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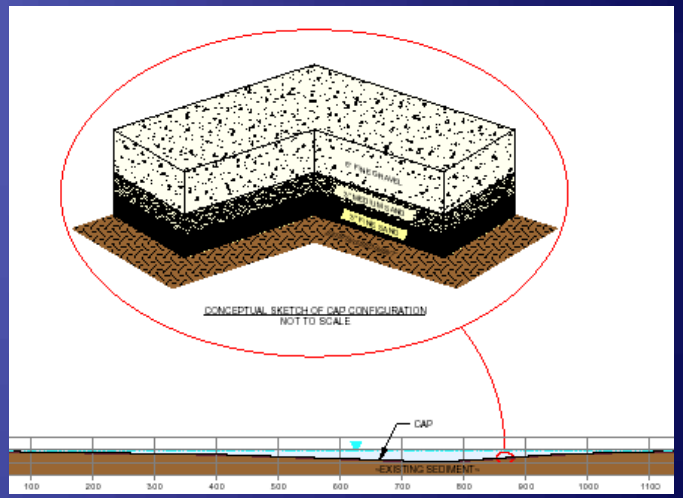
IN-SITU CAPPING ITS NOT JUST BURYING OUR HEAD IN THE SAND ANYMORE

Research supported by
EPA, DOD-ESTCP/SERDP, NIH & Industrial Sources

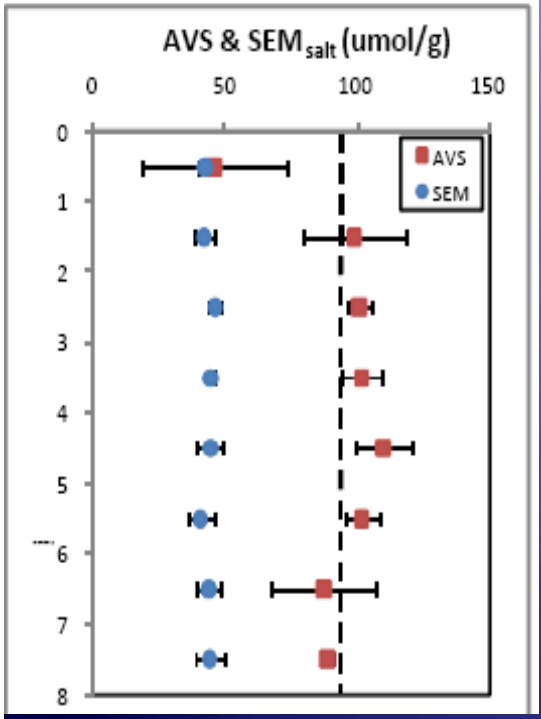
Sediment In-situ Capping

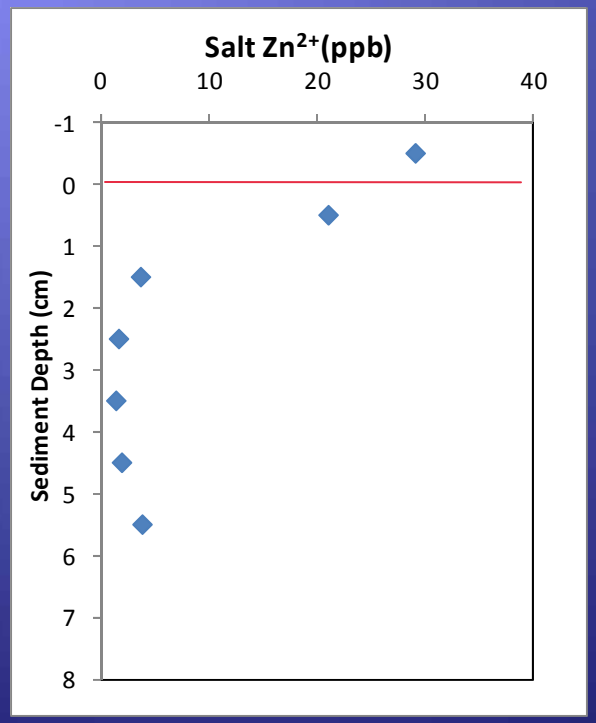
- Reduce risk by:
  - Stabilizing sediments
  - Physically isolating sediment contaminants from benthos
  - Reducing contaminant flux to benthos and water column
- Sand surprisingly effective for strongly solid associated contaminants
- "Amended caps" for other situations



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

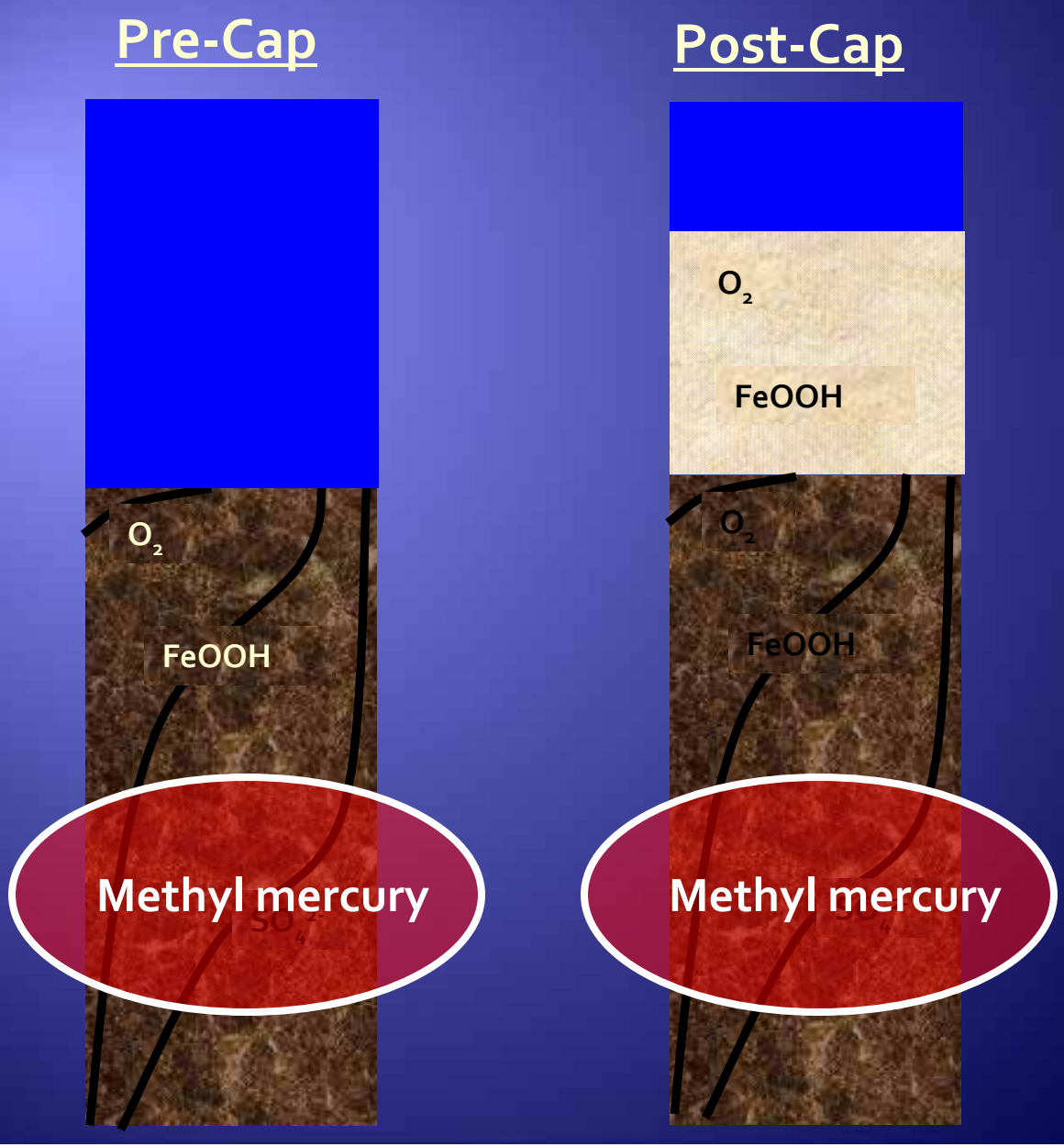
$M^{2+} + FeS_{(s)} \rightarrow MS_{(s)} + Fe^{2+}$

