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CONTAMINATED SEDIMENTS: ITS NOT JUST THE SOLIDS

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

Contaminated Sediments

- Solid associated contaminants ⇔ solid problem?
  - Risk defined by contaminant concentration on solids?
  - Risk defined by sediment fate and transport?
- Solid associated contaminants
  - Bioavailable?
  - Mobile?
- Aqueous and NonAqueous contaminants
  - Available
  - Mobile

DNAPLs in Sediments

- Groundwater/NAPL plumes intercepting a river
  - e.g. chlorinated solvents
- Creosote/MGP site NAPLs
  - Heavily weathered
  - Near neutral buoyancy
  - Often found in very large volumes
- PCBs
  - Typically found as discontinuous ganglia in oil or solid associated

Two goals

- How to manage NAPLS in sediment
- How to assess NAPLS mobility and availability in sediments
  - To assist design
  - To assist evaluation of remedy effectiveness

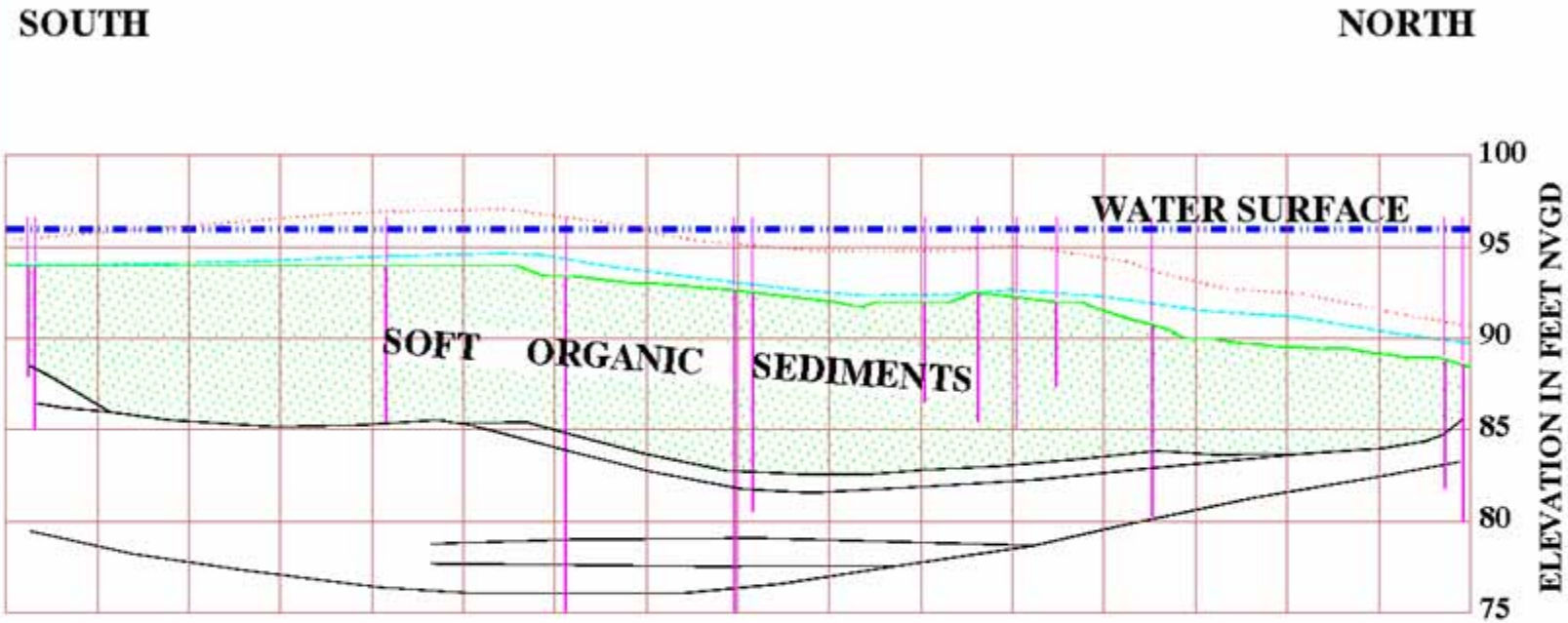
Managing Risks
What are the Options?

- Monitored Natural Recovery
  - Part of all remedies
  - May be an integral part of active remediation
- Dredging
  - Need to recognize impacts and limitations
  - Triggers a variety of onshore activities
- Capping/In-Situ Treatment
  - Clean sediment/sand layer over contaminated sediment
  - Can be rapidly implemented with minimal impact
  - Need to assess long-term protectiveness

Pine Street Canal, Burlington VT, *DNAPL*

Collaboration with Don Maynord/Johnson CO.

Sheens – Pine Street Canal



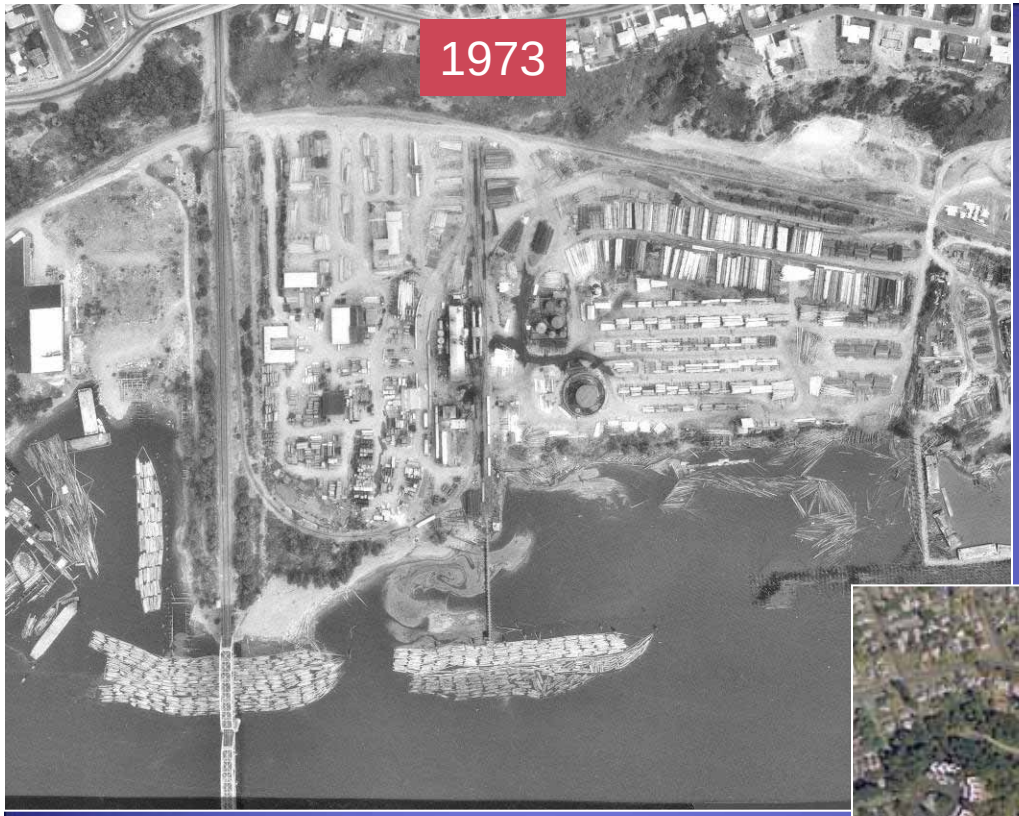
GEOLOGIC PROFILE T9 - T13
5:1 VERTICAL EXAGGERATION

