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National Institute of Environmental Health Sciences

RISKeLearning

Bioavailability – Metals, Organics, and Use at Hazardous Waste Sites

June 11th, 2008 Session 2: "Bioavailability of Organic Compounds: Methods and Case Studies"

Dr. Edward Neuhauser, National Grid
Determining True PAH Bioavailability in Sediments Using Solid-Phase Microextraction (SPME)

Dr. Danny Reible, University of Texas at Austin
Defining the Availability and Mobility of Contaminants in Sediments

sbrp Superfund Basic Research Program
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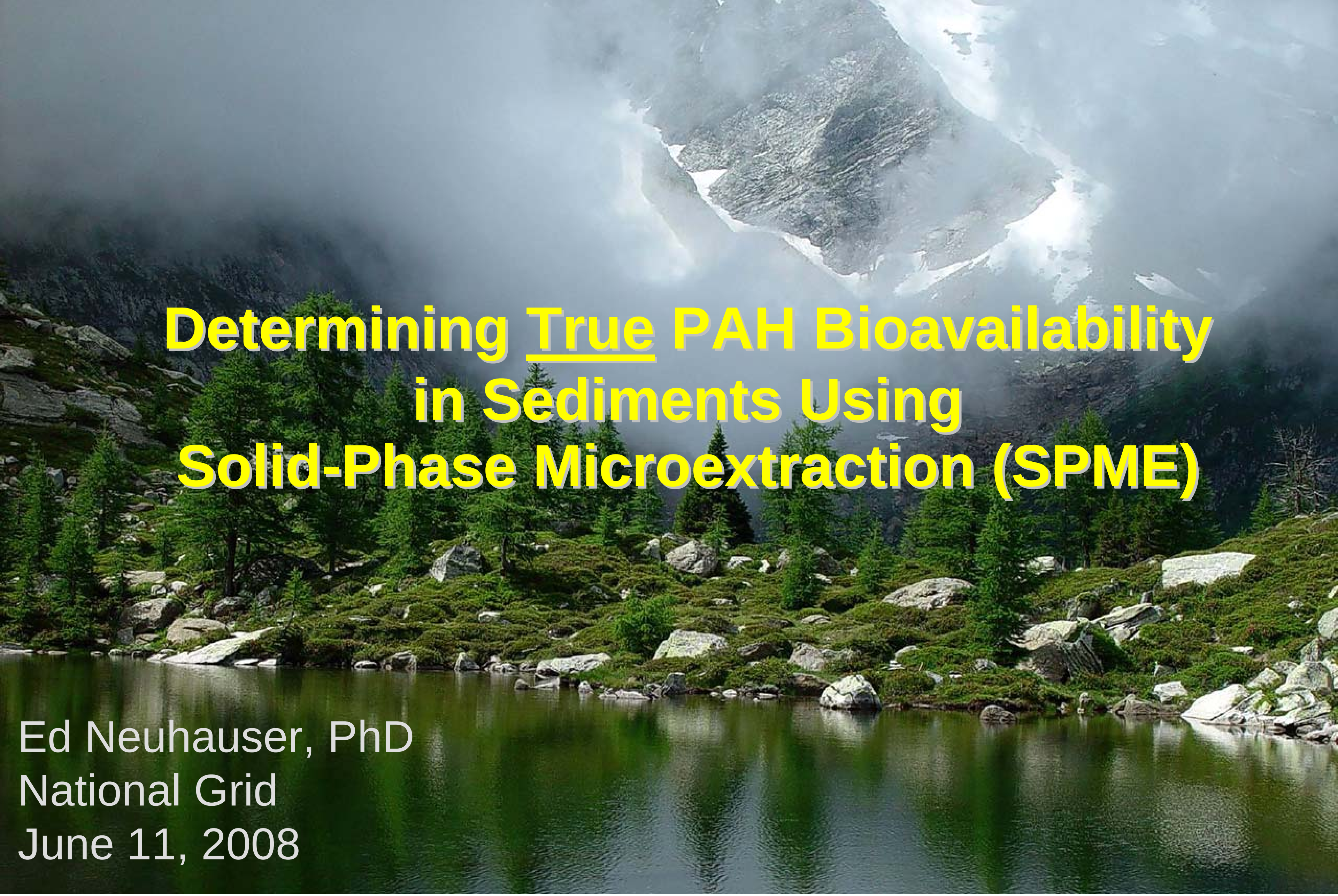


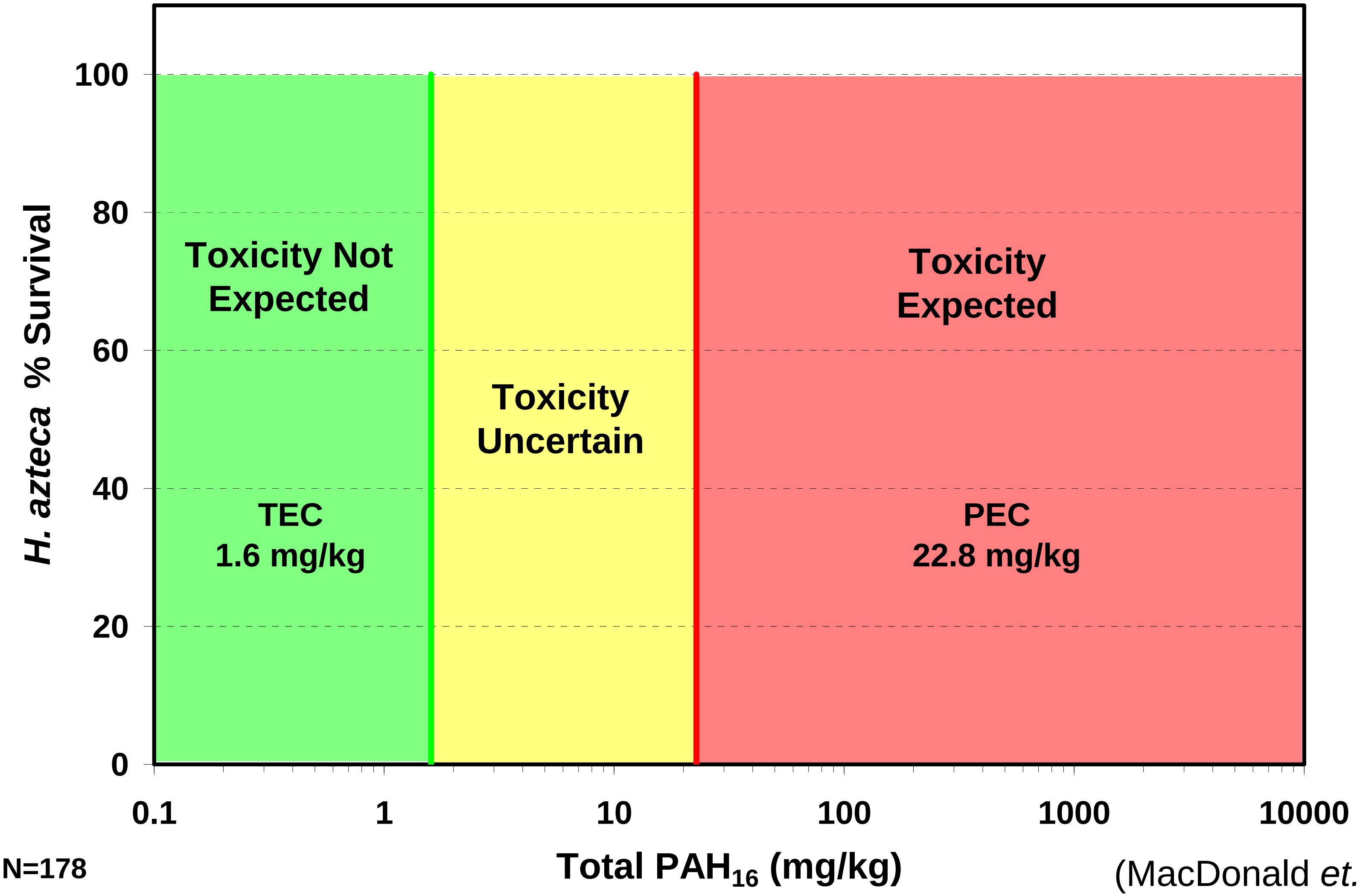
Determining True PAH Bioavailability in Sediments Using Solid-Phase Microextraction (SPME)

Ed Neuhauser, PhD
National Grid
June 11, 2008

Traditional Management Approaches Use NOAA Sediment Screening Criteria

	Total PAH_{16} (mg/kg)
MacDonald *et. al.* (2000) - Freshwater	
TEC – Threshold Effect Concentration	1.6
PEC – Probable Effect Concentration	22.8
Long *et. al.* (1998) - Marine	
ERL – Effects Range Low	4.0
ERM – Effects Range Median	44.8

Total [PAH_{16}] Sediment Screening Approach



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(MacDonald *et. al.* 2000)

Pore Water [PAH_{34}] Provides True Bioavailability

- Porewater is "the most accurate indicator of bioavailable exposure concentration" (USEPA 2007)
- Solid-Phase Microextraction (SPME)
  - ✓ Applied to >240 sediment samples (precise)
  - ✓ Rapid – 60 minute cycle time
  - ✓ Small sample size:
    - ✓ ~ 20 ml of sediment
    - ✓ ~ 1.5 ml of pore water
  - ✓ Low detection limit: ~ pg/mL (ppt) (sensitive)

(Hawthorne *et. al.* 2005)

SCBA Approach Builds Upon Existing EPA Framework

Measure 34 PAHs in Sediment (NOAA PAH_{34})

↓

Use Equilibrium Partitioning to Estimate Bioavailable PAH Concentrations

↓

Convert Bioavailable PAH Concentrations to Toxic Units ← SPME pore water PAH_{34} concentration

↓

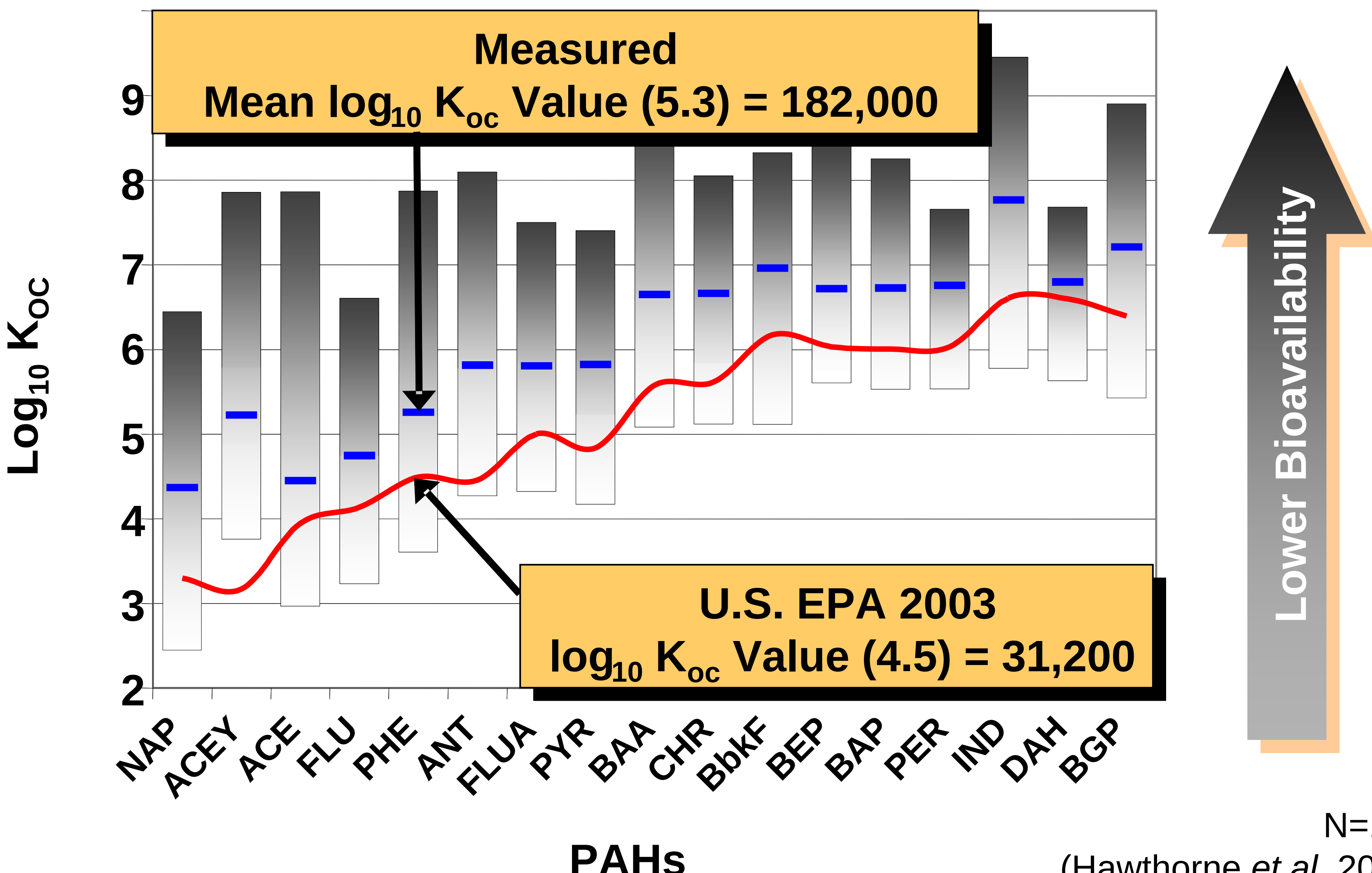
Sum PAH Toxic Units (TU_{34})

↓

If $TU_{34} > 1$, Toxicity is Expected

U.S. EPA (2007 Draft) *Evaluating ecological risk to invertebrate receptors from PAHs in sediments at hazardous waste sites*

K_{oc} Values Vary 1,000-fold in Sediments



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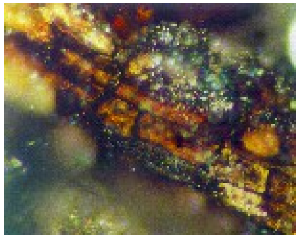
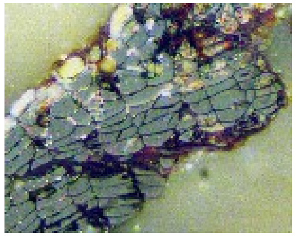
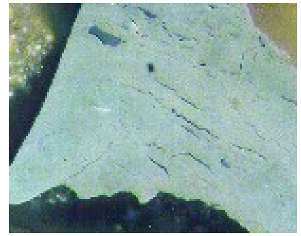
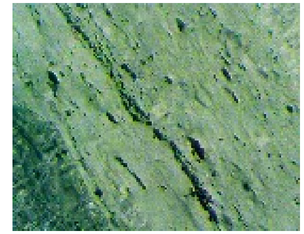
(Hawthorne *et al.* 2006)