AVS < SEM

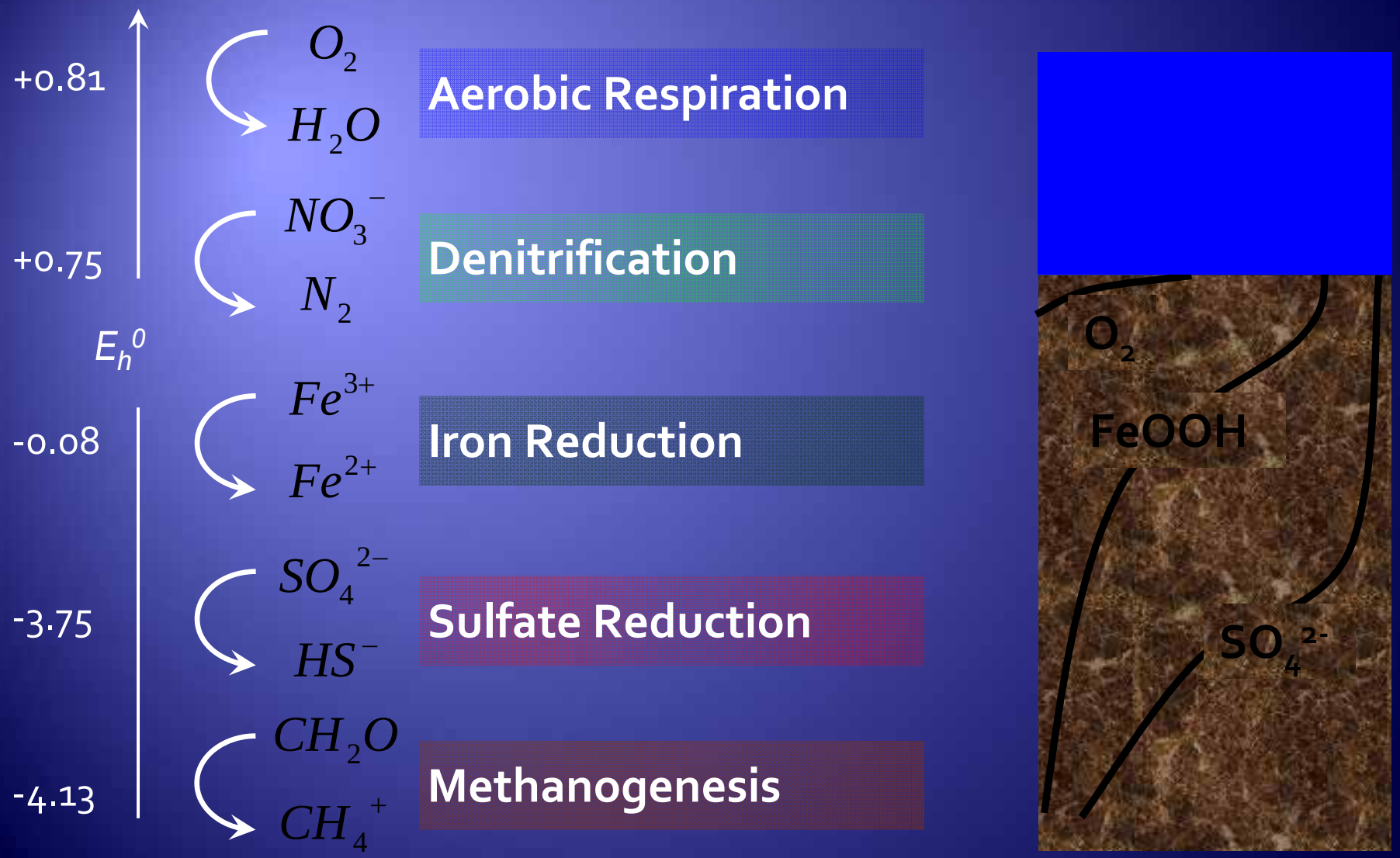
Divalent metals may be toxic

Work with YS Hong- now at Johns Hopkins

Conceptual Model



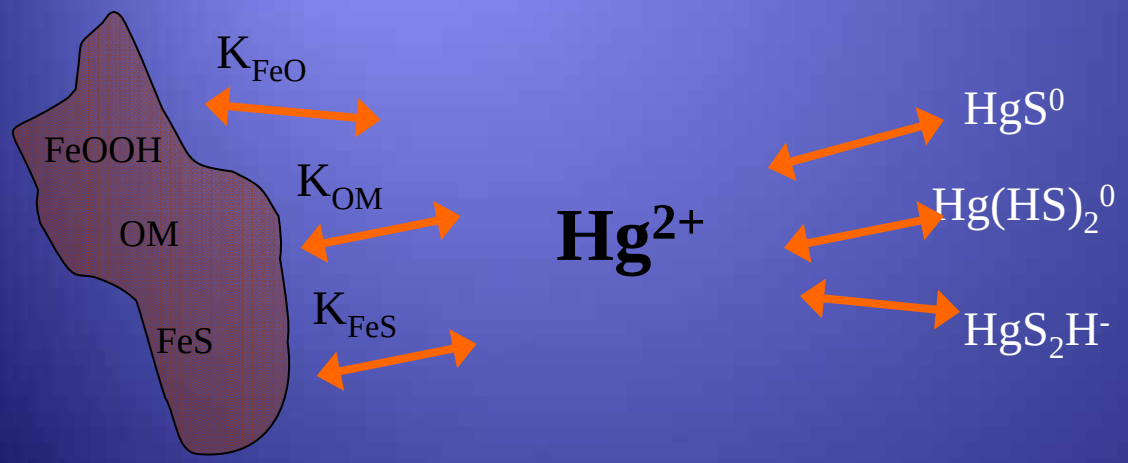
Conceptual Model

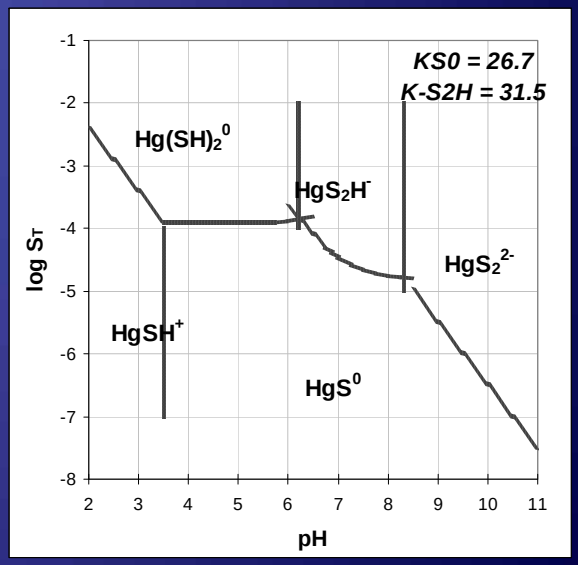


Detailed Conceptual Model

Methyl Mercury Modeling - Geochemical

- Availability of methylmercury to microbes affected by at least 2 factors: solid-phase sorption & aqueous speciation



