What can fingerprinting tell us about PCB sources in the Spokane River?

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PCB fingerprinting made possible by:

- Measuring most or all congeners
  - EPA method 1668 (all 209 congeners)
    OR
  - Analysis of a long list of congeners by ECD or other methods
    BUT
  - Virtually impossible to combine data from different methods

- Sophisticated source apportionment tools such as:
  - Polytopic Vector Analysis (PVA)
  - Positive Matrix Factorization (PMF)♥

But also by:

- Good data management!
  - Much more than just an Excel spreadsheet
  - All data is transmitted and maintained (inc. metadata, blanks, etc.)
  - Use an EDD (electronic data delivery) format
- Metadata!
  - Detection limits and surrogate recoveries
- Public availability of data
  - And metadata! (Ex: STORET doesn't include surrogate recoveries)
  - Query is easy, output makes sense!
- Good project planning
  - Using the same method for all media
  - Measuring all analytes in all samples
  - Making sure all partners follow the same procedures (USACE, USFWS, state, federal agencies)

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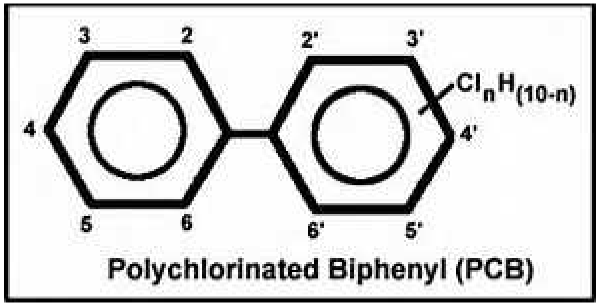
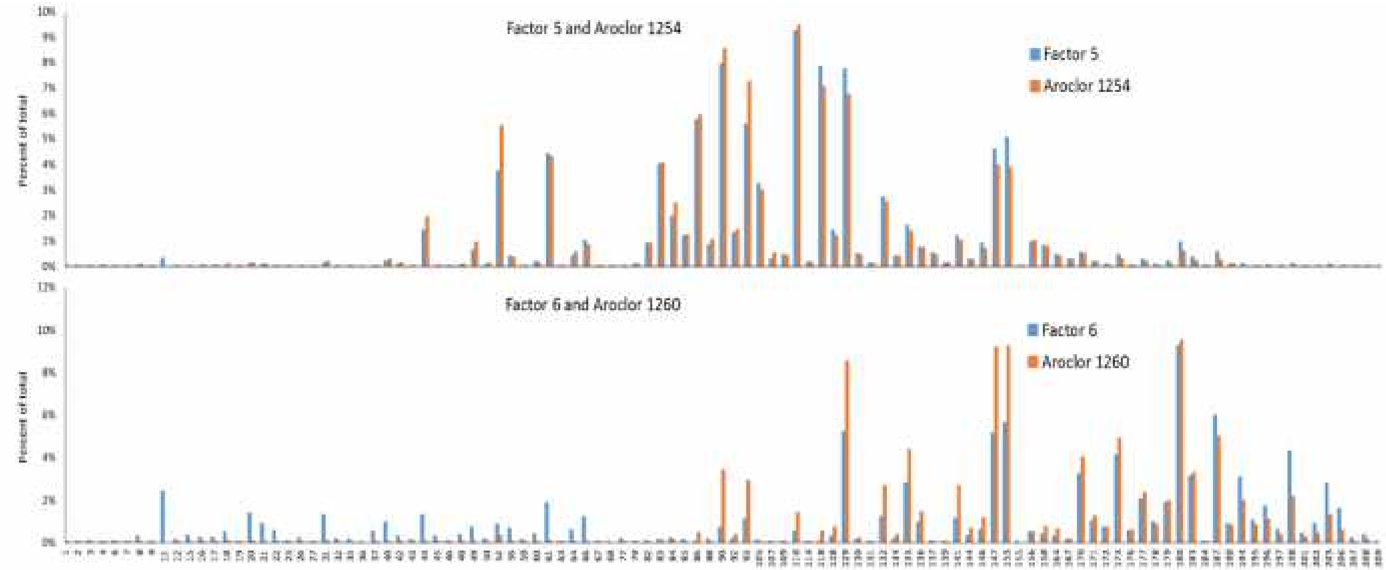
PCB source categories



- Non-Aroclor sources (esp. pigments)
- Dechlorination of Aroclors
- Aroclors



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Known inadvertent non-Aroclor PCB sources

- Organic pigments, especially diarylide yellow, contains primarily PCB 11, among others (like 12?, 13?, 35, 77, 52 etc)

- Titanium dioxide (white pigment) may contain PCBs 206, 208, and 209

- Silicone rubber tubing produces PCBs 68, 44 and 45, etc. (Perdih and Jan Chemosphere 1994)
  - Don't sample using silicone rubber tubing!

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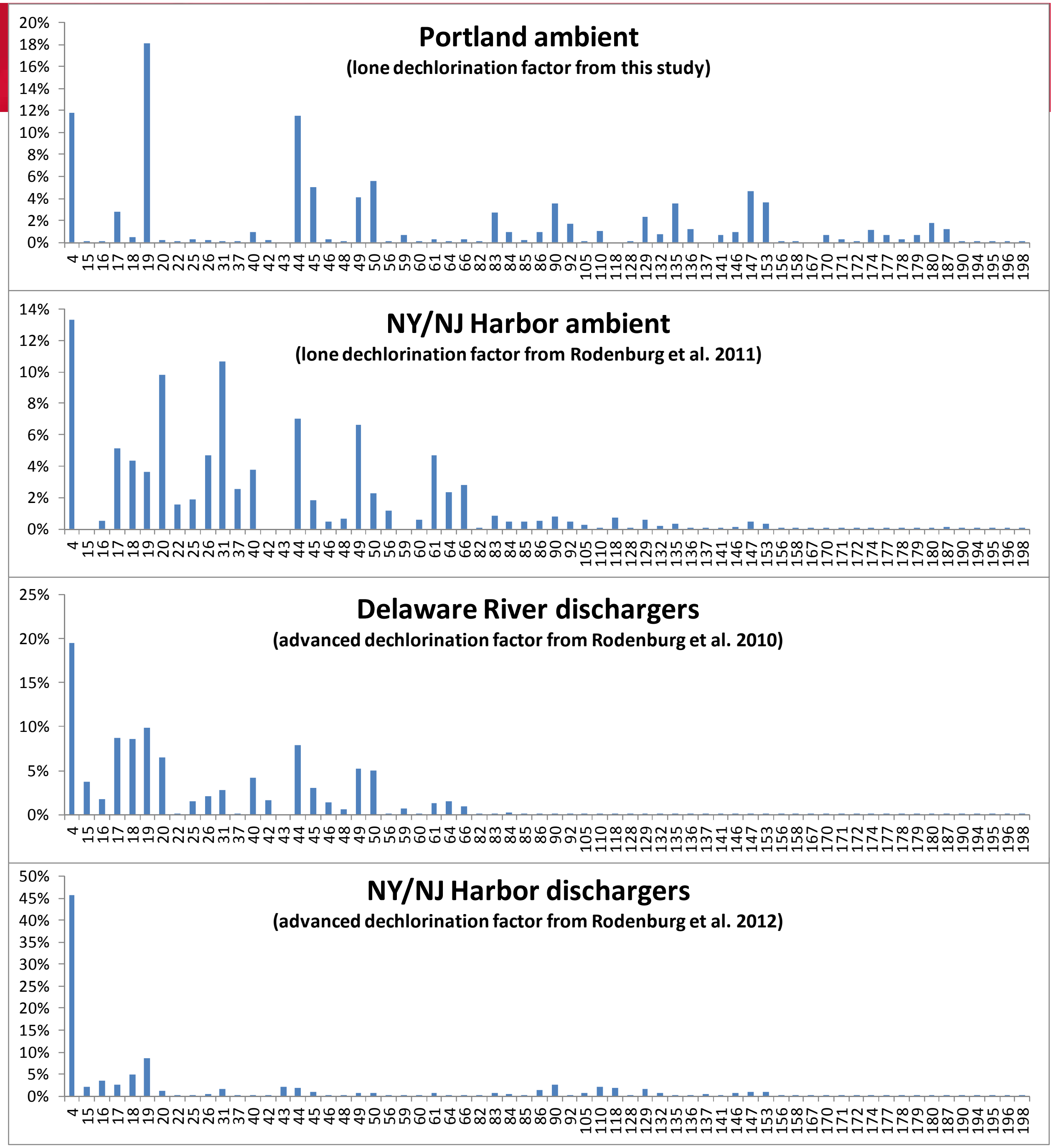
Comparison of dechlorination patterns



Factor Analysis Equation

Applies to Principle Components Analysis, PMF, PVA etc.

Use this equation to predict concentrations, then minimize the sum of squared residuals between measured and predicted concentrations (E) until a stable solution is found.

You do NOT need any information about the sources, such as their fingerprints, or even how many there are!

$$X = G\,F + E$$

$$(m \times n) \quad (m \times p) \quad (p \times n)$$

X = input data matrix
G = matrix of conc of each factor in each sample generated by model
F = matrix of fingerprint of each factor (p) generated by model
E = leftover or residual
n = number of analytes
m = number of samples
p = number of factors (sources)

Note: in all forms of factor analysis, the user has to decide what is the ‘correct’ number of sources based on model output.

Advantages of Positive Matrix Factorization

over other models, for example Principle Components Analysis

- Positive correlations only – mass balance model
- Assign a point-by-point uncertainty estimate
- Missing and below detection limit values can be included by assigning them a high uncertainty
- “Robust” mode can be used so that outlier values will not skew the factor profiles
- PMF provides the quantitative contribution estimate from each factor for each sample.

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PMF input matrixes

- For all matrixes:
  - 209 congeners measured in ~160 peaks
  - Discard any peaks that are BDL in more than ~50% of samples
  - Usually use about 90 peaks
  - Iterative process. Remember the Rodenburg principle:

> "Smaller data sets often yield more factors"

- Concentration matrix:
  - Replace missing data with geometric mean
  - Replace BDL data with random number between 0 and LOD
- Uncertainty matrix:
  - RSD of surrogate recoveries for detected concentrations
  - 3X this uncertainty for BDL and missing data (x,3x)
- LOD matrix:
  - Use actual LOD for every data point where possible.
  - If LODs all similar, then you can use an average.

