CURRENT STATUS OF IN-SITU CAPPING FOR SEDIMENT REMEDIATION

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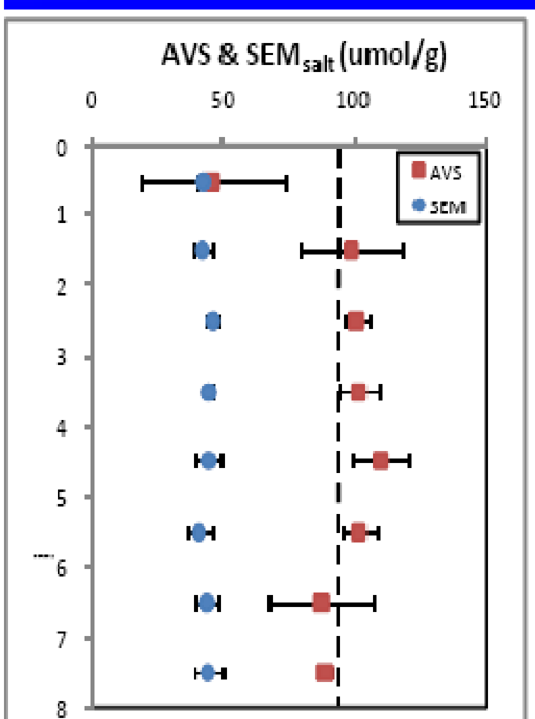
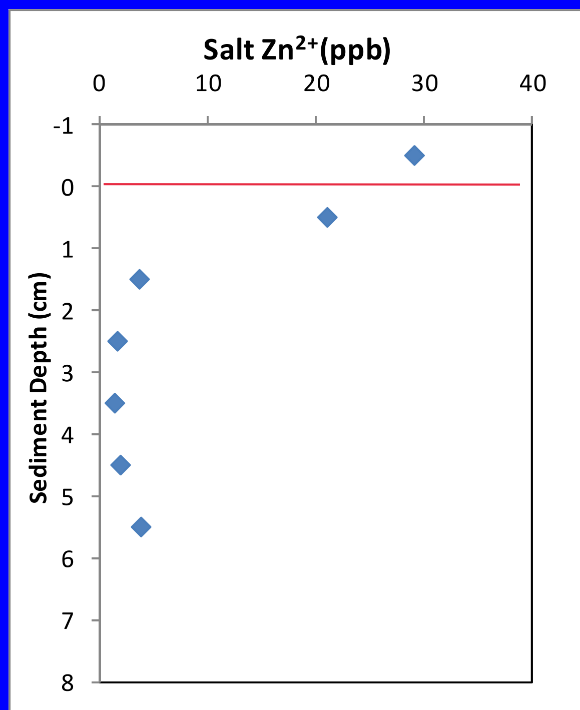
Current Issues in Capping

- Biogeochemistry beneath the cap
- Active Capping- Permeable adsorptive barrier
  - Material Options
  - Management of upwelling water /gas/NAPL
  - Effectiveness of materials
  - Placement of materials
  - Capping design- modeling
- Monitoring Cap Performance
  - *Definition of Cap Objectives*

Metals and Capping

- Metals often effectively contained by a conventional cap
- AVS vs. SEM- Capping will enhance reducing conditions





AVS > SEM

Metals will not be toxic

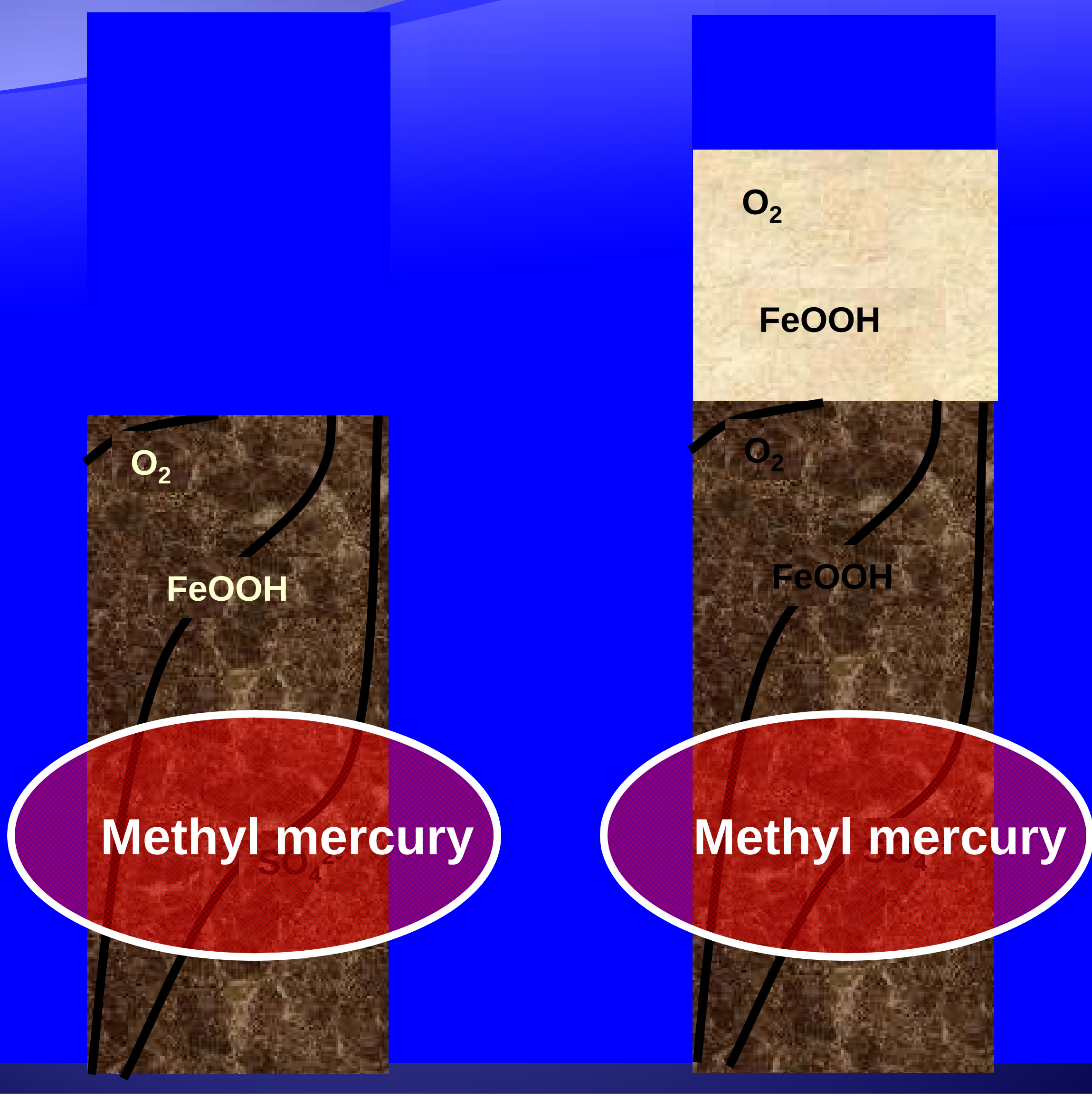
$M^{2+} + FeS_{(s)} \longrightarrow MS_{(s)} + Fe^{2+}$

