Fingerprinting of PCBs in Spokane River fish, biofilm, and SPMDs

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Abstract

PCB congener data from fish, biofilm, and Solid-Phase Microextraction Devices (SPMDs) were analyzed using Positive Matrix Factorization (PMF). The fish data included 135 samples of fish from various species, ages, locations, and tissue types. In addition, PCB concentrations in fish are the results of absorption, distribution, metabolism, and excretion (ADME) processes that can alter the fingerprints. These issues complicate the interpretation of the results. Nevertheless, PMF analysis identified three factors or source types in the fish (denoted FishA, FishB, and FishC) that each resemble one or more Aroclors, with some evidence of metabolism. PCB concentrations in fish appear to be declining over time based on samples of the same species collected at the same locations at 2-3 time points between 2003 and 2020. However, these declines are not statistically significant due to the small number of samples. There is some evidence that the PCB signal in the fish is shifting toward lower molecular weight (MW) congeners over time.

The 60 biofilm samples were combined with the 14 SPMD samples for PMF analysis, even though the SPMD samples displayed a lower MW pattern more similar to the water column, while the biofilm samples generally contained somewhat higher MW PCBs. The PMF analysis found six factors or source types in the biofilm+SPMD data set (denoted BF1 through BF6), with one factor dominated by the non-Aroclor congener PCB 11, while the others resembled Aroclors. The highest concentration biofilm samples tended to be dominated by BF4, which resembled Aroclor 1260, while the lower concentration samples were more likely to contain lower MW PCBs.

Introduction

The purpose of this work was to use Positive Matrix Factorization (PMF) to analyze data on polychlorinated biphenyl (PCB) congener concentrations in fish as well as biofilm and SPMDs (solid-phase microextraction devices) in order to understand the sources of PCBs to the Spokane River. Biofilm is defined as a film formed on a surface due to the actions of a consortium of microorganisms which secrete a slimy extracellular matrix that is composed of extracellular polymeric substances. These substances form the film that gives microorganisms a ‘home’ on the surface. Biofilms are ubiquitous and are formed on virtually any surface that stays wet, including surfaces submerged in natural waters. This work builds on other efforts to use PMF to analyze data from the water column, treated wastewater, untreated wastewater and combined sewer overflows (CSOs), stormwater, and other sources (Rodenburg, 2020).

In this analysis, 30 new samples of fish collected in 2020 were combined with fish data from previous years and analyzed anew. Notably, fish from hatcheries were not included in this analysis. Separately, 60 samples of biofilm from 2018 and 2019 were combined with 14 samples of SPMDs from 2020 and analyzed via PMF.

Methods

All new data (30 new fish samples and all biofilm and SPMD data) were provided by SRRTTF via Amy Sumner and Michael Hermanson. Fish from hatcheries were not included in the data analysis. Biofilm and SPMD data were blank corrected by censoring at one time the affiliated blank level. This blank correction made almost no change to the data because the samples masses were much higher than the blank masses. For this reason, blank correction was not required for the fish data.

The PMF analysis was performed using the PMF2 software of Paatero and Tapper (1994). This software requires three inputs: concentrations, limits of detection (LOD), and uncertainty of each data point. For both data sets (fish and biofilm/SPMD), the concentrations input was constructed by substituting one-half the detection limit for any measurements that were below detection after blank correction. LODs were taken directly from the data as provided. The standard deviations of the surrogate recoveries were used as the percent uncertainty for each detected concentration. For data points that were below detection, three times this uncertainty was used.

Fish

In 2020, the SRRTTF in cooperation with the Washington State Department of Fish and Wildlife (WDFW) and Washington State Department of Ecology (Ecology) assessed whole fish PCB levels in 1 year old wild Redband (Rainbow) Trout from the Spokane River (Lee et al., 2020) . The 30 new fish samples from this study were combined with the previous data set of 105 fish samples from various past Ecology studies, for a total of 135 fish samples of various species, age range, and both fillet and whole fish (see Appendix for details). The fish data therefore ranged from 2001 to 2020 and spatially ranged from River Mile (RM) 96.42 (Washington-Idaho border) to Lake Spokane. The 105 PCB peaks included in the PMF matrix included 96.2% of the PCB mass detected in the 2020 samples and 99.9% of the PCB mass in the previous 105 samples. Note that the various fish samples were analyzed using two different gas chromatography columns, giving rise to more than one coelution pattern. These patterns were rectified to make the various data sets compatible for pooled PMF analysis.

Biofilm and SPMD

In 2018, Ecology began characterizing PCB concentrations in biofilm from the Spokane River and evaluating its use in tracing PCB sources. The 60 biofilm samples were collected in 2018 and 2019 between RM 57.70 and 95.90 (Wong and Era-Miller, 2019, 2020). In 2020, the SRRTTF

recommended the use of SPMDs for long-term PCB monitoring in the Spokane River. They contracted with Gravity Consulting to implement sampling with SPMDs during 2020-2021. The SPMDs were deployed at Nine Mile Dam (RM 57.7), Mission Reach (RM 76.6), Upriver Dam (RM 79.8) and State Line (RM 95.9). The measured congener concentrations in the SPMD (not converted to water column equivalent) were used in the PMF model. The results of an alternate PMF run that used the SPMD data corrected to reflect whole water concentrations showed no difference with the model runs using the raw measured SPMD data.

Sixty-one peaks were included in the PMF model. They represented 96% of the PCB mass in the biofilm samples, but just 68% of the mass in the SPMD samples. This is in part because there were very few non-detects in the SPMD samples, so most of the congeners that were excluded from the PMF model were detected in the SPMDs.

Results

Fish

The previous analysis of the 105 fish samples found that the PMF model converged on a solution with six factors or source fingerprints, three of which were similar to Aroclor 1254. The new combined data set converged on just three factors, denoted FishA through FishC (Figure 1). Due to the absorption, distribution, metabolism, and excretion (ADME) processes that occur during uptake of PCBs by fish as well as their prey, PCB congener patterns can be very different in fish as compared to fresh Aroclors (Rodenburg et al., 2015; Rodenburg and Leidos, 2017). **Here we have compared the PMF factors for the fish data set with the Aroclors, but this should not be taken to mean that each factor represents one and only one Aroclor.** FishA was similar to Aroclor 1248 (R^2 = 0.83) and explained 10% of the PCB mass in the fish. FishB was similar to Aroclor 1254 (R^2 = 0.78) and explains 44% of the PCB mass in the fish. FishC was somewhat similar to Aroclor 1254 (R^2 = 0.50) and Aroclor 1260 (R^2 = 0.43) and explained 46% of the PCB mass in the fish. Therefore, the new PMF solution merged all of the 1254-like factors of the old PMF model into one. A multiple linear regression of each PMF factor versus the four main Aroclors (1016, 1248, 1254, and 1260) was conducted and the results indicated that all three factors have some similarity to additional Aroclors. The best-fit profile for FishA was 72% 1248, 16% 1254, and 11% 1260. The best-fit profile for FishB was 35% 1248, 53% 1254, and 13% 1260. The best-fit profile for FishC was 49% 1254 and 51% 1260 (Figure 1). None of the factors bore significant similarity to Aroclor 1016.

Notably, the PMF analysis did not generate a factor that is representative of non-Aroclor PCBs. PCB 11 is often used as an indicator of non-Aroclor PCBs because its abundance in the Aroclors is low (Rushneck et al., 2004) and it is often found in pigments (Litten et al., 2002; The Japanese Ministry of Economy Trade and Industry (METI), 2012, 2013). PCB 11 was included in the data set used in the PMF analysis, but it represents only about 0.04% of the PCB mass in the fish samples. Therefore, although non-Aroclor sources constitute about 10% of the PCBs in the water column (Rodenburg et al., 2020), they are negligible in the fish. This likely occurs because

the non-Aroclor sources are generally lower in MW, and low MW PCBs do not bioaccumulate as efficiently as higher MW congeners (Burkhard et al., 2012; Burkhard et al., 2013).

