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Identifying PCB sources through fingerprinting

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PCB fingerprinting made possible by:

- Measuring most or all congeners
  - EPA method 1668 (all 209 congeners)
- Sophisticated tools such as:
  - Factor analysis:
    - Polytopic Vector Analysis (PVA)
    - Positive Matrix Factorization (PMF)♥
  - GIS
- GOOD DATA MANAGEMENT

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Data management

- Good data management is…
  - 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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Method 1668: special considerations

- **Not all labs can do 1668 well!**

- 1668 allows two columns
  - Very different coelution patterns
  - DB-5 more rugged
  - SPB-octyl ♥ resolves all the dioxin-like congeners
  - Pick one and stick with it!

- Reporting standards are important!
  - Congener names - IUPAC♥ (i.e. PCB 11) or name ☹ (i.e. 3,3'-dichlorobiphenyl)
  - Co-elutions – leave blank♥ or report same concentration for all ☹
  - BDL values – leave blank♥ or report detection limit ☹
  - Report LOD for each analyte and surrogate recoveries for each sample

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Not an expert in data management?

- Just use the DRBC's protocols:
  - http://www.state.nj.us/drbc/quality/toxics/pcbs/monitoring.html

Delaware River Basin Commission

- These guidelines were developed so that dischargers (who know very little about PCB measurement) could send their samples to any one of a variety of contract labs and get a consistent, homogeneous data set.

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OK, I have some data.
What now?

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Low-tech fingerprinting (first steps)

- Check for specific non-Aroclor congeners
  - 11, 206/208/209, 44/45
- Check for dechlorination congeners
  - 4, 19, 44+47+65, and 45+51
- Correlation matrix

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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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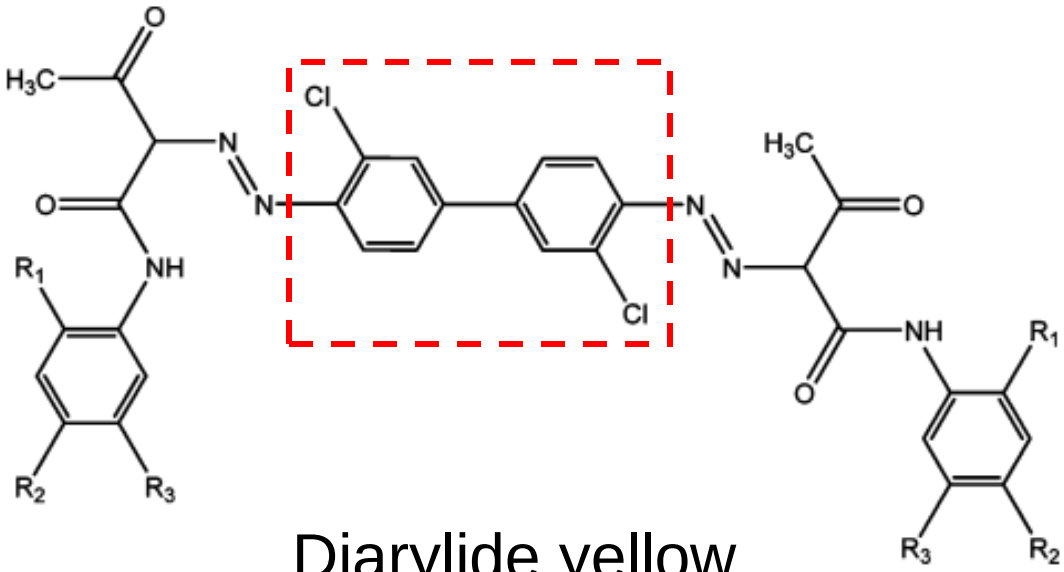
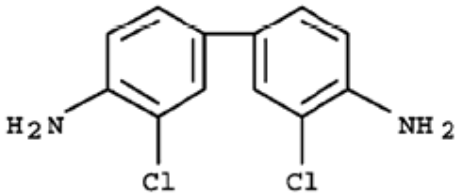
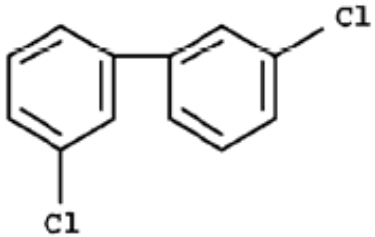
PCB 11 from Diarylide Yellows



Diarylide yellow



3,3'-dichlorobenzidine



PCB 11

R_1,R_2,R_3 = H	Pigment yellow 12
R_1,R_2 = CH_3, R_3 = H	Pigment yellow 13
R_1 = OCH_3, R_2, R_3 = H	Pigment yellow 17
R_1,R_3 = OCH_3, R_2 = Cl	Pigment yellow 83

→ All listed in EPA's Toxic Substances Control Act (ToSCA) inventory

(Basu et al. 2009)

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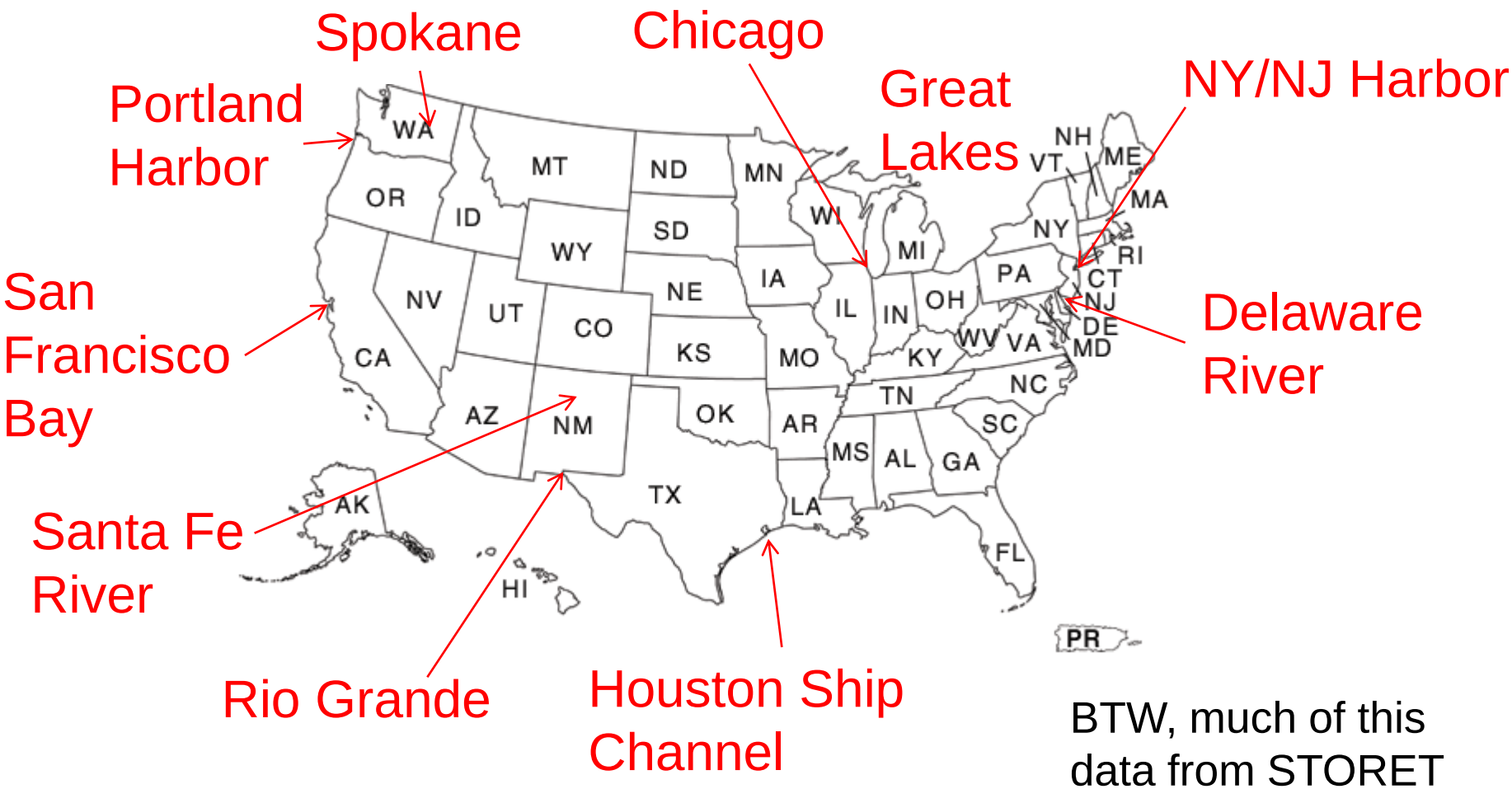
PCB 11 is everywhere…

in the water column



BTW, much of this data from STORET

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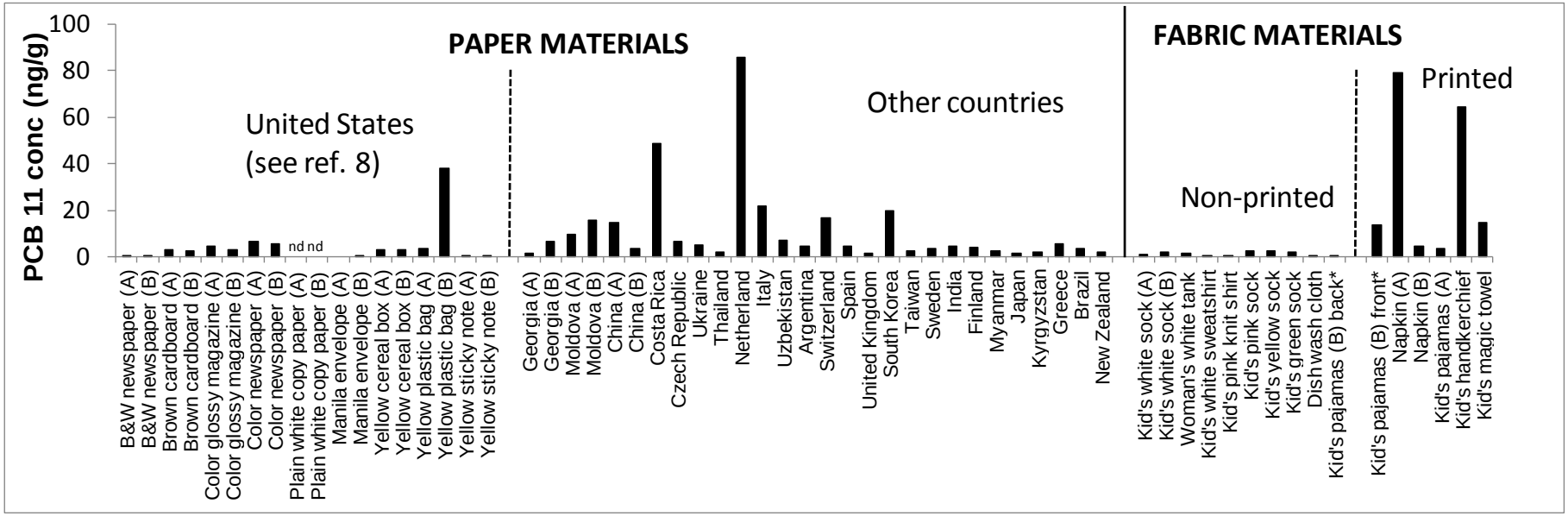
PCB 11 is everywhere, continued



