UMBC

Using passive sampling to develop an improved framework for Total Maximum Daily Loads of hydrophobic organic contaminants

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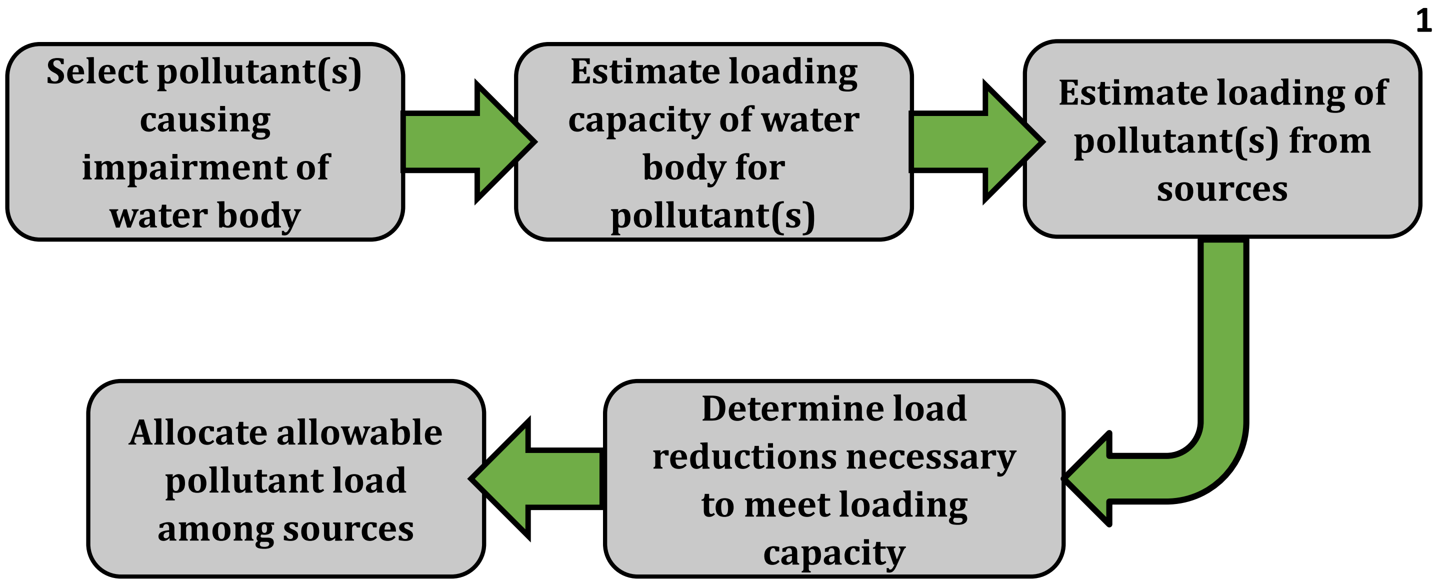
11th International Passive Sampling Workshop

Boston, MA. 11 – 13th September 2019

Chemical
Biochemical and
Environmental
Engineering

Total Maximum Daily Loads approach



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Select pollutant(s) causing impairment of water body

Estimate loading capacity of water body for pollutant(s)

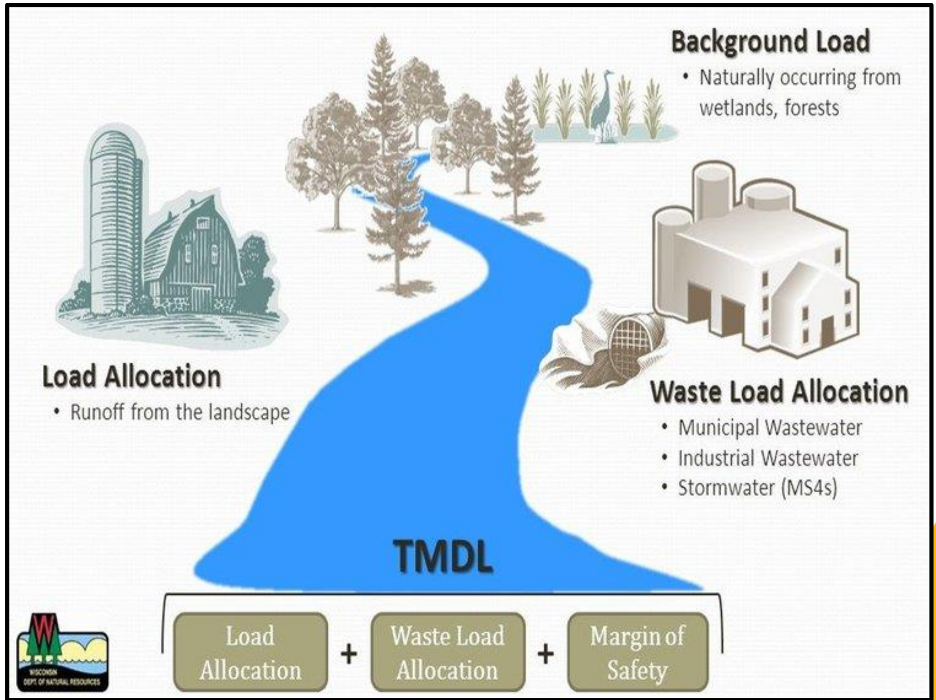
Estimate loading of pollutant(s) from sources

Determine load reductions necessary to meet loading capacity

Allocate allowable pollutant load among sources

The **total maximum daily load (TMDL)** is the maximum quantity of a pollutant that can enter a waterbody and attain water quality standards.

- ☐ Part of Clean Water Act (CWA)
- ☐ States required to develop pollution reduction targets for impaired water bodies
- ☐ Assign TMDLs to sources of pollutants



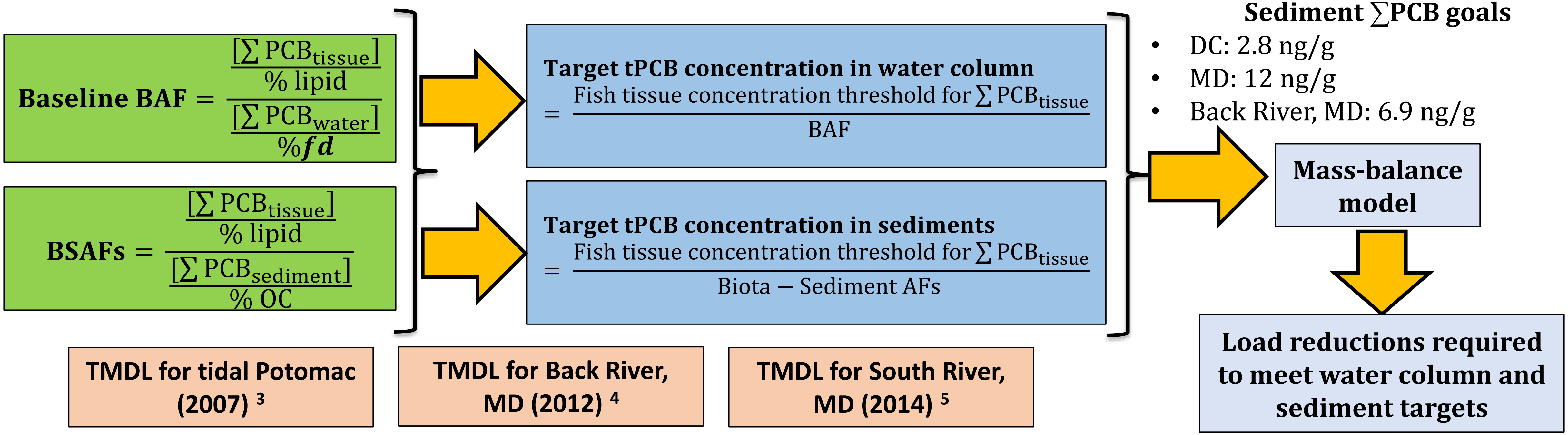
$$\text{TMDL (mass per unit time)} = \sum \text{WLA} + \sum \text{LA} + \text{Margin of Safety}$$

Load from point sources

Load from non-point and background sources

Image Source: Wisconsin DNR (https://www.lakepepinlegacyalliance.org/faq)

Issues with current TMDL approach for HOCs



$$\text{Baseline BAF} = \frac{\dfrac{[\sum \text{PCB}_{\text{tissue}}]}{\%\ \text{lipid}}}{\dfrac{[\sum \text{PCB}_{\text{water}}]}{\%\boldsymbol{fd}}}$$

$$\text{BSAFs} = \frac{\dfrac{[\sum \text{PCB}_{\text{tissue}}]}{\%\ \text{lipid}}}{\dfrac{[\sum \text{PCB}_{\text{sediment}}]}{\%\ \text{OC}}}$$

Target tPCB concentration in water column

$$= \frac{\text{Fish tissue concentration threshold for} \sum \text{PCB}_{\text{tissue}}}{\text{BAF}}$$

Target tPCB concentration in sediments

$$= \frac{\text{Fish tissue concentration threshold for} \sum \text{PCB}_{\text{tissue}}}{\text{Biota} - \text{Sediment AFs}}$$

Sediment $\sum$PCB goals

- DC: 2.8 ng/g
- MD: 12 ng/g
- Back River, MD: 6.9 ng/g

Mass-balance model

Load reductions required to meet water column and sediment targets

TMDL for tidal Potomac (2007) [3]

TMDL for Back River, MD (2012) [4]

TMDL for South River, MD (2014) [5]

For a site with high dissolved PCB levels in our study, congener-wise %fd varied from 0.45% (PCB 209) to 93% (PCB 4)

Average %fd calculated using the above equation: 53%

- **98% reduction in PCB loads** from Northeast and Northwest Branches of Anacostia to meet downstream TMDL targets[6]
- **96% reduction in PCB loads to Potomac and Anacostia** [3]
- **99.9% reduction in total PCB load** for Patuxent River (MD) [7]

Mass-balance models not linked to food-web bioaccumulation models

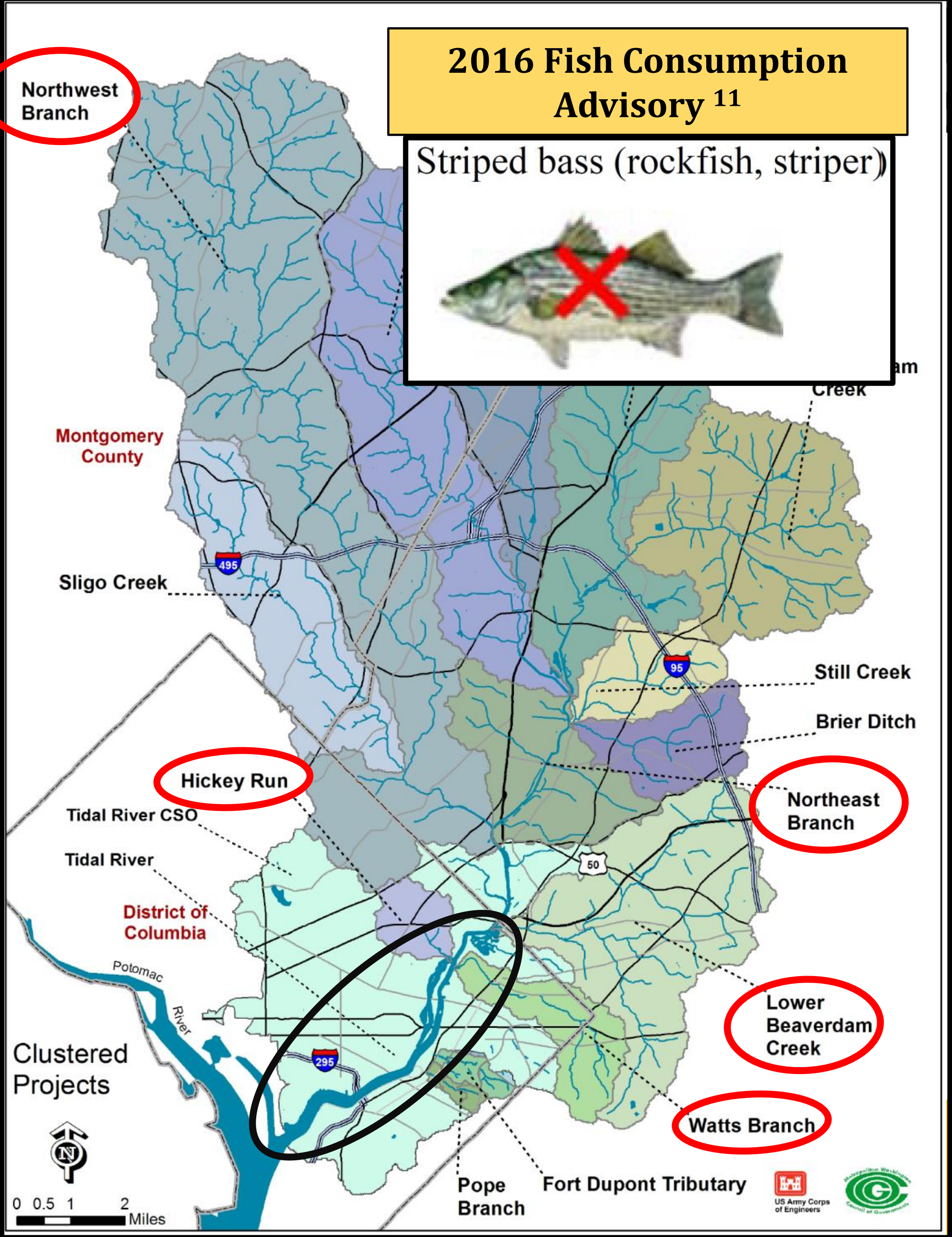
Diffusive exchange between air-water and sediment-water not included in mass-balance models

Area of study: Anacostia Watershed

- ❑ Drainage area of **173 square miles** [8]
- ❑ Almost **70 %** of the watershed is drained by the **Northeast and Northwest Branch tributaries** [8]
- ❑ Other major tributaries:
  - ➢ Lower Beaverdam Creek (LBC)
  - ➢ Watts Branch (WAB)
  - ➢ Hickey Run (HIR).

Anacostia River

- ❑ Length of main channel: **8.4 miles** [8]
- ❑ Discharges into the **Potomac River**; **108 miles** upstream of the Chesapeake Bay [8]
- ❑ Designated **"Region of concern"** in the Chesapeake Bay due to impaired water quality from Persistent Organic Pollutants (POPs)[9,10]



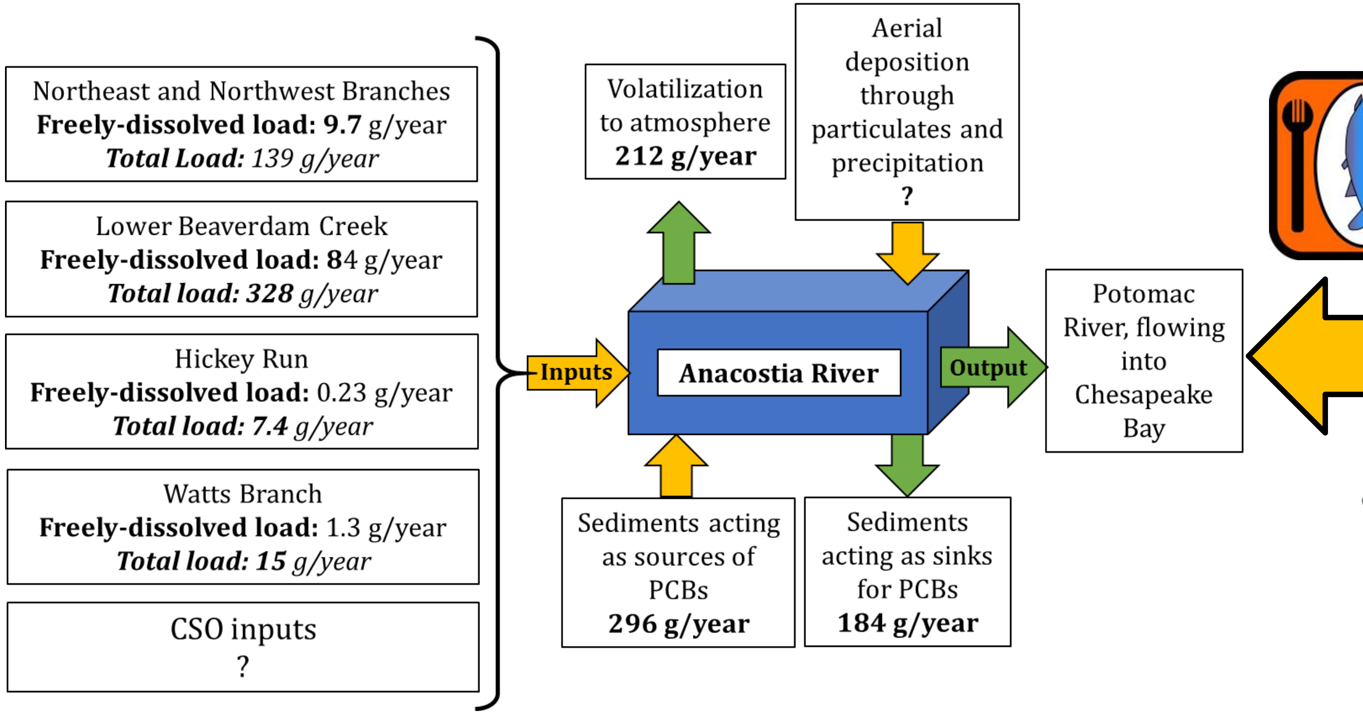
2016 Fish Consumption Advisory [11]

Striped bass (rockfish, striper)

Image Source: U.S Army Corps of Engineers (https://www.nab.usace.army.mil/portals/63/docs/Environmental/Anacostia/Anacostia2.pdf)

Improving existing TMDL framework by incorporating passive sampling

- ☐ Better delineation of freely-dissolved loads with high impacts
- ☐ Quantification of air-water and sediment-water diffusive exchange processes
- ☐ Link fate and transport of HOCs to their bioaccumulation in aquatic organisms



Northeast and Northwest Branches
Freely-dissolved load: 9.7 g/year
Total Load: *139 g/year*

Lower Beaverdam Creek
Freely-dissolved load: 84 g/year
Total load: *328 g/year*

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Total load: 7.4 *g/year*

Watts Branch
Freely-dissolved load: 1.3 g/year
Total load: 15 *g/year*

CSO inputs
?

Inputs

Anacostia River

Output

Volatilization to atmosphere
212 g/year

Aerial deposition through particulates and precipitation
?

