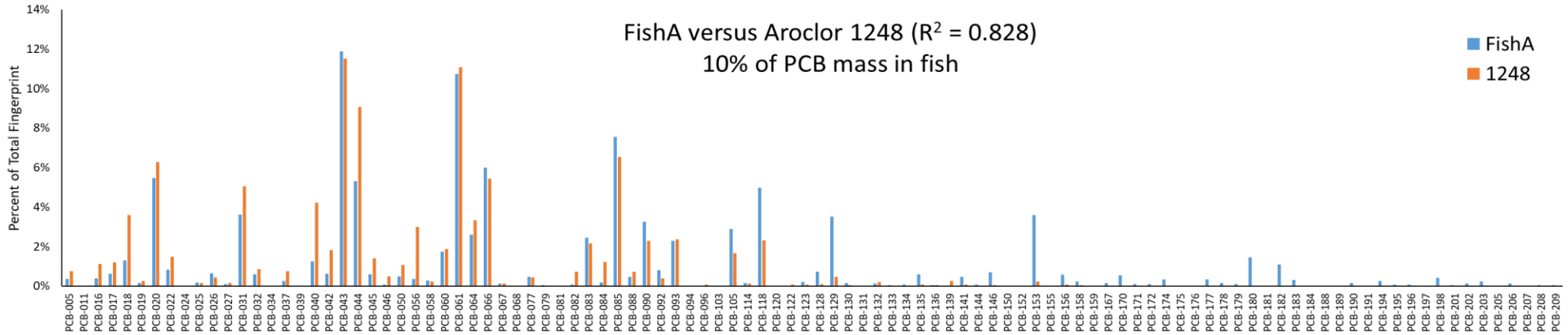
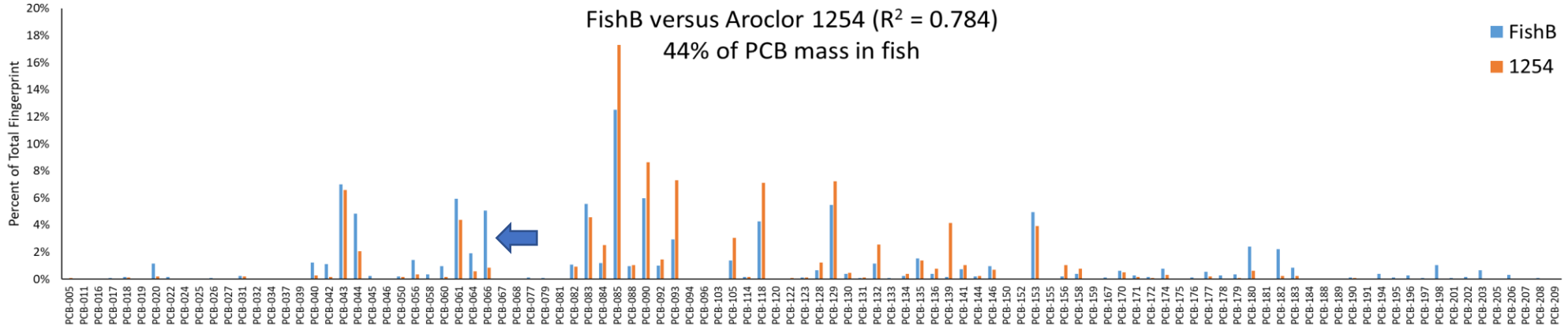
What have we learned about PCB sources to the Spokane River from the PMF analysis?