Guo et al. EST 2014

- PCB 11 inks used in printing on paper, plastic, and fabric, as well as pigments in plastics
- From 26 countries on five continents
- Washing of clothing introduces PCBs to wastewater

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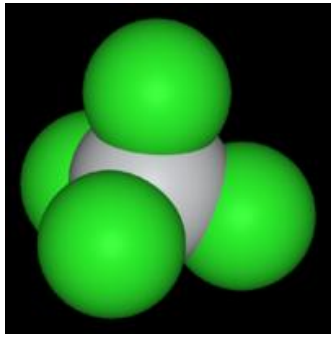
PCBs 206, 208, 209



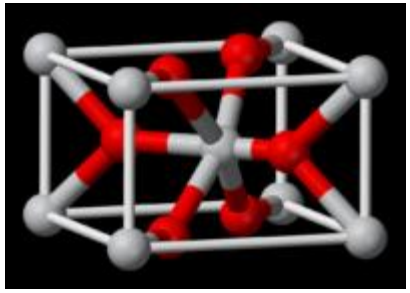
Produced inadvertently during the making of titanium tetrachloride

$$2\ FeTiO_3 + 7\ Cl_2 + 6\ C \rightarrow 2\ TiCl_4 + 2\ FeCl_3 + 6\ CO$$

This carbon is chlorinated to form PCBs

Often sold to water treatment plants as a flocculant

Most $TiCl_4$ is then used to make titanium dioxide (white pigment)



$$TiCl_4 + O_2 \rightarrow 2\ TiO_2 + 2Cl_2$$

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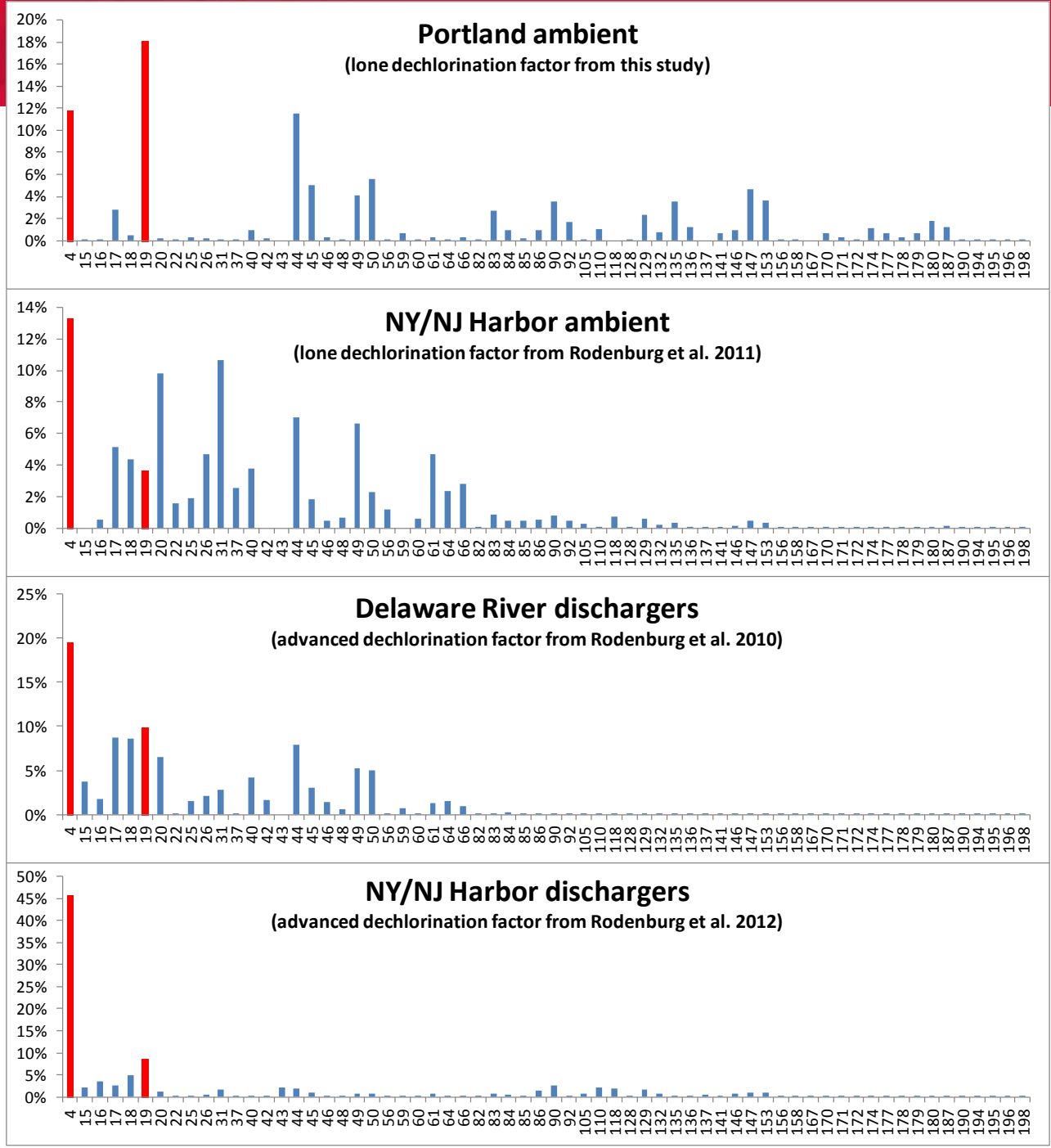
Various dechlorination profiles

- Seen in dischargers, groundwater, sewers, landfills
- Always contain lots of PCBs 4 and 19
- Sometimes 44 & 45 sort out separately



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What if I want to get more sophisticated?

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.

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PMF input matrixes

- **For all matrixes:**
  - 209 congeners measured in ~160 peaks
  - Usually use about 90 peaks (others usually BDL)
  - 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 when 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.

Case Study:

Delaware River

Du et al. ES&T 2008
Rodenburg et al. ES&T 2010
Praipipat et al. 2014

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Delaware discharger database

Delaware River Basin Commission

- Chose to use 89 peaks
- 546 effluent samples from 100 dischargers (identified by NPDES permits)
- 99 influent samples from 21 dischargers

7 factors resolved

- Q best match
- Low RSD (0.8%) compared to 85% for 8 factors
- R^2 between measured and modeled concentrations was 0.986 for the sum of PCBs and was greater than 0.8 for 61 congeners of the 87 congeners
- Easily interpretable factors

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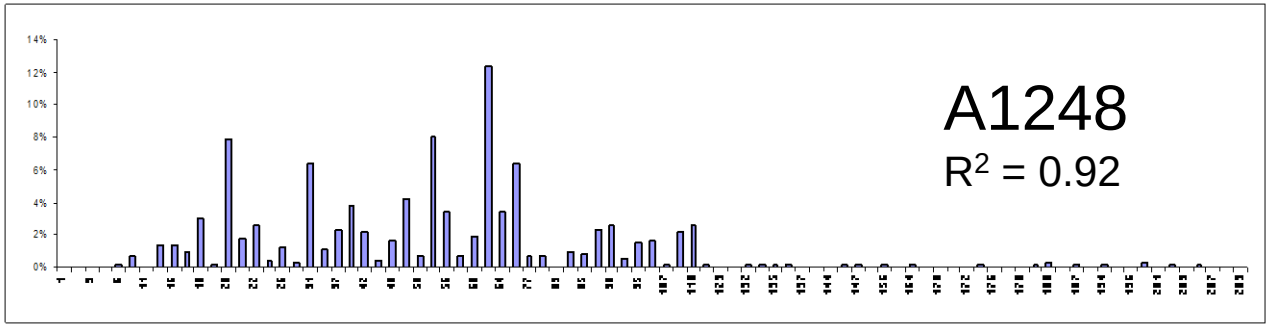
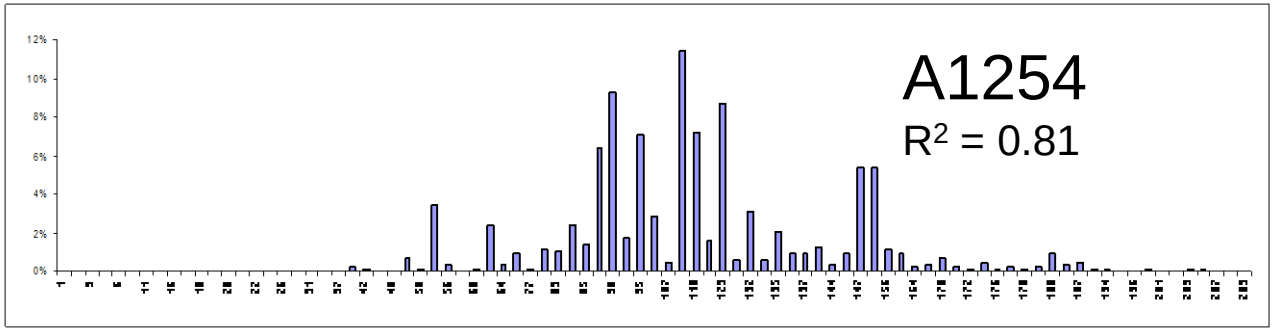
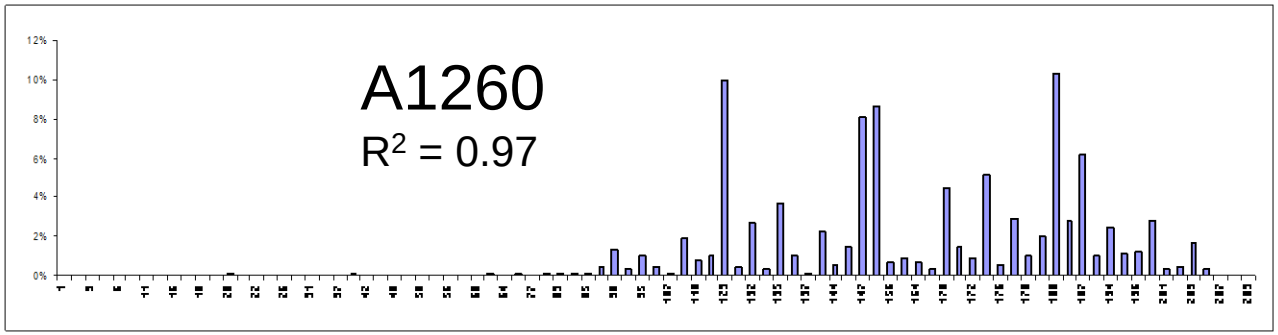
7 factors:

3 look like Aroclors



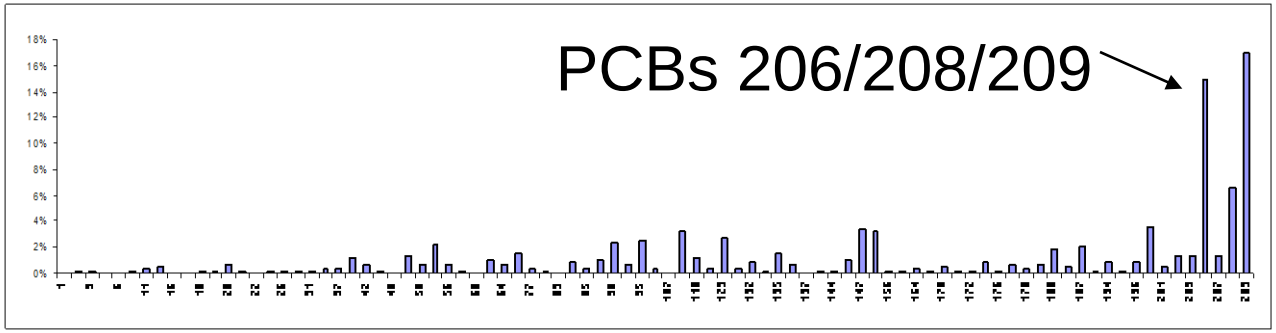




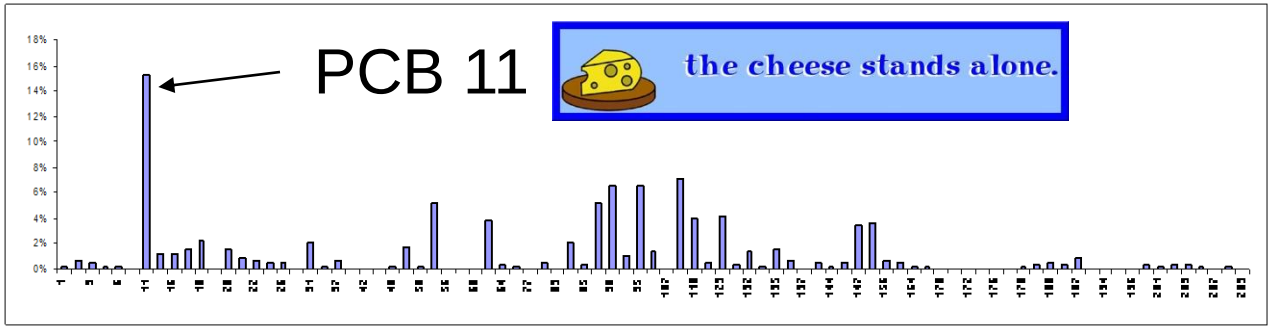
Aroclor 1242/1016 is often missing… not sure why

Two Non-Aroclor factors

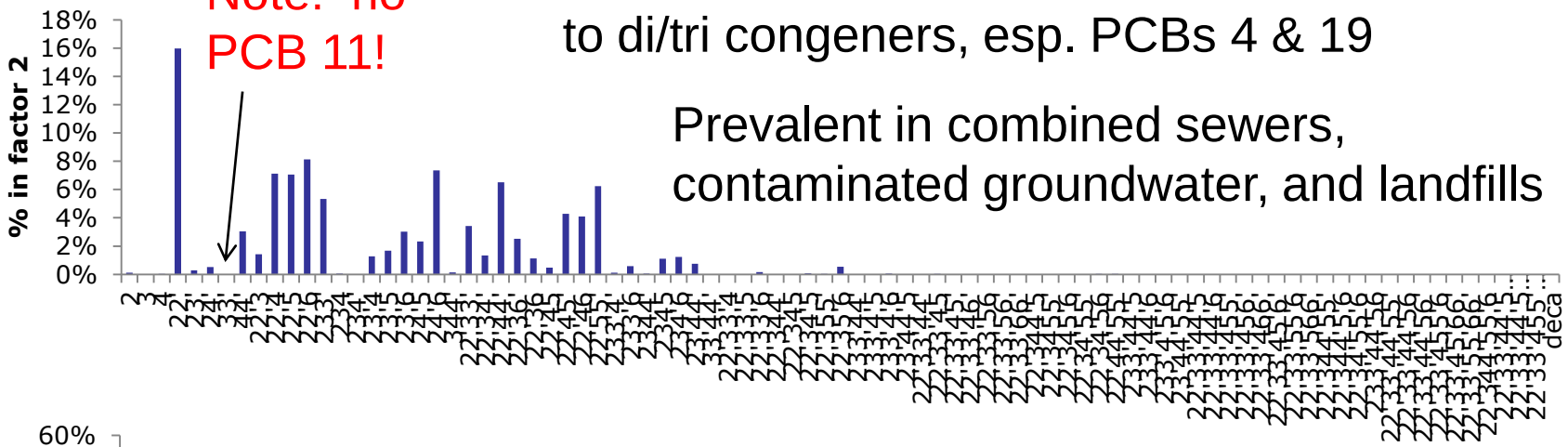
Production of TiO_2 at Edgemoor



PCB 11 from pigments – tracer for treated wastewater/ stormwater runoff



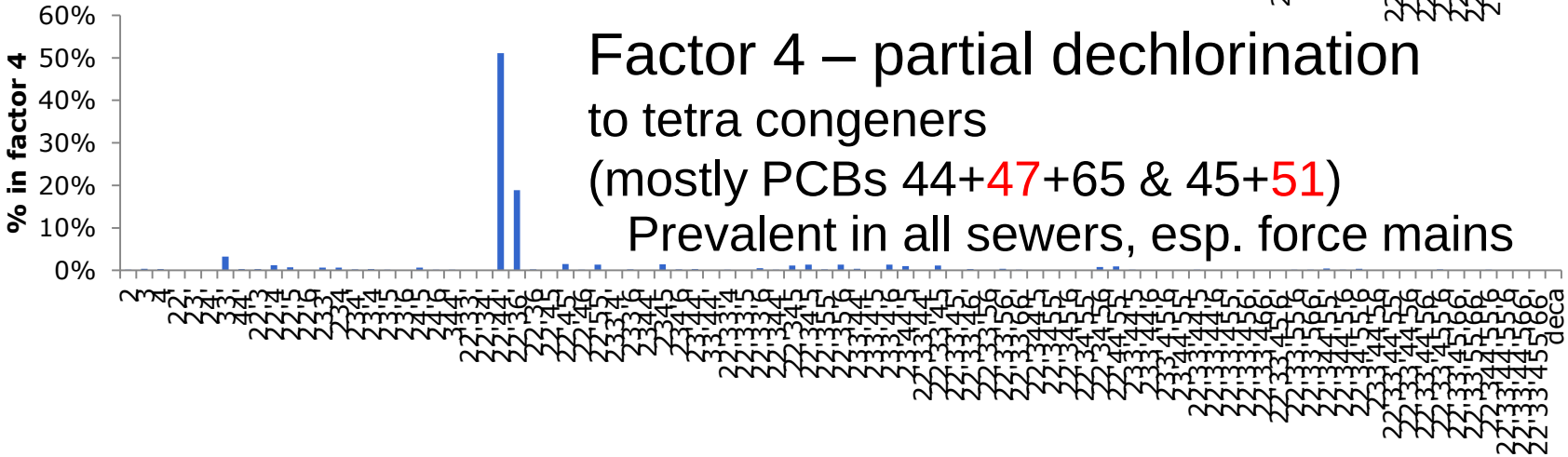
Two factors are dechlorination signals



Factor 2 – advanced dechlorination

to di/tri congeners, esp. PCBs 4 & 19

Prevalent in combined sewers, contaminated groundwater, and landfills



Factor 4 – partial dechlorination

to tetra congeners

(mostly PCBs 44+47+65 & 45+51)

Prevalent in all sewers, esp. force mains

Top emitters of advanced dechlorination factor are WWTPs, contaminated groundwater, and landfill leachate

Facilities in **green** are WWTPs

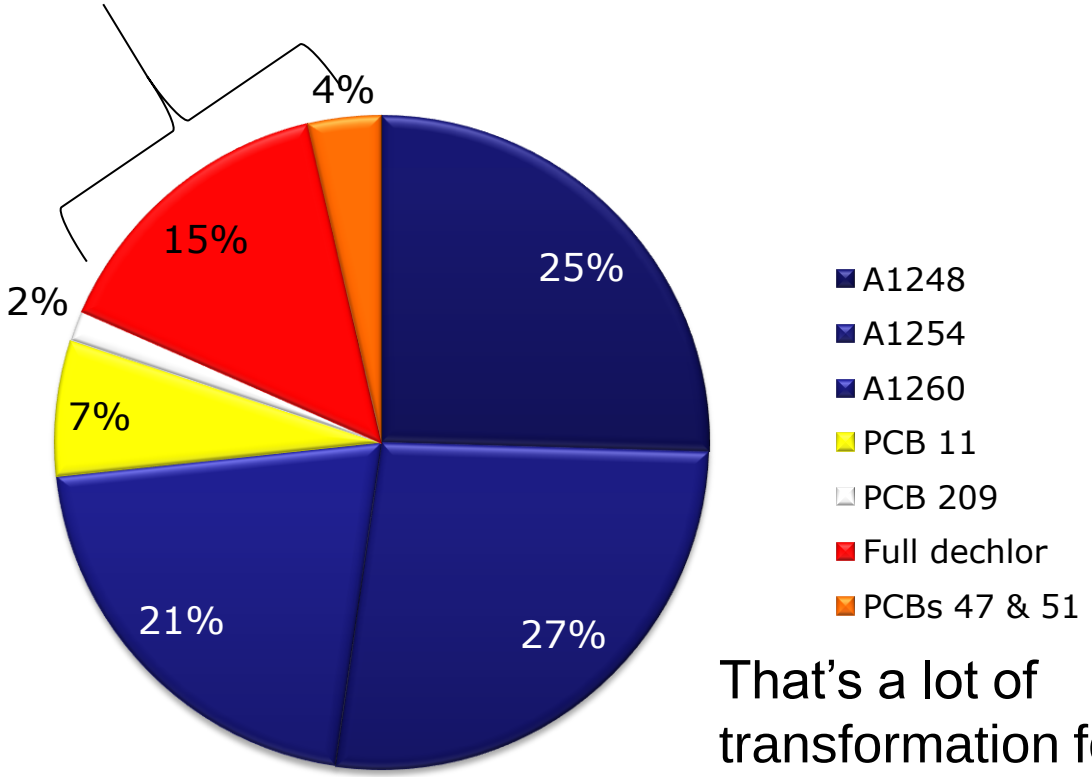
Facilities in **black** are sites with contaminated groundwater

