CURRENT APPROACHES TO SEDIMENT ASSESSMENT AND REMEDIATION

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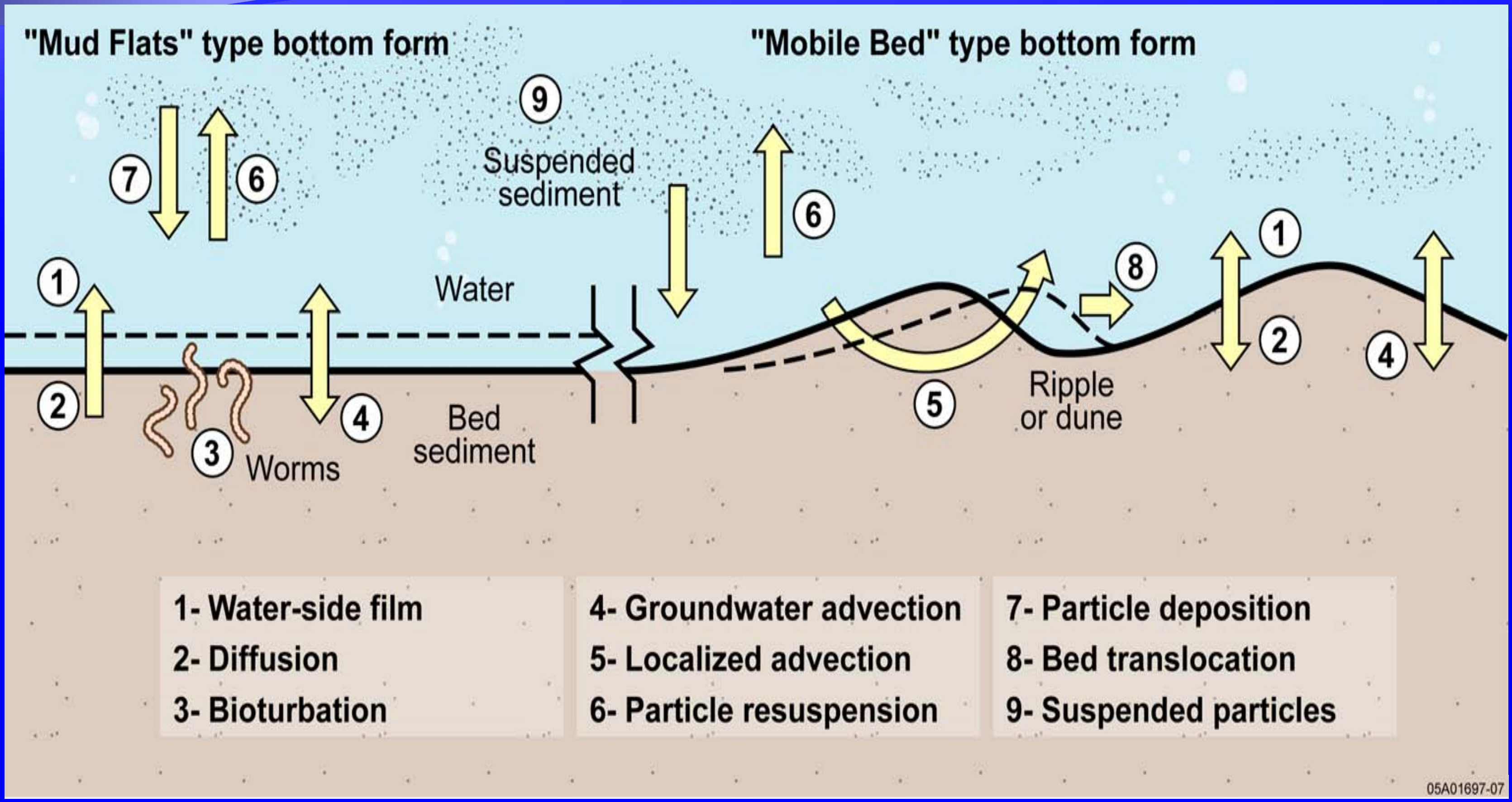
EPA, DOD-ESTCP/SERDP, NIH & Industrial Sources

