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PCB fingerprinting at the Newtown Creek Superfund Site

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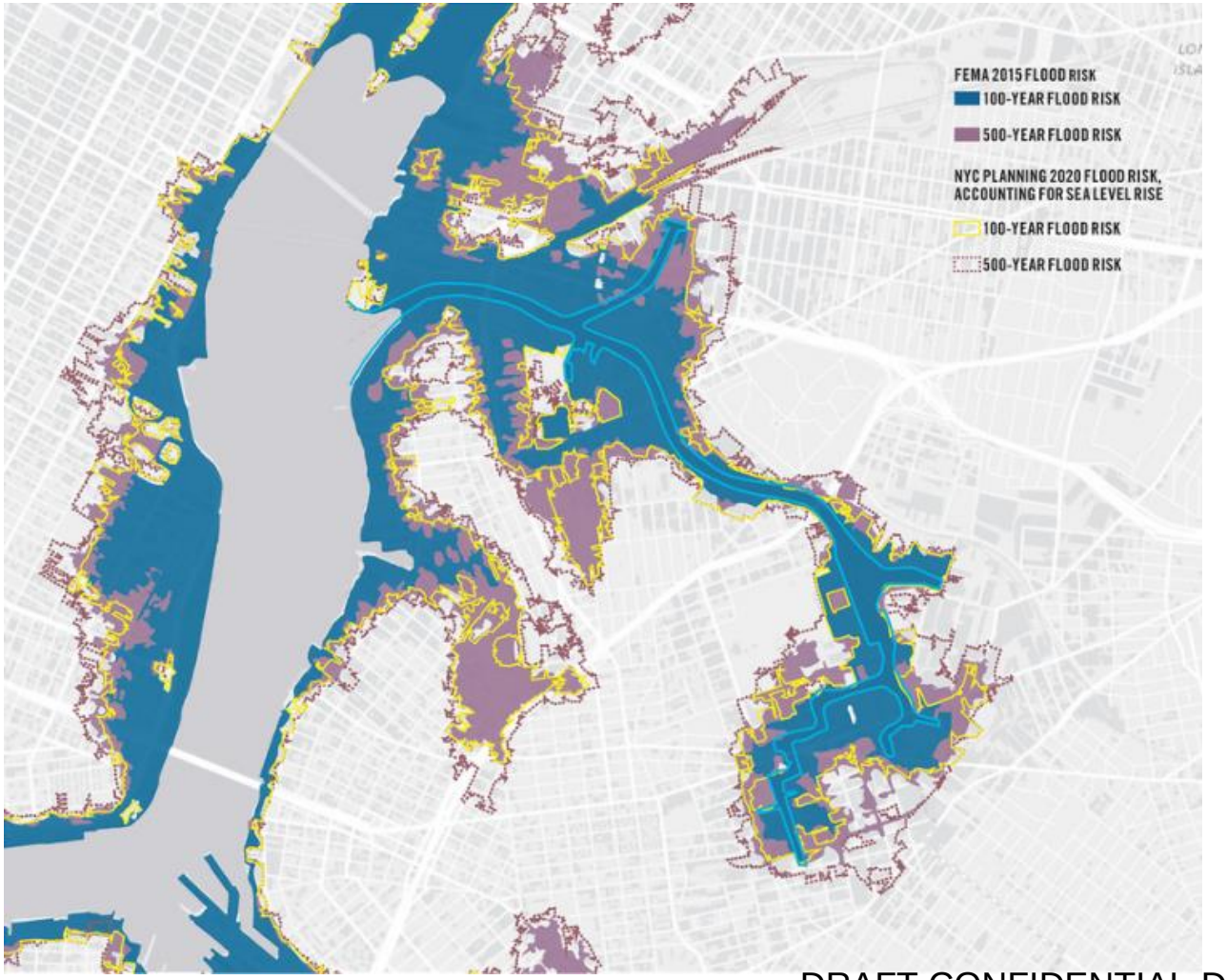
https://www.riverkeeper.org/campaigns/restore-nyc-waterways/newtown-creek-vision-plan/

Flood risk



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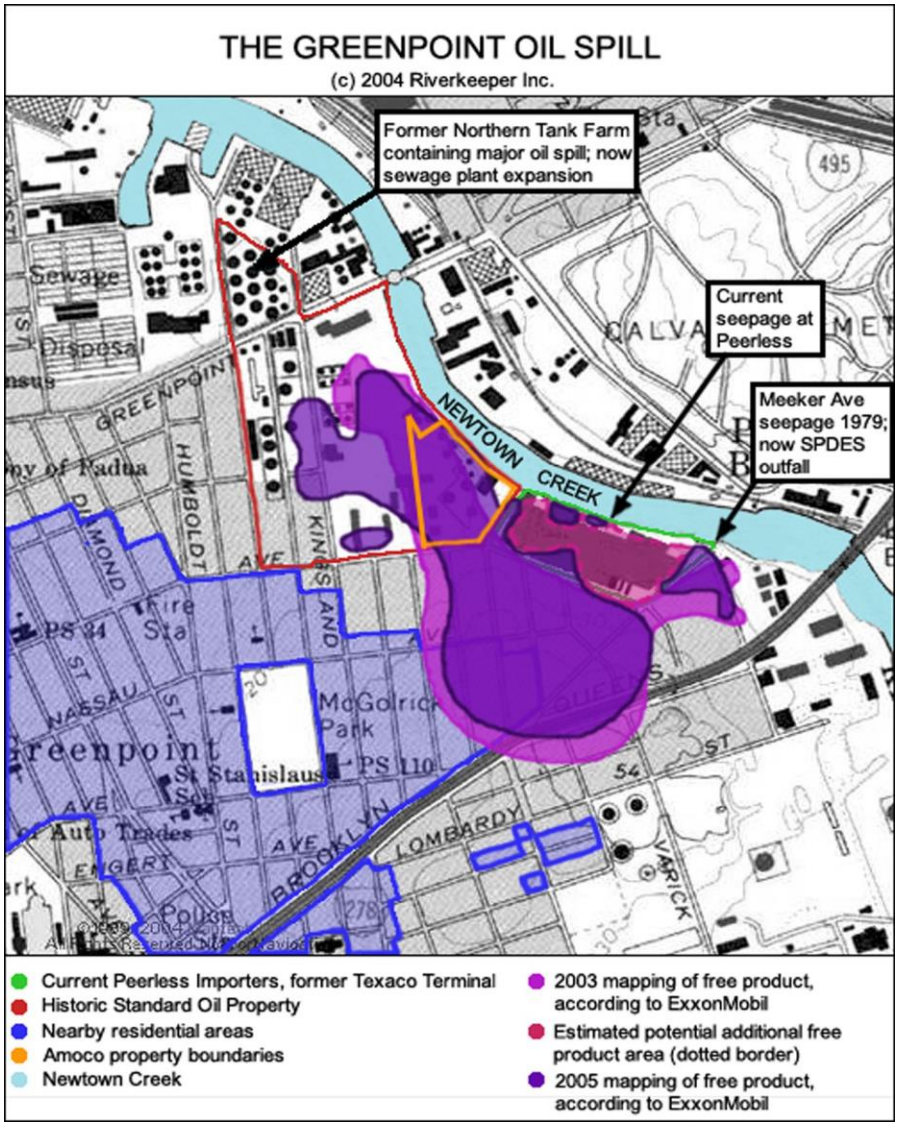
Newtown Creek