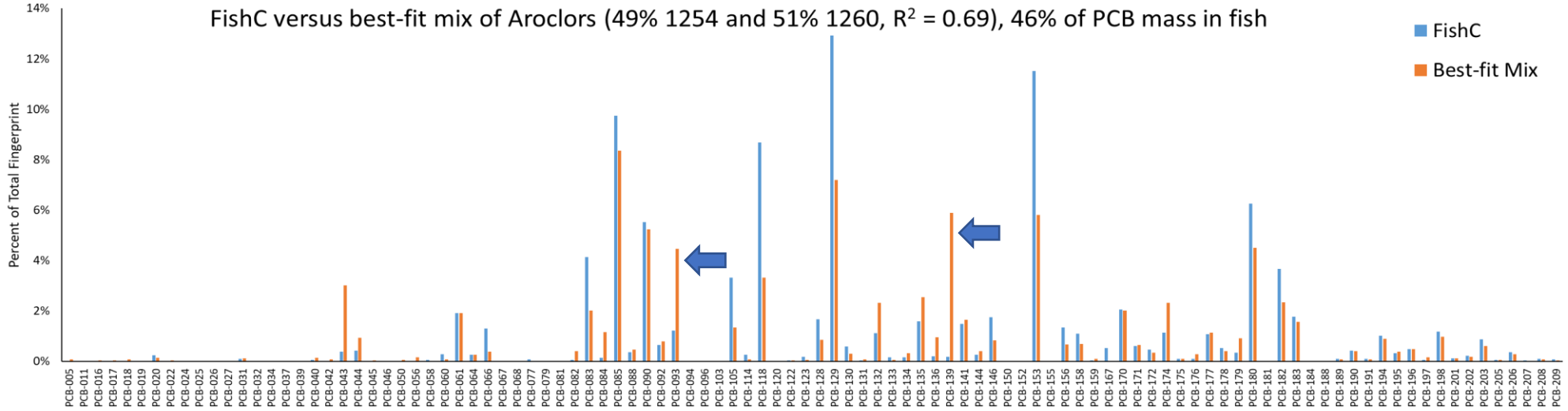
Lisa Rodenburg

Fish

Fish fingerprints

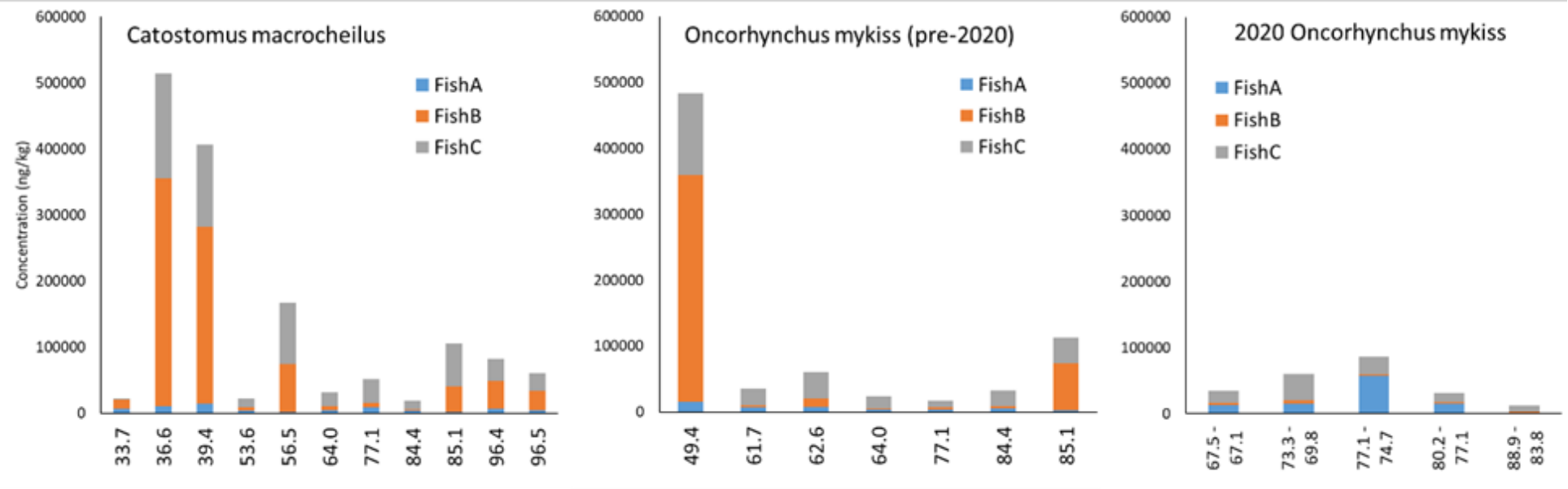






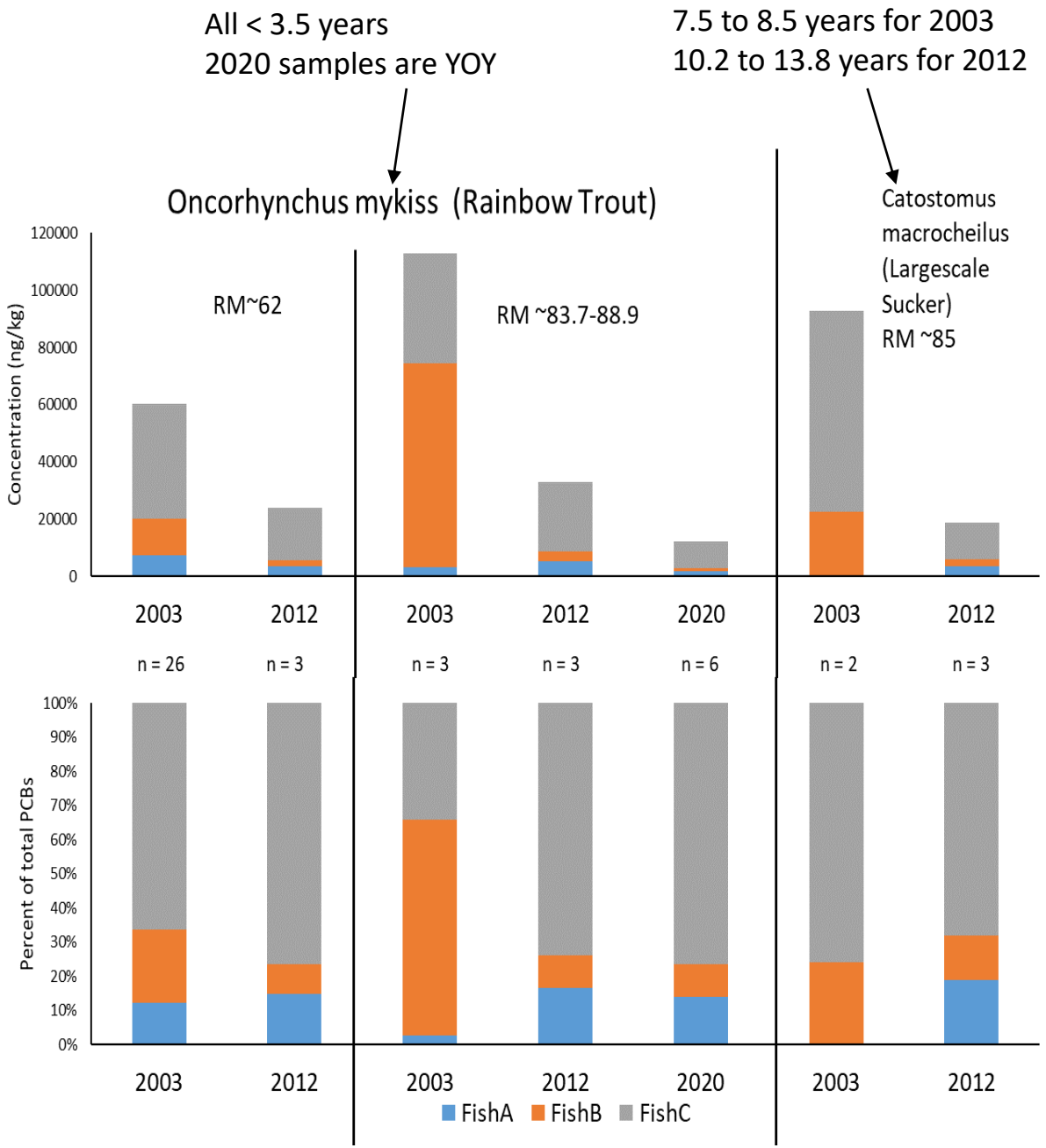
Fish-spatial trends

- Differences in fish age make it difficult to assess
- Concentrations of factors by RM or reach:



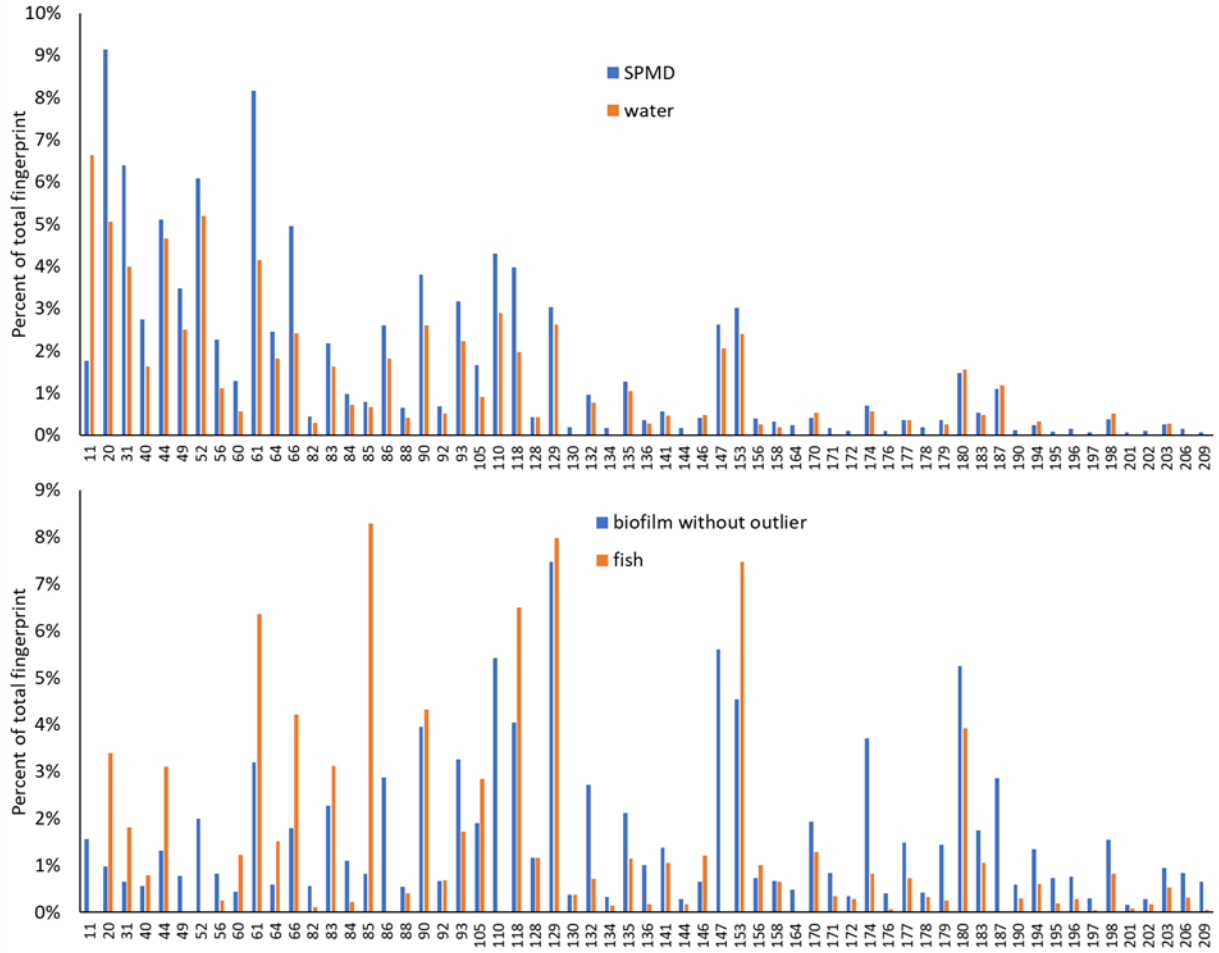
Fish – temporal trends

- Ecology's analysis (Seiders et al, 2014) generally found no significant temporal difference in total PCB concentration 2012-2005.
- Some are visually apparent in this analysis.
- Shift toward lower MW PCB sources over time??
  - FishA = 1248ish
  - FishB = 1254ish
  - FishC = 1254+1260ish



Biofilm and SPMD

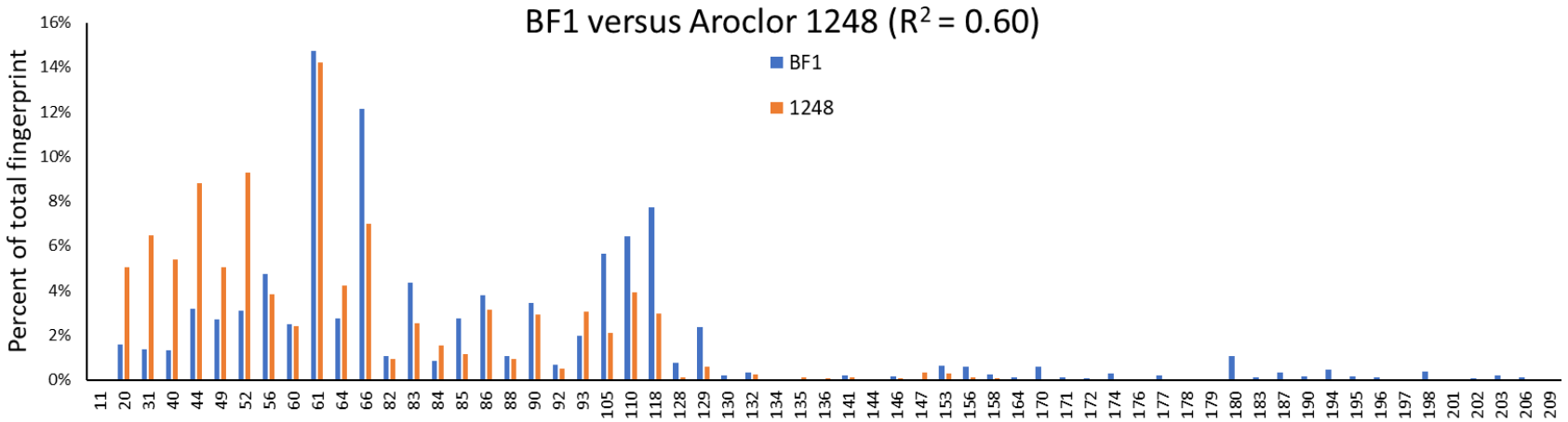
- SPMD have different congener patterns that biofilm
- SPMD very similar to water
- Biofilm higher in MW and more similar to fish
- They were combined for PMF analysis because not enough SPMD for separate analysis; no effect on PMF solution

