Evaluation of Passive Sampling Nonequilibrium Adjustment Methods of Sediment Porewater PCBs at Two Sites

Oindrila Ghosh[†], Nathalie Lombard[†], Mandar Bokare[†], James Sanders, Upal Ghosh[†]

† Department of Chemical, Biochemical and Environmental Engineering, University of Maryland Baltimore County, Baltimore, Maryland 21250, United States

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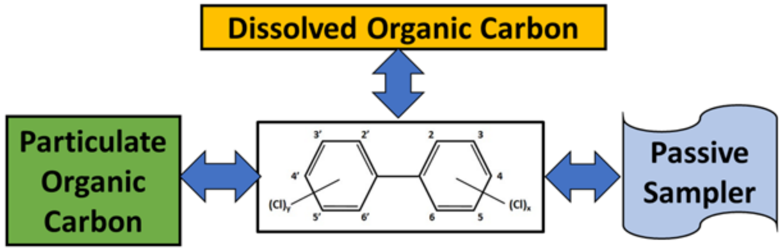
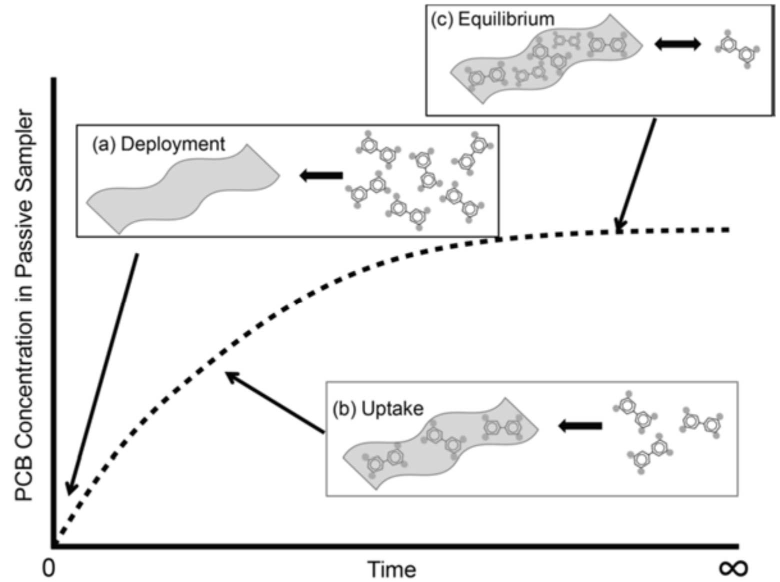
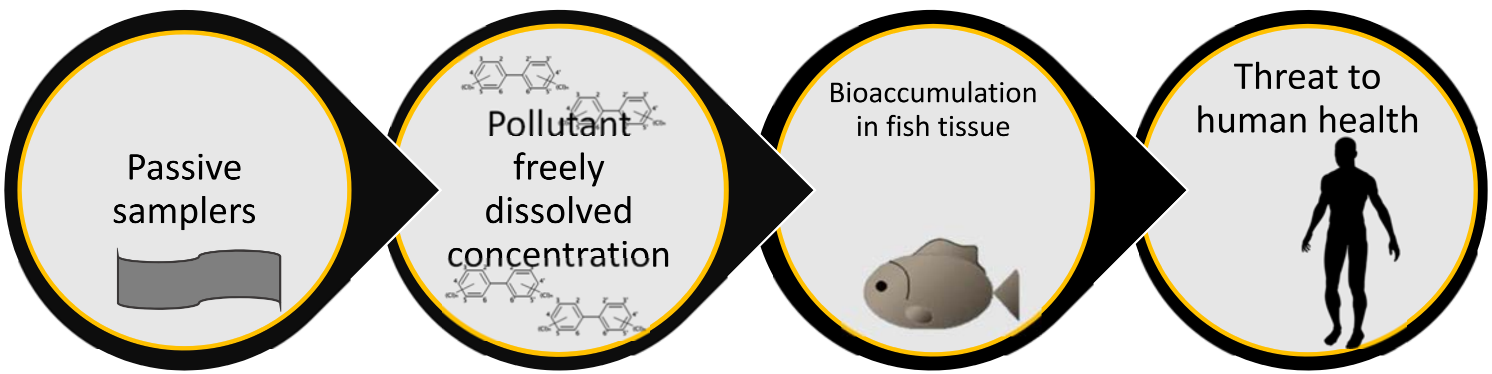
Introduction