Metadata matters!
When LOD and unc matrix are not correct, the model blows up and the output is not useful.

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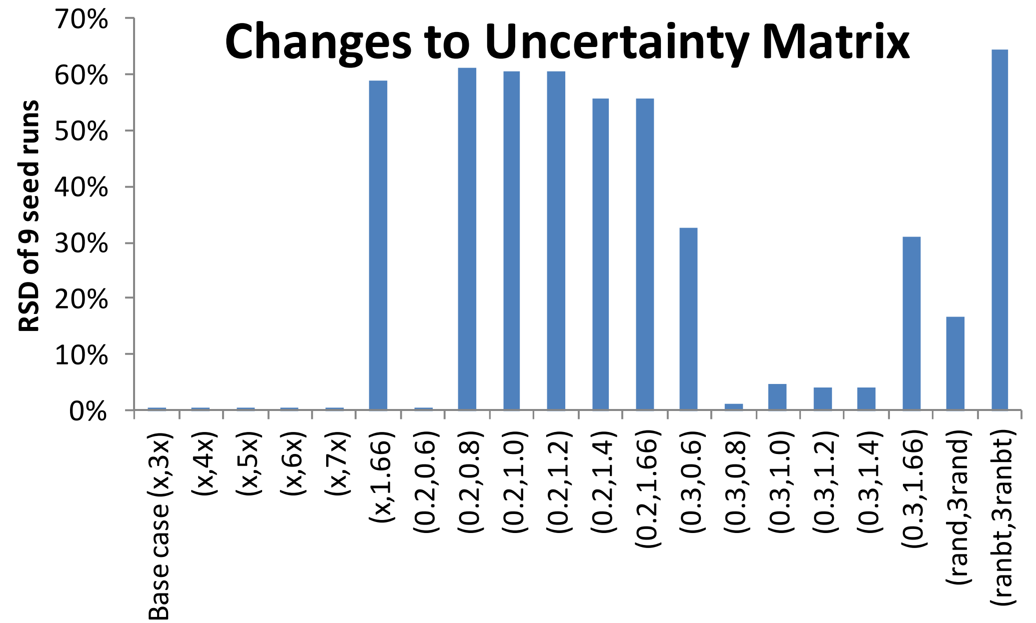
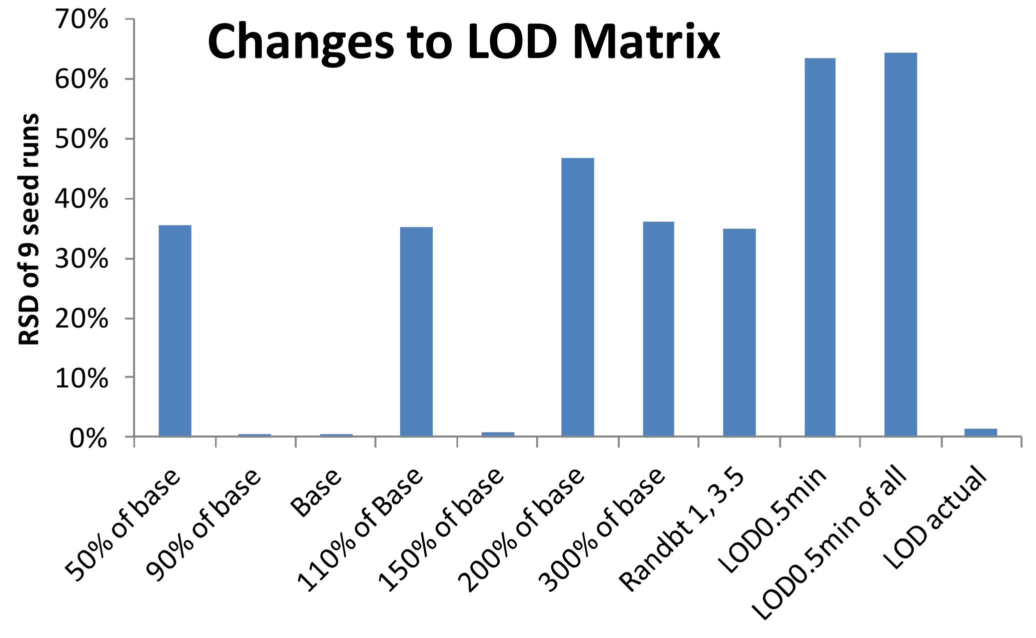
These matrixes matter!

- Changes to LOD and uncertainty matrices can make the output unstable
- In the worst case, if these matrices are not constructed correctly, the model output will be un-interpretable.





The “Suicide” Analogy

- Several different soft drinks to choose from
- Sometimes kids like to mix these…

- Say we have 100 kids who made mixed drinks from the same soda fountain

Data matrix

	Caramel color	sugar	aspartame	lemon-lime flavoring	cola flavoring	caffiene
Anna	0.50	0.62	0.41	0.58	0.99	0.87
Bruce	0.58	0.86	0.25	0.78	0.35	0.14
Carlos	0.65	0.06	0.68	0.75	0.50	0.06
Donna	0.33	1.00	0.98	0.39	0.63	0.92
Emily	0.38	0.10	0.40	0.14	0.11	0.06
Francis	0.67	0.60	0.44	0.60	0.50	0.10
George	0.07	0.23	0.65	0.37	0.82	0.54
Harriet	0.95	0.53	0.02	0.25	0.51	0.86
Inga	0.46	0.67	0.19	0.92	0.23	0.45
John	0.32	0.97	0.79	0.19	0.88	0.21
Karl	0.81	0.42	0.68	0.70	0.15	0.08
Lisa	0.22	0.62	0.47	0.94	0.52	0.75
Michael	0.00	0.95	0.98	0.19	0.45	0.88
Nick	0.49	0.46	0.25	0.02	0.97	0.02
Olga	0.36	0.49	0.55	0.62	0.94	0.07

& etc

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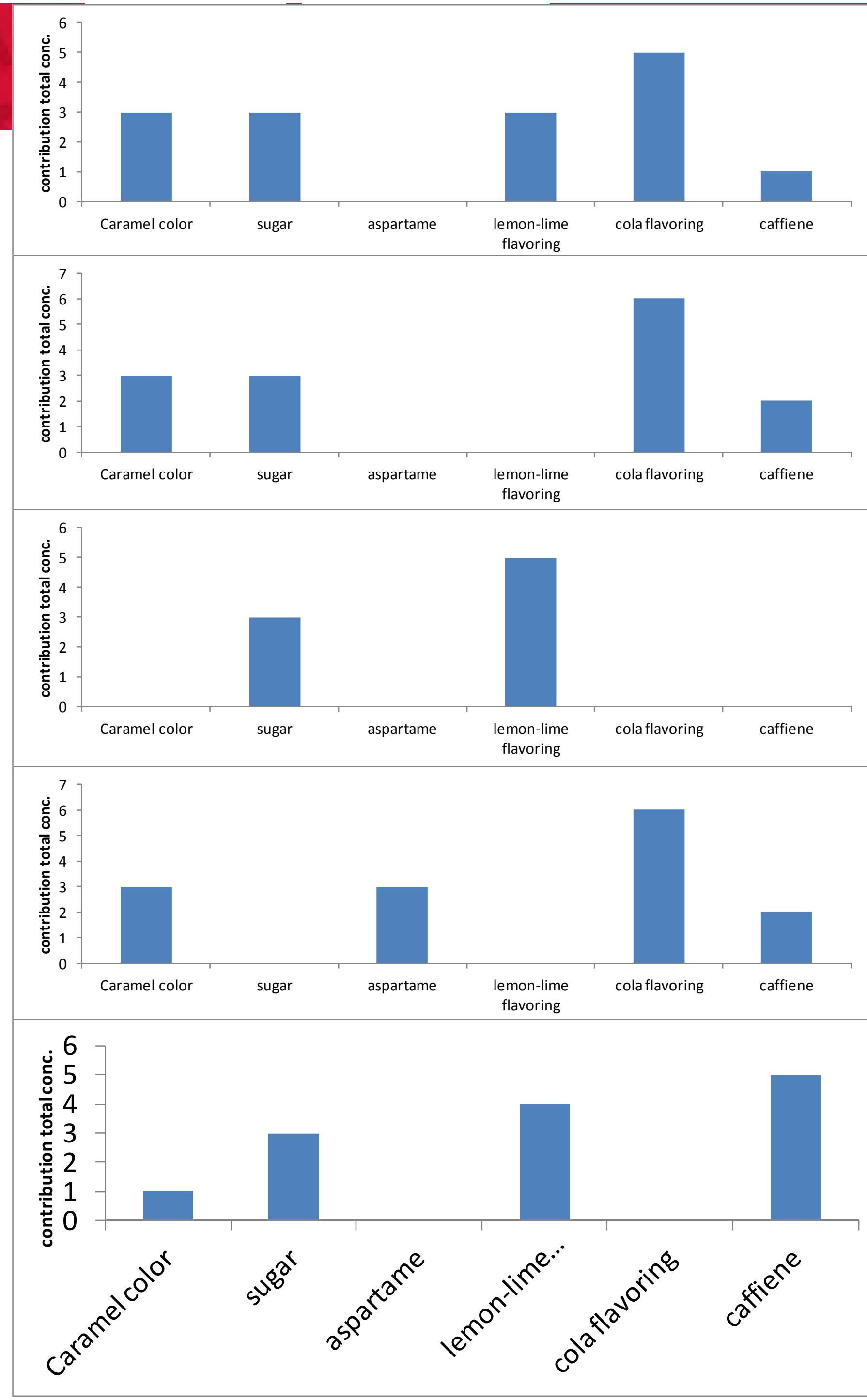
PMF results

PMF can tell you:

- How many sources (fingerprints, factors)
- Their fingerprints (F matrix)
- How abundant each fingerprint is in each sample (G matrix)

"F matrix"