(Not on this list: GROWS landfill leachate treatment plant)

Rank	Facility	F2 load (g/y)
1	US Steel Fairless	216
2	PWD-SW	198
3	PWD-NE	156
4	City of Wilmington	137
5	PWD-SE	92
6	CCMUA	39
7	Bridgeport Disposal	16
8	Dupont-Repauno	15
9	Metro Machine (Navy Yard)	10
10	Dupont-ChamberWorks 001	4.8
11	Dupont-ChamberWorks 662	4.7
12	US Steel Fairless	3.0
13	Bridgeport Disposal	2.6
14	Hamilton Township	2.4
15	GCUA	2.1
16	Rohm&Haas-Philadelphia	1.7
17	Morrisville WWTP	1.7
18	Aker Shipyard (Navy Yard)	1.7
19	LBCMUA	1.6
20	DELCORA	1.3
21	Ferro Delaware River Plant	1.1
22	Trenton	0.79
23	Dupont-Edgemoor 001	0.48

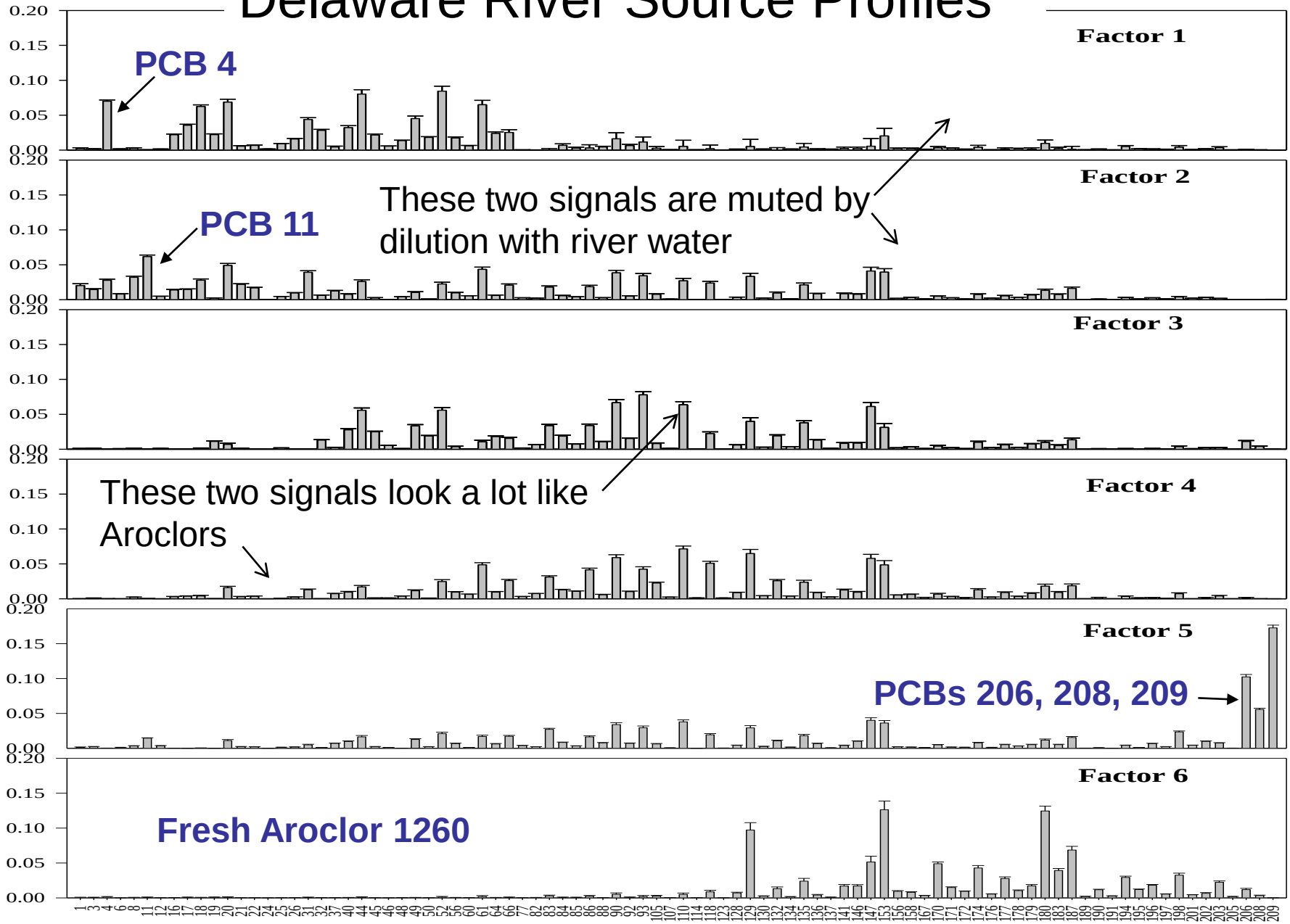
Composition of total PCBs loads by factor

Dechlorination products make up about 18% of total PCB loads to the Delaware River from NPDES dischargers



That's a lot of transformation for a chemical that is considered "persistent"!

Delaware River Source Profiles



Still resemble Aroclors, but not as strong

	A1242	A1248	A1254	A1260
Factor 1	**0.79**	**0.84**	0.55	0.14
Factor 2	0.69	0.56	0.47	0.40
Factor 3	0.40	0.72	0.82	0.38
Factor 4	0.37	0.56	**0.84**	0.71
Factor 5	0.10	0.16	0.22	0.22
Factor 6	0.01	0.02	0.38	**0.97**

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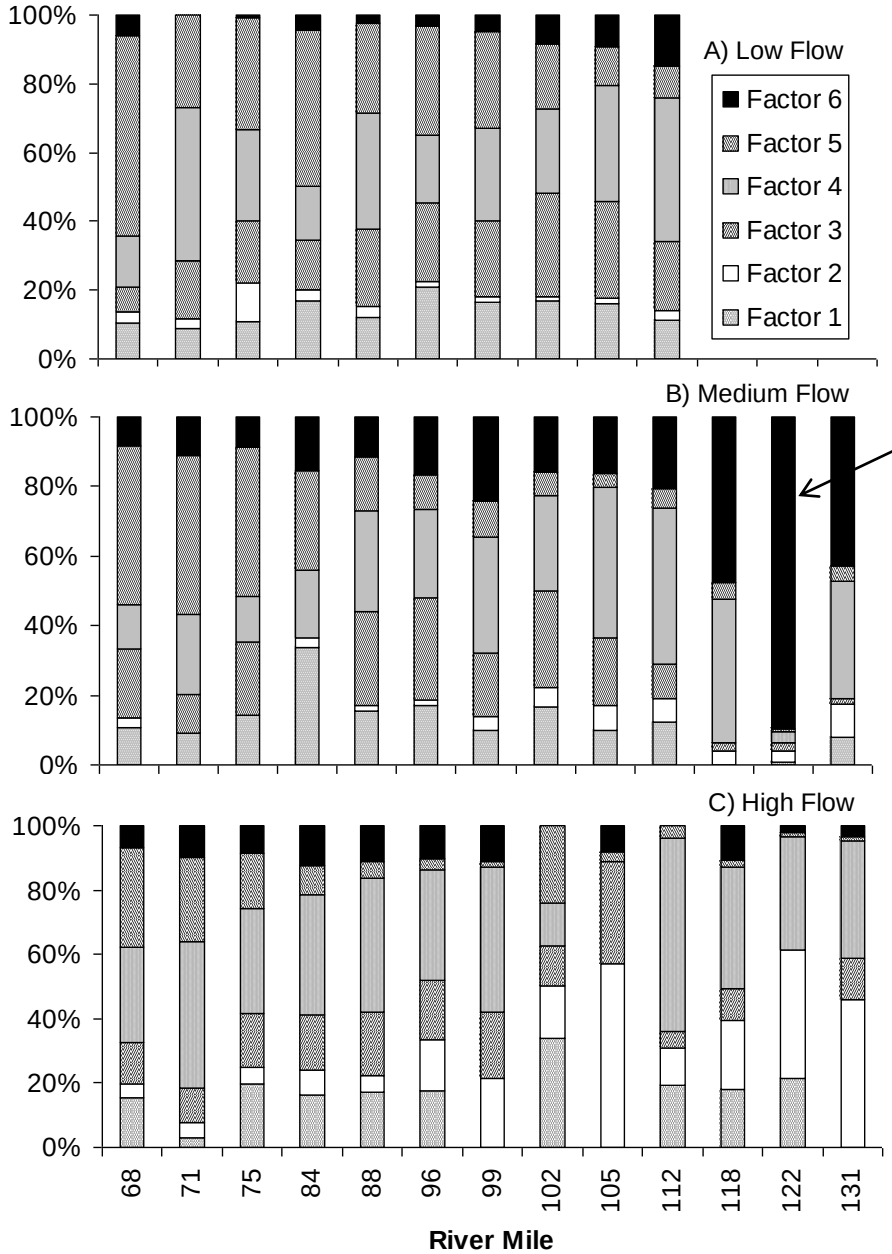


