Innovations in Sediment Assessment and Remediation

Danny Reible, PhD PE BCEE NAE
Donovan Maddox Distinguished Engineering Chair
Texas Tech University

Kappe Lecture

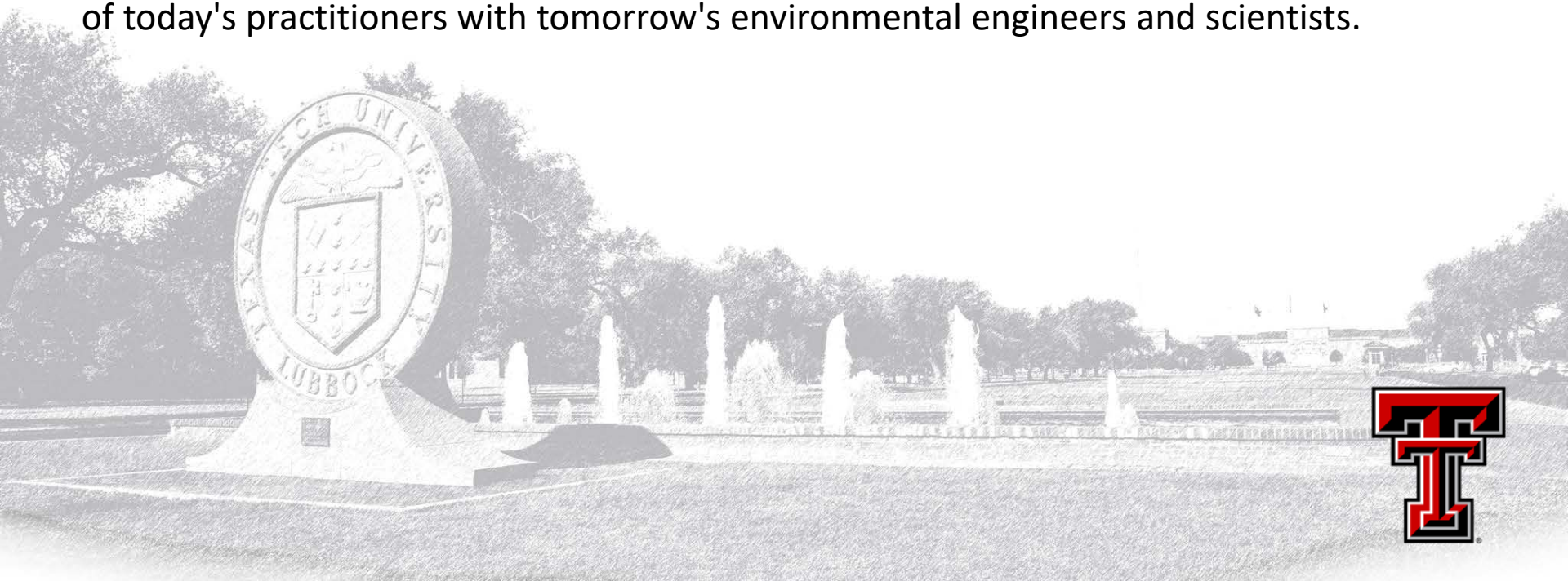
AMERICAN ACADEMY OF ENVIRONMENTAL ENGINEERS & SCIENTISTS®

AMERICAN ACADEMY OF ENVIRONMENTAL ENGINEERS & SCIENTISTS®

Protecting public health and the environment by:

- Recognizing leadership and excellence through Board Certification of Environmental Engineers and Scientists (BCEE)
- Providing professional development opportunities for students, engineers, and scientists

The Kappe Lecture Series was inaugurated by the Academy in 1989 to share the knowledge of today's practitioners with tomorrow's environmental engineers and scientists.

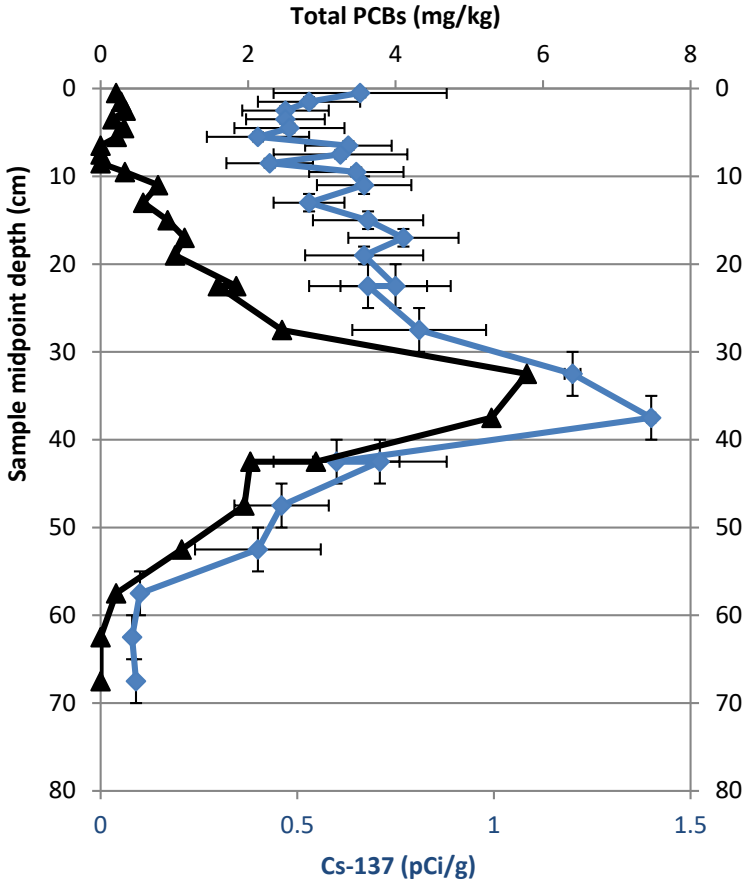


Contaminated Sediments

- **Industrial and municipal effluents managed effectively**
  - ✓ At least for historical sediment contaminants (metals and hydrophobic organics)
  - ✓ Concerns about perfluorinated compounds, pharmaceuticals, pesticides/herbicides
  - ✓ Current contaminant concerns often not sediment contaminants
- **Stormwater increasingly managed effectively**
  - ✓ Remains a source of sediment recontamination in some areas
  - ✓ Slowing or reversing remedial efforts
- **Legacy of strongly solid-associated refractory contaminants in sediments now pose substantial risk to bodies of water**
  - ✓ Polyaromatic hydrocarbons (PAHs)
  - ✓ Polychlorinated biphenyls and dioxins (PCBs)
  - ✓ Metals

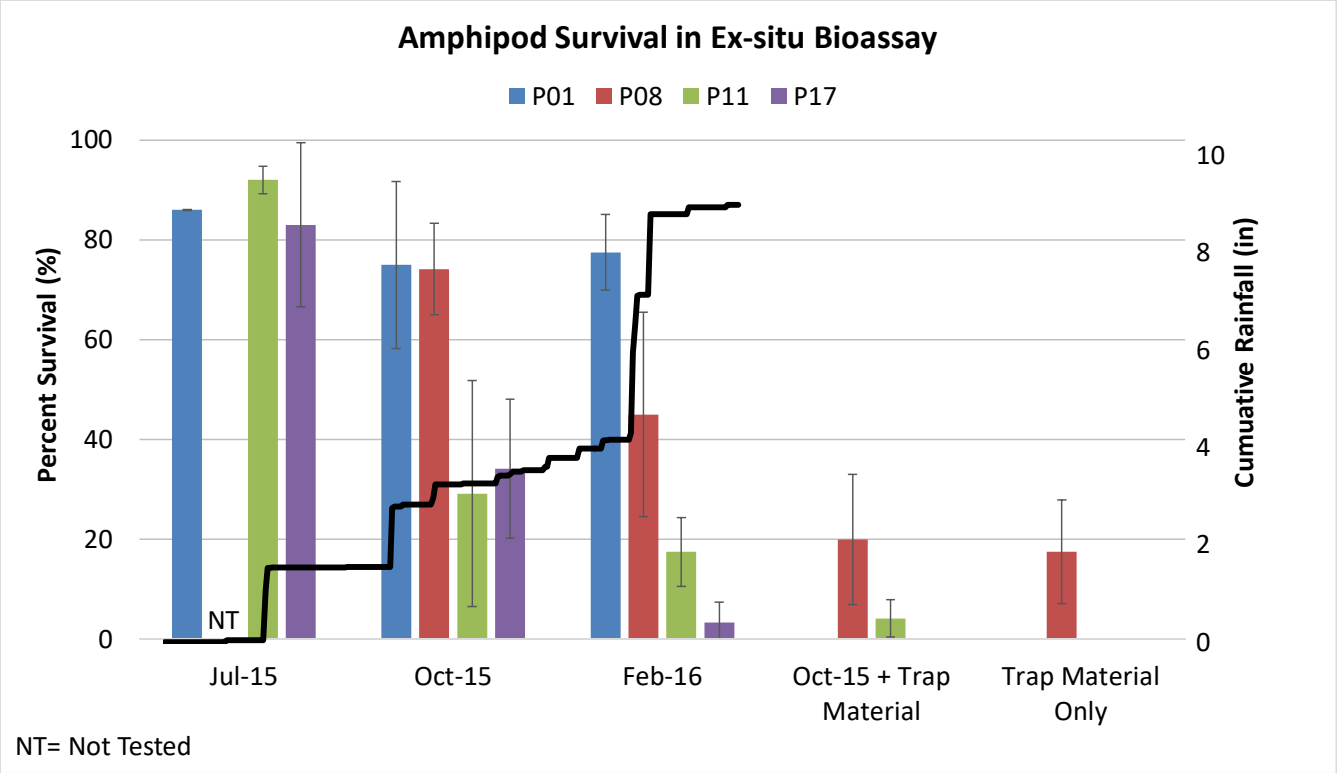
Risk-based Decision-Making

- Risk relates to exposures to contaminants above acceptable levels.
- Remediation should be designed to eliminate or reduce those exposures.
- Exposures are dictated by surface sediments – contaminants buried below the biologically-active zone are not available to organisms.
- Disrupting sediment beds to remove buried contaminants can expose organisms to otherwise inaccessible contaminants.
- However, removal of deeply buried contaminants may thwart future exposure and transport during severe events.



