What have we learned about PCB sources to the Spokane River from Positive Matrix Factorization analysis?

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Introduction

Polychlorinated biphenyls (PCBs) are toxic, persistent, and bioaccumulative chemicals that are regulated in the United States under several statutes including the Clean Water Act. The Spokane River is on the State of Washington's Clean Water Act 303(d) list for impairment by PCB contamination. The impairment is based on concentrations of PCBs in fish tissue that exceed a fish tissue equivalent concentration (FTEC) for applicable water quality standards (LimnoTech, 2016a). Levels of PCBs in mountain whitefish and rainbow trout sampled in 2012 were sometimes more than ten times the FTEC of 5.3 ug/kg (Seiders et al., 2015). There is also a health advisory limiting the consumption of fish caught in the river due to PCB concentrations in fish tissue.

Due to this impairment, there is a need to understand the sources of PCBs to the Spokane River. The Spokane River Regional Toxics Task Force (SRRTTF) has contracted with the author to examine the available congener-specific PCB data for the Spokane River via Positive Matrix Factorization (PMF) in order to identify and, if possible, quantify sources of PCBs to the river. These investigations have resulted in several reports and peer-reviewed publications (Rodenburg, 2020; Rodenburg et al., 2020; Rodenburg et al., 2022a).

Commented [LR1]: I will add a ref for the fish and biofilm report once it is finalized.

The purpose of this report is to integrate the various observations of these reports into a holistic examination of PCB sources to the Spokane River.

Methods

Data sources

Methods for each environmental compartment are detailed in the various reports referenced here (Rodenburg, 2020; Rodenburg et al., 2020; Rodenburg et al., 2022a). In general, the PMF analysis utilized the currently available measurements of PCB congeners in surface water, atmospheric deposition, wastewater treatment plant influents and CSOs, treated wastewater

effluents, biofilms, Semi Permeable Membrane Devices (SPMDs), fish tissue, stormwater, groundwater from the Kaiser site, and treated effluents from the Kaiser plant. For some other media, not enough data was available for PMF analysis, but congener patterns were still examined by comparing them with Aroclor patterns. This was done for bulk atmospheric deposition, river sediment, CLAM (Continuous low-level aquatic monitoring) samples, influent and effluent from the Inland Empire Paper facility, and groundwater from the General Electric (GE) site. To the extent possible, the PMF analysis utilized all of the available data. Data was excluded from the PMF model for three reasons. First, as noted above, for some compartments, insufficient data was available. In these cases, the data was examined by means other than PMF. Second, some samples were measured using different analytical techniques that resulted in different congener co-elution patterns. This data could not always be combined with data from the same compartment, but again, it was examined by other means. Third, in some samples and for many congeners, the measurements were below detection in enough samples that the data was no longer useful. In these cases, the data could not be included in the PMF models and could not be examined by other means.

For the surface water, blank correction was a significant issue. The method of blank correction had an observable impact on the PMF solutions. For this reason, SRRTTF commissioned a 'blank study' to determine the optimal methods of blank correction, which is described in (Rodenburg et al., 2020). This study suggested that censoring the data at one time the concentration in the event-specific blank was the optimal correction method. For all other compartments, the method of blank correction was not important.

Data for the PMF analysis was obtained from the entities that collected the data by Spokane County staff, formatted and blank corrected as appropriate, and provided to the author. All data was collected under approved quality assurance project plans.

PMF analysis

PMF is an advanced factor analysis technique developed by Paatero and Tapper (1994). This approach has been used extensively in the environmental literature to investigate PCB sources by the author of this report (Du and Rodenburg, 2007; Du et al., 2008; Rodenburg et al., 2010; Rodenburg et al., 2011; Rodenburg et al., 2012; Praipipat et al., 2013; Rodenburg and Meng, 2013; Rodenburg et al., 2015a; Rodenburg et al., 2015b; Praipipat et al., 2017; Rodenburg and Ralston, 2017) and many other researchers (Magar et al., 2005; Bzdusek et al., 2006a; Bzdusek et al., 2006b; Soonthornnonda et al., 2011; Uchimiya et al., 2011; Saba and Su, 2013; Karakas et al., 2017).

PMF defines the sample matrix as product of two unknown factor matrices with a residue matrix:

$$X = GF + E \quad (1)$$

The sample matrix (X) is composed of n observed samples and m chemical species. F is a matrix of chemical profiles of p factors or sources. The G matrix describes the contribution of each factor to any given sample, while E is the matrix of residuals. The PMF solution, i.e. G and F matrices, are obtained by minimizing the objective function Q through the iterative algorithm:

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} (e_{ij} / s_{ij})^2 \qquad (2)$$

Q is the sum of the squares of the difference (i.e. e_{ij}) between the observations (X) and the model (GF), weighted by the measurement uncertainties (s_{ij}).

The PMF2 software of Paatero and Tapper (1994) was used in all analyses. PMF2 requires three inputs: the concentration matrix, the uncertainty matrix, and the Limits of Detection (LOD) matrix. The concentration matrix used the concentrations as given. Concentrations below detection were replaced with half the LOD. The LOD matrix was constructed out of the LODs as provided. The uncertainty matrix was calculated by the method used previously (Du et al., 2008; Rodenburg et al., 2011; Praipipat et al., 2013; Rodenburg and Meng, 2013; Rodenburg et al., 2015a), i.e. the relative standard deviation of the surrogate recoveries was used as the base uncertainty, which was applied to all detected concentrations. Three times this uncertainty was applied to non-detects. Peaks were excluded from the input data sets when they were below detection in a majority of samples.

Results and Discussion

The PMF analysis of the various matrices from the Spokane River allows a holistic view of PCB sources. In all compartments, Monsanto's Aroclors are the main PCB sources, as opposed to inadvertent PCBs (iPCBs). For each compartment, the PMF analysis yielded a number of factors or source terms (fingerprints). These were labeled as SurfW1 through SurfW5 for surface water; FishA, FishB, and FishC for fish tissue; and Eff1 through Eff4 for the treated municipal WWTP effluent; BF1 through BF6 for biofilm and SPMD. Most of these factors are similar to one or more Aroclors.

Water column

The vast majority (~90%) of the PCBs in the water column come from the Aroclor formulations manufactured by Monsanto. This conclusion is definitive because of the close matches between the congener patterns found in Spokane River media and the Aroclors and because Monsanto manufactured virtually all of the PCBs sold in North America.

A small portion (~10%) of the PCBs in the water column come from sources with fingerprints that do not closely resemble Aroclors, suggesting that they are associated with in advertent (iPCB) sources, possibly with some input from Aroclors that have undergone varying degrees of weathering. This conclusion holds despite the presence of iPCB congeners in the laboratory

blanks. Even after blank correction by various means, PCB 11 in particular remains at significant concentrations in the water column Rodenburg et al. (2020). This observation is corroborated by the presence of PCB 11 in the biofilm samples, results that are not impacted blank contamination. Analysis of the groundwater and treated discharges suggests that iPCBs are present in CSOs, stormwater runoff, and treated wastewater from municipal plants as well as the IEP facility. In contrast, iPCBs are virtually absent in contaminated groundwater and Kaiser discharges. This pattern was expected based on the presence of PCB 11 and other iPCBs in consumer products (Stone, 2014; Stone, 2016), especially pigments used in printed paper and many other applications. Wastewater treatment processes (both conventional secondary treatment and membrane filtration) preferentially remove high MW PCBs, leaving behind low MW Aroclors and iPCBs such as PCB 11 (Rodenburg et al., 2022b).

