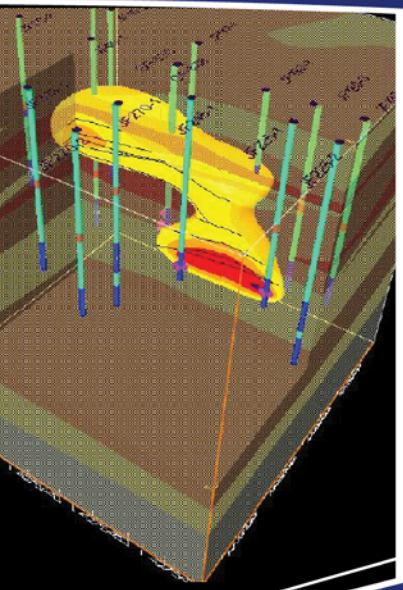


Porewater and Bioavailability at Contaminated Sediment Sites

Karl Gustavson
Army Engineer Research and Development Center (ERDC)

ERDC

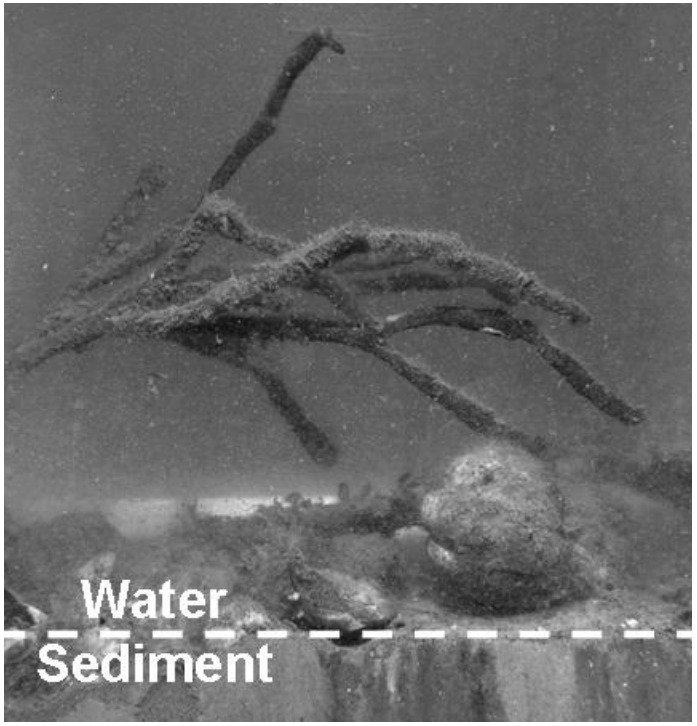
Outline

- Problem definition
- Porewater, bioavailability, and exposures
- Passive samplers for porewater assessment
- Passive sampler applications and environments
- Recommendations for use

Sediment Remediation

- Conducted to decrease risk to consumers of fish.

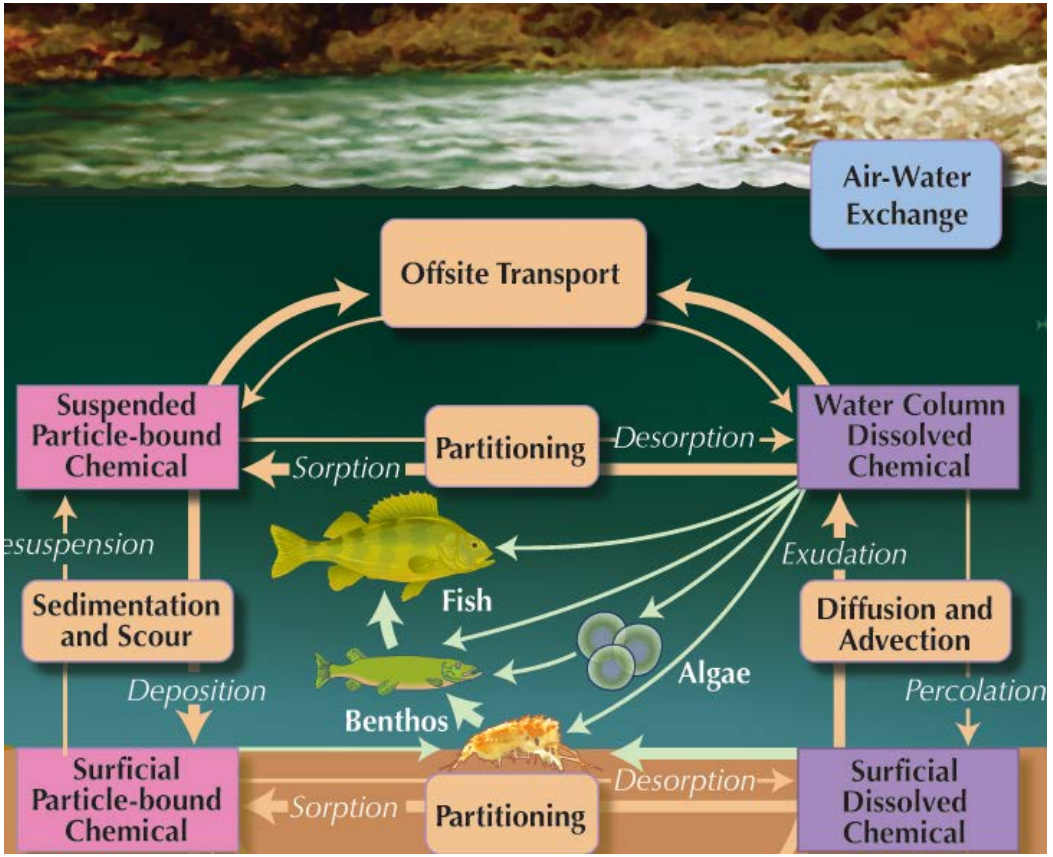
- Conducted to decrease risk to benthos.



Sediment – Biota Relationship

There is a complex relationship between sediment and biota contamination.

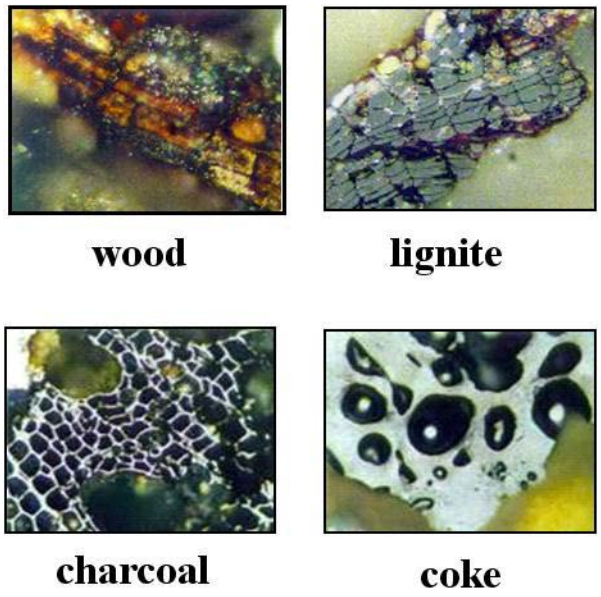
…influenced by concentration, bioavailability, fish diet, behavior, movement, etc.



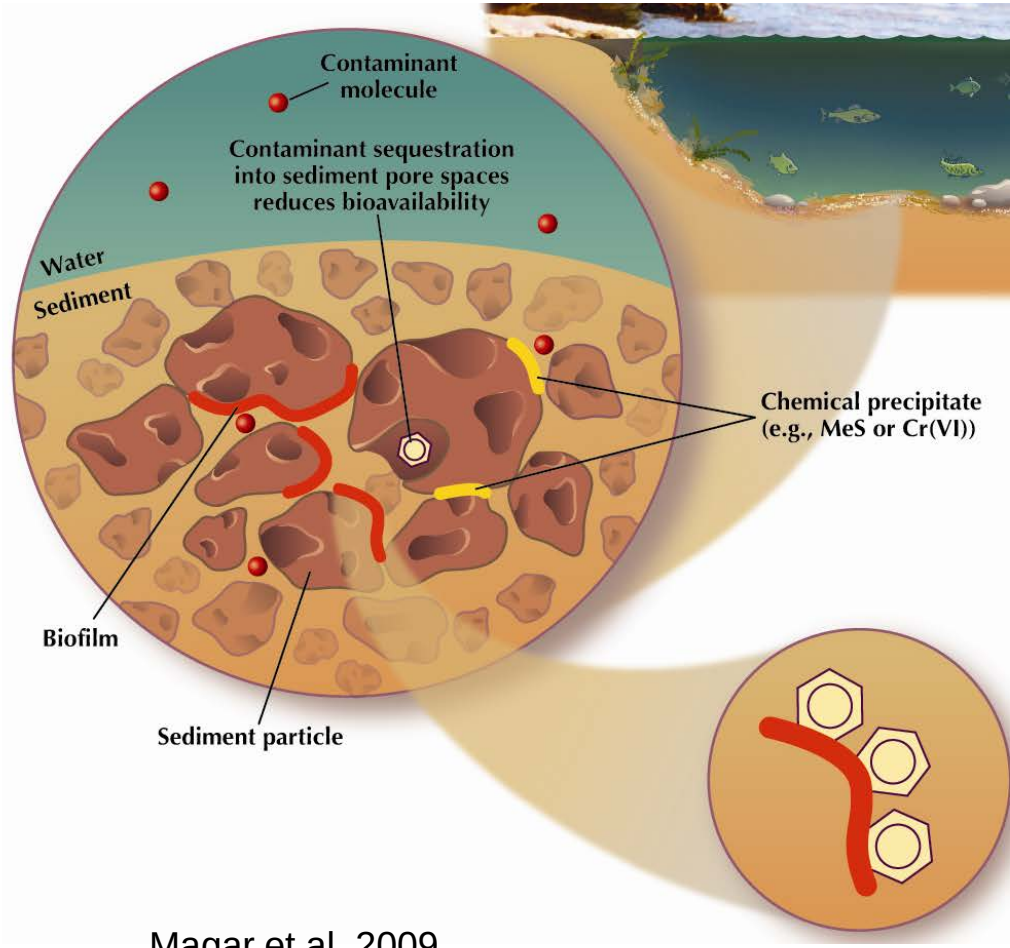
Magar et al. 2009

Sediment – Contaminant Dynamics

- All sediments aren't created equal…
- they vary in potential to drive contaminant uptake.