10-15 ft of soft NAPL laden sediments!

Hudson River Dredging

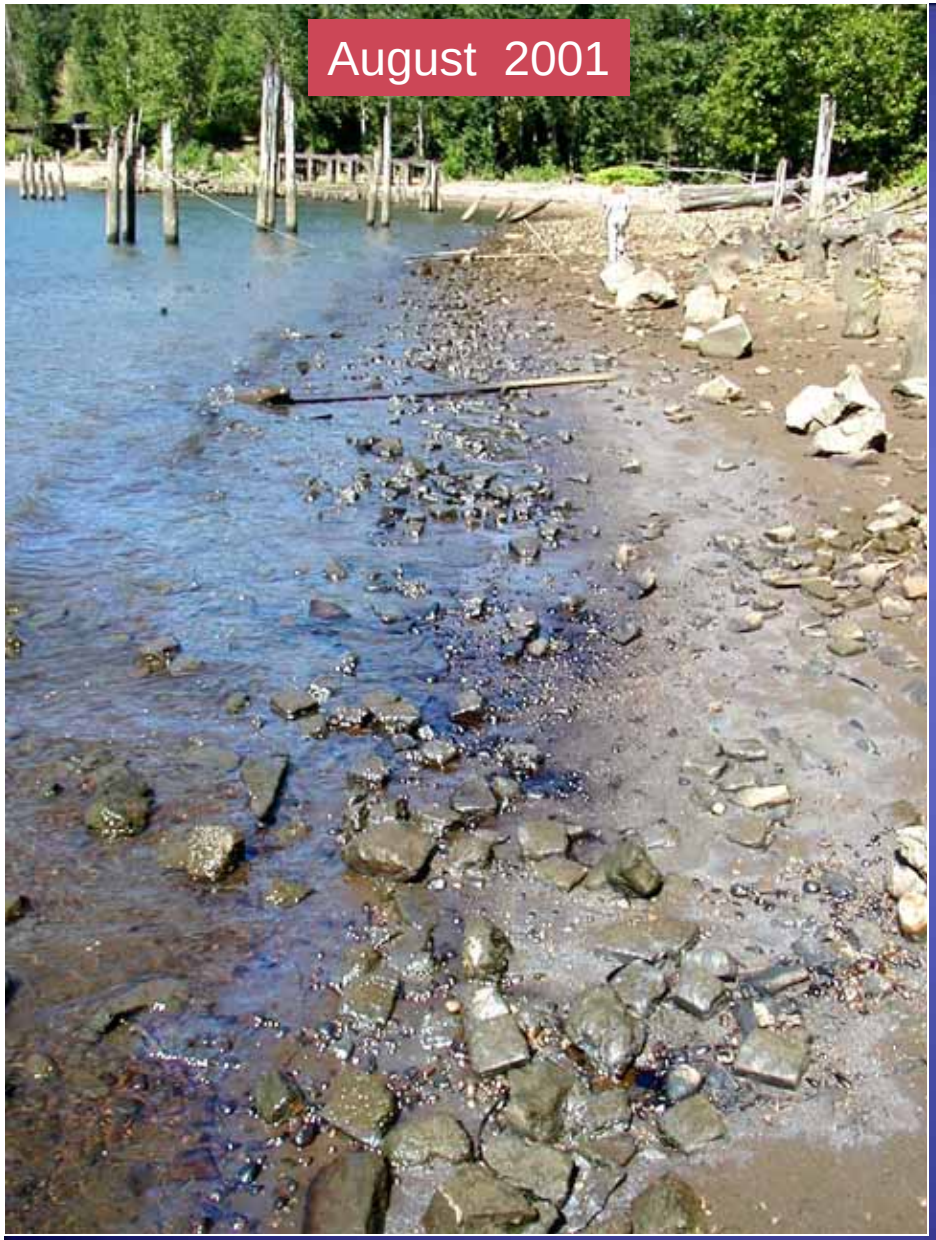
Dredging?
Sheens from NAPL in Hudson River