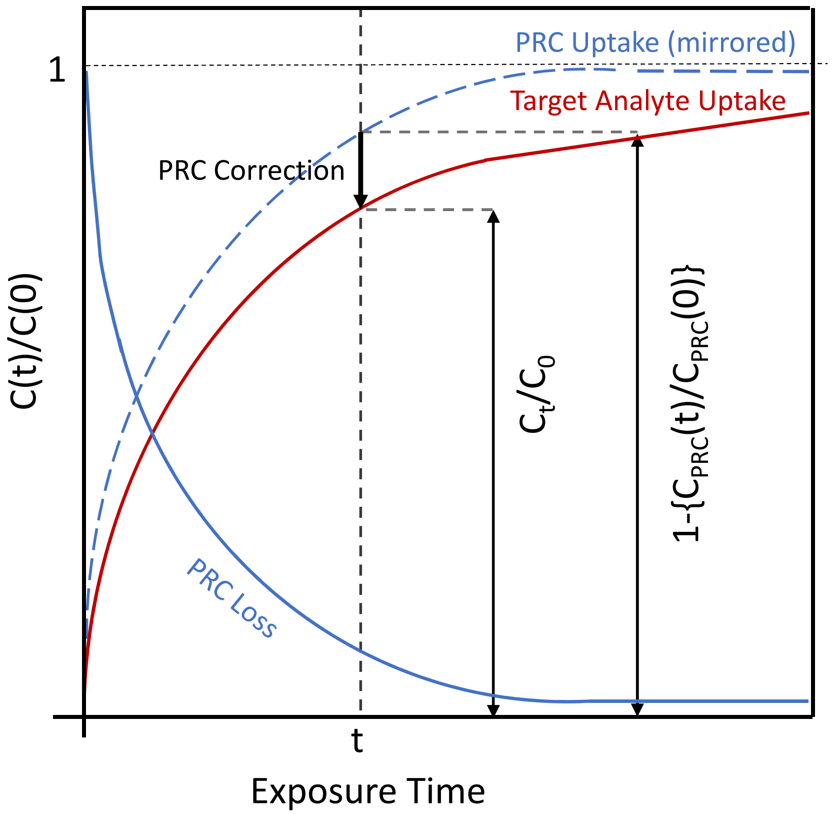
PASSIVE SAMPLING:

- Provides freely dissolved concentration
- Used for assessing pollutant bioavailability
- Calculating pollutant gradients
- Very low detection limits (ng/L to pg/L)
- Avoids need for collecting and extracting large volumes of water to meet instrument detection limits





Introduction



PRC Correction

- Kinetically inhibited to reach equilibrium within practical deployment times.
- Correction for non-equilibrium conditions – Use of PRCs
- How they work!
  - Samplers impregnated with PRCs before deployment.
  - While deployed, sorbed PRCs are released
  - Kinetics of analyte uptake can be estimate from the kinetics of PRC loss

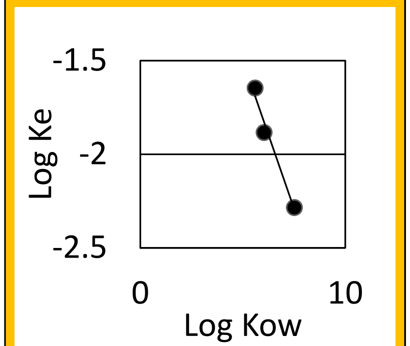
Objective

- Compare between the PRC adjustment methods applied to passive samplers deployed in sediment porewaters
- Evaluate the better suited PRC correction method for a given flow regime.

PRC Correction Methods

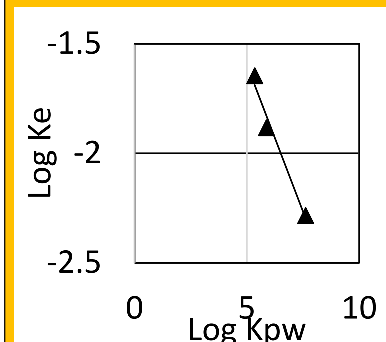
M1
Ke-Kow

Correlation between Exchange Coefficient and Hydrophobicity



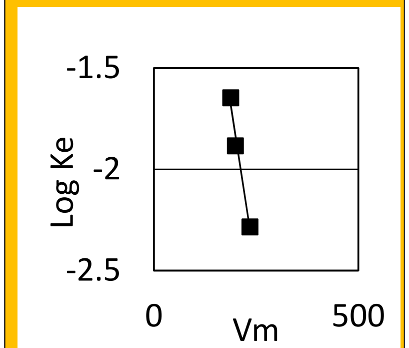
M2
Ke-Kpw

Correlation between Exchange Coefficient and Hydrophobicity



M3
Ke-Vm

Correlation between Exchange Coefficient and Molar Volume



M4
Molar Volume Adjustment

$$R_{s,PRC} = K_{e,PRC} K_{pw} \text{m(PE)}$$

$$R_s = R_{s,PRC} \left(\frac{V_{m,PRC}}{V_m} \right)^{0.39}$$

Recommended (Sanders et al., 2018)	
mono-tri	PRC 29
tetra-penta	PRC69
hexa	PRC155
hepta-deca	PRC 192

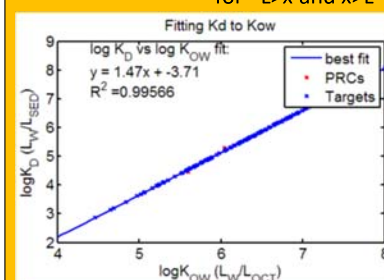
M5
Fickian Diffusion

Diffusivity b/w sediment and water

$$\frac{\partial C_{PE}}{\partial t} = D_{PE} \frac{\partial^2 C_{PE}}{\partial x^2} \quad \text{for } -L<x<L$$