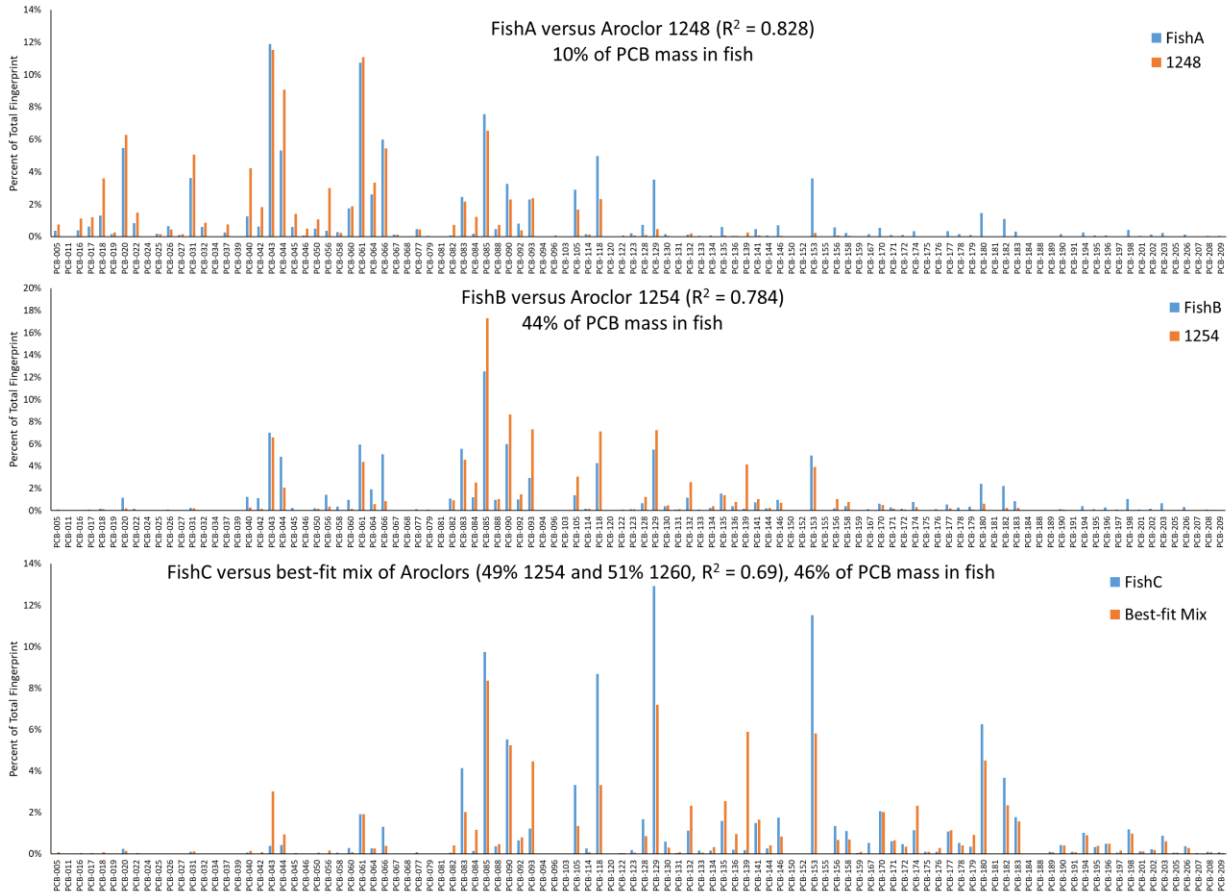


Figure 1. Fingerprints of the PCB source factors isolated from PMF analysis of the fish data.

In a previous publication (Rodenburg and Delistraty, 2019), we suggested some ratios of metabolizable versus recalcitrant congeners that could be used to quantify the extent of metabolism of PCBs in biota. The lower the ratio and more different it is from the ratio in the Aroclor, the more metabolism has occurred. The ratios for the Aroclors and the fish samples investigated here (Table 1) show extensive weathering of the higher molecular weight (MW) congeners (hexa and hepta) but minimal weathering of the penta congeners.

Table 1. Ratios of metabolizable versus recalcitrant congeners in fish PMF factors versus Aroclors calculated from Rushneck et al. (2004).

	90+101+113 83+99 (penta)	139+140+147+149 153+168 (hexa)	174 180+193 (hepta)
FishA (similar to 1248)	1.32	0.01	0.23
FishB (similar to 1254)	1.08	0.03	0.31
FishC (similar to 1260)	1.33	0.02	0.18
Aroclors:			
1016	1.66	1.09	0.43
1242	1.01	0.99	0.40
1248	1.07	1.16	0.49
1254	1.89	1.06	0.52
1260	32.00	0.99	0.52

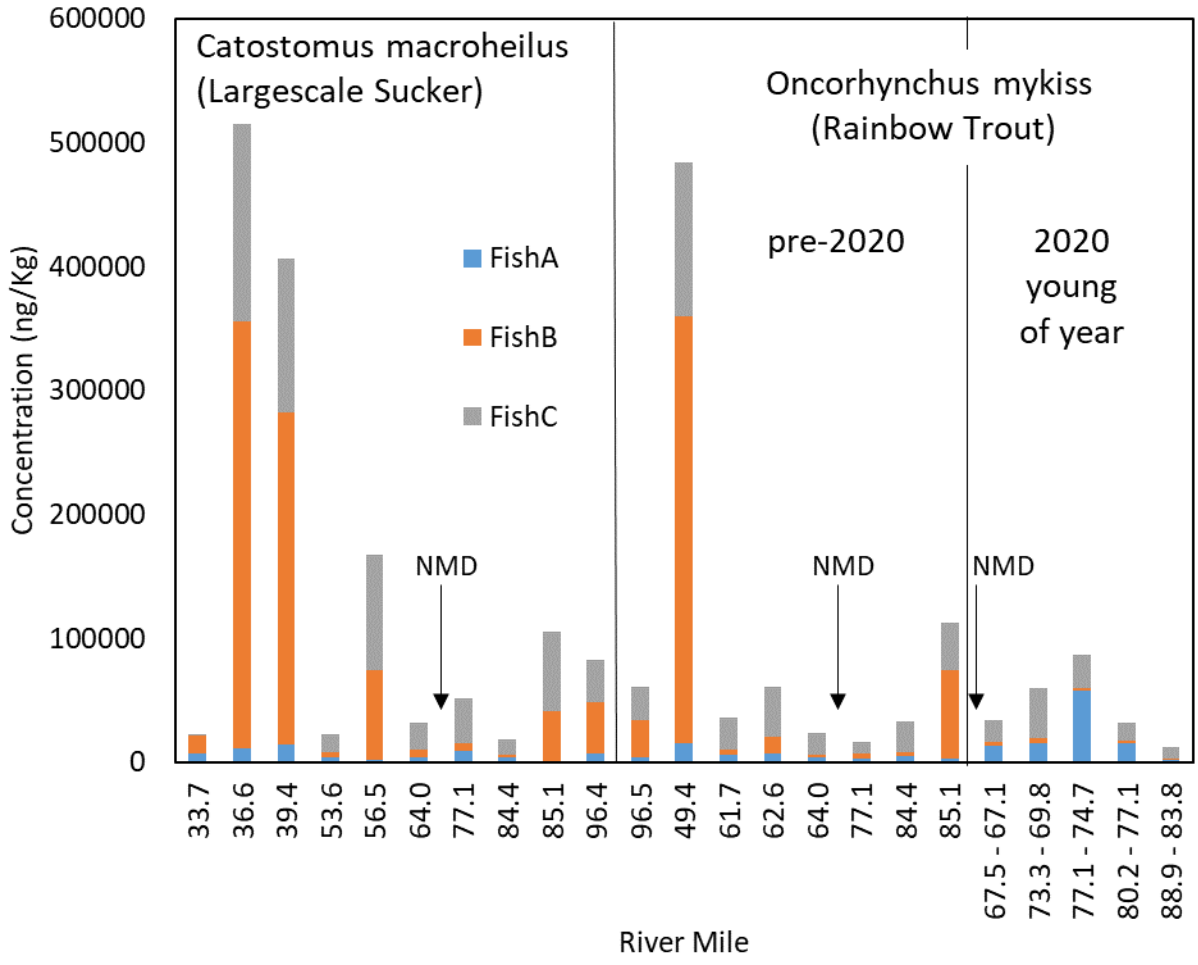


Figure 2. Concentrations of the three PMF-derived PCB source factors in select fish species averaged for river reach or mile. The location of Nine Mile Dam (NMD) is indicated with arrows. River flow is from right to left.

The various studies utilized in the fish analysis used different methodologies that complicate the interpretation of the results. These include differences in fish age, species, and trophic level (for example, older fish of the same species can have a different diet than younger fish), the type of tissue analyzed, the time of year and locations where fish were caught, the contract lab used, and perhaps other factors.

Of these, the type of tissue analyzed is not likely to be important in the context of PCB fingerprinting. Most studies analyzed either whole body or filet with skin, but 4 of the 135 samples were of gut contents. Previous work suggests that although absolute concentrations of PCBs may be different between whole body and filet samples, the congener patterns are typically the same (Rodenburg et al., 2015). However, gut contents may have very different congener patterns since they come from entirely different organisms. In the present work, there were no obvious differences between the 4 samples of gut contents versus the other tissues, but this comparison is difficult since the fish from which the gut contents were taken were not analyzed. Note that the type of tissue analyzed will affect the absolute concentrations of PCBs, but generally will not affect the relative contributions of the various congeners (i.e. the fingerprints).

