

Land Use and Era of Development Effects on PCB Contamination of Soils and Stormwater Sediments in the Chesapeake Bay Watershed

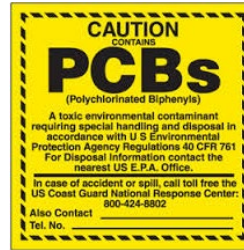


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Polychlorinated biphenyls: An environmental Legacy



1865



1970s



E.P.A. Bans Discharge of PCB's Directly Into the Nation's Waters

By RAYARD WEBSTER

The Environmental Protection Agency yesterday ordered the ban of the direct discharge of PCB's, a highly toxic industrial chemical, into United States waters.

The chemical, a close relative of DDT, has been found in scientific studies to cause deformities in fetuses, changes in liver function, nervous disorders and cancers in animals. Widespread in the environment, it is found in almost all major bodies of water in the world. Significant amounts have also been monitored in the air.

The ban follows results of recent studies that show that its levels in water and fish, exceed by several factors those standards set by the E.P.A. and the Food and Drug Administration.

The only plants covered by the ban are some 20 factories that manufacture electrical transformers and capacitors and discharge their PCB's, used in electrical insulation, into bodies of water.

The E.P.A. noted in announcing the ban yesterday that "past widespread use of the chemicals in the production of lubricants, additives, hydraulic and compressor fluid, carbonless copy paper, plasticizers, paints and other products has resulted in PCB's being present throughout the environment."

"Although most of these uses have now been substantially curtailed, PCB's which have entered the environment cannot in most cases be recovered and will require many years to degrade. The public will be alerted to potential hazards by careful long-term monitoring of PCB levels in food."

One of the most prominent PCB contamination cases involved the General Electric Company, which had been dumping its PCB wastes into the Hudson River, causing fish to accumulate many times the permissible level of the chemical. A negotiated settlement between the company and the State Department of Environmental Conservation resulted in G.E.'s agreeing to cease its dumping and to pay \$1 million toward cleaning the river and \$1 million for research toward ending the problem.

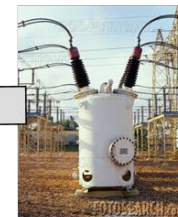
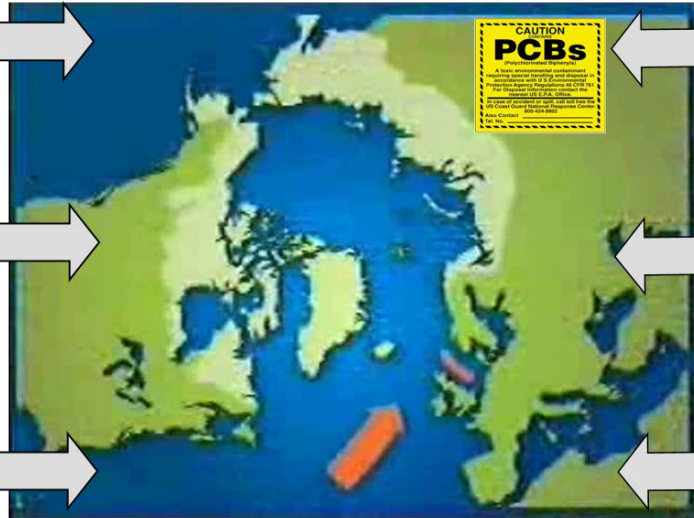
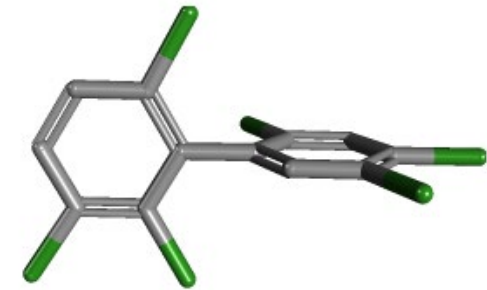
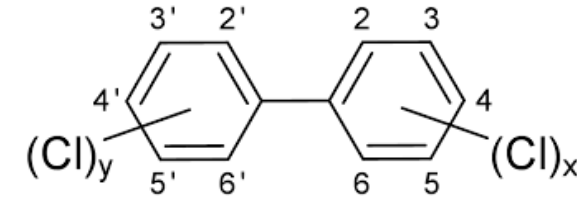
The ban did not cover the PCB wastes of transformer plants that discharge their wastes into municipal sewage systems. Such "indirect" discharges, the E.P.A. said, would be taken care of by additional regulations being prepared by the environmental agency.

The ruling, which in effect calls for the zero discharge of PCB's into major bodies of water, follows the recent studies that indicated that the recently proposed permissible standard of one part per billion of PCB's in transformer plant waste water could not be met.

The present problem of PCB contamination in the environment is so severe that in many waters throughout the United States PCB loads are already in excess of the criteria," E.P.A. Administrator Russell E. Train said in announcing the ban. His action came on the final day under the law for a decision in the PCB case, which had been argued most prominently by the Environmental Defense Fund, a Washington-based environmental law firm principally responsible for the banning of DDT in 1972.

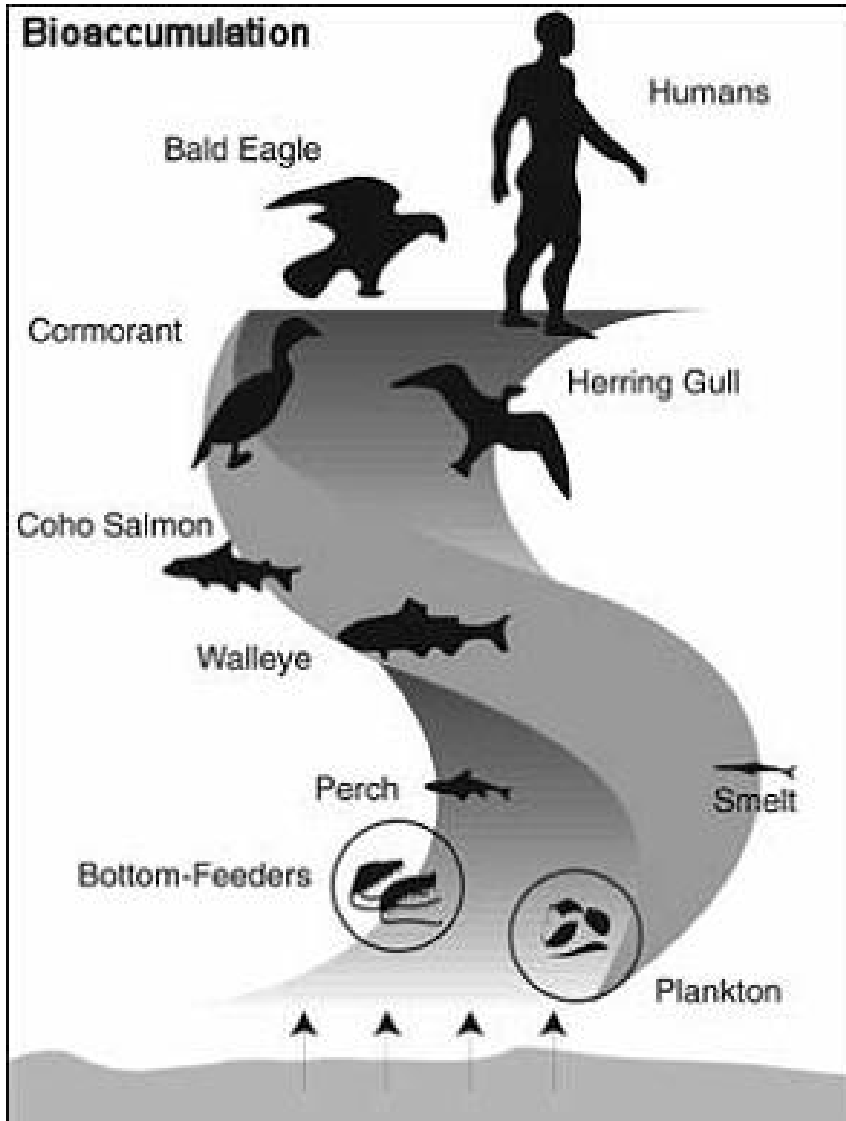
The industrial chemical is widely used for insulating electrical equipment, in the recycling of wastewater and in metal casting plants. Because of its widespread distribution in the environment, its resistance to biological degradation with a half-life of more than 25 years, PCB's are considered one of the most serious of the many environmental contamination problems prevalent today.

Monsanto Industrial Chemicals Company, the only American maker of the chemical, announced several months ago that it would quit production of the substance by October 31 of this year. There are no restrictions on the importation of PCB's. The Food and Drug Administration has already banned use of the chemical in the processing of food and feed, where it was sometimes used as cloth and paper insulation in containers and canisters.

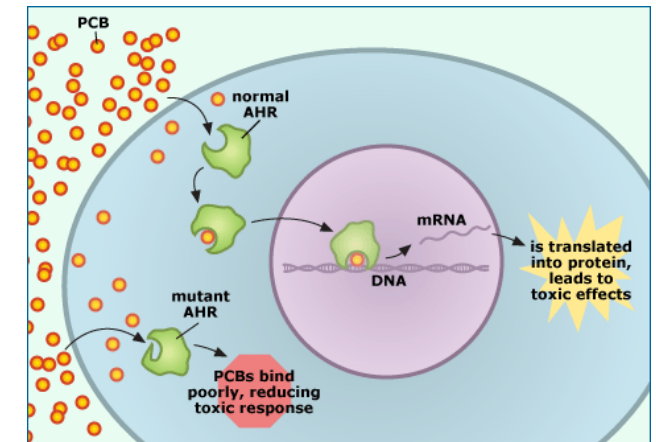
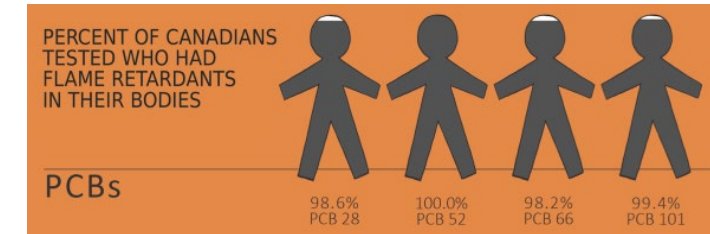


**Estimate:
0.6-1.2 billion
kg worldwide**

Why are PCBs of concern?

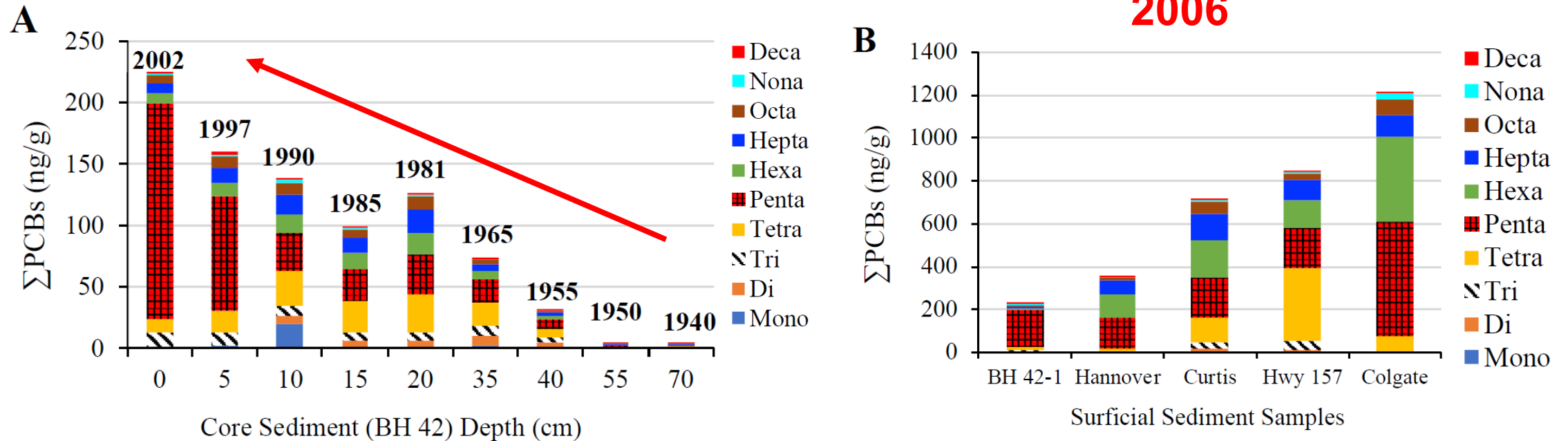


- **Bioaccumulates** and **biomagnifies** in the food chain
- Sediments/soils = **global sinks**
- **Toxicological effects**: Cancer, problems with endocrine and reproductive organs as well as immunological issues
- Humans: Source - ingestion (sea food, meat, poultry etc.)



