Defining the Availability of Contaminants in Sediments

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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 ?

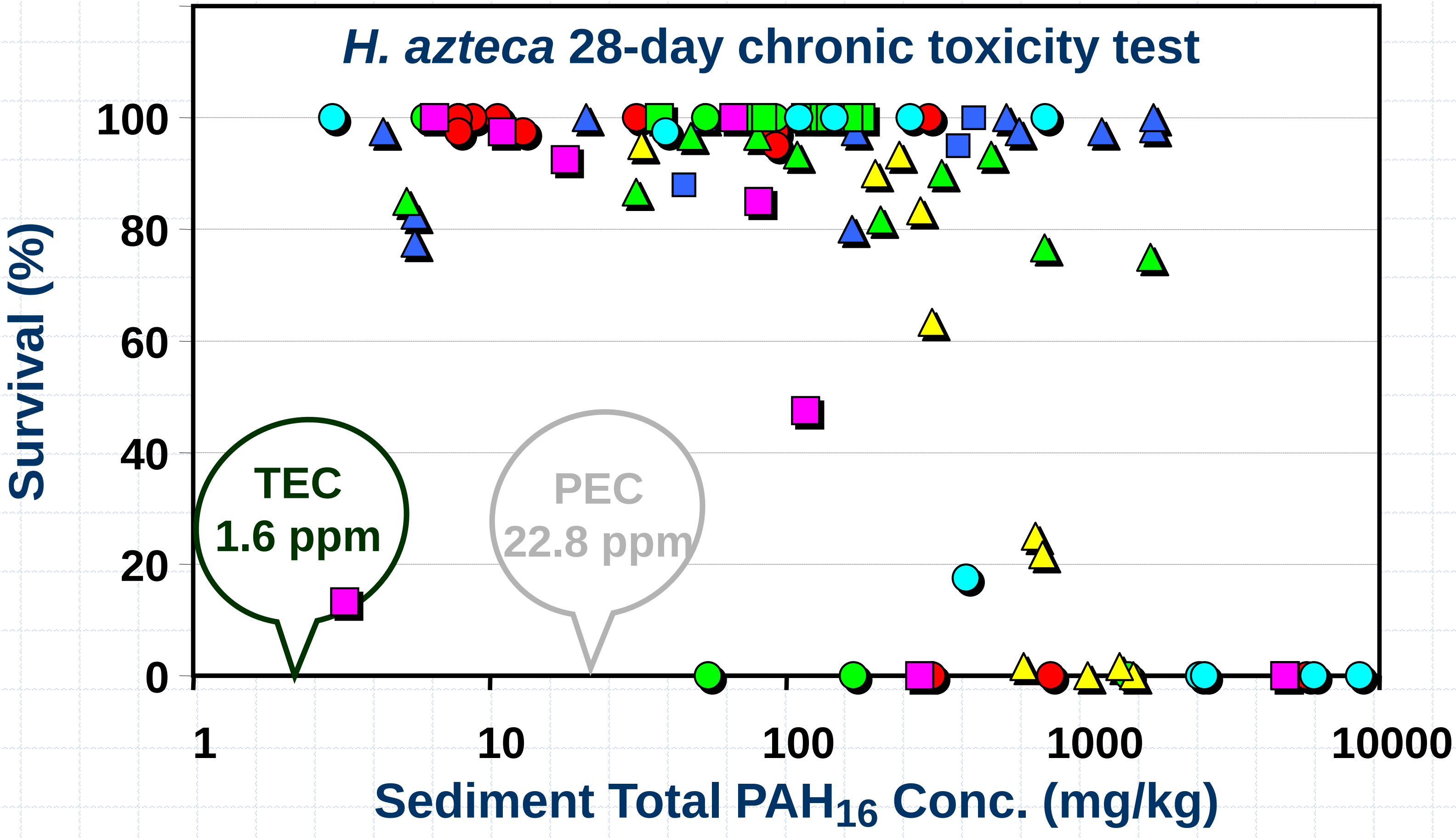
A Tale of Two Contaminants

- Hydrophobic Organic Contaminants
  - PAHs
  - PCBs
- Mercury

Hydrophobic Organic Compounds

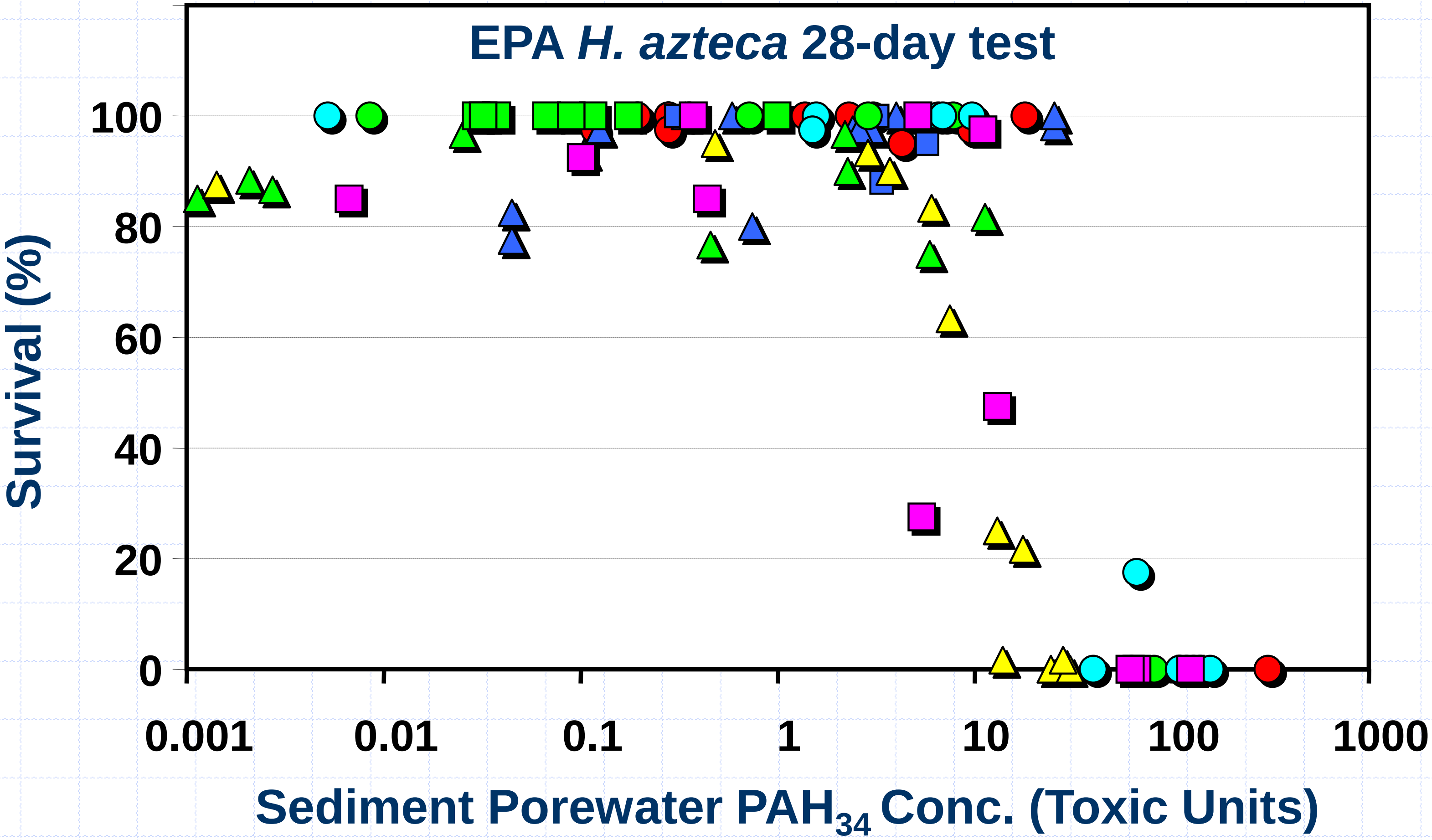
Does pore water concentration define exposure and risk?

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)

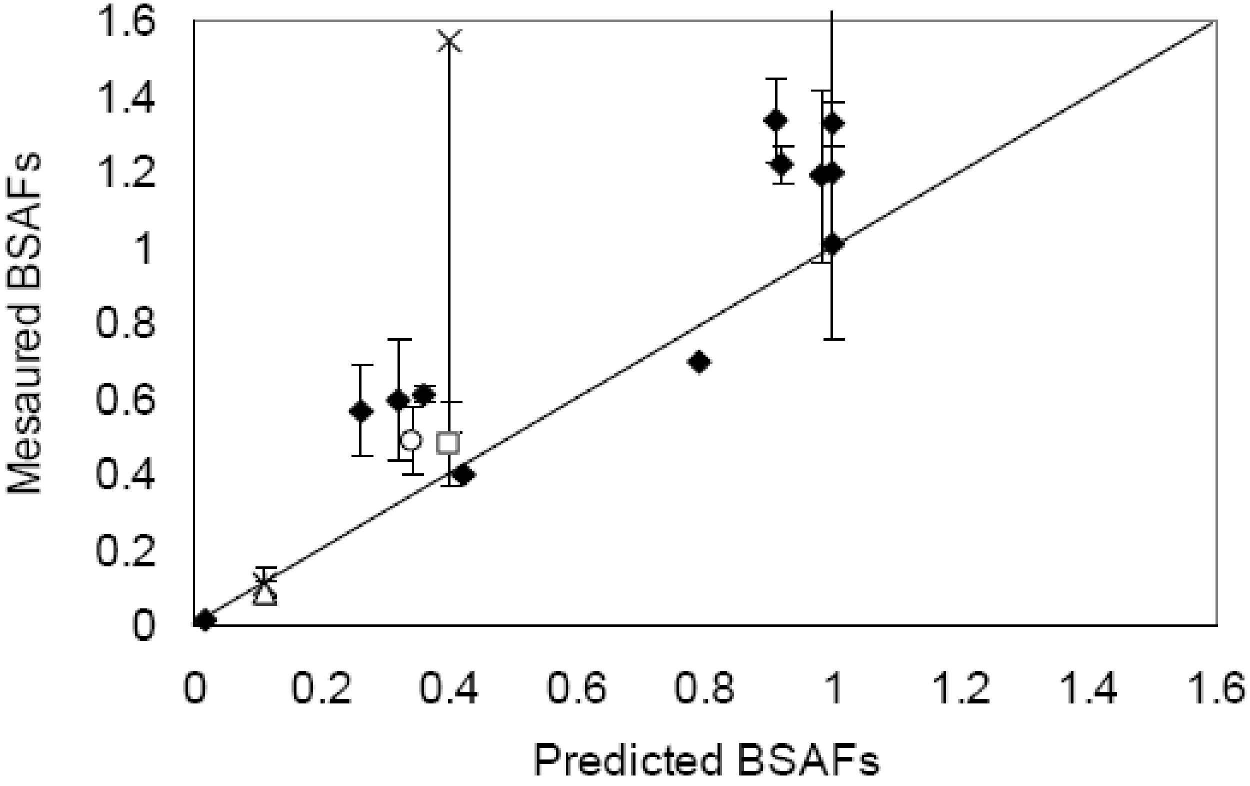
f_{oc} is total organic carbon content of the sediment (g TOC/g dry sediment).