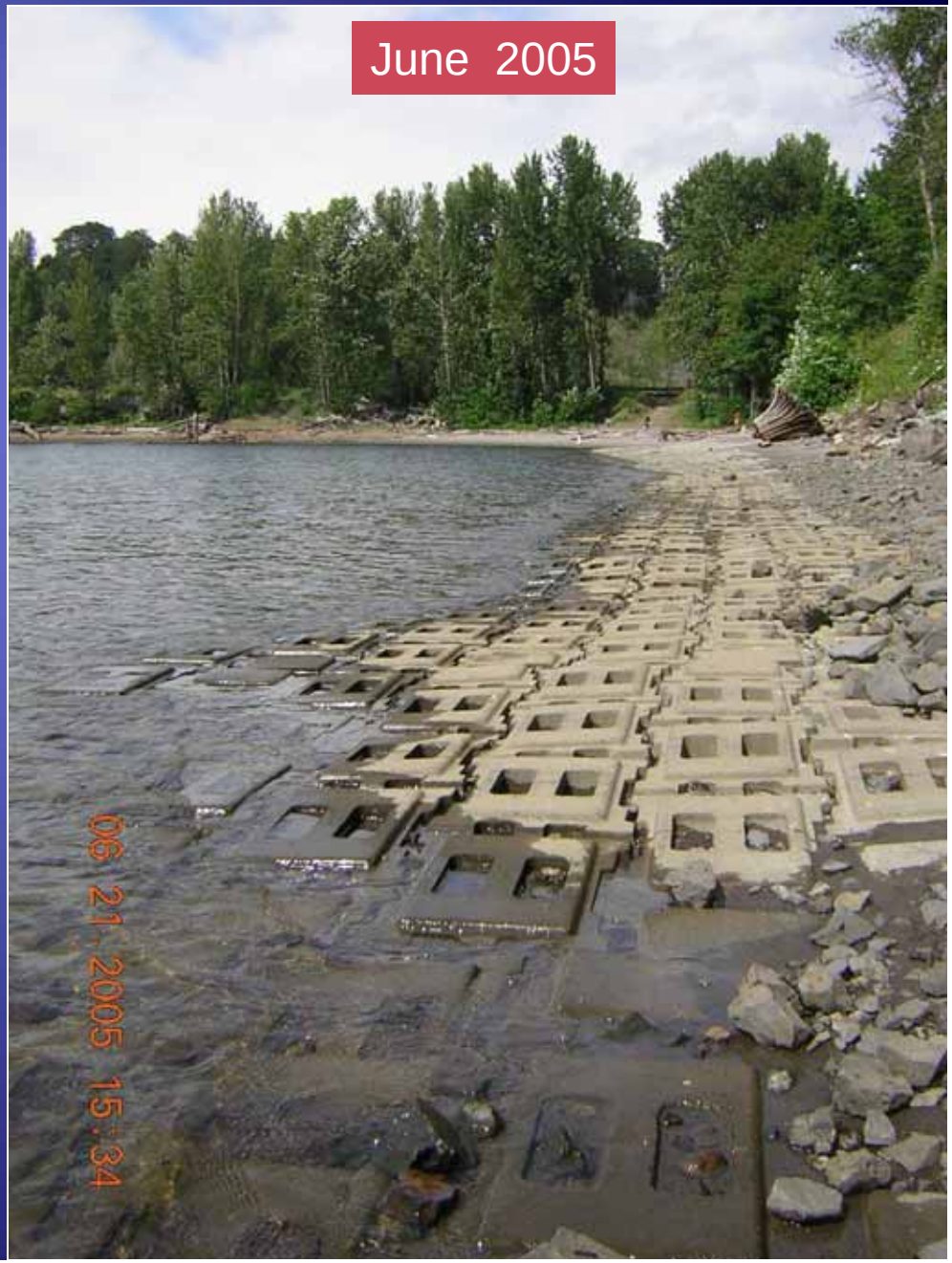
Ed Garvey
SETAC
2009



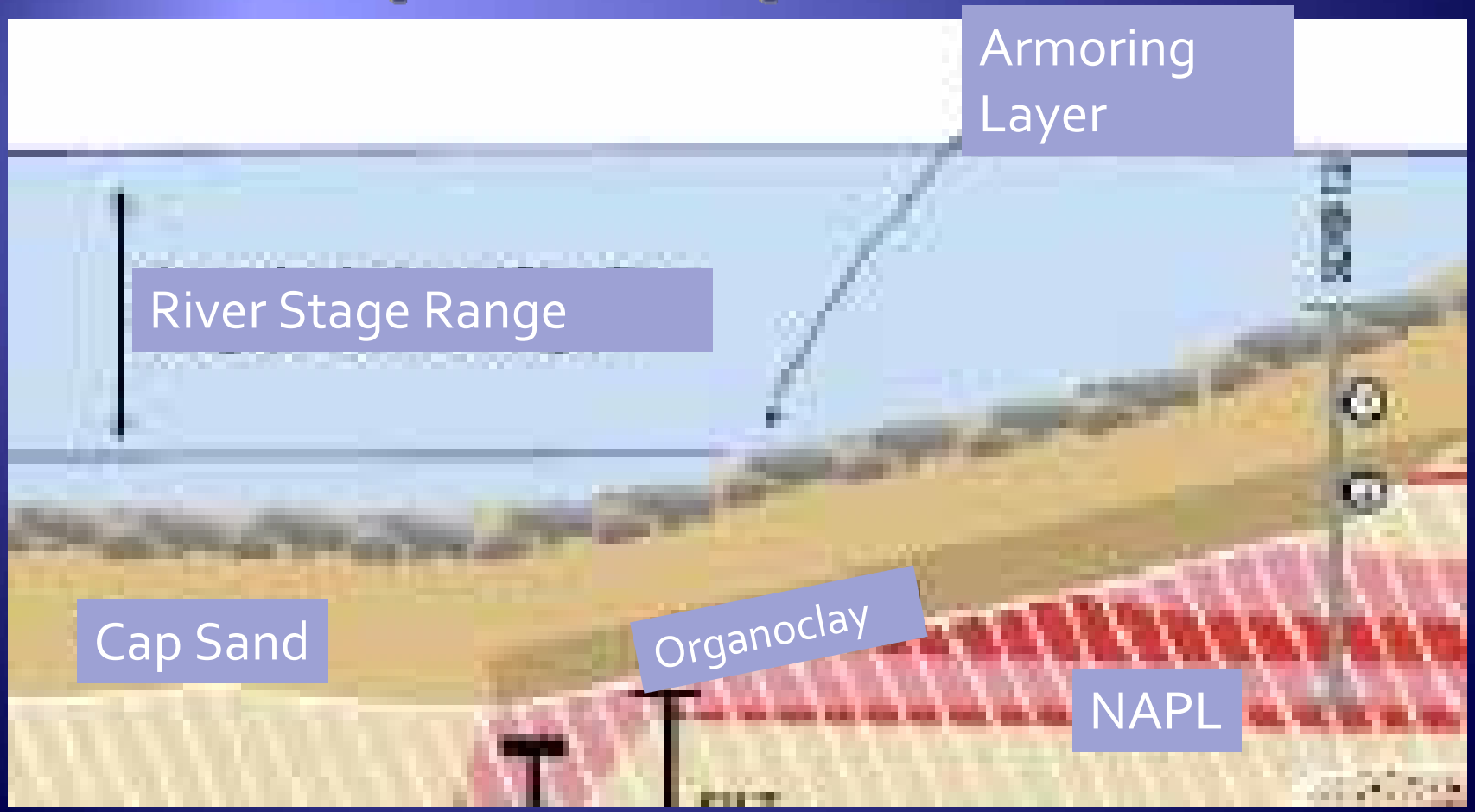
McCormick & Baxter Portland, OR

Before and After Remedy

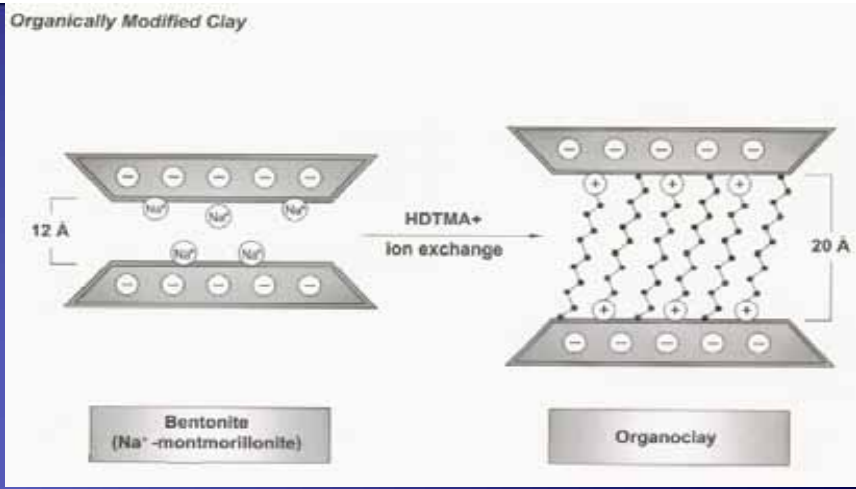




M&B Cap Conceptualization



Organic Retardation

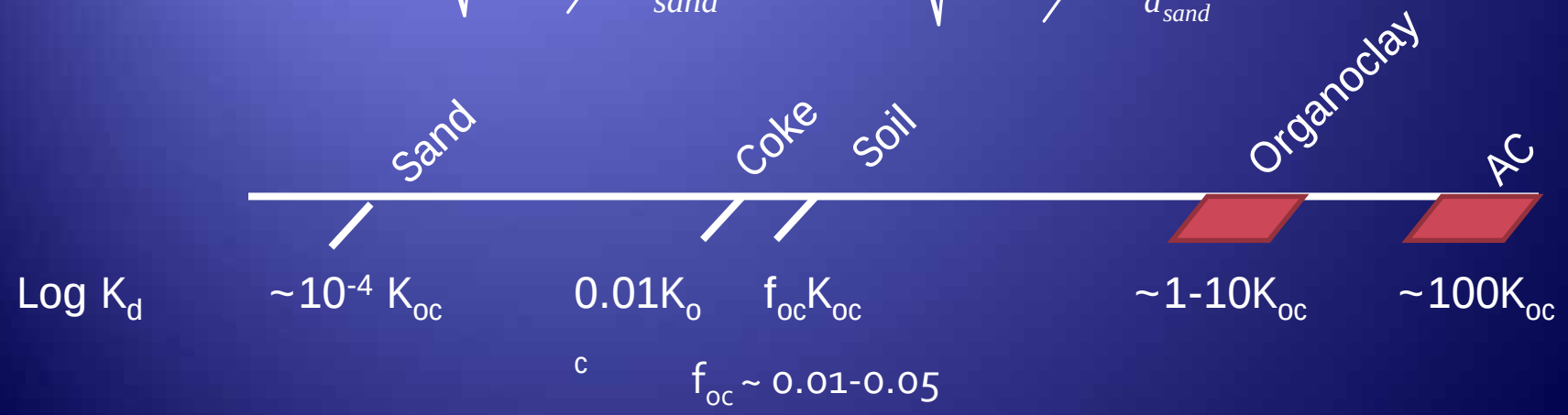


- NAPL present - Organoclays
  - Capacity of O(1 g NAPL/g organoclay)
  - Placement within a laminated mat for residual NAPL or to allow replacement if capacity exceeded
