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

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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
  - Biofilm
  - 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

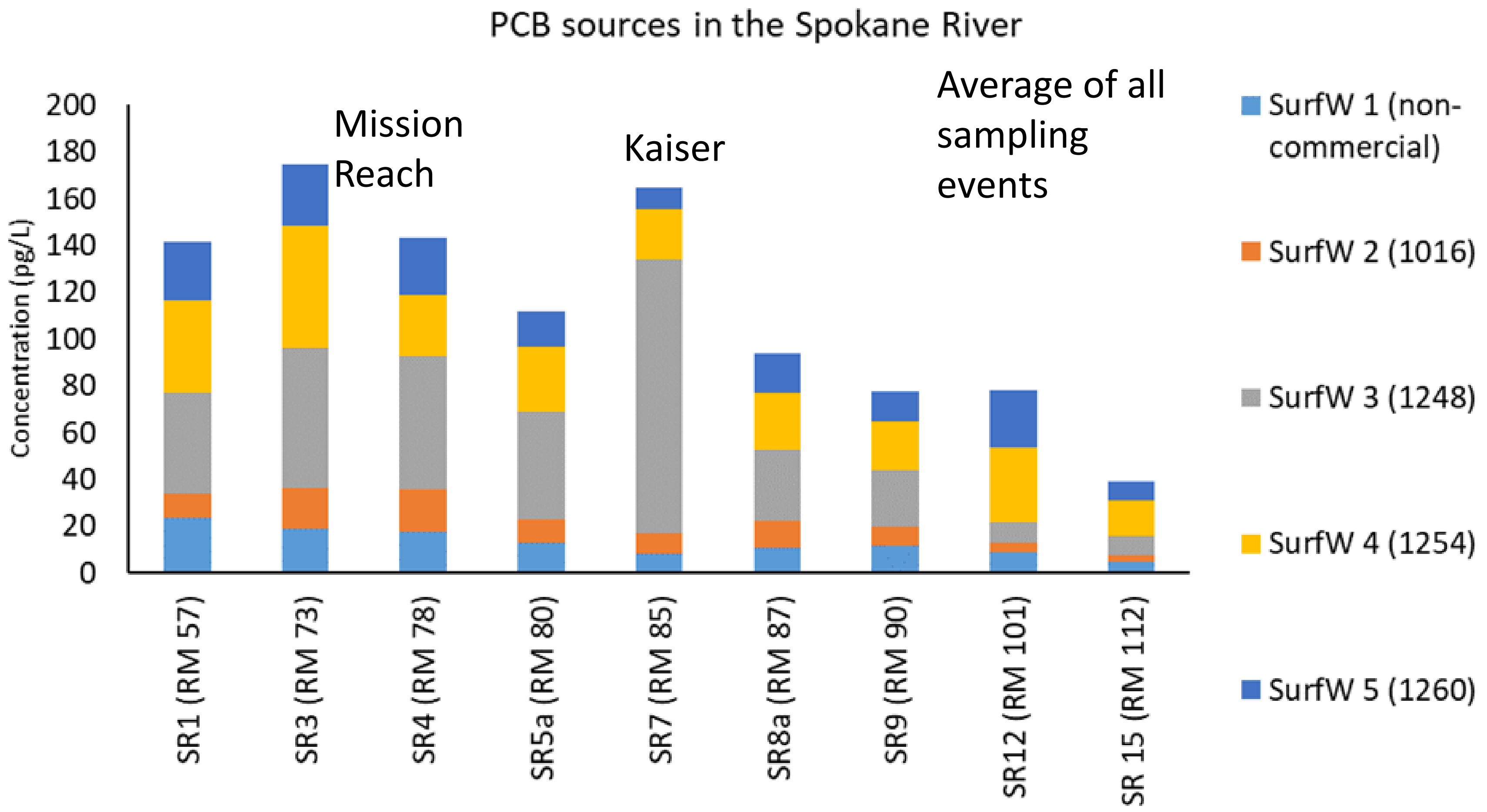
Quality and completeness

- 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 only 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

Surface water – flow correlations

Station	SurfW1 (PCB 11)	SurfW2 (1242)	SurfW3 (1248)	SurfW5 (1260)
SR3	negative	negative	negative	
SR4		negative		
SR7			negative	positive
SR8a		positive	positive	

Negative correlation at SR7 may result from GW inputs

One-box model set up

- Assumes the river is one well-mixed box, which it is not
- Puts too much weight on downstream sources
- Does not include infiltration as a loss process
- Input: $$I = C \cdot V \cdot (k_w + k_{vol} + k_{sed})$$

k_w = Q/V
Q at NMD,
V from MODFLOW

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

Sorbed PCBs can settle:

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

Dissolved PCBs can volatilize:

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

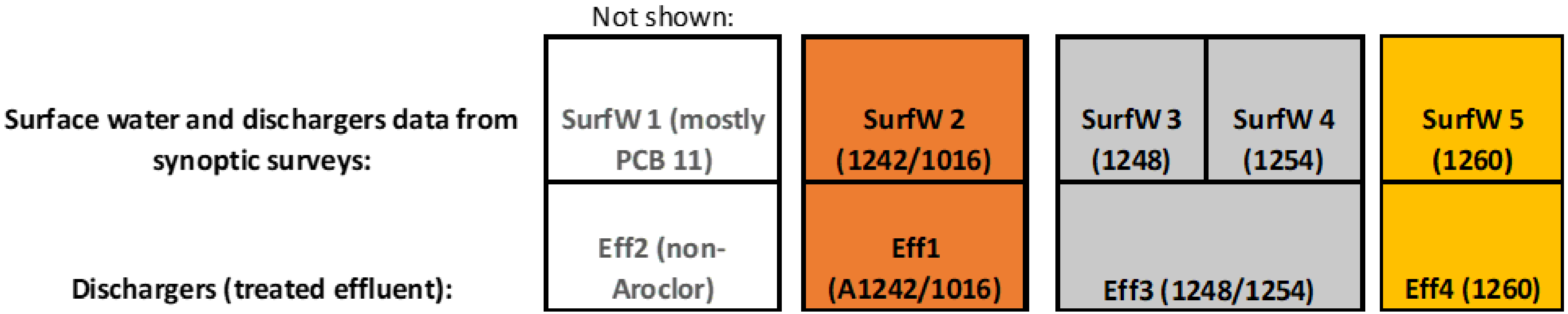
One-box model results

Rate constants

	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) flushing	**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) Concentration	**2014**	34	13	52	59	31	189
	2015	31	26	66	78	27	228
	2018	8	8	25	11	21	73
I (mg/d) Load	**2014**	330	126	496	561	284	1796
	2015	265	223	572	664	222	1946
	2018	89	86	258	113	217	763

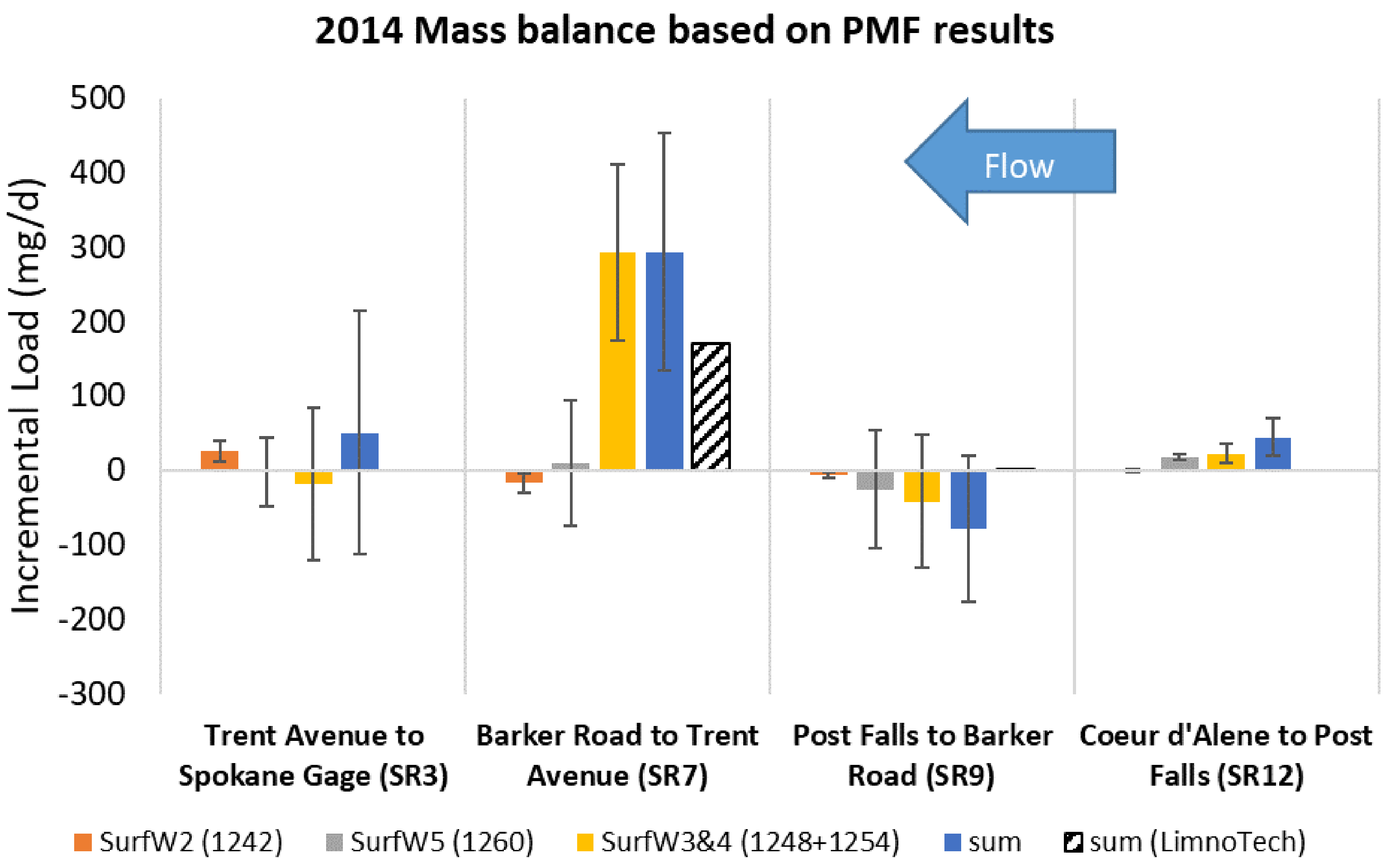
The one box model suggests that volatilization is important, but LimnoTech reports disagree.
Will the EPA TMDL include volatilization as a loss process?
Without volatilization, loads are about 200-600 mg/d