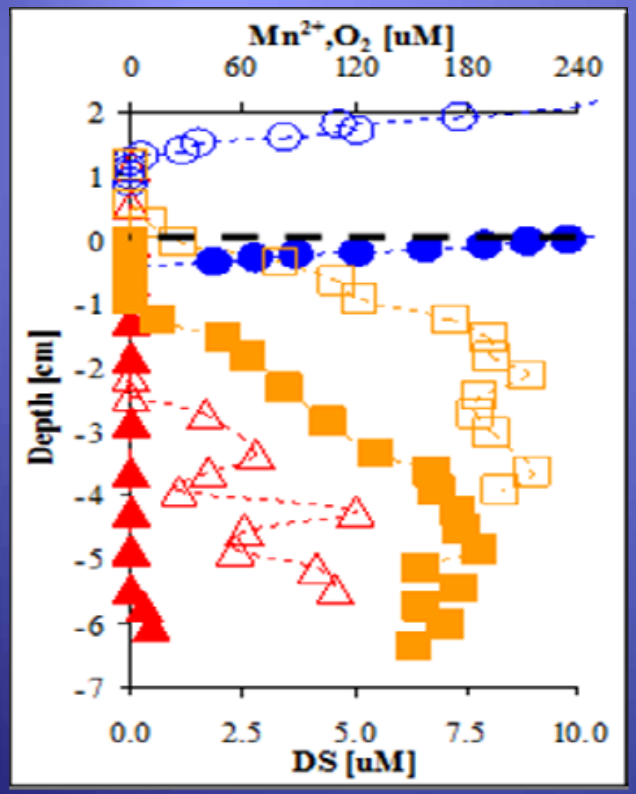


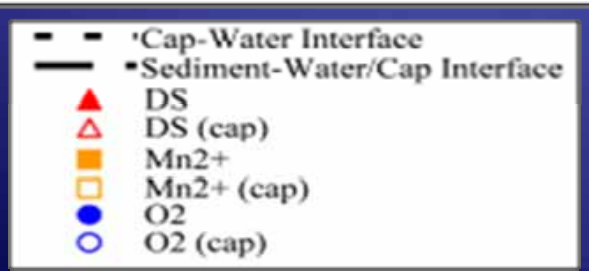
Solid phase sorption

Aqueous Speciation

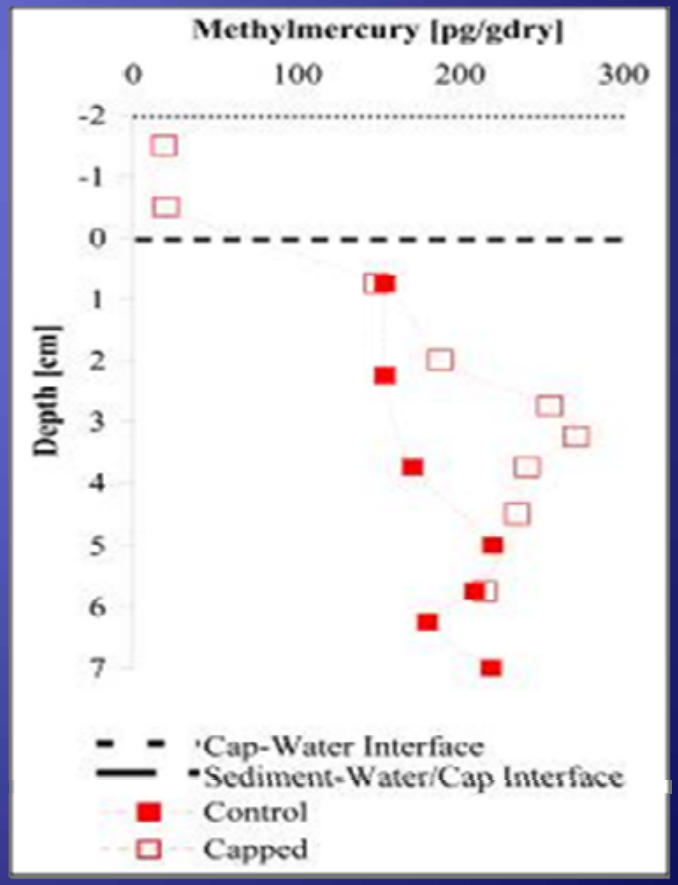
Cap redox changes and MeHg

Saltwater





Methylmercury



Work with Nate Johnson , now at UMn-Duluth

MeHg production slows down over time

- After 8 months in laboratory microcosms, short term increase of MeHg with capping replaced by decreases

Fractions of MeHg in Sediment profiles after 8 months

	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, 0 represents the interface of sand cap and sediment; for uncapped cells,0 represents the interface of water and sediment

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
  - Substantial groundwater upwelling of organics or potentially mobile NAPL most common reasons to consider active caps

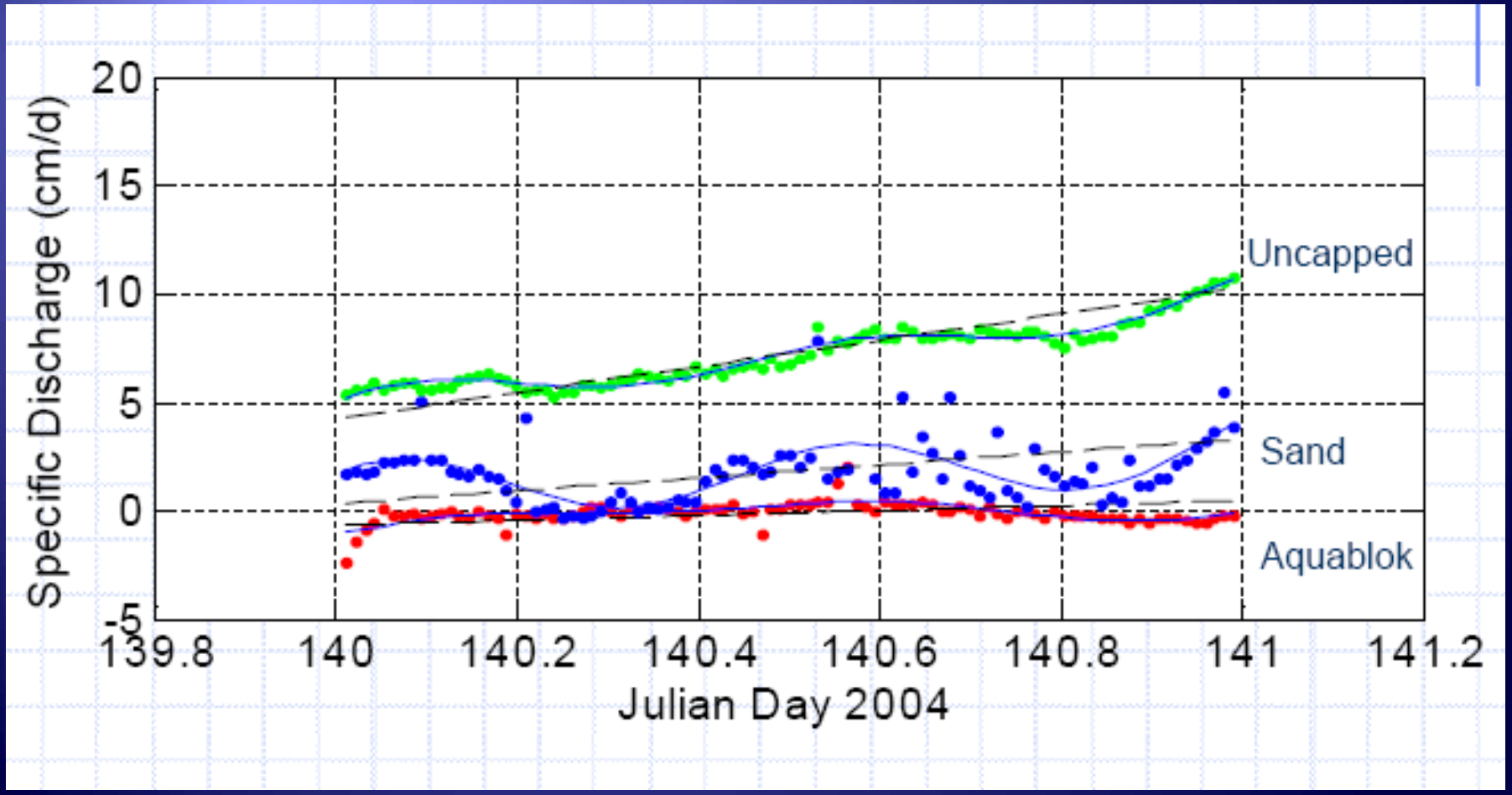
Goals of Capping Amendments

- **Permeability Control**
  - **Discourage upwelling through contaminated sediment by diverting groundwater flow**
  - **Example – Chattanooga Creek/AquaBlok Cap**
- Contaminant Migration Control
  - Slow contaminant migration, typically through sorption related retardation
  - Example – McCormick and Baxter/Organoclay Cap
- Contaminant Degradation Aid
  - Less well developed, contaminant specific but designed to encourage contaminant fate processes
  - Primary problem – maintaining appropriate conditions
  - Example – Electrode control of redox in a cap (Lab studies)

