Passive Sampling of Porewater for the In-situ Assessment of Bioavailability

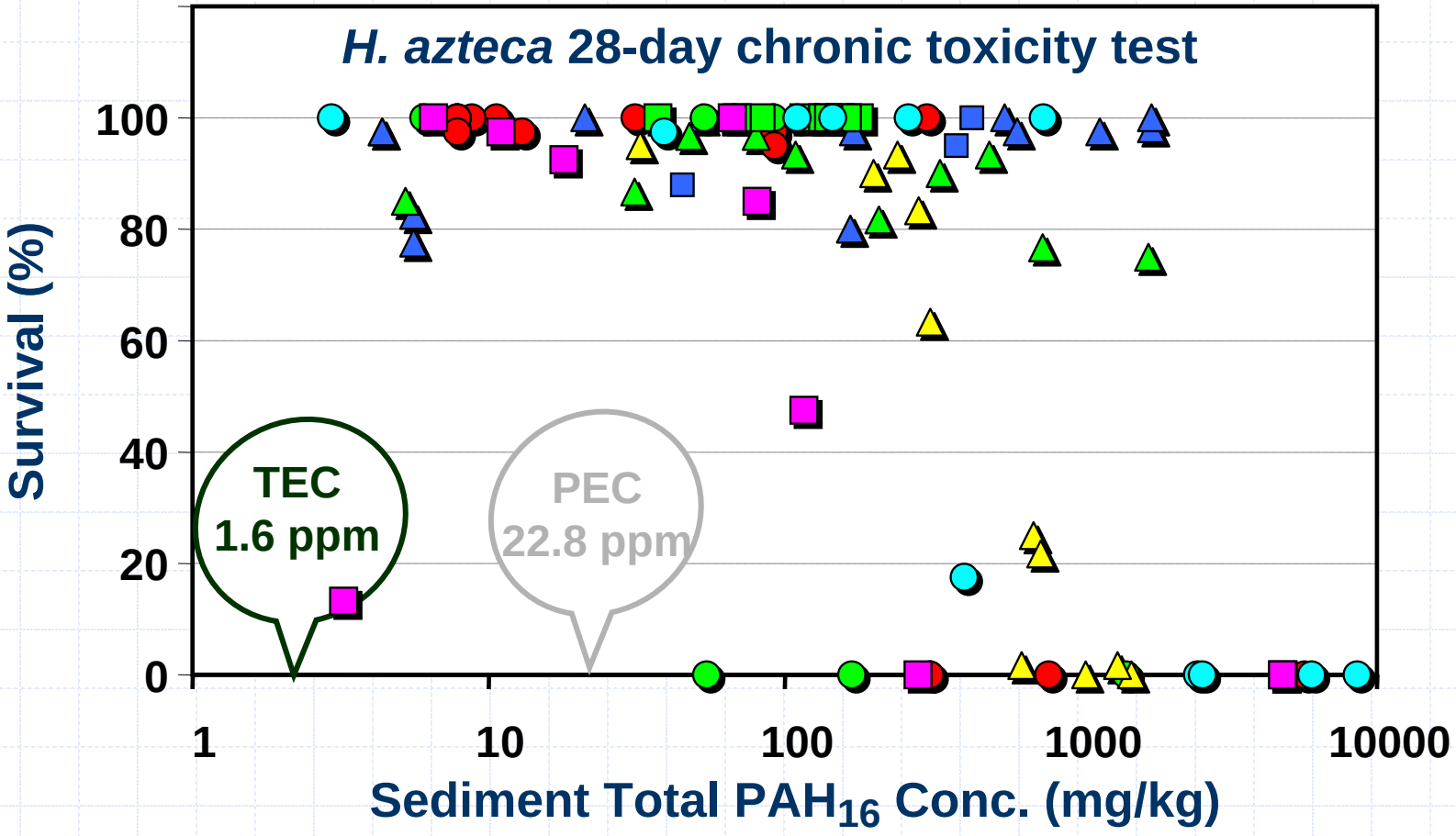
Danny D. Reible, PhD, PE, DEE, NAE

University of Texas

Linking Sediment Exposure and Risk

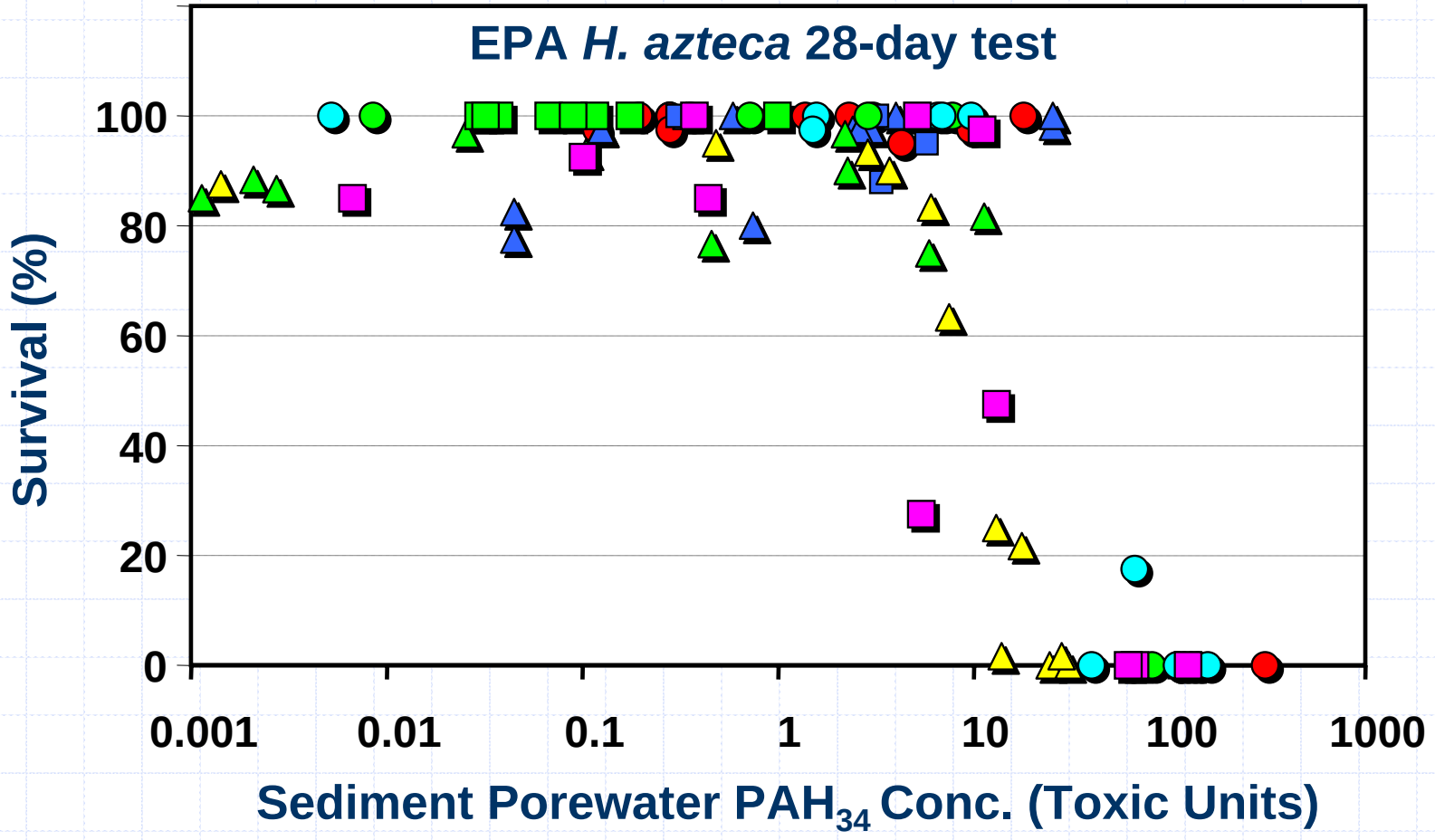
- Relevance of bulk sediment concentration
  - Erosive sediments if complete desorption possible
  - Surficial sediments if complete desorption possible or if organisms can access all of contaminant
- Relevance of pore water concentration
  - Mobile fraction of buried stable sediments
  - Indicator of bioavailability of surficial or erodible sediments ?