AVS < SEM

Divalent metals may be toxic

Conceptual Model

Pre-Cap **Post-Cap**



Organics and Capping

- Mobility and toxicity generally not redox sensitive
- Degradation is redox sensitive
  - Hydrocarbon degradation facilitated aerobically
  - Chlorinated organics reductively dechlorinate but many sediment contaminants refractory
- Dynamics controlled by sorption in cap and groundwater upwelling

Active Capping

- Potentially greater effectiveness than with sand can be achieved with "active" or amended caps
  - Encourage fate processes such as sequestration or degradation of contaminants beneath cap
  - Discourage recontamination of cap
- Feasible if high value components are placed in thin layer in a controllable manner
- Effective if time/capacity of active cap sufficient to manage finite mass of contaminants
- Significant stakeholder acceptance advantage

Goals of Capping Amendments

- Permeability Control
  - Discourage upwelling through contaminated sediment by diverting groundwater flow
- Contaminant Migration Control
  - Slow contaminant migration, typically through sorption related retardation
- Contaminant Degradation Aid
  - Less well developed, contaminant specific but designed to encourage contaminant fate processes

Potential Active Cap/Treatment Materials

Demonstrated

- Clays for permeability control
- Activated Carbon or other carbon sequestration agent
- Organoclays for NAPL control & some dissolved control
  - Significant swelling and permeability reduction with NAPL
- Clay and sequestration agent mixtures
- Phosphate additives for metals
  - Rock phosphate (i.e. apatite) demonstrated
- Iron Sulfide for Hg and MeHg control
- Siderite ($FeCO_3$) for pH control
- Zero valent iron
- Oxygen or hydrogen release compounds/technologies
- Biopolymers
- Electrochemical controls on redox conditions

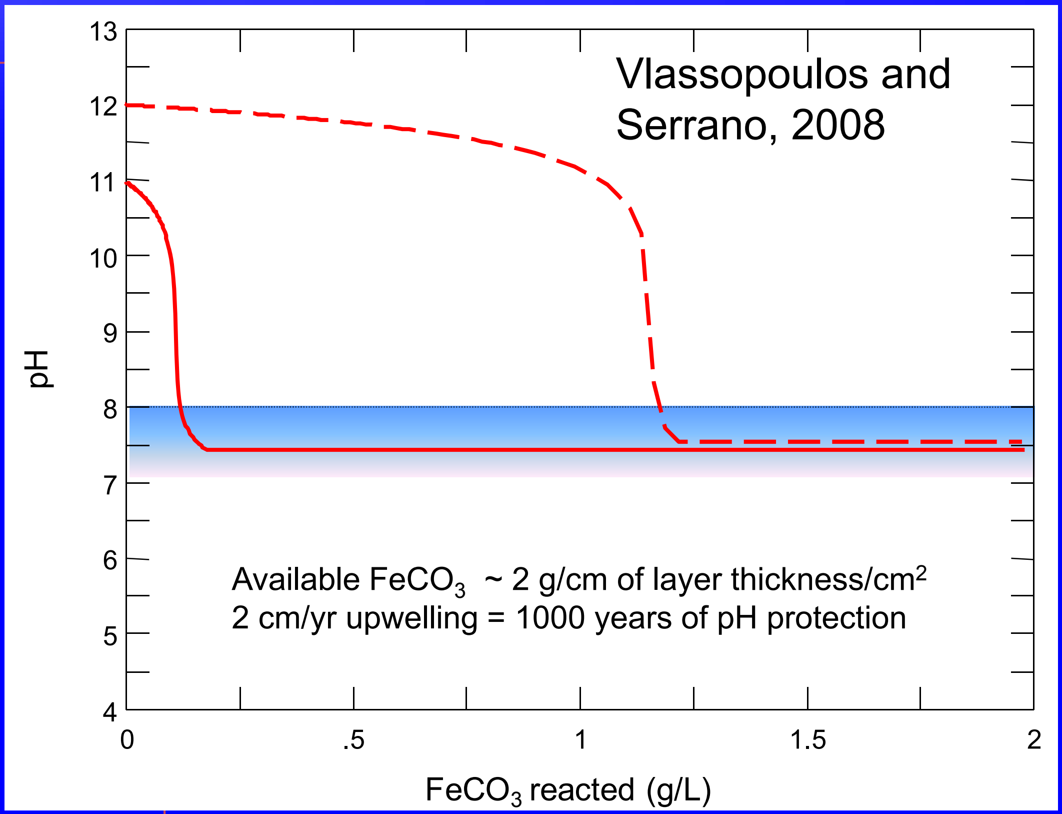
Speculative

Impermeable Caps

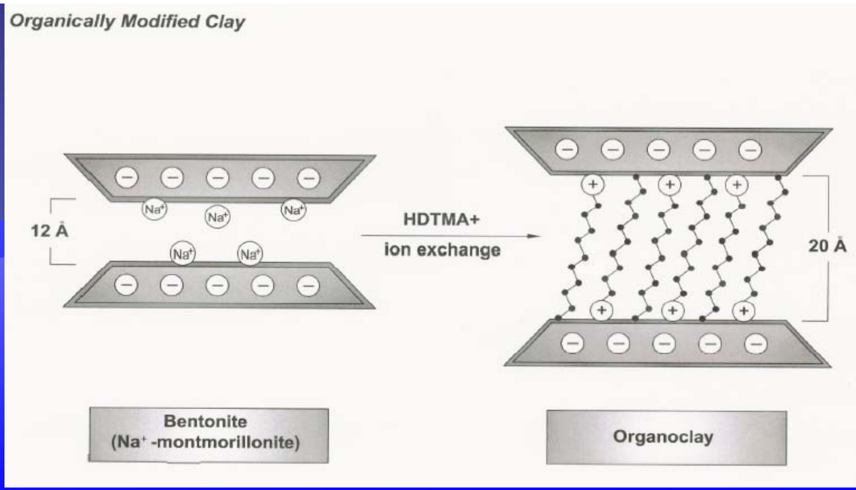
- Commercially available
  - AquaBlok
  - Bentomat
  - HDPE
- Can successfully divert groundwater upwelling
  - Where will the groundwater go?
  - Plan for gas accumulation and release
  - Long term effectiveness in the face of gas/tidal dynamics?