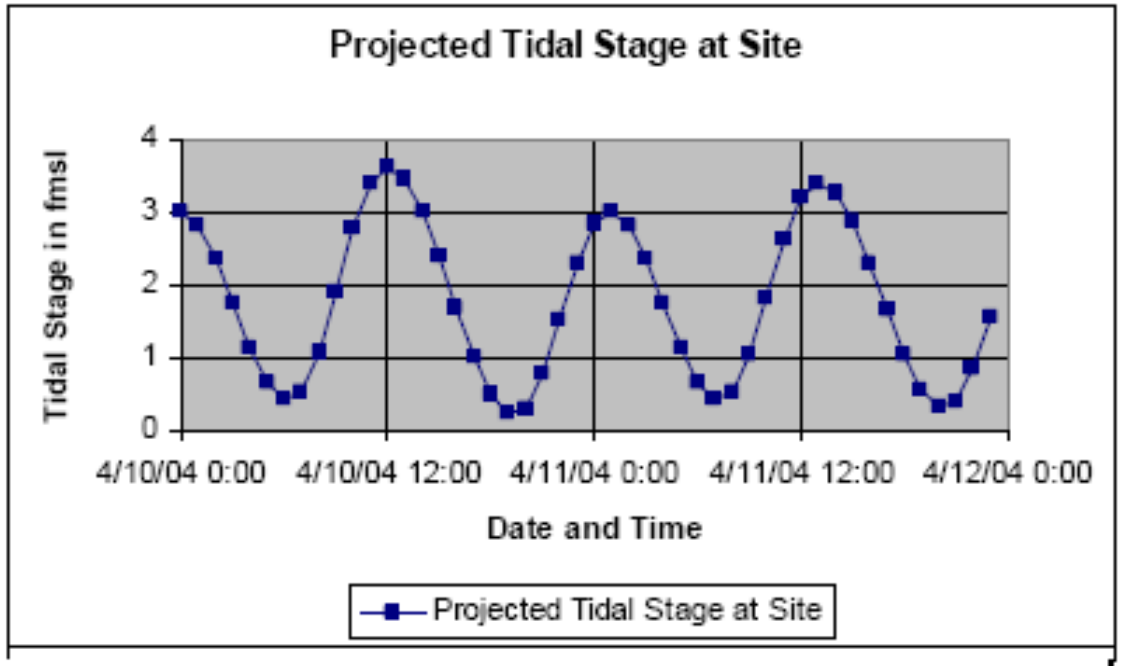
Impermeable Caps

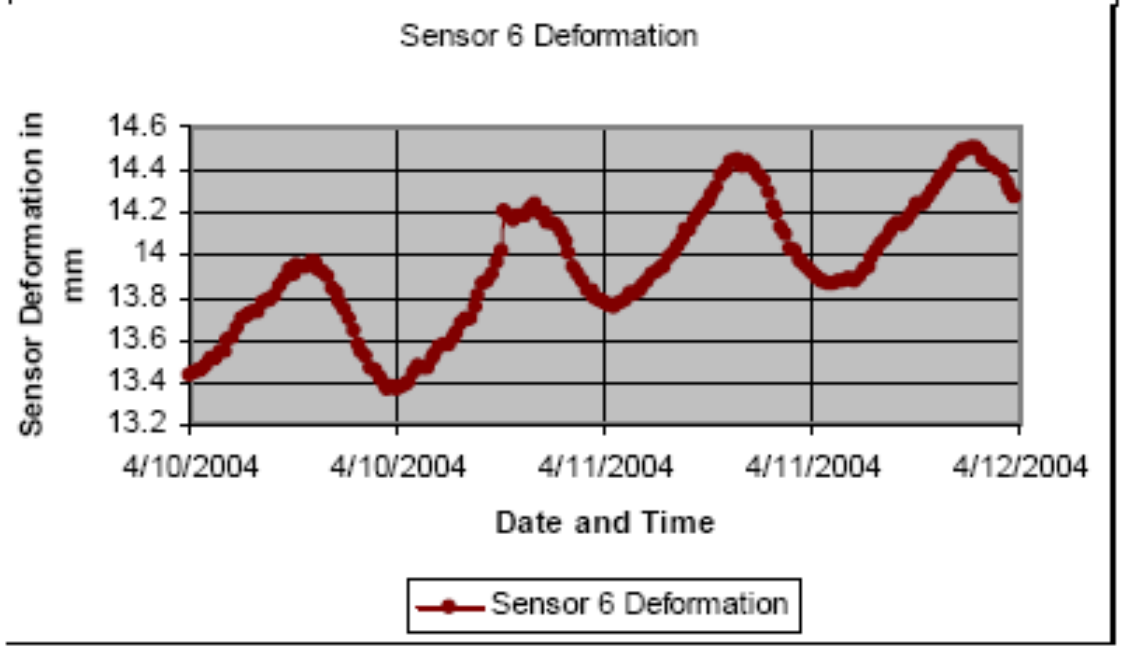
- Commercially available
  - AquaBlok
  - Bentomat
  - HDPE
- Can successfully divert groundwater upwelling
  - Where will the groundwater go?
  - Plan for gas accumulation and release
  - Long term effectiveness in the face of gas/tidal dynamics?

Seepage Rates - Anacostia Post AquaBlok Placement



Tidal Pumping Anacostia





Uplift in direct response to tidal forcing with little or no lag time

Chattanooga Creek

- AquaBlok
  - Placed in response to observation of NAPL in sediments
- Overlain by Clays
- Sampling by interstitial water

In cooperation with TetraTech, EPA Cincinnati & Reg. 4 and Tenn. Div. of Remediation

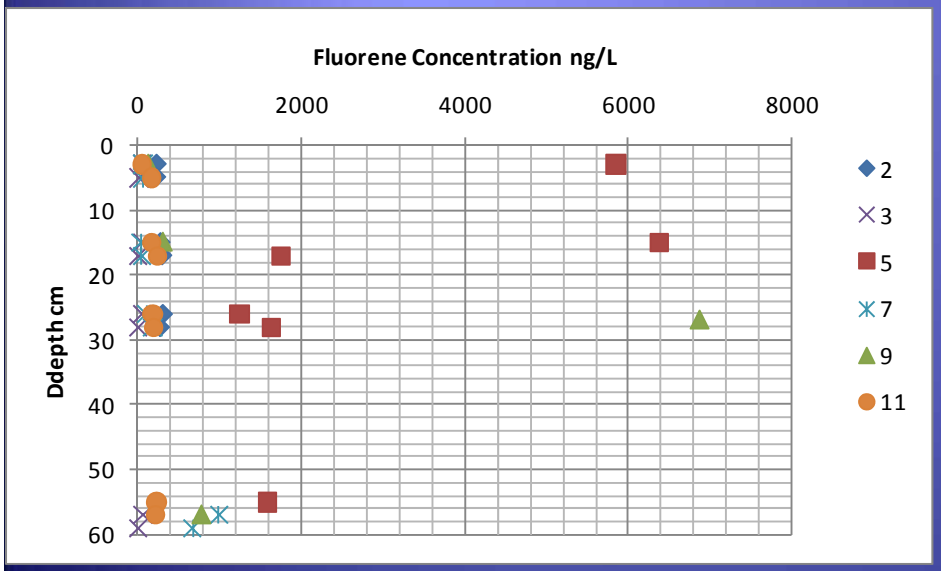
Profiling SPME

Large shielded sampler- 36”