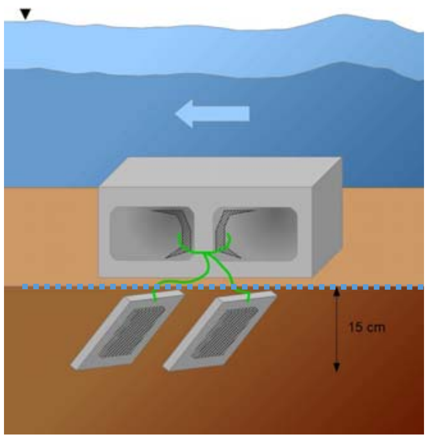
$$\frac{\partial C_{SED}}{\partial t} = D_{SED} \frac{\partial^2 C_{SED}}{\partial x^2}$$

for –L>x and x>L



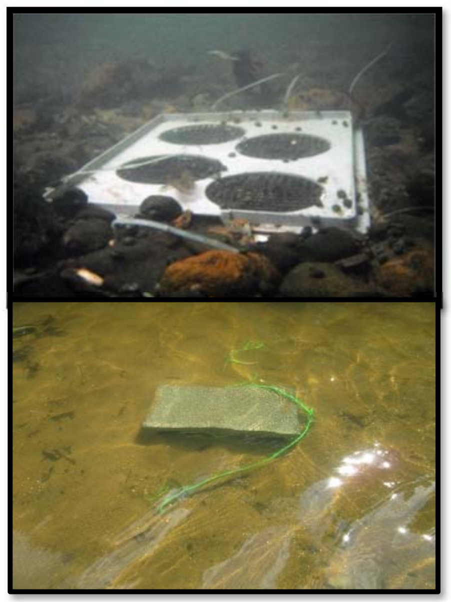
Site 1: Anacostia River tributaries

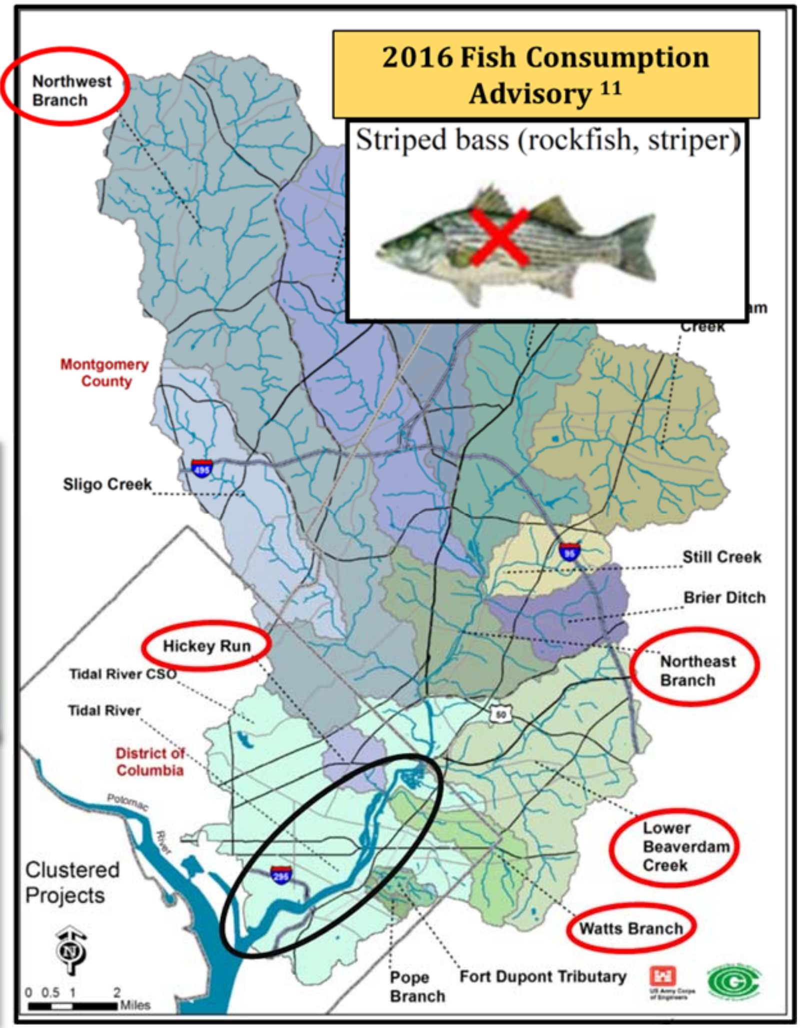
- ❑ Flashy urban streams
- ❑ Drainage area of **173 square miles** [8]
- ❑ Almost **70 %** of the watershed is drained by the **Northeast and Northwest Branch tributaries** [8]
- ❑ Other major tributaries:
  - ➢ Lower Beaverdam Creek (LBC)
  - ➢ Watts Branch (WAB)
  - ➢ Hickey Run (HIR).