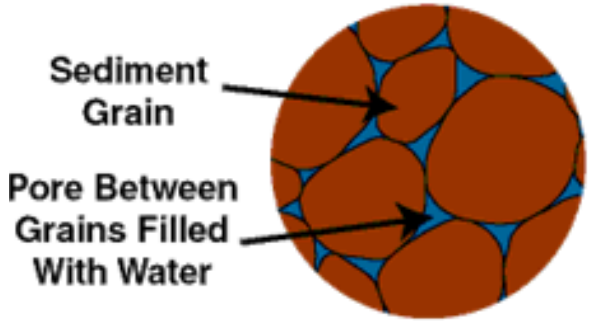
Gosh 2003



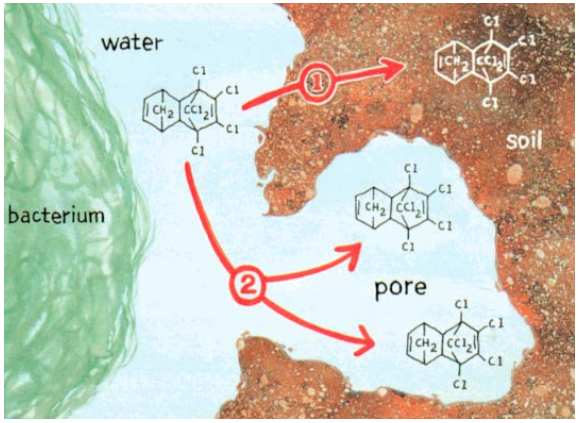
Magar et al. 2009

Terms

- Porewater (interstitial water)
  - Water residing in the pore space of sediments.



USGS.gov



Alexander, 2000. ES&T 34: 4259-4265.

- Bioavailability
  - The individual physical, chemical, and biological interactions that determine exposure of organisms to chemicals associated with soils and sediments.

Bioavailability Driving Exposures and Effects

- "Only a portion of the sediment-bound contamination is bioavailable, and there is no simple way of determining the available fraction through the use of extractants"
- "For several kinds of pollutants the interstitial water fraction has been shown to be most available to the benthos" (Swartz and Lee, 1980)

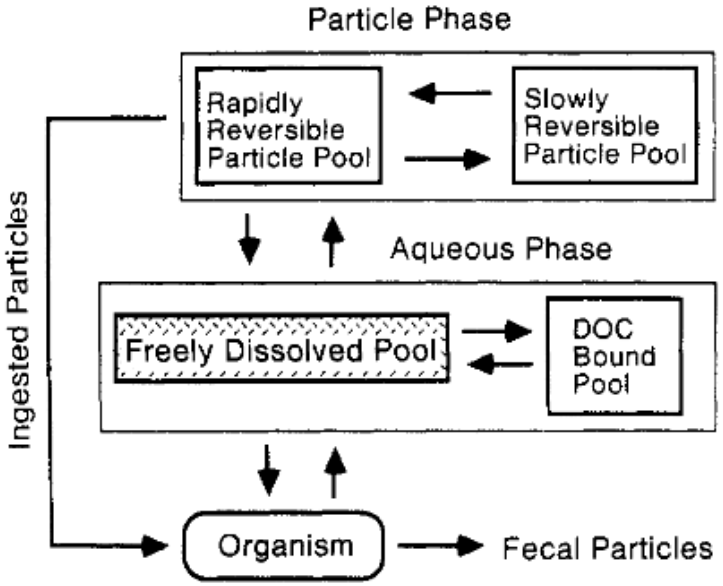
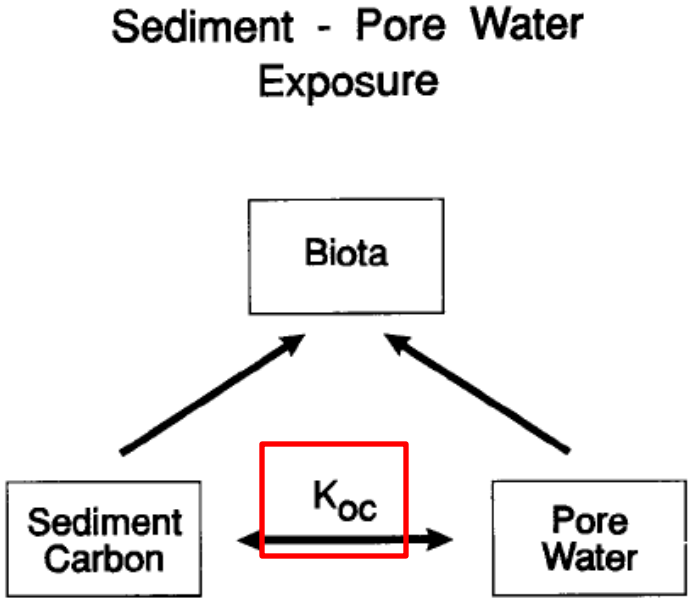


Figure 6. Conceptual model for accumulation of sediment-associated contaminants.