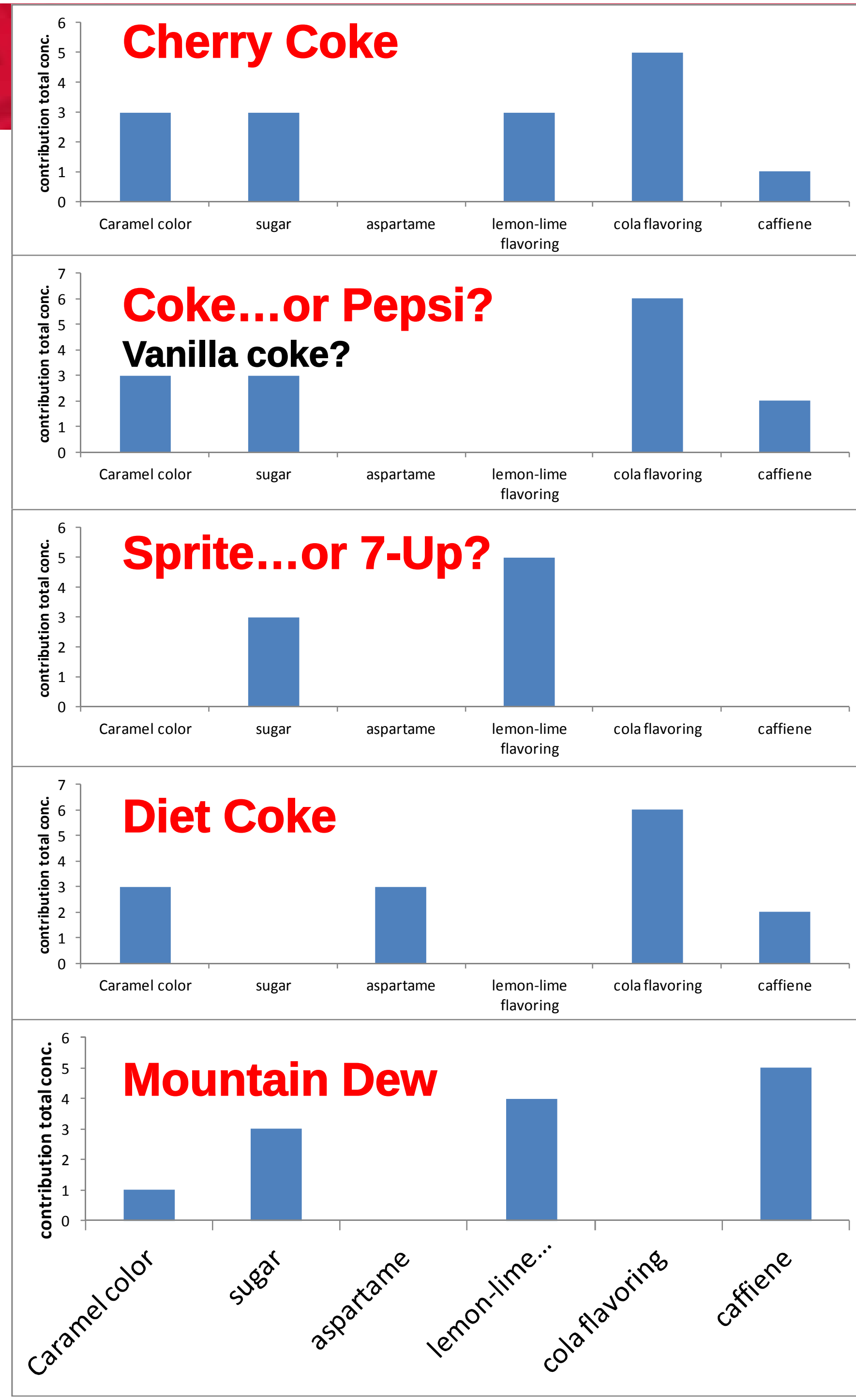


PMF results

PMF can't tell you:

- What it all means

- YOU have to interpret this information



PMF Results

- G matrix: abundance of each factor in each sample

- Helps with Q's like:
  - Older people prefer diet soda?
  - Women prefer non-caffeinated drinks?
  - More caffeine consumed later at night?

	Cherry Coke	Coke	Sprite	Diet Coke	Mt Dew
Anna	16%	20%	13%	19%	32%
Bruce	20%	30%	9%	28%	13%
Carlos	25%	2%	26%	29%	19%
Donna	10%	30%	29%	12%	19%
Emily	34%	9%	35%	12%	10%
Francis	24%	21%	16%	21%	18%
George	3%	11%	30%	17%	38%
Harriet	42%	23%	1%	11%	23%
Inga	19%	27%	8%	37%	9%
John	10%	31%	25%	6%	28%
Karl	29%	15%	25%	25%	5%
Lisa	8%	22%	17%	34%	19%
Michael	0%	37%	38%	7%	18%
Nick	22%	21%	11%	1%	44%
Olga	12%	16%	19%	21%	32%

Rows sum to 100%→

Need ancillary info, such as age, gender, time of day etc.

Case Study:

Portland Harbor Superfund Site

(Rodenburg et al. ES&T 2015)

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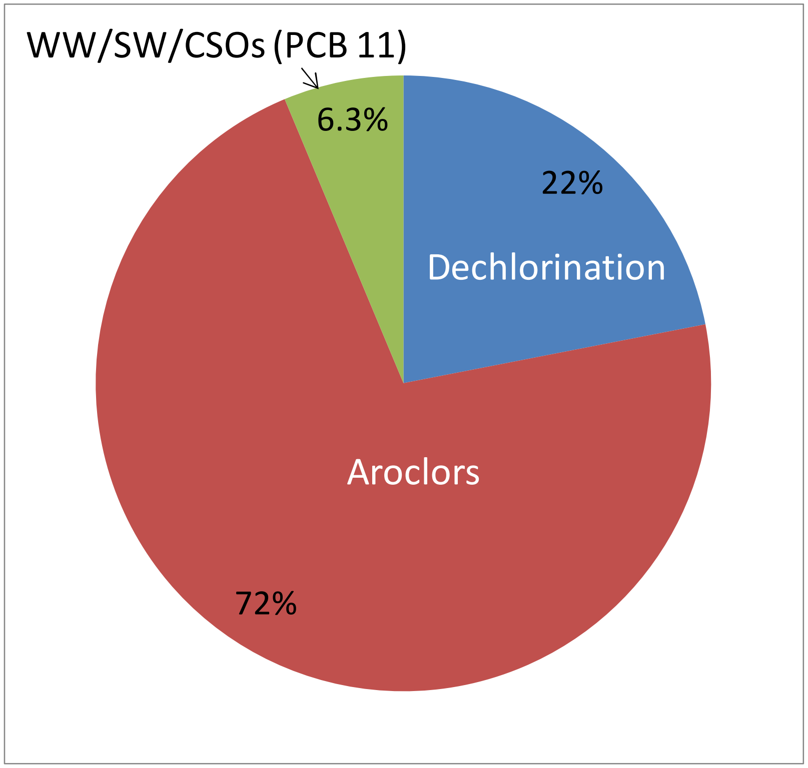
Portland Harbor – water column

- SPB-octyl column (I prefer!)
- Dissolved + particle phase summed
- 85 PCB peaks (congeners) in 120 samples

- Five source terms (factors) identified
  - Three resemble Aroclors
  - One factor is rich in PCB 11 probably wastewater/ stormwater/CSOs
  - One factor is dominated by PCBs 4 and 19 = dechlorination



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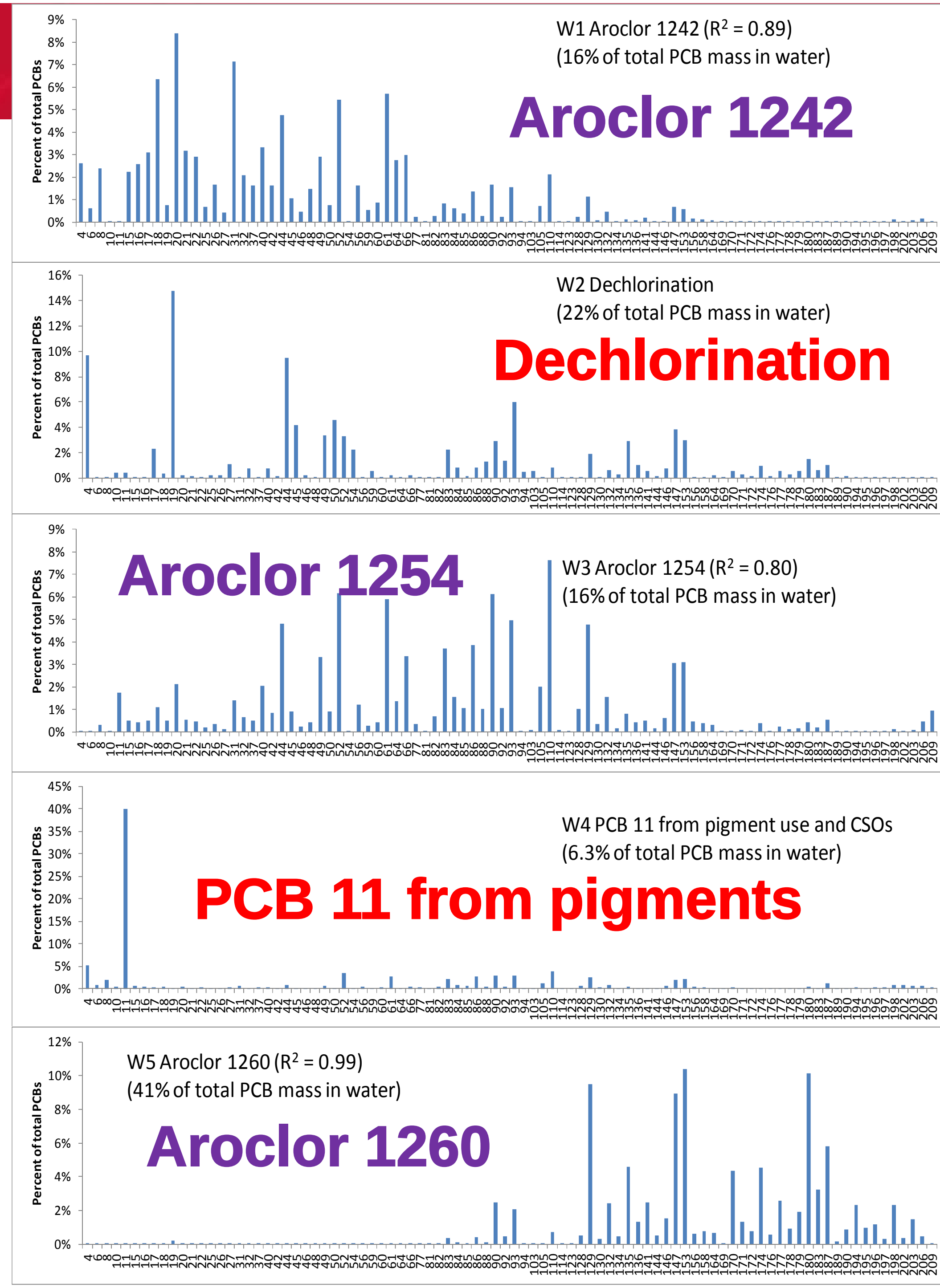
Water column factors - fingerprints

