Water Column and Biofilm Fingerprinting near GE Site via Polytopic Vector Analysis

The impact of GE groundwater on river PCBs

Scope

1. How many distinct sources and processes contribute to the observed PCB congener compositions (i.e., number of end members)?
2. What is the PCB congener composition of each end member?
3. What is the identity of each end member in terms of Aroclors and alteration mechanisms (degradation, weathering, uptake, etc.)
4. Can some of these end members be linked uniquely to groundwater inputs, to the original groundwater composition at the GE source, or to the mass-balance changes by congener?
5. What is the magnitude of the contribution of the GE-linked end members in the biofilm samples?
6. What is the trend of the GE-linked contributions downstream of the suspected input?
7. Can this contribution be used to estimate the significance of GE PCB inputs to the river as a whole?

PVA background (concise version)

Conceptual process:

- Using information about which **congeners tend to associate together,** PVA finds original compositions (**assuming** that mixing within river is incomplete and original associations among congeners are preserved as spatial and temporal gradients)

Inputs:

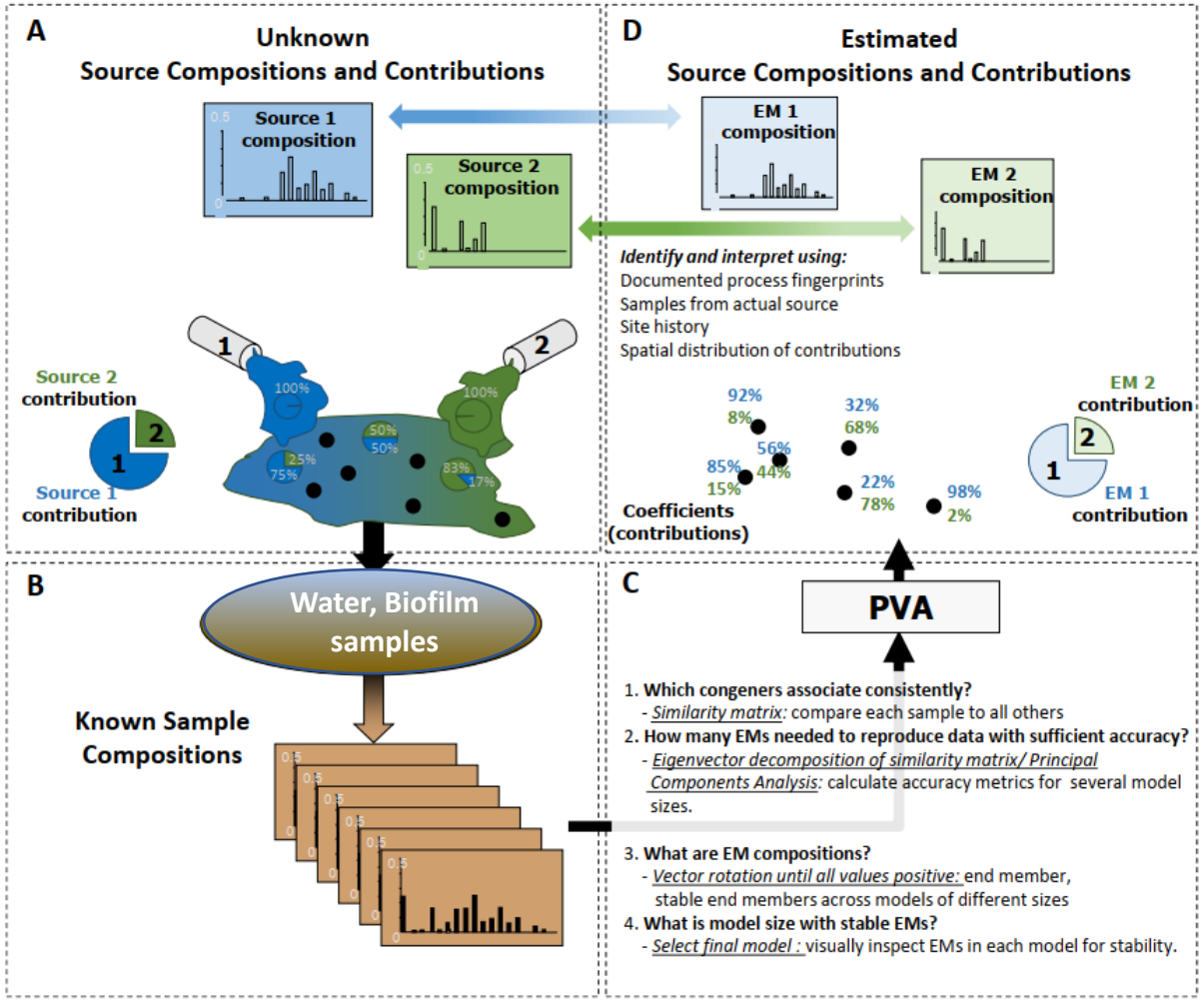
- **NDs and censoring** can skew results towards artifact compositions so the input data are filtered
- Used 128 congeners without censoring, (it generated a large proportion of zeros in the dataset eliminating information.)
- The input **data is normalized** so concentrations do not affect the results.

Mathematical process:

- **PVA starts with PCA and** rotates the principal component axes until all compositions and their contributions are positive. This makes compositions interpretable physically.
- The EMs are compared to knows Aroclor compositions and information about alteration processes.

Intpretation of results:

- Loadings are interpreted spatially and temporally



EMs

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	Model Size >>	**3 EMs**	**4 EMs**	**5 EMs**	**6 EMs**	**7 EMs**	**8 EMs**	**9 EMs**	**10 EMs**	**11 EMs**	**12 EMs**	**13 EMs**
EMs Identified in 10-EM Model >>	GE A1260 altered (EM10)								19%			
	IEP A1242/1016								15%			
	Kaiser A1248								15%			
	A1260 Dechl Backgr								16%			
	A1254 Dechl Bckgr								12%			
	PCB11mix SCRWRF								8%			
	PCB11 mix 1 @ SR8a/9								5%			
	PCB11 mix 2 @ SR8a/9								5%			
	A1260 at SR8a/9								5%			
	Dechlorination end-point								2%			

Grey shading indicates that EMs have stable composition

Percentages indicate how much of the data variability is explained by each EM

10 EMs

(EMs have stable composition for model size 10)

- 4 Aroclors across 6 EMs: 1242, 1248, 1254, 1260 (as point sources and background)
- 3 PCB11 mixes (as point sources)
- Dechlorination prevalent
- Chromatographic shifting of composition in GE gw with approach to river: less heavy congeners and more light congeners.
- GE EM could also reasonably be a mix of A1260 and 1254.