PCB profiles and Cs-137 dating
Location in the Kalamazoo River

Stormwater can create new problems

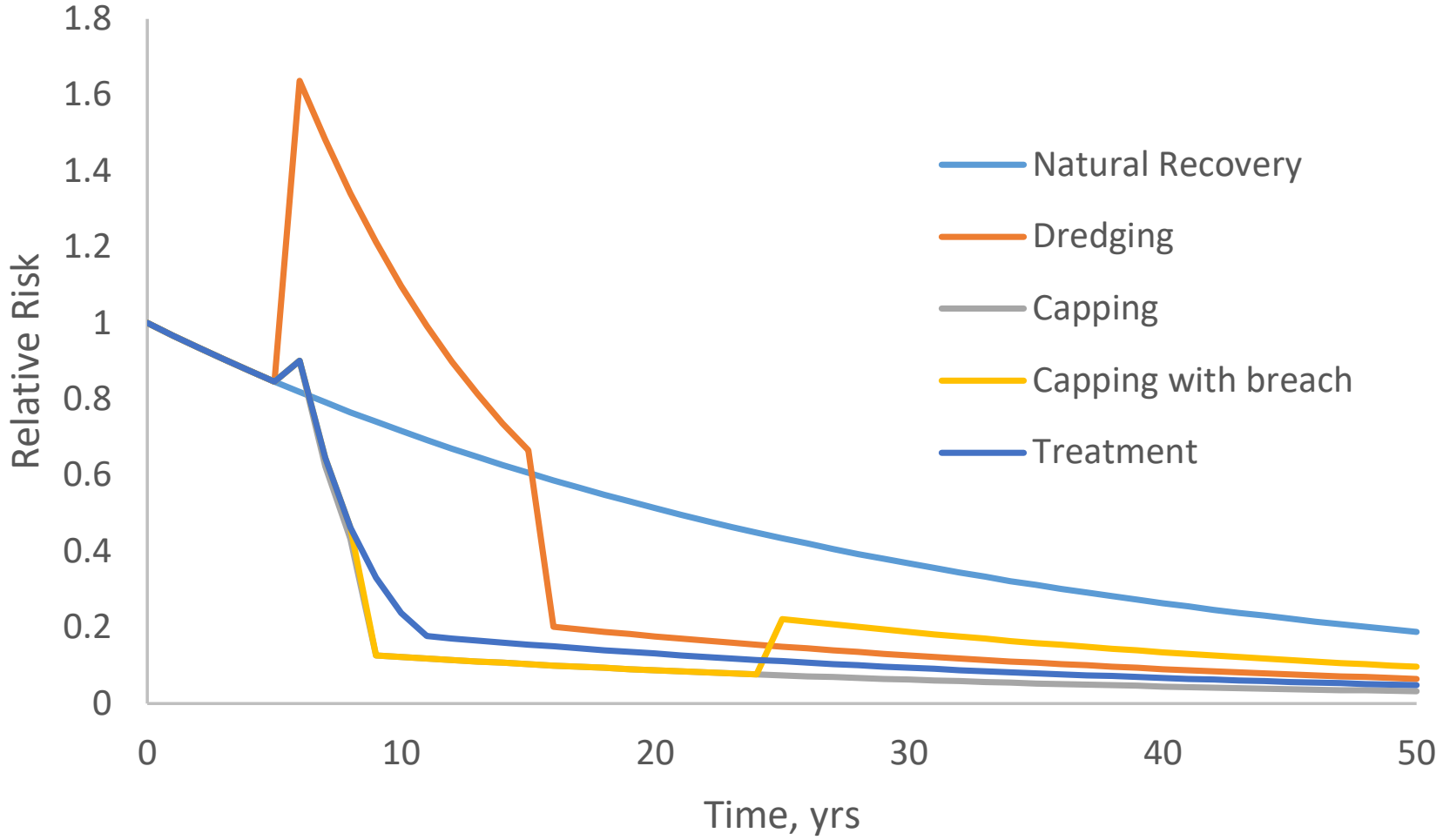


- Increasing toxicity from non-toxic summer condition as storm season progressed, particularly at stations closest to creek mouth
- Addition of sediment trap material to surface of cores collected in October 2015 were more toxic than without the trap material
- Trap material was highly toxic at Stations P17 and P11, those closest to creek mouth

Managing Risks
What are the options?

- **Monitored Natural Recovery**
  - ✓ Depends upon effective monitoring
- **Dredging**
  - ✓ Potentially effective but subject to resuspension/residuals
  - ✓ Current targets are mass and volume oriented- needs refocusing on risk reduction
- **Capping and In-Situ Treatment**
  - ✓ Effective/Efficient/Sustainable
  - ✓ Bulk solid measures not directly applicable
  - ✓ Depends upon effective monitoring and effective long-term stability

Performance of Remedial Alternatives

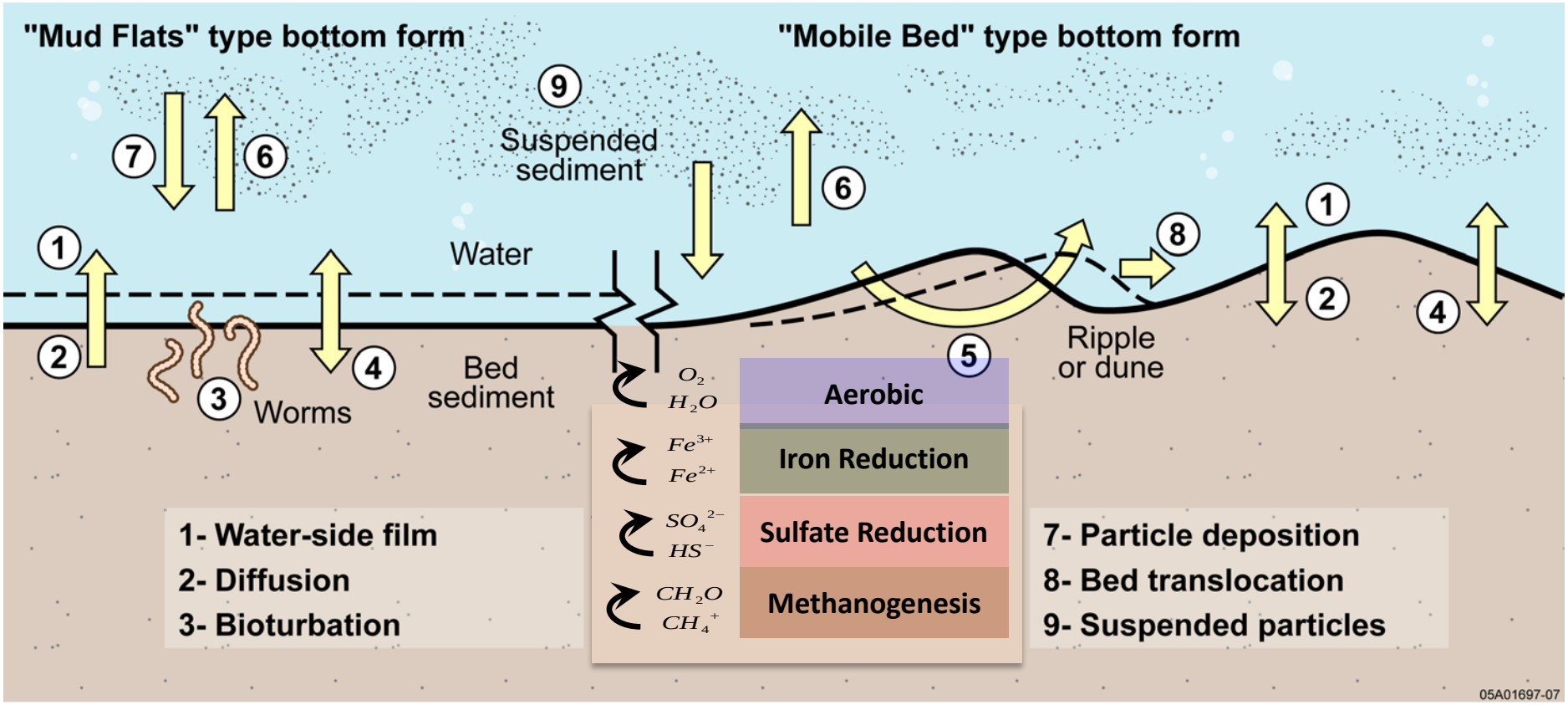


Dredging Limitations

- **All dredges resuspend sediment**
- **All dredging operations leave residual contamination**
- **Increased resuspension and residual**
  - ✓ During debris removal and if significant debris present
  - ✓ With hardpan or bedrock
  - ✓ Poor operational controls
- **Dredging most cost-effective**
  - ✓ If disposal onsite or as fill available
  - ✓ Without local disposal, additional costs
    - **Dewatering**
    - **Water treatment**
    - **Transportation**
    - **Disposal**