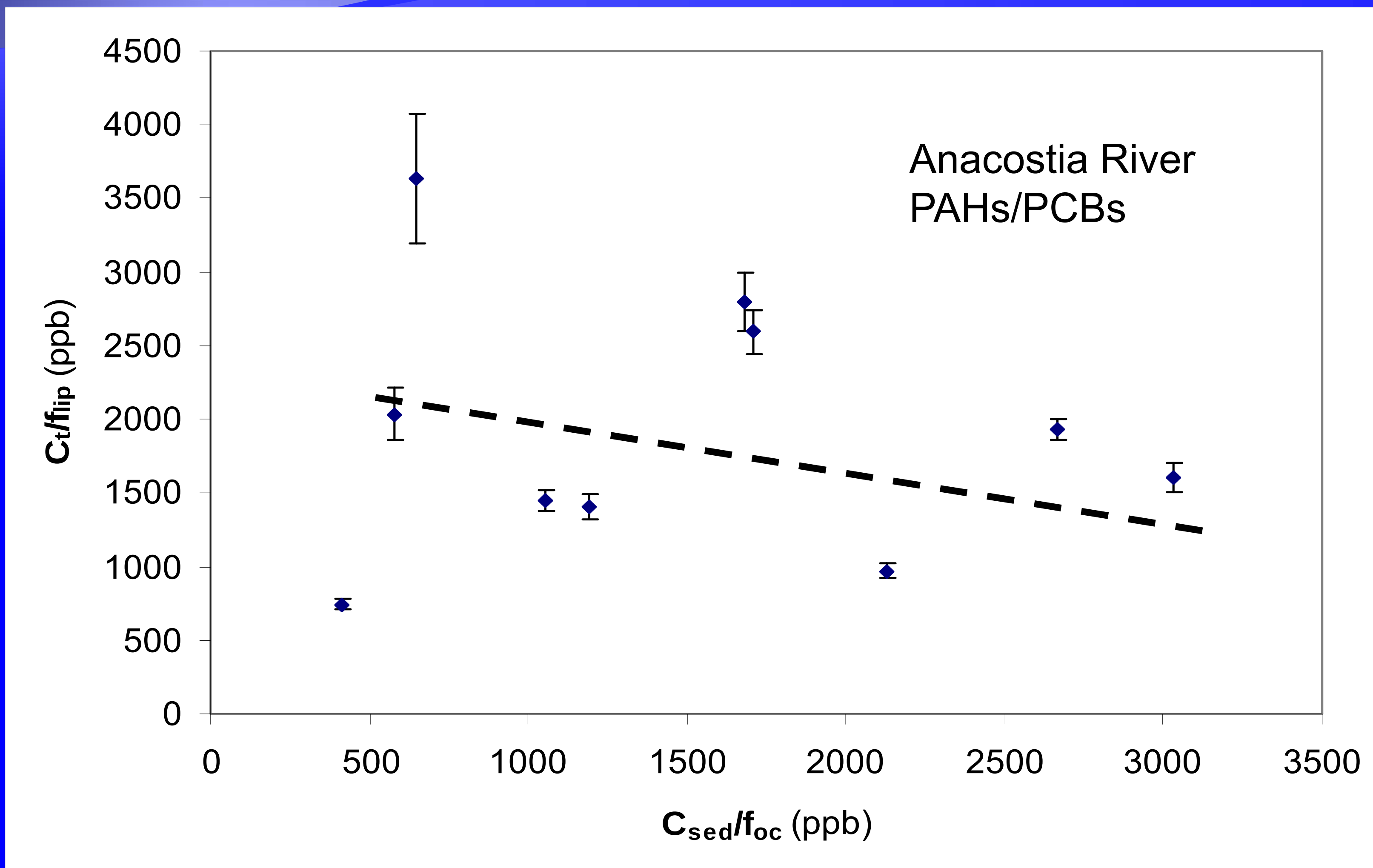
Danny Reible - Bio

- PhD Chemical Engineering Caltech
  - Long range transport of atmospheric pollutants