EMs

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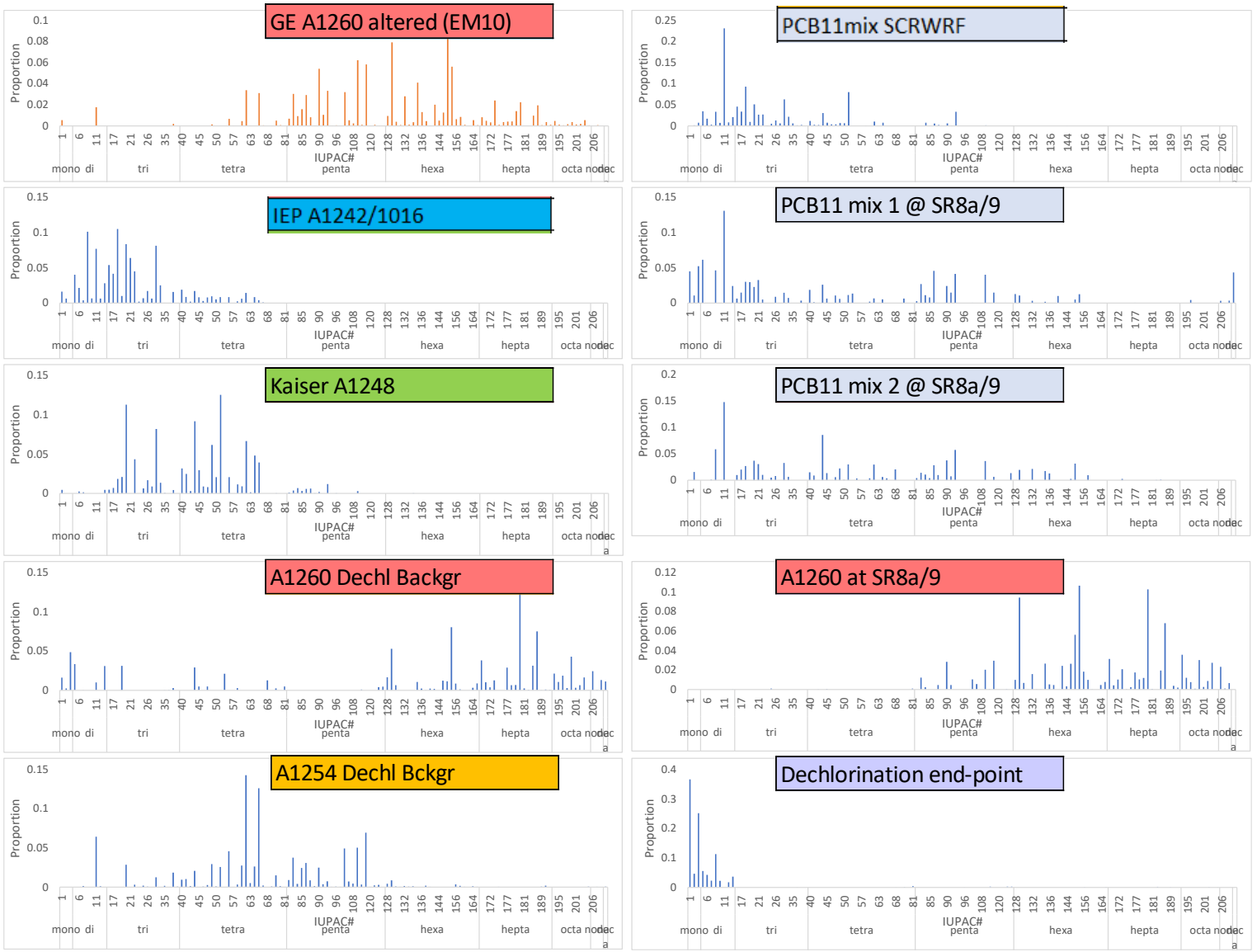


EMs: what composition can we expect the GE PCBs (A1260) to have upon seepage into river?

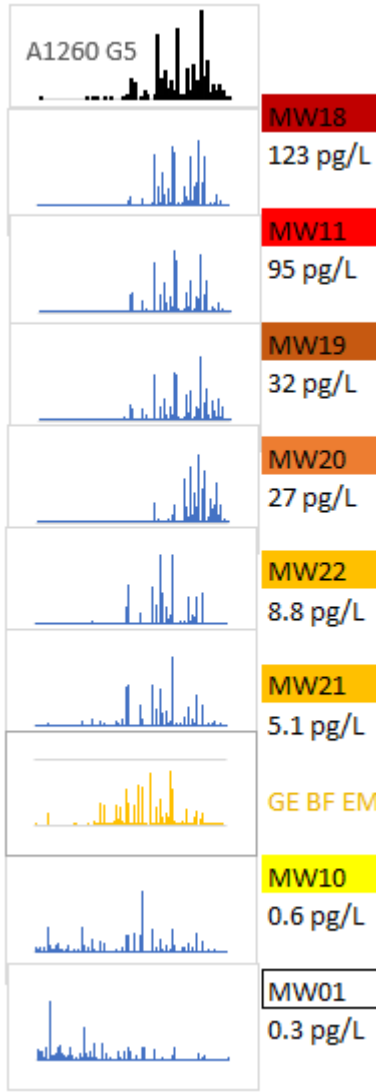
4. **Can some of these end members be linked** uniquely **to groundwater inputs, to the original groundwater composition at the GE source,**
   - or to the mass-balance changes by congener?