Bulk Sediment Concentration Correlates only Weakly with PAH Toxic Endpoints



Dave Nakles, RETEC

Porewater Concentration Better Correlates with Survival



Dave Nakles, RETEC

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 MT resistances?)
- Measure of bioavailability= steady state BSAF

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

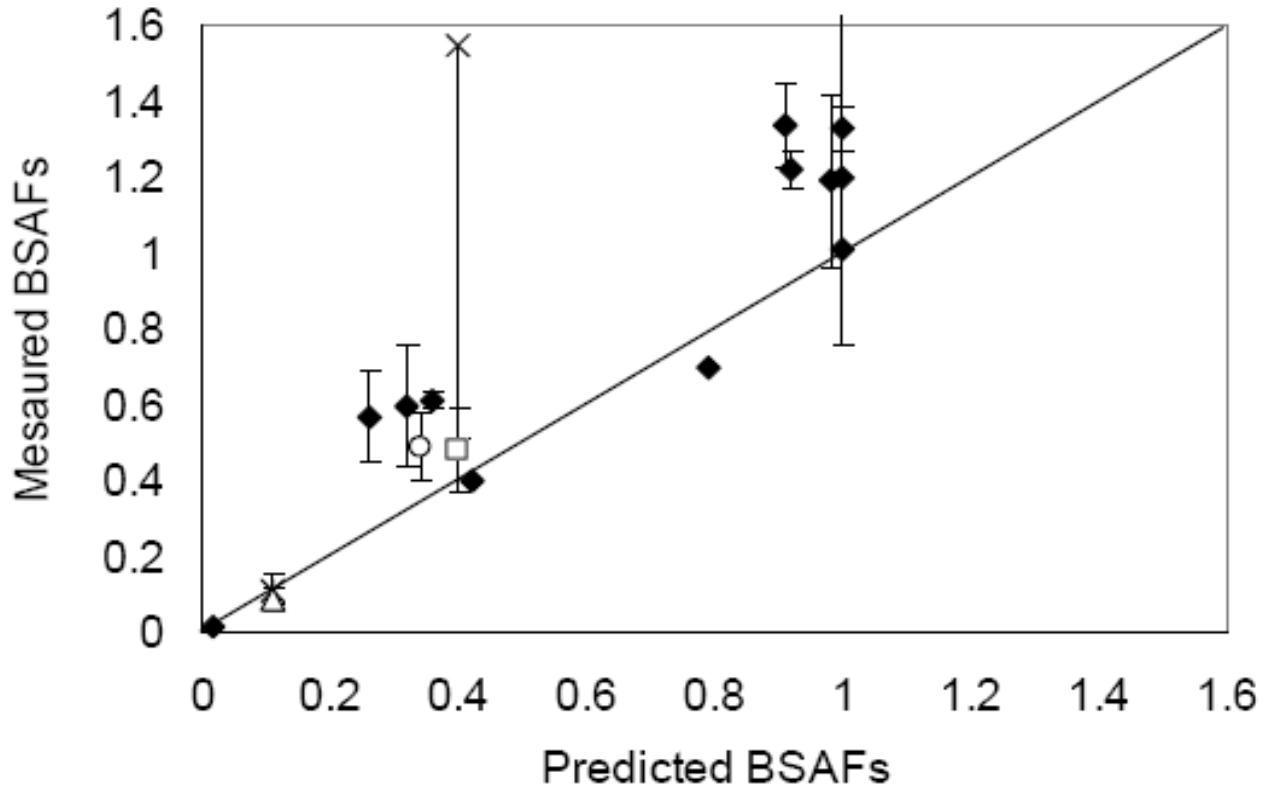
Where
C_t is contaminant concentration accumulated in organisms' tissue (μg/g)
f_{lip} is organisms' lipid content (g lipid/g dry worm)
C_s is the sediment concentration (μg/g dry sediment)
f_{oc} is total organic carbon content of the sediment (g TOC/g dry sediment).