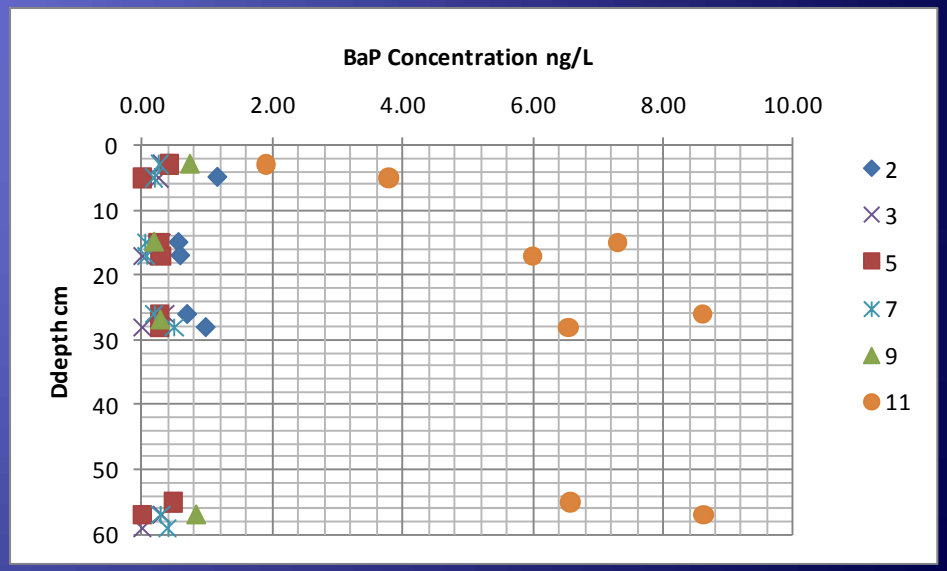
Small unshielded sampler- 14”

Chattanooga Creek Example Profiles

- LPAH



HPAH



- No evidence of NAPL penetration through AquaBlok
- Site 5 – some evidence of runoff associated contaminants
- Site 11 – some evidence of intermixing of strongly solid associated HPAHs

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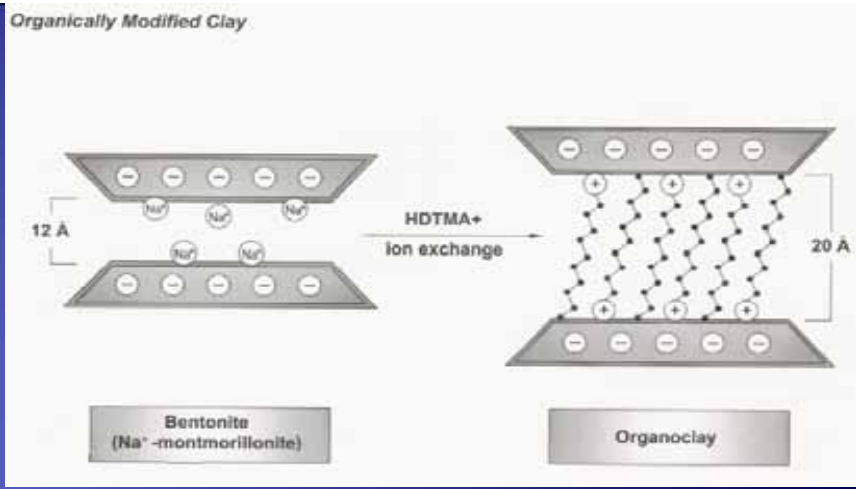
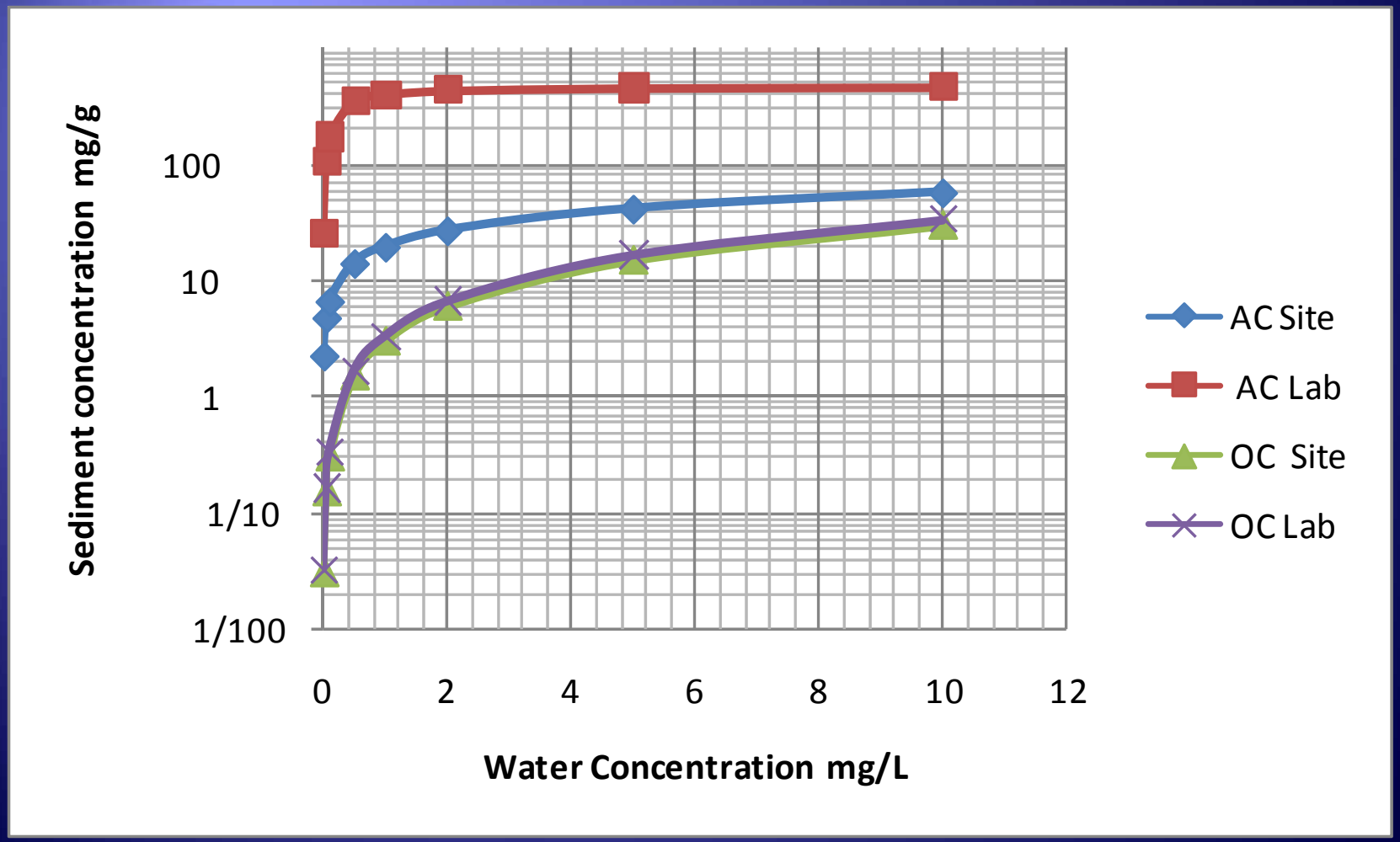
Organic Retardation