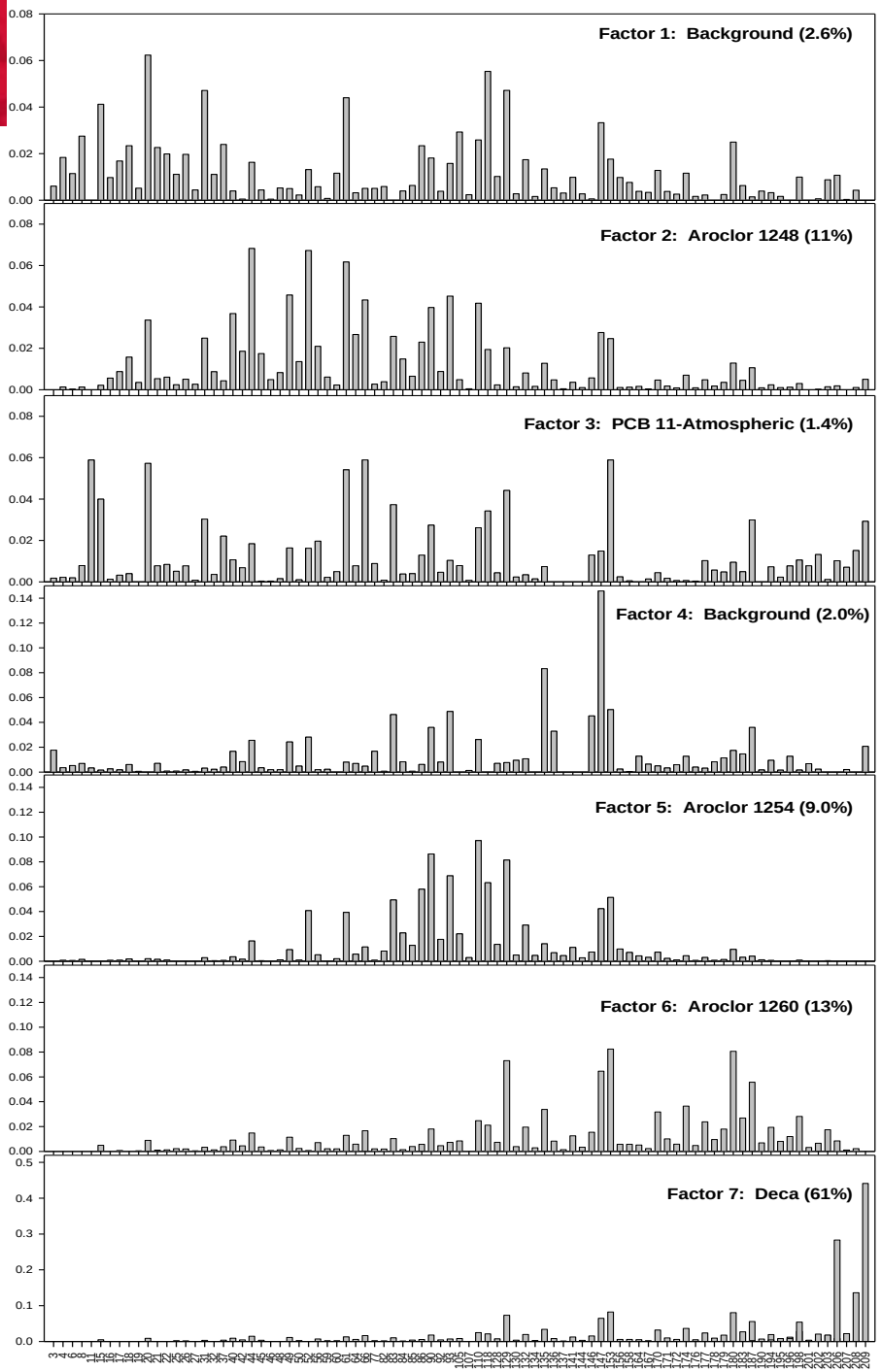
Spatiotemporal variability

Large source of unweathered Aroclor 1260 near RM 122

- Spatial variability by river mile
- Temporal variability by low/medium/high flow

Sediment

- Aroclors still discernible
- Factor with lots of PCB 11 is probably atmospheric deposition (evenly spread across estuary)
- PCBs 206/208/209 localized around the source



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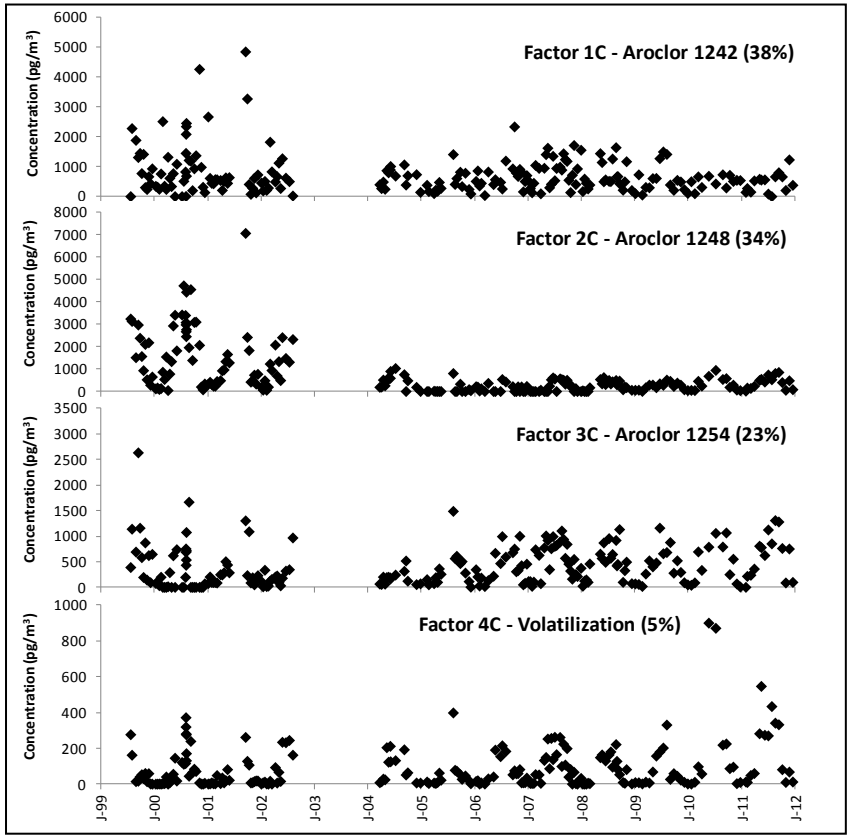
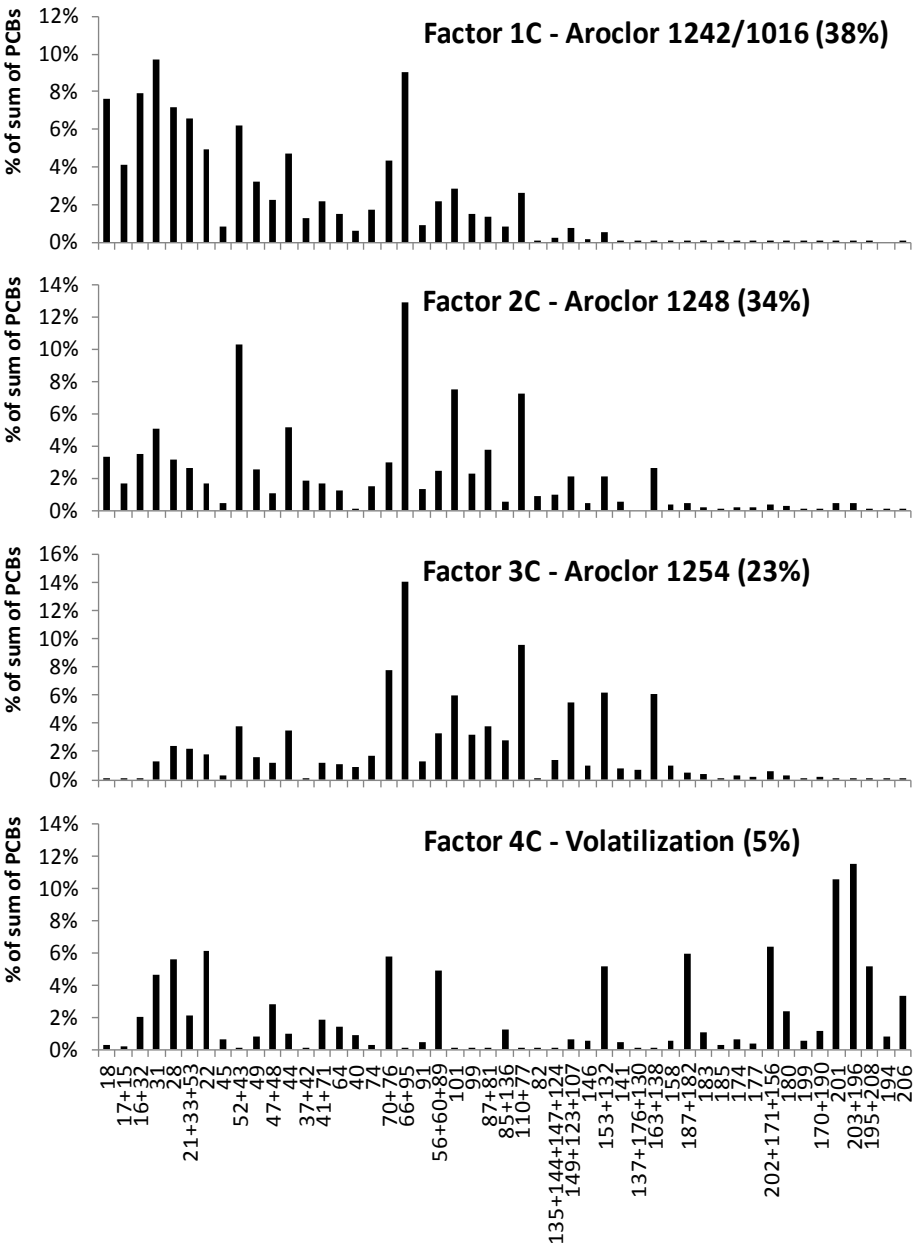
Air at Camden, NJ

- Used ECD detector
- Congener patterns very different
- Not necessarily declining





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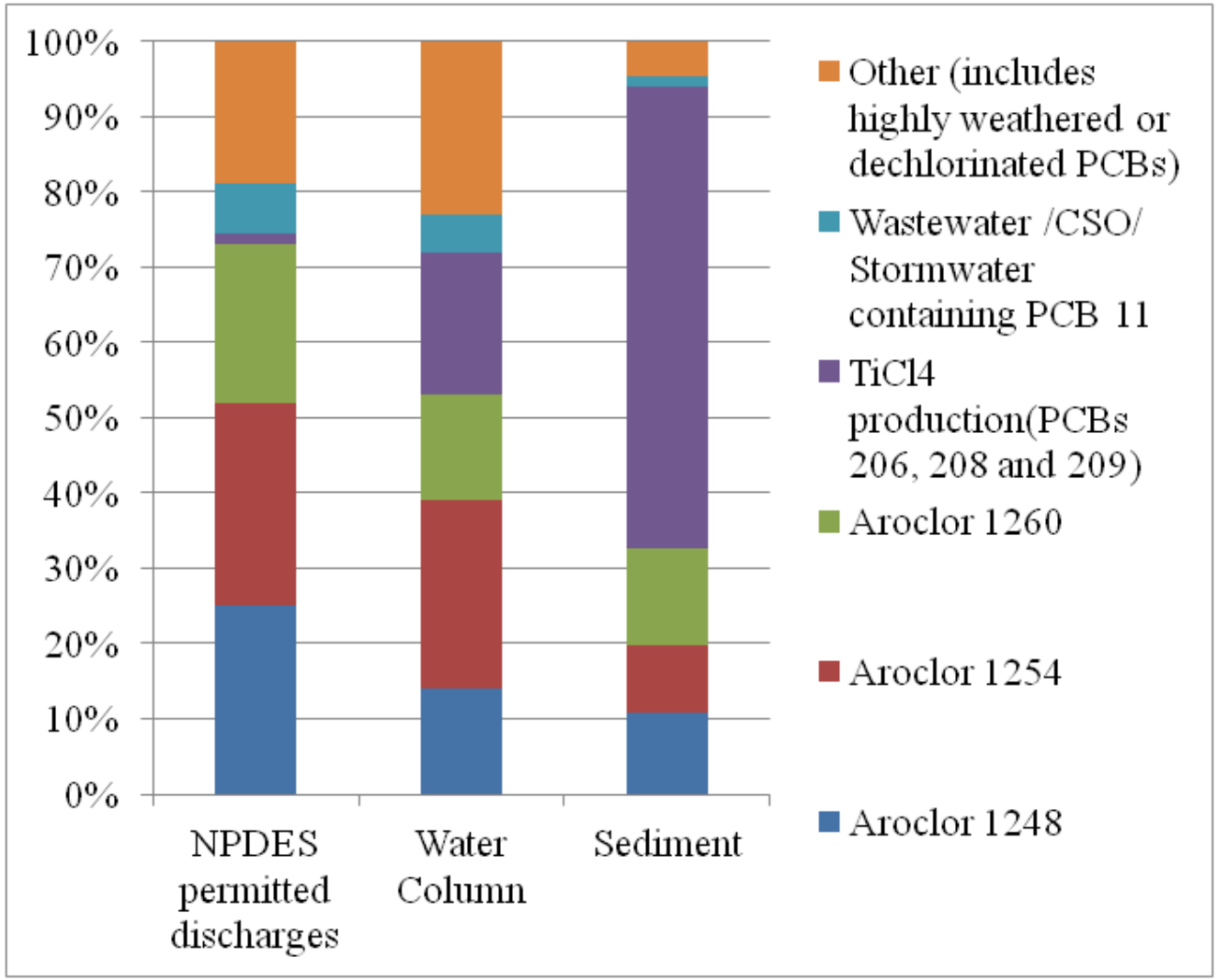
Compare across media



