PCB Symposium:

Source Identification & Tracking

Cross Program Contaminant Working Group

June 15, 2023

PCB Symposium | Source Identification & Tracking

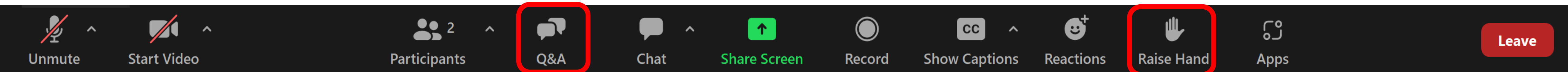
We’ll officially start at 9 am PT/12 pm ET

Informal networking in the breakout rooms

1. Introduce yourself
2. Why did you sign-up for the PCB symposium and what are you excited to learn about today?

Navigating the workshop

- Update your name to include your pronouns and organization
- Message Marielle with any access needs
- Add questions to the Q&A or raise your hand and we’ll unmute you



Agenda

Time Pacific	Time Eastern	Topic
09:00 am	12:00 pm	**Introduction**
09:15	12:15	**Source Tracking in Anacostia River/Lower Beaverdam Creek** Elisabeth Green & Mark Mank, Maryland Department of the Environment
10:00	1:00	**Field-based Source Tracking in San Francisco Bay** Jay Davis, San Francisco Estuary Institute
10:45	1:45	**Break**
11:00	2:00	**PCB fingerprinting at the Newtown Creek Superfund Site** Lisa Rodenburg, Rutgers University
11:45	2:45	**Panel Discussion**
12:30	3:30	**Closing**

PCB Symposium

Cross Program Contaminant Working Group

Symposium Steering Committee

Andy James	University of Washington Tacoma Puget Sound Institute
Greg Allen	US EPA Chesapeake Bay Office
Joel Baker	University of Washington Tacoma Puget Sound Institute
Will Hobbs	Washington State Department of Ecology
Marielle Larson	University of Washington Tacoma Puget Sound Institute
Katrina Radach	Puget Sound Partnership

PCB Symposium
Cross Program Contaminant Working Group

BACKGROUND:

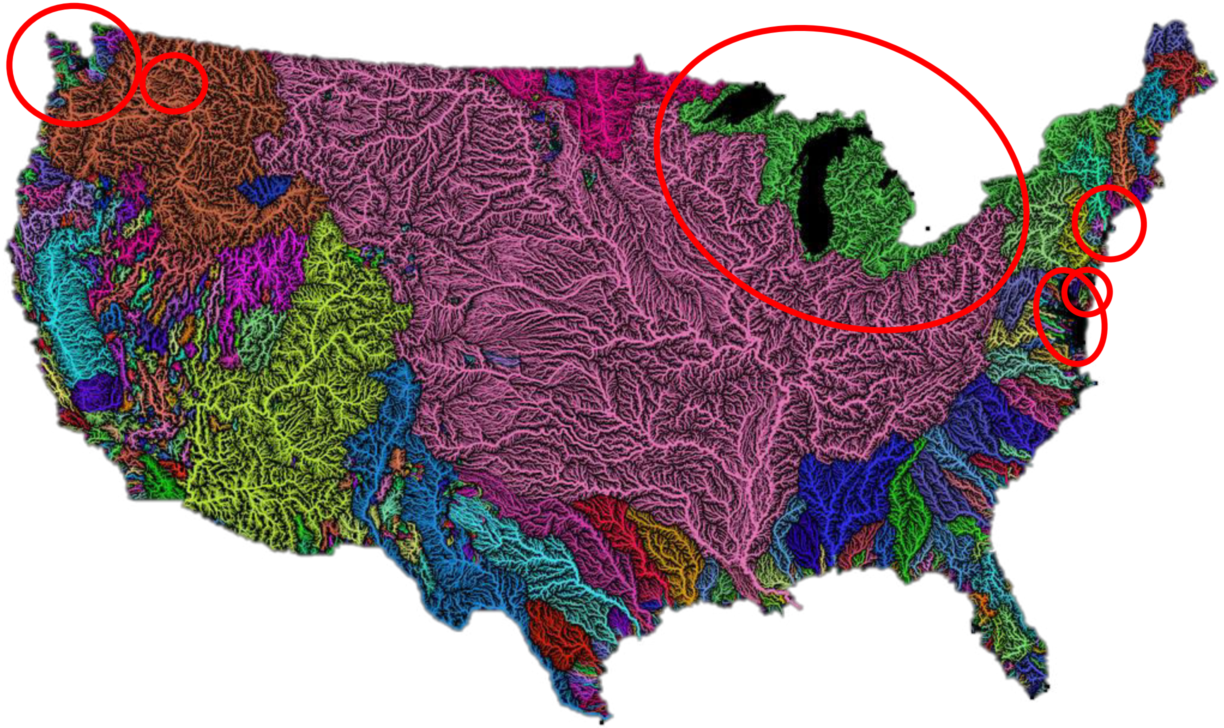
- Many estuaries (and river systems) are dealing with anthropogenic contaminants. Face similar challenges in this work.
- Premise:
  Share information on programs, projects, and best practices across regions to improve the effectiveness by which toxics contaminants are managed, controlled, and remediated.
- Approach:
  Initial focus on PCBs.
  Poll those who are involved in contaminant management, and address the topics that are of interest.

PCB Symposium

Cross Program Contaminant Working Group

January 2023

- Presentations on Status and Trends and approaches for PCB Management
- Six regions across U.S.
- Information is compiled on UW Puget Sound Institute website
  https://www.pugetsoundinstitute.org/about/cross-program-contaminant-working-group/



Map from Grasshopper Geography

PCB Symposium

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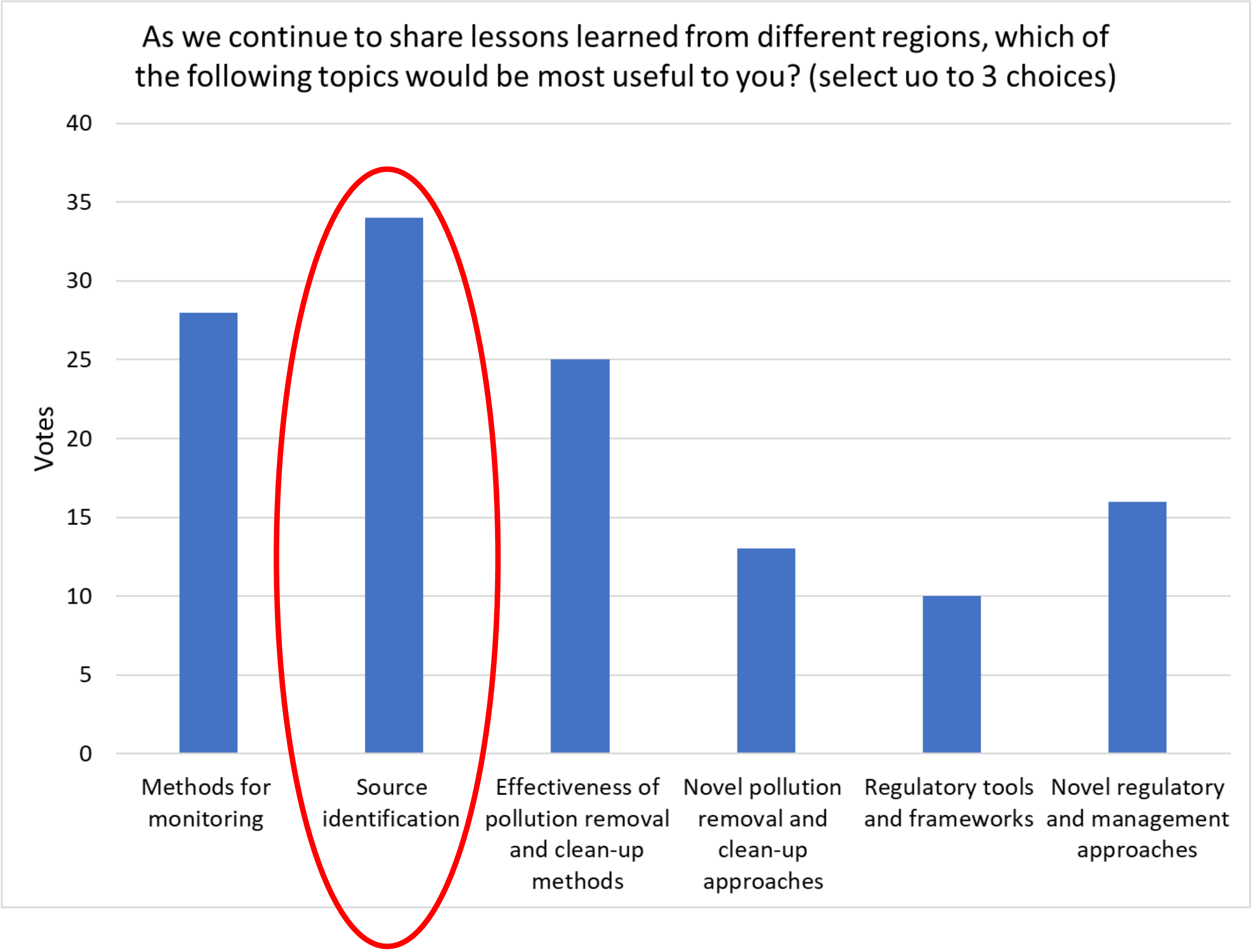


<u>June 2023</u>

PCB Symposium #2:

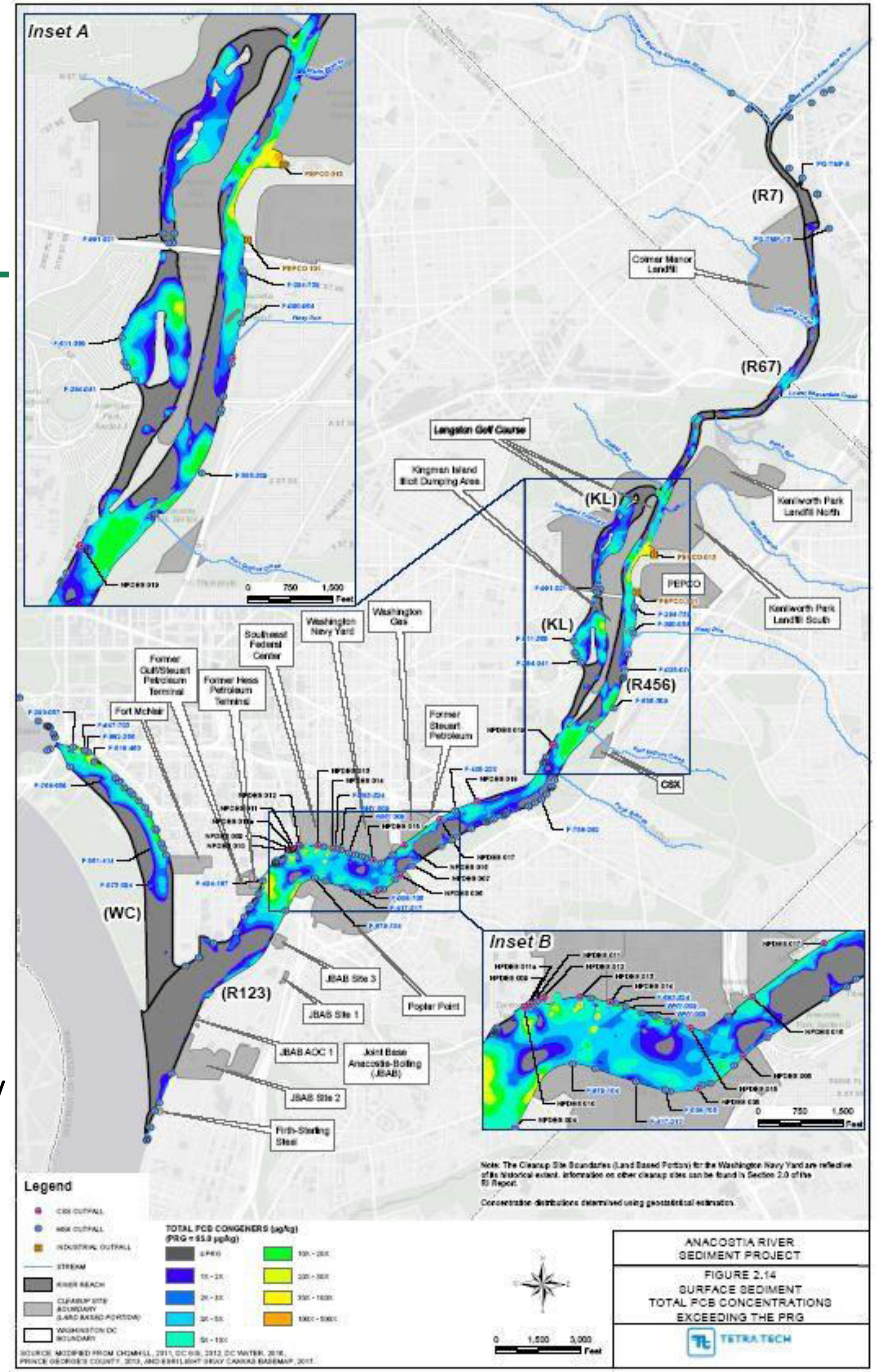
Source Identification & Source Tracking

Maryland's PCB Source Trackdown Study in Lower Beaverdam Creek

EPA PCB Coastal Symposium
June 15, 2023

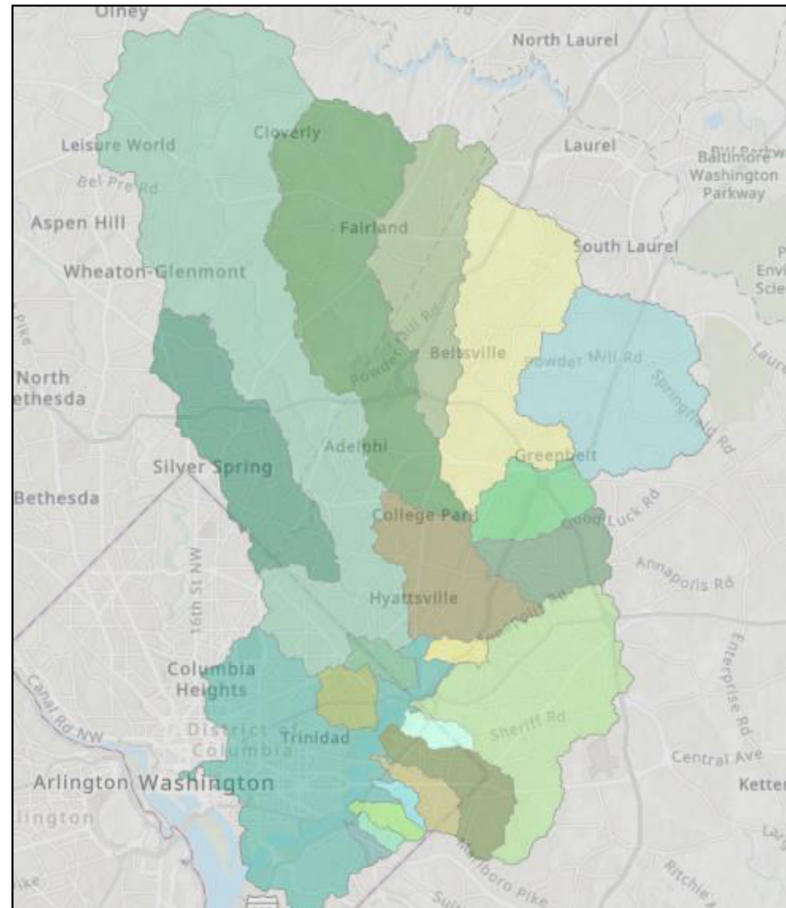
Anacostia River Sediment Project

- Washington D.C.'s Department of Energy and the Environment (DOEE) is working towards a fishable and swimmable Anacostia River.
  - Remedial Investigation – Dec. 2019
  - Focused Feasibility Study – Dec. 2019
  - Interim Record of Decision issued by D.C. – Sept. 2020
- Nine miles of river that are tidally influenced
- 176 square miles of watershed in Maryland (Montgomery County, Prince George's County) and D.C.
- Other stakeholders include U.S. Fish and Wildlife Service, National Park Service, Maryland Department of the Environment, National Oceanic and Atmospheric Administration, U.S. Environmental Protection Agency, and the counties in Maryland.
- PCBs are primary contaminants of concern because they drive fish consumption advisories
- Six early action areas in the tidal Anacostia identified in the Interim ROD, combination of dredging and capping PCB hot spots – action planned by DOEE over the next 3 years



Lower Beaverdam Creek: Previous Studies

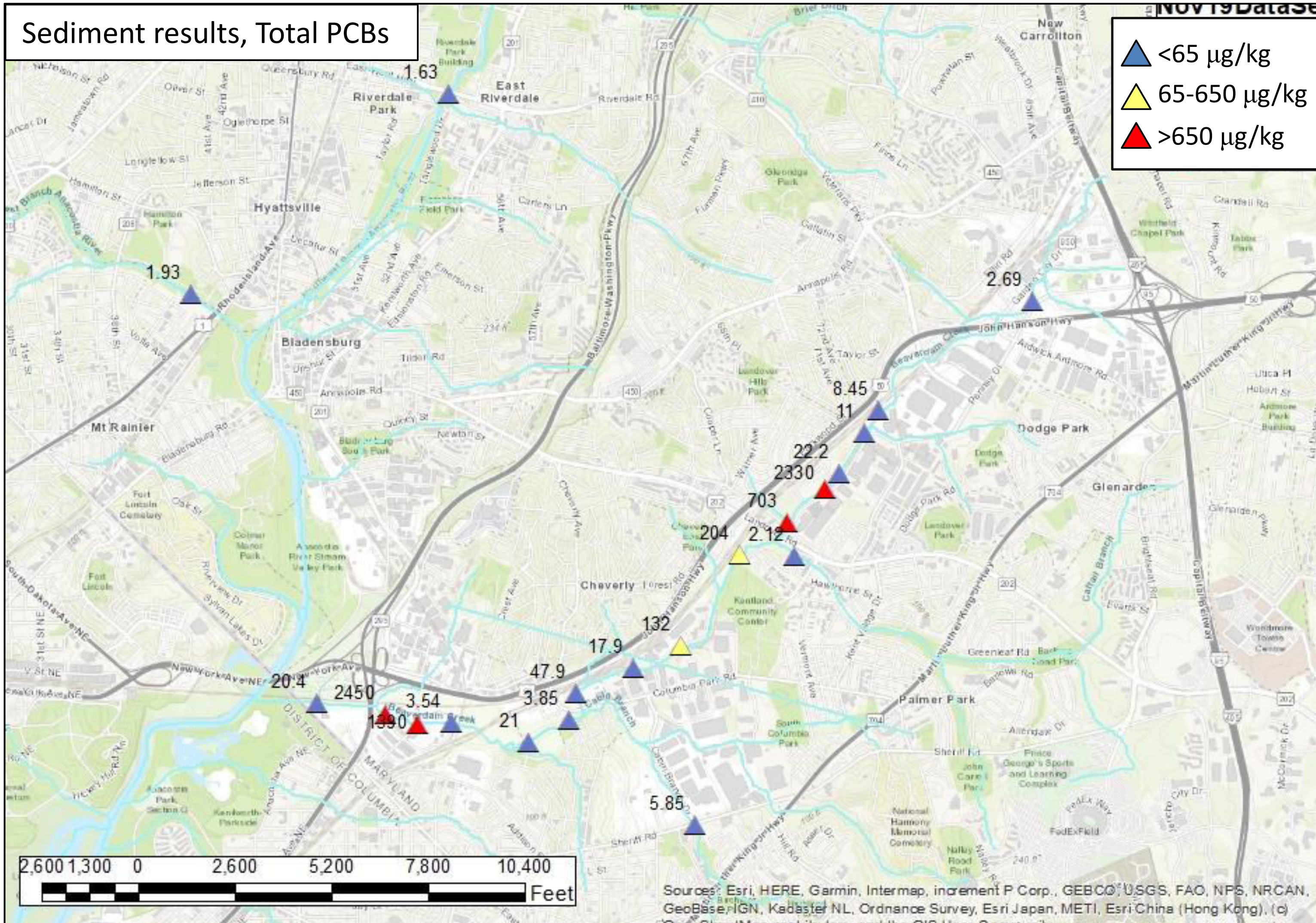
- Studies done in cooperation with reaching goals of ASRP, and led by DOEE
- USGS Tributary Study (2017)
  - 5 tributaries, LBC contributes 14% of sediment, but highest sediment-bound PCB concentration (74% of total annual PCB load from the 5 tributaries)
- NPS Background Study (2019)
  - Several elevated PCB sediment concentrations in LBC measured as part of study of Anacostia tributary sediment study
- UMBC Passive Sampler and Mussel Study (2020)
  - Elevated dissolved PCB concentrations in water column (freely dissolved PCBs) relative to other tributaries and tidal Anacostia
  - Porewater in LBC also elevated
  - Total annual estimated load of PCBs from LBC is 285 g/yr
  - Storm loading and base flow approximately equal contributors
- USFWS small fish studies (2022)
  - PCB concentrations in tissue of mummichogs and killifish in LBC higher than other tributaries and tidal Anacostia
- Previous PCB work by MDE in the LBC watershed
  - Multiple discrete actions and investigations were completed in and around LBC since the 1990s, but did not consider the creek holistically



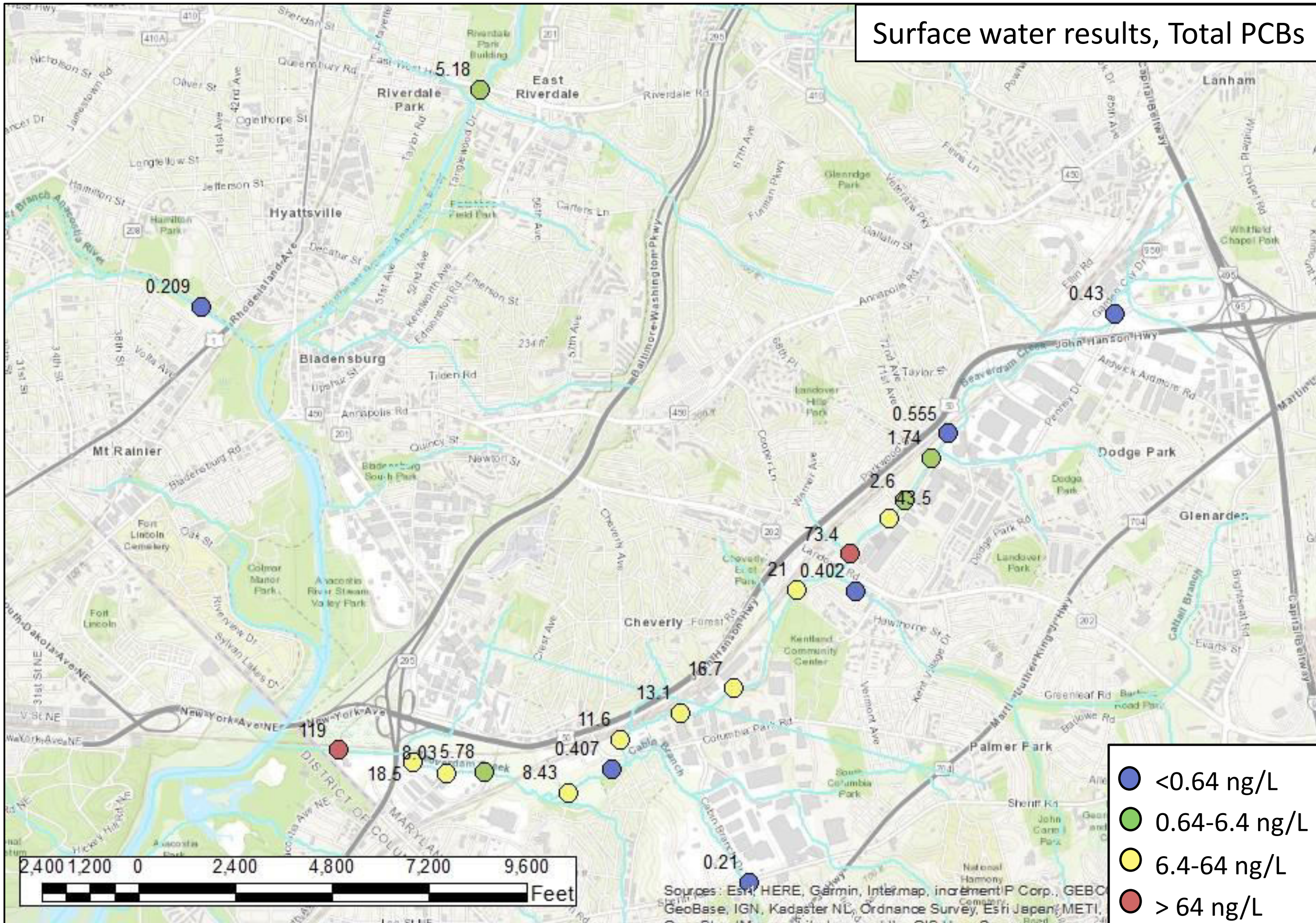
MDE's PCB Source Trackdown

- 18 locations sampled within Lower Beaverdam Creek in November 2019
- Aqueous samples for PCBs (EPA Method 1668c)
- Sediment samples for PCBs (EPA Method 1668c), Total Organic Carbon, and Grain Size Distribution
  - Composite of 3 samples from stream transect