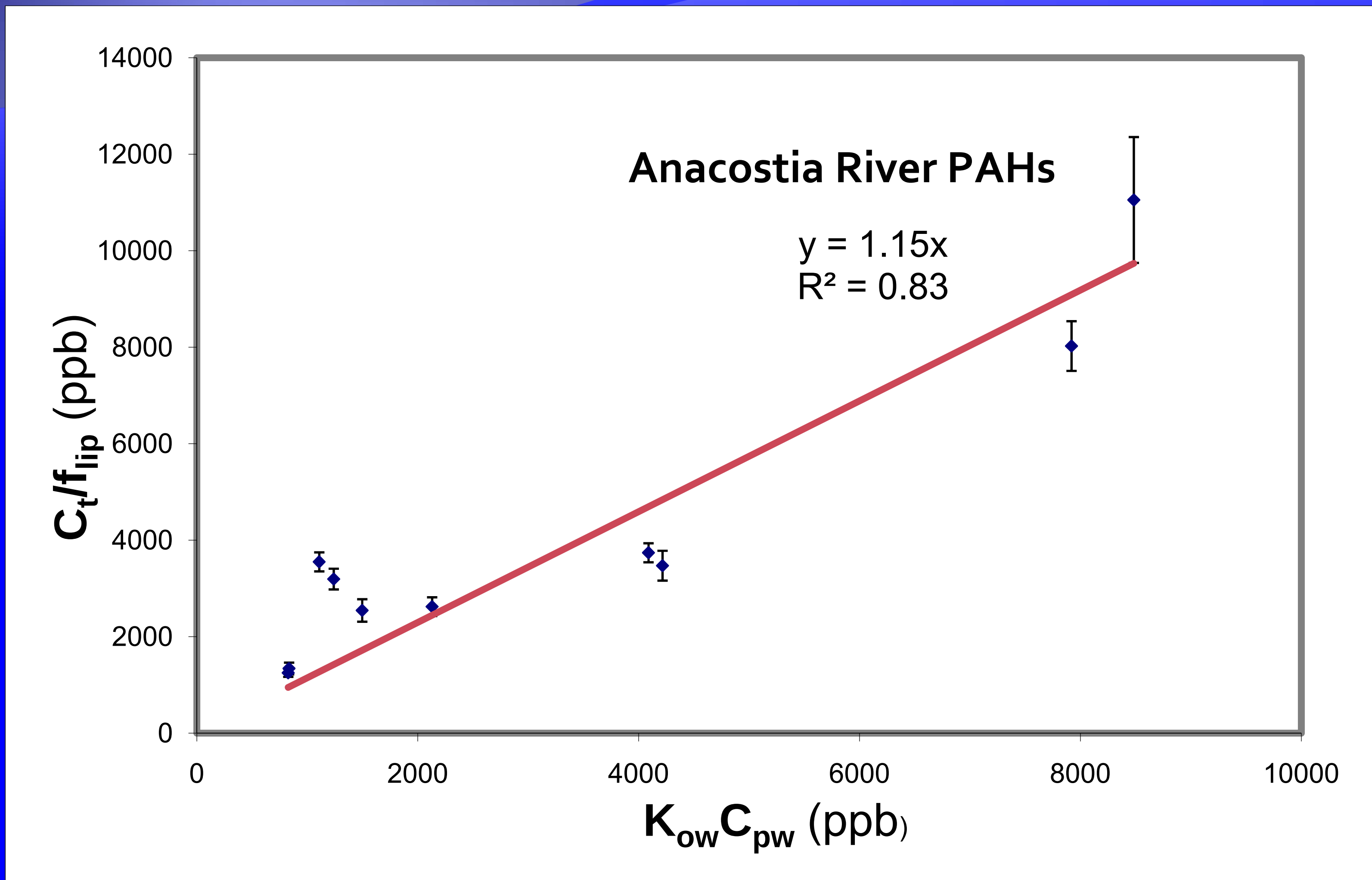
Sediment Processes



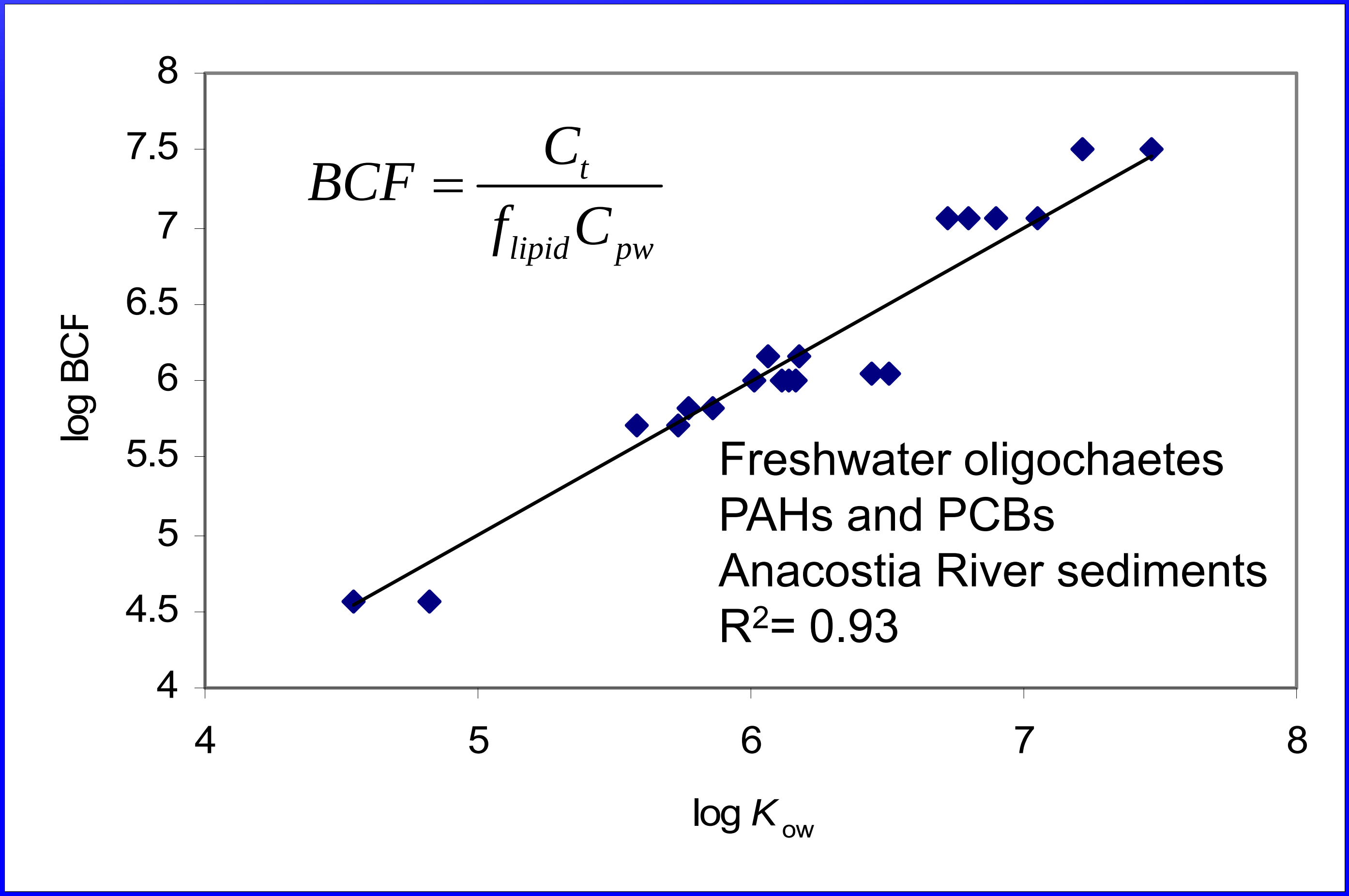
Should We Estimate Exposure-Risk from *Whole Sediment* Concentration?