- 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

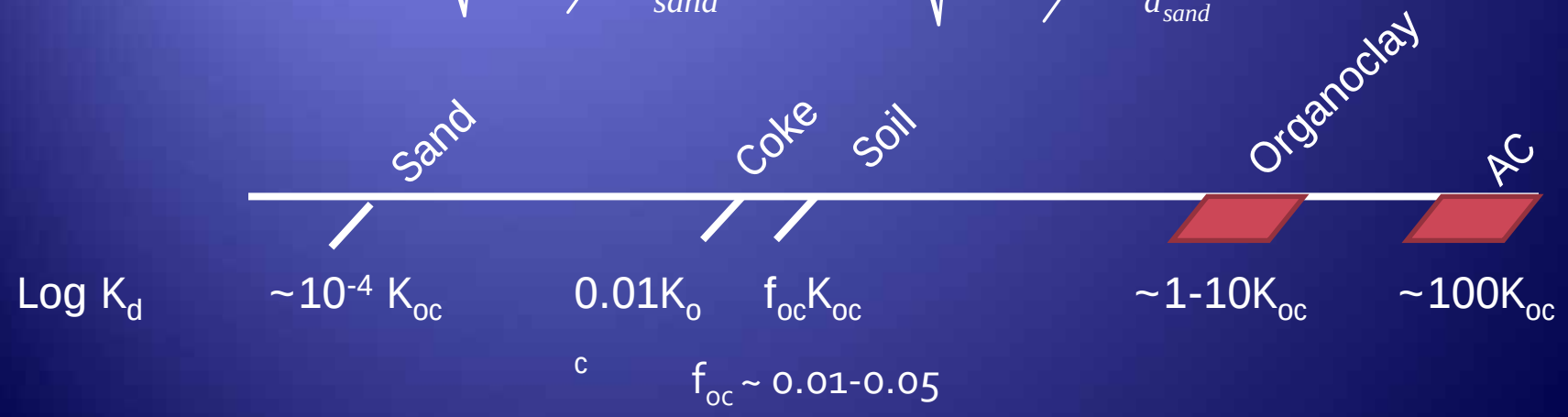
AC/OMC Relative Effectiveness Matrix Effects (Naphthalene)



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)

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



McCormick and Baxter

- Portland, OR
- Is visible success supported by measurements?

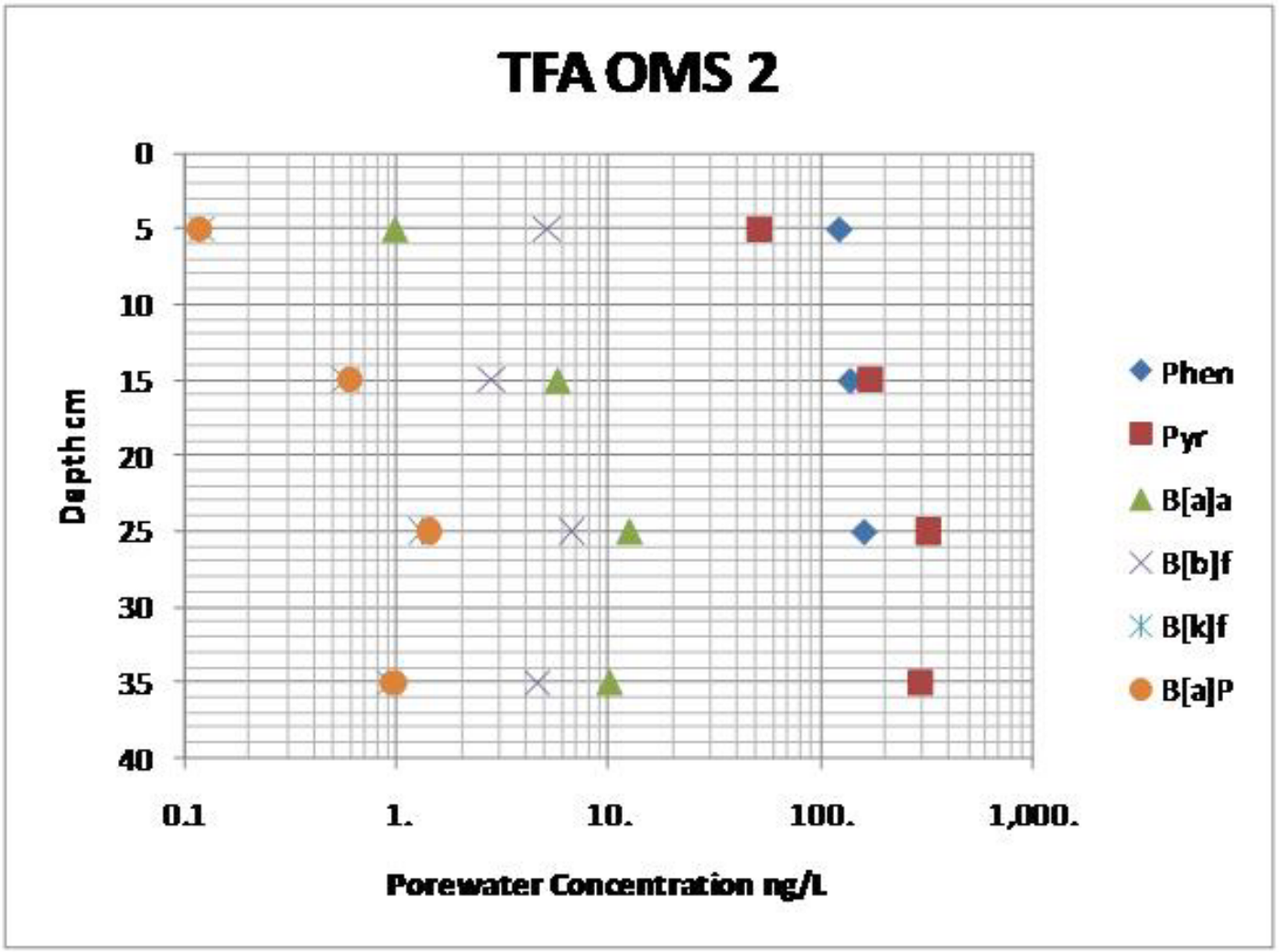
Before (2001)

After (2005)

In cooperation with Oregon DEQ and GSI, Inc.

