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Inadvertent PCBs: An Introduction

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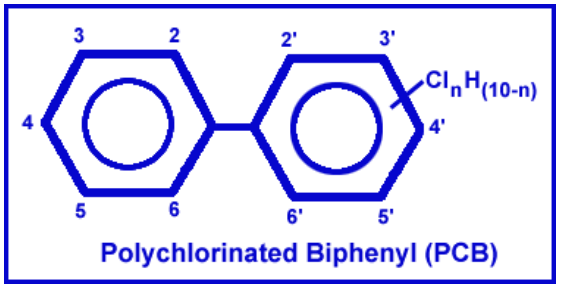
PCBs



PCBs consist of 209 congeners, which may have 1 to 10 chlorines.

A group of congeners having the same number of chlorines is a "homolog group"

PCBs were previously sold as "Aroclors" and used as fluids in electrical equipment, particularly transformers and capacitors.

They were used for their high dielectric properties and flame resistance.

Many other uses: carbonless copy paper, plasticizer in paint, etc.

The manufacture, processing, and distribution in commerce of PCBs were 'banned' in 1976 due to concerns over their toxicity and persistence in the environment.

About 1.3 million metric tons of PCBs were produced world-wide.

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TSCA contains a loophole allowing for inadvertent production of PCBs

Under TSCA, the inadvertent production of PCBs is allowed.

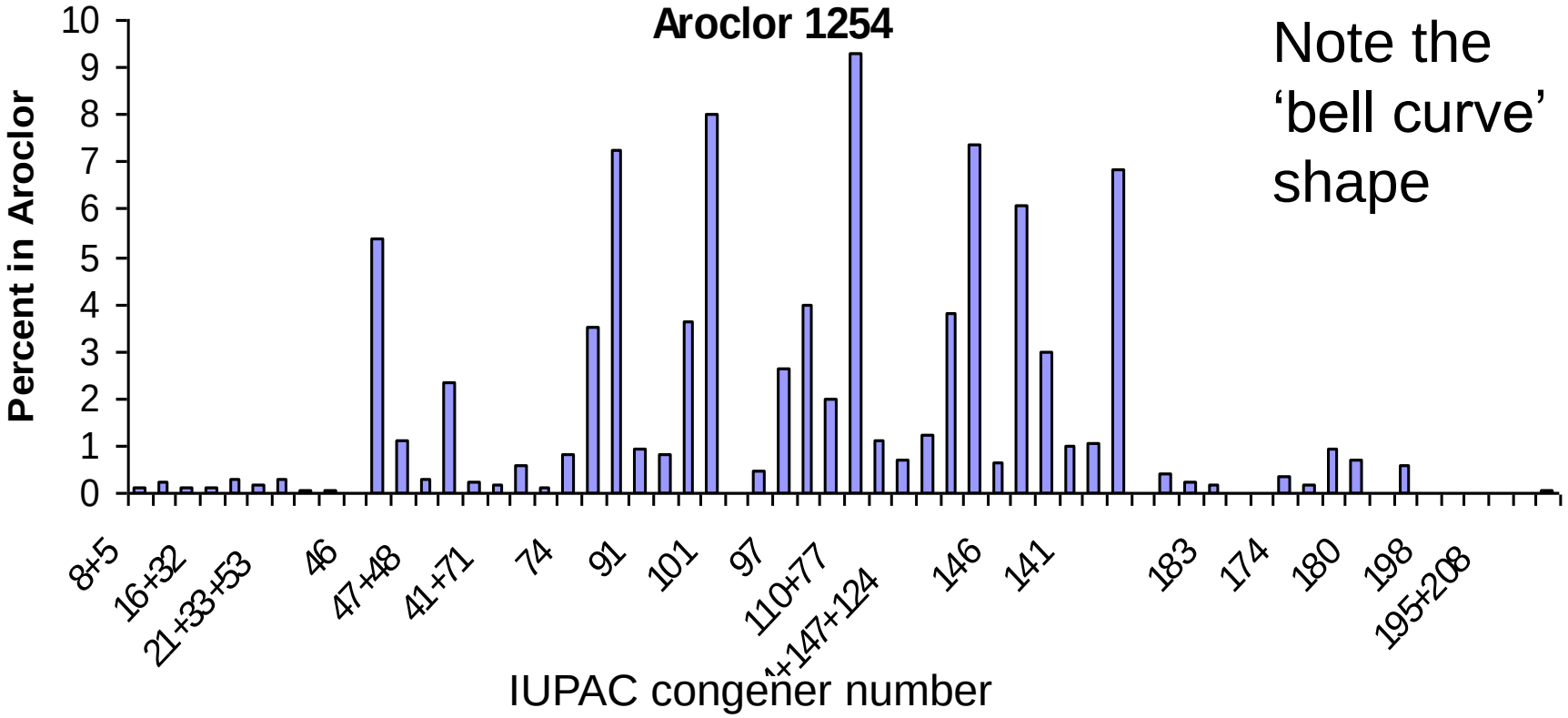
PCB concentrations in the product have to average less than 25 ppm and can be no higher than 50 ppm

BUT, the concentrations of monochlorobiphenyls are divided by 10, and dichlorobiphenyls by 5.

(Pigment process waste is classified as hazardous waste)

Transfer of PCBs in a concentration of 50 mg/kg or over is prohibited by the Stockholm Convention on Persistent Organic Pollutants.

PCBs size affects physical properties



Note the 'bell curve' shape

Fewer Cl → **More Cl**

Lighter MW → **Heavier MW**

More in gas/dissolved phase → **More in solids**

Aroclor Production

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

(Brown 1994)

Last two numbers represent chlorine content (wt%)