- Superfund site in NYC
- Greenpoint Oil "Spill"
  - PAH contamination
- PCBs still a main driver of remedy
- ROD due in 2028
- Chevron has funded our work on fingerprinting of PCBs at the site
- Multiple PCB sources!



Fingerprinting Methodology

Relies primarily on Positive Matrix Factorization (PMF)

- EPA has used PMF 5.0
- We use PMF2
- Testimony under Daubert rules

Looks for co-varying analytes (unsupervised machine learning)

Identifies ‘factors’ (fingerprints) which are likely to represent specific sources

If you would like more info, watch “PMF for dummies” on YouTube

Factor Analysis Equation

Applies to Principal Components Analysis, PMF, PVA etc.

View the PCB signal as a mixture of mixtures

Some of those mixtures are **Aroclors** …some are not.

Use this equation to predict concentration of each congener, based on number, fingerprint and concentration of sources.

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 'optimal' number of sources based on model output.

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Advantages of Positive Matrix Factorization

over other models, for example Principal 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.

How to ensure good quality data

- 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)
- 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, surrogate recoveries, lat/long projection, etc.
- Public availability of data
  - And metadata! (Ex: STORET doesn't include surrogate recoveries)
  - Query is easy, output makes sense!

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Three GC columns used for method 1668

- **SPB-octyl**
  - Separates all the dioxin-like congeners except 156+157
  - **PCB 21+33, 20+28**
- **DB-5 (HP-5, RTX-5 etc.)**
  - Old faithful
  - Does not separate all dioxin-like congeners
  - **PCB 20+21+33**
  - PCB 4+10, 5+8
- **SGE-HT8**
  - Newest(?)
  - Separates all dioxin-like congeners
  - Pattern is similar to DB-5 but with fewer coelutions
  - **PCB 20+33** (21 is resolved)
  - PCB 5+8 (4 and 10 are resolved)

I have spreadsheets of the Aroclor compositions on the SPB-octyl and SGE-HT8 columns. Just ask!

PMF2 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 > 90 peaks
  - Iterative process
- **Concentration matrix:**
  - Replace BDL data with:
    - Random number between 0 and **LOD**
    - Half **LOD**
- **Uncertainty matrix:**
  - RSD of **surrogate recoveries** for detected concentrations
  - 3X this uncertainty for BDL values
- **LOD matrix:**
  - Use actual **LOD** for every data point where possible.

Metadata matters!
When LOD and unc matrix are not correct, the model doesn't always converge.

Fingerprinting of Newtown Creek sediment

- PMF analysis of PCB congener concentrations
- Mapping of PMF results against probable sources
- Inventory of PCBs, by mass, in the sediment

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Newtown Creek sediment data

- ~870 PCB samples
  - 602 in which both PCBs and PCCD/F were measured
    - 490 in which most analytes were detected
- Final data set: 490 samples, 137 peaks