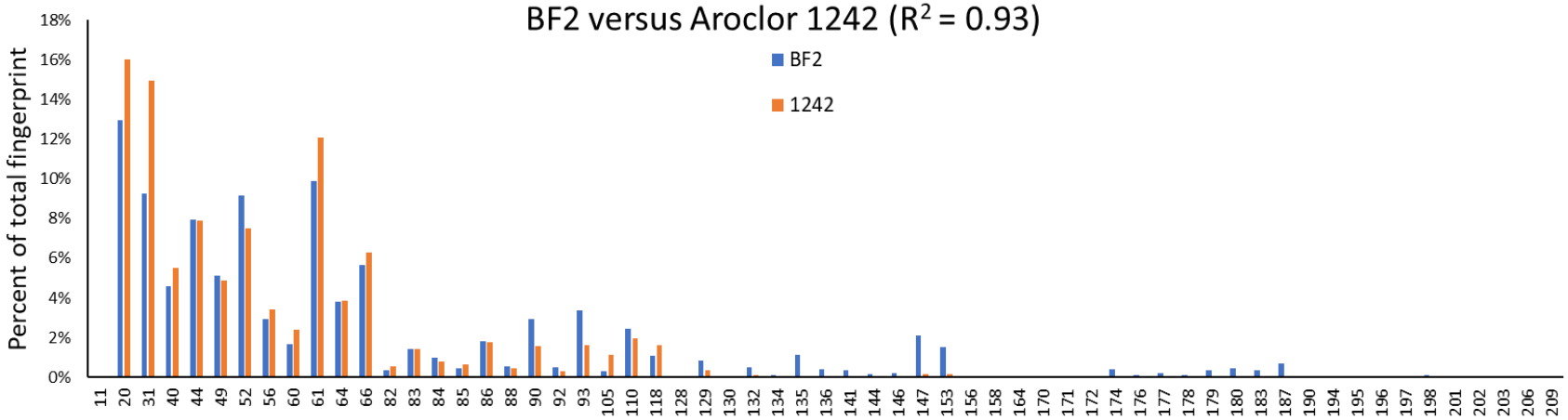


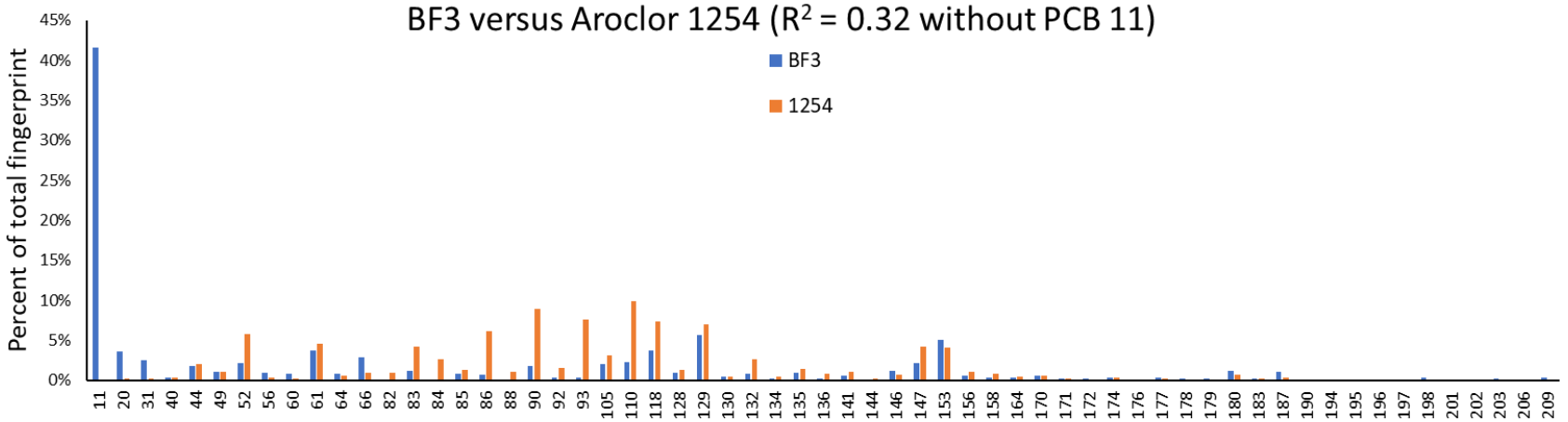
Note: differences in coelution patterns make this figure inexact.