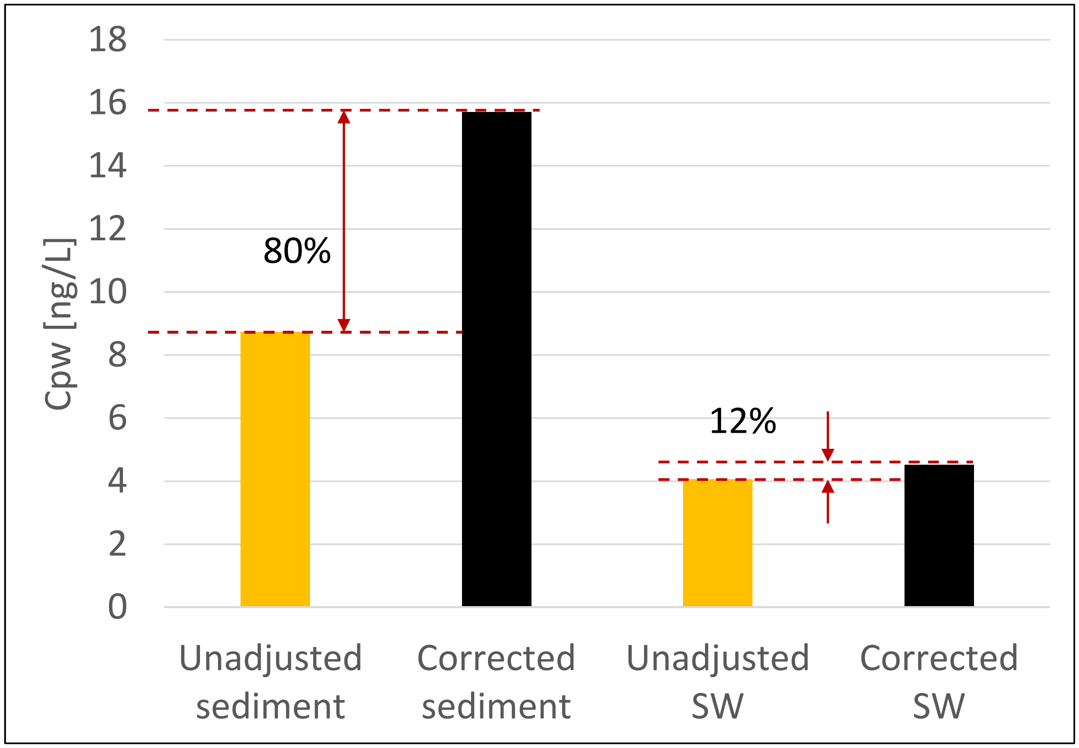
Water column measurement

Sediment pore water measurement





Observations: Correction with Surface Water



- Lesser corrections for surface water than sediment porewater
- Surface water concentrations reach equilibrium faster

