POREWATER CONCENTRATION AND BIOAVAILABILITY

Upal Ghosh

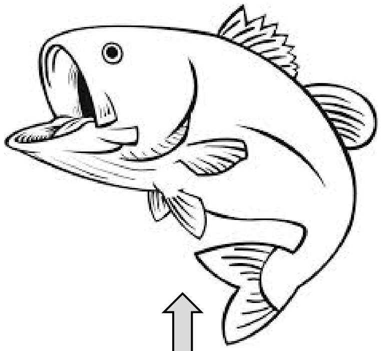
Department of Chemical, Biochemical, & Environmental Engineering
University of Maryland Baltimore County

FRTR
May 11, 2016

Outline

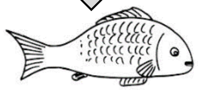
- Pollutant bioavailability in sediments
- Freely dissolved concentration in porewater
- Measurement using passive sampling
- Application case studies:
  - site-specific sediment risk assessment
  - remedy monitoring

Bioaccumulation And Exposure of DDD

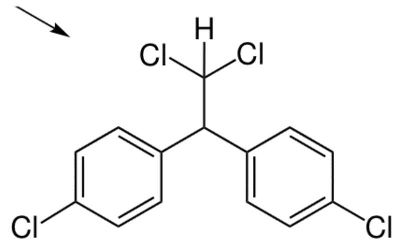


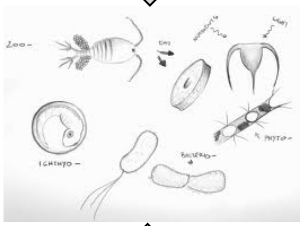
Large fish
1.7 ppm

$\xrightarrow{\text{100g fish}}$ **0.17** mg DDD

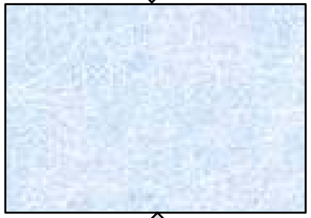


Small fish
0.5 ppm



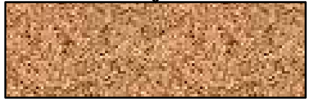


Plankton
0.0265 ppm



Water
0.0001 ppm

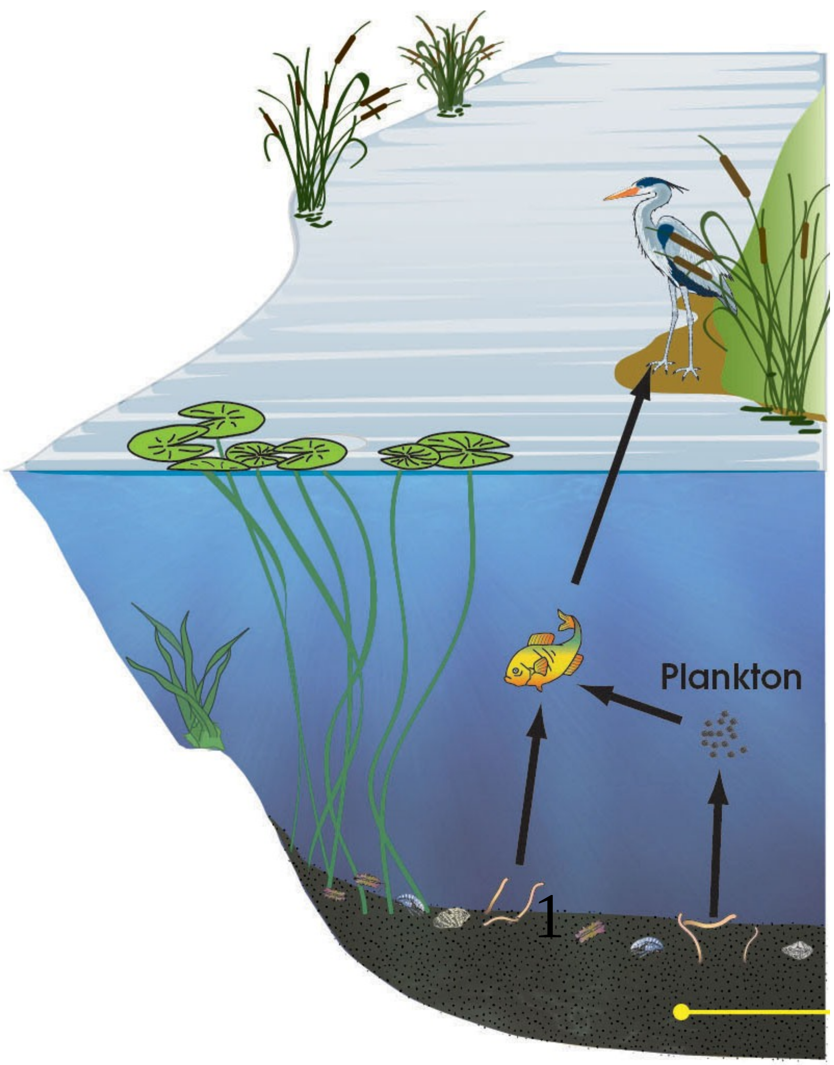
$\xrightarrow{\text{2 L water}}$ 0.0002 mg DDD



Sediment
1 ppm

K_{oc} = 151,000

Bioaccumulation of Hydrophobic Compounds



Contaminated sediment

Legacy contaminants in exposed sediment contaminates the food chain through:

1) bioaccumulation in benthic organisms

2) flux into the water column, and uptake in the pelagic food web.

- Predictions work reasonably well for natural systems

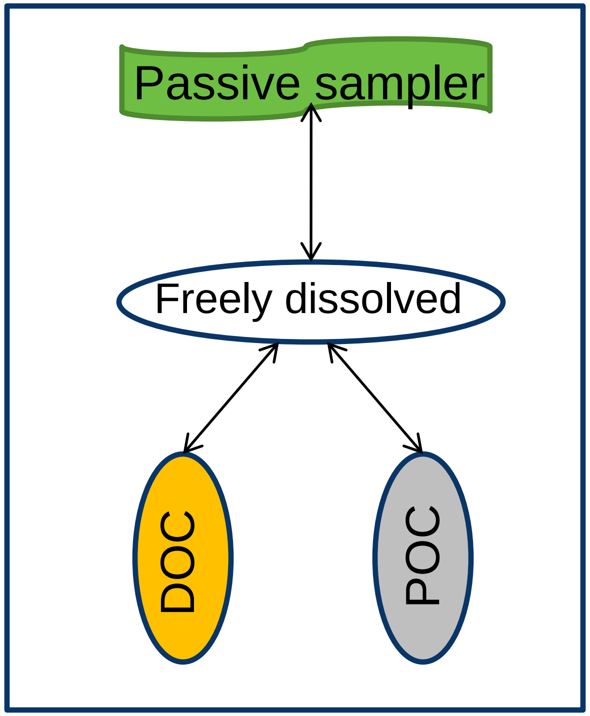
- Predictions become more challenging for industrially impacted sediments

Conceptual Understanding of Passive Sampling

1) Hydrophobic chemicals partition among the aqueous and different solid phases

2) Equilibrium distribution can be described by linear free energy relationships

$$C_{total} = C_{free} + \boxed{DOC*K_{DOC}*C_{free}} + \boxed{POC*K_{POC}*C_{free}}$$

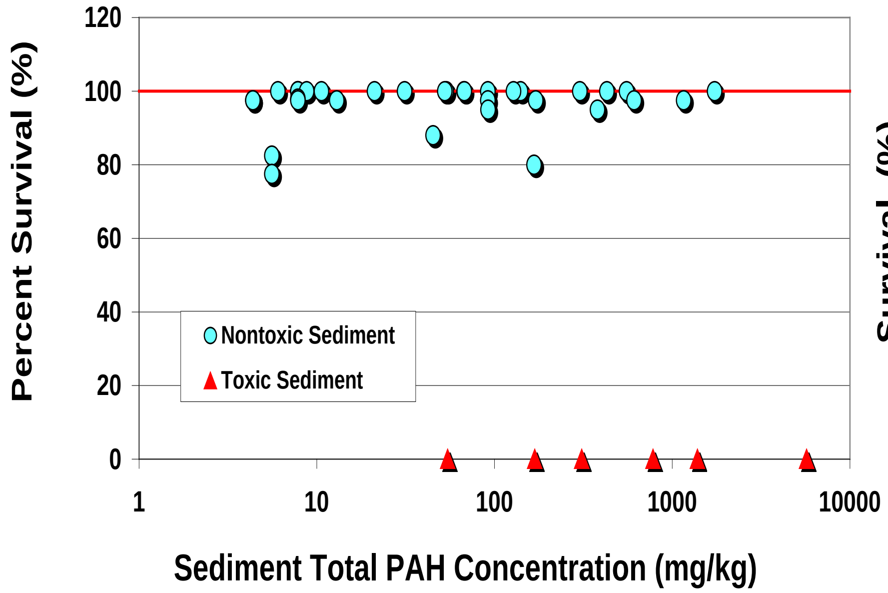


Two approaches to measure total and freely dissolved concentrations:

1) Remove POC by centrifugation/flocculation, measure total dissolved concentration and DOC, and estimate freely dissolved concentration.