Or Based on *Porewater* Concentration?



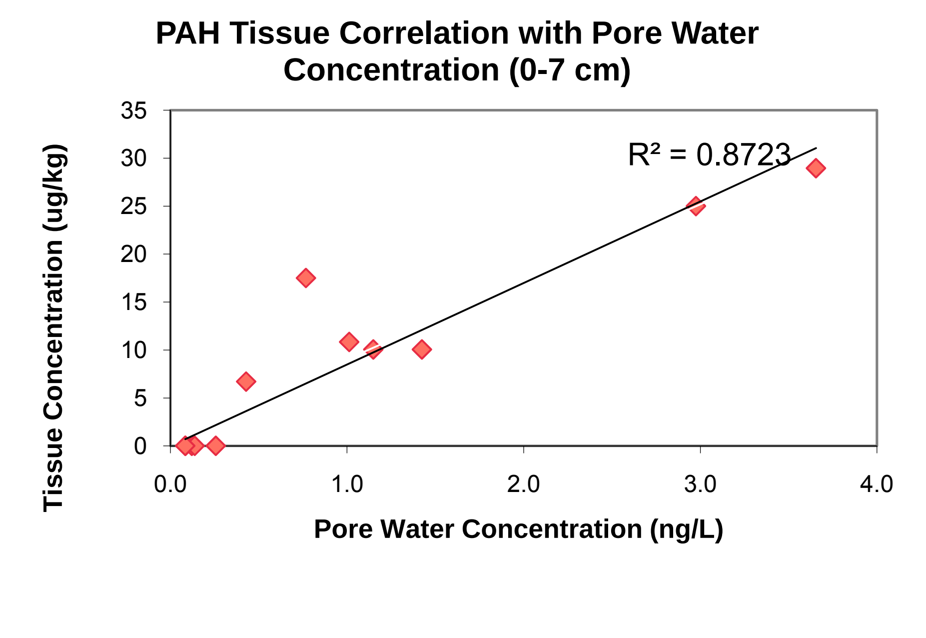
Bioconcentration Factor Applicable to Deposit Feeders In-Situ?