November 2019 Sediment Results



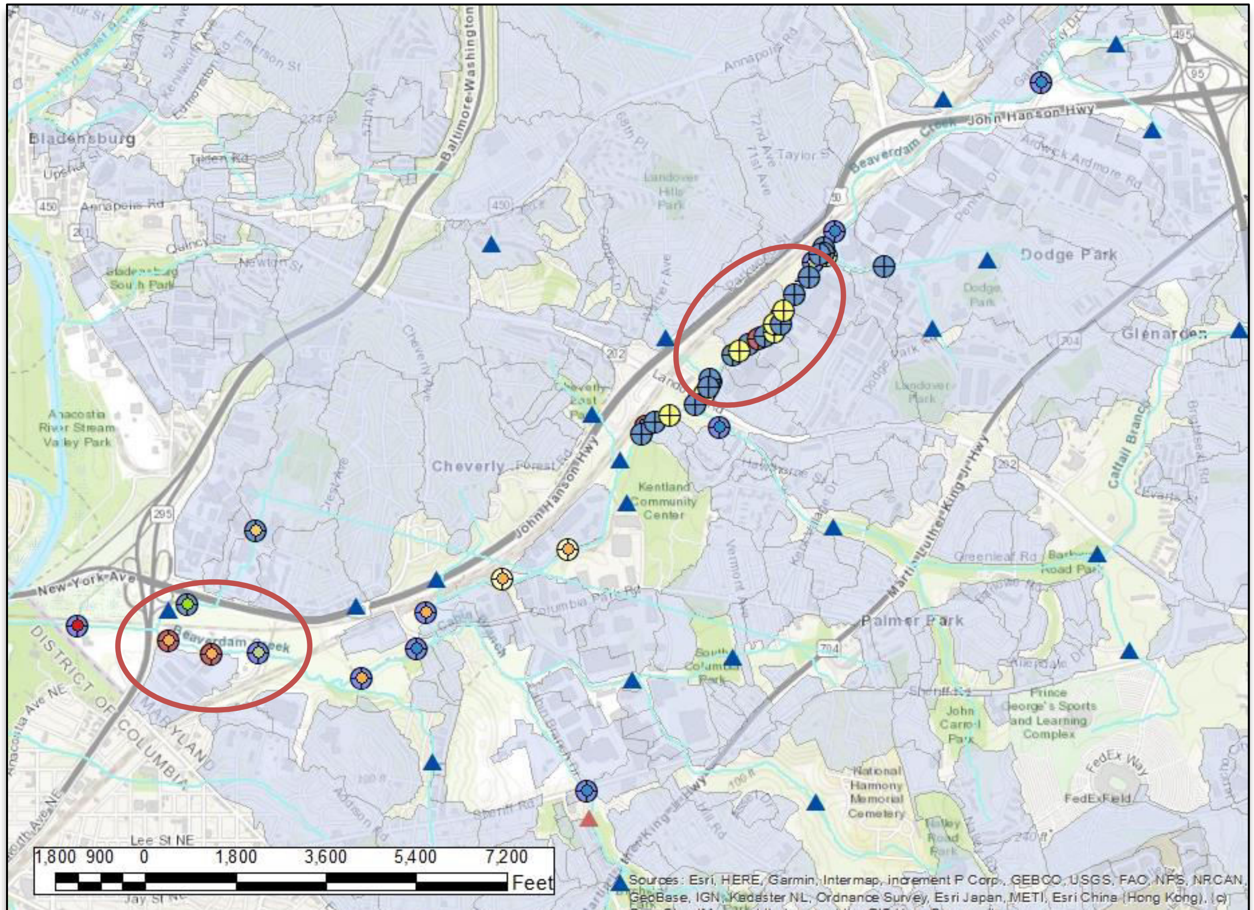
November 2019 Surface Water Results



0.64 ng/L is MDE's Ambient Water Quality Criteria for PCBs

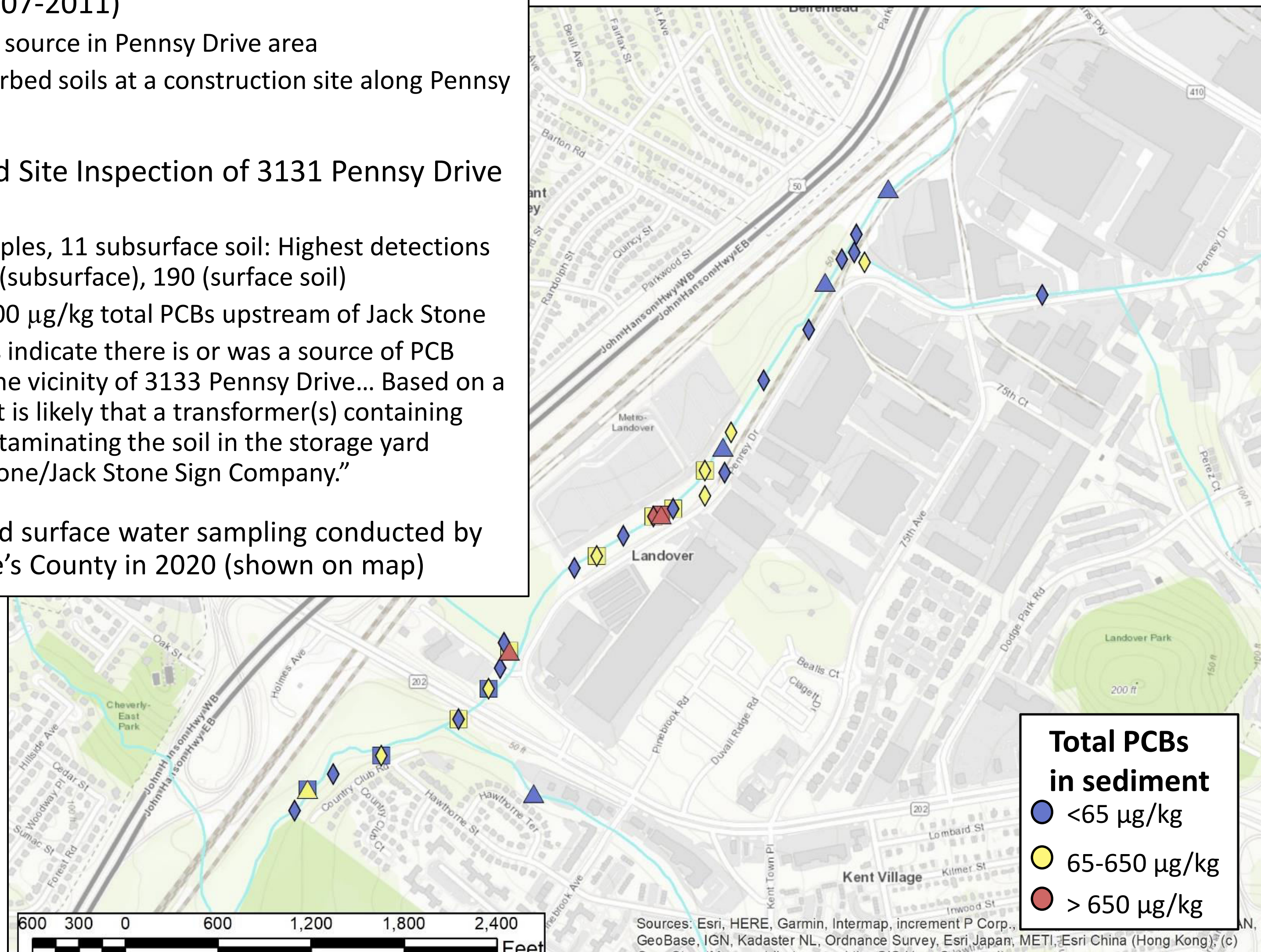
Lower Beaverdam Creek: Areas of Concern

- Several additional sampling efforts by MDE and Prince George's county in 2020 confirmed two primary areas of concern within LBC:
  - Pennsy Drive
  - Joseph Smith and Sons Property



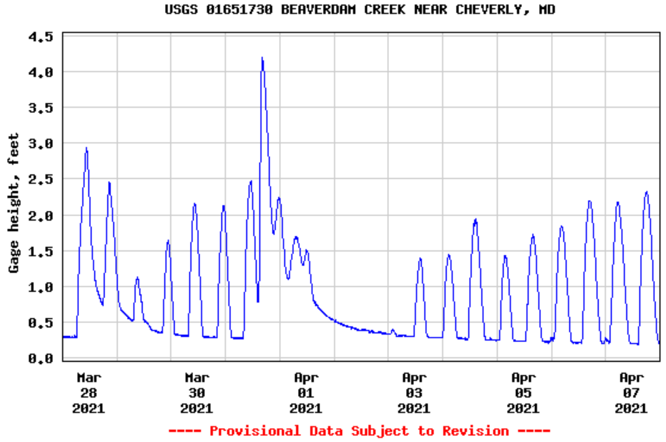
Pennsy Drive Investigations

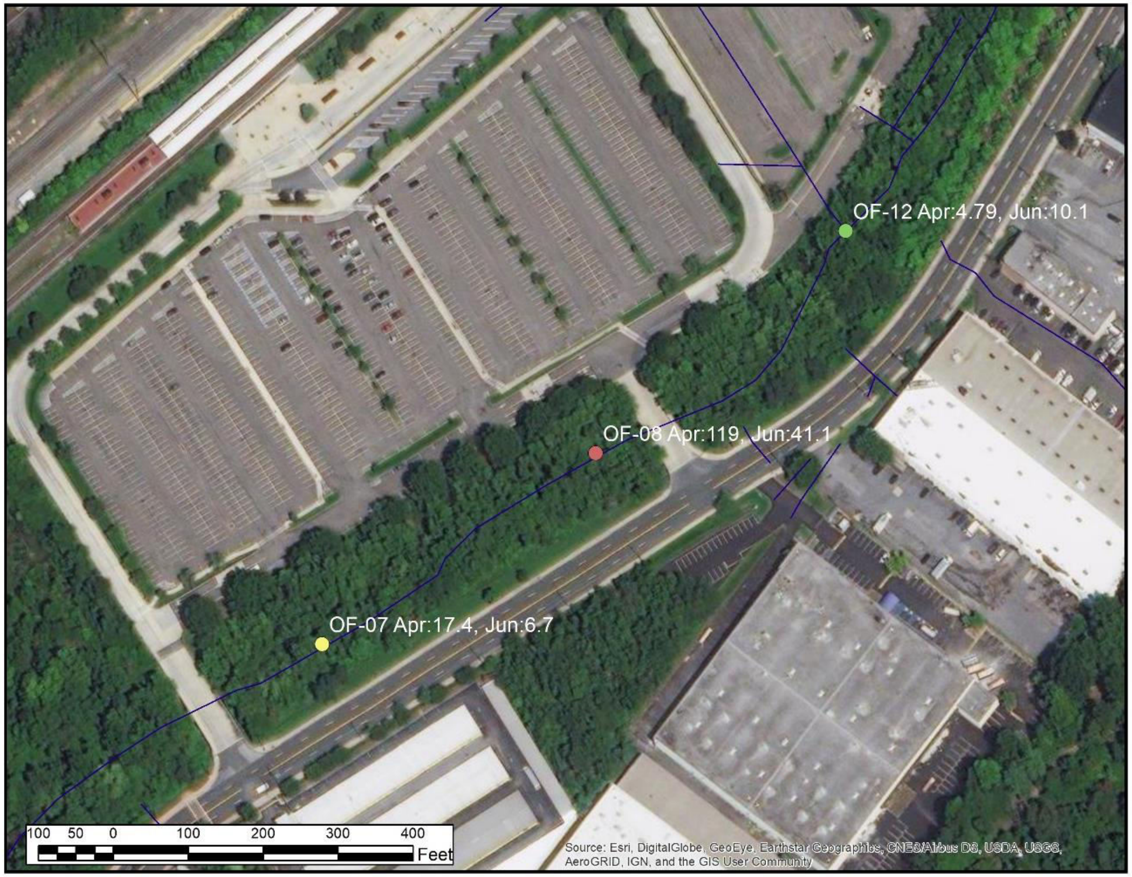
- MDE Clam studies (2007-2011)
  - Indicated potential source in Pennsy Drive area
  - Possibly from disturbed soils at a construction site along Pennsy Drive
- Jack Stone – Expanded Site Inspection of 3131 Pennsy Drive (2012):
  - 11 surface soil samples, 11 subsurface soil: Highest detections of PCBs 380 µg/kg (subsurface), 190 (surface soil)
  - Sediment data: 1100 µg/kg total PCBs upstream of Jack Stone
  - "Laboratory results indicate there is or was a source of PCB contamination in the vicinity of 3133 Pennsy Drive… Based on a history of the site it is likely that a transformer(s) containing PCB oil leaked, contaminating the soil in the storage yard behind the John Stone/Jack Stone Sign Company."
- Additional sediment and surface water sampling conducted by MDE and Prince George's County in 2020 (shown on map)



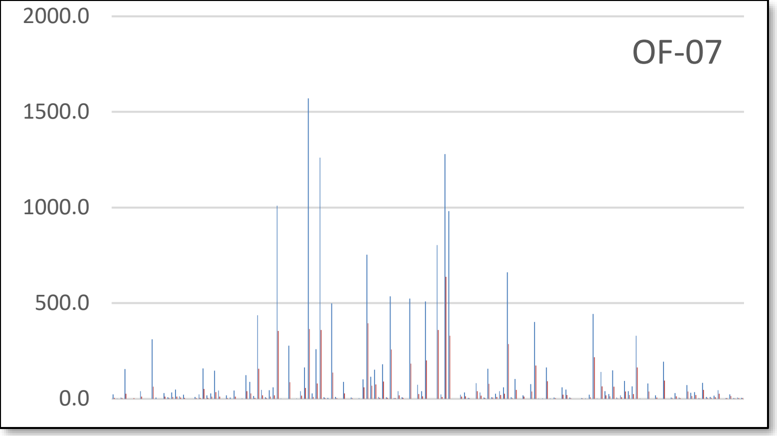
Pennsy Drive: Spring 2021 ISCO Outfall Sampling

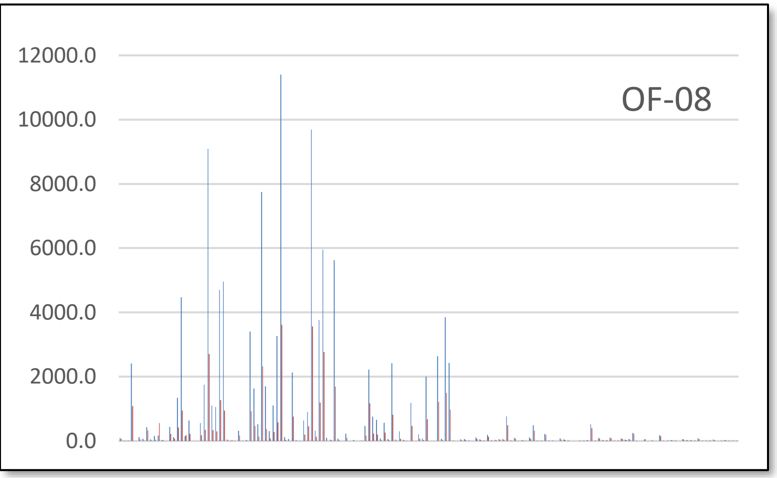
- ISCO samplers installed in 3 outfalls of question
- 2 storm events captured in 2021 (March 31, June 4), samplers ran 10 minutes every hour for 24 hours
- June event was not as significant as hoped, but samples reflect first flush out of storm drains

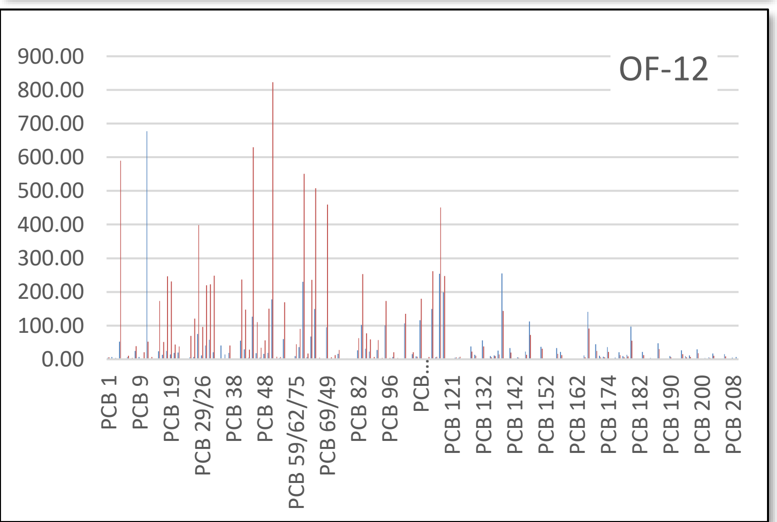


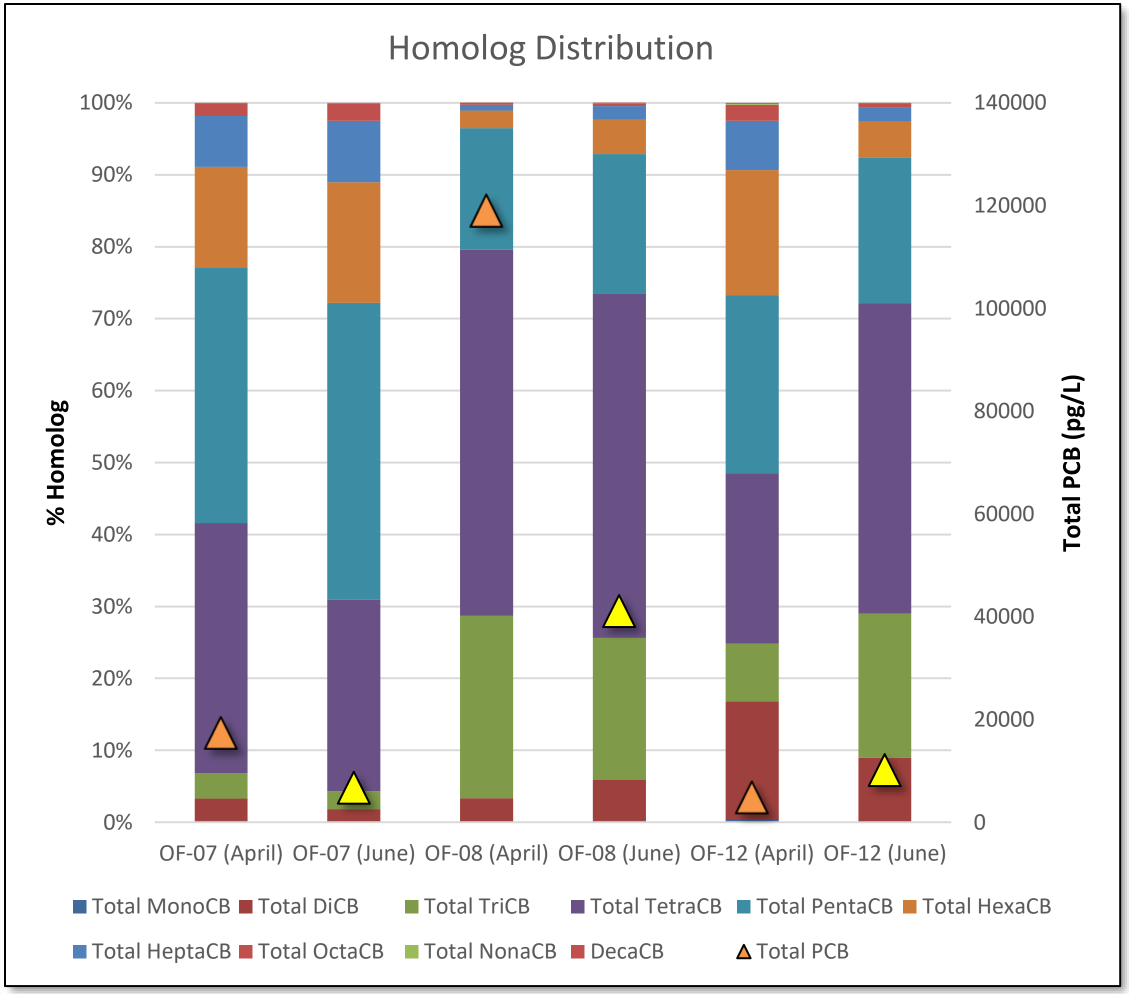


Pennsy Drive 2021 ISCO Outfall results









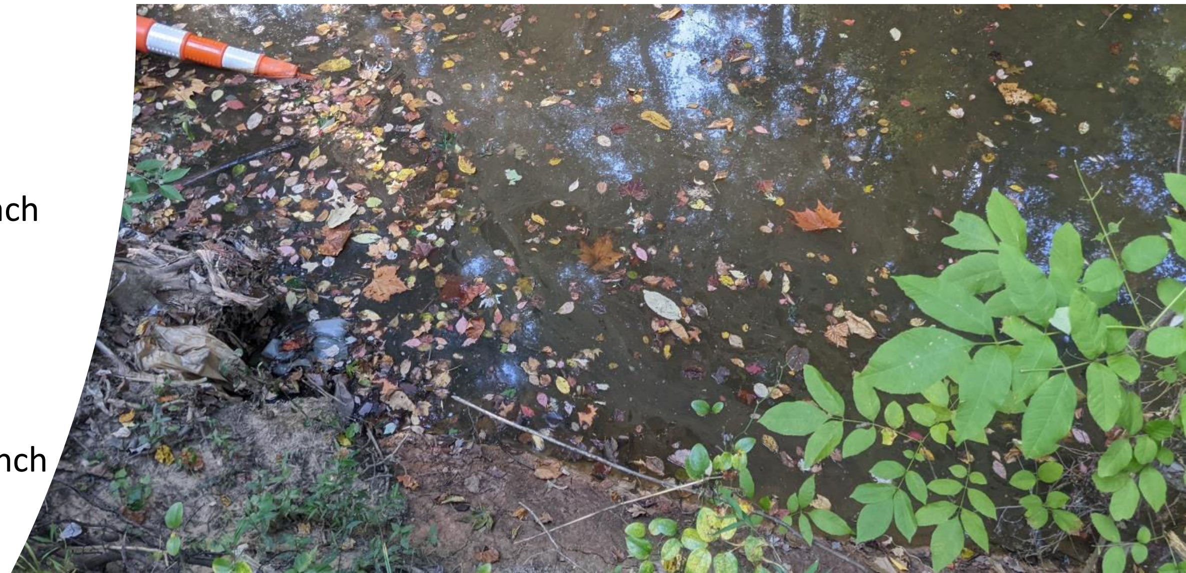
EPA Site Assessment: Pennsy Drive trackdown work

Historical research, aerial photography, and a site visit has identified several potential suspect areas as sources of PCBs:

Old Landover Road
- Equipment storage (potential junkyard) located on Lower Beaverdam Creek
- Old substation
- Printing facility
- Potential Construction Landfill

Pennsy Drive
- Unnamed outfalls along Pennsy Drive (pictured) have concrete bottoms
- Various areas of discrete dumping with potential migration pathways (pictured)
- Former GE Hotpoint factory and repair
- Conducting more in-depth research on each facility

Country Club Road
- Dead end street with various areas of dumping in Beaverdam (pictured)
- Concrete bottom observed on Cattail Branch confluence area of Beaverdam Creek



EPA Site Assessment, Pennsy Drive: Phase II MS4 Outfall and Stream Sampling

- Currently working on the Field Sampling and Analysis Plan for the upcoming sampling.
- Looking to sample outfall locations requested by MDE and outfall locations in the vicinity of Old Landover road and the former GE facility.
- Plan on conducting video studies in the MS4 system and dye tracer studies to determine the integrity and flow of the MS4 system.
- Will attempt to collect sediment in the MS4 system and may need to install passive samplers if sediment is not available.
- Will collect sediment, surface water, and porewater in Lower Beaverdam Creek analyzing for PCB Aroclors and PCB congeners. The investigation is expected to commence in the Fall of 2023.

Joseph Smith and Sons: Site Overview

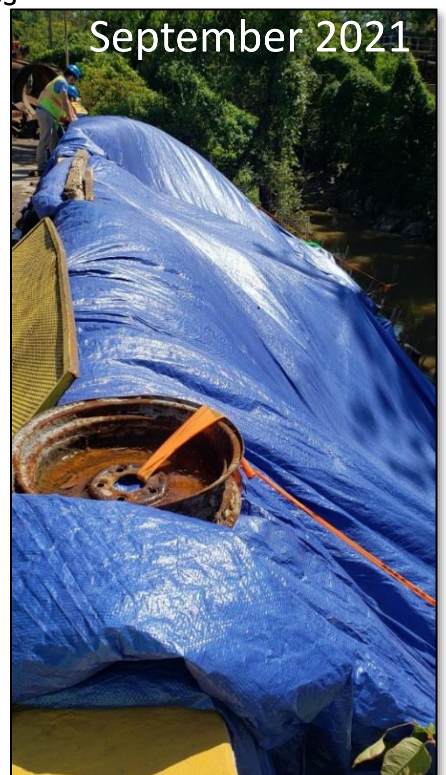
- ~32 acres, bisected by Lower Beaverdam Creek
- In operation since 1952
- Processing of automobiles, larger household appliances, and other metal-bearing finished goods to recover metals for reclamation and recycling
- 300 employees, estimated to support another 3000 people in the community indirectly
- 0.5M tons of metal processed per year
- Concrete-lined to capture stormwater and prevent run-off
- Routinely inspected by MDE's Water and Science Administration Compliance Group

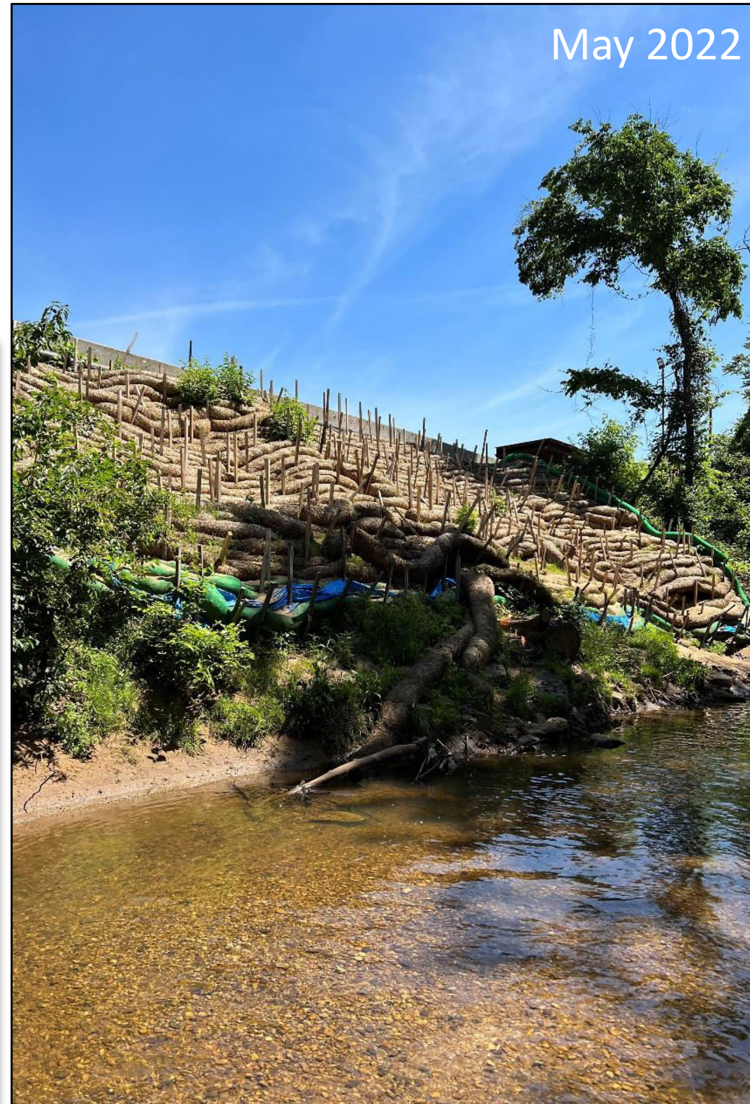
Joseph Smith and Sons: 2021 Sampling and Analysis Plan Report

- Sampling and Analysis Plan approved in October 2020 on Joseph Smith & Sons (JSS)
- Multi-media sampling onsite in December 2020
- Overview of results
  - Banks of LBC ~5-10 mg/kg total PCBs
  - One soil sample over 50 mg/kg total PCBs
  - Ponded process water on-site elevated in total PCBs (1,300 - 110,000 ng/L)