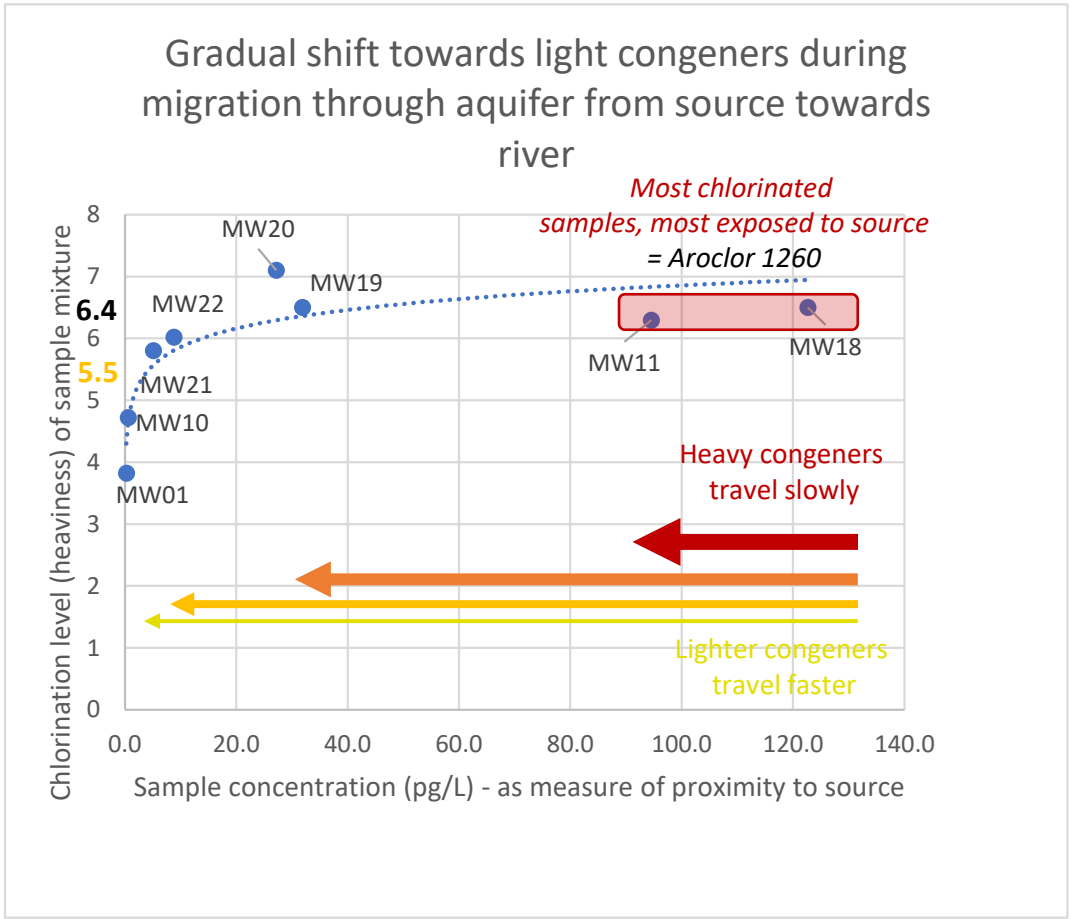
<u>Effect of migration through aquifer matrix</u>:

- may allow for light congeners to volatilize: enrichment with heavy congeners, especially in vadose zone.
- Enrichment of light congeners with distance due to less retardation and faster movement.
- Both effects are observed, but in most cases, light congeners are enriched

<u>GE EM</u>:

- Chlorination level = 5.5, halfway between MW10 and MW21
- GE EM is similar to MW21 and to a 6:4 mixture of M21 and M10.



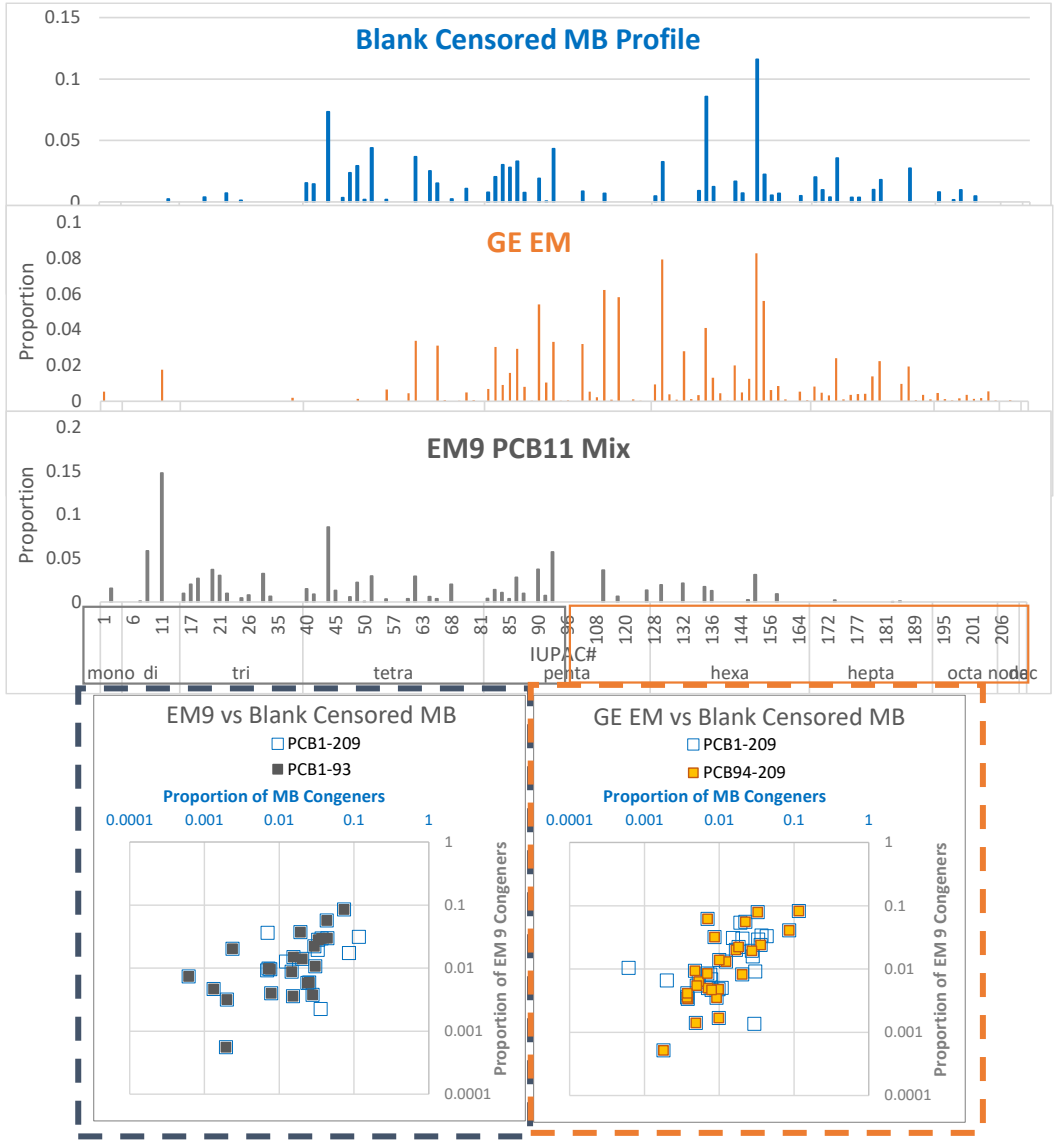


EMs: Mass-balance compositions vs. GE EM

4. **Can some of these end members be linked** uniquely to groundwater inputs, to the original groundwater composition at the GE source,
   - or **to the mass-balance changes by congener?**

Uncensored Mass Balance Composition

- Similar to EM9, PCB11 mix, up to PCB93 where both profiles have positive values
- Similarity with GE EM between PCB94 and PCB209 where both profiles have positive values



EMs: Mass-balance compositions vs. GE EM

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Uncensored Mass Balance Composition