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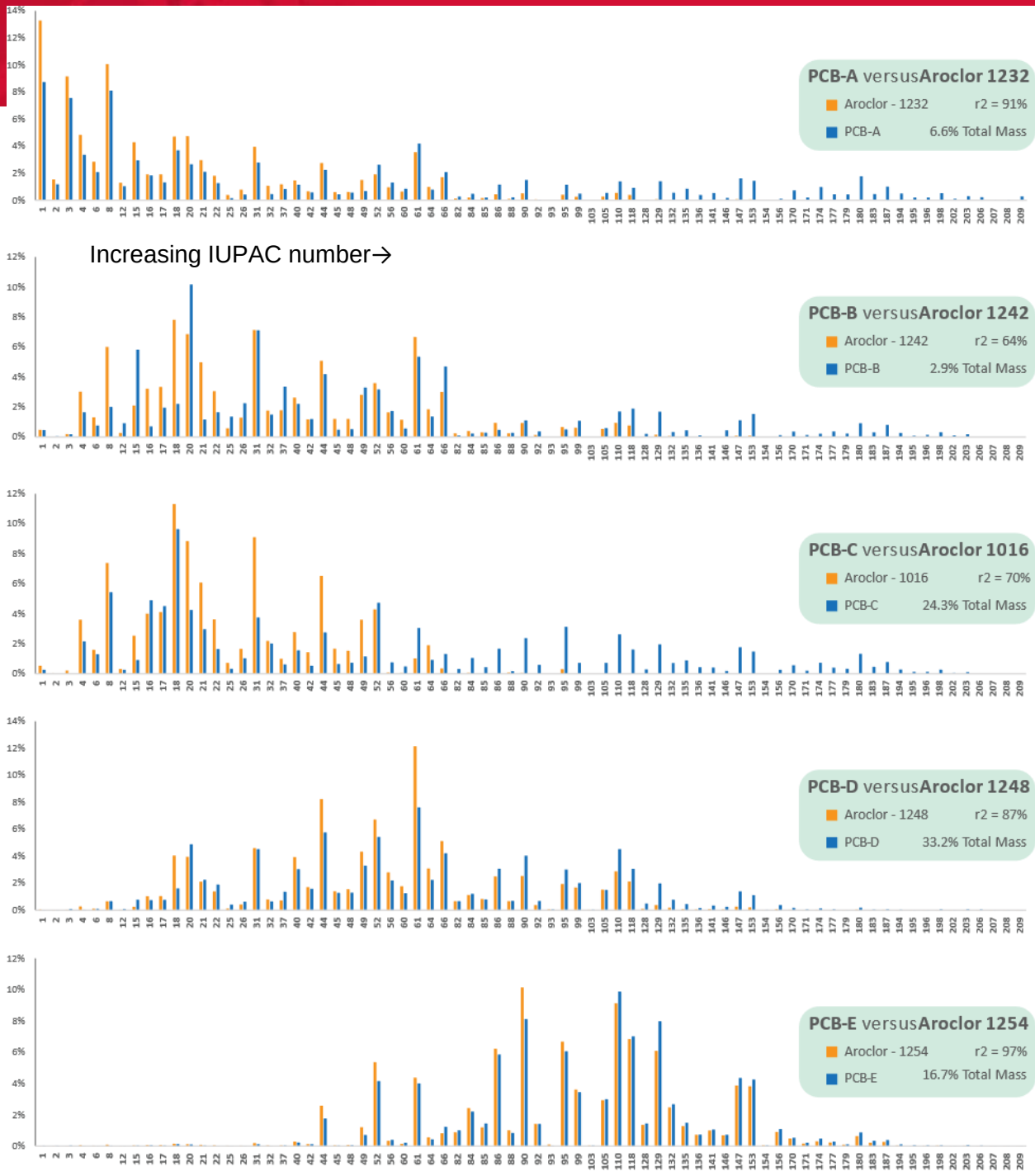
Results

- PMF analysis found 8 fingerprints or source terms
- Some resemble Aroclors



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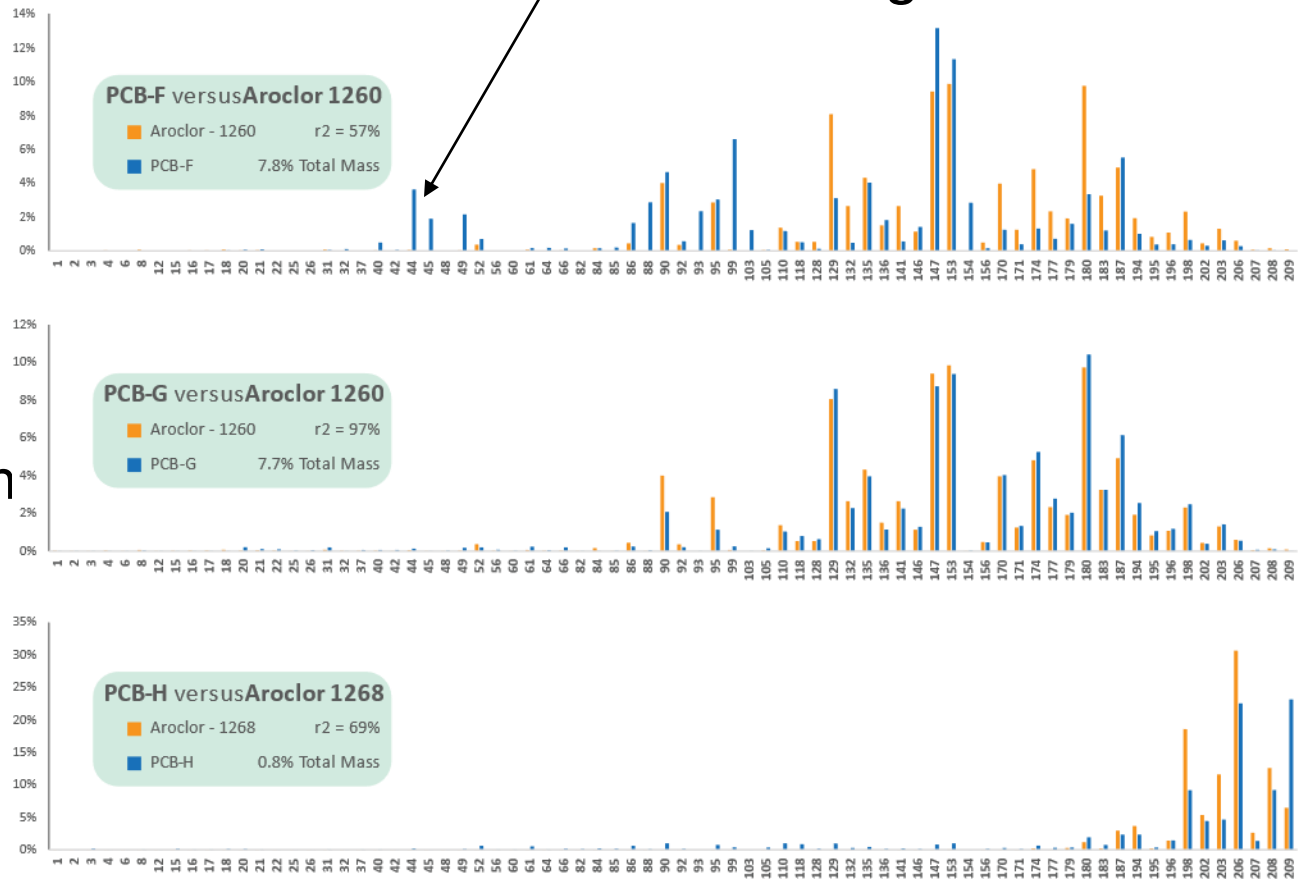
Identifying fingerprints