Contaminant Migration Control

- pH
  - Siderite
  - Ferrous Sulfate
  - Alum
- Metals
  - Apatite
  - Iron Sulfide
- Organics
  - Organoclay
  - Activated carbon



Organic Retardation

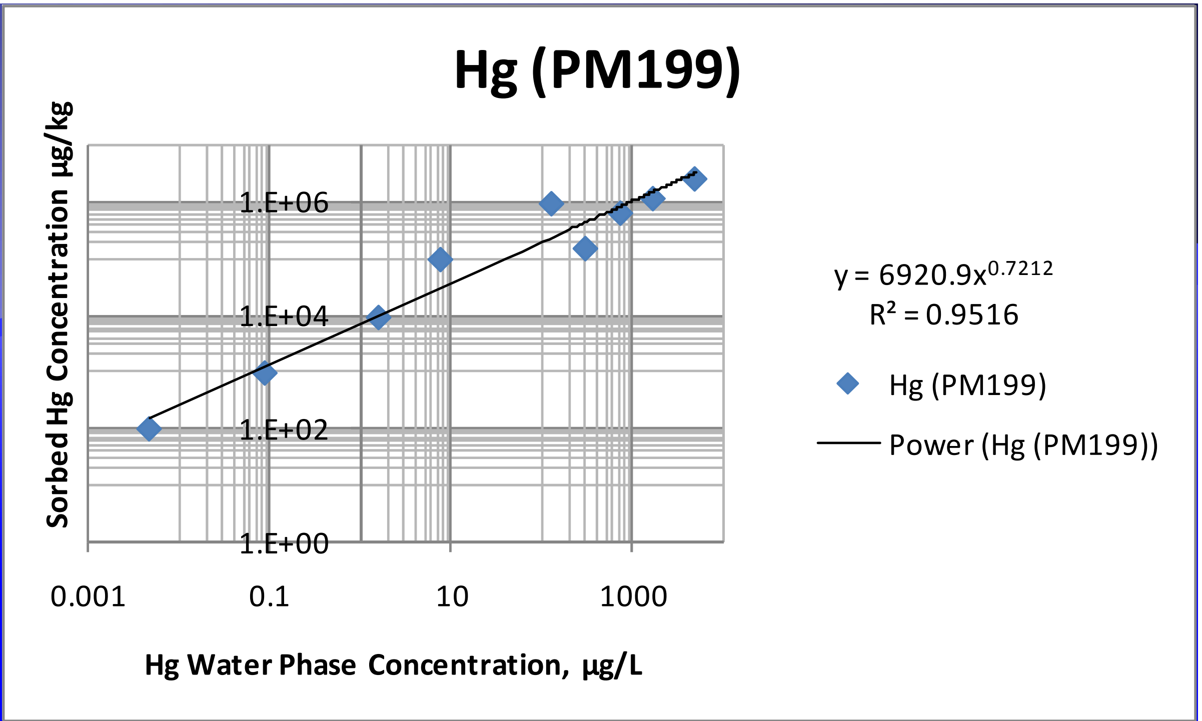


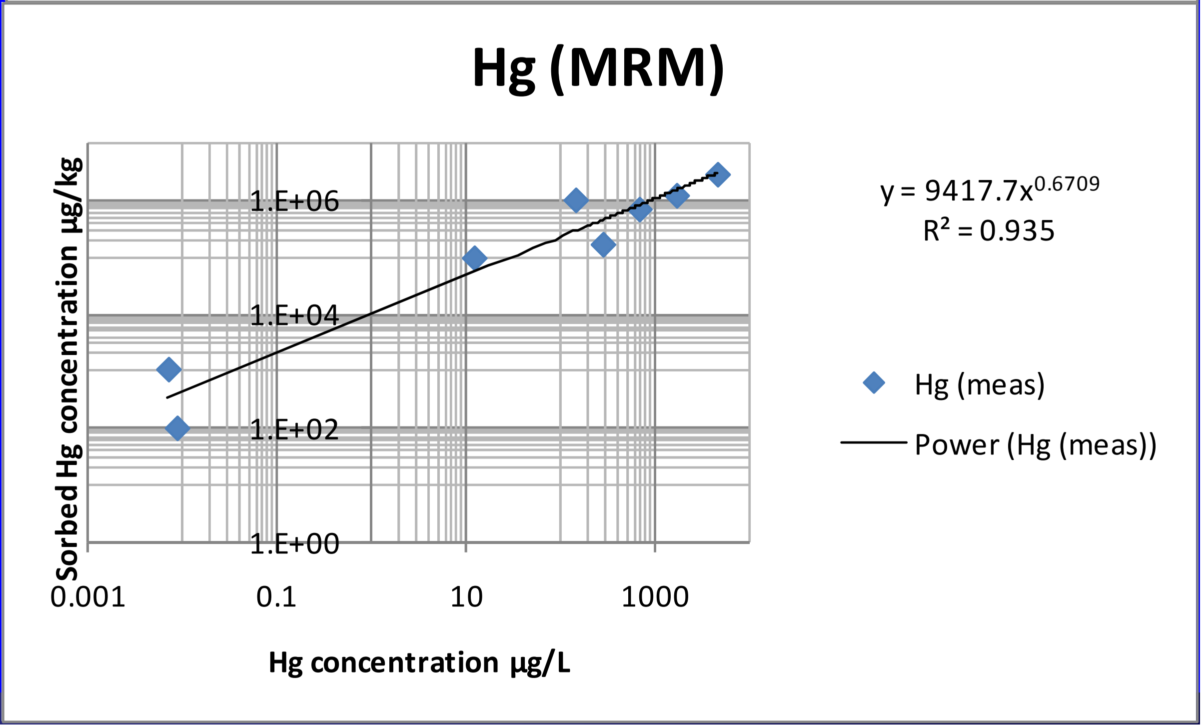
- NAPL present - Organoclays
  - Capacity of O(1 g NAPL/g organoclay)
  - Placement within a laminated mat for residual NAPL or to allow replacement if capacity exceeded
  - Placement in bulk for significant NAPL volumes
  - Multiple organoclay layers or organoclay/activated carbon layer for both NAPL and dissolved contaminant control
- Dissolved contaminants only - Activated carbon
  - Placement in mat may be necessary to allow easy placement
  - Placement as amendment also possible
  - Activated carbon typically more subject to fouling than organoclay