- Similar to EM9, PCB11 mix, up to PCB93
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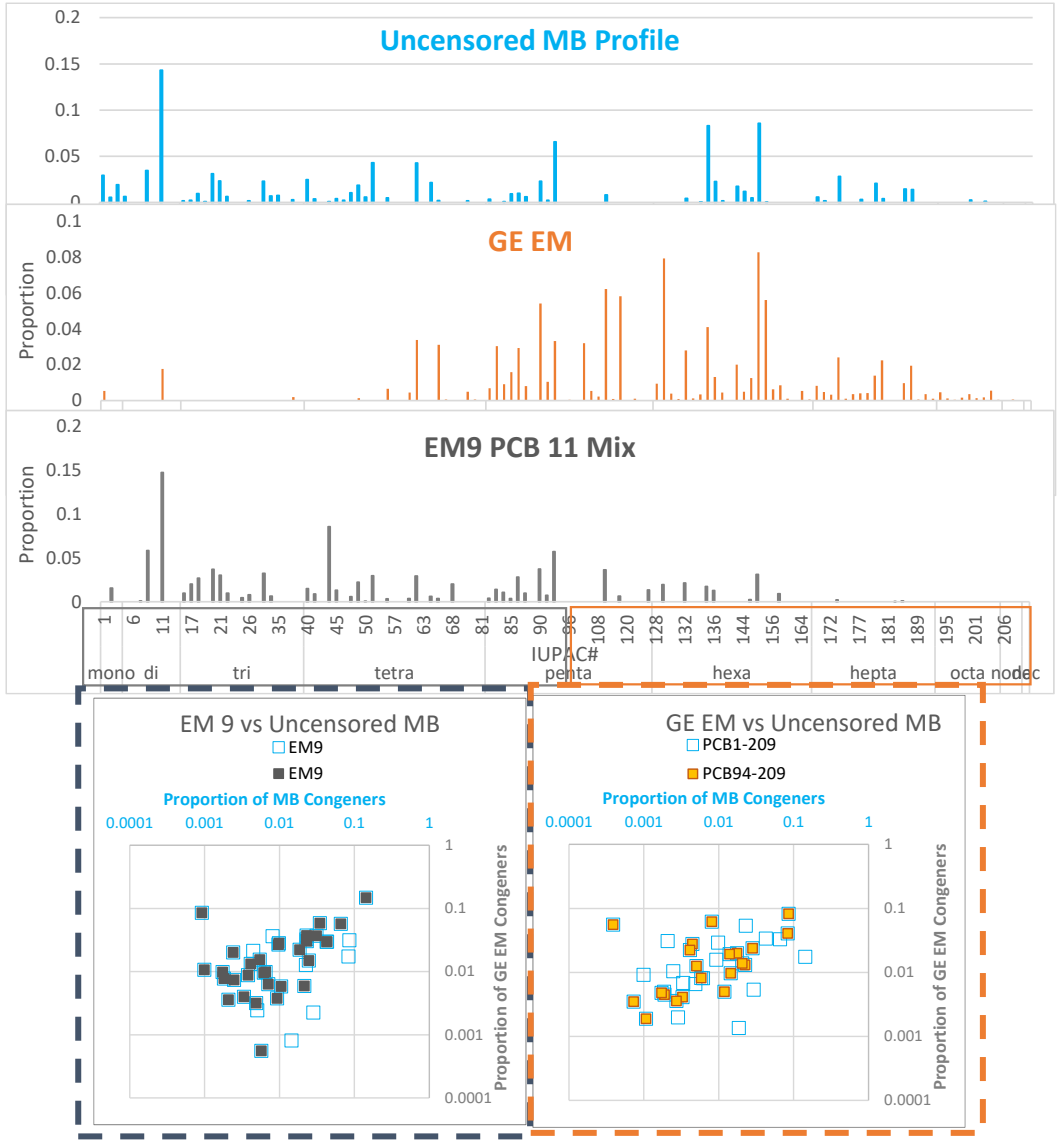
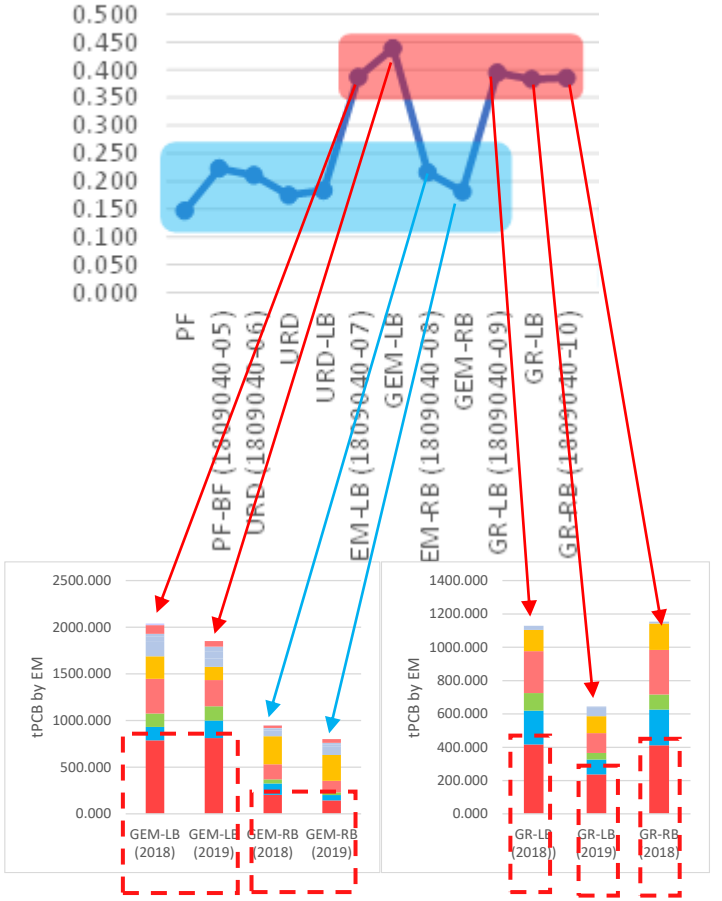
- Yes: the mass balance composition contains inputs from GE groundwater as well as an additional source of PCB11 and other lighter congeners.
- PVA can help separate these two sources



Loading contribution to GE biofilm

5. What is the magnitude of the contribution of the GE-linked end members in the biofilm samples?
   - Up to 40% contributed by EM on left bank
   - Double the contribution at upstream baseline and in samples on right bank.