Normalized Accumulation as Indicator of Bioavailability

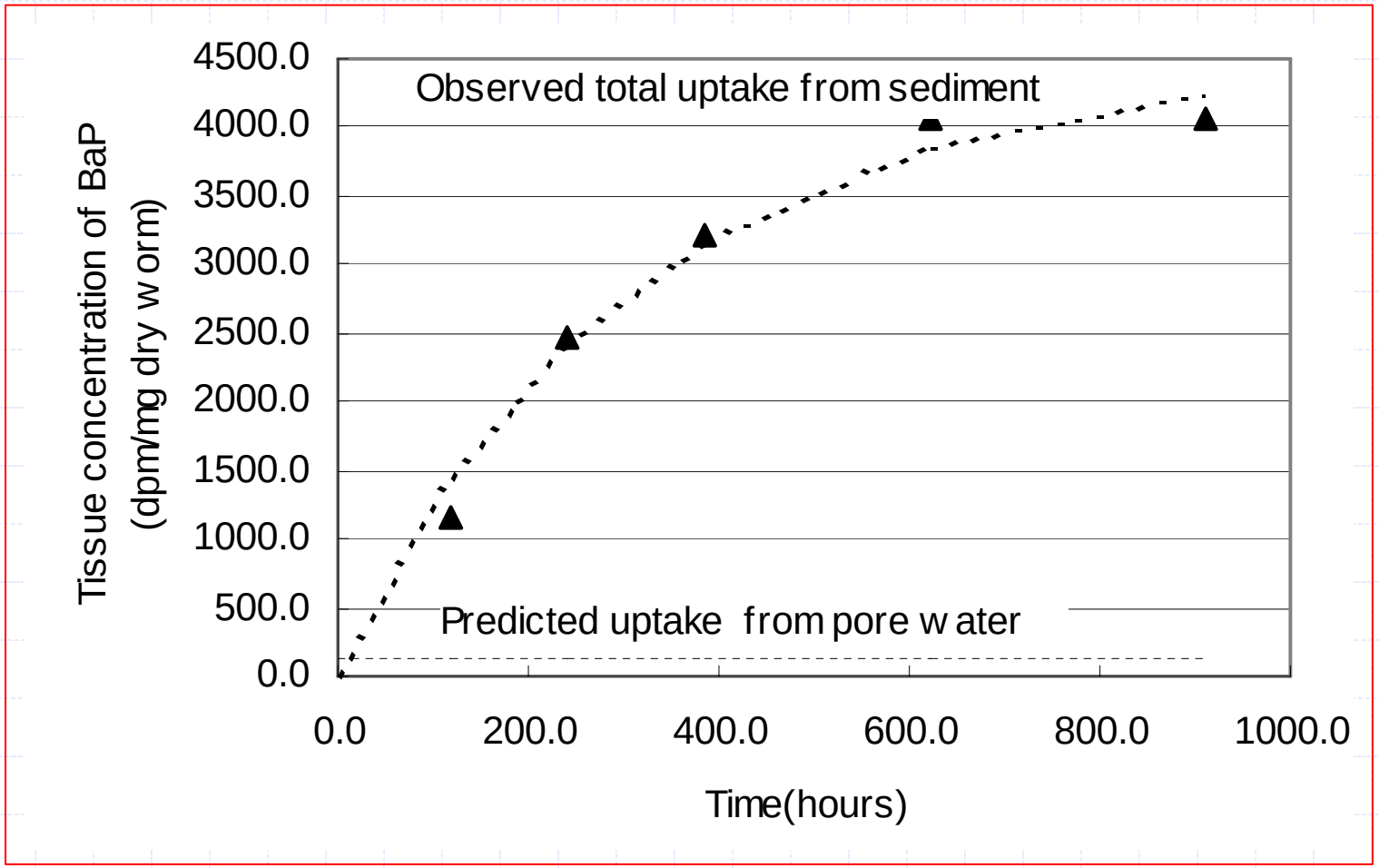
- BSAF of O(1) for reversibly sorbed non-metabolizing contaminants in directly exposed organisms at steady state (e.g. benthic deposit feeders)
- If accumulation indicated (not necessarily caused) by porewater concentration

$$BSAF_{predicted} = \frac{K_{lipid}}{K_{oc}} \times \left(\frac{C_{porewater,observed}}{C_{porewater,reversible}} \right)$$