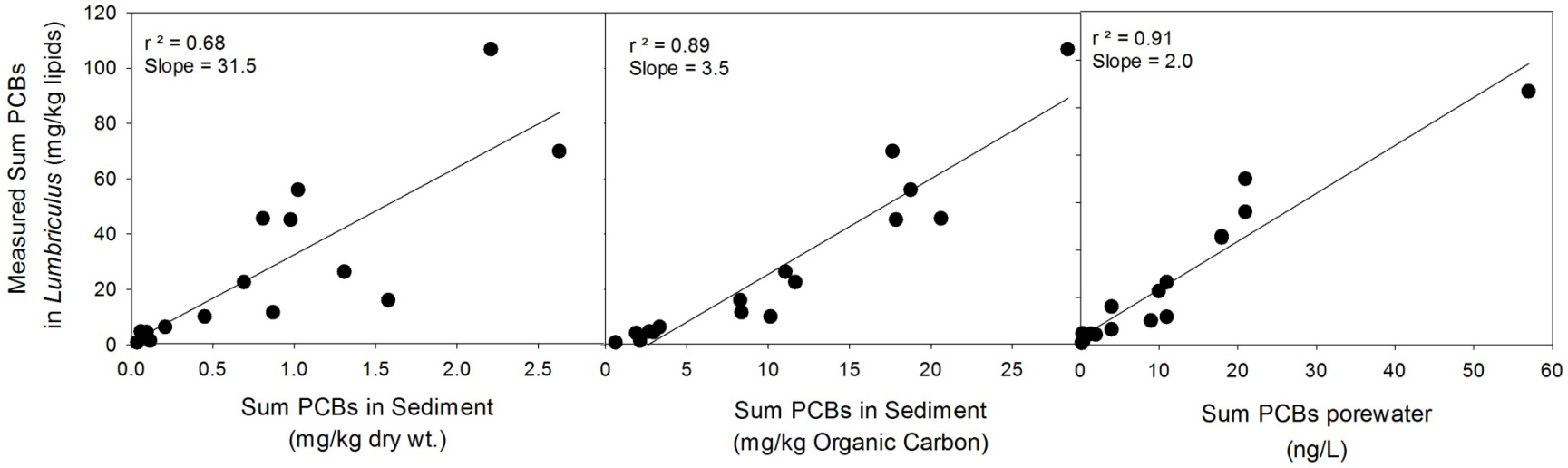
Landrum 1989, ES&T 23:588



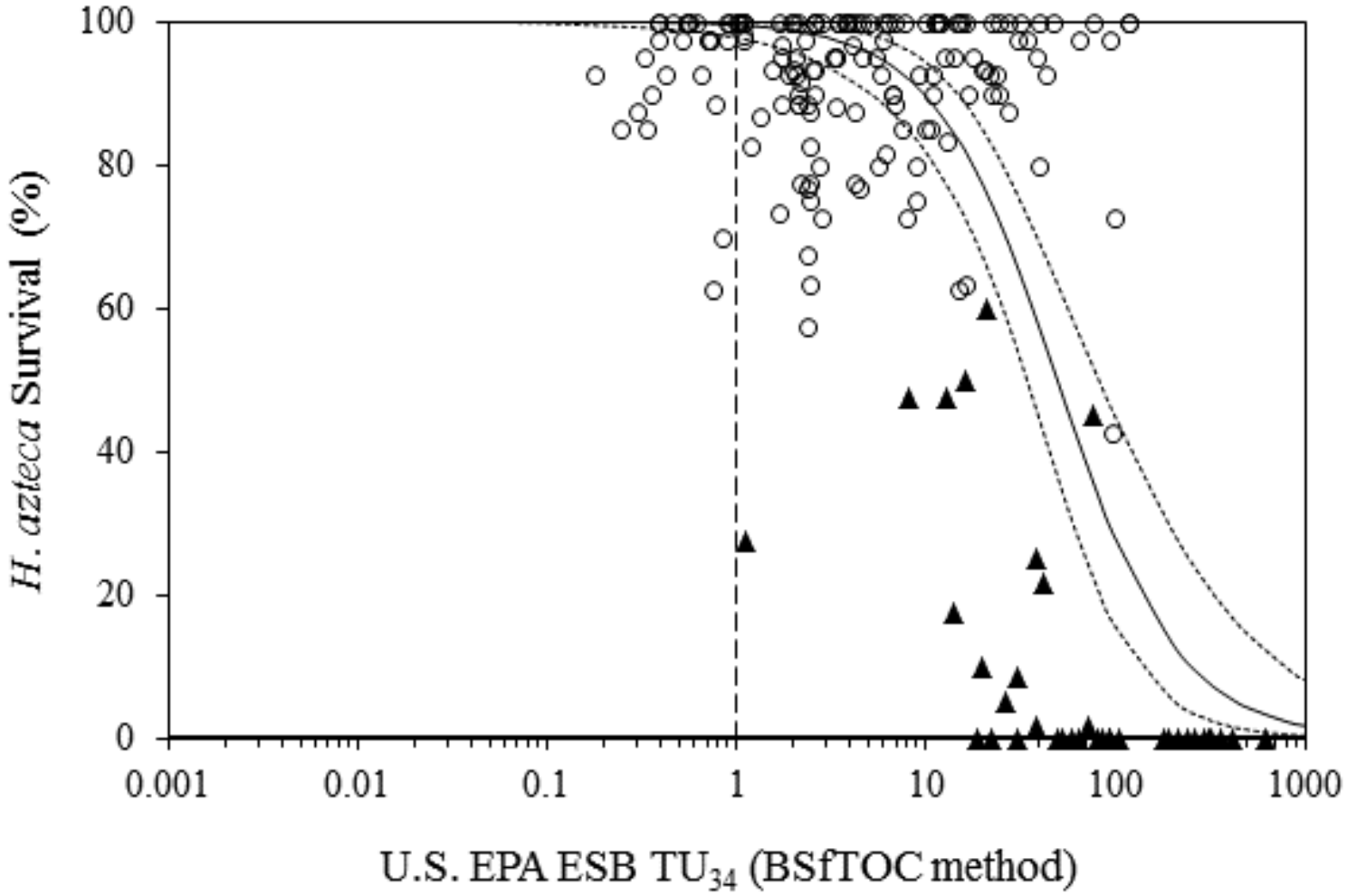
DiToro 1991, ET&C 10:1541

Bioavailability Driving Exposures and Effects

- Lack of concordance between toxicity and bioaccumulation and contaminant concentrations in bulk sediment.

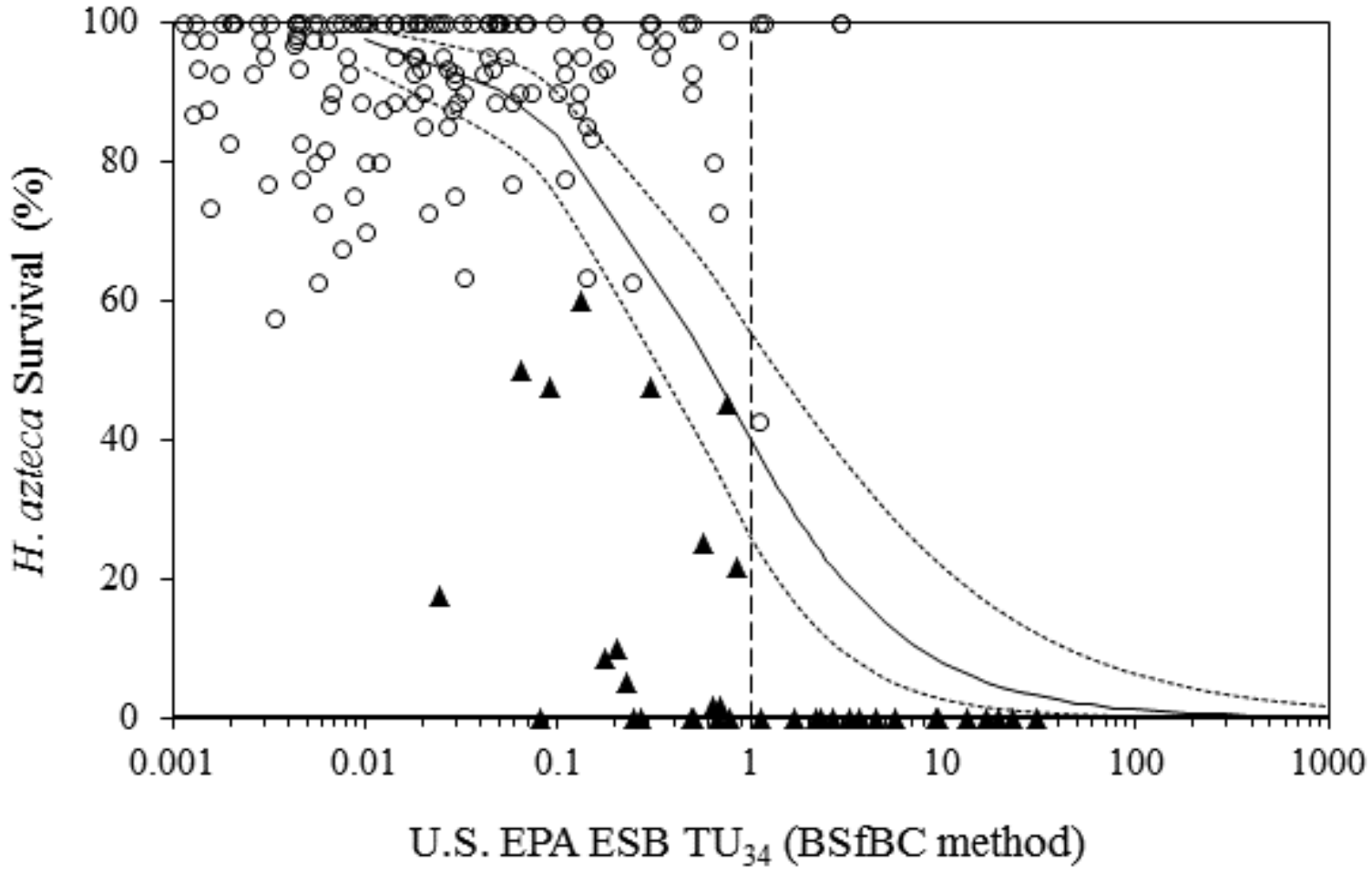


Using EqP with lit. Koc and sediment PAH-34 *grossly* over-predicts mortality, and does not separate toxic from non-toxic sediments.



Courtesy of Steve Hawthorne, Univ North Dakota

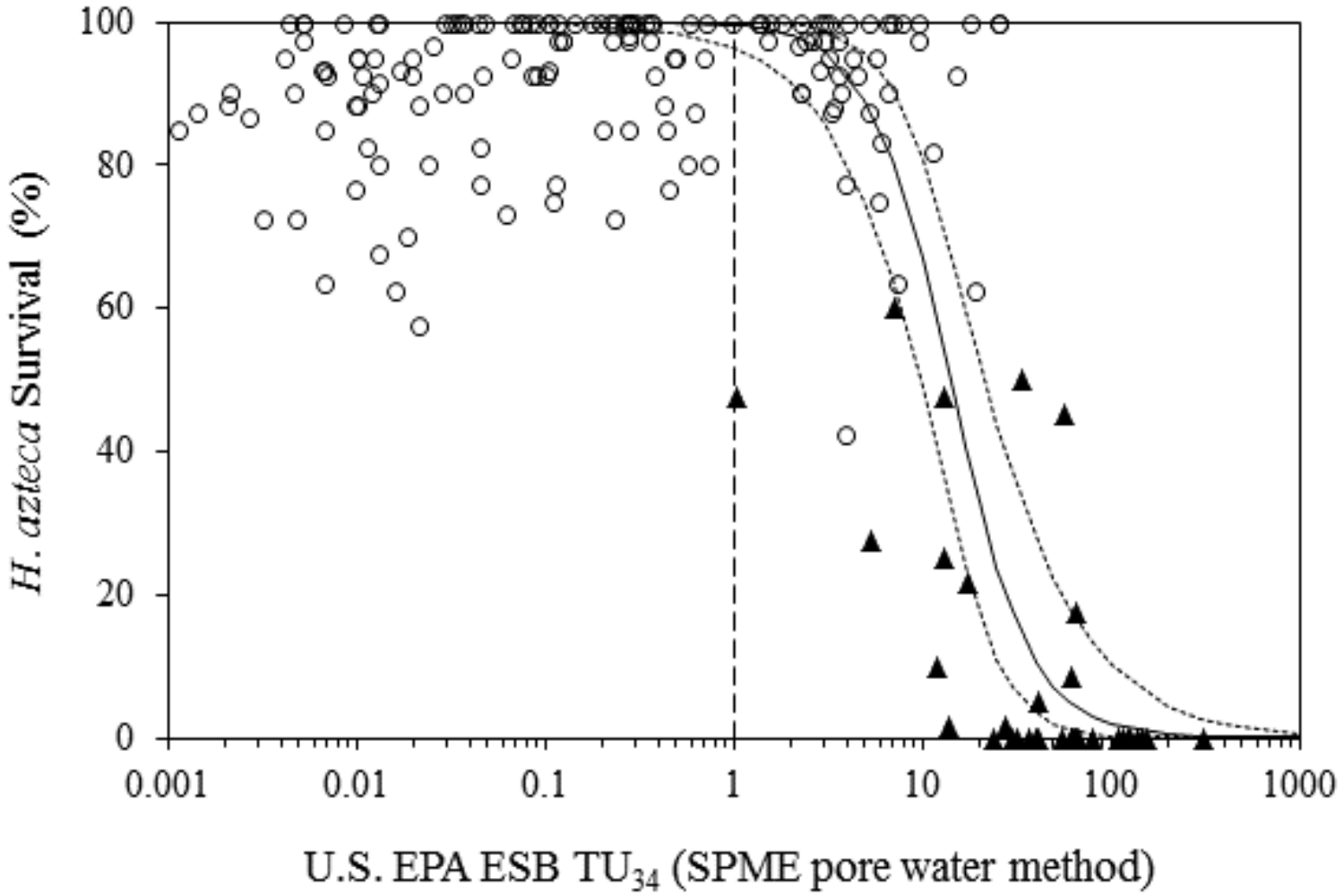
The two carbon (Koc/K_{BC}) model and sediment PAH-34 *grossly* under-predicts mortality, and does not separate toxic from non-toxic sediments.