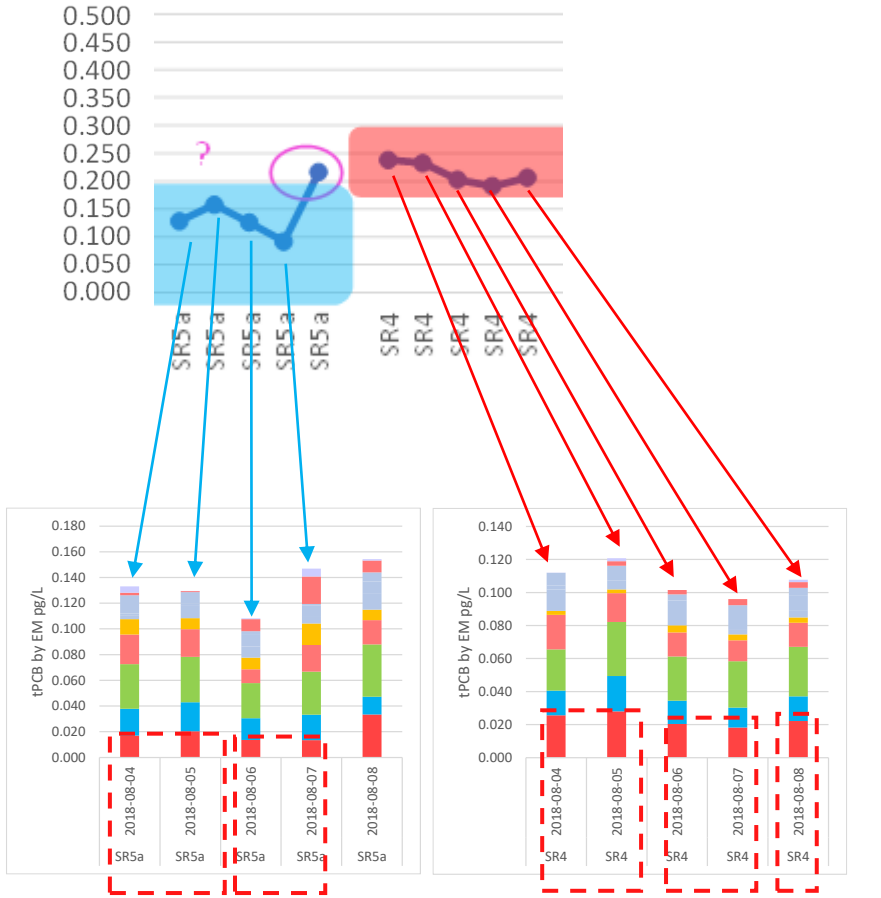
40% of total PCBs in GE LB samples

20% of total PCBs in RB samples

36-37% of total PCBs in downstream samples

Loading contribution to water column at Greene St. (and downstream)?

6. What is the trend of the GE-linked contributions downstream of the suspected input?
   - GE's impact is discernible downstream in both BF and SW
7. Can this contribution be used to estimate the significance of GE PCB inputs to the river as a whole?
   - Can use PVA to identify GE-linked congeners to fine tune mass loading estimate from GE-impacted groundwater.



10-15% of total PCBs in upstream samples

20-25% of total PCBs in downstream samples

Summary

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1. **10** EMs: 4 Aroclors, 3 media (groundwater, surface water/background, atmospheric + blank cont.), alteration dechlorination, separation by molecular weight
2. Aroclor 1260, with and without alterations, Aroclor 1254 dechlorinated, Aroclor 1248, Aroclor 1242 or 1016, dechlorination and PCB11 mixes.
3.
4. Yes, groundwater input with separation by molecular weight is present in both GE LB biofilm samples and downstream water samples. The original input looks like Aroclor 1260.
5. GE EM explains 19% of overall sample variability (this percentage is dependent on the number of samples and whether certain locations are under or over represented) and 20-40% of sample concentrations in affected reaches. (This percentage is more robust, as it is specific to samples)
6. At GE groundwater reach, GE EM contribution increases in BF, and downstream water samples are enriched in the GE EM relative to upstream
7. PVA results can tease apart the congeners most likely associated with GE impacted groundwater, and mass-balance calculations can better account for PCB loading by GE alone into the river.

Extra material

Comparison to Lisa Rodenburg Results

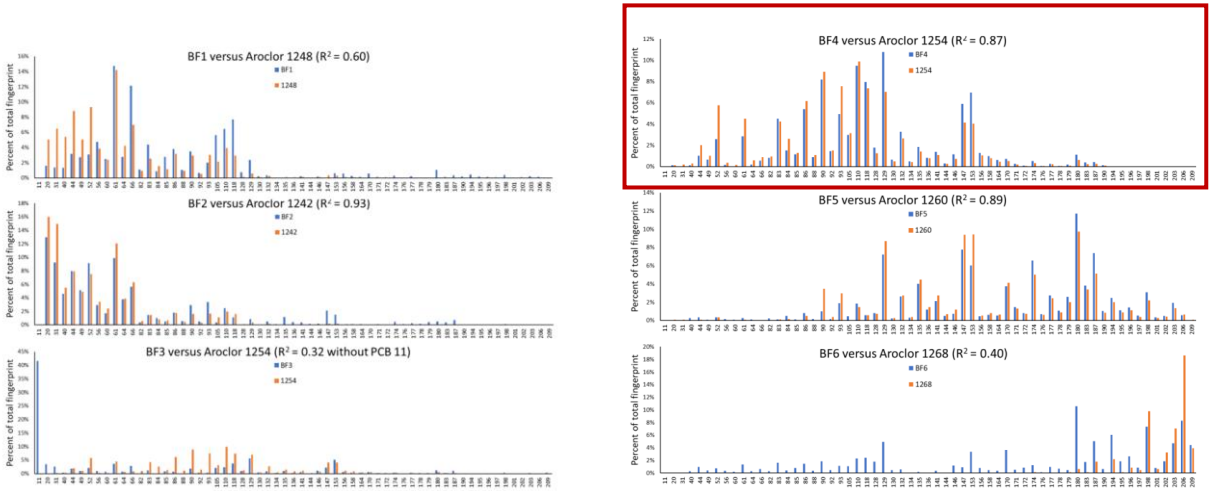

Figure 5. Fingerprints of the six factors resolved from PMF analysis of the biofilm/SPMD data set.