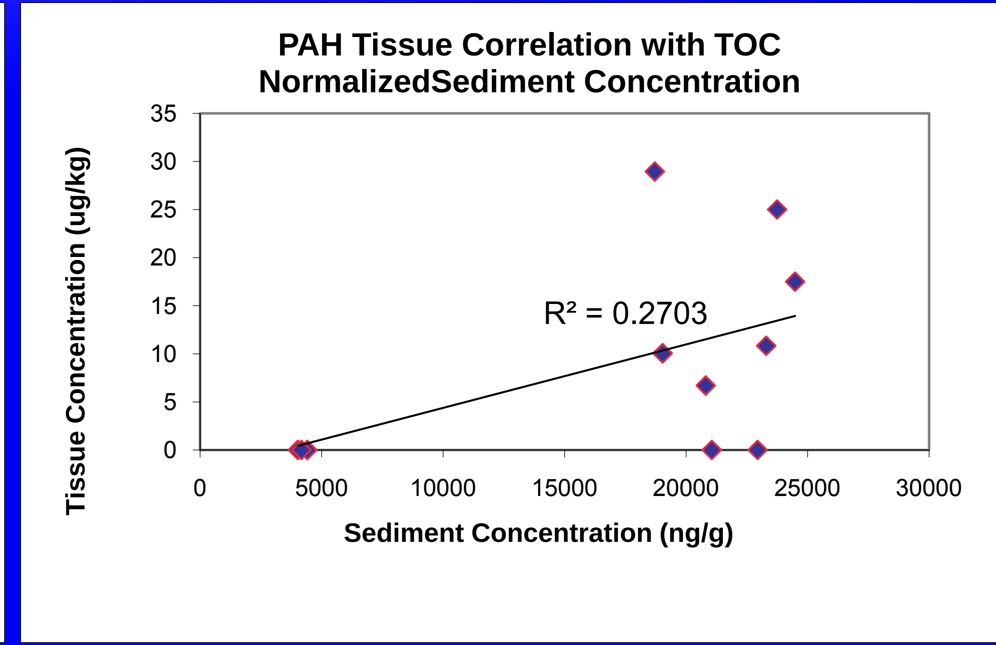


In sediments and in deposit-feeding organism (porewater not route of exposure)

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

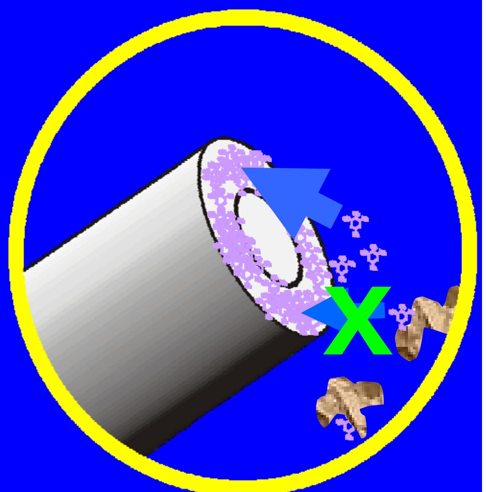
Implications & Measuring Porewater

- Bulk sediment concentration is less useful as indicator of exposure-risk
- **Porewater concentration** is better indicator (*even for active benthic uptake by ingestion)*
- Growing ability to measure porewater with solid phase micro extraction (SPME) and other passive approaches


Field deployable SPME, capable of measuring porewater with vertical resolution

How to Measure Porewater?

- Extraction/centrifugation – stability? accuracy?
- Direct in-situ measurement (PE, POM, SPME)
- Solid phase microextraction (SPME)
  - 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