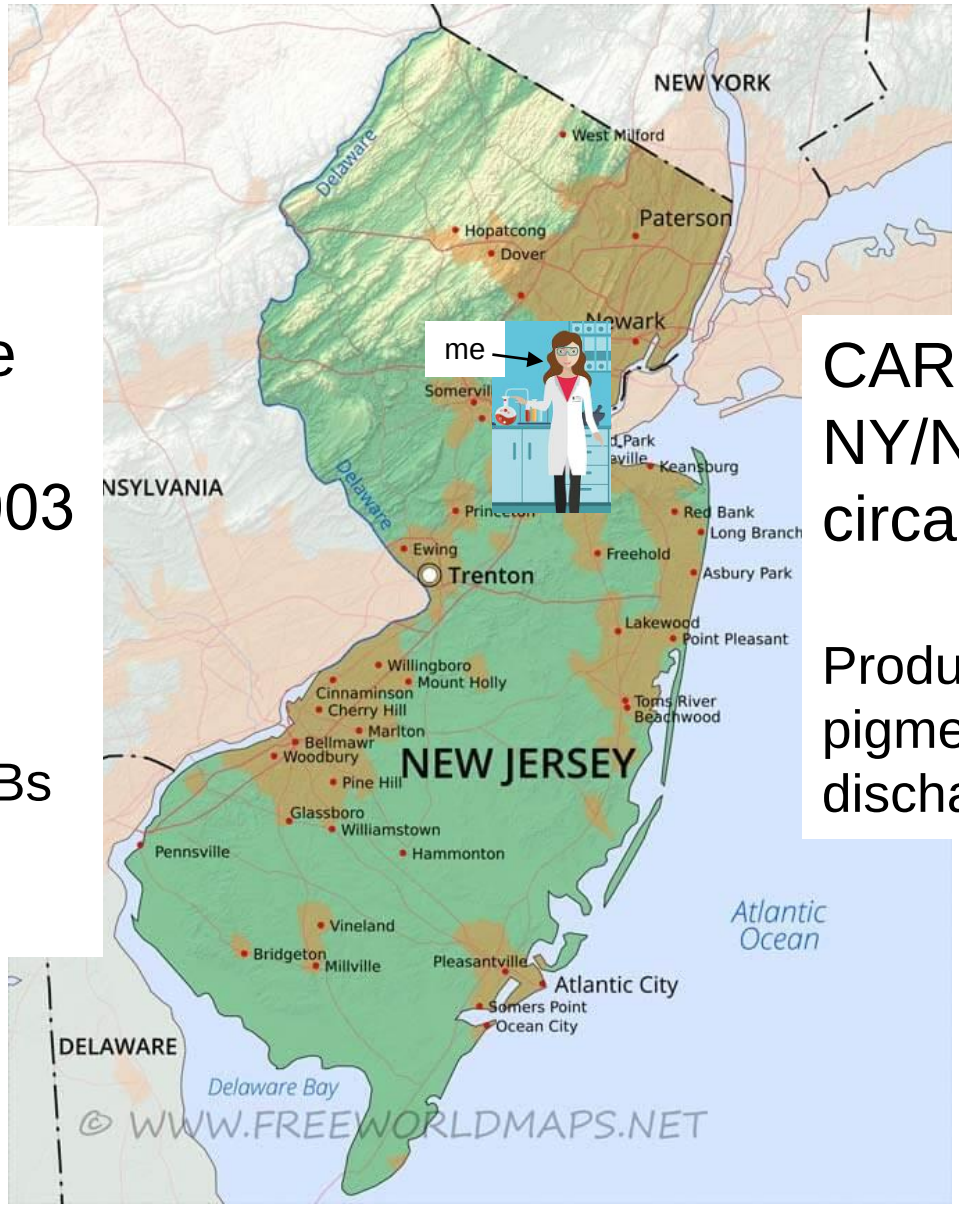
Usually can't discern between 1016 and 1242

And other Aroclors: 1270, 1272, which were mostly PCB 209

My history

TMDL for PCBs in the Delaware 'done' in 2003

Production of $TiCl_4 \rightarrow TiO_2$ produced PCBs 206/208/209 (a lot!)



CARP in the NY/NJ Harbor circa 2001

Production of pigments discharged PCB 11

Since then, I've looked at PCB data from:

- NY/NJ Harbor
- Delaware River
- Chicago
- San Francisco Bay
- Duwamish River
- Portland Harbor SS
- Newtown Creek SS
- Upper Hudson River
- New Mexico
- Houston Ship Canal
- Washington, DC
- Passaic River

- Surface Water
- Sediment
- Air/atm deposition
- Biota
- Dischargers
- Groundwater
- Stormwater
- Wastewater/CSO
- Biofilm
- Consumer products

Main PCB sources in most watersheds

- **AROCLORS!**
  - Legacy?
- Inadvertent PCBs
- Things that alter Aroclor fingerprints and can *seem* like a different source:
  - Reductive dechlorination by bacteria
  - Metabolism by biota

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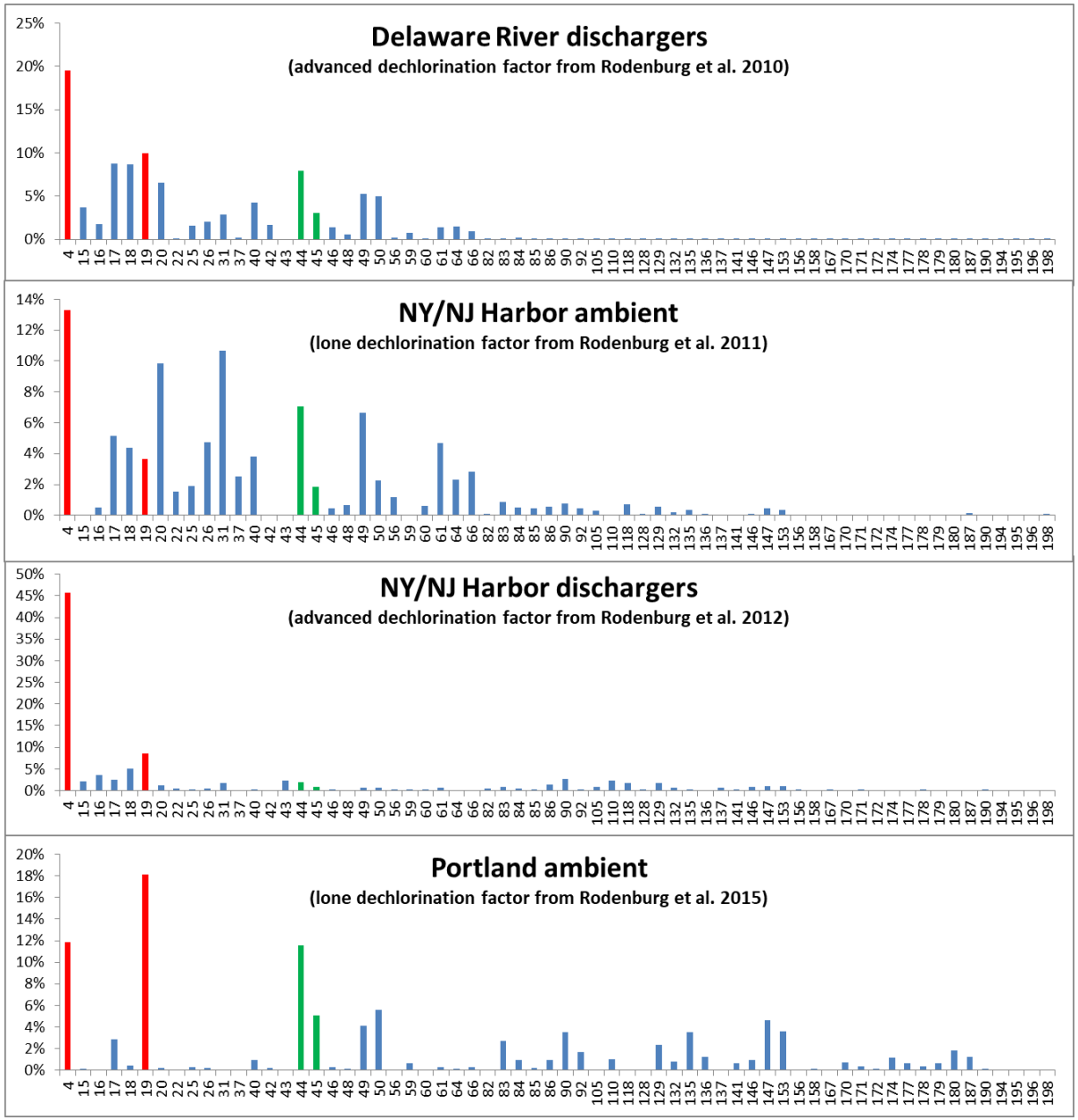
Various dechlorination profiles