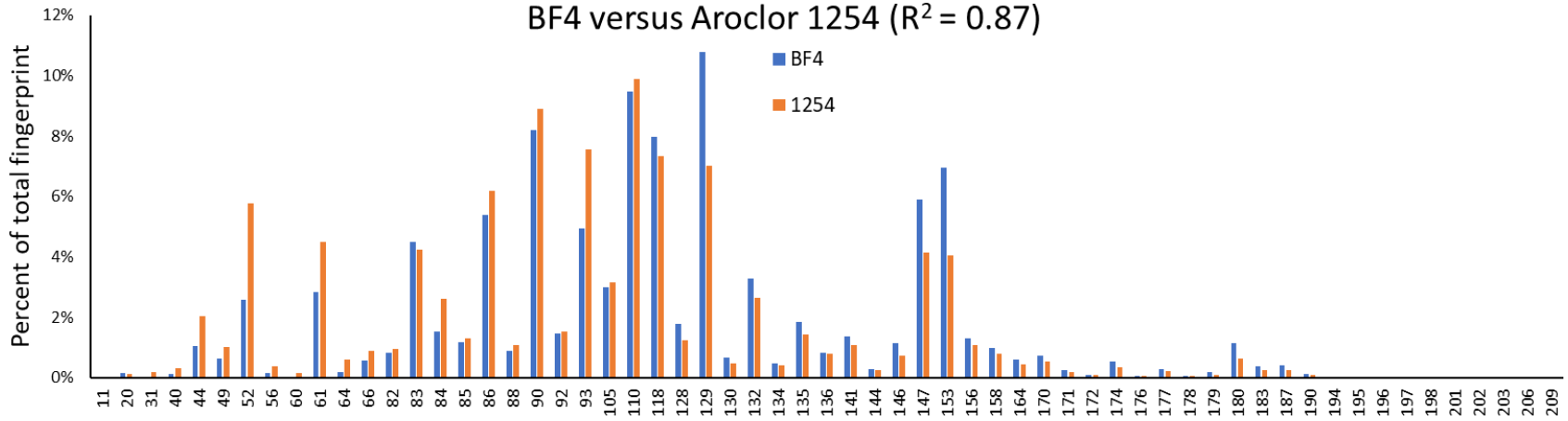
Biofilm and SPMD

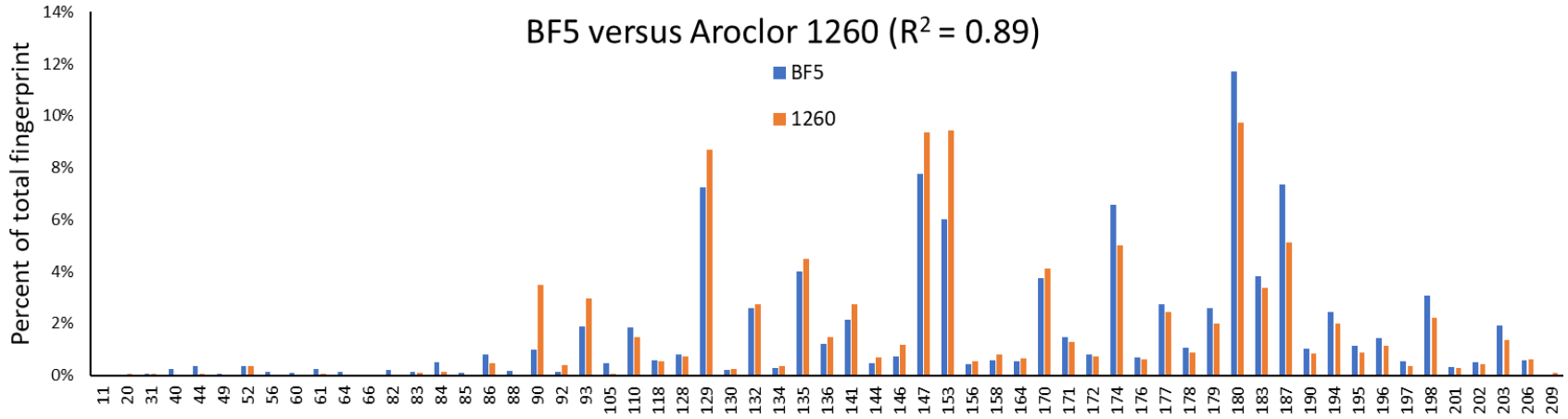
Biofilm and SPMD: 6 factors

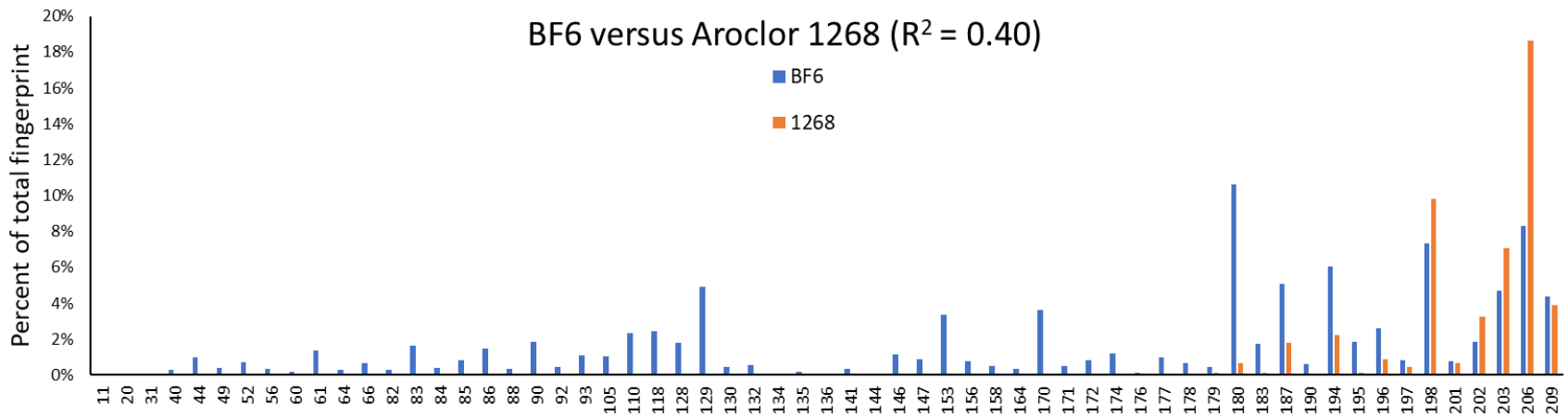




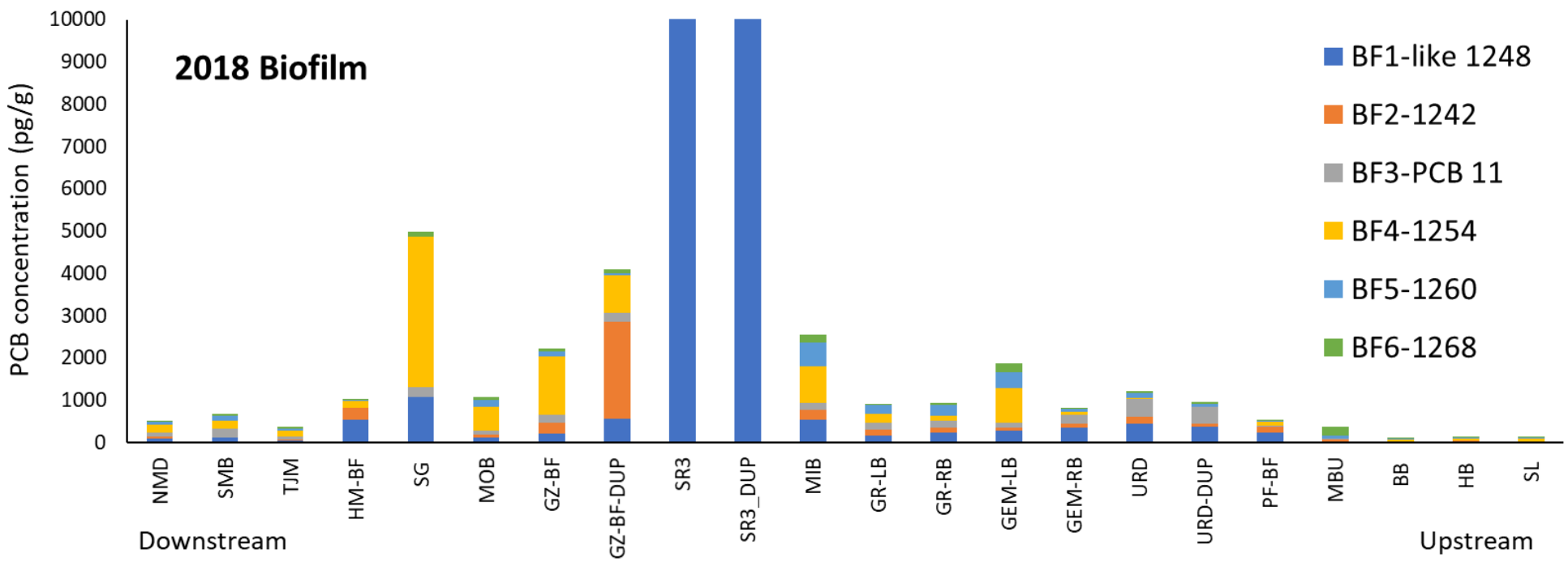


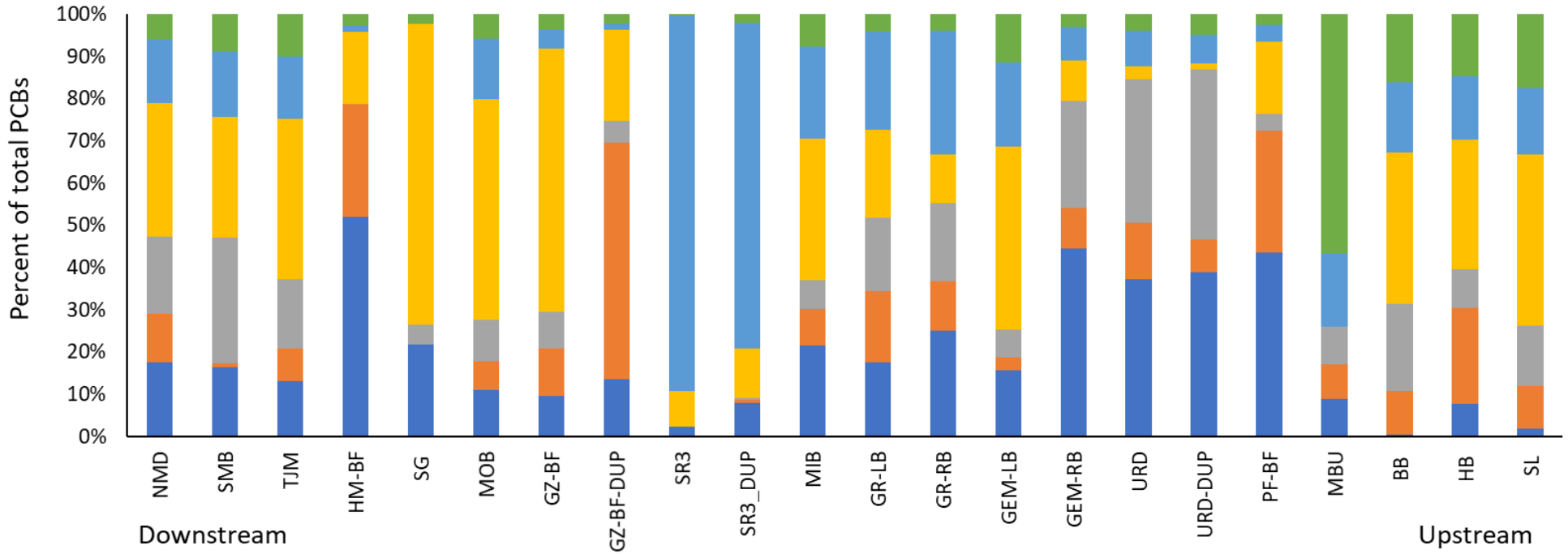

BF4 versus Aroclor 1254 (R^2 = 0.87)
BF4
1254
Percent of total fingerprint
12%
10%
8%
6%
4%
2%
0%
11 20 31 40 44 49 52 56 60 61 64 66 82 83 84 85 86 88 90 92 93 105 110 118 128 129 130 132 134 135 136 141 144 146 147 153 156 158 164 170 171 172 174 176 177 178 179 180 183 187 190 194 195 196 197 198 201 202 203 206 209


BF5 versus Aroclor 1260 (R^2 = 0.89)
BF5
1260
Percent of total fingerprint
14%
12%
10%
8%
6%
4%
2%
0%
11 20 31 40 44 49 52 56 60 61 64 66 82 83 84 85 86 88 90 92 93 105 110 118 128 129 130 132 134 135 136 141 144 146 147 153 156 158 164 170 171 172 174 176 177 178 179 180 183 187 190 194 195 196 197 198 201 202 203 206 209

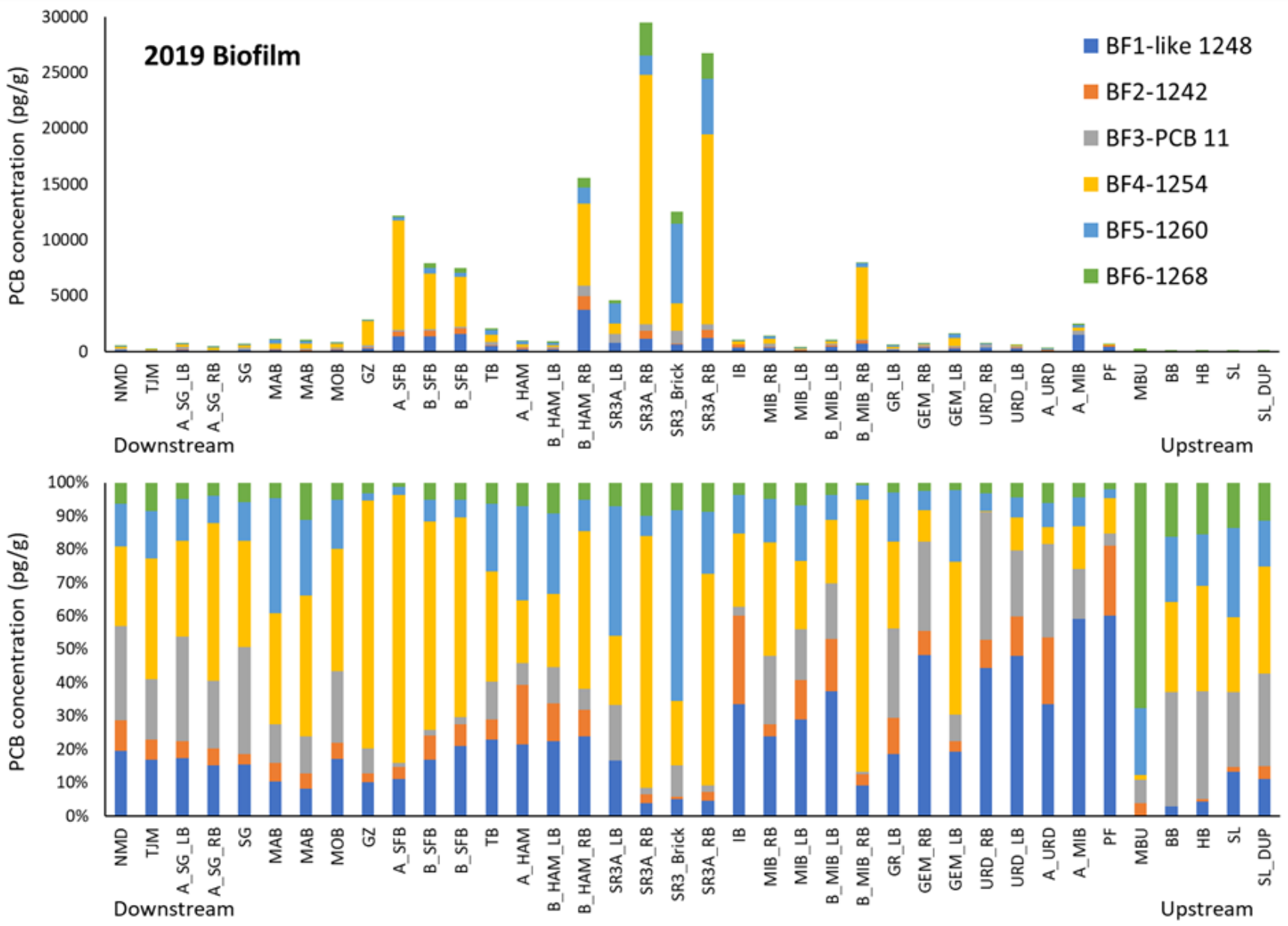

BF6 versus Aroclor 1268 (R^2 = 0.40)
BF6
1268
Percent of total fingerprint
20%
18%
16%
14%
12%
10%
8%
6%
4%
2%
0%
11 20 31 40 44 49 52 56 60 61 64 66 82 83 84 85 86 88 90 92 93 105 110 118 128 129 130 132 134 135 136 141 144 146 147 153 156 158 164 170 171 172 174 176 177 178 179 180 183 187 190 194 195 196 197 198 201 202 203 206 209