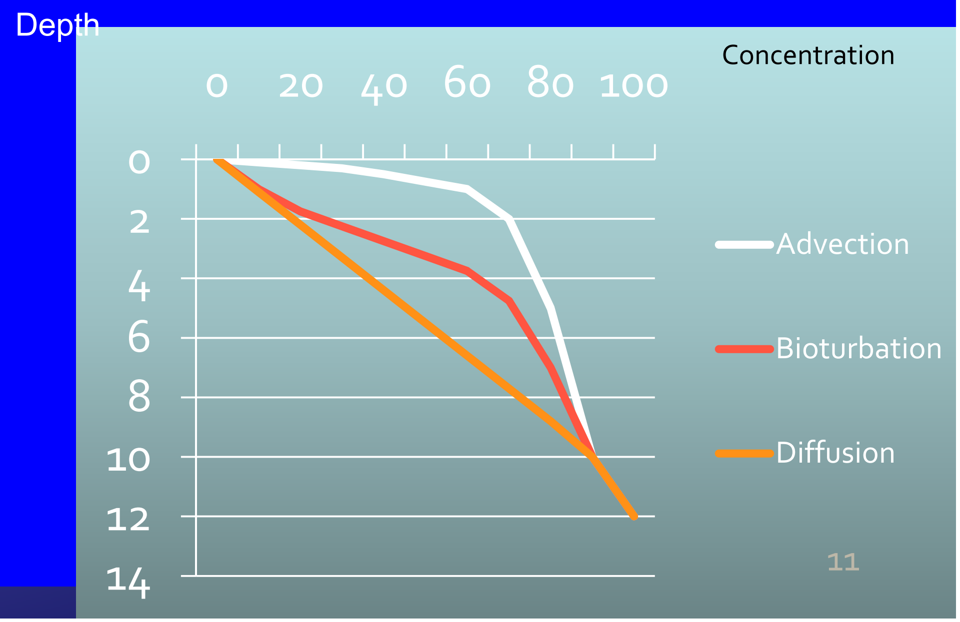


Comparison of Porewater Concentrations – Hunter's Point

PCB Congener	SPME (UT) pg/L	POM (EERC) pg/L	PE** (MIT) pg/L	Air Bridge (MIT) pg/L	Extracted Porewater Raw pg/L	Extracted Porewater TOC corr. pg/L***	Predicted Porewater Kd=Kocfoc pg/L
101	902	<915	230	602	5260	2400	6480
87	125	124	NR	NR	NR	NR	788
110	320	492	410	433	2850	1800	2340
95	880*	1460	330	667	3300	1900	8400
151	303	101	130	365	4820	670	5680
153	347	416	NR	NR	NR	NR	5440
141	134	133	NR	NR	NR	NR	1670
138	352	<2090	79	626	16300	5200	4910
149	750*	650	130	1180	15600	6200	9470
132	350*	408	720	866	20000	6100	12100

Why Field Deployable SPME?

- Avoids concerns about contaminant dynamics associated with porewater extraction
- Provides in-situ profile with up to 1 cm vertical resolution depending on detection limits
  - Profiles provide rate/mechanism information
- Disadvantages
  - Deployment time
  - Analytical requirements
  - Complexity
  - Volatile Losses

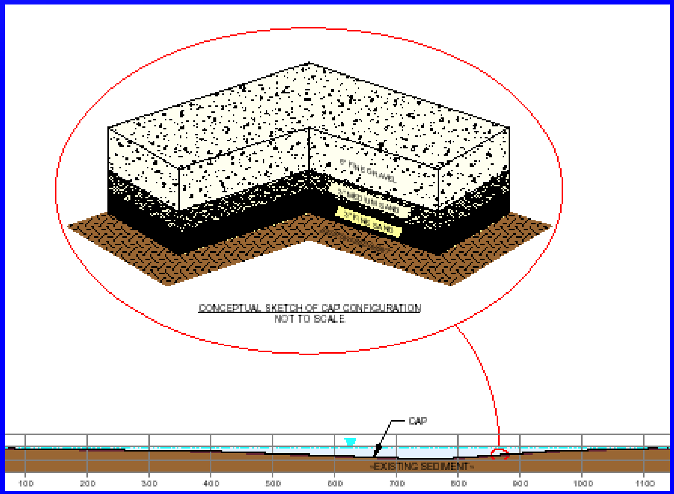


Managing Risks What are the Options?

- 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
  - Clean sediment/sand layer over contaminated sediment
  - Can be rapidly implemented with minimal impact
  - Need to assess long-term protectiveness