Observations: Homolog Distribution of Feq for MVA Method

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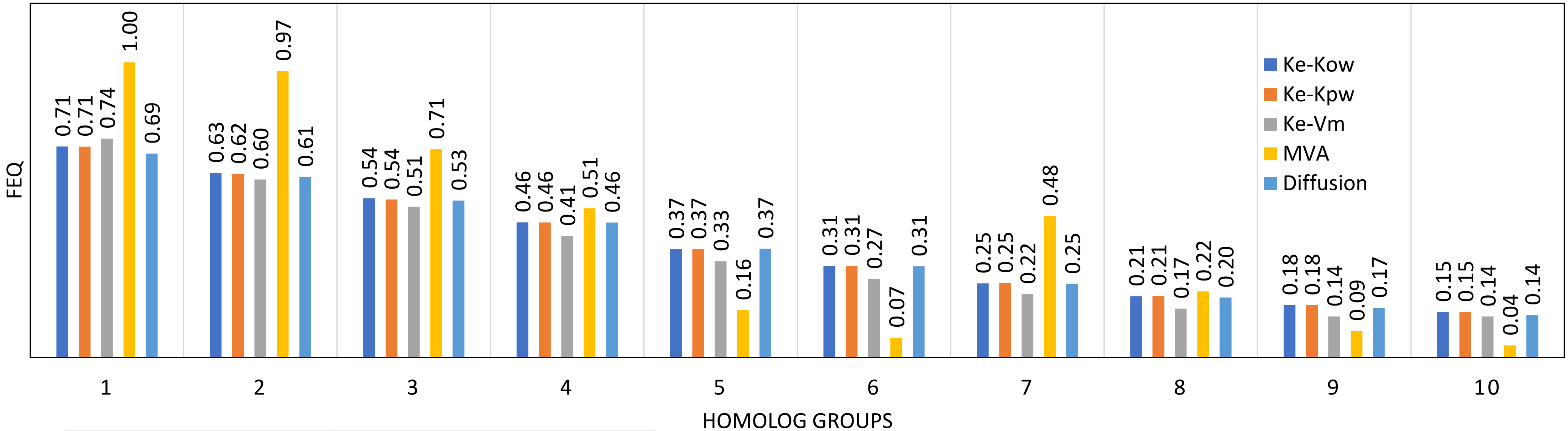
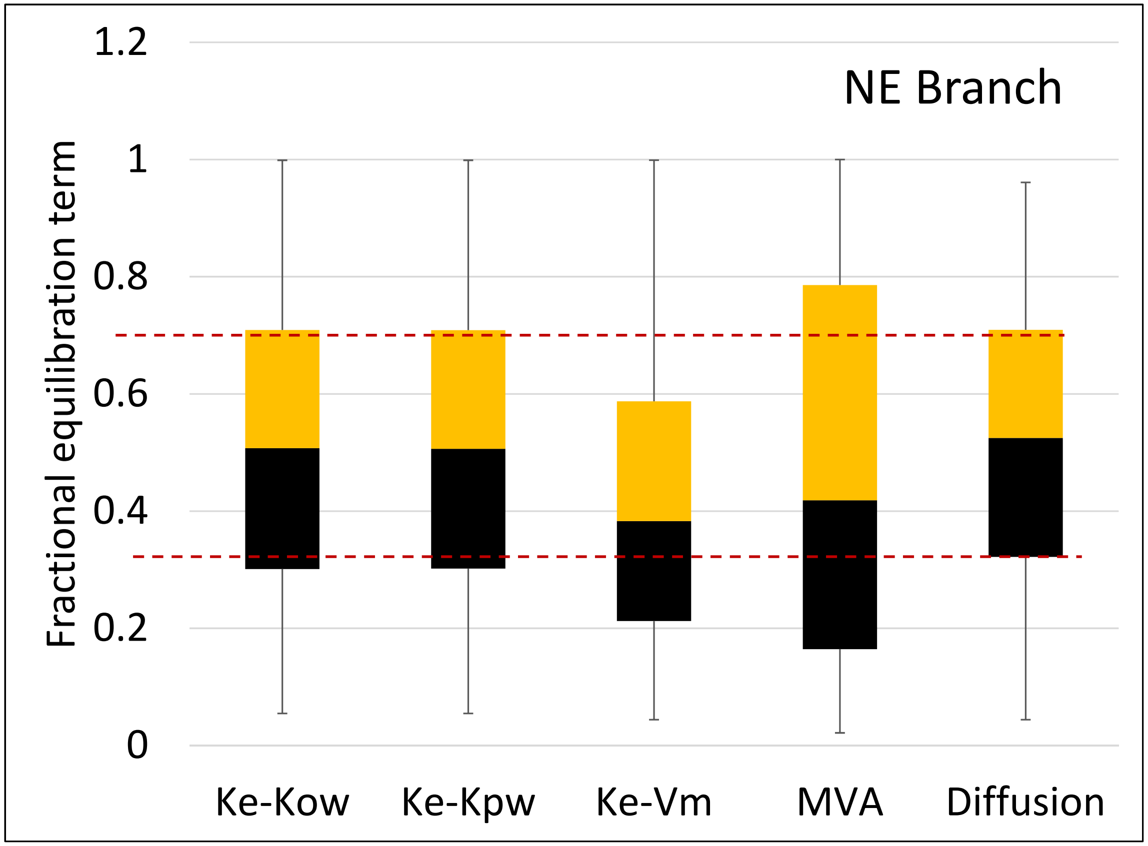


Recommended (Sanders et al., 2018)		**This Study**	
mono-tri	PRC 29	mono-tri	PRC 29
tetra-penta	PRC69	tetra-hexa	PRC69
hexa	PRC155		
hepta-deca	PRC 192	hepta-deca	PRC 192

MVA Method is prone to give errors when all the PRCs are not considered

Observations: Comparison of Fractional Equilibration Term



- The fractional equilibration term (Feq) accounts for how close to equilibrium the system is
- The range of Feq for the first order models are almost similar to the Diffusion Model
- MVA method has more deviation