2018

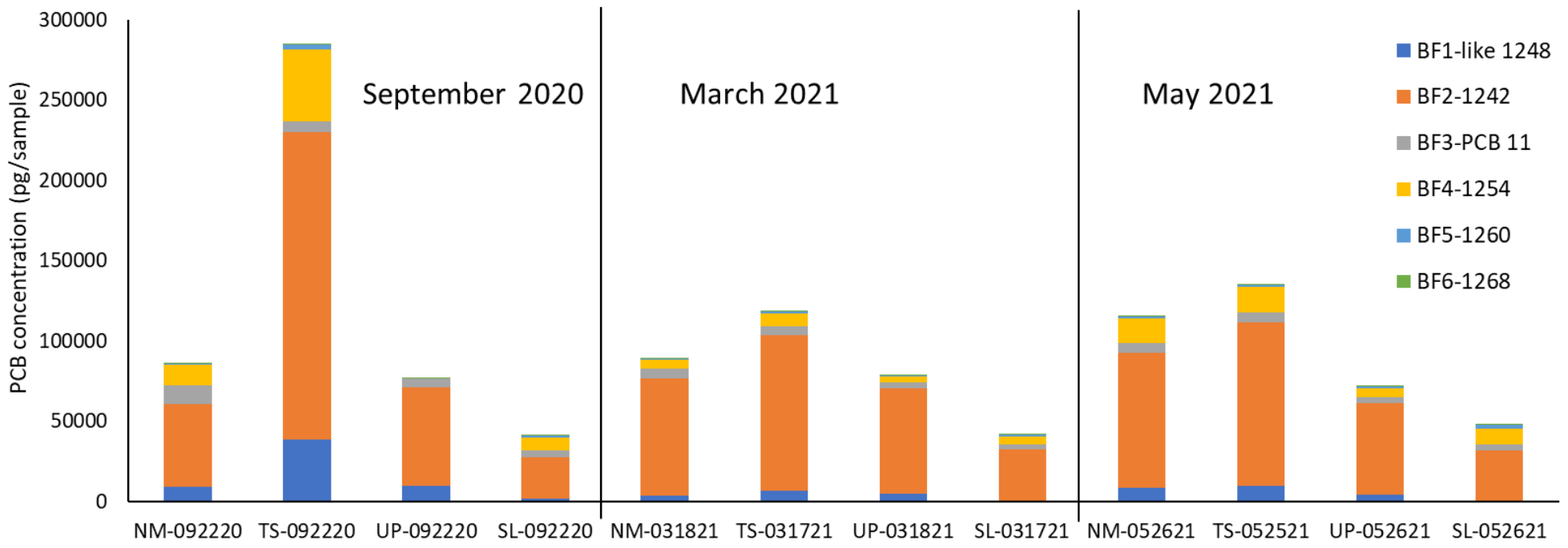

2018 Biofilm
PCB concentration (pg/g)
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
BF1-like 1248
BF2-1242
BF3-PCB 11
BF4-1254
BF5-1260
BF6-1268
NMD
SMB
TJM
HM-BF
SG
MOB
GZ-BF
GZ-BF-DUP
SR3
SR3_DUP
MIB
GR-LB
GR-RB
GEM-LB
GEM-RB
URD
URD-DUP
PF-BF
MBU
BB
HB
SL
Downstream
Upstream

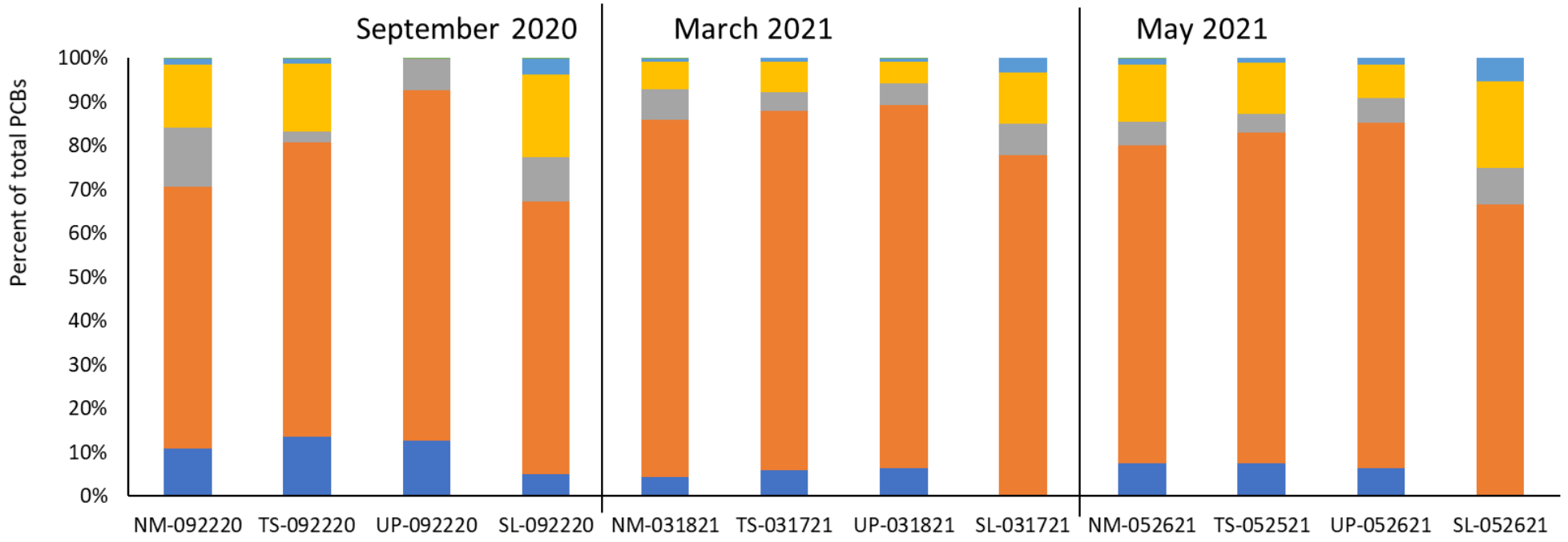

Percent of total PCBs
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
NMD
SMB
TJM
HM-BF
SG
MOB
GZ-BF
GZ-BF-DUP
SR3
SR3_DUP
MIB
GR-LB
GR-RB
GEM-LB
GEM-RB
URD
URD-DUP
PF-BF
MBU
BB
HB
SL
Downstream
Upstream

Mission Reach source is mostly 1260 and some 1254



SPMD


PCB concentration (pg/sample)
300000
250000
200000
150000
100000
50000
0
September 2020
March 2021
May 2021
BF1-like 1248
BF2-1242
BF3-PCB 11
BF4-1254
BF5-1260
BF6-1268
NM-092220
TS-092220
UP-092220
SL-092220
NM-031821
TS-031721
UP-031821
SL-031721
NM-052621
TS-052521
UP-052621
SL-052621


Percent of total PCBs
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
September 2020
March 2021
May 2021
NM-092220
TS-092220
UP-092220
SL-092220
NM-031821
TS-031721
UP-031821
SL-031721
NM-052621
TS-052521
UP-052621
SL-052621

Conclusions

- Fish may show evidence of decline in PCB concentrations over time, but Ecology's assessment showed no significant change.
- Fish may show evidence of a shift toward lower MW PCB sources over time:
  - WWTP upgrades preferentially remove higher MW PCBs
- Biofilm data shows that hot spots tend to be dominated by higher MW PCBs:
  - SR3 is dominated by 1260
  - Other are usually dominated by 1254
- SPMD data also suggests that hot spots are dominated by high MW PCBs

Holistic Report

Data sets analyzed:

- With PMF
  - Ambient water
  - Stormwater/CSOs
  - WWTP influent
  - WWTP effluent
  - Biofilm+SPMD
  - Fish
  - Kaiser outfalls
  - Kaiser groundwater
- With MLR:
  - Bulk Atmospheric Deposition
  - Sediment (including suspended particulates)
  - Surface water CLAM (Continuous low-level aquatic monitoring) samples
  - Groundwater from the GE plant
  - Inland Empire Paper outfalls
  - Storm drain solids
  - Municipal products

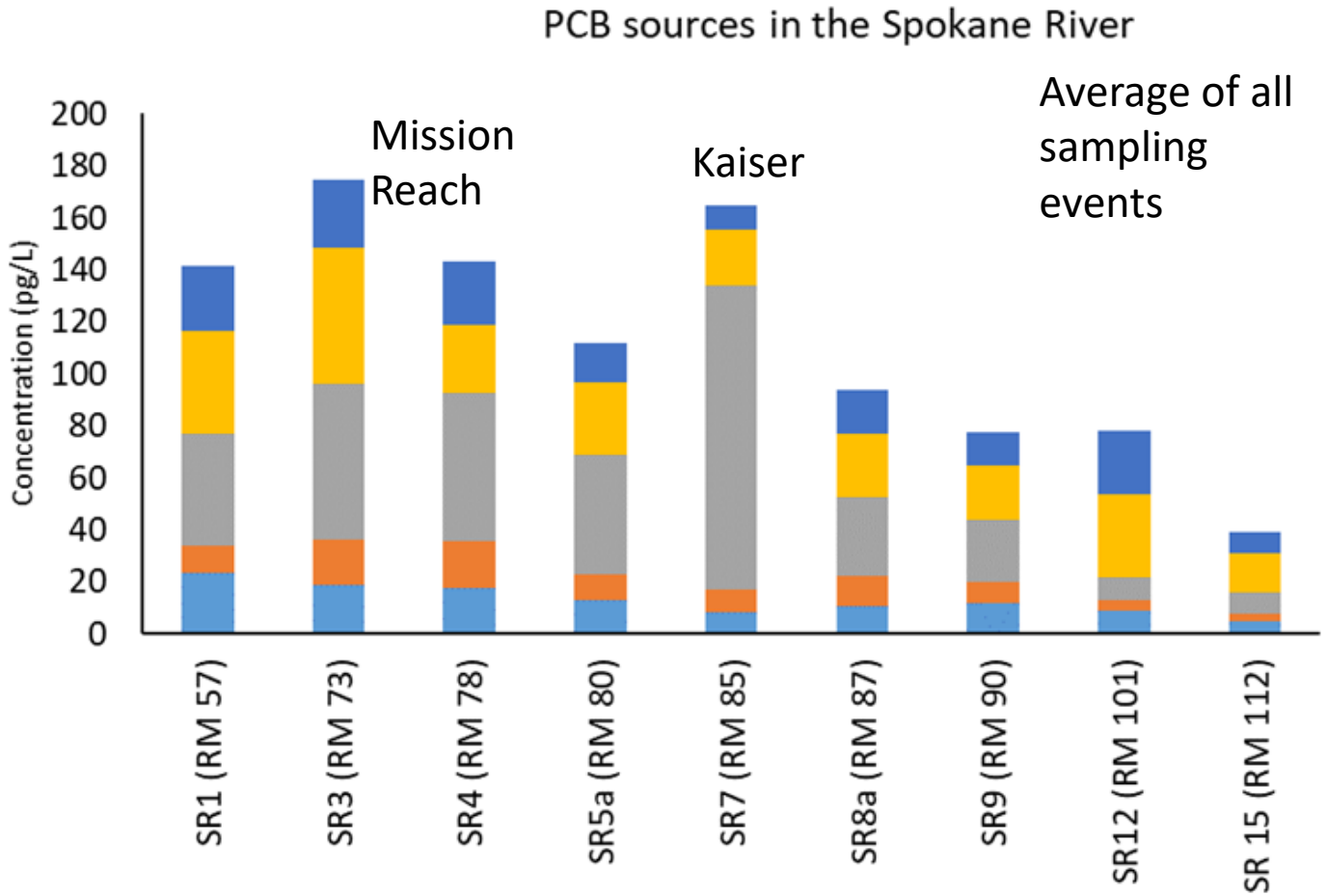
Quality and completeness

- I examined all the available method 1668 PCB data
- Data was excluded from PMF analysis only when:
  - Insufficient data was available for that compartment. This data was examined by other means.
  - It was measured using a different GC column that the bulk of the data for that compartment. This data was examined by other means.
  - Congeners that were below detection in a majority of samples were not included. Care was taken not to exclude congeners from PMF that were important indicators of source types.
- Blank masses were significant for surface water. Peer-reviewed blank correction study determined the best method of blank correction (Rodenburg et al. 2020)