  - Placement in bulk for significant NAPL volumes
- Dissolved contaminants only - Activated carbon
  - Placement in mat may be necessary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

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)

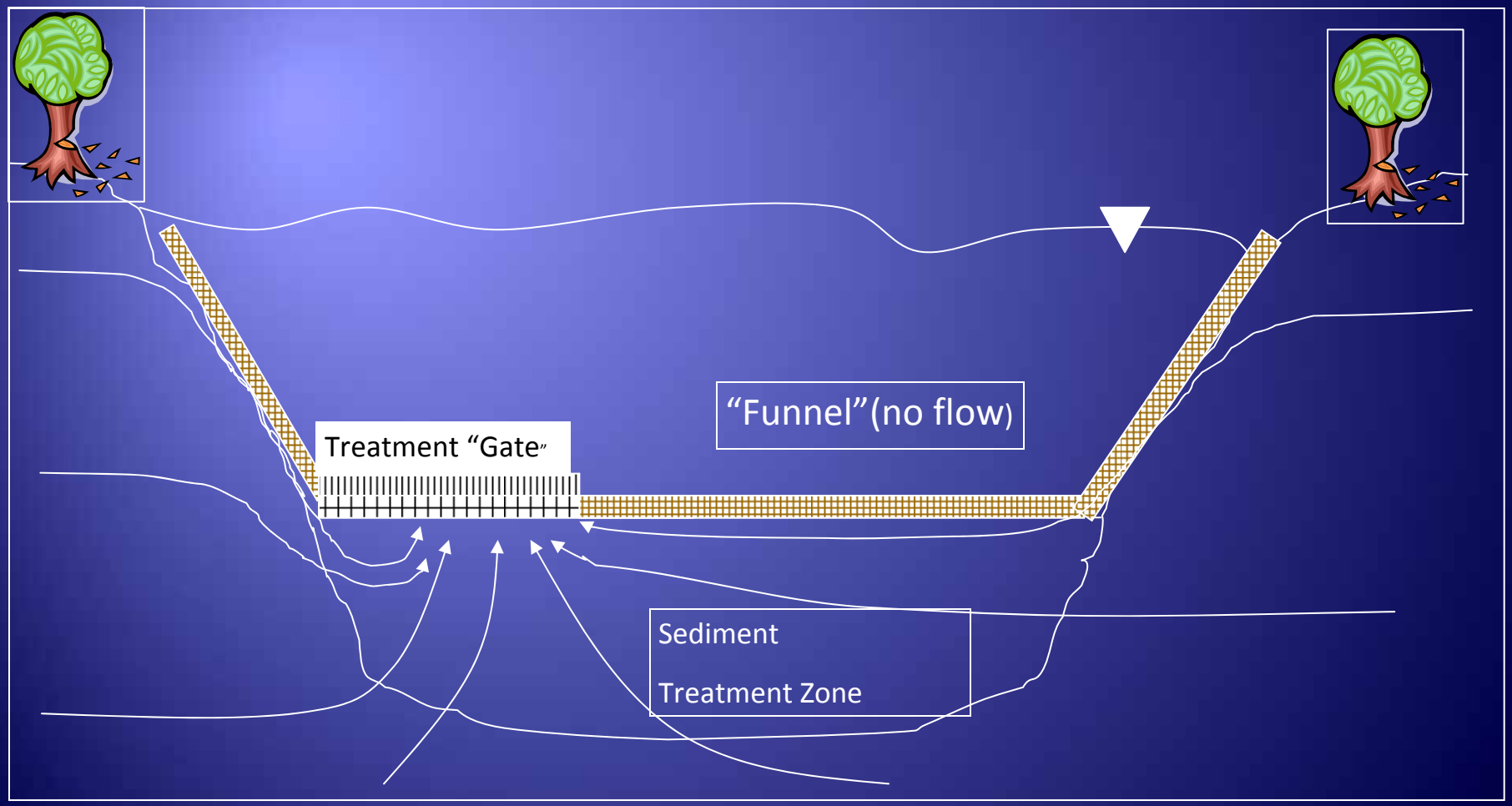
$$L_{eff} = L_{active}\sqrt{R_{active}/R_{sand}} \sim L_{active}\sqrt{K_{d_{active}}/K_{d_{sand}}}$$