Note:
no Aroclor 1248 factor



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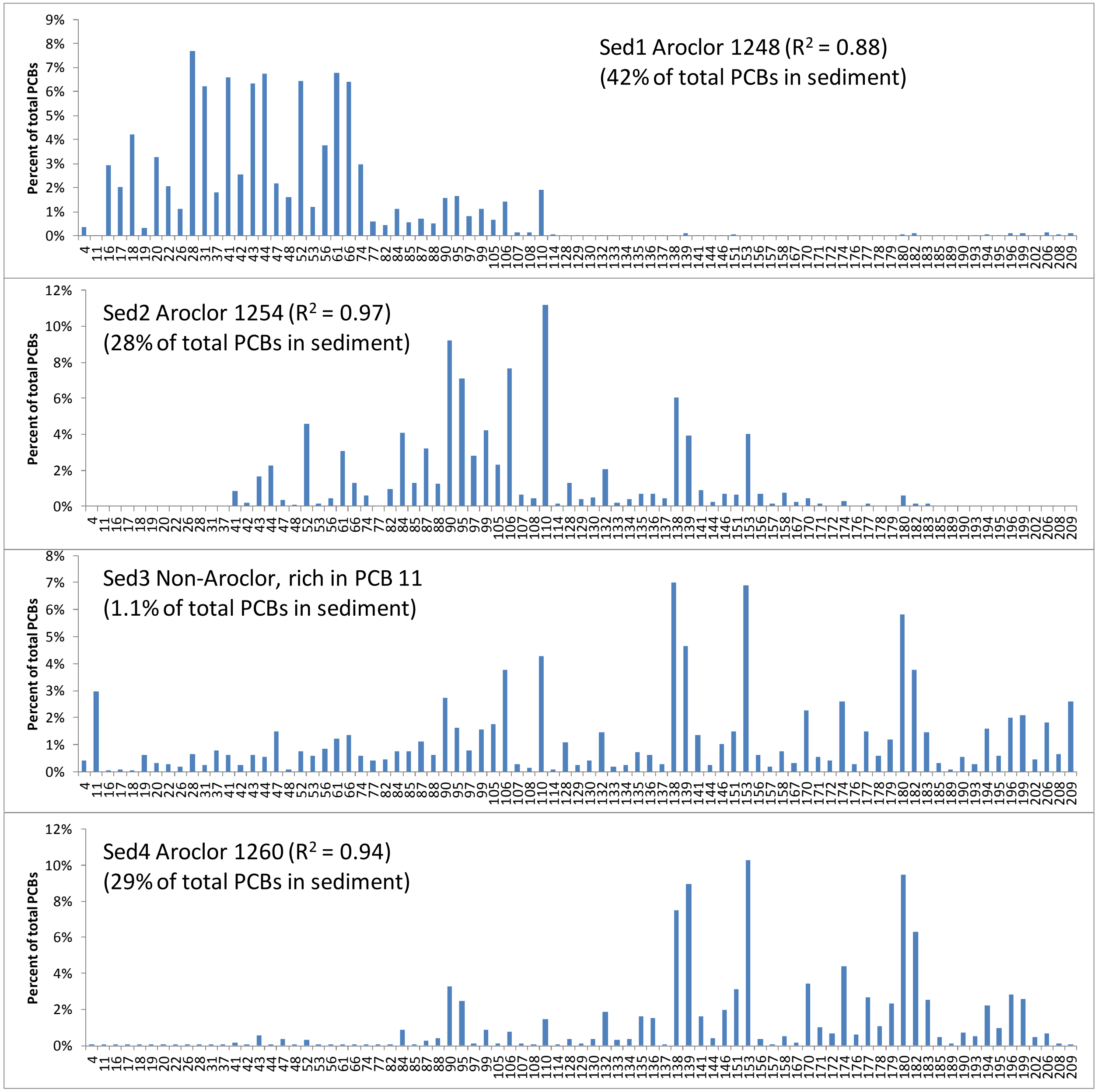
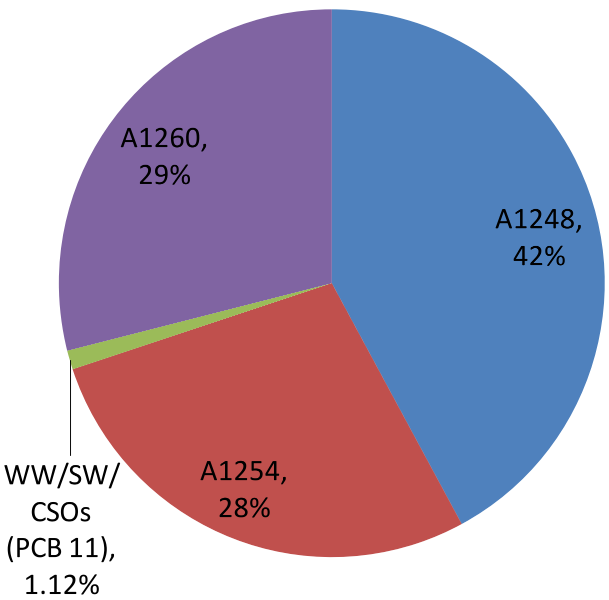
Portland Harbor sediment

Note: No Dechlorination





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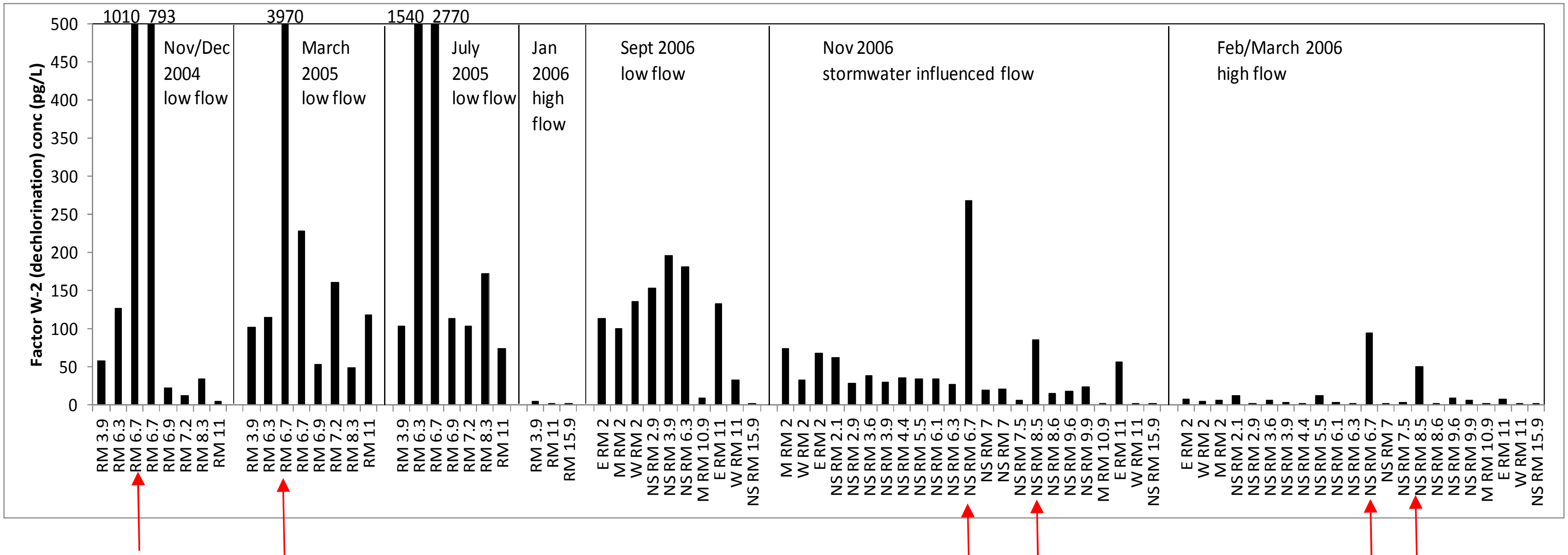
If dechlorination doesn't happen in the sediment, then where?