Mass balances on PMF factors

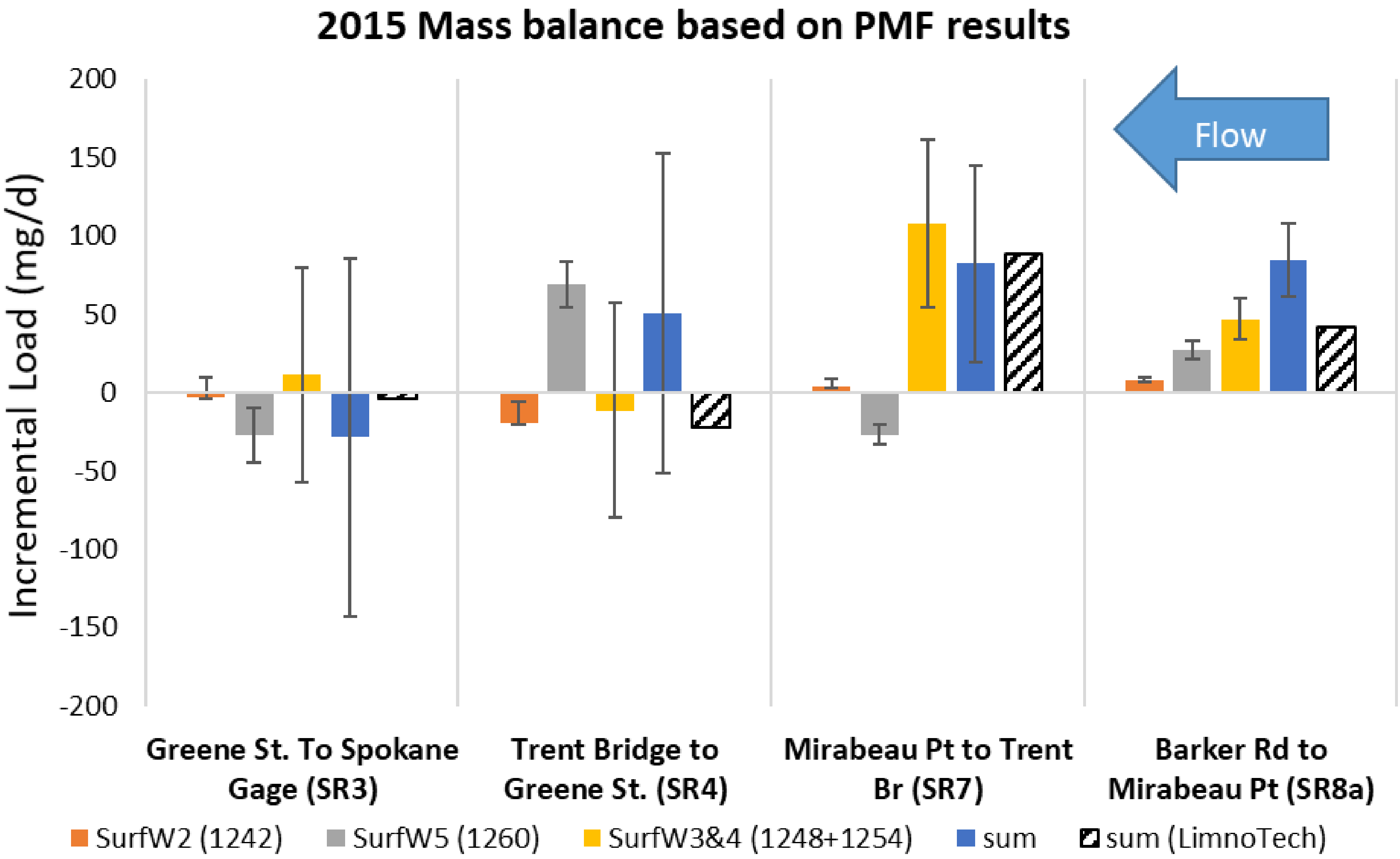


- Mass balance flows from LimnoTech
- Uncertainty propagated by assuming 20% unc in conc, 0% in flows