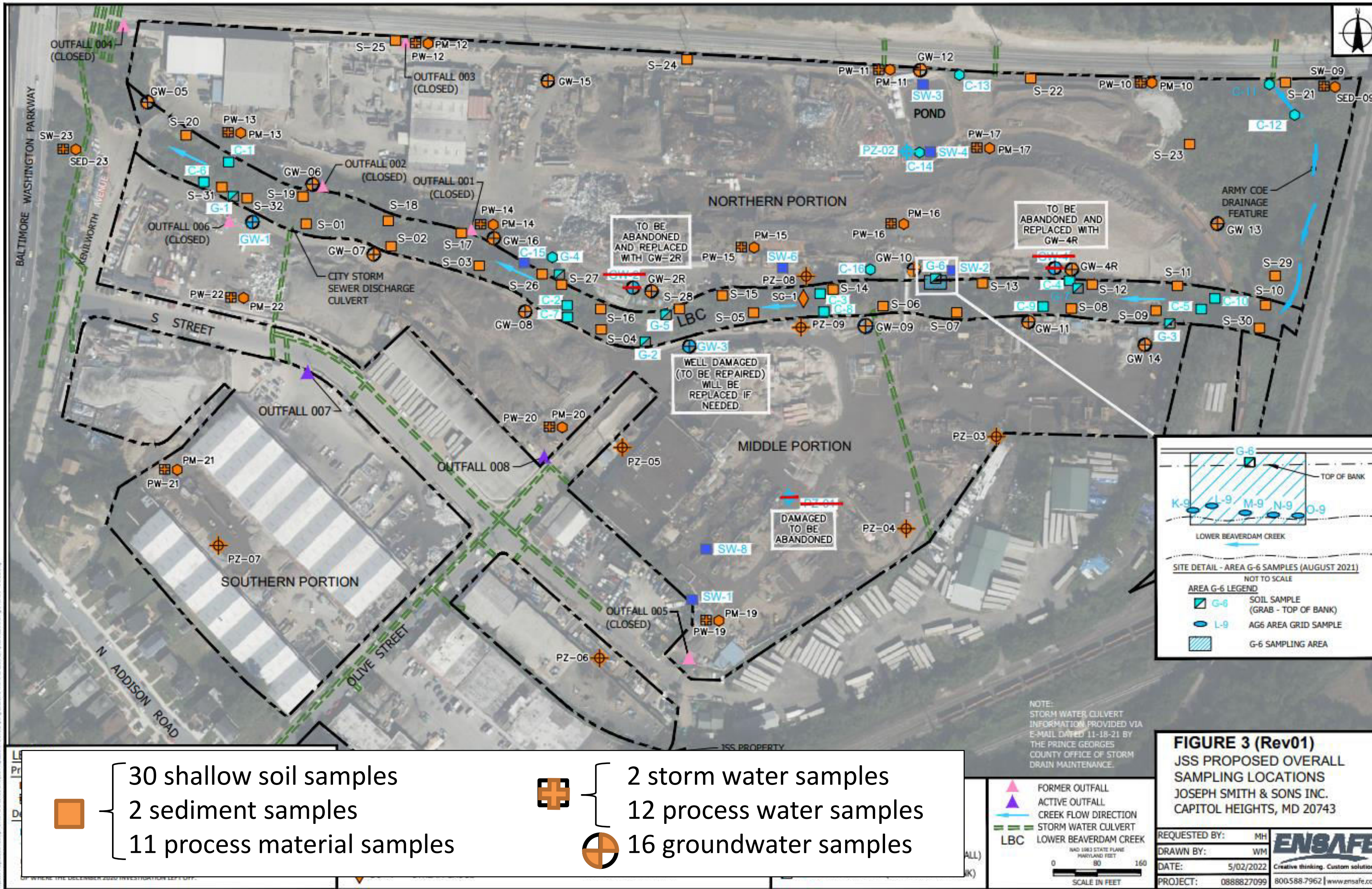
Joseph Smith and Sons: G-6 hot spot

- Initial Site Characterization in February 2021 identified one location with > 50 mg/kg total PCBs
- Follow-on hot spot delineation in August 2021:
  - One additional location > 50 mg/kg total PCBs
  - 11 locations > 1 mg/kg total PCBs
  - Remainder < 1 mg/kg total PCBs
- Excavation and stabilization work plan approved in December 2021
- Removal of soils over 50 mg/kg total PCBs in the G-6 area (~7 cubic yards), and permanent bank stabilization completed in March 2022





Joseph Smith and Sons: Site-Wide Characterization June-Dec 2022

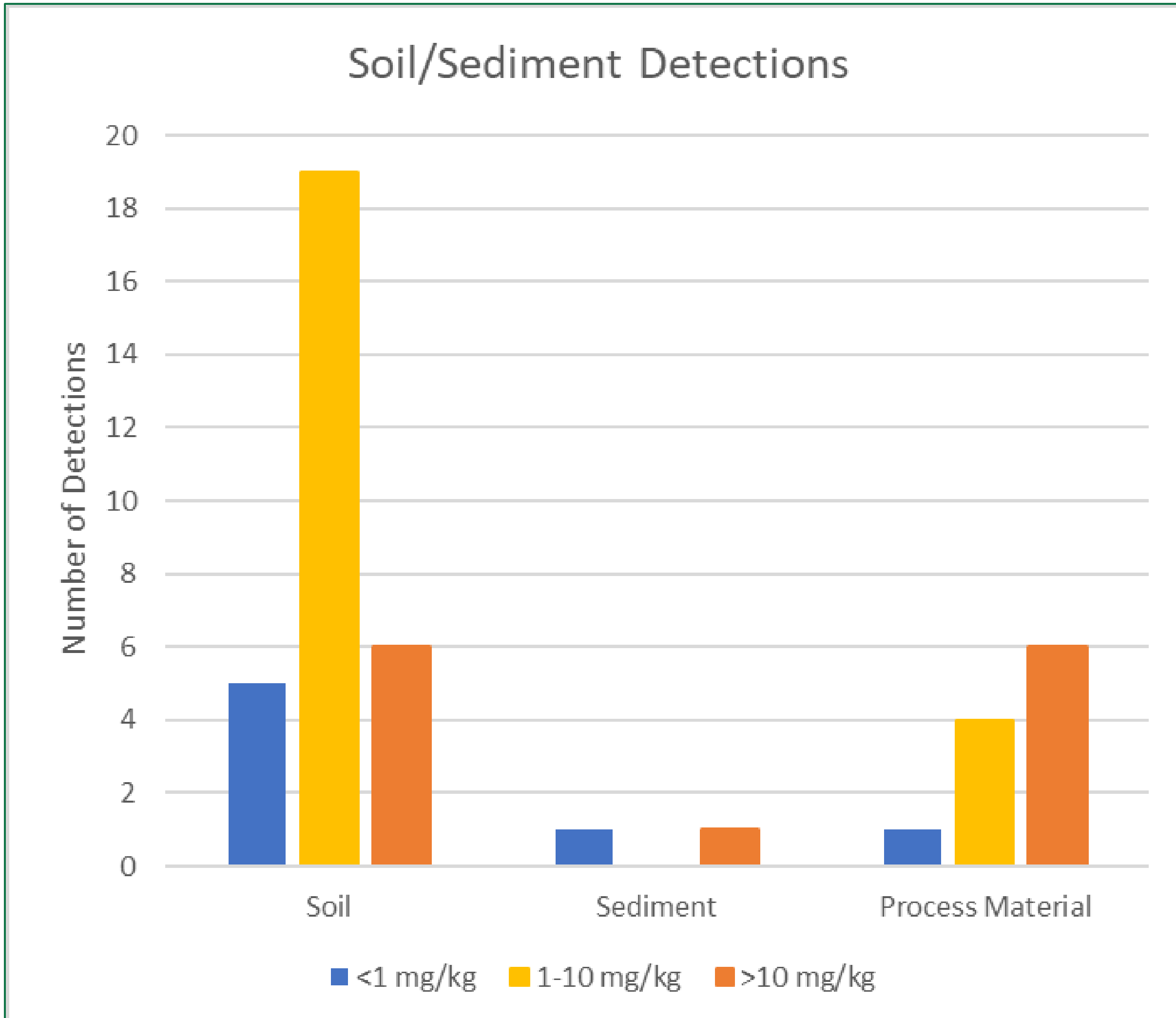


- 30 shallow soil samples
- 2 sediment samples
- 11 process material samples

- 2 storm water samples
- 12 process water samples
- 16 groundwater samples

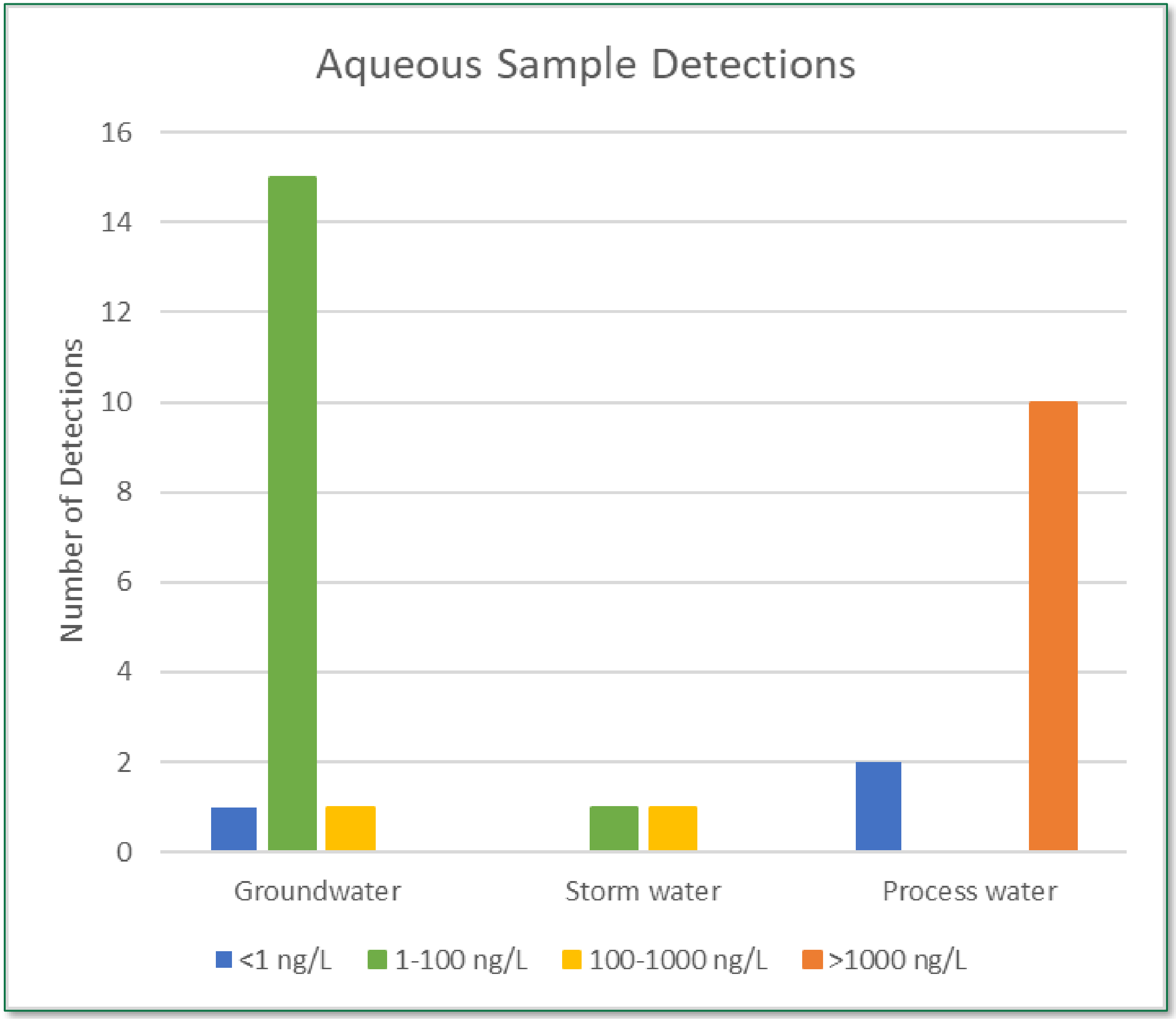
Joseph Smith and Sons: Site-Wide Characterization Report

- 30 soil samples
  - 0.1 – 30 mg/kg
  - Primarily LBC bank samples
- 2 sediment samples
  - 0.36-18 mg/kg
  - Drainages at east and west ends of property
- 11 process material samples
  - 0.11 – 69 milligrams per kilogram (mg/kg) total PCBs
  - Interior to the site



Joseph Smith and Sons: Site-Wide Characterization Report

- 16 groundwater samples
  - 0.6 – 210 ng/L
  - Interior to the site, mostly near the banks of LBC
- 2 storm water samples
  - 4 – 160 ng/L
  - Drainages at east and west ends of property
- 12 process water samples
  - Non-detect – 37,000 ng/L total PCBs
  - Interior to the site, areas where water collects



Characterization of total PCBs in surface water in LBC through Joseph Smith and Sons by MDE

Joseph Smith and Sons: MDE sampling of LBC outfalls

Surface Water sample date	OF-06 (ng/L)	OF-11 (ng/L)
Feb 2021	917	1190
Oct 2021	560	11.4
Nov 2021	215	NS
Mar 2022	136	23.1
May 2022	127	NS
Dec 2022	23.4	1160
Mar 2023	280	85.9

Sediment sample date	OF-06 (ug/kg)	OF-11 (ug/kg)
May 2022	355	NS
Dec 2022	330	3600

Joseph Smith and Sons: Next Steps

- JSS has agreed to Risk-Based Disposal Approval Application under EPA, and Response Action Plan under MDE's Controlled Hazardous Substance Division.
- Remedial Action Objectives (RAOs) to include protecting creek, workers, and natural resources
- Ongoing improvements to stormwater capture and management through work with MDE's Water Compliance group

Small Fish Sampling

- Previous work by Dr. Fred Pinkney (USFWS) indicates that small fish in LBC are elevated in PCBs relative to other tributaries
- Samples throughout Anacostia watershed over several years
- Mummichogs
- Banded killifish
- Elevated concentrations of PCBs in fish tissue found within LBC relative to other Anacostia tributaries

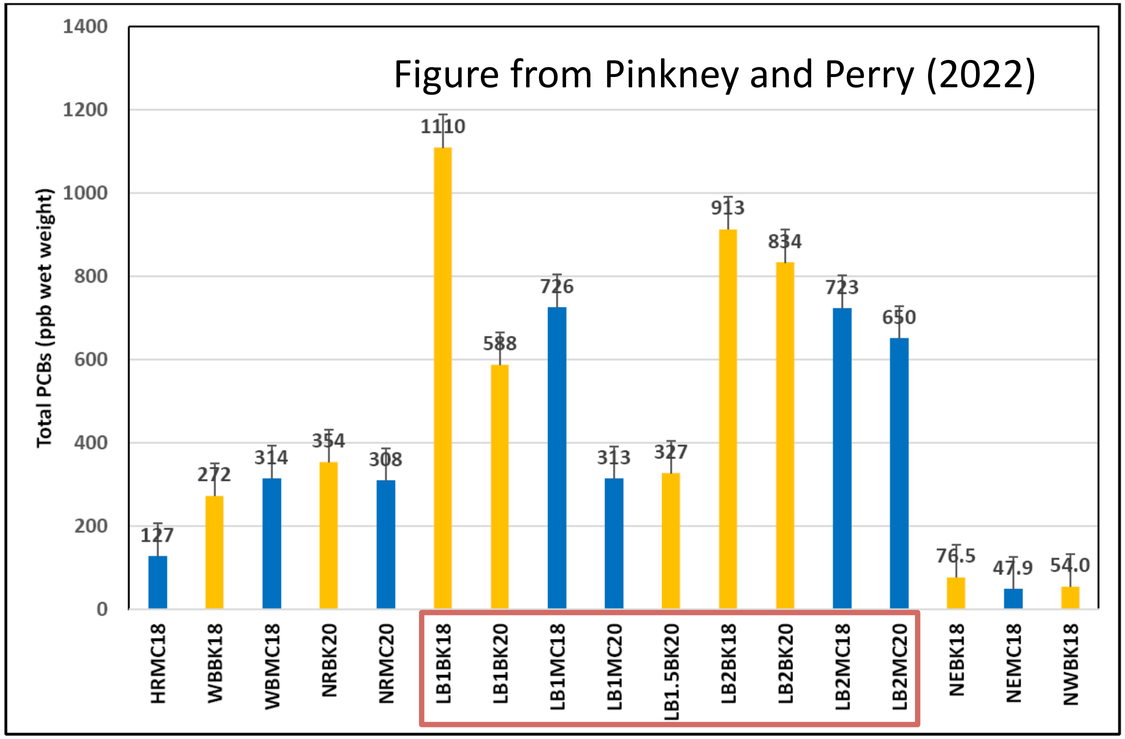
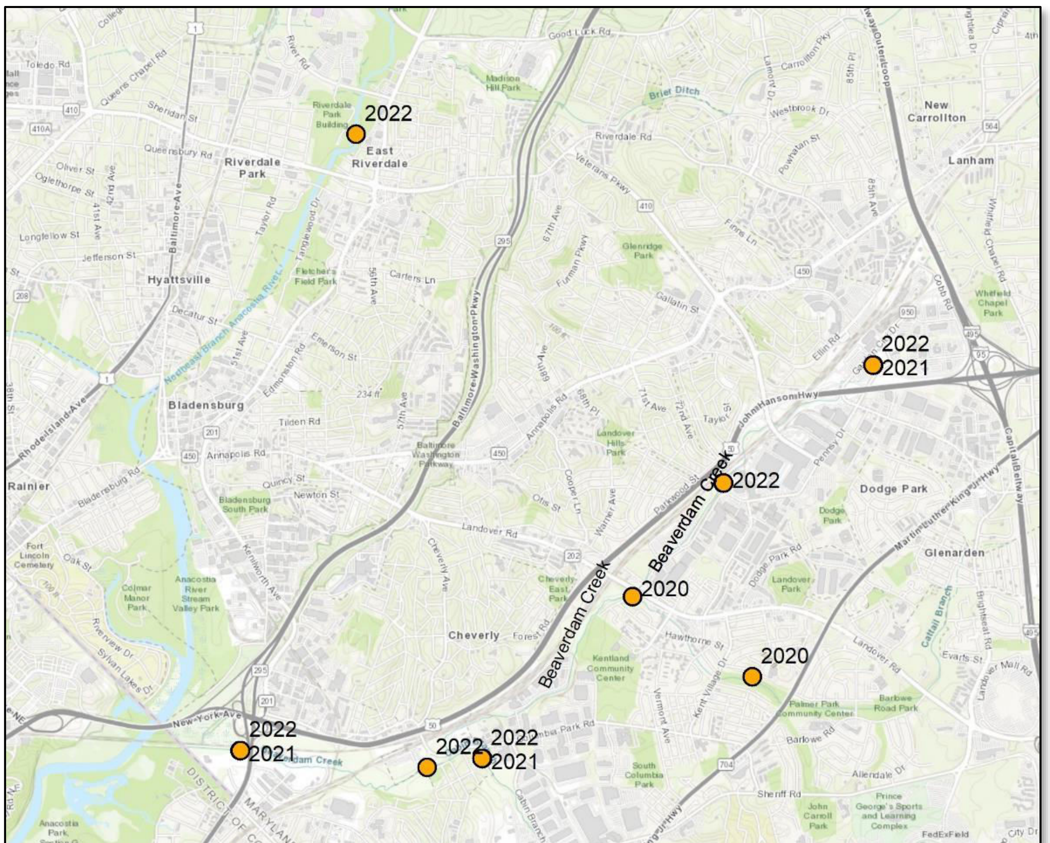


Figure 3 Total PCBs (ppb wet wt., mean + standard deviation) in mummichogs (MC) and banded killifish (BK) from Anacostia Tributaries. See Table 1 for location/collection abbreviations.

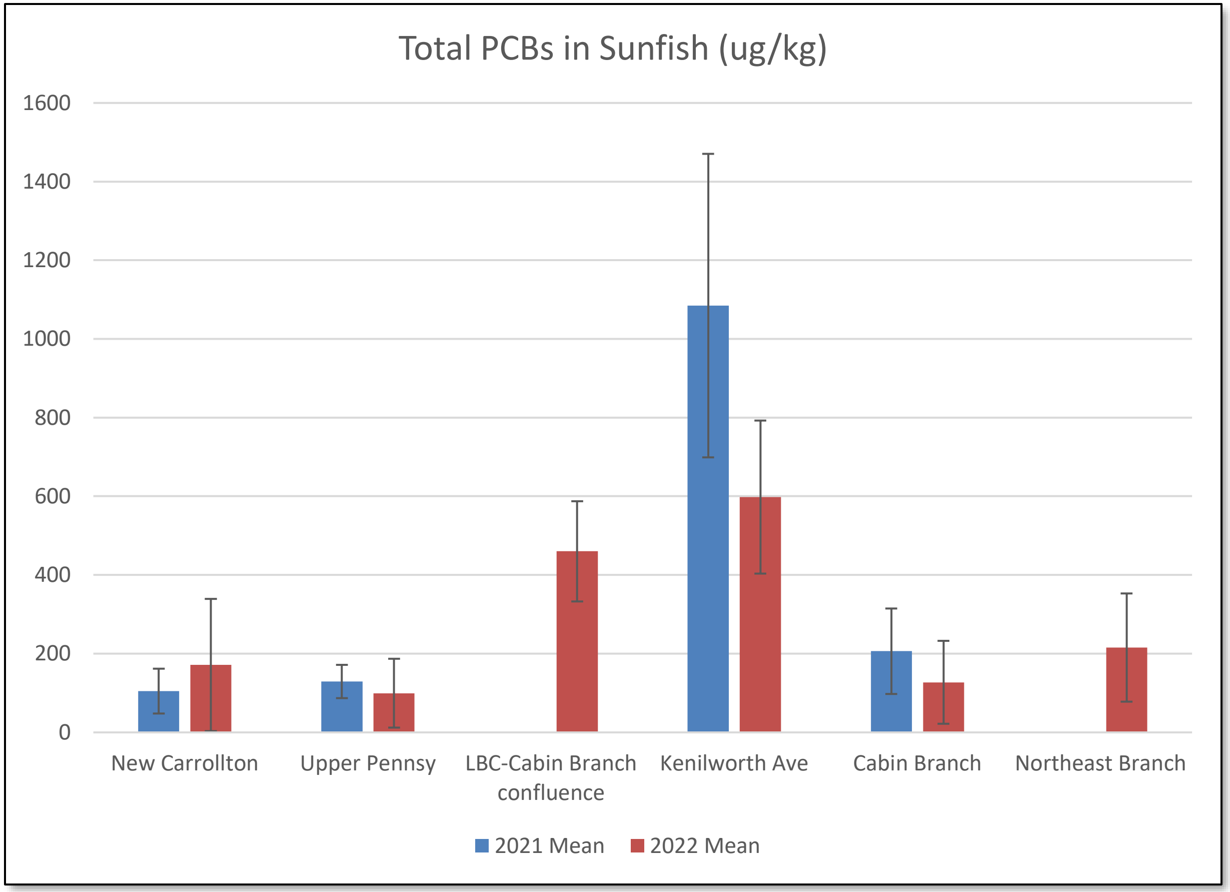
MDE Fish Collection

- Small fish collection by MDE started at limited locations in 2020
- Expanded to 4 locations in 2021, and 6 locations in 2022 (35 samples, two different species)
- Thanks to Metropolitan Washington Council of Governments staff for assistance with electroshocking and fish species identification



Locations (2022)	Fish Species	Number of lab samples
New Carrollton	Sunfish	6
Upper Pennsy	Sunfish	6
LBC-Cabin Branch Confluence	Sunfish	6
Kenilworth Ave	Sunfish	5
Kenilworth Ave	Banded Killifish	2
Cabin Branch	Sunfish	4
Northeast Branch	Sunfish	6

2022 Fish Collection Results

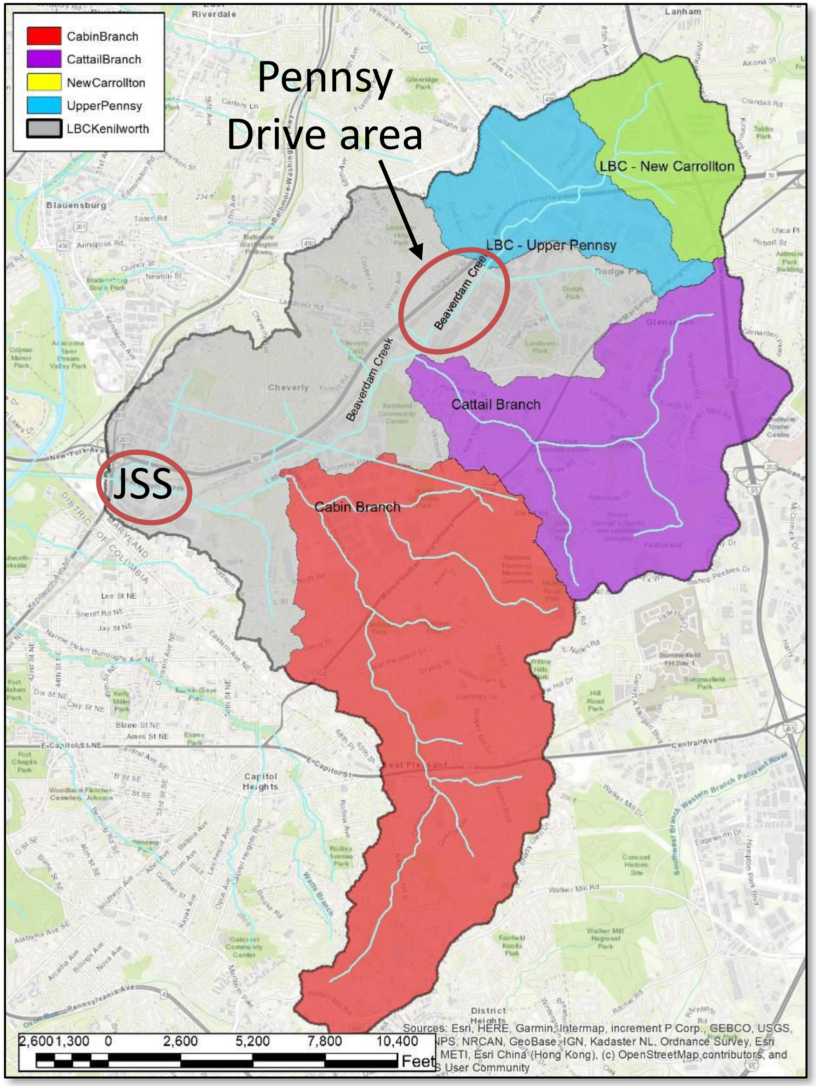


Banded killifish total PCBs (ug/kg)	2020	2021	2022
Upper Cattail Branch	54	Not Sampled (NS)	NS
Lower Cattail Branch	72	NS	NS
Kenilworth Ave	NS	555	47