These iPCBs, mostly characterized by PCB 11, do appear in the biofilm, but are virtually absent in the fish. This may be because lower MW PCBs do not bioaccumulate as extensively in fish tissue as higher MW congeners. This lower bioaccumulation is partly due to the lower hydrophobicity of lower MW PCBs, but it may also be related to the fact that low MW congeners are metabolized. Cytochrome P-450 metabolism of PCBs can result in hydroxylated PCBs that are sometimes more toxic than the parent congeners (Tehrani and Van Aken, 2014).

With respect to the Aroclors, the PMF model suggests that the dominant Aroclor in the Spokane River ambient water is Aroclor 1248, which accounts for 36% of total PCB mass across all of the surface water samples. Aroclor 1242/1016 accounts for 8.3%. (The congener patterns of Aroclors 1016 and 1242 are similar and cannot be discerned from each other in this analysis.) Aroclors 1254 and 1260 account for 27% and 18% of total PCBs, respectively, with iPCBs explaining the remaining ~10%. Matching the PMF-generated fingerprints with Aroclors is relatively easy, while matching the Aroclors with specific sources to the river such as treated wastewater or stormwater is more difficult. The one exception is the influx of groundwater from the Kaiser site, which consists entirely of Aroclor 1248 and therefore matches the PMF factor dubbed SurfW3 (i.e. surface water factor number 3). However, this does not mean that the Kaiser groundwater is the only source of SurfW3.

The dominance of Aroclor 1248 in the Spokane River is somewhat surprising given that this Aroclor accounted for only about 7% of the US production of Aroclors (Brown, 1994). However, the input of Aroclor 1248 via Kaiser groundwater near SR7 or SR8a may explain much of this discrepancy. The mass balance analysis presented below calculates that this load ranges from 116 mg/d during the 2018 survey to 293 mg/d during the 2014 survey. All of these surveys were conducted at low flow. It is not clear how river flow may affect the size of this groundwater PCB load.

Table 1 is reproduced from the Agency for Toxic Substances and Disease Registry (ATSDR) (2000) and shows the end uses of each of the Aroclors. This table is not complete. Notable omissions include the use of Aroclor 1268 in Galbestos and the use of Aroclor 1242 in capacitors. However, it does indicate the main uses of the Aroclors. Aroclor 1260 was used for

a relatively short list of applications, which may facilitate the trackdown of such sources in the Spokane River watershed.

	Aroclor								
End use	1016	1221	1232	1242	1248	1254	1260	1262	1268
Capacitors	•	•				•			
Transformers				•		•	•		
Heat transfer				•					
Hydraulics/lubricants									
Hydraulic fluids			•	•	•	•	•		
Vacuum pumps					•	•			
Gas-transmission turbines		•		•					
Plasticizers:									
Rubbers		•	•	•	•	•			•
Synthetic resins					•	•	•	•	•
Carbonless paper				•					
Miscellaneous:									
Adhesives		•	•	•	•	•			
Wax extenders				•		•			•
Dedusting agents						•	•		
Inks						•			
Cutting oils						•			
Pesticide extenders						•			
Sealants and caulking compounds						•			

Source: IARC 1979

Table 1. Main uses of the Aroclors. Reproduced from Agency for Toxic Substances and Disease Registry (ATSDR) (2000).

Surf1 and Surf2 are both low-MW fingerprints that probably represent dissolved phase contamination. They are therefore more likely to arise from sources such as treated wastewater and atmospheric deposition than the higher MW fingerprints. These higher MW fingerprints, such as SurfW4 (1254) and SurfW5 (1260) are more likely to come from untreated water inputs that are high in particulate matter, such as stormwater runoff or soil erosion. The PMF analysis of the stormwater data indicates that many of the locations with the highest total PCB concentrations were dominated by StormW5 (1260).

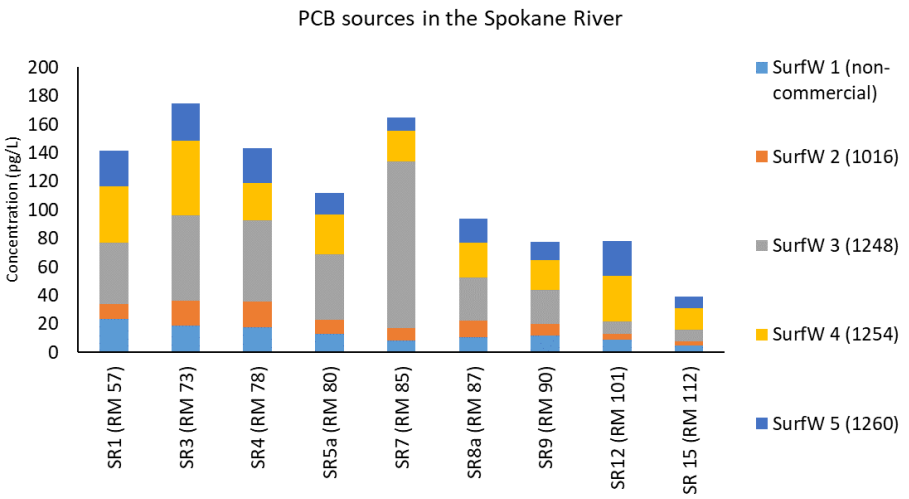

Figure 1. Spatial variation in the abundance of various PCB sources in the water column of the Spokane River, averaged over all sampling campaigns.

Total PCB concentrations are low at SR15 and increase as the river flows through the urban area around Spokane. There is a notable increase in concentration around SR7 and SR8a which is driven by SurfW3 (Aroclor 1248). This presumably represents in the inflow of contaminated groundwater from the Kaiser site. Note that bacteria appear to be dechlorinating some of the PCBs in the Kaiser groundwater, which may reduce the overall load of PCBs to the river from this site. These dechlorination products are not noticeable in the surface water nearby. This may be because the dechlorination products are low MW congeners that readily volatilize. Notably, the analysis of how treatment of blank contamination affects the surface water PMF results found that a signal dominated by PCB 44+47+65 and 45+51 was present in the surface water data that was not blank corrected, but blank correction largely made it disappear. It is likely that this signal, which was also found in the blanks themselves, represents contamination from silicone products, it is also possible that it represents the dechlorination occurring around the Kaiser site, which produces these congeners.

Are PCB concentrations in the water column a function of water flow rate?

Where correlations of PCB concentrations with river flow are significant, they usually display a negative slope, suggesting that PCBs are diluted by higher river flows. This dilution effect is typical of many contaminants in many rivers. This negative correlation is seen for several factors (SurfW1 (non-Aroclor PCBs), SurfW2 (1016/1242) and SurfW3 (1248)) at SR3 and for SurfW5 (1260) at SR5a and SurfW3 at SR7. Only one factor (SurfW5) displays a positive correlation with flow at one station (SR7).