2) Use calibrated passive sampler to measure freely dissolved concentration, measure DOC, and estimate total dissolved concentration.

Prediction of **Toxicity**: Sediment vs. Freely Dissolved Conc.



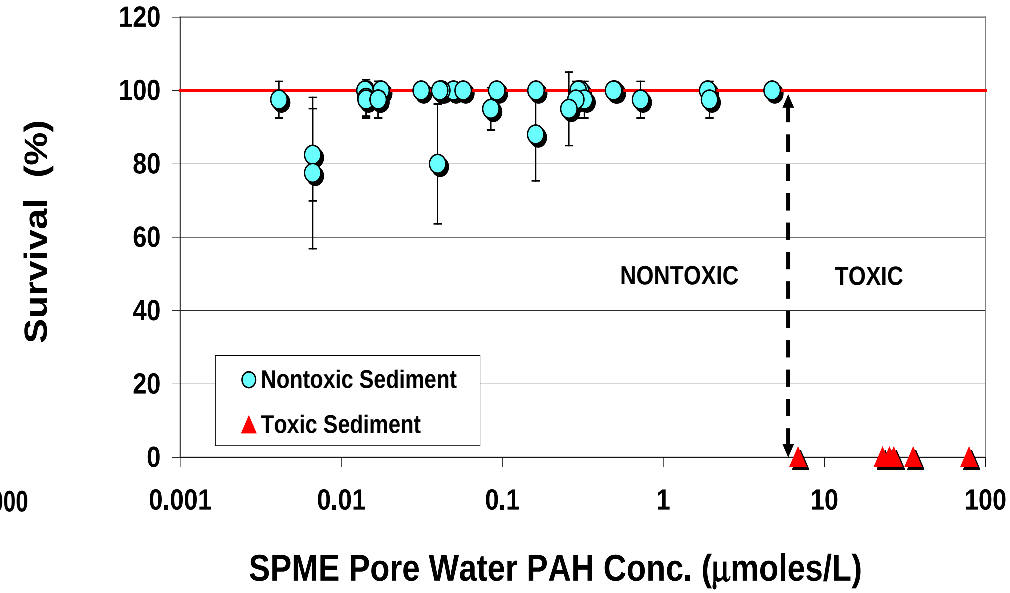


Figure 1. Chronic toxicity to *H. azteca* (28-day) can not be predicted from total PAH concentration in MGP sediment

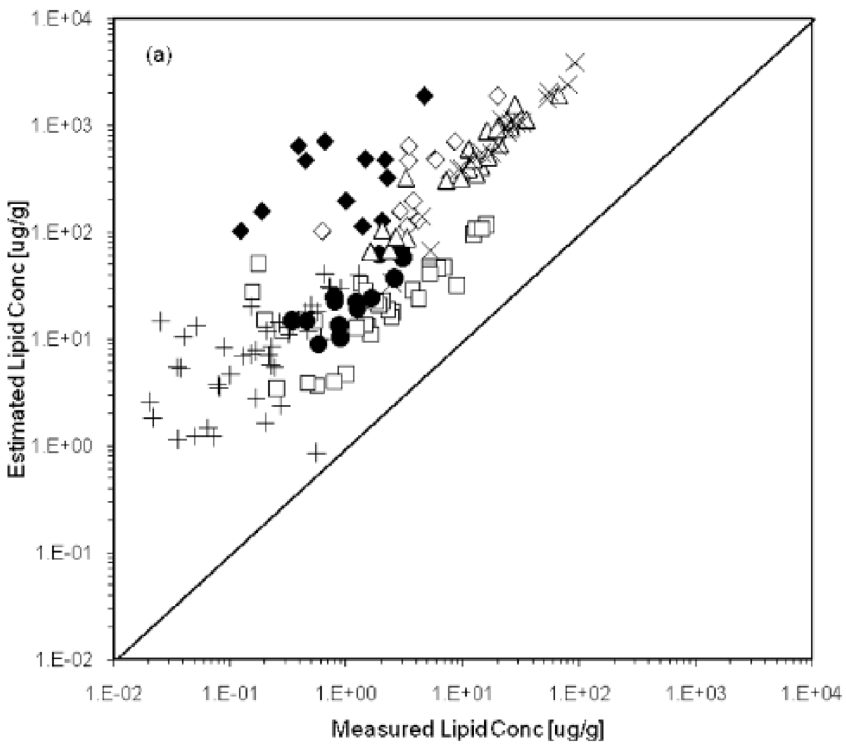
Figure 2. Chronic toxicity to *H. azteca* (28-day) can be predicted by estimating PAHs in sediment pore water.

Kreitinger et al , ETC 2007

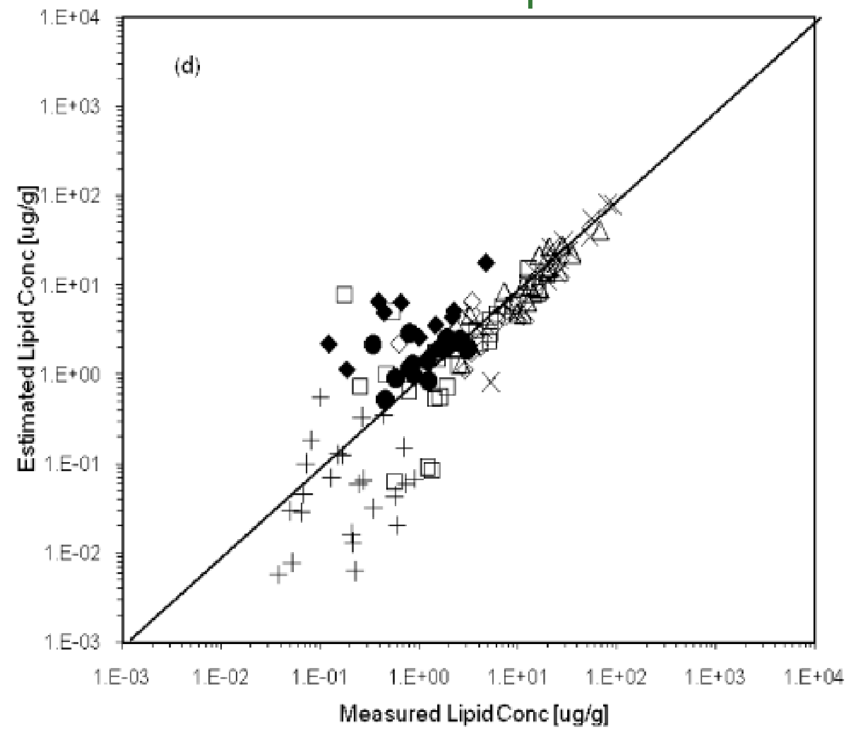
Prediction of **Biouptake** in Benthic Organisms: Sediment vs. Freely Dissolved Conc.