ID based on weight of evidence, including:

- Similarity to Aroclors
- Knowledge about degradation processes
- Spatial distribution
- Temporal distribution (depth)
- Knowledge of your system

These congeners are often products of dehalogenation



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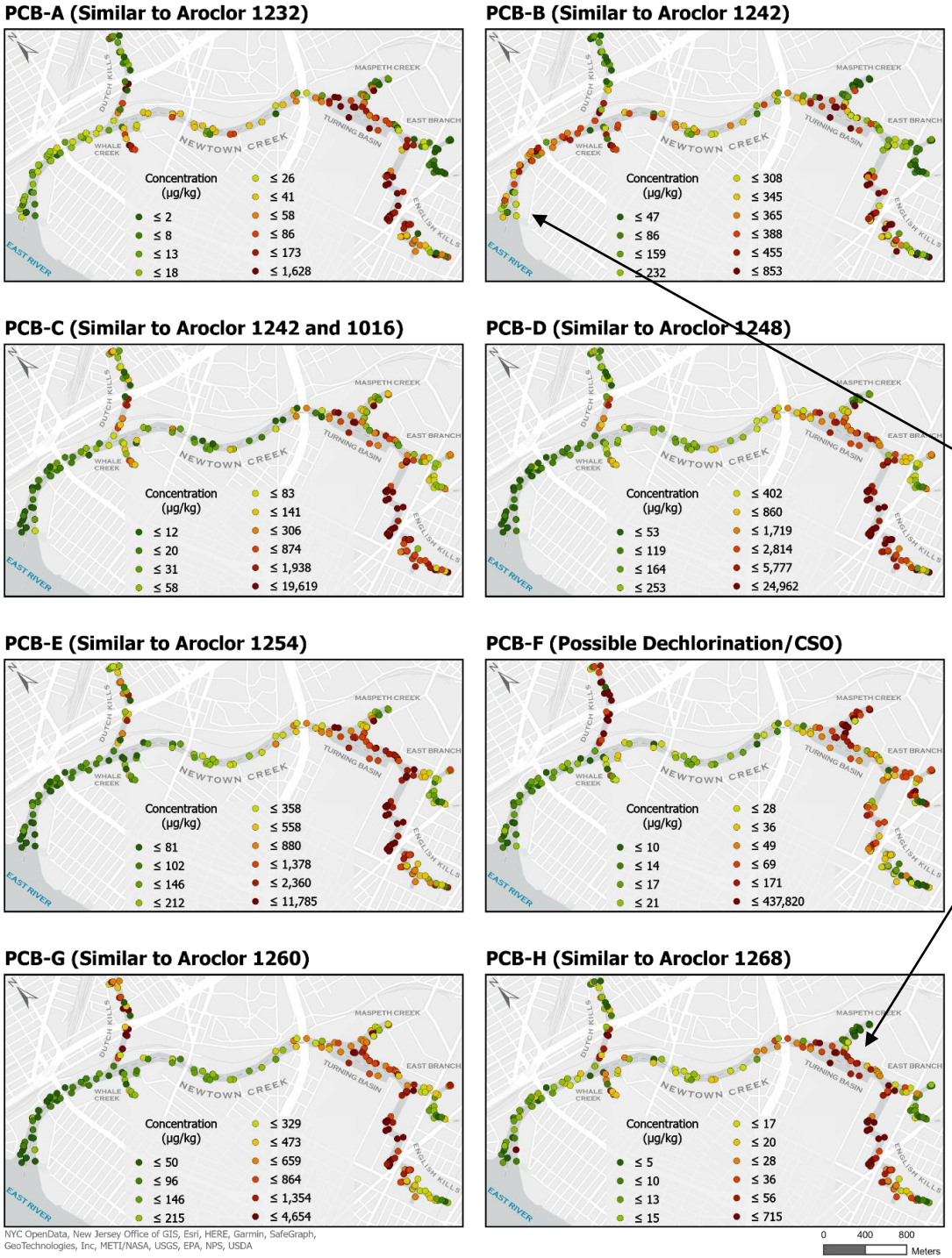


Spatial distribution of sources

- Source of PCBs from East River similar to 1242 & 1016 used by GE in the UHR
- Aroclor 1268 near former ALCOA plant

Hudson River (GE) as a source of PCBs

DRAFT

Attorney work product/ attorney-client privilege

CARP I model indicates:

- Upper Hudson River is projected to continue to be the dominant source throughout much of the Lower HR
- Significant source to Newtown Creek (projected 17% in 2023)
- Reasonable agreement with Rodenburg and Ralston (2017) fingerprinting (27% in 2000)