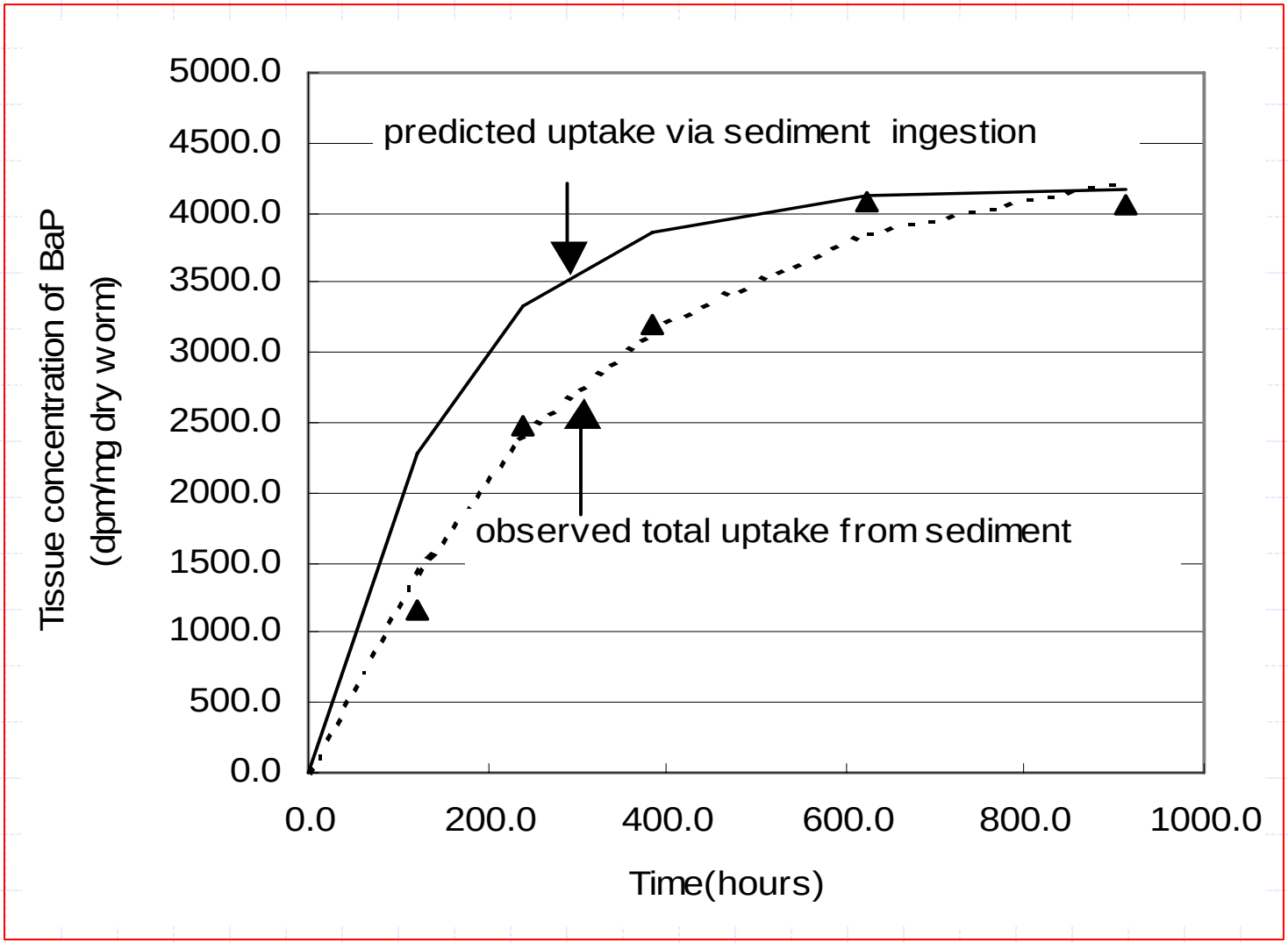
Does it predict uptake of PAHs ?



Uptake of benzo[*a*]pyrene from water



Contribution of ingestion to the uptake of benzo[*a*]pyrene



Measurement of Porewater Concentrations

- Problems
  - Low porewater concentrations limits the measurement of more hydrophobic compounds like PCBs
  - Solvent extraction overestimates the freely dissolved pore-water concentration due to the absorption by DOC
  - Errors due to the measurement of DOC and uncertainties in determination of K_{DOC}
- Solution – solid phase microextraction SPME
  - Potential extremely low detection limits due to high fiber-water partition coefficients
  - Decouple sampling from water-DOC matrix effects
  - High spatial resolution, rapid dynamics
  - Employed ex-situ by National Grid/RETEC (Nakles)

Other Porewater Measurement Approaches

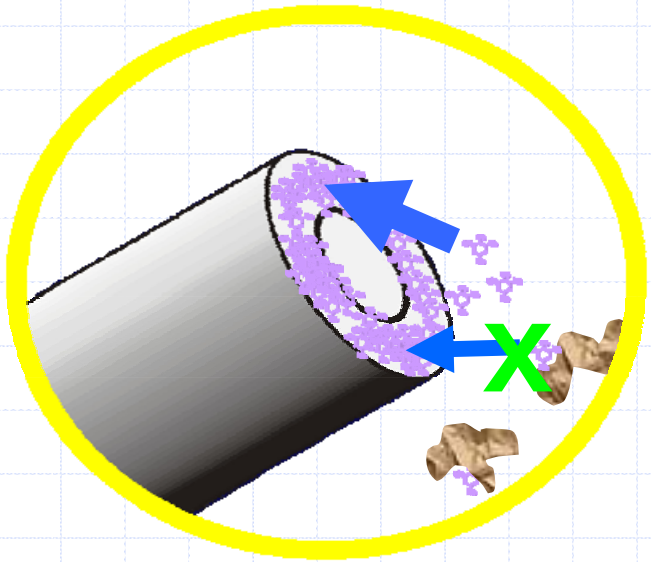
- Ex-situ SPME
  - Proving to be valid approach
  - Maintenance of profiles?
  - Maintenance of sample integrity?
- Semi-permeable membrane devices
  - Dynamics?
  - Spatial resolution?
- Passive Polyethylene Samplers
  - Currently under development (P. Gschwend)