Surface water data suggests dechlorination hot spots at:

Willamette Cove (RM 6.7) and Swan Island Basin (RM 8.5)

Highest conc at low flow suggest groundwater inputs

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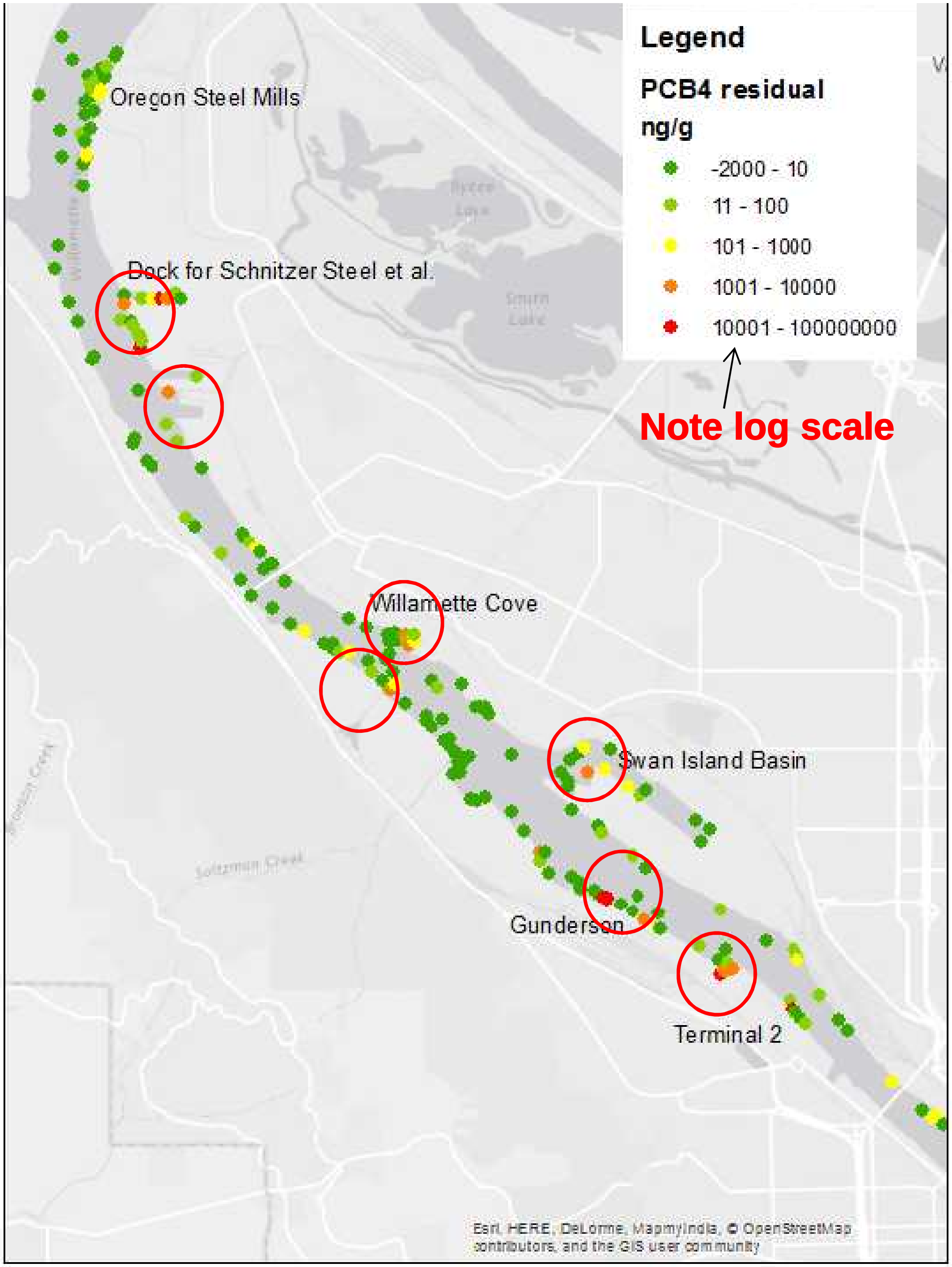
Groundwater inflows

Based on PCB 4 residual*, dechlorination products enter the river at several points along the river bank

* i.e. PCB 4+10 concentration in excess of that predicted by the model



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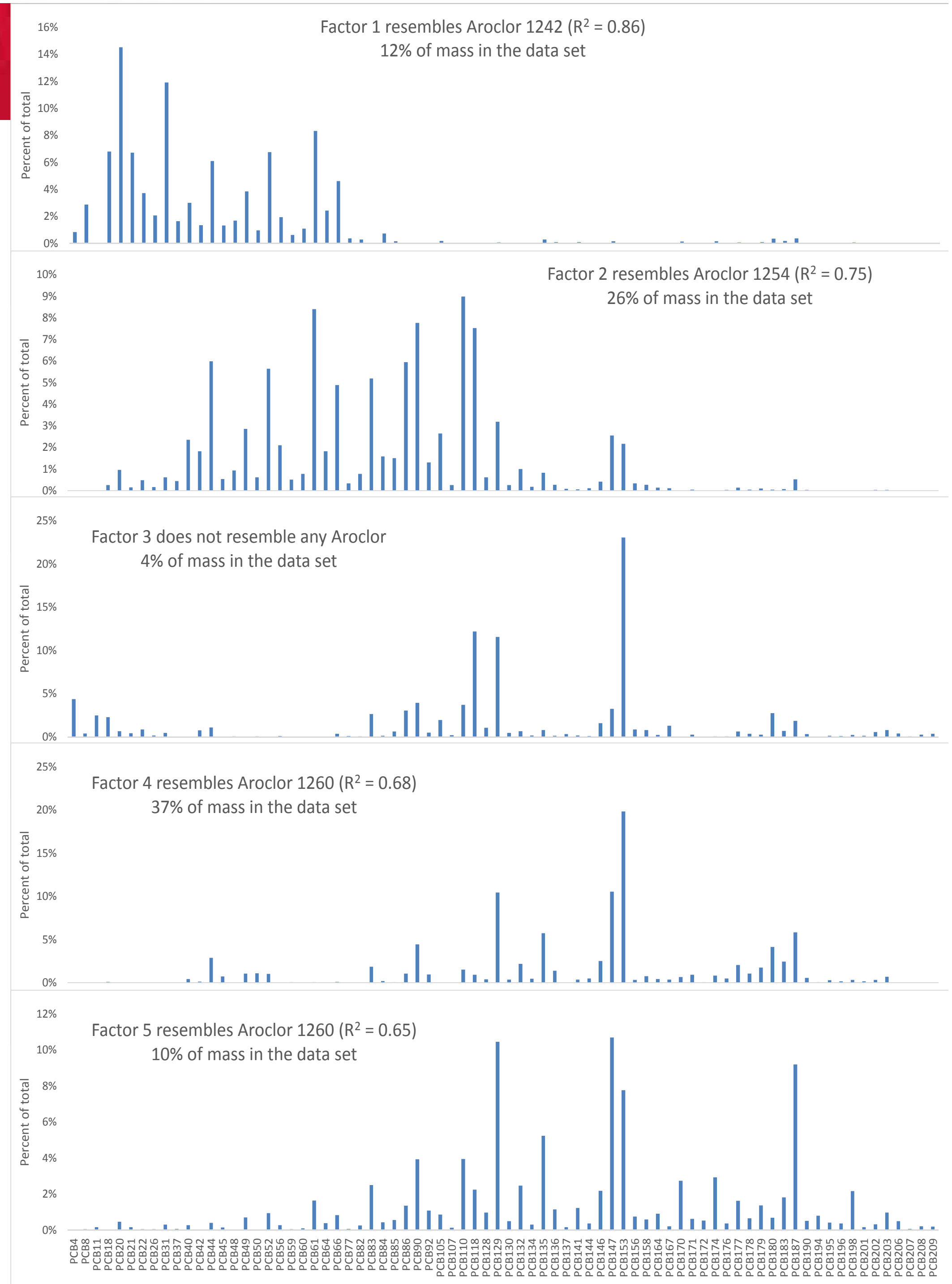
Portland Harbor benthic organisms

(in prep.)