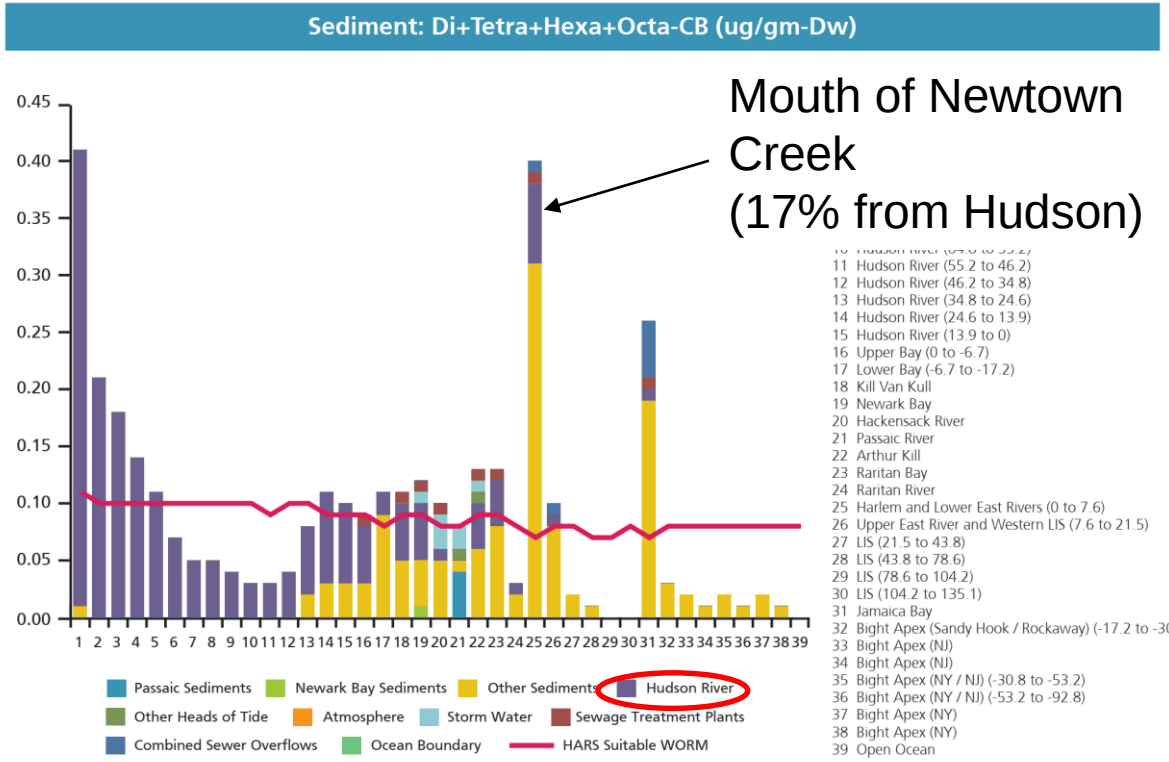
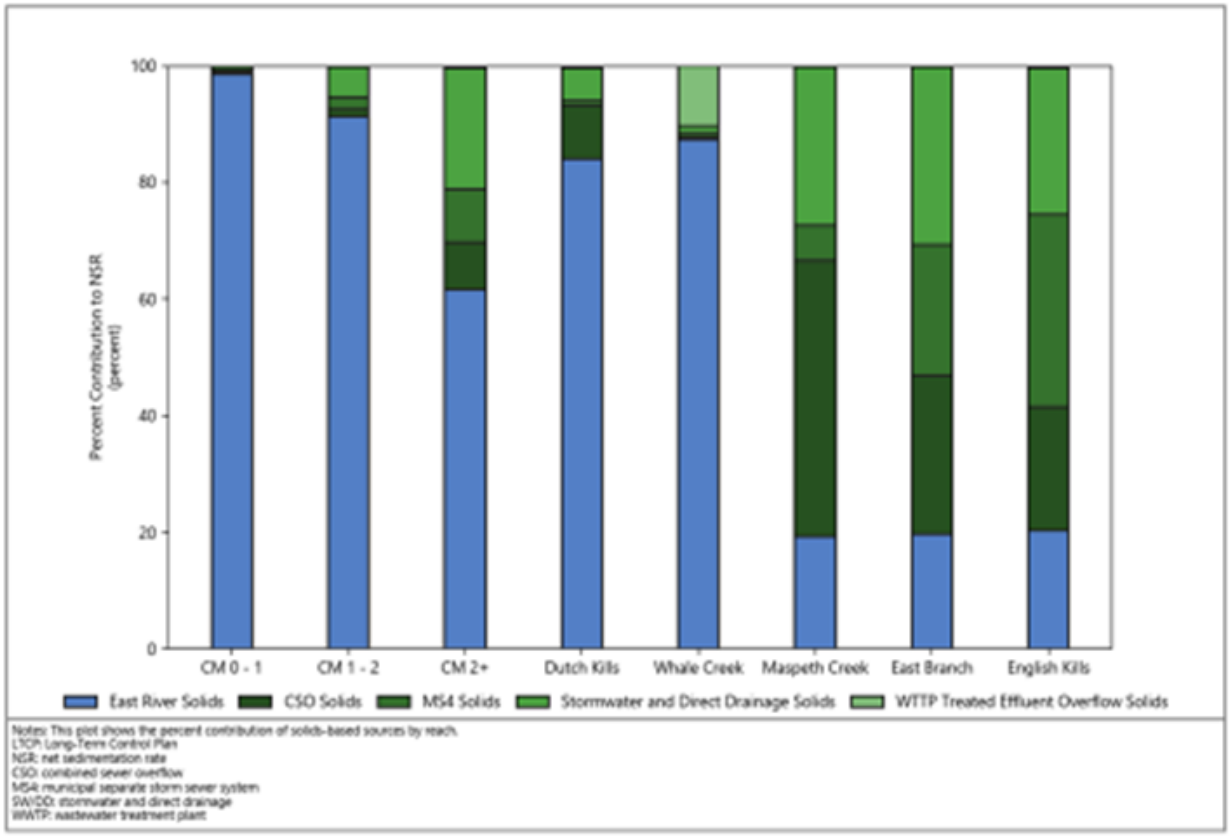