Normalized Accumulation as Indicator of Bioavailability

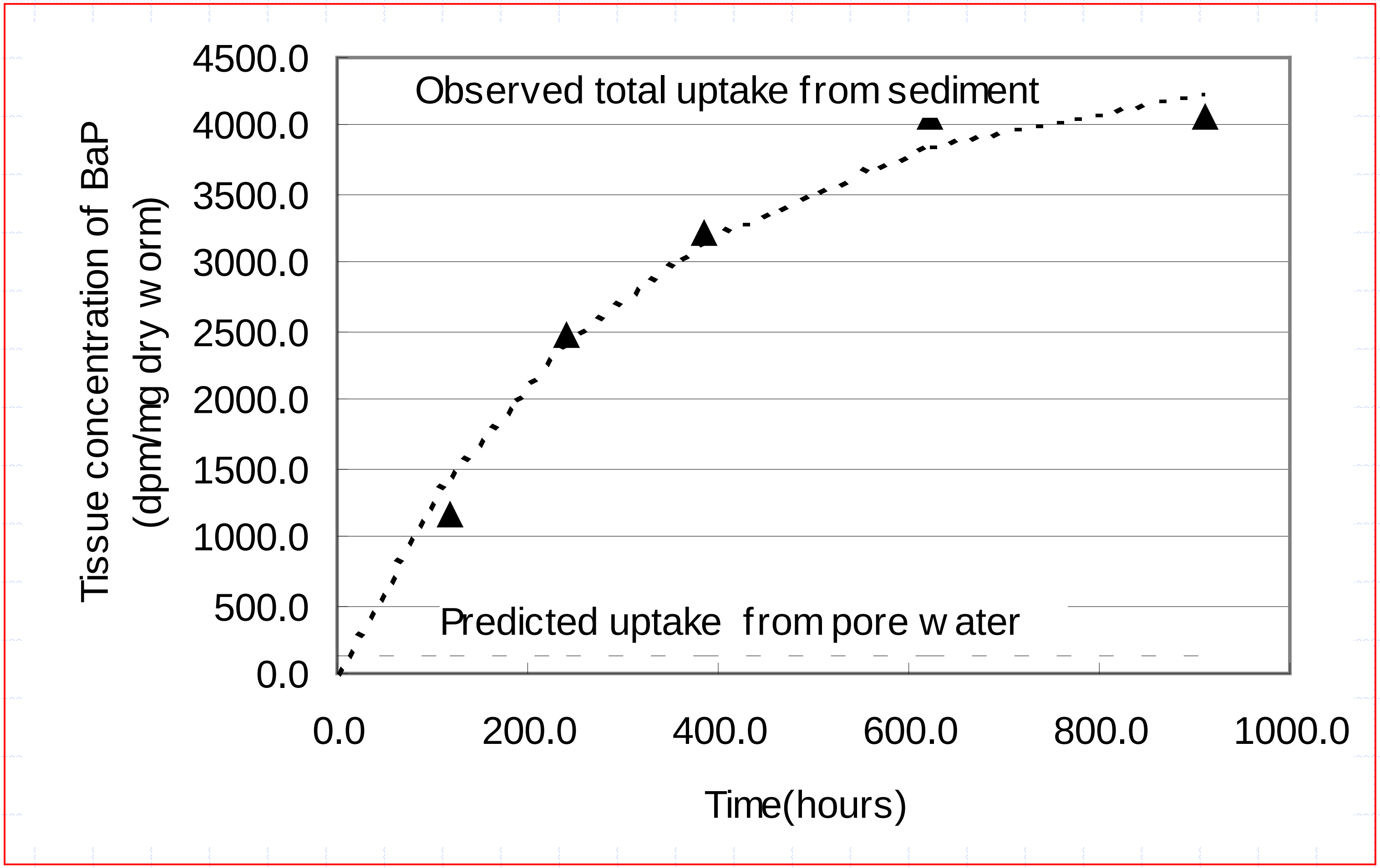
- BSAF of O(1) for reversibly sorbed non-metabolizing contaminants in directly exposed organisms at steady state (e.g. benthic deposit feeders)
- If accumulation indicated (not necessarily caused) by porewater concentration

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

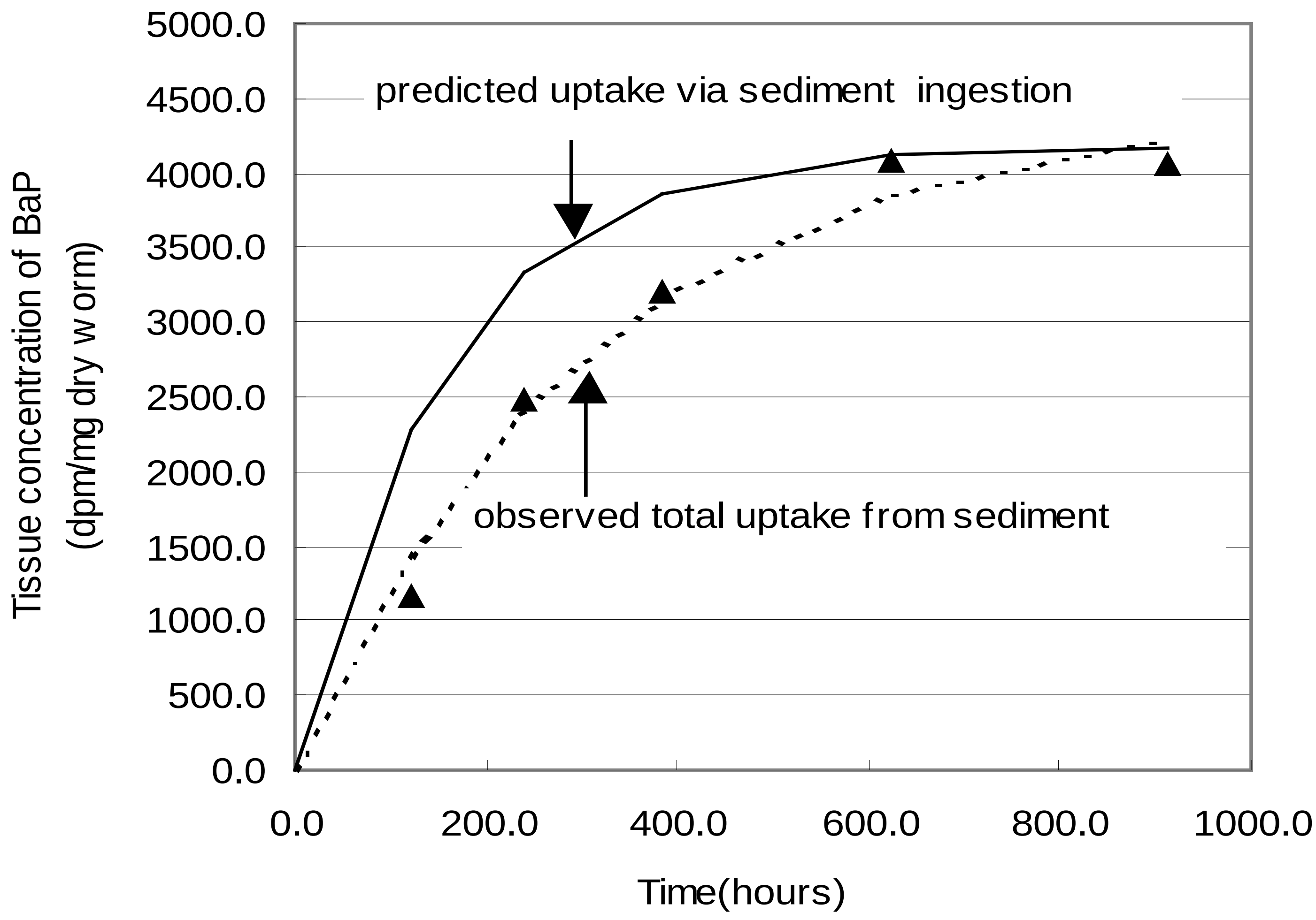
Does it predict uptake of PAHs ?



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

Overall Project plan

- Laboratory
  - Optimization of Deployment Conditions
  - Correlation with uptake in benthic organisms under controlled conditions
- Field
  - Demonstration of relationship between measured pore water and organism uptake
  - Comparison to conventional measurements
- Commercial Laboratory
  - Demonstrate potential for routine availability

Laboratory efforts

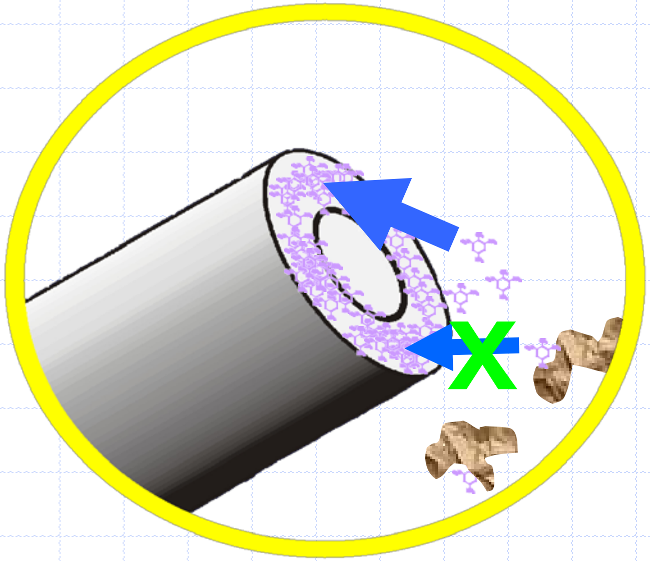
- Evaluate key implementation characteristics
  - Fiber-water partition coefficient
  - Dynamics of uptake
  - Reproducibility
  - Accuracy
- Confirm relationship to availability
  - PCBs/ PAHs
  - Freshwater/ Marine Organism
  - Endpoint- Accumulation
  - Methods
    - “Raw” Sediment exposure
    - Sequential dilution exposure

Field efforts

- Freshwater and Marine Sites
- Opportunistic organisms and controlled (caged) organism studies
- PAHs/PCBs
- Adherence to DoD QA/QC guidelines
- Cooperative efforts where possible
  - Anacostia Active Capping Demonstration (Reible)
  - Hunters Point Demonstration (Luthy)
  - PET development (Gschwend)
  - Survival endpoint (Nackles)

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,

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

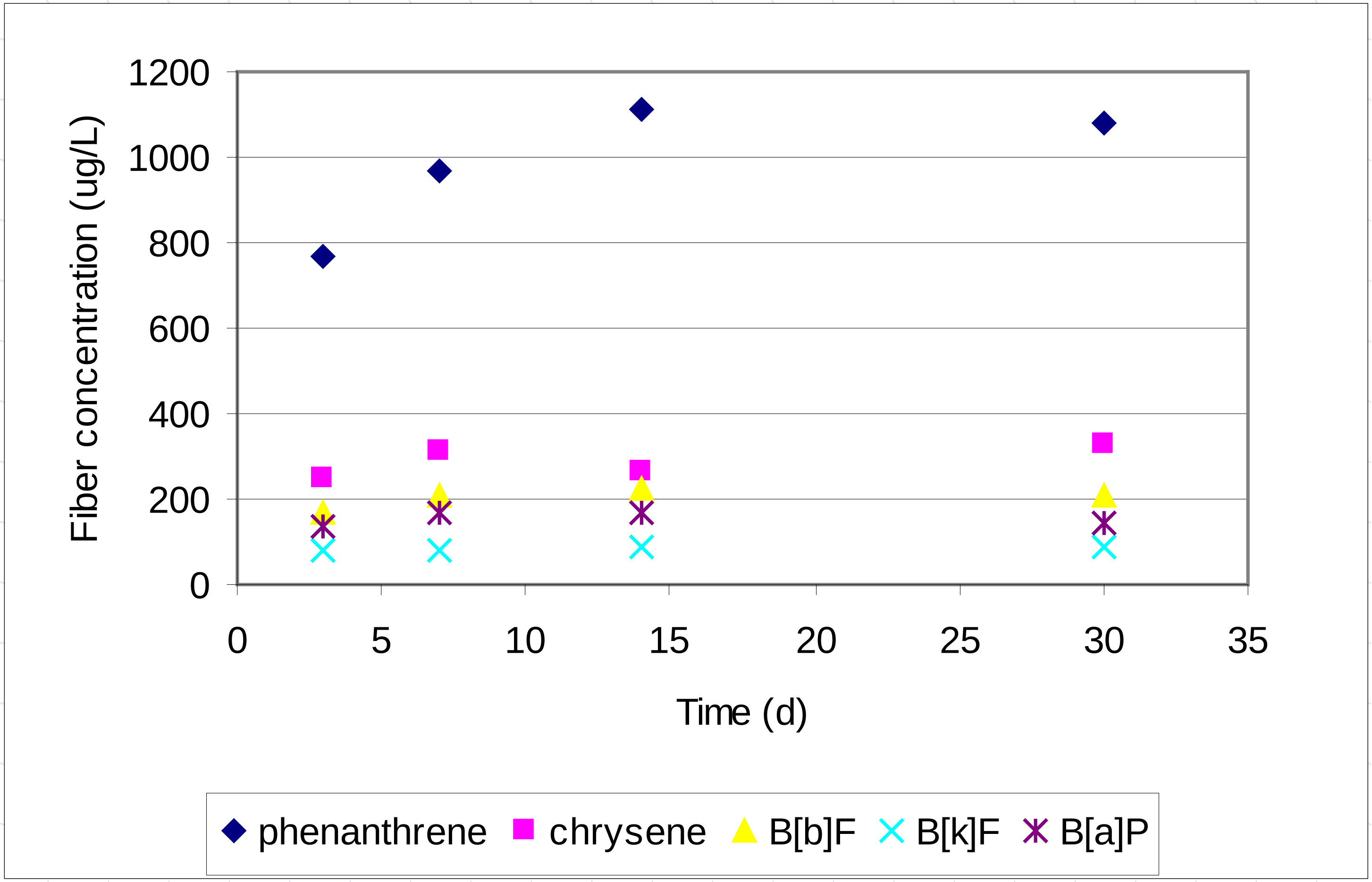
C_{fiber}=mass of contaminant absorbed by fiber/fiber volume (volume of PDMS)