A factor that could affect both PCB fingerprints and concentrations is the age of the fish. The 2020 study collected only young of year (YOY), while the other studies determined fish age (See Appendix). FishA is relatively abundant in *Oncorhynchus mykiss* (Rainbow Trout) collected in 2020 (Figure 2), which may imply that FishA is increasing in concentration over time. However, this abundance of FishA could also be related to the use of a different contract lab, the lower total PCB concentrations found in 2020, or the age of fish.

In general, FishA is a higher proportion of total PCBs in the fish when the total PCB concentrations are low (Figure 2). Conversely, FishB is proportionately more abundant at high concentrations. This may be because more recent samples have lower PCB concentrations overall, and the sources of PCBs to the river are shifting toward lower MW PCB formulations. Alternatively, this correlation could be due to the fact that the 2020 study used only YOY fish, making it difficult (or impossible) to separate the effects of fish age from time from concentration. This correlation may also partially explain the relatively low degree of metabolism of the lower molecular weight congeners found in FishA: low PCB concentrations may be less likely to promote metabolism in the fish (Wirgin et al., 2011). Again, it is difficult to separate the various issues at work, because there is some evidence that larger (i.e. older) fish have less cytochrome activity (Couillard et al., 2004). On the other hand, Hudson River fish exposed to high PCB levels have evolved changes in their cytochrome structure to make them more resistant to PCB toxicity (Wirgin et al., 2011), implying that some fish species do respond to changes in PCB levels with changes in their cytochrome pathways.

It is not possible to make meaningful comparisons between species due to the species, times, and locations at which fish were caught across the various studies. In contrast, it is possible to make some limited temporal assessments. Figure 3 shows the distribution of the PMF factors for two species at two river segments at several time points. Despite the different fish ages, the comparisons in the lower panel of Figure 3 (percent of total) are deemed reliable because the *Oncorhynchus mykiss* (Rainbow Trout) samples from 2003 and 2012 were never more than 3.5 years old with an average age of 1.75 years. Similarly, the *Catostomus macrocheilus* (Largescale Sucker) samples shown in Figure 3 are all from relatively old fish with ages ranging from 7.5 to 8.5 years for the 2003 samples and from 10.2 to 13.8 years for the 2012 samples. This figure suggests that FishB and FishC concentrations have declined sharply in both species at both locations since 2003, but FishA has not. However, the absolute concentrations of PCBs can be affected by the type of tissue analyzed, and this renders the upper panel of Figure 3 to be less reliable since the 2003 and 2012 samples are fillet while the 2020 is whole body. However, the trends show in Figure 3 are in general agreement with the hypothesis presented above that the PCB burden in the Spokane River is shifting toward lower MW PCBs as it is generally declining over time. FishA has in some cases increased in concentration over this period in the fish shown in Figure 3. The surface water data indicated that a fingerprint representing Aroclor 1248 was increasing in abundance at SR8a (RM 87) and SR9 (RM 90). This may be related the groundwater inputs of 1248 from the Kaiser facility just upstream of SR8a (LimnoTech, 2016). The analysis of the treated discharges suggested that upgrades of wastewater treatment facilities to membrane filtration are most effective at removing high MW PCBs (Rodenburg et al., 2022). Taken together, these results suggest a shift toward lower MW PCB sources in the Spokane River since about 2014, perhaps as a result of the implementation of PCB management plans.

Adult *Catostomus macrocheilus* feed primarily on benthic aquatic invertebrates, diatoms, and other plant material. In contrast, *Oncorhynchus mykiss* occupy a higher trophic level, eating insects and small fish. This difference in trophic level may explain why the PCB concentrations are generally higher in *Oncorhynchus mykiss* than *Catostomus macrocheilus* in fish caught in the same year around river mile 85 (Figure 3).

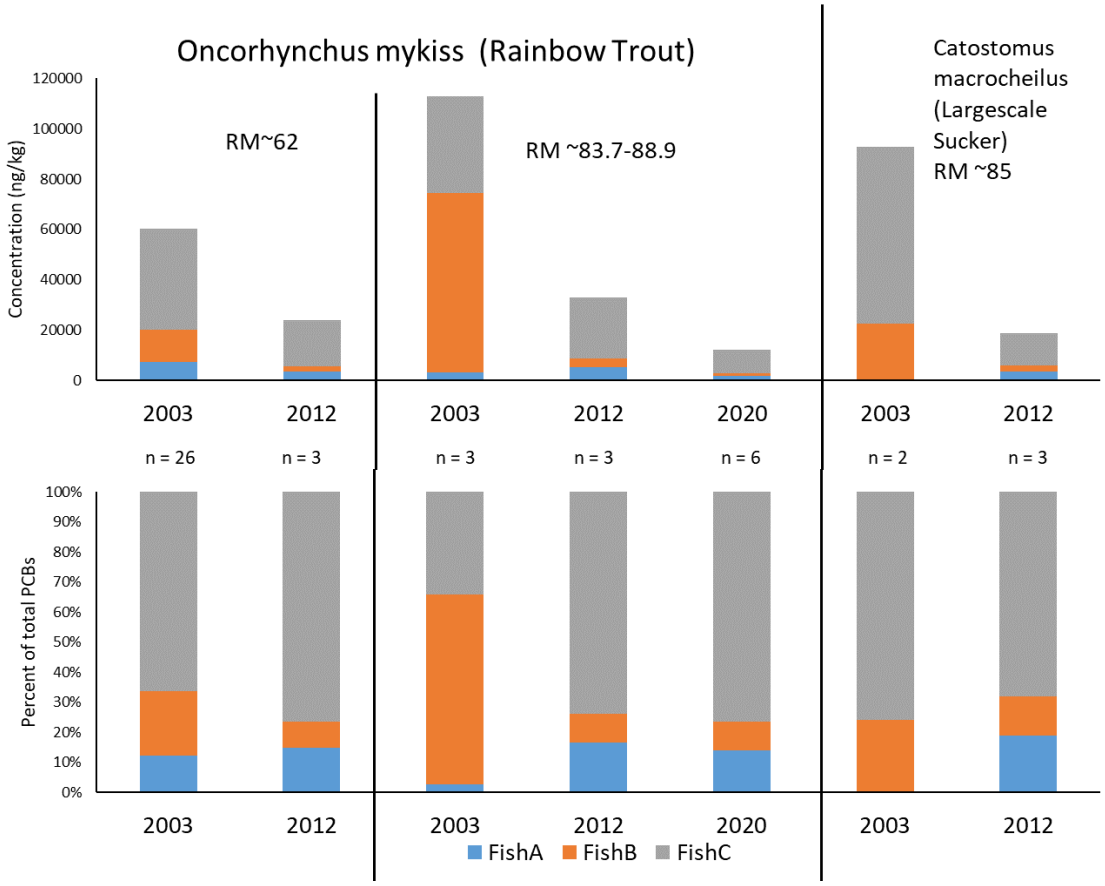


Figure 3. PCB sources in two species from a few general locations averaged by year of collection. FishA (blue) is similar to Aroclor 1248. FishB (orange) is similar to Aroclor 1254. FishC (grey) is similar to Aroclor 1260.

Biofilm and SPMD

The SPMD and biofilm samples have somewhat different congener patterns. The SPMD samples closely resemble the water samples. This is good news as it indicates that SPMDs are a good way to assess not only the concentrations of PCBs in the water column, but also their fingerprints. In contrast, the biofilm has a higher MW pattern that is more similar to the fish. Biofilm fingerprints are much more variable than the fingerprints in the SPMD. In Figure 4, the fingerprint in 'baseline' biofilm samples is compared to the pattern in the fish. For purposes of this report, the baseline is defined as < 1000 pg/g, which is the median concentration in the biofilm samples.

The decision to combine the biofilm and SPMD samples into one data set for the PMF analysis was based on the assumption that both represent passive sampling of the water column, and the fact that there were not enough SPMD samples to analyze them separately via PMF. To assess the impact of adding the SPMD samples to the biofilm PMF analysis, the biofilm data was

analyzed without the SPMD. The PMF solution was virtually identical to the solution obtained when SPMD samples were included, so the SPMD samples were retained in the final data set.