Figure 11: CARP Matrix Results: Projected PCB Concentrations in Sediment, by Source, for Various Portions of the Estuary. Concentrations Above the Red Line Indicate Exceedances of the HARS PCB Bioaccumulation Limit

Lodge et al. 2015 CARP Summary Report

Sources of solids to Newtown Creek



Percent Contribution of Solids-Based Sources to the NSR for the Post-LTCP Scenario
Interim Estimates of Long-Term Equilibrium Surface Sediment Background Concentrations
Newtown Creek RI/FS

East River solids dominate throughout much of Newtown Creek

Remedial Investigation Report

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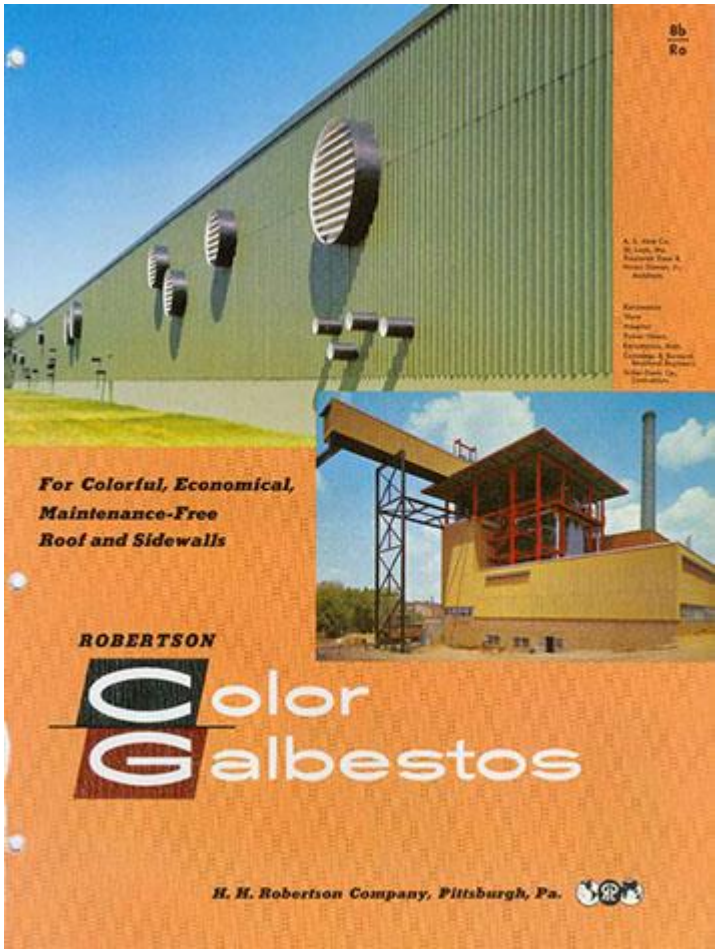
Aroclor 1268

- Less than 1% of Monsanto's Aroclor production in US
- Used in Galbestos building material
  - Used to make many military buildings during and shortly after WWII
  - Used in some foreign countries
- Primarily nona- and deca-PCBs
  - These can also sometimes be inadvertent PCBs



https://www.structuretec.com/galbestos-what-is-it-and-why-is-it-dangerous.html

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Main inadvertent non-Aroclor PCB sources

- Organic pigments, especially diarylide yellow, contains primarily PCB 11, among others

- Titanium dioxide (white pigment) may contain PCBs 206, 208, and 209
  - Kinda looks like Aroclor 1268, 1270, 1272
  - Also, Caffaro PCBs from Italy

- Silicone from chlorophenyl silanes produces PCBs 1, 2, 3 etc.
  - Kinda looks like Aroclor 1221

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

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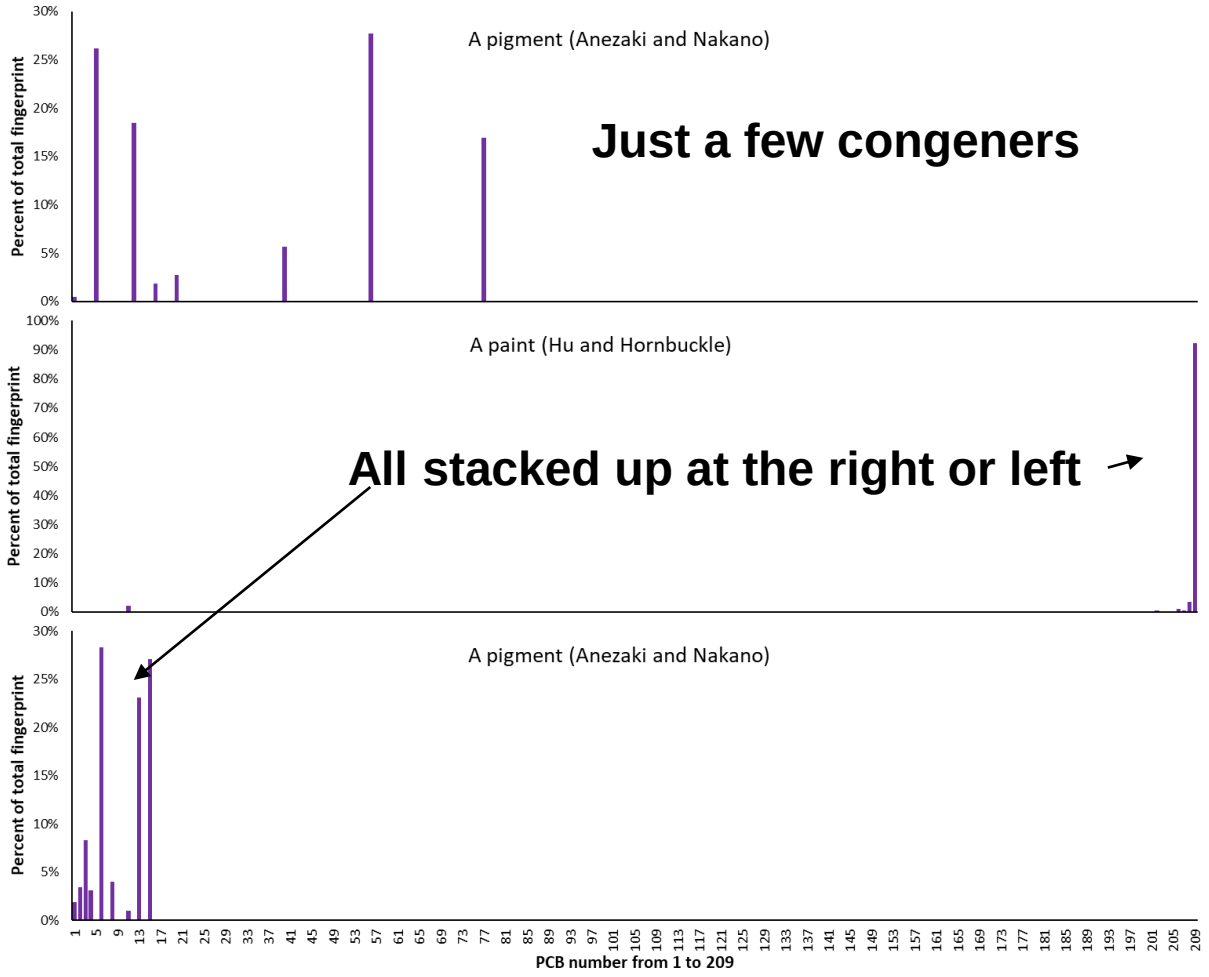
Non-Aroclor fingerprints