Courtesy of Steve Hawthorne, Univ North Dakota

log K_{BC}=0.6997 log Kow + 2.822, Koelmans, 2006

Measured freely-dissolved PAH-34 greatly improve mortality predictions, while still being conservative.

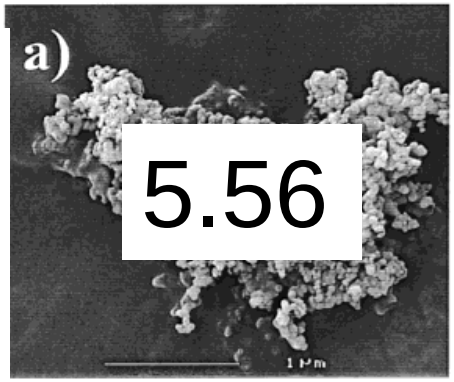


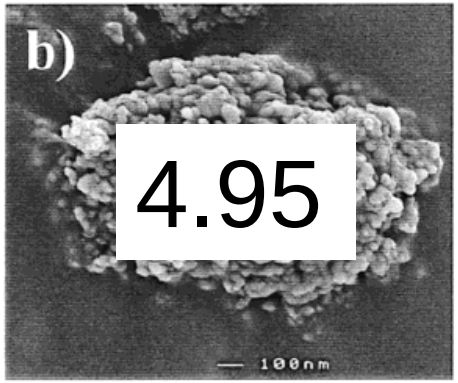
Courtesy of Steve Hawthorne, Univ North Dakota

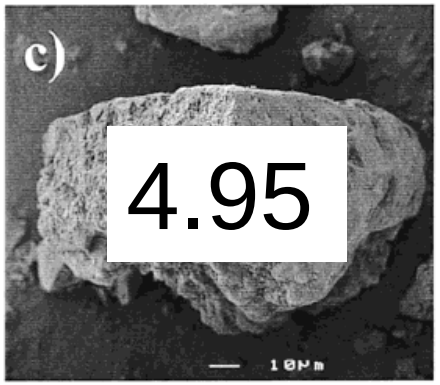
PCB-18 (2,2',4) Log Kow: 5.24

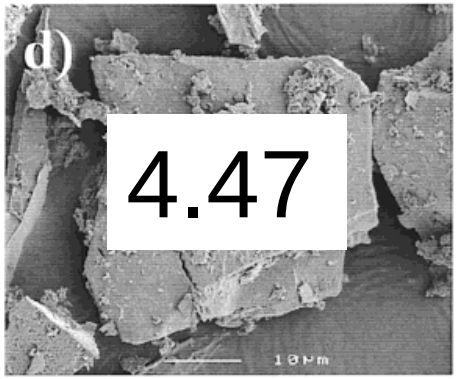
Compared to Koc of :

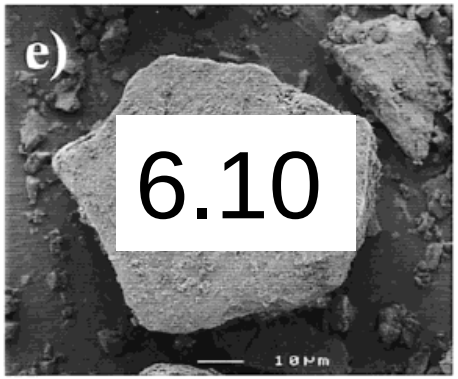
a) Traffic soot
b) Oil soot
c) Wood soot
d) Coal soot
e) Coal
f) Charcoal
g) Flyash
h) Activated carbon
i) Graphite