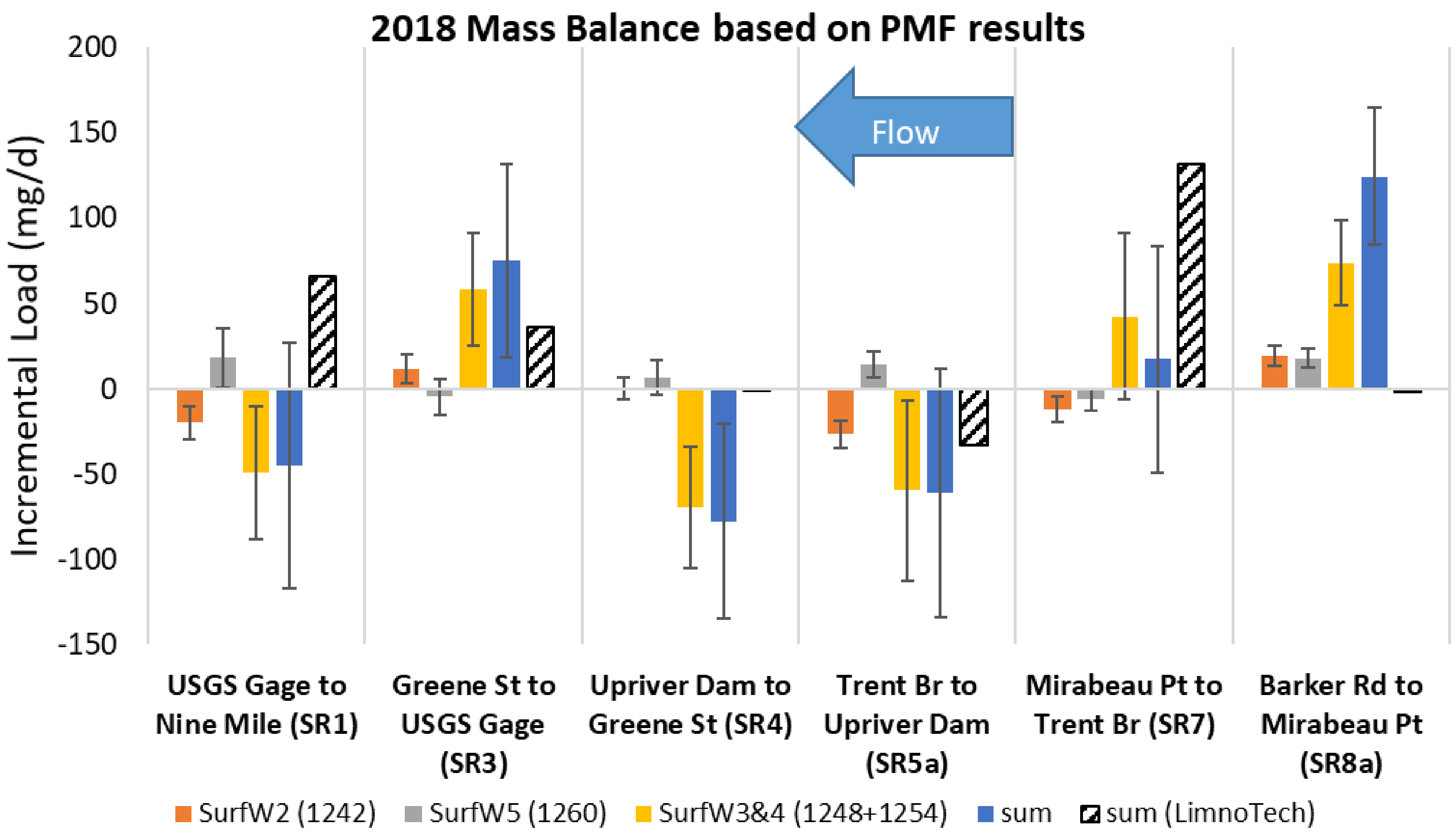
2014 mass balance



2015 mass balance

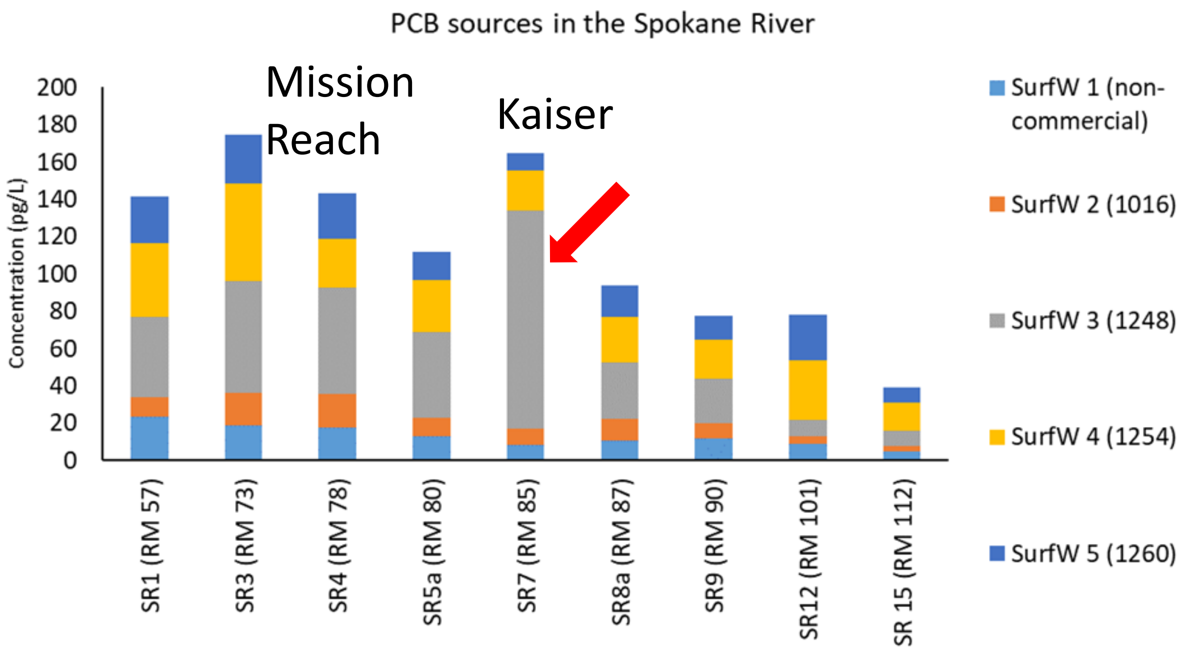