Hg sorption

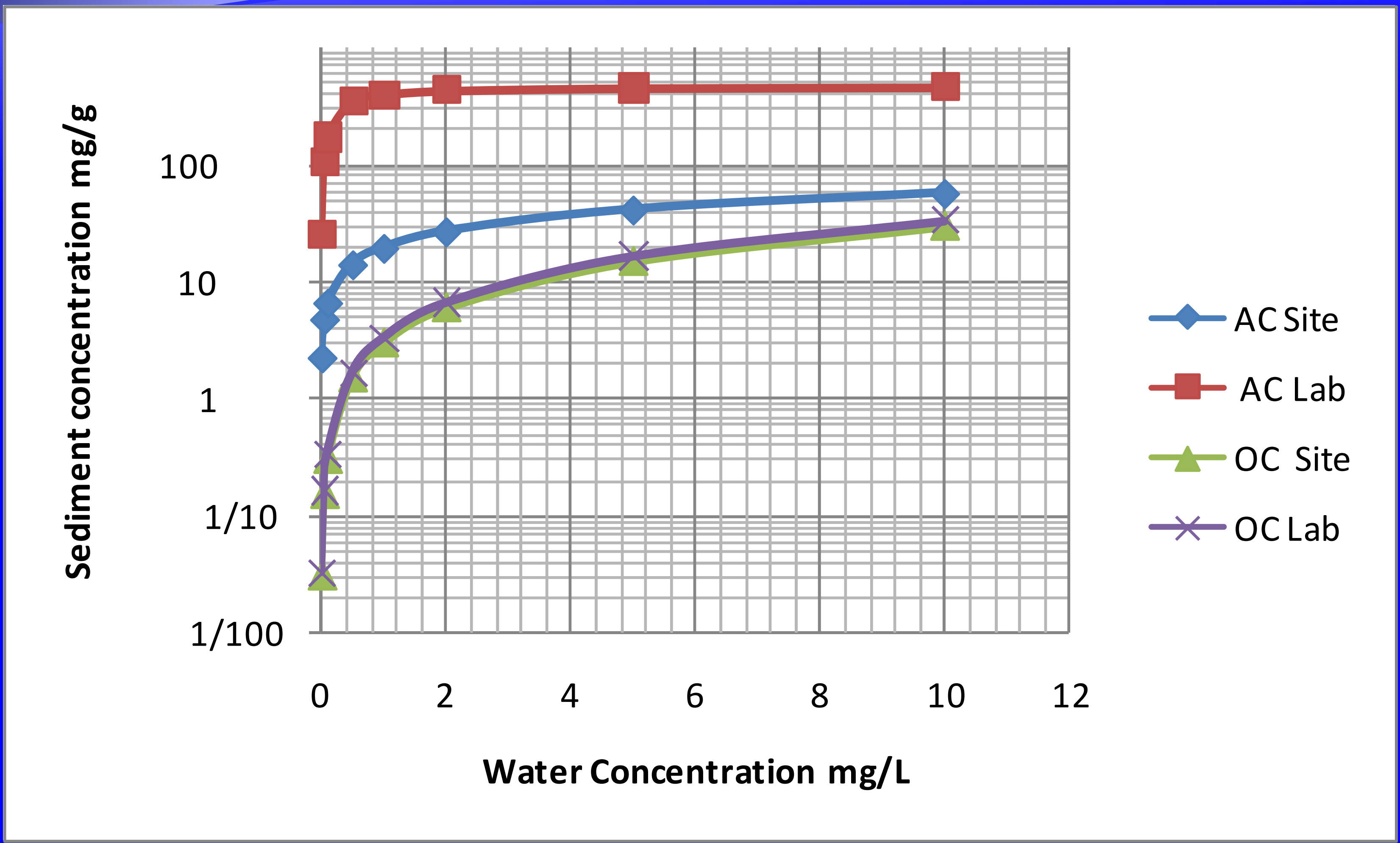
Special Hg formulations exist

Conventional formulations may be similarly effective if Hg complexed with suspended organic matter

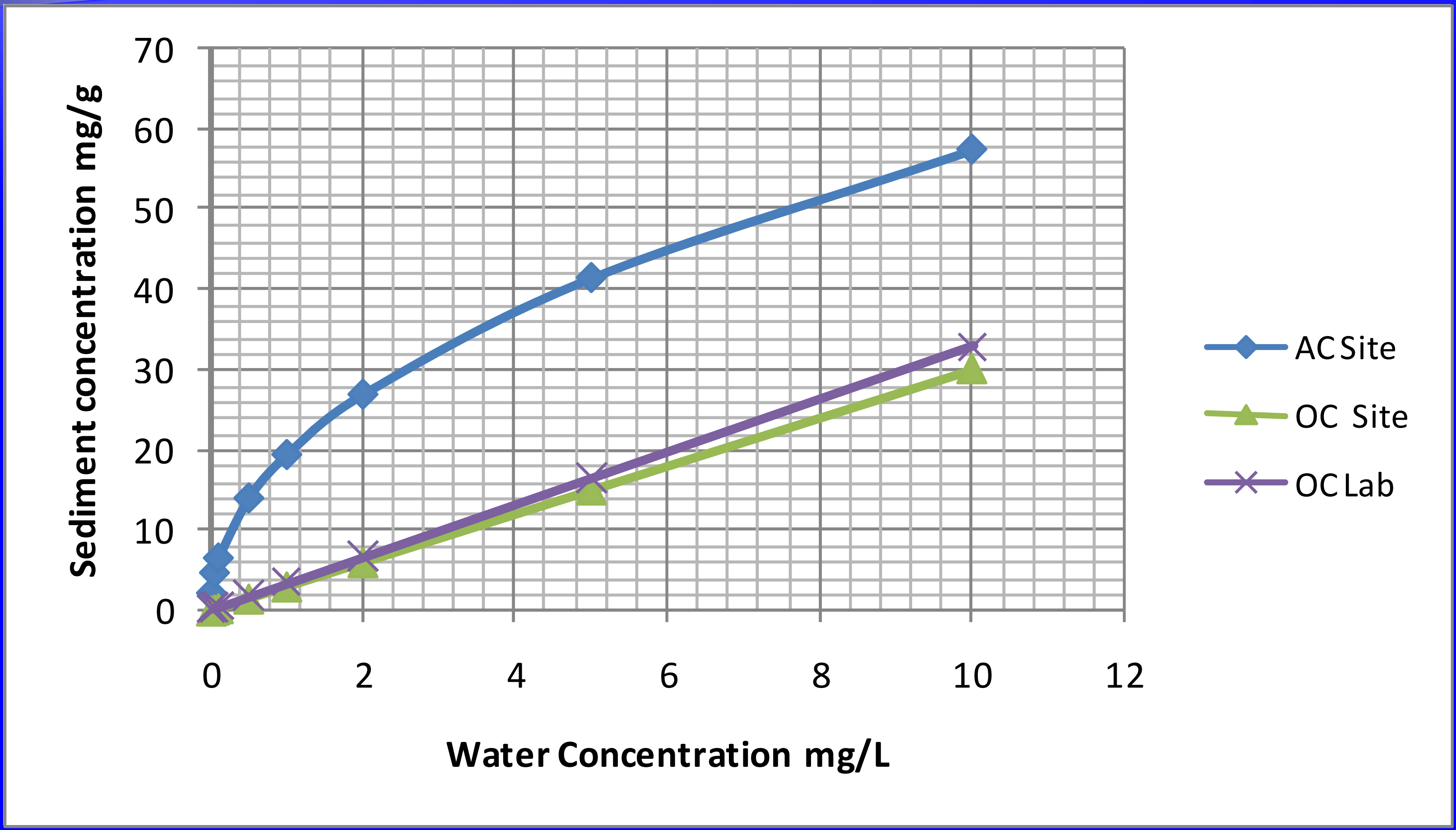




AC/OMC Relative Effectiveness Matrix Effects (Naphthalene)