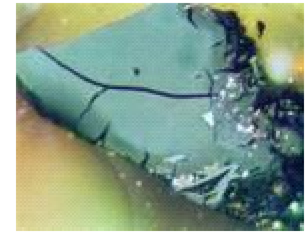
Urban River Sediments Contain Natural and Anthropogenic Carbon

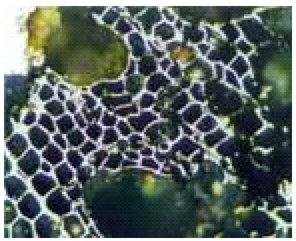

wood

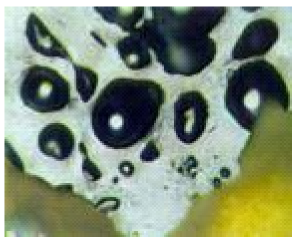

lignite

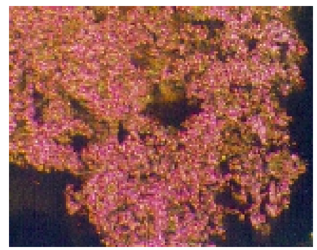

bituminous coal

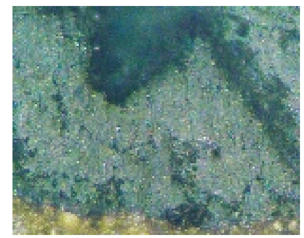

anthracite coal

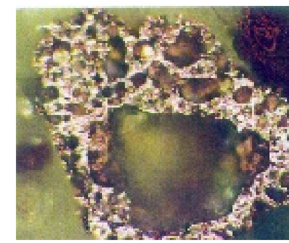

oxidized coal


charcoal


coke


soot carbon


coal tar pitch

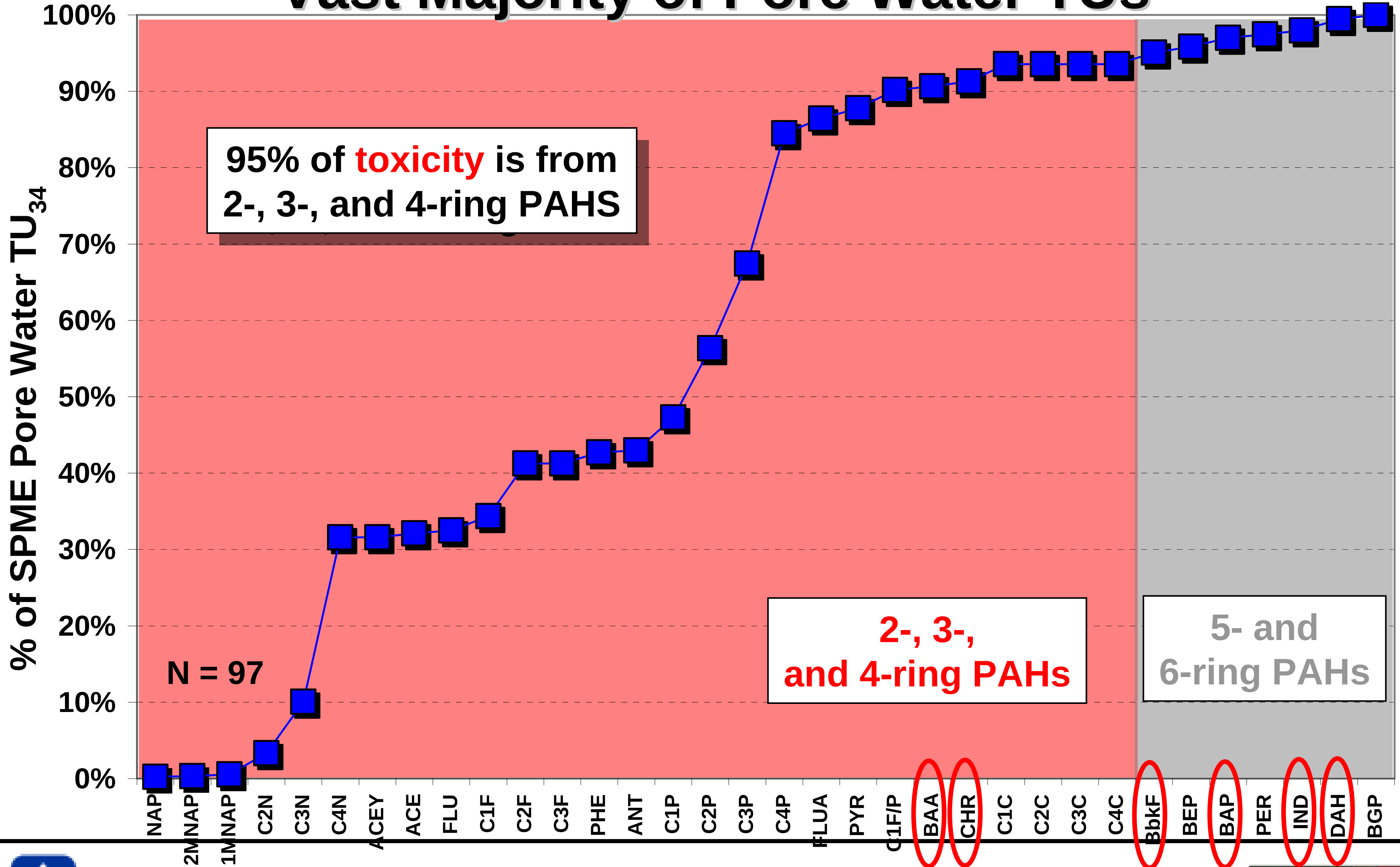

cenosphere

PAH binding (K_{oc}) is very different for different types of carbon.

Quantity and type of carbon are important!

(U. Ghosh *et al.* 2003)