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

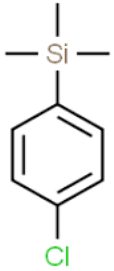


Main inadvertent non-Aroclor PCB sources

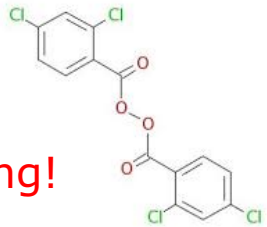
- Organic pigments, especially diarylide yellow, contains primarily PCB 11, among many others
  - PCB 11 sometimes correlated with 35 and 77

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

- Silicone from chlorophenyl silanes produces PCBs 1, 2, 3 etc.



- Peroxide-cured polymers produces PCBs 68, 44 and 45, etc.
  - Don't sample using silicone rubber tubing!



bis(2,4-dichlorobenzoyl) peroxide

This list is not complete…

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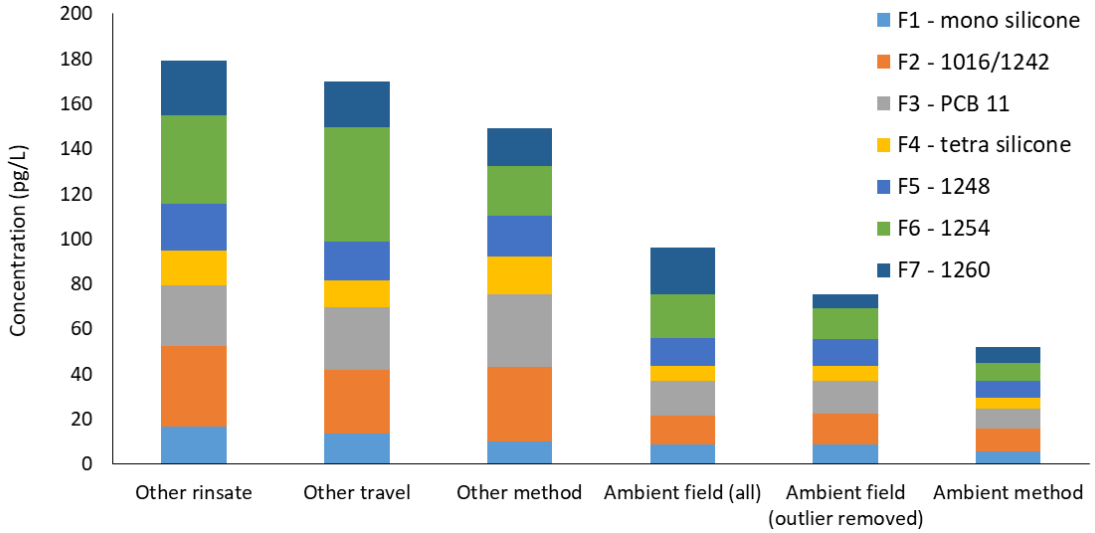
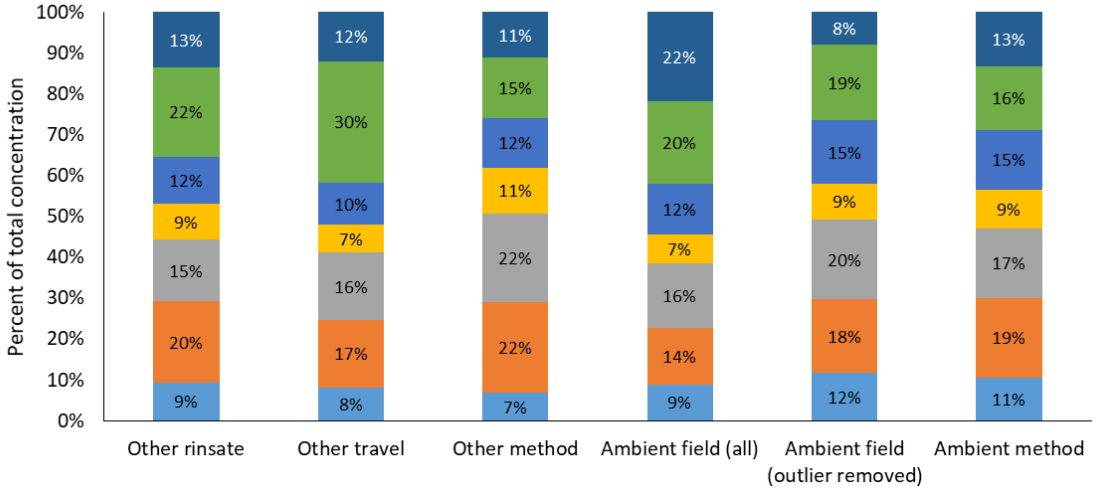
Lab blanks – PCB sources





Are the PCBs in your samples really from the river?

Or are they from blank contamination?

About 1/3 of the PCBs in blanks are inadvertent

Rodenburg, Hermanson, and Sumner, *Environmental Forensics*, in review

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Are the PCBs you see inadvertent?