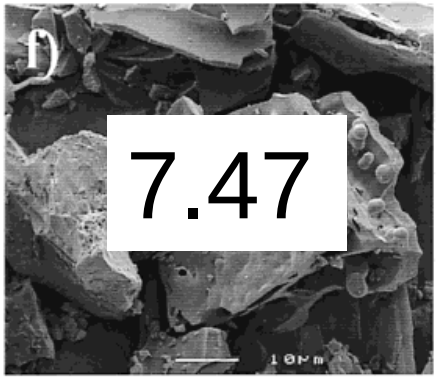


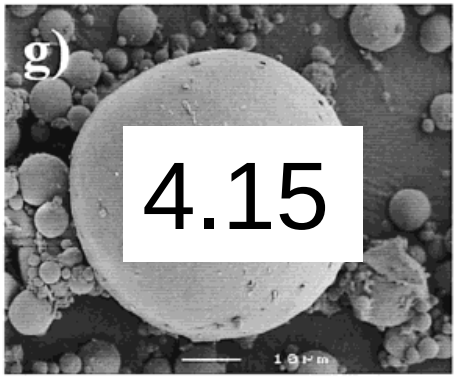


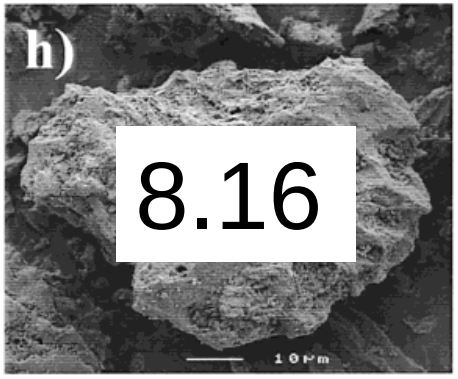


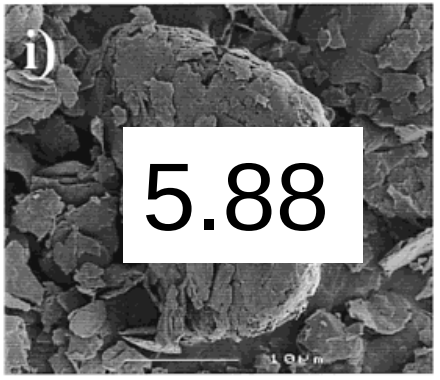






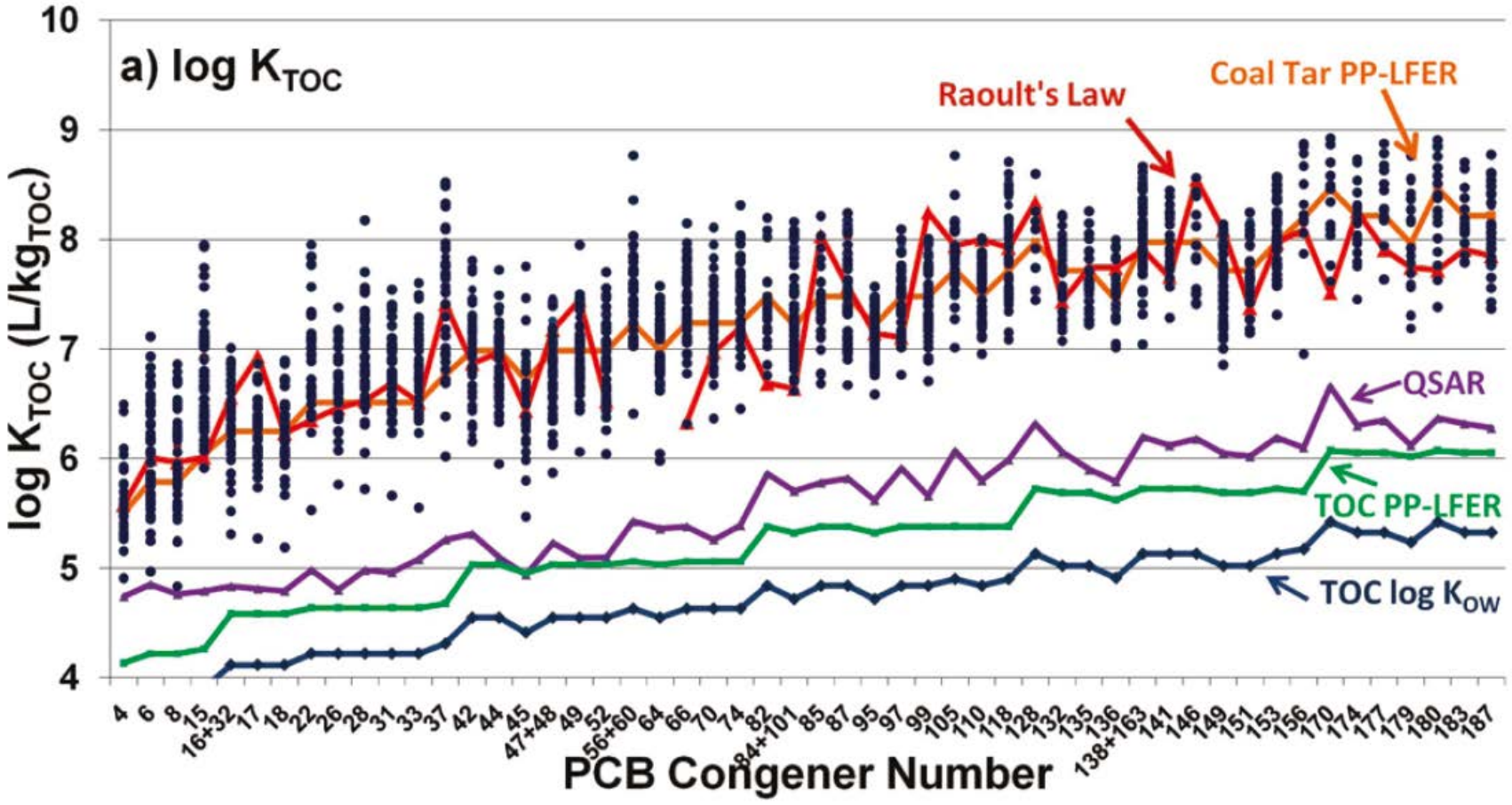






Jonker and Koelmans. 2002

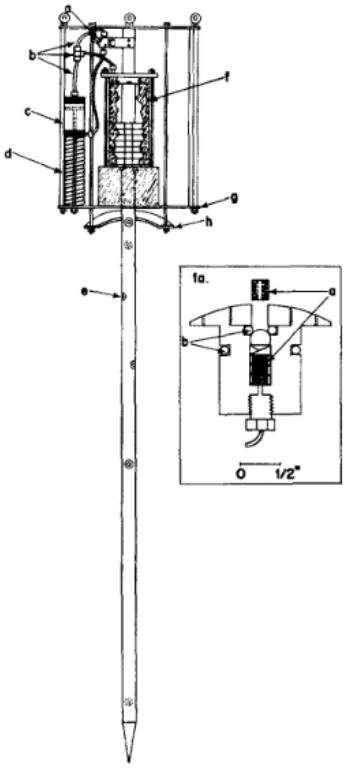
Variation in Contaminant Partitioning



Hawthorne et al. 2011

Porewater Sampling

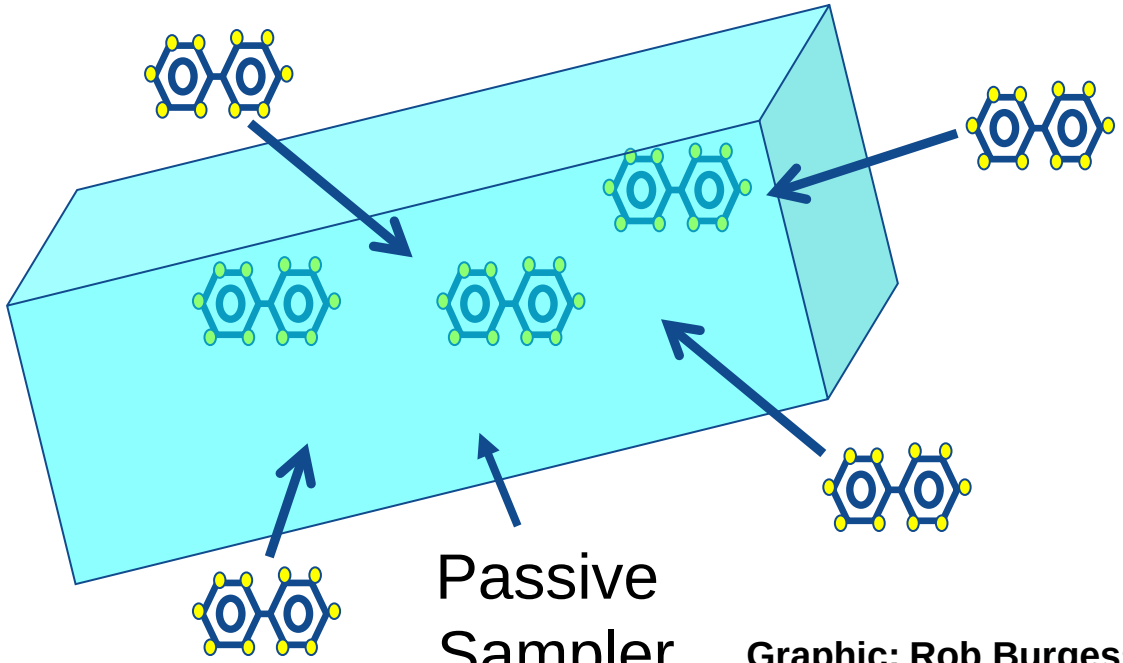
- Importance long recognized.
  - Variety of techniques: squeezing, centrifugation, leaching, filtering, direct sampling
  - Issues
    - sampling altering chemistry
    - including DOC- and POC-associated contaminants
  - Need to measure freely-dissolved fraction
  - More detail in Mark Cantwell's Presentation



Sayles et al. 1976

Passive Samplers

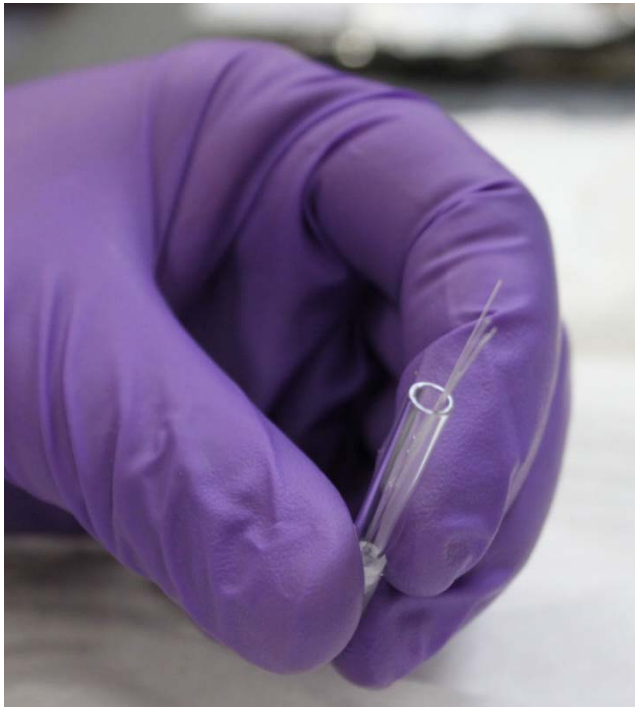
- Accumulate freely-dissolved organic contaminants from surrounding water into a solid phase.
- Contaminant concentrations of the samplers are measured.
- Circumvent problems associated with colloids, rapid- and slow-desorbing contaminants, and accounting for carbon content and variation.