Objectives of ESTCP effort

- Demonstrate solid-phase micro extraction (SPME) for the in-situ assessment of bioavailability
- Demonstrate viable deployment approach
- Demonstrate relationship' to sediment pore water concentrations
- Demonstrate relationship to benthic organism body burdens

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 fibre



Using SPME to Measure Porewater Concentration

- Matrix-SPME ---A nondepletive, equilibrium extraction
  - "nondepletive" refers to an extraction that is limited to a minor part of the analyte and which does not deplete the analyte concentration
  - "equilibrium" refers to extraction times are sufficiently long to bring the sampling phase into its thermodynamic equilibrium with the surrounding matrix.
    - At equilibrium,

$$C_{porewater} = C_{fiber} / K_{fiber-water}$$

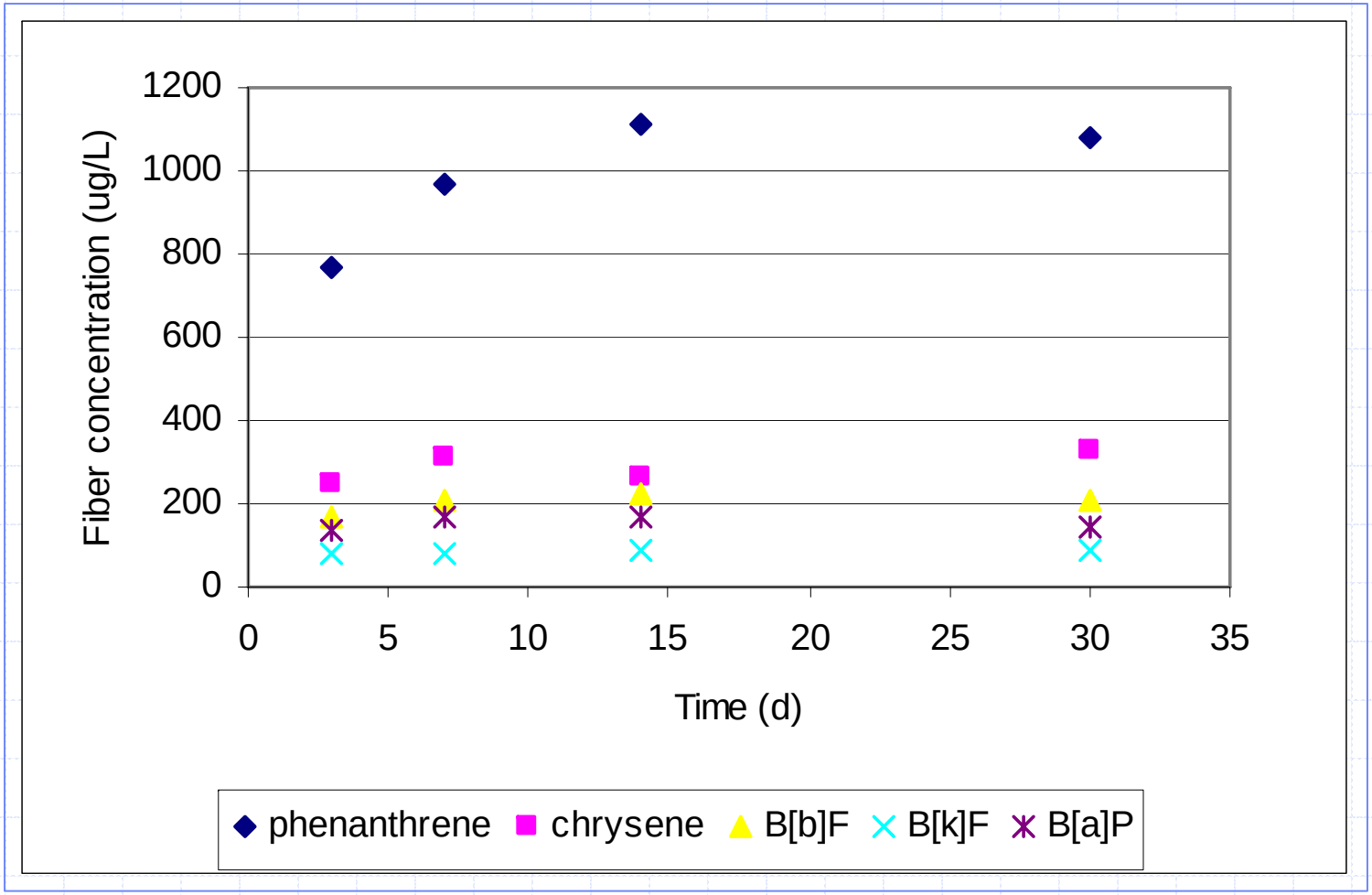
C_{fiber}=mass of contaminant absorbed by fiber/fiber volume (volume of PDMS)