- Some congeners are in both Aroclors and inadvertent sources:
  - PCB 209 can come from TiO_2, green pigment, foundry wax or Aroclors 1260, 1262, 1268, 1270, and 1272.
  - PCBs 44+47+65 and 45+51 can come from Aroclors, peroxide-cured polymers, dechlorination
  - PCBs 1, 2, 3, 4, 8, 15, etc. can come from dechlorination, phenyl silicone, or Aroclor 1232

- Use fingerprinting, spatial and temporal variations, history, and judgement to determine sources

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Examples

- PCB 209 is probably from…
  - TiO_2 production in the Delaware River
  - Green pigment in hydroseed
  - Foundry wax in very old sediment (pre-WWII)
  - Aroclors in Los Alamos stormwater, because we also found Aroclor 1262
- PCBs 1, 2, and 3 are probably from…
  - Adhesives in an unnamed Superfund Site
  - Dechlorination in the Upper Hudson River
- PCB 44+47+65 and 45+51 are probably from…
  - Aroclors when they fit the Aroclor profile (most places)
  - Peroxide-cured silicone when PCB 68 is also present
  - Dechlorination when PCBs 4 and 19 are also present

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Fingerprinting

- Uses software to find co-varying congener patterns
- Works best when you have:
  - A lot of samples
  - Many congeners measured, hopefully by Method 1668
- Can (often) tell you:
  - Which Aroclors are present
  - Which inadvertent sources are present
  - Which processes are occurring (dechlorination, metabolism)
- BUT, sometimes PCBs travel together even though they are from a different primary source

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!

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

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

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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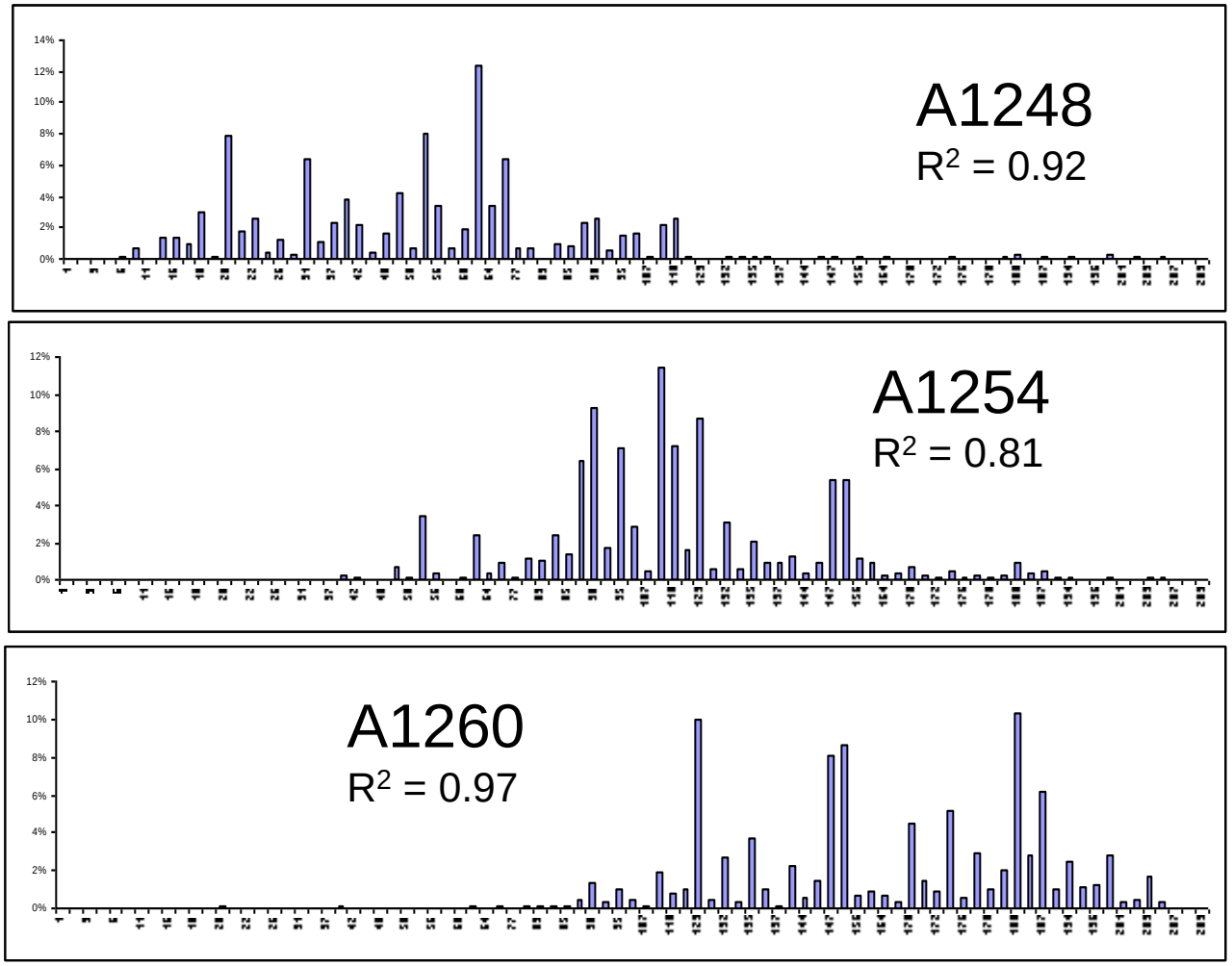
Delaware River Dischargers

(Rodenburg et al. ES&T 2010)

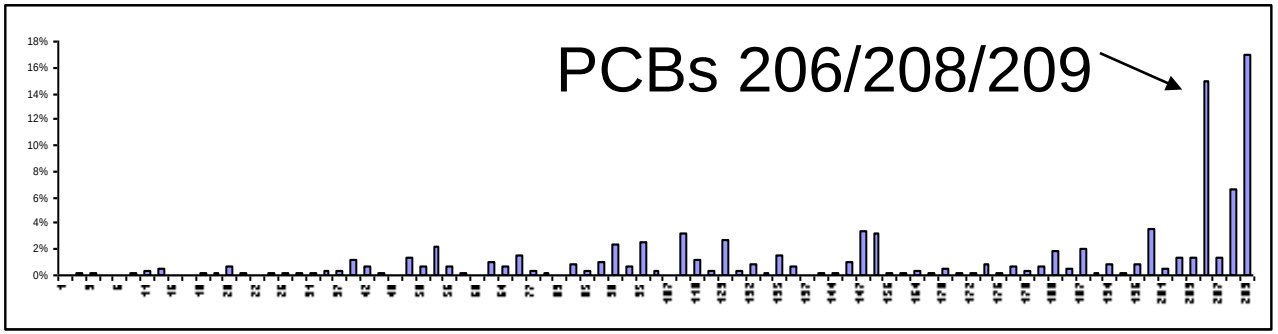
7 factors:

3 look like Aroclors

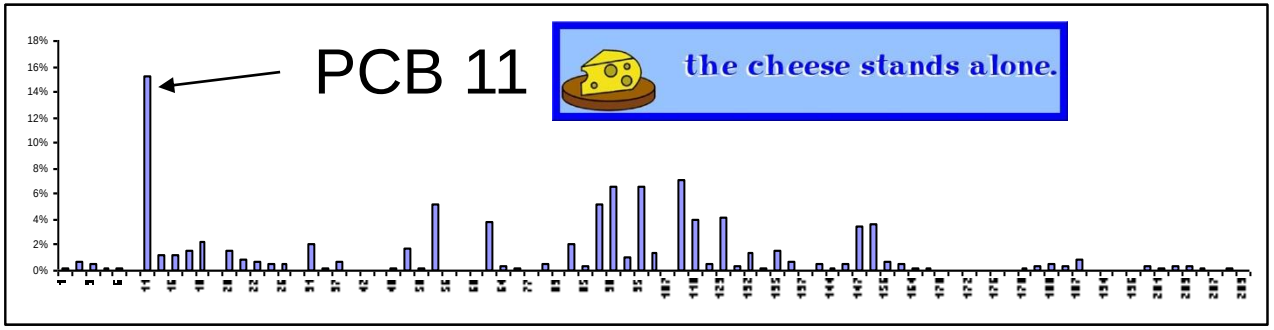


Two Non-Aroclor factors

Production of TiO_2 at Edgemoor

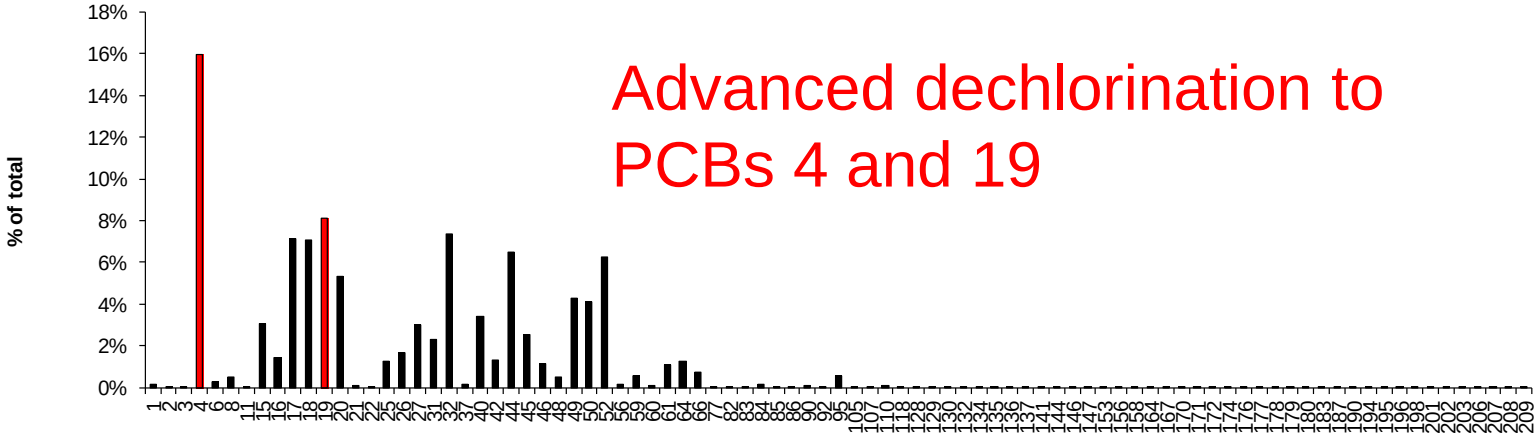


PCB 11 from pigments – tracer for treated wastewater/CSO/ stormwater runoff

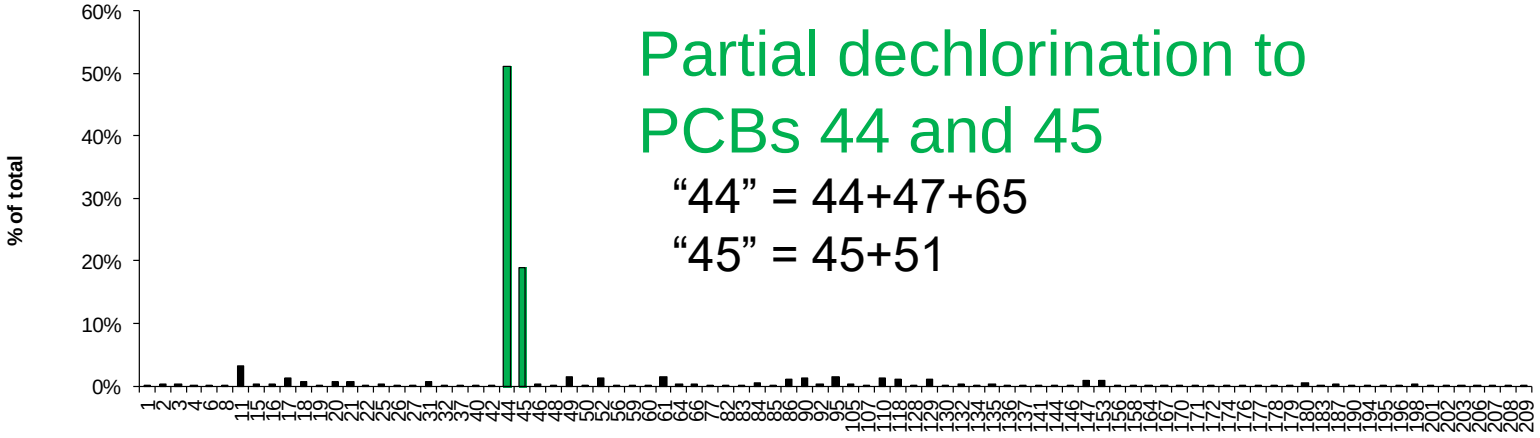


See Du et al. ES&T 2008; Rodenburg et al. ES&T 2010

Two factors are dechlorination signals



Advanced dechlorination to PCBs 4 and 19



Partial dechlorination to PCBs 44 and 45

"44" = 44+47+65

"45" = 45+51

See Du et al. ES&T 2008; Rodenburg et al. ES&T 2010