- 7 freshwater and marine sediments
- Freely dissolved conc. measured by passive sampling and also directly
- Lipid concentrations better predicted from freely dissolved porewater

Predicted from sediment



Predicted from porewater



$$C_S = (f_{OC} - f_{BC}) K_{AOC} C_{aq} + f_{BC} K_{Fr,BC} C_{aq}^n$$

$$\log(C_{lipid}) = 0.91 \cdot \log(K_{OW}) + 0.50 + \log(C_{aq})$$

$$C_{lipid} \approx K_{LIP} \cdot C_{aq}$$

Werner et al. ES&T 2010

Measurement of HOCs in Water is Challenging

Need to measure <ng/L concentrations in sediment porewater

Two approaches to get to this concentration:

1) Modeling based on partitioning calculations:
   A) Sediment concentration and fraction OC
   B) Model presumes a certain partitioning behavior for the OC
   C) Complication from the presence of BC
   D) Difficult to characterize BC partitioning

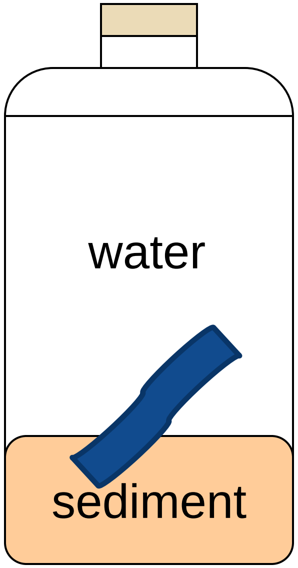
2) Direct measurement:
   A) Detection limits associated with manageable grab sampling
   B) Separation of colloids challenging
   C) Passive sampling

Examples of Passive Sampling Use

1) Batch equilibrium measurements for low aqueous concentrations (PCBs, PAHs, dioxins)

2) In-situ probing to assess ambient contaminant concentrations or to assess changes with time or with treatment

Pictures of typical applications:



Laboratory batch equilibrium

Stream water quality assessment

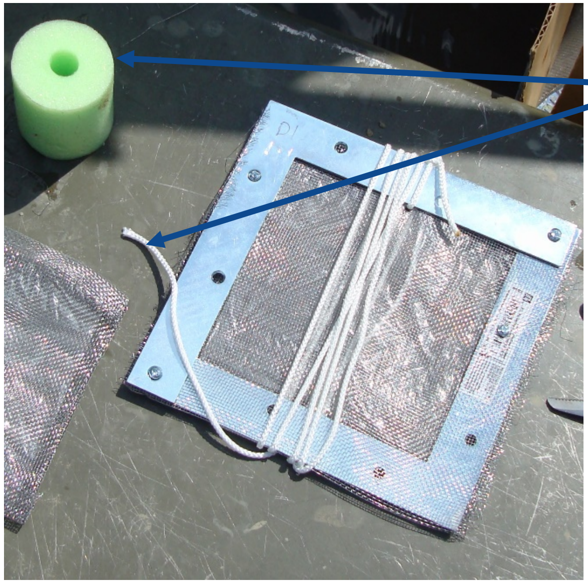
Field evaluation of treatment performance

Depth profiling of porewater in sediment

Deployment of Passive Samplers into Surface Sediments

Underwater video camera for confirming placement depth

Tool for inserting passive sampler frame in sediment. The 8' pole allows deployment from a boat in shallow water sediments



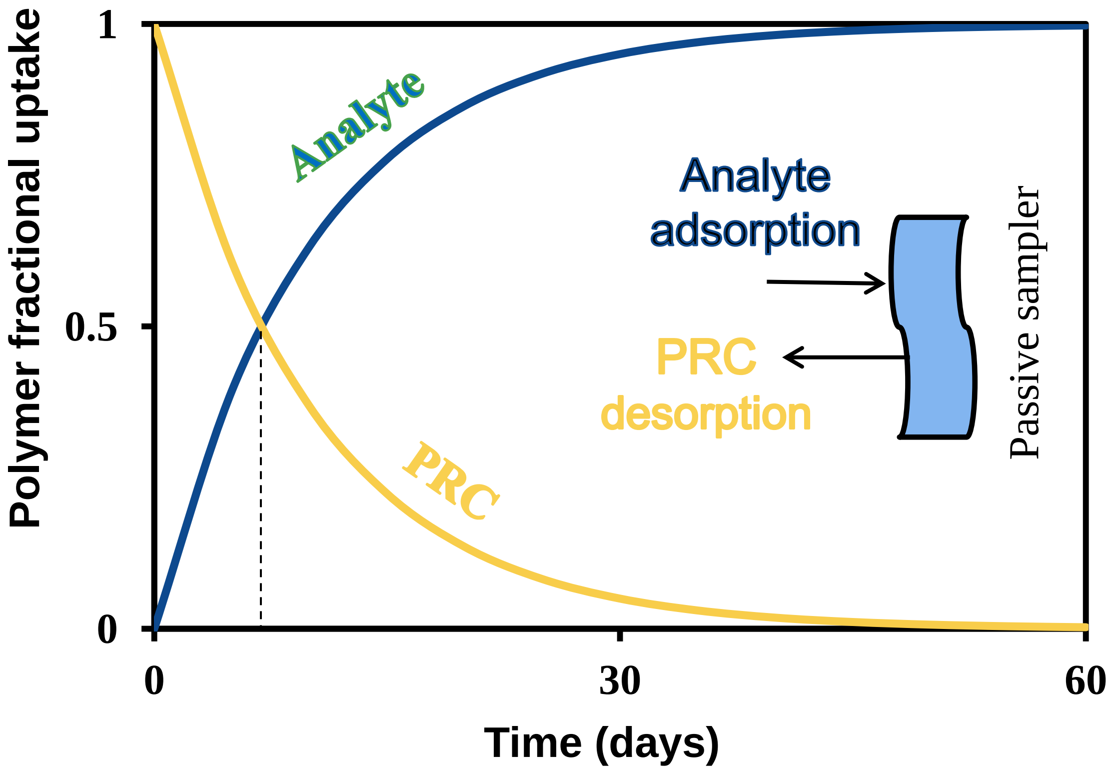
Rope and buoy for retrieval after deployment

Passive sampler encased in stainless steel mesh and framed for sediment deployment

Image from underwater camera showing the passive sampler being inserted into sediment

Uptake of Pollutants in Passive Sampler

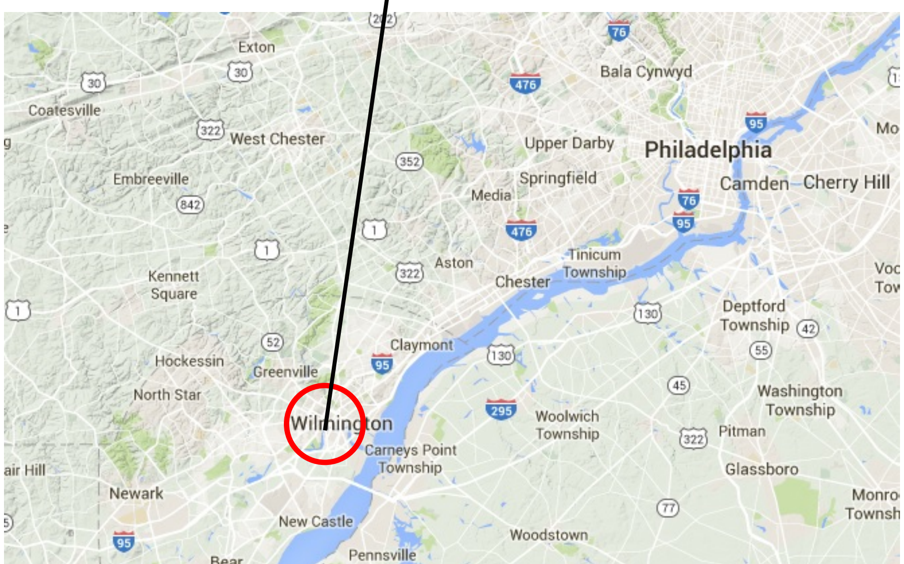
- Equilibrium slow for: 1) high K_{ow}; 2) static porewater
- Mass transfer in sediment side difficult to predict
- Performance Reference Compounds (PRCs) are used to correct for non-equilibrium
- PRCs have similar diffusion properties as analytes



$$k_e = -\frac{\ln(C_{PRC,f}/C_{PRC,i})}{t}$$

$$C_p = K_{pw}C_w[1 - exp(-k_e t)]$$

Case Study 1:Site Specific Risk Assessment



27-acre degraded wetland

Contaminants detected in marsh soil:

- Metals (e.g. As, Pb, Cr)
- PAHs
- PCBs
- Pesticides

Benthic Organism-Based PRGs

(Equilibrium Partitioning Approach):

$$PRG_{sediment} = \text{Toxicity Value} \times CF \times foc \times Koc$$

- PRG, concentration in sediment (mg/kg DW sediment)
- Toxicity Value , Aquatic community-based toxicity value (µg/L)
- CF, Conversion factor of mg/1,000 µg
- foc, Organic carbon fraction (2 % default used in initial calculation, average of 4% TOC was detected in sediments)
- Koc, Organic carbon partition constants (default value from HHRAP used in initial calculation, measured specific Koc used in revised version)

EPA, 2003c, 2003d, 2003e, 2005j, 2008b
Human Health Risk Assessment Protocol (HHRAP 2012)

Food Web Modeling Based PRGs

(bioamagnification and trophic transfer through dietary exposure)

$$PRG_{sediment} = \frac{THQ * TRV}{FT * (FIR * \frac{BCF}{foc K_{oc}} + SIR)}$$

Parameter	Definition	Value
$PRG_{sediment}$	Concentration of COPEC in sediment (mg COPEC/kg DW sediment).	
THQ	Target hazard quotient (unitless)	1
TRV	Toxicity reference value (mg COPEC/kg BW-day)	Class- and COPEC-specific
FT	Fraction of foraging time in the exposure area (unitless)	Receptor-specific
FIR	Food ingestion rate (kg WW tissue/kg BW-day)	Receptor-specific
SIR	Sediment ingestion rate (kg DW sediment/kg BW-day)	Receptor-specific
Log K_{ow}	Log octanol-water partitioning coefficient (unitless)	COPEC-specific

- Local receptors: American robin, Raccoon, **Spotted sandpiper**, etc.
- Spotted sandpiper was selected due to its most rigid sediment concentration criteria.

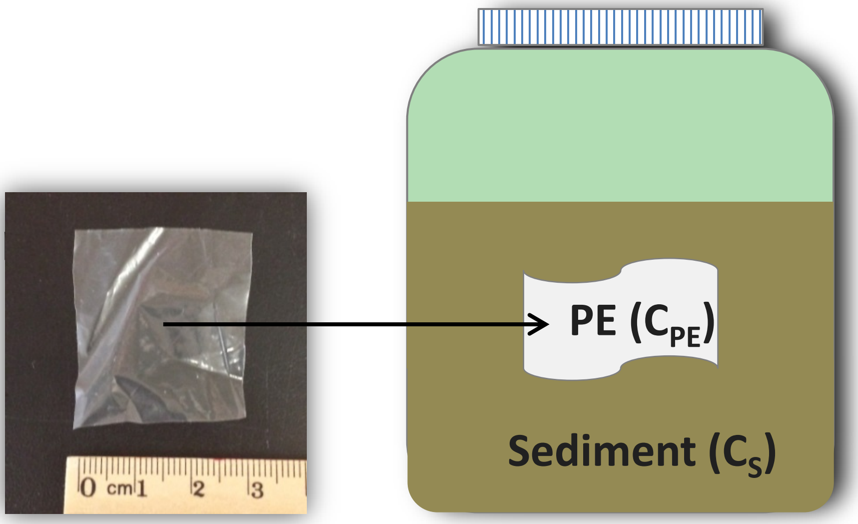
(EPA 2007a, 1999, 1993)

Study Objectives

Evaluate site specific bioavailability of PAHs and PCBs in South Wilmington Wetland sediment and refine risk assessment.

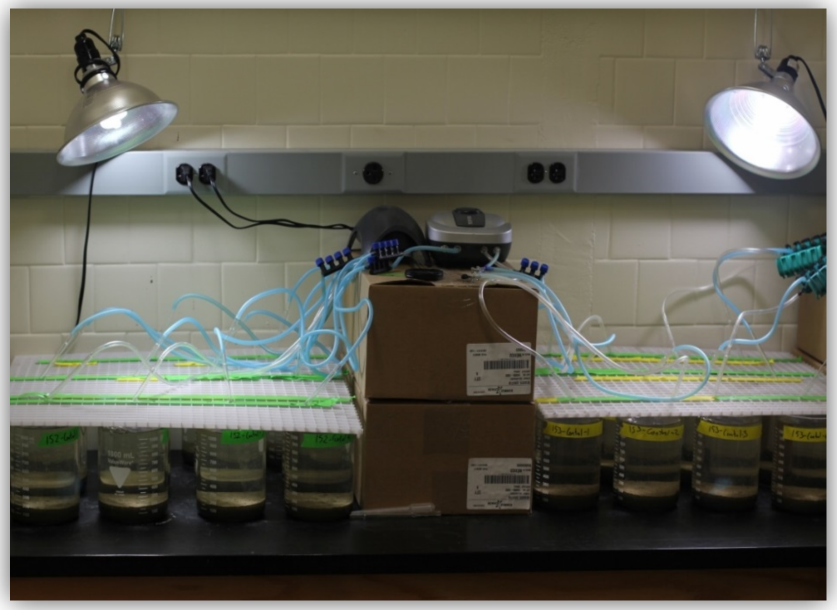
Methods

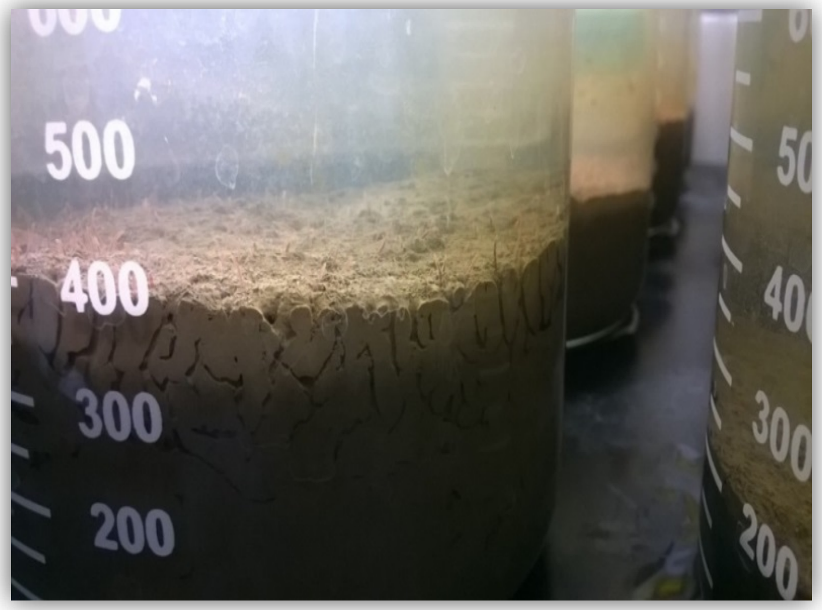
- Sediment samples collected from 15 sites.
- Measurement of PCB, PAH, and pesticide concentrations in sediment samples.
- Laboratory partitioning study for PCBs and PAHs using passive sampler
  - Four weeks partitioning test
  - Polyethylene (PE) as passive sampler
  - $C_W = C_{PE}/K_{PE}$
  - K_{PE} previously determined