- Non-Aroclor fingerprints look very different from the Aroclors



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How do you know if the PCBs are inadvertent?

- Some congeners are in both Aroclors and inadvertent sources:
- PCB 209 can come from TiO_2, green pigment, foundry wax (Caffaro products from Italy) or Aroclors 1260, 1262, 1268, 1270+
- PCBs 44+47+65 and 45+51 can come from Aroclors, peroxide-cured polymers, and dechlorination of Aroclors by bacteria
- Use a weight of evidence approach to assign sources

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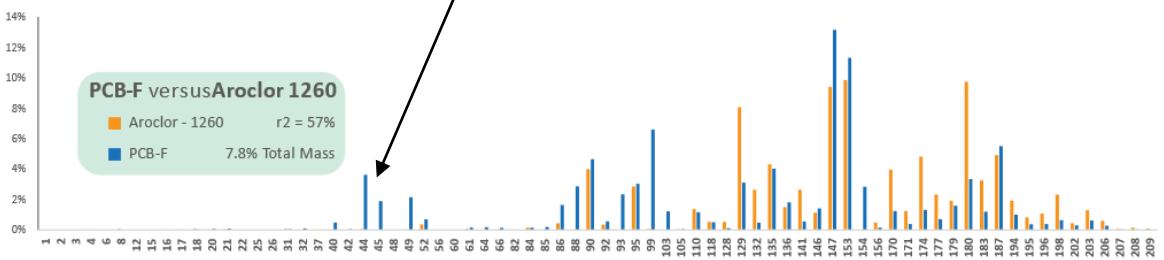
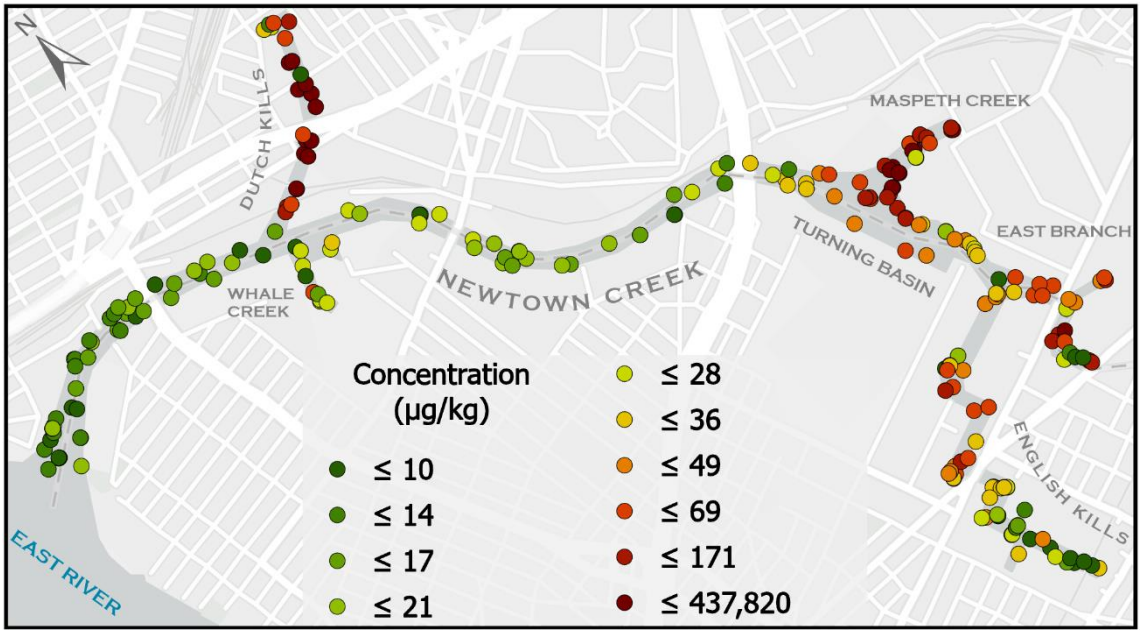
PCB-F

- Contains Aroclors & (presumably) dechlorinated PCBs
- Dechlorination definitely occurs in the sewers (Rodenburg et al. 2012)
- Dechlorination is inhibited at moderate salinity (Abramowicz et al., 1993; TAMS Consultants and the Gradient Corporation, 1997)