Sediments acting as sources of PCBs
296 g/year

Sediments acting as sinks for PCBs
184 g/year

Potomac River, flowing into Chesapeake Bay

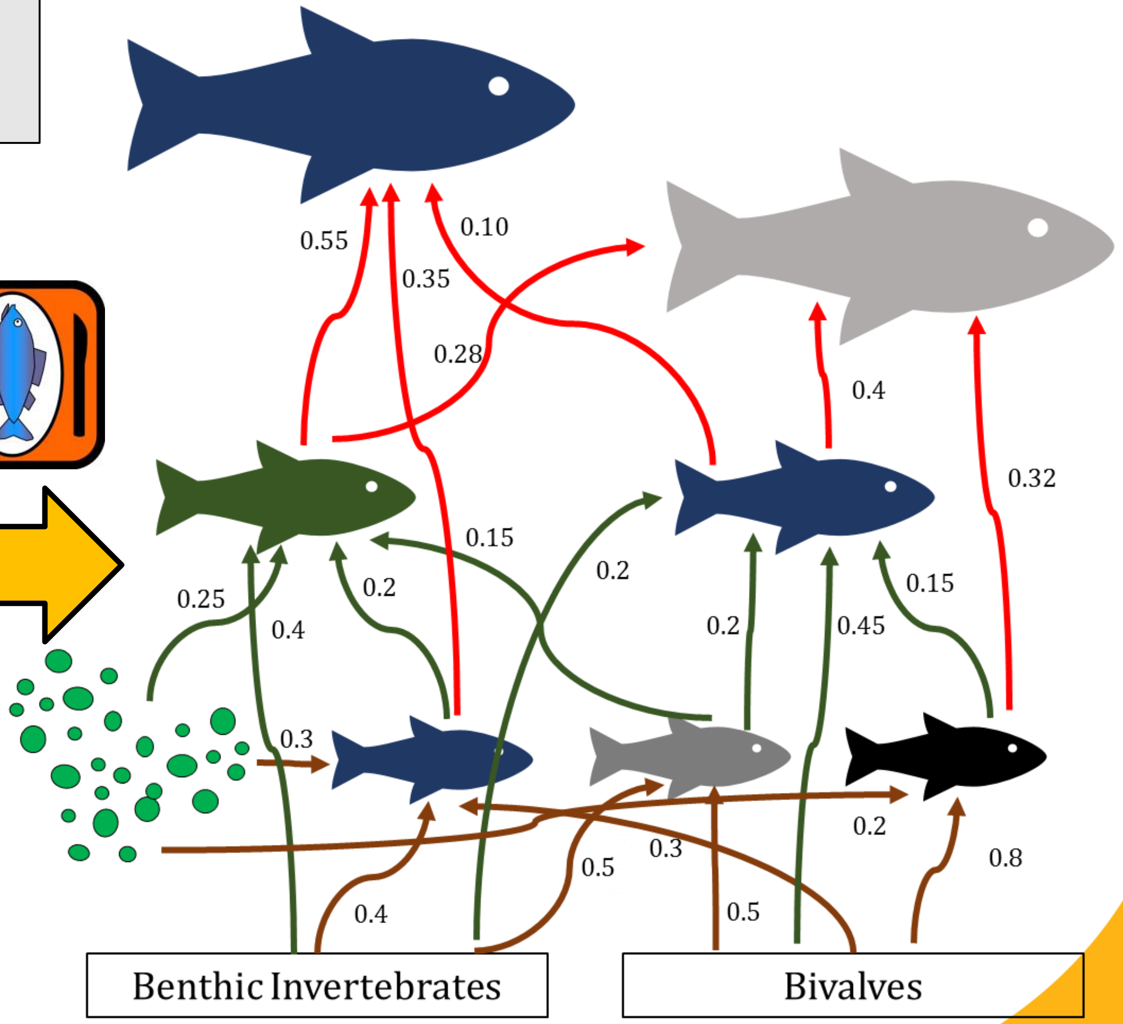
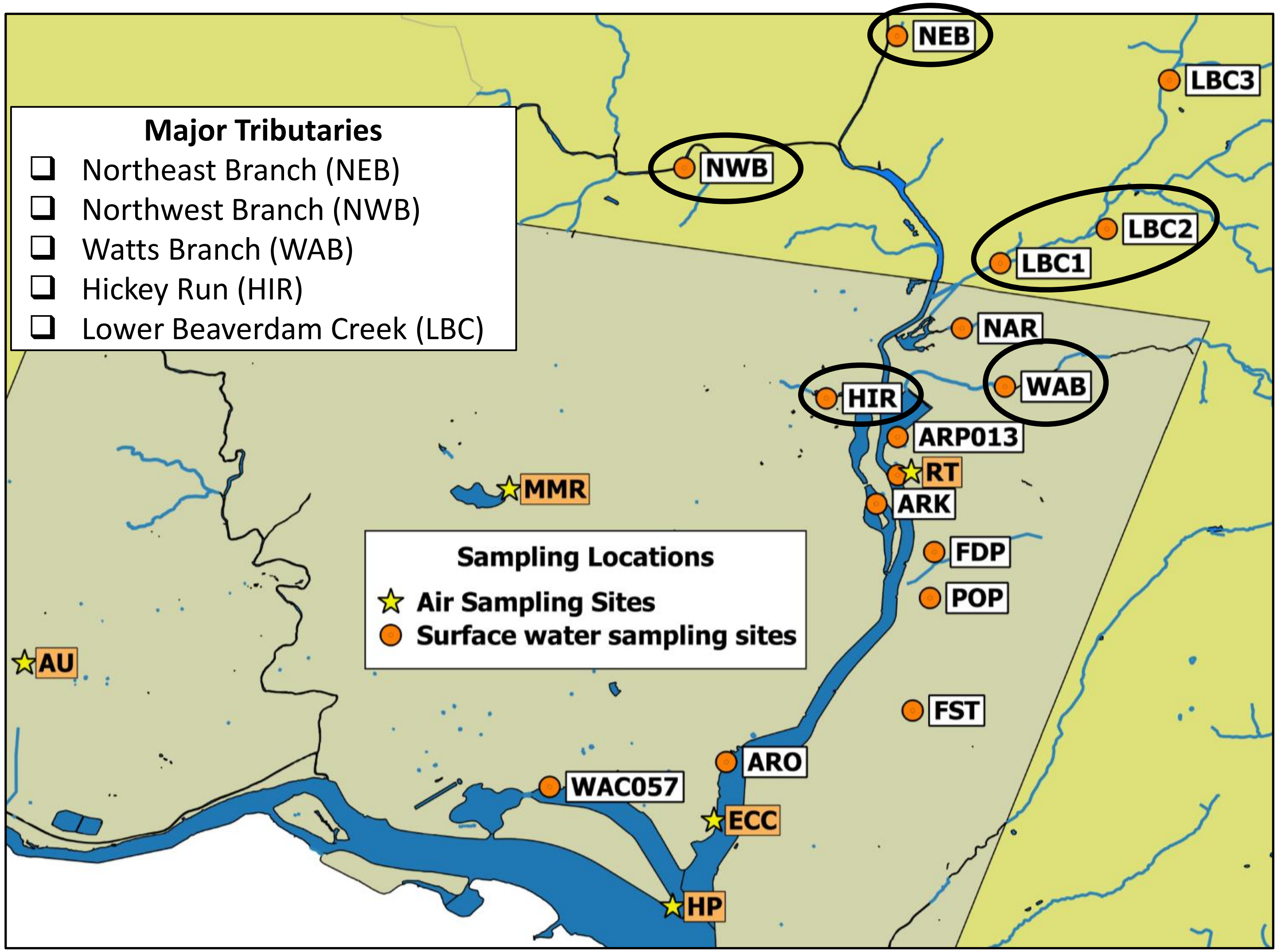


Image Source: Grand Lake Watershed Mercury Study
(http://www.grandlakemercurystudy.org/Fish_Consumption.html)

Research Approach: Sampling locations

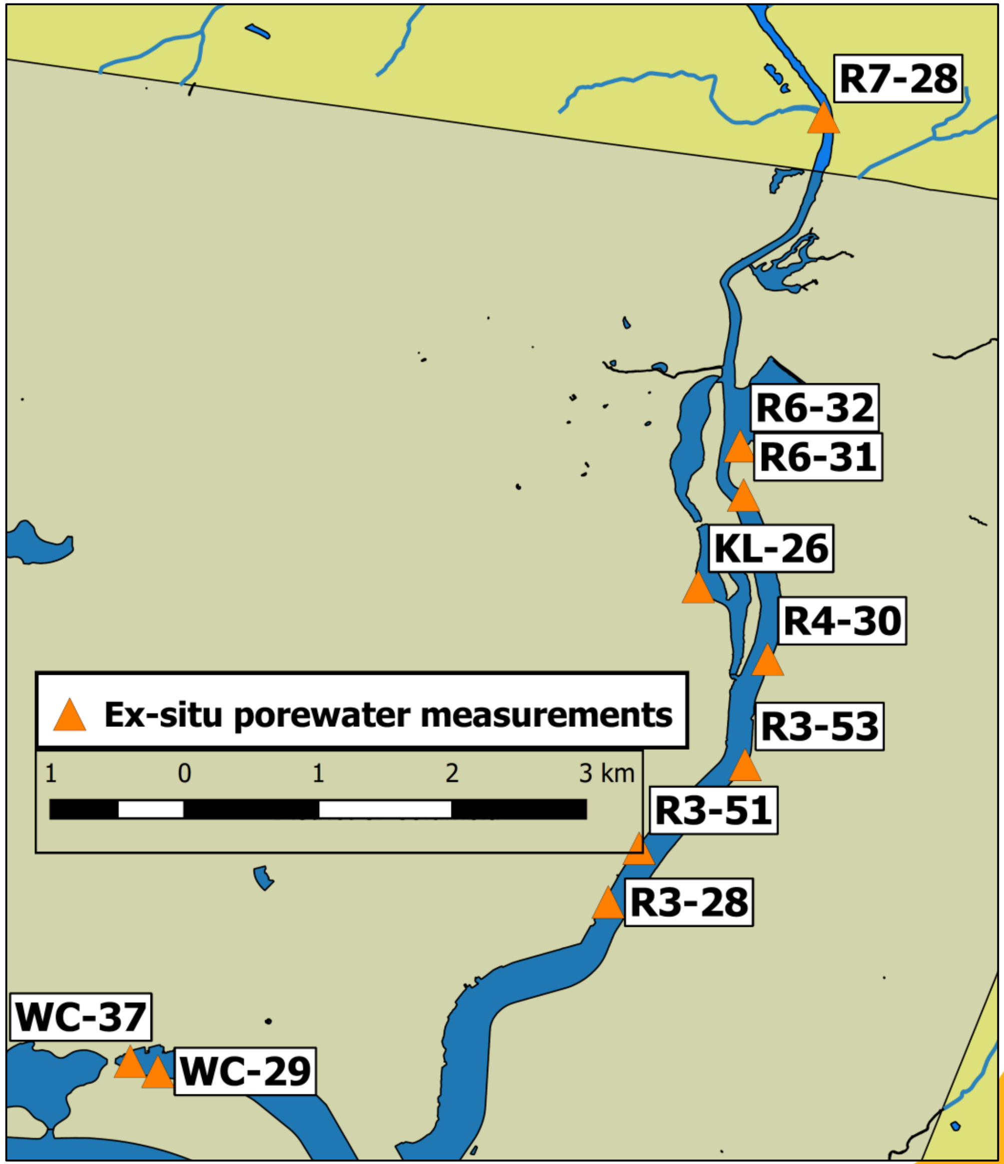


Major Tributaries

- ☐ Northeast Branch (NEB)
- ☐ Northwest Branch (NWB)
- ☐ Watts Branch (WAB)
- ☐ Hickey Run (HIR)
- ☐ Lower Beaverdam Creek (LBC)

Sampling Locations

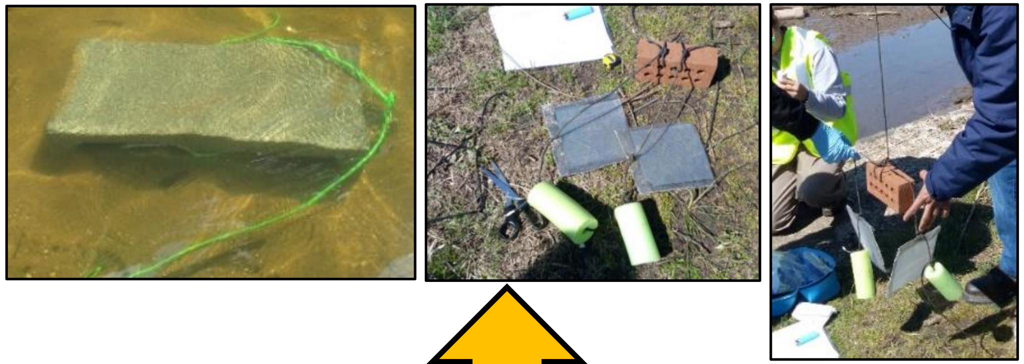
- ☆ Air Sampling Sites
- ● Surface water sampling sites



▲ Ex-situ porewater measurements

Research Approach: Passive sampler deployment

Water-phase sampling



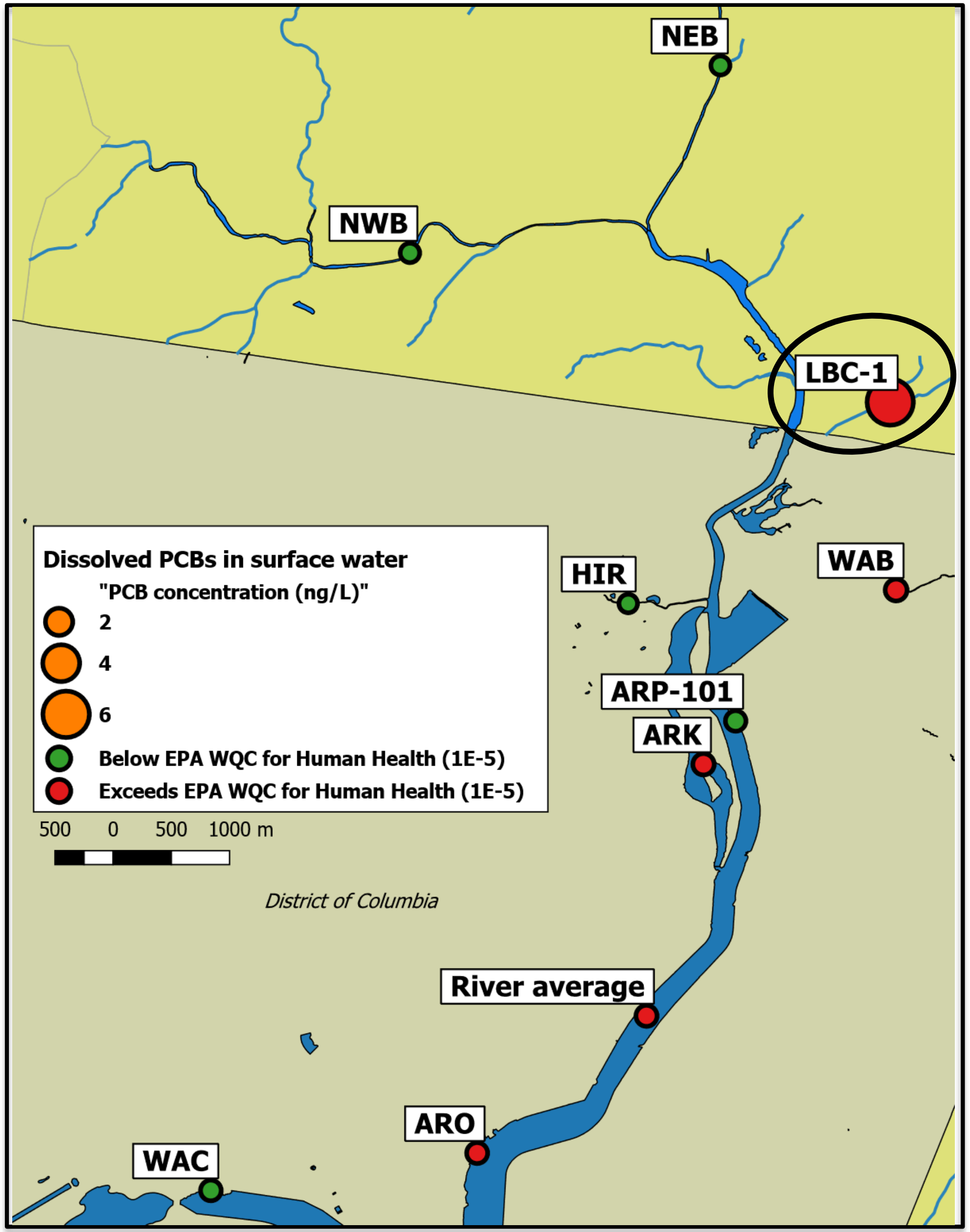
Gas-phase sampling

- ☐ Low-density polyethylene (LDPE) passive samplers
- ☐ Performance reference compounds used to correct for non-equilibrium
- ☐ 1-2 g of PE deployed in field for ~ 3 months

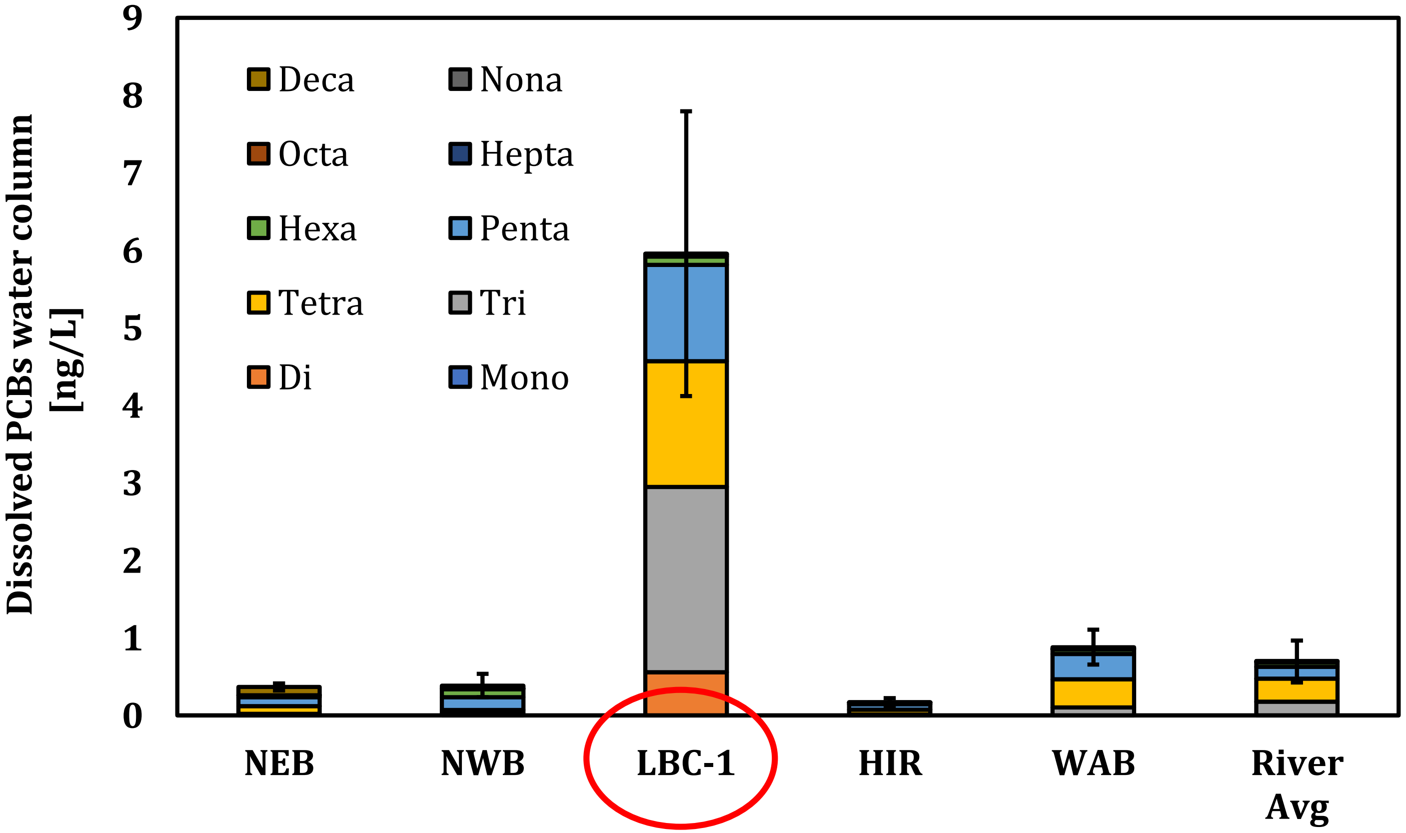
Porewater-phase sampling

- ☐ Ex-situ measurement of porewater concentrations
- ☐ ~ 130 mg of PE equilibrated for 1 month with sediment core samples