Graphic: Rob Burgess, EPA-ORD

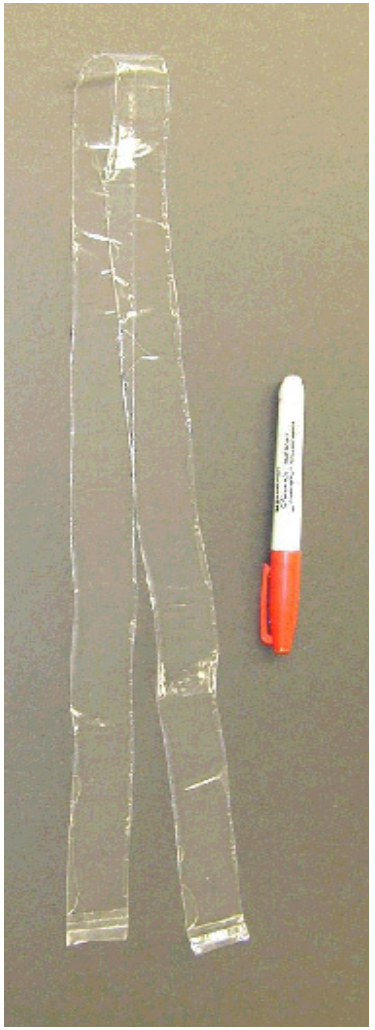
Diversity of Passive Samplers

SPME
solid phase microextraction



PED
polyethylene device

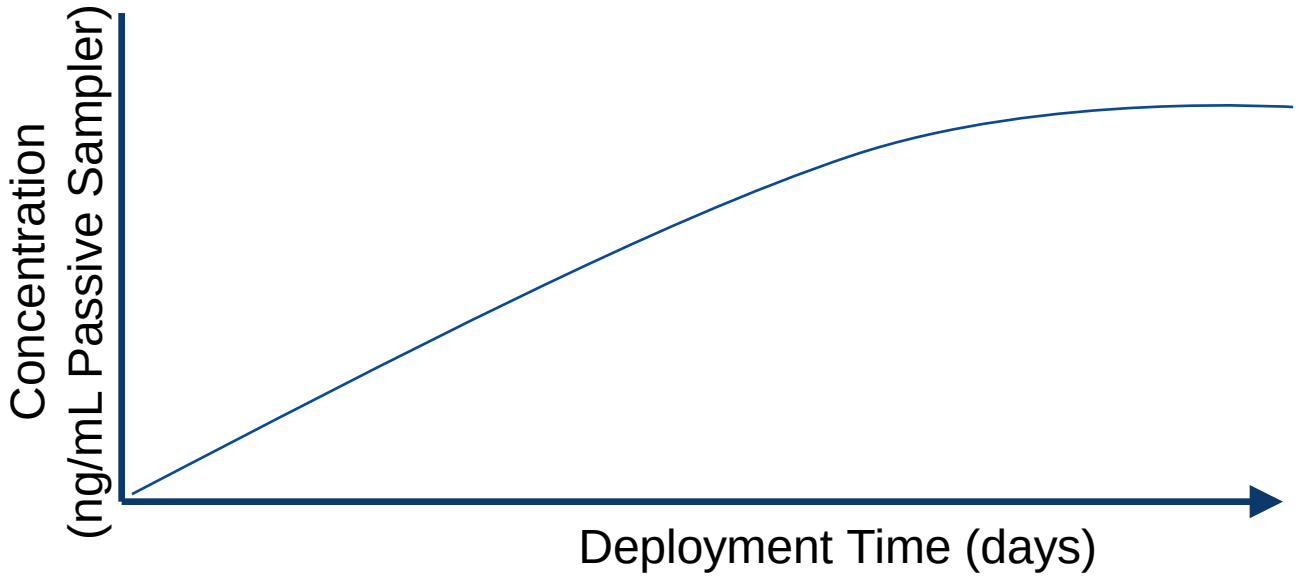
SPMD
semi-permeable membrane devices



POM
polyoxymethylene samplers

Prediction of Dissolved Concentration

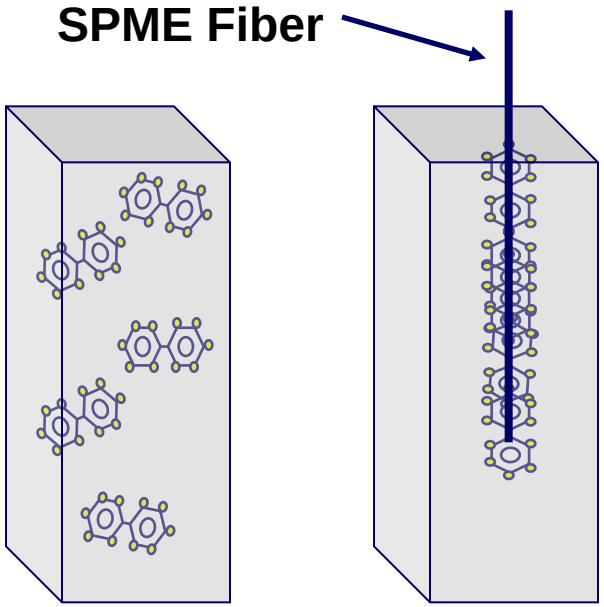
"Equilibrium" Sampling



$$C_{dissolved} = \frac{C_{passive\ sampler}}{K_{passive\ sampler/water}}$$

Quantification of Dissolved Concentration

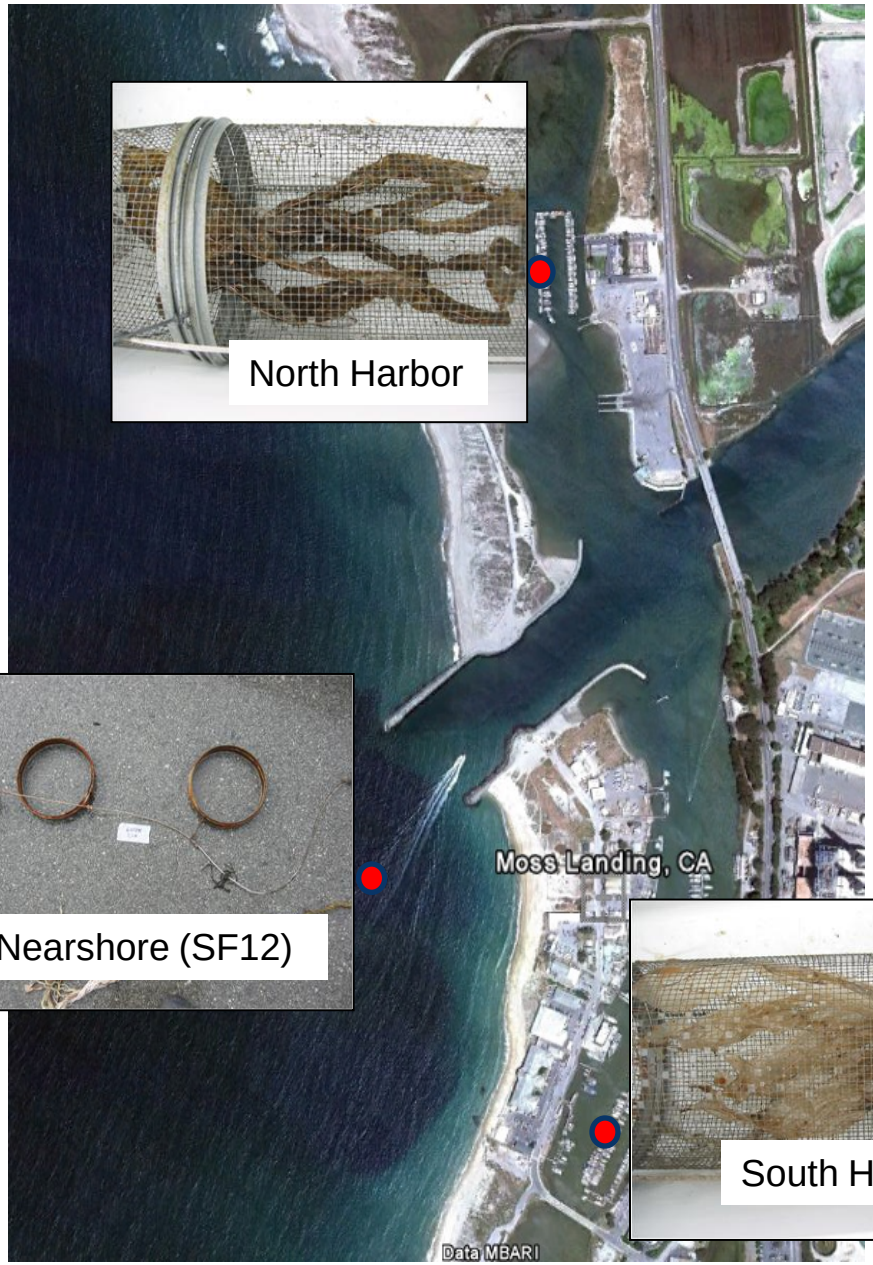
"Depletive" Sampling



~1.5 mL porewater

Courtesy of Joseph Kreitinger, USACE

Water Column Contaminant Analysis

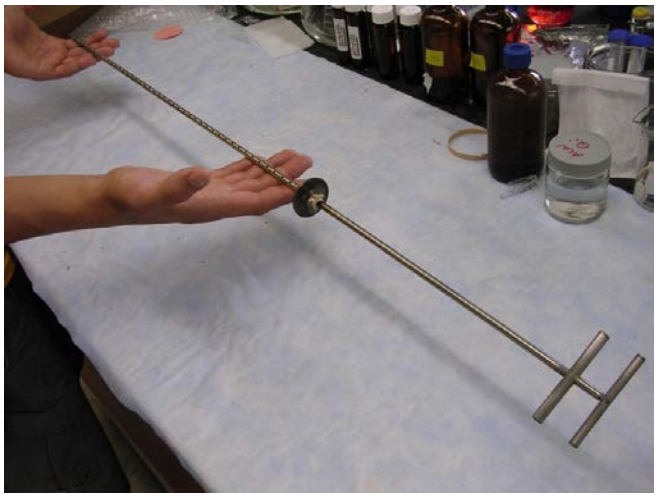


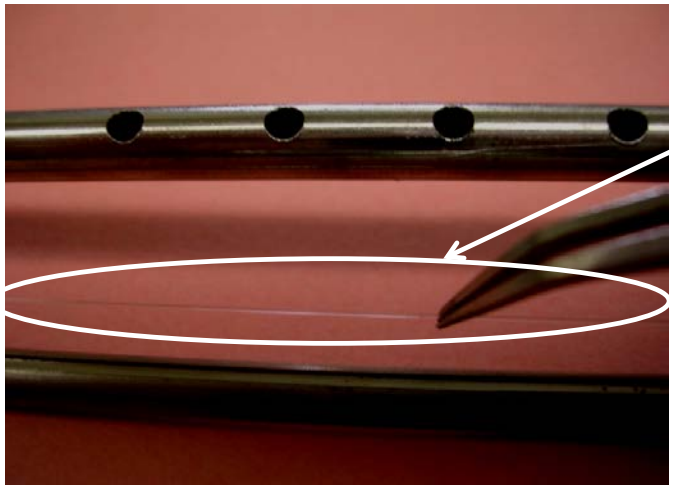
Area	Total DDx (ng/L)
North Harbor	0.2
South Harbor	1.5
Nearshore (SF-12)	Not recovered