- *GE BF samples are enriched in A1254 EM. I interpret this as Aroclor 1260 that has shifted to a more 1254-like lighter composition during migration to river seepage zone. Similar enrichment on LB of Green Rd BF sample, relative to RB.*

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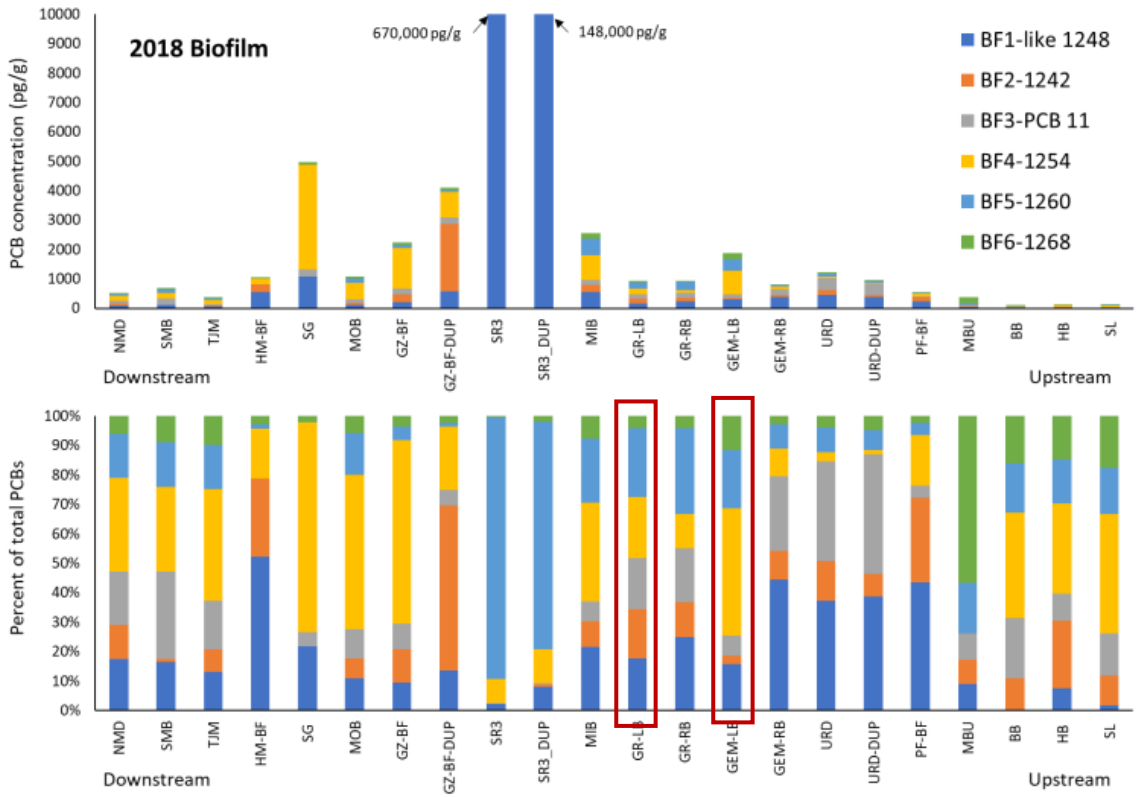

Figure 6. Abundance of the six biofilm PMF factors in biofilm samples collected in 2018.

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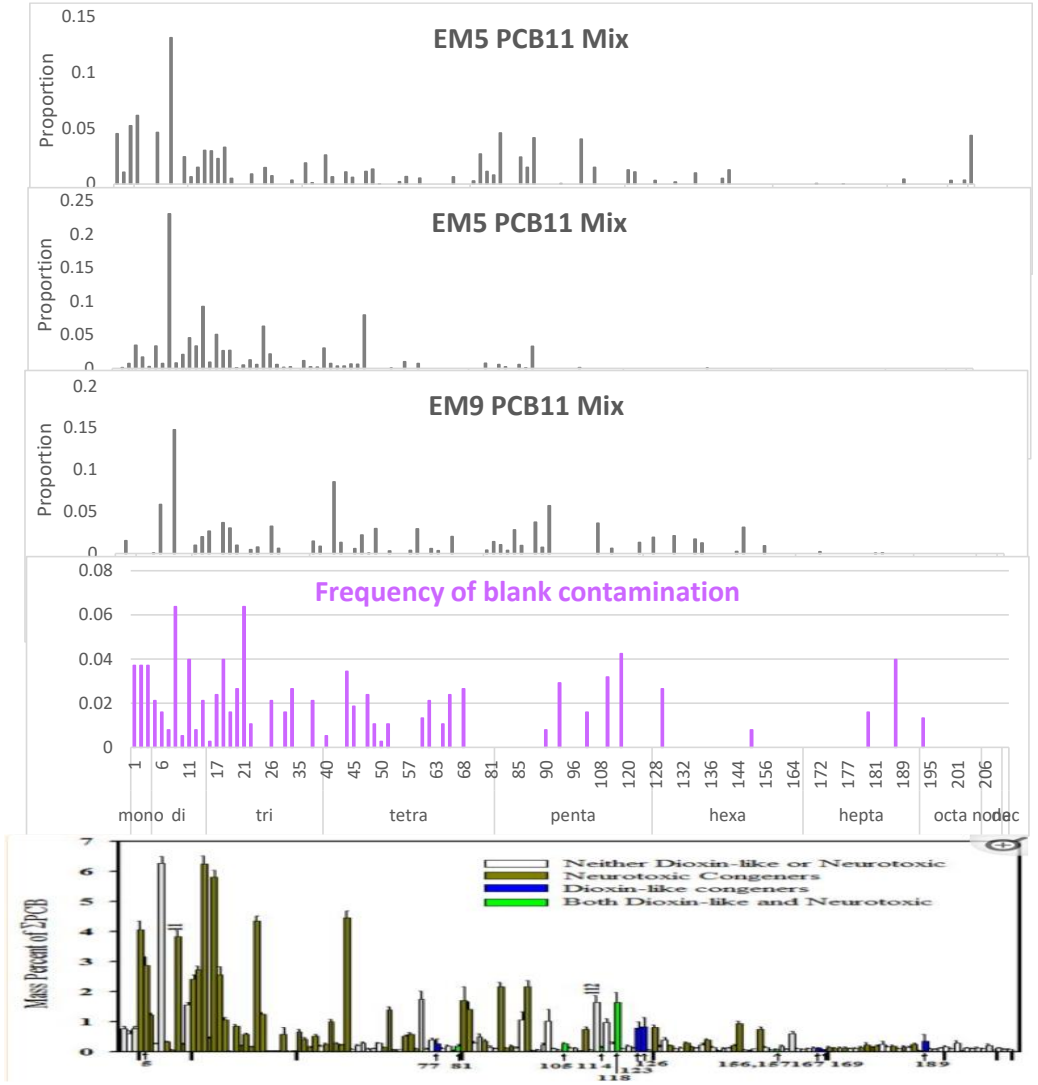
\\LTIaaFile01.limno.com\surface\SRRTTF10\DataSynthesisWorkshop\Presentations\Rodenburg_suggestions.pptx

EMs: Mass-balance compositions vs. and blank contamination

- Three EMs have a pattern dominated by PCB mixed with other lighter congeners.
- The frequency of blank contamination is similar to these patterns
- Hu et al, 2010 measured atmospheric PCB congeners in Chicago air samples. This pattern resembles our PCB mix EMs to a great extent.
- It is likely that the blank contamination stems from airborne PCBs
- It is also likely that atmospheric PCBs contribute to groundwater and surface water.
- Which one of these EMs represents actual surface water or groundwater PCBs needs further study.
- Lisa Rodenburg also investigated blanks, however, her results are not directly comparable, as she decomposed the composition of the blank samples directly into multiple Aroclor components as well as PCB 11.
- 3x blank correction is probably too extreme for fingerprinting, however, subtracting 1xblank C from the sample C is likely a better approach. Lisa Rodenburg suggests a similar approach.