2018 mass balance



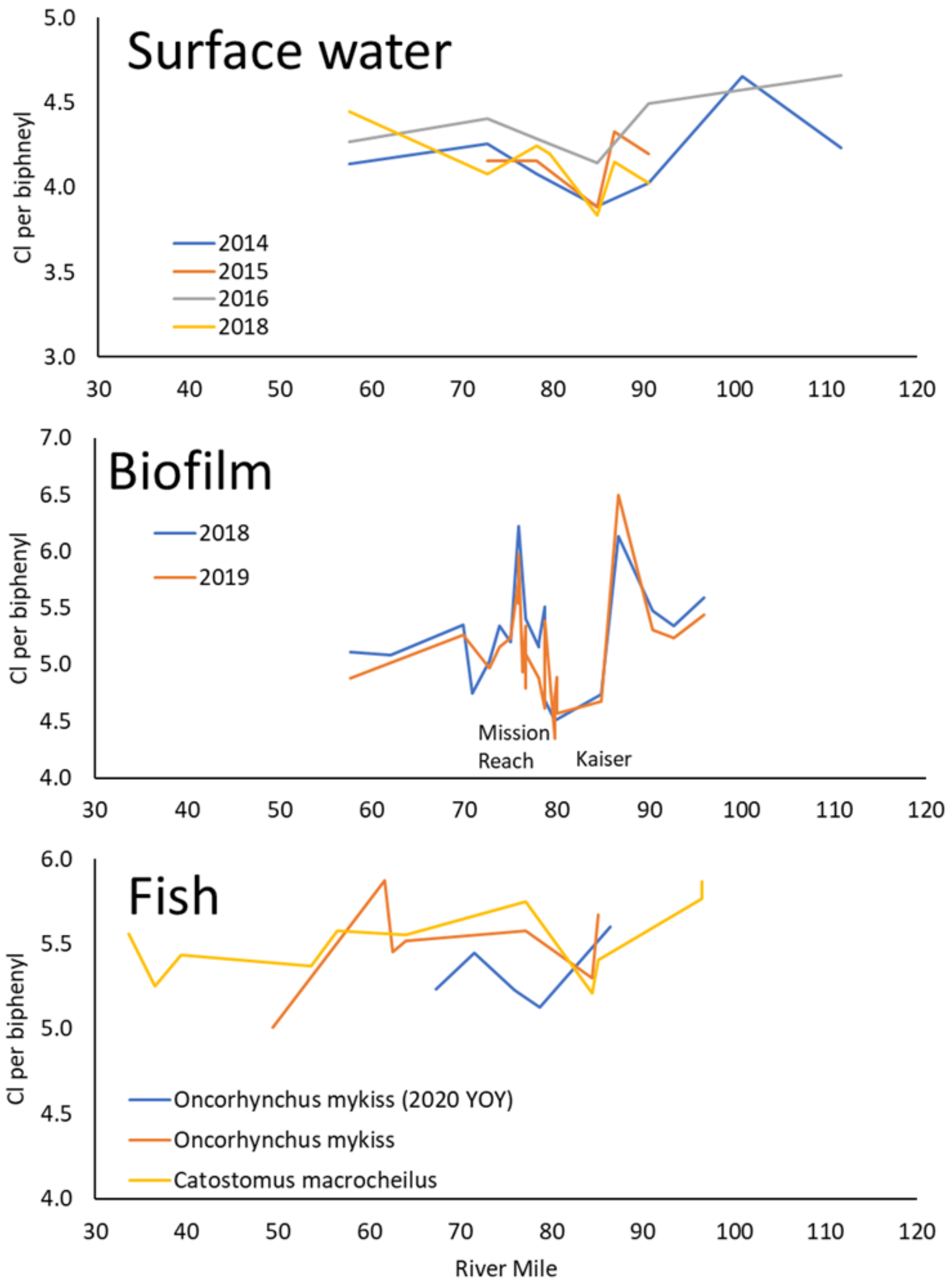
Mass balance takeaways:

- 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)