- ADME changes congener patterns in biota

- absorption, distribution, metabolism, and excretion

- PCBs 153, 180 etc. are bioaccumulated



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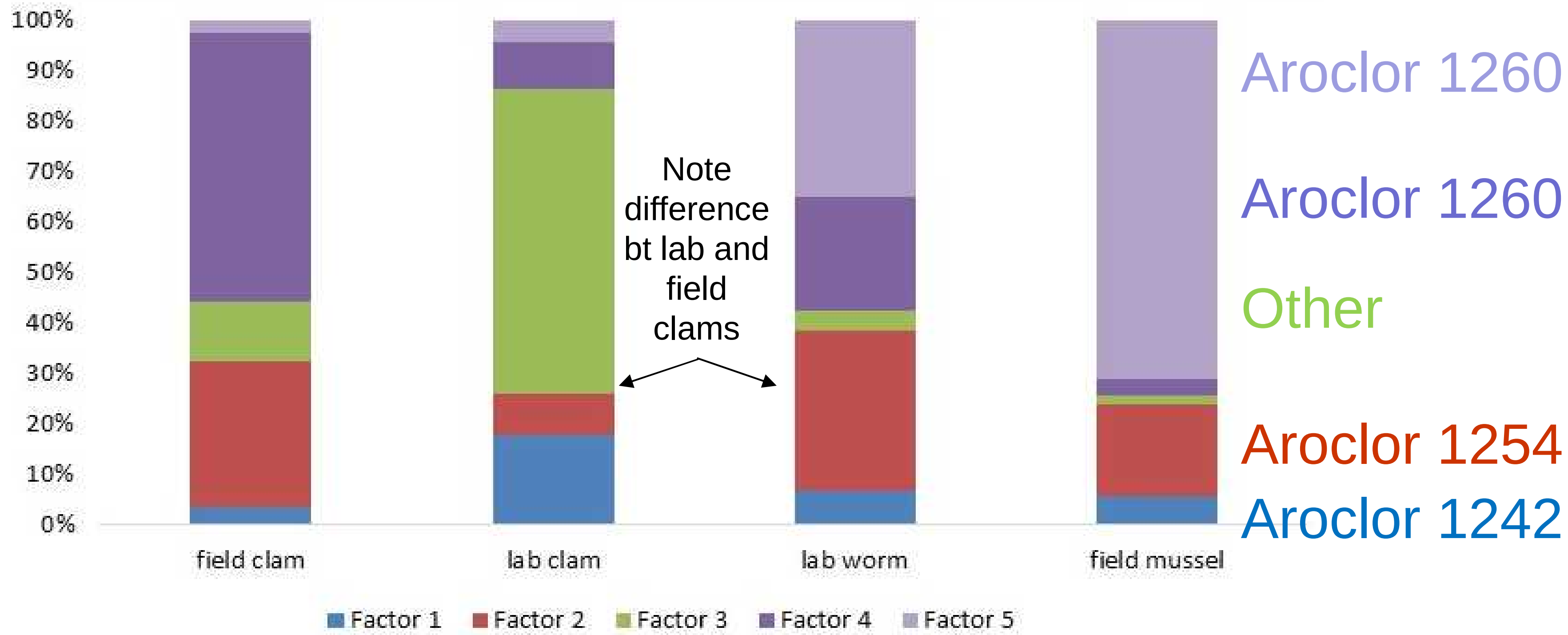
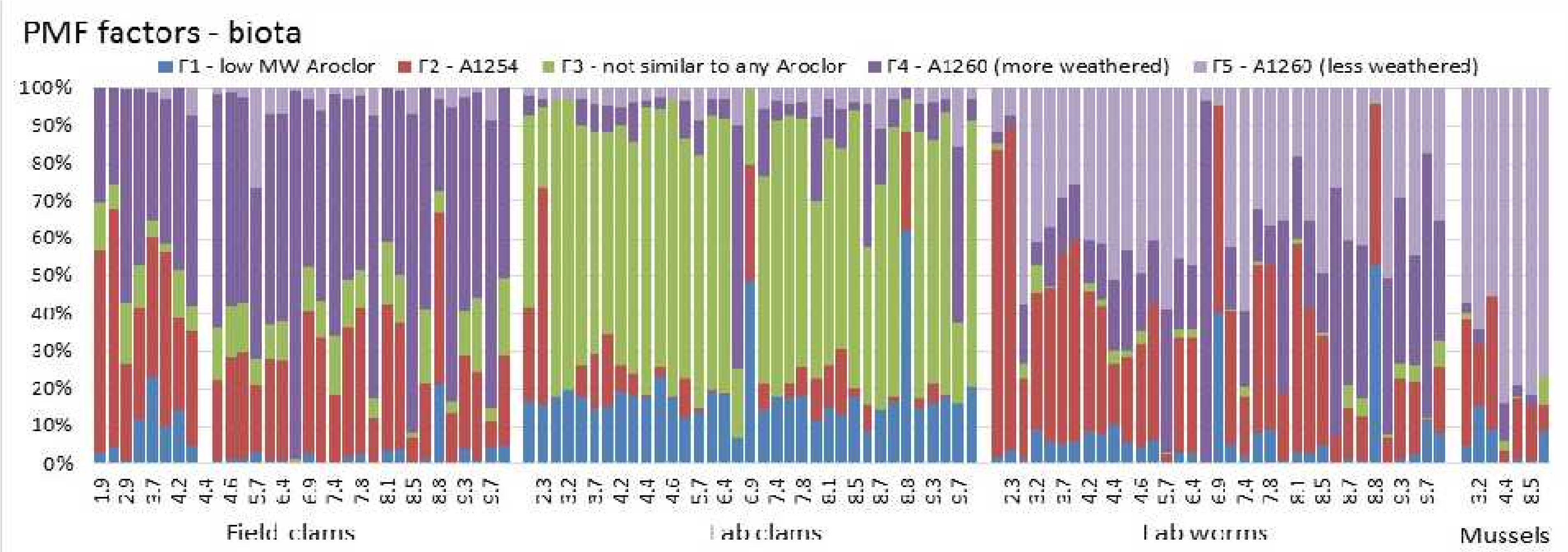
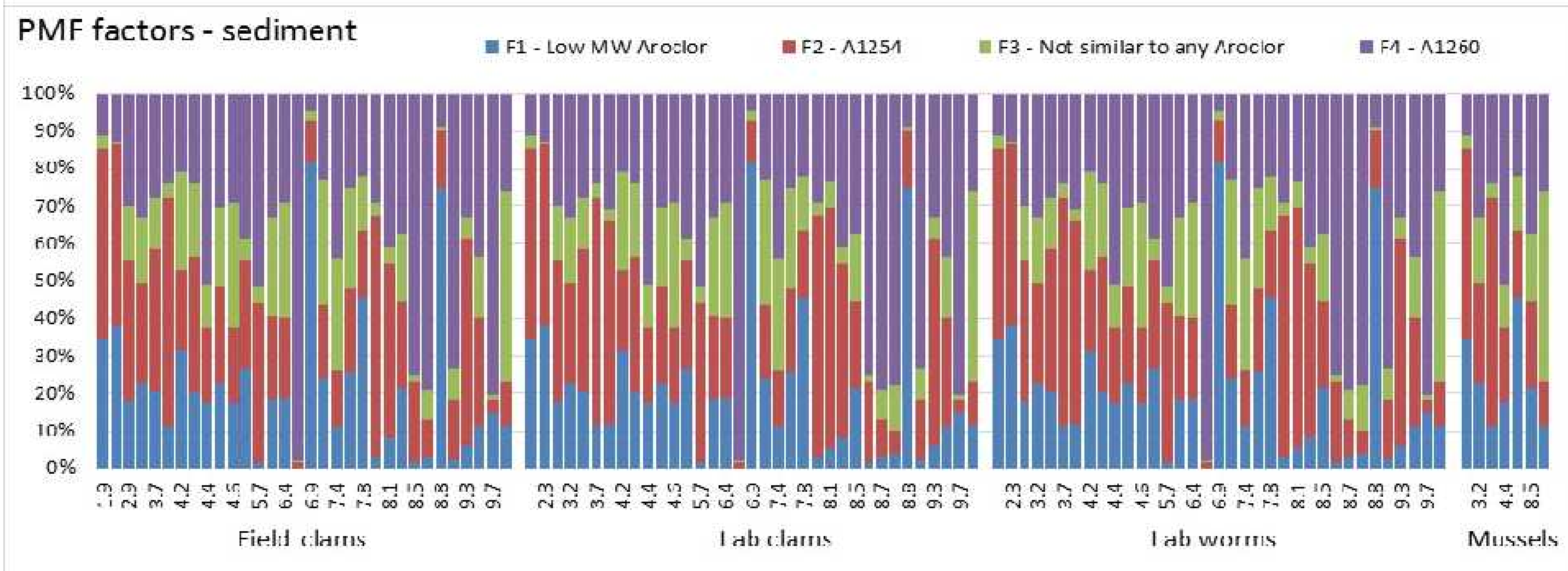
PCB sources to benthic biota



Factors 4 and 5 both resemble Aroclor 1260, but factor 4 has more evidence of bioaccumulation


PMF factors - biota
F1 - low MW Aroclor
F2 - A1254
F3 - not similar to any Aroclor
F4 - A1260 (more weathered)
F5 - A1260 (less weathered)
Field clams
Lab clams
Lab worms
Mussels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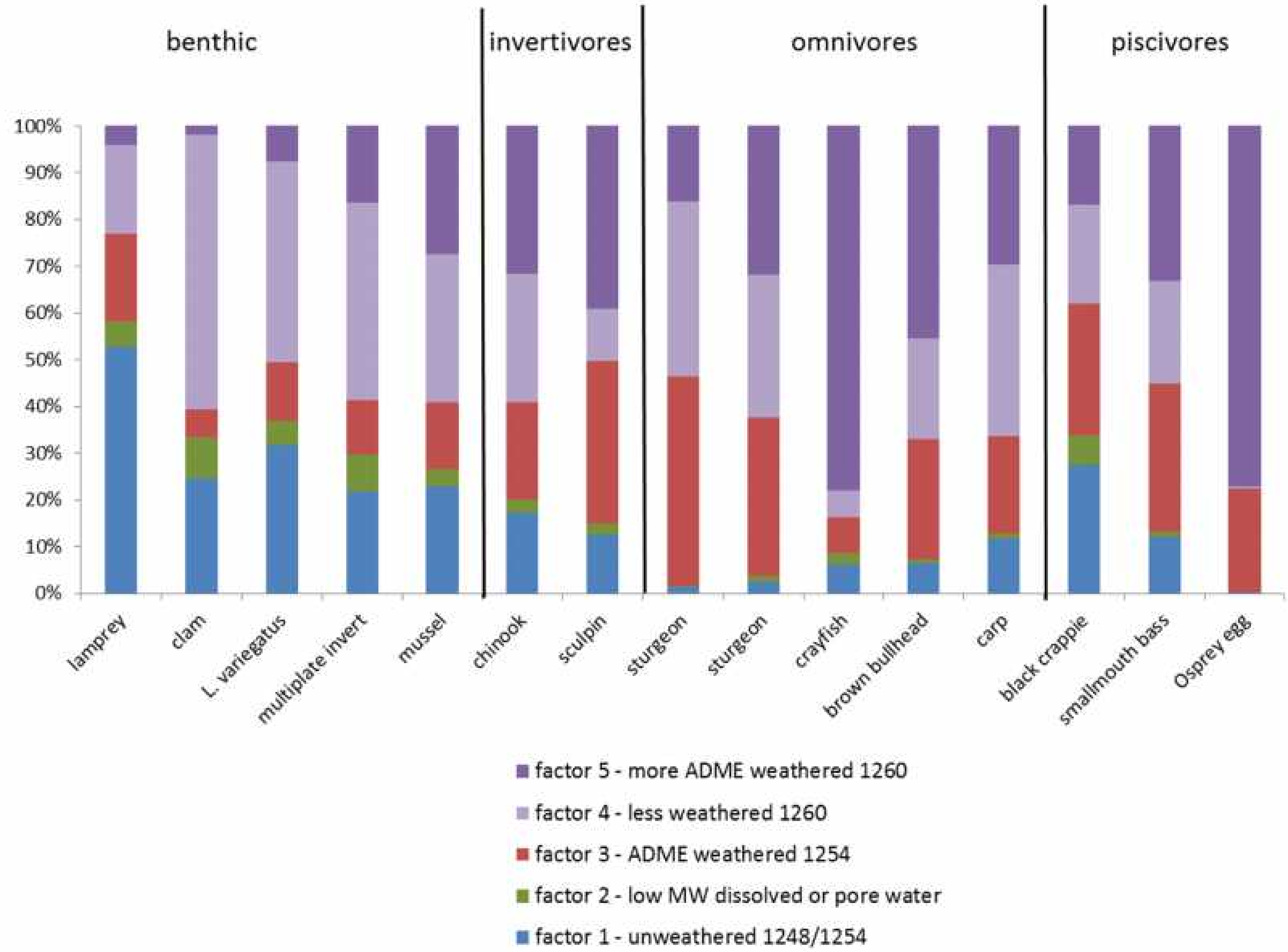
Fish and benthics