Could add fish, biota to this

What is YOUR endpoint?

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Case Study:

Portland Harbor Superfund Site

(unpublished)

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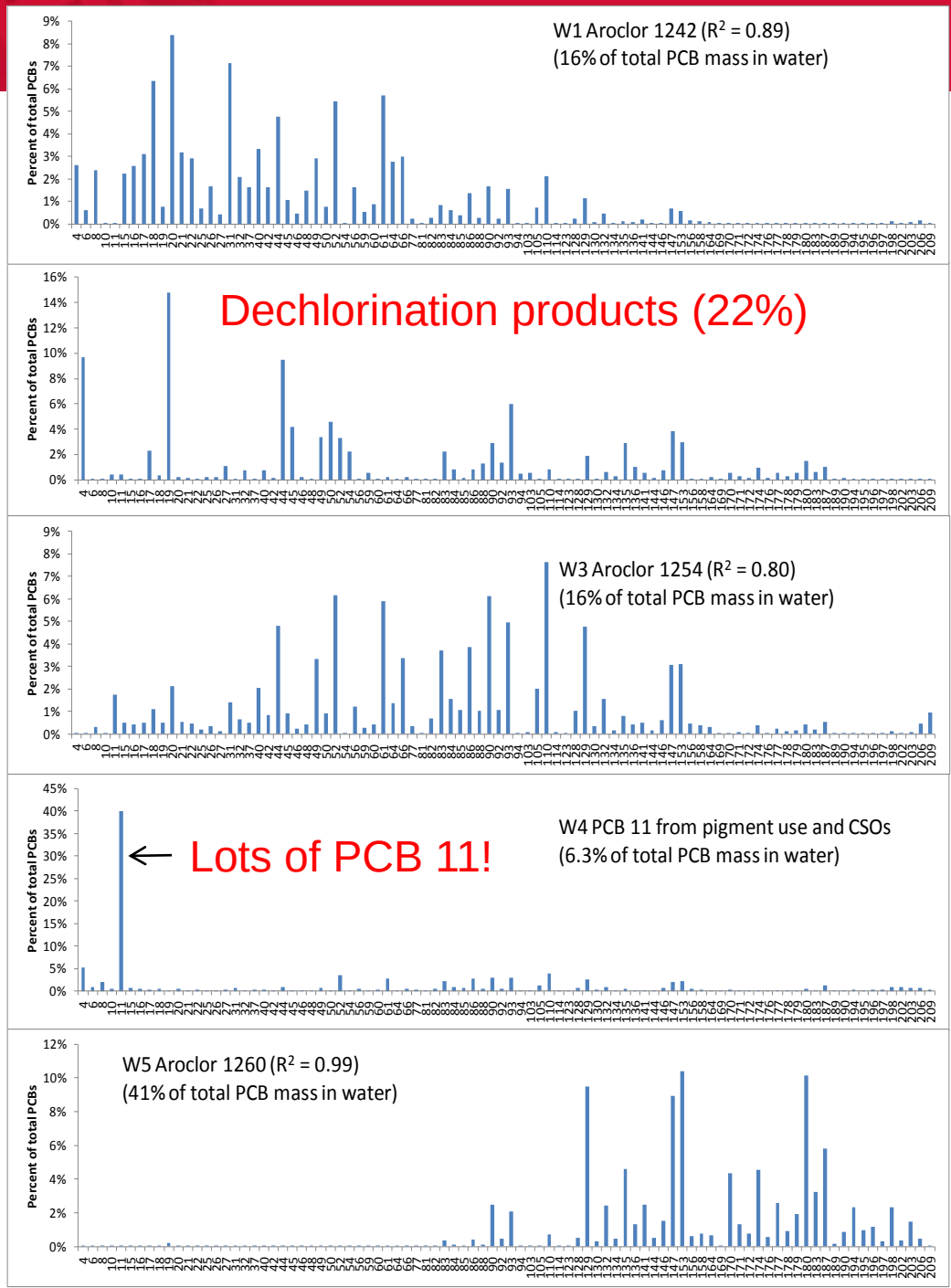
Portland Harbor superfund site

- Water column contains dechlorinated PCBs
- Sediment does not
- Spatial pattern suggests dechlorination occurs in groundwater

- Ergo: proof that groundwater is a source of PCBs to the water column



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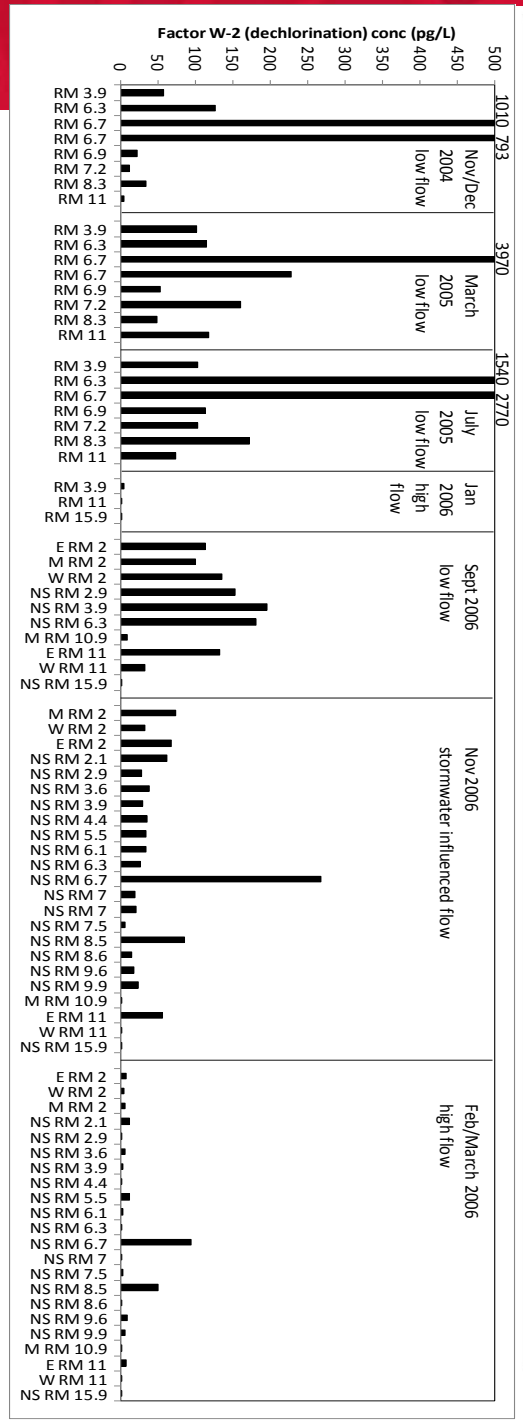
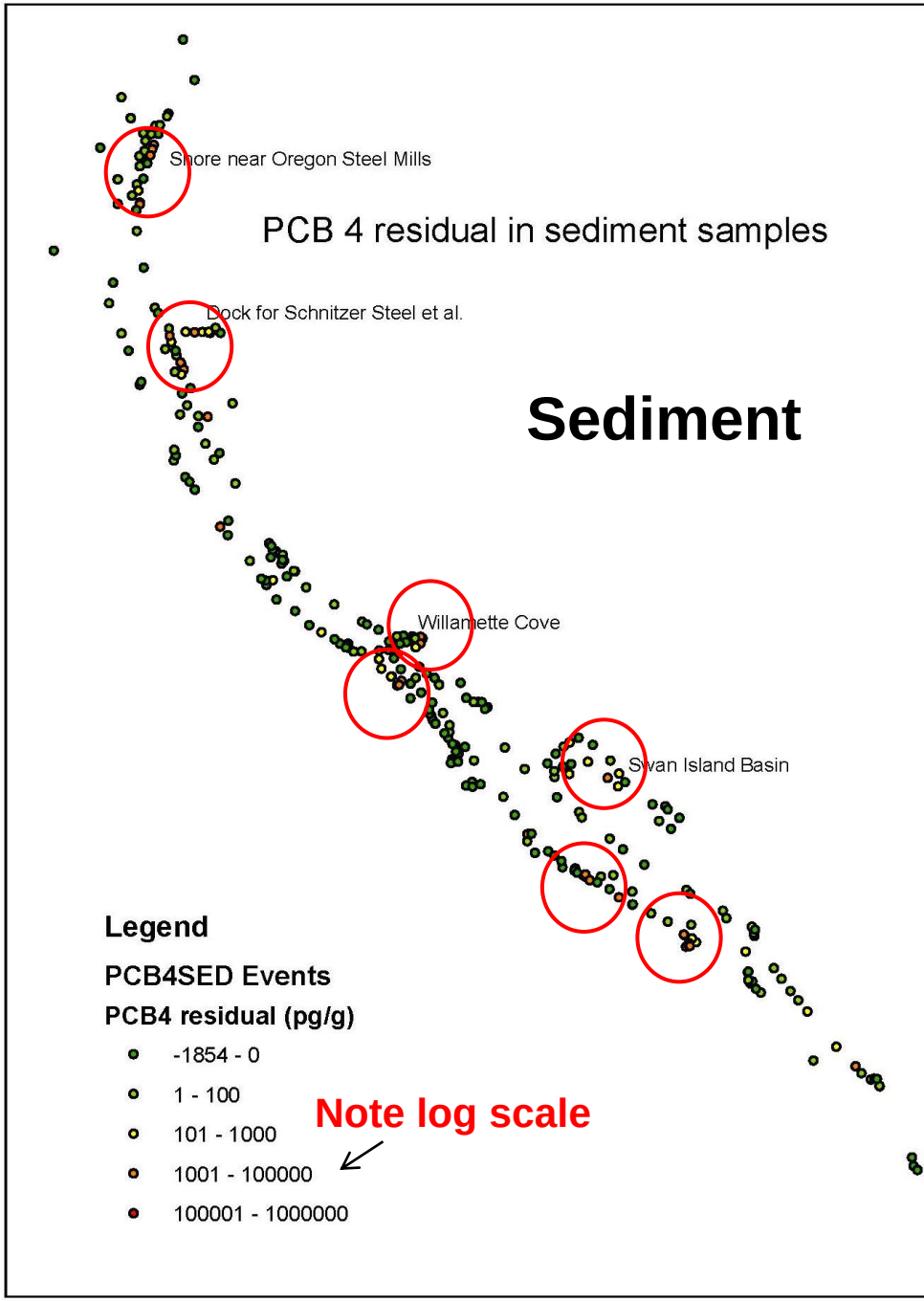
Spatial patterns