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

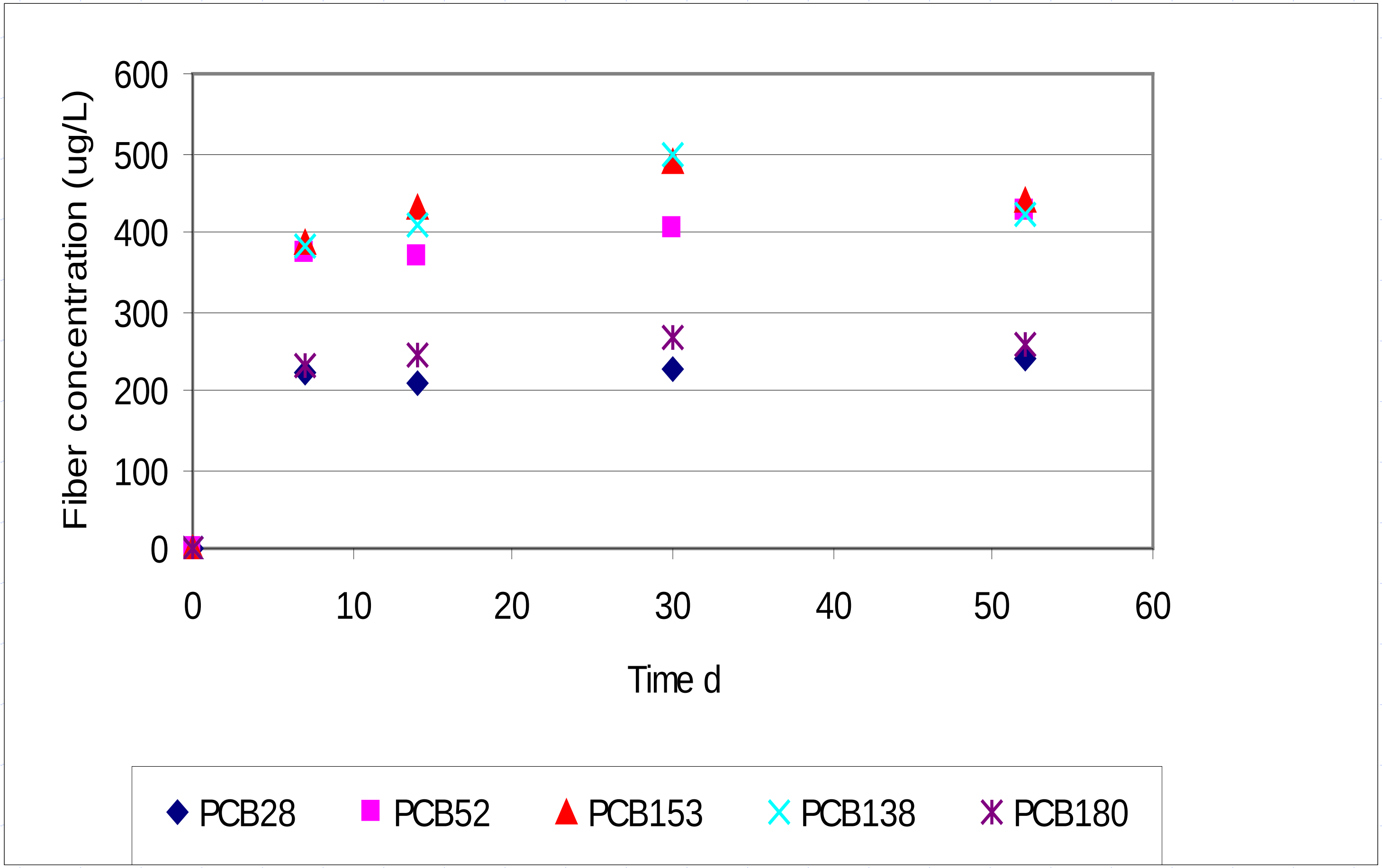
Expected detection limit PDMS fiber

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**

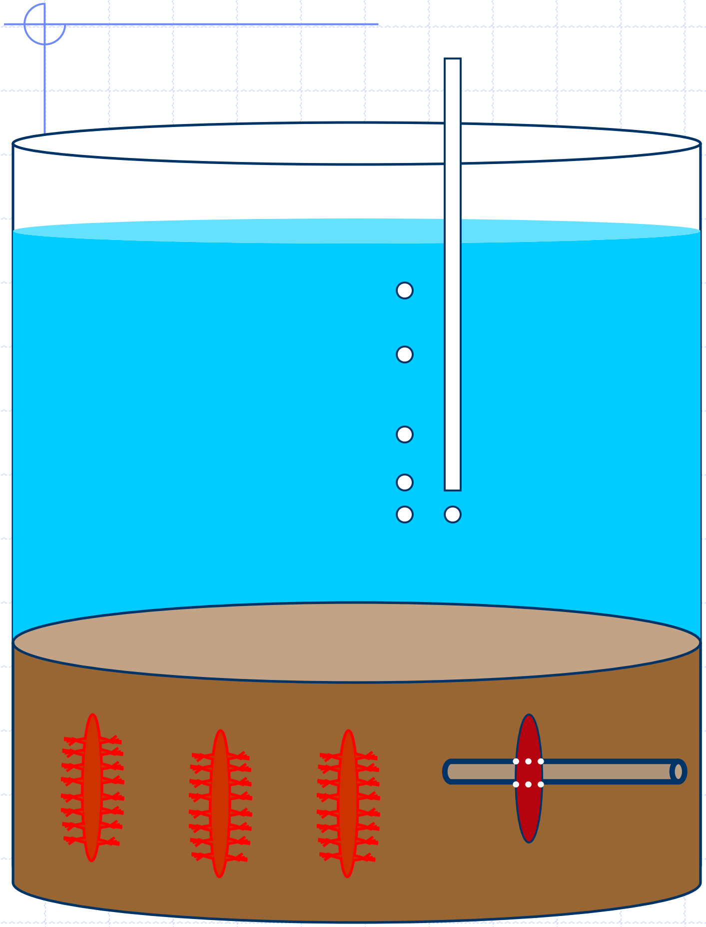
Uptake of PAHs in PDMS fiber (Sediment)



Uptake of PCBs in PDMS fiber (Sediment)



Benthic Bioaccumulation Experiments

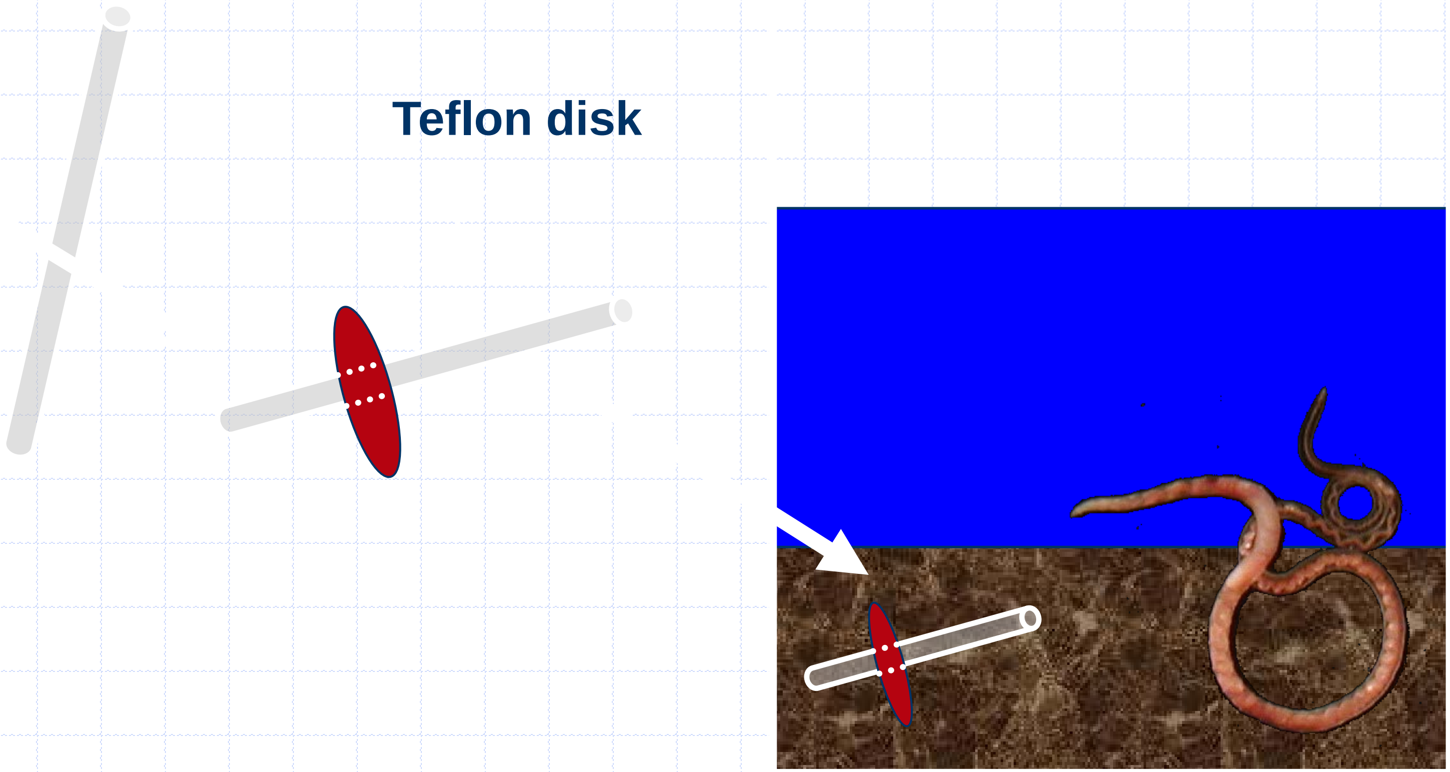


- Conduct whole-sediment exposures to simultaneously measure bioaccumulation and fiber uptake.

Exposure design

- Mass of exposure organism per replicate approximately 50 mg
- Ratio OC to biomass > 50:1
- 21-day exposure duration
- No feeding
- Gentle aeration
- Overlying water exchanged 2x weekly