It is notable that SurfW3 (1248) displays a negative correlation with flow at station SR7, meaning that concentrations are lower at higher river flow. The slope of this correlation is the highest among all of the flow correlations. Such a correlation was expected since there is clearly a substantial load of SurfW3 entering the river near SR7 via groundwater. In the Portland Harbor Superfund Site, a PCB source that entered the river via groundwater showed much higher concentrations in the river at low flow (Rodenburg et al., 2015b).

How big are the loads of PCBs to the Spokane River?

A simple way to estimate total loads of PCBs to the Spokane River is to apply a one box model. This model assumes that the stretch of river for the Coeur d'Alene outlet to the Nine Mile Dam is one well-mixed box, which it certainly is not. Despite this limitation, the one box model can give an order of magnitude estimate of the loads necessary to support the concentrations observed.

If there are no loss processes for PCBs other than flushing downstream, then total PCB loads required to produce the concentrations observed at Nine Mile Dam are simply equal to the load flowing over the dam, i.e. the flow rate times the concentration. These loads range from about 200 to 600 mg/d for the three sampling campaigns conducted at low flow during 2014, 2015, and 2018.

Loss processes that might be important are settling with particles and volatilization. Particle settling is probably not significant on an annualized basis, but could be important at low flow. Volatilization is a direct function of the surface area of the river, which is relatively small. However, the various falls of the river probably increase the mass transfer across the air/water interface and thereby enhance volatilization.

The load of PCBs (I) required to maintain a measured concentration is given by:

$$I = C \cdot V \cdot (k_w + k_{vol} + k_{sed})$$

Where C is the PCB concentration at Nine Mile Dam, V is the volume of the river, k_w is the rate constant for flushing (which is calculated from Q/V where Q is the flow rate), k_{vol} is the rate constant for volatilization, and k_{sed} is the rate constant for settling with particles (sedimentation). Using the river geometry from the SVRP USGS MODFLOW model (Hsieh et al., 2007) and assuming the river is a rectangle of the given width and depth, the volume (V) of the river from the Lake Coeur d'Alene outlet to Nine Mile Dam is about 2.9×10^{10} L at low flow. The flow (Q) at Nine Mile Dam ranged from 700 cfs to 1478 cfs during the summer low flow periods that were sampled in 2014, 2015, and 2018. Dividing V/Q gives residence times ranging from 8 to 17 days.

The rates of volatilization and sedimentation depend on the water column partitioning of PCBs. Only PCBs in the dissolved phase can volatilize, and only those in the particle phase can settle. The fraction of the PCBs that are in the dissolved phase (f_w) was calculated using:

$$f_w = \frac{1}{1 + K_{OC} \cdot POC}$$

Where K_{oc} is the equilibrium constant describing partitioning between the water and the organic carbon, and POC is the concentration of organic carbon in the sediment. K_{oc} values were taken from Hansen et al. (1999). POC was measured to average about 0.13 mg/L during the SPMD deployments. Partitioning was calculated for each congener included in the surface water PMF analysis, and a weighted average f_w was calculated for each PMF-derived factor. These ranged from 98% for SurfW1 (which is mostly PCB 11) to 84% for SurfW5 (Aroclor 1260).

The mass transfer coefficient across the air/water interface (v_{aw}) was assumed to be 1 m/d as in other studies (Contamination Assessment and Reduction Project (CARP), 2007). Using this, k_{vol} is calculated as:

$$k_{vol} = \frac{v_{aw} \cdot f_w}{d}$$

Where d is the average depth of the river, taken from the MODFLOW model to be 4.15 m. Similarly, k_{sed} was calculated from:

$$k_{sed} = \frac{v_{sed} \cdot (1 - f_w)}{d}$$

Where v_{sed} is the settling velocity of sediment, assumed to be 0.7 m/d (Schwarzenbach et al., 2003).

Using this framework, the loads required to maintain the measured concentrations are shown in Table 2. Loads for the sum of PCBs range from about 763 mg/d in 2018 to around 1946 mg/d in 2015. This table reveals that settling is relatively unimportant as a loss process, but volatilization is significant, with k_{vol} similar in magnitude to the rate constant for flushing.

	year	SurfW1	SurfW2	SurfW3	SurfW4	SurfW5	Sum
fraction dissolved		98%	96%	98%	92%	84%	
k sed (1/d)		0.00	0.01	0.00	0.01	0.03	
k vol (1/d)		0.24	0.23	0.24	0.22	0.20	
k w (1/d)	**2014**	0.09	0.09	0.09	0.09	0.09	
	2015	0.06	0.06	0.06	0.06	0.06	
	2018	0.13	0.13	0.13	0.13	0.13	
C (pg/L)	**2014**	34	13	52	59	31	189
	2015	31	26	66	78	27	228
	2018	8	8	25	11	21	73
I (mg/d)	**2014**	330	126	496	561	284	1796
	2015	265	223	572	664	222	1946
	2018	89	86	258	113	217	763

Table 2. Loads needed to support the measured concentrations at Nine Mile Dam for the five PMF factors derived from the surface water data set, based on the one-box model.

These calculated loads serve as a useful order of magnitude estimate that allows some perspective on the loads calculated from the mass balance (see below). Note that some of the loads of PCBs could be internal loads. For example, resuspension of contaminated sediment represents a large internal PCB load in many systems. However, since the Spokane River has relatively little sediment, this is less likely to be an important source of PCBs here. LimnoTech (2016a) include a small load of 0.2 to 20 mg/d from "bottom sediments" in their loading assessment.

The estimated loads from this simple one box model are in reasonable agreement with the loads tabulated by LimnoTech (2016a). In that report, total PCB loads were calculated to be between about 285 mg/d and 1,363 mg/d. Loads from fish hatcheries and atmospheric deposition were assumed to be zero in calculating the sums shown here. This sum included loads from upstream, groundwater, tributaries, WWTPs, MS4 stormwater/CSOs, and bottom sediments. Since the synoptic surveys on which this box model is based were conducted at low flow, stormwater and CSOs input would have been zero at these times. Without these, the total loads are between 270 mg/d and 1,269 mg/d.

Commented [HM2]: The way the table in that report is presented is a bit confusing. If you just add up the columns the municipal loads will be double counted. So the range is actually 300 – 1,563 mg/day. Also it counts the Little Spokane which enters below Nine Mile so without that it is 285-1,363. The high estimate includes two loads that are believe are not likely, 444 from Lake CdA (very low concentration with high flows) and 215 for Latah Creek which is based on very few high samples that are likely from a City of Spokane stormwater input just upstream of the mouth. I think the 200 to 600 mg/d actually makes sense.

Commented [LR3R2]: I fixed the numbers in the report. I'm leaving your comment here because I think this will be the subject of much discussion.

As described above, if volatilization and sedimentation are assumed to be negligible, the one box model predicts loads of about 200 to 600 mg/d. These seem too low given the estimated loads of LimnoTech (2016a), which suggests that volatilization is an important loss process in the Spokane River. Volatilization is recognized as an important loss process for PCBs in surface waters, for example the Delaware River (Fikslin and Suk, 2003), Hudson River (Connolly et al., 2000; TAMS Consultants Inc. et al., 2000), and New York/New Jersey Harbor (Farley et al., 1999; Contamination Assessment and Reduction Project (CARP), 2007), among many others. These systems have longer residence times for water, which may allow for more volatilization. However, the Spokane River has various falls which might enhance volatilization.