Observations: Distribution of C_{pw} across various flow regimes

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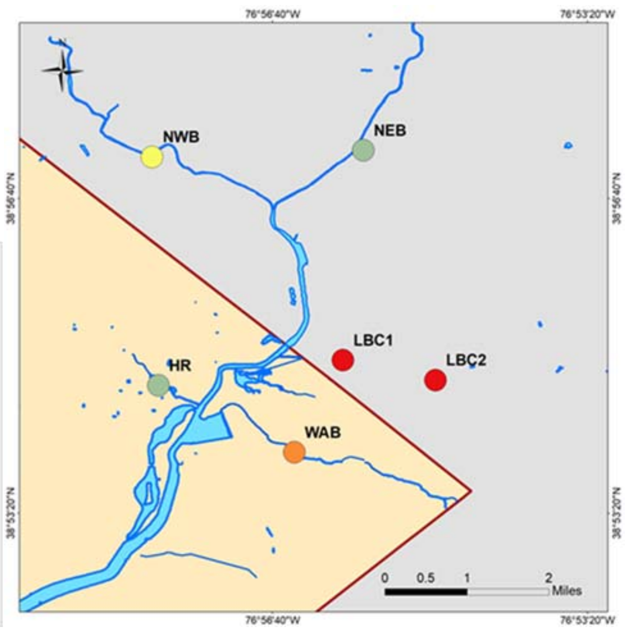
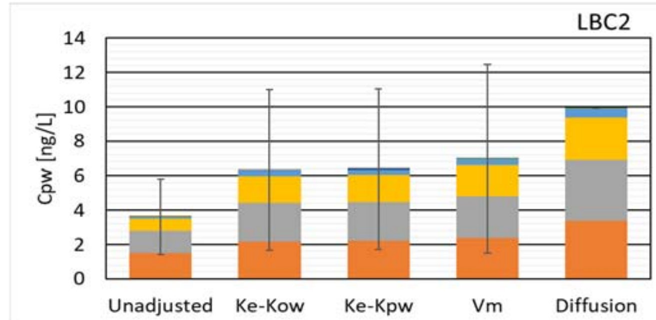
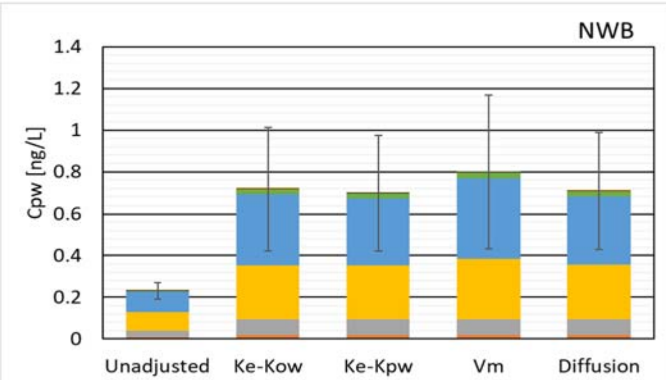
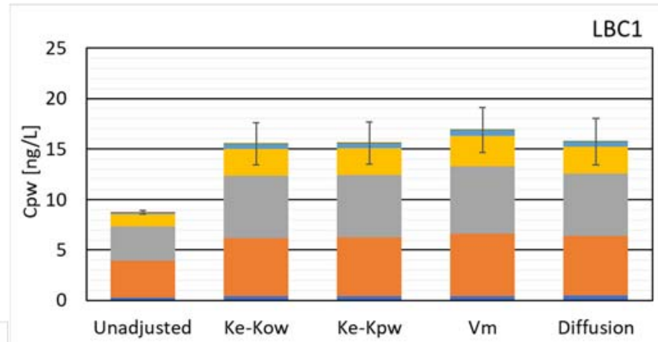
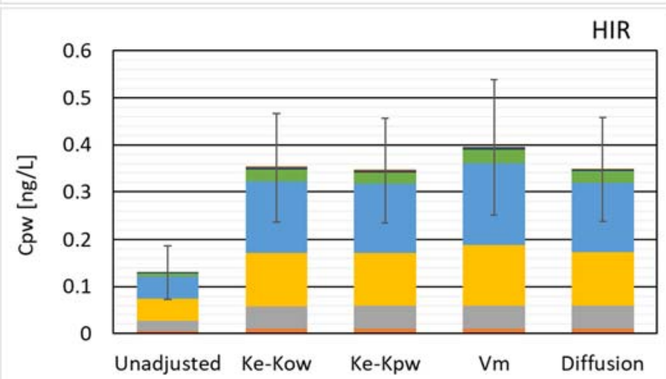
LBC1, LBC2 - highest porewater concentrations