In situ management requires process understanding

Sediments- a *perfect storm* of chemistry, physics and biology

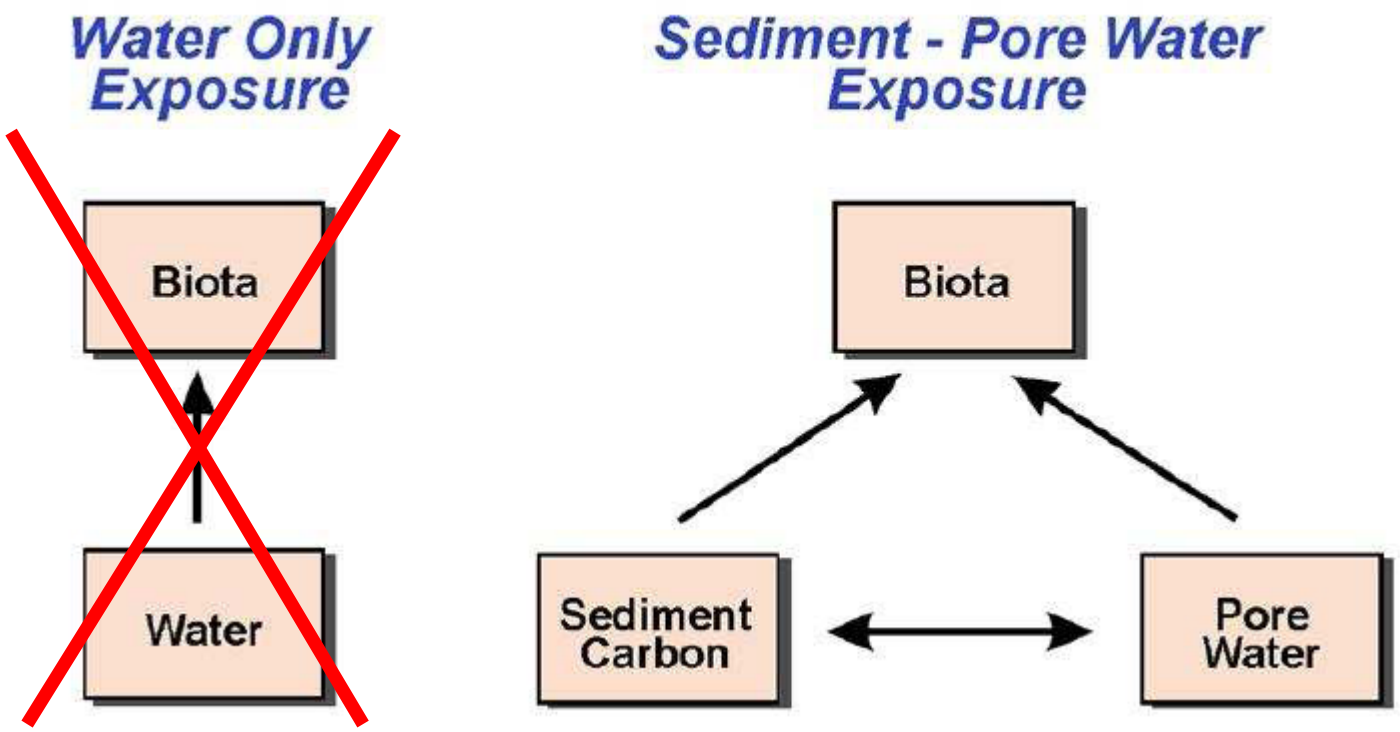


Indicators of Exposure and Risk

- **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 (Porewater)**
  - ✓ Indicator of mobility and availability
  - ✓ Does not indicate route of exposure

Porewater Contaminants
Mobile and Available

Does not imply porewater only exposure

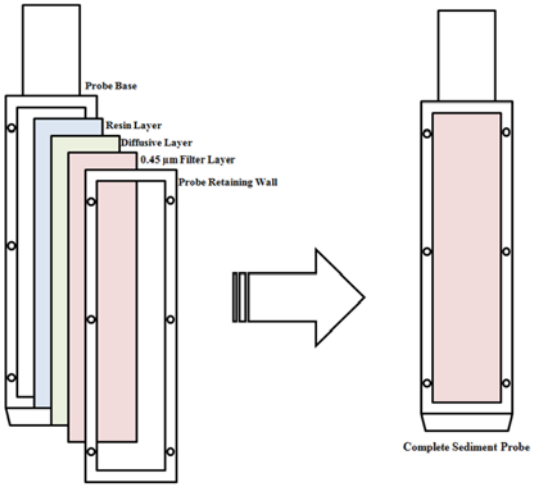


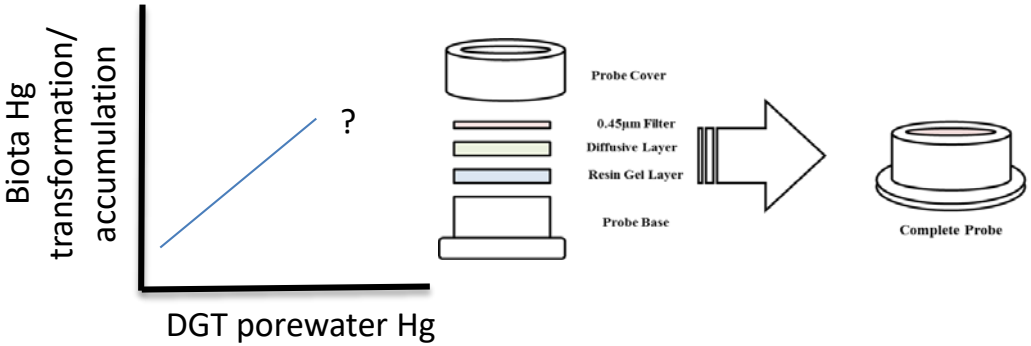
So How to Measure Porewater?

- **Challenge**
  - ✓ Concentration very low for hydrophobic contaminants (O(1ng/L) or less)
- **Approach**
  - ✓ Expose sorbents to porewater, concentrate *in situ* and analyze sorbent
- **Inorganic Species - Diffusion gradient thin film (DGT)**
  - ✓ *nonequilibrium* devices
  - ✓ Chelating resin (infinite sink) uptake controlled by thin diffusion gel uptake
- **Organic Species - Polymer sorbent (PDMS,PE, POM)**
  - ✓ *equilibrium* devices
  - ✓ Partitioning proportional to porewater concentration
  - ✓ Low detection limit = Long equilibrium times

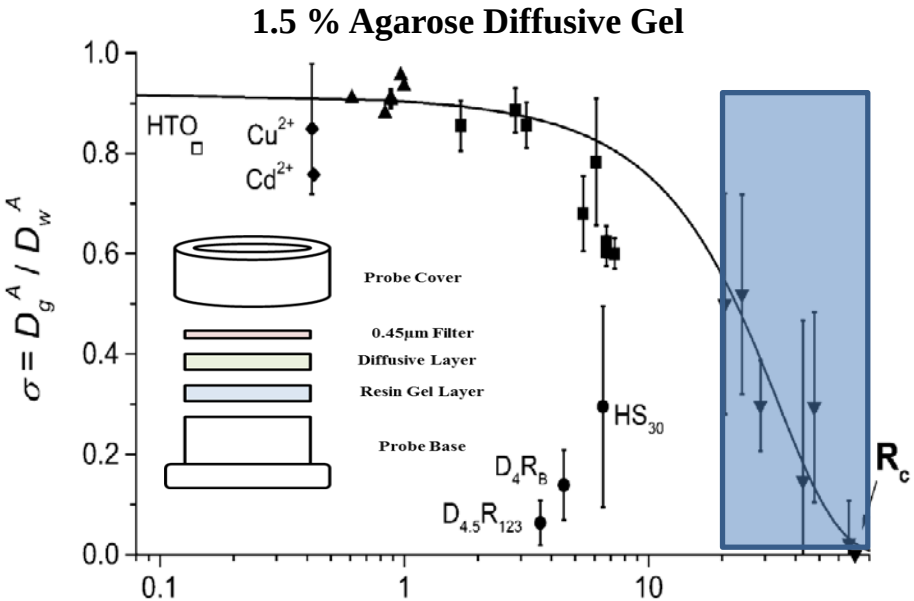
Measurement of Bioavailable Hg

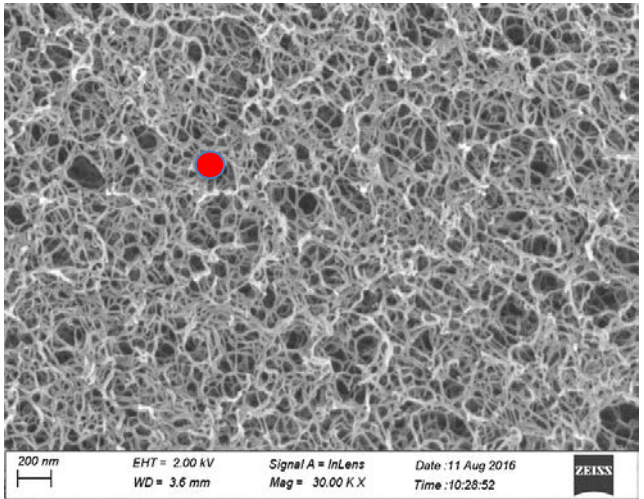
- **Direct porewater extraction and analysis**
- **Sediment Core Expression**
- **Passive Samplers—DGTs**
  - ✓ Davison & Zhang – Lancaster, UK
  - ✓ Based on Fick's 1st Law of Diffusion-Measures flux Hg into the sampler
- **Advantages**
  - ➢ Less invasive
  - ➢ Time averaged pore-water concentration
  - ➢ Higher depth resolution ~ 1cm
  - ➢ Potential ability to measure bioavailable relevant Hg