Water column

Highest conc at low flow and near RM 6.7 (Willamette Cove)





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Case study:

Fish from Hanford Nuclear Site

In press with ES&T

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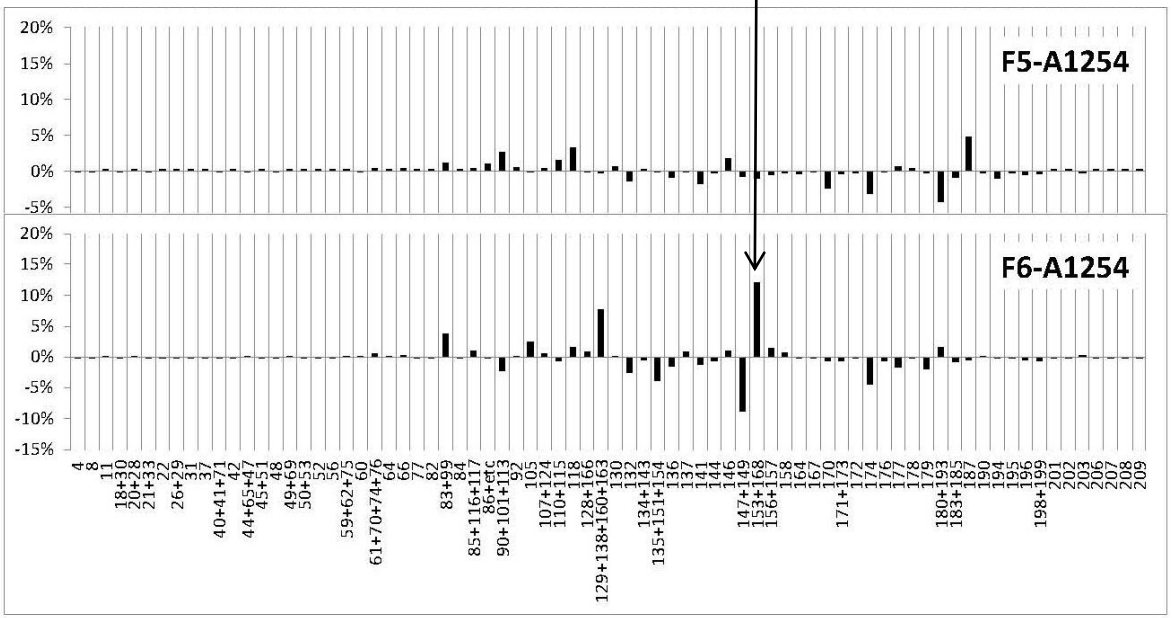
Hanford Nuclear Site fish data

	Single Aroclors Cos Θ			
Factor	**1242**	**1248**	**1254**	**1260**
F1	0.60	0.87	0.74	0.28
F2	0.16	0.37	0.94	0.58
F3	0.17	0.36	0.90	0.63
F4	0.10	0.21	0.62	0.59
F5	0.06	0.14	0.61	0.91
F6	0.04	0.08	0.44	0.79

Factors look less like Aroclors, with signature changes such as accumulation of PCB 153

Compare Factors 5 and 6 with the parent Aroclor



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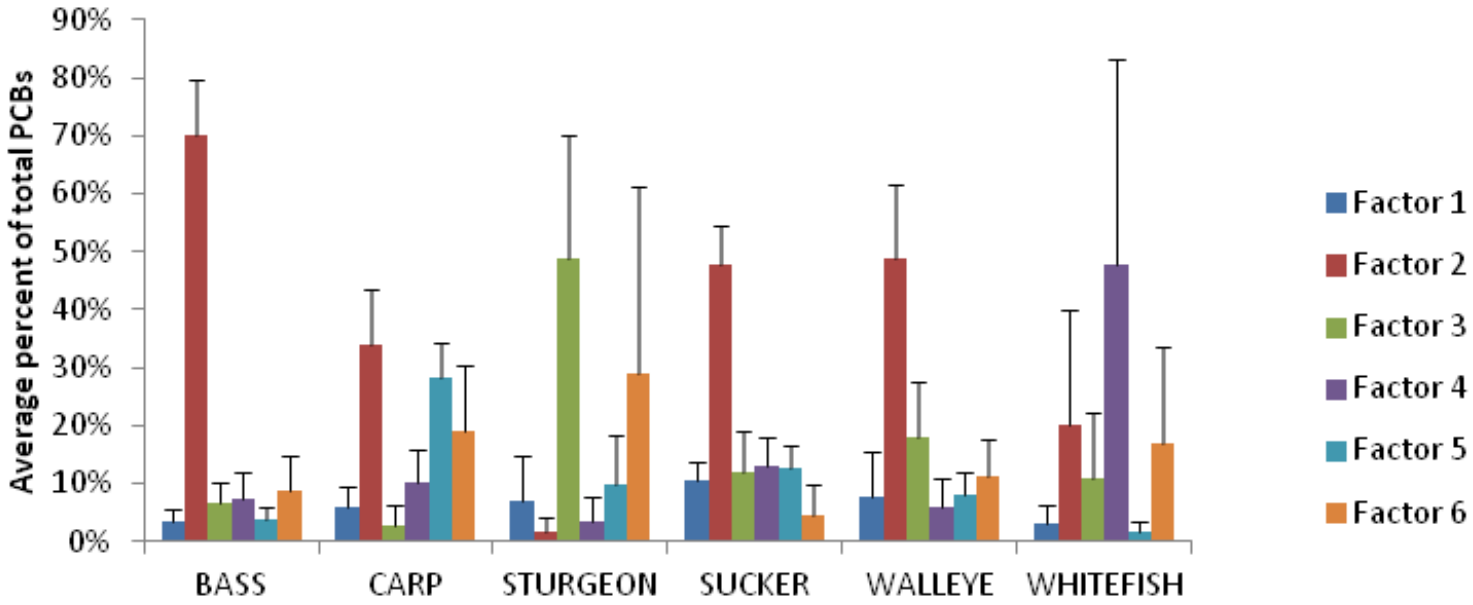
Species differences



Very different bioaccumulation patterns across species

What is YOUR endpoint?

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Case study:

Influent and effluent to Spokane County Regional Water Reclamation Facility

unpublished

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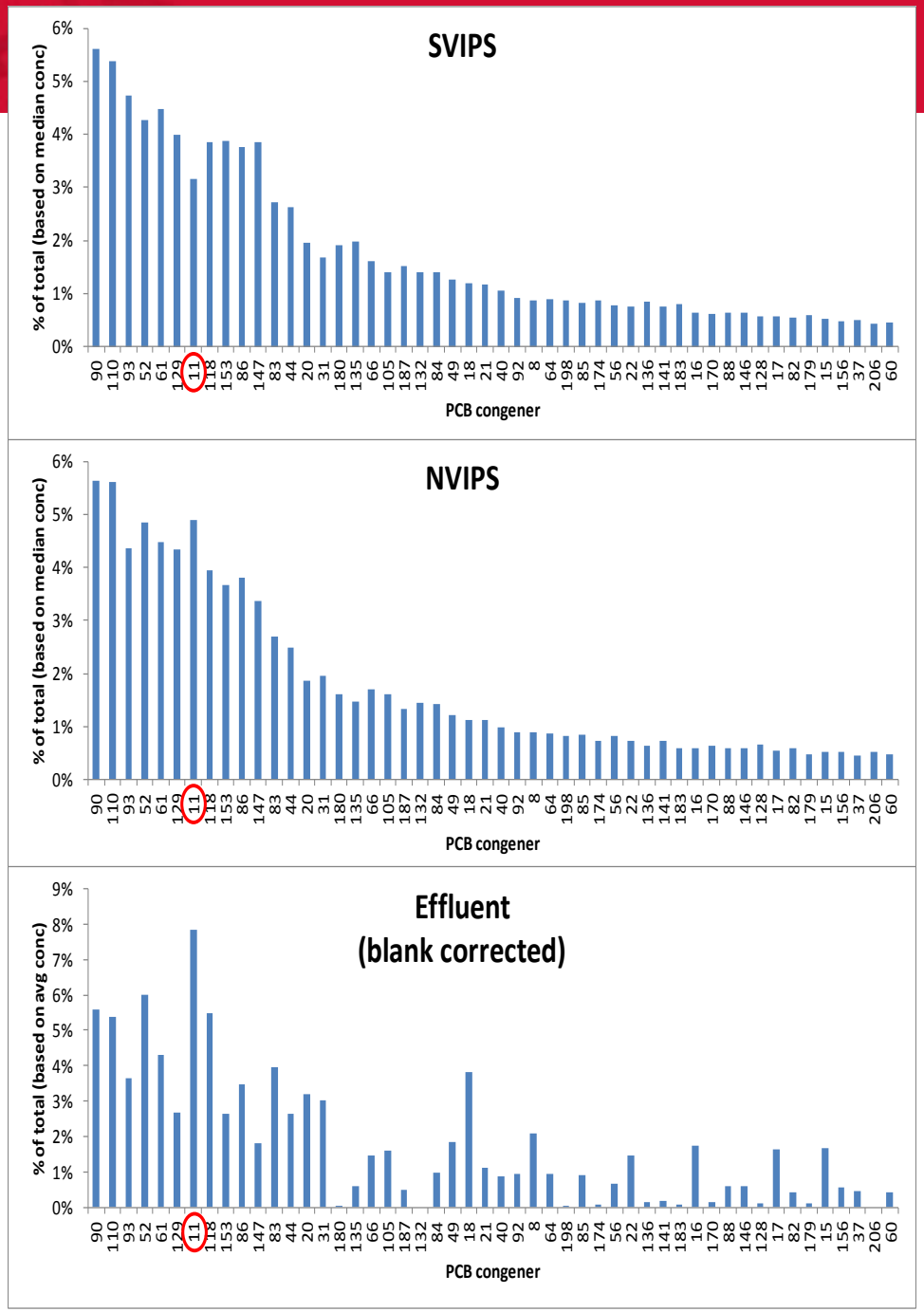
Check for specific non-Aroclor congeners

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.