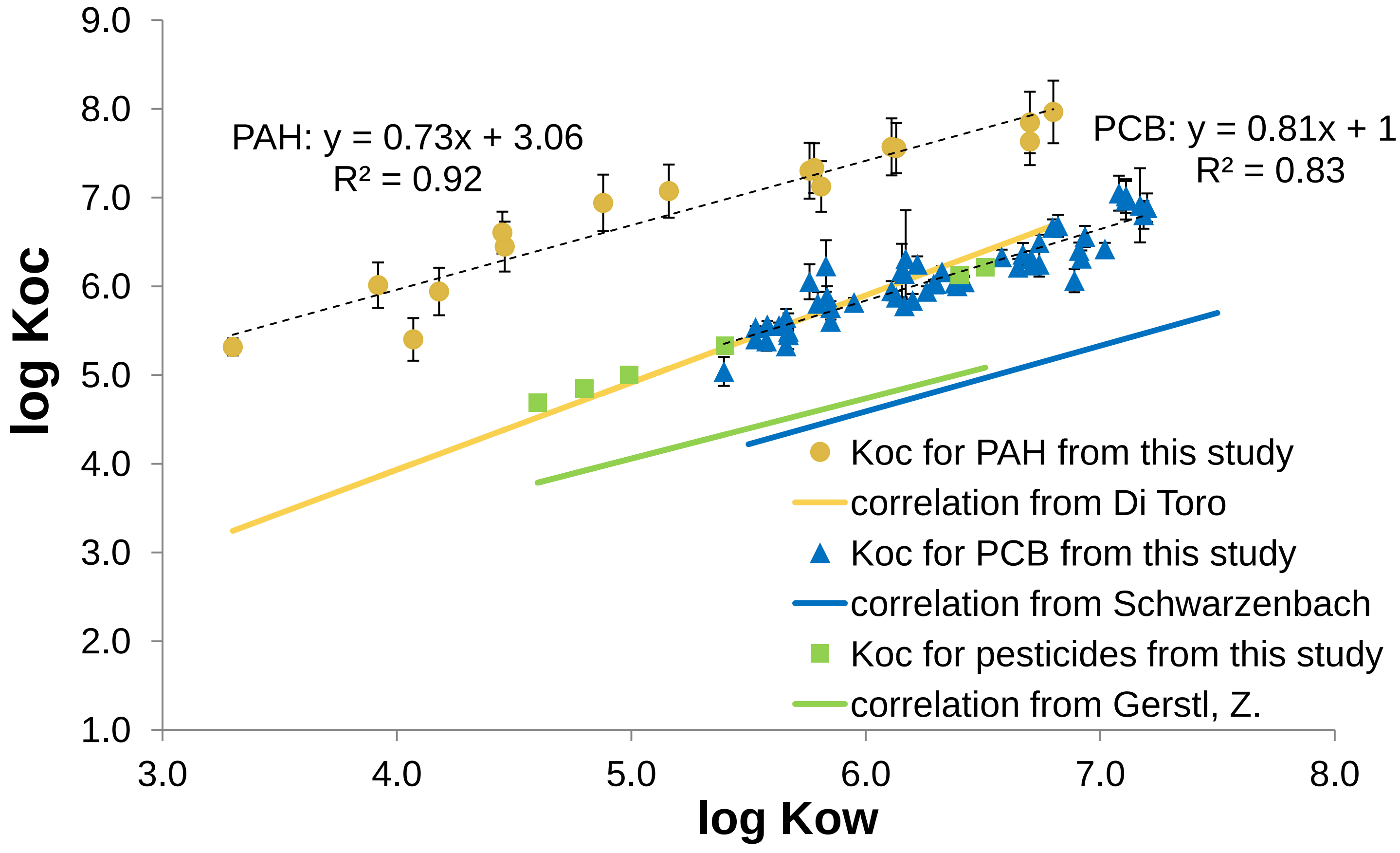
Bioaccumulation in Benthic Organisms

- Organism: *Lumbriculus variegatus*
- Daily water exchange and quality monitoring
- 28 days exposure
- Worm collection and depuration
- Cleanup and analysis for PCBs





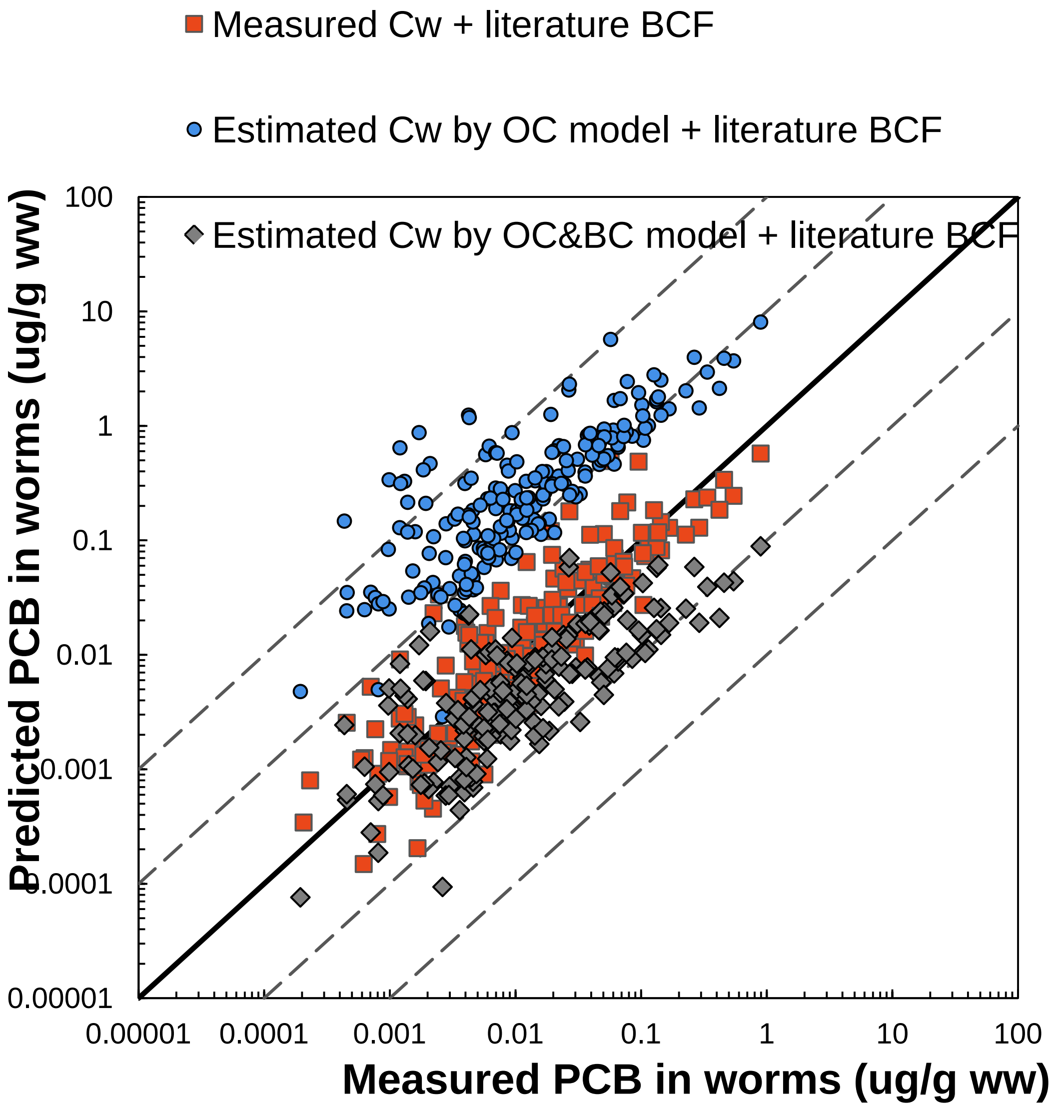
Partition Constants For PAHs, PCBs, Pesticides



- Measured Koc values for both PAHs and PCBs were 1-2 orders of magnitude higher than the generic values used in preliminary risk assessments