$K_{fiber\text{-}water}$ is fiber-water partition coefficient

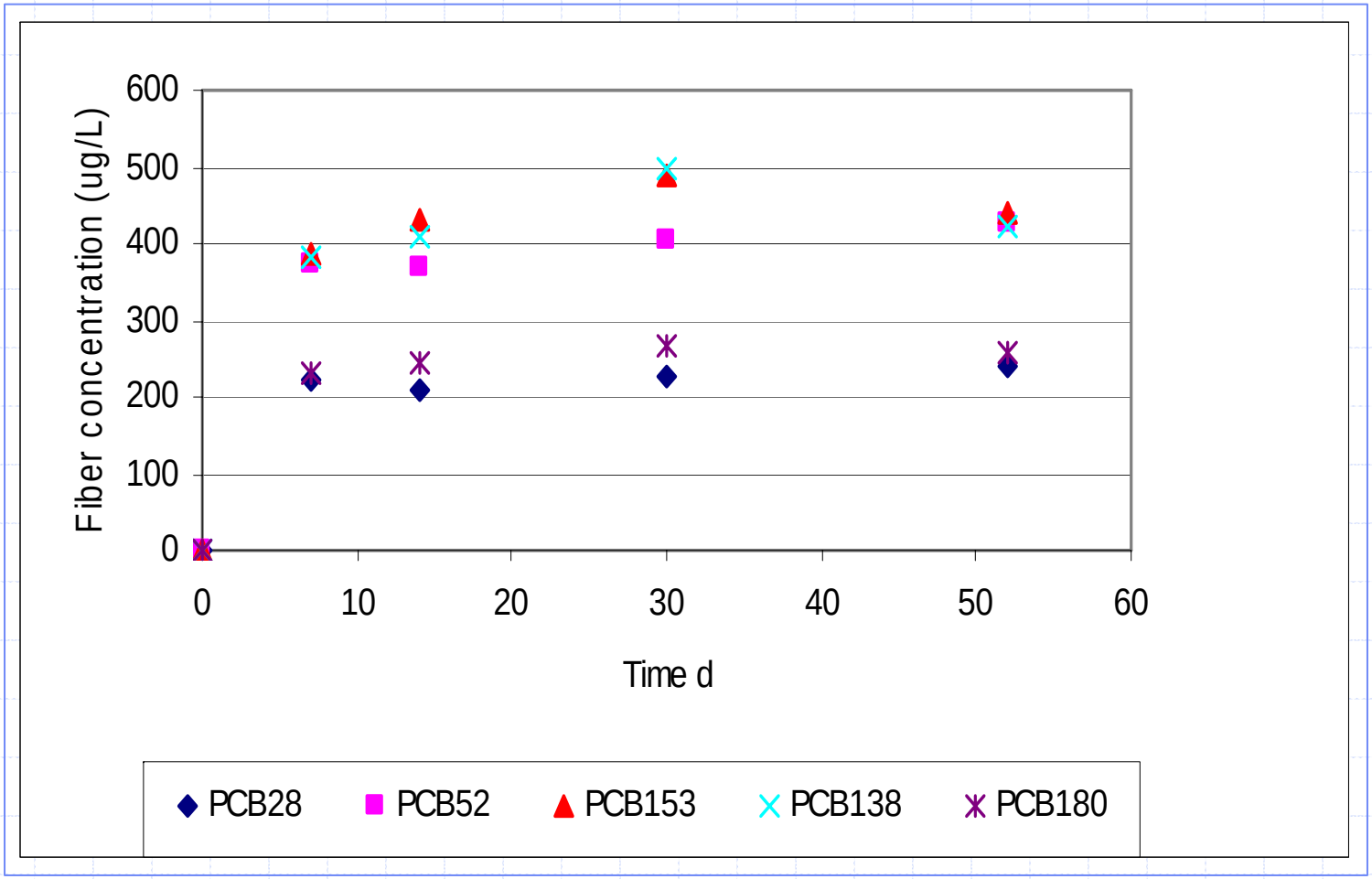
Expected detection limit PDMS fiber

Compounds	Log $K_{PDMS,water}$	Method detection limit	$C_{det,water}$ (1 cm fiber)	**$C_{det,water}$ (5cm fiber)**
Phenanthrene	3.71	1.14 µg/L	164.6	**32.9 ng/L**
pyrene	4.25	3.44	143.3	**28.7**
chrysene	4.66	0.79	12.8	**2.56**
B[*b*]F	5.0	0.32	2.37	**0.47**
B[*k*]F	4.77	0.15	1.89	**0.38**
Benzo[*a*]pyrene	4.87	0.17	1.70	**0.34**
PCB 28	5.06	0.5	3.22	**0.645**
PCB 52	5.38	0.5	1.54	**0.31**
PCB 153	6.15	0.2	0.11	**0.021**
PCB 138	6.20	0.2	0.0935	**0.019**
PCB 180	6.40	0.2	0.059	**0.012**

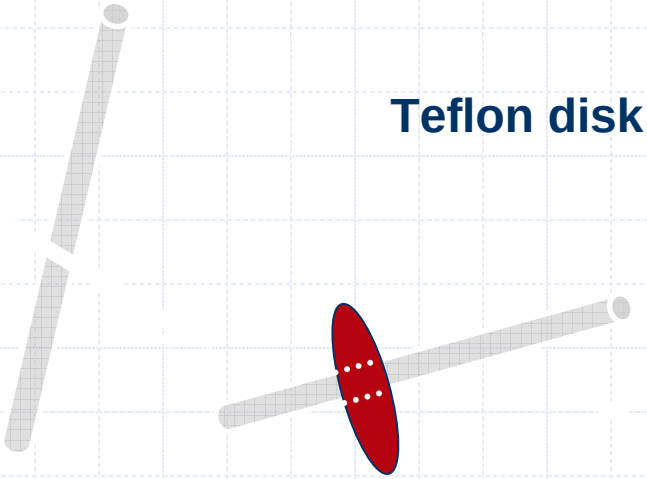
Uptake of PAHs in PDMS fiber (Sediment)