Sediment Remedy – Cap (2004/05)

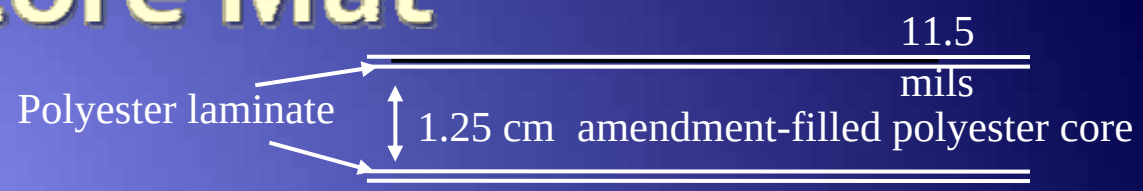
- *Granular organoclay (1 ft) in active seeps*
- *Organoclay blankets to manage gas release carrying small mass of NAPL to surface*

Depiction of Funnel and Gate



Amenable to more complicated treatment , e.g. organoclay/activated carbon sequence

Reactive Core Mat



- Thickness
  - ~0.5 in. (1.25cm)
- Loading
  - ~0.8-1.0 lb/ft^2

- Costs
  - Materials ($2700)
  - Lamination ($1750)
  - Labor ($2850)
  - Coke ($950) Anacostia
  - Shipping ($2900)
  - Total <u>($11,100)</u> ($1.11/ft^2)

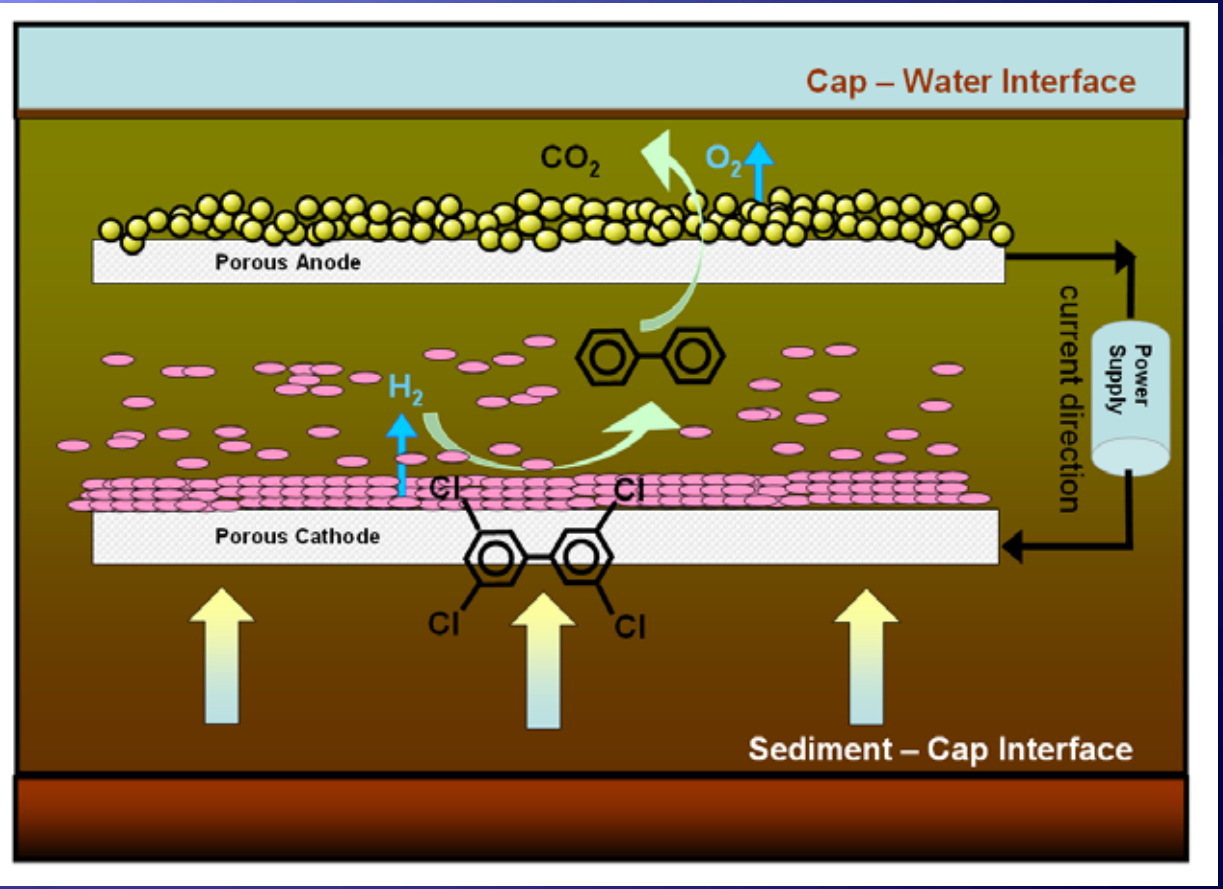
RCM- Reactive Core Mat

If activated carbon ~ $2.00/ft^2 (0.4 lb/ft^2)
If organoclay ~$2.00/ft^2 (0.8 lb/ft^2)
If iron - $1.25/ft^2 (bulk iron)
$3.62/ft^2 (10% nano-iron)