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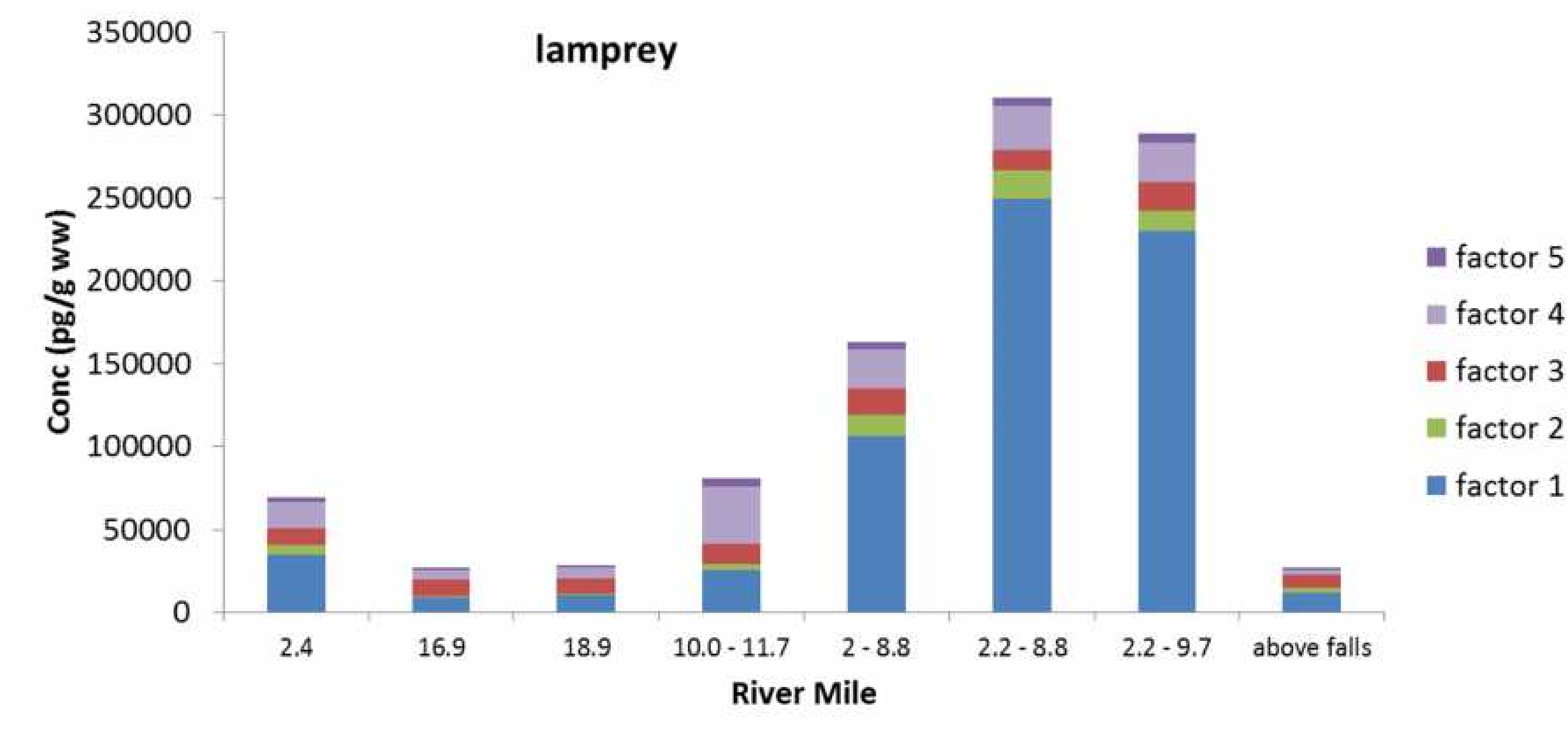
Fish by location



Location matters for fish, too

Lessons

- Congener fingerprints change from water to sediment to biota
- Still, can generally identify the proportions of the different Aroclors in the all compartments
- High MW Aroclors bioaccumulate more, esp. at higher trophic levels
- For benthic organisms, location matters a lot
- For fish, location matters some, tooi
- Lab bioaccumulation studies give very different results than field

Spokane River

- Limited fish data
- Good amount of water column data
- WWTP data
- Blank issues

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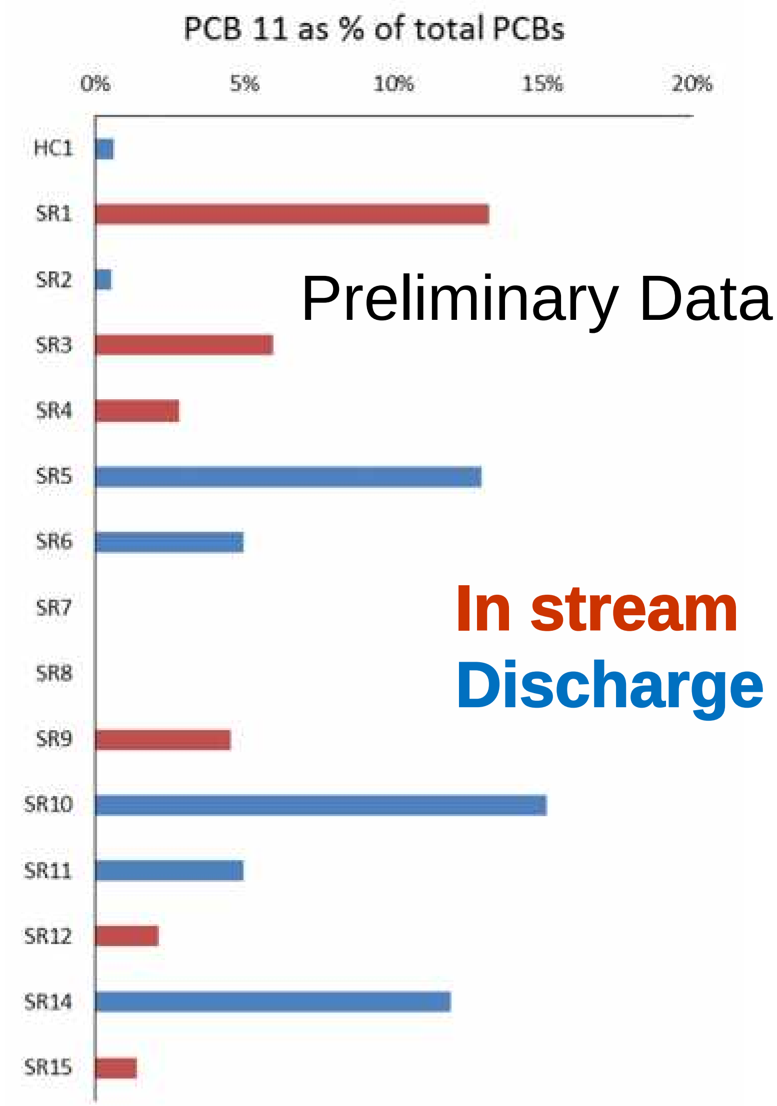
Water column – some PCB 11, but mostly Aroclors



Station	Location	Type of Sample
SR-1	Spokane River Below 9 Mile Dam	In-stream
HC-1	Latah (Hangman) Creek	Discharge
SR-2	City of Spokane Riverside Park Advanced WWTP	Discharge
SR-3	Spokane River at Spokane	In-stream
SR-4	Spokane River at Greene Street Bridge	In-stream
SR-5	Spokane County Regional Water Reclamation Facility	Discharge
SR-6	Inland Empire Paper	Discharge
SR-7	Spokane River at Below Trent Bridge	In-stream
SR-8	Kaiser Aluminum	Discharge
SR-9	Spokane River at Barker Road Bridge	In-stream
SR-10	Liberty Lake Sewer & Water District	Discharge
SR-11	Post Falls WWTP	Discharge
SR-12	Spokane River at Post Falls	In-stream
SR-13**	Hayden Area Regional Sewer Board WWTP	Discharge
SR-14	Coeur d'Alene Advanced WWTP	Discharge
SR-15	Lake Coeur d'Alene Outlet	In-stream

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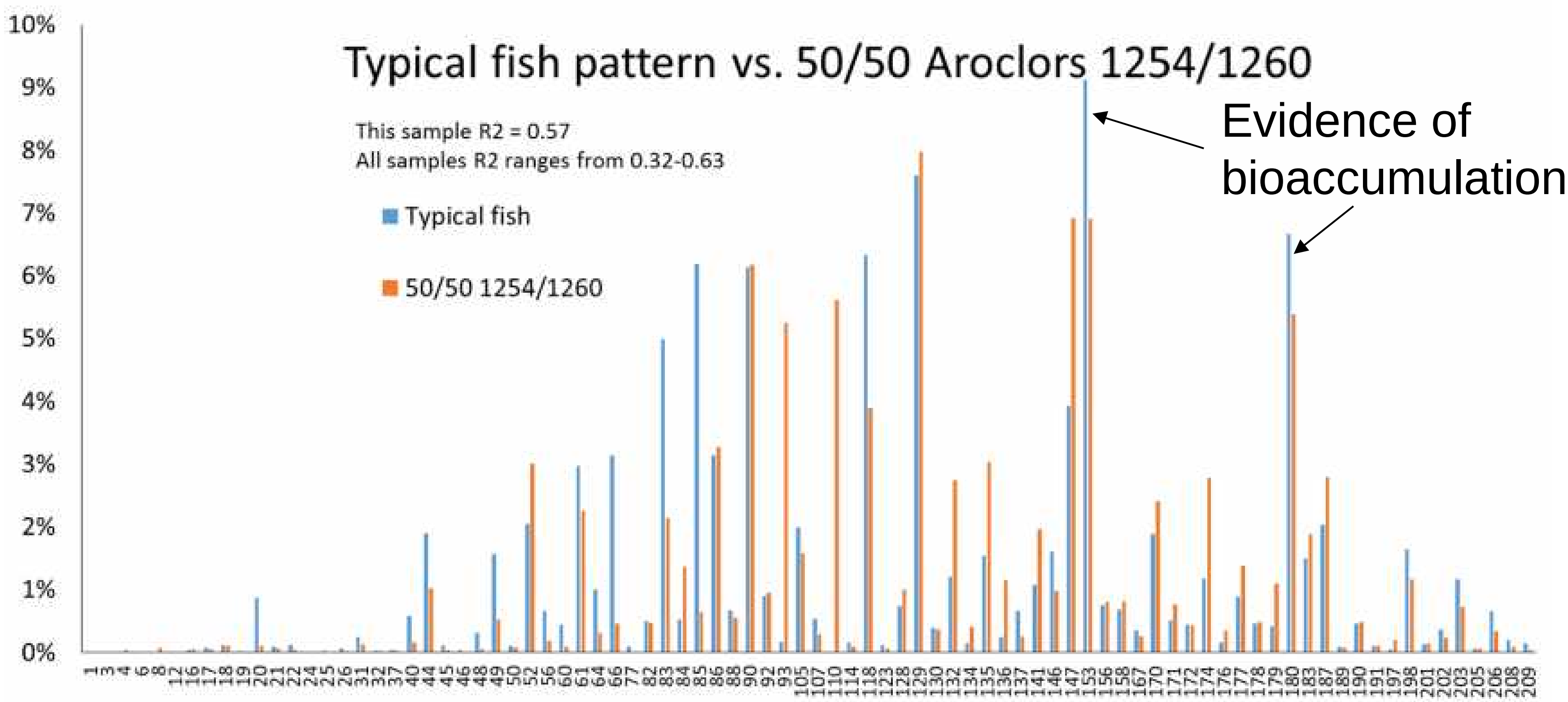
Fish fingerprints look like Aroclors 1254+1260