Legacy contamination or current sources?

Kaya et al (2019), STOTEN



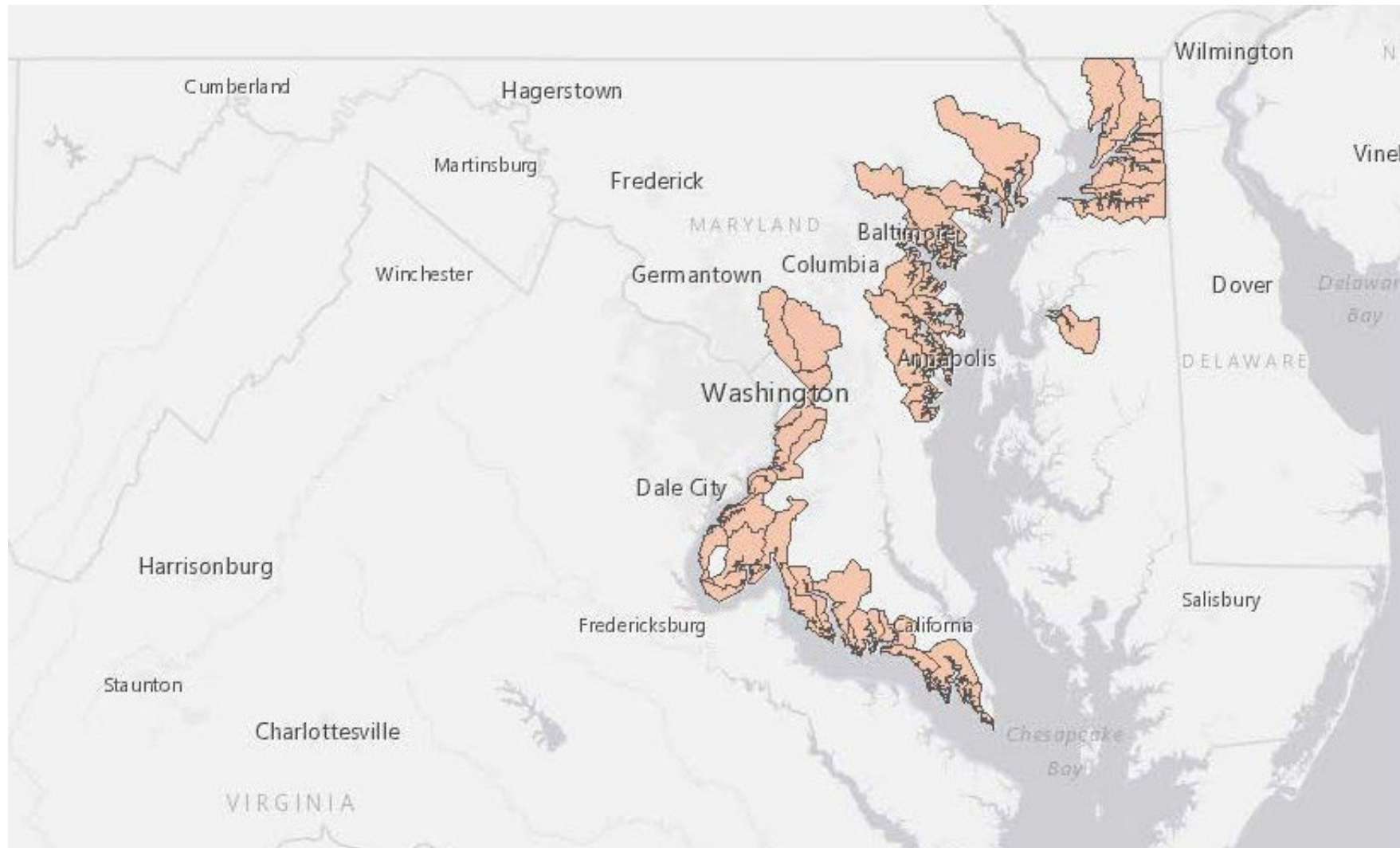
Conclusion:

Not only legacy PCBs (Example of Baltimore Harbor)

⇒ **Current sources** are increasing the contamination level

⇒ **TMDLs in place** for watersheds in the Chesapeake Bay

PCB TMDLs in Maryland



Impact of land development on PCB contamination

- Land-use categories

- Residential
- Commercial
- Institutions
- Industrial areas (light vs heavy)
- Energy sites
- Green spaces



- Land development era

Pre 1979

PCBs
banned

Post 1979

Objectives

- Assess the **land use** and **time of development** impact on the presence of PCBs in soils and stormwater sediments
- Identify the **potential sources** of stormwater PCBs
- Provide information and **guidance** on PCBs presence (and removal) in stormwater

Residential neighborhoods

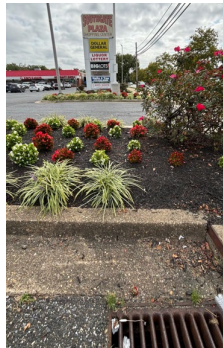


Before 1970es



After 1970es

Light commercial areas



Before 1970es

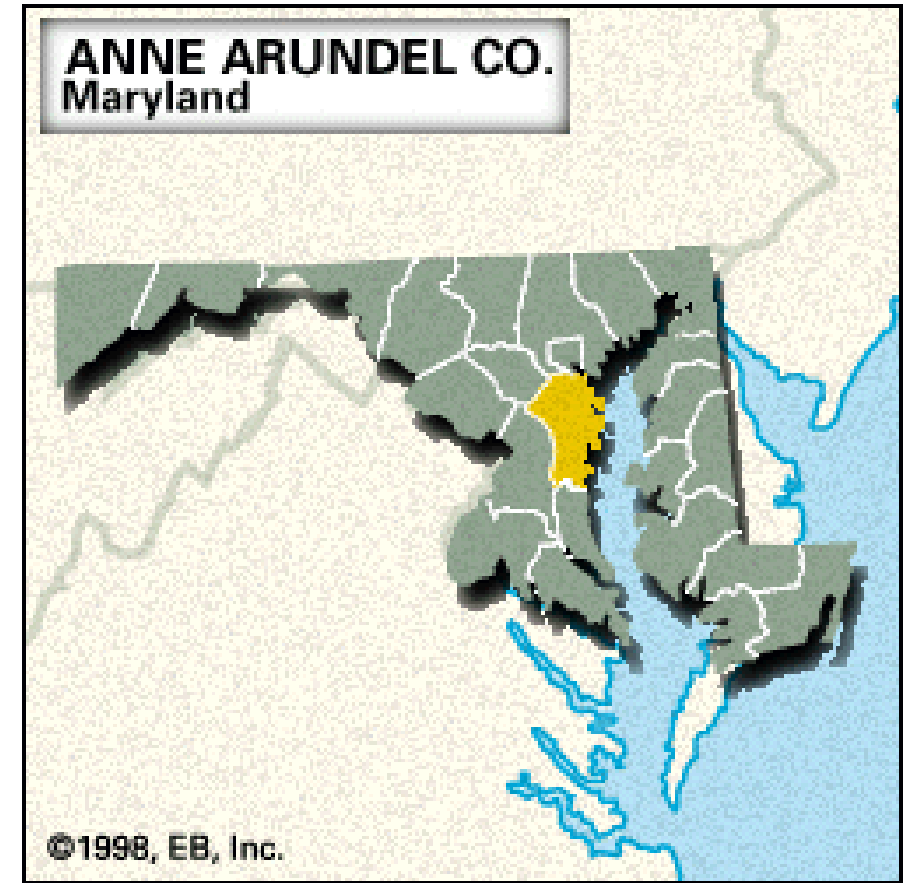


After 1970es

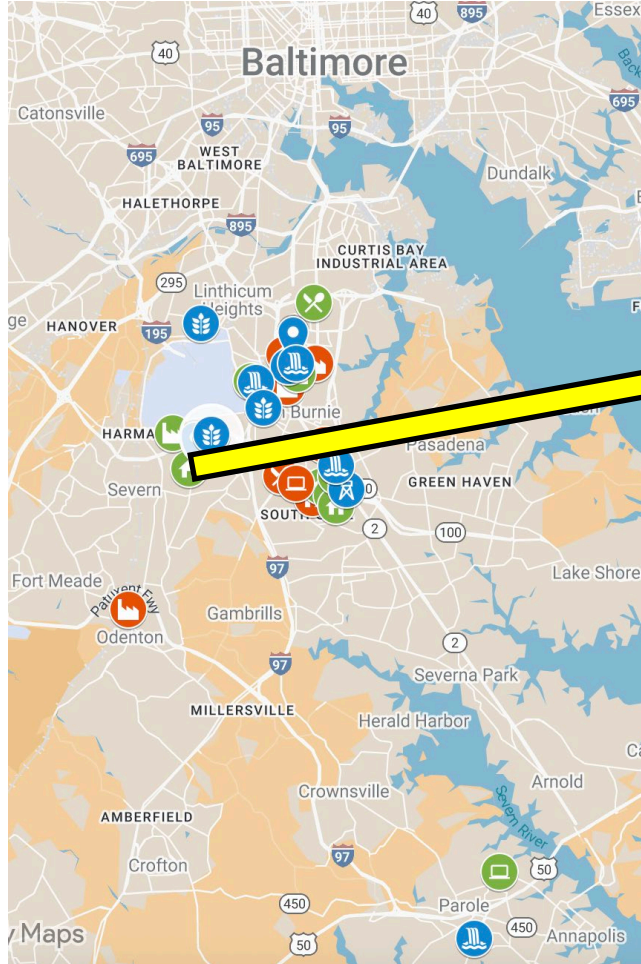
Energy site



Sampling locations

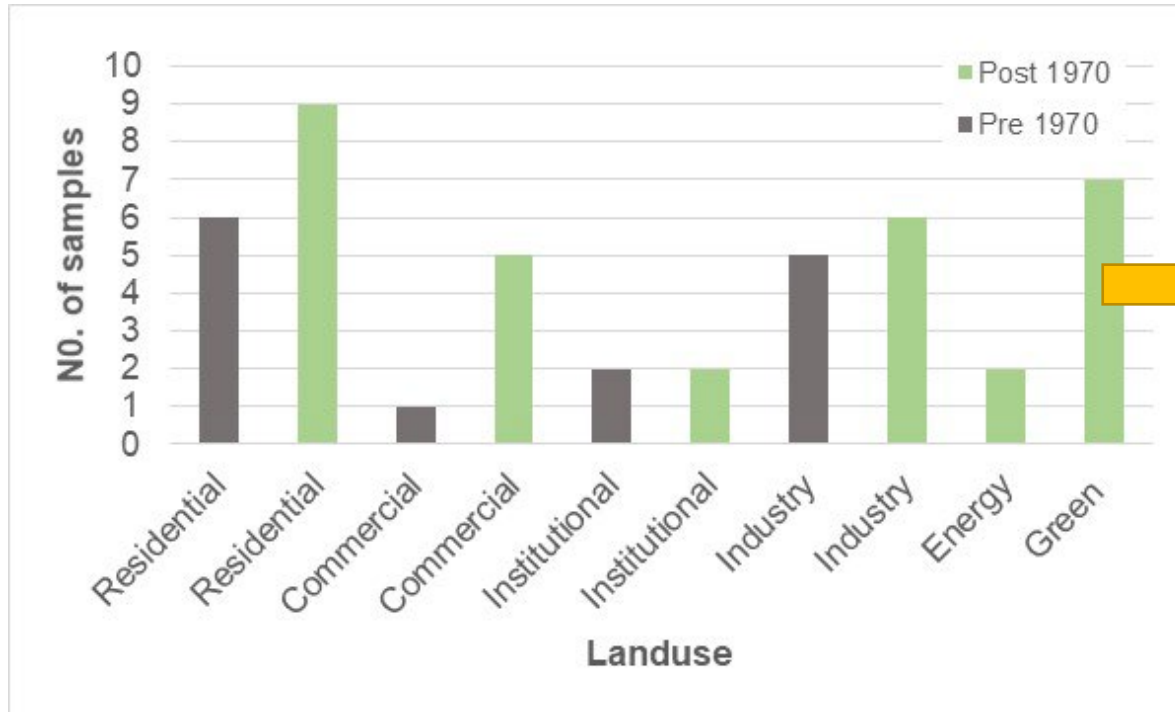


Map of the sampling sites



Abbreviation	Meaning
Res	Residential Area: Neighborhood
ID	Industry Area: Metal scrap yard, Automotive sales industry
Com	Commercial Area: Retail Shop
IN	Institutional area: Hospital
GS	Greenspace: Park
Pre70	Developed before 1970s (before PCB banned)
Po70	Developed after 1970s (after PCB banned)