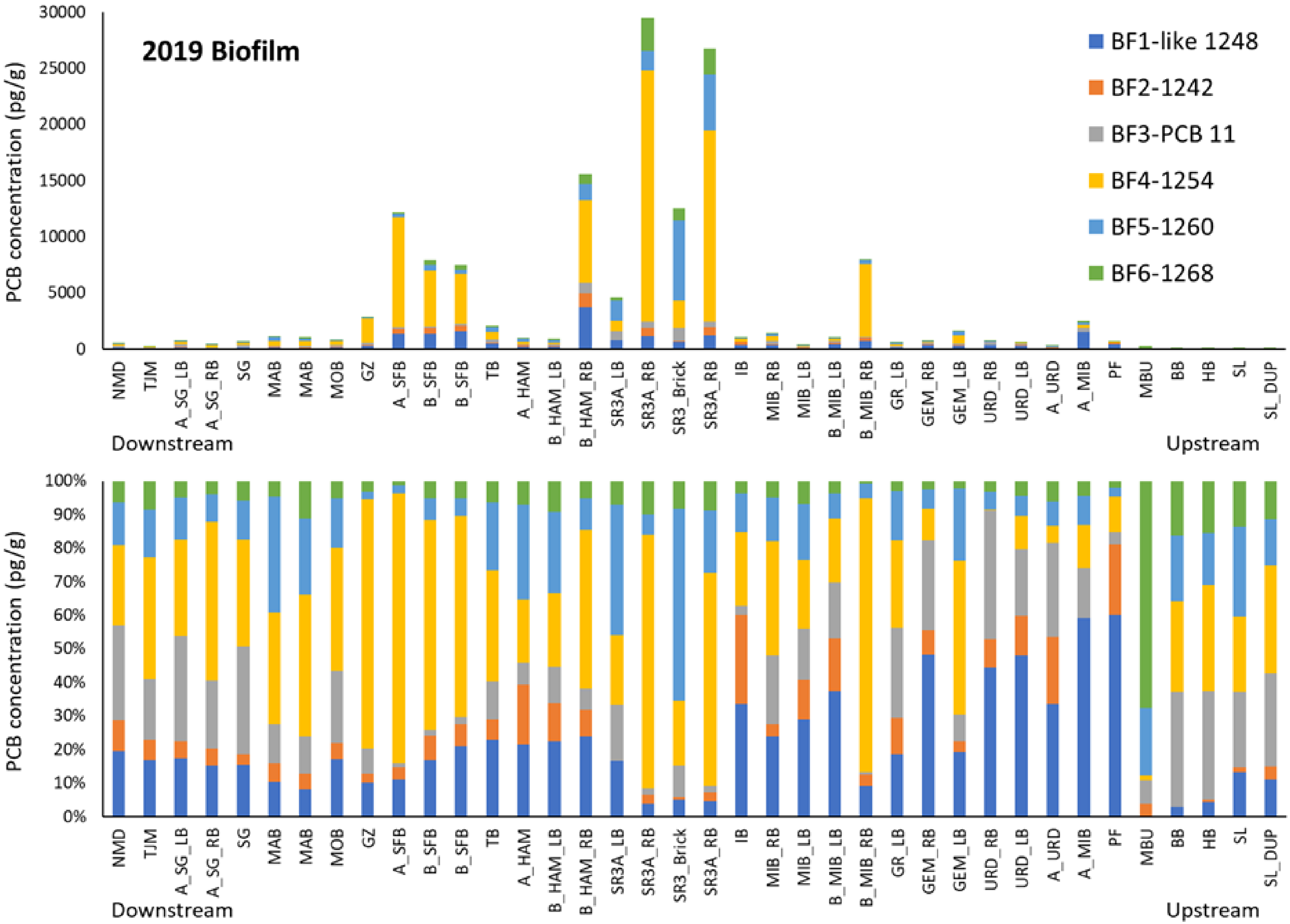


Sources by RM

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



Mission Reach source is mostly 1260 and some 1254



Time trends: surface water

- Not enough data over long enough time to accurately identify trends
- Implementation of tertiary treatment reduces WWTP PCB loads, especially high MW congeners