Low and Mid-MW PAHs Account for the Vast Majority of Pore Water TUs

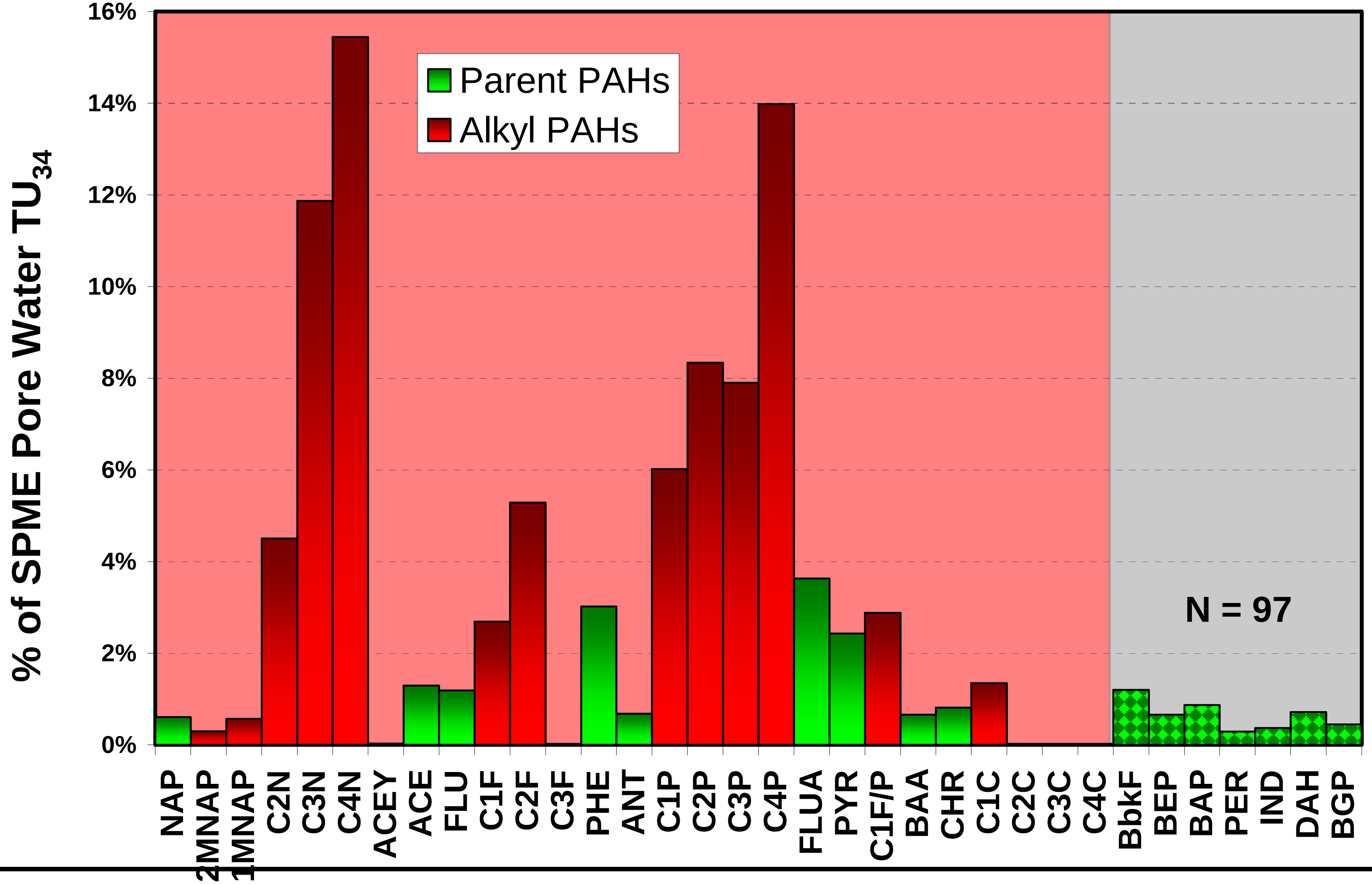


ALCOA

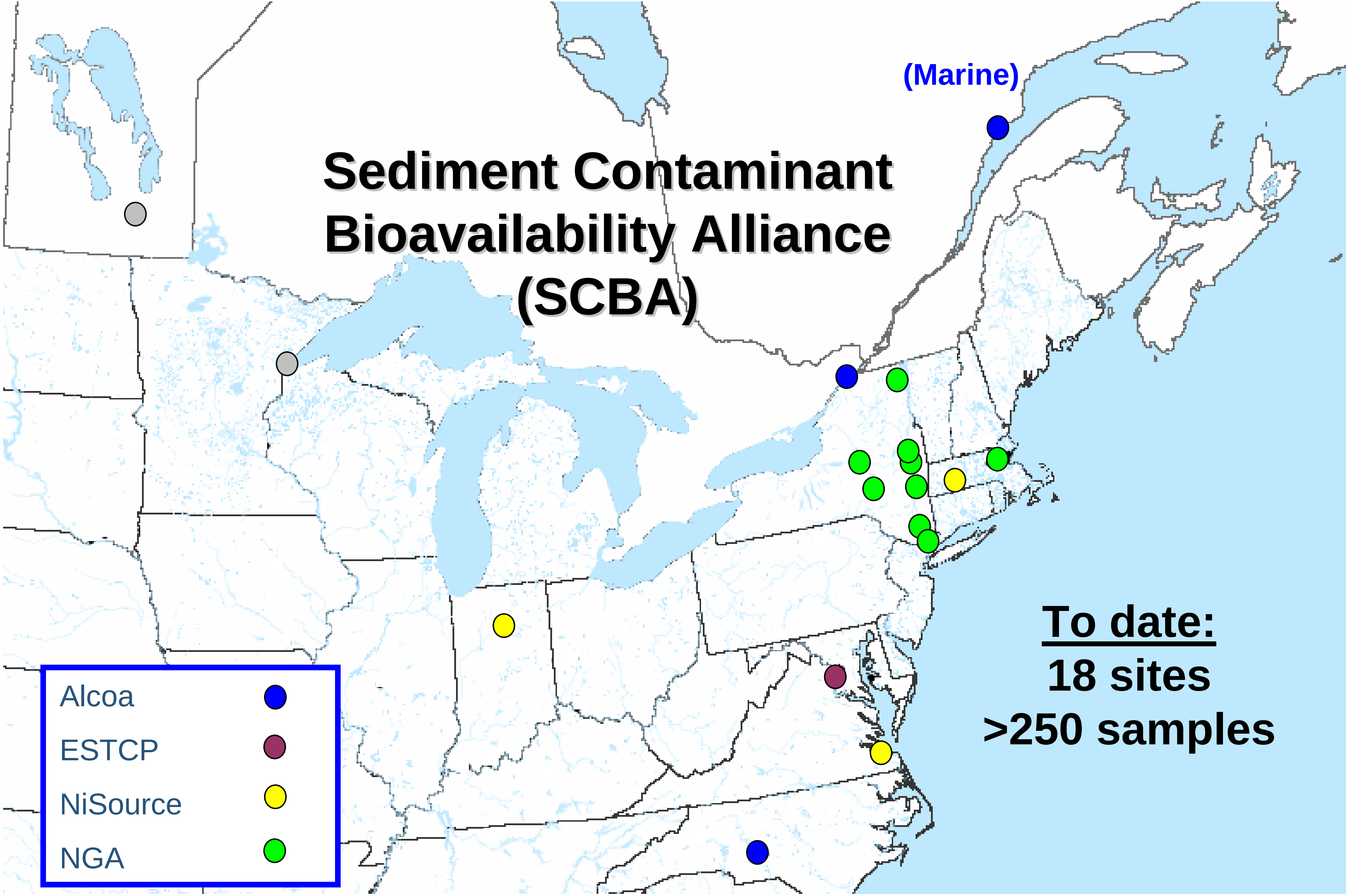
nationalgrid

SCBA

Alkylated PAHs Account for ~75% of Pore Water TUs



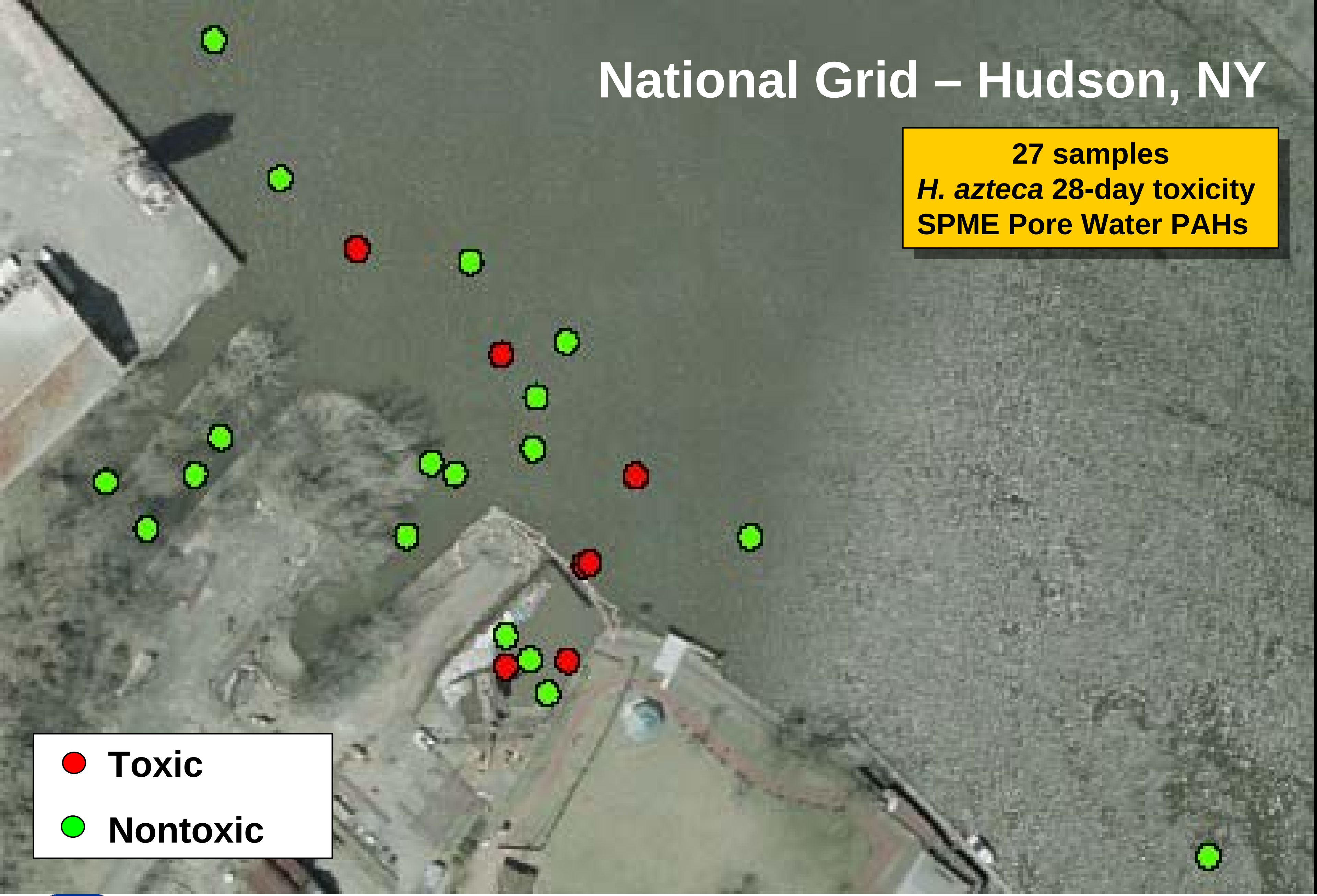
Sediment Contaminant Bioavailability Alliance (SCBA)



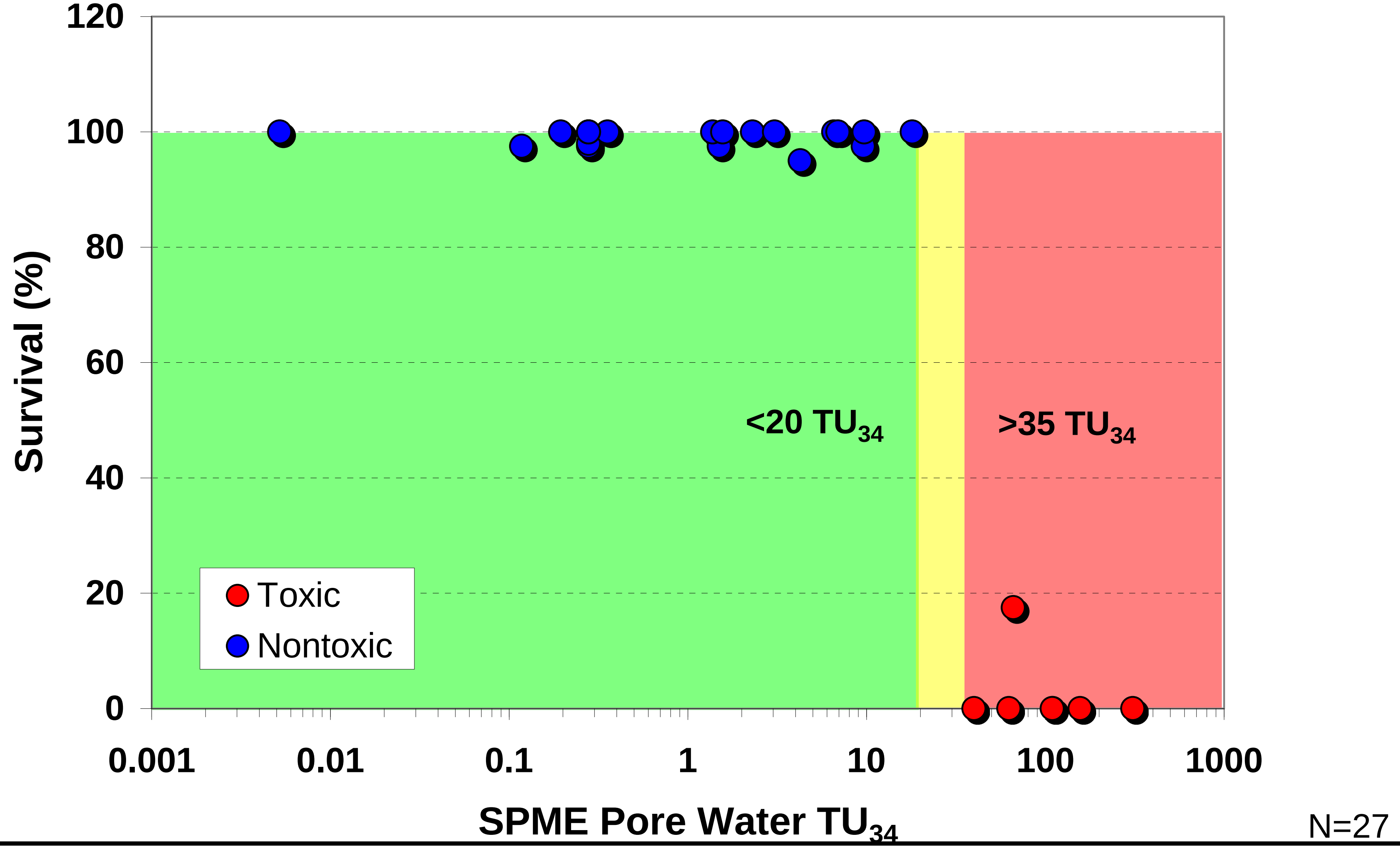
To date:
18 sites
>250 samples

National Grid – Hudson, NY

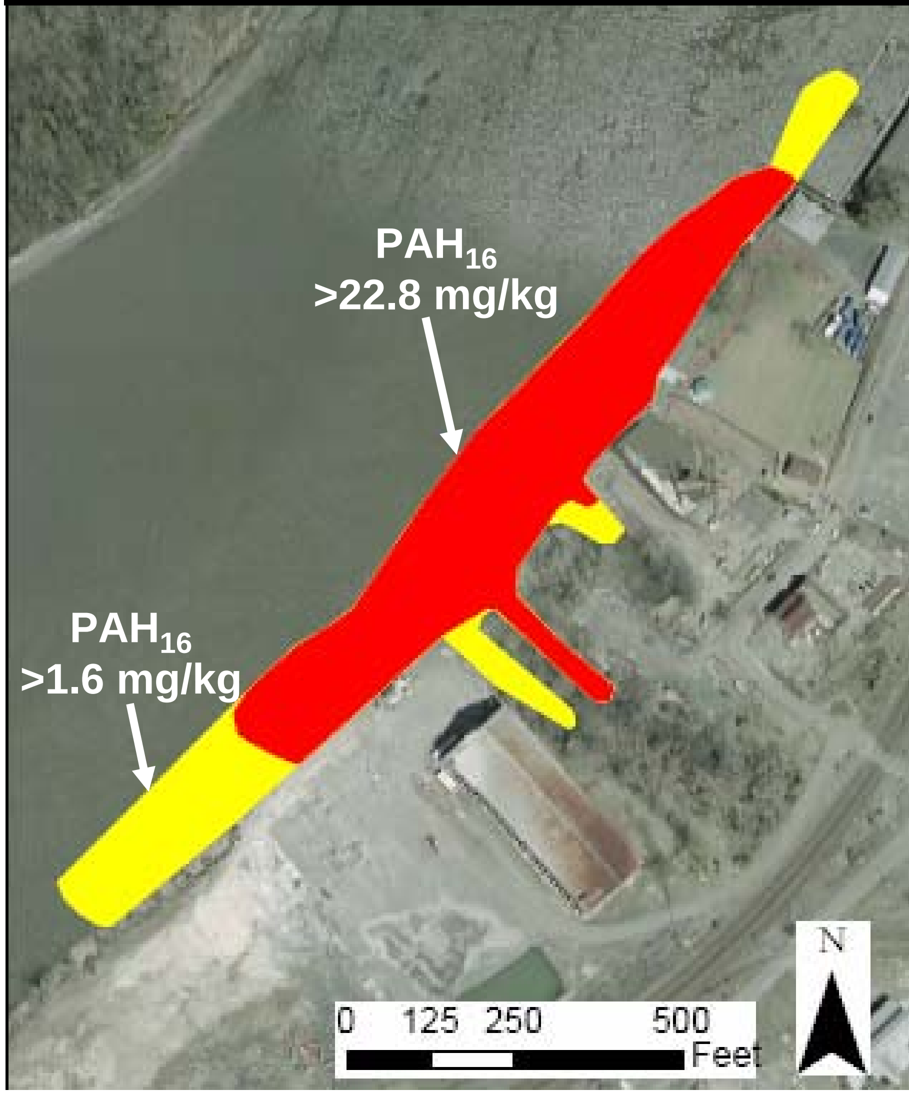
27 samples
H. azteca **28-day toxicity**
SPME Pore Water PAHs

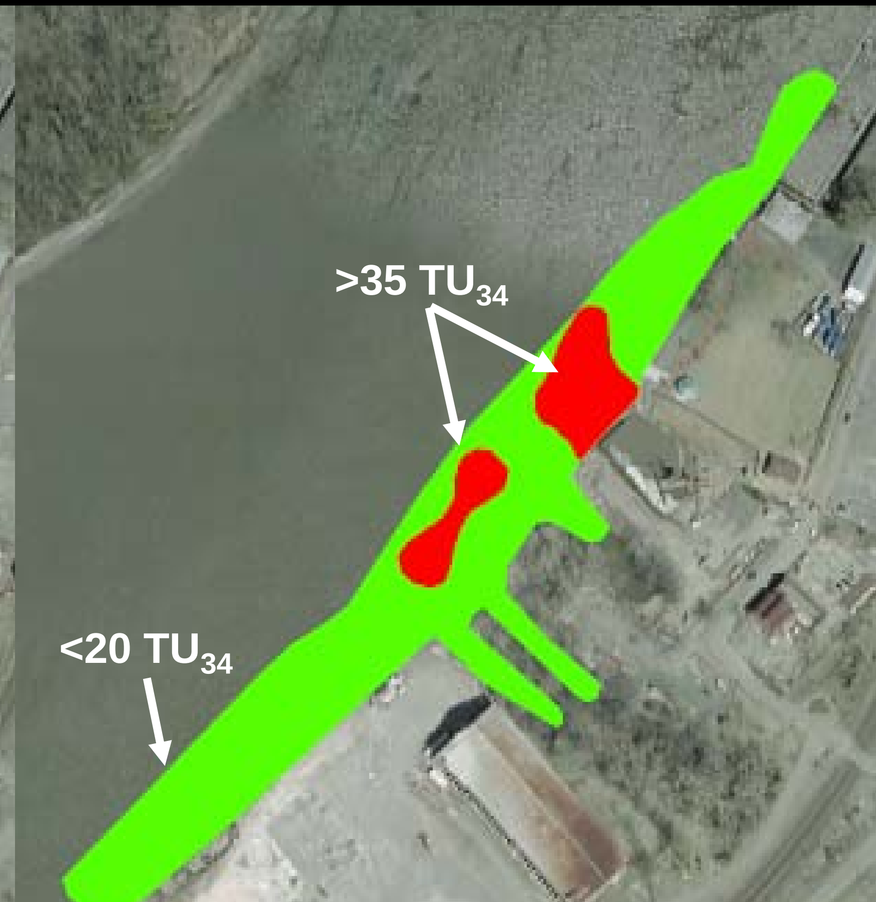


Hudson Site-Specific Dose-Response Provides an Accurate Characterization Tool



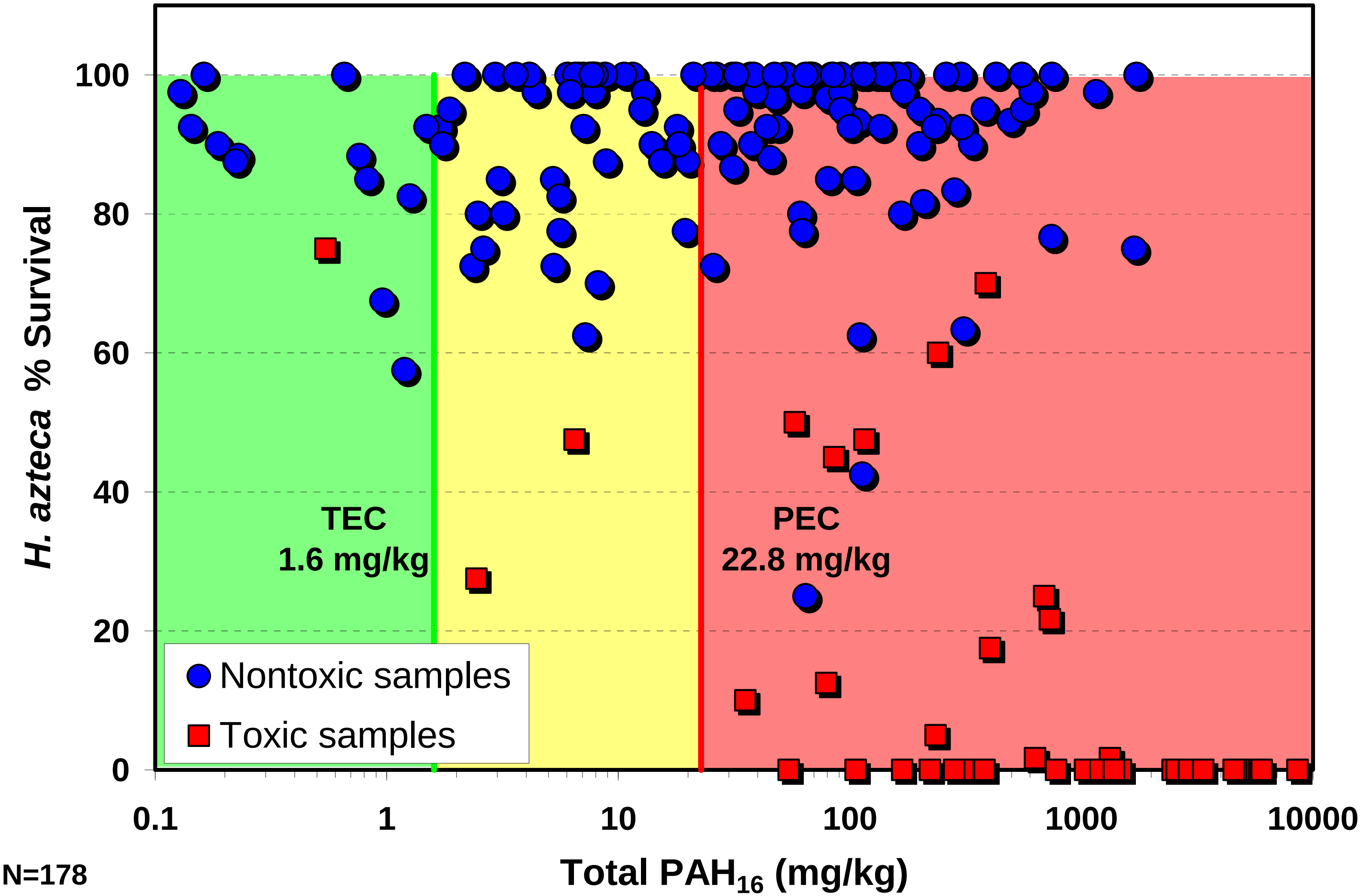
SPECIFICITY – Focused on Measured Toxicity