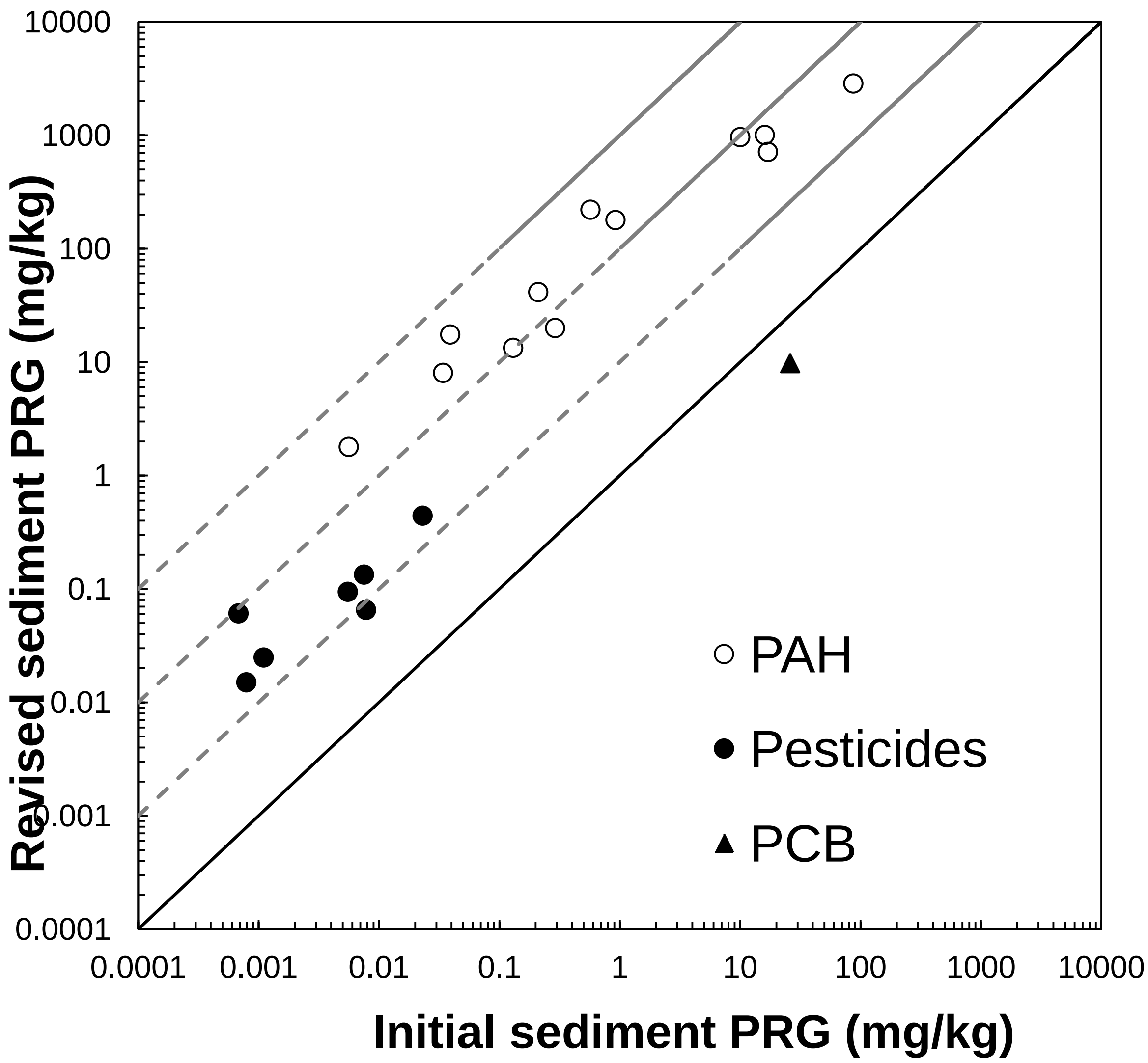
- Literature median value of BC/OC ratio : 9%, n=300 (Cornelissen et al. 2005)
- Measured BC/OC ratio: 17-36%

PCB Bioaccumulation



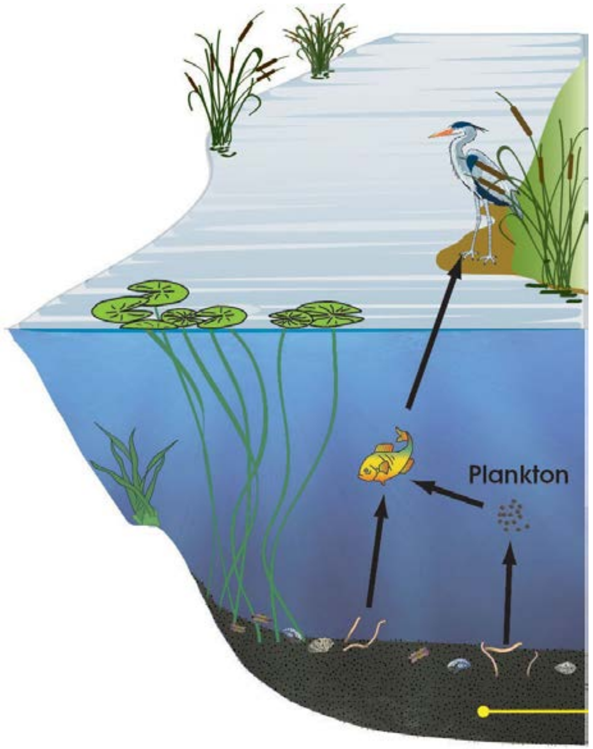
Measured Cw provides best prediction of PCB bioaccumulation

Benthic Organism-Based PRGs Using Site Specific Koc

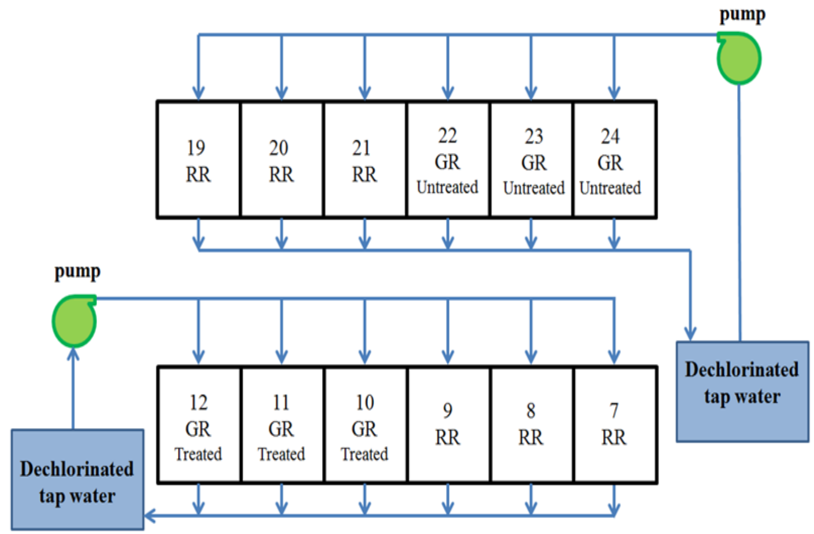


Case Study 2: Predicting Uptake in Fish After in situ Treatment

- Evaluate the effect of sediment amendment with AC on PCB uptake in fish
- Test the ability of existing PCB bioaccumulation models to predict changes observed in fish uptake upon AC amendment of sediment
- Incorporate measured freely dissolved concentrations by passive sampler in food chain models