Number of collected samples



Greenspaces – 'control' areas

Summary:

- 45 samples were collected over 2 years
- 6 different land-uses
- 2 time eras
- Analyzed in triplicate

Experimental process



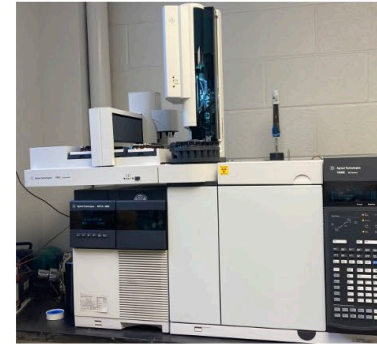
**Sample
Collection**



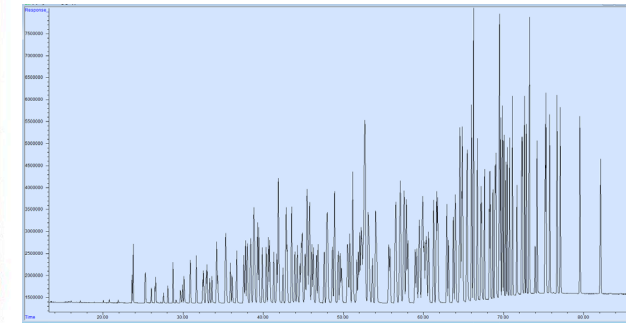
**Microwave
Extraction**



Clean up



**Gas
Chromatograph
(ECD) analysis**



**Data
Analysis**

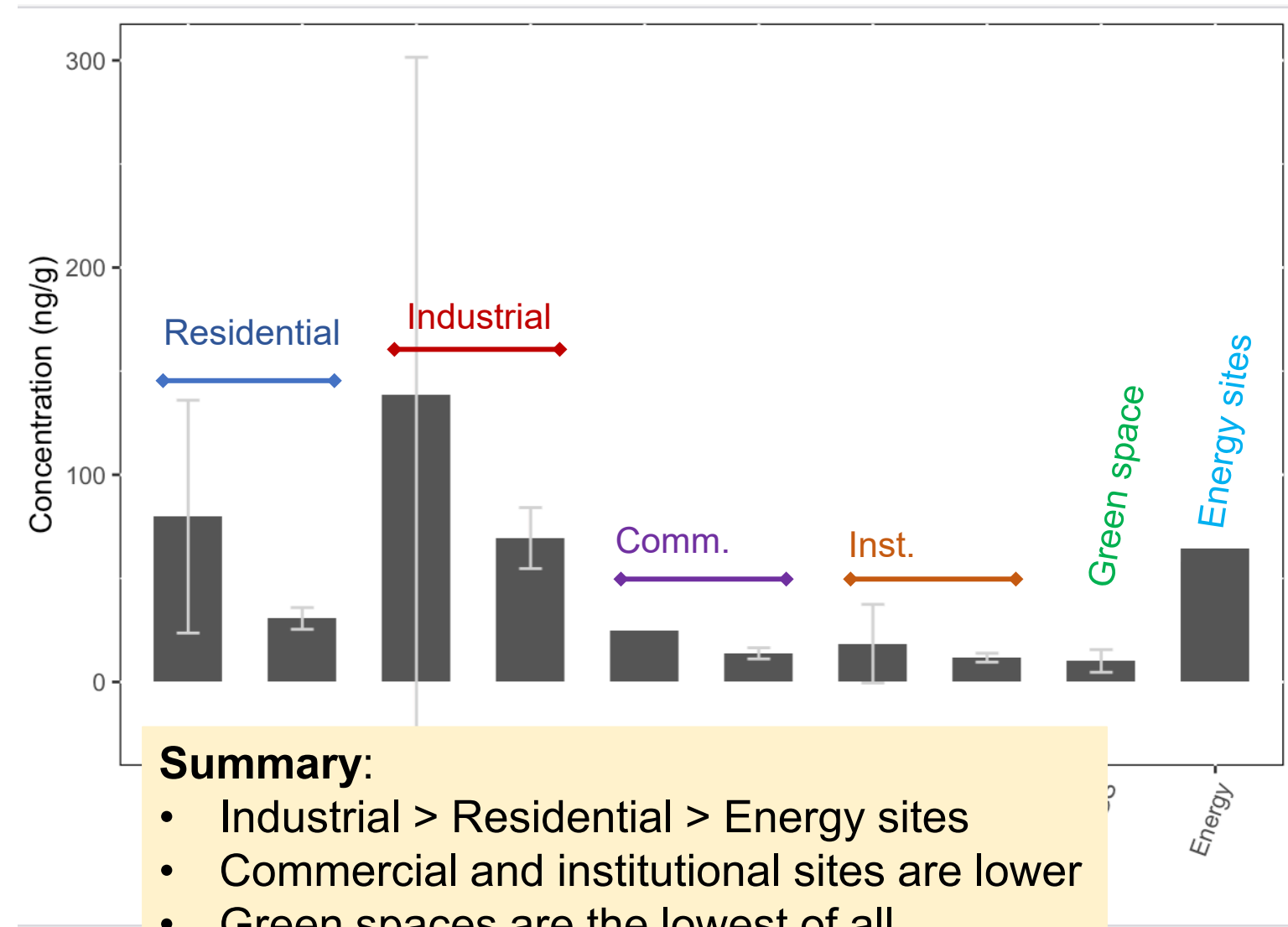
Detection Limit vs Below Quantifiable Limit

- Not all 209 PCB congeners are quantifiable in each sample
- How can we determine the **Total PCB concentration**?
 - Define BQL = 0 → Underestimation
 - Define BQL = $\frac{1}{2}$ QL → Overestimation
- **Kaplan-Meier** ranking assessment
 - Statistical method using a value between 0 and $\frac{1}{2}$ QL
- Provides **more accurate** estimate of data BQL for use in total pollutant measurements

Summary:

- Detection Limit (DL): 0.0420-2.85 ug/mL
- Methods Detection Limit (MDL): 0.00841-0.570 ng/g

Landuse Type - Total PCB concentration

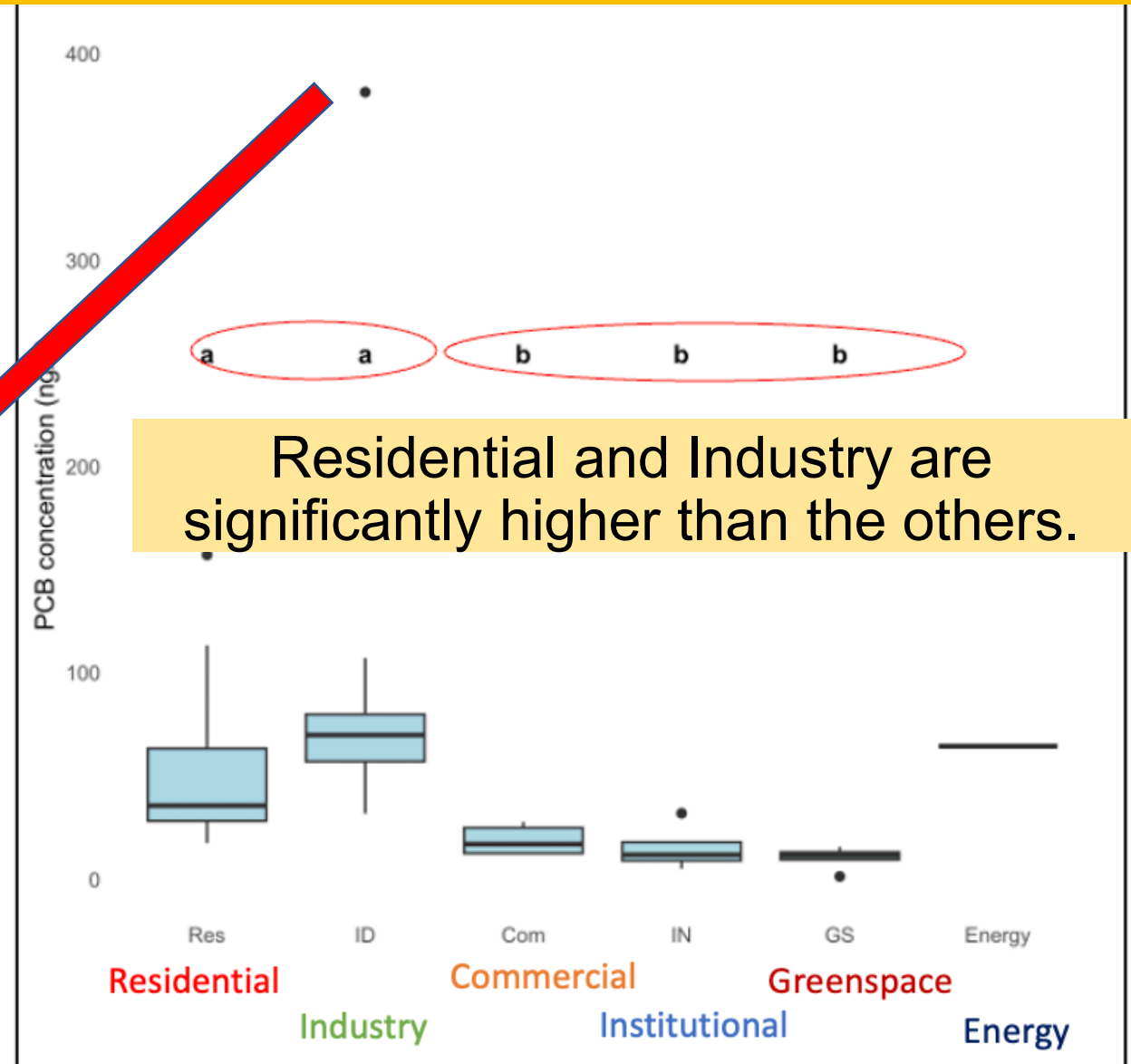


Summary:

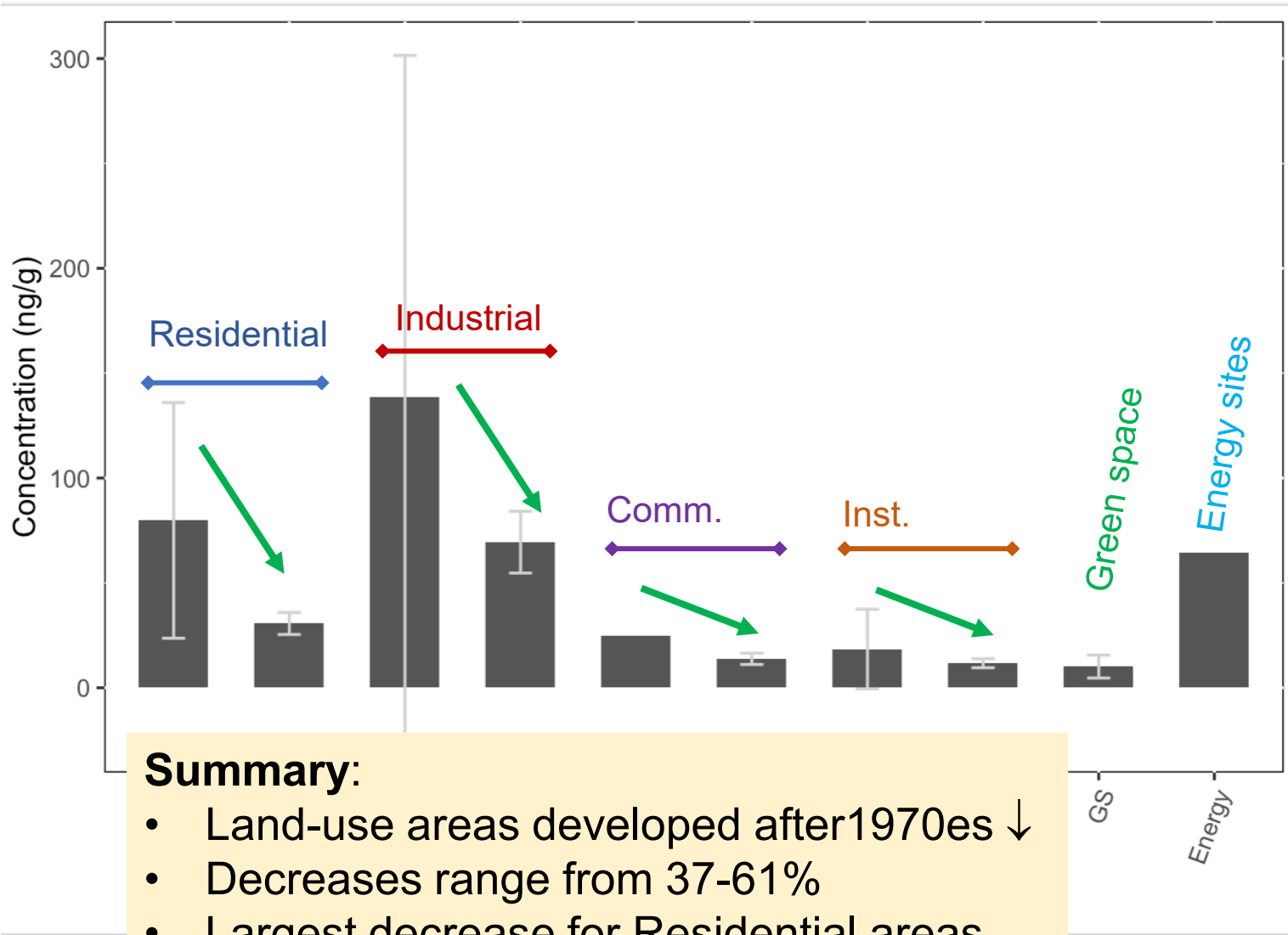
- Industrial > Residential > Energy sites
- Commercial and institutional sites are lower
- Green spaces are the lowest of all
- Large range of concentrations

Category	Range (ng/g)	Average (ng/g)
Residential (Pre)	17.4-157	79.8
Residential (Post)	24.1-37.4	30.6
Industrial (Pre)	31.7-381.3	140
Industrial (Post)	59.0-79.8	69.4
Commercial (Pre)	24.9	24.9
Commercial (Post)	12.1-24.9	13.8
Institutional (Pre)	5.05-31.9	18.5
Institutional (Post)	10.2-12.3	11.7
Green Space	1.27-13.0	10.1
Energy sites	64.4	64.4

Effect of Land Use



Development time - Total PCB concentration



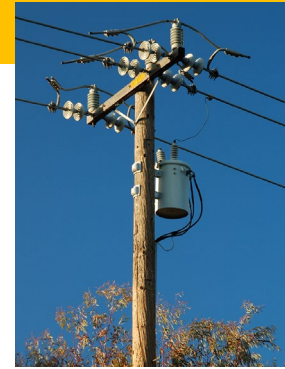
Category	Average (ng/g)	Reduction
Residential (Pre)	79.8	61%
Residential (Post)	30.6	
Industrial (Pre)	140	50%
Industrial (Post)	69.4	
Commercial (Pre)	24.9	44%
Commercial (Post)	13.8	
Institutional (Pre)	18.5	37%
Institutional (Post)	11.7	
Green Space	10.1	-----
Energy sites	64.4	-----

Summary:

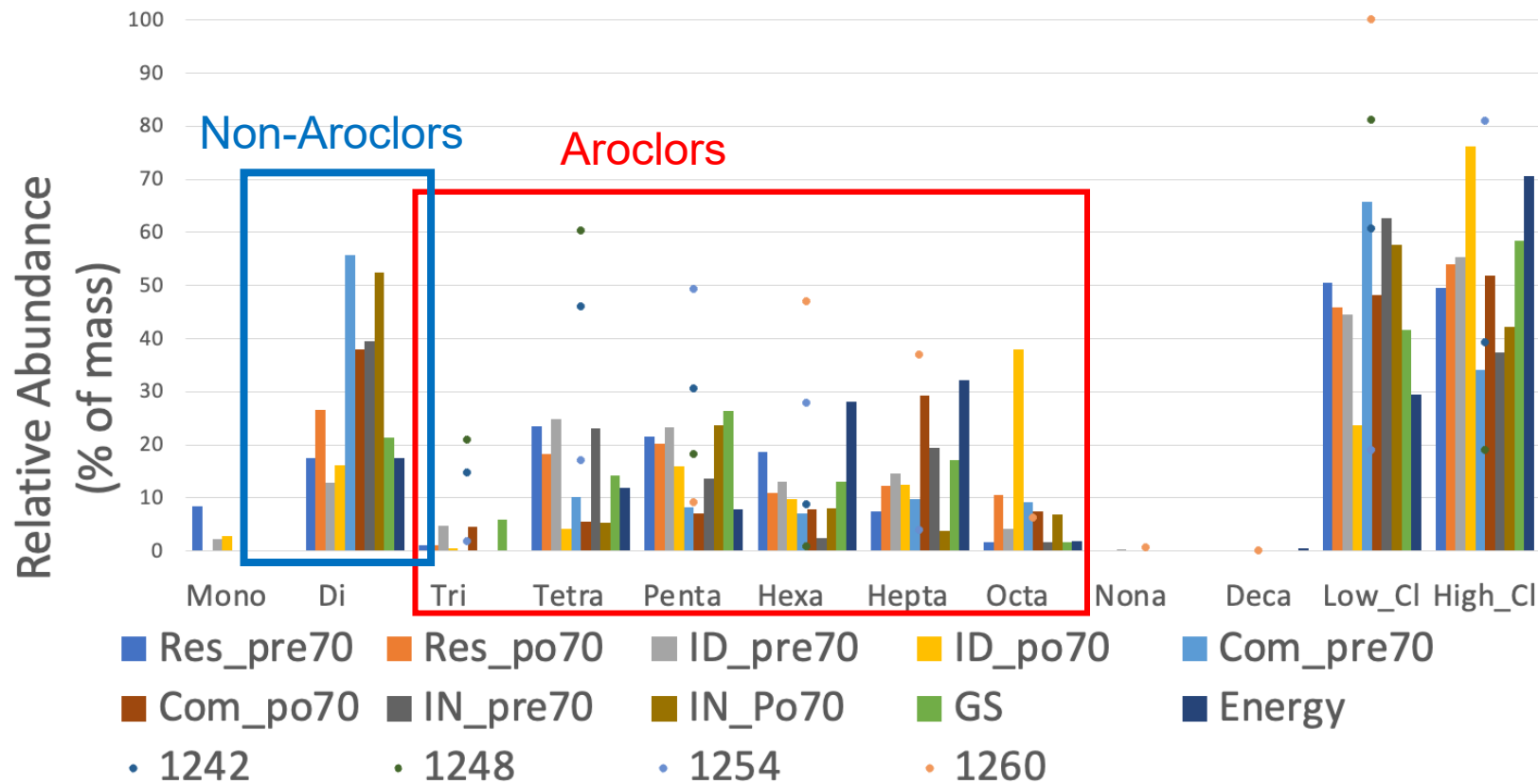
- Land-use areas developed after 1970es ↓
- Decreases range from 37-61%
- Largest decrease for Residential areas
- Difficult to determine re-development time

Known sources of PCBs

- Industrial products: Aroclors, A1242, A1248, A1254, A1260
 - ❖ Last two digits indicate chlorine % by weight
 - ❖ EX: Aroclor 1254 contains approximately 54% chlorine
 - ❖ Found in: Electrical transformers, capacitors, heat transfer fluids
- Building materials (recycled material)
 - ❖ Found in: Sealants, caulks, paints
- Other products
- Road paints



PCB sources – landuse category

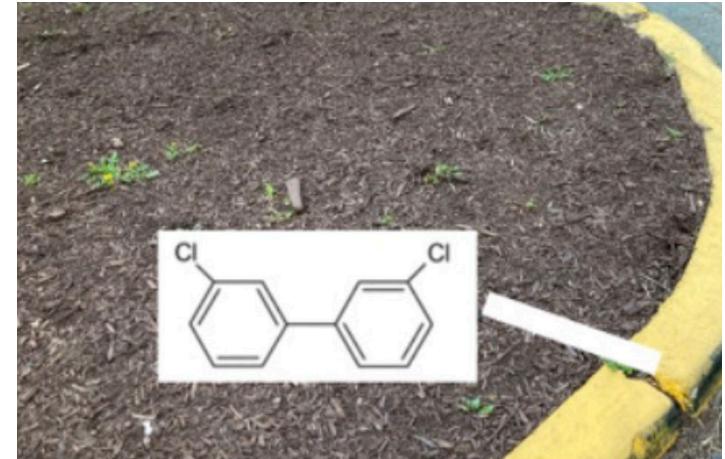
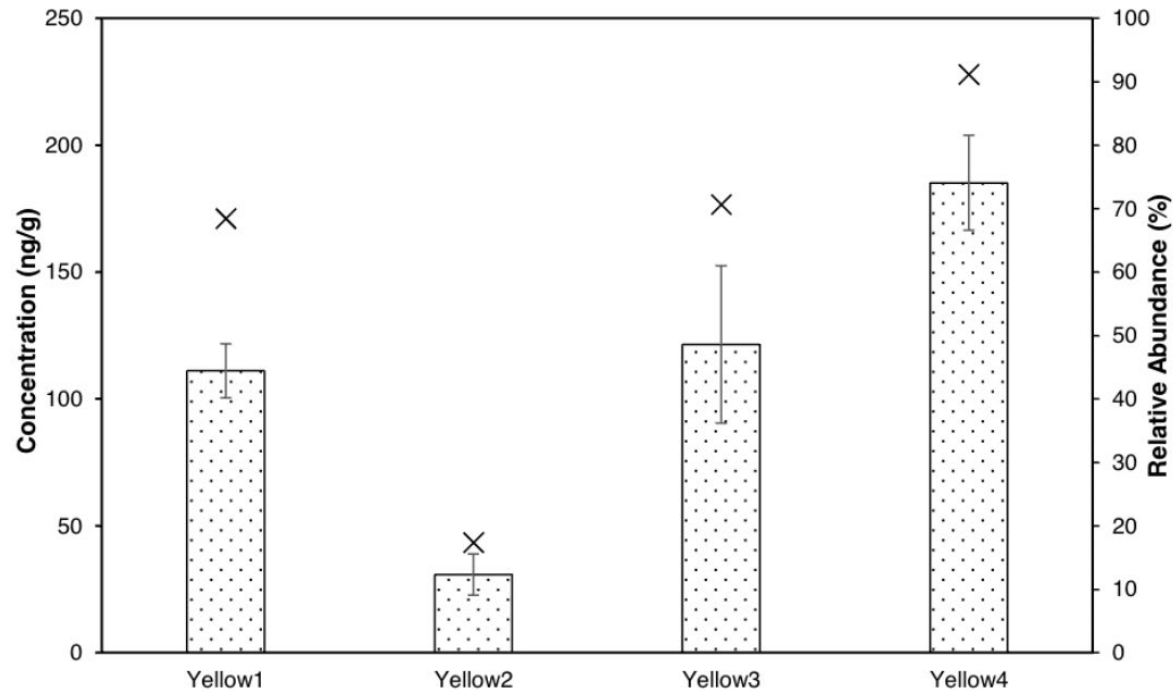