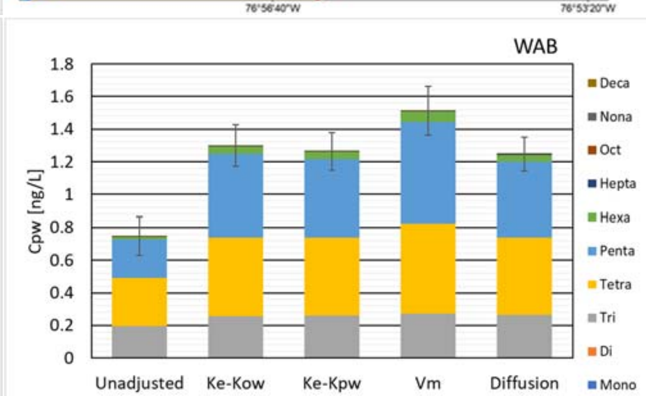


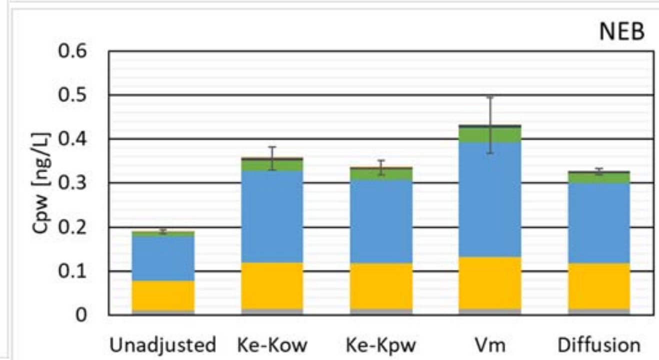




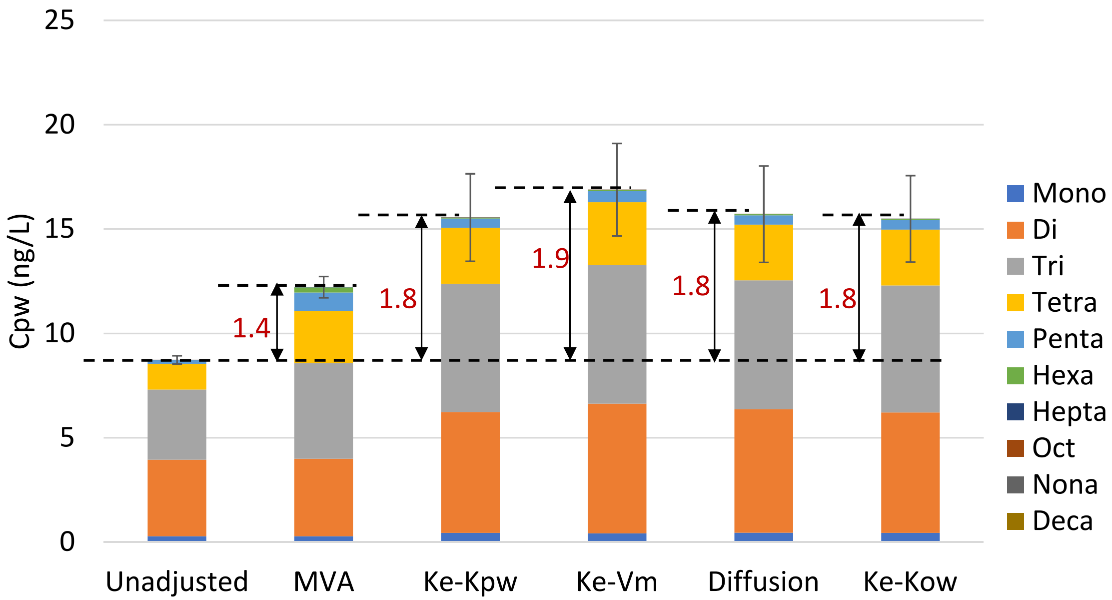








Observations: Relative Correction with unadjusted concentrations



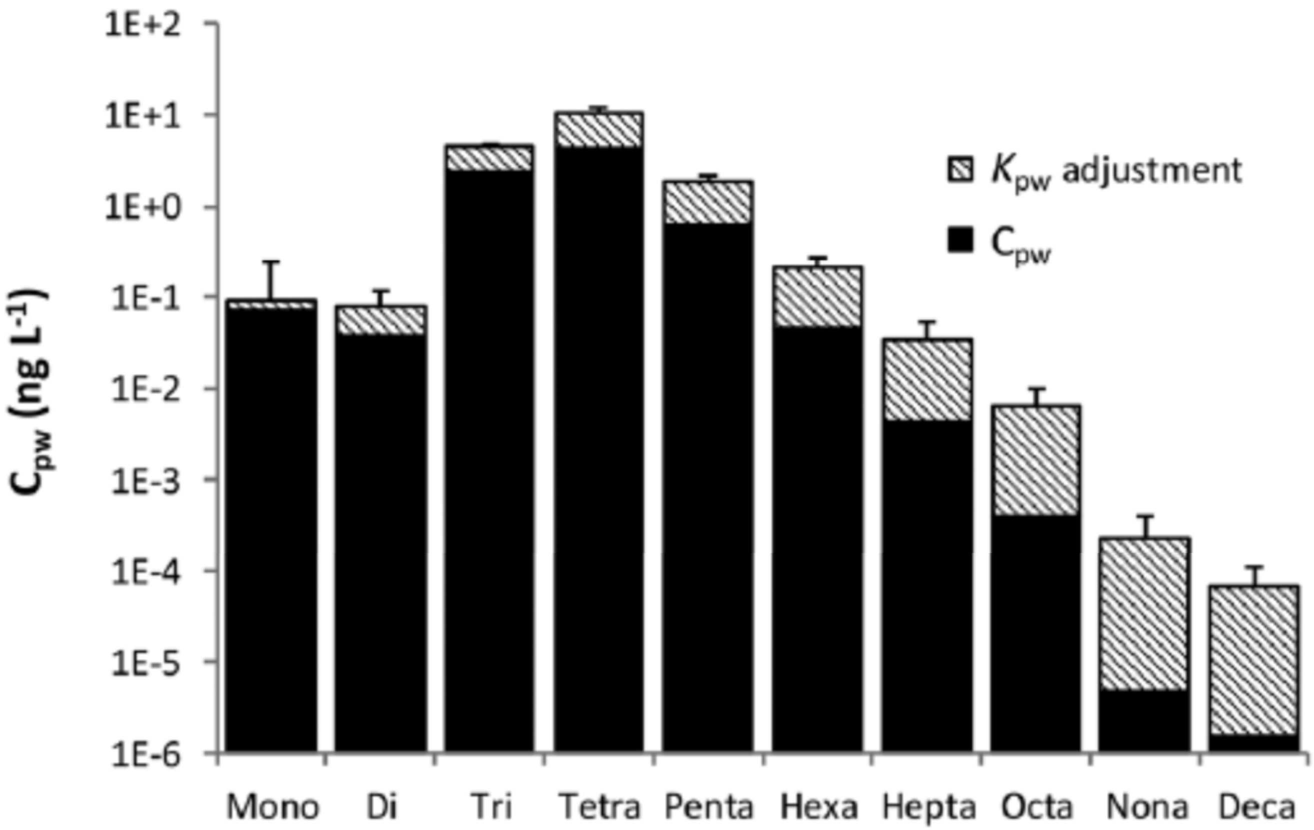
C_{free} of PCBs in upper 15 cm of unamended Lower Lower Beverdam Creek Study area sediment