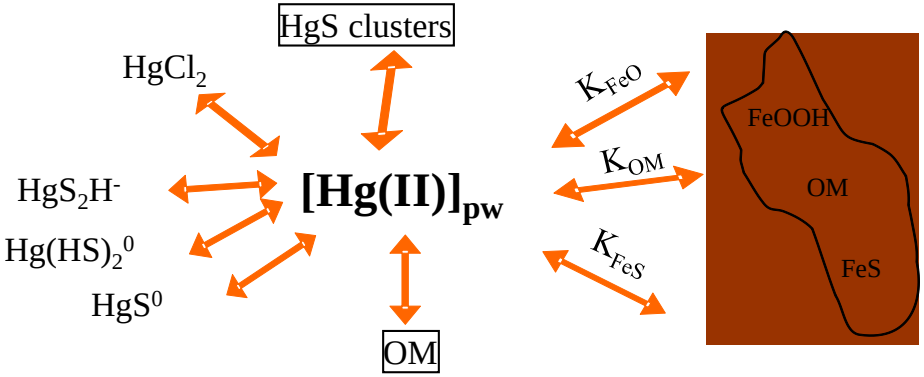




Can DGT effectively measure biological relevant Hg?







Dissolved < 1 nm | **Colloidal** | **Particulate > 0.2 µm**

Decreasing Methylation potential →

← Increasing DGT relevance

$$R_{MeHg} = k(\mathrm{THg}_{pw})(\phi_{bio})(RR)$$

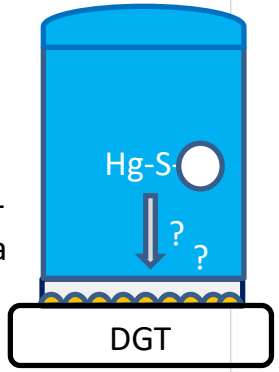
Can DGT measure this?

Reduction rate of dominant e^- acceptor (e.g., SRB)

Do DGTs uptake coarse particulate Hg?

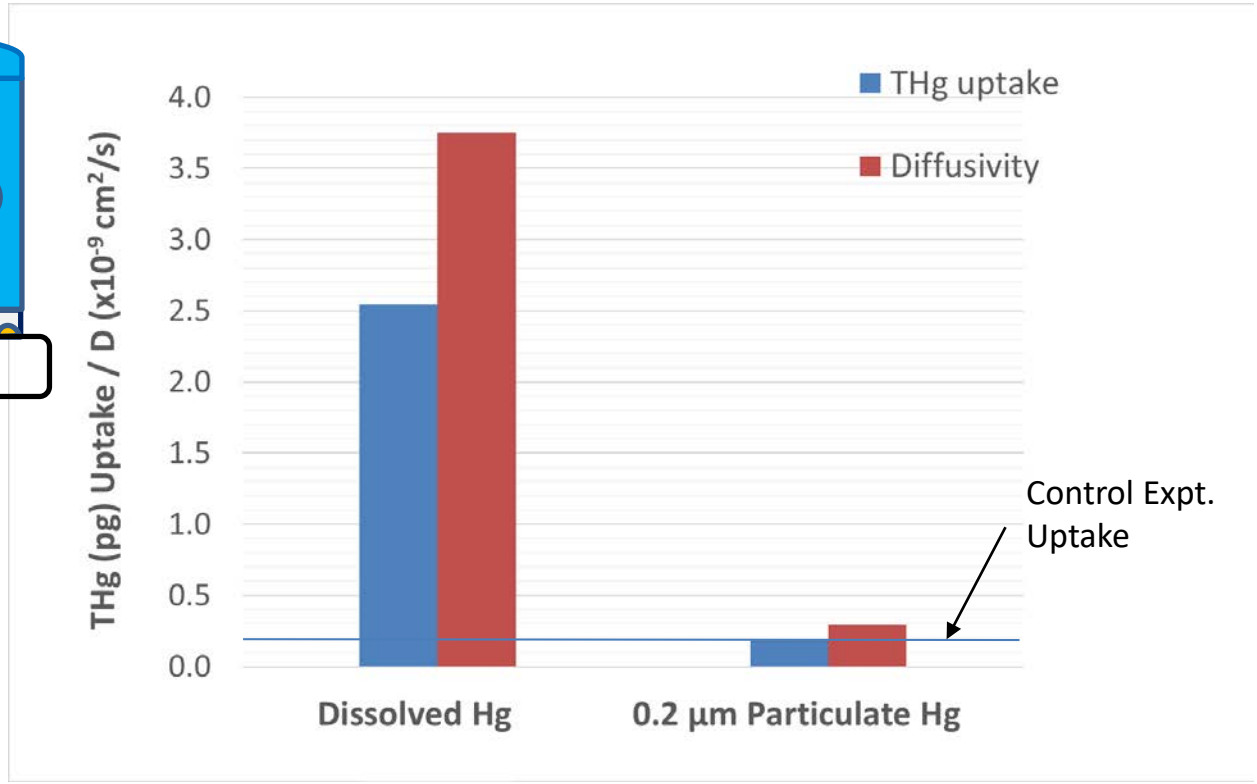
Expt. Parameters

- Uptake time: 6h
- THg: 1ppb
- Particulate Hg: Hg(II) + 200 nm thiolated silica



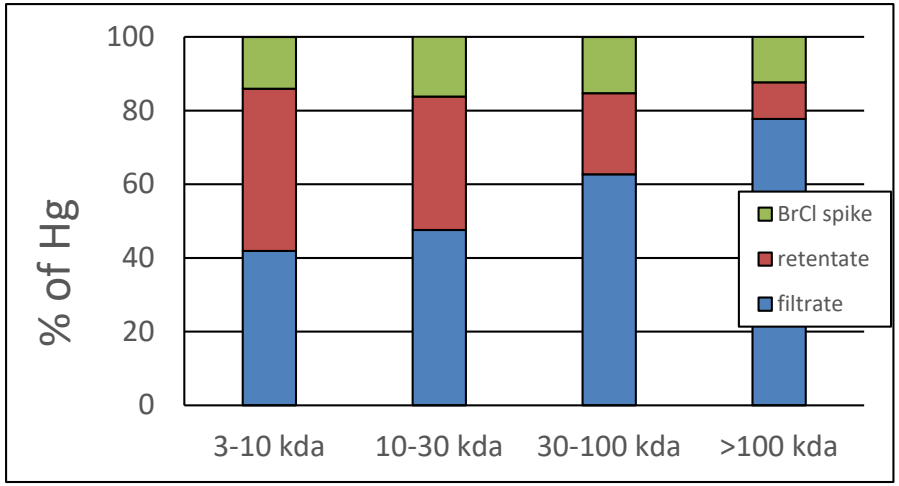
Results

- Particulate non-colloidal forms Hg forms (200 to 450 nm) are unlikely to pass though DGT.
- Represents the upper bound in particle size for Hg that is accessible by DGT.

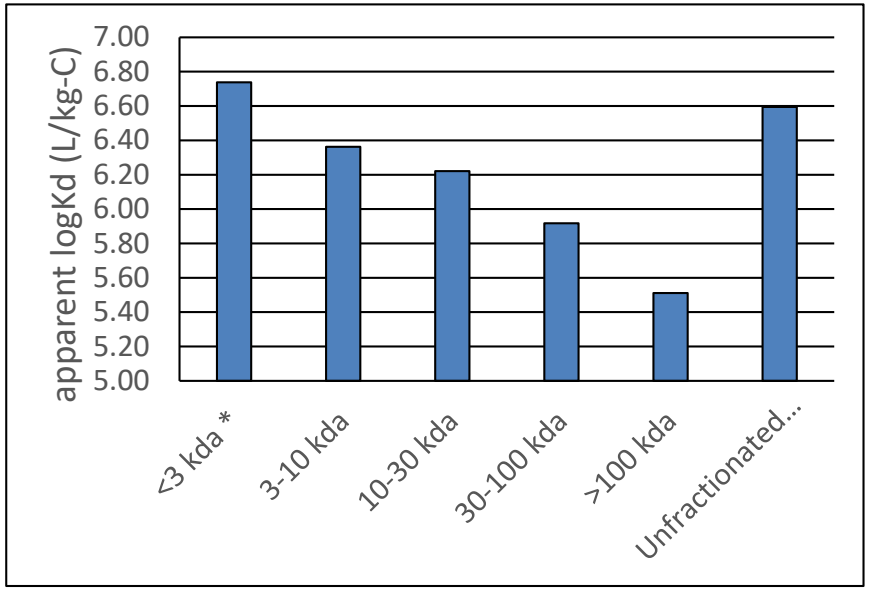


Size Fractionated Partition Coefficients

Suwannee River NOM, exposed to Hg then size fractionated by ultrafiltration



Plot of Hg distribution in different size fractions of SRNOM. Loss/BrCl spike are recorded as filtrate for Kd calculation