Summary:

- Samples are not originating from Aroclors (dots are not matching samples)
- Large presence of di-chlorinated PCB homologs
- Other sources for PCBs should be considered

Earlier study of yellow road paint

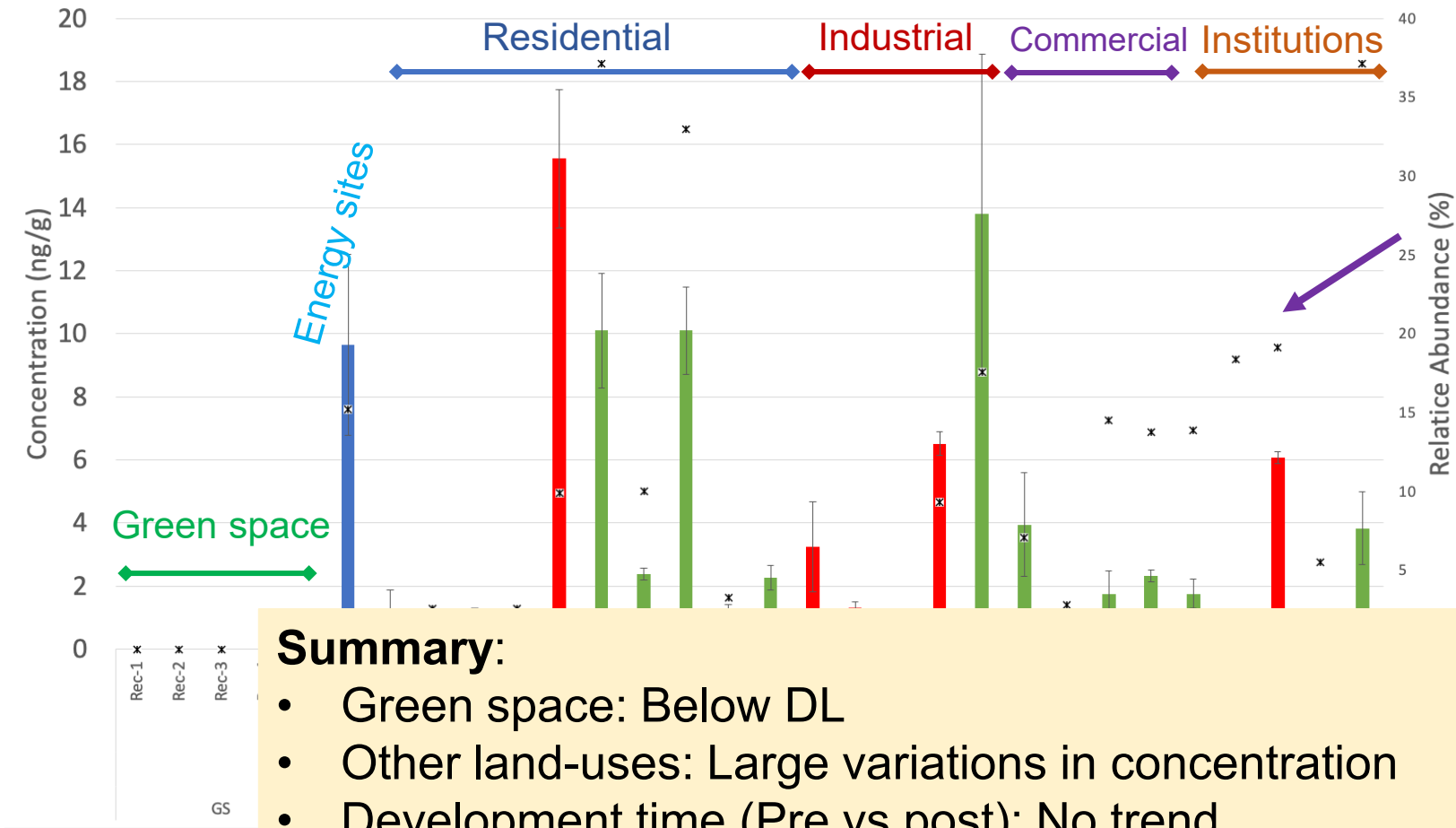
PCB 11 in yellow road paints



- The relative abundance of PCB 11 ranged from 17% to 91% of total PCB concentrations in yellow roadway paints
- Road paint flake exist in the soil/sediment sample might impact the concentration of samples.

PCB-11 in the collected samples (this study)

PCB-11 Concentration and relative abundance (% of total PCB mass)



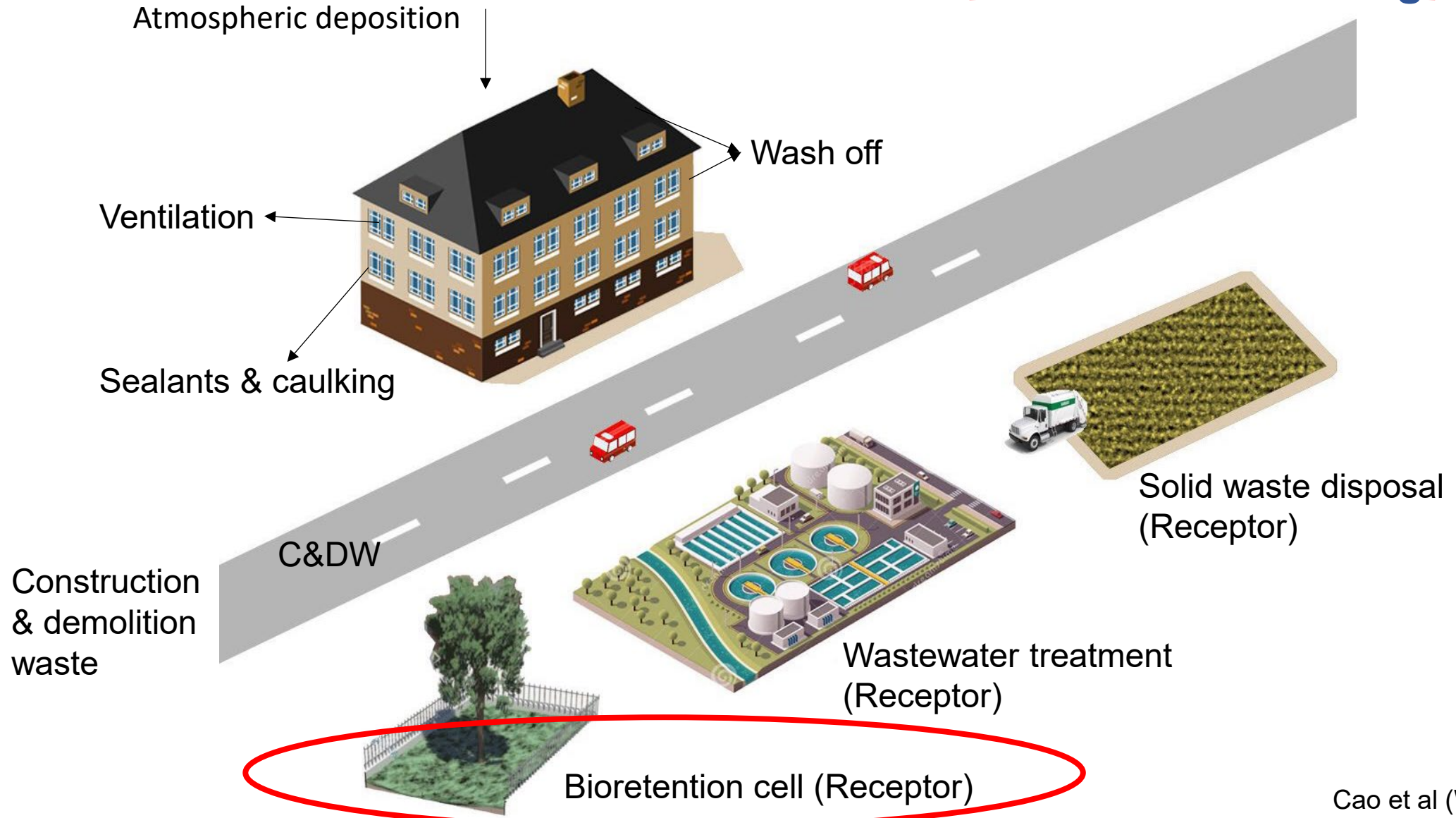
PCB-11 is non-Aroclor

Summary:

- Green space: Below DL
- Other land-uses: Large variations in concentration
- Development time (Pre vs post): No trend
- Total PCB mass: Ranges from 0-36%
- Removal of road yellow road paints can reduce the PCB-11 level