Aroclor vs. non-Aroclor sources

- Water column is about 90% Aroclors, 10% non-Aroclor, mostly PCB 11
  - Biofilm corroborates the presence of PCB 11 in the water column (not a blank issue)
- PCBs in fish are virtually entirely from Aroclors, PCB 11 usually BDL
- Integrated sources such as surface water, biofilm, stormwater, WWTP influent and effluent, and fish are a mixture of Aroclors
- Groundwater at Kaiser is almost entirely Aroclor 1248 with some microbial dechlorination occurring
- IEP influent and effluent are primarily Aroclor 1242 with some PCB 11
  - Indicates that A1242 from carbonless copy paper is still circulating in the recycled paper stream

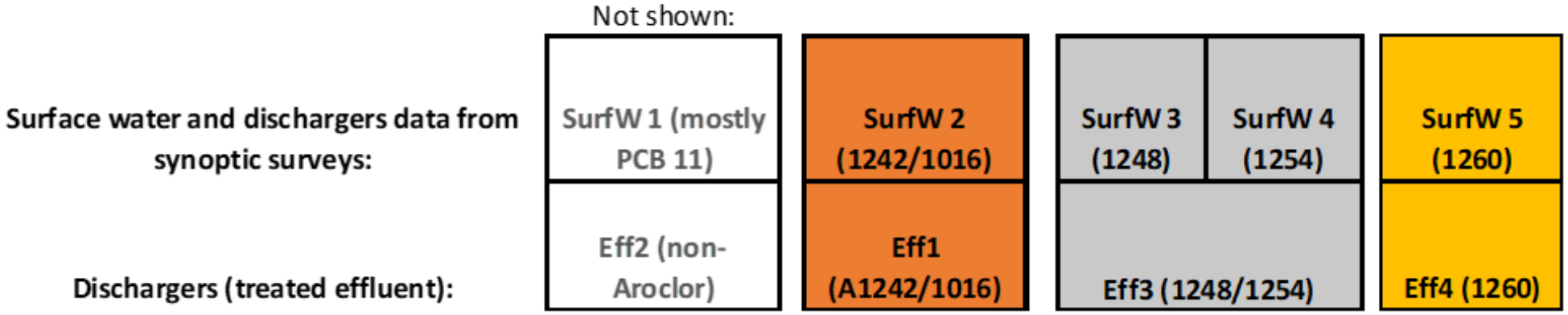
Surface water - spatial variations in sources



Aroclor	1957–1977 U.S.prodn (%)
1221	0.96
1016	12.88
1232	0.24
1242	51.76
1248	6.76
1254	15.73
1260	10.61
1262	0.83
1268	0.33
mean	100.00

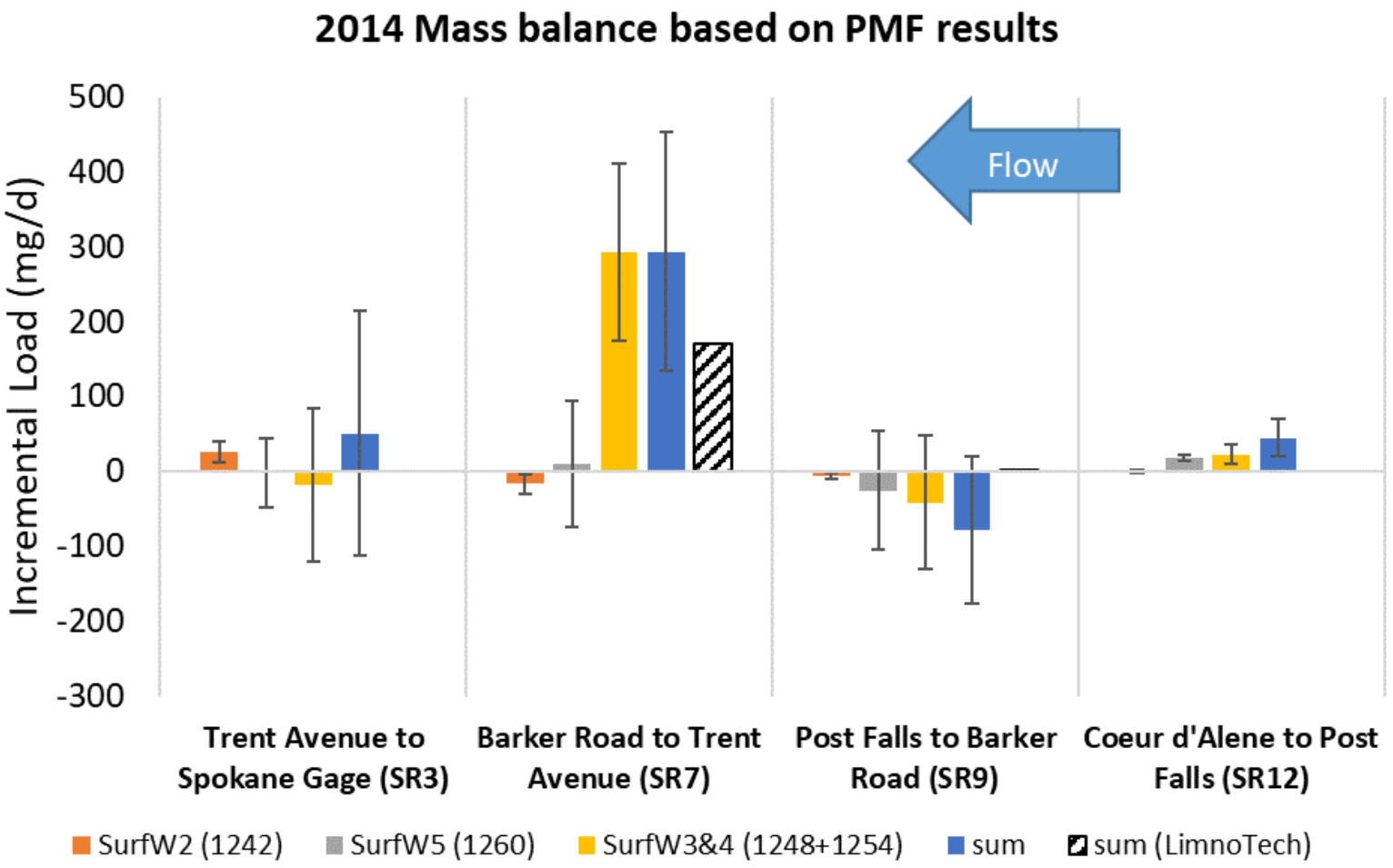
1248 is about 36% of total PCB mass in the water column

Mass balances on PMF factors

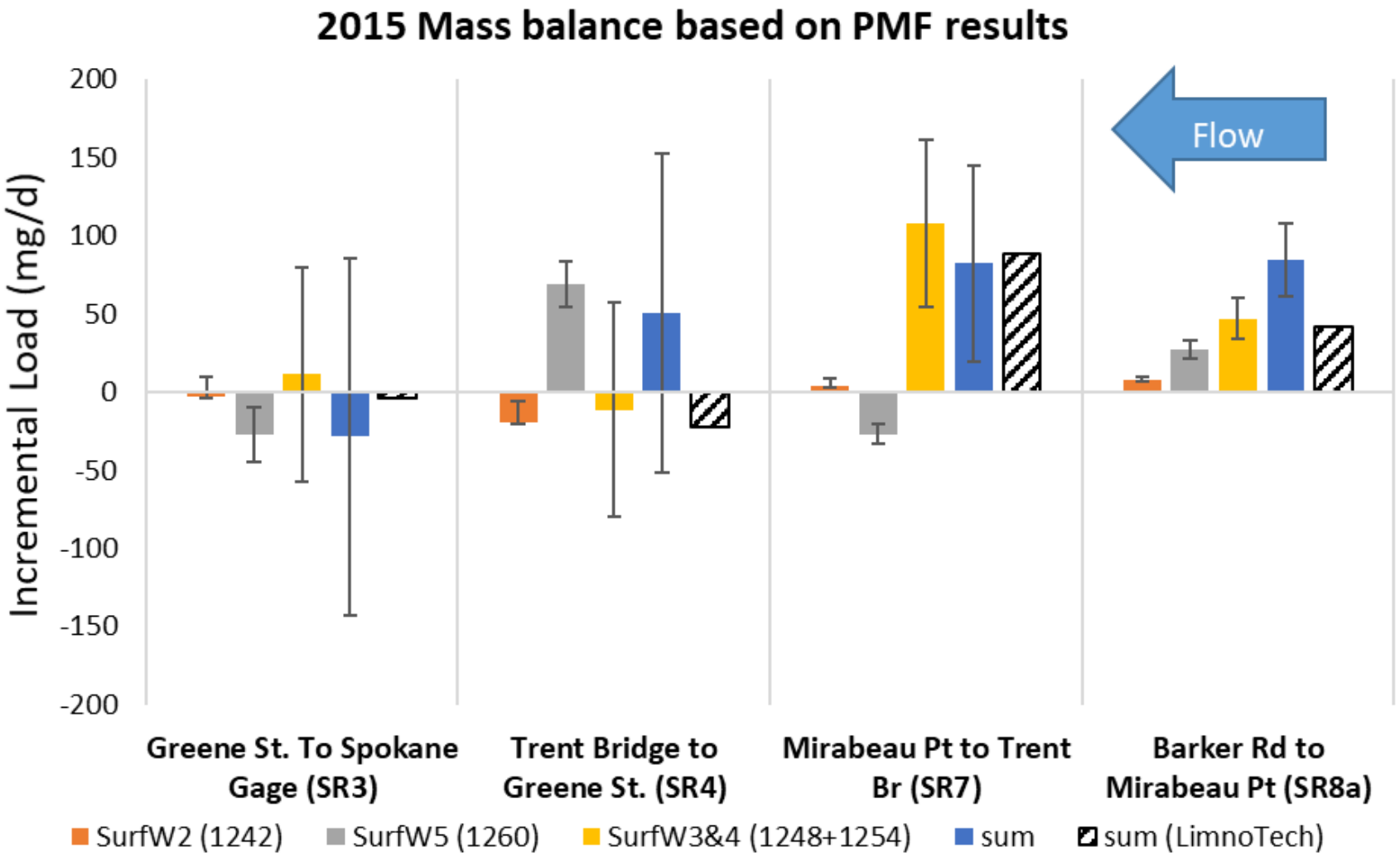


- Mass balance flows from LimnoTech
- Uncertainty propagated by assuming 20% unc in conc, 0% in flows