Commented [LR4]: Dave Dilks says there is a LimnoTech report that shows volatilization is negligible. My question is whether EPA is going to include volatilization in its TMDL model. If they do, their calculated TMDL will be higher.

On another note, the residence time of water in the system is already built into the volatilization calculations. Volatilization occurs over the whole surface area and reduces the concentration across the whole volume. Volume divided by SA = depth, which is where the depth comes from in the equation.

Insights from the mass balance

A mass balance on PCBs in the Spokane River was conducted via the methodology of LimnoTech (LimnoTech, 2016b, 2019). The flows were used as provided in these reports. The concentrations of the PMF-derived factors for surface water and dischargers were used as depicted in Figure 2. The surface water PMF analysis yielded five factors. Of these, SurfW3 resembled Aroclor 1248, while SurfW4 resembled Aroclor 1254. The discharger PMF analysis yielded four factors, of which Eff3 resembled a mixture of Aroclors 1248 and 1254. Therefore, a mass balance was conducted on the sum of SurfW3 and SurfW4, which was assumed to be equivalent to Eff3. SurfW1 consisted primarily of PCB 11. Since LimnoTech already performed a mass balance on PCB 11, the results of the SurfW1 mass balance are not presented separately, but the sum of PCBs loads in Figure 3, Figure 4, and Figure 5 do include SurfW1. The discharger PMF analysis yielded a factor (Eff2) that was dominated by PCBs 44 and 45 which is

thought to be an artifact of blank contamination, so the mass balance did not include this factor.

In order to use the measurements of discharger loads from the synoptic surveys for the IEP and Kaiser loads, the synoptic discharger data was analyzed using multiple linear regression as follows. The congener patterns of each synoptic sample were normalized such that the sum of the congeners equaled 100%. This congener pattern was then designated as the Y variable, and the congener patterns of the PMF-derived SurfW factors were designated as the X variables. The coefficients of this regression were a measure of the percent of each sample that was attributable to each factor. These percentages were then multiplied by the measured sum of PCBs to generate concentrations of each SurfW PMF factor in each synoptic discharger sample. The R^2 values for these regressions averaged 0.91. The lowest R^2 value was 0.76 for sample SR6.081815.1535.

Notably, the concentration data used in the various PMF analyses (and the multiple linear regression) was blank-corrected less aggressively than the data used by LimnoTech, which was censored at three times the concentration in the corresponding blank. In contrast, concentrations used in the PMF mass balance were censored at one times the concentration in the corresponding blank.

Uncertainty in the mass balance was estimated by assuming that the uncertainty in the PCB concentrations was 20% and the uncertainty in the flows was negligible. The error bars in Figure 3, Figure 4, and Figure 5 are the result of propagating this 20% uncertainty.

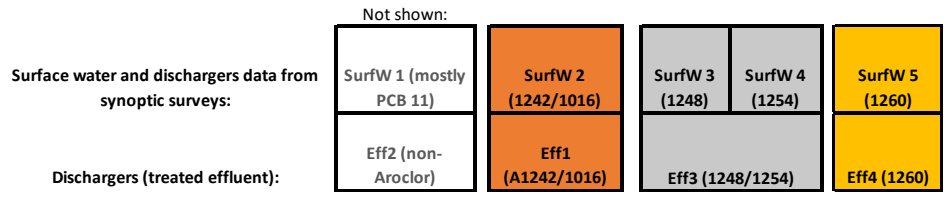

Figure 2. Schematic of the mass balance calculations showing which PMF-derived factors were pooled for the mass balance assessment.

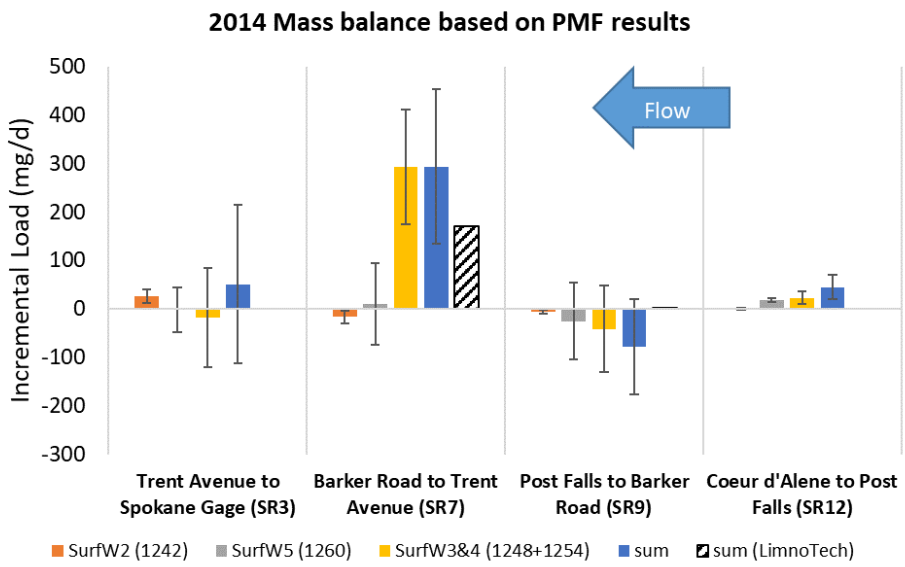

Figure 3. Mass balance on PCBs in the Spokane River during the August 2014 synoptic survey based on PMF results. The results of the mass balance of LimnoTech (2016b) are shown for comparison.

The 2014 PMF is largely consistent with that of LimnoTech. The PMF mass balance shows small loads at Post Falls that are balanced by small losses at Barker Road. There is a large load of 293 mg/d of SurfW3&4 at Trent Ave (SR7). The LimnoTech mass balance similarly showed a significant load here. The PMF identifies this as a combination of Aroclors 1248 and 1254, which presumably represents the inflow of Aroclor 1248 with groundwater near SR7. The remaining loads/losses are low and often not statistically significant. The one box model suggests that the total load of PCBs required to support the measured concentration at Nine Mile Dam during the 2014 mass balance was about 1750 mg/d. Therefore, the load from Kaiser groundwater is a substantial part of the overall load, perhaps 10-20%.

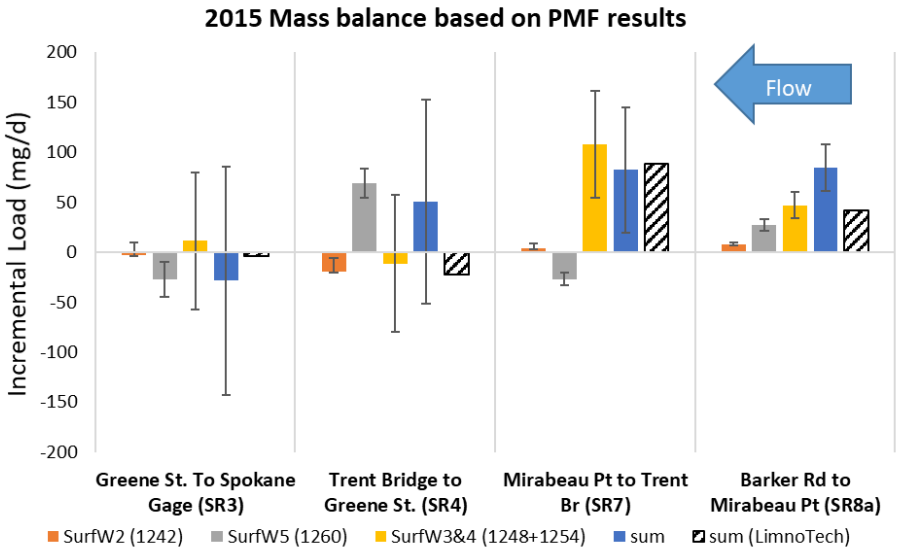

Figure 4. Mass balance on PCBs in the Spokane River during the August 2015 synoptic survey based on PMF results. The results of the mass balance of Dilks (LimnoTech, 2019) are shown for comparison.