Hu, D., Lehmler, H. J., Martinez, A., Wang, K., & Hornbuckle, K. C. (2010). Atmospheric PCB congeners across Chicago. *Atmospheric environment*, *44*(12), 1550-1557.

Dr. Lisa Rodenburg’s presentation

PMF Assessment Summary
Dr. Lisa Rodenburg

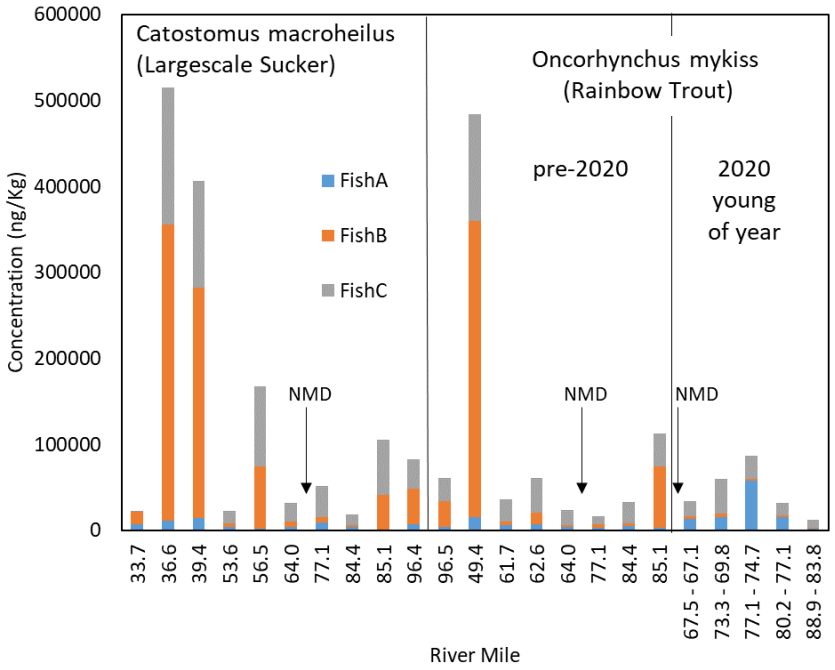
SRRTTF Data Synthesis Workshop

January 31, 2022

Summary

- Fish
  - PCB burden is shifting toward lower MW PCBs and likely declining over time
  - Non-Aroclor sources are negligible
- Biofilm
  - Lower concentration samples have very different relative abundance of factors from the high concentration samples.
  - 2018 spike resembles 1260; 2019 hits are primarily 1254
- Water column
  - 1242 is the most prominent component, non-Aroclor sources about 10%
  - Mass balance across Mission Reach inconclusive, but shows potential for load
  - Chlorination levels increase downstream of the Mission Reach, presumably reflecting inputs