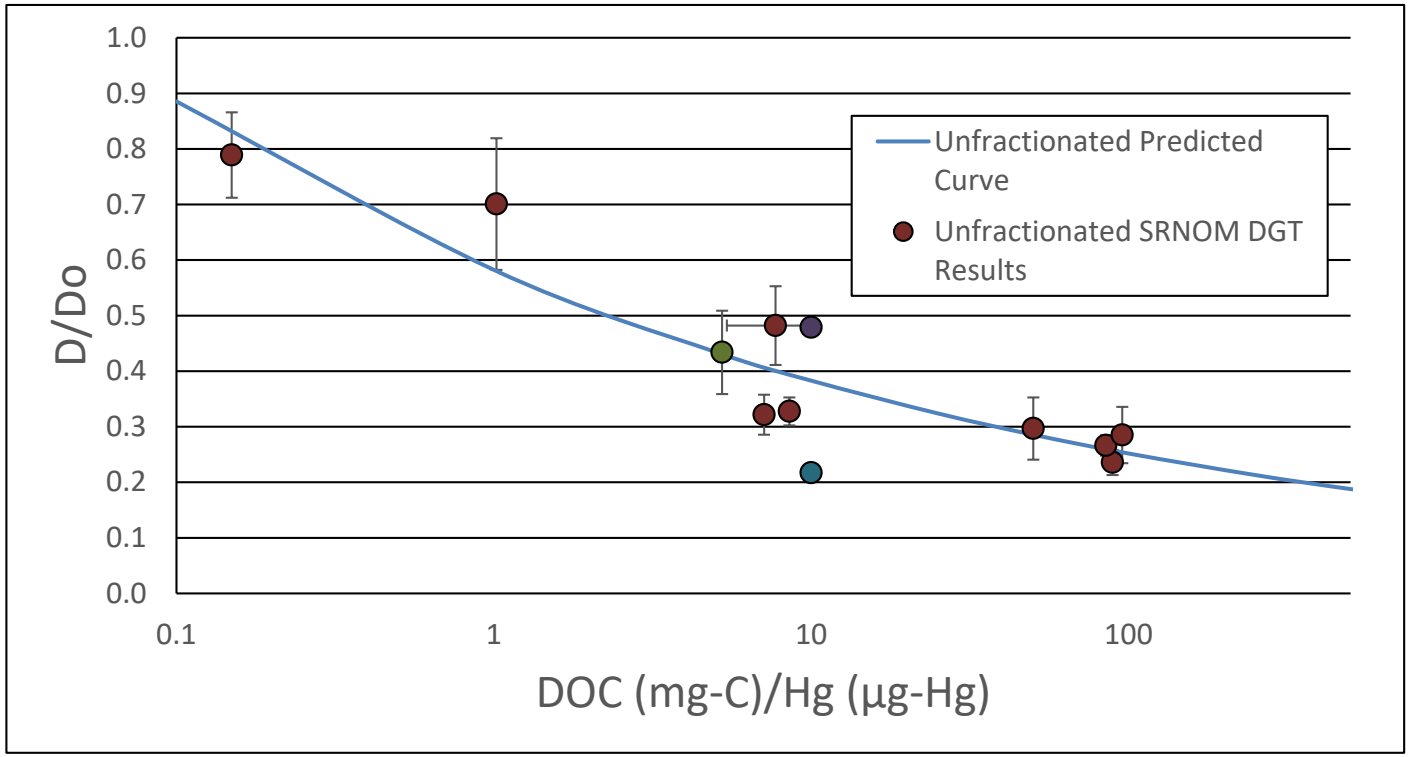


Plot of apparent log Kd values for each NOM size fraction assuming loss and BrCl spike is filtrate

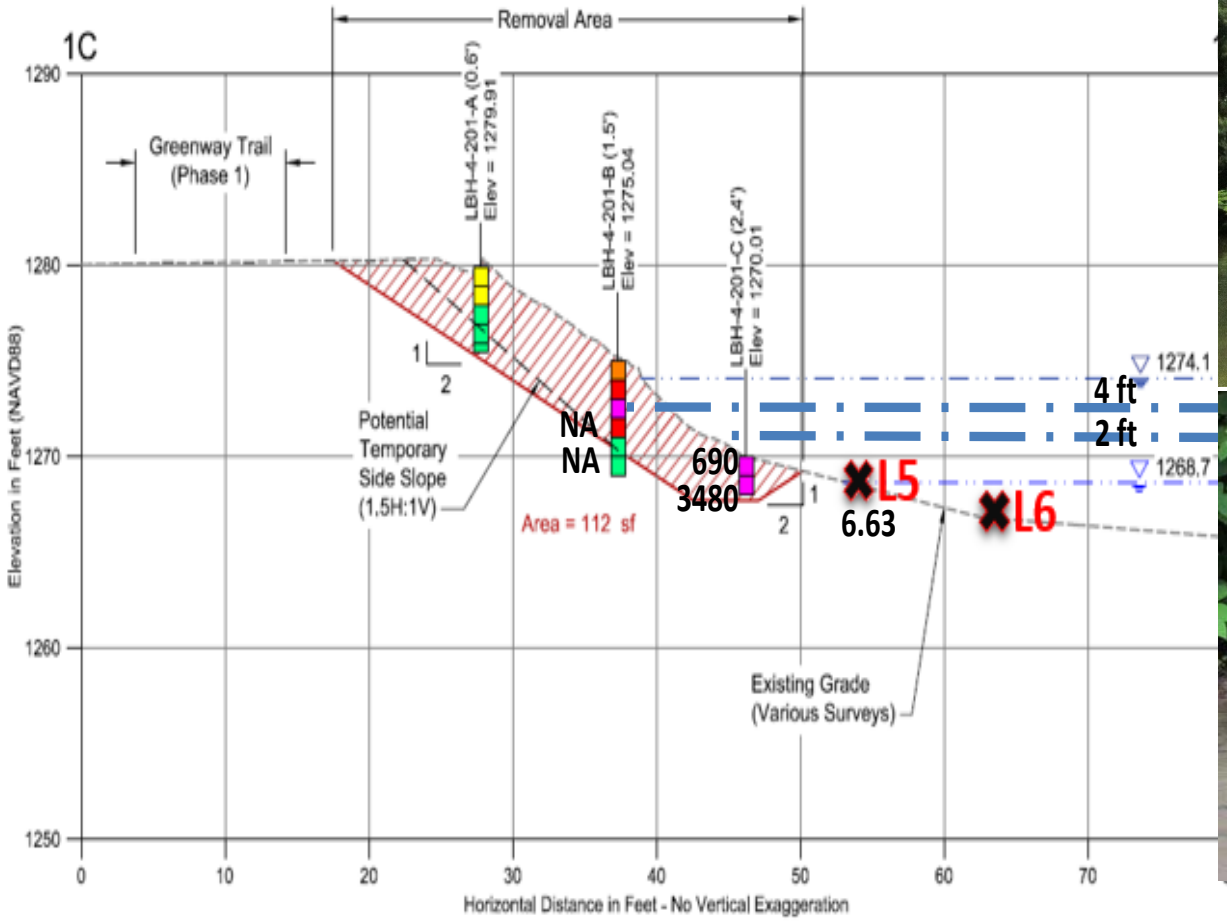
D/Do Size fraction estimated curves

Buffle (2007)

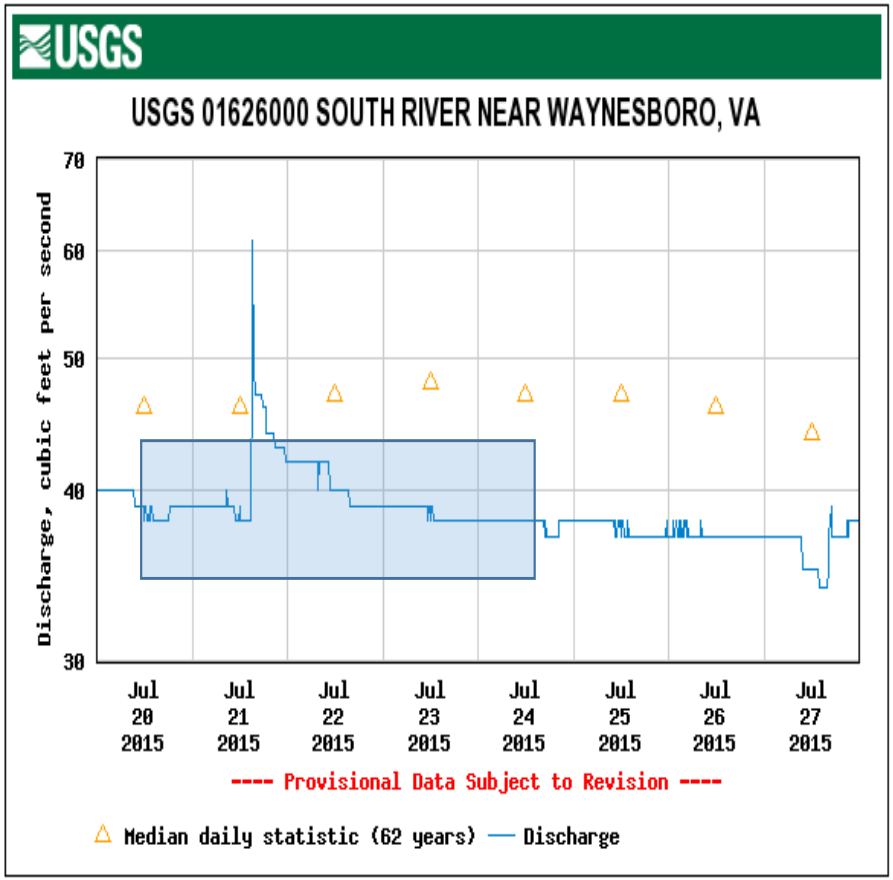
$$D = \frac{2.84\ x\ 10^{-5}}{{M_w}^{1/3}}$$