SPME Deployment in Sediment



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

Experimental Species

Leptocheirus plumulosus

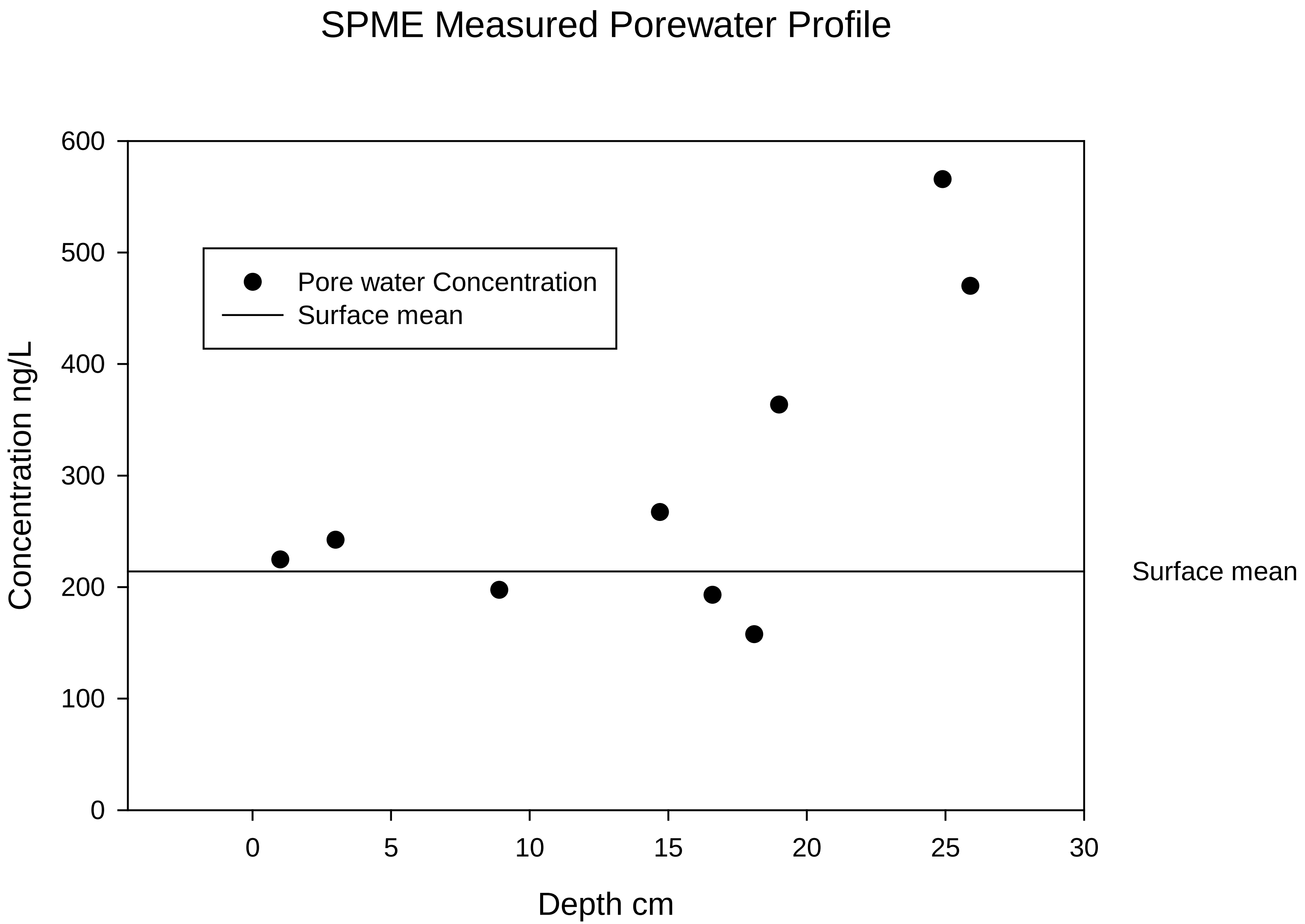
Neanthes arenaceodentata

Lumbriculus variegatus

Tubifex tubifex

Field Deployment System

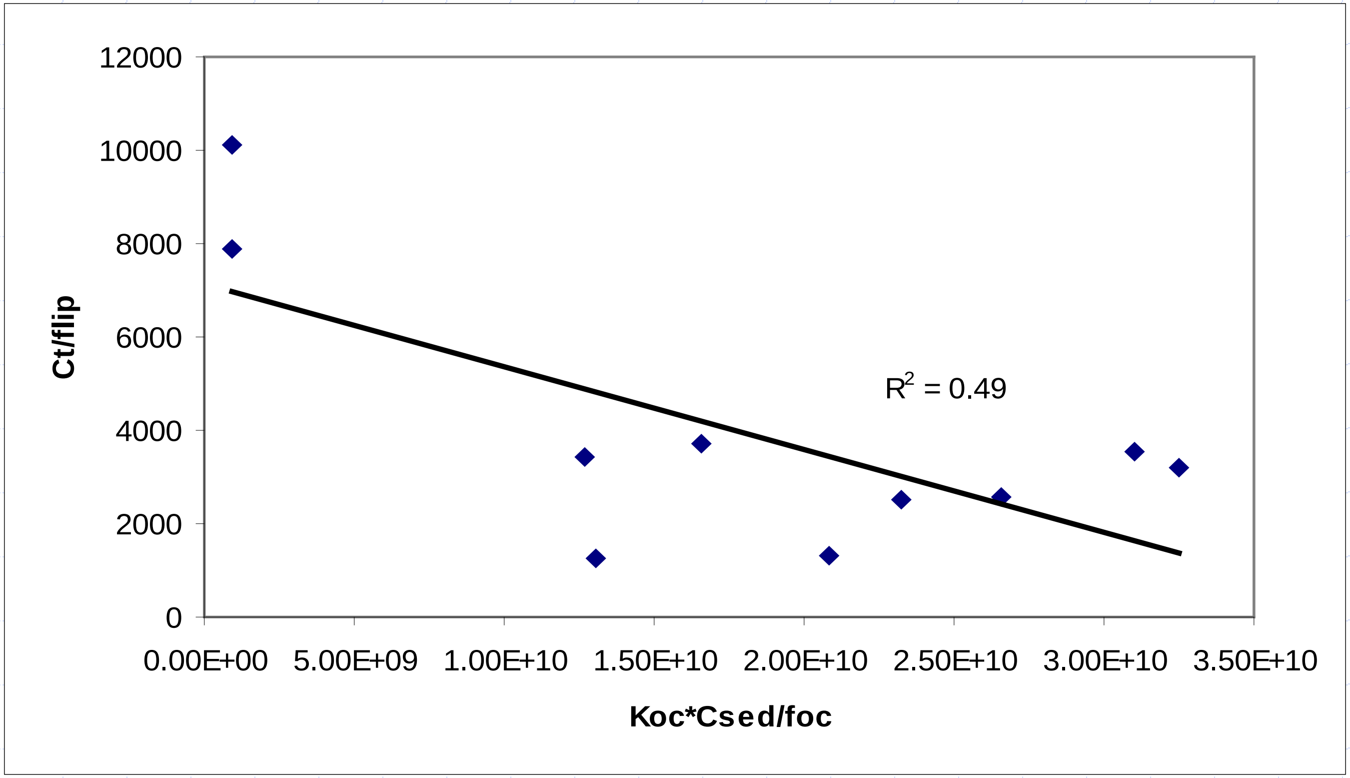
Porewater Concentration Profiles



Anacostia Sediment Porewater Concentration

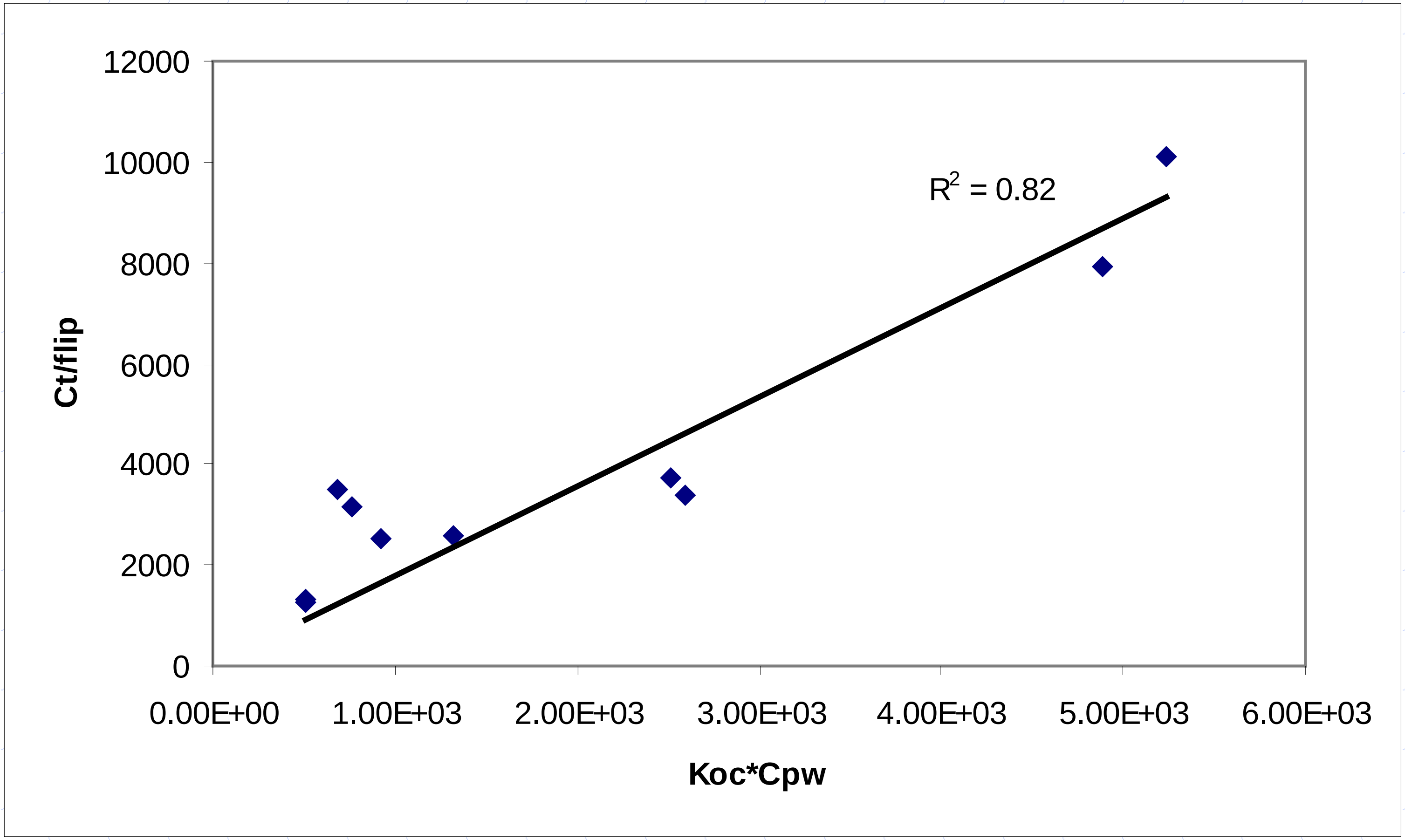
PAH	Measured SPME	Measured by LLE	If Reversibly Sorbed
Phenanthrene	210	370	1810
pyrene	610	730	990
chrysene	7.1	7.8	83
B[*b*]F	2.1	5.3	70
B[*k*]F	1.8	2	55
B[*a*]P	1.9	2	68

PAHs correlated with:



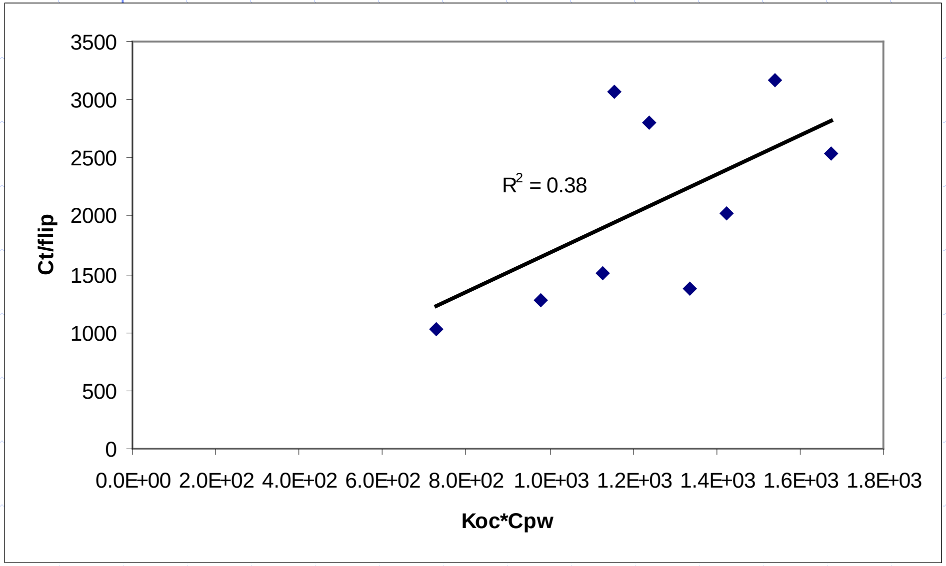
Bulk Sediment

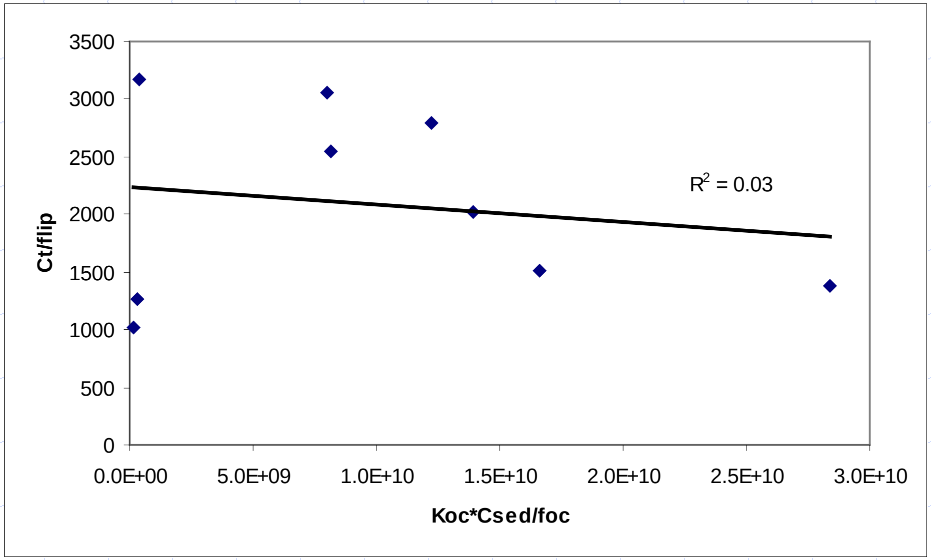
PAHs correlated with:



Pore water

PCBs correlated with:

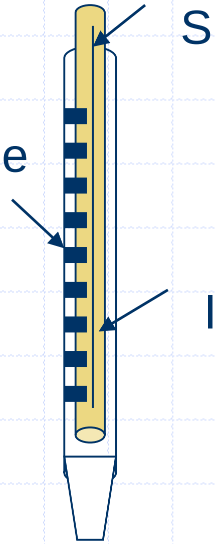




Pore water

Bulk Sediment

- Transition to the field
  - Optimization of the field implementation approach



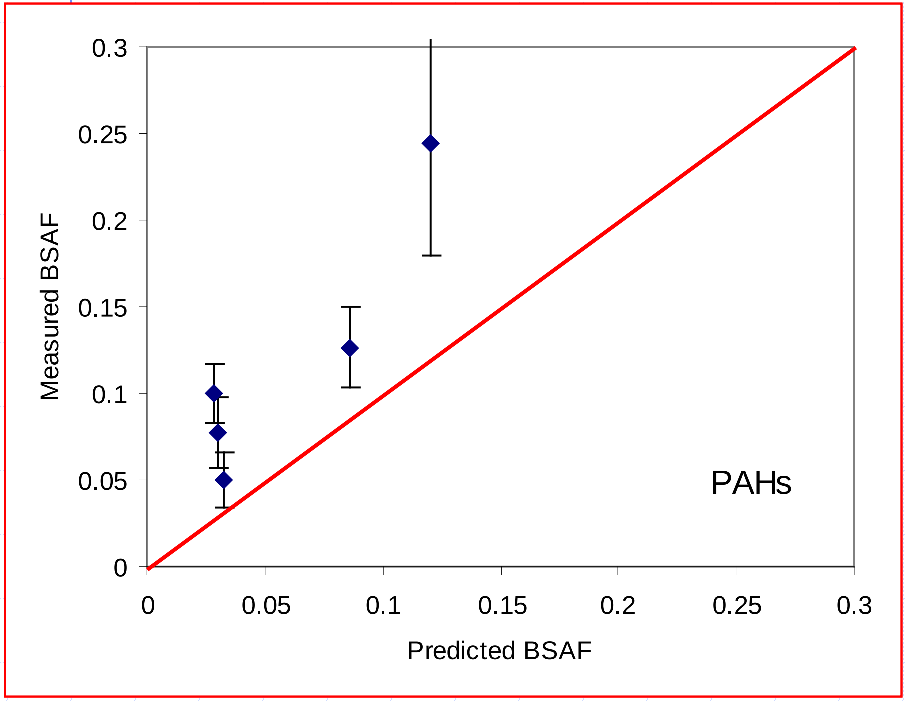
SPME Fiber

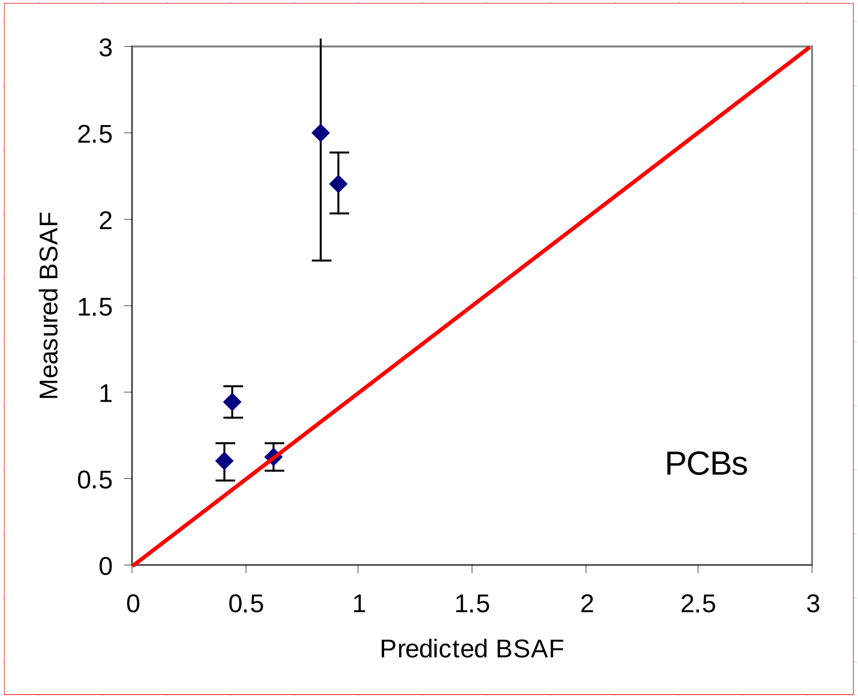
Outer slotted tube

Inner rod – SPME support

Field Deployment System

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



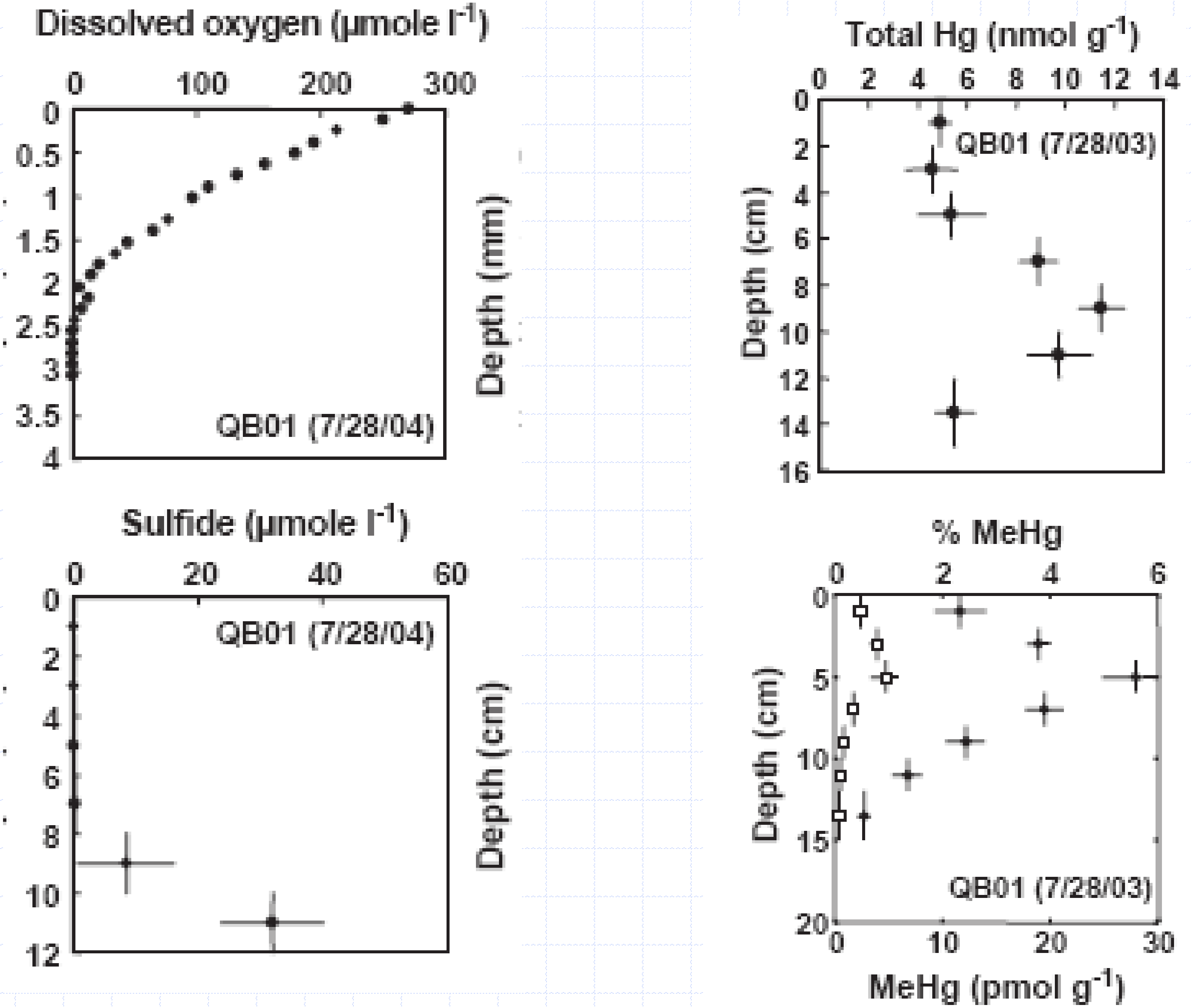


Preliminary Conclusions

- 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 - $K_{lipid}/K_{oc} \sim 1.25 - 2$
  - PCB - $K_{lipid}/K_{oc} \sim 1\text{-}3$
  - PAHs – BSAF<<1 indicates desorption resistance in complex field-contaminated sediment

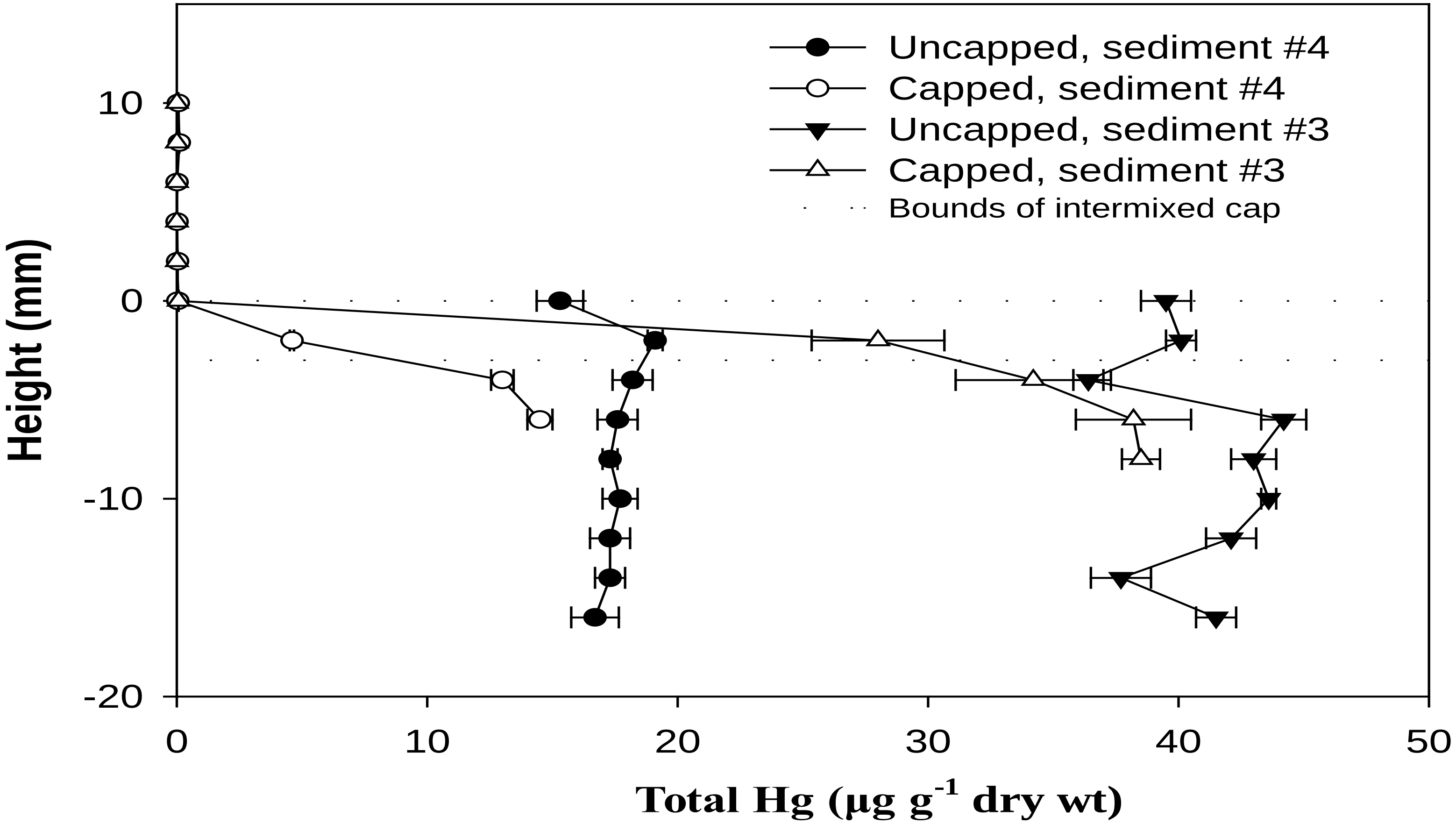
Mercury

Do soluble species define exposure and risk?