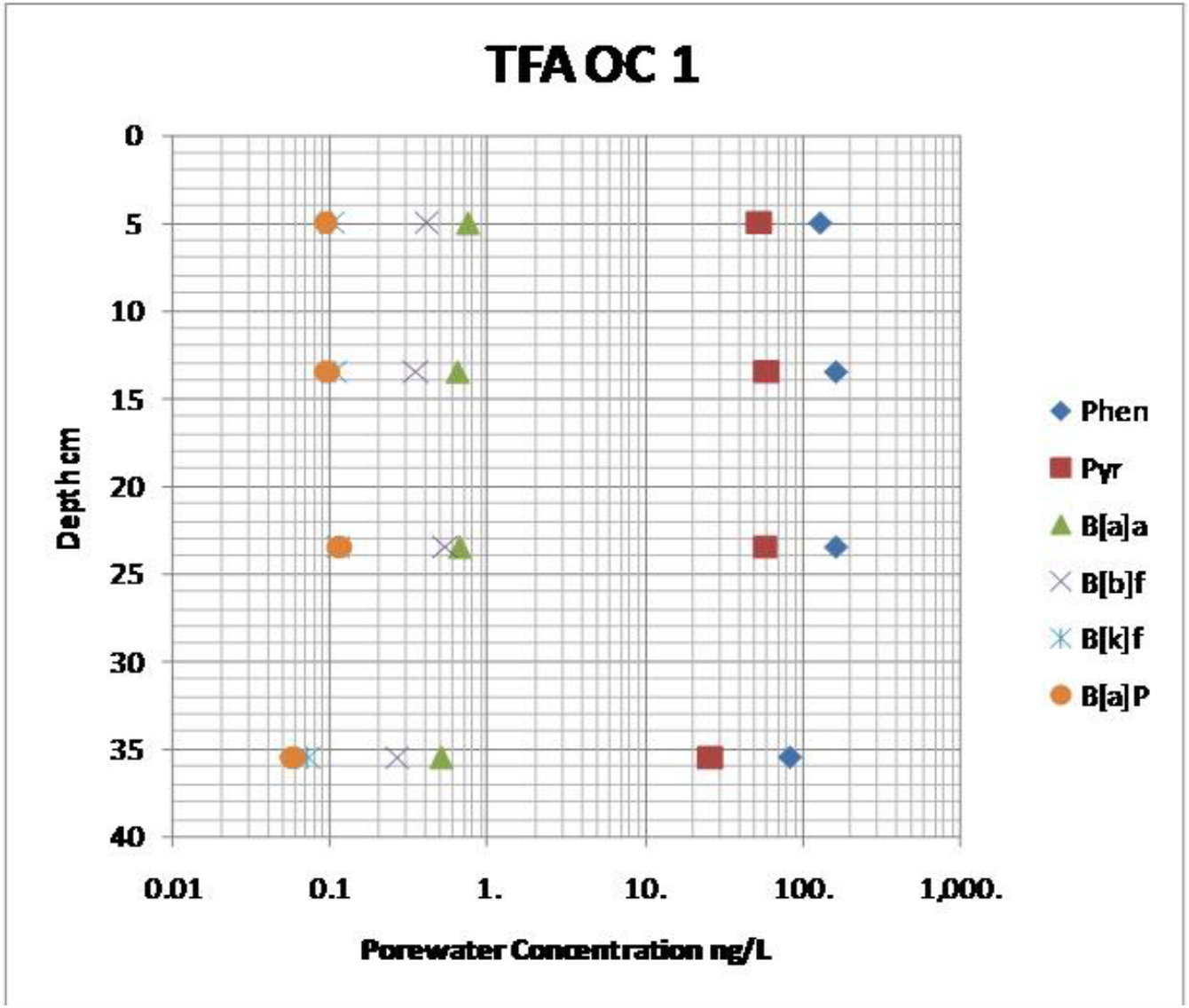
McCormick and Baxter, Portland

Example of location showing gradient to the surface



McCormick and Baxter Portland, OR

Example of location showing uniform vertical concentrations



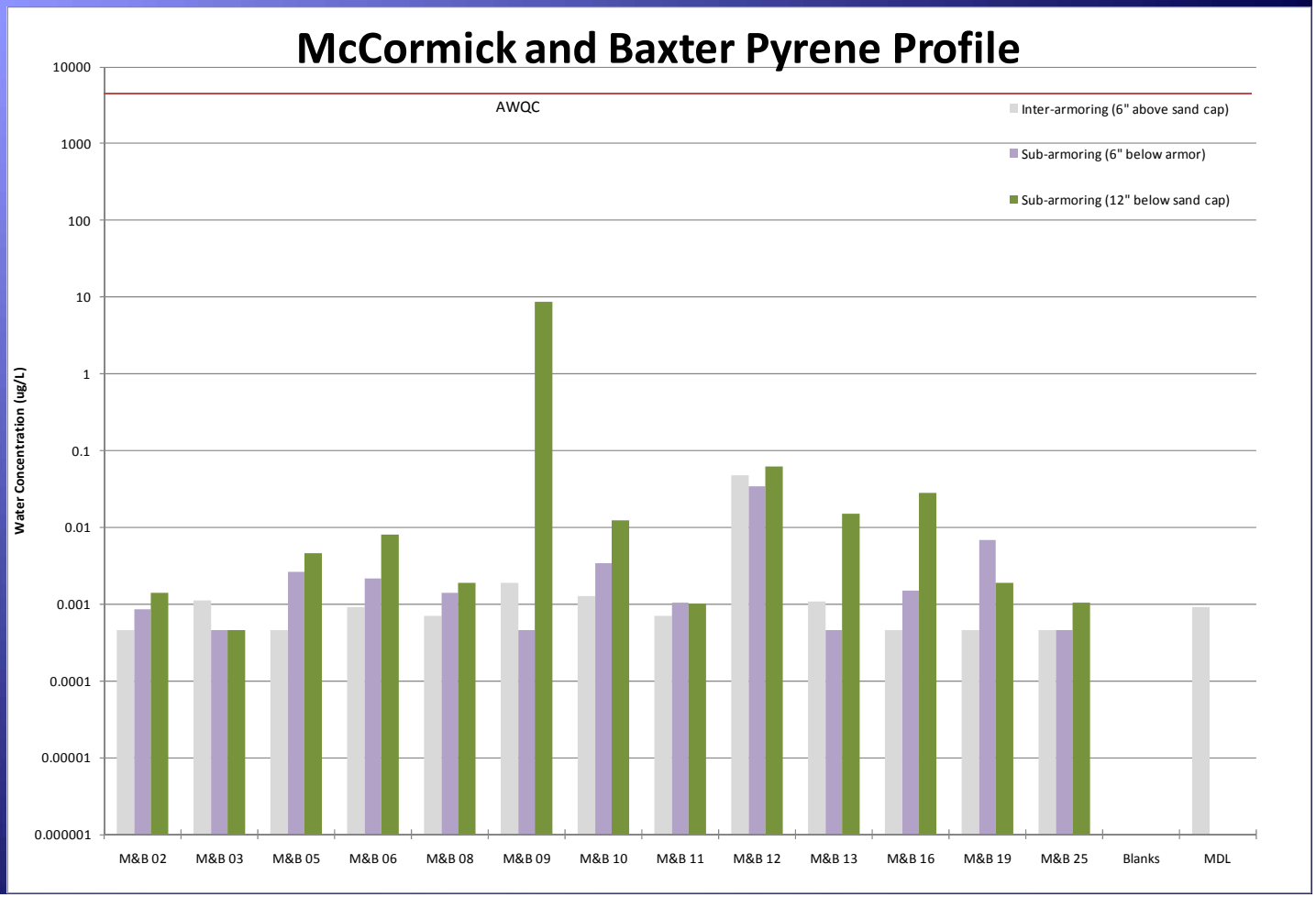
M&B Current Porewater Sampling

Conclusions

No evidence of NAPL migration

Some evidence of partial degradation of one type of organoclay

Dissolved contaminants in porewater<surface water AWQC except occasionally at deepest sample



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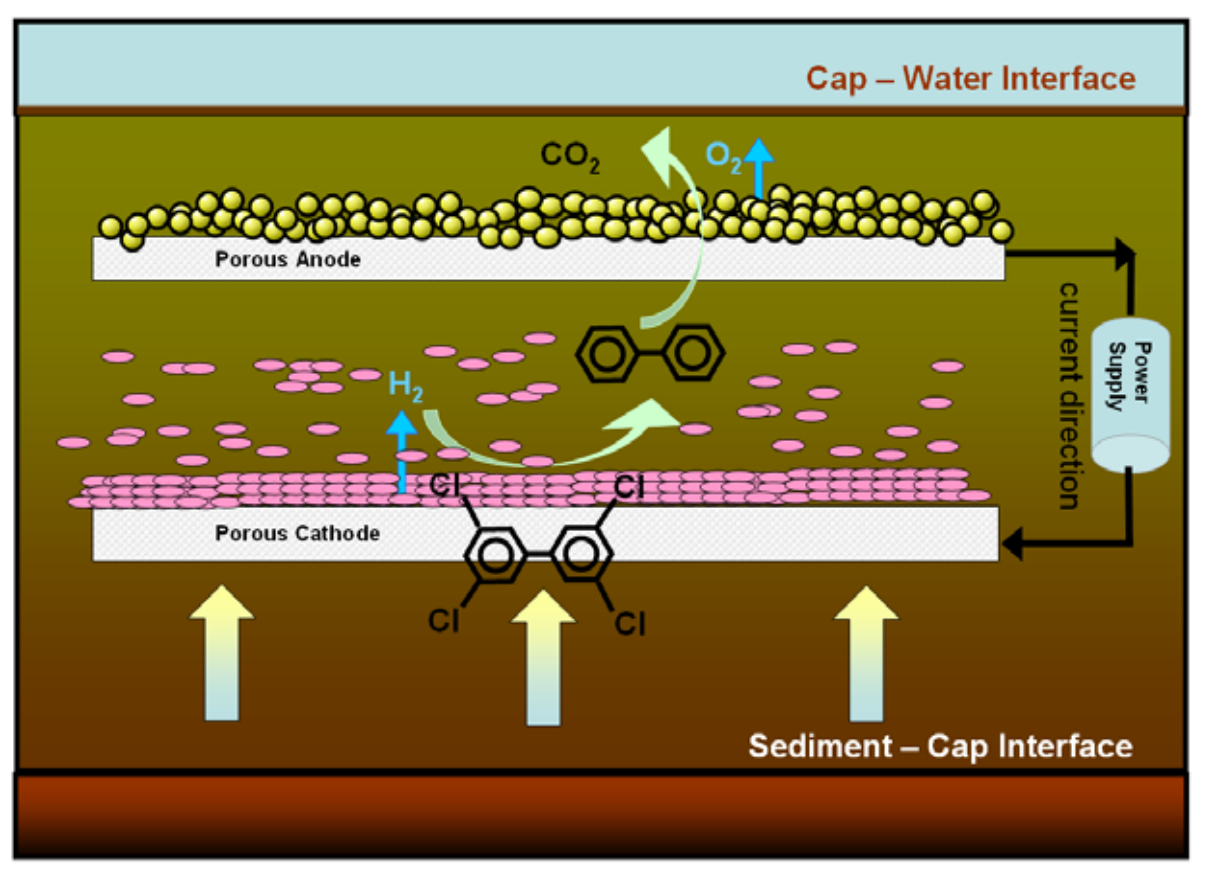
Conceptualization of electrode cap