Dissolved PCBs in surface water

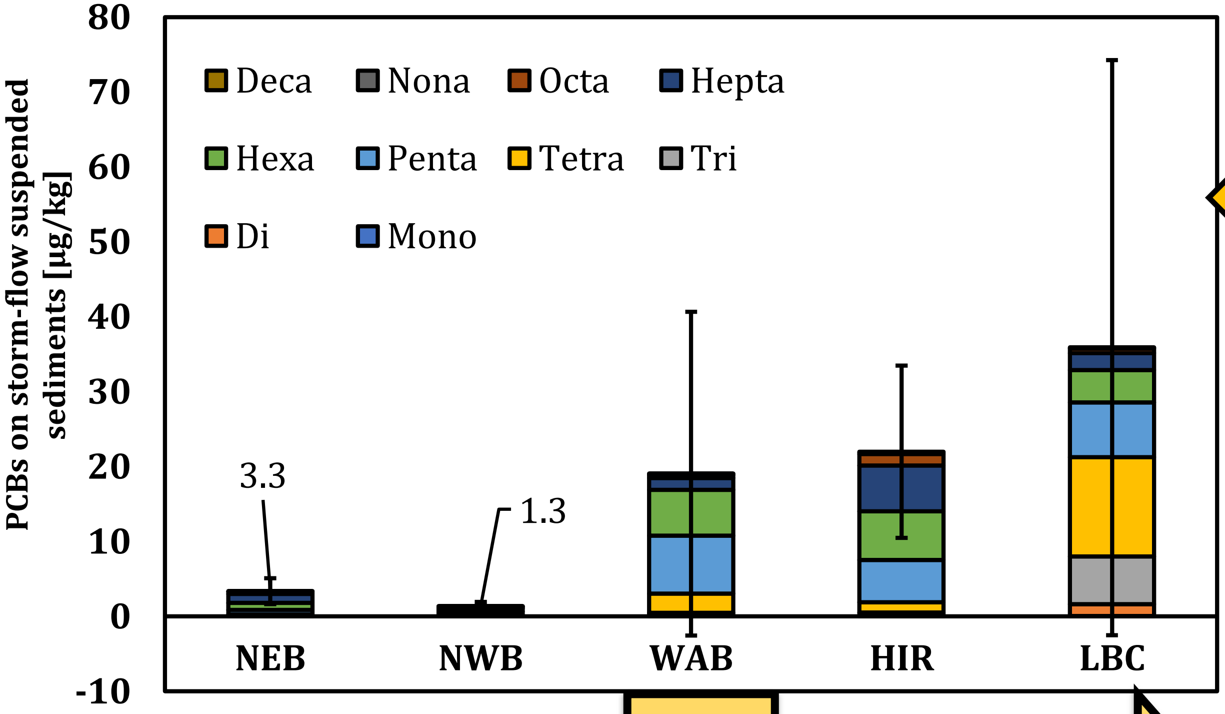


Average dissolved PCB levels from 4 deployments



Dissolved PCBs at storm and base flow conditions

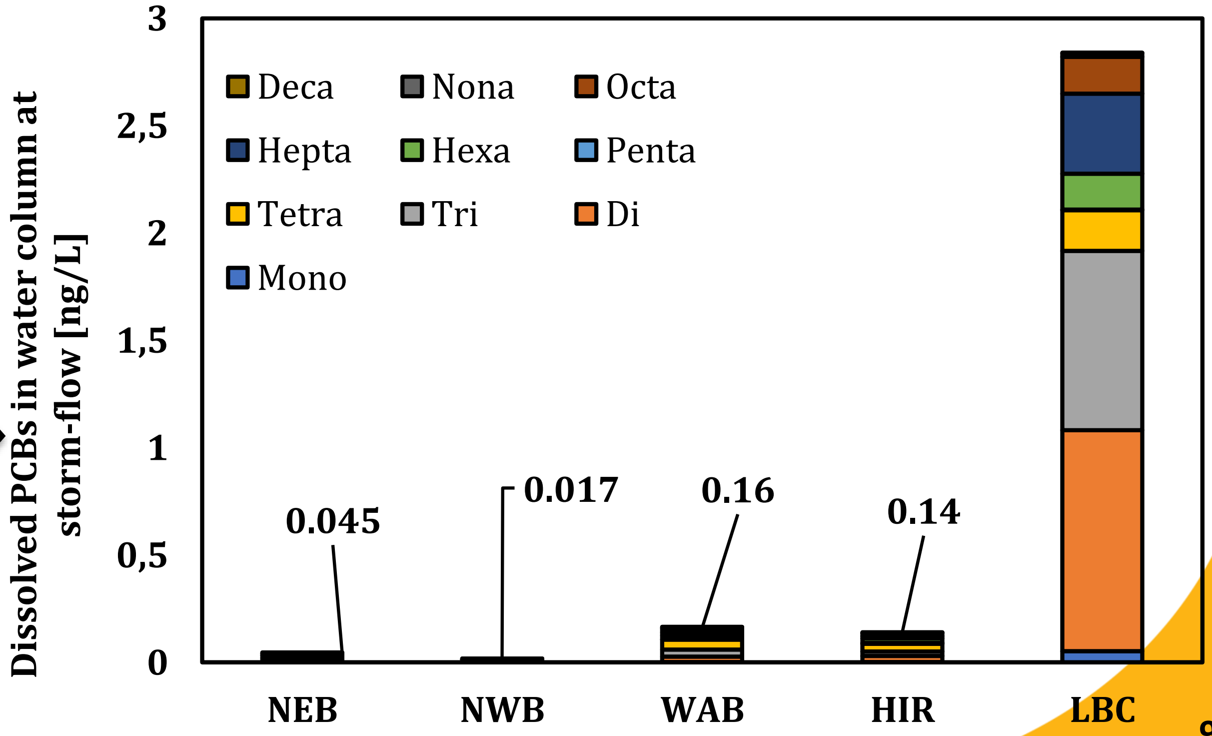
PCBs on suspended sediments at storm-flow



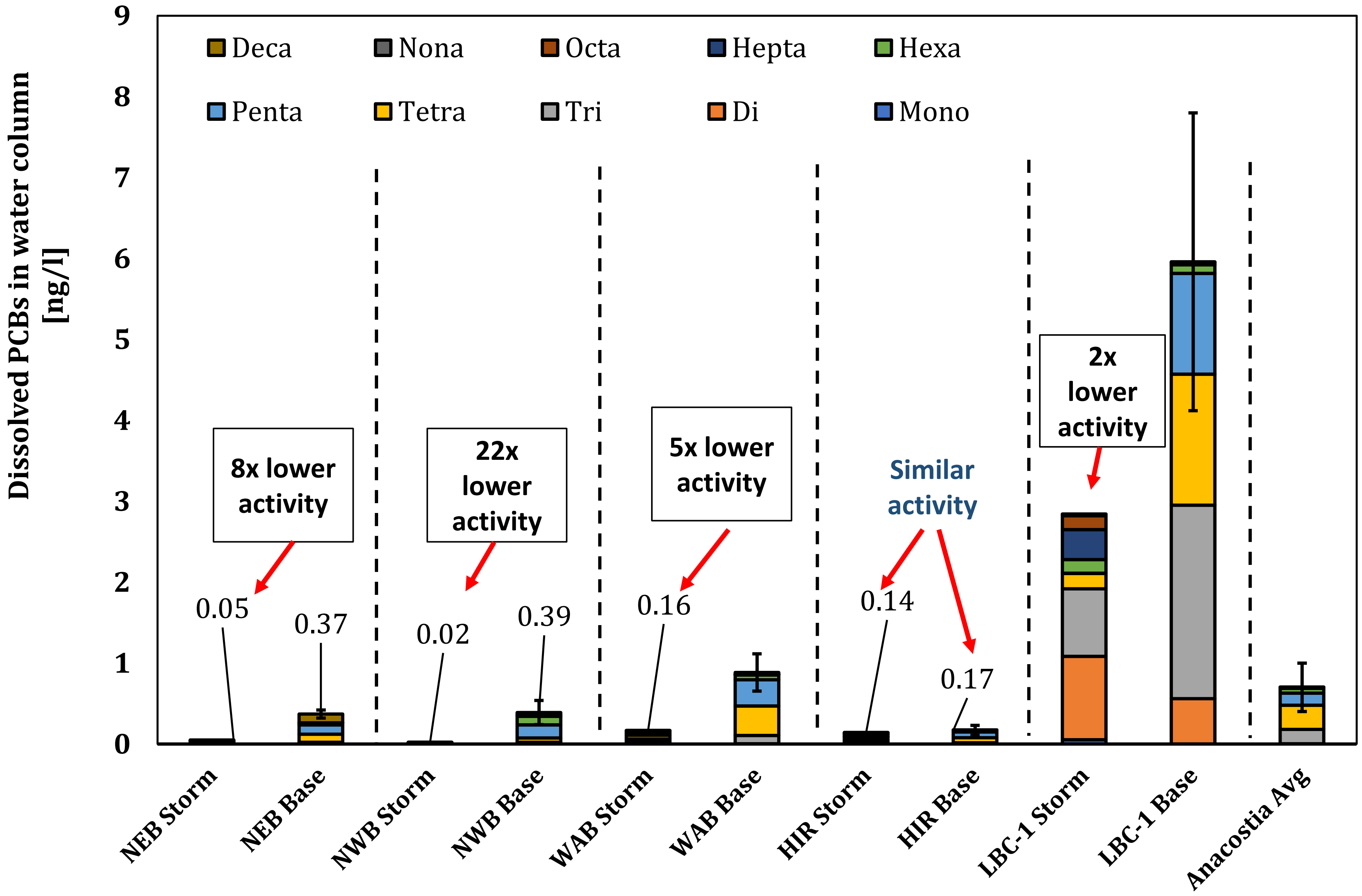
Dissolved PCBs in water column at storm-flow

Suspended sediments collected by USGS during storm flow conditions by stream-side filtering using automated samplers

$$C_{\text{Free}} = \frac{C_{\text{Sed}}}{f_{OC} \times K_{OC}}$$



Dissolved PCBs at storm and base flow conditions



For most tributaries, storm flows and the sediments that they carry lower the activity of dissolved PCBs

Activity of PCBs (with respect to PCBs in Anacostia River) lowered during storm flows

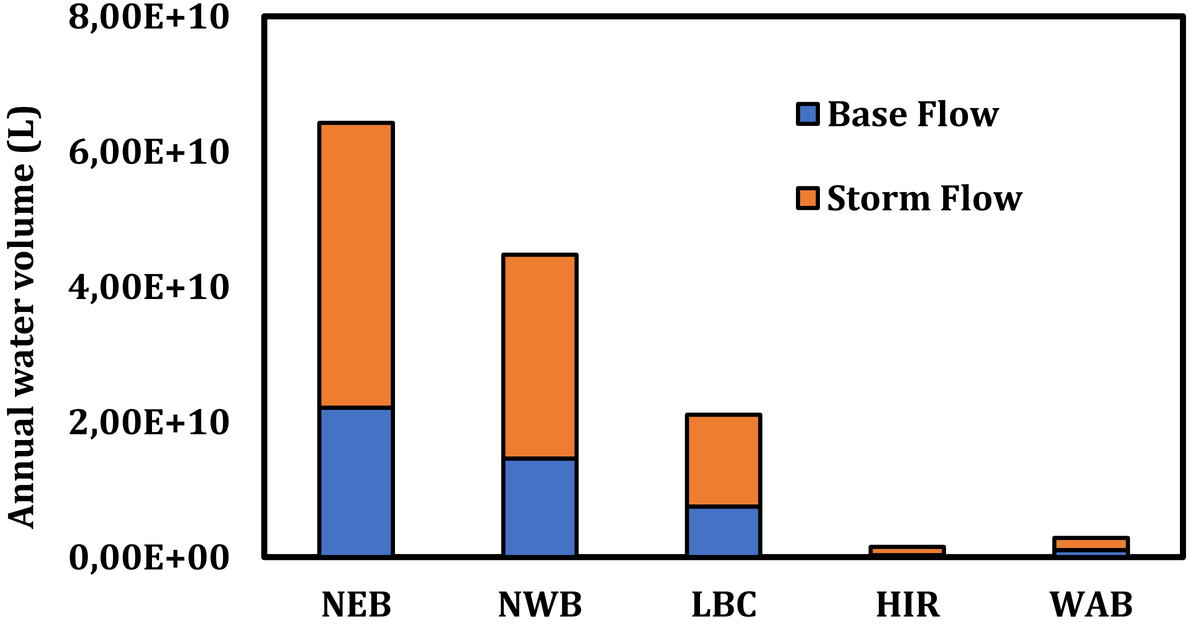
Water and sediment loads for major tributaries

USGS Station ID	Site Name	Average flow (2017, cfs)	Average turbidity during base flow (2017, FNU)	Average turbidity during storm flow (2017, FNU)
1651000	**NWB**	47.1	9.0	82
1649500	**NEB**	67.4	9.2	64
1651730	**LBC**	21.2	14	99
1651800	**WAB**	2.98	5.4	56
1651770	**HIR**	1.68	11	55

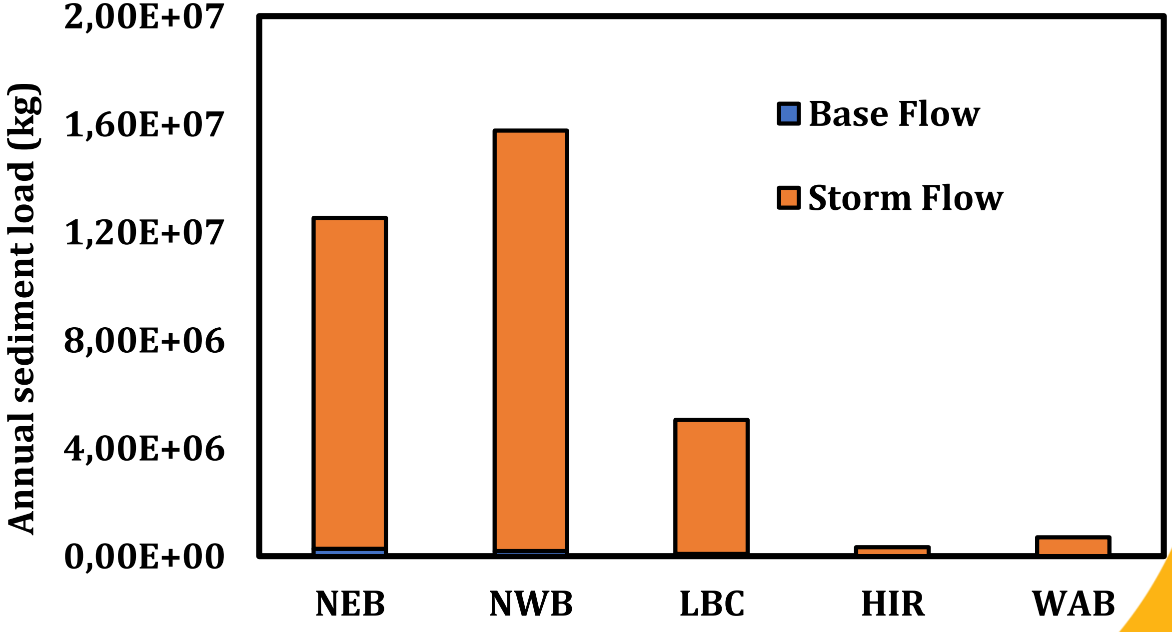
Streamflow data obtained from USGS National Water Information System (NWIS, https://waterdata.usgs.gov/nwis) [12]

Average streamflow during 2017 used for delineating base and storm flow conditions

Annual water volume



Annual sediment load

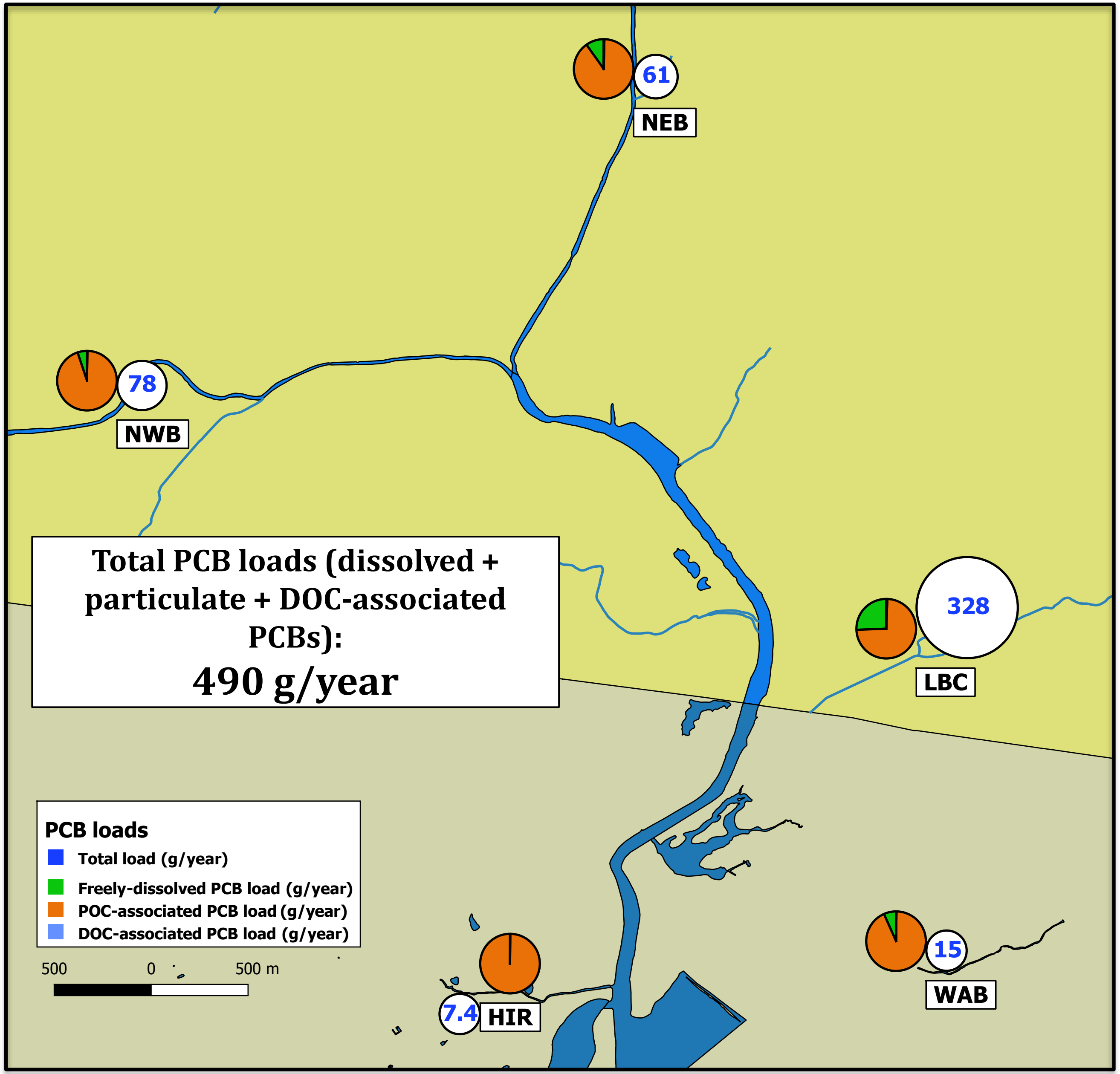


$$\textbf{Volume of water } V = \int_{t=0}^{t=T} Q.\,dt$$

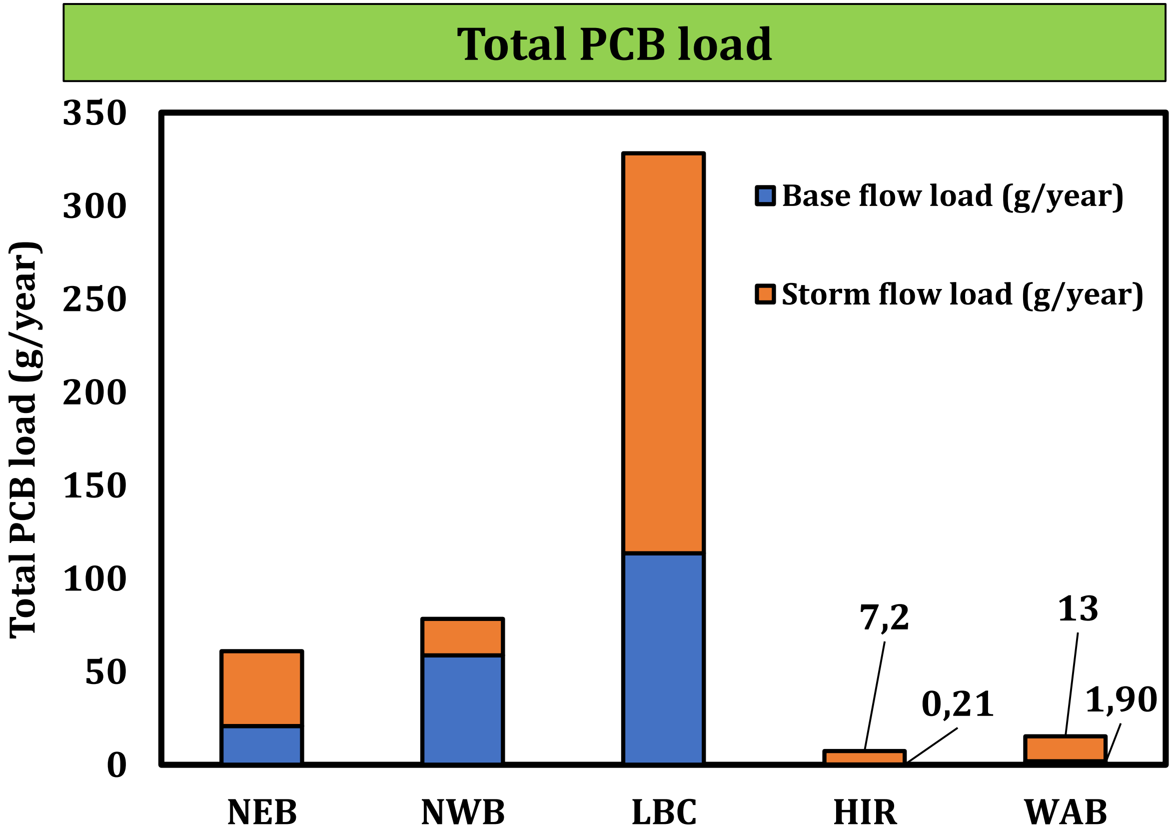
$$\log_{10}(TSS) = A * \log_{10}(Turbidity) + B * \log_{10}(Q) + C$$