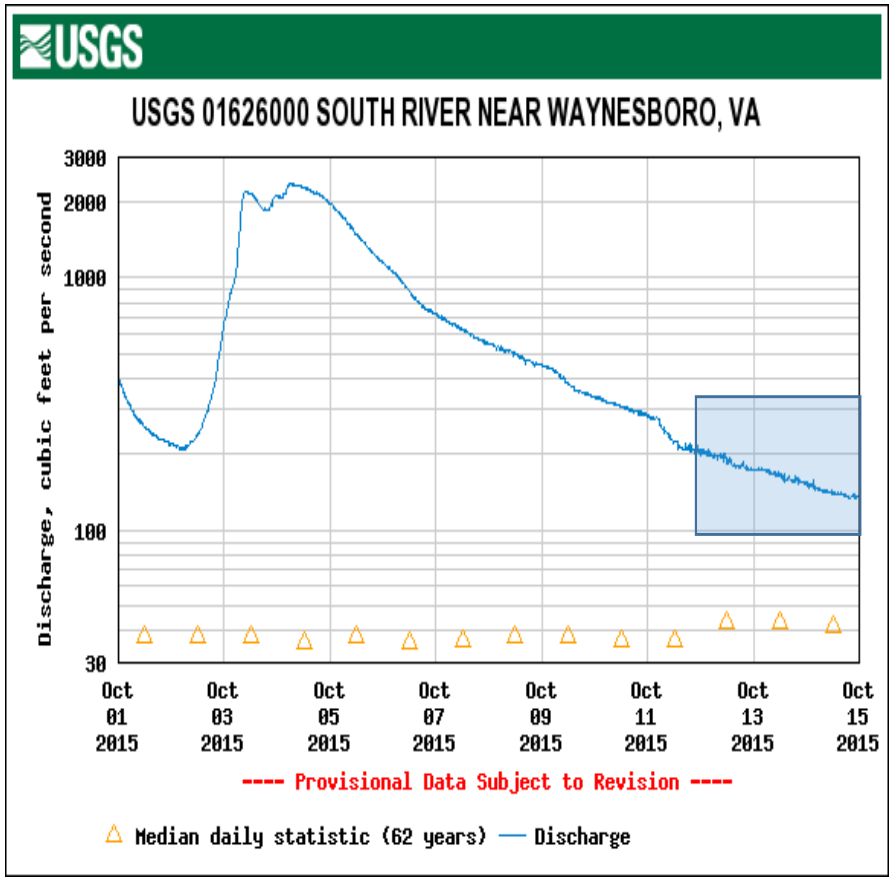


Bank leaching during drainage

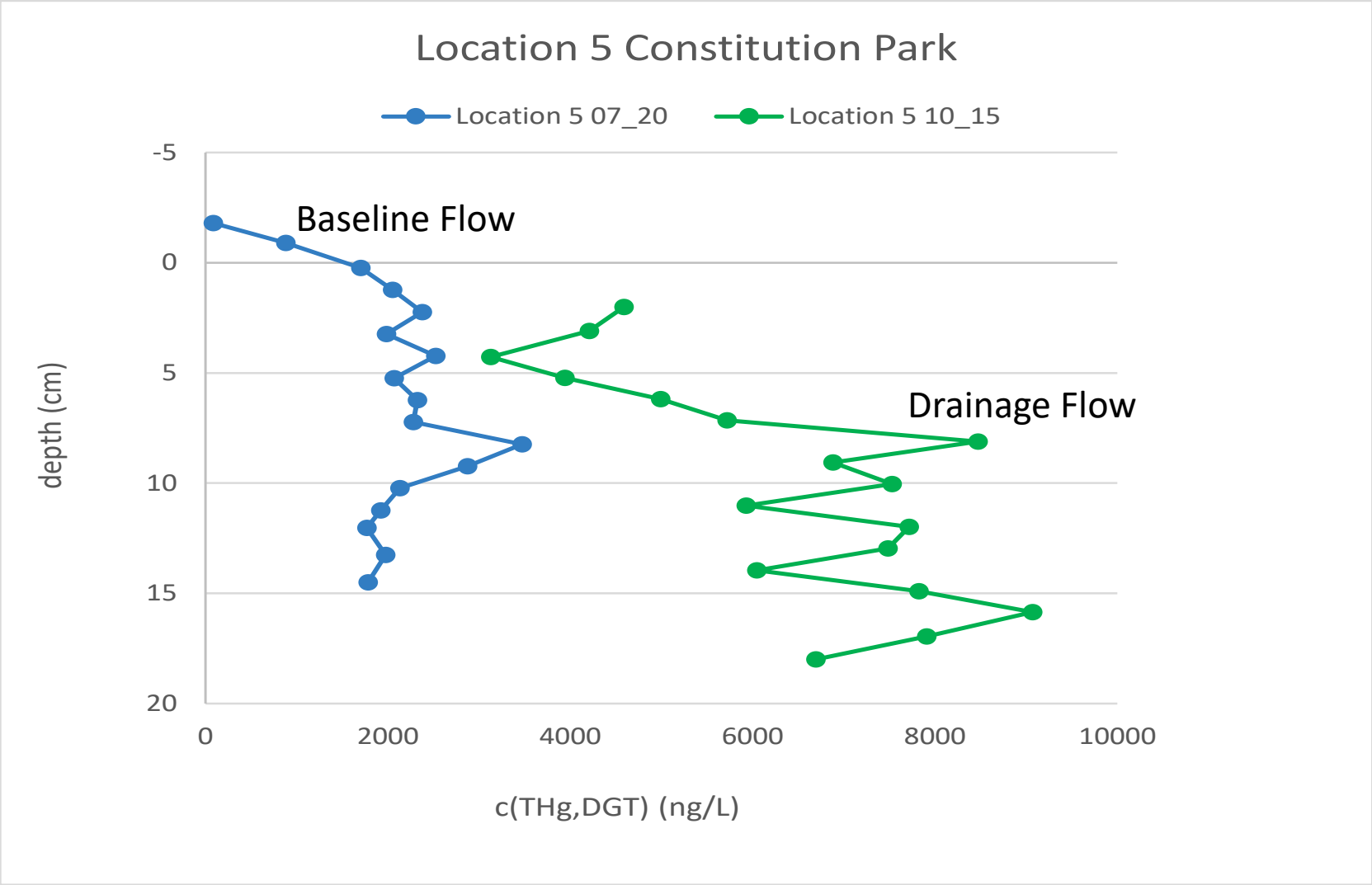


River Flow during Sampling 2015





Increased THg release during drainage

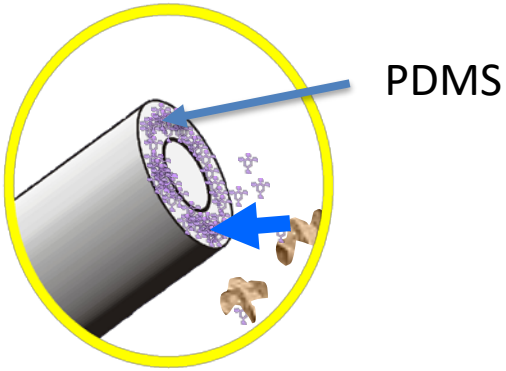


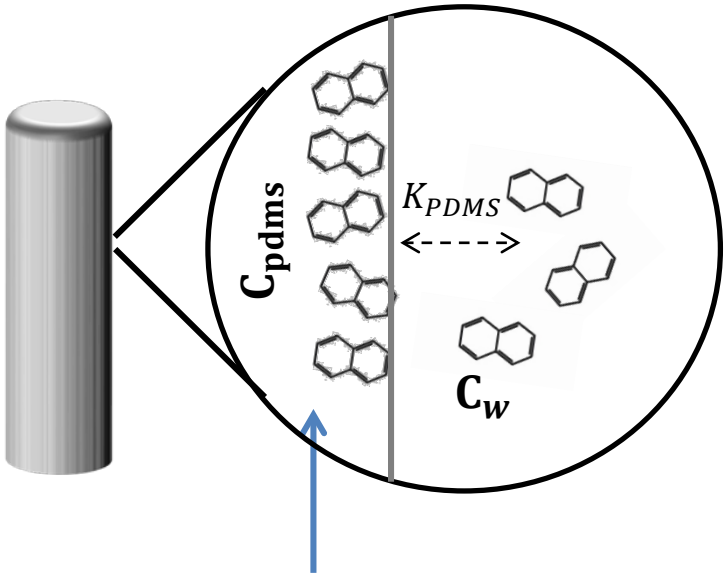
DGTs

- **DGTs can measure contaminants that are freely dissolved or associated with molecular size complexes**
- **Generally exclude particle associated contaminants greater than 20-100 nm in size**
  - ✓ Likely not biologically relevant?
- **May provide better indication of biologically relevant contaminants**
  - ✓ Limited scientific data to support this hypothesis at this time
  - ✓ Likely much better than traditional 0.45 µm filtered sample