Conceptualization of electrode cap

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

For NAPL applications perhaps a treatment layer above an organoclay layer



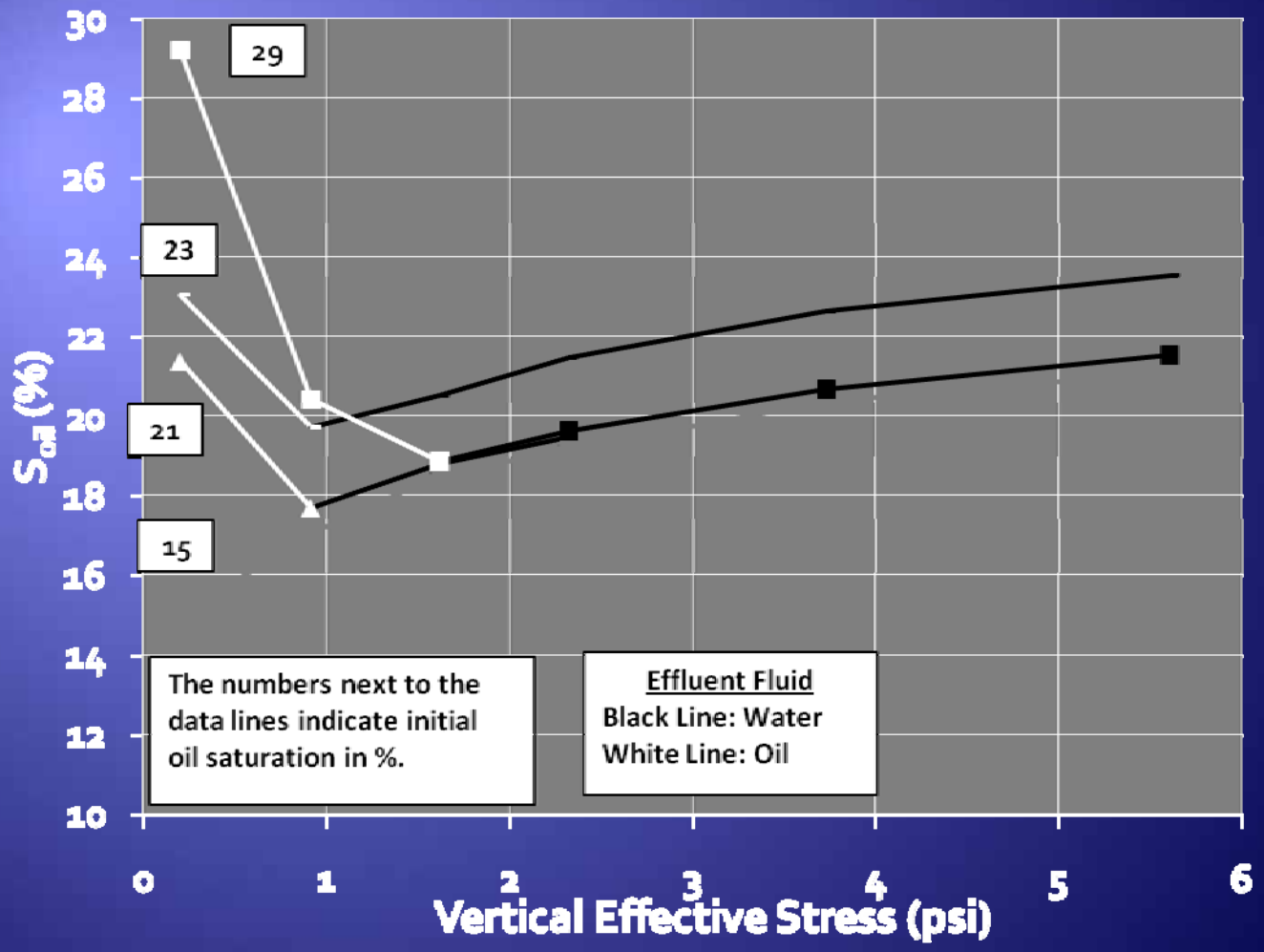
Assessment of NAPL in Sediments

- Before Remedy
  - Is NAPL mobile either currently or with the application of the load of a cap?
  - Capacity of organoclay sufficient?
    - Source controlled sufficiently?
    - Capacity of the organoclay for NAPL?
    - Capacity of the organoclay for dissolved constitutents?
    - Matrix effects that limit either?
  - Coupling with a second treatment possible/needed?
- Post-Remedy
  - Is the cap effective?
  - Are there early warning indicators of failure?