AC/OMC Relative Effectiveness Linear Scale (Naphthalene)

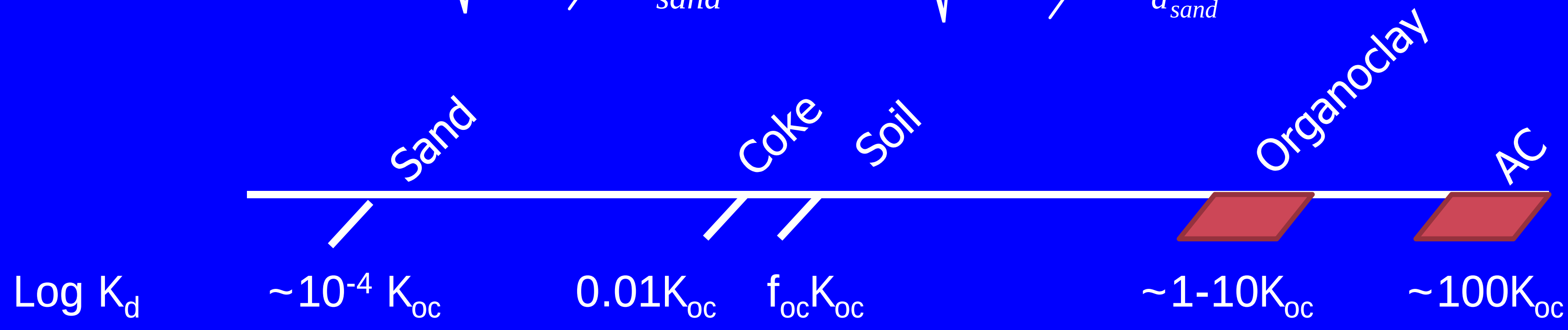


Dense Non-Aqueous Phase Liquid, *DNAPL*

Sorbents for Sequestration and Bioavailability Reduction

- Expect bioavailability reduction proportional to porewater concentration (inversely proportional to partition coefficient, K_d)
- Equivalent sand cap thickness – diffusion/dispersion dominated (u<<1 cm/day)

$$L_{eff} = L_{active}\sqrt{R_{active}/R_{sand}} \sim L_{active}\sqrt{K_{d_{active}}/K_{d_{sand}}}$$



f_{oc} ~ 0.01-0.05

Spreadsheet Model of Active Cap

To Appear Journal of Soil and Sediment Contamination – Summer 2009

ACTIVE CAP DESIGN MODEL

including steady state design model from Lampert and Reible (2009)*
Version 3.13
2/9/2008

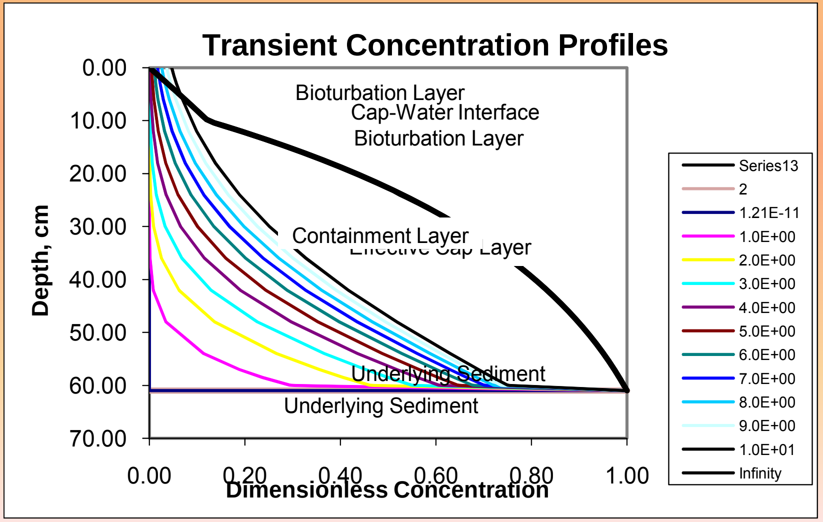
Instructions: This spreadsheet determines concentrations and fluxes in a sediment cap at steady-state worksheet 1), unsteady state (worksheet 2), assuming advection, diffusion, dispersion, bioturbation, deposition/erosion, sorption onto colloidal organic matter, and boundary layer mass transfer. An active cap layer with enhanced sorption is considered by converting to an equivalent conventional cap thickness. Depth is defined from the cap-water interface. A constant deposition rate can be entered but is not allowed to result in a net contaminant velocity <0 (relative to the changing cap-water interface). The cells in blue are input cells; these can be changed for the design of interest. DO NOT CHANGE THE CELLS IN RED (or the spreadsheet will not function properly). A second worksheet calculates the transient profiles for a semi-infinite case. The third worksheet title "array" allows the user to create an array of outputs for a given input (e.g. to study different compounds for a given site).

Contaminant Properties

Contaminant	Chlorobenzene	
Organic carbon partition coefficient, log K_{oc}	2.52	log L/kg
Colloidal organic carbon partition coefficient, log K_{DOC}	2.15	log L/kg
Water diffusivity, D_w	6.0E-06	cm^2/s
Cap decay rate (porewater basis), λ_1	0.00	yr^{-1}
Bioturbation layer decay rate (porewater basis), λ_2	0.00	yr^{-1}

Sediment/Bioturbation Layer Properties

Contaminant pore water concentration, C_0	1	ug/L
Biological active zone fraction organic carbon, $(f_{oc})_{bio}$	0.05	
Colloidal organic carbon concentration, ρ_{DOC}	10	mg/L
Darcy velocity, V	2	cm/yr
Depositional velocity, V_{dep}	0	cm/yr
Bioturbation layer thickness, h_{bio}	10	cm



Design Models

- Spreadsheet model
  - Transient model until penetration of chemical isolation layer
  - Steady state model (bioturbation &isolation layer)
  - Variant for additional active cap layer- transient and ss
- Numerical model
  - Matlab version
  - Multiple layers, nonlinear sorption, finite source
- Available at http://www.caee.utexas.edu/reiblegroup/