Provides accurate characterization tool

Total [PAH_{16}] DOES NOT Predict Toxicity



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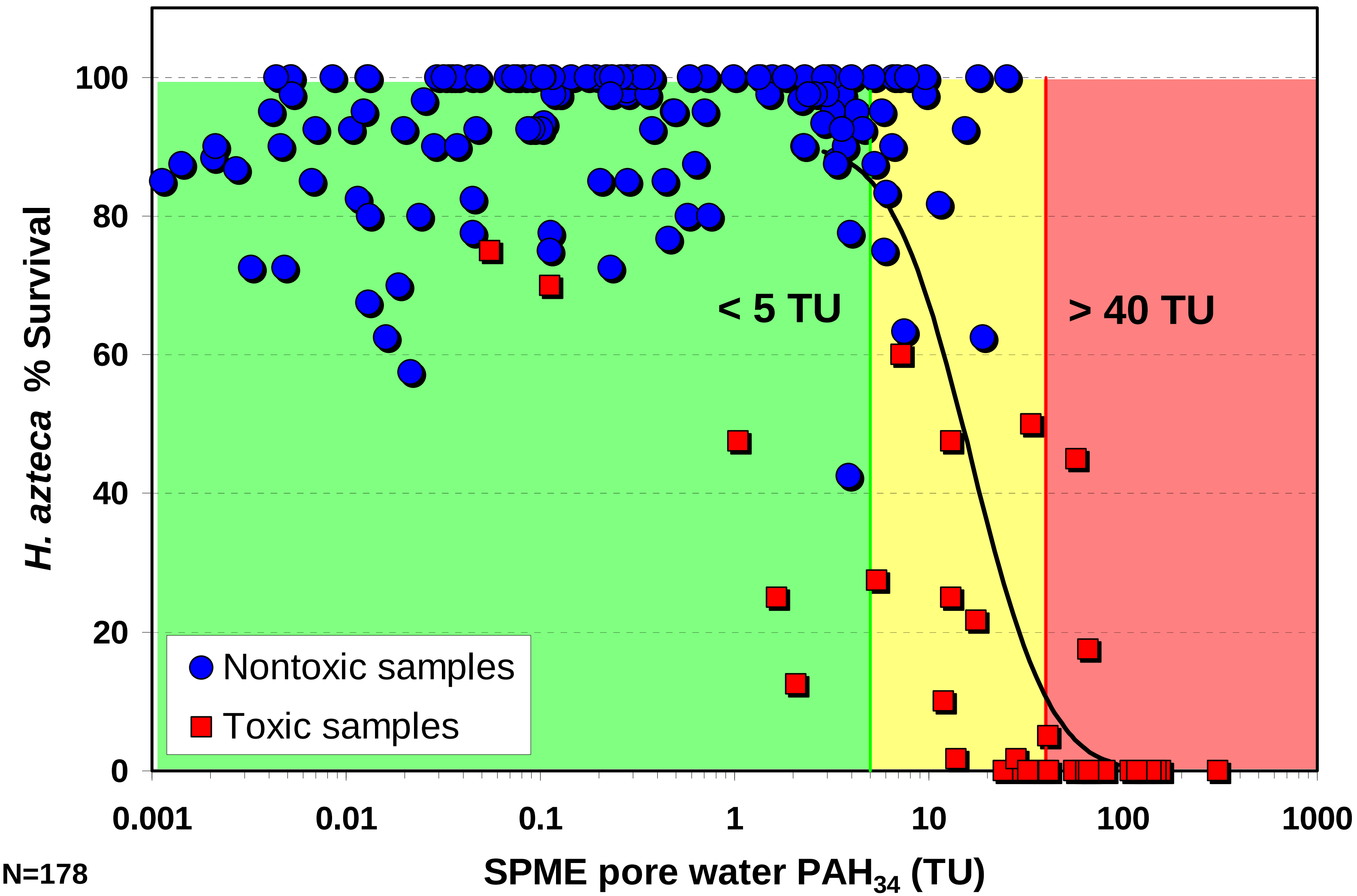
SCBA [PAH_{34}] Method Allows Better Decisions



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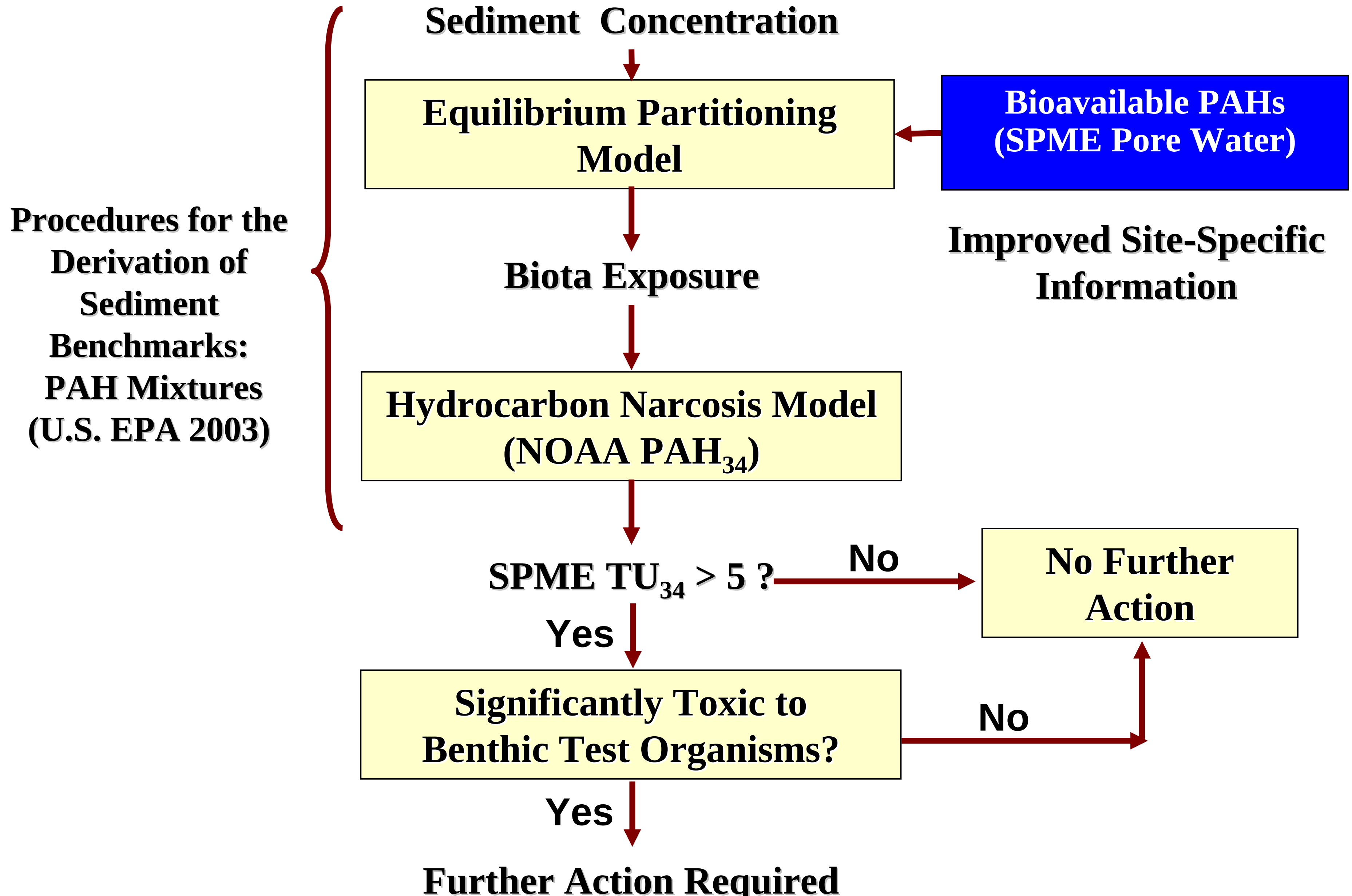
SPME Pore Water Prediction Efficiency is Better

Screening Criteria	% of Total No. of Samples Above Criteria*	Chance of Correctly Predicting Toxicity†	Chance of Correctly Predicting Nontoxicity‡
> 1.6 mg/kg PAH_{16}	86%	23%	93%
> 22.8 mg/kg PAH_{16}	55%	32%	95%
> 1 EPA-modeled TU_{34}	87%	25%	96%
> 1 SPME TU_{34}	44%	45%	98%
> 5 SPME TU_{34}	29%	67%	97%
> 40 SPME TU_{34}	11%	100%	89%

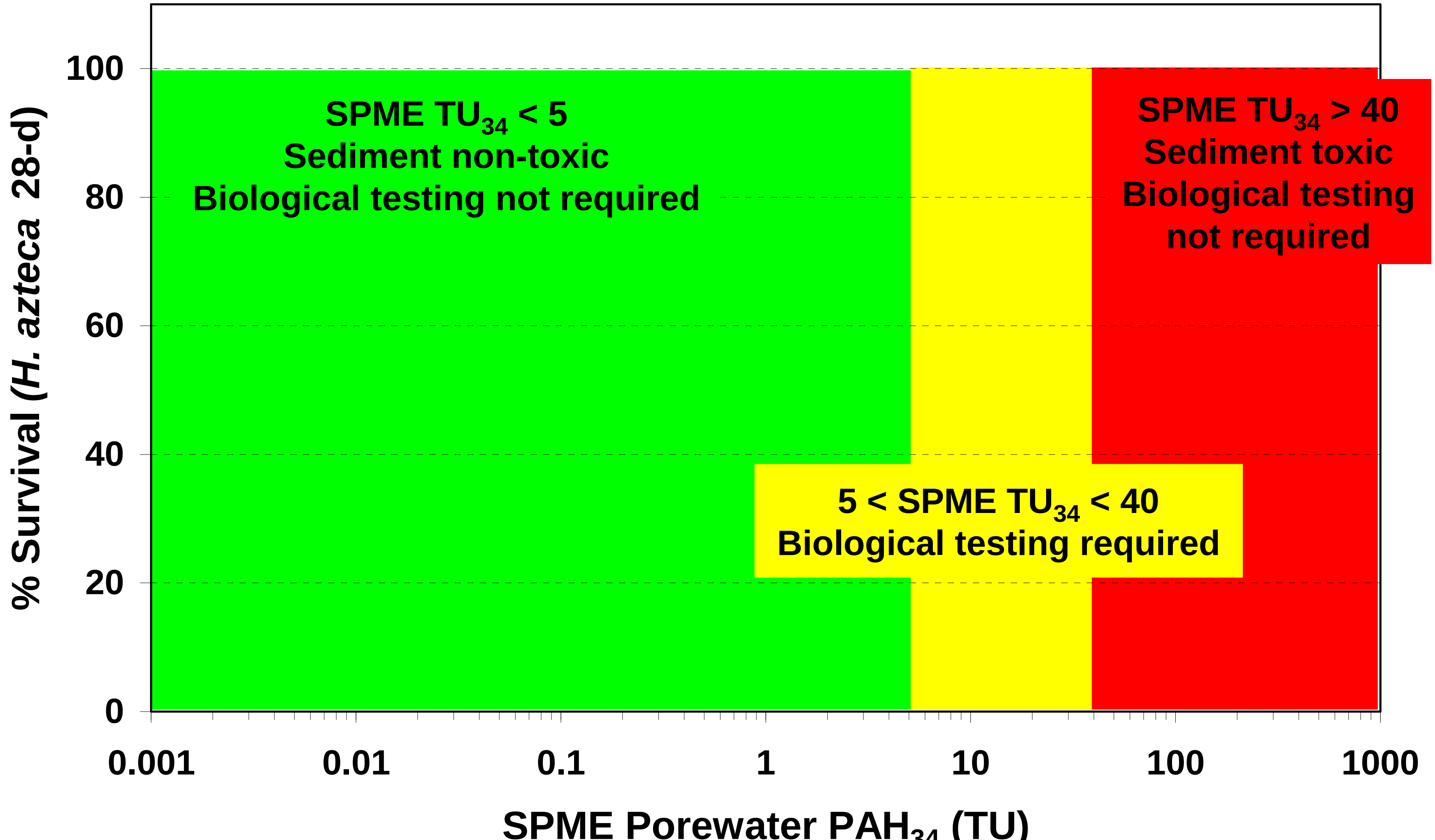
*Total N = 178

†Positive predictive value - the likelihood that a sample exceeding the threshold criteria is truly toxic

‡Negative predictive value - the likelihood that a sample below the threshold criteria is truly nontoxic


Procedures for the Derivation of Sediment Benchmarks: PAH Mixtures (U.S. EPA 2003)
Sediment Concentration
Equilibrium Partitioning Model
Bioavailable PAHs (SPME Pore Water)
Biota Exposure
Improved Site-Specific Information
Hydrocarbon Narcosis Model (NOAA PAH_{34})
SPME TU_{34} > 5 ?
No
No Further Action
Yes
Significantly Toxic to Benthic Test Organisms?
No
Yes
Further Action Required