Next round of sampling scheduled for July 2023. To be continued…

Upcoming activities within LBC

- **JSS property**
  - Finalize Site-Wide Characterization Report
  - Develop of MDE Response Action Plan and EPA TSCA Region 3 Risk-Based Disposal Approval Application to reduce PCB migration from the site
- **Pennsy Drive area**
  - MS4 stormwater network mapping
  - Continued sampling and source trackdown, introducing new field methodologies
  - Funding from EPA Region 3 Site Assessment
- **Lower Beaverdam Creek**
  - Fish sampling planned for summer 2023
  - Continued characterization of surface water and soils in the vicinity of JSS along the lower reaches of LBC



Current Status

- Multiple lines of evidence allow us to eliminate sub-watersheds in LBC and isolate significant contributors
- JSS Conceptual Site Model complete and adaptive
- Multi-media RAOs under development by JSS in cooperation with MDE and EPA
- Strong evidence that materials managed on-site at JSS are a primary source of PCBs in lower section of LBC
- Mitigative strategies on-going and anticipate implementation of remedial measures over next several years
- Continuing multi-media monitoring in LBC to quantify changes in water quality over time

Mitigation Strategies and Future Work

- Source trackdown in areas without obvious responsible parties is less straight forward

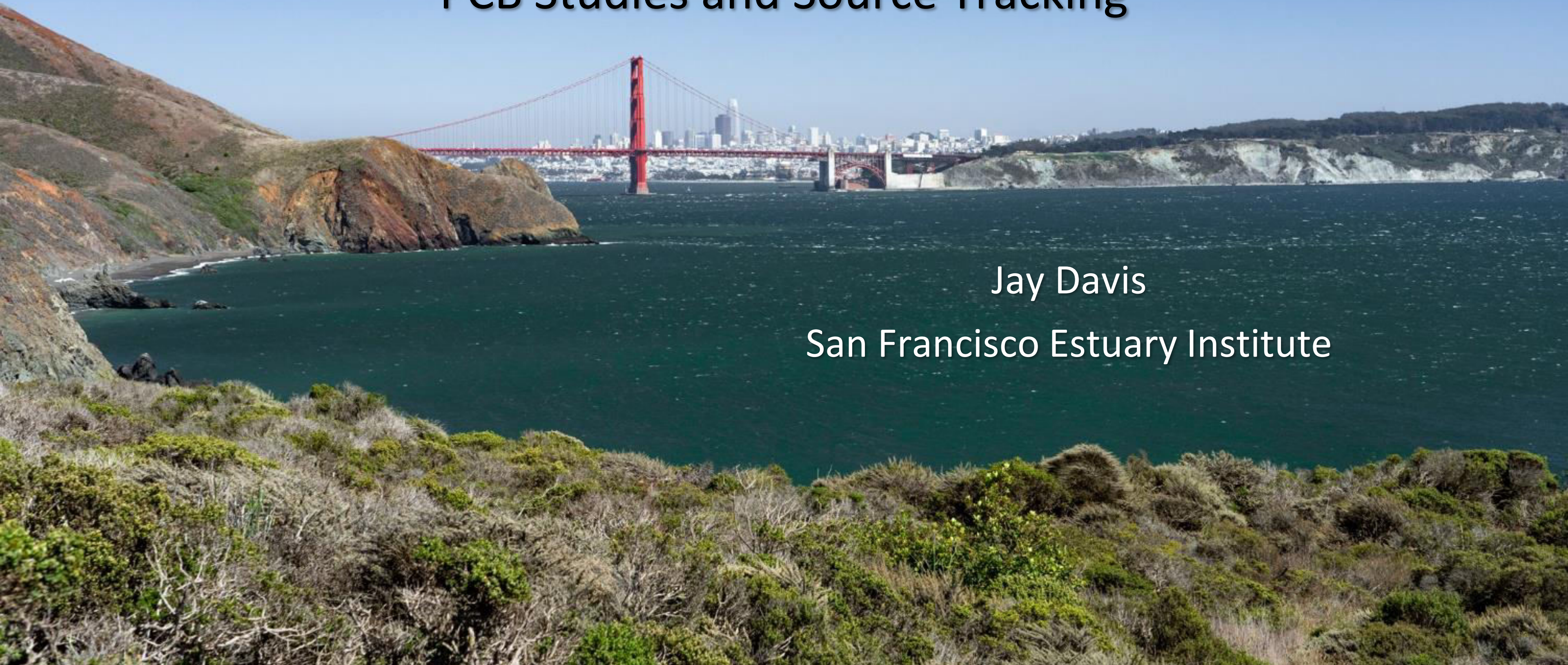
- MDE will continue multi-media monitoring in LBC to quantify changes in water quality and fish tissue over time

- Post discrete source trackdown mitigative measures, additional PCB source reduction processes will be considered

- Adaptive management potentially including BMPs and diffuse source mitigative strategies may be best in these types of areas

Regional Monitoring Program for Water Quality in San Francisco Bay

PCB Studies and Source Tracking



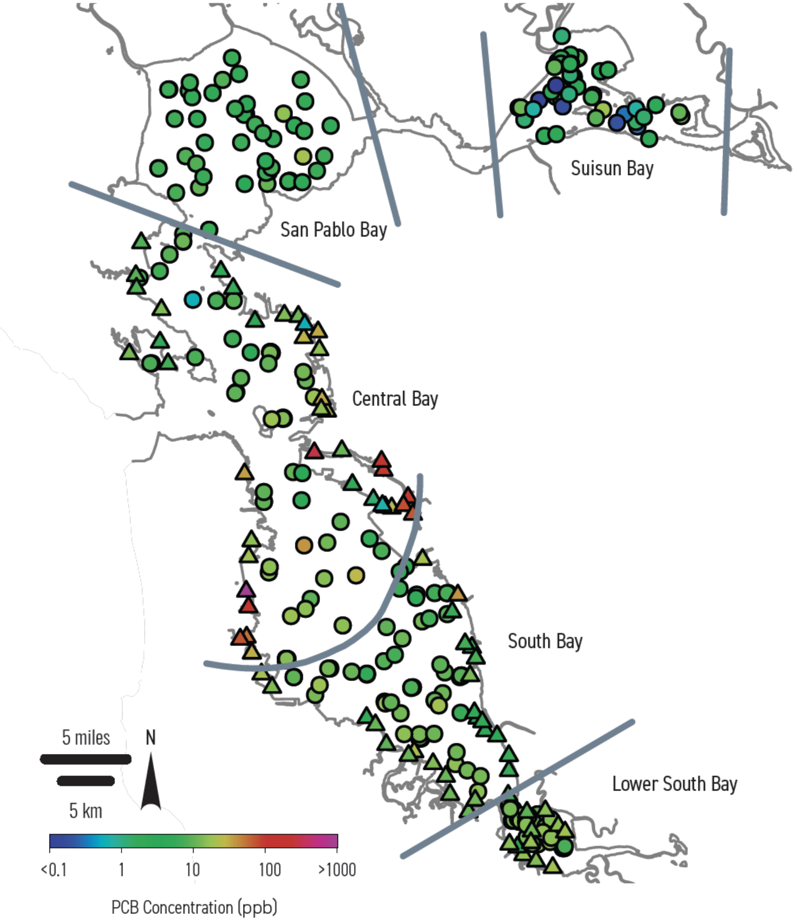
Jay Davis

San Francisco Estuary Institute

Regional Monitoring Program for Water Quality in San Francisco Bay

- Began in 1993
- $4 million/year of stable funding
- Multi-faceted
- Continually adapting – recent shift toward CECs
- PCB Workgroup (2011)

PCBs in Sediment, 2002-2018

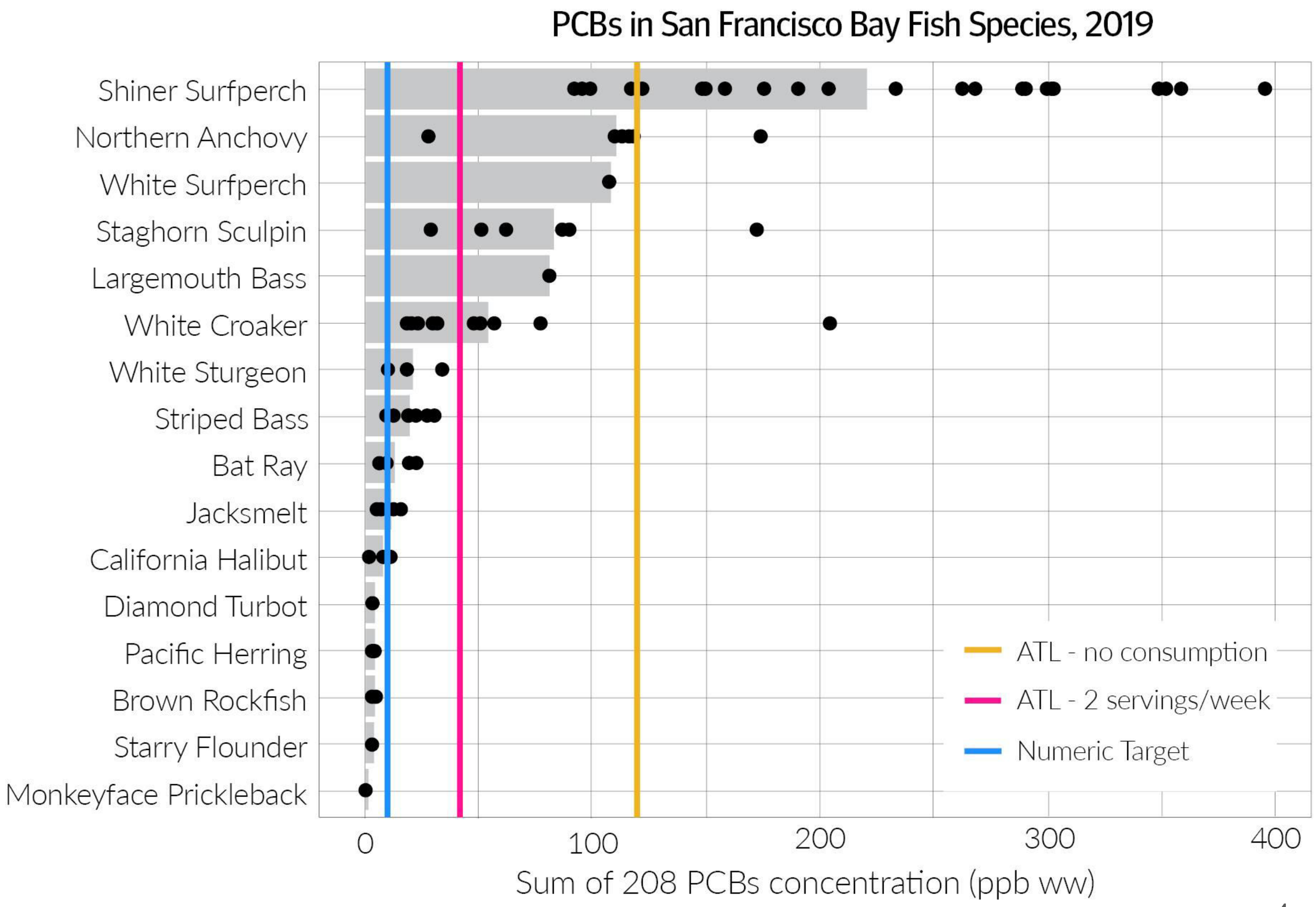


FOOTNOTE: Points on the map show all available dry season RMP data from 2002-2018 (circles) along with Central Bay and South Bay margin data (triangles) from 2015 and 2017, respectively.

PCBs: A Persistent Challenge

This is the dataset that defines the problem

Many species have average concentrations well above thresholds

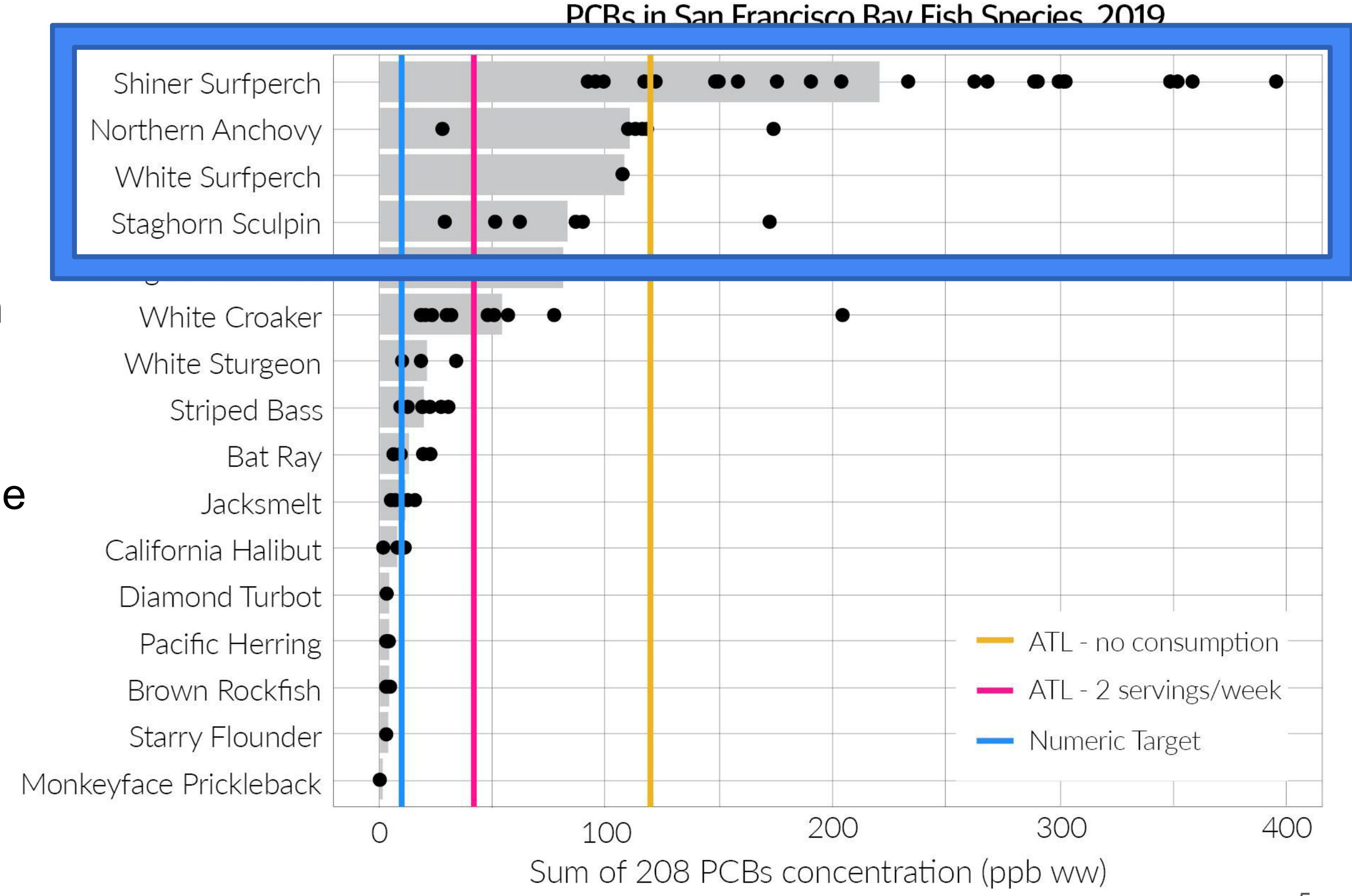


Buzby, N., Davis, J., Sutton, R., Yee, D., Miller, E., Wong, A., Sigala, M., Bonnema, A., Heim, W., Grace, R. 2021. Contaminant Concentrations in Sport Fish from San Francisco Bay: 2019. SFEI Contribution No. 1036. San Francisco Estuary Institute, Richmond, CA.

Understanding the Problem

Part A:
Localized margin contamination

- Very high levels
- More controllable



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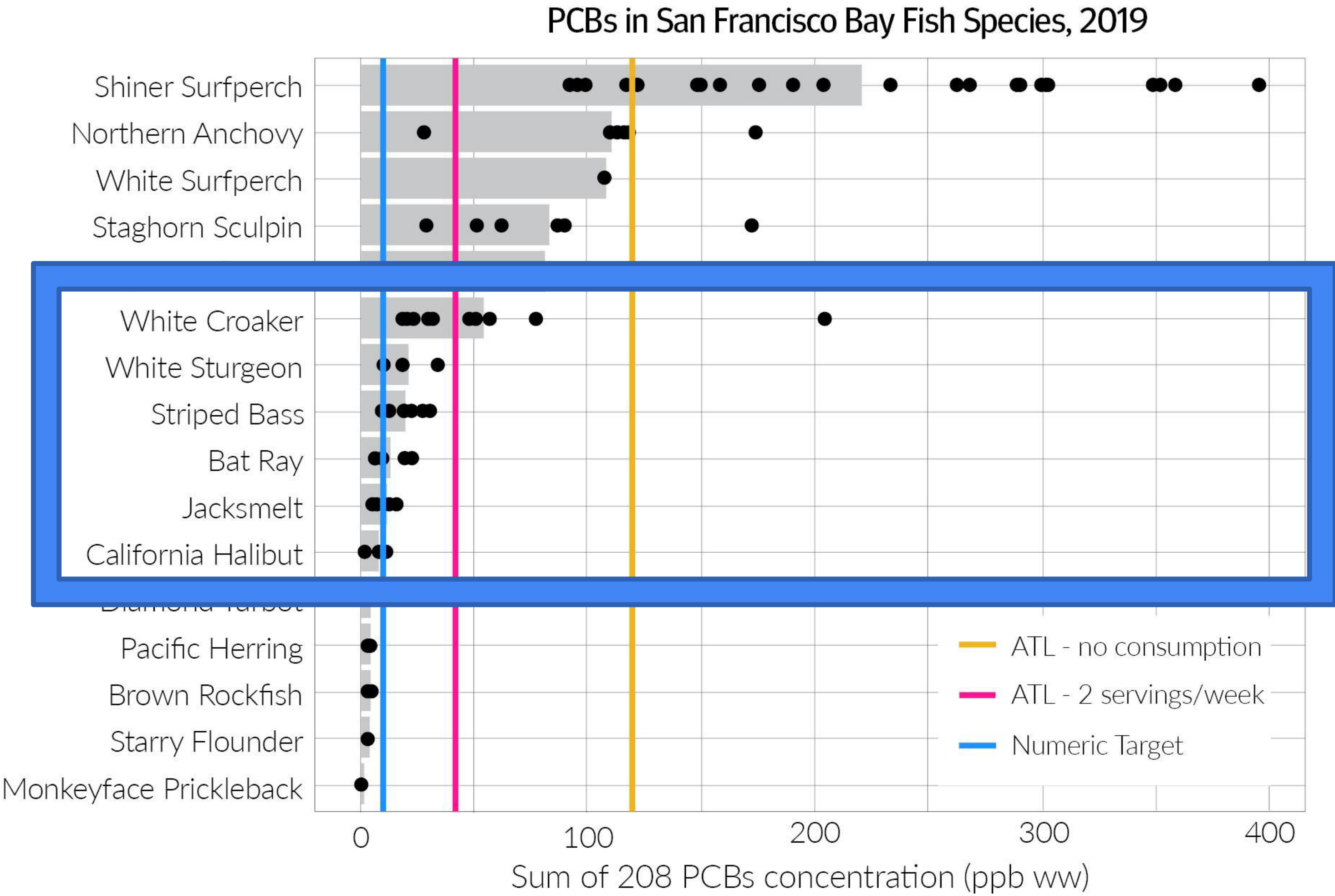
Understanding the Problem

Part B:

Regional Bay contamination

- Moderate levels
- Harder to control



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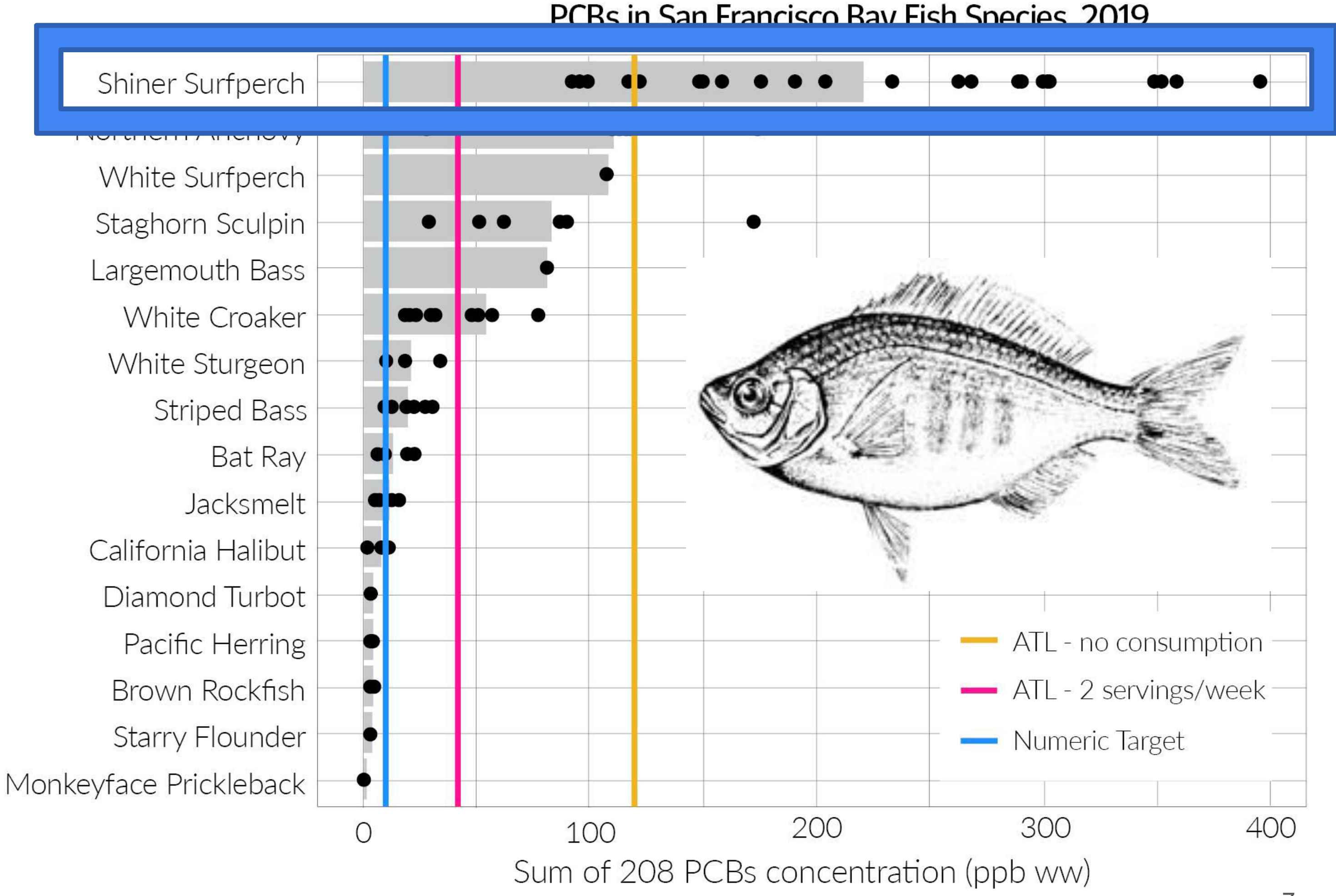
Understanding the Problem

Part A:
Localized margin contamination

- Shiner surfperch



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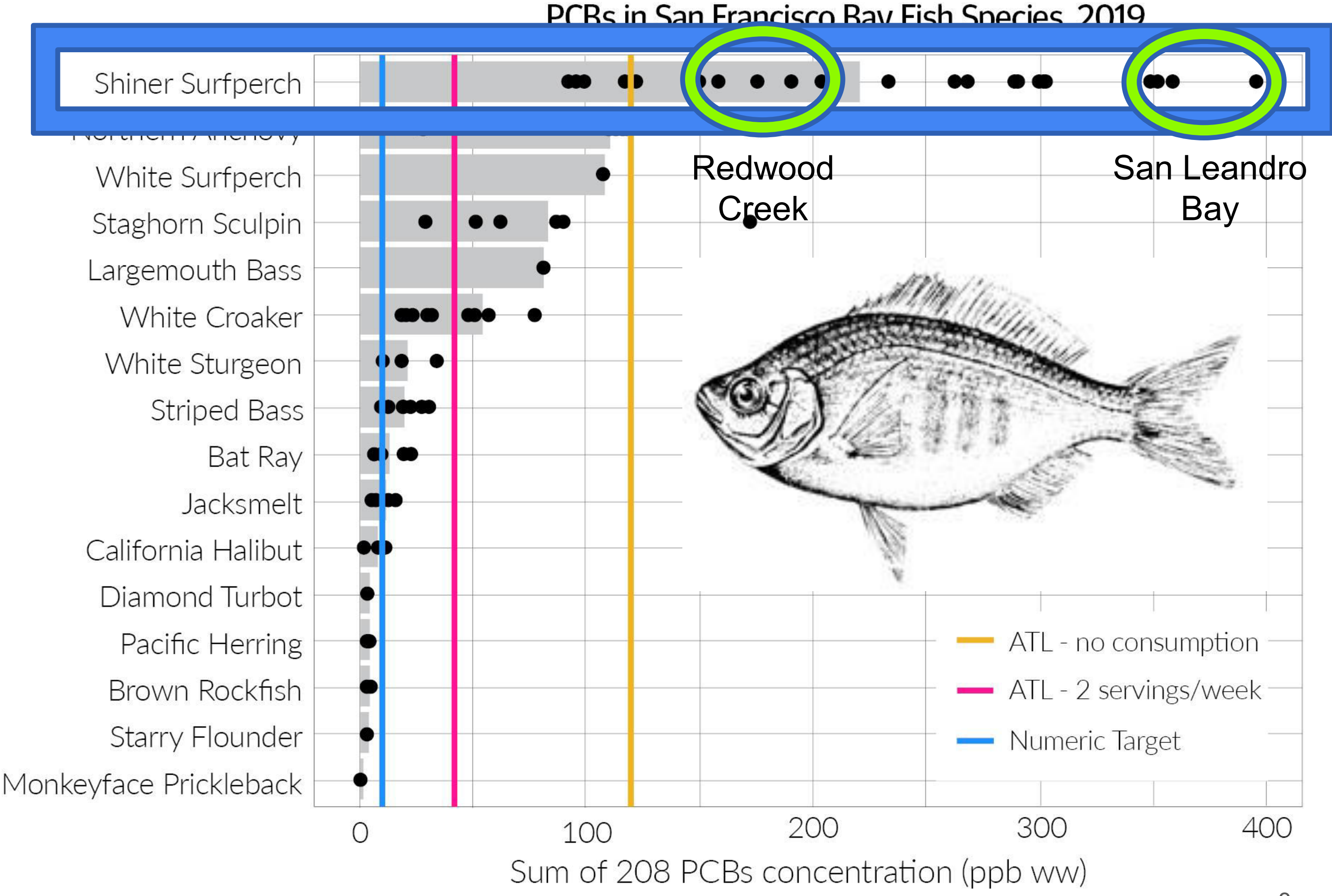
Understanding the Problem