What is YOUR endpoint?



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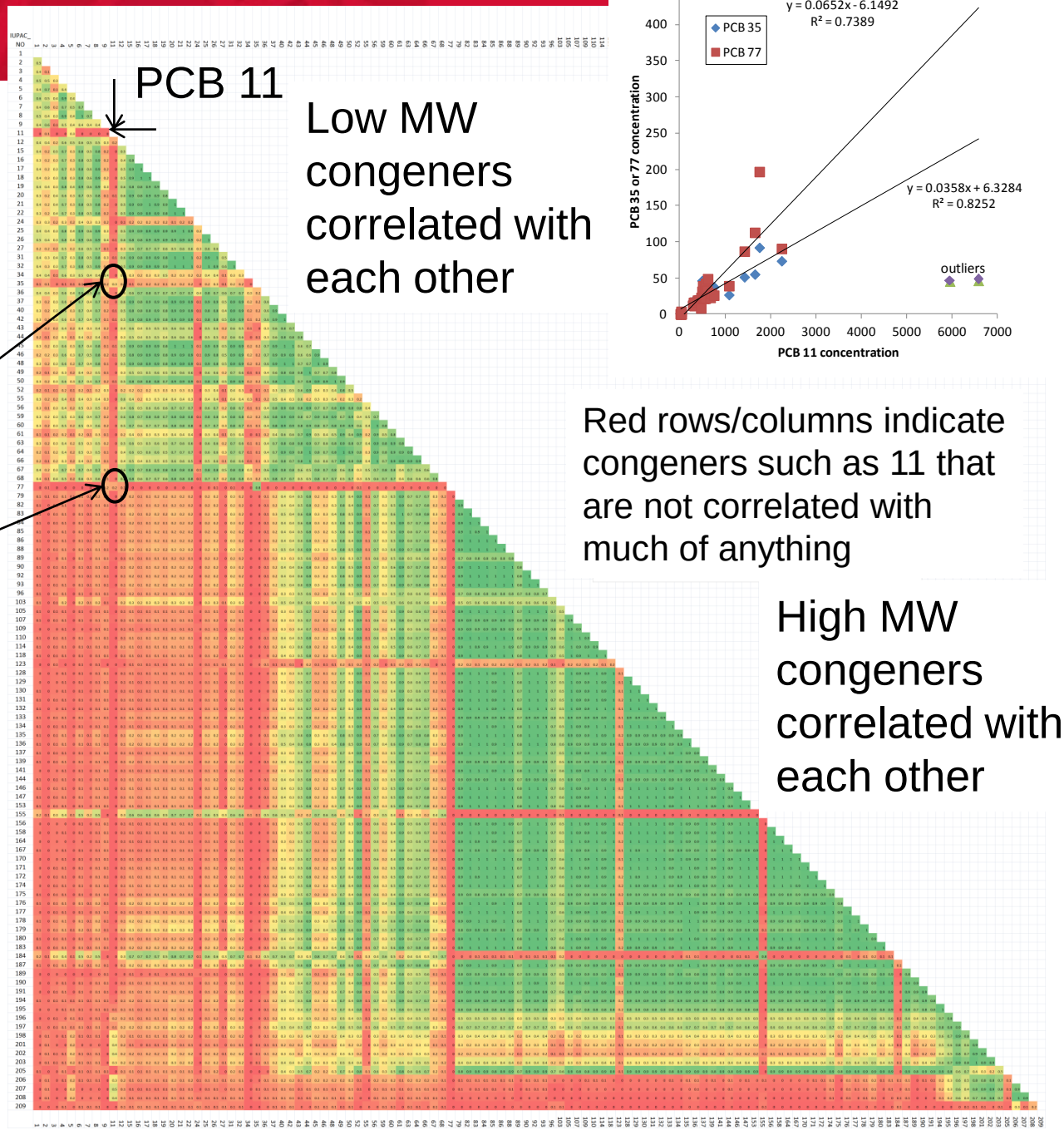
Correlation matrix

Red = low R
Green = high R

PCB 11 (3,3')
correlated
with PCB 35
(3,3',4)
and PCB 77
(3,3',4,4')
(see also Litten et al. 2002)

PCB 77 is dioxin-like and accounts for 0-25% (median 1.8%) of TEQ.



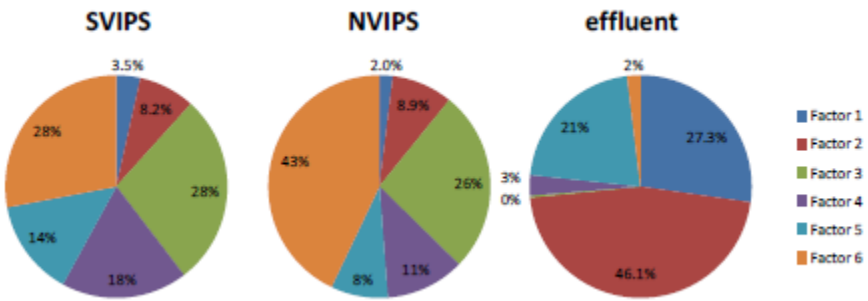
Low MW congeners correlated with each other

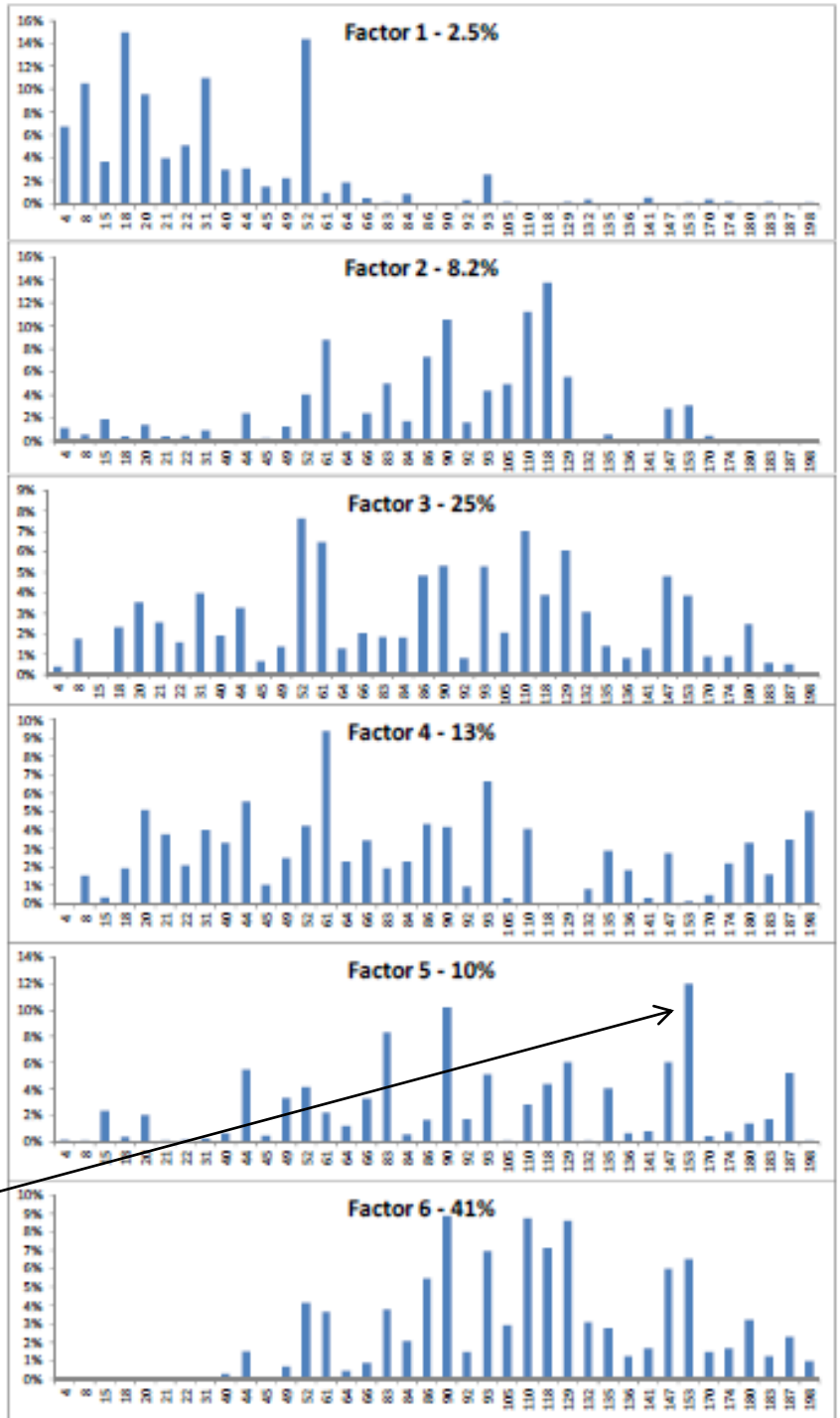
Red rows/columns indicate congeners such as 11 that are not correlated with much of anything

High MW congeners correlated with each other

PMF results

- Not yet enough data to do a full PMF analysis (will be soon)
- Factors 2, 3, and 6 look like Aroclors





Lots of PCB 153 might indicate bioaccumulation (i.e. food)

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Conclusions

- 1668 yields powerful data but…
  - It has to be collected and managed carefully
  - And analyzed with powerful tools
- Fingerprinting can help track down sources and processes
- Non-Aroclor sources are showing up everywhere (more than just PCB 11)
- Dechlorination (with its weird congener pattern) can happen in more places than you think
- Fingerprints look more like Aroclors close to the source in time and space, but less and less as they move away

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Acknowledgements:

Money ± Data:

HUDSON RIVER FOUNDATION for Science & Environmental Research

new jersey department of environmental protection

Environmental Sciences Rutgers University

Delaware River Basin Commission

RUTGERS New Jersey Agricultural Experiment Station

Rutgers Office of Technology Commercialization

Spokane County, WA

Data:

NEW YORK STATE DEPARTMENT OF ENVIRONMENTAL CONSERVATION

United States Environmental Protection Agency