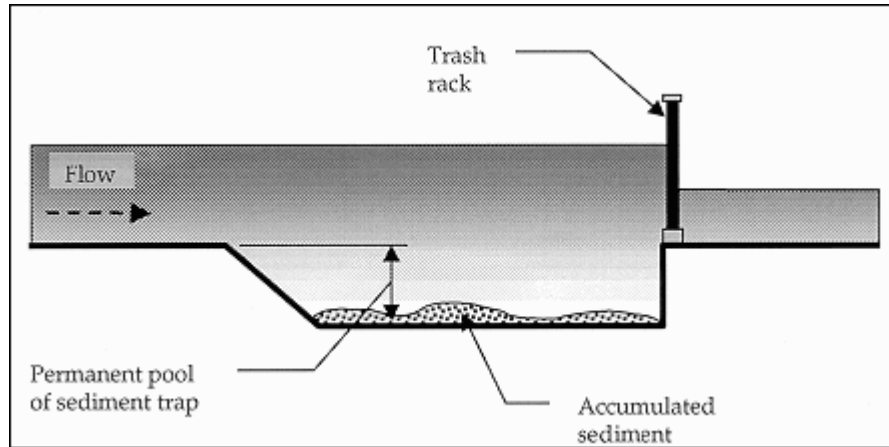
Current sources and receptors of PCBs

PCBs: ~~An environmental~~ Legacy

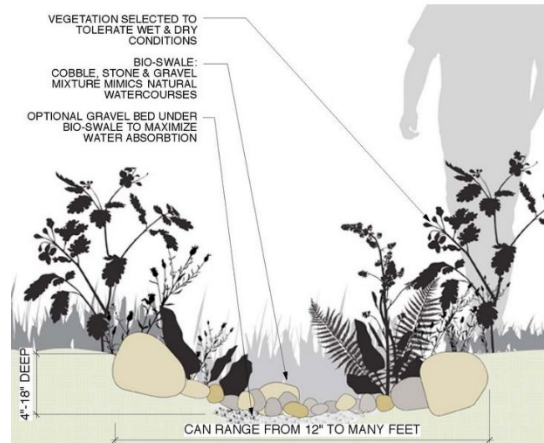


Stormwater treatment options

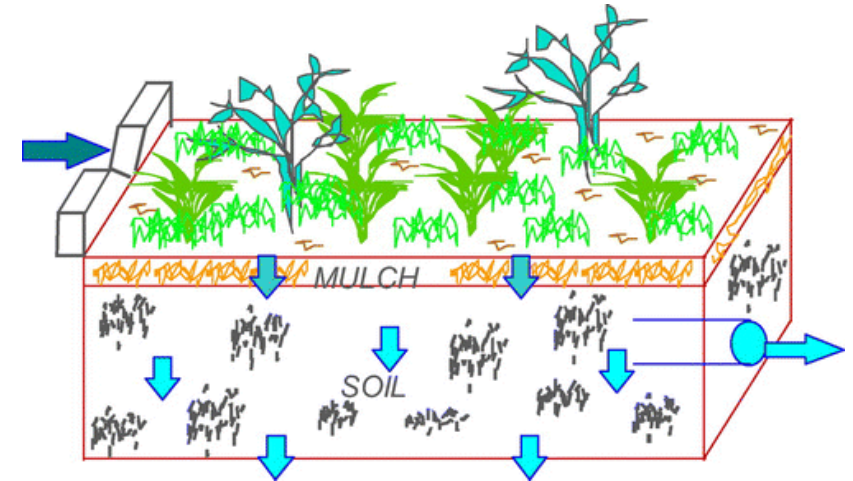
Sediment trap



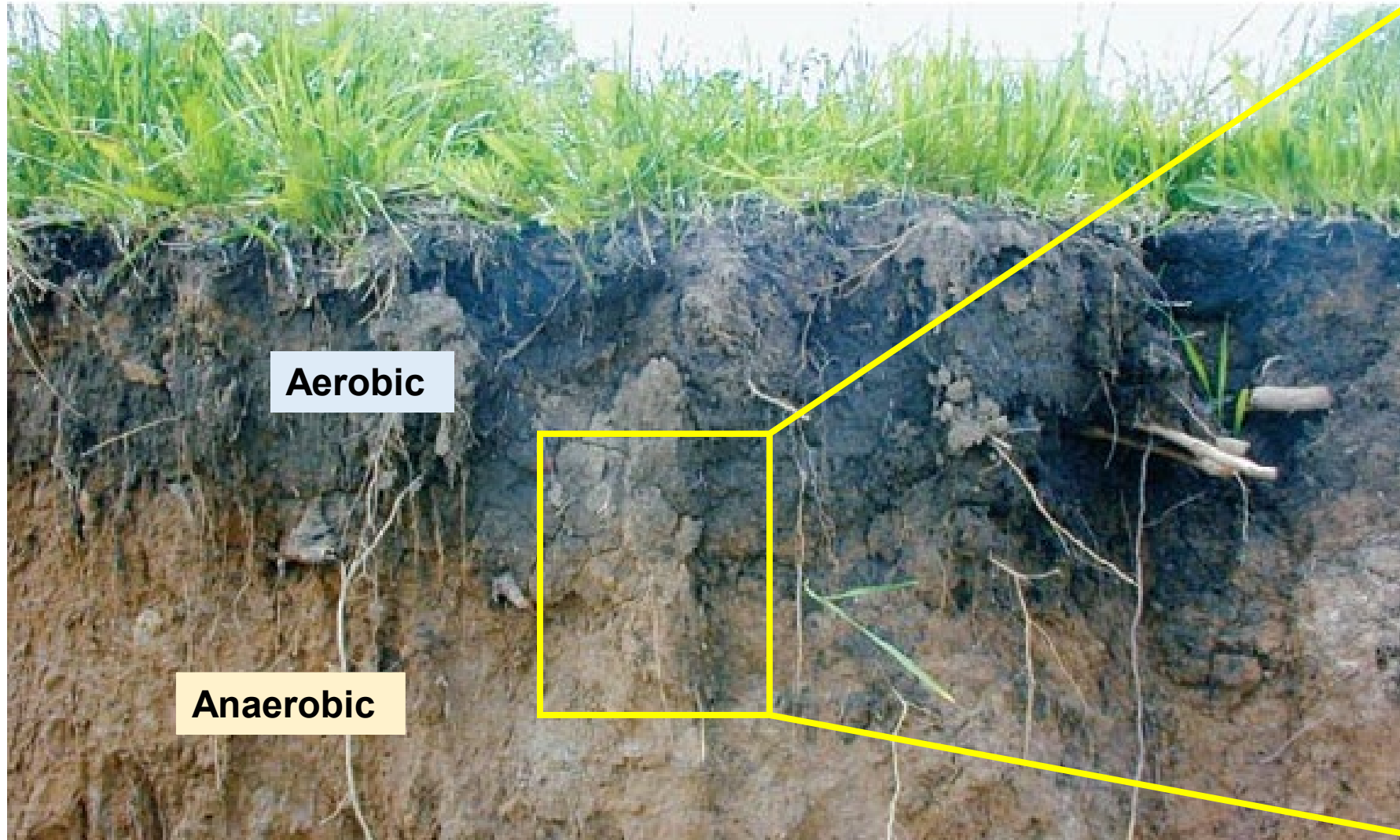
Swales



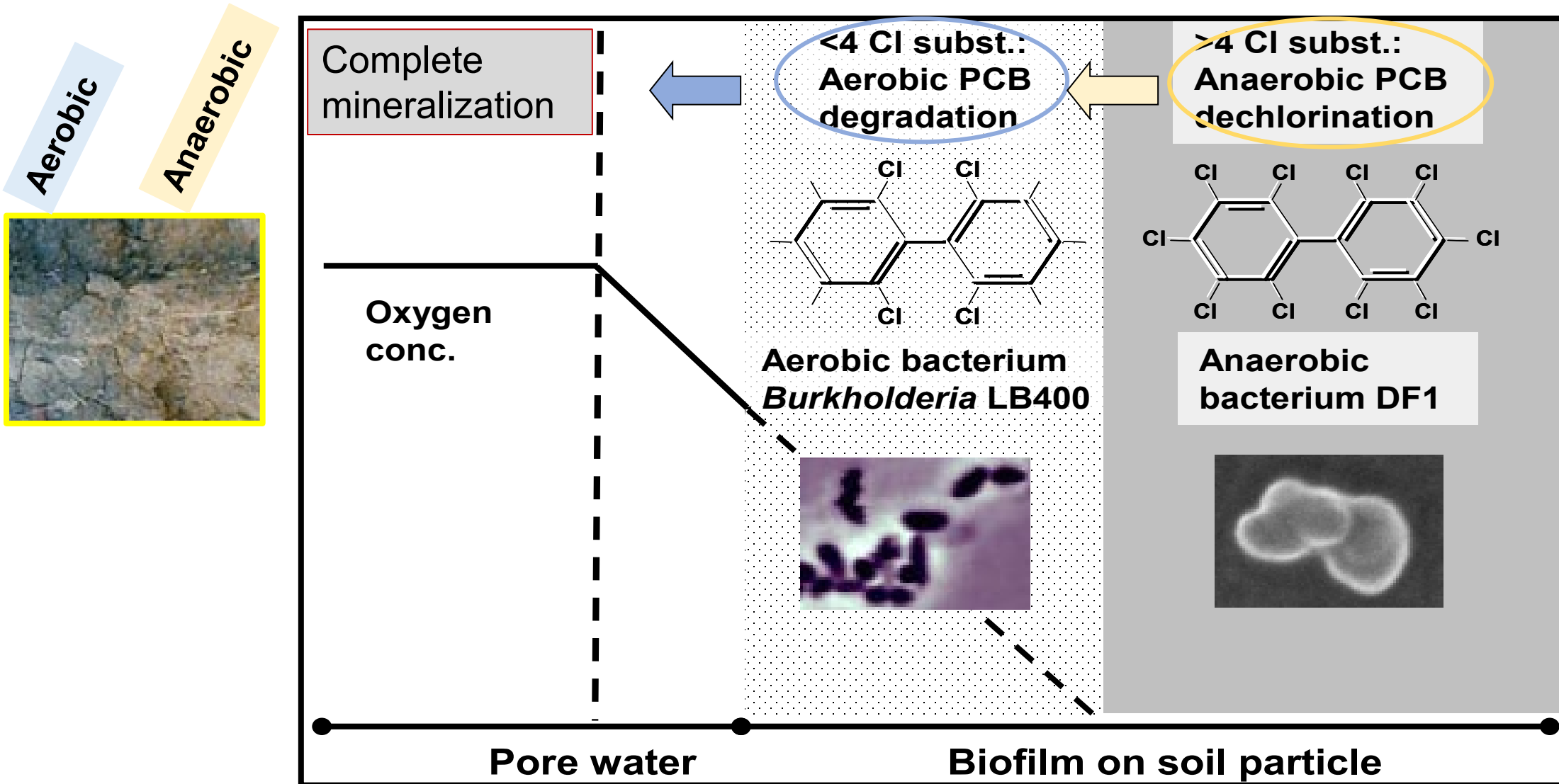
Bioretention cells



The Microbial Fate of PCBs in soil biofilm

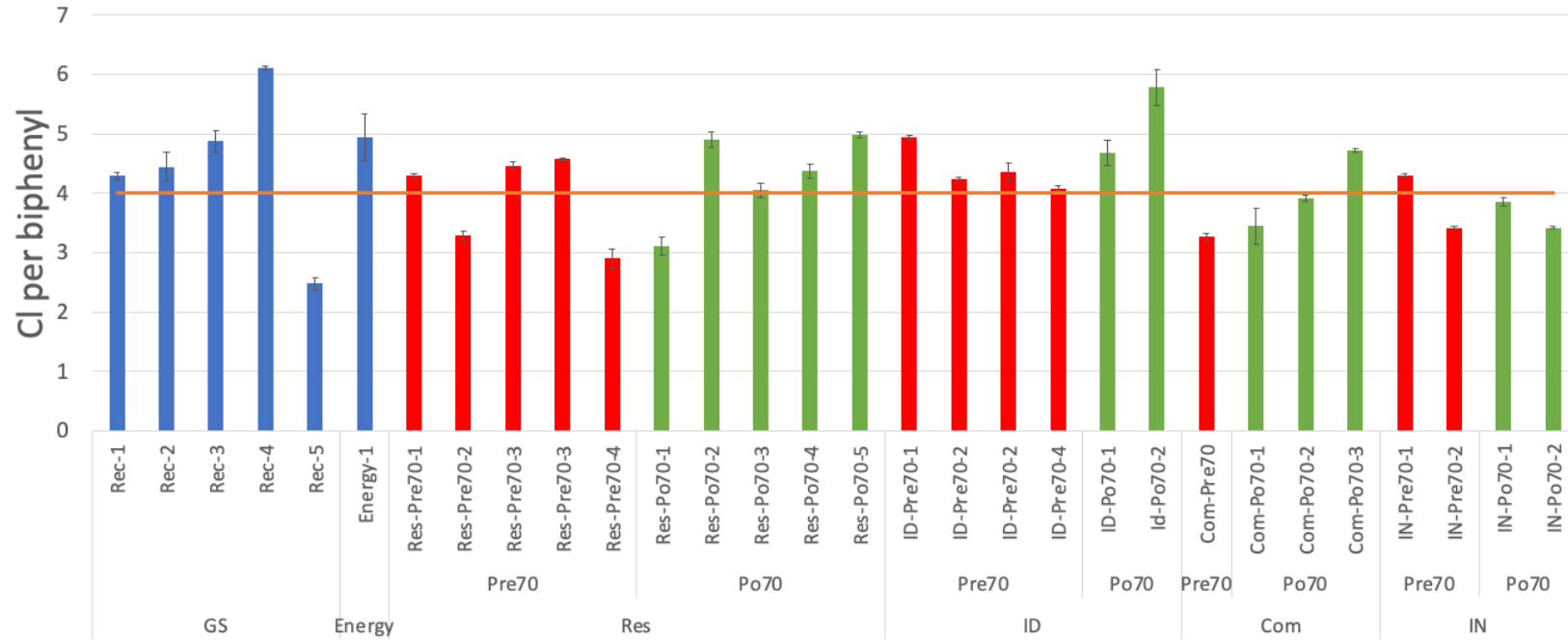


The Microbial Fate of PCBs in soil

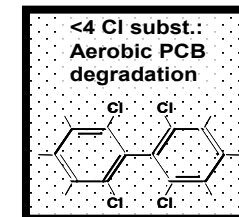
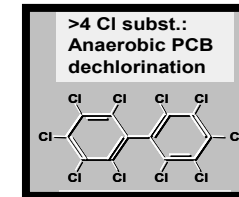


Signs of PCB biodegradation?