$$\textbf{Sediment load} = V.\int_{t=0}^{t=T} TSS.\,dt$$

PCB loads at storm and base flow conditions

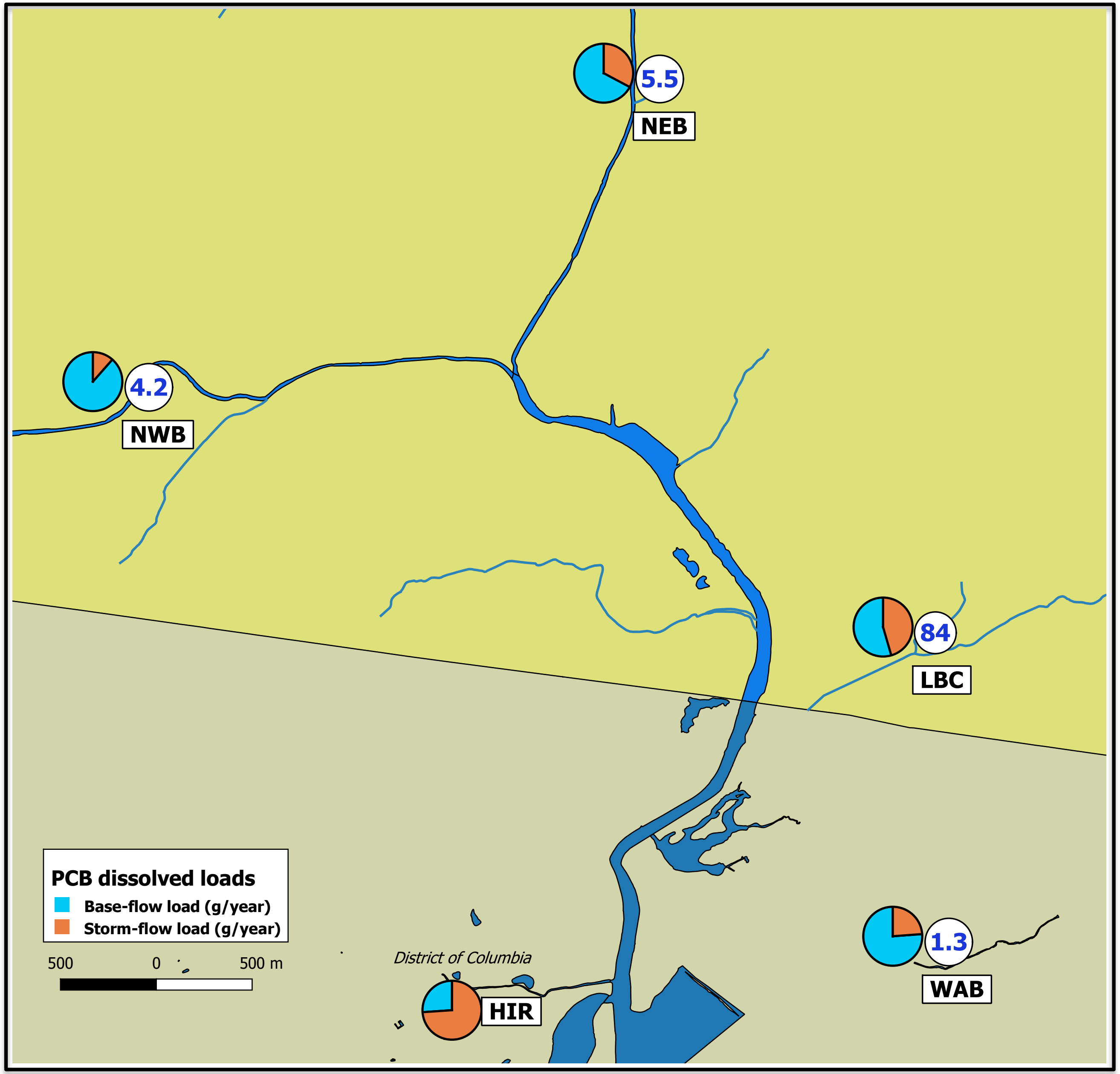


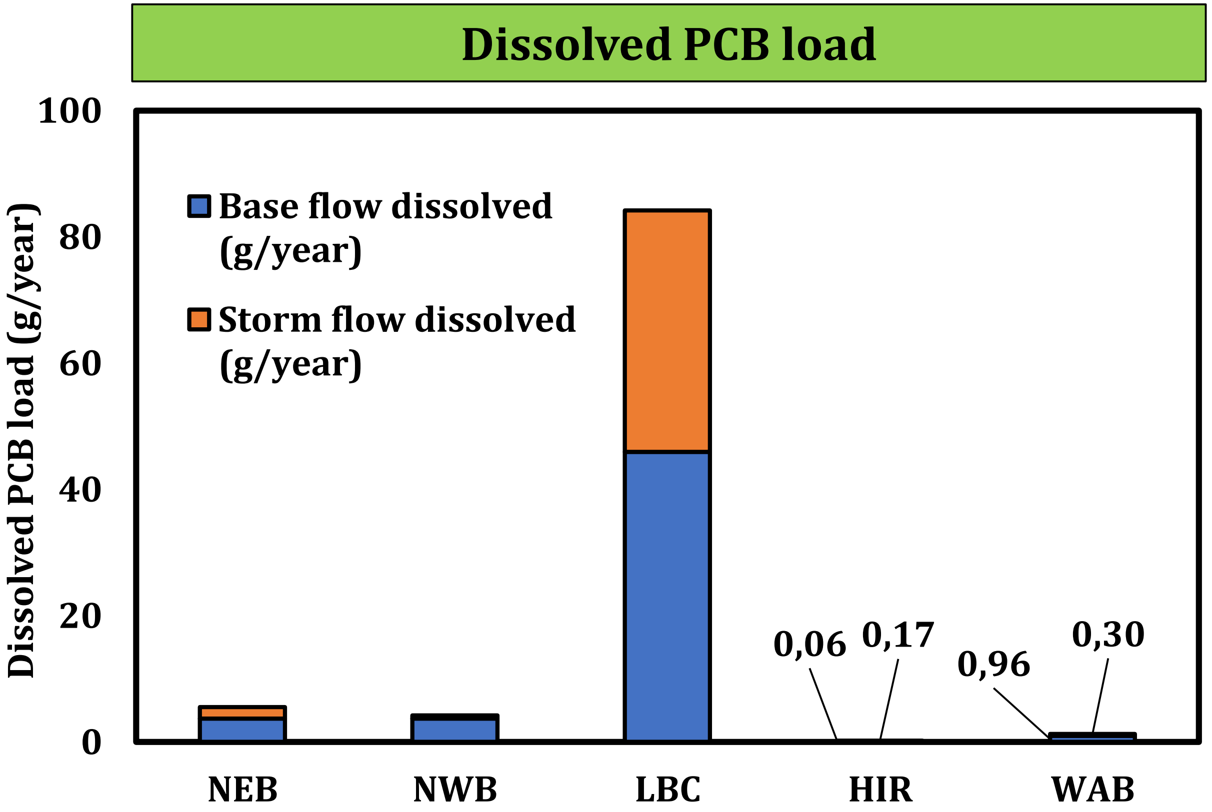
Total PCB loads (dissolved + particulate + DOC-associated PCBs):
490 g/year


Total PCB load

Total loads dominated by storm-flow associated suspended sediments

Dissolved PCB loads at storm and base flow conditions

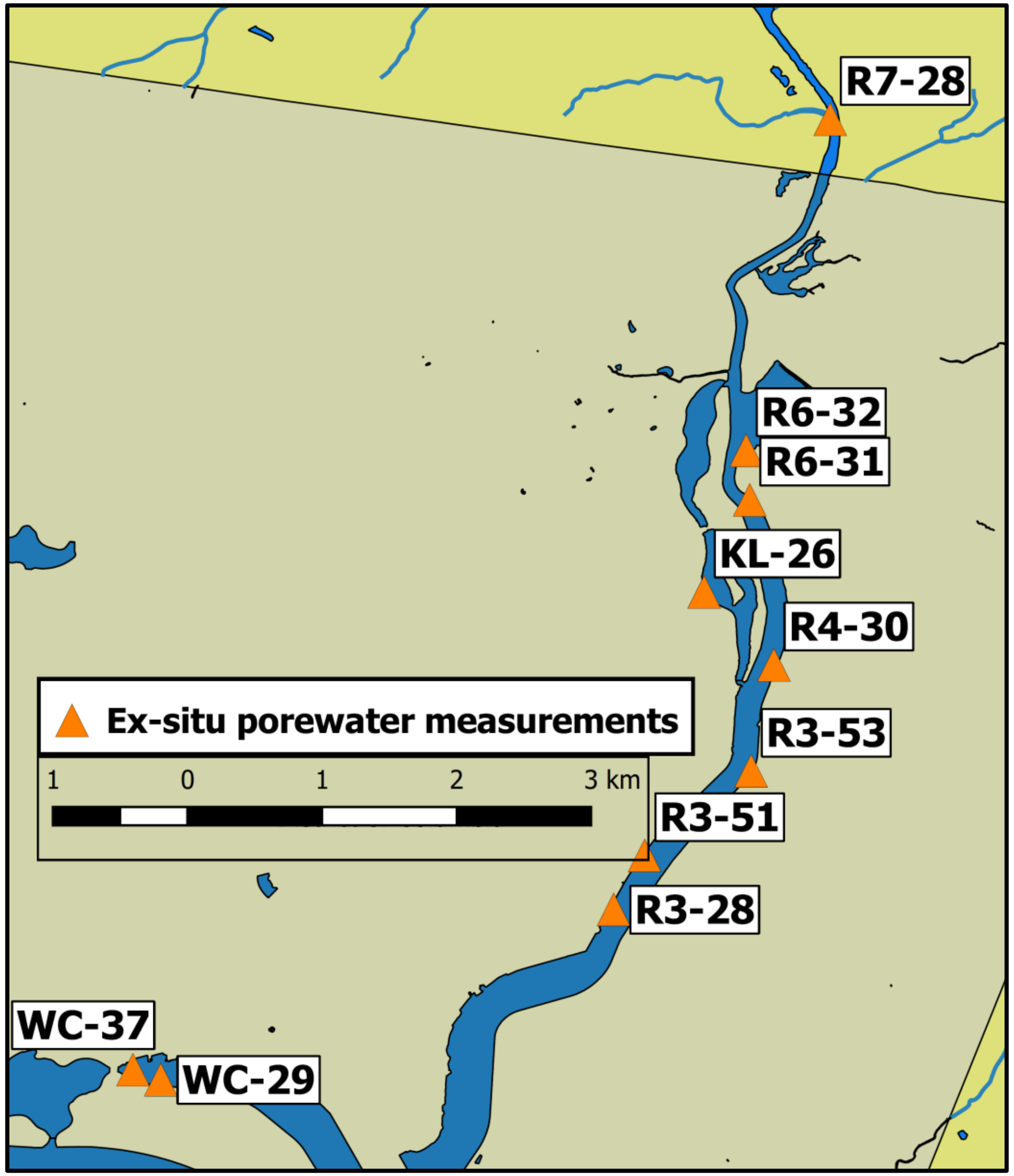




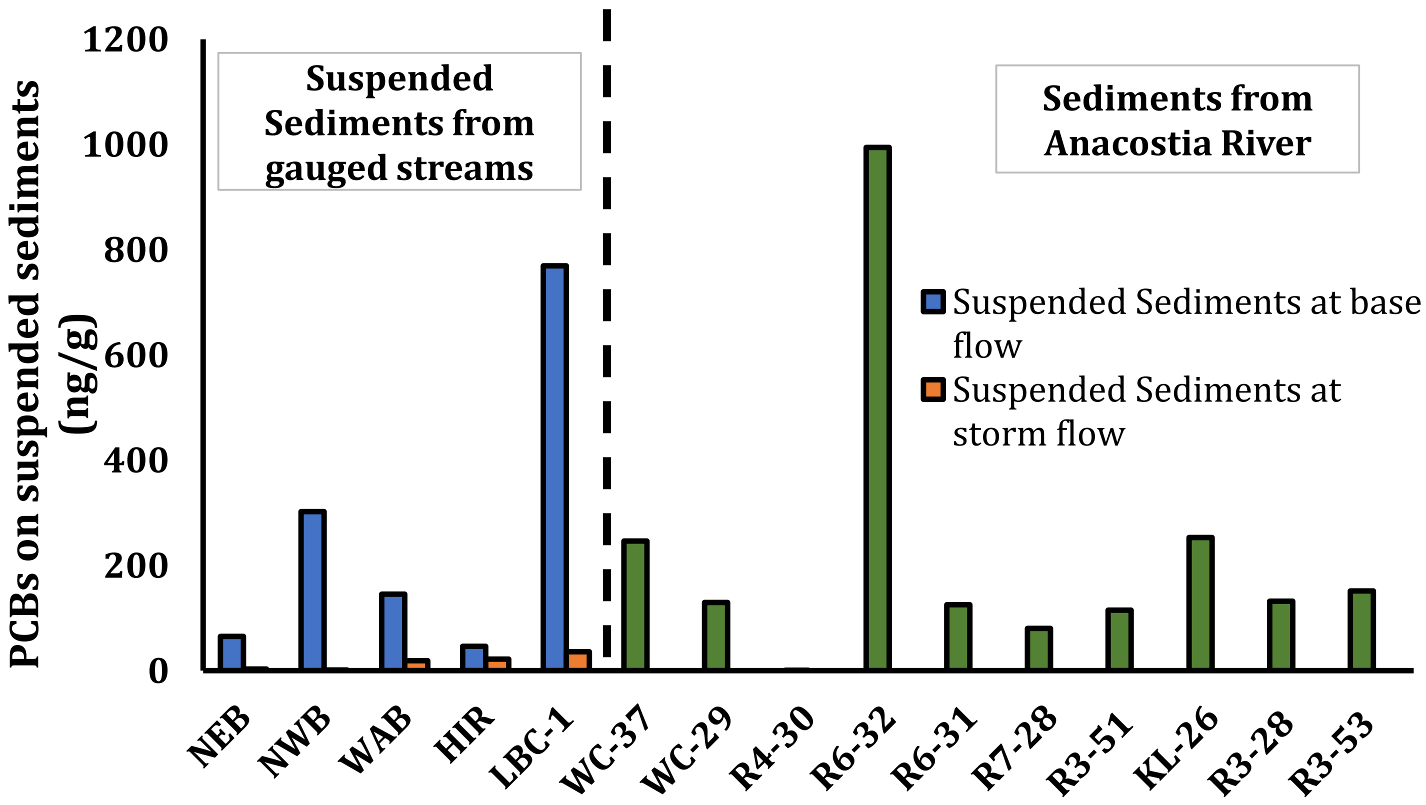
Dissolved loads mostly delivered at base flow conditions

Focus on total loads can mask importance of dissolved loads at base flow

PCBs on suspended sediments in tributaries



Comparison of PCBs on suspended and bed sediments



Suspended sediments at storm flow have PCB concentration lower than bed sediments from the river

Could assist in natural recovery of river

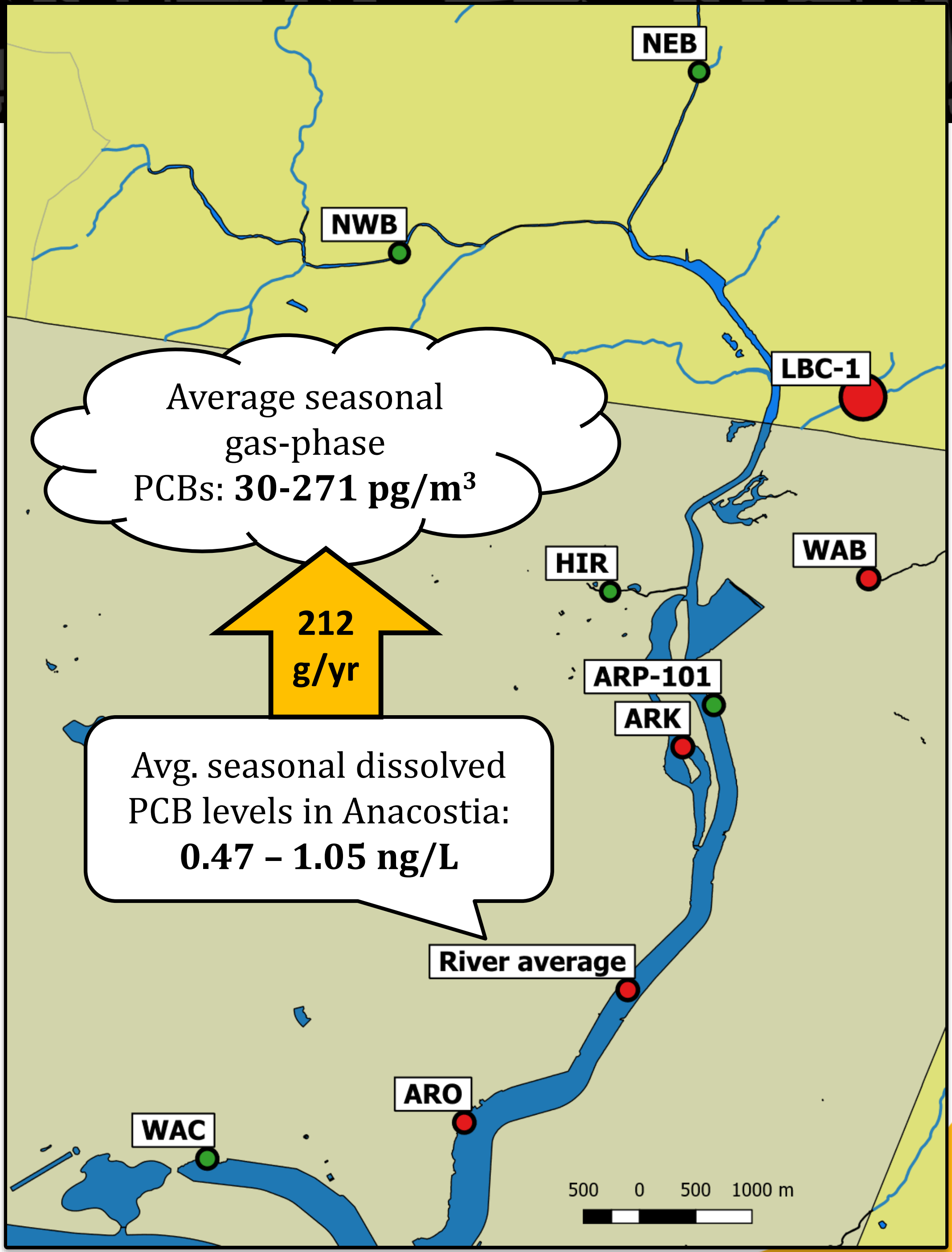
Air-water diffusive exchange of PCBs

- Volatilization of PCBs from surface water across all deployment periods
- Volatilization rate of **212 g/year** from river to atmosphere
- Estimates of aerial deposition rates: **5.5 to 56 g/year** [13]

Important data gap for this watershed

"Iterative model runs determined that atmospheric deposition to the Anacostia River must be reduced by 93%, which set the level of atmospheric reductions for the entire watershed. That reduction in the atmospheric deposition source category was, by itself, sufficient to meet PCB targets in some of the impairments in the lower part of the watershed. *Thus no reductions are required for tributary and direct drain loads to these impairments.*"

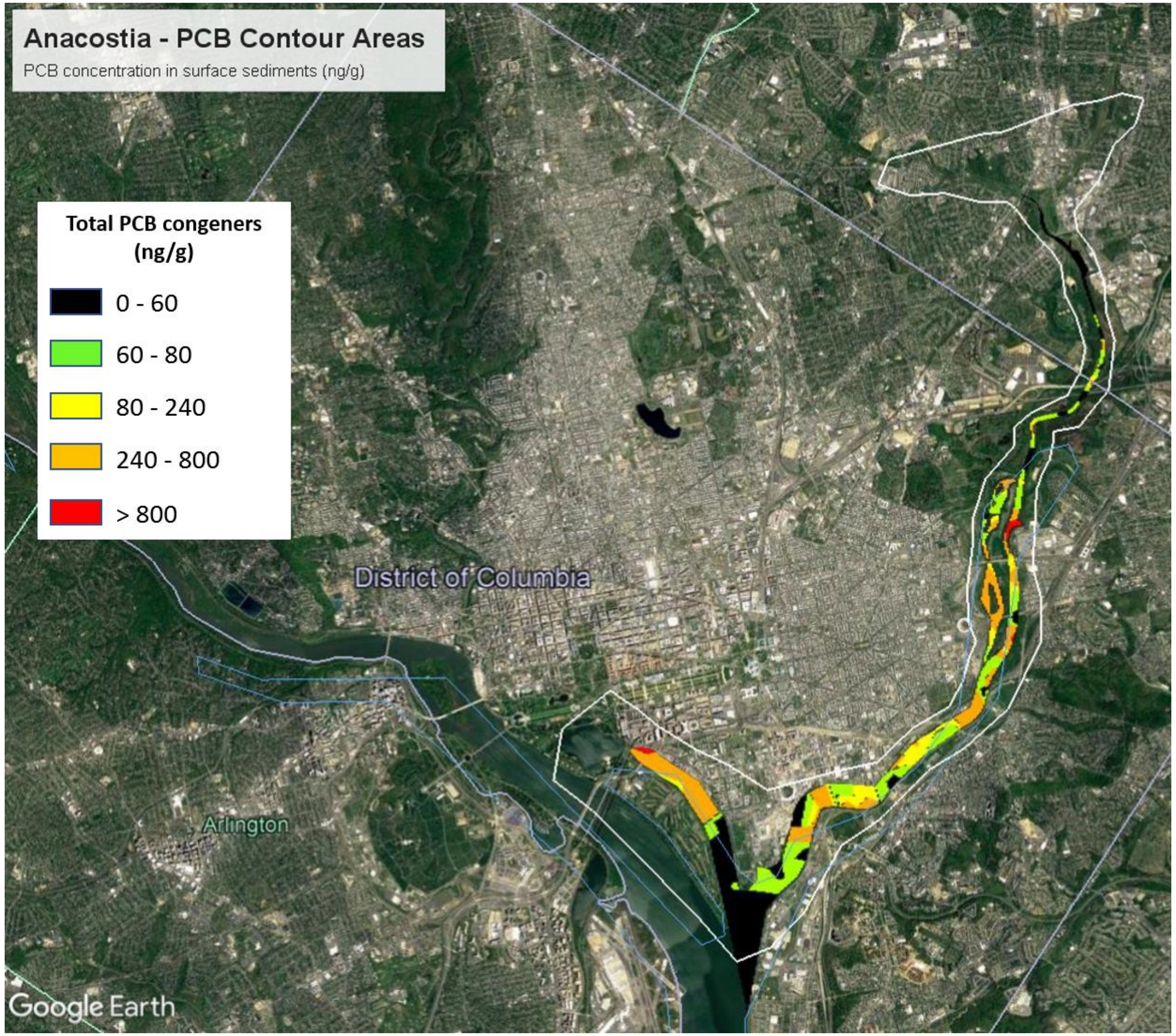
- TMDL for Tidal Potomac and Anacostia (2007)