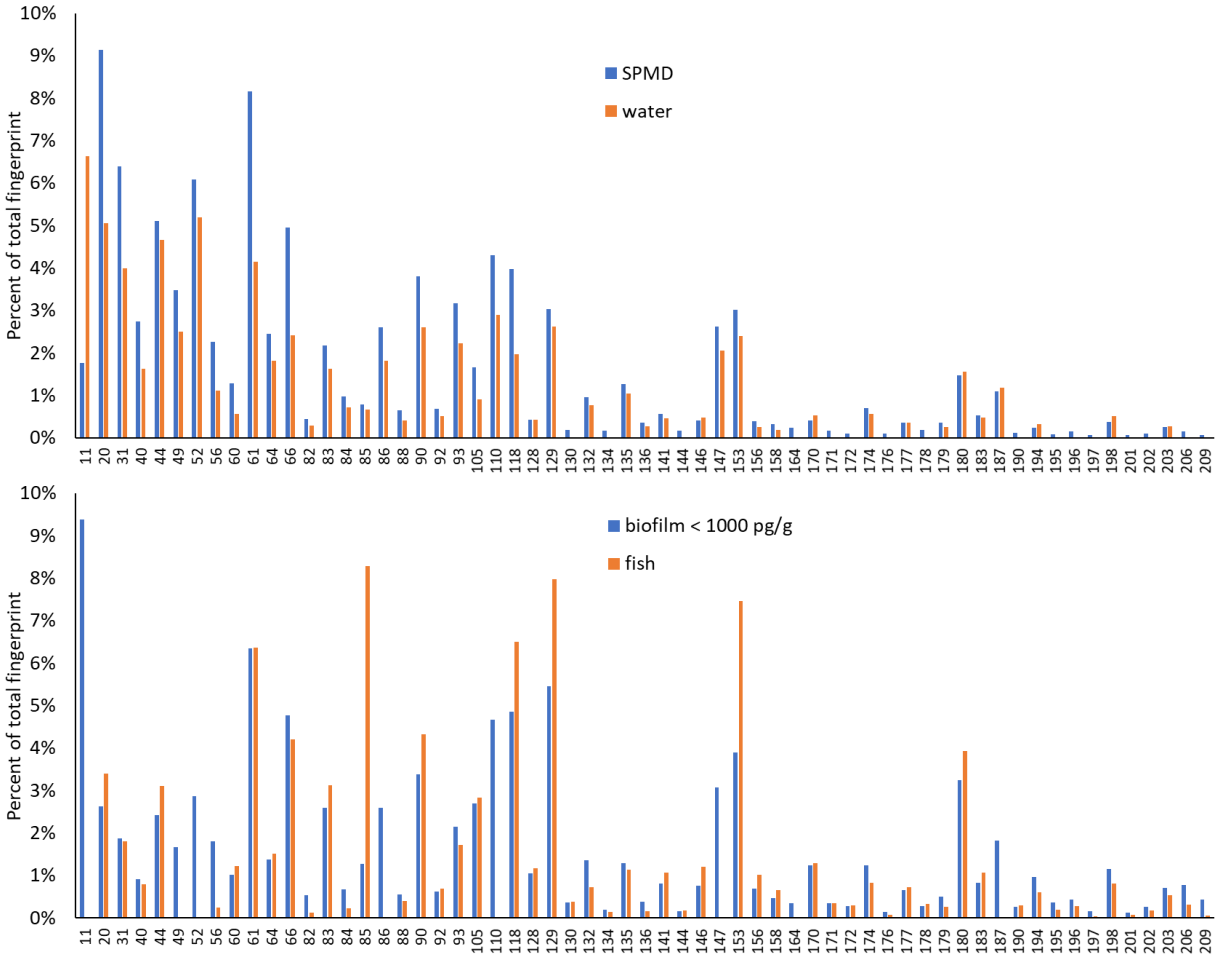
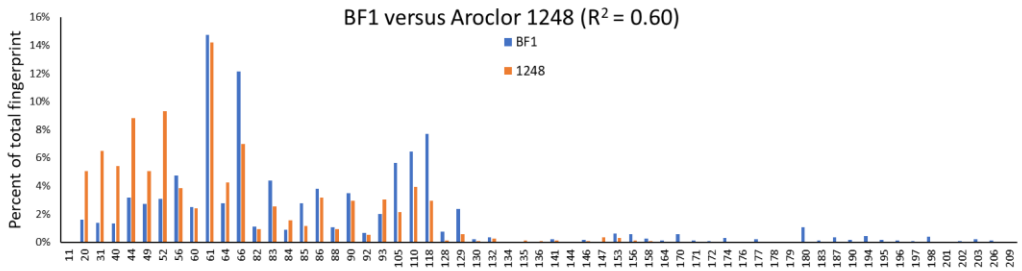


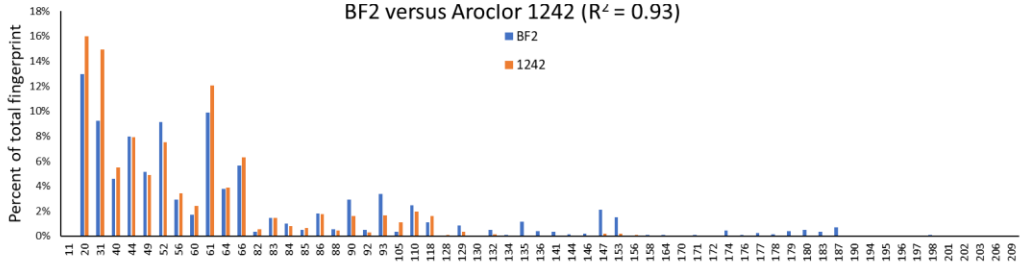
Figure 4. Average congener patterns in the 2020 SPMD (top, blue) and 2018-2019 biofilm (bottom, blue) samples in which the total PCB concentration was less than 1000 pg/g compared to water from 2018 (top, orange) and fish collected in 2020 (bottom, orange). Note that due to differences in coelution patterns, these comparisons are inexact and are presented here only to illustrate the differences between the two matrices.

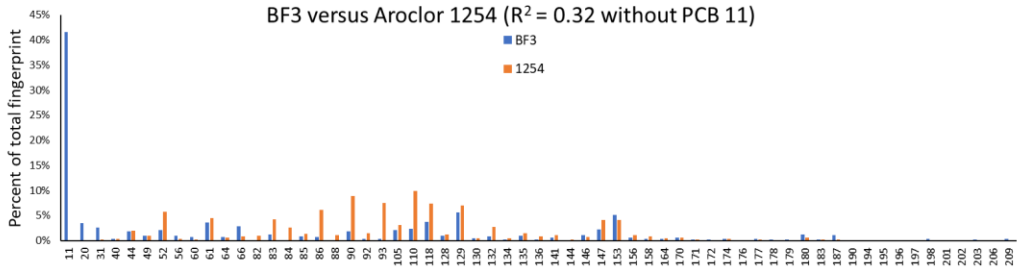
PMF analysis of the biofilm/SPMD data set yielded six factors, denoted BF1 through BF6 (Figure 5). BF2, BF4, and BF5 were very similar to Aroclors 1242, 1254, and 1260, respectively, with R^2 values all above 0.87. These high R^2 values indicate minimal weathering. BF3 contains a high contribution (42%) from PCB 11, but the remainder of the BF3 fingerprint somewhat resembles Aroclor 1254 (R^2 = 0.32), suggesting that is a mixed source. In the Delaware River, a factor containing both PCB 11 and some Aroclor congener showed a positive correlation with river flow, suggesting that it might be related to stormwater and/or CSOs (Du et al., 2008). BF1 is similar to Aroclor 1248 (R^2 = 0.60). BF6 contains high MW congeners such as PCBs 206 and 209. 206 is more abundant than 209 in this signal, which probably indicates that it is not related to

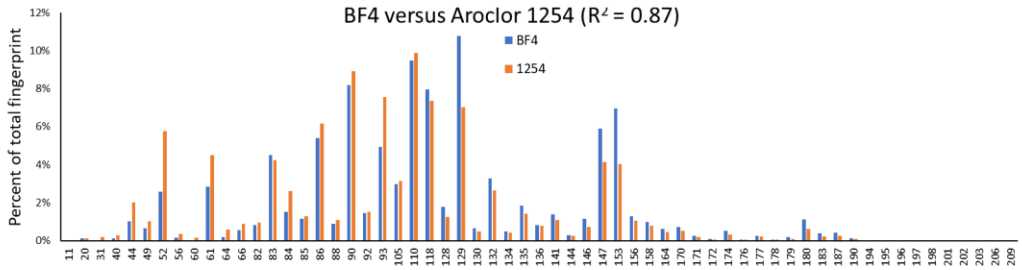
pigments such as titanium dioxide or phthalocyanine green. Instead, the fact that PCB 206 is more abundant than PCB 209 suggests it results from high MW Aroclors such as 1260, 1262, and 1268. It resembles each of these Aroclors with R^2 values of 0.2 versus 1260 and around 0.4 for 1262 and 1268. The mix of Aroclors that best fits this profile is 2% 1248, 17% 1254, 56% 1262, and 25% 1268 with an R^2 value of 0.74. The PMF analysis of the influents to the Spokane area dischargers indicated that Aroclor 1268 was present in the influents of the Hayden area wastewater treatment plant. We have speculated that this signal results from the use of Galbestos building material somewhere in the watershed. BF6 is most abundant in some of the samples from the Mission Reach hotspot area. Thus, BF6 could be related to the use of these high MW Aroclors in the Spokane River. It is possible that BF4 represents the high MW fraction of Aroclor 1260 which is relatively unreactive and insoluble.