Summary: Possible Approach for Using SPME Data



DEFINING THE AVAILABILITY AND MOBILITY OF CONTAMINANTS IN SEDIMENTS

Danny Reible
Civil, Architectural and Environmental Engineering
The University of Texas at Austin
Work supported by ESTCP/EPA/NIEHS

Focus

- Relationship between sediment contaminants and potential for exposure and risk
- Contaminants- Hydrophobic organics
  - PAHs and PCBs
- Metric – Accumulation in benthic organisms
  - Benthic organisms often control contaminant exposure to higher organisms through food chain transfer and direct release (via bioturbation)
  - Accumulation provides a dose proportionate response

Traditional indicators of risk

- Bulk sediment concentration
  - Relatively easily measured
  - If equilibrium partioning to porewater bulk sediment is also indicates porewater/mobile phase concentrations
  - In the absence of direct partitioning information

$$K_d = \frac{W_s}{C_{pw}} = K_{oc} f_{oc}$$

  - Reality – porewater concentration typically much less than predicted by this equation due to desorption resistant phenomena

Bioavailability Studies

- Test organism
  - Deposit-feeding freshwater tubificide oligochaete
  - *Ilyodrilus templetoni*
    - Ease to culture
    - High tolerance to contaminants and handling stress
    - Intense sediment processing environment (overcome mass transfer resistances?)
- Measure of bioavailability
  - steady state biota-sediment accumulation factor, BSAF

$$BSAF = \frac{C_t / f_{lip}}{C_s / f_{oc}} = \frac{K_{lip}}{K_{oc}}$$

Where

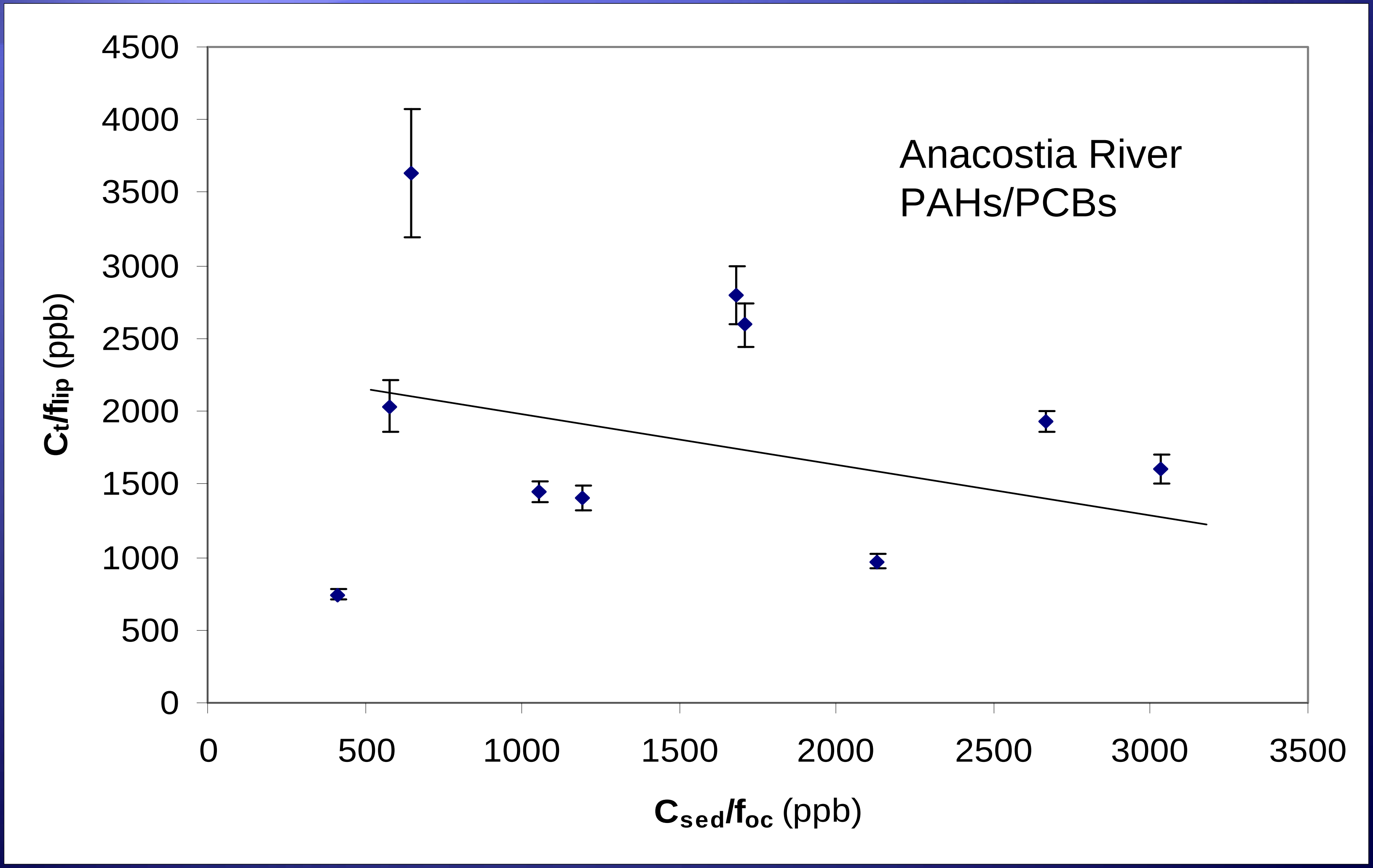
C_t is contaminant concentration accumulated in organisms' tissue (μg/g)

f_{lip} is organisms' lipid content (g lipid/g dry worm)

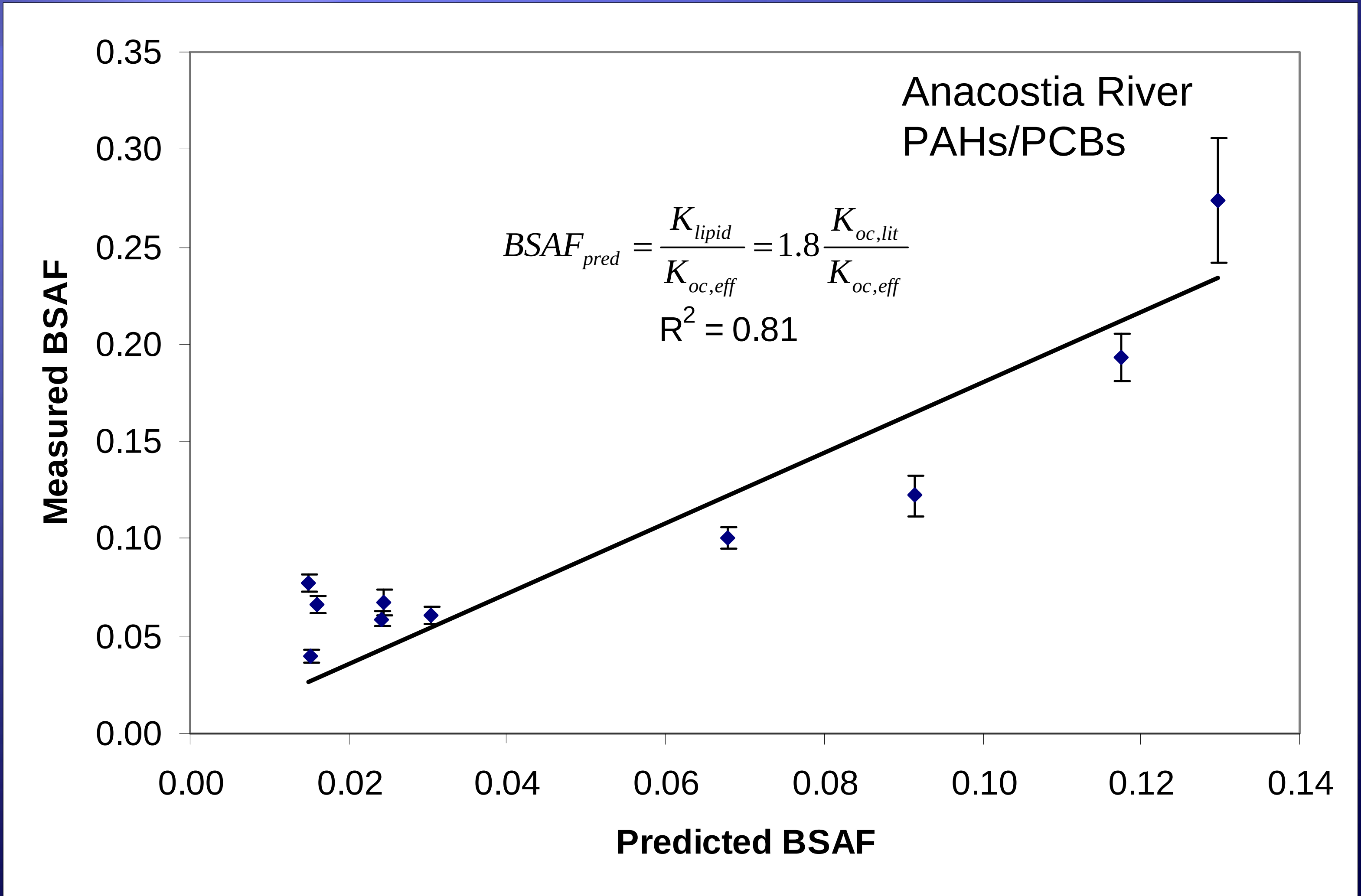
C_s is the sediment concentration (μg/g dry sediment)

f_{oc} is total organic carbon content of the sediment (g TOC/g dry sediment).

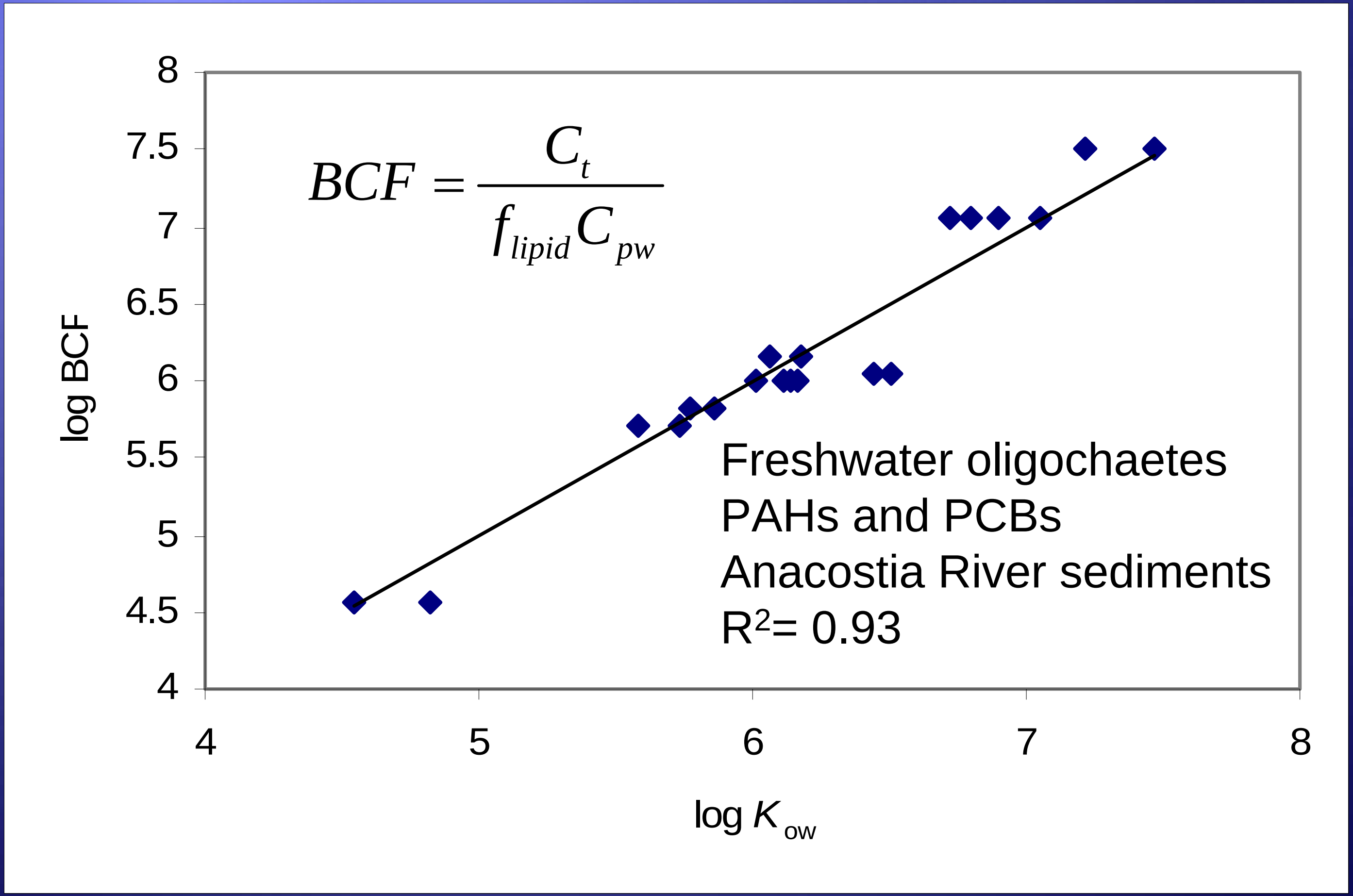
Measuring Risks
Whole Sediment Concentration?



Measuring Risks
Porewater Concentration?