These congeners are often products of dehalogenation



PCB-F (Possible Dechlorination/CSO)



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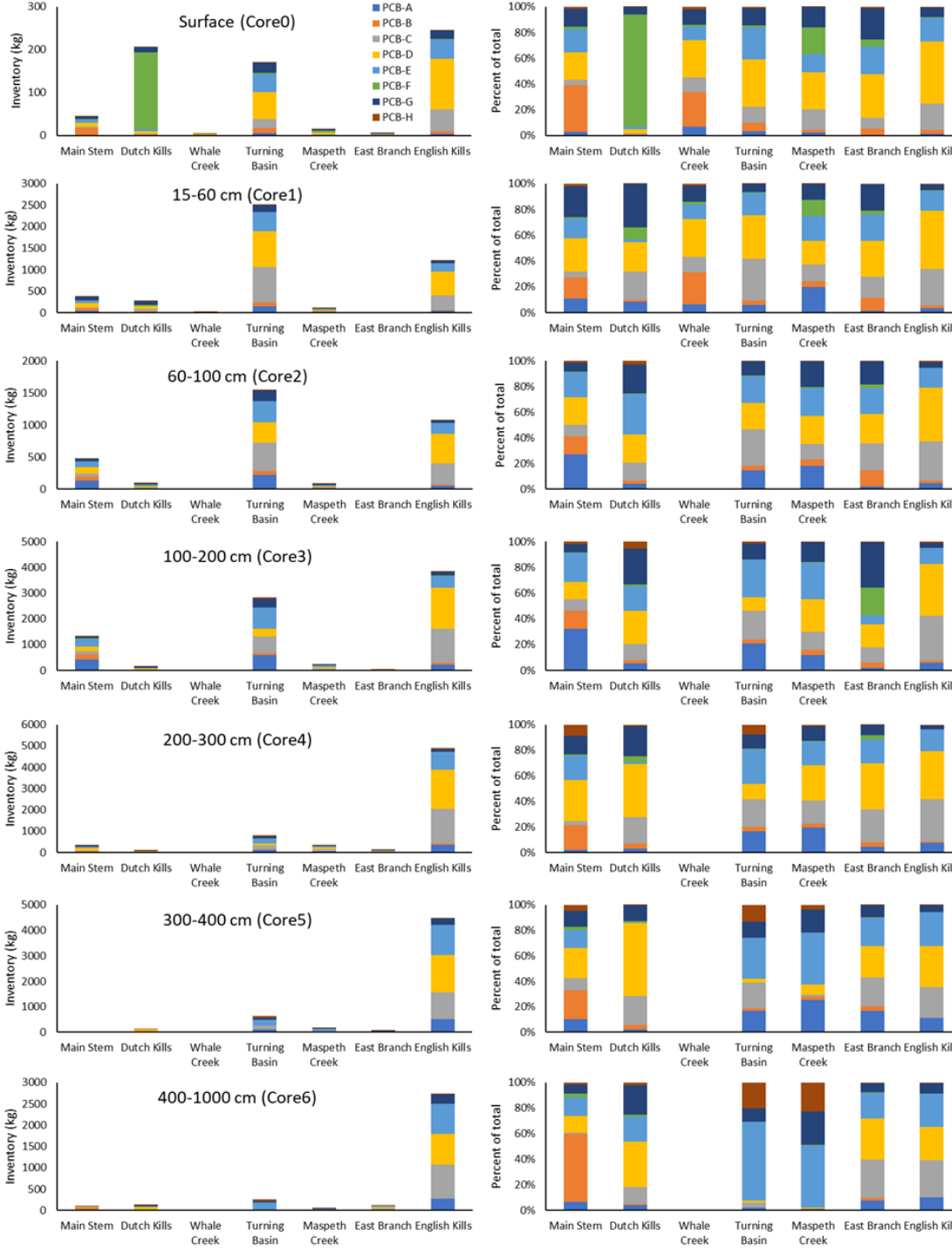
Inventory

- Different sources in surface vs deeper
- PCD-F (CSOs) more important at surface
- Aroclors more important at depth
  - Esp. 1268 (PCB-H)

- Note: horizontal migration of hydrocarbon NAPL



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Conclusions

- Data management is hugely important
- High quality data is necessary for fingerprinting
- Fingerprinting can identify both sources and processes
  - Sources like Aroclors
  - Processes like transport via East River or CSOs
- Low production volume Aroclors can still be found in the environment
- Consider inadvertent PCB sources
  - PCB 11 often travels via sewers, tracer for sewage, stormwater, or CSOs?
- PCB 68 might indicate that silicone rubber tubing was used for sampling

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PCBs vs. PFAS

PCB	PFAS
•One US manufacturer	•Many manufacturers, some overseas
•Less international trade 1930-1970s	•Globalized trade
•Same formulations 1930s to 1970s until ban	•Many formulations, constantly changing
•Primary chemical is regulated and measured	•Many PFAS are products of the reactions of thousands of precursors that are not measured
•Monsanto voluntarily restricted some uses and formulations prior to ban	•Only a few PFAS are regulated
	•Voluntary phase-outs
•Industrial uses	•Consumer products
•Hydrophobic, less mobile in the environment	•Much less hydrophobic, more soluble in water and mobile
•Sediment, stormwater	•Ground water, drinking water

Acknowledgements

Chevron

HUDSON RIVER FOUNDATION

RUTGERS New Jersey Agricultural Experiment Station

RUTGERS School of Environmental and Biological Sciences

ES Environmental Sciences Rutgers University

Disclaimer:

- Dr. Lisa Rodenburg provides expert witness testimony to cities and states that are suing Monsanto regarding PCBs
- She is an unpaid science advisor to Made Safe
- She does other consulting work for Chevron and Weston Solutions