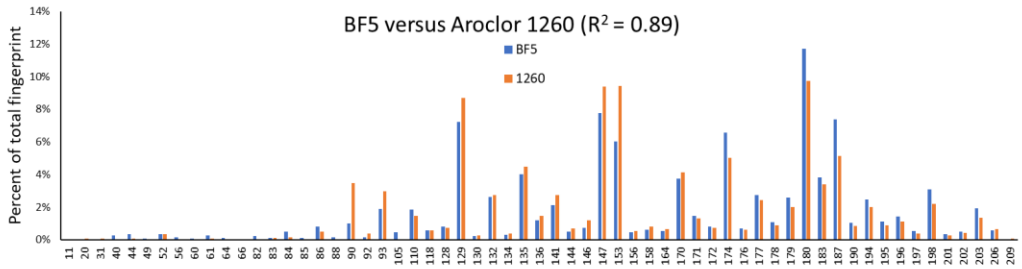
As the raw congener patterns suggested, the abundance of the PMF factors was very different between biofilm and SPMD samples. As depicted in Figure 4, SPMD samples resembled the water column, which contains proportionately more low MW PCBs relative to the biofilm, which appeared to preferentially accumulate the higher MW PCBs based on the results of this study. The relative abundance of each of the factors is greatly skewed by the extremely high concentration (about 615,000 pg/g) in sample SR3A (1809040-12). Even without this sample, the abundance of factors in the biofilm is still quite different from the SPMD samples. Lower concentration biofilm samples (less than 1,000 pg/g) have very different relative abundance of factors from the high concentration biofilm samples.


BF1 versus Aroclor 1248 (R^2 = 0.60)
BF1
1248
Percent of total fingerprint


BF2 versus Aroclor 1242 (R^2 = 0.93)
BF2
1242
Percent of total fingerprint


BF3 versus Aroclor 1254 (R^2 = 0.32 without PCB 11)
BF3
1254
Percent of total fingerprint


BF4 versus Aroclor 1254 (R^2 = 0.87)
BF4
1254
Percent of total fingerprint


BF5 versus Aroclor 1260 (R^2 = 0.89)
BF5
1260
Percent of total fingerprint

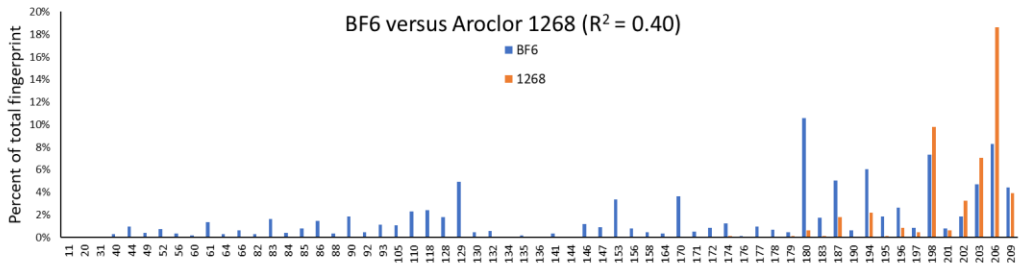

BF6 versus Aroclor 1268 (R^2 = 0.40)
BF6
1268
Percent of total fingerprint

Figure 5. Fingerprints of the six factors resolved from PMF analysis of the biofilm/SPMD data set.

The 2018 biofilm sampling campaign results are shown in Figure 6. Both the outlier sample SR3A (1809040-12) and its reanalysis were included in the PMF input and are shown here Figure 6. This sample (both the original and the reanalyzed version) consisted mostly of BF4 (Aroclor 1260). The 2019 biofilm sampling campaign results are shown in Figure 7. Here, the highest concentration samples are dominated by BF2 (Aroclor 1254). Taken together, these two campaigns demonstrate that high MW PCB formulations can dominate at a small number of locations (hotspots), whereas the low concentration 'baseline' samples contain proportionately more of the low MW PCB formulations. The baseline concentration is roughly below about 1,000 pg/g in the biofilm. The samples below this concentration contain proportionately more BF1 and BF3 (**Error! Reference source not found.**).

The similarity between the congener patterns in the fish and biofilm (Figure 4) suggests that it is reasonable to compare these two sets of samples. The biofilm samples are of recent vintage, so they are best compared with the 2020 fish samples. This comparison suggests that the small number of high concentration biofilm samples, which are dominated by high MW PCBs, are not driving the concentrations in the fish, which are increasingly over time dominated by factors that represent lower MW PCB formulations. Since feeder fish have, in general, a higher MW pattern than the water column, this shift may indicate that the fish are increasingly accumulating PCBs via bioconcentration (i.e. direct uptake from water) rather than from biomagnification (i.e. uptake via food). In particular, at around RM 75.9 (SR3) the biofilm is dominated by high MW sources, but the 2020 fish contain a ~50/50 mix of FishA (similar to 1248) and FishC (similar to 1260), which is a higher proportion of FishA and lower proportion of FishC than at any other site sampled in 2020 except RM 78.2 (site SR4).

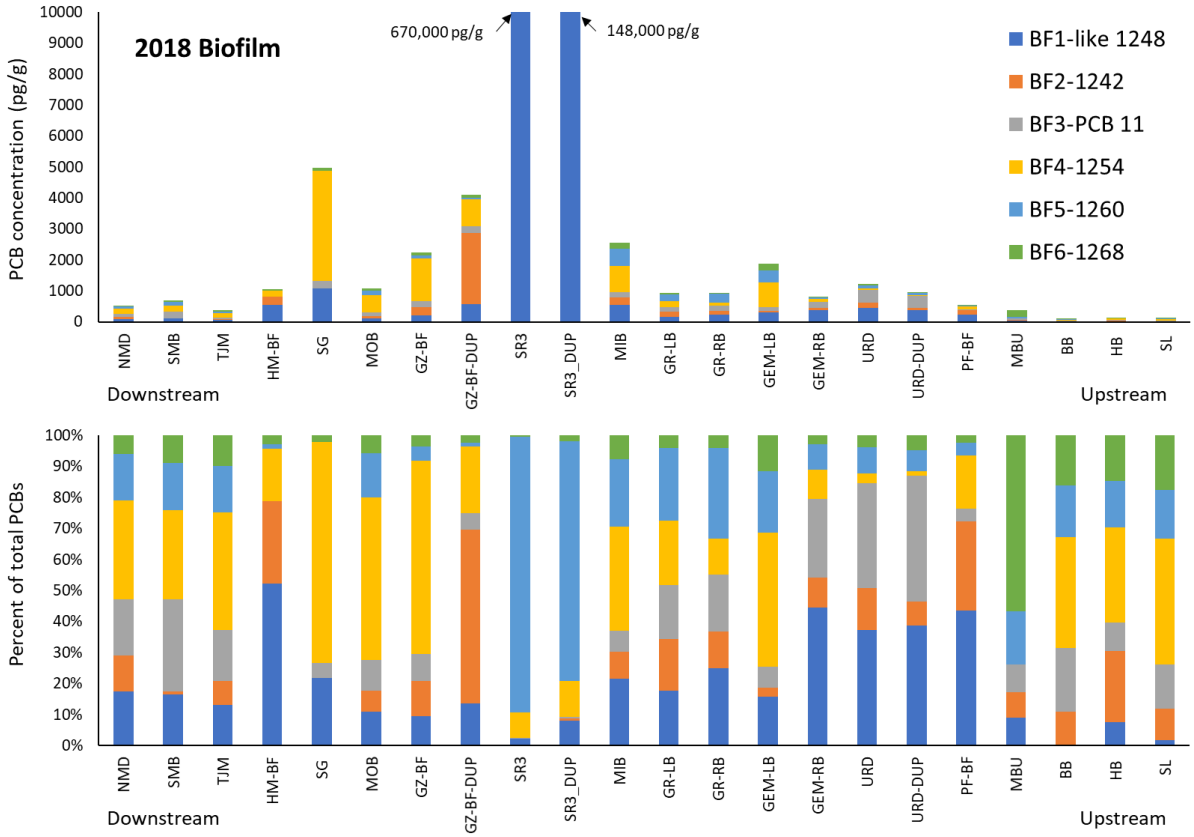


Figure 6. Abundance of the six biofilm PMF factors in biofilm samples collected in 2018.

