-based multivariate analysis used for exploring data complicated datasets.

Stormwater: The portion of precipitation that does not naturally percolate into the ground or evaporate but instead runs off roads, pavement, and roofs during rainfall or snowmelt. Stormwater can also come from hard or saturated grass surfaces such as lawns, pastures, playfields, and from gravel roads and parking lots.

Watershed: A drainage area or basin in which all land and water areas drain or flow toward a central collector such as a stream, river, or lake at a lower elevation.

Water year: As defined by the United States Geological Survey (USGS), the term refers to the period between October 1st of one year and September 30th of the next. The water year is designated by the calendar year in which it ends, so the 2010 water year (USGS) started on October 1, 2009 and ended on September 30, 2010.

303(d) list: Section 303(d) of the federal Clean Water Act requires Washington State to periodically prepare a list of all surface waters in the state for which beneficial uses of the water – such as for drinking, recreation, aquatic habitat, and industrial use – are impaired by pollutants. These are water quality-limited estuaries, lakes, and streams that fall short of state surface water quality standards and are not expected to improve within the next two years.

Acronyms and Abbreviations

Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
MEL	Manchester Environmental Laboratory
MQO	Measurement Quality Objective
PBDE	polybrominated diphenyl ethers
QAPP	Quality Assurance Project Plan
RPD	Relative percent difference
SRRTTF	Spokane River Regional Toxics Task Force
TOC	total organic carbon
USGS	U.S. Geological Survey
WRIA	Water Resource Inventory Area

Units of Measurement

cfs	cubic feet per second
dw	dry weight
g	gram, a unit of mass
g/cm^2	gram per centimeter squared, a measure of biomass
kg	kilograms, a unit of mass equal to 1,000 grams
km	kilometer, a unit of length equal to 1,000 meters
mg/d	milligrams per day
pg/g	picograms per gram (parts per trillion)
per mil	part per thousand; often written as ‰
ug/Kg	micrograms per kilogram (parts per billion)
ww	wet weight