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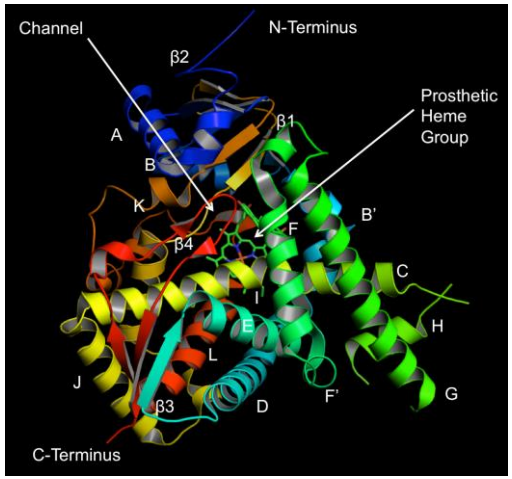
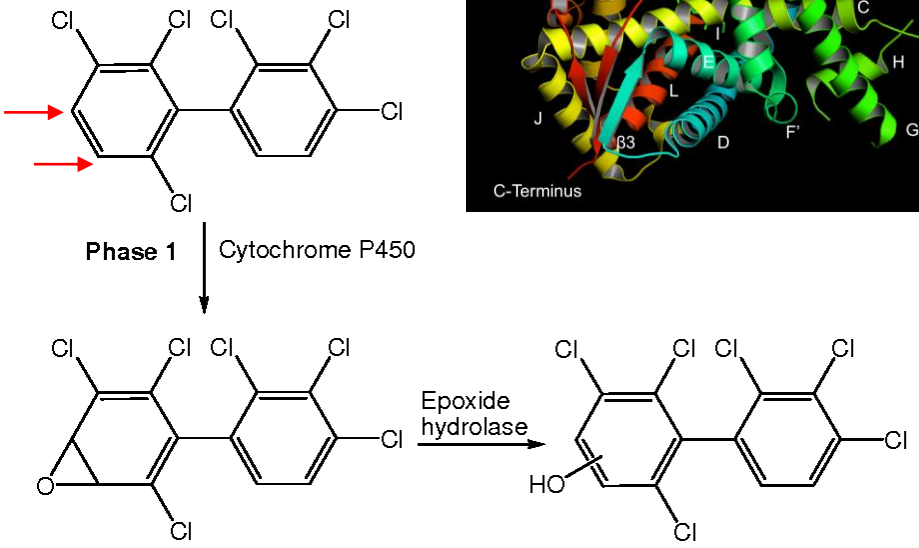
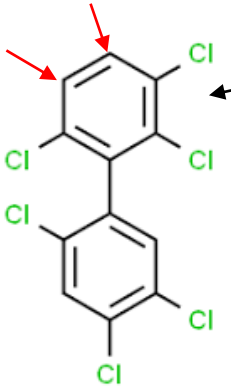
Metabolism by biota

- Cytochrome P450 (CYP) can oxygenate some PCB congeners
- CYP450 likes to attack two adjacent unsubstituted carbons

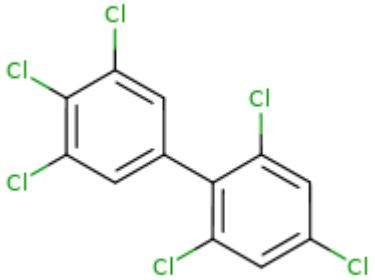






PCB 149 has two adjacent open positions

PCB 168 does not



Both have 6 Cl, so should behave the same otherwise

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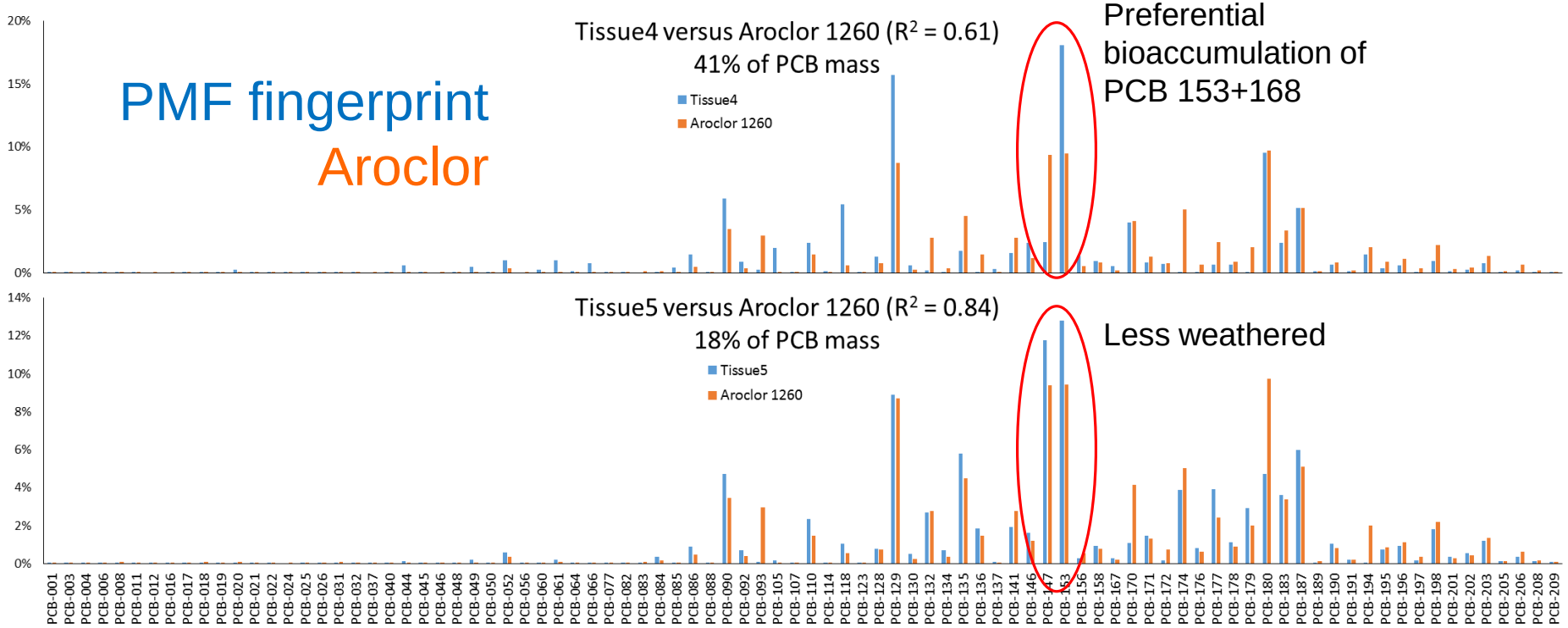
Biota from Duwamish