The 2015 LimnoTech mass balance shows a large load at Trent. The PMF mass balance shows a load of similar size (mostly SurfW3&4) entering both at Trent Bridge (SR7) as well as further upstream above Mirabeau Point (SR8a). The total of these two SurfW3&4 loads is 155 mg/d. The difference in location is probably not meaningful and instead both approaches show a load from groundwater inflow in this area. Both approaches show that the reach from Trent Bridge to Upriver Dam loses PCBs, presumably due to groundwater infiltration and an overall loss of flow. The PMF mass balance shows meaningful loads of SurfW5 (Aroclor 1260) at Greene St. and Mirabeau Point (SR8a). The one box model suggests that the load required to maintain the concentrations measured at Nine Mile Dam during the 2015 sampling event was about 1900 mg/d. The Kaiser groundwater load was therefore about 10% of the total load.

Commented [HM5]: If the outliers are not included is there still a load?

Commented [LR6R5]: After processing the data through the lens of PMF, they aren't outliers anymore.

Commented [HM7]: This seems high to me.

Commented [LR8R7]: Yes, we need to talk about the one-box model. I don't think it is correct to ignore volatilization entirely, but my estimate for that might be too high.

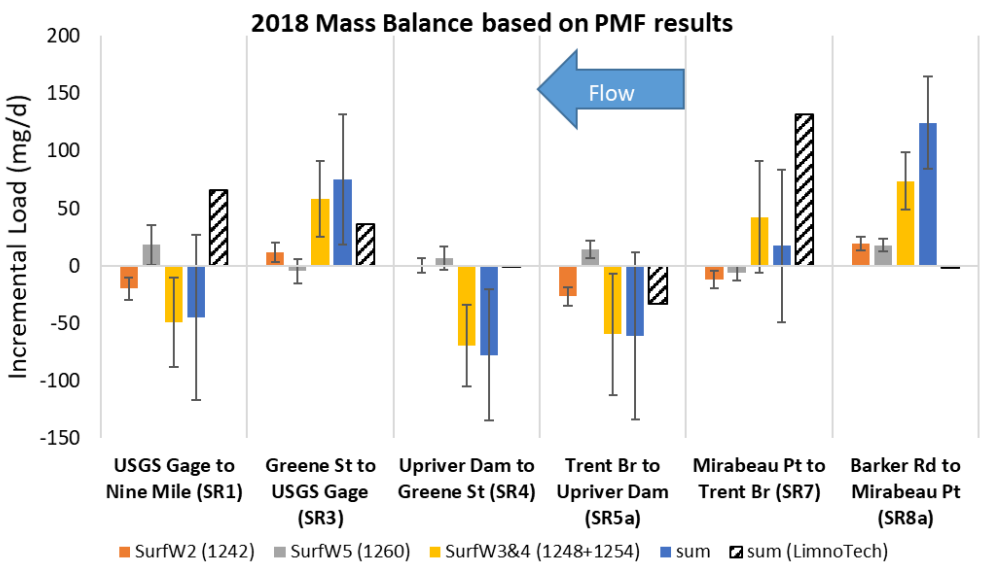

Figure 5. Mass balance on PCBs in the Spokane River during the August 2018 synoptic survey based on PMF results. The results of the mass balance of Dilks (LimnoTech, 2019) are shown for comparison.

Similar to 2015, the 2018 LimnoTech mass balance shows a large load at Trent while the PMF mass balance shows a similar load of SurfW3&4 entering at both SR7 and SR8a (total load = 116 mg/d). Again, the difference in location is probably not meaningful. The load of SurfW3&4 at SR8a is calculated to be 74 mg/d. Both approaches shows that the reach from Trent Bridge (SR7) to Upriver Dam (SR5a) loses PCBs, presumably due to groundwater infiltration and an overall loss of flow. Despite the loss of the sum of PCBs, the PMF analysis suggests a small load of SurfW5 (Aroclor 1260) in this reach. Further downstream, the PMF and LimnoTech mass balances diverge. The PMF approach shows a large loss of PCBs from SR5a to SR4, balanced by a gain from SR4 to SR3, followed by another loss from SR3 to SR1. The Limnotech approach shows no change from SR5a to SR4, a small gain from SR4 to SR3, and a larger gain from SR3 to SR1. The one box model suggests that the load required to maintain the concentration measured at Nine Mile Dam during the 2018 sampling event was about 750 mg/d. Again, the Kaiser groundwater load is a substantial fraction of this total, around 10-20%.

Taken together, the mass balances based on the three synoptic surveys suggest that the groundwater source of Aroclor 1248 is a significant source of PCBs to the river, with a load on the order of 116 to 293 mg/d under low flow conditions. The LimnoTech and PMF mass balances agree on that conclusion. The PMF mass balance further suggests some additional meaningful sources of Aroclor 1260 above SR8a and SR4, although the significance of this

source depends on how some outlier data points are handled. Across the entire study area, the cumulative load of SurfW5 (Aroclor 1260) is about 40 mg/d.

In comparison, the total load of the sum of PCBs from the WWTPs was estimated to be 51-125 mg/d in 2016 (LimnoTech, 2016a) and should be slightly lower now that several plants have upgraded their processes to include tertiary treatment by membrane filtration (Rodenburg et al., 2022a). Calculations based on the discharger data analyzed by Rodenburg et al. (2022a) suggest that cumulative PCB load from the Coeur d'Alene, Hayden, Post Falls, Spokane County, and Spokane City WWTPs was about 89 mg/d during 2015-2017 and dropped slightly to about 86 mg/d after the Coeur d'Alene plant upgraded its treatment process in 2018 (these calculations assume that the factor containing PCBs 44 and 45 is an artifact, i.e. this mass is not actually in the effluent). Rodenburg et al. (2022a) estimated that if the City of Spokane were to upgrade its plant to include membrane filtration, it would further reduce these loads by more than 40 mg/d.

The one box model suggests that the total of all PCB loads to the Spokane River required to support the measured concentrations are around 750 to 1900 mg/d under low flow conditions. The mass balance results suggest that the Kaiser groundwater load is substantial but still accounts for much less than half of the total load. Even the Aroclor 1260 (F5) loads estimated from the mass balance and the WWTP loads cannot account for the total measured PCBs in the water column. Thus, there are 'missing' loads of PCBs that the mass balance model cannot identify due to the uncertainties in the measured concentrations.

Is the atmosphere a significant source of PCBs to the Spokane River?