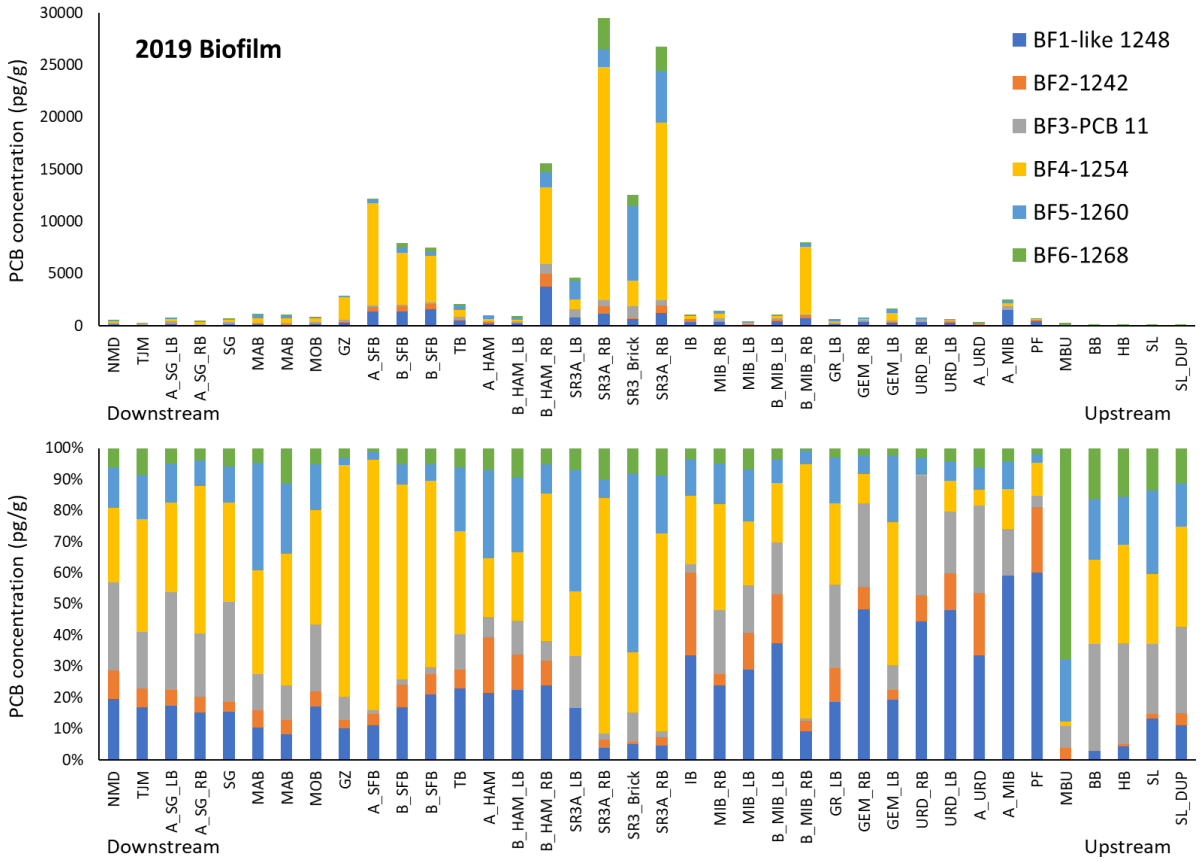


Figure 7. Abundance of the six biofilm PMF factors in biofilm samples collected in 2019.

The SPMD samples (Figure 8) display comparatively little variation in the relative abundance of the six PCB factors. However, because they integrate sources over a long period of time, this is to be expected. Even small differences in the abundance of the various factors may be significant for SPMD samples. The highest concentrations were always observed at Mission Reach (station name TS in Figure 8). The September 2020 sample from TS shows proportionately more BF2 and less of the three higher MW fingerprints (BF4, BF5, and BF6) than the other stations during this deployment. However, in the other two deployments, the relative abundance of the six factors is not noticeably different between TS, NM (Nine Mile Dam) and UP (Upriver Dam). In all three deployments, however, SL (State Line) shows a higher molecular weight pattern with proportionately more BF4 (similar to Aroclor 1254) and BF5 (similar to Aroclor 1260).

Figure 8. Abundance of the six biofilm PMF factors in SPMD samples collected during three deployment periods.

Conclusions

The addition of new fish samples has allowed the PMF model to group all of the Aroclor 1254-like fingerprints into one PMF factor. The fish PMF model results suggest that the overall fish PCB signal may be shifting toward lower molecular weight congeners. This may also suggest that fish are increasingly taking up PCBs via direct uptake from water (i.e. bioconcentration) rather than from indirect uptake via diet (biomagnification).

The biofilm samples are a highly effective means of characterizing PCB sources to the river on a relatively fine spatial scale. They have allowed the identification of PCB sources near Mission Reach. The PMF analysis indicates that these sources are dominated by Monsanto's Aroclors 1260 and 1254. Biofilm samples have also identified a source of Aroclor 1268 in the Spokane River. This source should be relatively easy to track down because Aroclor 1268 was used in a very limited number of applications. The biofilm samples corroborate the finding that PCB 11 is a significant contributor to total PCBs in the water column of the Spokane River. This is important because the water column samples are difficult to interpret due to the interference of PCB from the blanks. The biofilm samples contain high enough PCB masses that the blanks

are negligible, so they indicate that PCB 11 is truly a contaminant in the water column of the Spokane River and not a blank artifact.

The SPMD samples were less helpful in identifying PCB sources, due to the limited number of samples collected. Because their congener patterns are different from the biofilm samples, they should be analyzed separately, if there are enough SPMD samples to allow a separate PMF analysis.

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Table A-1: Details of fish samples. YOY = young of year. NA = not available.

Location	Sample ID	Study ID	Sample Date	River Mile	Taxon Name	Tissue Type	Age (years)
LAKE SPOKANE	1611047-10	mifr0003	9/23/2016	49.4	Oncorhynchus mykiss	Whole organism	NA
LAKE SPOKANE	1611047-11	mifr0003	9/23/2016	49.4	Oncorhynchus mykiss	Whole organism	NA
LAKE SPOKANE	1611047-12	mifr0003	9/23/2016	49.4	Oncorhynchus mykiss	Whole organism	NA
LAKE SPOKANE	1611047-14	mifr0003	9/23/2016	49.4	Oncorhynchus mykiss	Whole organism	NA
LONG LAKE	1410029-02	BERA0011	9/28/2014	50.5	Cyprinus carpio	Whole organism	14
LONG LAKE	1410029-03	BERA0011	9/28/2014	50.5	Cyprinus carpio	Whole organism	11
LONG LAKE	1410029-04	BERA0011	9/28/2014	50.5	Cyprinus carpio	Whole organism	17
LONG LAKE	1410029-06	BERA0011	9/28/2014	50.5	Cyprinus carpio	Whole organism	5
LONG LAKE	1410029-09	BERA0011	9/28/2014	50.5	Cyprinus carpio	Whole organism	10
LONG LAKE	1410029-10	BERA0011	9/28/2014	50.5	Cyprinus carpio	Whole organism	10
LONG LAKE	1410029-12	BERA0011	9/28/2014	50.5	Cyprinus carpio	Whole organism	5
LONG LAKE	1410029-13	BERA0011	9/29/2014	50.5	Cyprinus carpio	Whole organism	13
LONG LAKE	1410029-14	BERA0011	9/29/2014	50.5	Cyprinus carpio	Whole organism	10
LONG LAKE	1410029-15	BERA0011	9/29/2014	50.5	Cyprinus carpio	Whole organism	10
Lower Long Lake	2138288	RJAC002	6/19/2001	36.6	Catostomus macrocheilus	Fillet, skin on	10.6
Lower Long Lake	2138289	RJAC002	6/19/2001	36.6	Catostomus macrocheilus	Fillet, skin on	4.7
Lower Long Lake	2138290	RJAC002	6/19/2001	36.6	Catostomus macrocheilus	Fillet, skin on	8.9
Lower Long Lake	2158303	RJAC002	6/19/2001	36.6	Micropterus salmoides	Fillet, skin on	9
Lower Long Lake	2158304	RJAC002	6/19/2001	36.6	Micropterus salmoides	Fillet, skin on	7.5
Lower Long Lake	2158305	RJAC002	6/19/2001	36.6	Micropterus salmoides	Fillet, skin on	6.8
LONGLOW-F	4324444	DSER0010	7/13/2004	39.4	Catostomus macrocheilus	Whole organism	8.2
LONGLOW-F	4324446	DSER0010	7/13/2004	39.4	Catostomus macrocheilus	Whole organism	7.6
NINEMILE-F	4188310	DSER0010	9/16/2003	61.7	Oncorhynchus mykiss	**Gut contents**	1.6
NINEMILE-F	4324447	DSER0010	7/13/2004	61.7	Catostomus columbianus	Whole organism	9.1
NINEMILE-F	4324448	DSER0010	7/13/2004	61.7	Catostomus columbianus	Whole organism	NA
NINEMILE-F	4324449	DSER0010	7/13/2004	61.7	Catostomus columbianus	**Gut contents**	6
NINEMILE-F	4324450	DSER0010	7/13/2004	61.7	Catostomus columbianus	Whole organism	5.4