Organics Passive Sampling Polymer Sorbents

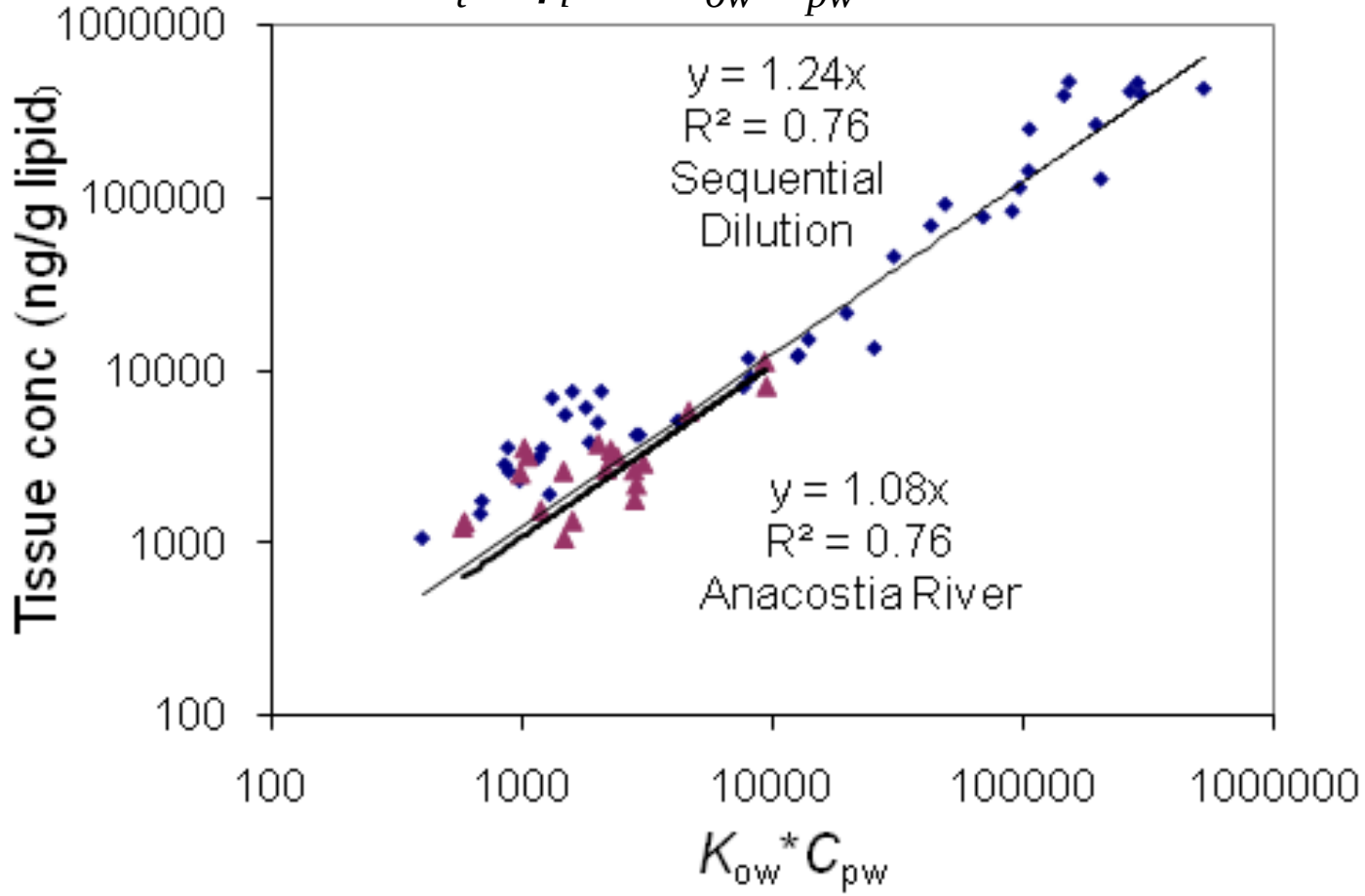
- **Polyethylene (PE)**
  - ✓ Sheets (planar geometry)- High volume, good surface area to volume ratio, moderate internal diffusion rates, marginal insitu feasibility
- **Polyoxymethylene (POM)**
  - ✓ Molded thermoplastic, planar geometry - High volume, fair surface area to volume ratio, slow internal diffusion rates, marginal insitu feasibility
- ***Polydimethylsiloxane (PDMS)***
  - ✓ Thin annular coating on glass fibers- Moderate volume, good surface area to volume ratio, high internal diffusion rates, good insitu feasibility
- **Goal- Equilibrium with porewater**
- **Similar sorption (POM~PE>PDMS)**