Five factors:

All resemble single Aroclor or mix

Two factors resemble 1260, one more weathered



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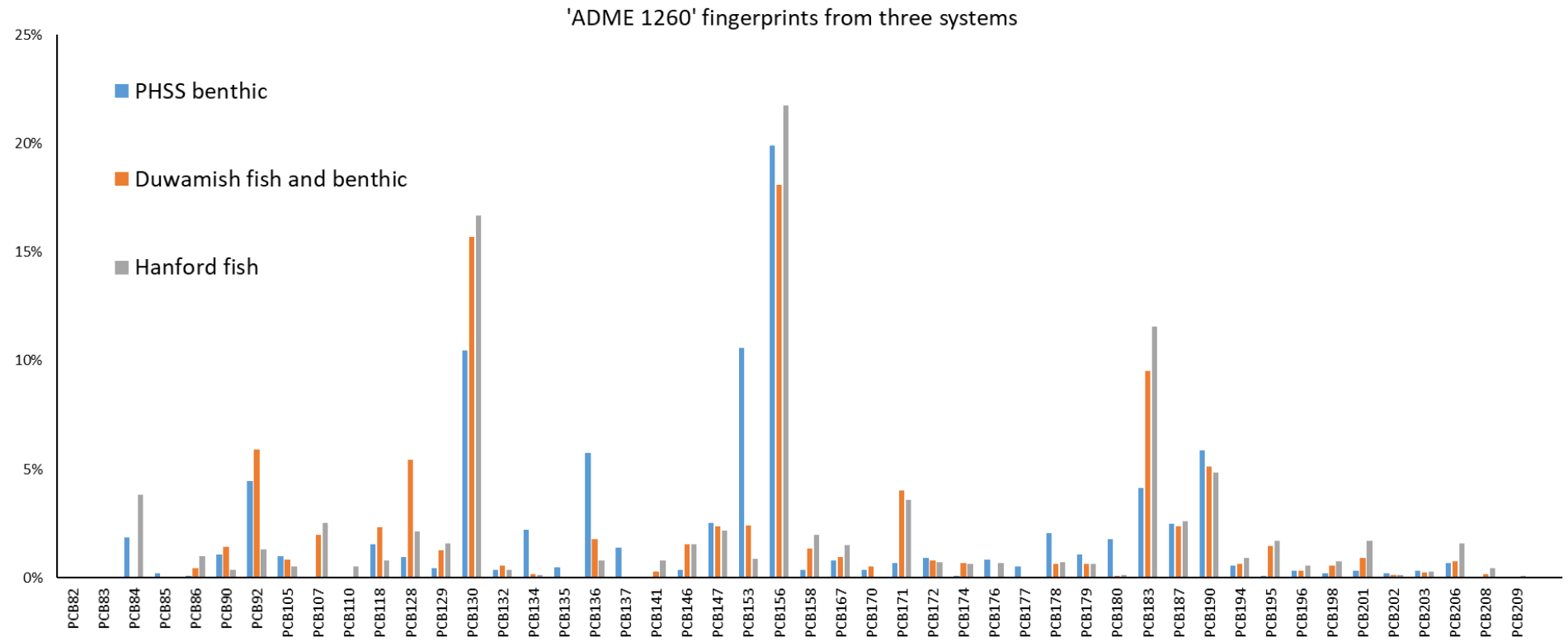
Metabolism looks the same everywhere



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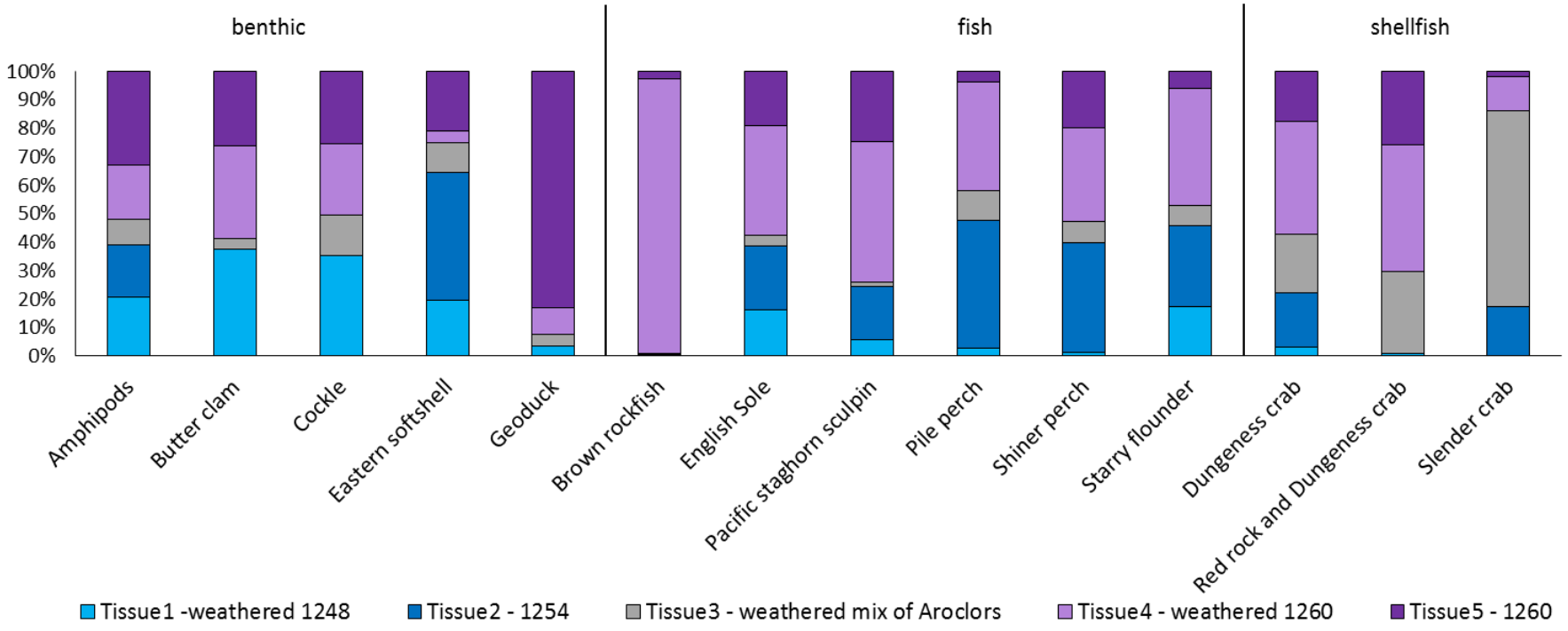
And in all species