Conventional Sampling was Non-detect

- "Freely dissolved" DDx concentration in surface water.
  - Nature and Extent
  - Relative Contamination
  - Exposure Assessment
  - Inclusion in food web modeling

Use of Passive Samplers in Cap Performance Monitoring



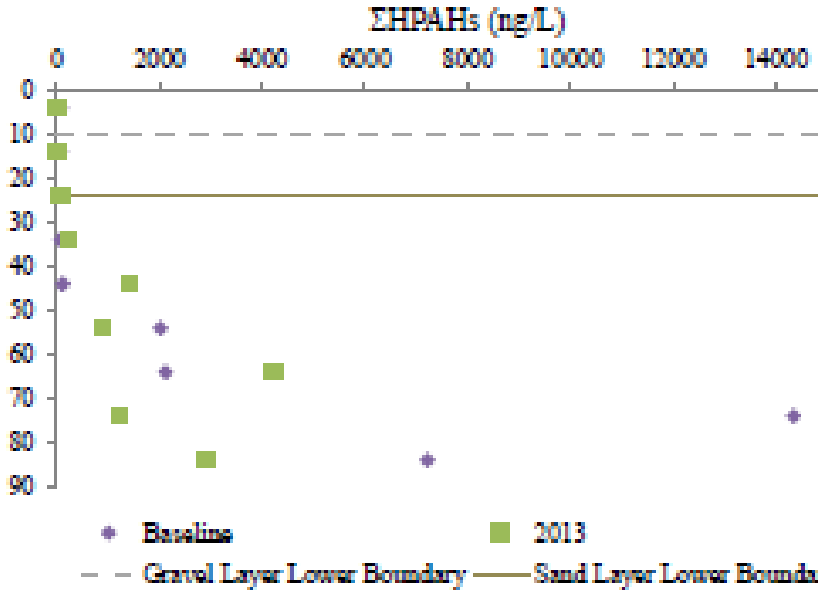


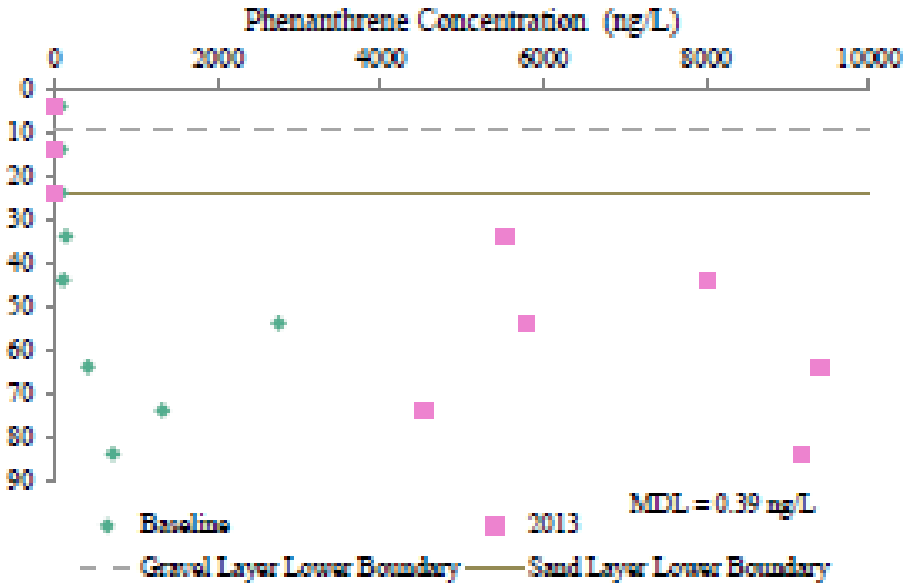
D. Reible, Texas Tech University

In-situ SPME Samplers and Associated Cores

PAH Profiles through Isolation Cap

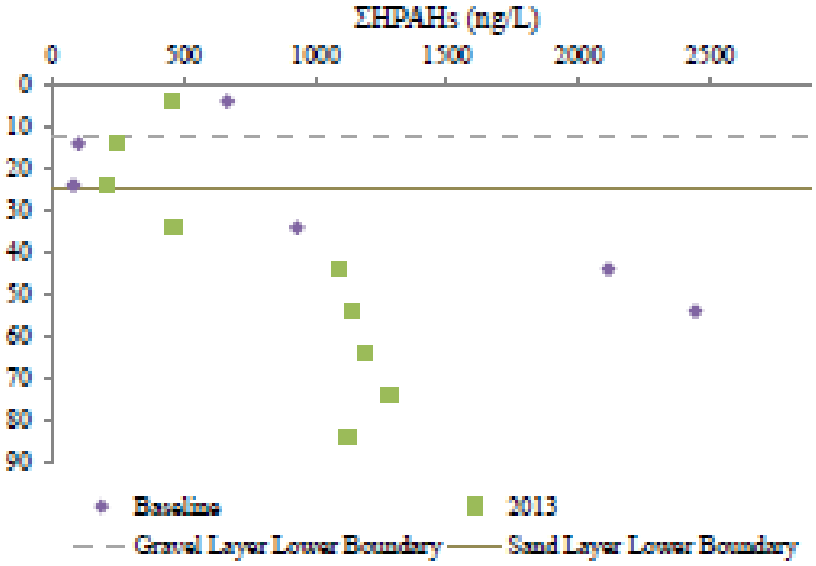
- Cap profile shows performance as expected (isolation)