NAPL Mobility Testing

RESULTS Oil Saturation

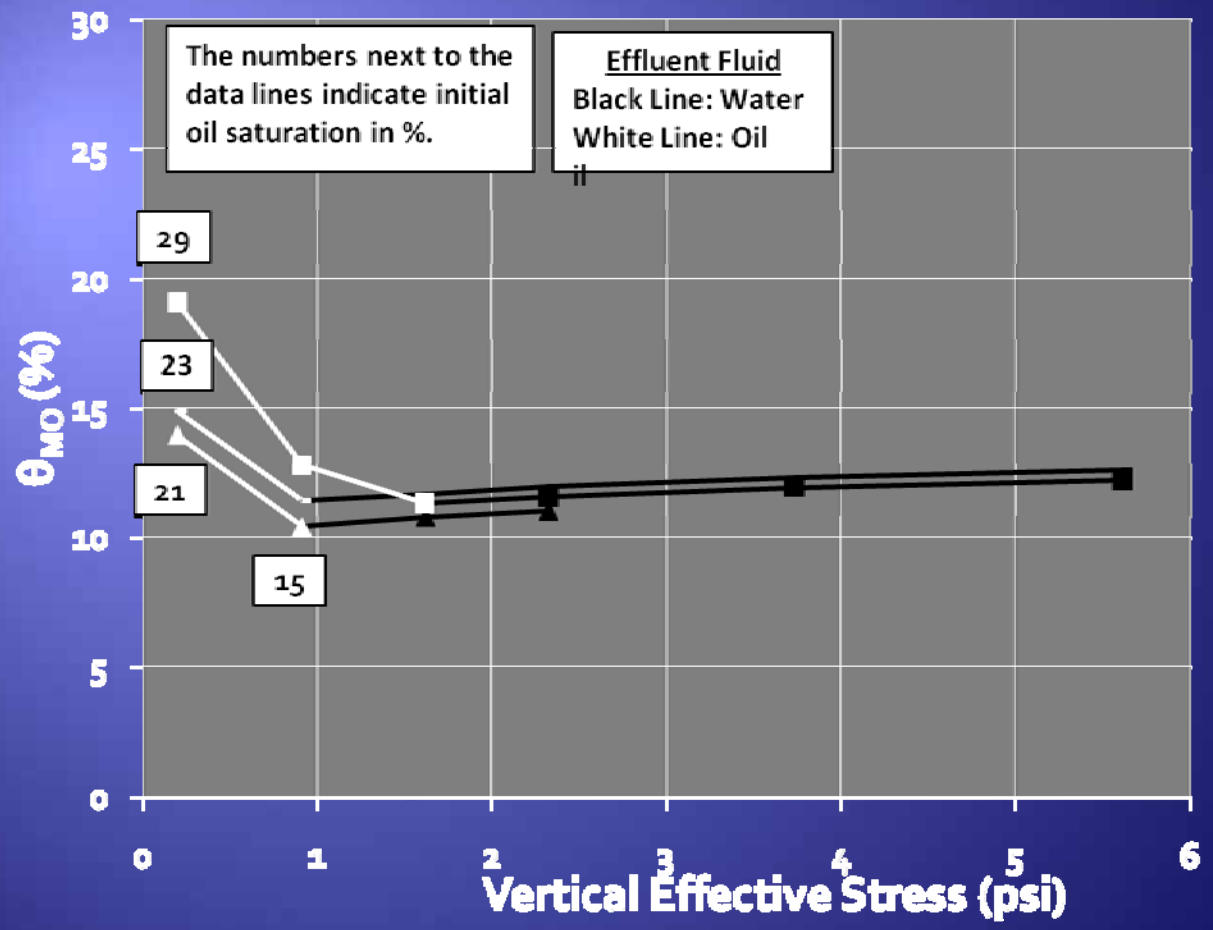
Initial Porosity (n) = 67%



When Oil Saturation ~ 20% The draining fluid switches from oil to water

RESULTS – Oil Content

Initial Porosity (n) = 67%



When volumetric oil content ~ 10-15% The draining fluid switches from oil to water

Monitoring Remedy Performance

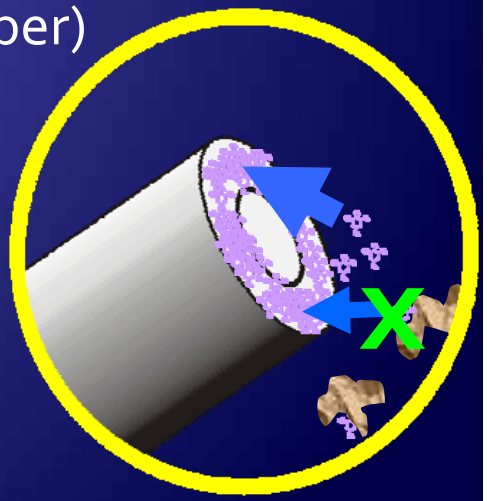
- Do we have effective means of monitoring remedy performance?
- Are our existing approaches to evaluating dredging and capping remedies consistent?
- Do we have tools for assessing when remedies will fail sometime in the future?

Indicators of Exposure and Risk

- Bulk Sediment Concentration
  - Relatively easy to measure
  - Good indicator of contaminant mass
  - Confusing indicator of risk
  - Largely irrelevant to capping and insitu treatment
- Interstitial Water Concentration
  - Indicator of availability
  - Does not indicate route of exposure

How to Measure Porewater?

- Direct in-situ measurement
  - Polydimethylsiloxane (PDMS)
    - Thin coating on glass fibers- Moderate volume, good surface area to volume ratio, high internal diffusion rates, good insitu feasibility
  - Polyethylene (PE)
    - Thin rectangular sheets - High volume, good surface area to volume ratio, moderate internal diffusion rates, marginal insitu feasibility
  - Polyoxymethylene (POM)
    - Molded thermoplastic- High volume, fair surface area to volume ratio, slow internal diffusion rates, marginal insitu feasibility
- Sorbent polymer PDMS (poly-dimethylsiloxane)
  - 30 µm fiber on 110 µm core (13.6 µL PDMS/m of fiber)
  - 10 µm on 230 µm core (7 µL /m)
  - 30 µm on 1 mm core (94 µL /m)
- ng/L detection with 1 cm resolution
- Profiling field deployable system
- May require 7->30 days to equilibrate



PDMS/SPME as passive sampler

- Commercial fabrication readily available in variety of dimensions
- Easy analysis - wipe fiber, rinse and insert in autosampling vial with injection solvent
- Concentrates porewater for hydrophobic contaminants (Log Kow≥ 4)
  - Little advantage and special handling required for volatile, less hydrophobic compounds
- Slow kinetics for very hydrophobic (Log Koc≥6)
- Kinetics governed by surface area to volume ratio
- Detection limit governed by volume of sorbent

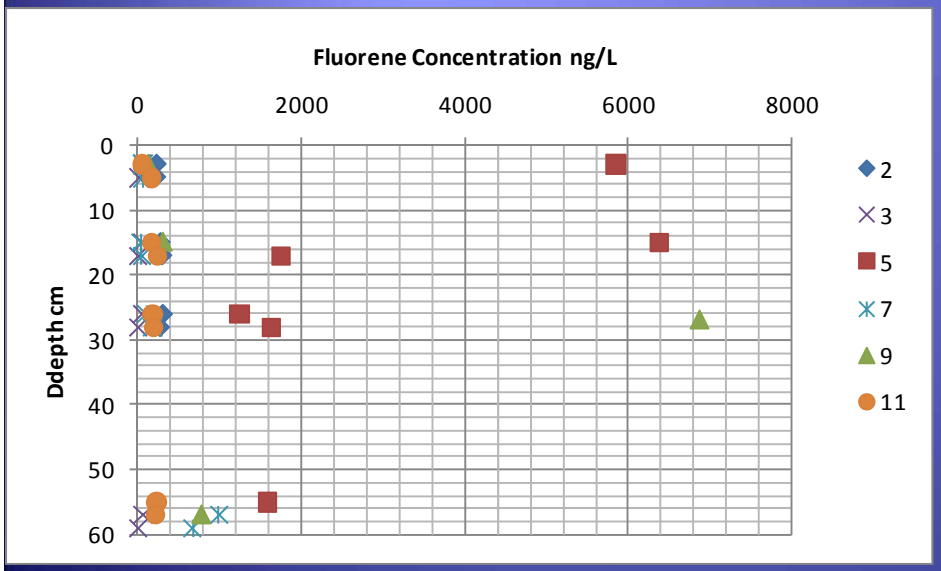
Profiling SPME

Large shielded sampler- 36”