- Species vary in their ability to metabolize PCBs
  - Data from Duwamish River

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Other indicator congeners for metabolism

Ratio	90+101+113/ 83+99	147+149/ 153+168	134+143+139+140+ 146+147+149+165/ 153+168	141/ 153+168	174/ 180+193
Homologue	**penta**	**hexa**	**hexa**	**hexa**	**hepta**
Organisms:					
Field clam	**1.7 ± 0.1**	0.46 ± 0.1	**0.62 ± 0.13**	**0.0195 ± 0.008**	**0.22 ± 0.06**
Lab clams	**1.6 ± 0.1**	0.25 ± 0.1	**0.36 ± 0.13**	**0.016 ± 0.011**	**0.14 ± 0.09**
Lab worms	**1.7 ± 0.2**	1.1 ± 0.1	**1.4 ± 0.3**	**0.080 ± 0.032**	**1.2 ± 0.3**
Mussels	**1.7 ± 0.2**	0.78 ± 0.07	**1.1 ± 0.1**	**0.18 ± 0.01**	**0.42 ± 0.05**
Sediment	105 ± 110	Not available	4.2 ± 1.5	3.4 ± 0.4	0.6 ± 0.07
Aroclors:*					
1016	1.7	1.1	1.2	0.12	9.3
1242	1.1	0.93	1.3	0.29	15
1248	1.161 ± 0.004	1.10 ± 0.01	1.50 ± 0.01	0.328 ± 0.001	6.0 ± 0.3
1254	2.1	1.0	1.3	0.26	7.2
1260	35	0.99	1.2	0.29	5.7

Data from Portland Harbor SS (Rodenburg et al. 2019)

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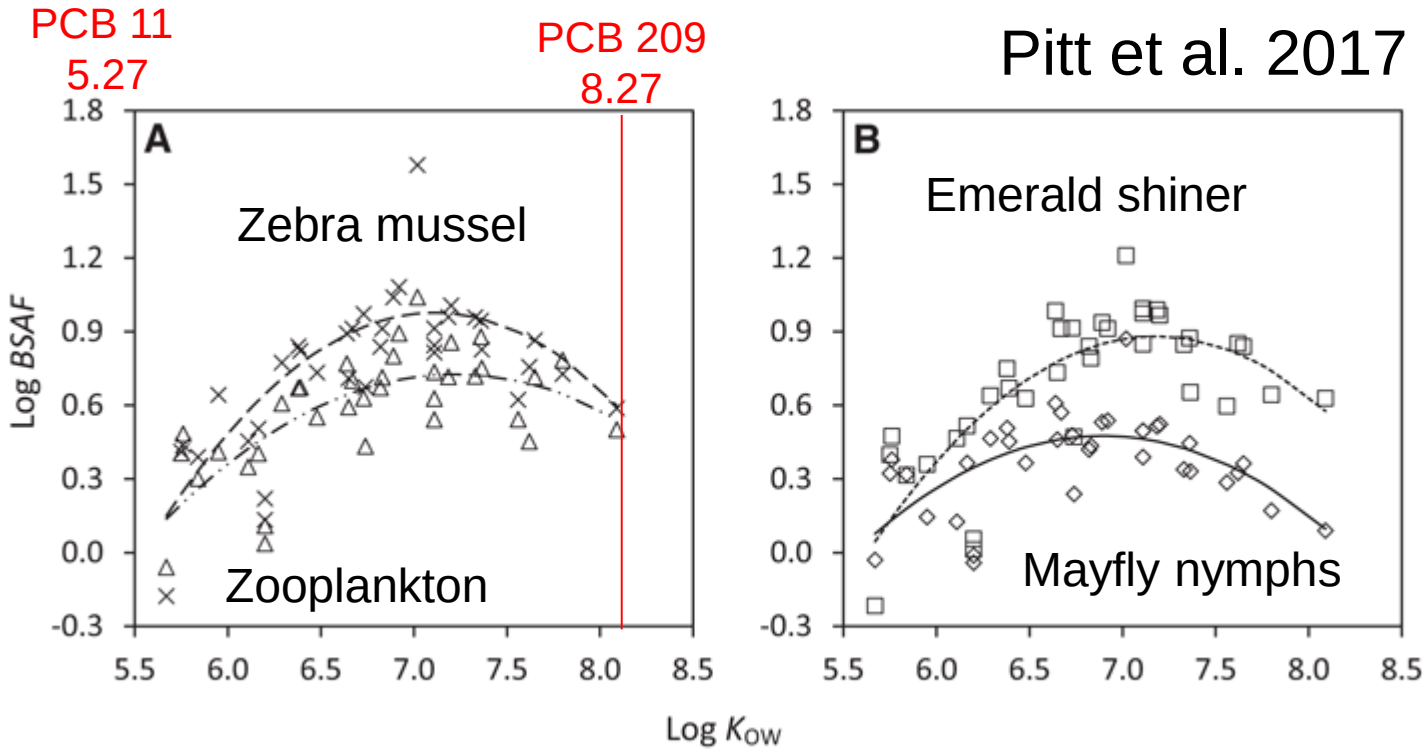
Really advanced metabolism (otter scat)

- Very little of the original Aroclor left

Bioaccumulation



- Bioaccumulation (BSAF) is not a direct function of size/hydrophobicity
- Some of the most common iPCBs don't bioaccumulate as efficiently as other PCBs

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Toxicity of PCB 11

- Not a lot known
- Kodavanti 1995:
  - neurochemical effects in rat cerebellar granule cells
- Roy et al. 2019:
  - can affect liver development
  - act as a partial agonist/antagonist of the Ahr pathway
  - and act as an antagonist of Cyp1a activity to modify the toxicity of compounds that interact with the Ahr pathway
- Pradeep et al. 2019:
  - Has a relatively high (top 20% among PCBs) Neurotoxic Equivalency Factor (NEF) of 0.336
- Tehrani and Van Aken 2014:
  - Hydroxylation of low MW PCBs yields toxic products

Notably, PCBs 1, 4, 19, 47, and 51 have even higher NEFs

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Conclusions

- Aroclors are still usually the main source of PCBs
- Inadvertent PCBs are showing up nearly everywhere
- But maybe they're just coming from blank contamination?
- It's not just PCB 11
- Some of the most common iPCBs are not bioaccumulated as efficiently as other PCBs
- Not a lot known about the toxicity of iPCBs, but what we know isn't good