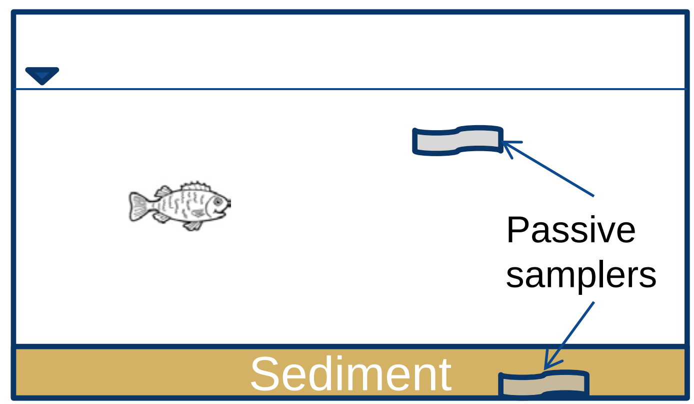


Laboratory Exposure Experiments



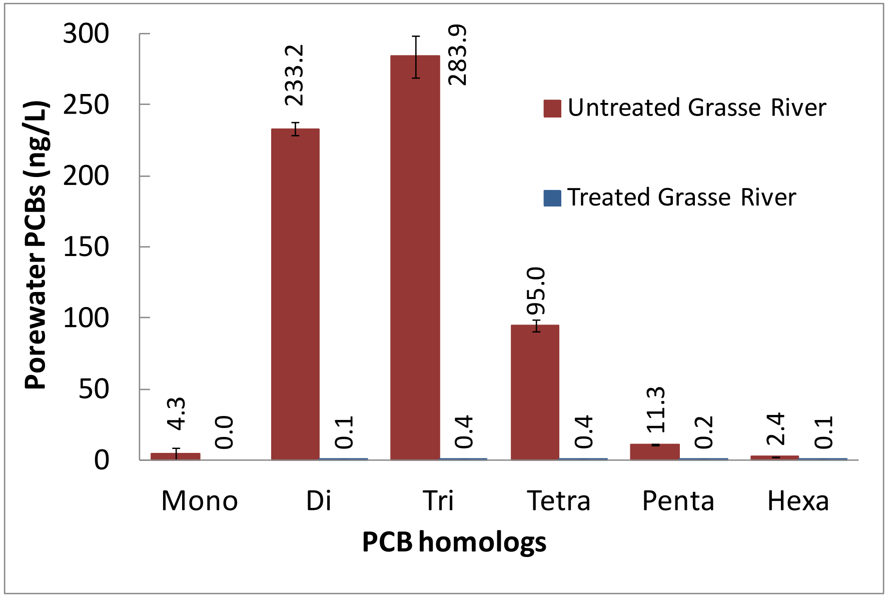
Water flow in aquaria tanks

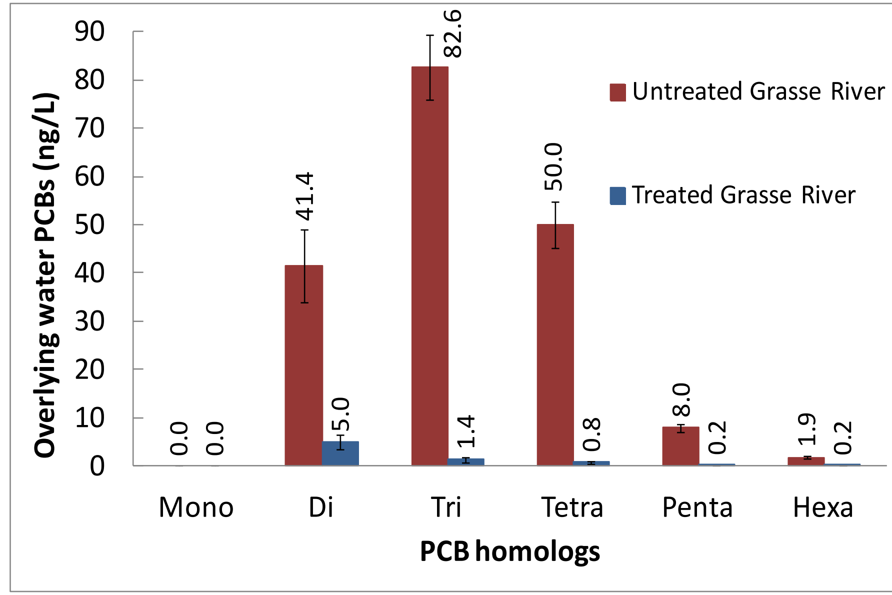
- Treatments:
  - Clean sediment (Rhode River)
  - PCB impacted sediment (Near-shore Grasse River)
  - PCB impacted sediment-AC treated in the lab
- Replicate aquaria with passive samplers in water column and sediment
- Fish species: Zebrafish
- PCB-free diet
- Sampling after 45 and 90 days



Components in each aquaria

Porewater and Overlying Water PCBs

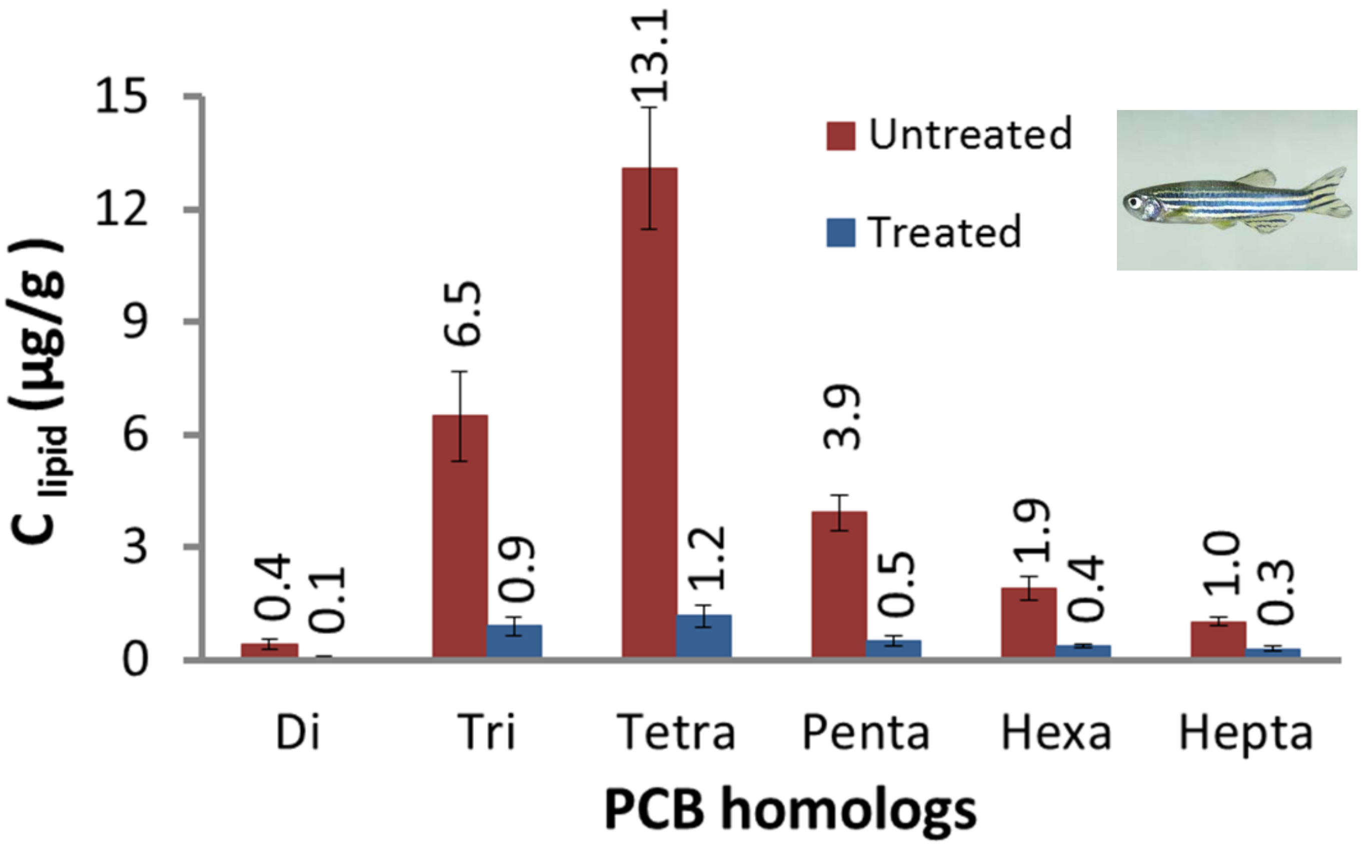




- Porewater and Overlying PCB concentrations in PCB impacted untreated sediment were high and were reduced by **more than 95%** upon amendment with AC.

- In the PCB-impacted untreated sediment tanks, porewater PCB concentrations were **3-7 fold** higher than the overlying concentrations indicating sediment as the PCB source to the water column.