Generally, atmospheric deposition is a small source of PCBs. For example, in relatively urbanized areas such as the Delaware River and NY/NJ Harbor, atmospheric deposition represents a few percent of the total PCB loads (Totten et al., 2004; Totten, 2005; Praipipat et al., 2013). In contrast, atmospheric deposition is proportionately more important in remote areas, and was once an important source of PCBs to Lake Michigan, although it is now considered negligible (Guo et al., 2017). Given the lower concentrations of PCBs measured in the Spokane River relative to more urbanized water bodies, it is reasonable to ask whether atmospheric deposition is an important source of PCBs there. Bulk atmospheric deposition of PCBs was measured in study BERA0013. The geometric mean flux across 21 samples was 3.6 $ng/m^2/d$. This may be biased high due to blank contamination issues in the bulk deposition samples. The geometric mean flux is 3.2 $ng/m^2/d$ when the silicone-related congeners are excluded (PCBs 1, 2, 3, 4, 8, 9, 11, 15, 18+30, 20+28, 21+33, and 31). In comparison, bulk deposition fluxes measured using essentially the same methodology in the Green-Duwamish River basin ranged from 1.1 $ng/m^2/d$ in remote Enumclaw, WA to 16.9 $ng/m^2/d$ at South Park in the city of Seattle (Rodenburg et al., 2019).

One way to estimate the impact of atmospheric deposition on the water column is to use the one box model of the river. If all other loss processes (such as volatilization and sedimentation) are negligible, the concentration in the river at steady state (C_{ss}) is given by:

$$C_{ss} = \frac{I}{Q}$$

Where I is the load of PCBs. The load can be calculated as the flux (3.2 ng/m^2/d) times the surface area, which is calculated from the MODFLOW model geometry to be 5.88 km^2. This gives an atmospheric deposition load of 18 mg/d. The calculation suggests that C_{ss} is on the order of 5 pg/L for the sum of PCBs.

A second way to estimate the impact of atmospheric deposition on the water column is to assume that it is in equilibrium with the gas phase in the overlying air. This requires knowledge of the gas phase concentrations, which have not been measured. The Delaware Atmospheric Deposition Network measured PCB concentrations in both urban and rural areas. The regional background of the sum of PCBs in New Jersey was found to be about 125 pg/m^3 in the gas phase. It not clear whether this concentration is typical of the atmosphere above the Spokane River. The concentrations of PCBs found in wastewater influents and stormwater in Spokane are similar to those found in cities along the Delaware River, suggesting that the atmospheric concentrations in the Spokane River valley are probably similar to those observed near the Delaware River, i.e. the 125 pg/m^3 noted above. This is a regional background concentration. Atmospheric concentrations of PCBs are usually highest in urban areas (Harner et al., 2004). Du and Rodenburg (2007) calculated that PCB concentrations can drop by half over a distance of just 2 km. This although concentrations are probably higher in downtown Spokane than in more remote areas, over most of the surface area of the Spokane River, concentrations are closer to regional background. Assuming an average temperature of 15°C, using the Henry's Law Constants (Bamford et al., 2000; Bamford et al., 2002), and using the same congener distribution as seen in New Jersey gives a dissolved phase total PCB concentration of about 16 pg/L at equilibrium. This dissolved phase number can be used to predict the concentrations on particles and in the dissolved organic carbon (DOC) by using the K_{oc} values of Hansen et al. (1999) and assuming that the partitioning coefficient between water and DOC is an order of magnitude lower than K_{oc} (Farley et al., 1999; Yagecic et al., 2003; Rowe et al., 2007). The SPMD surveys showed an average POC value of 0.13 mg/L. Dissolved organic carbon (DOC) at Barker Road averaged 1.6 mg/L during the synoptic surveys. The partitioning of PCBs onto these phases would result in an additional 7.4 pg/L on DOC and 3.7 pg/L on particles, for a whole water concentration of about 27 pg/L. Concentrations of PCBs expected in the fish can be estimated from the dissolved concentration by applying biota accumulation factors (BAFs). For this purpose, the BAFs calculated for PCB homologs in Striped Bass in the NY/NJ Harbor were used (Contamination Assessment and Reduction Project (CARP), 2007). This results in an estimated 8 ug/kg ww total PCBs in predator fish in the Spokane River based solely on atmospheric PCB concentrations. While low, this number is still slightly above the FTEC of 5.3 ug/kg ww. The main uncertainty in this calculation is the background atmospheric PCB concentration.

These calculations suggest that atmospheric deposition is not a significant source of PCBs to the Spokane River, but it does present a lower bound below which the PCB levels in the river cannot go unless atmospheric concentrations of PCBs decline.

Other compartments

Compared to the water column, biofilm and fish are more likely to display a higher MW PCB congener pattern. This largely reflects the partitioning of PCBs between the dissolved phase and those with a more organic (non-polar) nature. Because such partitioning is driven by hydrophobicity, higher MW congeners partition more extensively into these other phases. The fact that the biofilm samples show a higher MW distribution of PCBs than the water column samples is useful, because it better reflects the fish. However, this partitioning can cause a low MW Aroclor source to the water column to resemble a higher MW pattern in the biofilm and fish.

The biofilm data indicates that iPCBs are present in the Spokane River, confirming that they are not simply introduced to sample via blank contamination. PCB 11 contributes an average of 6% of total PCBs in biofilm samples. This is slightly less than the ~10% non-Aroclor PCBs found in the water column, but the difference can probably be attributed to the partitioning effect, which causes the biofilm to have a slightly higher MW signal overall compared to the water column.

PCB congener patterns in fish from the Spokane River are dominated by higher MW formulations, particularly Aroclors 1254 and 1260. Although PCB 11 is a significant congener in the water column and is present in the biofilm, it is insignificant in the fish, often below detection. Given that fish consumption is the primary route of human exposure to PCBs in the Spokane River region, this suggests that efforts to reduce the impacts of PCBs on the ecosystem should focus on reducing the inputs of Aroclor PCBs to the river. The upgrading of WWTPs to include tertiary treatment via membrane filtration has contributed to this goal (Rodenburg et al., 2022a). Reductions in the amounts of solids reaching the river via stormwater should also contribute to this goal. Effective control of the Kaiser groundwater plume would also be an important component of reducing fish PCB levels.

Mission Reach hot spot

The Mission Reach hot spot is a zone of high PCB concentrations detected in biofilm and SPMD samples around RM 76 and SR3a. The biofilm results suggest that the dominant source of PCBs in the samples of biofilm with the highest concentrations is BF5, i.e. Aroclor 1260. BF4 (Aroclor 1254) is also important in this area. The loads of SurfW5 (Aroclor 1260) calculated in the PMF mass balance are not entering at the correct locations to explain this source around RM 76.