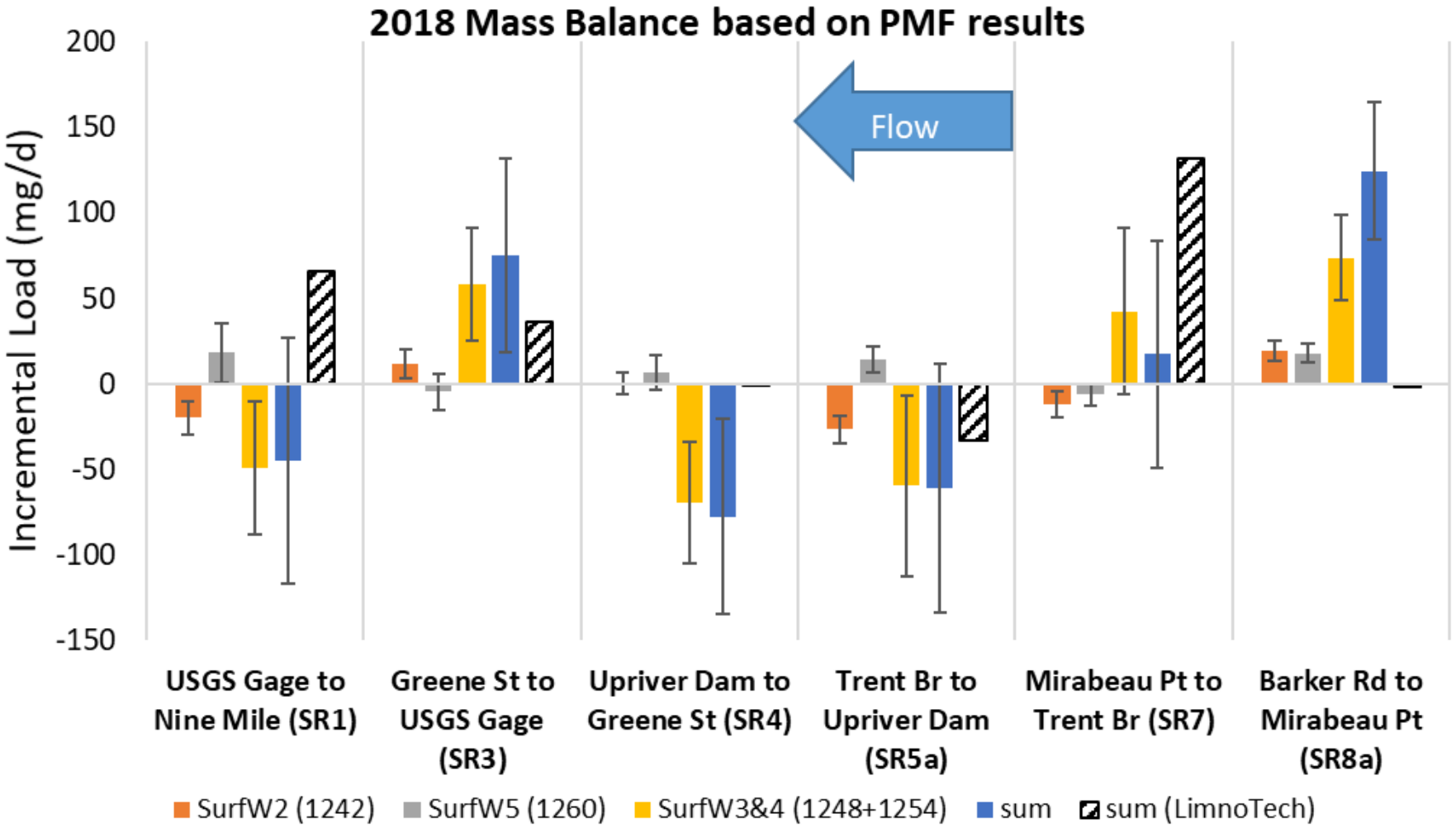
2014 mass balance



2015 mass balance

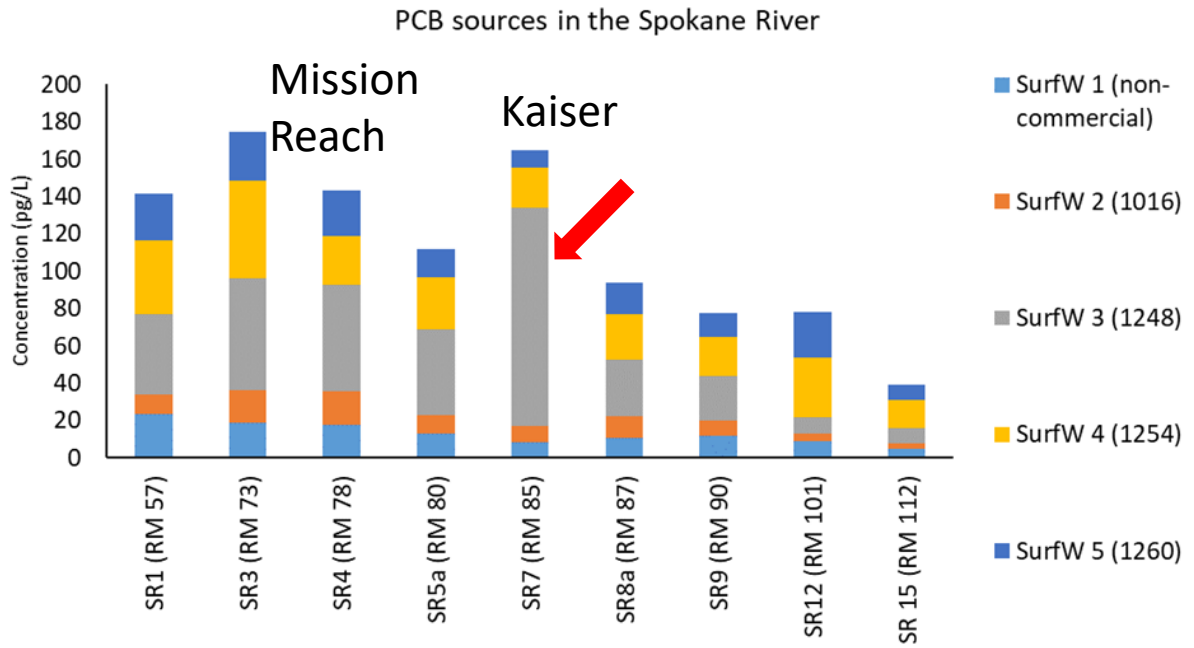


2018 mass balance



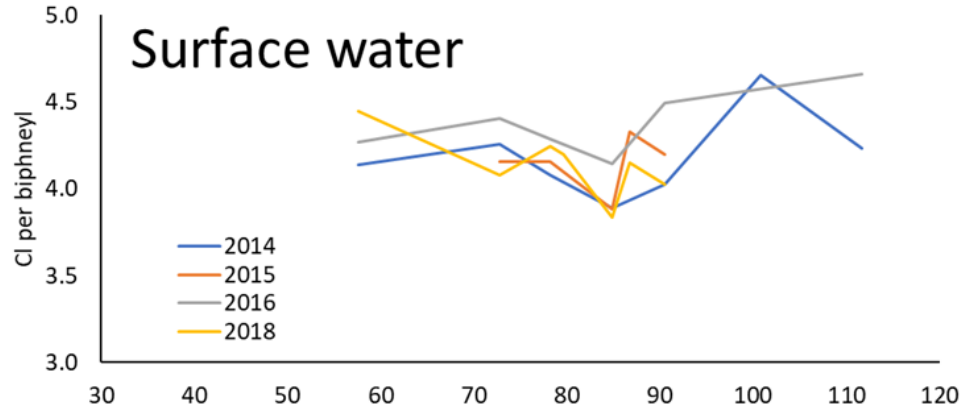
Mass balance takeaways:

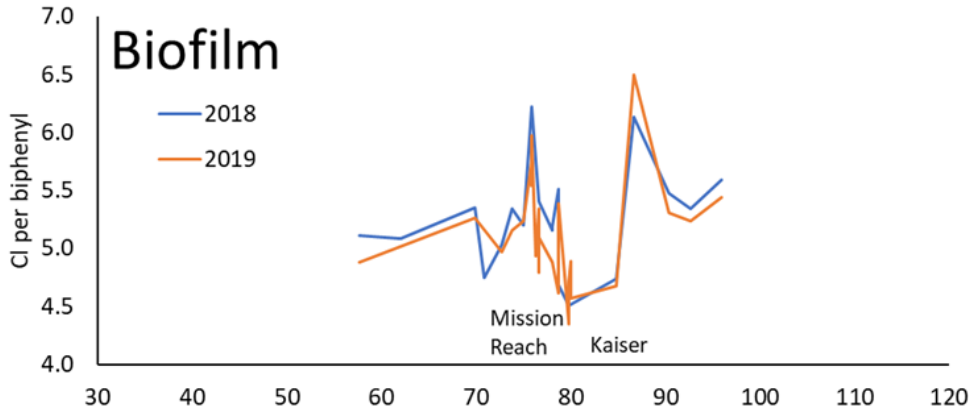
- PMF-based mass balance in good agreement with LimnoTech
- The Kaiser GW source is significant, about 116 to 293 mg/d under low flow.
- Some additional meaningful sources of 1260 above SR8a and SR4?
- Influence of GW is visible ⇒
- 1260 sources and Mission Reach are not obvious (no big jump in the dark blue bar)