- Correlation coefficients for the Ke-Vm method were in most cases slightly higher than the K_e–K_{pw} (or K_e –K_{ow}) method
- F_{eq} and C_{pw} for the K_e–K_{pw} (or K_e –K_{ow}) and the diffusion methods similar for almost all the sites.

Site 2: Berry’s Creek, NJ

- Tidal marsh covered with phragmites
- USEPA Superfund site
- Primary COCs: PCBs and Hg
- Site for a demonstration of in-situ treatment with AC

Observations: PRC Corrections for porewater



- PCB porewater in unamended plot (0-10 cm)
- ke-K_{PW} correction
- Note logarithmic scale

Observations: Berry's Creek PRC correction comparison

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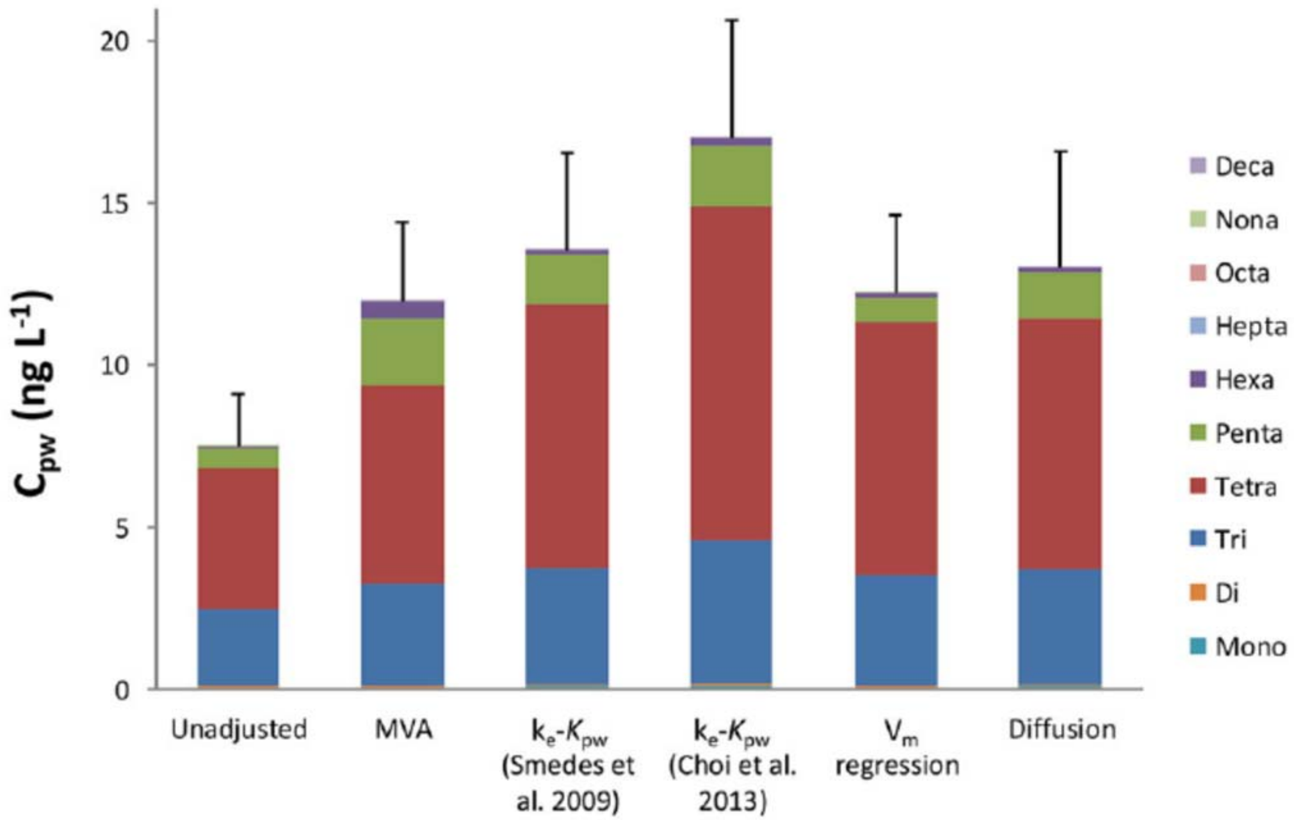

- Top 2.5 cm sediment porewater PCBs
- Comparison of 5 correction methods

Key Conclusions

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- Surface water needs lower correction as compared to sediment porewater
- The **first order linear regression model** estimates are **close to those of the diffusion model**
- The **MVA method was not consistent** across the sites

Thank You

Funding sources:

DOEE and SERDP

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