No. of chlorines per biphenyl at each site



Anaerobic conditions required



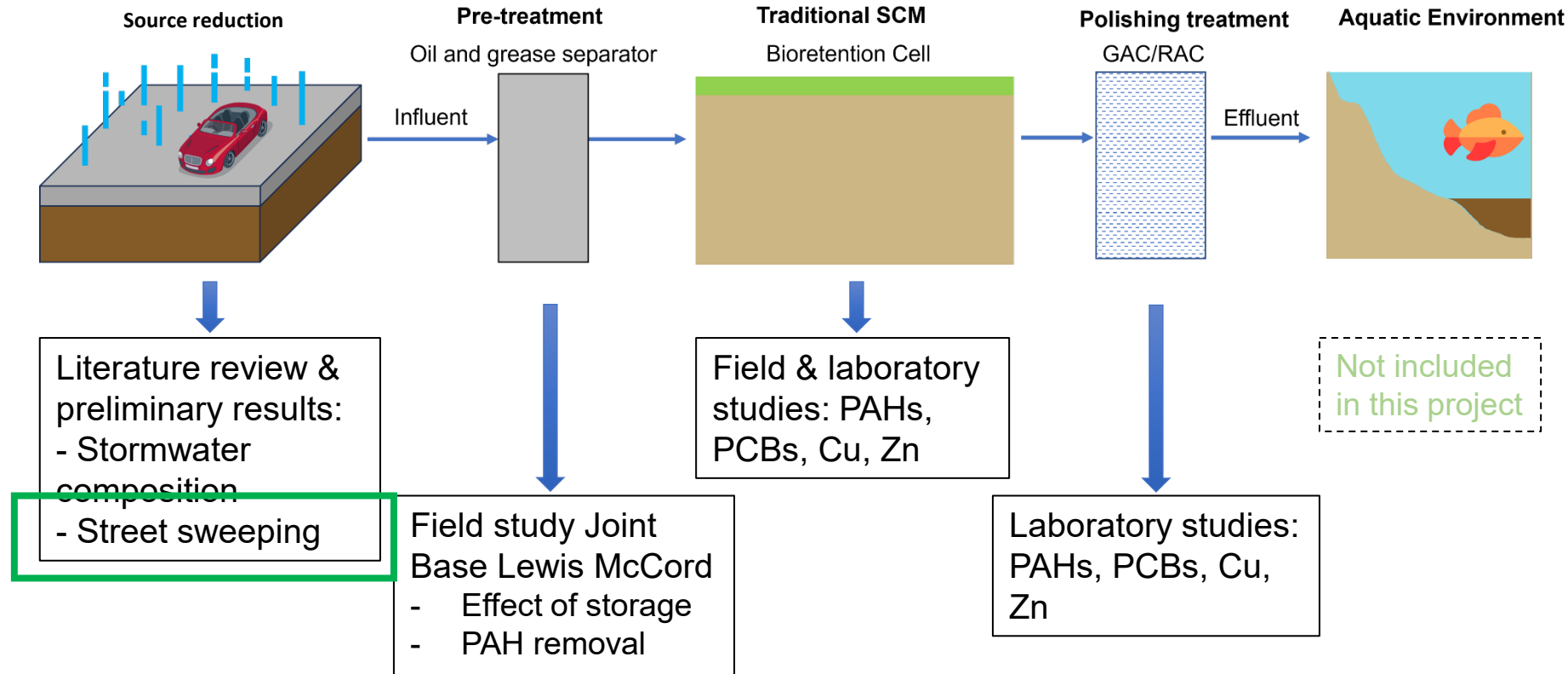
Aerobic conditions required

Summary:

- 66% of samples have >4 chlorines – anaerobic conditions are required
- 33% of samples have <4 chlorines – aerobic conditions are required
- Mass from samples <4 chlorines can be removed 'easily'

Stormwater Treatment Train System

Results from completed SERDP-DOD project:



Outcome: Demonstrated effect of the treatment train by use of project data for Mass Balance Estimation for each process step

Effect of Street Sweeping?



POLLUTANT LOADING			SOURCE REDUCTION (STREET SWEEPING) ²			PRE-TREATMENT (OIL GRIT SEPARATOR) ³			STORMWATER BMP ³			POLISHING TREATMENT (BIOCHAR) ⁴		
Pollutant	Concentration (mg/L) ¹	Annual Load (lbs)	% Reduction	Load Reduction (lbs)	Reduced Load (lbs)	% Reduction	Load Reduction (lbs)	Reduced Load (lbs)	% Reduction	Load Reduction (lbs)	Reduced Load (lbs)	% Reduction	Load Reduction (lbs)	Reduced Load (lbs)
Total Cu	0.013	0.120	31	0.037	0.083	10	0.008	0.075	23.5	0.018	0.057	77	0.044	0.013
Diss Cu	0.0065	0.060	10	0.006	0.054	0	0.000	0.054	0	0.000	0.054	77	0.042	0.012
Total Zn	0.0757	0.700	75	0.525	0.175	10	0.017	0.157	71.7	0.113	0.045	37	0.016	0.028
Diss Zn	0.029	0.268	10	0.027	0.241	0	0.000	0.241	0	0.000	0.241	37	0.089	0.152
PAHs (sum of reported PAHs)	0.00141	0.013	unk	0.000	0.013	unk	0.013	0.013	unk	0.000	0.013	90	0.012	0.001
1: Source: Chapter 6 Site Assumptions Drainage Area: 1ac Impervious Cover: 80% Annual Rainfall: 59" Runoff Coefficient: 0.77 Annual Runoff: 40.9"			2: Source: Chapter 11; assumes regenerative air sweepers with monthly sweeping; portional reduction in efficiency made for diss metals to account for reduced efficiency; note this does not account for accumulation that may occur between sweeping events			3: Based on oil grit separators which are known poor pollutant removal performers			3: Source: Chapter 3; no significant difference reported between dissolved metals influent and effluent so assumed 0% reuduction			4: Source: Chapters 7 and 8; assumed eff for biochar (vs GAC); applied dissolved metals eff to total metals		

Conclusion:

- Pollutant removal efficiencies > 70% may be achievable across contaminants
- A treatment train can:
 - Improve performance for a broad range of COCs
 - Reduce maintenance burden
 - Extend the life of the structural BMP

Effect of Street Sweeping?

Estimated removal of PCBs based on collected data in this study

- Street sweeping FY24: Collection of **234 tons** of debris
- Using 'typical' street sweeping calculations:
 - 234 tons (assume US & wet) x 0.7 = 164 US dry tons = **148,750 kg** street sediment/solids
- Using PCB conc. of ~ 50 ng/g = 50 ug/kg [Low-mid range of our data]

= ~ 7.4 g of PCBs collected

Street sweeping in this area:

- Targeted areas include
- "Arterial Roads, Industrial/Business districts, and NPDES Priority Areas."
- Sweeps are performed twice per month

→ Can Street Sweeping become more targeted?



Summary & conclusions

- 45 samples were collected over 2 years, 6 different land-uses, 2 time eras (Pre and Post PCB ban in 1970s)
- **Highest** total PCB concentrations in **Pre-1970s Residential** and **Industrial** areas
- **Reductions** in total PCB concentrations from **37-61%** were observed **Post-1970s**
- Sources of PCBs are not 'clean' Aroclors, but are mixed
- **PCB-11** (non-Aroclor) from yellow road paint contributes from **0-33%** of the total PCB mass
- Stormwater is an important carrier of PCBs
- **Street sweeping, catchment basin clean-outs** and **biodegradation** in BMPs can reduce PCB mass

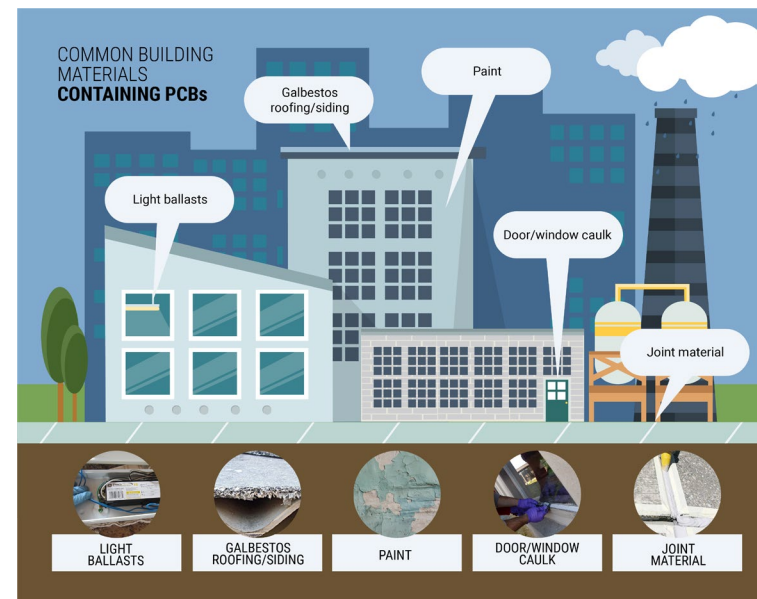


PCBs FREE



Next steps

- Assess the impact of soil and particle types
- Expand the road pain study to include other paint colors
- Assess presence of other PCB sources and their contributions
- Investigate if stormwater BMPs can be designed to remove PCBs simultaneously with other contaminants (N, P) via biodegradation, bioaugmentation?



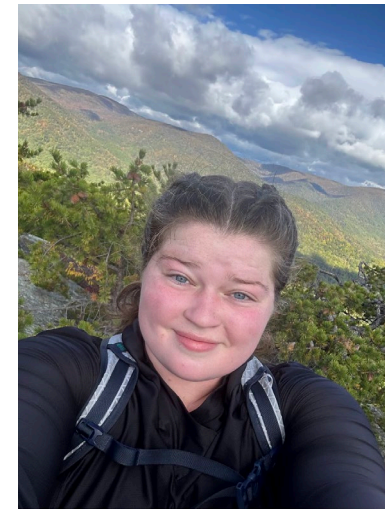
Acknowledgements



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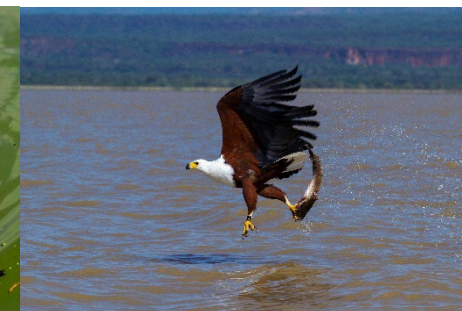
UMD, Civil and Environmental Engineering
Capstone Group: Genevieve Sullivan, Geoffrey
Dochat, Graham Simon, and Brett Strauss

[Collaborations and interactions overall are appreciated. Please reach out if you are interested – bvk@umd.edu]



QUESTIONS?

Contact: bvk@umd.edu

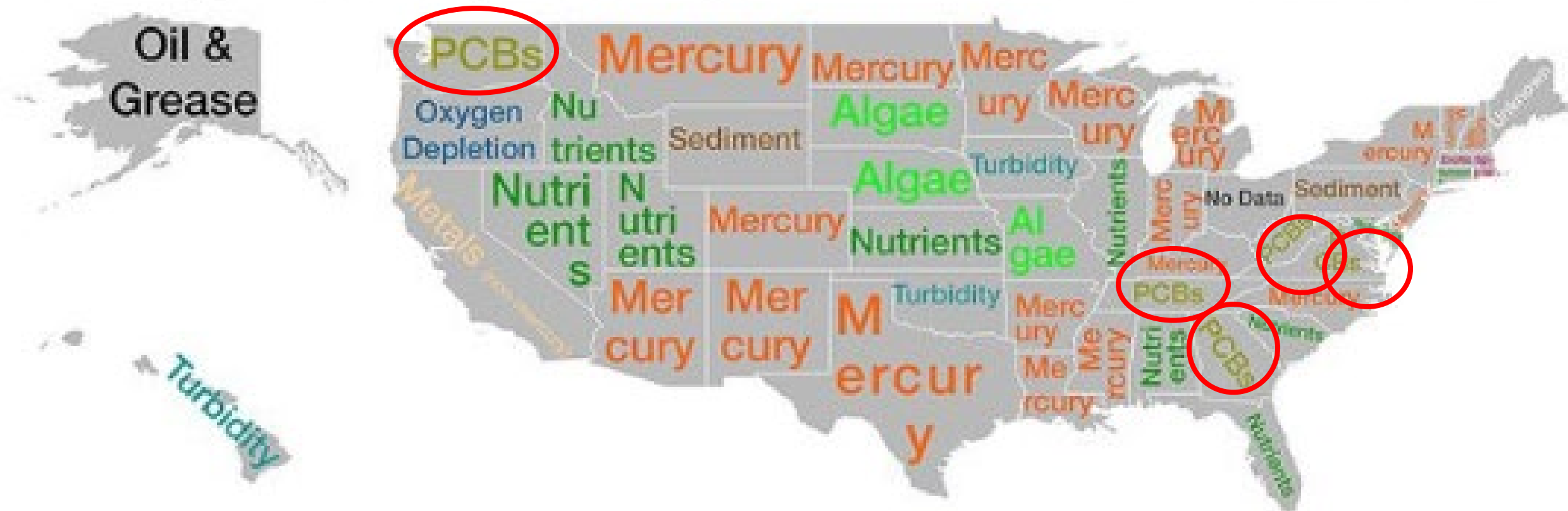


Land Use and Era of Development Effects on PCB Contamination of Soils and Stormwater Sediments in the Chesapeake Bay Watershed

EXTRA SLIDES

Causes of water impairment in the US

Leading Cause of Impairment by Acres of Lakes, Reservoirs and Ponds



Impact of soil physicochemical properties?