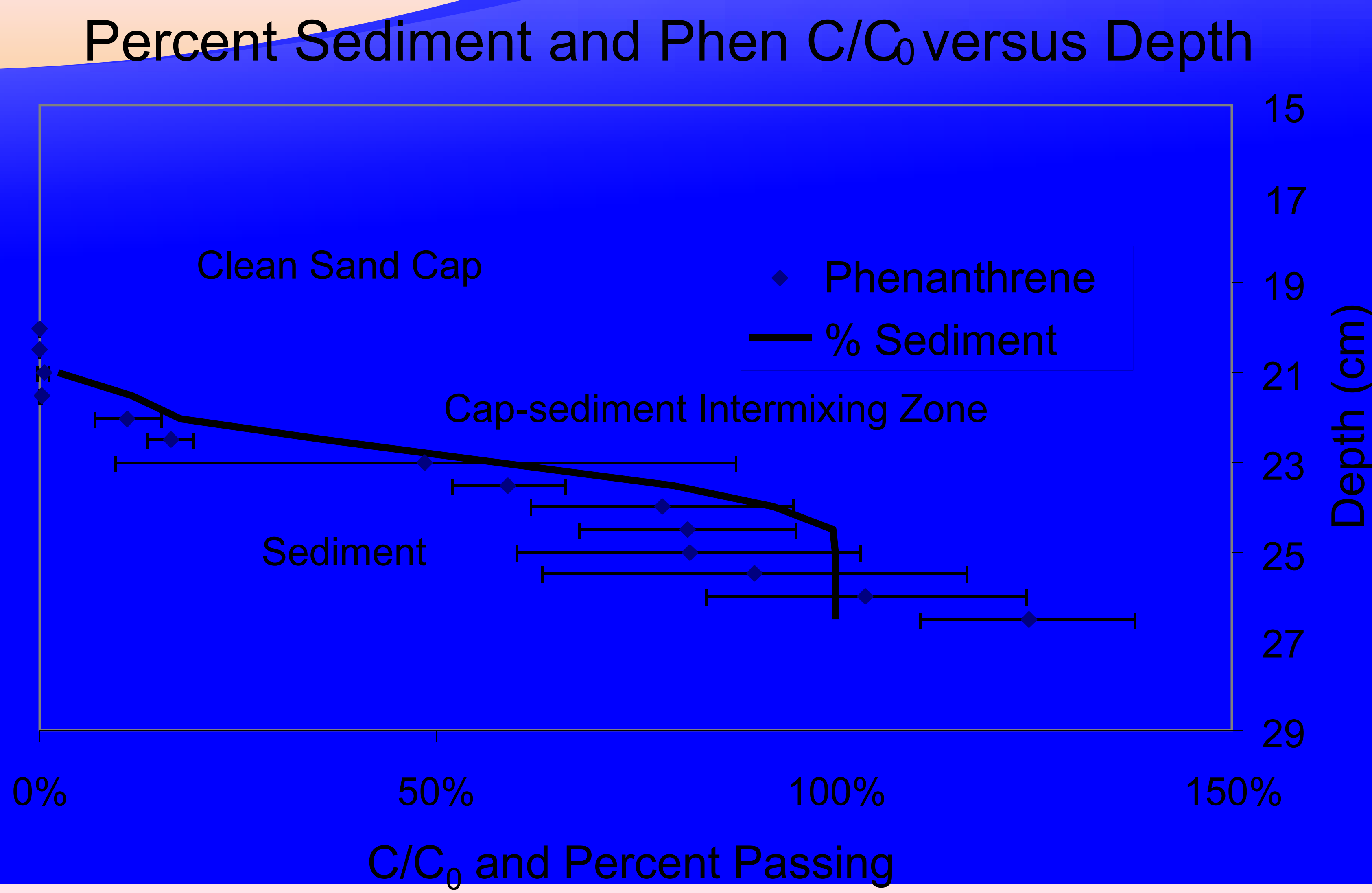
Performance Measures

- Isolation of contaminated sediment- *Cap stability?*
- Elimination of sediment resuspension – *Cap stability?*
- Reduction in contaminant flux to water – *Flux?*
- Reduction in contaminant accumulation in benthic organisms- *Flux? Contaminant isolation? Bioaccumulation?*

Thin Layer Capping

Thick Layer Capping

Effectiveness from Bulk Solids?