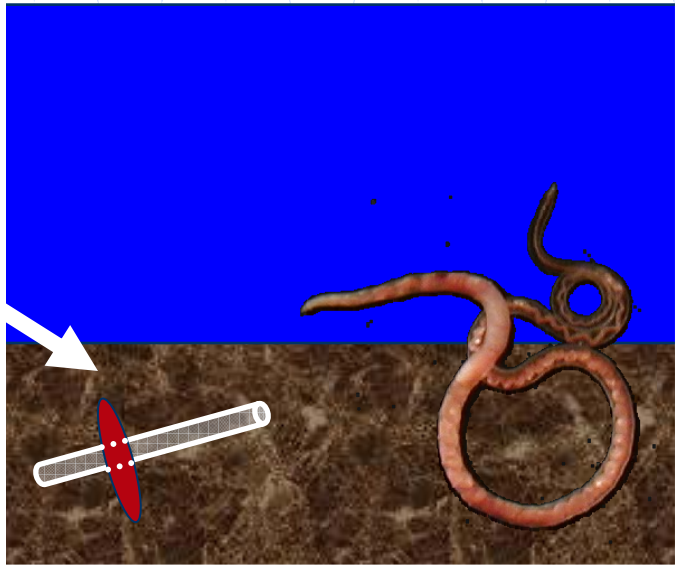
Uptake of PCBs in PDMS fiber (Sediment)