Part A: Localized margin contamination

- Shiner surfperch



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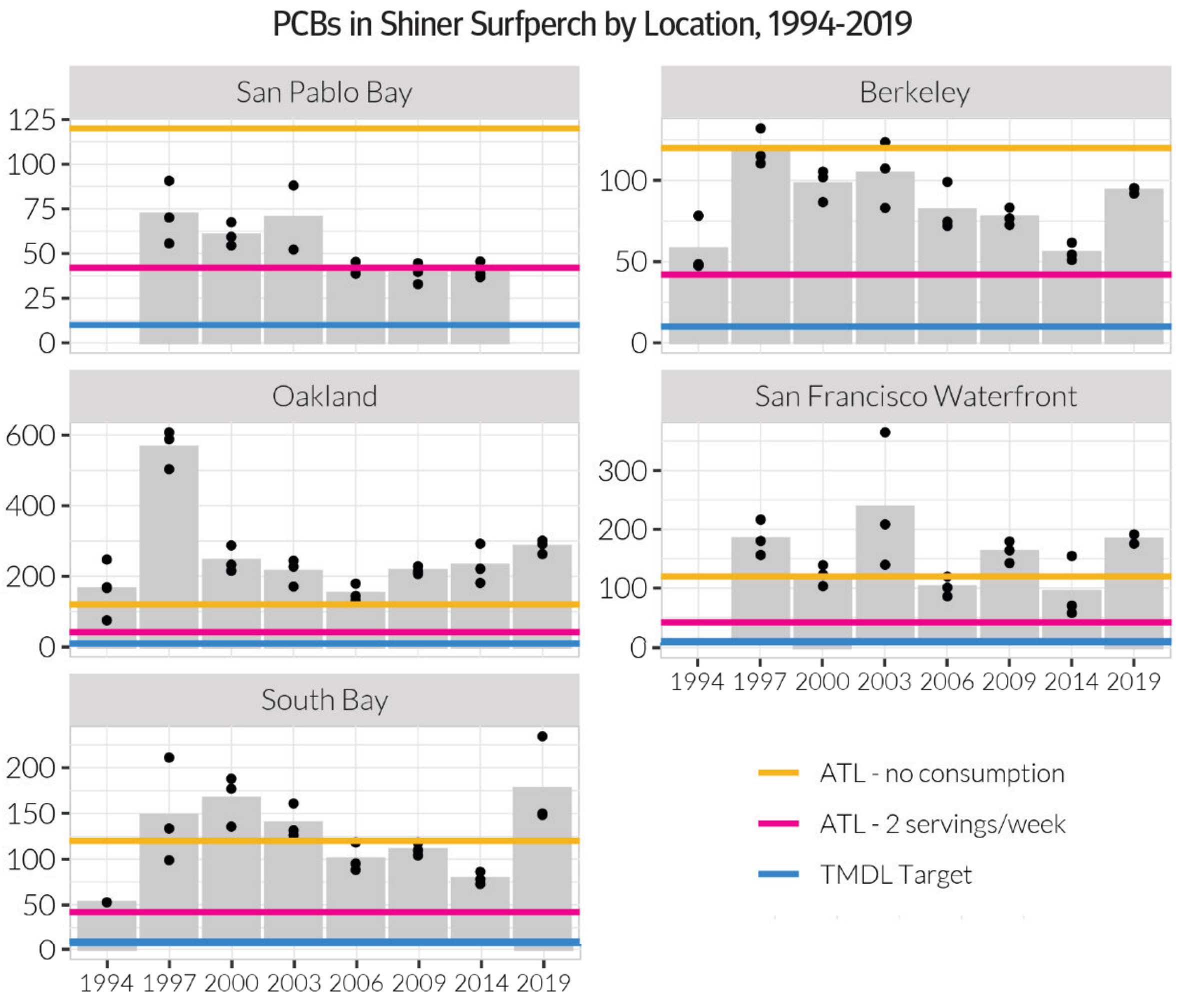
Negligible improvement in the last 25 years



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PCBs in Prey Fish, 2010

- Higher concentrations than sport fish!
- Focused attention on contaminated margin areas

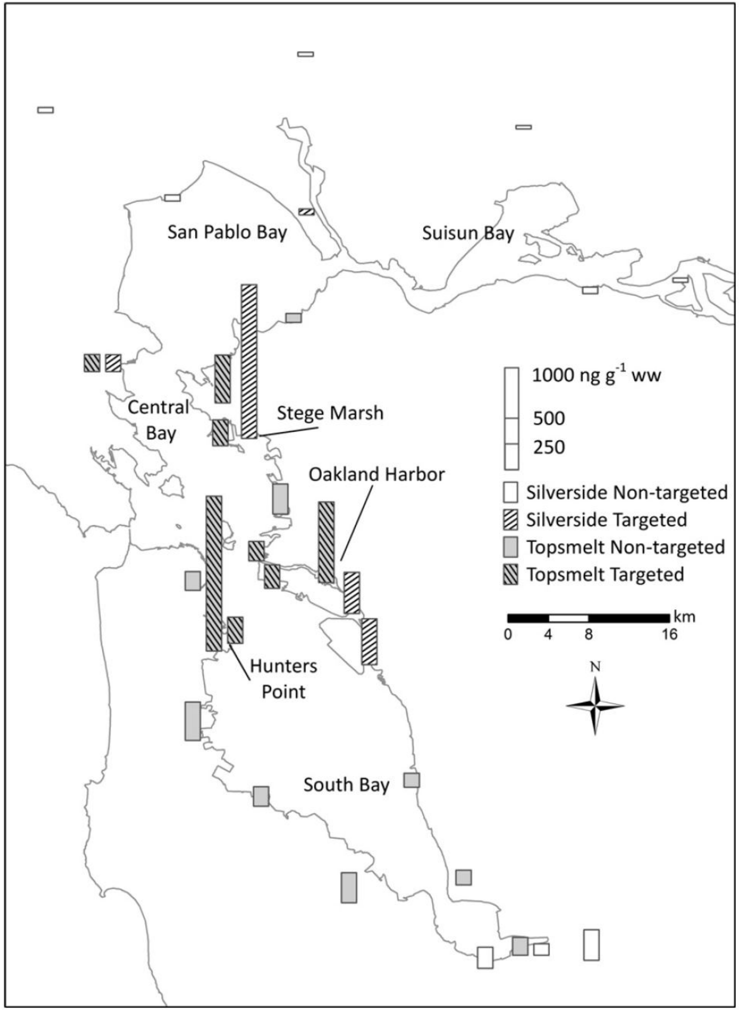


Fig. 1. Sum of 209 PCB wet weight concentrations at each location.

Greenfield, B.K. and Allen, R.M., 2013. Polychlorinated biphenyl spatial patterns in San Francisco Bay forage fish. Chemosphere, 90(5), pp.1693-1703.

Stormwater Reconnaissance

- 2015-2020
- Single grab samples
- Estimated particle concentrations

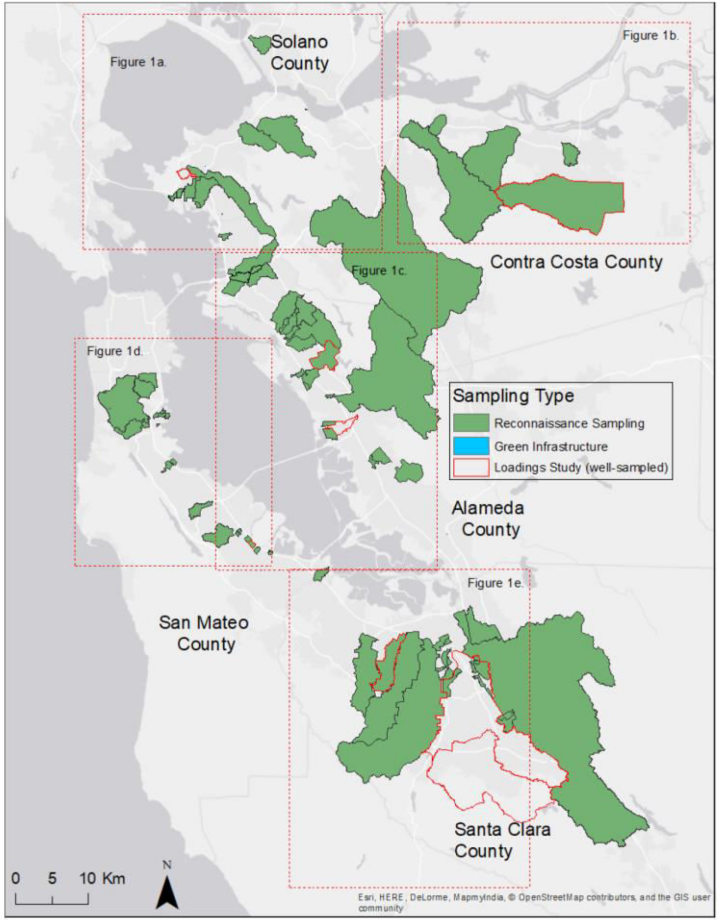
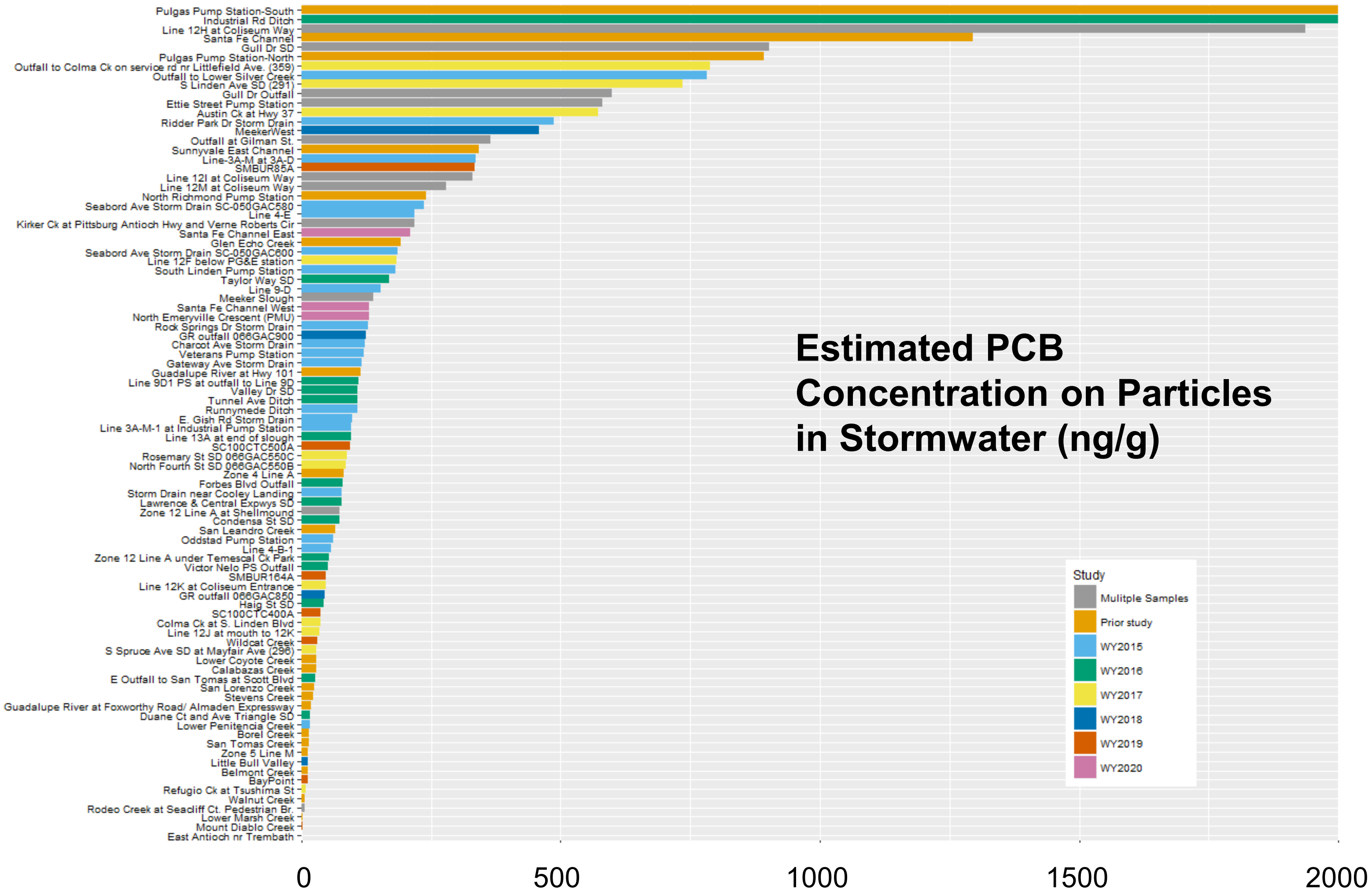


Figure 1. Watersheds/catchments sampled to date. Note: The drainage management areas (DMAs) of the green stormwater infrastructure sampling sites are so small they are not visible, though they are given a numeric map key identifier.

Gilbreath, A.N. and McKee, L.J. 2021. Pollutants of Concern Reconnaissance Monitoring Progress Report, Water Years 2015-2020. SFEI Contribution No. 1061. San Francisco Estuary Institute, Richmond, California.



Gilbreath, A.N. and McKee, L.J. 2021. Pollutants of Concern Reconnaissance Monitoring Progress Report, Water Years 2015-2020. SFEI Contribution No. 1061. San Francisco Estuary Institute, Richmond, California.

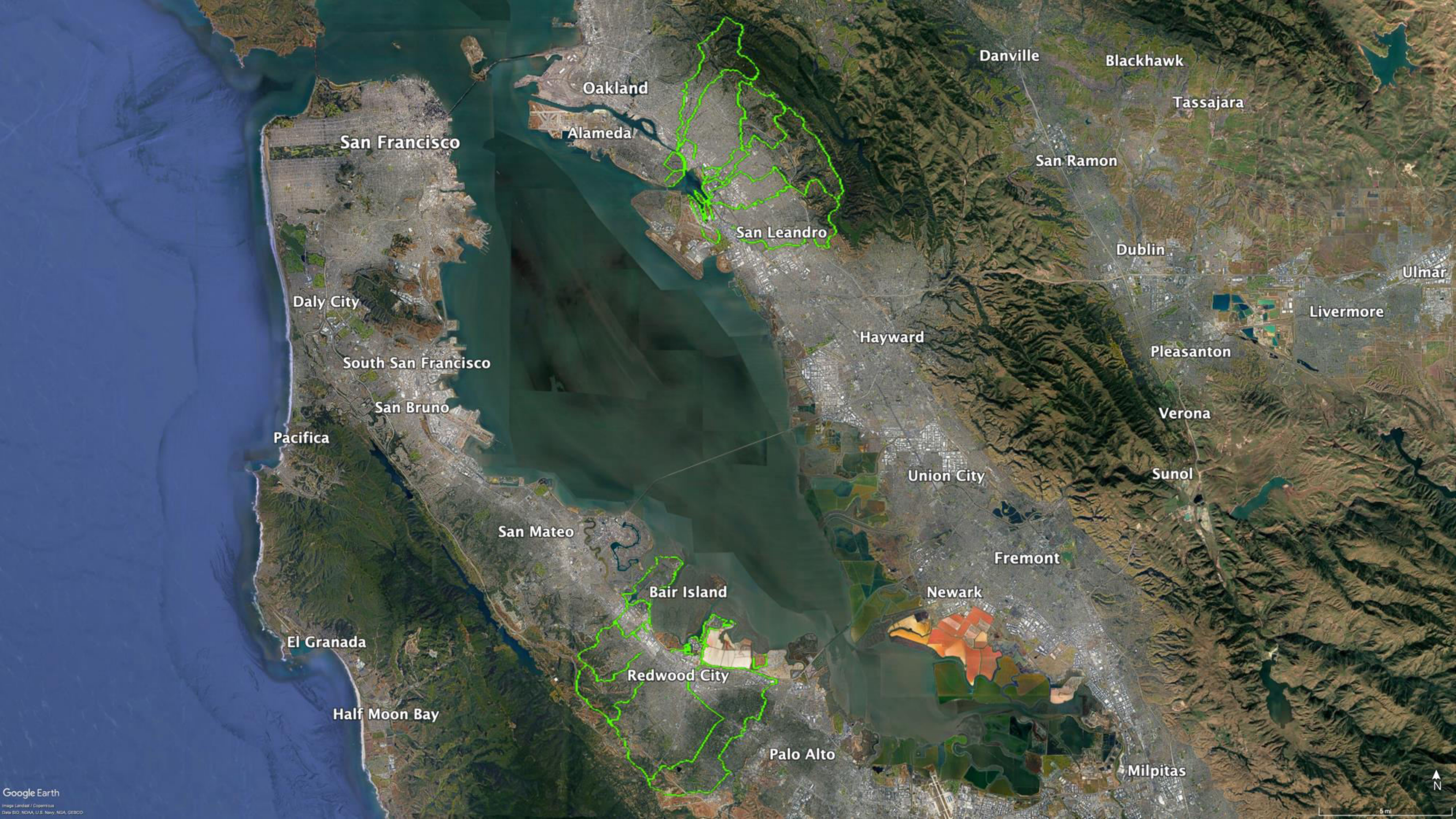

Danville
Blackhawk
Oakland
Tassajara
Alameda
San Francisco
San Ramon
San Leandro
Dublin
Ulmar
Daly City
Livermore
Hayward
Pleasanton
South San Francisco
San Bruno
Verona
Pacifica
Union City
Sunol
San Mateo
Fremont
Bair Island
Newark
El Granada
Redwood City
Half Moon Bay
Palo Alto
Milpitas
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Image Landsat / Copernicus
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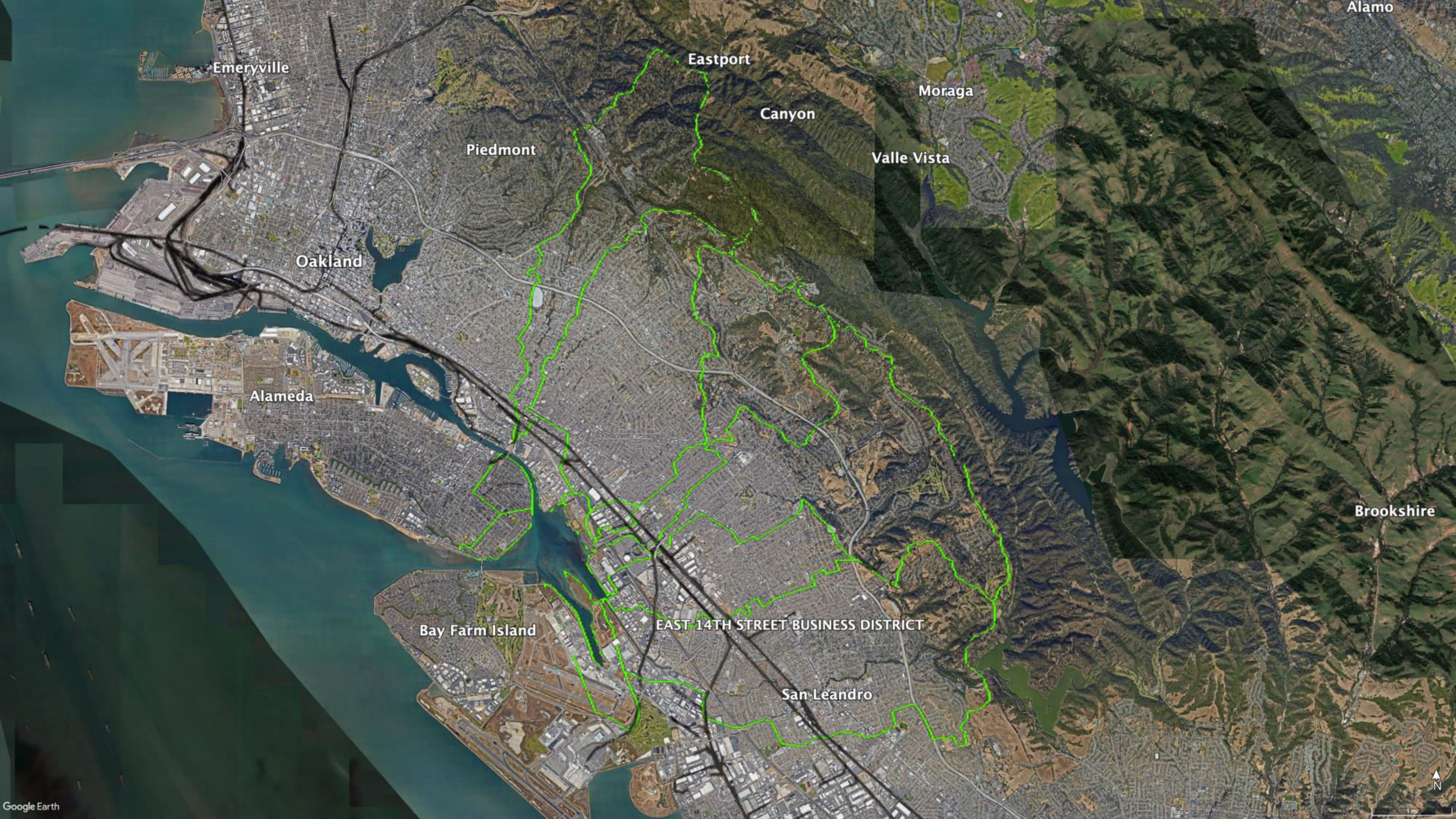
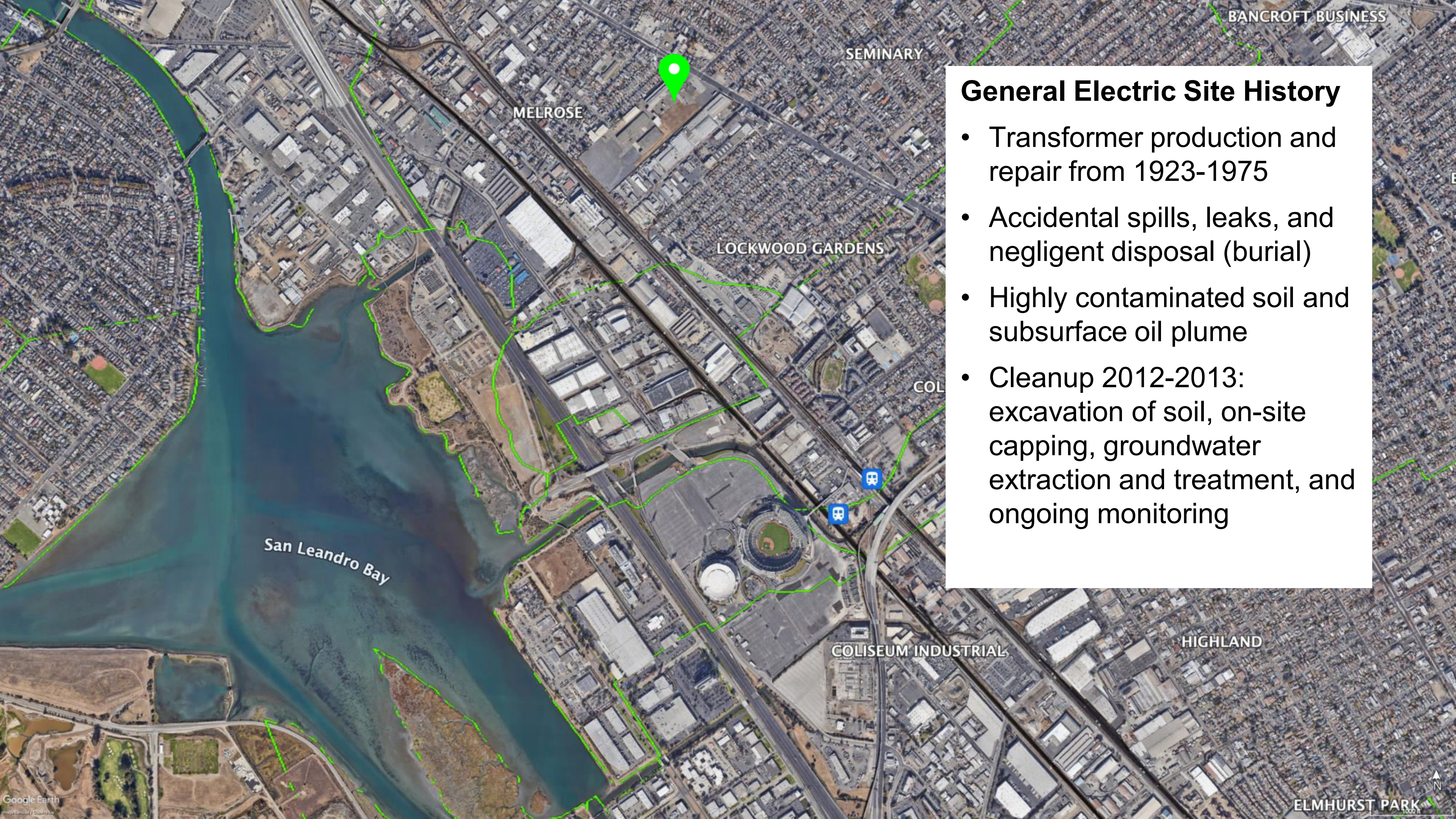


Alamo
Eastport
Emeryville
Moraga
Canyon
Piedmont
Valle Vista
Oakland
Alameda
Brookshire
Bay Farm Island
EAST 14TH STREET BUSINESS DISTRICT
San Leandro
Google Earth
N

General Electric Site History

- Transformer production and repair from 1923-1975
- Accidental spills, leaks, and negligent disposal (burial)
- Highly contaminated soil and subsurface oil plume
- Cleanup 2012-2013: excavation of soil, on-site capping, groundwater extraction and treatment, and ongoing monitoring



Stormwater (RMP)