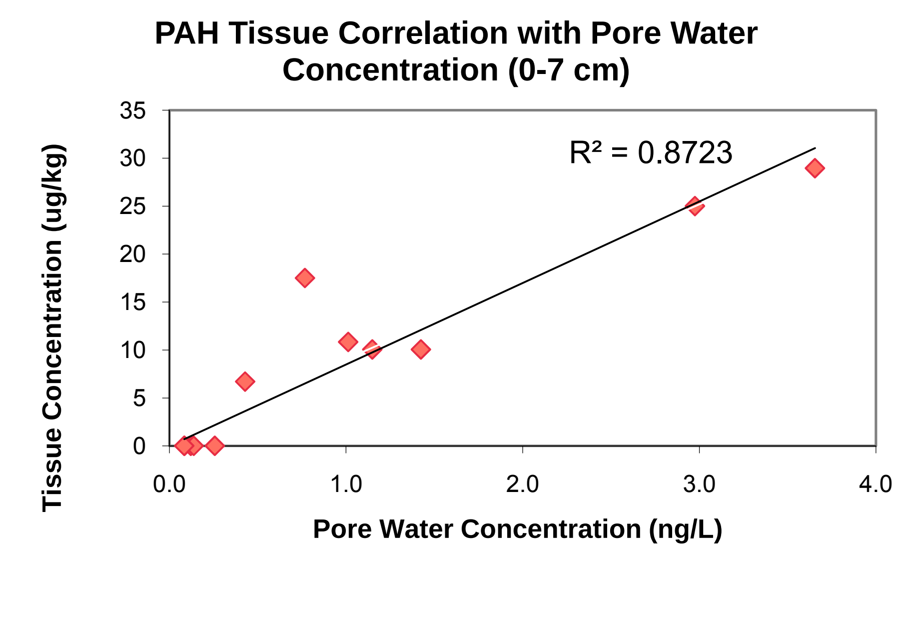
In. Situ Porewater Measurement

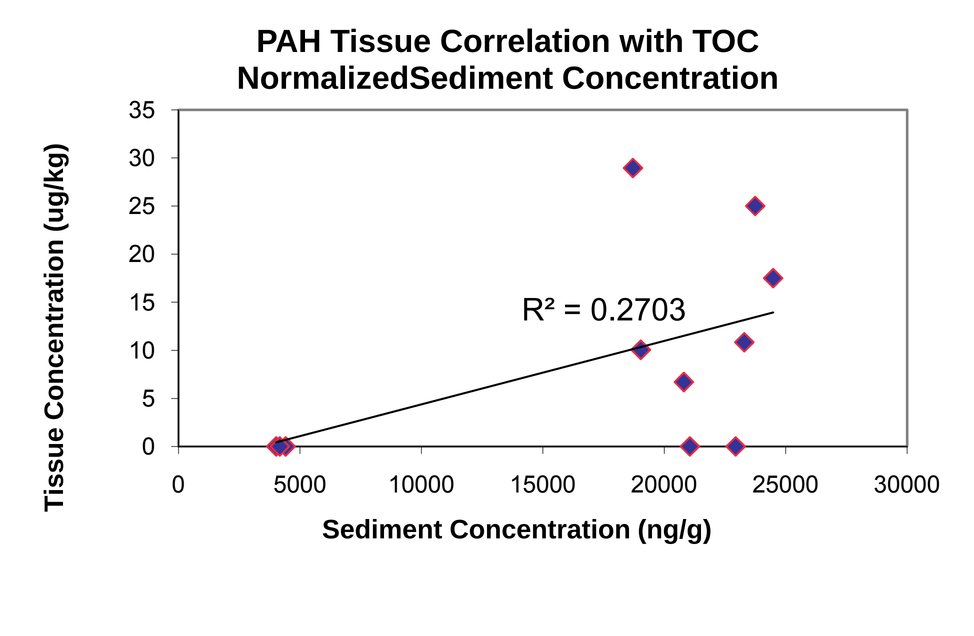
- Bulk sediment concentration is less useful as indicator of exposure-risk
- **Porewater concentration** is better indicator (*even for active benthic uptake by ingestion)*
- Porewater is difficult to measure, but possible with solid phase micro extraction (SPME)

Field deployable SPME, capable of measuring porewater with vertical resolution

SPME and Body Burden San Diego Bay

PAHs – B(b)F, B(k)F, BaP in *Muscalista*





Single correlation with porewater concentrations works well for all three compounds