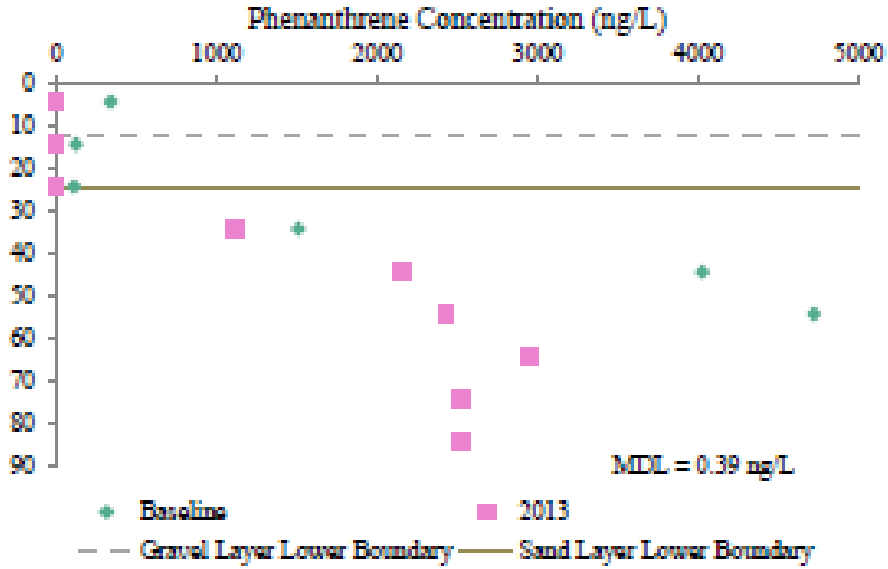




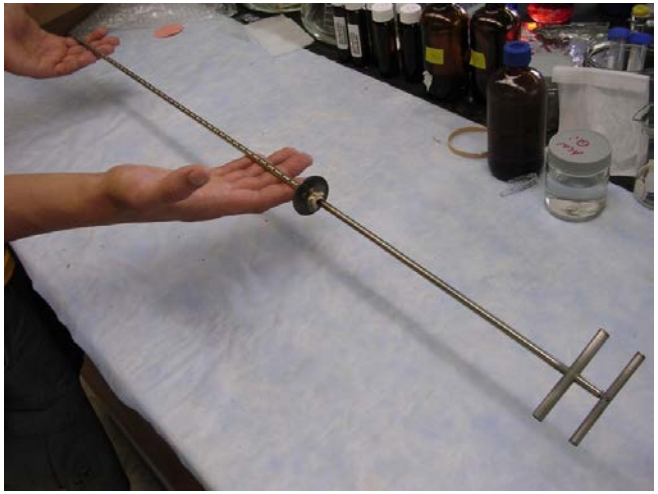
PAH Profiles through Isolation Cap

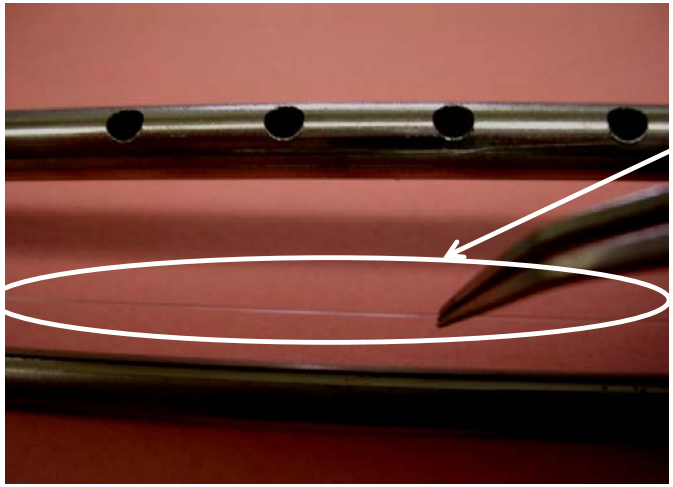
- Evidence of recontamination





Use of Passive Samplers in Cap Performance Monitoring

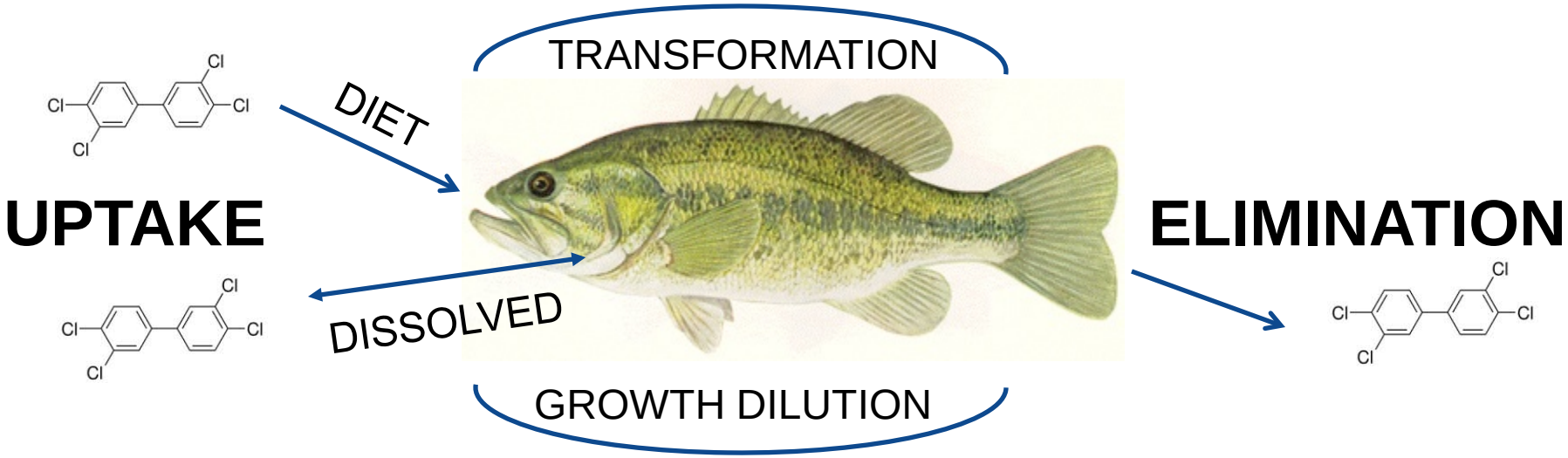




D. Reible, Texas Tech University

- Freely-dissolved PAH profiles through cap
  - Nature and extent
  - Changes over time
  - Cap performance
  - Recontamination
  - Source ID

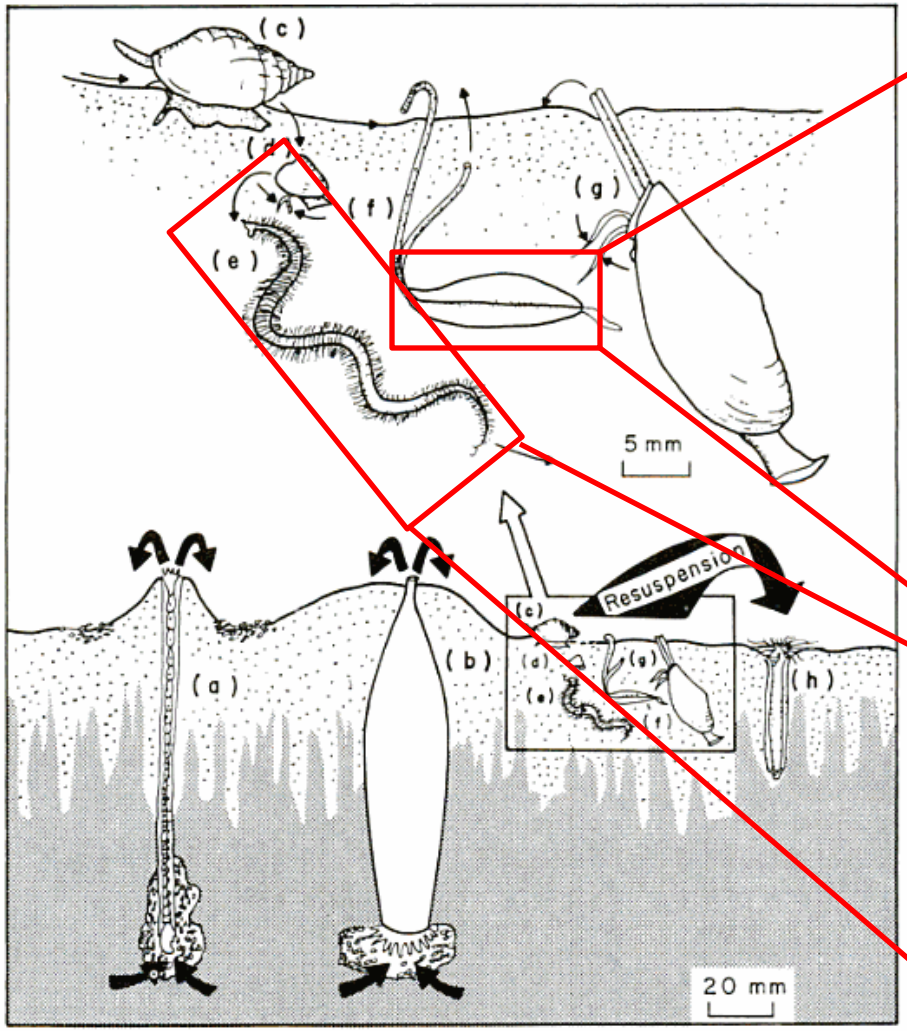
Surrogates for Aquatic Organisms?



Aquatic organisms vary in their interaction with the environment and physiology

- Gradient from sessile to highly mobile
- Large differences in food preference and feeding behavior
- Gradient from poor metabolizes (e.g., mussels) to efficient biotransformers (e.g., fish from contaminated environments)

Benthic Invertebrate Feeding Strategies

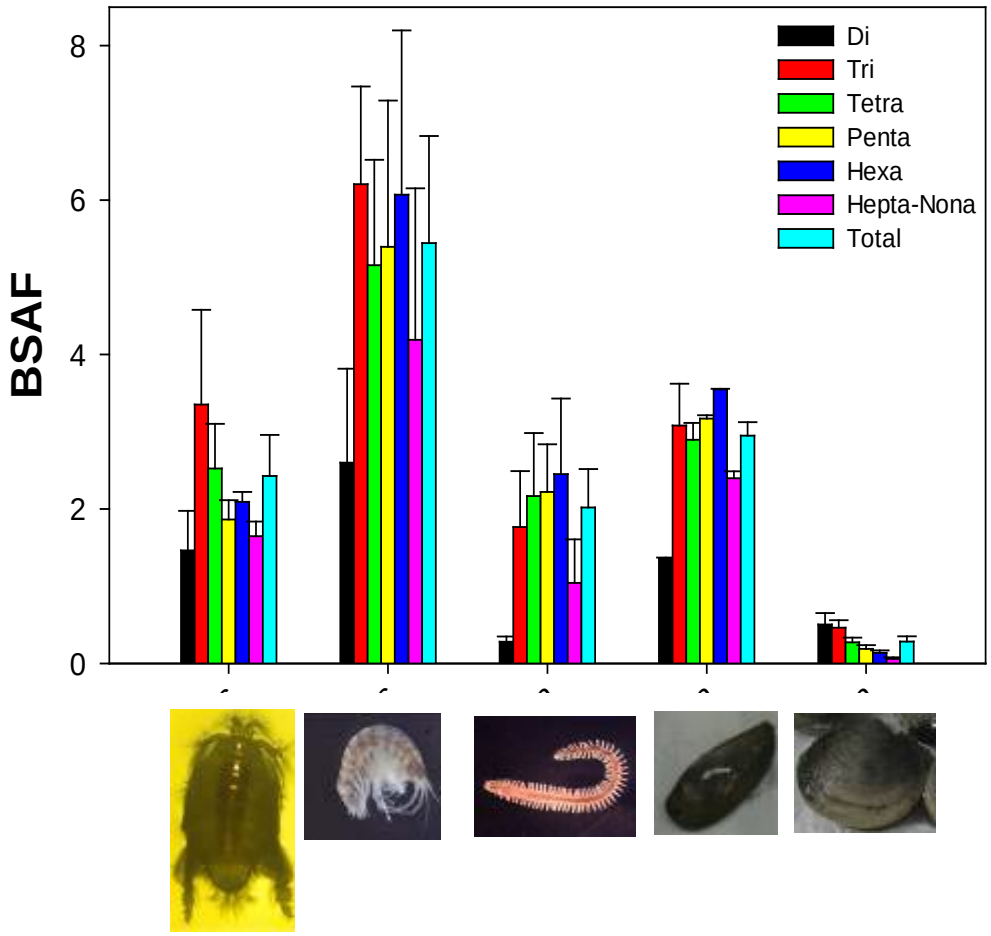


Rhoads 1974

Al Kennedy, USACE ERDC

Variability in Bioaccumulation Potential

- Comparison of PCB uptake among organisms with different feeding strategies.
- All organisms exposed to the same PCB-contaminated sediment.



Lotufo, USACE ERDC

Where Porewater/Bioavailability Assessments are Useful?

- Where bulk sediment concentrations aren't sufficient.
- To define
  - Nature and Extent of Contamination
  - Concentration-Toxicity Relationships
  - Definining Exposure Concentrations
    - "Truly-dissolved" pore- or surface-water
    - Flux from sediment bed
  - Remedial Effectiveness Evaluations

Questions

- gustavson.karl@epa.gov
  703-603-8753