SPME Deployment in Sediment



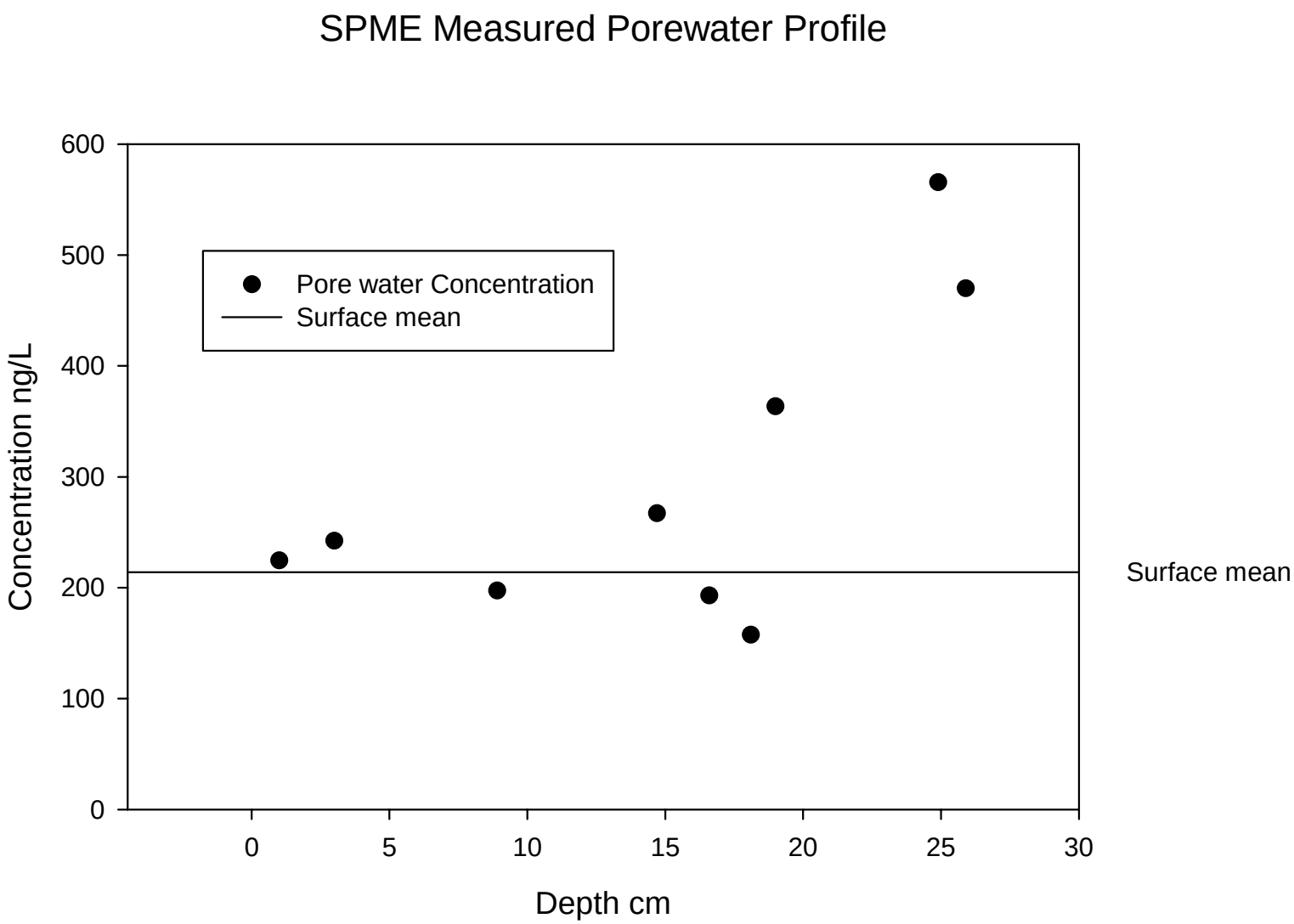
Teflon disk



Conder and La Point (2004): *Env. Tox. Chem. 23*:141

Field Deployment System

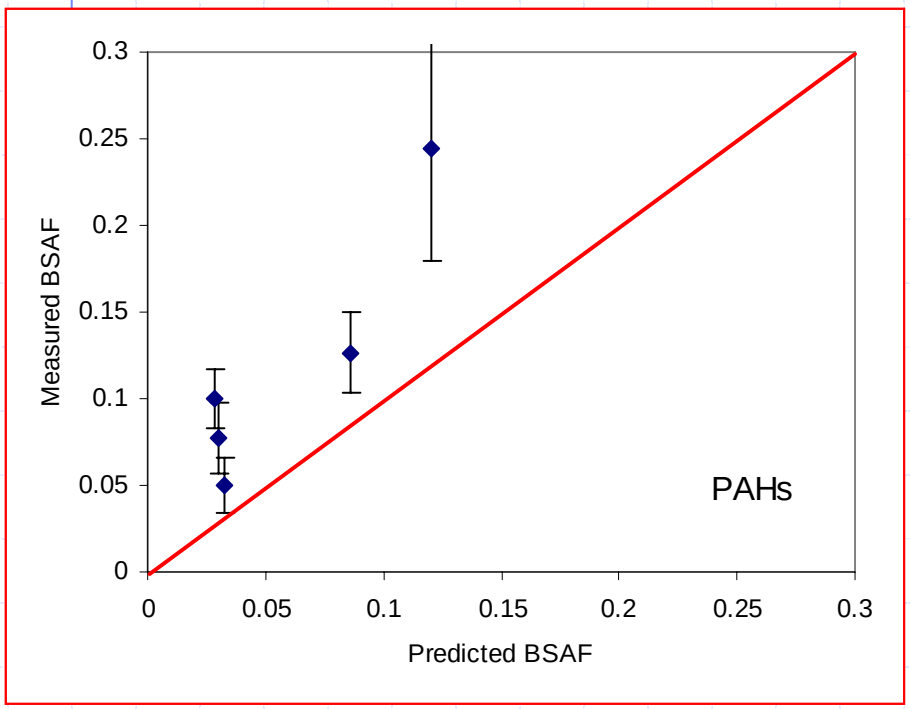
Porewater Concentration Profiles

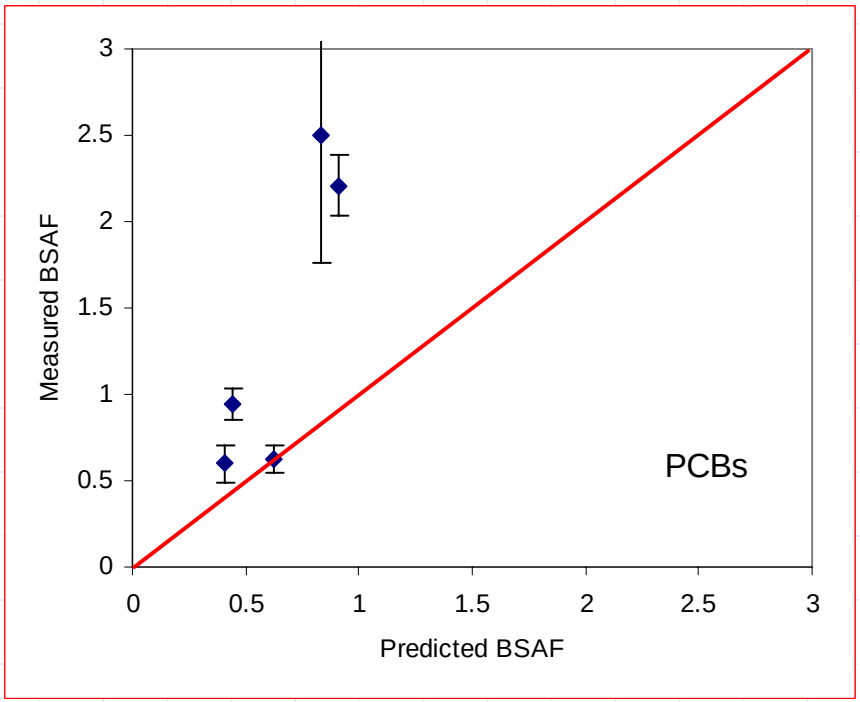


Anacostia Sediment Porewater Concentration

PAH	Measured SPME	Measured by LLE	If Reversibly Sorbed
Phenanthrene	210	370	1810
pyrene	610	730	990
chrysene	7.1	7.8	83
B[*b*]F	2.1	5.3	70
B[*k*]F	1.8	2	55
B[*a*]P	1.9	2	68

Biota-sediment accumulation factors of PAHs and PCBs(Measured vs predicted)





Preliminary Conclusions

- Good correlation of porewater concentration with uptake for all compounds
- SPME provides excellent indication of porewater concentration and uptake (within a factor of two in this preliminary assessment)
- Measured BSAF for both PAHs and PCBs were greater than predicted
- Indicates $K_{lipid}/K_{oc} > 1$
  - PAH - K_{lipid}/K_{oc}~ 1.25 - 2
  - PCB - K_{lipid}/K_{oc} ~ 1-3
  - PAHs – BSAF<<1 indicates desorption resistance in complex field-contaminated sediment