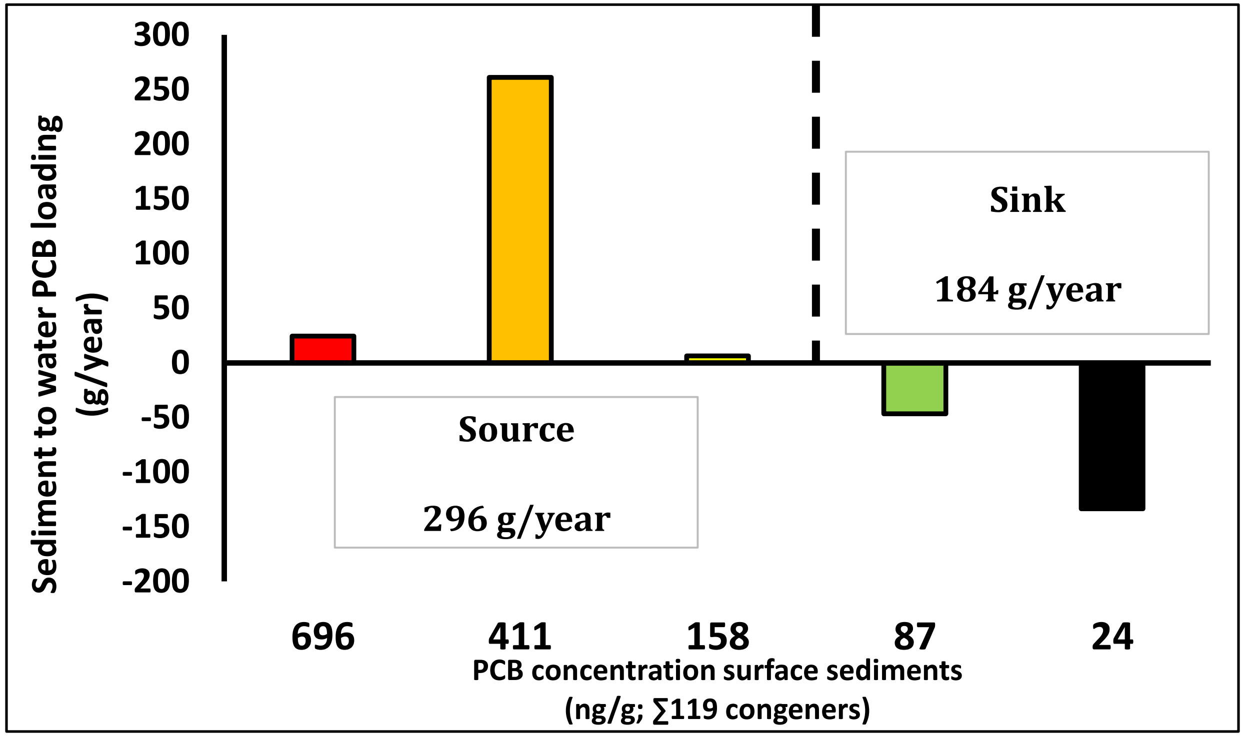


Average seasonal gas-phase PCBs: **30-271 pg/m³**

Avg. seasonal dissolved PCB levels in Anacostia: **0.47 – 1.05 ng/L**

Porewater-surface water diffusive exchange of PCBs

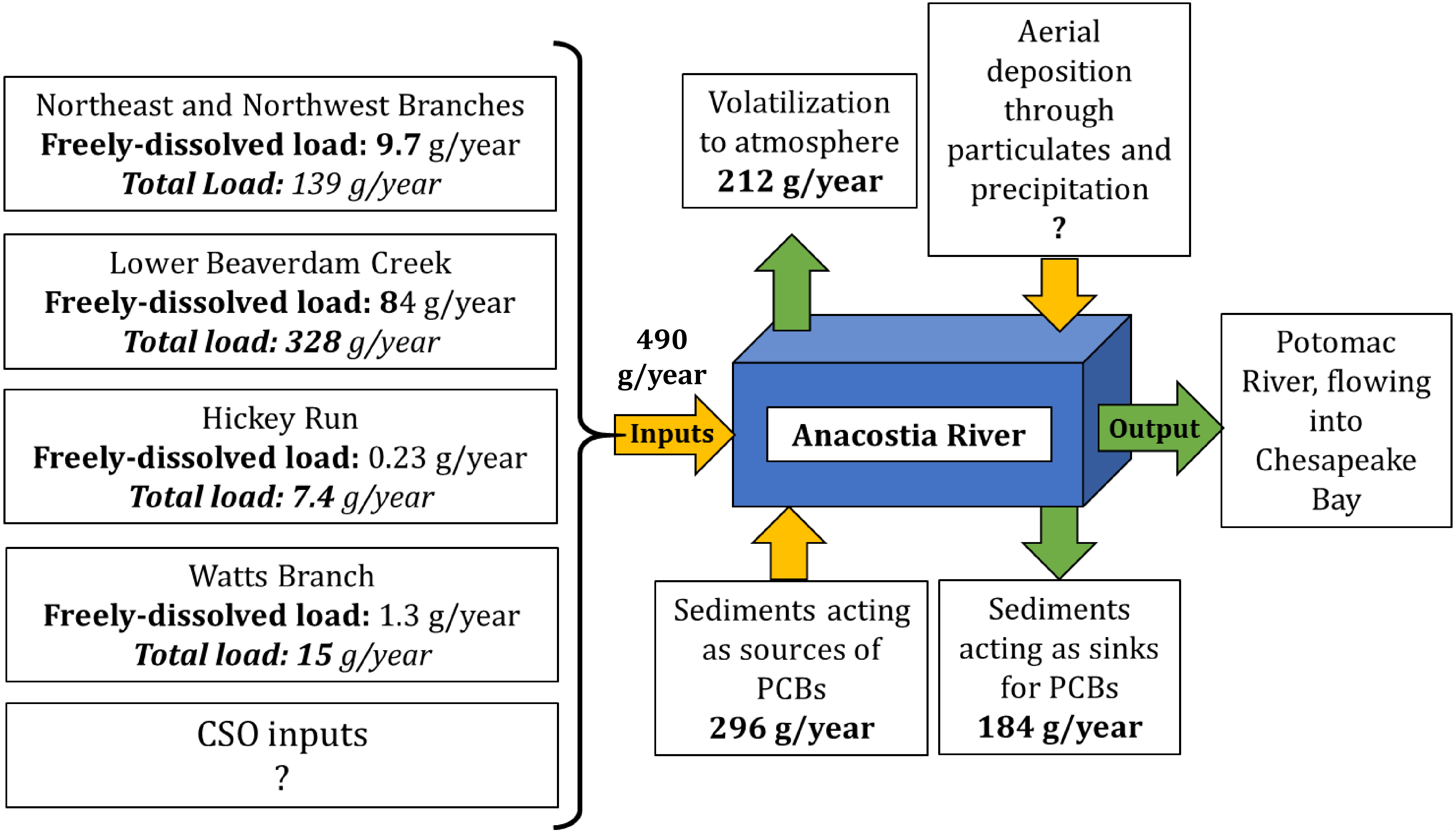




Important data gap for this watershed

Arriving at sediment remediation goals based on delineation between sediments that serve as sources of PCBs to overlying water and those that act as sinks for PCBs in overlying water

PCB inputs and outputs



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CSO inputs
?

490 g/year

Inputs

Anacostia River

Output

Volatilization to atmosphere
212 g/year

Aerial deposition through particulates and precipitation
?

Potomac River, flowing into Chesapeake Bay

Sediments acting as sources of PCBs
296 g/year

Sediments acting as sinks for PCBs
184 g/year

Acknowledgements

- **Dr. Upal Ghosh (PhD advisor)**

Group Members

- Dr. Nathalie Lombard
- Dr. Trevor Needham
- Dr. James Sanders
- Dr. Hilda Fadaei
- Samuel Magee
- Jada Damond
- Oindrila Ghosh
- Sarahana Joshee
- Robin Sevell
- Taylor Stephen
- Adam Haj-Hamad
- Louis Cheung

Project Sponsors

DEPARTMENT OF ENERGY & ENVIRONMENT

Collaborators

U.S. FISH & WILDLIFE SERVICE
DEPARTMENT OF THE INTERIOR

USGS
science for a changing world

Questions?

References

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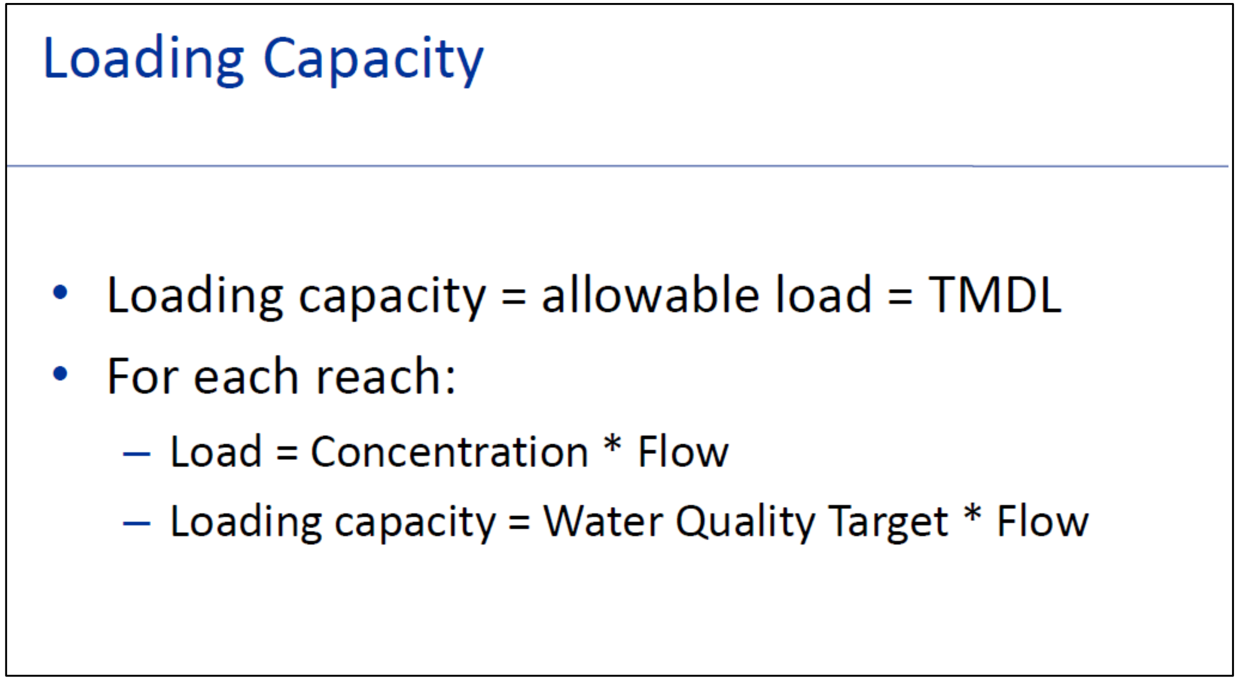
11. Department of Energy and Environment. Fish Consumption Advisory Information. (2016).
12. USGS National Water Information System (NWIS, https://waterdata.usgs.gov/nwis)
13. US EPA (US Environmental Protection Agency). 1999. Chesapeake Bay Basin Toxics Load and Release Inventory. Annapolis, MD: U.S. Environmental Protection Agency with Chesapeake Bay Program.

Additional slides for reference

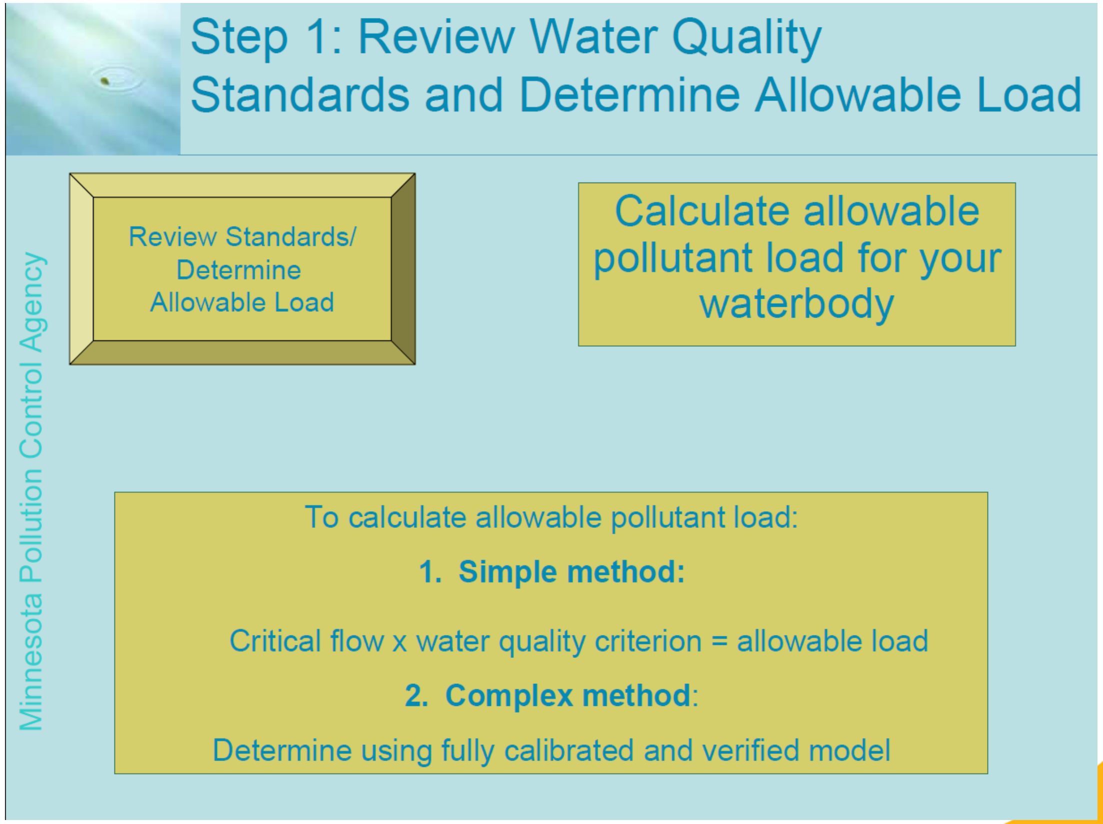


Loading Capacity

- Loading capacity = allowable load = TMDL
- For each reach:
  - Load = Concentration * Flow
  - Loading capacity = Water Quality Target * Flow

Sediment PCB goals for TMDLs

- San Francisco Bay: 1 µg/kg
- DC: 2.8 ng/g
- MD: 12 ng/g
- VA: 7.6 ng/g
- Back River, MD: 6.9 ng/g



Step 1: Review Water Quality Standards and Determine Allowable Load

Minnesota Pollution Control Agency

Review Standards/ Determine Allowable Load

Calculate allowable pollutant load for your waterbody

To calculate allowable pollutant load:

1. **Simple method:**

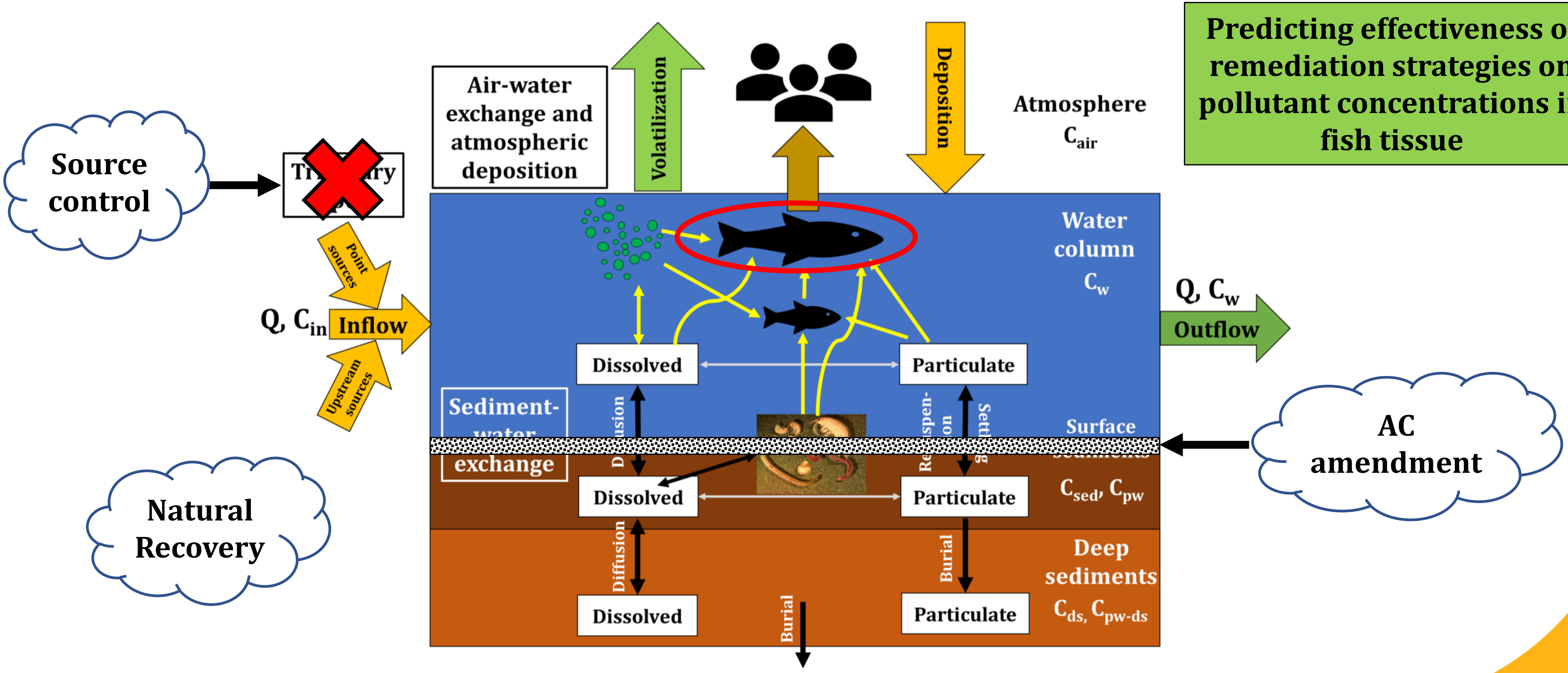
   Critical flow x water quality criterion = allowable load

2. **Complex method**:

   Determine using fully calibrated and verified model

Research Objective #3
Coupling fate, transport and bioaccumulation

Predicting effectiveness of remediation strategies on pollutant concentrations in fish tissue



Research Objective #2
Improved framework for TMDLs

- ☐ Evaluate (any) seasonal variations in total and dissolved pollutant loads
- ☐ Calculating annual pollutant loads

Data Interpretation

- ☐ Changes in chemical activities of dissolved pollutants at base and storm flow conditions
- ☐ Trends in dissolved loads at storm and base flow conditions
- ☐ Freely-dissolved, POC-associated and DOC-associated loads
- ☐ TMDL calculation for Anacostia River based on dissolved pollutant loads

Error Propagation

Based on calculated or measured uncertainties in:

a) Freely-dissolved pollutant concentrations **(δC_{Free})**

b) DOC **(δ[DOC])**, TSS and f_{OC} measurements

c) Volume of water **(δV_{Base})** and sediment load

d) Pollutant concentration on suspended sediments.