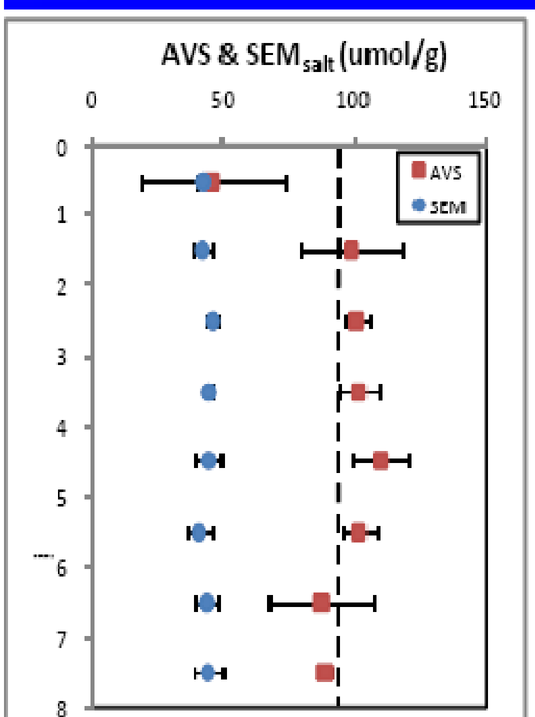
Sediment In-situ Capping

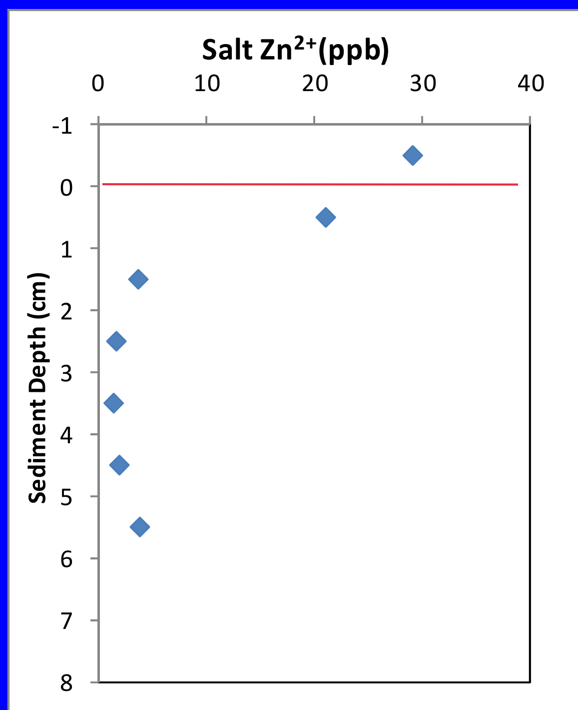
- Reduce risk by:
  - Stabilizing sediments
  - Physically isolating sediment contaminants
  - Reducing contaminant flux to benthos and water column
- Sand surprisingly effective for strongly solid associated contaminants
- "Active caps" for other situations



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

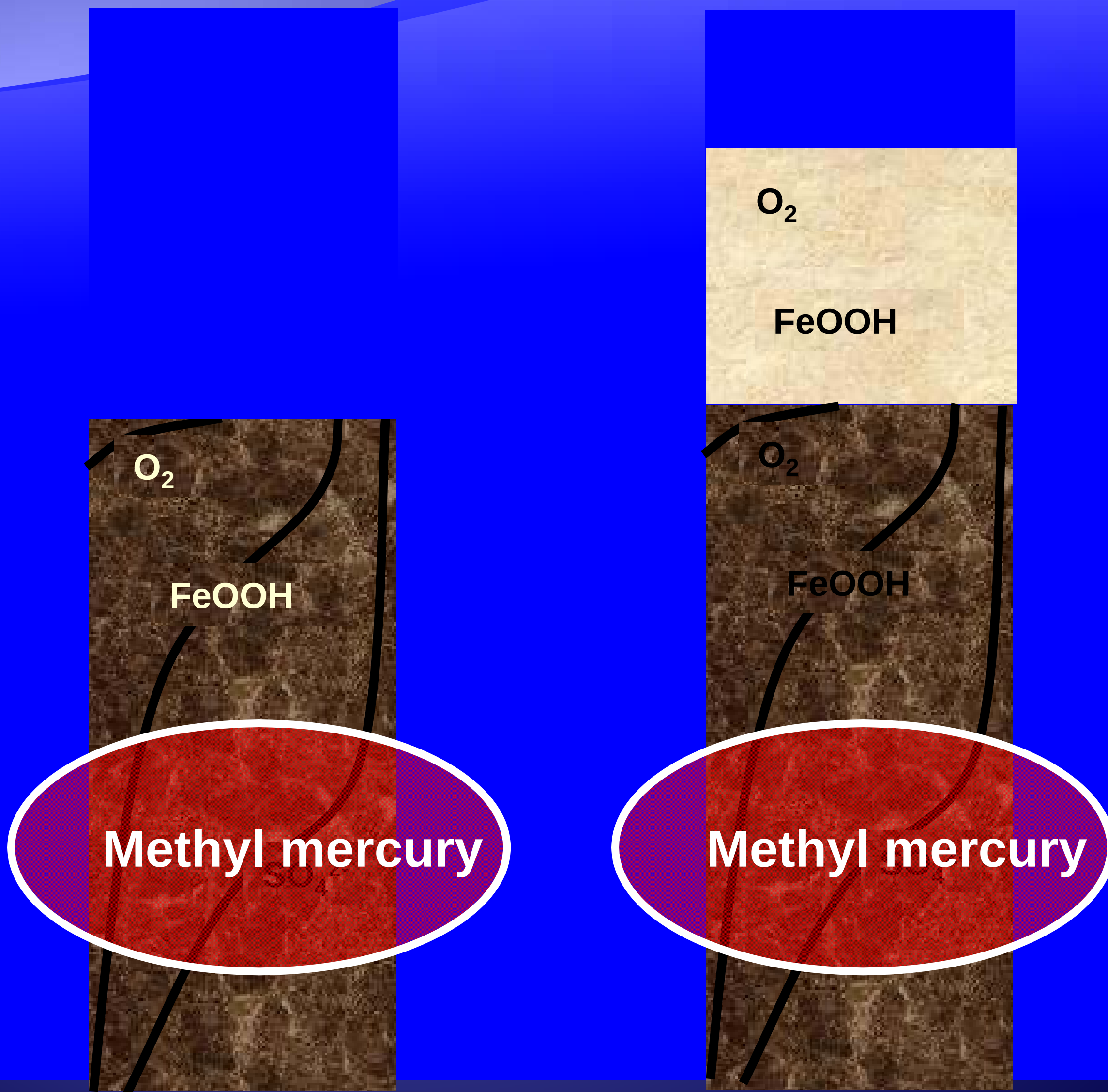
$M^{2+} + FeS_{(s)} \rightarrow MS_{(s)} + Fe^{2+}$