Location	Sample ID	Study ID	Sample Date	River Mile	Taxon Name	Tissue Type	Age (years)
PLANTE-F	4188308	DSER0010	9/15/2003	85.1	Oncorhynchus mykiss	Fillet, skin on	2.9
PLANTE-F	4188309	DSER0010	9/15/2003	85.1	Oncorhynchus mykiss	Fillet, skin on	3.2
PLANTE-F	4188311	DSER0010	9/15/2003	85.1	Oncorhynchus mykiss	**Gut contents**	2.6
PLANTE-F	4324440	DSER0010	9/15/2003	85.1	Catostomus macrocheilus	Whole organism	7.9
PLANTE-F	4324441	DSER0010	9/15/2003	85.1	Catostomus macrocheilus	Whole organism	7.5
PLANTE-F	4324445	DSER0010	9/15/2003	85.1	Catostomus macrocheilus	**Gut contents**	8.5
Spokane River (River Mile 56.5 - 57.1)	1301011-49	WSTMP12	9/26/2012	56.5	Catostomus macrocheilus	Whole organism	17.6
Spokane River (River Mile 56.5 - 57.1)	1301011-50	WSTMP12	9/26/2012	56.5	Catostomus macrocheilus	Whole organism	13.6
Spokane River (River Mile 56.5 - 57.1)	1301011-51	WSTMP12	9/26/2012	56.5	Catostomus macrocheilus	Whole organism	19.8
Spokane River (River Mile 56.5 - 57.1)	1301011-68	WSTMP12	9/26/2012	56.5	Prosopium williamsoni	Fillet, skin on	2.2
Spokane River (River Mile 56.5 - 57.1)	1301011-69	WSTMP12	9/26/2012	56.5	Prosopium williamsoni	Fillet, skin on	2.4
Spokane River (River Mile 56.5 - 57.1)	1301011-70	WSTMP12	9/26/2012	56.5	Prosopium williamsoni	Fillet, skin on	2
Spokane River (River Mile 64.0)	1301011-27	WSTMP12	9/25/2012	64.0	Catostomus macrocheilus	Whole organism	9.2
Spokane River (River Mile 64.0)	1301011-28	WSTMP12	9/25/2012	64.0	Catostomus macrocheilus	Whole organism	9.4
Spokane River (River Mile 64.0)	1301011-29	WSTMP12	9/25/2012	64.0	Catostomus macrocheilus	Whole organism	10.4

Location	Sample ID	Study ID	Sample Date	River Mile	Taxon Name	Tissue Type	Age (years)
Spokane River (River Mile 64.0)	1301011-61	WSTMP12	9/25/2012	64.0	Prosopium williamsoni	Fillet, skin on	2.6
Spokane River (River Mile 64.0)	1301011-62	WSTMP12	9/25/2012	64.0	Prosopium williamsoni	Fillet, skin on	3.3
Spokane River (River Mile 64.0)	1301011-83	WSTMP12	9/25/2012	64.0	Oncorhynchus mykiss	Fillet, skin on	3.5
Spokane River (River Mile 64.0)	1301011-84	WSTMP12	9/25/2012	64.0	Oncorhynchus mykiss	Fillet, skin on	2
Spokane River (River Mile 64.0)	1301011-85	WSTMP12	9/25/2012	64.0	Oncorhynchus mykiss	Fillet, skin on	1.4
Spokane River (River Mile 77.0)	1301011-20	WSTMP12	9/19/2012	77.1	Catostomus macrocheilus	Whole organism	14.2
Spokane River (River Mile 77.0)	1301011-21	WSTMP12	9/19/2012	77.1	Catostomus macrocheilus	Whole organism	11.2
Spokane River (River Mile 77.0)	1301011-22	WSTMP12	9/19/2012	77.1	Catostomus macrocheilus	Whole organism	15.6
Spokane River (River Mile 77.0)	1301011-56	WSTMP12	9/19/2012	77.1	Prosopium williamsoni	Fillet, skin on	5.6
Spokane River (River Mile 77.0)	1301011-57	WSTMP12	9/19/2012	77.1	Prosopium williamsoni	Fillet, skin on	4.2
Spokane River (River Mile 77.0)	1301011-58	WSTMP12	9/19/2012	77.1	Prosopium williamsoni	Fillet, skin on	4
Spokane River (River Mile 77.0)	1301011-60	WSTMP12	9/19/2012	77.1	Prosopium williamsoni	Fillet, skin on	11
Spokane River (River Mile 77.0)	1301011-80	WSTMP12	9/19/2012	77.1	Oncorhynchus mykiss	Fillet, skin on	3.4
Spokane River (River Mile 77.0)	1301011-81	WSTMP12	9/19/2012	77.1	Oncorhynchus mykiss	Fillet, skin on	2.4
Spokane River (River Mile 77.0)	1301011-82	WSTMP12	9/19/2012	77.1	Oncorhynchus mykiss	Fillet, skin on	1.3
Spokane River (River Mile 96.0)	1301011-42	WSTMP12	9/24/2012	96.4	Catostomus macrocheilus	Whole organism	12.4

Location	Sample ID	Study ID	Sample Date	River Mile	Taxon Name	Tissue Type	Age (years)
Spokane River (River Mile 96.0)	1301011-43	WSTMP12	9/24/2012	96.4	Catostomus macrocheilus	Whole organism	13.2
Spokane River (River Mile 96.0)	1301011-44	WSTMP12	9/24/2012	96.4	Catostomus macrocheilus	Whole organism	12.4
Spokane River (River Mile 33.7)	1301011-13	WSTMP12	10/2/2012	33.7	Catostomus macrocheilus	Whole organism	8.6
Spokane River (River Mile 33.7)	1301011-14	WSTMP12	10/2/2012	33.7	Catostomus macrocheilus	Whole organism	9.6
Spokane River (River Mile 33.7)	1301011-15	WSTMP12	10/2/2012	33.7	Catostomus macrocheilus	Whole organism	8.4
Spokane River (River Mile 84.4)	1301011-34	WSTMP12	9/20/2012	84.4	Catostomus macrocheilus	Whole organism	12.4
Spokane River (River Mile 84.4)	1301011-35	WSTMP12	9/20/2012	84.4	Catostomus macrocheilus	Whole organism	13.8
Spokane River (River Mile 84.4)	1301011-36	WSTMP12	9/20/2012	84.4	Catostomus macrocheilus	Whole organism	10.2
Spokane River (River Mile 84.4)	1301011-86	WSTMP12	9/20/2012	84.4	Oncorhynchus mykiss	Fillet, skin on	3.3
Spokane River (River Mile 84.4)	1301011-87	WSTMP12	9/20/2012	84.4	Oncorhynchus mykiss	Fillet, skin on	2
Spokane River (River Mile 84.4)	1301011-88	WSTMP12	9/20/2012	84.4	Oncorhynchus mykiss	Fillet, skin on	1.4
Spokane-F	3084281	WSTMP03T	9/16/2003	62.6	Oncorhynchus mykiss	Fillet, skin on	1
Spokane-F	3084282	WSTMP03T	9/16/2003	62.6	Oncorhynchus mykiss	Fillet, skin on	2
Spokane-F	3084283	WSTMP03T	9/16/2003	62.6	Oncorhynchus mykiss	Fillet, skin on	1
Spokane-F	3084284	WSTMP03T	9/16/2003	62.6	Oncorhynchus mykiss	Fillet, skin on	1
Spokane-F	3084285	WSTMP03T	9/16/2003	62.6	Oncorhynchus mykiss	Fillet, skin on	3
Spokane-F	3084286	WSTMP03T	9/16/2003	62.6	Oncorhynchus mykiss	Fillet, skin on	1
Spokane-F	3084287	WSTMP03T	9/16/2003	62.6	Oncorhynchus mykiss	Fillet, skin on	1
Spokane-F	3084288	WSTMP03T	9/16/2003	62.6	Oncorhynchus mykiss	Fillet, skin on	1
Spokane-F	3084289	WSTMP03T	9/16/2003	62.6	Oncorhynchus mykiss	Fillet, skin on	3