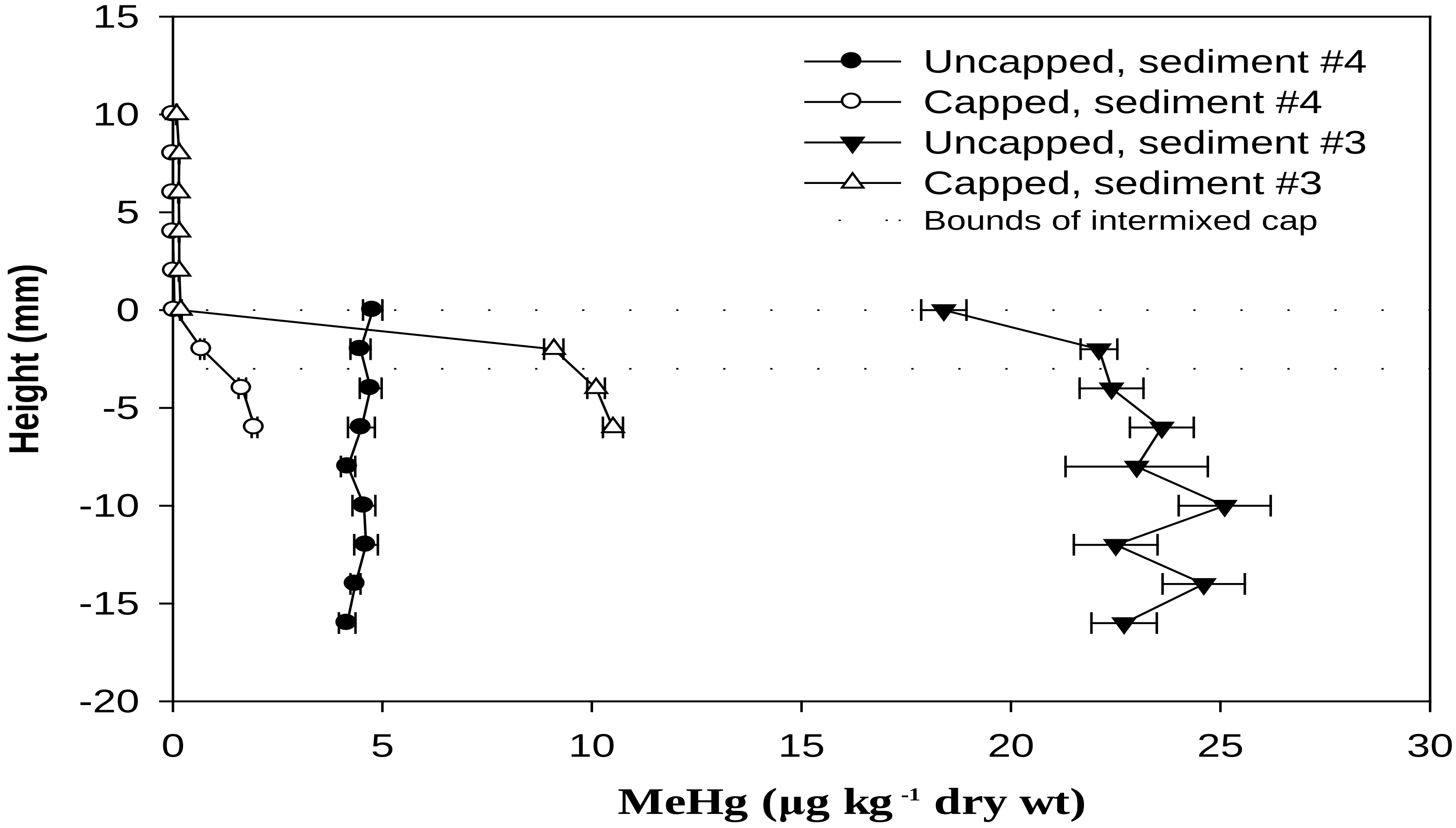

Dissolved oxygen (µmole l-1)
0
100
200
300
0
0.5
1
1.5
2
2.5
3
3.5
4
Depth (mm)
QB01 (7/28/04)
Sulfide (µmole l-1)
0
20
40
60
0
2
4
6
8
10
12
Depth (cm)
QB01 (7/28/04)
Total Hg (nmol g-1)
0
2
4
6
8
10
12
14
0
2
4
6
8
10
12
14
16
Depth (cm)
QB01 (7/28/03)
% MeHg
0
2
4
6
0
5
10
15
20
Depth (cm)
QB01 (7/28/03)
0
10
20
30
MeHg (pmol g-1)

Benoit et al.

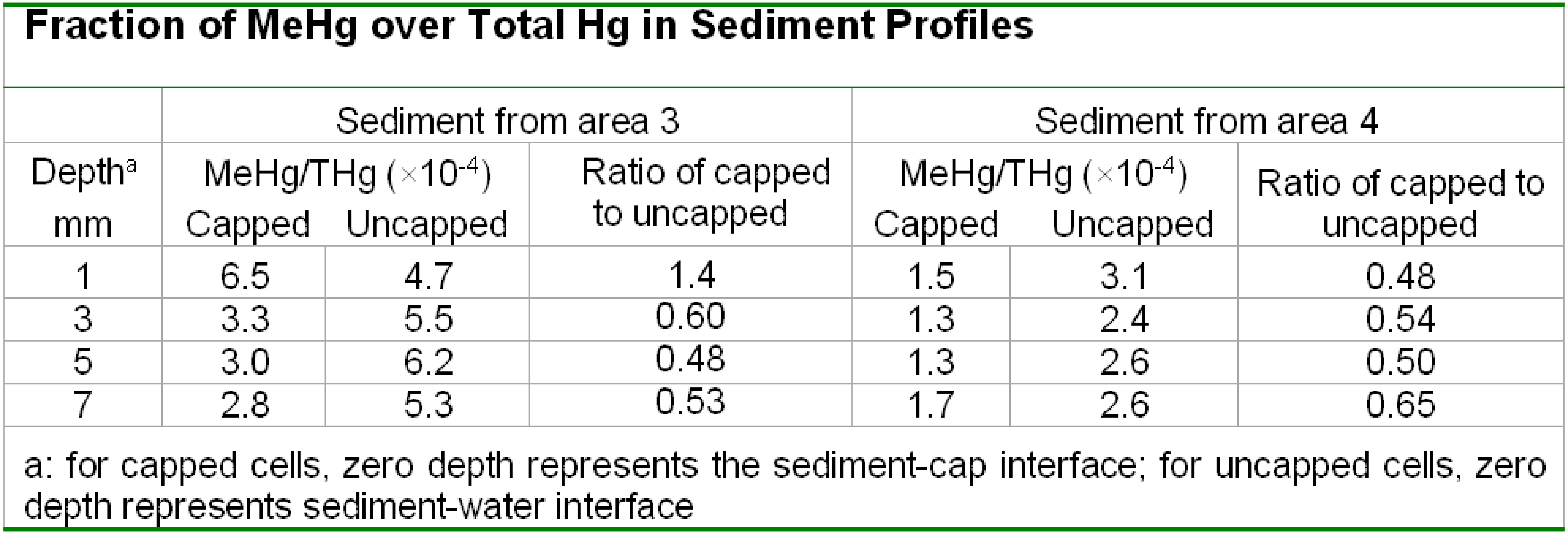
Mercury Containment by a Cap



Methylmercury Containment by a Cap



Methylmercury Production

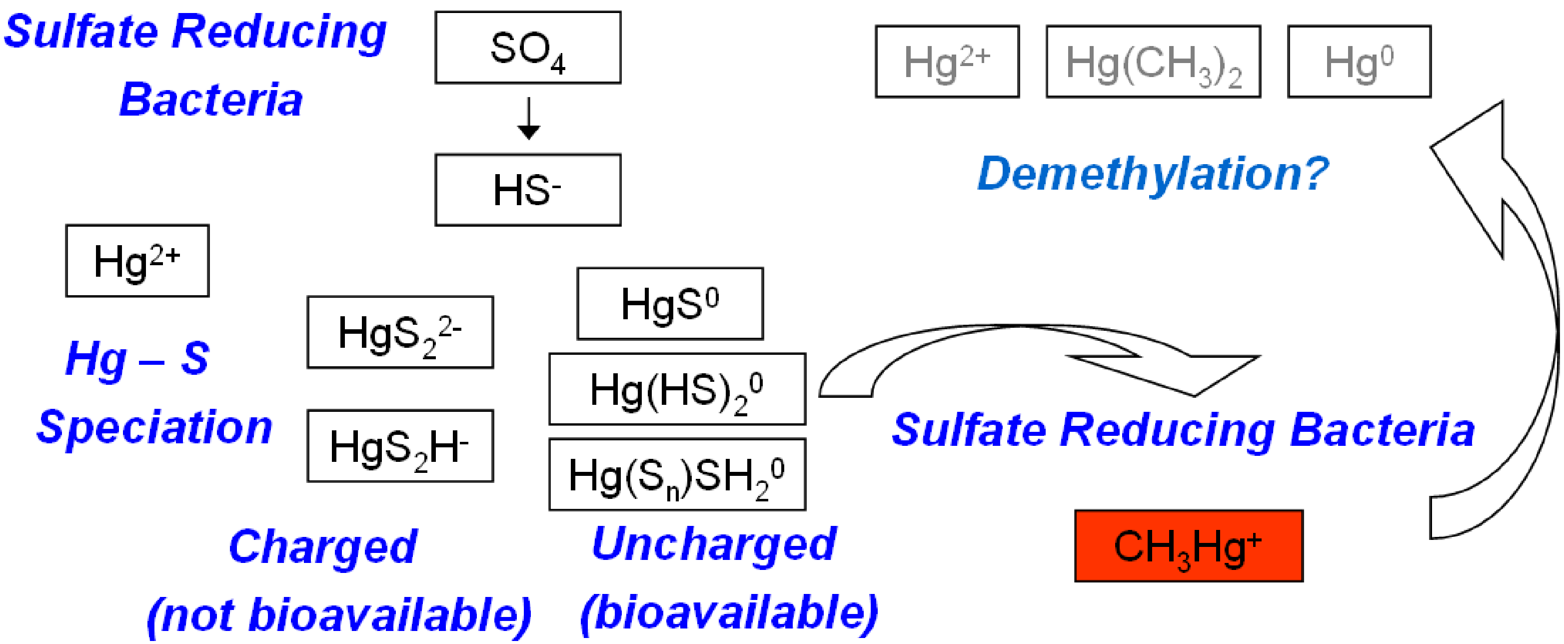


Fraction of MeHg over Total Hg in Sediment Profiles

	Sediment from area 3			Sediment from area 4		
Depth[a] mm	MeHg/THg ($\times 10^{-4}$) Capped	MeHg/THg ($\times 10^{-4}$) Uncapped	Ratio of capped to uncapped	MeHg/THg ($\times 10^{-4}$) Capped	MeHg/THg ($\times 10^{-4}$) Uncapped	Ratio of capped to uncapped
1	6.5	4.7	1.4	1.5	3.1	0.48
3	3.3	5.5	0.60	1.3	2.4	0.54
5	3.0	6.2	0.48	1.3	2.6	0.50
7	2.8	5.3	0.53	1.7	2.6	0.65

a: for capped cells, zero depth represents the sediment-cap interface; for uncapped cells, zero depth represents sediment-water interface

Mercury Fate in Sediments



Sulfate Reducing Bacteria

SO_4

HS^-

Hg^{2+}

Hg – S Speciation

HgS_2^{2-}

HgS_2H^-

HgS^0

$Hg(HS)_2^0$

$Hg(S_n)SH_2^0$

Charged (not bioavailable)