PCB 11 is never more than 0.3% in fish

Preliminary Data

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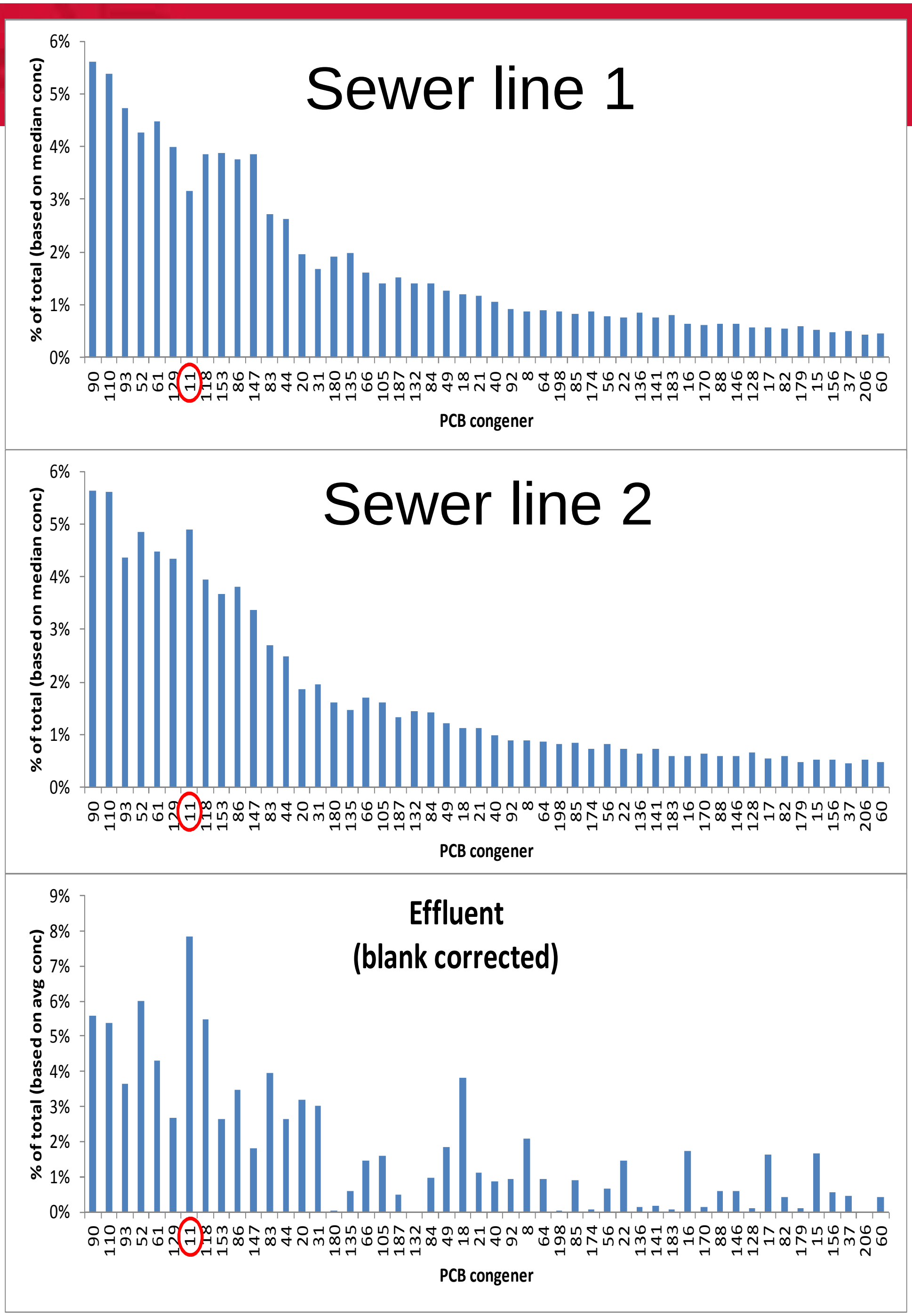
Wastewater

PCB 11 is significant in influent, but *most abundant* congener in effluent due to excellent solids removal.

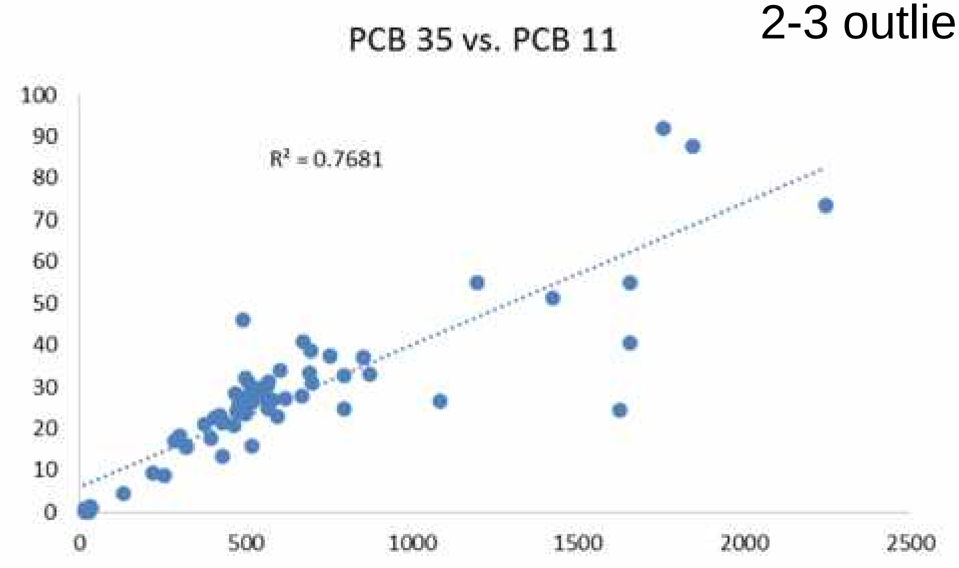
Pigments are a major source of PCBs in this system.

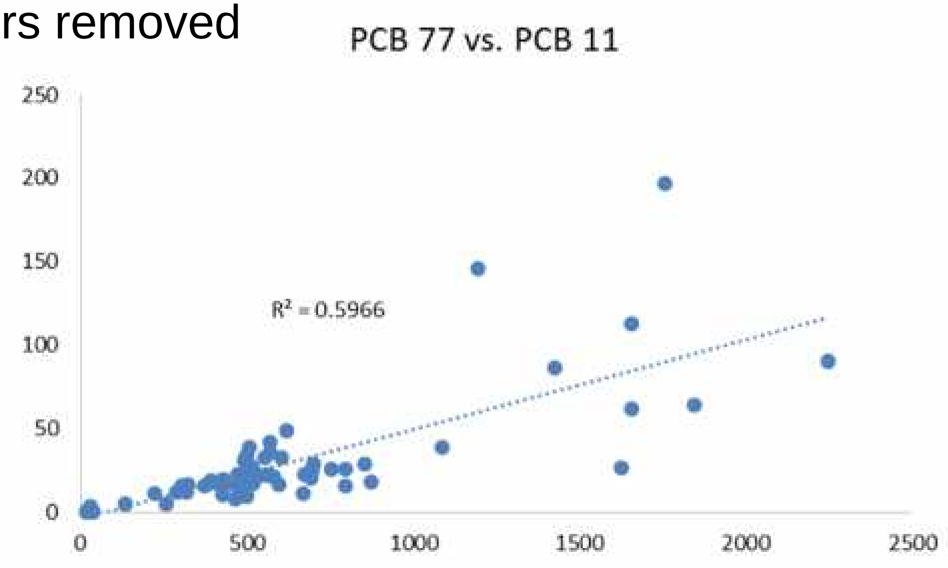
Reducing legacy PCB sources will not fix this problem.

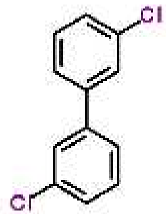


PCB 11 is strongly correlated with PCBs 35 and 77 (dioxin-like)

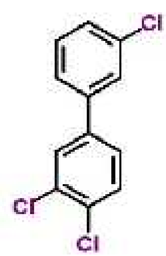
2-3 outliers removed



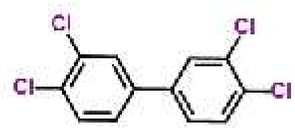




PCB 11



PCB 35



PCB 77 (TEF = 0.0001)

Also seen in raw pigments.(Litten et al., 2002; Anezaki and Nakano, 2014)

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Conclusions

- Fingerprinting can help determine where and when certain types of PCB sources are important
- Non-Aroclor sources are a problem in the Spokane River
  - Correlation between PCB 11 and PCB 77 is troubling
- Fingerprints look more like Aroclors close to the source in time and space, but less and less as they move away and as they are processed by fish
- In the Spokane River, Aroclors are the most important source to fish

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