Comparisons of spatial trends in PCB sources across media

One way to assess the significance of each load or source of PCBs to the Spokane River is to examine whether each has a significant impact on the PCB fingerprint measured in environmental media near the point of release. Because the PMF-derived factors were different for each receptor (surface water, fish, etc.), examining these trends in terms of PMF factors is problematic. Therefore, this comparison was instead made by calculating the average

number of chlorines per biphenyl (i.e. the chlorination level of the PCB mixture). For this analysis, data from surface water, biofilm, and fish are presented because these three media (a) reflect the integration of all sources to the river and (b) have enough data for a meaningful analysis by river mile. The results are shown in Figure 6. These plots become hard to understand when each individual data point is plotted, so the lines in Figure 6 are averages for the fish and the surface water. The chlorination level is overall lower for the surface water (around 4-4.5 chlorines per biphenyl) than in the fish (5-6 chlorines per biphenyl) due to the partitioning effect, but the important feature of these plots is how chlorination level increases or decreases with river mile. All three media generally show a higher level of chlorination upstream which decreases until around RM 85. The increase in chlorination level around RM 85 presumably reflects the input of Aroclor 1248 from the Kaiser groundwater plume. Around RM 80, chlorination levels decrease, then increase again around RM 75, presumably reflecting inputs from the Mission Reach hotspot. The analysis presented above suggests that the PCB load associated with this hotspot is probably the high MW formulation Aroclor 1260, which would explain the increase in chlorination level in this area. This analysis therefore suggests that both the Kaiser groundwater and the source(s) that contribute to the Mission Reach hotspot are significant enough to affect the water column and the fish nearby. Notably, the 2020 young of year Oncorhynchus mykiss do not display the increase in chlorination level around the Mission Reach hotspot, which may indicate that control measures have been effective in reducing the PCB load in this area.

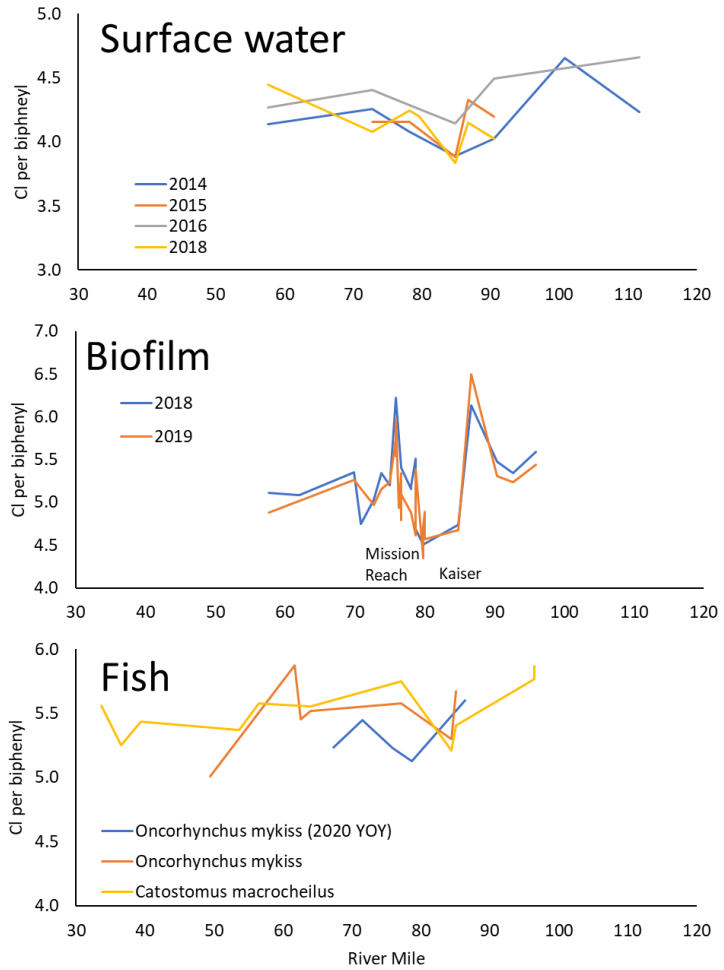

Figure 6. Chlorines per biphenyl across three media (surface water, biofilm, and fish) by River Mile. Multiple surface water and fish samples were average for this plot.

Are PCB levels in the Spokane River declining?

There is not enough data to make any definitive statement with respect to the time trends of PCBs in the Spokane River. In the water column, some of the PMF factors were declining over time, but this data set covers only a few years and is biased toward collection of samples at lower flow rates. In the fish, there is some indication that PCB burdens may be declining, but more sampling is needed to make this conclusion statistically robust.

The various PMF analysis suggest that over time, the PCB burden in the river may be shifting toward lower MW PCBs. The fish display this trend. The water data suggested that PCB sources resembling Aroclors 1242 and 1248 are decreasing at SR3, while they are increasing at SR8a. Upgrades of wastewater treatment facilities will preferentially remove high MW congeners, leaving behind a lower MW signal. CSOs and stormwater runoff contain a wide variety of PCB sources, including high MW formulations, so reductions in these inputs may contribute to a shift toward lower MW PCBs in the river. This is especially true if the stormwater management techniques remove solids but allow the dissolved phase PCBs to enter the river.

Time trends in fish PCB concentrations are not statistically significant due to the relatively small number of samples (Seiders et al., 2015). However, visually, it does appear that fish concentrations are declining (Figure 7) and that fish are increasing dominated by low MW sources. This may indicate that they are shifting from getting their PCBs primarily through food (biomagnification) to getting PCBs primarily from water (bioconcentration). However, these observations may not be valid because the fish samples displayed in Figure 7 are of different ages. In Figure 7, 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 and the 2020 samples are young of year. Similarly, the *Catostomus macrocheilus* (Largescale Sucker) samples 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.

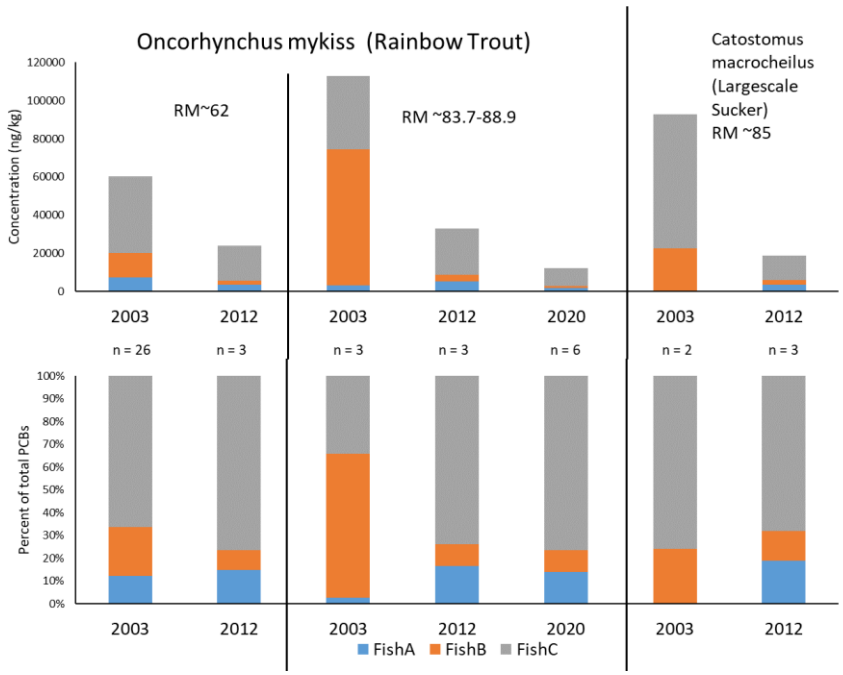

Figure 7. PCB sources in two species from a few general locations averaged by year of collection. FishA (blue) is similar to Aroclor 1248. FishB (orange) is similar to Aroclor 1254. FishC (grey) is similar to Aroclor 1260.

Is degradation of PCBs occurring anywhere in the watershed?

There are three main mechanisms by which PCB can be degraded in the environment.