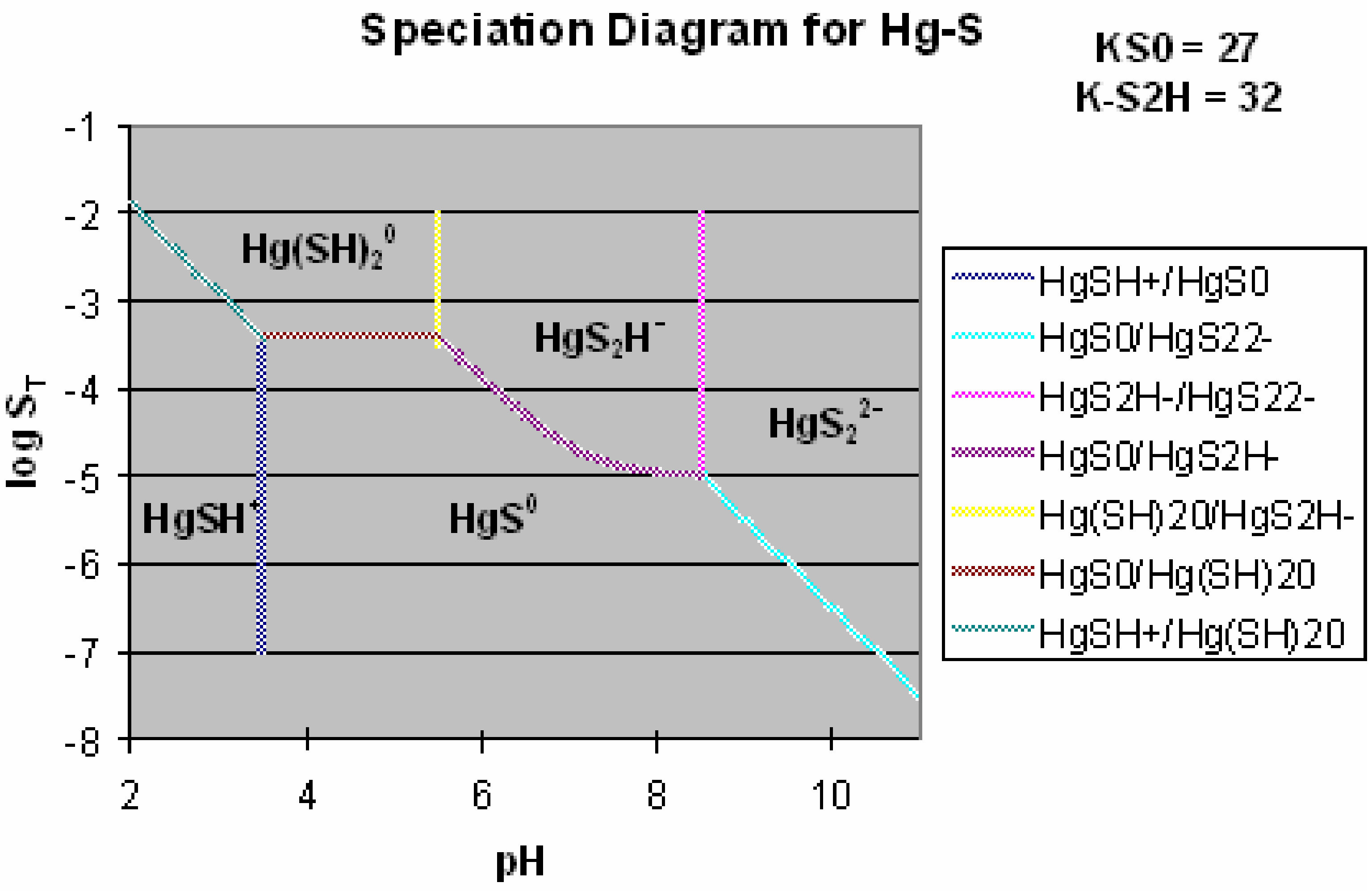
Uncharged (bioavailable)

Hg^{2+} $Hg(CH_3)_2$ Hg^0

Demethylation?

Sulfate Reducing Bacteria

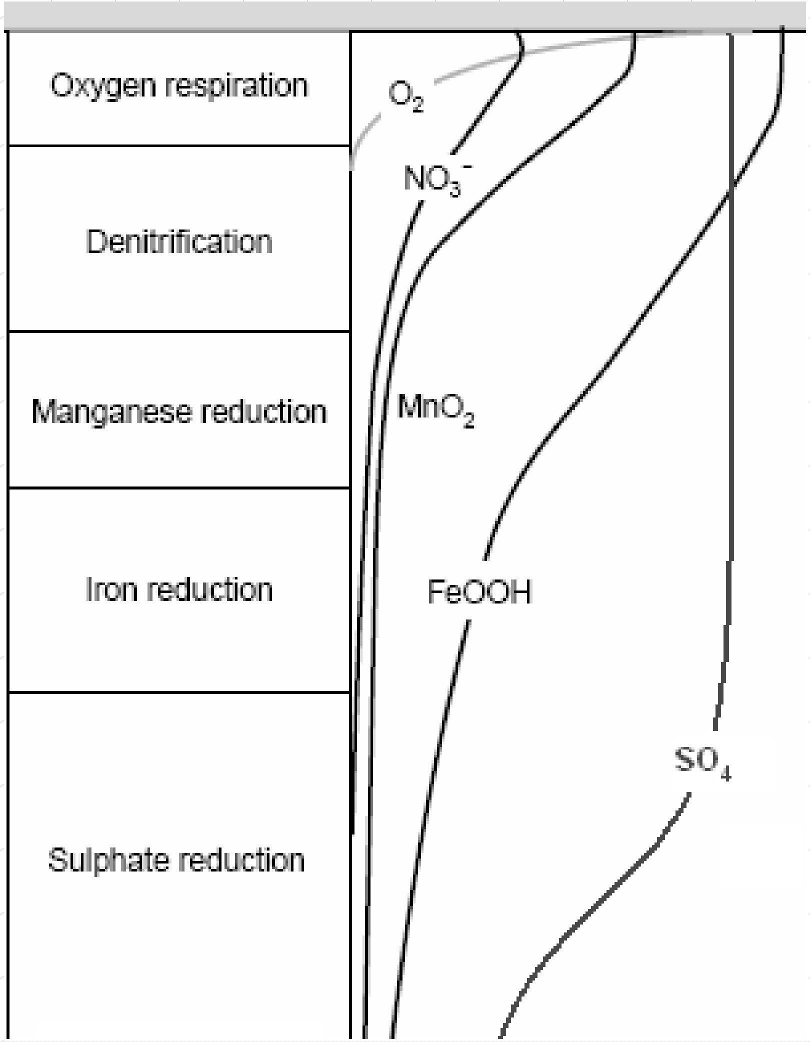
CH_3Hg^+


Speciation Diagram for Hg-S

KS0 = 27
K-S2H = 32

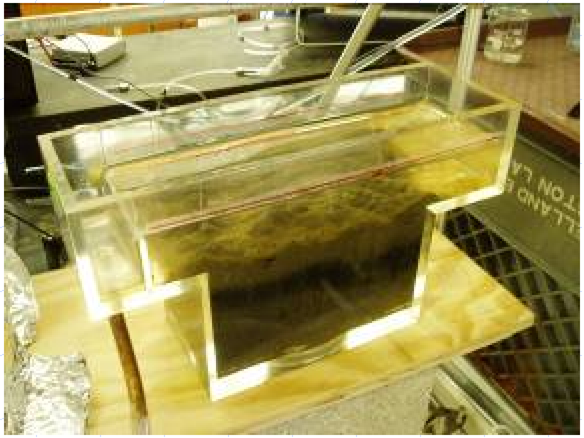
Motivation

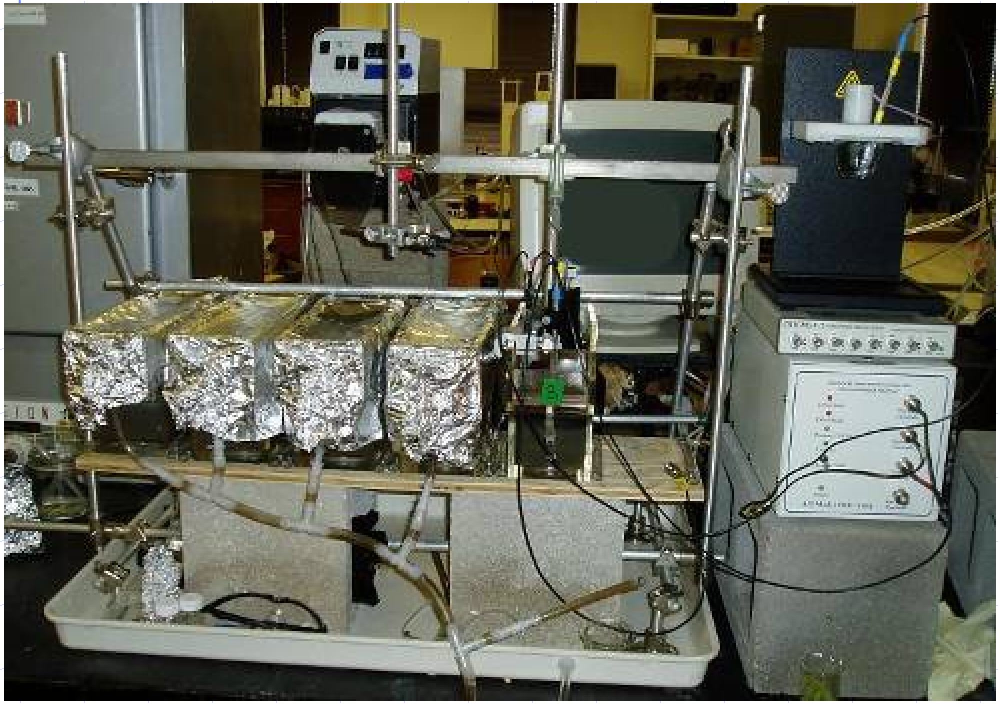
- Nutrient Cycling in Sediments
  - *Nutrient gradients governed by bacterial activity.*
  - *Mercury methylation mediated by Sulfate Reducing Bacteria.*
- Mercury Methylation tied to Sulfate Reduction