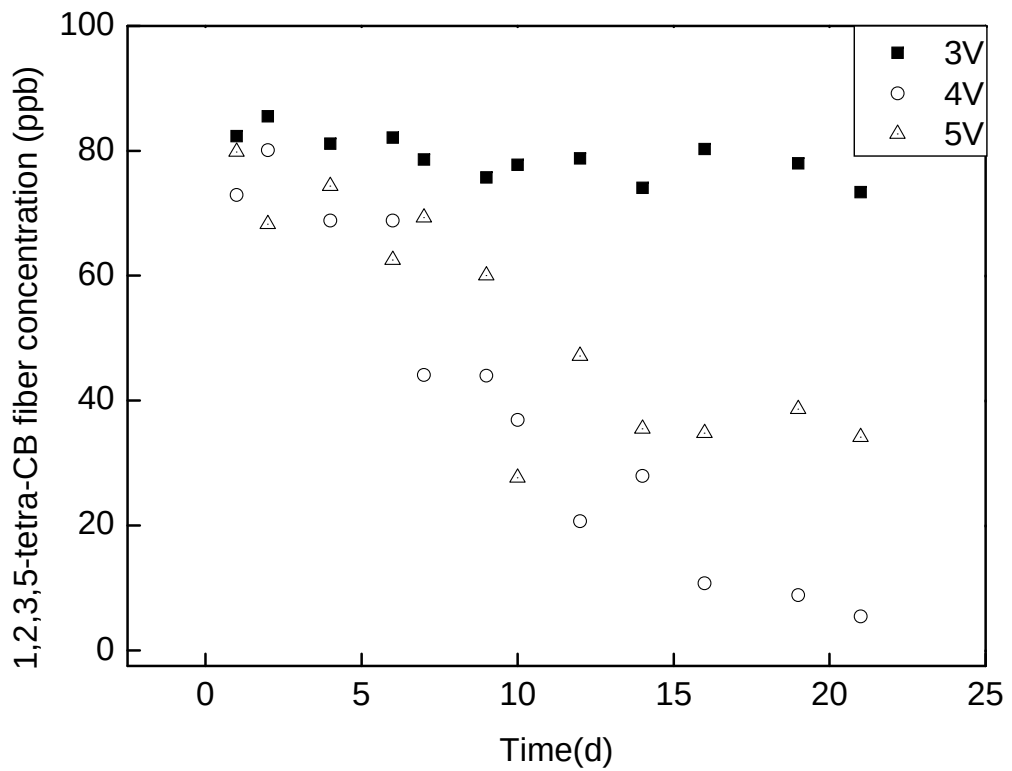
Being developed in cooperative effort between Univ of Texas and Carnegie Mellon Univ (Greg Lowry & Kelvin Gregory) with NIEHS Support



Degradation of TetraClBenzene with applied voltage

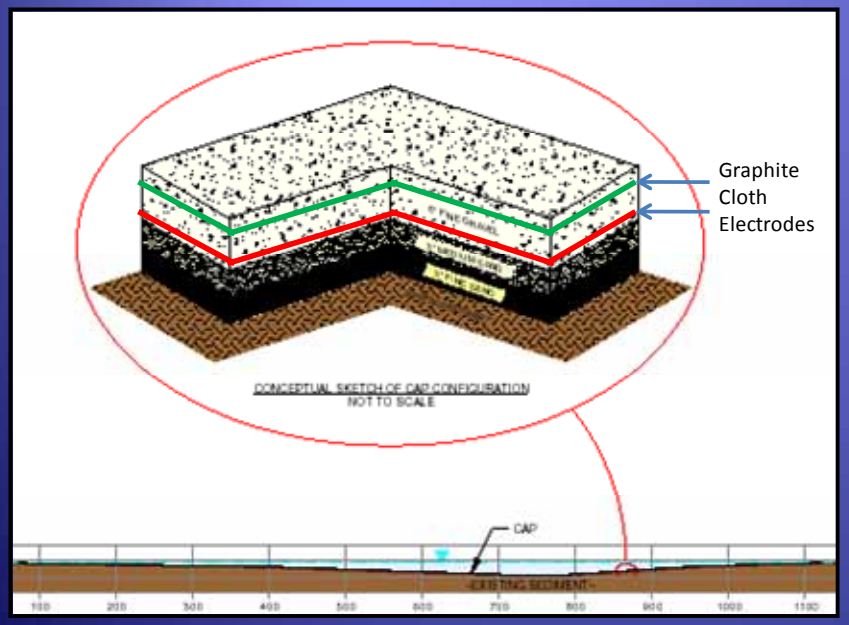
Measured H_2 evolution

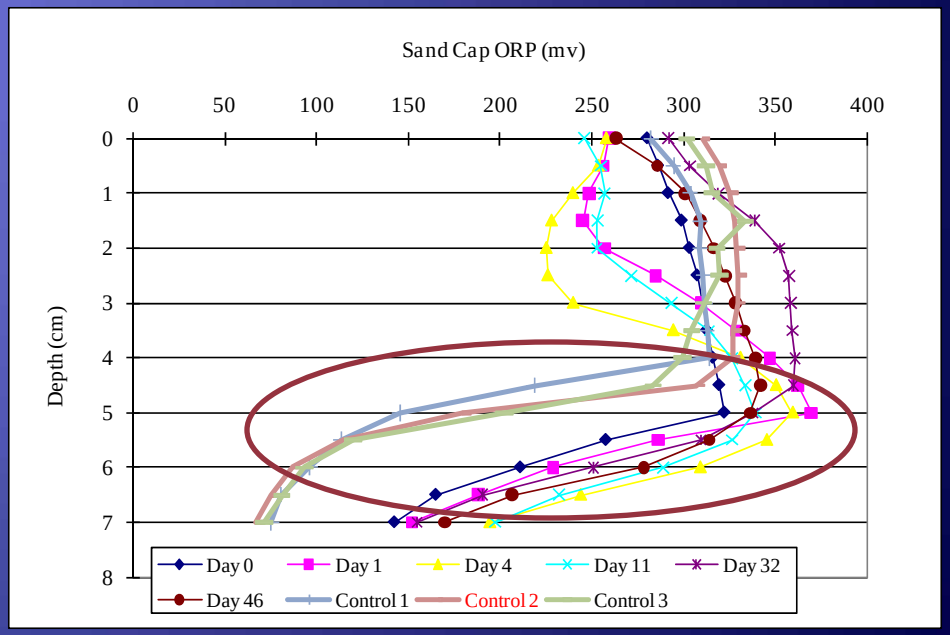
Degradation of Tetrachlorobenzne by reductive dechlorination



The degradation of 1,2,3,5-Tetra-CB fiber concentration versus time

Oxidation Cap Design





Low voltage, low current resulting in 200 mV increase in redox at sediment –cap interface
Conditions appropriate for improved oxidation of hydrocarbons

Conclusions

- Sand Cap can be effective for strongly solid associated contaminants
  - Metals
  - Organics in low advective flow conditions
- Amended caps
  - Permeability control (AquaBlok/Bentonite) can be effective but must design for water/gas accumulation
  - Contaminant control can be effective but must manage sources (finite capacity)
  - Degradation amendments developing option but currently very limited