Thin Layer Capping

4-cm Sand Cap

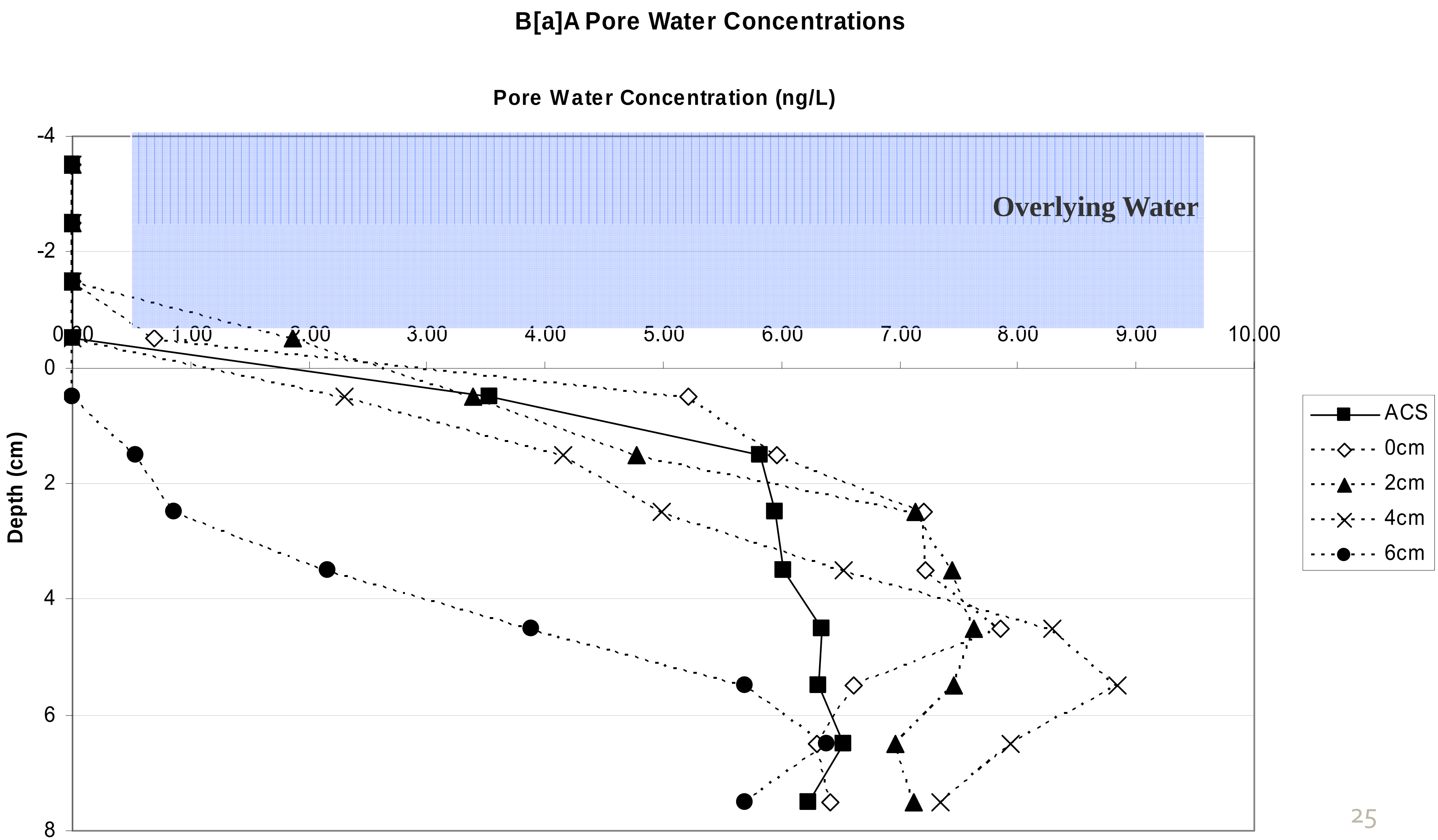
Day 28

Laboratory Studies of Thin Layer Capping

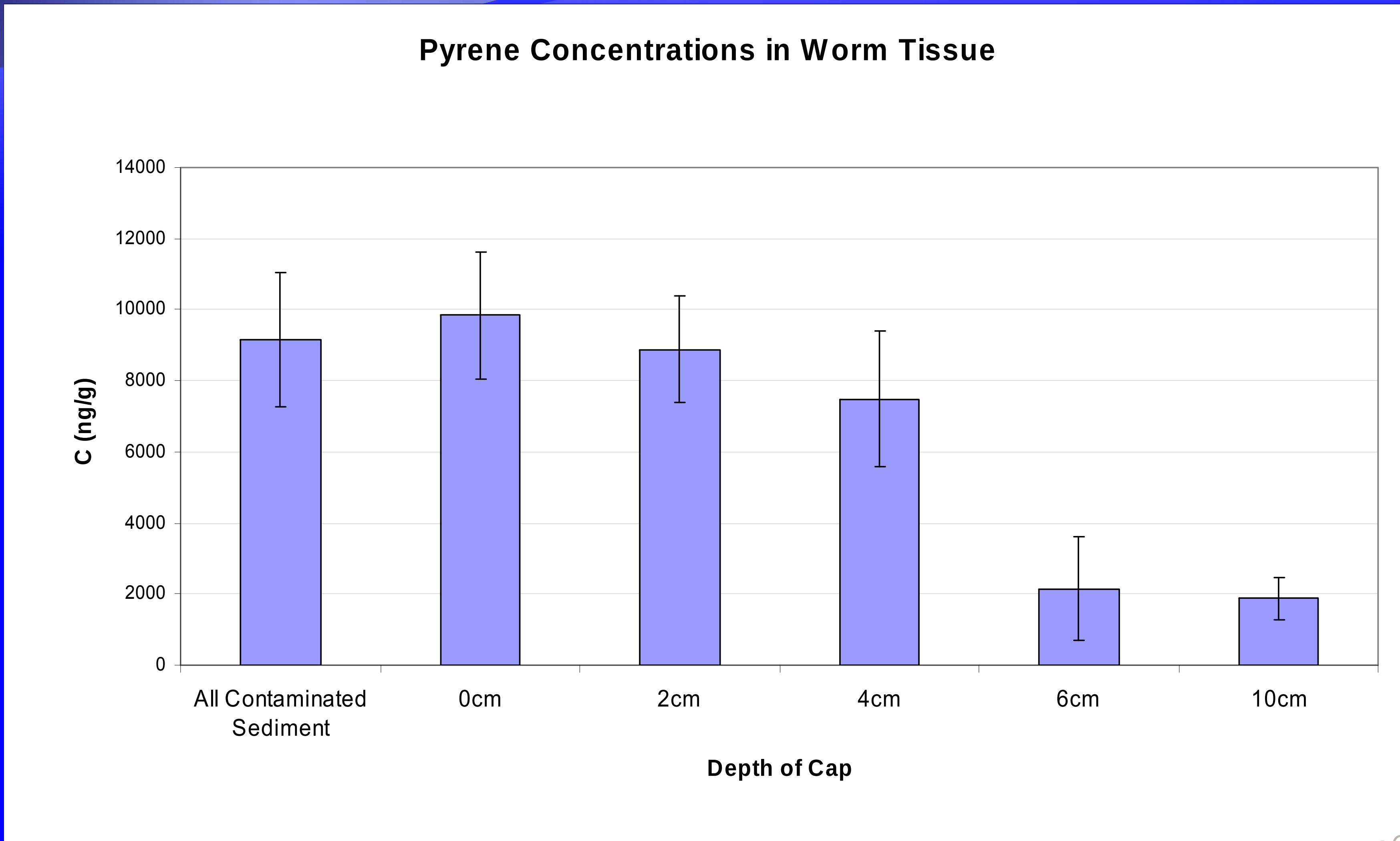
4-cm Sand Cap

Day 28

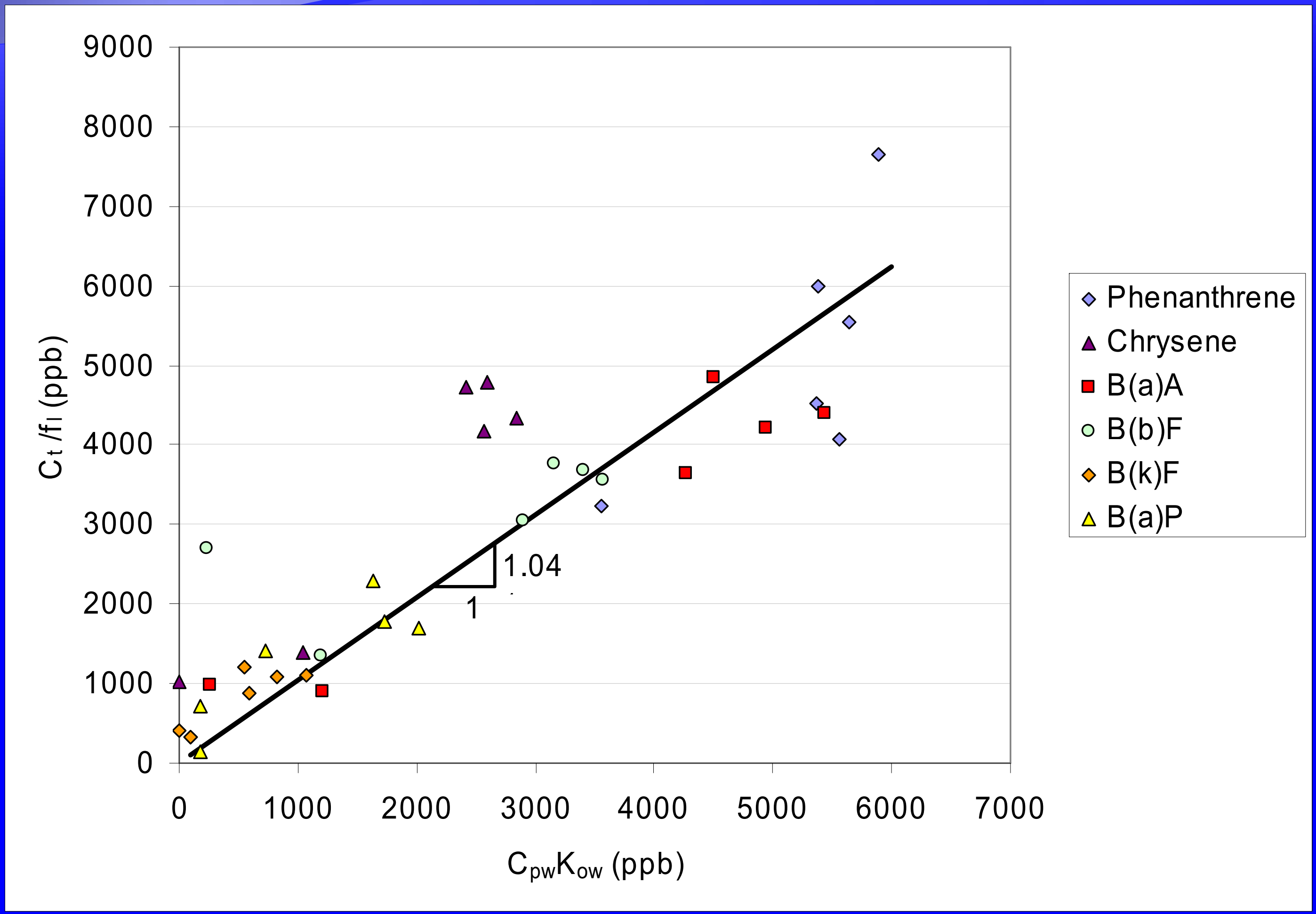
Capping Performance



Thin Layer Capping to Manage Residuals



Correlation of Bioaccumulation with Porewater Concentration



Unit slope is BSF estimated by K_{ow}

Capping Summary

- Conventional sand caps easy to place and effective
  - Contain sediment
  - Retard contaminant migration
  - Physically separate organisms from contamination
- There are existing and developing alternatives when a conventional cap is not sufficiently protective
  - Permeability Control
  - Adsorptive Caps
- Porewater concentrations /profiles can be an effective tool for defining contaminant migration, exposure and risk