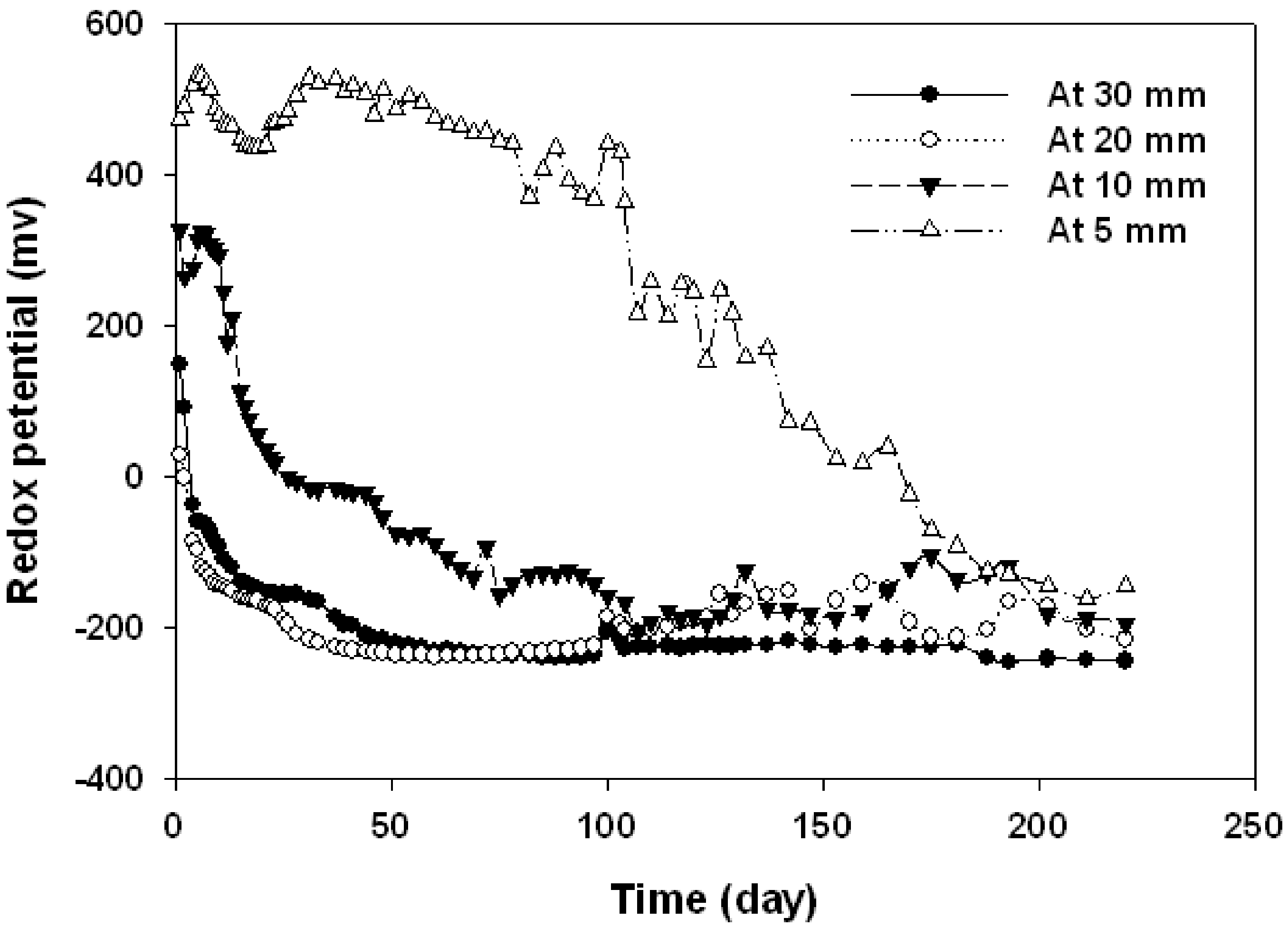
Experimental Set-up

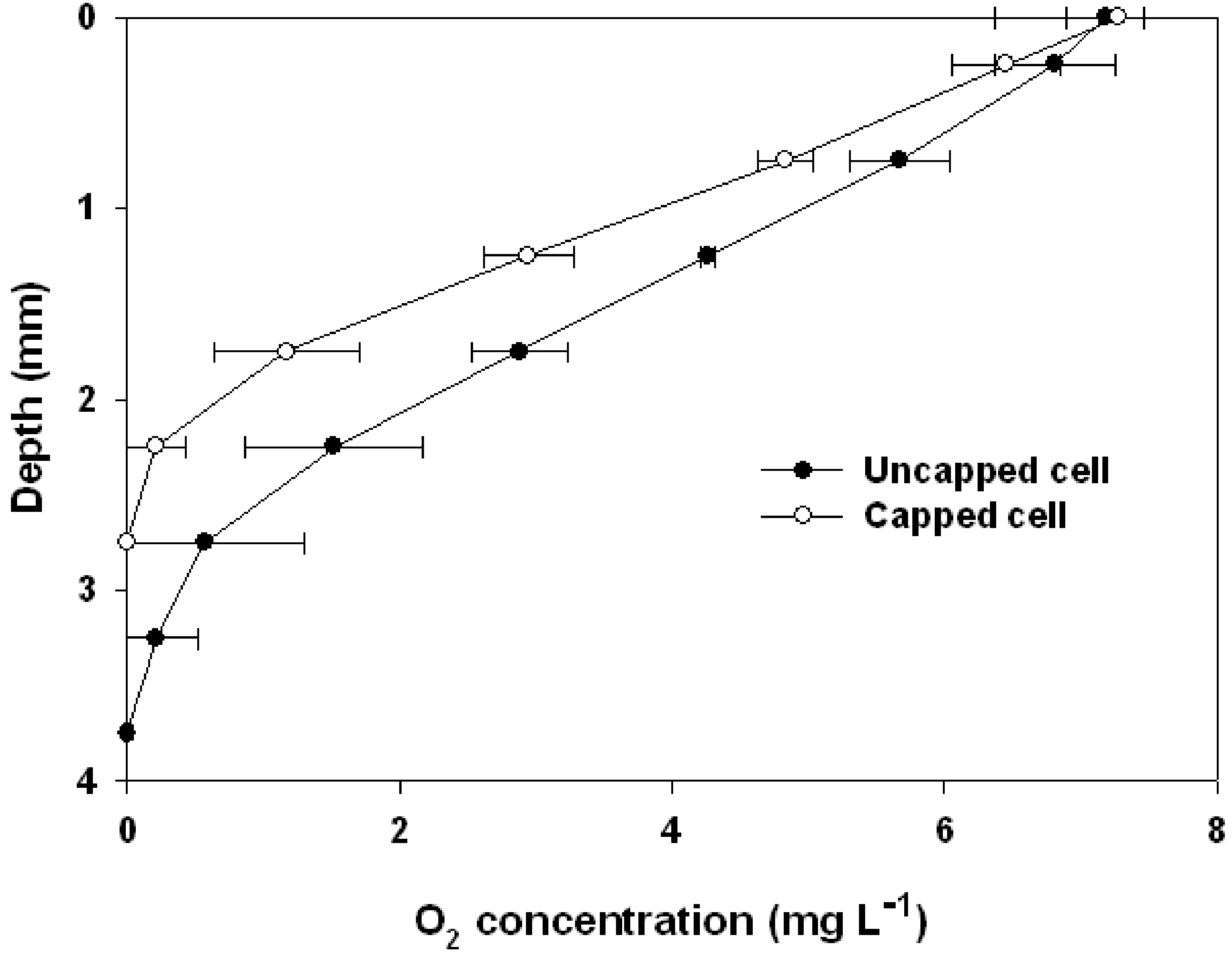
Bulk sediment samples placed in experimental microcosms and allowed to equillibrate





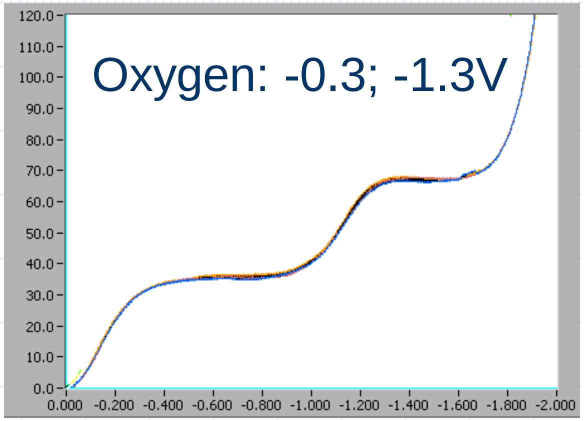
Aluminum support and micromanipulator used to hold electrodes in place

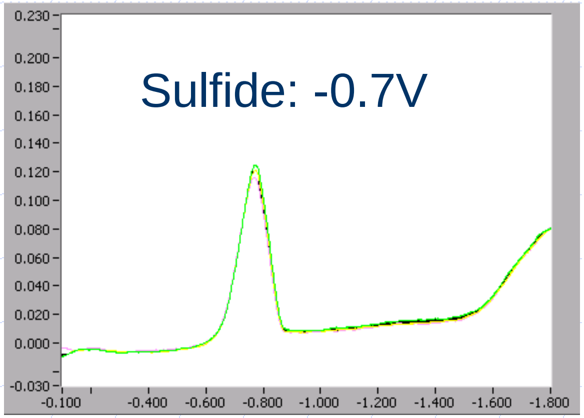

600
400
200
0
-200
-400
Redox petential (mv)
0
50
100
150
200
250
Time (day)
At 30 mm
At 20 mm
At 10 mm
At 5 mm

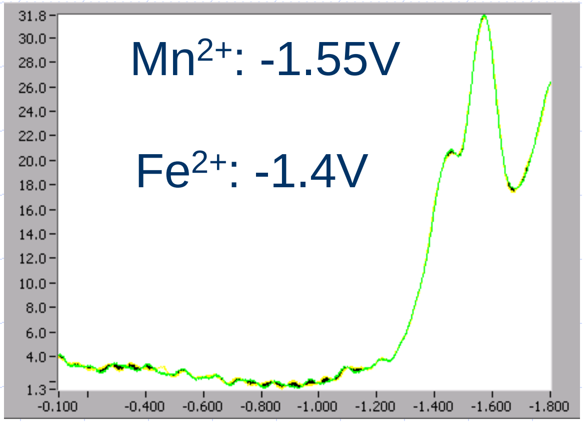

0
1
2
3
4
Depth (mm)
0
2
4
6
8
O$_2$ concentration (mg L^{-1})
Uncapped cell
Capped cell

Voltammetric Microelectrodes

- **Theory**
  - ***Apply sweeping electric potential to electrode***
  - ***Electroactive species in porewater are oxidized/reduced at characteristic potentials***
- **Capabilities**
  - ***Gold-Mercury amalgam microelectrode (ideally <1mm) measures O_2, Fe^{2+}, Mn^{2+}, HS^-, and $FeS_{(aq)}$, all environmentally important for redox cycling in sediments***


Oxygen: -0.3; -1.3V

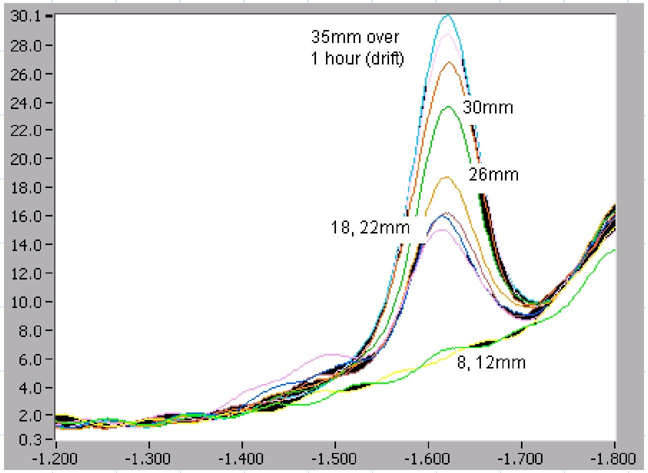

Sulfide: -0.7V

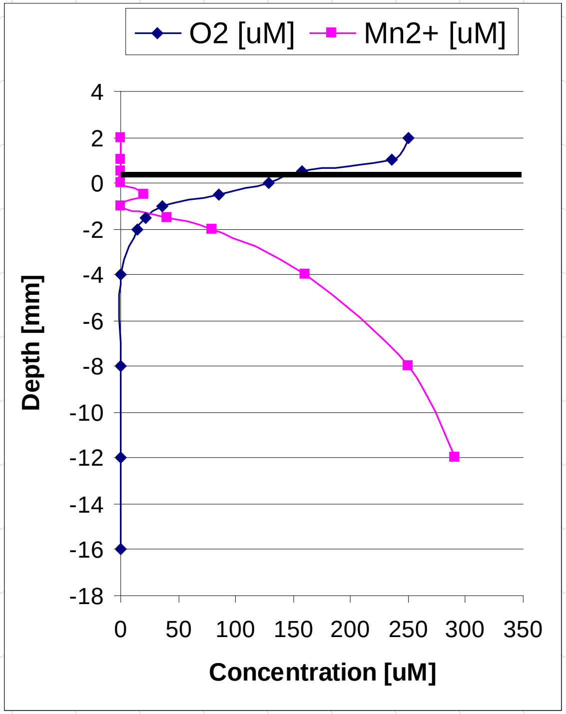

Mn^{2+}: -1.55V

Fe^{2+}: -1.4V

Preliminary Findings

- **Preliminary Profiles**
  - ***Oxygen disappears in first 2-3 mm in sediment***
  - ***Increasing amounts of Mn^{2+} (>200 uM) and Fe^{2+} observed***
  - ***No sulfide observed, but evidence of $FeS_{(aq)}$ complex***
- **Probing dynamics**
  - ***Size of electrode used for profiling important***
  - ***Should be <1mm for reasonable time to equilibrium***





Future Plans

- Capping Simulation
  - *Install electrodes at depths in and above sediment*
  - *Monitor to observe steady behavior*
  - *Place 1-2cm cap and monitor dynamics of changes in O_2, Mn^{2+}, Fe^{2+} due to cap placement.*
- Mercury Implications
  - *Before and after capping simulation, core column and measure total and methyl mercury.*
- Geochemical Modeling
  - *Calibrate geochemical model with results of experimental observations*
  - *Link mercury methylation to sulfate reduction in model*

Conclusions

- Hydrophobic organic uptake controlled by pore water concentration
- SPME promising method for determining pore water concentrations in-situ
- Mercury risk controlled by methyl mercury formation which is a strong function of sediment biogeochemistry and soluble species in pore water
- Capping appears to reduce methylation and effectively contains all mercury species
- Voltametry promising characterization method