PMF: Fish

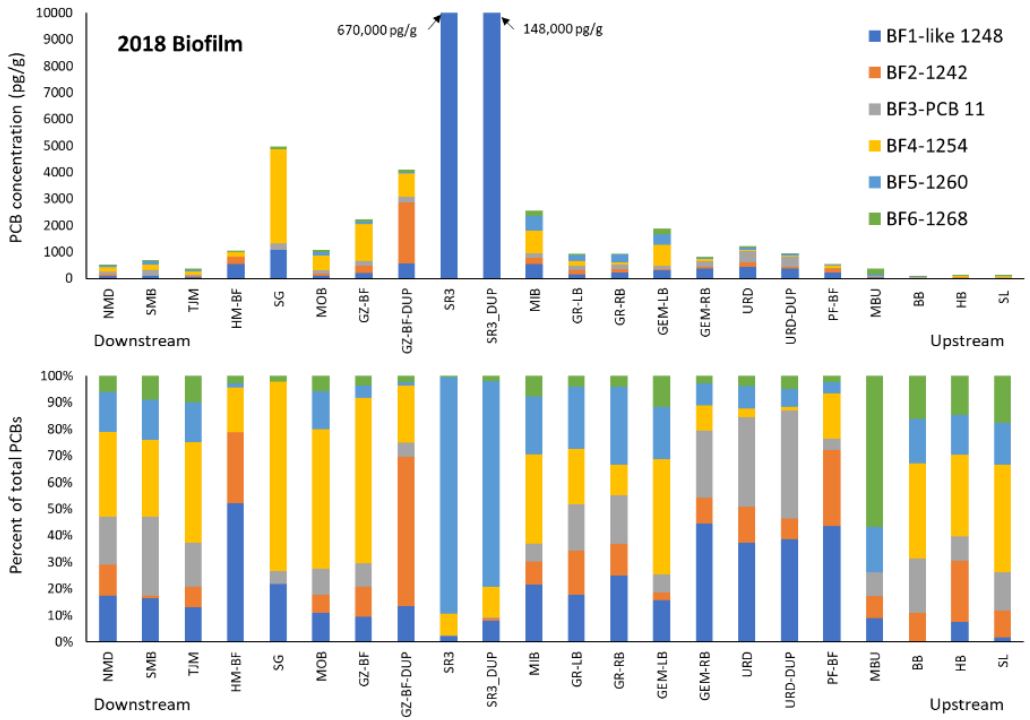


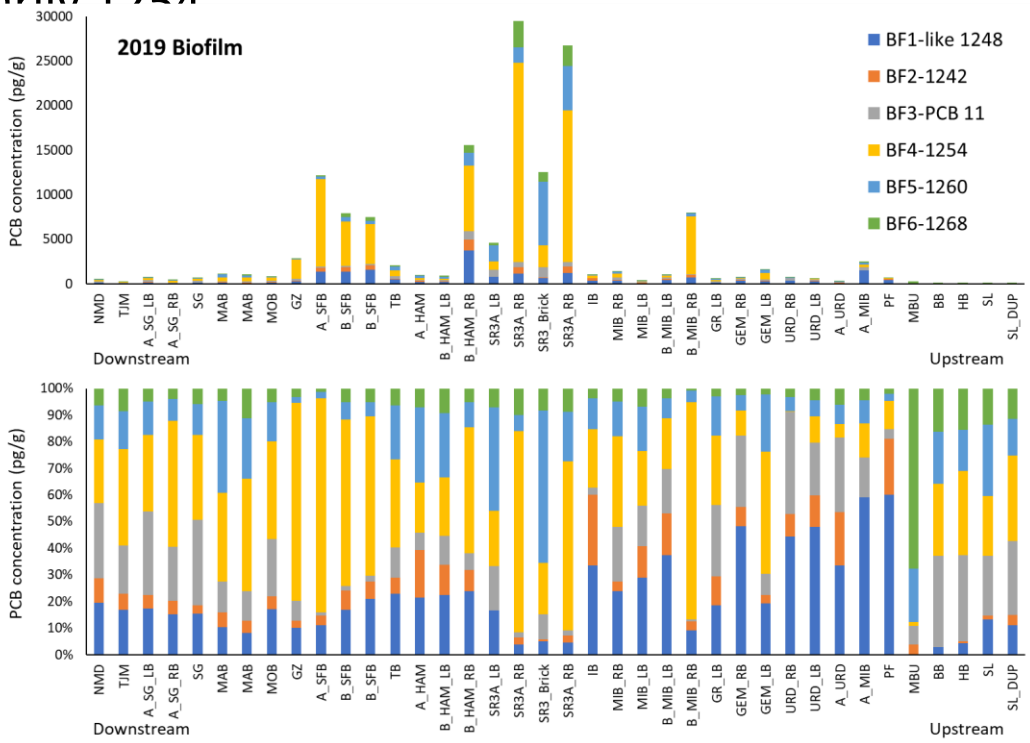
Can we crop to study area, and show where Mission is?

PCB burden is shifting toward lower MW PCBs and generally declining over time

PMF: Biofilm

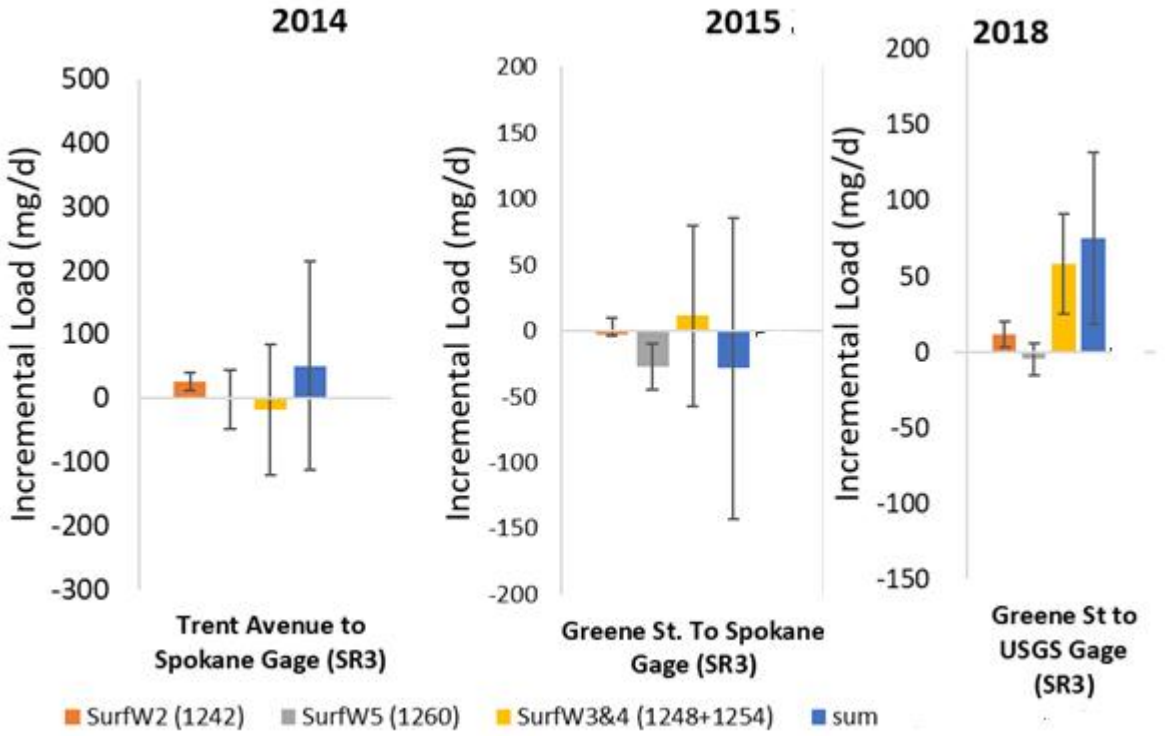
- Lower concentration biofilm samples (less than 1,000 pg/g) have very different relative abundance of factors from the high concentration biofilm samples.
  - 2018 spike resembles 1260; 2019 hits are primarily 1254





PMF: Water Column

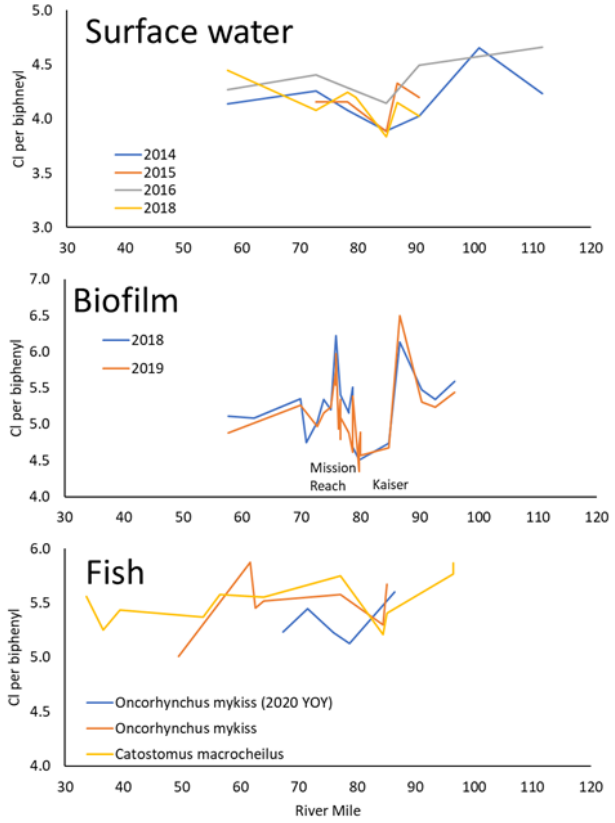
- Mass balance across Mission Reach suggests apparent loading of (1254+1248) in 2018, inconclusive in 2014 and 2015



Suggest extracting out just the Mission Reach mass balance results, as in the example here

PMF: Water Column

- Chlorination levels increase around RM 75, presumably reflecting i on Reach hotspot



Helpful to truncate spatial scale to Study area, highlight Mission Reach