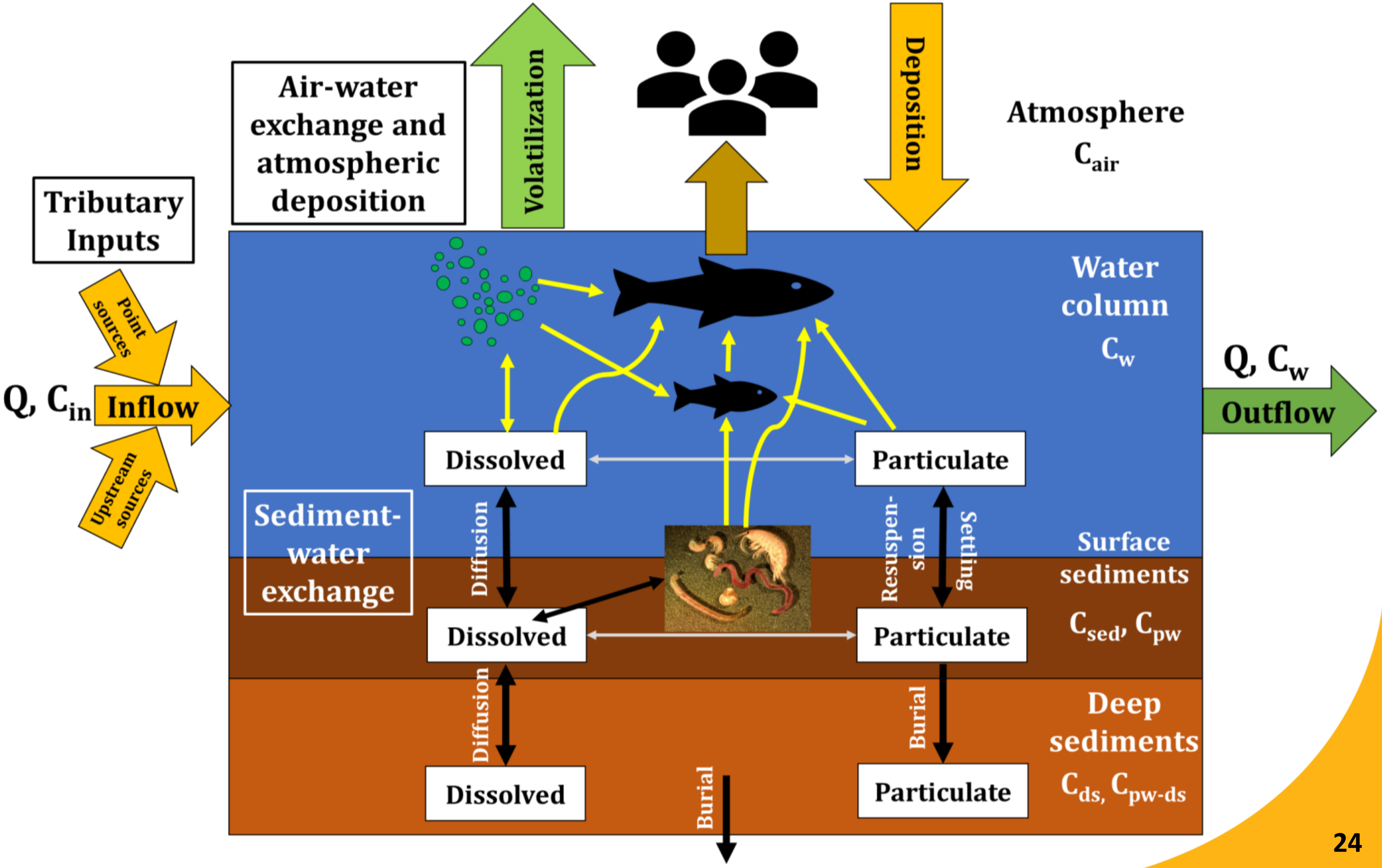
$$\mathbf{M_{Base} = C_{Free} * V_{Base} * (1 + [DOC].K_{DOC} + f_{OC}.[TSS].K_{OC})}$$

$$\delta M_{Base} = \sqrt{\left(\frac{\partial M_{Base}}{\partial C_{Free}}\right)^2 .(\delta C_{Free})^2 + \left(\frac{\partial M_{Base}}{\partial [DOC]}\right)^2 .(\delta [DOC])^2 + \left(\frac{\partial Flux}{\partial V_{Base}}\right)^2 .(\delta V_{Base})^2 + \cdots}$$

Research Objective #3
Coupling fate, transport and bioaccumulation

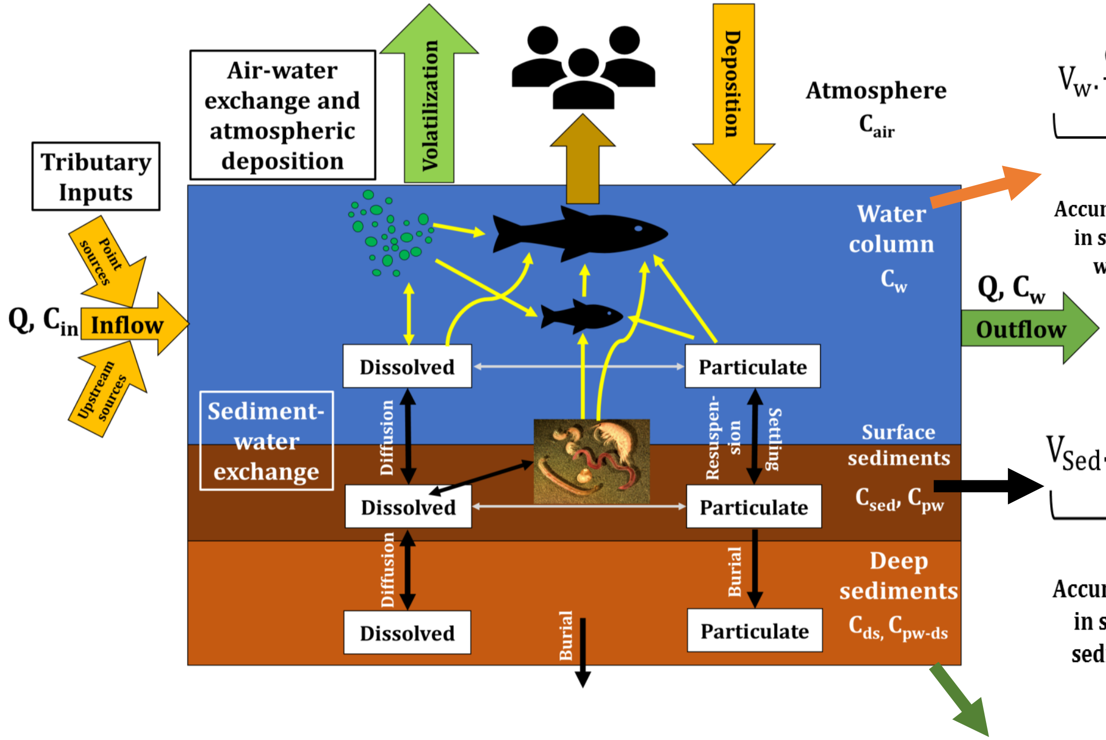
Fish consumption is a major pathway for human exposure to PCBs, PAHs and OCPs

Predicting effectiveness of remediation strategies requires coupling of mechanistic fate, transport, and bioaccumulation models



Research Objective #3

Coupling fate, transport and bioaccumulation



Contaminant mass balance for water column [20-22]

$$\underbrace{V_w.\frac{dC_w}{dt}}_{\text{Accumulation in surface water}} = \underbrace{Q.C_{in} - Q.C_w}_{\text{Inputs from tributaries and output from the river}} - \underbrace{v_{aw}.\left(C_{Free} - \frac{C_{air}}{K_{aw}}\right).A_w}_{\text{Rate of volatilization}} - \underbrace{v_s.A_w.f_{POC}.C_w}_{\text{Sediment settling}} + \underbrace{v_r.A_m.C_{sed}}_{\text{Sediment resuspension}} - \underbrace{v_d.(C_{pw} - C_{Free}).A_m}_{\text{Diffusive transfer between porewater and surface water}} + \underbrace{W}_{\text{Input from point sources}}$$

Contaminant mass balance for surface sediments [20-22]

$$\underbrace{V_{Sed}.\frac{dC_{sed}}{dt}}_{\text{Accumulation in surface sediments}} = \underbrace{v_d.(C_{pw} - C_{Free}).A_m}_{\text{Diffusive transfer between porewater and surface water}} + \underbrace{v_s.A_w.f_{POC}.C_w}_{\text{Sediment settling}} - \underbrace{v_r.A_m.C_{sed}}_{\text{Sediment resuspension}} - \underbrace{v_b.A_m.C_{sed}}_{\text{Sediment burial}} + \underbrace{v_d.(C_{pw-DS} - C_{pw}).A_m}_{\text{Diffusive transfer between surface and deep sediments}}$$

Contaminant mass balance for deep sediments [20-22]

$$\underbrace{\frac{\partial C_{DS}}{\partial t}}_{\text{Rate of concentration change in deep sediments}} = \underbrace{C_{pw-DS}.D_{DS}.\frac{\partial^2 C_{DS}}{\partial z^2}}_{\text{Rate of diffusive pollutant transfer in porewater}} - \underbrace{v_b.\frac{\partial C_{DS}}{\partial z}}_{\text{Rate of pollutant transfer due to sediment burial}}$$

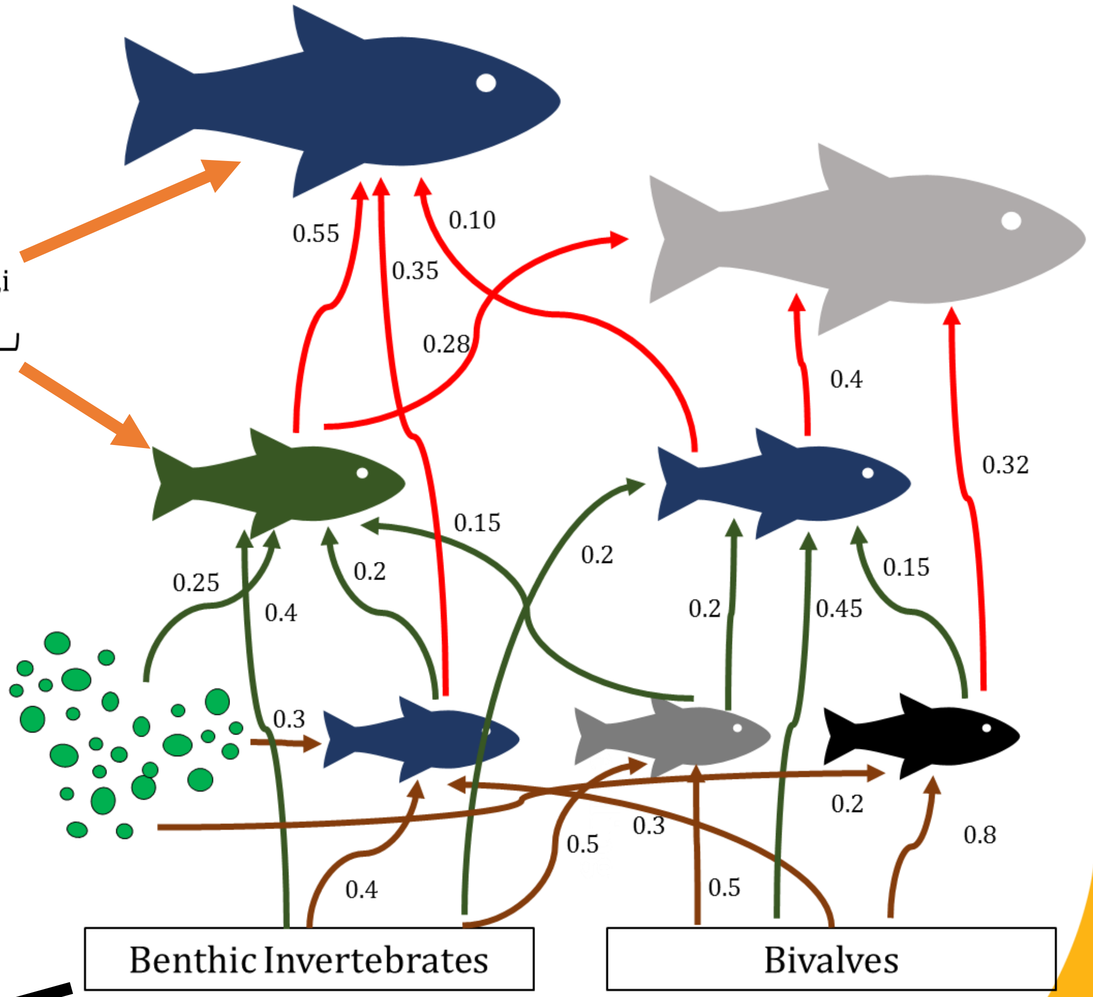
Research Objective #3
Coupling fate, transport and bioaccumulation

Bioaccumulation in aquatic organisms [23,24]

$$\underbrace{\frac{dC_{B,i}}{dt}}_{\text{Rate of change of pollutant concentration}} = \underbrace{k_1.\left(m_{pw}.\boxed{C_{pw}} + m_{cw}.\boxed{C_W}\right)}_{\text{Rate of pollutant uptake from surface water and porewater}} + \underbrace{k_D.\sum_{j=1}^{n} P_j.C_{D,j}}_{\text{Rate of pollutant uptake from through diet}} + \underbrace{IR.\beta.C_{sed}}_{\text{Rate of pollutant uptake from incidental sediment ingestion}} - \underbrace{(k_2 + k_E + k_M + k_G).C_{B,i}}_{\text{Rate of pollutant elimination from organism}}$$

$$C_{lipid}\left(\frac{\mu g}{kg}\right) = BAF.\boxed{C_W}$$

$$\log BAF_{Algae}(PCBs) = 0.69 \log K_{OW} + 2.84$$ [25]



$$C_{lipid}\left(\frac{\mu g}{kg}\right) = BAF.\boxed{C_{PW}}$$

$$\log BAF_{L.variegatus}(PCBs) = 0.9172 \log K_{OW} + 0.8953$$ [26]

Research Objective #3

Coupling fate, transport and bioaccumulation

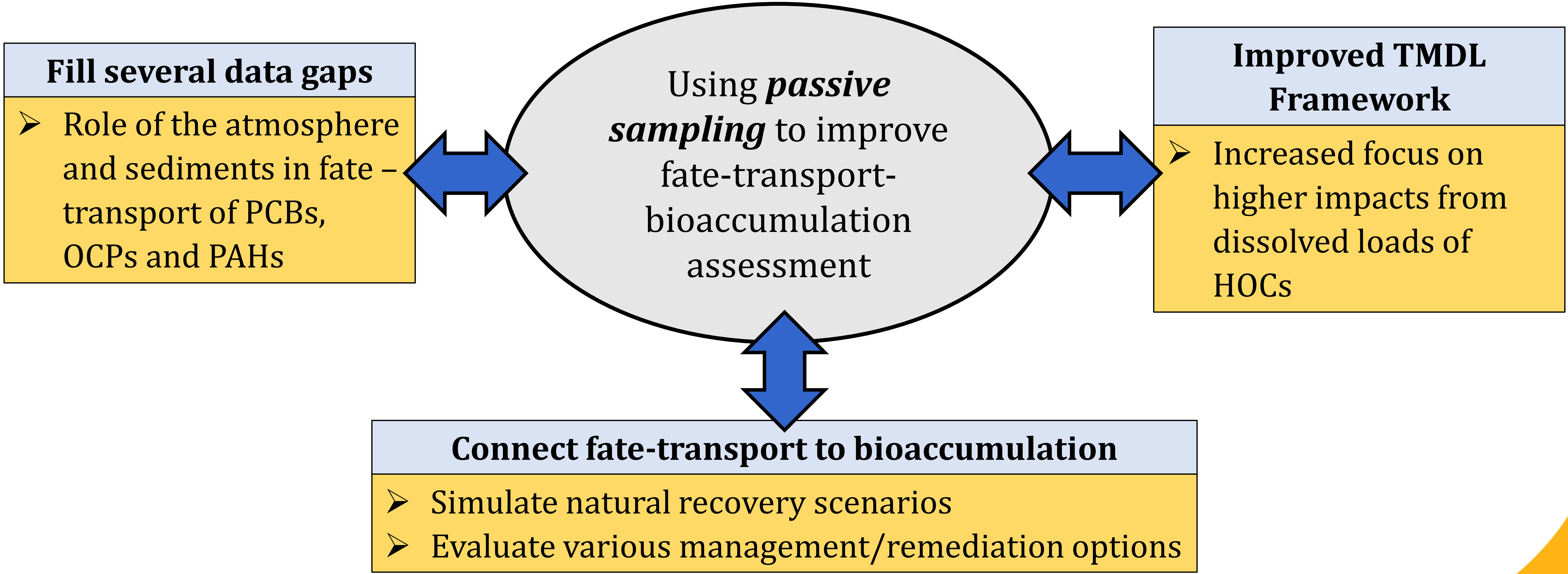
Validation of models

Predictions from fate and transport model validated against measured pollutant concentrations in Anacostia River

Predictions from fate-transport model used as inputs for bioaccumulation model

Results validated against fish concentrations measured in previous studies, ongoing RI-FS and in-lab measurements

Implications of proposed research



Using ***passive sampling*** to improve fate-transport-bioaccumulation assessment

Fill several data gaps

- Role of the atmosphere and sediments in fate – transport of PCBs, OCPs and PAHs

Improved TMDL Framework

- Increased focus on higher impacts from dissolved loads of HOCs

Connect fate-transport to bioaccumulation

- Simulate natural recovery scenarios
- Evaluate various management/remediation options

Research Objective #1

Seasonal variations in air-water exchange of HOCs

Mass-transfer velocity in gas-phase

$$v_a = v_{water,a}\ X \left(\frac{M_{target}}{M_{water}}\right)^{-0.5\ X\ a_D}$$

$$a_D = 0.67\ for\ u_{10} < 5\ m/s$$

$$a_D = 0.5\ for\ u_{10} > 5\ m/s$$

$$v_{water,a} = 0.2\ u_{10}\ (m.s^{-1}) + 0.3$$

Mass-transfer velocity in water-phase

$$v_w = v_{CO2,w}\ X\ (\frac{Sc_{Target,w}}{Sc_{CO2,w}})^{-a_{Sc}}$$

$$a_{Sc} = 0.67\ for\ u_{10} < 4.2\ m/s$$

$$a_{Sc} = 0.5\ for\ u_{10} > 4.2\ m/s$$

$$Sc_{CO2,w} = 600\ at\ 298\ K$$

$$Sc_{Target,w}(298\ K) = \frac{v_w(298\ K)}{D_{Target,w}\ (298\ K)}$$

$$D_{Target,w}\ (cm^2.s^{-1}, 298\ K) = \frac{2.7\ X\ 10^{-4}}{M_{Target}^{0.71}}$$

$$V_{CO2,w} = \begin{cases} 0.65\ X\ 10^{-3} & u_{10} \leq 4.2\ m.s^{-1} \\ (0.79\ u_{10} - 2.68)\ X\ 10^{-3} & 4.2 \leq u_{10} \leq 13\ m.s^{-1} \\ (1.64\ u_{10} - 13.69)\ X\ 10^{-3} & u_{10} \geq 13\ m.s^{-1} \end{cases}$$

Research Objective #1

Seasonal variations in air-water exchange of HOCs

Gas-particles partitioning of HOCs

Junge-Pankow model

$$\varphi = \frac{c.\theta}{p_L^0 + c.\theta}$$

Particle surface area per volume of air (m^2/m^3)

Particle-bound HOC fraction (%)

Constant (depends on heat of condensation and particle surface properties)

Wet deposition of particle-bound and vapour-phase HOCs

Overall Washout Ratio W

(ng/m^3 rain)/(ng/m^3 air) → $W = W_V(1 - \varphi) + W_P\,\varphi$

Washout ratio of vapours → $W_V = \frac{RT}{H} = \frac{1}{K_{aw}}$

$$W_P(\text{SOCs}): 2 \text{ x } 10^3 - 1 \text{ x } 10^6$$

Washout ratio of particles

Dry deposition of particle-bound and vapour-phase HOCs

Particle dry deposition velocity $V_{D,p}$

0.1 – 1 cm/s → $V_{D,p} = \frac{F_P}{C_P}$

Particle Flux (ng/cm^2-s)

Particle-phase HOC concentration (ng/cm^3)

Research Objective #2
Improved framework for TMDLs

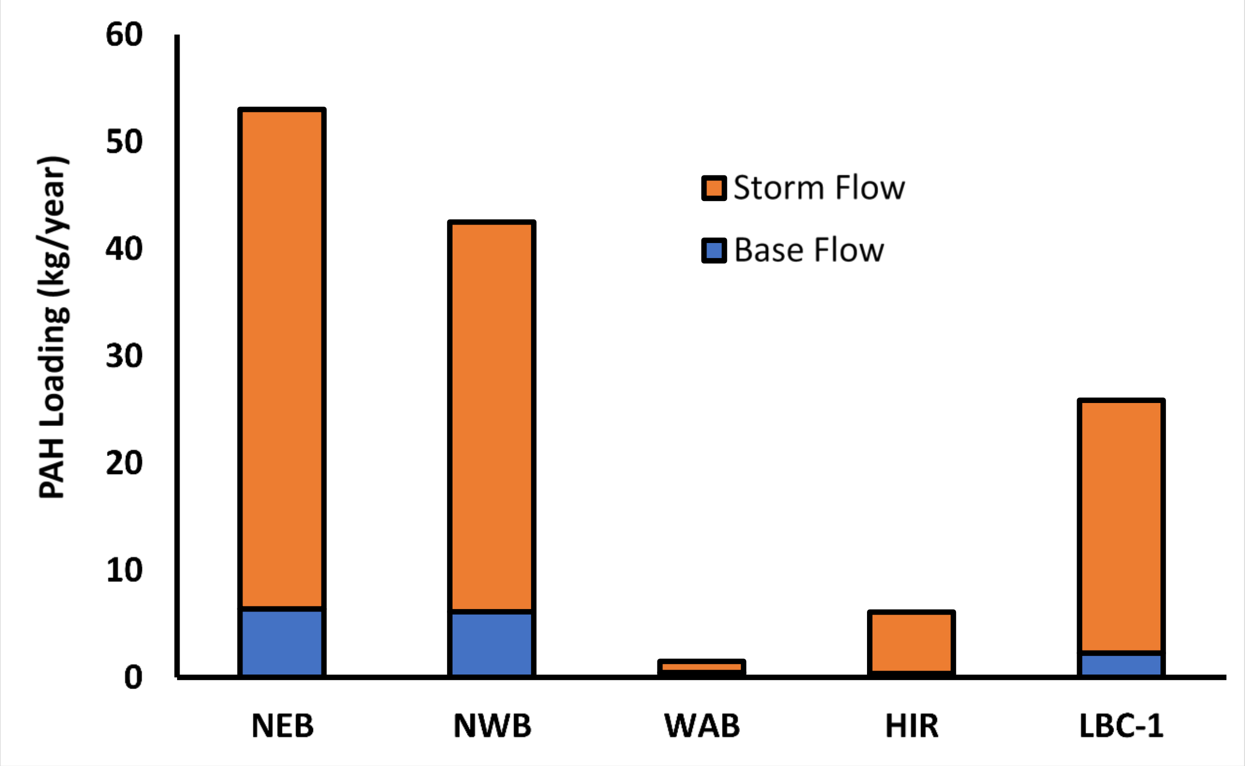


Figure 3-70: PAH loads (kg/year) from gauged tributaries at storm and base flow conditions.