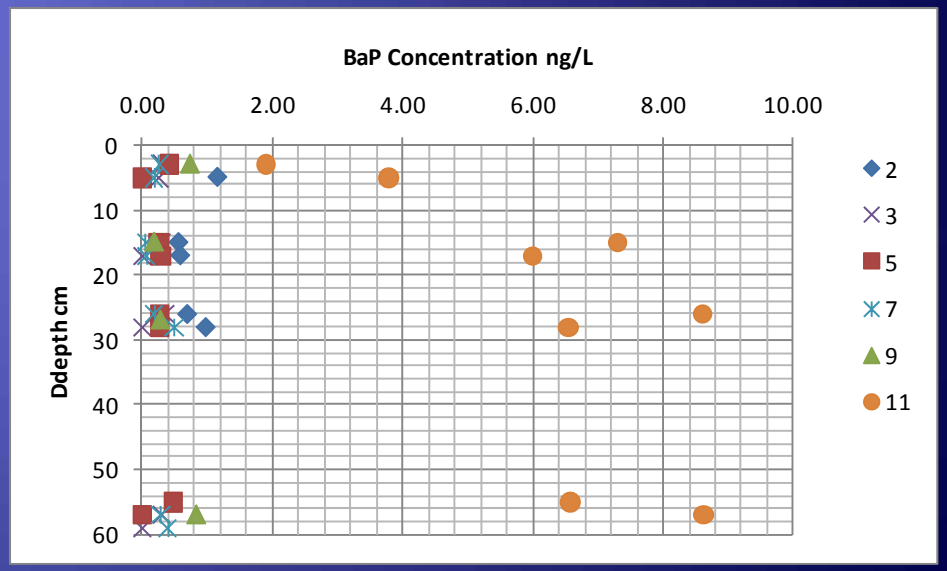
Small unshielded sampler- 14”

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

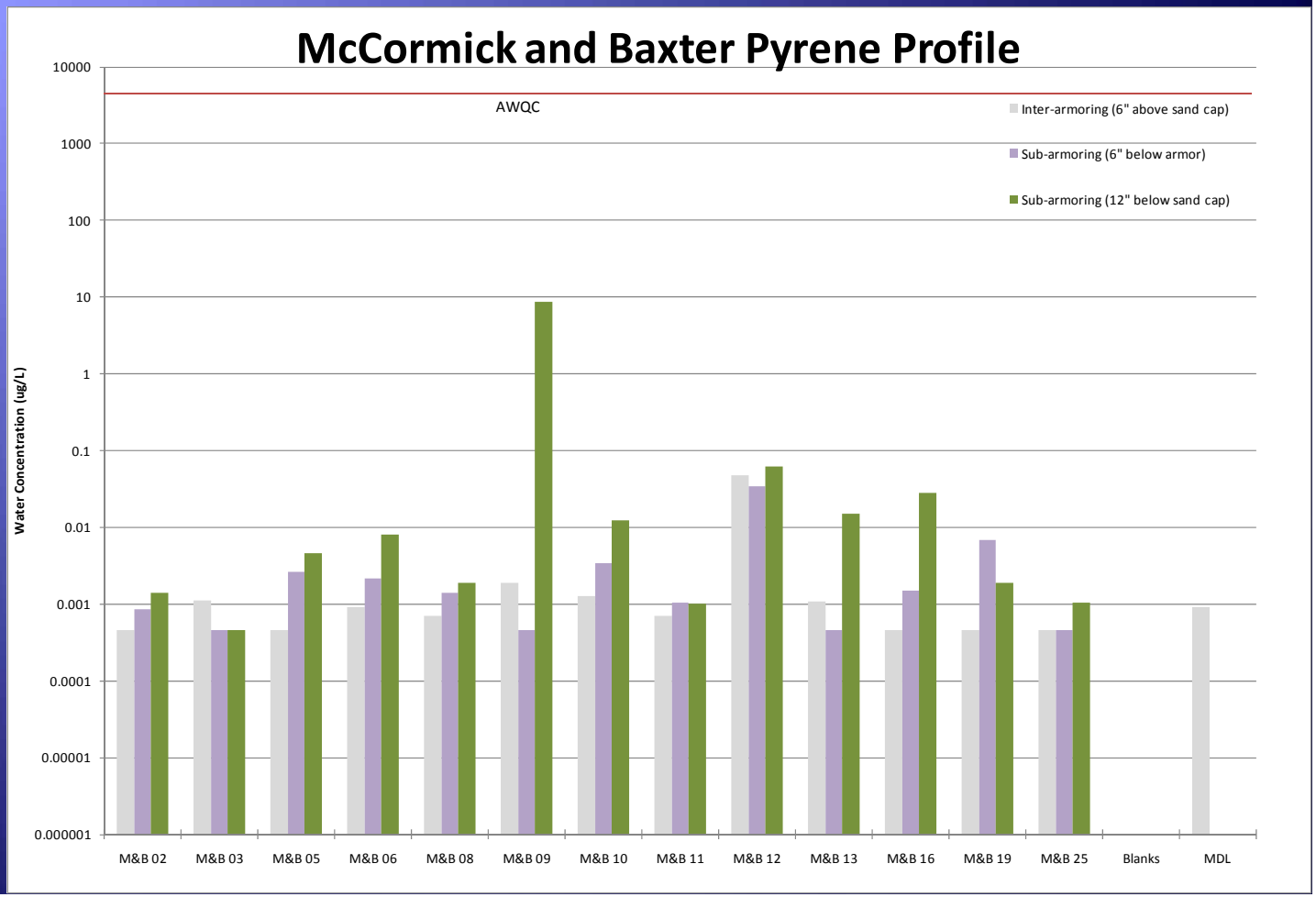
M&B Current Porewater Sampling

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



Conclusions

- NAPL is a problem in sediments as well
- No good NAPL remedies available
- In-situ containment with organoclay can be effective and protective
  - Placed in bulk
  - Placed in a thin layer (reactive core mat)
  - Placed as a replaceable treatment gate
  - Placed in concert with other materials
- Mobility can be assessed with lab testing
- Performance can be monitored with profiling passive samplers