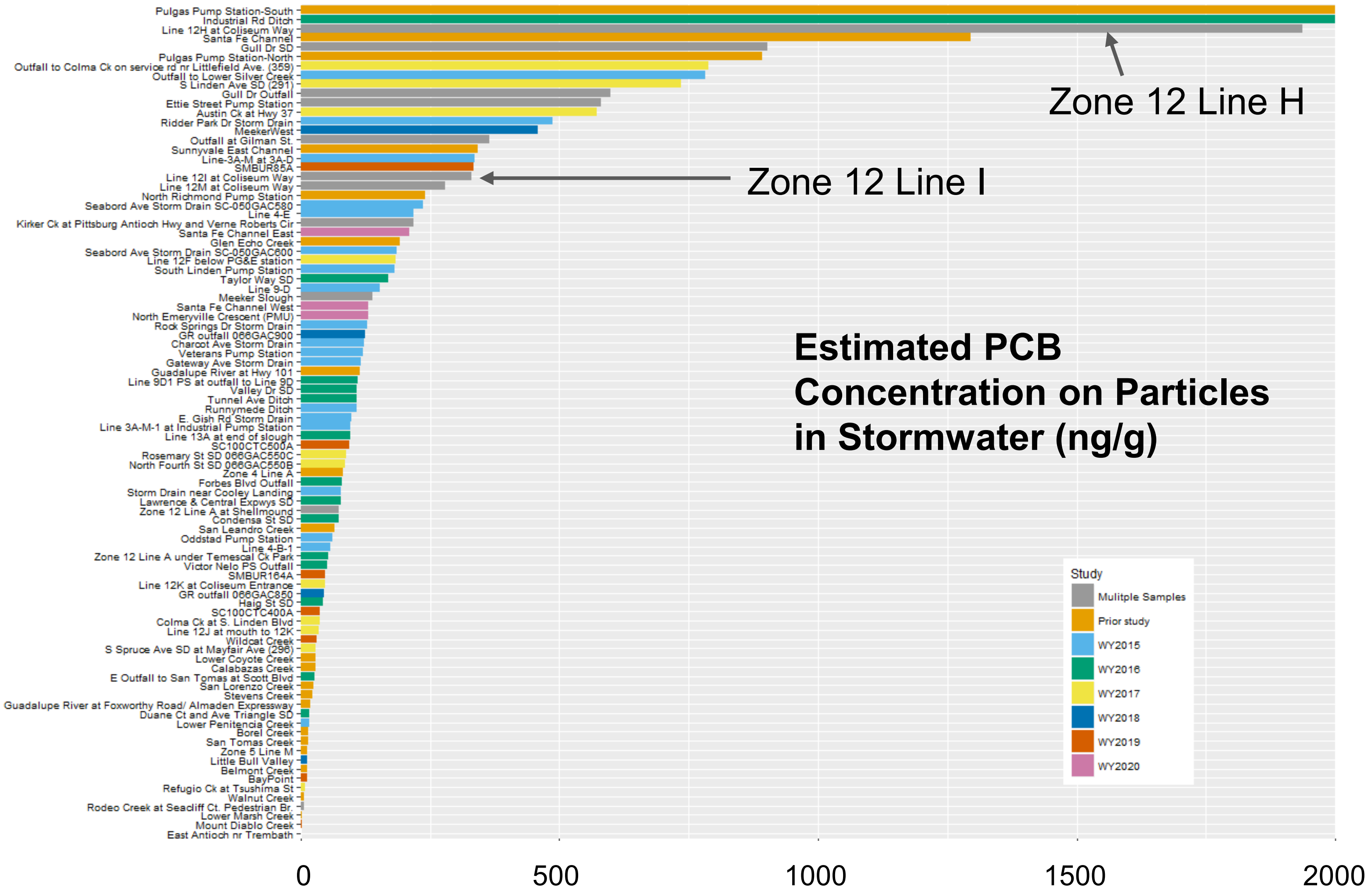
Zone 12, Line H
2017: 2,601 ng/g
2020: 1,271 ng/g

Stormwater (RMP)

Zone 12, Line I

2017: 398 ng/g

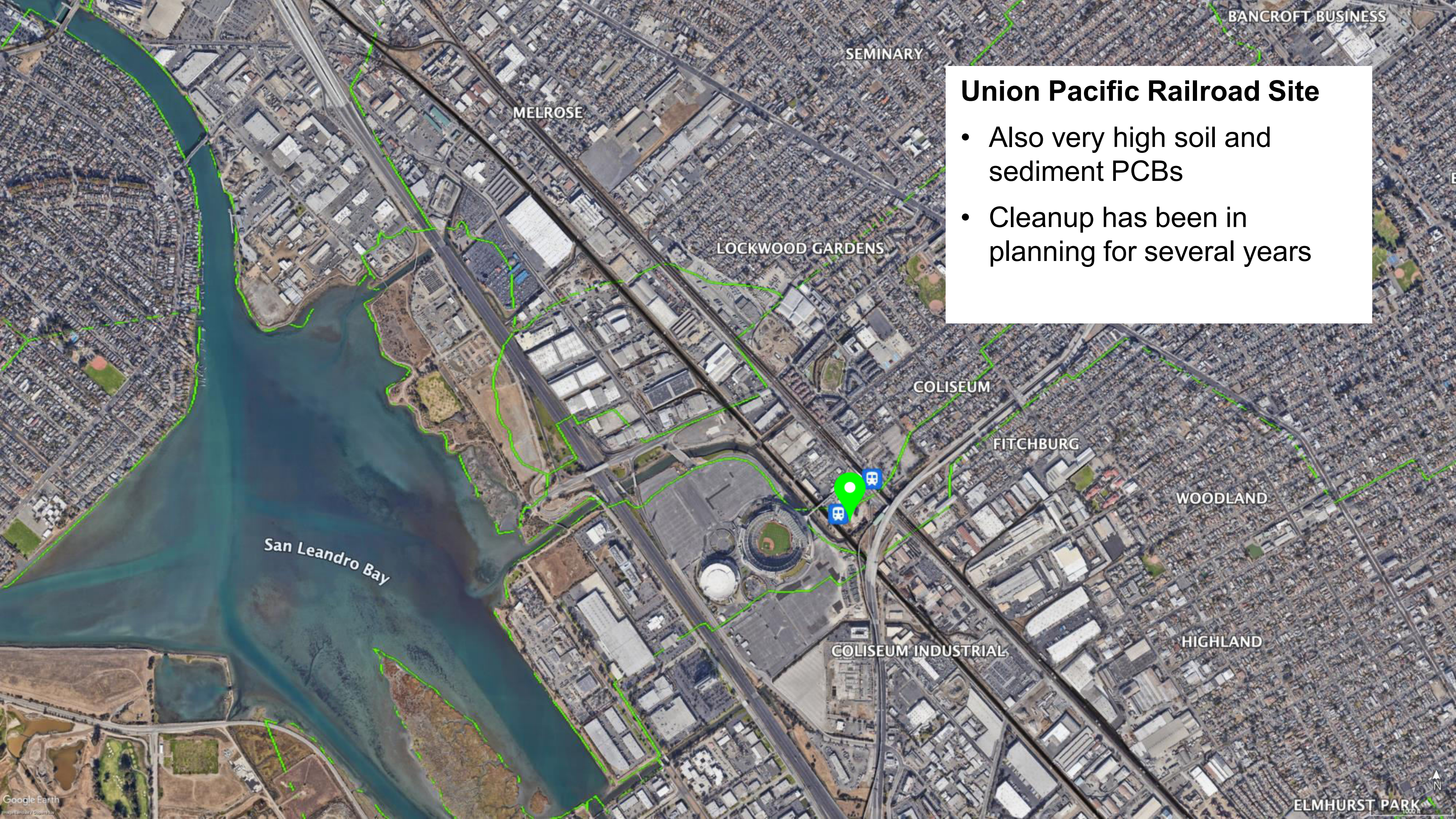
2020: 263 ng/g



Gilbreath, A.N. and McKee, L.J. 2021. Pollutants of Concern Reconnaissance Monitoring Progress Report, Water Years 2015-2020. SFEI Contribution No. 1061. San Francisco Estuary Institute, Richmond, California.

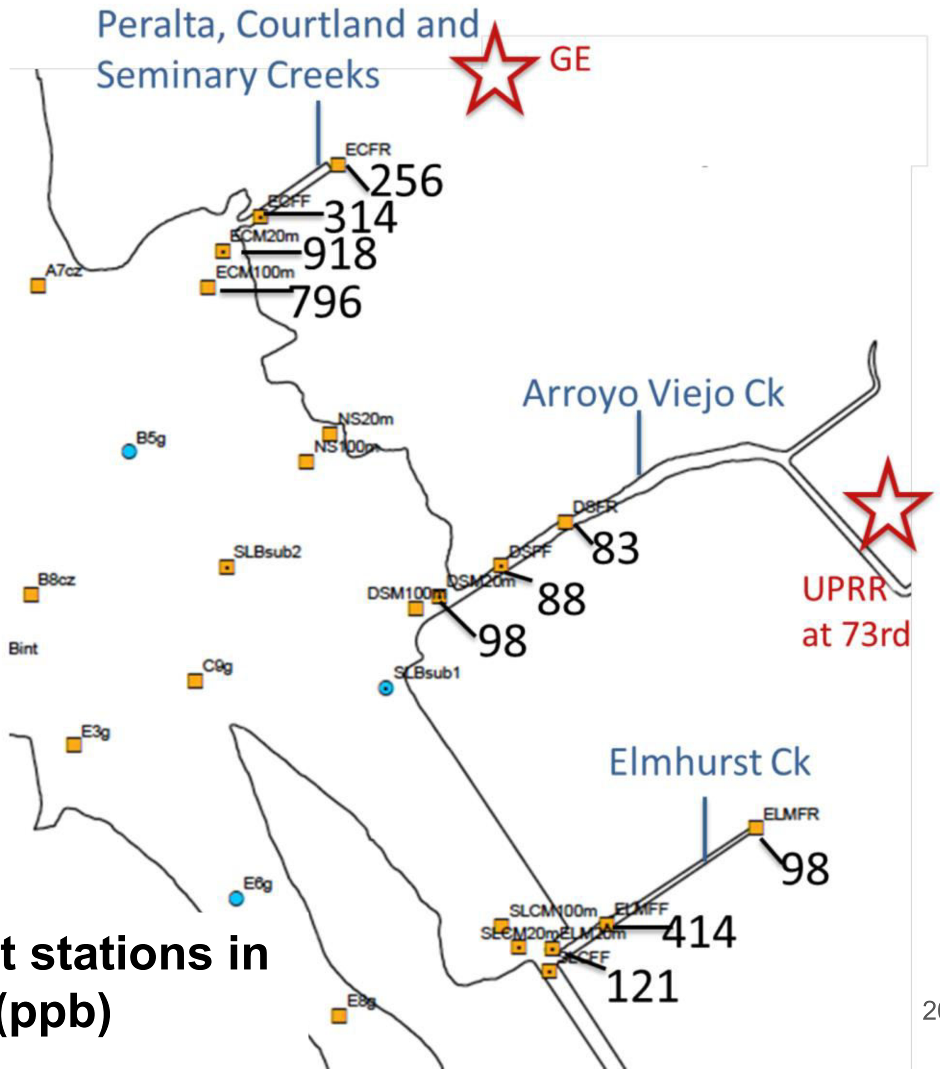
Union Pacific Railroad Site

- Also very high soil and sediment PCBs
- Cleanup has been in planning for several years



Real-world complexities demand a data-driven approach

- Straightforward expectations may be wrong
- Cleanup actions may not work as expected

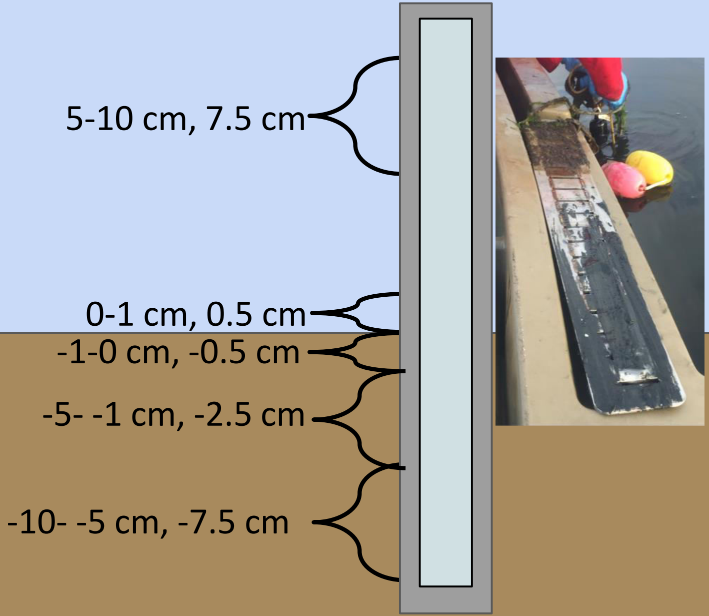


Sediment PCBs at select stations in San Leandro Bay, 2016 (ppb)

Passive Sampler Monitoring

Passive sampler
(PCB analysis, C_{PE} and C_{free})

Collaboration of Stanford University (Richard Luthy, Yeo-Myoung Cho) and SFEI



PRELIMINARY UNPUBLISHED DATA:
DO NOT CITE OR QUOTE

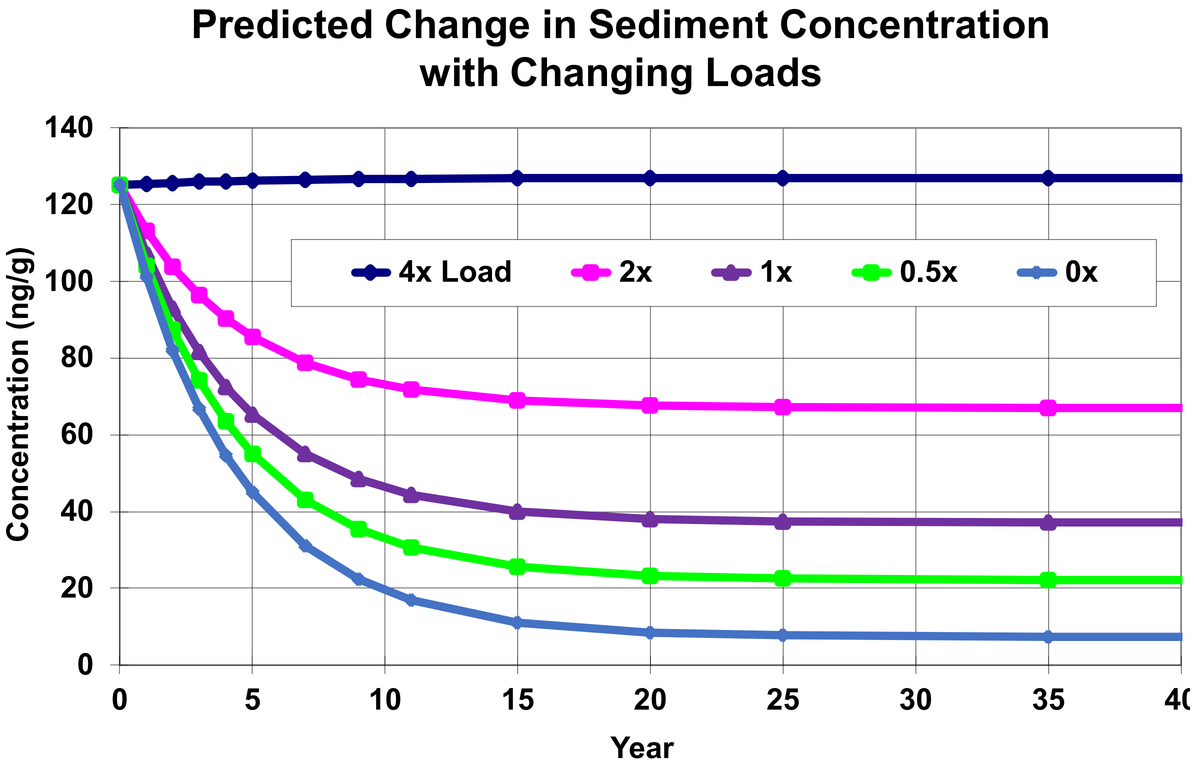
Relatively high Cfree concentrations near the GE area

PRELIMINARY UNPUBLISHED DATA:
DO NOT CITE OR QUOTE

- **Very high** suspended sediment concentration observed near GE site (27 ppm)
- Re-confirmed heavier contamination in GE downstream than in UPRR downstream

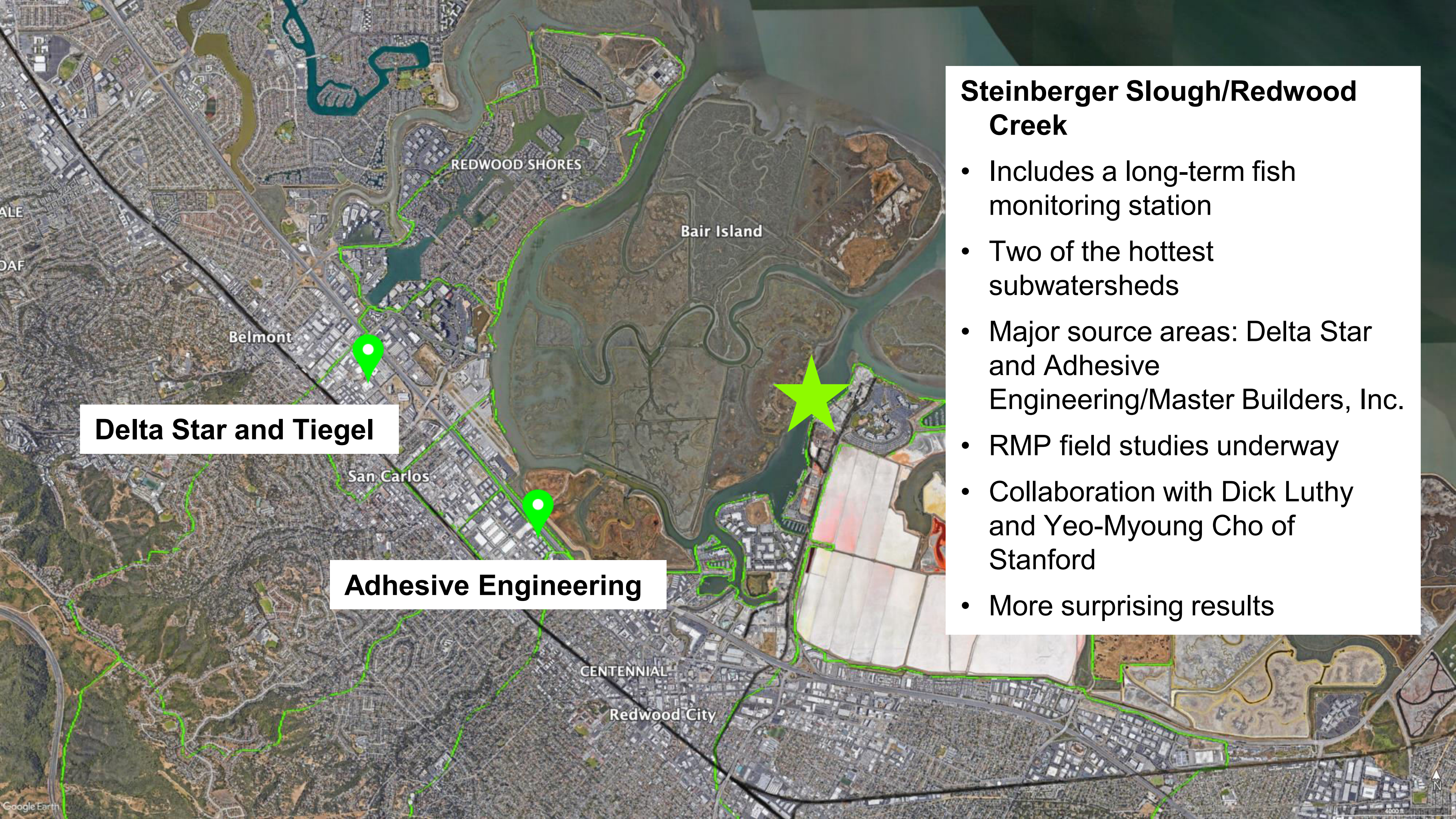
Simple Mass Budget Model for San Leandro Bay

- PMUs will vary
- Fish will follow sediment
- Suggests inputs are continuing
- Reducing watershed inputs would greatly accelerate recovery
- High uncertainty



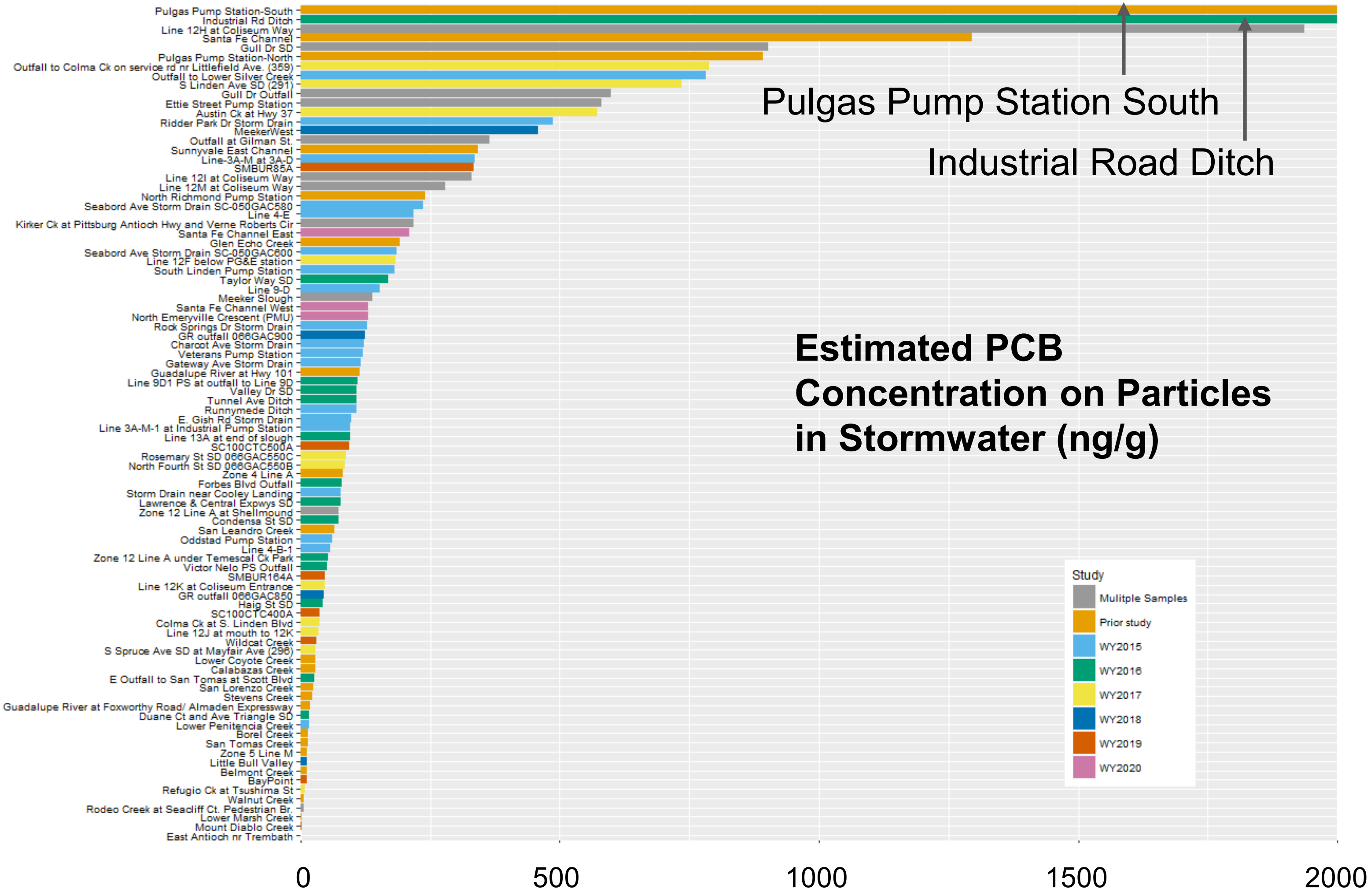
Loads shown as multiples of estimated current stormwater load

D. Yee, A.N. Gilbreath, L.J. McKee, and J.A. Davis. 2019. Conceptual Model to Support PCB Management and Monitoring in the San Leandro Bay Priority Margin Unit – Final Report. SFEI Contribution No. 928. San Francisco Estuary Institute Richmond, CA.



Steinberger Slough/Redwood Creek

- Includes a long-term fish monitoring station
- Two of the hottest subwatersheds
- Major source areas: Delta Star and Adhesive Engineering/Master Builders, Inc.
- RMP field studies underway
- Collaboration with Dick Luthy and Yeo-Myoung Cho of Stanford
- More surprising results

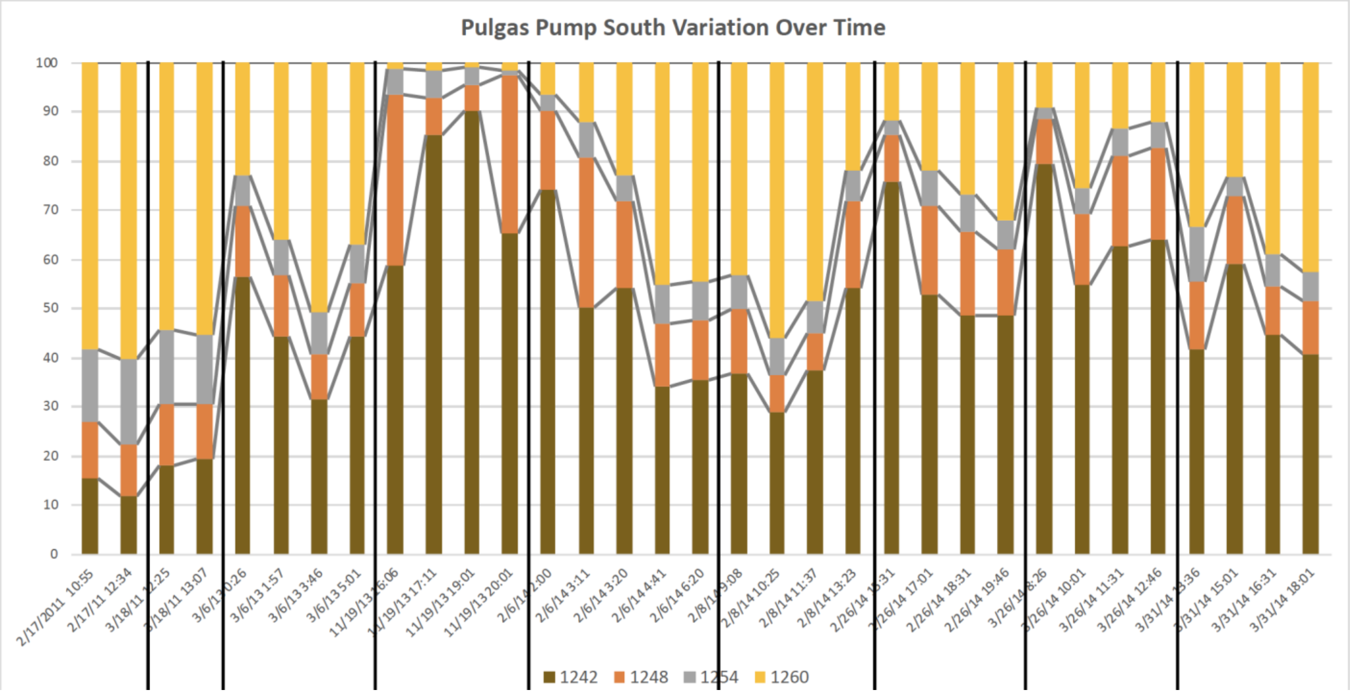


Gilbreath, A.N. and McKee, L.J. 2021. Pollutants of Concern Reconnaissance Monitoring Progress Report, Water Years 2015-2020. SFEI Contribution No. 1061. San Francisco Estuary Institute, Richmond, California.