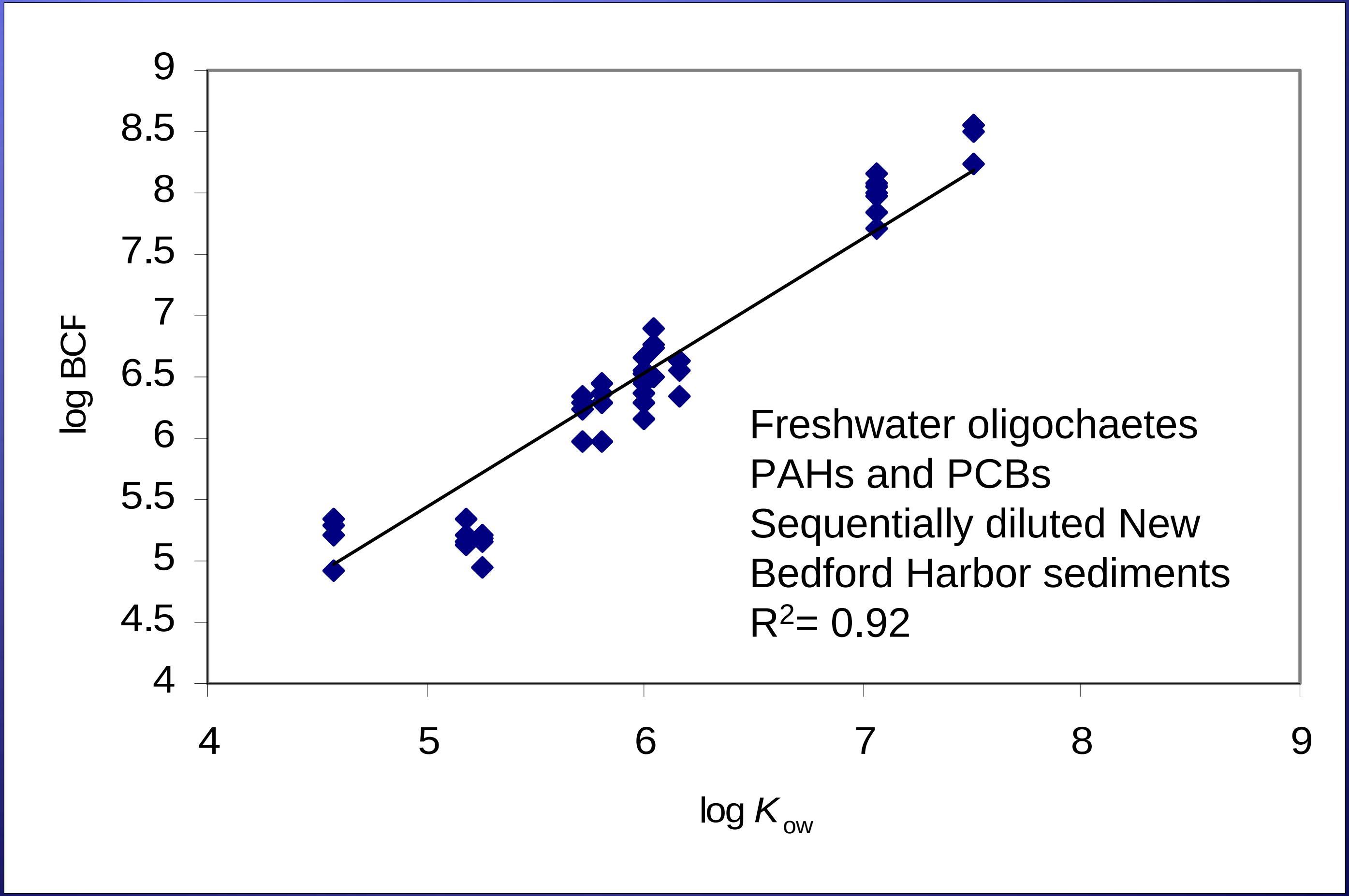


Bioconcentration Factor
Applicable to deposit feeders in-situ?

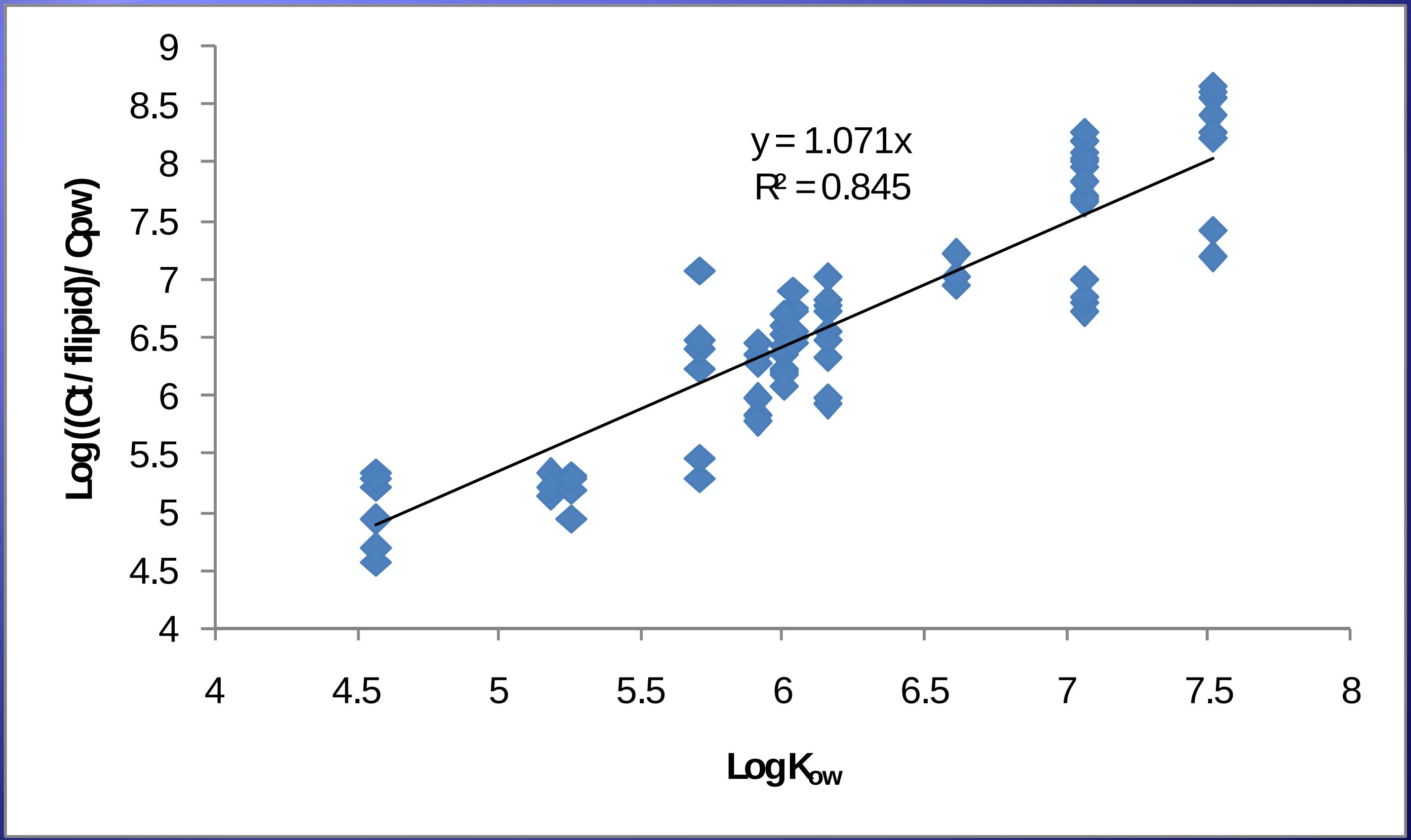


In sediments and in deposit feeding organism (porewater not route of exposure)

Additional data



Cumulative dataset



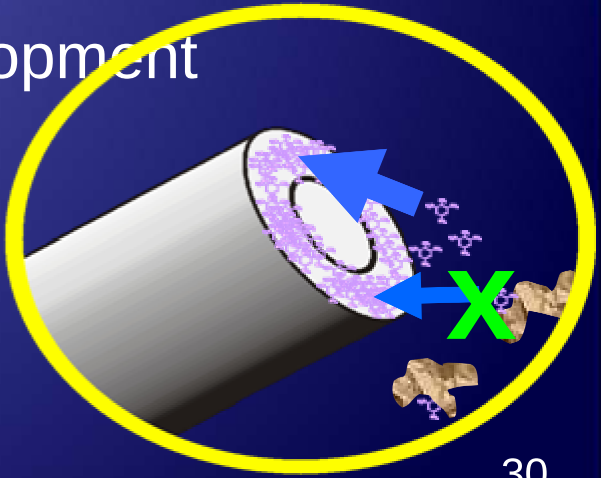
Saltwater/Freshwater sediments & organisms, PAHs and PCBs

Conceptual Model

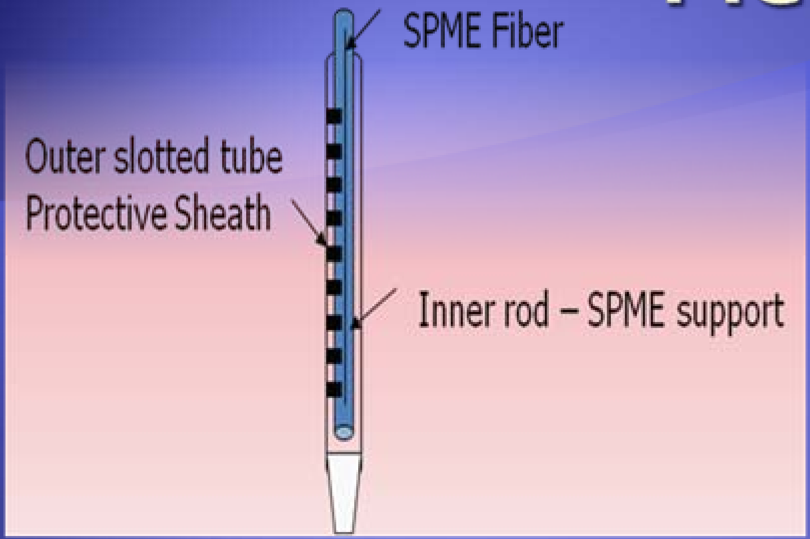
- Strongly sorptive phases cause desorption resistance and decreased porewater concentration
- Slow transport processes in porewater results in achievement of apparent equilibrium
  - Rapid transport processes would yield kinetic limited desorption and ultimately complete release of sorbed contaminants
  - No unavailable fraction – assumed to be strictly a kinetic phenomena
- Deposit feeding benthic organisms rapidly equilibrate with local solid phases
  - Route of exposure controls dynamics of uptake
  - Extent of uptake controlled by apparent equilibrium

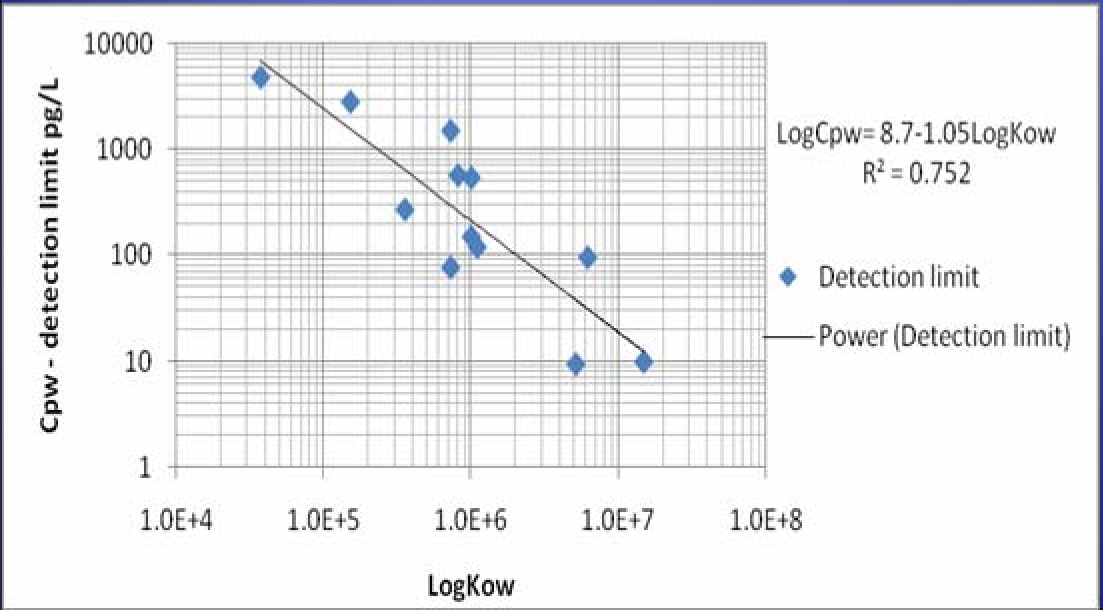
But How to Measure Porewater ?

- Solid Phase MicroExtraction
- Sorbent Polymer PDMS (poly-dimethylsiloxane)
  - Thickness of glass core: 114-108 µm
  - Thickness of PDMS coating: 30-31 µm
  - Volume of coating: 13.55 (±0.02) µL PDMS per meter of fiber
  - Easily capable of measuring ng/L concentrations
- Field deployable system under development
- ng/L detection with 1 cm resolution
- May require 10-30 days to equilibrate
- Recent work with thin coating
  - 10 µm on 230 µm core
  - 9 times faster dynamics
  - ~ 7 µL PDMS per meter of fiber