Location	Sample ID	Study ID	Sample Date	River Mile	Taxon Name	Tissue Type	Age (years)
Spokane-F	3084290	WSTMP03T	9/16/2003	62.6	Oncorhynchus mykiss	Fillet, skin on	3
Spokane-F	3084291	WSTMP03T	9/16/2003	62.6	Oncorhynchus mykiss	Fillet, skin on	3
Spokane-F	3084292	WSTMP03T	9/16/2003	62.6	Oncorhynchus mykiss	Fillet, skin on	1
Spokane-F	3084293	WSTMP03T	9/16/2003	62.6	Oncorhynchus mykiss	Fillet, skin on	1
Spokane-F	3084294	WSTMP03T	9/16/2003	62.6	Oncorhynchus mykiss	Fillet, skin on	1
Spokane-F	3084295	WSTMP03T	9/16/2003	62.6	Oncorhynchus mykiss	Fillet, skin on	1
Spokane-F	3084296	WSTMP03T	9/16/2003	62.6	Oncorhynchus mykiss	Fillet, skin on	1
Spokane-F	3084298	WSTMP03T	9/16/2003	62.6	Oncorhynchus mykiss	Fillet, skin on	1
Spokane-F	3084299	WSTMP03T	9/16/2003	62.6	Oncorhynchus mykiss	Fillet, skin on	1
Spokane-F	3084301	WSTMP03T	9/16/2003	62.6	Oncorhynchus mykiss	Fillet, skin on	1
Spokane-F	3084302	WSTMP03T	9/16/2003	62.6	Oncorhynchus mykiss	Fillet, skin on	1
Spokane-F	3084303	WSTMP03T	9/16/2003	62.6	Oncorhynchus mykiss	Fillet, skin on	2
Spokane-F	3084304	WSTMP03T	9/16/2003	62.6	Oncorhynchus mykiss	Fillet, skin on	1
Spokane-F	3084305	WSTMP03T	9/16/2003	62.6	Oncorhynchus mykiss	Fillet, skin on	1
Spokane-F	3084306	WSTMP03T	9/16/2003	62.6	Oncorhynchus mykiss	Fillet, skin on	1
Spokane-F	3084308	WSTMP03T	9/16/2003	62.6	Oncorhynchus mykiss	Fillet, skin on	NA
STATELINE-F	4324442	DSER0010	7/14/2004	96.5	Catostomus macrocheilus	Whole organism	11.6
STATELINE-F	4324443	DSER0010	7/14/2004	96.5	Catostomus macrocheilus	Whole organism	8.6
Upper Long Lake	2138280	RJAC002	6/19/2001	53.6	Catostomus macrocheilus	Fillet, skin on	6
Upper Long Lake	2138286	RJAC002	6/19/2001	53.6	Catostomus macrocheilus	Fillet, skin on	16.3
Upper Long Lake	2138287	RJAC002	6/19/2001	53.6	Catostomus macrocheilus	Fillet, skin on	9.4
Upper Long Lake	2158306	RJAC002	6/19/2001	53.6	Micropterus salmoides	Fillet, skin on	6.2
Upper Long Lake	2158307	RJAC002	6/19/2001	53.6	Micropterus salmoides	Fillet, skin on	6.7
Upper Long Lake	2158308	RJAC002	6/19/2001	53.6	Prosopium williamsoni	Fillet, skin on	3.5
Upper Long Lake	2158309	RJAC002	6/19/2001	53.6	Prosopium williamsoni	Fillet, skin on	3.5
Upper Long Lake	2158310	RJAC002	6/19/2001	53.6	Prosopium williamsoni	Fillet, skin on	3.3
Upper Long Lake	2158311	RJAC002	6/19/2001	53.6	Micropterus salmoides	Fillet, skin on	6.9
2020-SR2 (01-05)	2020-SR2 (01-05)		2020	Reach 2 (RM 88.9 - 83.8)	Oncorhynchus mykiss	Whole organism	YOY

Location	Sample ID	Study ID	Sample Date	River Mile	Taxon Name	Tissue Type	Age (years)
2020-SR2 (06-10)	2020-SR2 (06-10)		2020	Reach 2 (RM 88.9 - 83.8)	Oncorhynchus mykiss	Whole organism	YOY
2020-SR2 (11-15)	2020-SR2 (11-15)		2020	Reach 2 (RM 88.9 - 83.8)	Oncorhynchus mykiss	Whole organism	YOY
2020-SR2 (16-20)	2020-SR2 (16-20)		2020	Reach 2 (RM 88.9 - 83.8)	Oncorhynchus mykiss	Whole organism	YOY
2020-SR2 (21-25)	2020-SR2 (21-25)		2020	Reach 2 (RM 88.9 - 83.8)	Oncorhynchus mykiss	Whole organism	YOY
2020-SR3 (01-05)	2020-SR3 (01-05)		2020	Reach 3 (RM 80.2 - 77.1)	Oncorhynchus mykiss	Whole organism	YOY
2020-SR3 (06-10)	2020-SR3 (06-10)		2020	Reach 3 (RM 80.2 - 77.1)	Oncorhynchus mykiss	Whole organism	YOY
2020-SR3 (11-15)	2020-SR3 (11-15)		2020	Reach 3 (RM 80.2 - 77.1)	Oncorhynchus mykiss	Whole organism	YOY
2020-SR3 (16-20)	2020-SR3 (16-20)		2020	Reach 3 (RM 80.2 - 77.1)	Oncorhynchus mykiss	Whole organism	YOY
2020-SR3 (21-25)	2020-SR3 (21-25)		2020	Reach 3 (RM 80.2 - 77.1)	Oncorhynchus mykiss	Whole organism	YOY
2020-SR4 (01-05)	2020-SR4 (01-05)		2020	Reach 4 (RM 77.1 - 74.7)	Oncorhynchus mykiss	Whole organism	YOY
2020-SR4 (06-10)	2020-SR4 (06-10)		2020	Reach 4 (RM 77.1 - 74.7)	Oncorhynchus mykiss	Whole organism	YOY
2020-SR4 (06-10) (Duplicate)	2020-SR4 (06-10) (Duplicate)		2020	Reach 4 (RM 77.1 - 74.7)	Oncorhynchus mykiss	Whole organism	YOY
2020-SR4 (11-15)	2020-SR4 (11-15)		2020	Reach 4 (RM 77.1 - 74.7)	Oncorhynchus mykiss	Whole organism	YOY
2020-SR4 (16-20)	2020-SR4 (16-20)		2020	Reach 4 (RM 77.1 - 74.7)	Oncorhynchus mykiss	Whole organism	YOY
2020-SR2 (11-15) Rep	2020-SR2 (11-15) Rep		2020	Reach 2 (RM 88.9 - 83.8)	Oncorhynchus mykiss	Whole organism	YOY
2020-SR3 (16-20) Rep	2020-SR3 (16-20) Rep		2020	Reach 3 (RM 80.2 - 77.1)	Oncorhynchus mykiss	Whole organism	YOY

Location	Sample ID	Study ID	Sample Date	River Mile	Taxon Name	Tissue Type	Age (years)
2020-SR4 (21-25)	2020-SR4 (21-25)		2020	Reach 4 (RM 77.1 - 74.7)	Oncorhynchus mykiss	Whole organism	YOY
2020-SR5 (01-05)	2020-SR5 (01-05)		2020	Reach 5 (RM 73.3 - 69.8)	Oncorhynchus mykiss	Whole organism	YOY
2020-SR5 (01-05) Rep	2020-SR5 (01-05) Rep		2020	Reach 5 (RM 73.3 - 69.8)	Oncorhynchus mykiss	Whole organism	YOY
2020-SR5 (06-10)	2020-SR5 (06-10)		2020	Reach 5 (RM 73.3 - 69.8)	Oncorhynchus mykiss	Whole organism	YOY
2020-SR5 (11-15)	2020-SR5 (11-15)		2020	Reach 5 (RM 73.3 - 69.8)	Oncorhynchus mykiss	Whole organism	YOY
2020-SR5 (16-20)	2020-SR5 (16-20)		2020	Reach 5 (RM 73.3 - 69.8)	Oncorhynchus mykiss	Whole organism	YOY
2020-SR5 (21-25)	2020-SR5 (21-25)		2020	Reach 5 (RM 73.3 - 69.8)	Oncorhynchus mykiss	Whole organism	YOY
2020-SR6 (01-05)	2020-SR6 (01-05)		2020	Reach 6 (RM 67.5 - 67.1)	Oncorhynchus mykiss	Whole organism	YOY
2020-SR6 (06-10)	2020-SR6 (06-10)		2020	Reach 6 (RM 67.5 - 67.1)	Oncorhynchus mykiss	Whole organism	YOY
2020-SR6 (11-15)	2020-SR6 (11-15)		2020	Reach 6 (RM 67.5 - 67.1)	Oncorhynchus mykiss	Whole organism	YOY
2020-SR6 (16-20)	2020-SR6 (16-20)		2020	Reach 6 (RM 67.5 - 67.1)	Oncorhynchus mykiss	Whole organism	YOY
2020-SR6 (16-20) (Duplicate)	2020-SR6 (16-20) (Duplicate)		2020	Reach 6 (RM 67.5 - 67.1)	Oncorhynchus mykiss	Whole organism	YOY
2020-SR6 (21-25)	2020-SR6 (21-25)		2020	Reach 6 (RM 67.5 - 67.1)	Oncorhynchus mykiss	Whole organism	YOY