PCB Residue in Fish after 90 Days



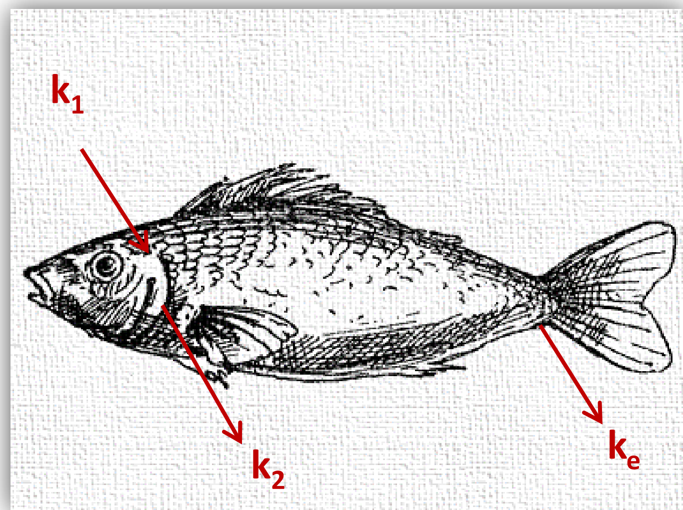
The AC amendment reduced the PCB uptake in fish **by 87%** after 90 days of exposure.

Predicting PCB Uptake in Fish

Equilibrium Approach

$$C_{lipid} = K_{lipid}\, C_{w,o} \qquad K_{lipid} \approx K_{ow}$$

Kinetic Approach

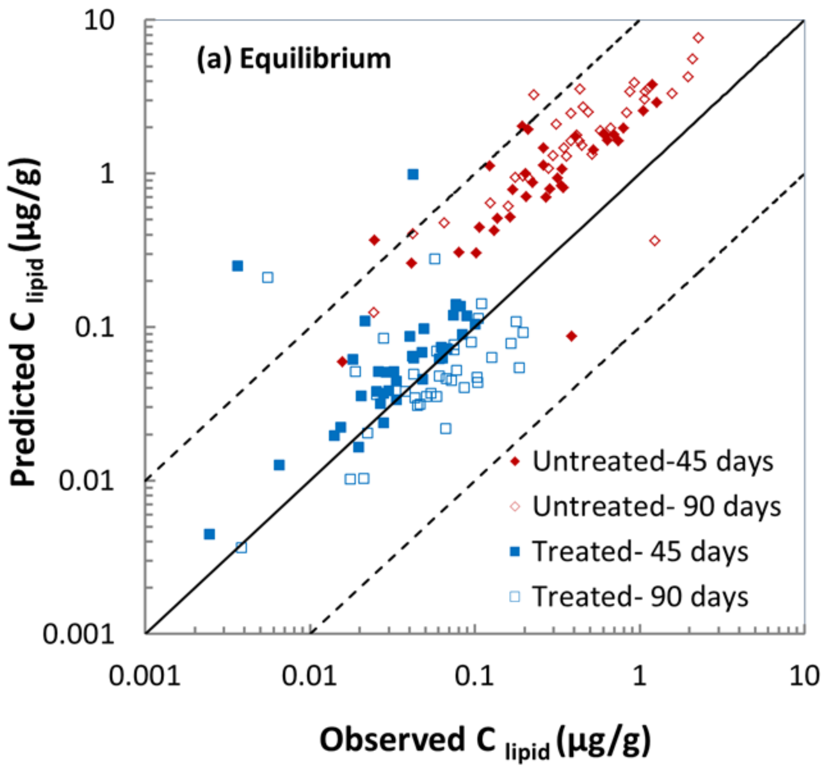


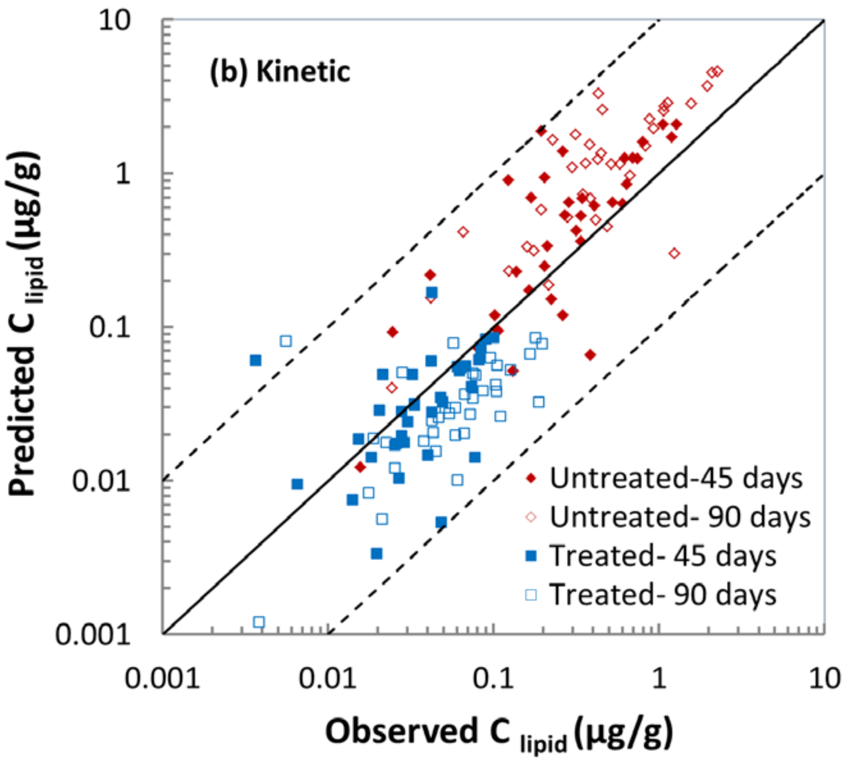
$$\frac{dM_B}{dt} = W_B k_1 C_{w,o} - (k_2 + k_e)\, M_B$$

(Arnot and Gobas 2004)

$$M_B = \frac{W_B k_1 C_{w,o}}{} \left(1 - e^{-(k_2+k_e)t}\right)$$

Equilibrium and Kinetic Model Predictions





- Worms in sediment come close to equilibrium in 1 month
- Fish do not reach equilibrium even after 90 day exposure

Key Conclusions

- Passive samplers can be used to accurately measure C_{free}
- Site-specific C_{free} values provide improved prediction of toxicity and bioaccumulation
- Incorporating C_{free} measurements in bioaccumulation model allows better prediction of uptake in fish

Future needs

- Inter-laboratory tests for greater confidence in precision
- Development of SRMs to check method accuracy
- More organic compounds with known K_{PW}

Acknowledgments

- Funding support from SERDP/ESTCP programs, NIEHS, USEPA GLNPO, and Alcoa
- Graduate students at UMBC

PASSIVE SAMPLER PREPARATION AND PROCESSING

- Polymers need to be cleaned before use in the field
- PRCs have to be added to the polymers
- Samplers need to be mounted in some form to allow water exposure while proving rigidity for deployment
- Important to make sure polymer sheets do not fold up during deployment
- Upon retrieval, surface deposits need to be removed
- After surface cleaning, the polymers are extracted in appropriate solvent.
- Surrogate standards added to extraction vial
- An accurate weight measurement of the polymer is taken
- Field blanks analyzed for exposure during transport and handling

DETECTION LIMITS

- PE and POM sheets generally have lower detection limits than PDMS-coated SPME fibers due to their larger mass and absorptive capacities

- The mass of polymer needed depends on the detection limit of the chosen analytical method (e.g., regular GC-ECD or GC-MS vs HR-GC/HR-MS)

Example C_{free} detection limits for PCBs using POM

	POM MDL	1g POM PQL	0.2g POM PQL
	ng/g	pg/L	pg/L
PCB-3	0.542	17	83
PCB-6	0.05	0.37	1.8
PCB-18	0.019	0.14	0.70
PCB-53	0.048	0.29	1.5
PCB-44	0.029	0.23	1.2
PCB-101	0.014	0.12	0.62
PCB-153	0.011	0.05	0.23
PCB-180	0.03	0.16	0.81

REVISED PRGS BASED ON EXPOSURE TO SPOTTED SANDPIPER