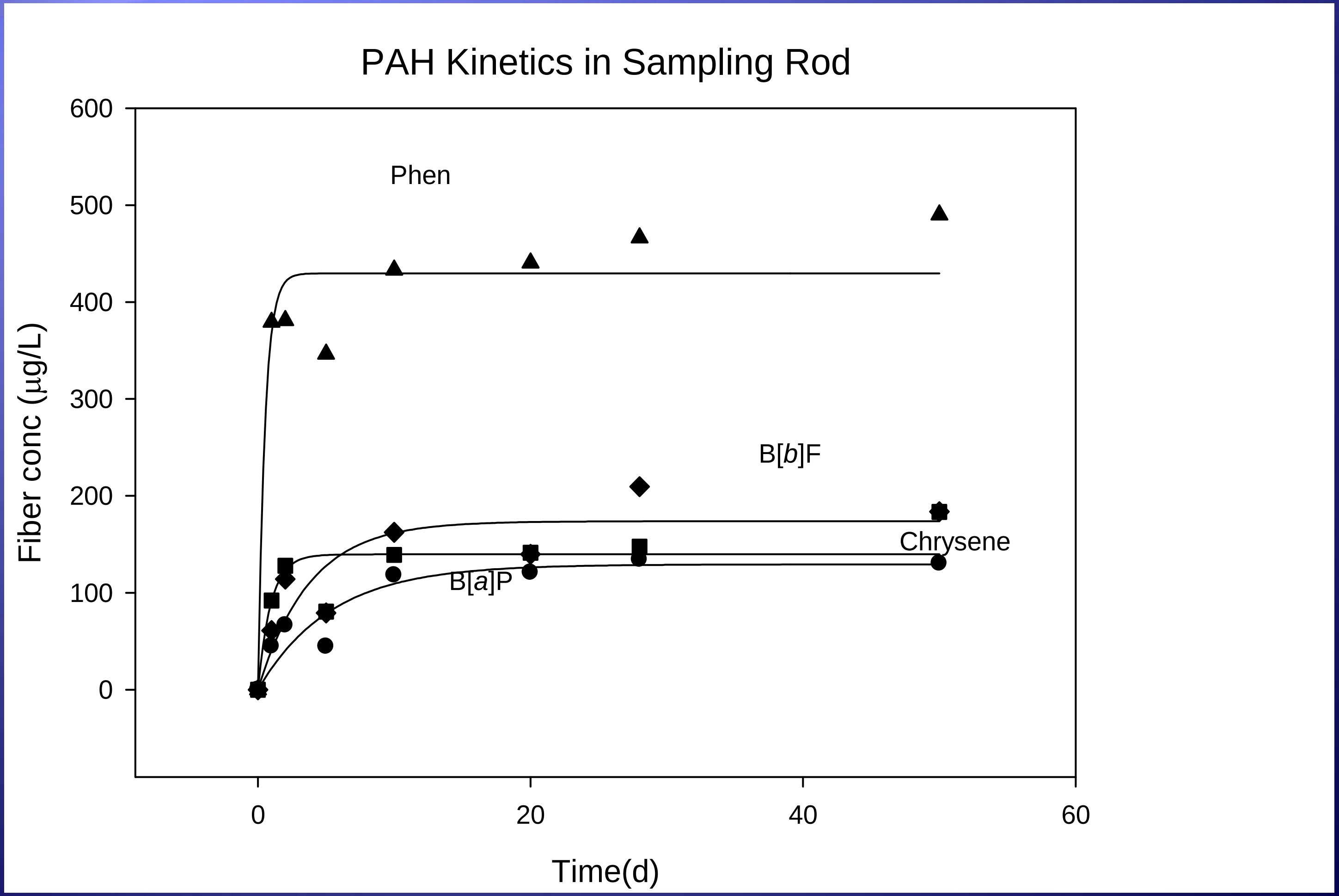


Field Deployable SPME

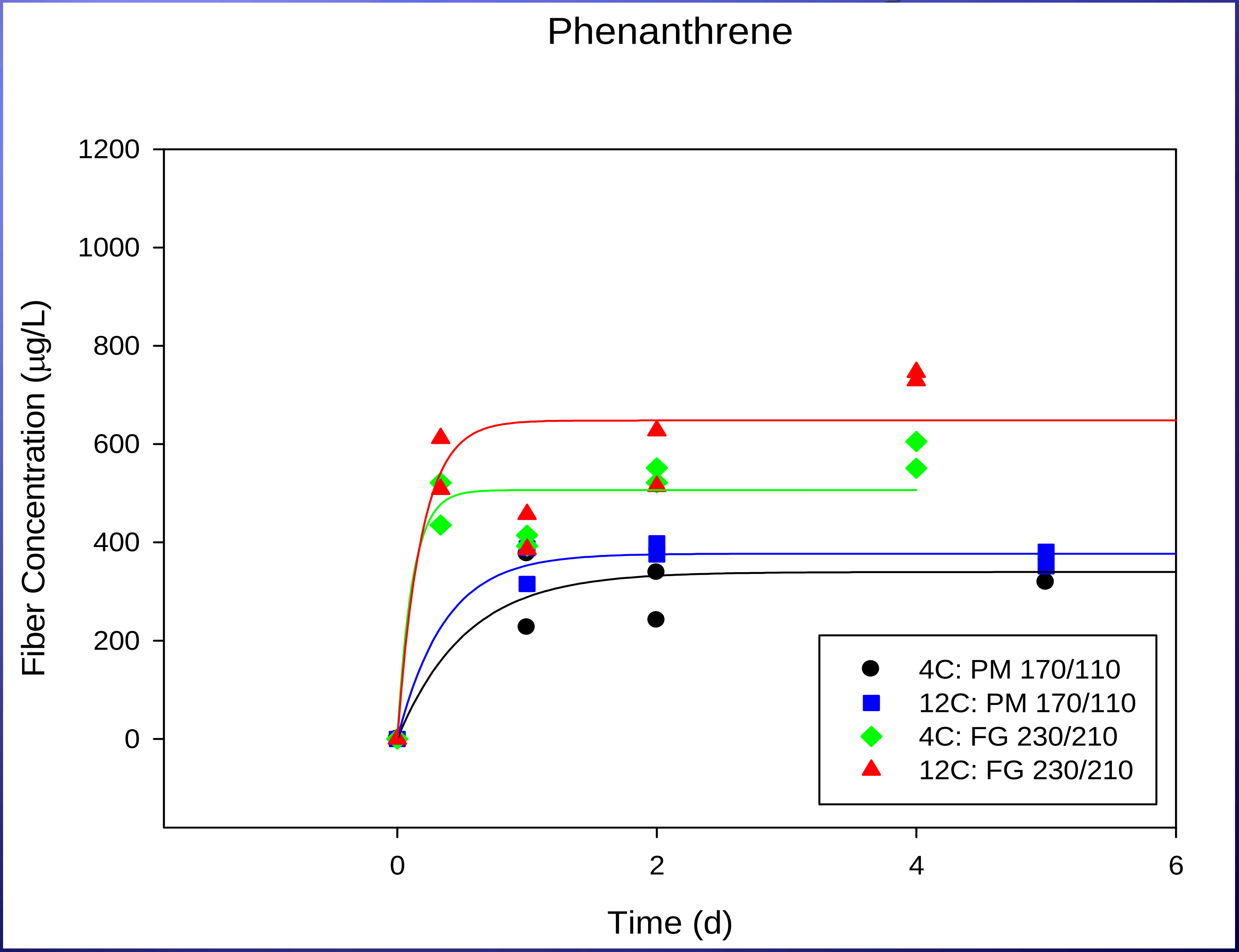




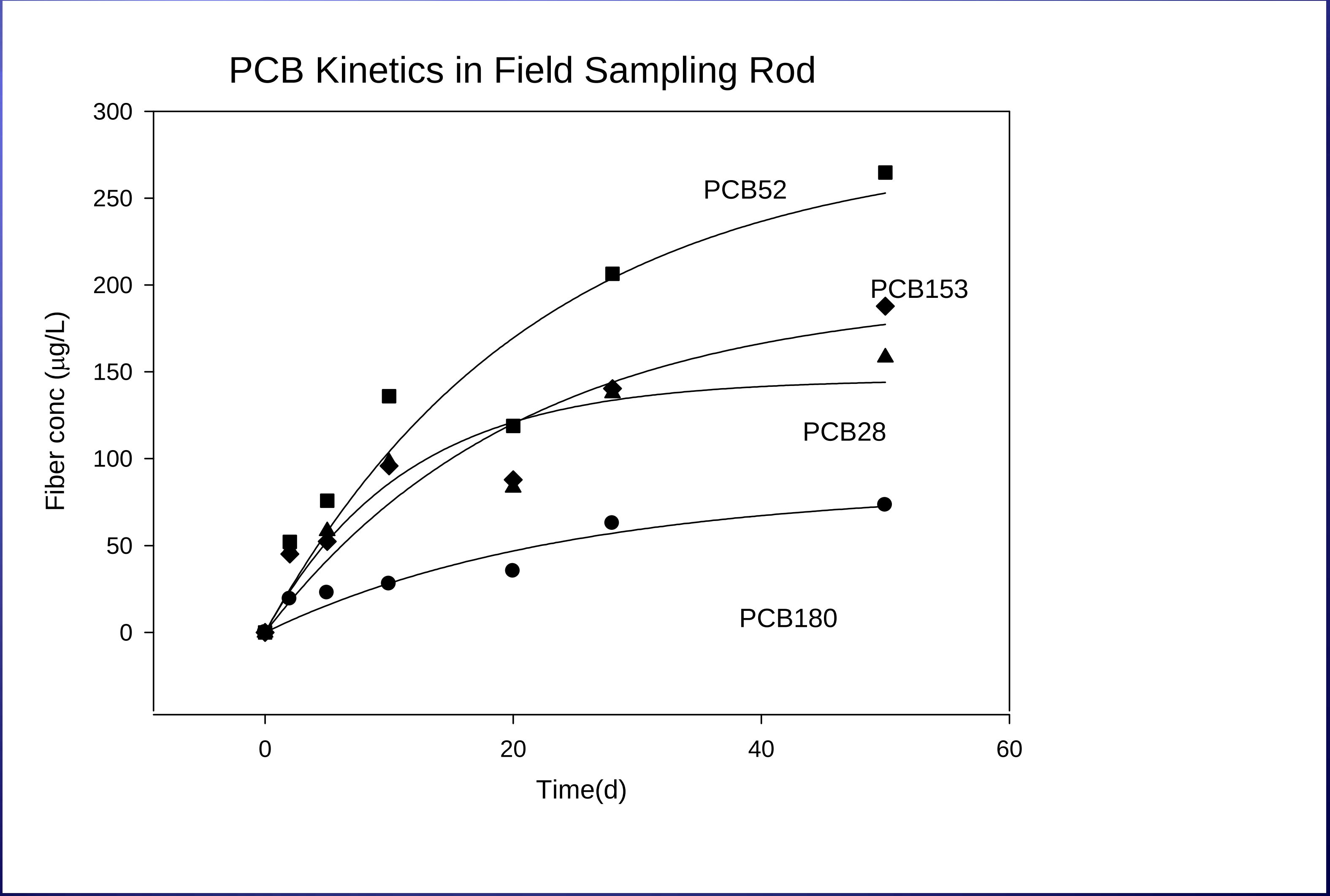
Kinetics of SPME Uptake - PAHs



Kinetics of SPME Uptake – Minimal effect of temperature



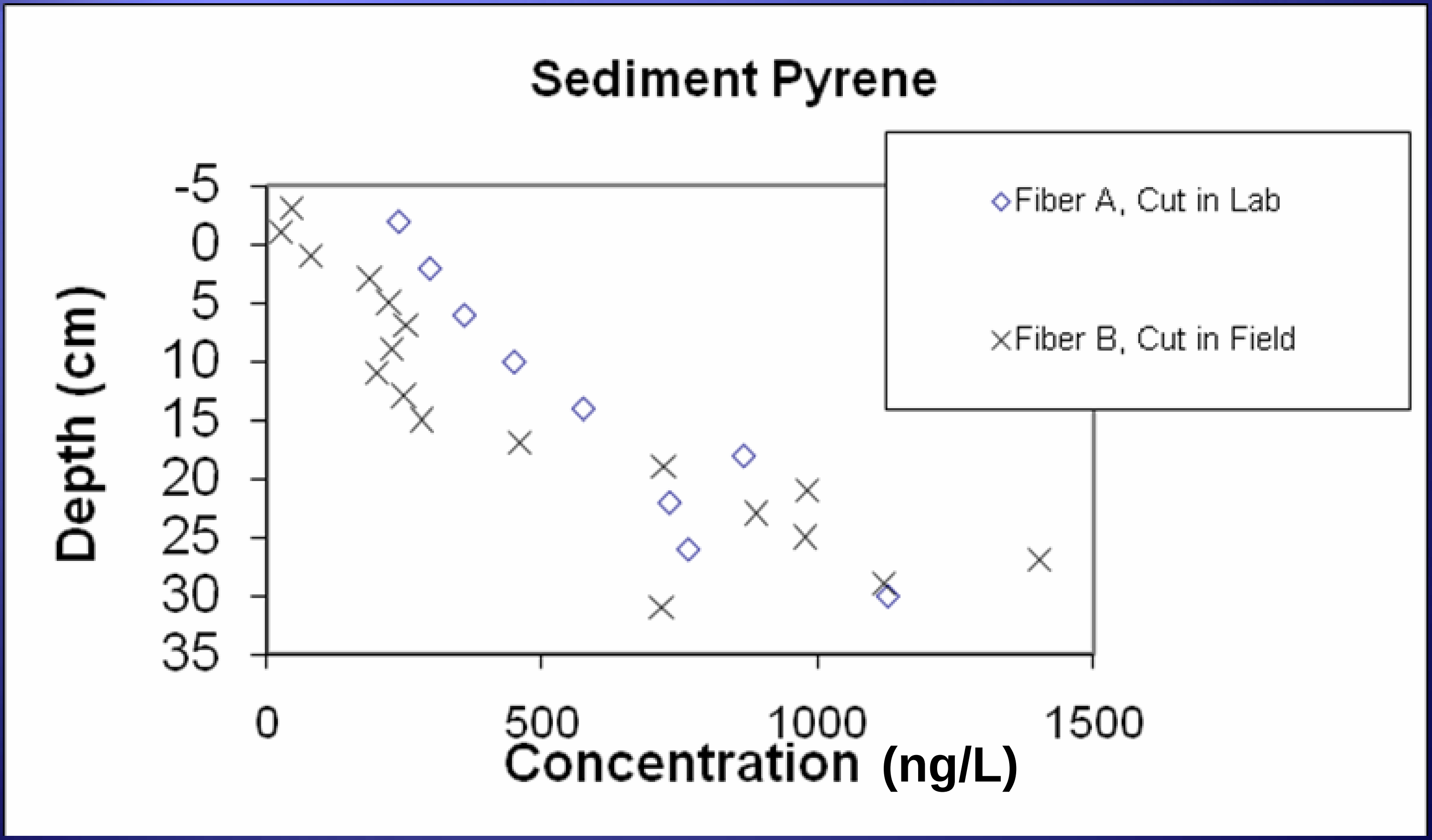
Kinetics of SPME Uptake - PCBs



TECHNICAL APPROACH

- Deployment for ~10-30 days (or shorter for nonequilibrium deployment or for light PAHs)
- In-situ
  - when sediment cannot be removed without compromising porewater integrity
  - when porewater chemical gradients must be retained or to assess field migration processes
- Ex-situ
  - Box cores can be collected and maintained
  - Field deployment is hazardous (e.g. divers in chemically or physically hazardous environments)
- Retrieval and sectioning for desired resolution
- Extraction
- Analysis

SPME Measured Porewater Concentration Profile Anacostia River (In-Situ)