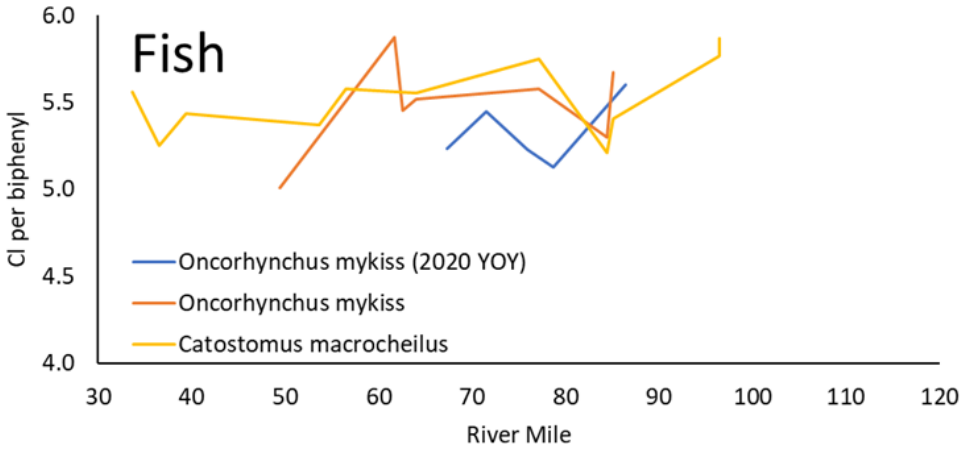


Sources by RM

- These three compartments show an increase in Cl level around the Kaiser inputs and to a lesser extent around Mission Reach







Comparisons to other systems

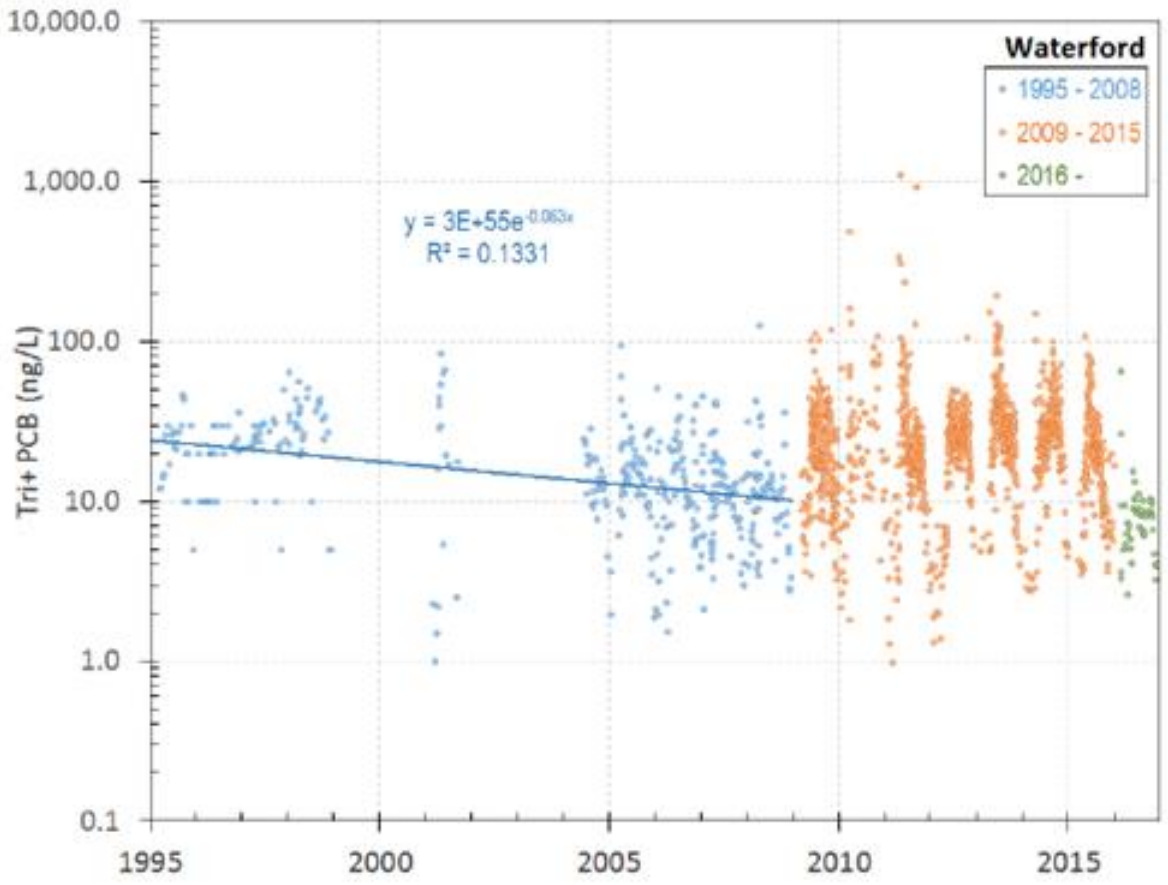
- Levels of PCBs in stormwater and CSOs in Spokane are about the same as other urban areas.
- Therefore, lower conc in surface water in Spokane is due to:
  - Lower population density
  - Better source control (newer WWTPs, fewer CSOs, etc.)
  - Less sediment
- Physical characteristics of the Spokane River are different:
  - Little or no sediment means no big reservoir of PCBs to buffer concentrations
  - Might mean faster response times to changes in loads
- Contaminated sites are important in most systems, including Spokane River
- Levels of non-Aroclor PCBs in the Spokane River are similar to other waterways

Conclusions – data collection

- A lot of very high-quality data have been collected
- More data are needed to see long-term time trends in water and fish
  - Blank problems in water are only going to get worse if PCB concentrations decline
- SPMDs are not very useful for source identification, but they might be good for measuring long-term declines in the water column
- Biofilm is very useful for identifying source areas and characterizing the river as a whole
- Volatilization/Atm Deposition may be data gaps
  - These affect low MW congeners most, which are not in fish

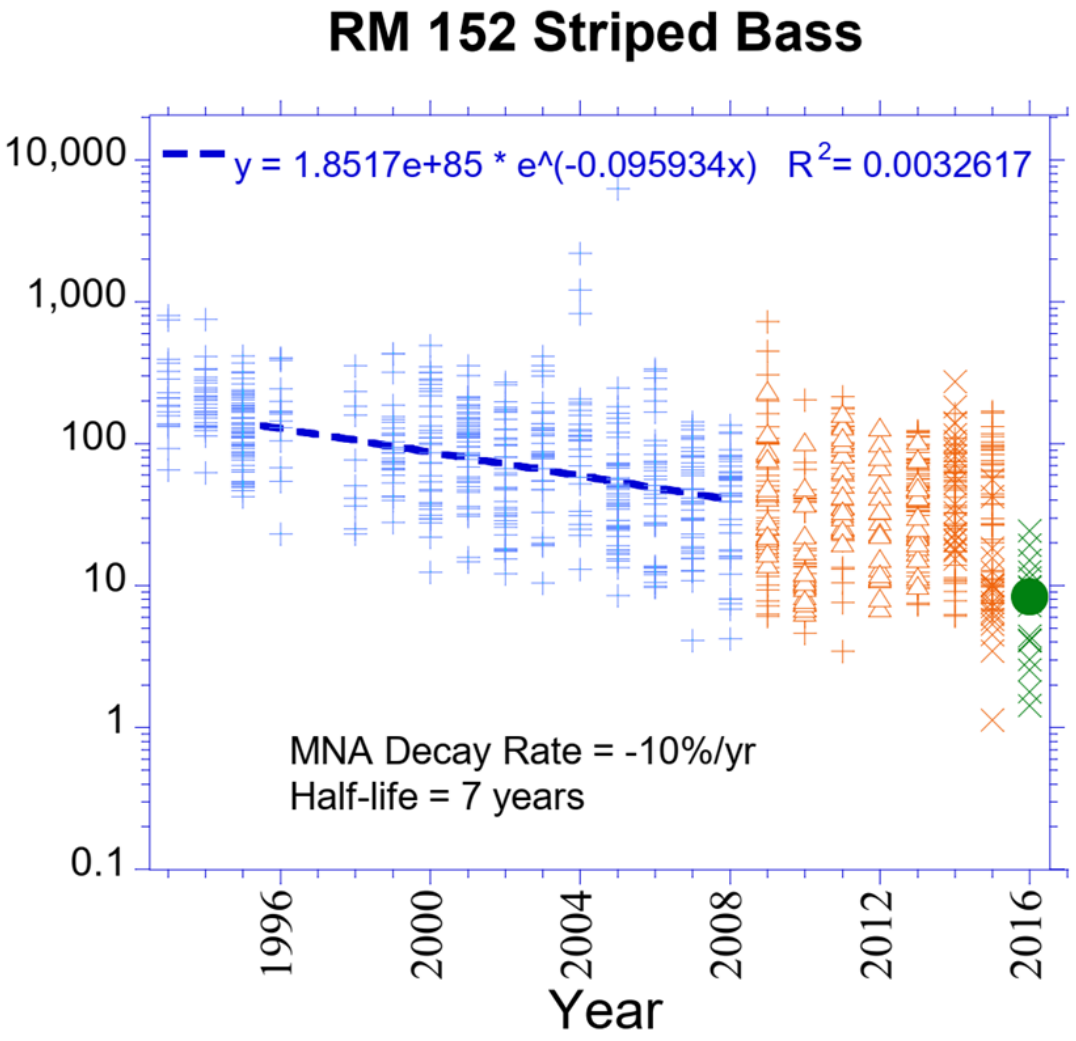
PCBs in the surface water of the Hudson River

- Because of natural variability, you need a LOT of data to be able to see trends in the water data (and they don’t have blank issues)
- Note log scale!



PCBs in Hudson River fish

- Detecting time trends in fish isn't easy either



Conclusions – PCB sources

- Water column is about 90% Aroclors, 10% non-Aroclor, mostly PCB 11
- PCBs in fish are virtually entirely from Aroclors, PCB 11 usually BDL
- Upgrades in WWTPs are effective at removing high MW PCBs
- Kaiser GW is significant
- There are source(s) around Mission Reach that do seem to be meaningful contributors to the water column and fish
- There are diffuse sources that are hard to find/quantify/shut down
- IEP influent and effluent are primarily Aroclor 1242 with some PCB 11
  - Indicates that A1242 from carbonless copy paper is still circulating in the recycled paper stream