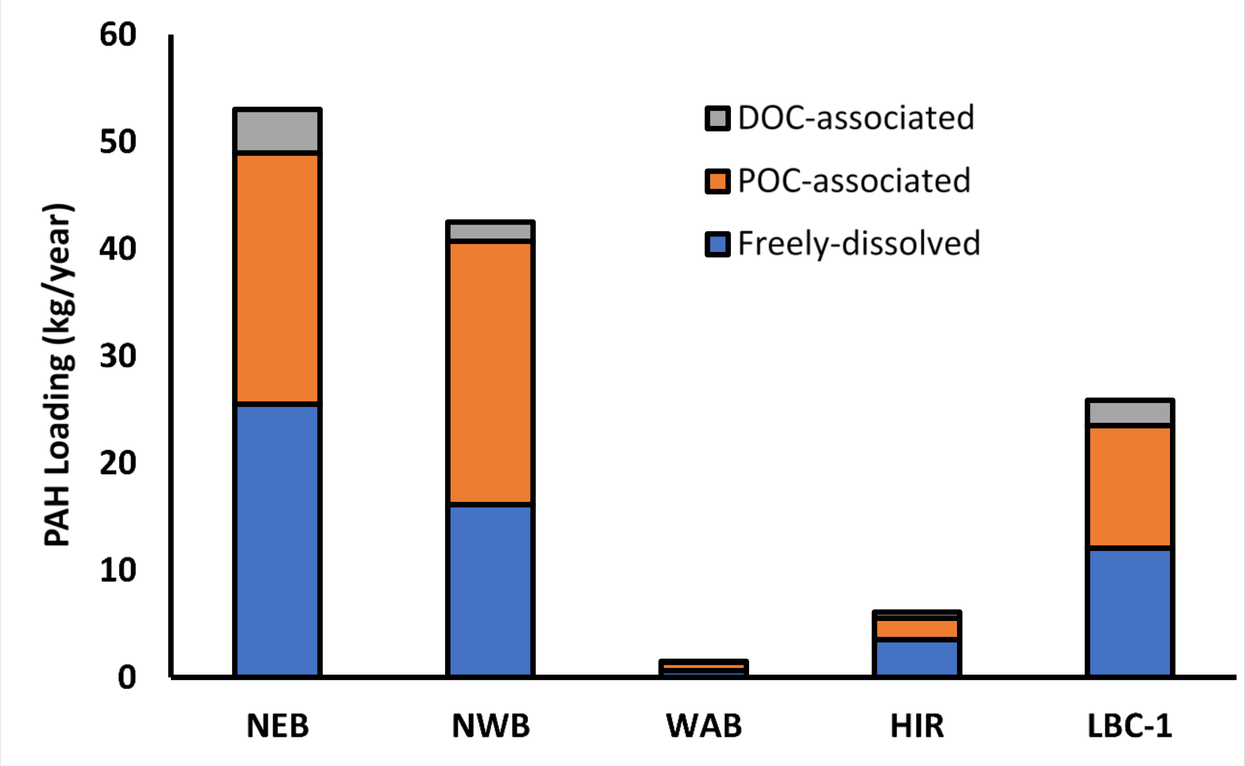


Figure 3-71: PAH loads associated with different phases (kg/year) from gauged tributaries.

Research Objective #2
Improved framework for TMDLs

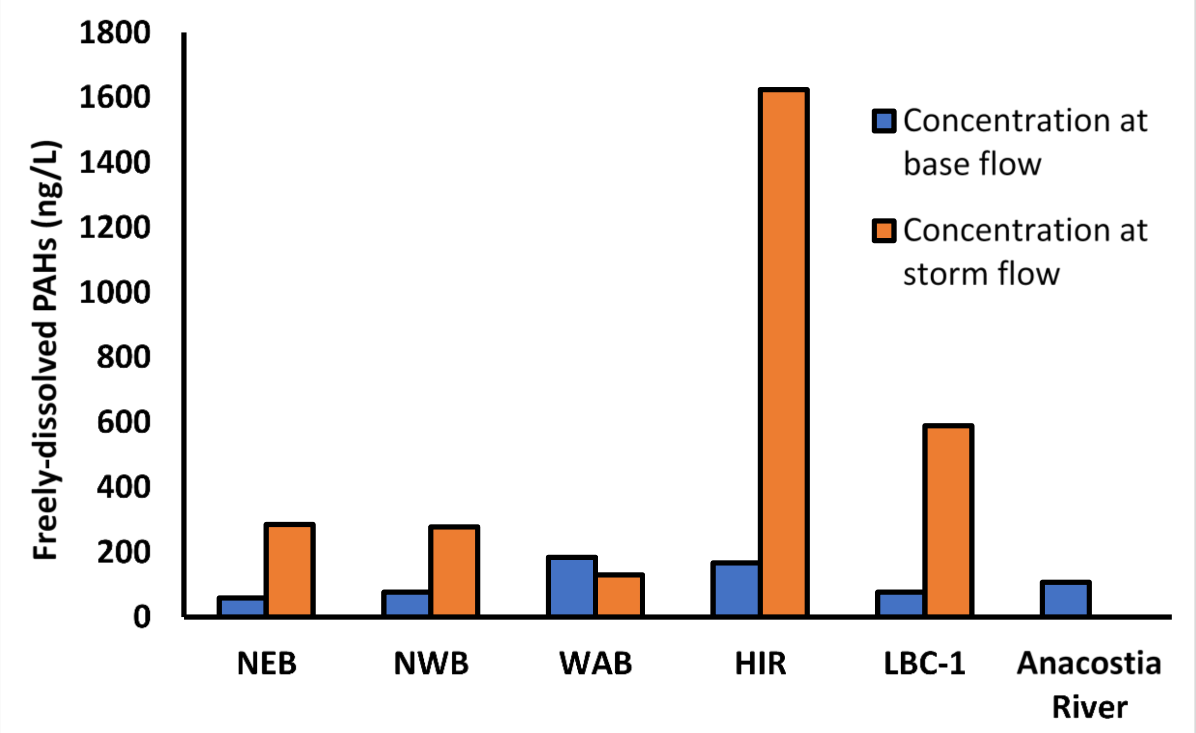


Figure 3-75: Comparison of freely-dissolved parent PAH concentration at base and storm flow events across gauged tributaries and the Anacostia River.

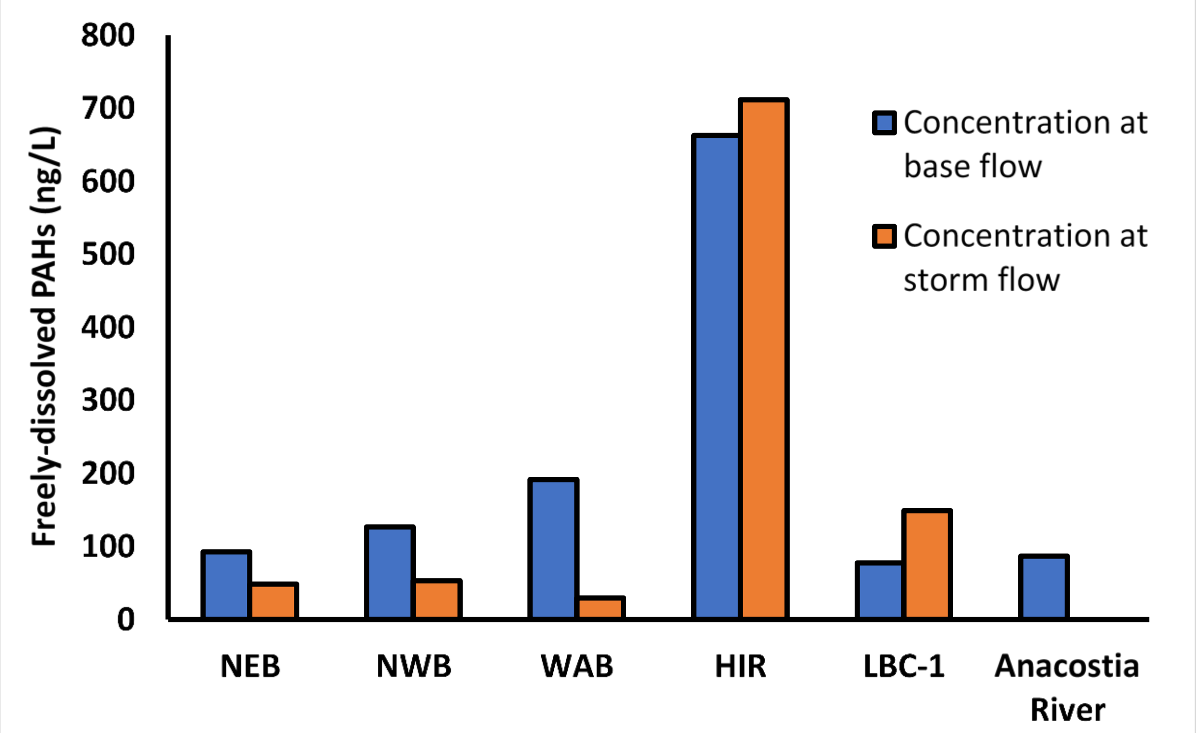
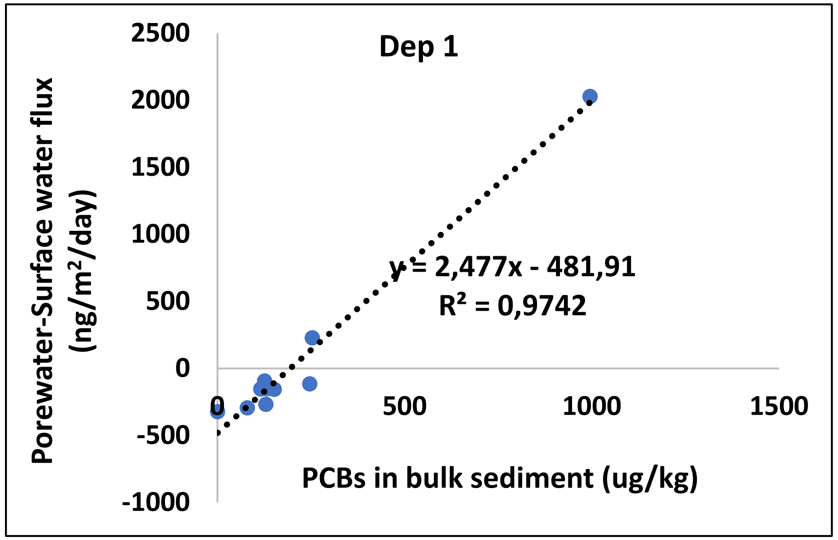
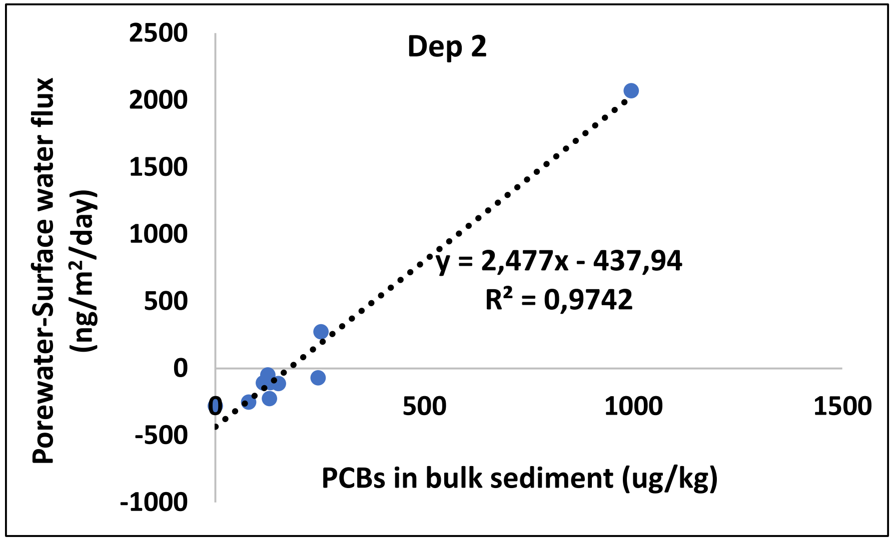
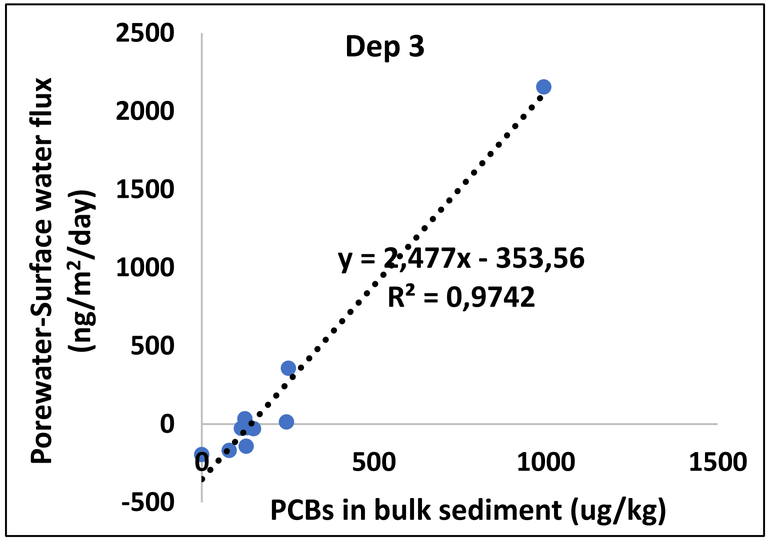
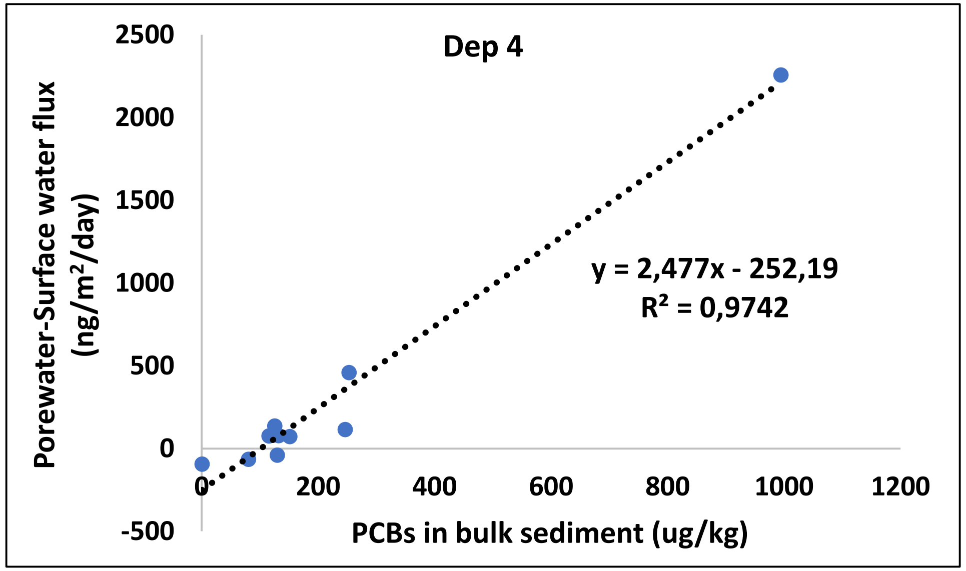


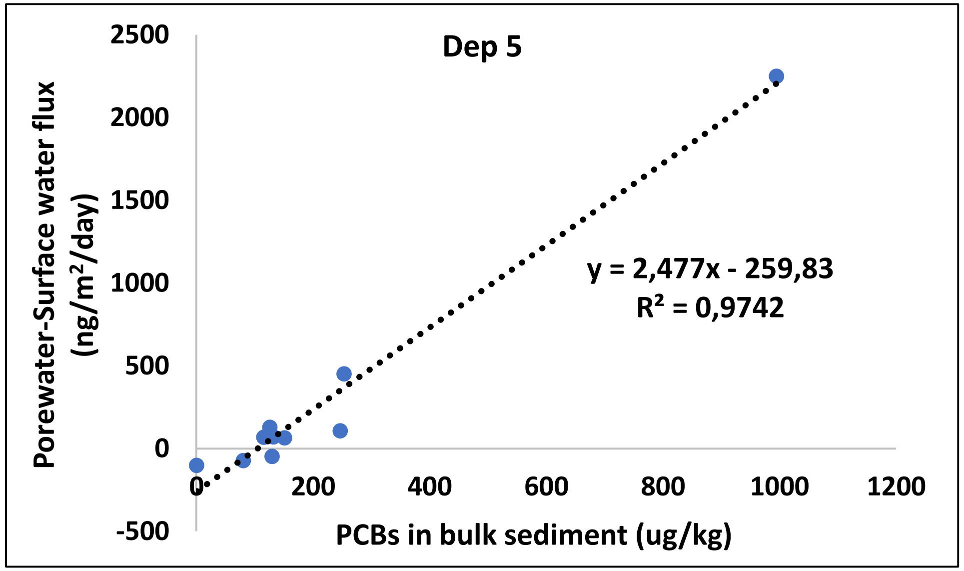
Figure 3-76: Comparison of freely-dissolved alkylated PAH concentration at base and storm flow events across gauged tributaries and the Anacostia River.