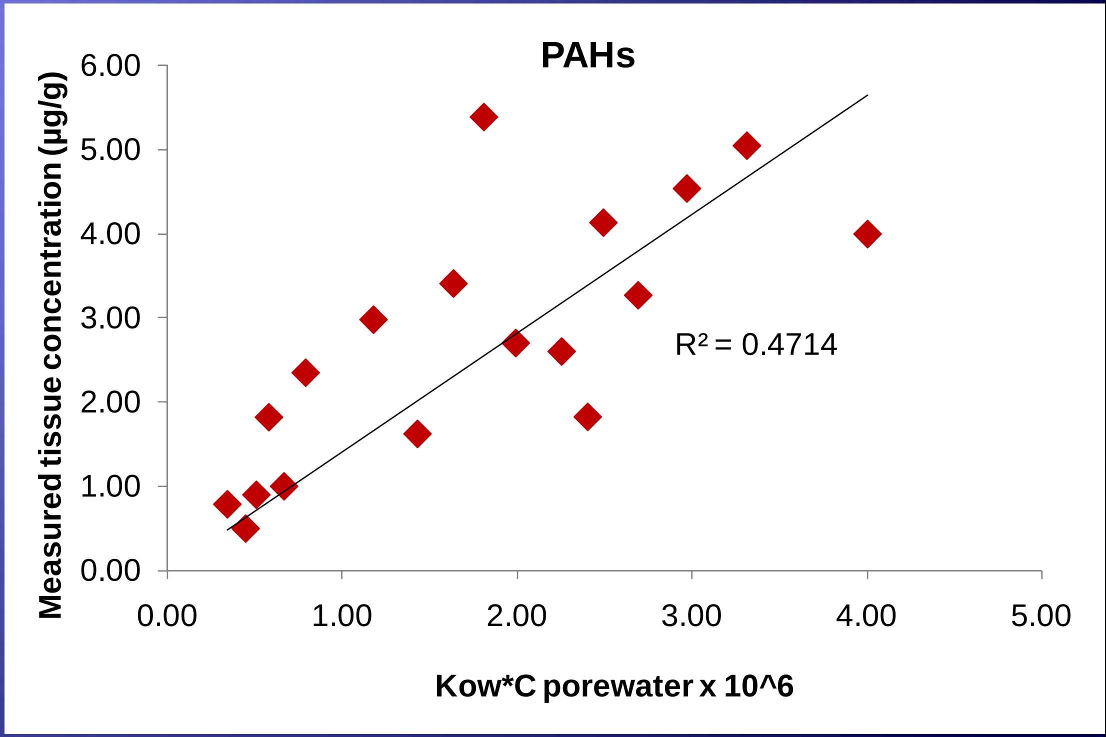


Bulk sediment concentration does not reflect high gradient near surface

Preliminary Correlation with Caged Organisms in the Field

Anacostia Active Capping Demonstration Site

- *Lumbriculus* – freshwater deposit feeder
- Preliminary Data
  - Variety of uncontrolled factors
- Still promising correlation
- Additional field demonstration planned Summer 2008

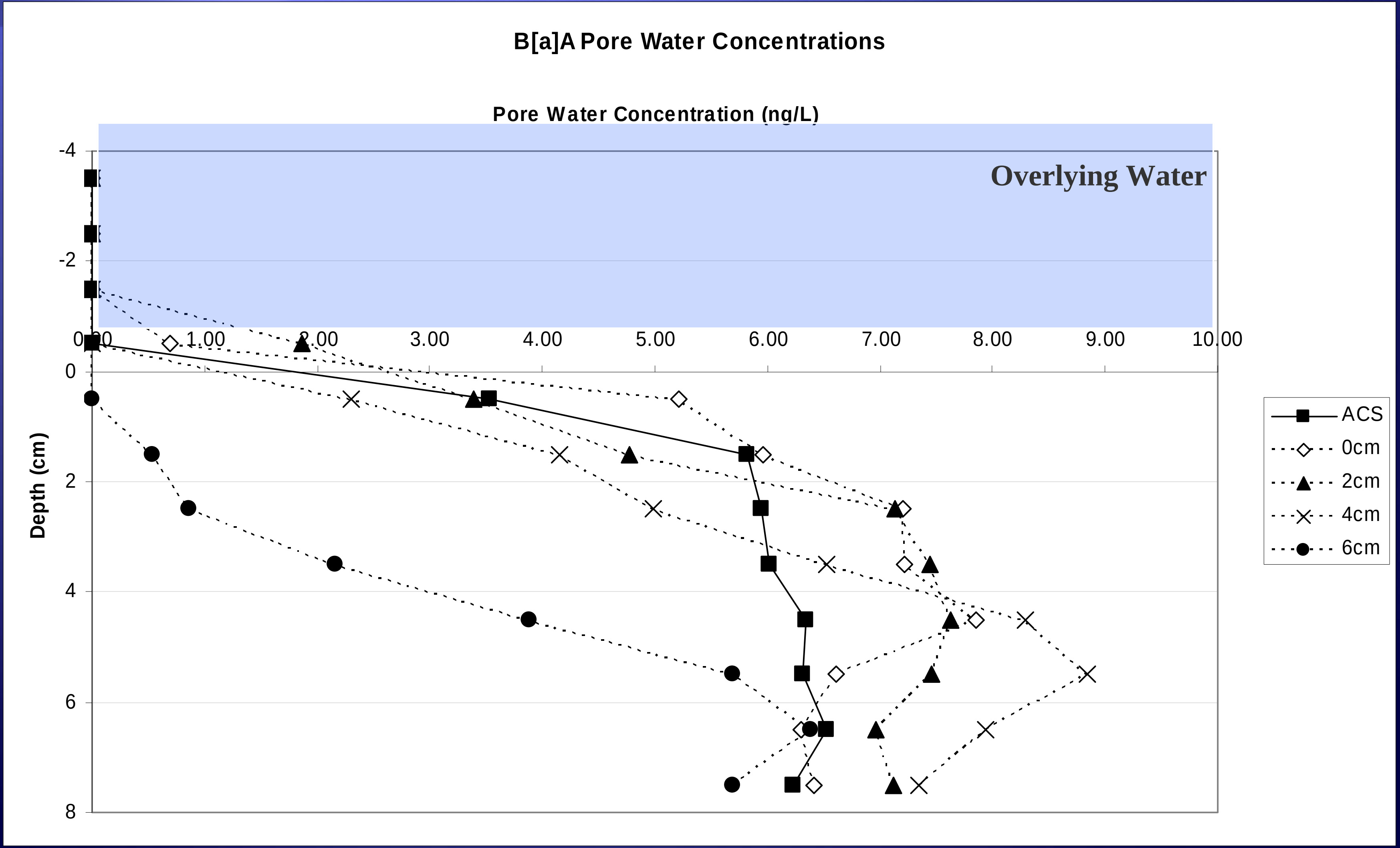


Bioavailability Assessment Thin Layer Capping

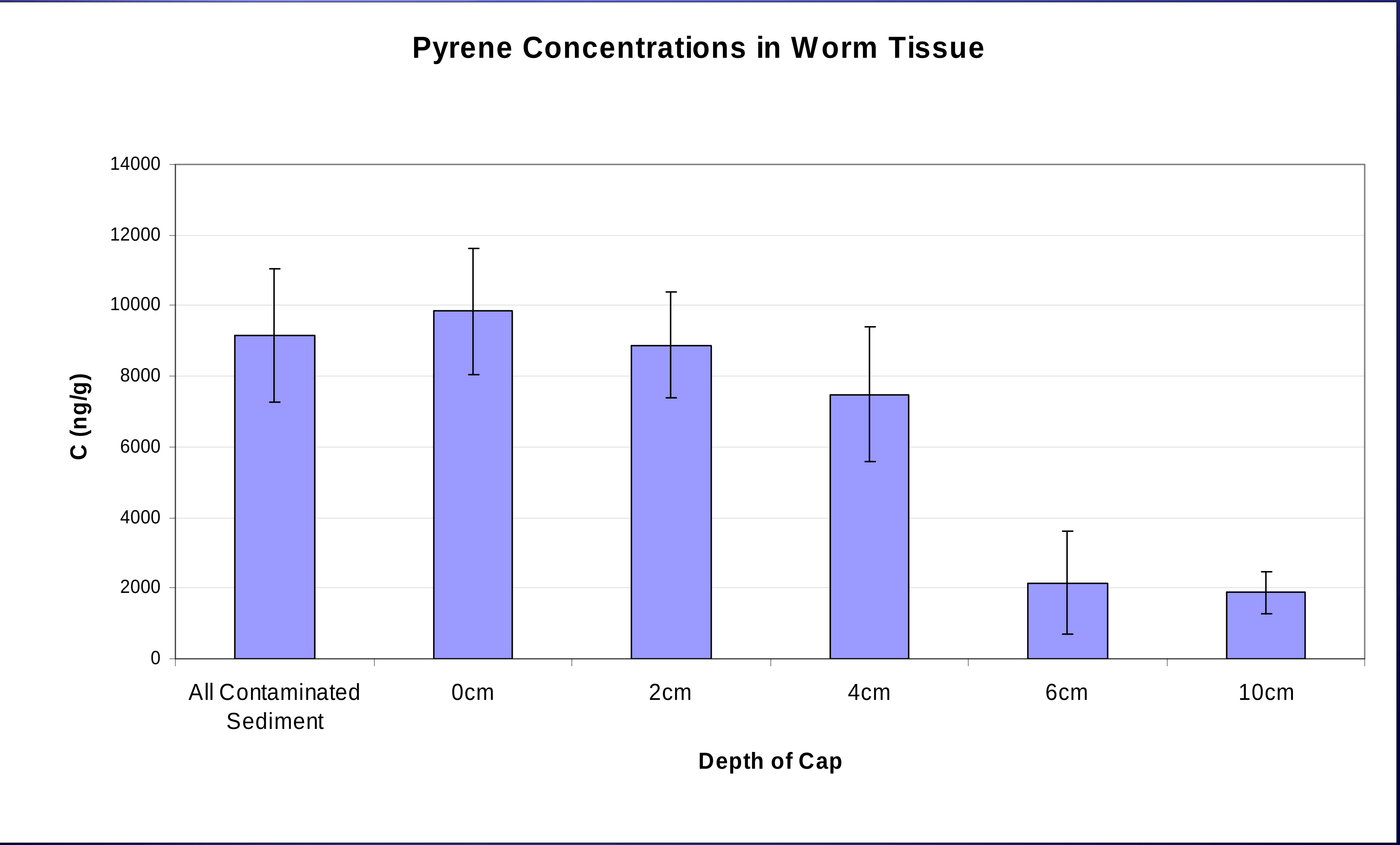
- Thin layer sand capping (10-15 cm) often used to provide clean surface over dredging residuals
- Assessed via bioaccumulation experiments with deposit feeding organism with layers of varying thickness
  - Thin (0.5 cm) of fine grained sediment above thin layer sand cap to simulate deposition of new sediment (allowing recolonization by deposit feeders)
  - Porewater and bioaccumulation testing after 28/ 56 days
  - No porewater advection
- Objectives
  - Can a thin layer sand cap reduce bioaccumulation?
  - Can porewater concentrations indicate bioaccumulation?

Experimental Setup

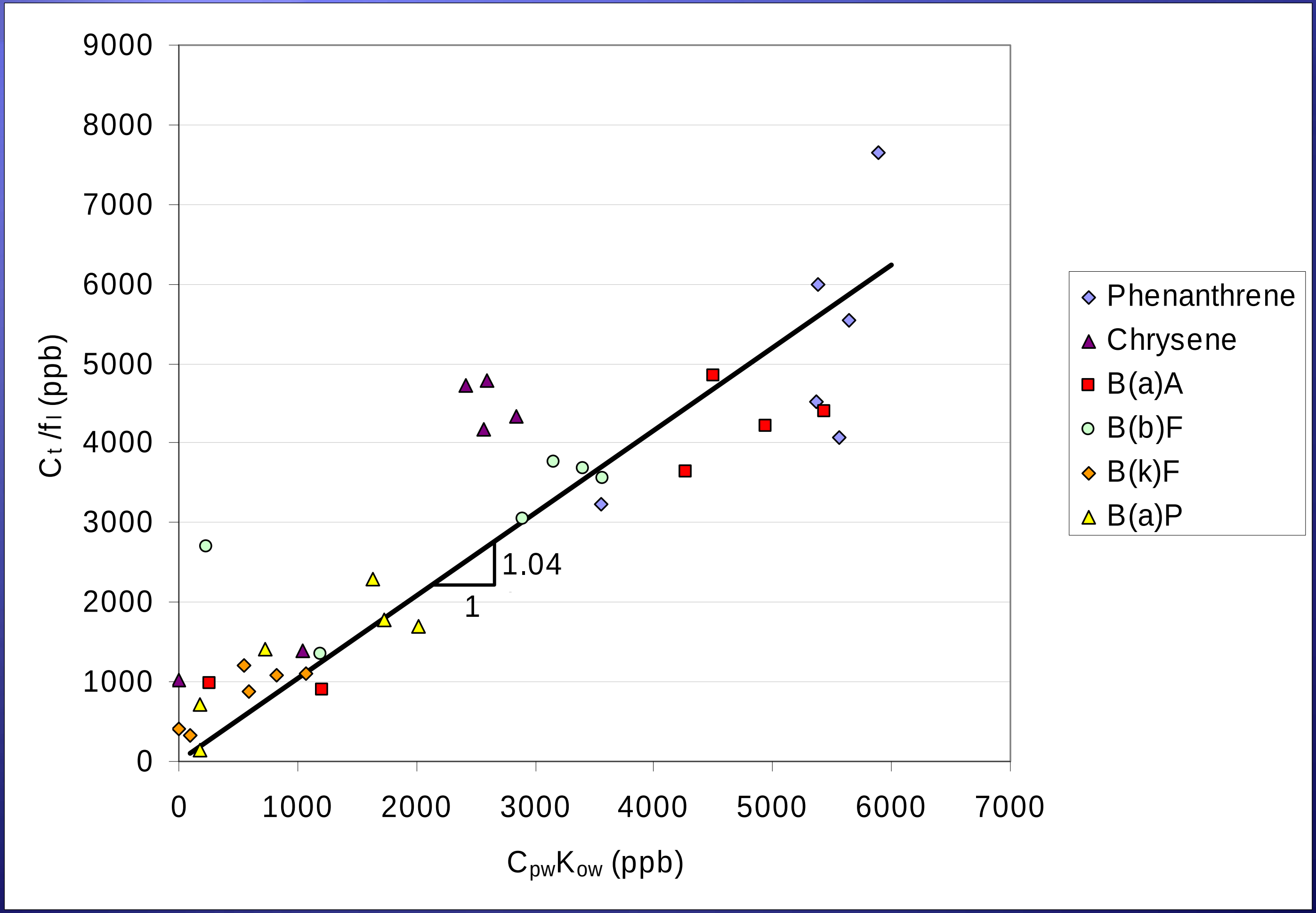
Thin Layer Capping to Manage Residuals



Thin Layer Capping to Manage Residuals



Correlation of Bioaccumulation with Porewater Concentration



Unit slope is BSF estimated by K_{ow}

Summary and Conclusions

- Interstitial water concentration indicative of available and mobile contaminants
  - Typically much lower than predicted by W_s/ (Koc foc) due to desorption resistance
- Interstitial water concentration indicative of bioaccumulation in deposit feeding organisms
  - Not indicative of route of exposure but of ss accumulation
  - PAHs and PCBs (although less data for PCBs)
  - BCF useful in-situ for deposit feeders as well as for passive uptake in organisms in overlying water
- SPME a useful tool for measuring interstitial water concentration
  - Field deployable tool useful for indicating interstitial water concentration and gradients to understand chemical migration

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