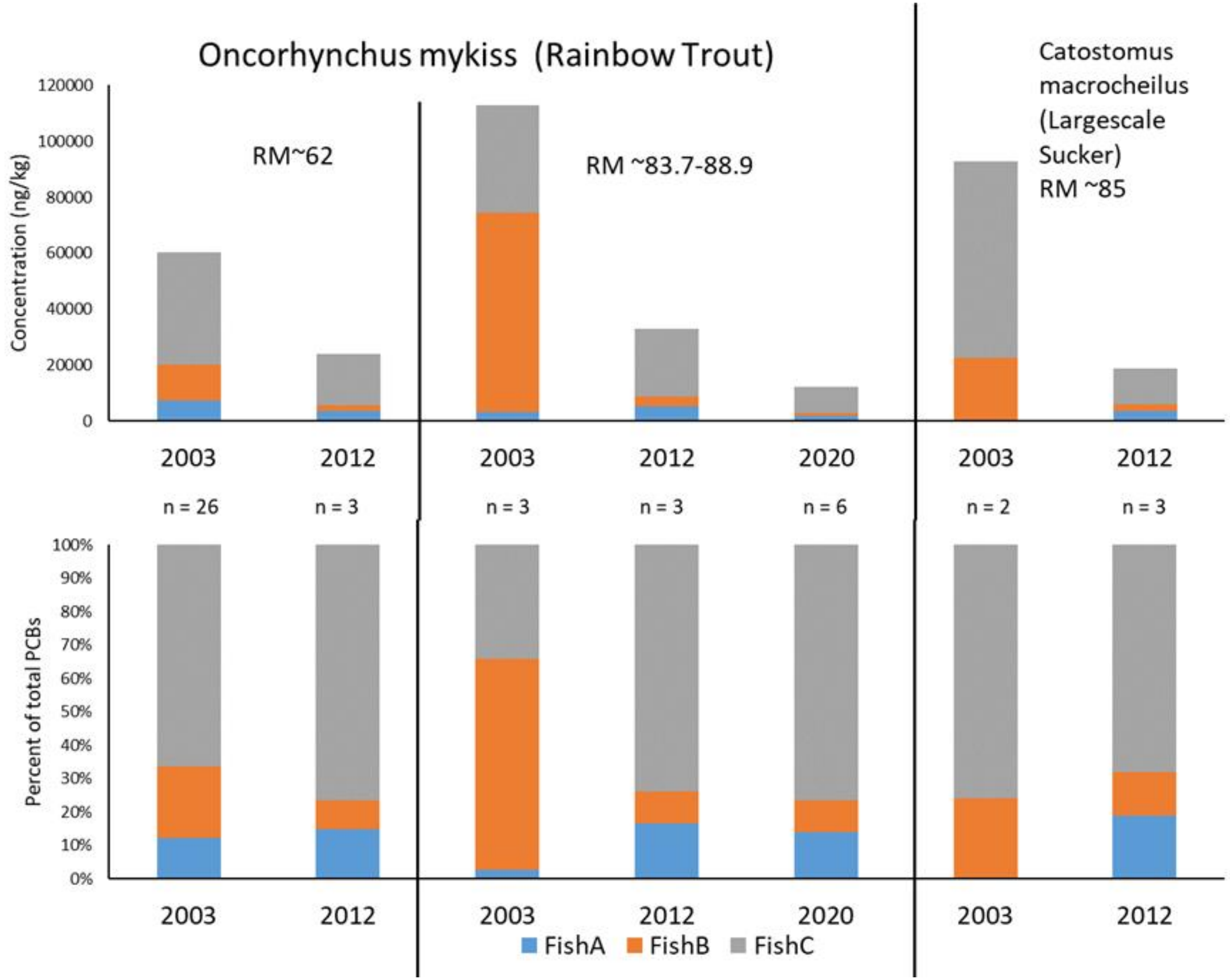
	SurfW1 (PCB 11)	SurfW2 (1242)	SurfW3 (1248)	SurfW4 (1254)	SurfW5 (1260)	Sum of PCBs
HC1				Decrease		
SR1		Decrease	Decrease	Decrease		
SR3		Decrease	Decrease	Decrease	Decrease	Decrease
SR4	Decrease	Decrease	Decrease	Decrease	Decrease	Decrease
SR7		Increase	Decrease	Decrease	Increase	Decrease
SR8a	Increase		Increase			
SR9			Increase			Increase

Decreasing upstream

Increasing downstream

Changes over time

- PCB levels in fish might be declining
  - Hard to discern because of differences in species, location, tissue type, fish age….
- Shifting toward lower MW sources over time?



Comparisons to other systems

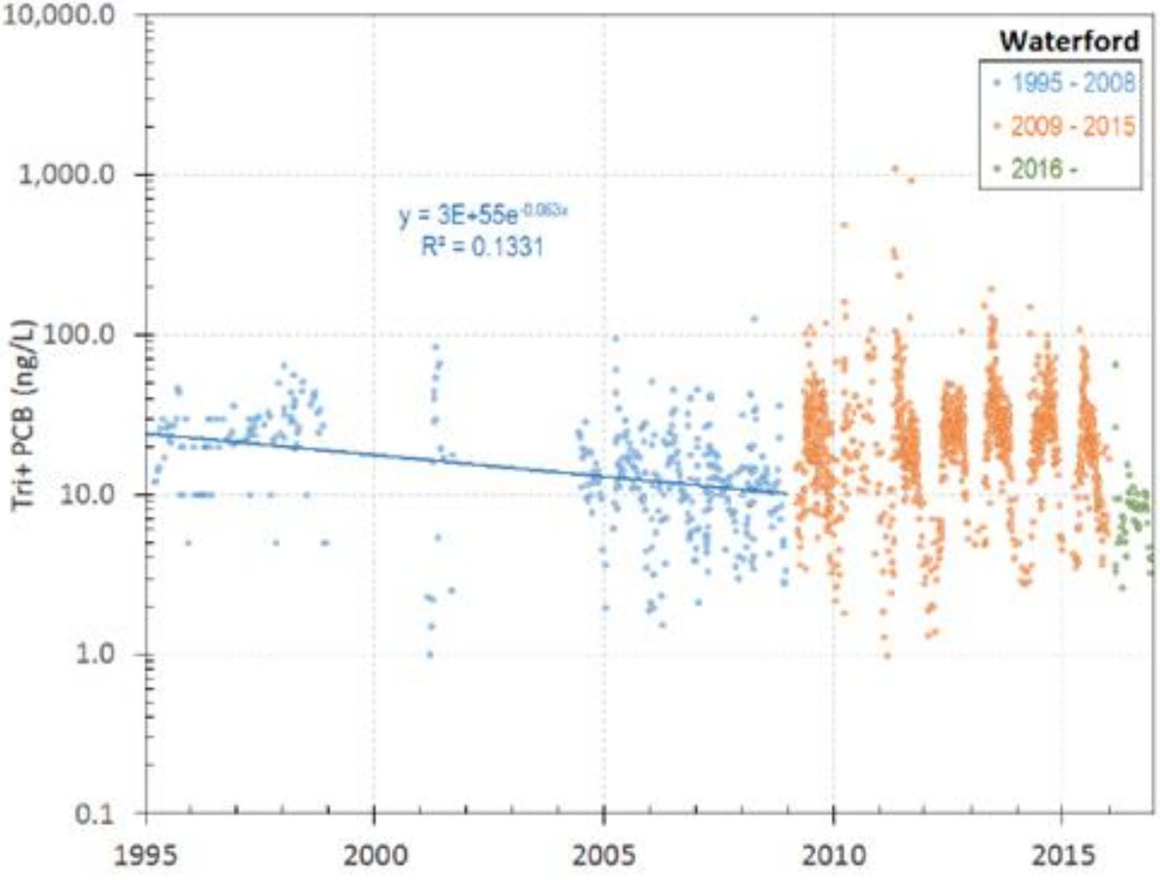
- Levels of PCBs in stormwater and CSOs in Spokane are about the same as other urban areas.
- Therefore, lower conc in surface water in Spokane is due to:
  - Lower population density
  - Better source control (newer WWTPs, fewer CSOs, etc.)
  - Less sediment
- Physical characteristics of the Spokane 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