Dep 1
Porewater-Surface water flux (ng/m²/day)
2500
2000
1500
1000
500
0
-500
-1000
0
500
1000
1500
y = 2,477x - 481,91
R² = 0,9742
PCBs in bulk sediment (ug/kg)


Dep 2
Porewater-Surface water flux (ng/m²/day)
2500
2000
1500
1000
500
0
-500
-1000
0
500
1000
1500
y = 2,477x - 437,94
R² = 0,9742
PCBs in bulk sediment (ug/kg)


Dep 3
Porewater-Surface water flux (ng/m²/day)
2500
2000
1500
1000
500
0
-500
0
500
1000
1500
y = 2,477x - 353,56
R² = 0,9742
PCBs in bulk sediment (ug/kg)


Dep 4
Porewater-Surface water flux (ng/m²/day)
2500
2000
1500
1000
500
0
-500
0
200
400
600
800
1000
1200
y = 2,477x - 252,19
R² = 0,9742
PCBs in bulk sediment (ug/kg)


Dep 5
Porewater-Surface water flux (ng/m²/day)
2500
2000
1500
1000
500
0
-500
0
200
400
600
800
1000
1200
y = 2,477x - 259,83
R² = 0,9742
PCBs in bulk sediment (ug/kg)

Research Objective #1

Air-water exchange of HOCs

Magnitude of flux

$$\mathbf{Flux_{w\rightarrow a}} = \nu_{a/w} \times \left(C_{water} - \frac{C_{air}}{K_{aw}} \right)$$

- ☐ $\boldsymbol{\nu_{a/w}}$ **:** Overall mass transfer velocity, (m/day)
- ☐ $\mathbf{K_{aw}}$ **:** Temperature-corrected air-water partitioning coefficient
- ☐ $\boldsymbol{\nu_{w}}$ **and** $\boldsymbol{\nu_{a}}$: compound-specific mass transfer velocities in the water and air phases respectively (m/day)

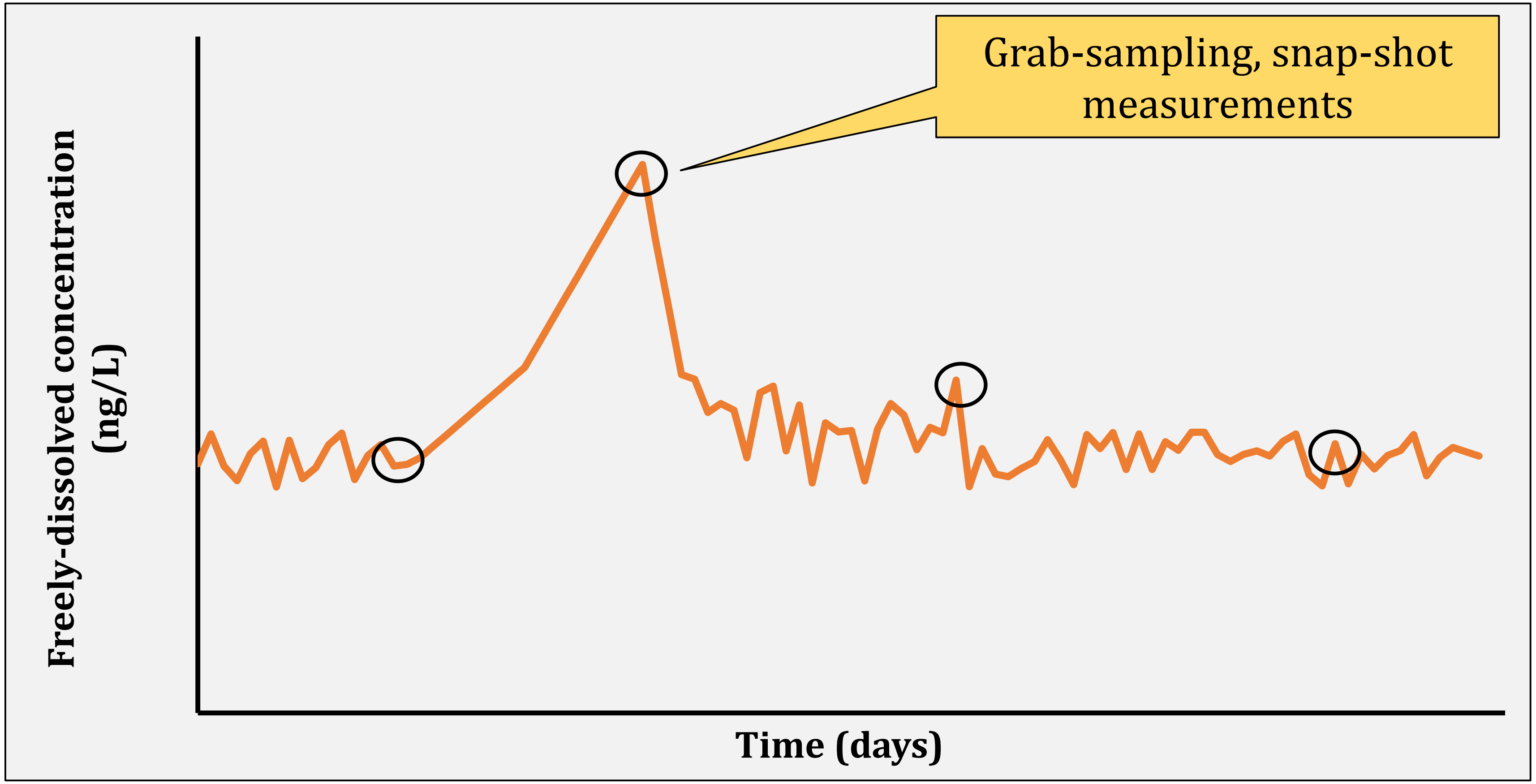
$$\frac{\mathbf{1}}{\boldsymbol{\nu_{a/w}}} = \frac{1}{\nu_w} + \frac{1}{\nu_a . K_{aw}}$$

Can be calculated using:

- ☐ Average wind speed over the deployment period
- ☐ Average ambient temperature over deployment period
- ☐ Molecular weight of PCB congeners (and analytes of interest)

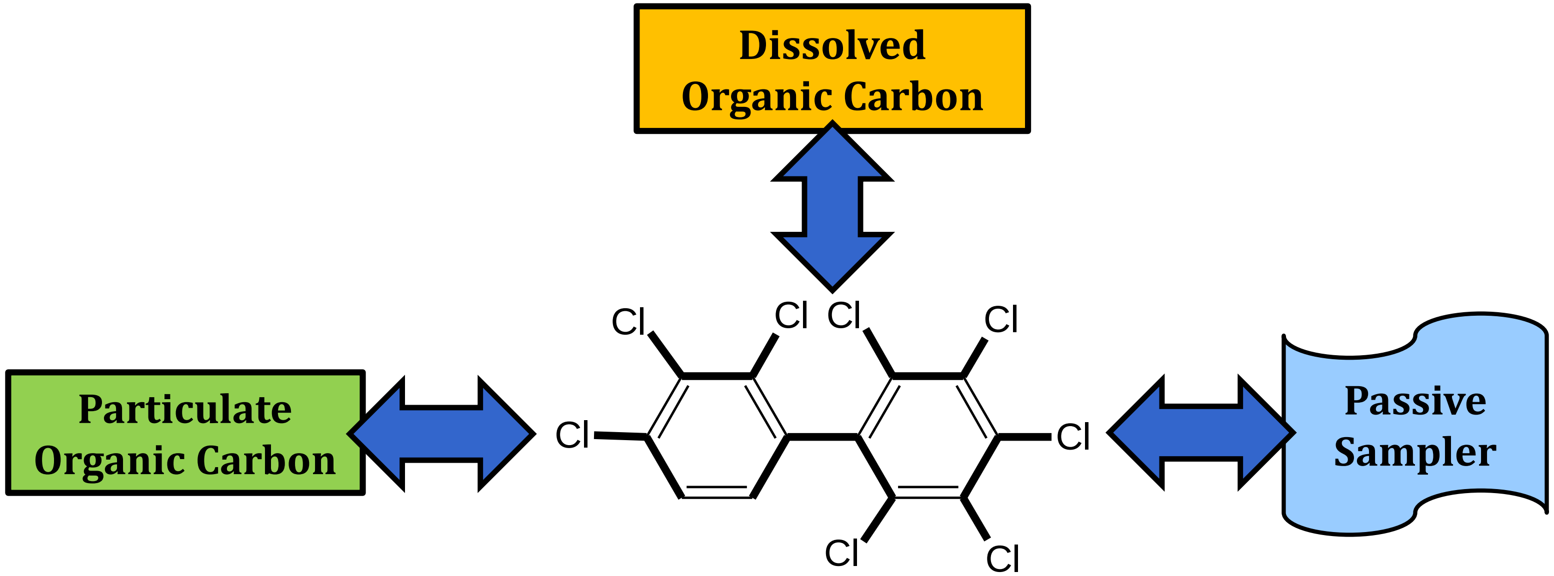
Existing knowledge gaps

1. Limited understanding of dissolved concentrations of hydrophobic organic contaminants in Anacostia Watershed



Grab-sampling, snap-shot measurements

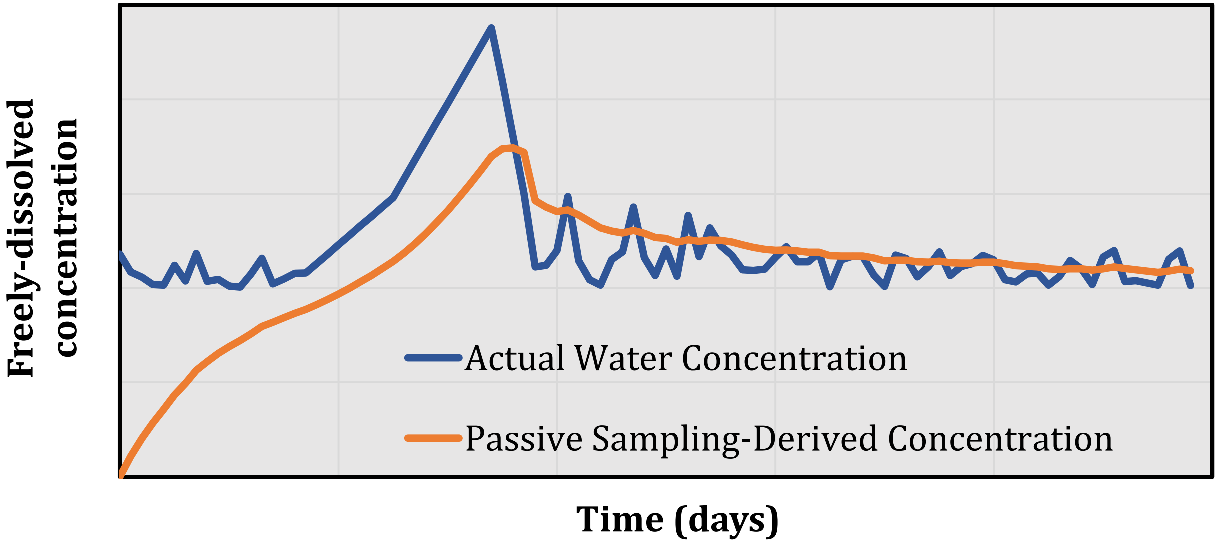
Research Approach: Passive Sampling



Dissolved Organic Carbon

Particulate Organic Carbon

Passive Sampler



Freely-dissolved contaminants partition between water and polymer

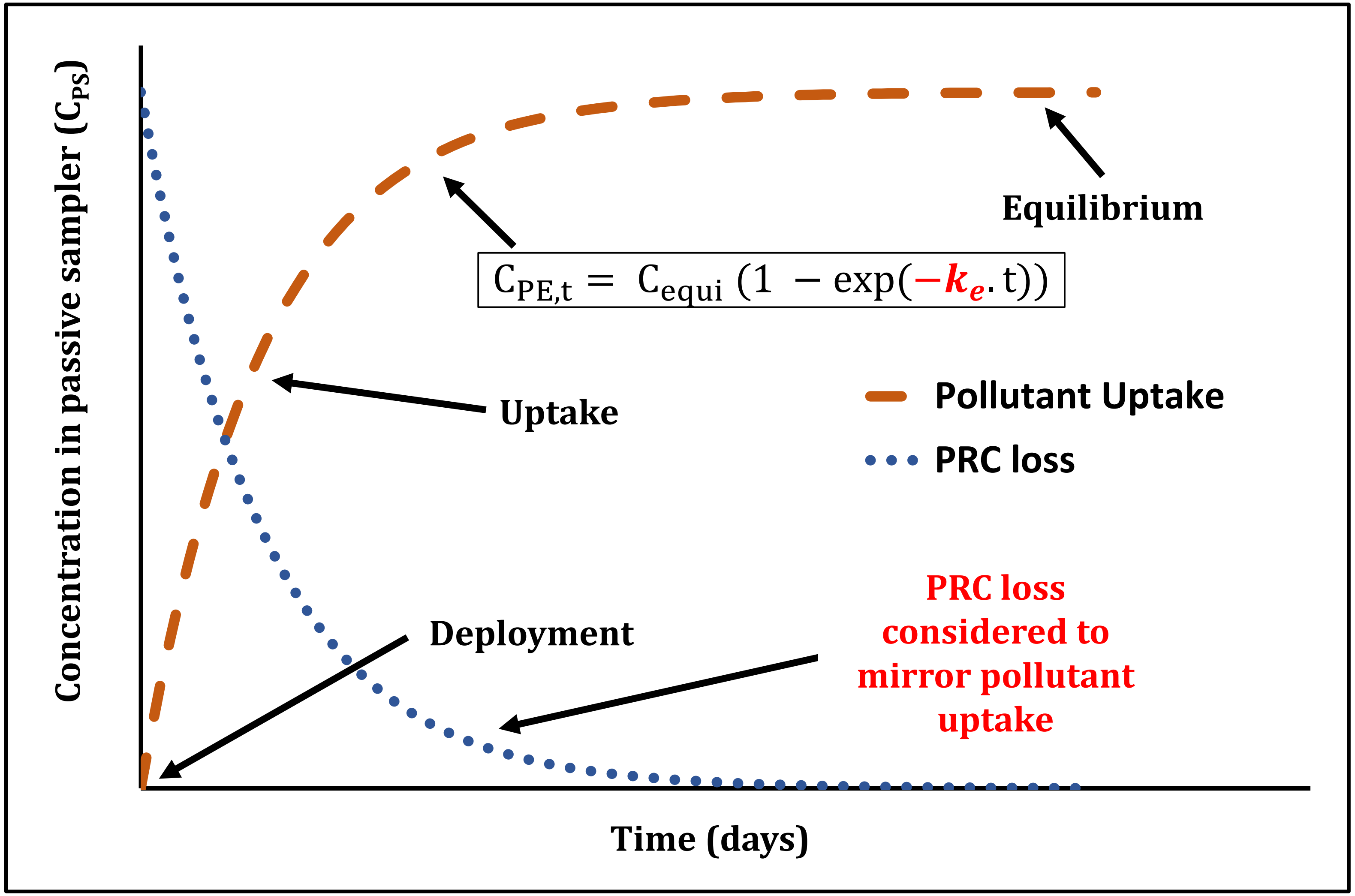
Advantages of passive sampling

- ☐ Very low detection limits (ng/L to pg/L)
- ☐ Measures freely-dissolved concentration
- ☐ Time-weighted average concentration
- ☐ Avoids need for collecting large volume samples

Polymer specifications

- ➢ Low-density polyethylene (PE)
- ➢ 50 µm thickness
- ➢ 15 cm x 15 cm (~ 1 g)

Research Approach: Passive Sampling



$$C_{PE,t} = C_{equi}\,(1 - \exp(-k_e . t))$$

PRC loss considered to mirror pollutant uptake

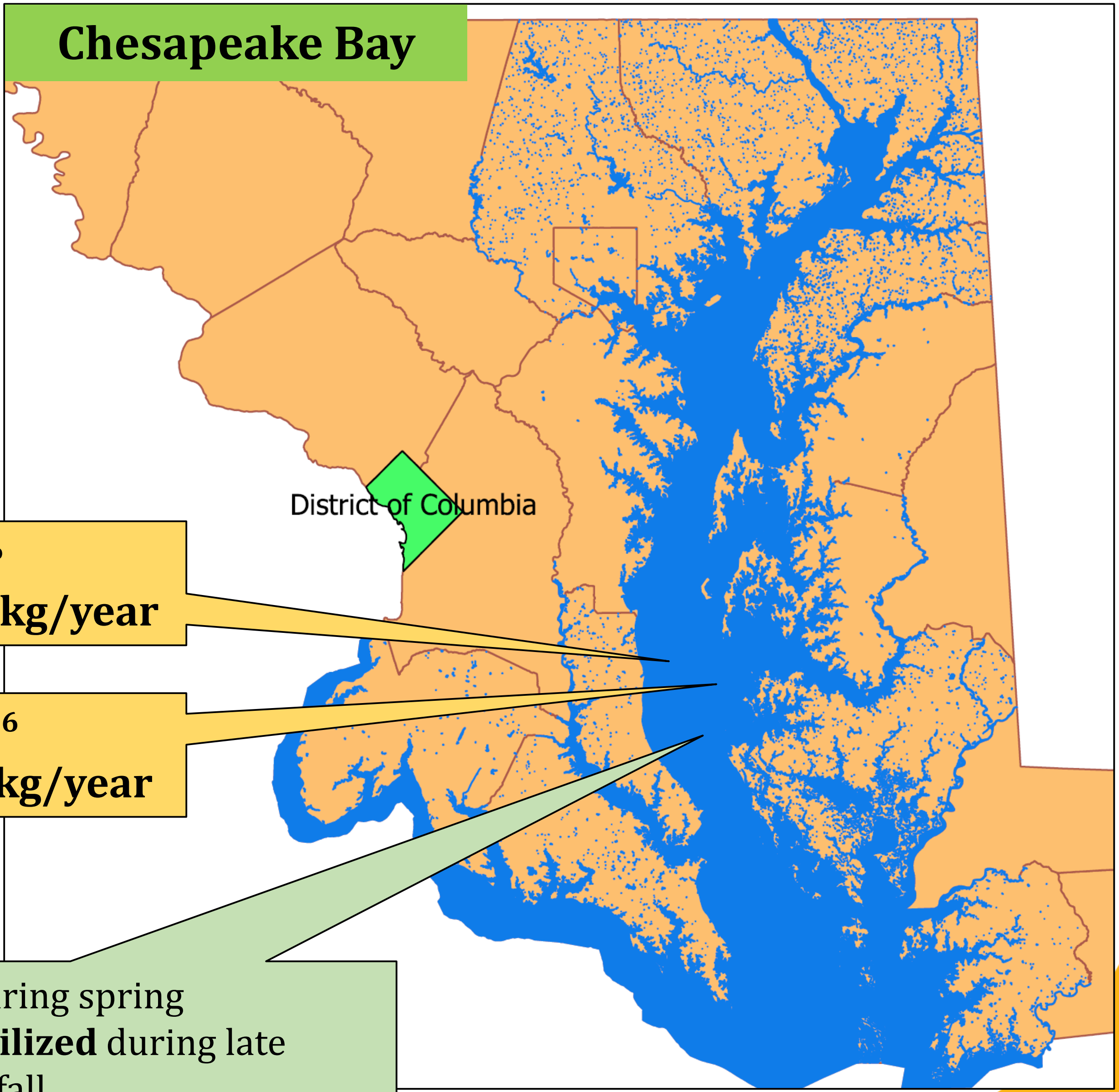
- ❑ LDPE passive samplers do not typically reach equilibrium for highly hydrophobic compounds within practical deployment times
- ❑ **Performance reference compounds (PRCs)** used to correct for non-equilibrium conditions
- ❑ PRCs can be:
  - ➢ **Deuterated** or **^{13}C** labeled analogues
  - ➢ Congeners not typically detected in the environment

$$k_e(\text{day}^{-1}) = \frac{\ln\left(\frac{C_{PRC,\ Initial}}{C_{PRC,\ Final}}\right)}{t}$$

Research Objective #1
Air-water exchange of HOCs

- ❑ Important component of environmental fate and transport
- ❑ Atmosphere can act as a sink or source of pollutants
- ❑ Direction of flux determined by concentration gradient across air-water interface

Chesapeake Bay



Atmosphere as sink for PCBs [16]
Volatalization rate of t-PCBs (1998): **400 kg/year**

Atmosphere as source of PAHs [16]
Absorption rate of 9 PAHs (1998): **5433 kg/year**

- ❑ PAHs **absorbed** during spring
- ❑ Lighter PAHs **volatilized** during late summer and early fall

Research Objective #1
Air-water exchange of HOCs

Direction of flux

$$\textbf{Fugacity ratio} = \frac{f_w}{f_a} = \frac{C_{PE(water)}}{C_{PE(air)}}$$

< 1 Flux from air to water

= 1 Equilibrium

> 1 Flux from water to air

Magnitude of flux

$$\mathbf{Flux_{w \rightarrow a}} = \nu_{a/w} \times \left(C_{water} - \frac{C_{air}}{K_{aw}} \right)$$

- ☐ **$\nu_{a/w}$:** Overall mass transfer velocity, (m/day)
- ☐ **K_{aw} :** Temperature-corrected air-water partitioning coefficient
- ☐ **ν_w and ν_a**: compound-specific mass transfer velocities in the water and air phases respectively (m/day)

Can be calculated using:
- ☐ Average wind speed and average ambient temperature over deployment period
- ☐ Molecular weight of analytes of interest

$$\frac{\mathbf{1}}{\boldsymbol{\nu}_{\mathbf{a/w}}} = \frac{1}{\nu_w} + \frac{1}{\nu_a . K_{aw}}$$

Research Approach: Dissolved and gas-phase concentrations

$$C_{water/air} = \frac{C_{PE-water(air)}}{K_{PE-water(air)} * (1 - \exp(-ke * t))}$$

$K_{PE\text{-}water(air)}$: Partitioning coefficient between PE and water (air) (L/kg)

Partitioning coefficients can be related to physical properties of pollutants

Gas-phase sampling

$$\log K_{PE-air}(\text{PCBs}) = -0.82 \log p_L + 6.22$$ [14]

p_L: Subcooled liquid vapor pressure (Pa)

Water-phase sampling

Porewater-phase sampling

$$\log K_{PE-water}(\text{PCBs}) = 1.18 \log K_{OW} - 1.26$$ [15]

K_{OW}: Octanol-water partitioning coefficient (L/L)