Soil Physicochemical

- Moisture Content (MC)
- Organic Matter (OM)
- pH
- Electricity Conductivity (EC)

	Range	
Parameter	Max	Min
MC (%)	42.3	< MC% limit
OM (%)	32.4	0.24
EC (μS/cm)	806	62.3
pH	8.84	6.15

Total PCB Concentrations

	Range	
	Min.	Max.
Total PCB concentration (ng/g)	1.27	381

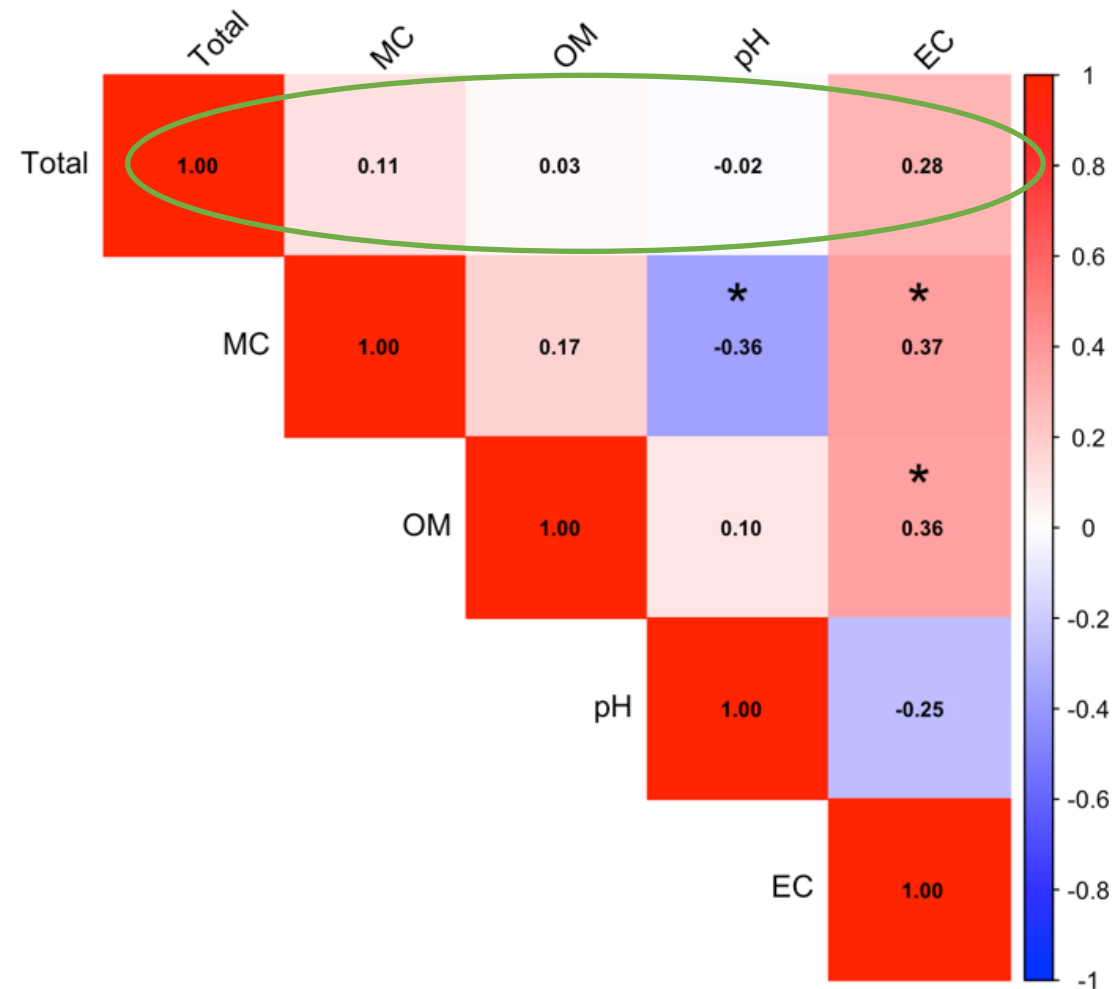
Impact of soil physicochemical properties?

Soil Physicochemical

- Moisture Content (MC)
- Organic Matter (OM)
- pH
- Electricity Conductivity (EC)

VS

Total PCB Concentrations



No Significant Correlation

Road paint calculator (Capstone Project)

Estimate the area of road paint in a watershed:



Color	White	Yellow
Length (ft)	184120.91	34486.91
Total Polylines	9426	298
+/- Error	6880.98	217.54
Area (sqft)	85260.68	28477.47
Volume (Cubic ft)	106.57585	35.5968375



PCB Calculator

Length of Roadway

Parking Lot Area (ft²)

☒ Make More Specific Calculation

Number of Stop Bars

Number of Crosswalks

Calculate

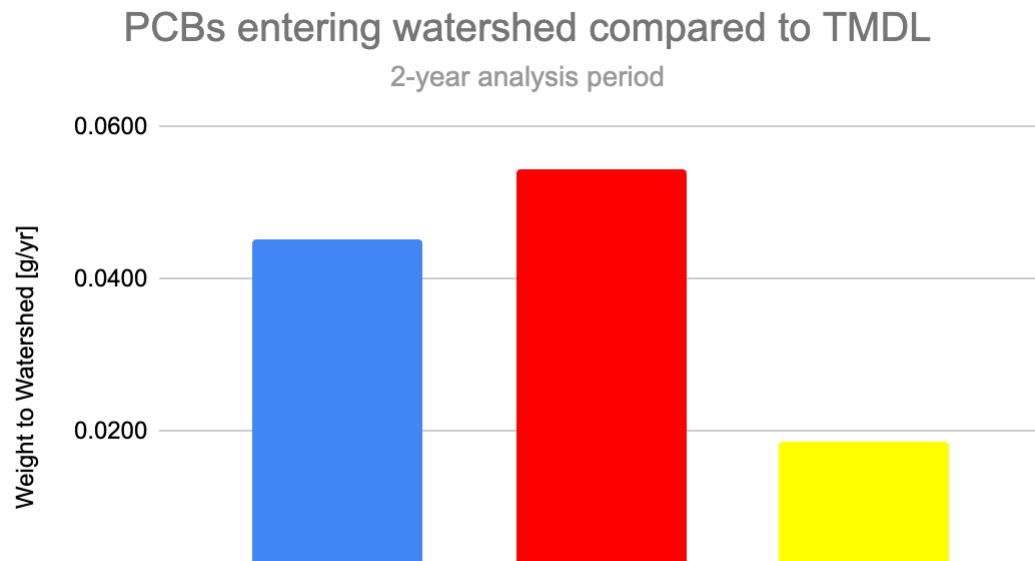
Reset

Summary of College Park Drafting Data

Road paint calculator (Capstone Project)

PCB Concentration	Low (g/ft ³)	High (g/ft ³)	Average (g/ft ³)
Yellow	0.0000727	0.001771	0.0011730
White	0.0000514	0.000074	0.0000584

PCB Calculator Concentrations



Summary:

- Estimate road paint areas (each color)
- Determine PCB concentration in paints
- Mass of PCBs from road paint in a watershed



PCB Runoff Calculator

Estimate paint volume and annual PCB leaching for roadways and parking lots

Roadway Length (ft)

Parking Lot Area (ft²)

☒ **Advanced Calculation**

Number of Stop Bars

Number of Crosswalks

Calculate

Reset

Enter values and click Calculate to see results

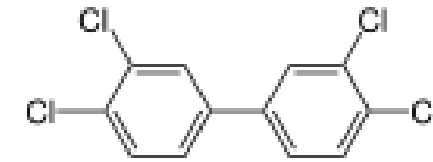
PCB Calculator User Interface

PCB Toxicity

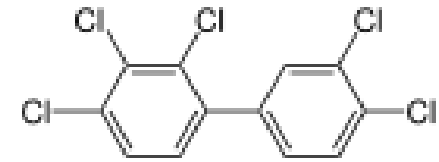
- 12 PCB congeners (of total 209) are **VERY** toxic
- **“Dioxin-like PCBs”** – due to chemical structure
- Can be caused by bacterial degradation in **soil biofilms**

Toxicity Equivalency Factors

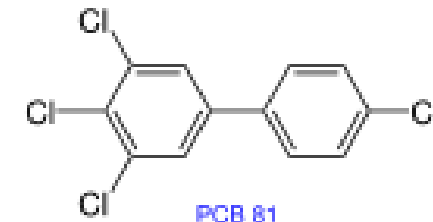
PCB congener	IUPAC No.	Mammals	Fish	Birds
Non-ortho PCBs				
3,4,4',5-	81	0.0001 ^{a,b,c,e}	0.0005	0.1 ^e
3,3',4,4'-	77	0.0001	0.0001	0.05
3,3',4,4',5-	126	0.1	0.005	0.1
3,3',4,4',5,5'-	169	0.01	0.00005	0.001



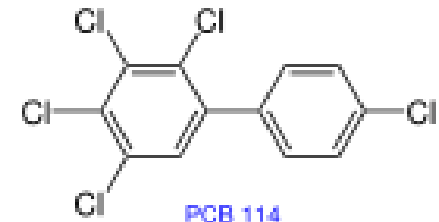
PCB 77



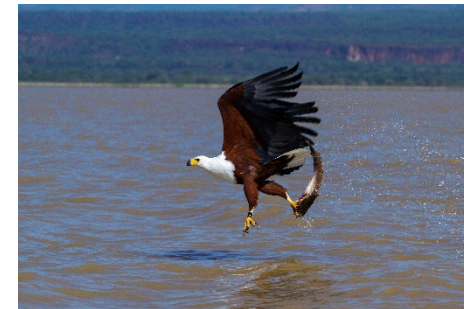
PCB 105



PCB 81



PCB 114



Toxicity Equivalency Factors

Dioxin-like PCB	TEF
77	0.0001
81	0.0003
126	0.1
169	0.03
105	0.00003
114	0.00003
118	0.00003
123	0.00003
156	0.00003
157	0.00003
167	0.00003
189	0.00003

TEQ_{PCB} **Safe sediment Value = 20 pg TEQ/g** (Eljarrat et al., 2001)

Date from this study:

Land Use	Development	Sample information	TEQ-PVB
Residential	Pre-1970s	Res-Pre70-3	26.3±36.9
Industrial	Pre-1970s	ID-Pre70-1	41.2±2.02
Industrial	Pre-1970s	ID-Pre70-4	41.2±2.02

Summary:

- Samples which TEQ exceed the safe sediment value are listed
- 3 of 45 samples **exceeded** the Safe Sediment Value
- These 3 samples were from **Pre-1970s: Residential** and **Industrial**
- All other samples are below the safe limit or <MDL