AVS < SEM

Divalent metals may be toxic

Conceptual Model

Pre-Cap | **Post-Cap**



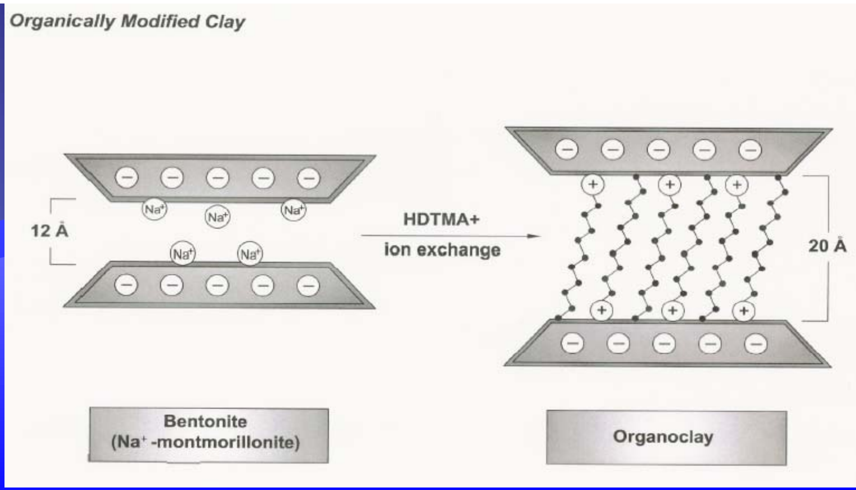
Organics and Capping

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

Goals of Active Capping

- 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

Organic Retardation

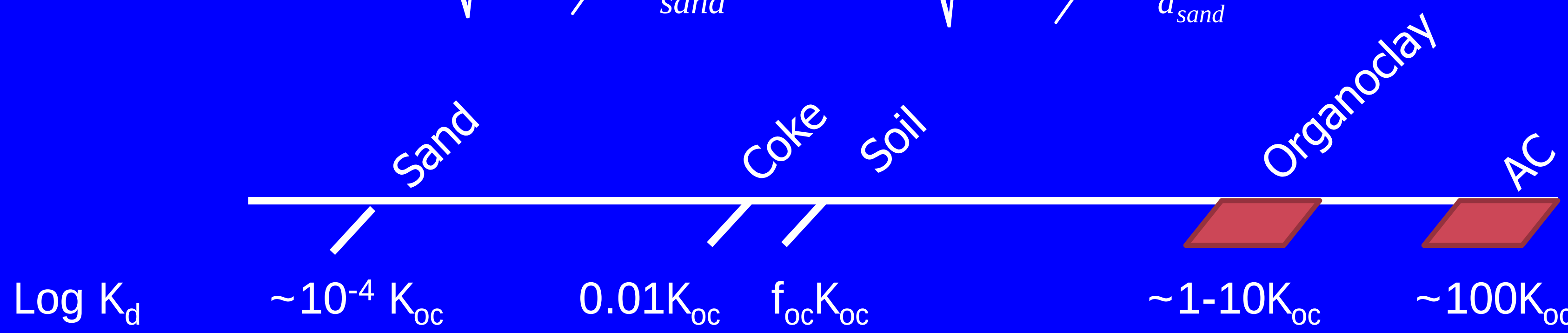


- NAPL present - Organoclays
  - Capacity of O(1 g NAPL/g organoclay)
  - Placement within a laminated mat for residual NAPL or to allow replacement if capacity exceeded
  - Placement in bulk for significant NAPL volumes
  - Multiple organoclay layers or organoclay/activated carbon layer for both NAPL 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 more subject to fouling than organoclay

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)

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



$f_{oc} \sim 0.01\text{-}0.05$

Conclusions for Sediment Management

- It's about ***risk,*** not whether a contaminant is present
- ***Benthic community*** is critical indicator of risk and transport
- ***Porewater*** may be better indicator than bulk sediment
- There are risks associated with ***both action and inaction***
- As with other media, ***containment*** can be effective
  - Inorganic contaminants often "self-contained"
  - Organic contaminant containment can be enhanced with sorbents
    - Organoclay – NAPL, fouling environments
    - Activated Carbon – Dissolved organic contaminants