Stormwater

- 2011-2014

Figure 3. Aroclor indices in stormwater at the outlet of Pulgas Pump Station South over time.



Davis, J.A. and Gilbreath, A.N., 2019. Small Tributaries Pollutants of Concern Reconnaissance Monitoring: Pilot Evaluation of Source Areas Using PCB Congener Data. SFEI Contribution No. 956. San Francisco Estuary Institute, Richmond, California.

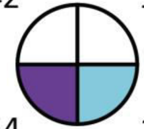
Sediment in Source Areas

- One very hot source area with unique profile

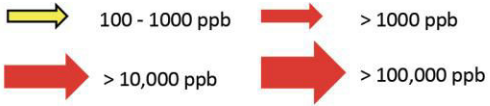
Davis, J.A. and Gilbreath, A.N., 2019. Small Tributaries Pollutants of Concern Reconnaissance Monitoring: Pilot Evaluation of Source Areas Using PCB Congener Data. SFEI Contribution No. 956. San Francisco Estuary Institute, Richmond, California.

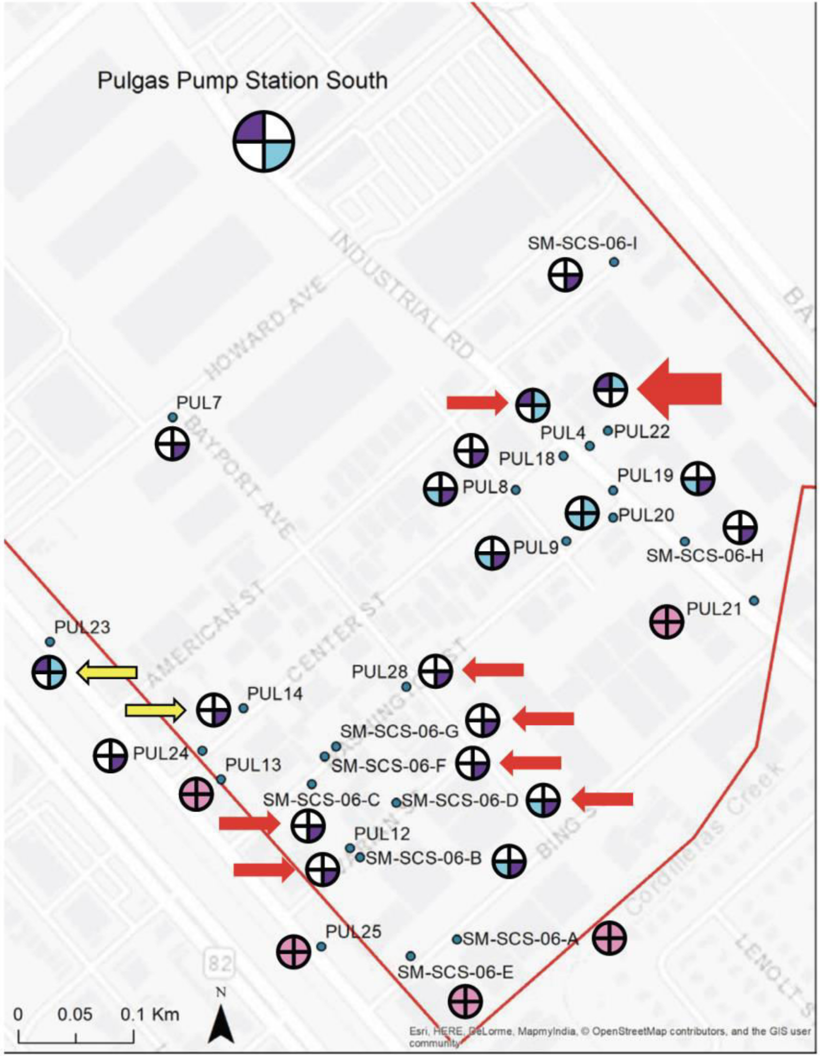
Figure 4. Aroclor indices in sediment in the Pulgas Pump Station South watershed.

Purple: Primary contributor (>40% of sum of indices)
Blue: Secondary (20-40%)
White: Low contributor (<20%)
Pink: Unreliable profiles due to low concentrations



Sum of 40 Congeners (ppb)

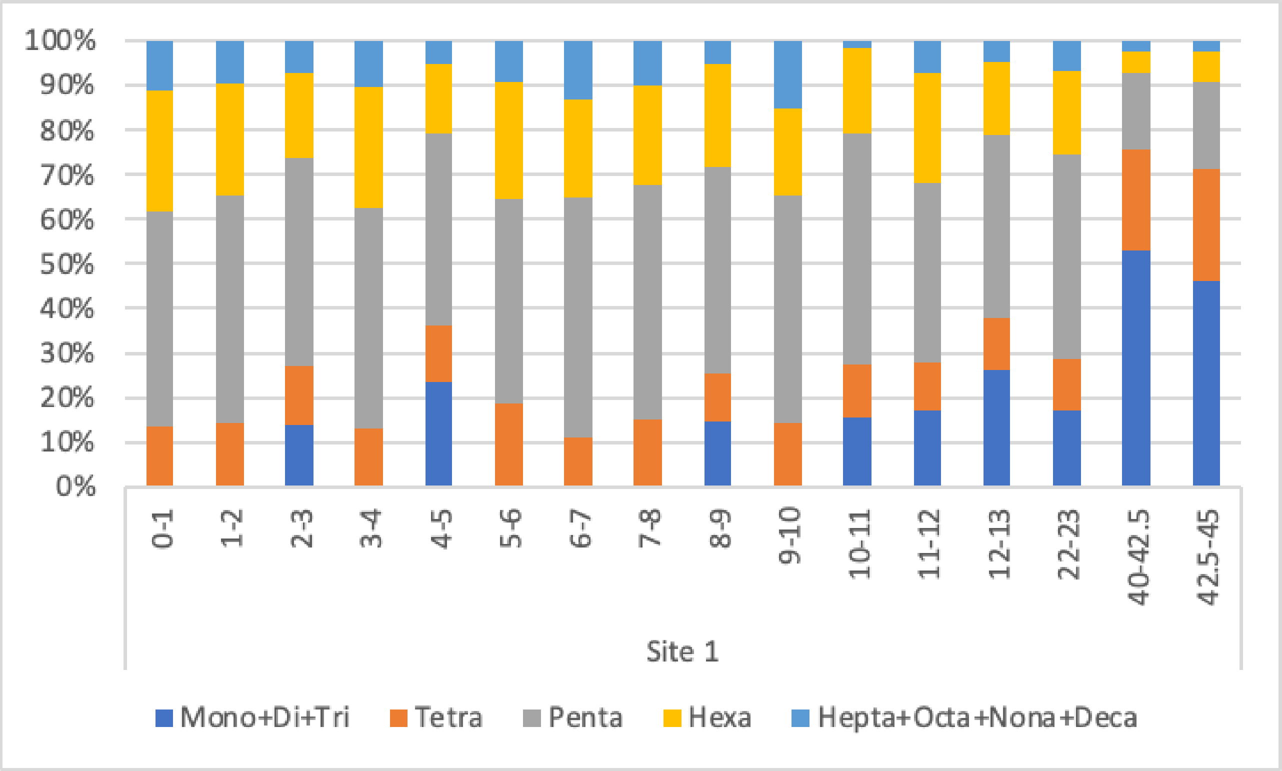




Passive Sampler at Pour Point

- 2020
- Sediment and prey fish data coming soon
- Strong Aroclor 1242 signal at depth

PRELIMINARY UNPUBLISHED DATA: DO NOT CITE OR QUOTE



Bay Science Needs and Plans

- Adequate **monitoring**
  - Establish baselines
  - Identify most important sources
  - Support modeling
  - Track improvement
- More robust fate **modeling** for SLB, SS/RC, other margin areas, and the whole Bay
- The RMP (PCB Workgroup) has been laying the groundwork and guiding studies to meet these needs

Model Grid for San Leandro Bay

Other Projects

- PCB-sniffing dog (proposal in development)
- Remote samplers

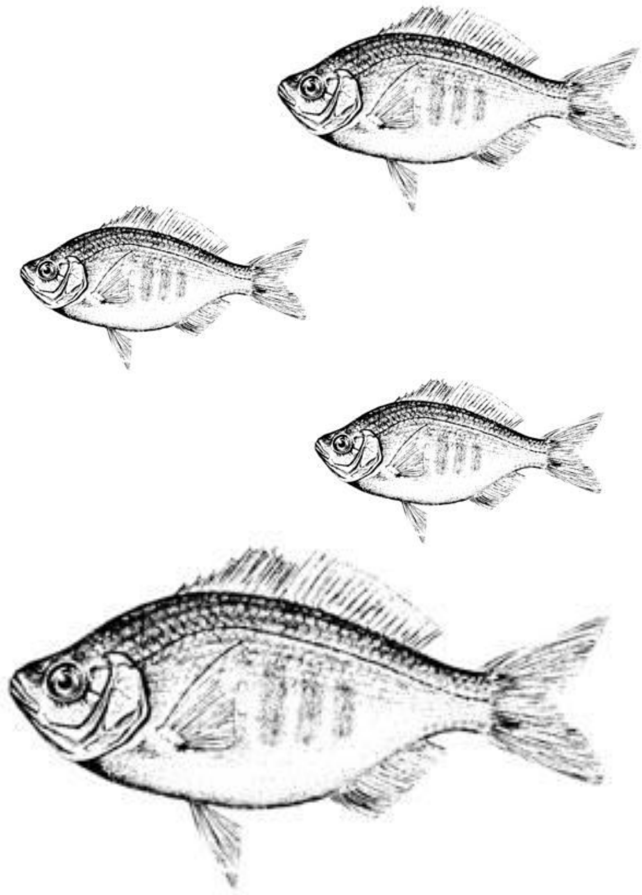
Acknowledgements

Co-Investigators

- Don Yee
- Alicia Gilbreath
- Lester McKee
- Diana Lin
- Yeo-Myoung Cho
- Dick Luthy
- Craig Jones
- Marco Sigala

RMP PCB Workgroup

- Setenay Frucht
- Frank Gobas
- Jon Konnan
- Ned Black
- Luisa Valiela
- Bridgette DeShields
- Bryan Frueh
- + the investigators



More Information

San Leandro Bay Conceptual Model Report

- https://www.sfei.org/documents/conceptual-model-support-pcb-management-and-monitoring-san-leandro-bay-priority-margin-1

Steinberger Slough/Redwood Creek Conceptual Model Report

- https://www.sfei.org/documents/conceptual-model-support-pcb-management-and-monitoring-steinberger-sloughredwood-creek

Emeryville Crescent Conceptual Model Report

- https://www.sfei.org/documents/conceptual-model-support-pcb-management-and-monitoring-emeryville-crscent-priority-margin

PCBs in Shiner Surfperch in Priority Margin Areas

- https://www.sfei.org/documents/pcbs-shiner-surfperch-priority-margin-areas-san-francisco-bay

Me

- jay@sfei.org

RMP

- sfei.org/rmp

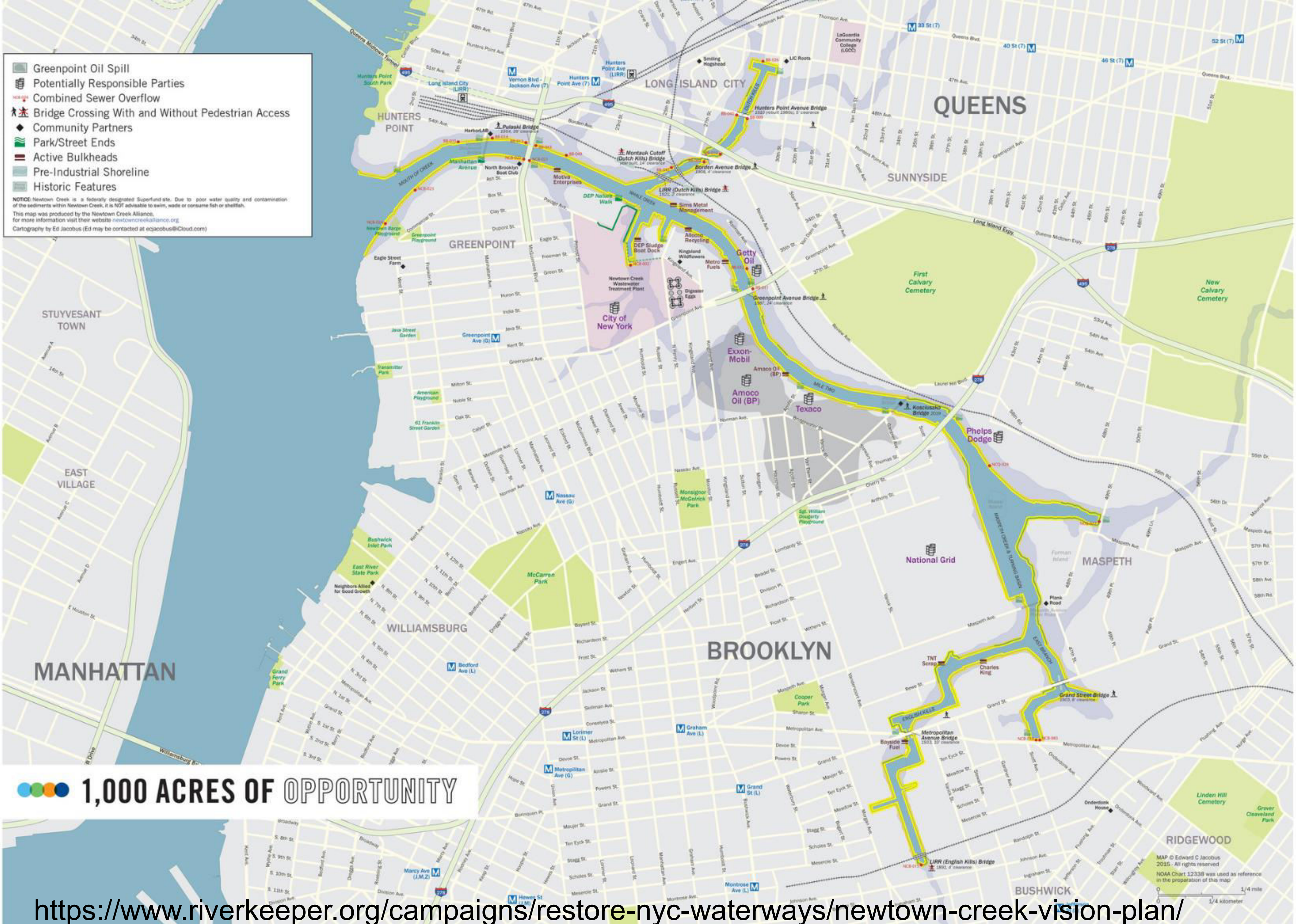
My son's band: Hot Flash Heat Wave

- Spotify, Apple Music, etc.

PCB fingerprinting at the Newtown Creek Superfund Site

Lisa A. Rodenburg, Mahdi Chitsaz, Mohson Al Hello, Kelly Francisco

Department of Environmental Sciences
Rutgers, the State University of New Jersey



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

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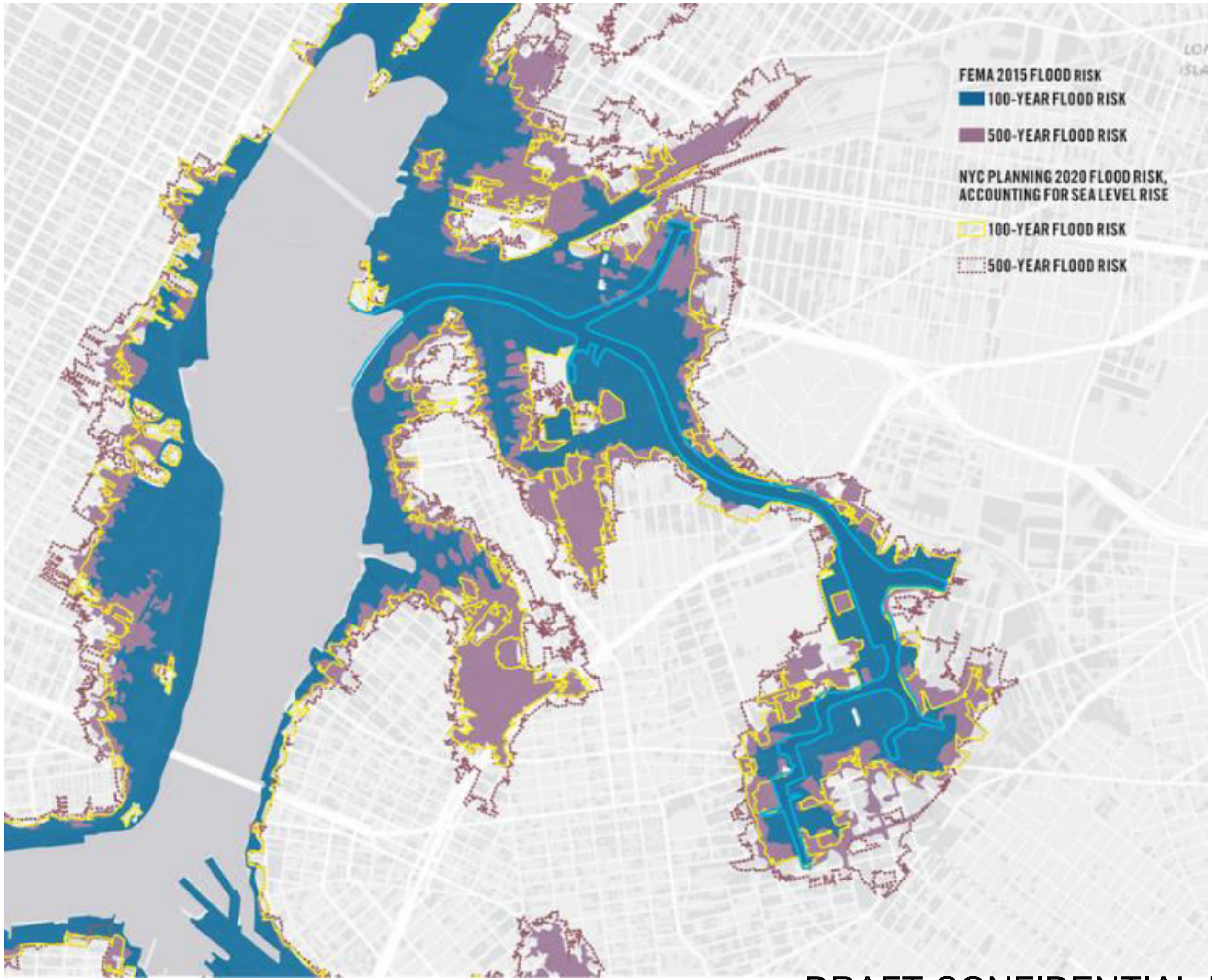
Flood risk



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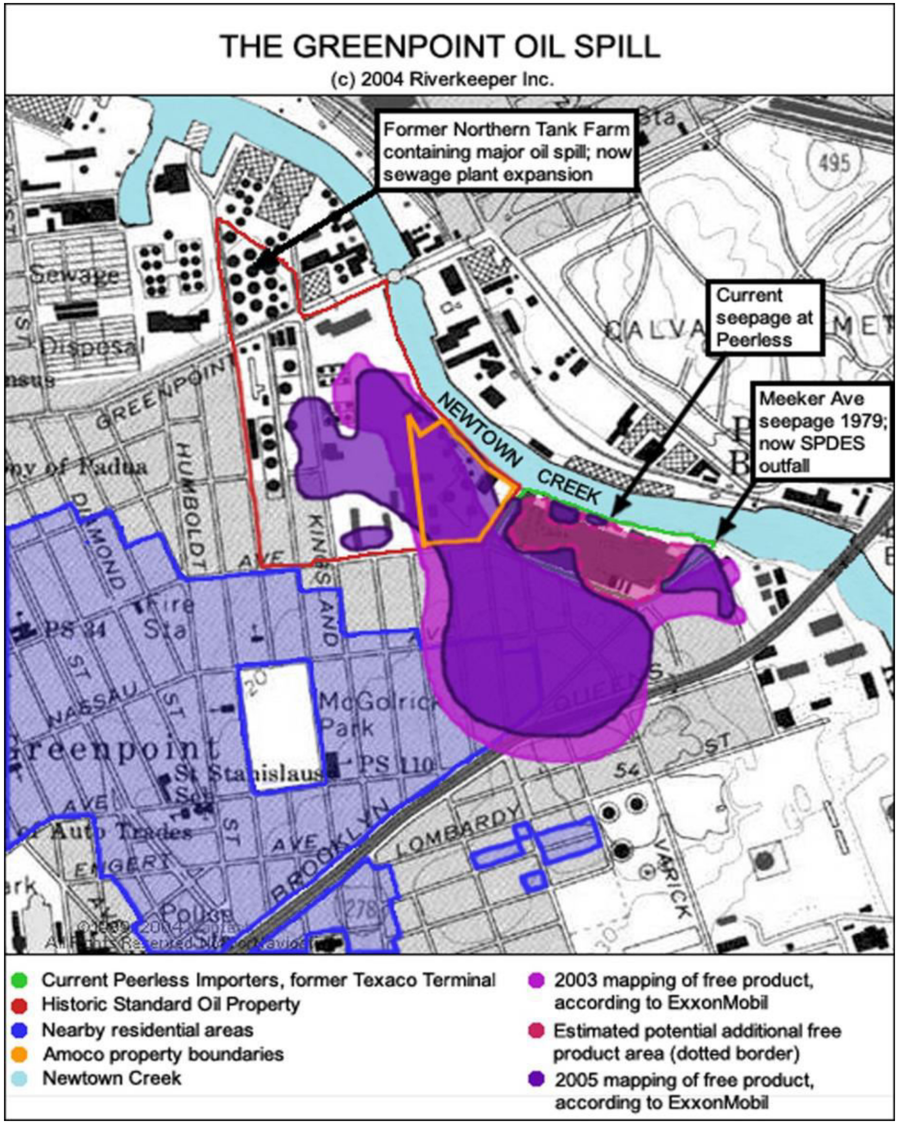
Newtown Creek

- 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!



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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!

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

$$X: (m \times n) \qquad G: (m \times p) \qquad F: (p \times n)$$

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.

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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!

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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

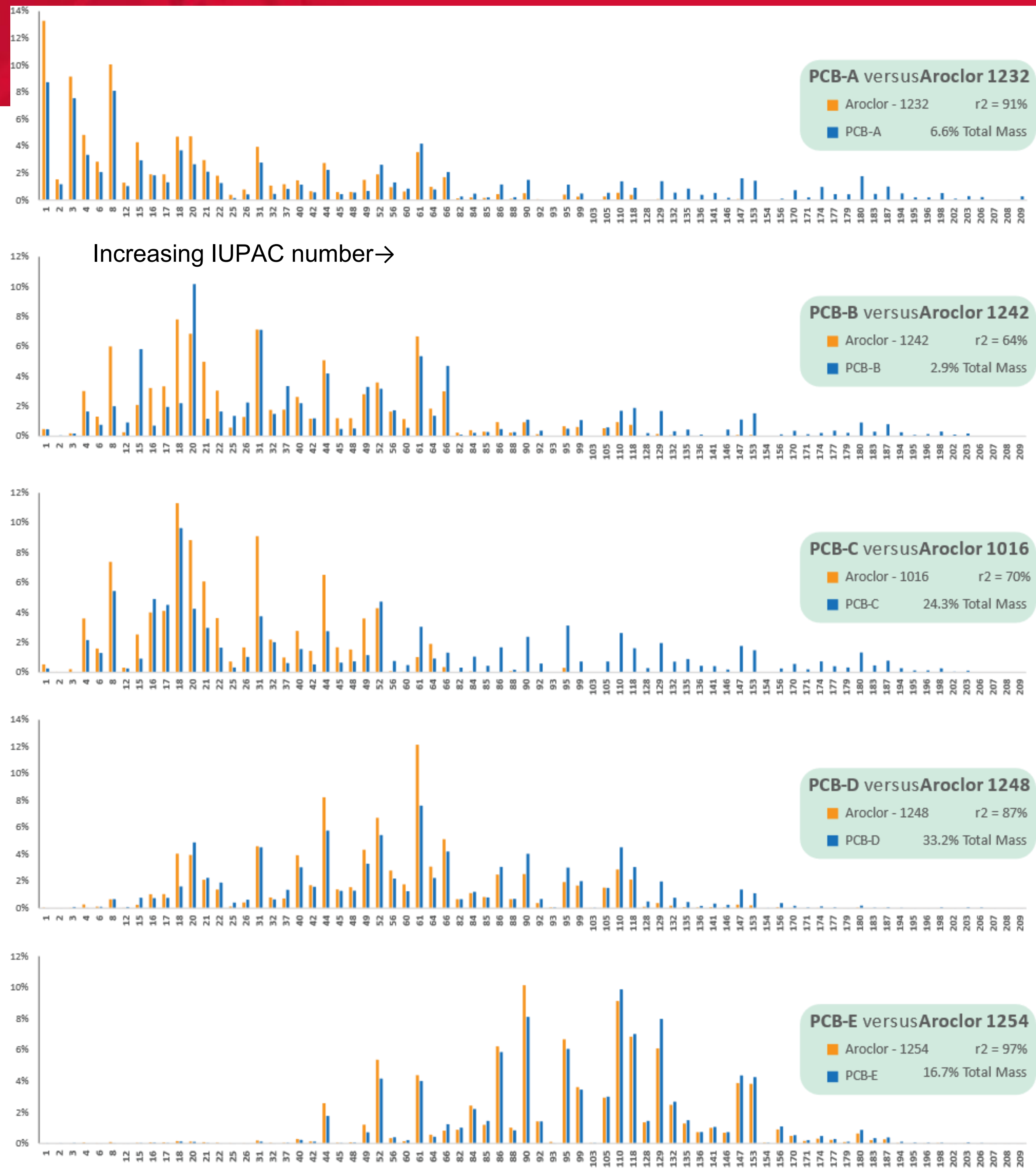
- PMF analysis of PCB congener concentrations
- Mapping of PMF results against probable sources
- Inventory of PCBs, by mass, in the sediment