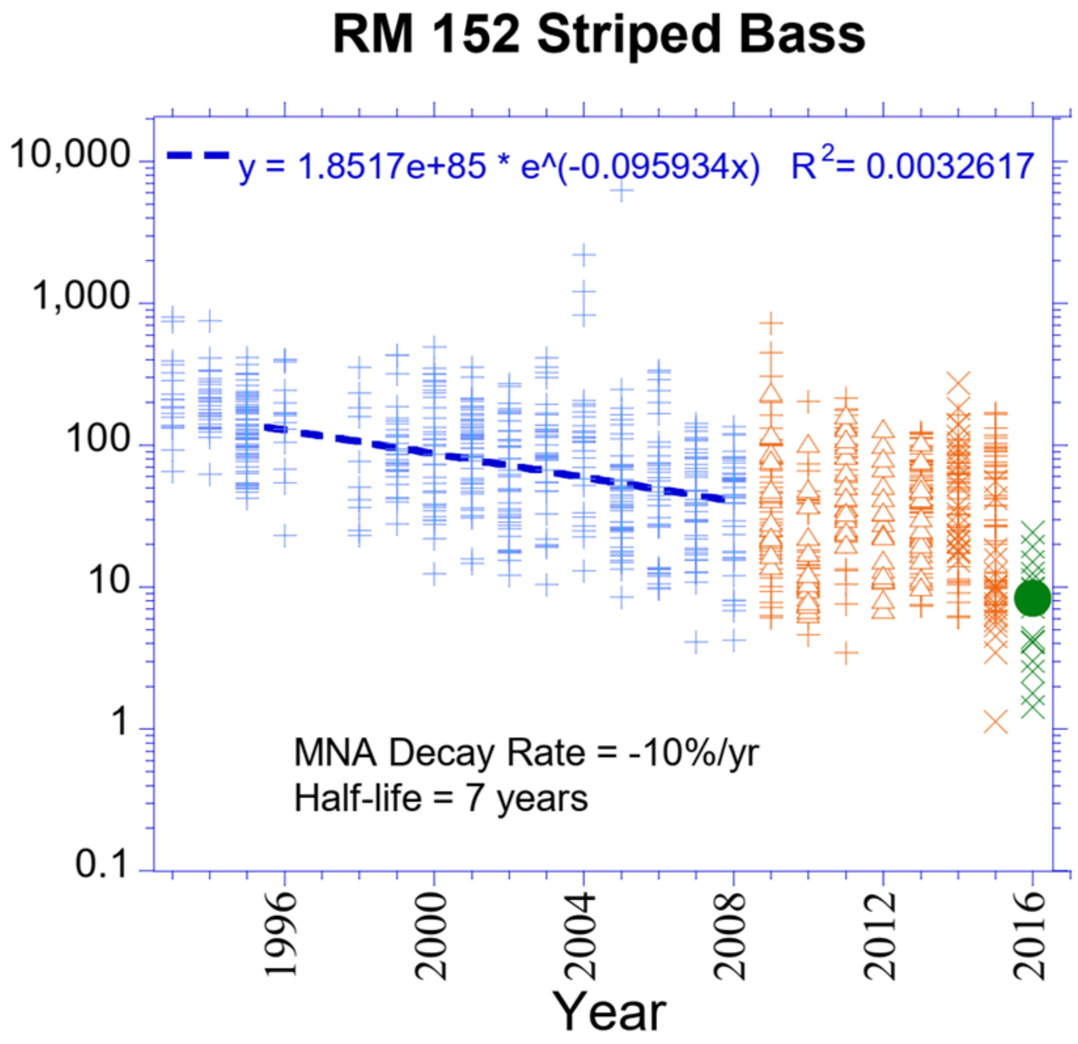
PCBs in the surface water of the Hudson River

- 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
- 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