PCBs, especially lower MW congeners, are susceptible to aerobic degradation (Abramowicz, 1990). The products of this process are not PCB congeners. For this reason, the PMF approach (which included only PCB congeners) cannot identify this process. It may be significant in the Spokane River watershed but will not be discussed here.

Under anaerobic conditions, bacteria can dechlorinate PCBs, converting PCB congeners with many chlorines to those with fewer (Brown et al., 1984). The products of dechlorination typically have a very different congener pattern from those of the Aroclors, such that the PMF approach can identify the products of dechlorination and in some cases can suggest which Aroclors were the substrates (starting material) for dechlorination (Bzdusek et al., 2006a; Bzdusek et al., 2006b; Rodenburg et al., 2010; Rodenburg et al., 2015b; Capozzi et al., 2019). PMF analysis of treated municipal wastewater effluents has identified dechlorination products in many cities, especially those with combined sewers (Rodenburg et al., 2010). The city of

Spokane has some combined sewers. Despite this, the PMF analysis of the treated wastewater does not identify any dechlorination occurring there. Dechlorination products have also been found in groundwater (Rodenburg et al., 2010; Rodenburg et al., 2015b). For example, at the Portland Harbor Superfund Site, dechlorination appears to occur in the groundwater, leading to dechlorination products that are a significant fraction (~20%) of the PCBs in the water column of the river. In the Spokane River watershed, the PMF analysis of the Kaiser groundwater and the Kaiser effluents identified dechlorination products. However, these dechlorination products do not appear to be a significant contributor to the surface water PCBs, i.e. the surface water PMF analysis did not identify a dechlorination signal. This may be because the products of dechlorination, being low MW congeners, volatilize and therefore have relatively little impact on water quality.

The third mechanism of PCB degradation commonly seen in the environment is metabolism by organisms, particularly via the cytochrome P450 enzymatic pathway. Rodenburg and Delistraty (2019) describe some ratios of congeners that are readily metabolized to those that are not that can be used to identify metabolism based on the PCB fingerprints. The lower the ratio, especially relative to the ratio in the Aroclors, the more metabolism has occurred. For example, the ratio of PCB 147+149/153+168 is about 1 in the Aroclors but can approach zero in organisms. Using this ratio, there is no clear evidence of metabolisms occurring in surface water or dischargers. However, in fish, there is clear evidence that metabolism has occurred, which was expected. More interestingly, there is evidence that PCBs are metabolized within the biofilms. The three metabolic ratios identified by Rodenburg and Delistraty (2019) are all significantly lower in the biofilm samples than in the SPMDs ($p << 0.05$ via an unpaired two-tailed t-test assuming unequal variances). While interesting, this metabolism is not expected to have any significant impact on the fate of PCBs in the Spokane River.

How does the Spokane River compare with other water bodies for which PCB sources have been evaluated?

In general, the Spokane River has lower overall water column PCB concentrations than most of the other rivers for which PCB sources have been apportioned using PMF. These include the Delaware River, New York/New Jersey Harbor, Green/Duwamish River and Portland Harbor Superfund Site. The Green River is the sole example of a river with PCB concentrations similar to those found in the Spokane River, i.e. they are so low that they become difficult to measure accurately. In Spokane, the concentrations of PCBs in the influents to the WWTPs averaged 45 ng/L versus 16 ng/L in the CSO/stormwater samples. In comparison, stormwater in Seattle, WA had a geometric mean concentration of 0.7 ng/L (Leidos, 2015; Rodenburg and Leidos, 2017a, b). Municipal wastewater influents averaged 62 ng/L in the District of Columbia circa 2015 (Capozzi et al., 2019), 27 ng/L in several municipal WWTP on the Delaware River circa 2000 (Rodenburg et al., 2010), and over 17,000 ng/L in several New York City WWTPs circa 2000 (Rodenburg et al., 2012). In all three of these systems, there are some combined sewers, such that wet-weather WWTP influent concentrations may be assumed to equal concentrations in CSO outfalls. Concentrations of PCBs the WWTP influents and storm water of Spokane are therefore similar to those observed in other urban areas. The lower concentrations prevailing

in the water column therefore presumably arise from a lower overall population density in the Spokane River watershed, as well as better controls on wastewater, stormwater, and CSO inputs to the river.

In addition, one reason for the lower PCB concentrations in the Spokane River is its physical characteristics, which are quite different from the other systems that have been examined using PMF. Rivers that have been previously assessed, such as the Delaware River, New York/New Jersey Harbor, Green/Duwamish River and Portland Harbor Superfund Site, are tidal systems with relatively deep sediment beds. In contrast, the Spokane River is not tidal and experiences fast flows, particularly during the spring freshet, and relatively shallow depths that allow for the scour of most sediments. Only above dams does the Spokane River build up deep beds of sediment. These differences are important with respect to PCB sources, because in these other systems, the sediment retains a large reservoir of PCBs that bleed out over time (this is the 'internal load' noted above). As a result, the response time of these systems to changes in load is relatively long. For example, in the NY/NJ Harbor, fish are expected to reach steady state with respect to changes in PCB loads on a time scale of about 30 years (Contamination Assessment and Reduction Project (CARP), 2007). The dearth of sediment in the Spokane River suggests that it might respond faster to changes in load than these other systems. However, the fish tissue concentrations of PCBs are similar to those from these other systems despite the dearth of sediment, which suggests that the mechanism of uptake of PCBs by the fish in the Spokane River is not well understood, so speculation about their rate of response to changes in PCB load is not wise.

Another reason for the higher PCB concentrations in other systems is the presence of Superfund Sites that could be major PCB sources. For example, the Hudson River Superfund Site is thought to contribute about half of the PCBs entering the NY/NJ Harbor. (Farley et al., 1999; Contamination Assessment and Reduction Project (CARP), 2007). The Green-Duwamish River terminates at the Harbor Island Superfund Site, which certainly contributes PCBs to the Duwamish River, although the amount is unknown (Rodenburg and Leidos, 2017a). The Delaware River and Portland Harbor Superfund Site have numerous facilities on their banks that may be sources of PCBs. Superfund sites and industrial sites are almost always sources of PCBs in the form of Monsanto's Aroclors.

Some of the other systems that have been investigated are impacted by non-Aroclor or inadvertent PCBs (iPCBs). The Delaware River in particular houses a large reservoir of iPCBs in its sediment. They are thought to have come from the production of titanium dioxide at a plant in Edgemore, DE. High MW PCBs (nona- and decachlorobiphenyls) from this plant contributed more than half of the PCBs in the sediment (Praipipat et al., 2013), and 19% in the water column (Du et al., 2008). All of these previously investigated systems contained some PCB 11 in the water column. PCB 11 concentrations in the NY/NJ Harbor averaged about 100 pg/L. PCB 11 averaged about 20 pg/L in both the Delaware River and the Portland Harbor Superfund Site, versus about 11 pg/L in the Spokane River. Notably, the data from these other systems was not blank-corrected with as much care as the Spokane data, so these average PCB 11 concentrations may be overestimates. Nevertheless, this comparison illustrates that the PCB

11 concentrations in the Spokane River are not unusually high. Instead, PCB 11 makes up a larger percent of total PCBs in the water column in Spokane because concentrations of the other congeners are comparatively low.

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