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

Results

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



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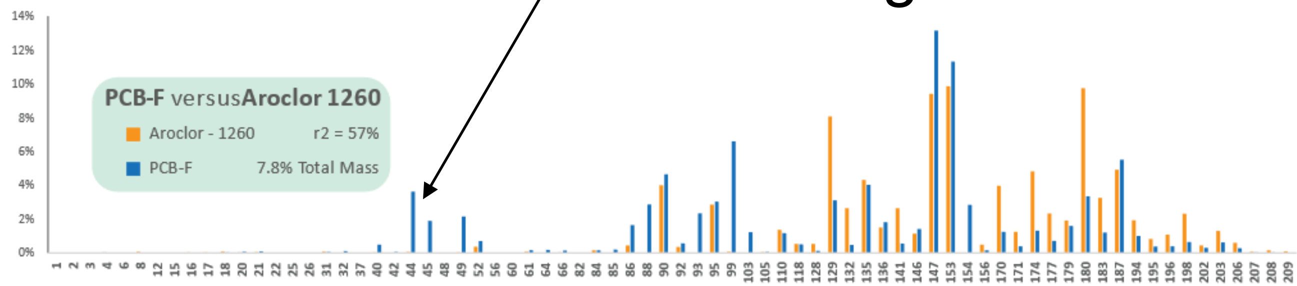
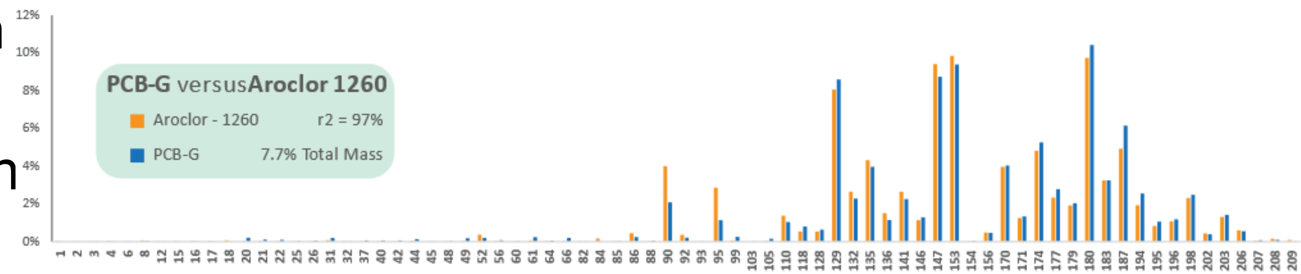
Identifying fingerprints

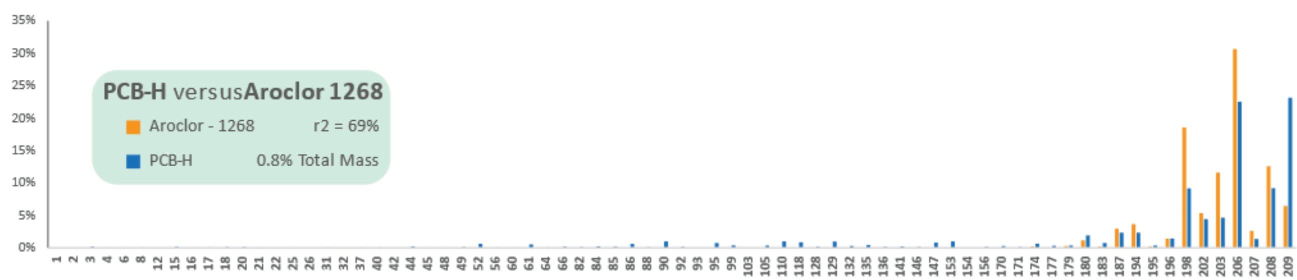
These congeners are often products of dehalogenation

ID based on weight of evidence, including:

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







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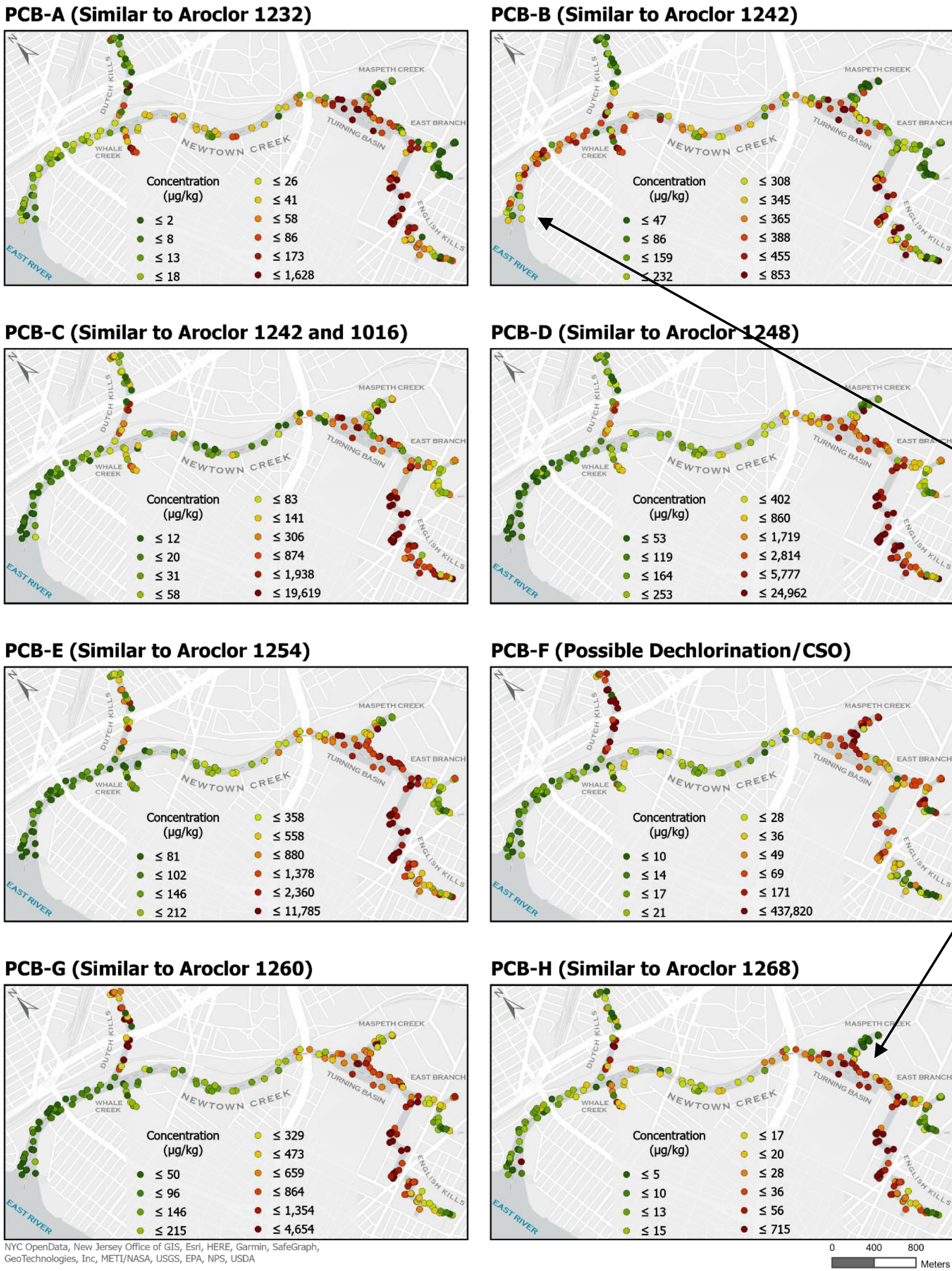

Spatial distribution of sources

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

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Hudson River (GE) as a source of PCBs

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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)

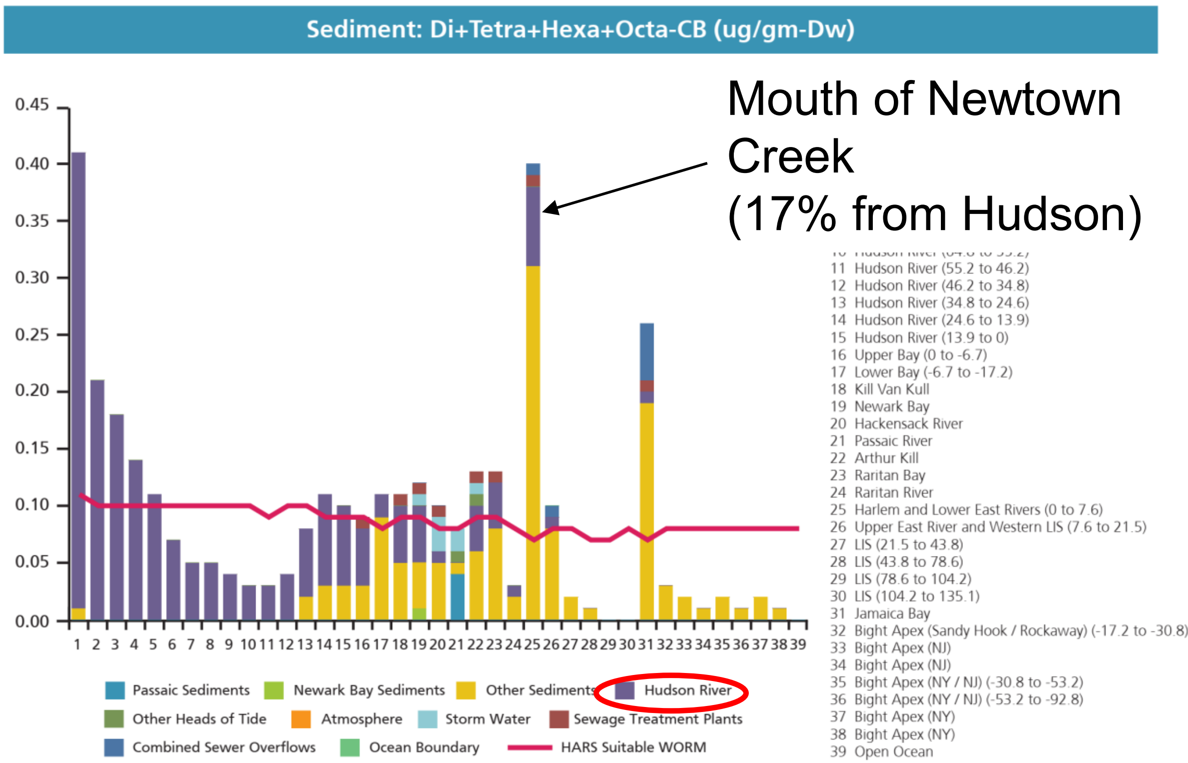

Figure 11: CARP Matrix Results: Projected PCB Concentrations in Sediment, by Source, for Various Portions of the Estuary. Concentrations Above the Red Line Indicate Exceedances of the HARS PCB Bioaccumulation Limit

Lodge et al. 2015 CARP Summary Report

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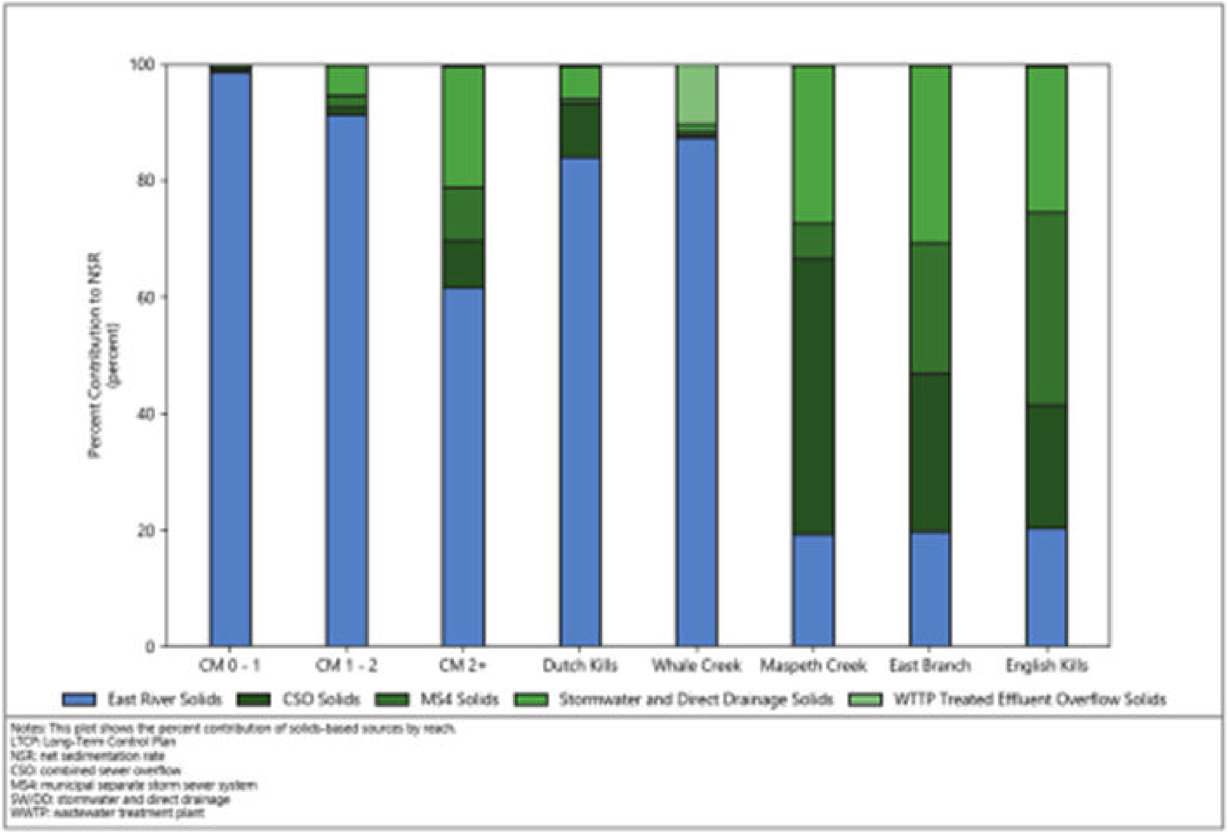
attorney-client privilege

Sources of solids to Newtown Creek



East River solids dominate throughout much of Newtown Creek

Remedial Investigation Report

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

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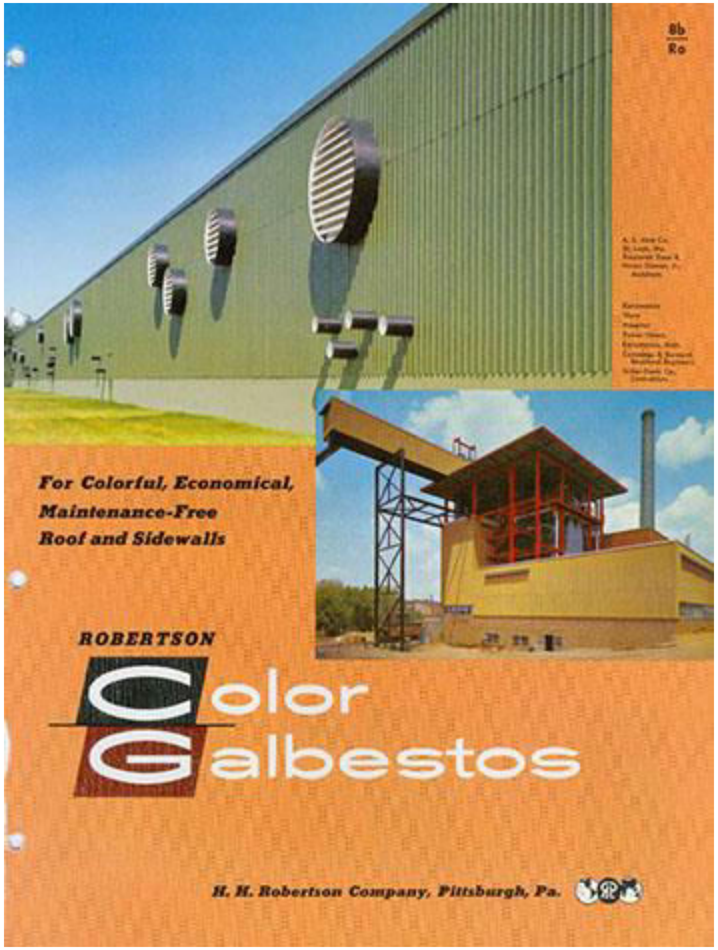
Aroclor 1268

- 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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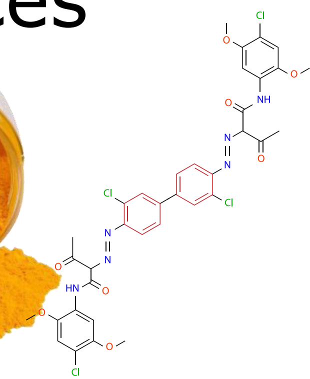
Main inadvertent non-Aroclor PCB sources



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

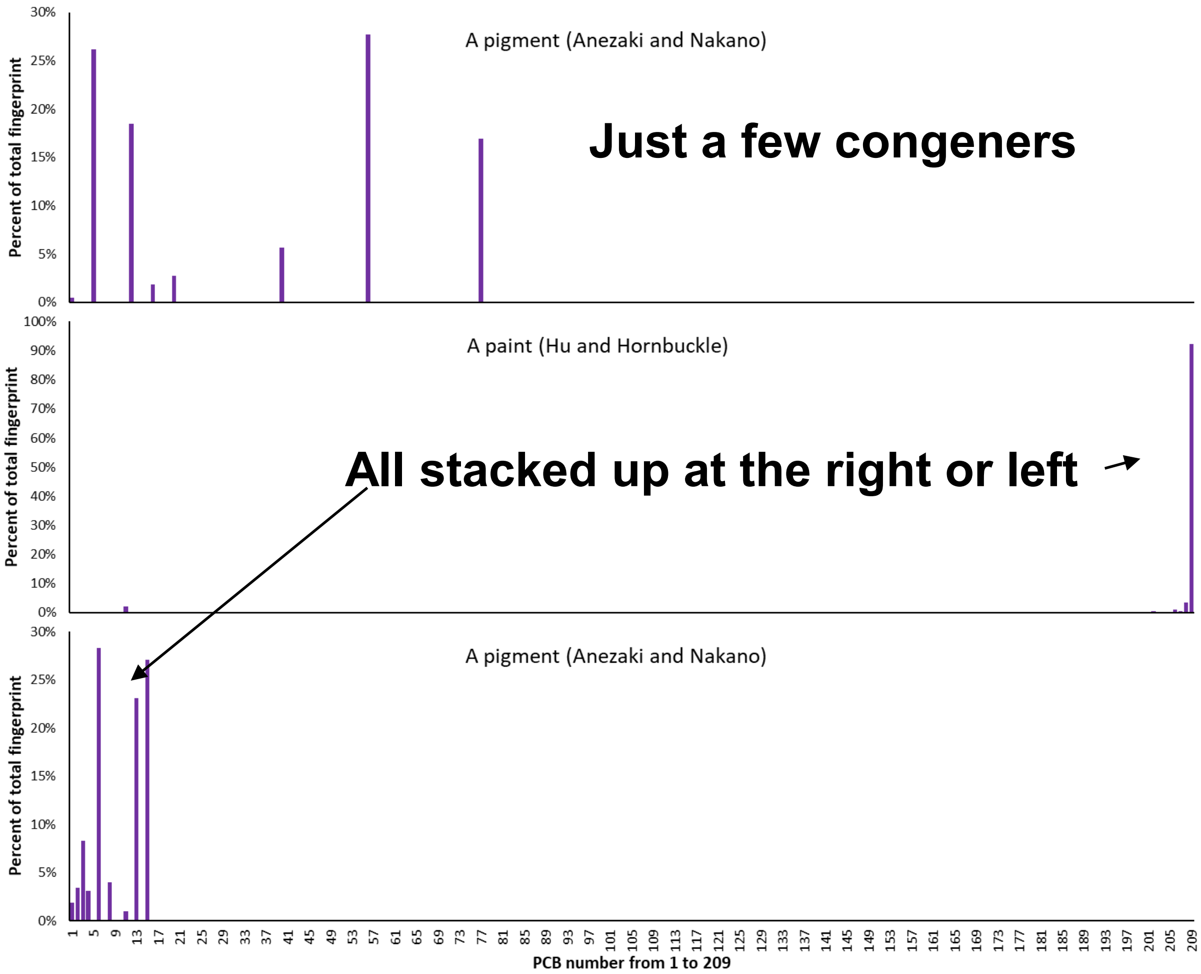
- Titanium dioxide (white pigment) may contain PCBs 206, 208, and 209
  - Kinda looks like Aroclor 1268, 1270, 1272
  - Also, Caffaro PCBs from Italy

- 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!

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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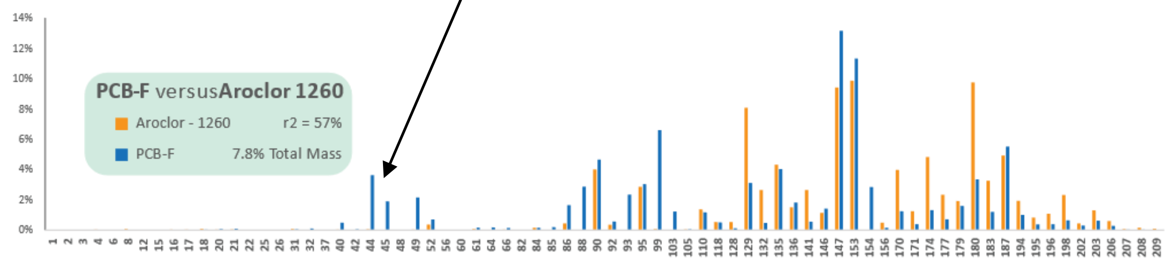
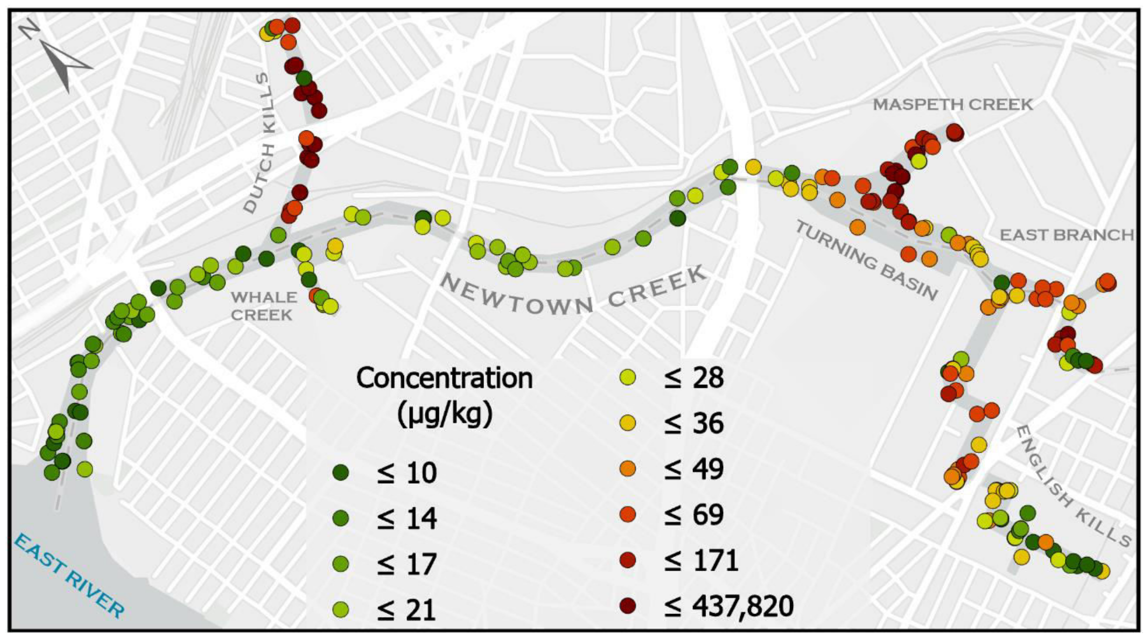
PCB-F

- 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



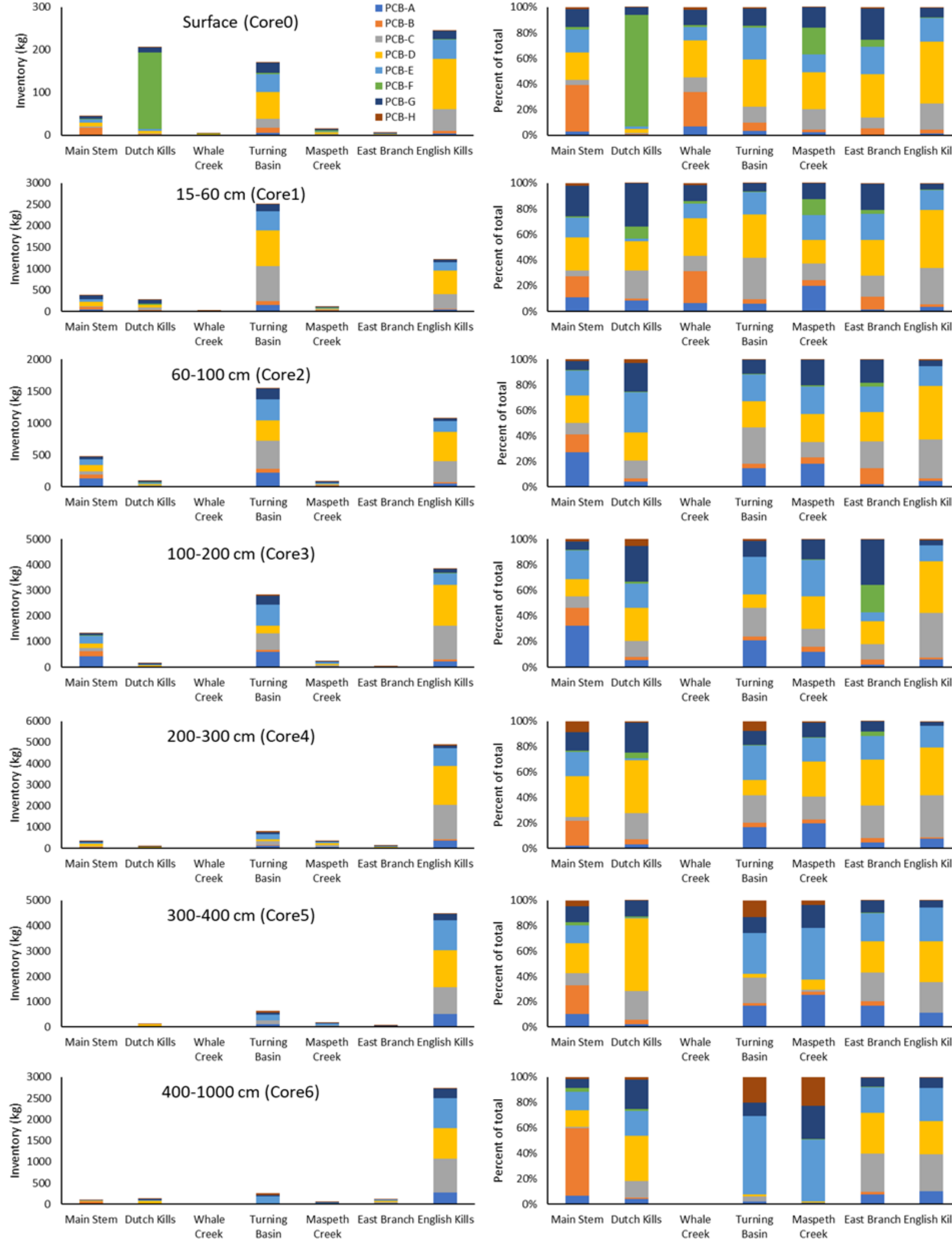
PCB-F (Possible Dechlorination/CSO)



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

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Disclaimer:

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