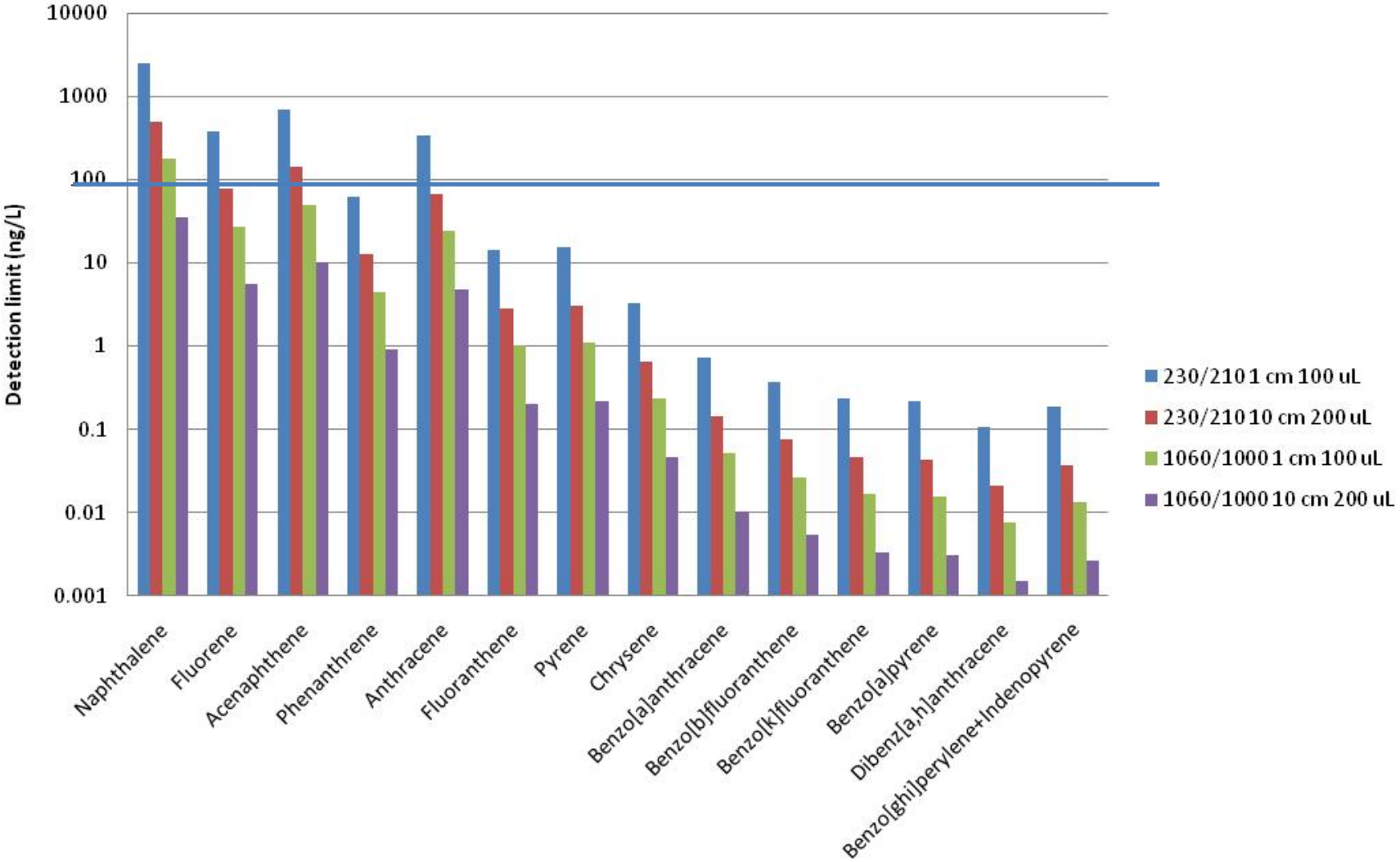


Bioaccumulation Predicted by PDMS Measured Porewater Concentration

$$C_t / f_l \approx K_{ow} C_{pw}$$



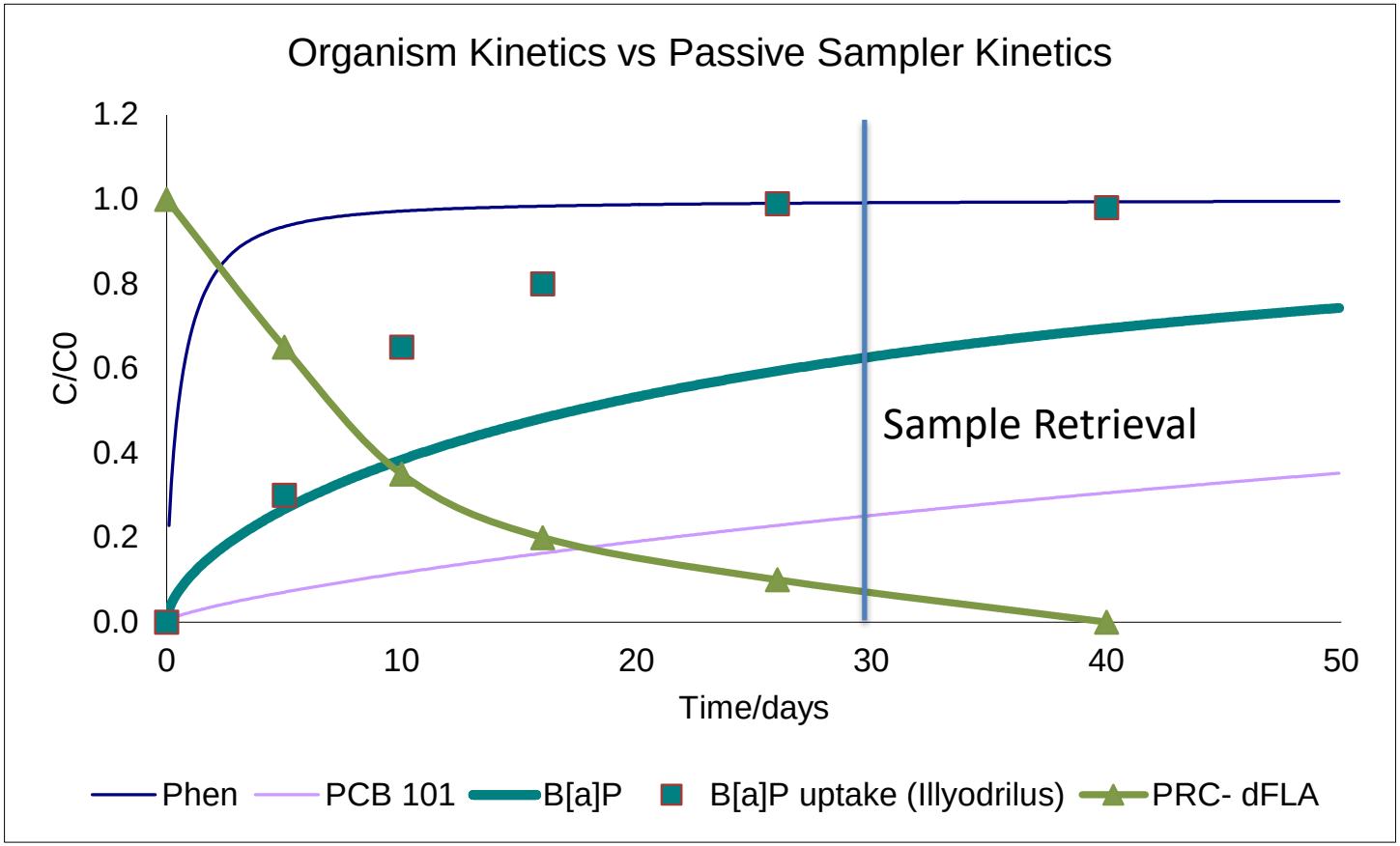
Challenges- Variable Detection Limits



Challenges- Kinetics of Uptake

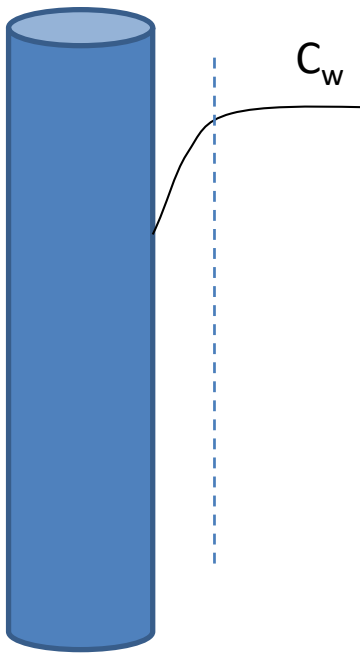
Performance Reference Compounds (PRCs) typically deuterated or C-13 substituted form of target compound

$$C_{pw} = \frac{C_{PDMS}}{K_{PDMS-w} f_{ss}} = \frac{C_{PDMS}}{K_{PDMS-w}} \frac{C_{PRC}(0)}{C_{PRC}}$$



Modeling Kinetics for other Compounds

- **Simple model**
  - ✓ External resistances often control
  - ✓ 1-D, diffusion model
  - ✓ Parameters RD (Rectangular) or α (Cylindrical)



- **Rectangular Coordinates (POM/PE)**

$$M(t) = K_{sw} C_0 (V/A)\left[1 - \exp\left(\frac{RDt}{(V/A)^2 K_f^2}\right)\operatorname{erfc}\left(\frac{\sqrt{RDt}}{(V/A)K_f}\right)\right]$$

- **Cylindrical Coordinates (PDMS)**

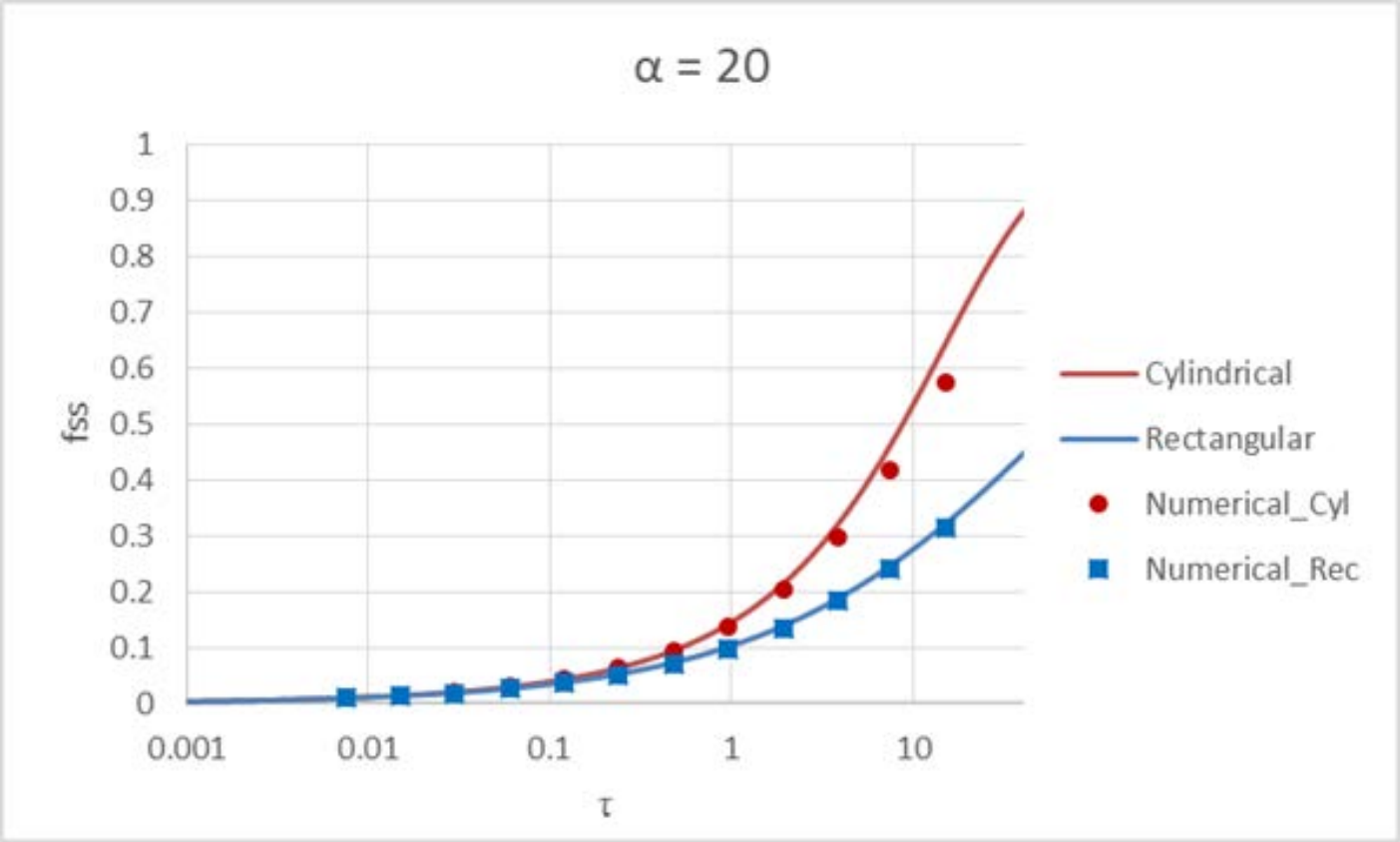
$$\frac{M}{M_t} = 1 - \frac{1}{2\beta}\left(\left(\frac{1}{a}+\beta\right)e^{\left(\frac{1}{a}+\beta\right)^2\tau}\operatorname{erfc}\left(\left(\frac{1}{a}+\beta\right)\sqrt{\tau}\right) - \left(\frac{1}{a}-\beta\right)e^{\left(\frac{1}{a}-\beta\right)^2\tau}\operatorname{erfc}\left(\left(\frac{1}{a}-\beta\right)\sqrt{\tau}\right)\right) \quad (1)$$

Where $\alpha = \frac{K_{pw}A}{R\pi L_o^2}$, $\beta = \frac{\sqrt{\alpha-1}}{\alpha}$ or $\frac{\sqrt{1-\alpha}}{\alpha}j$, $\tau = \frac{tD}{RL_o^2}$

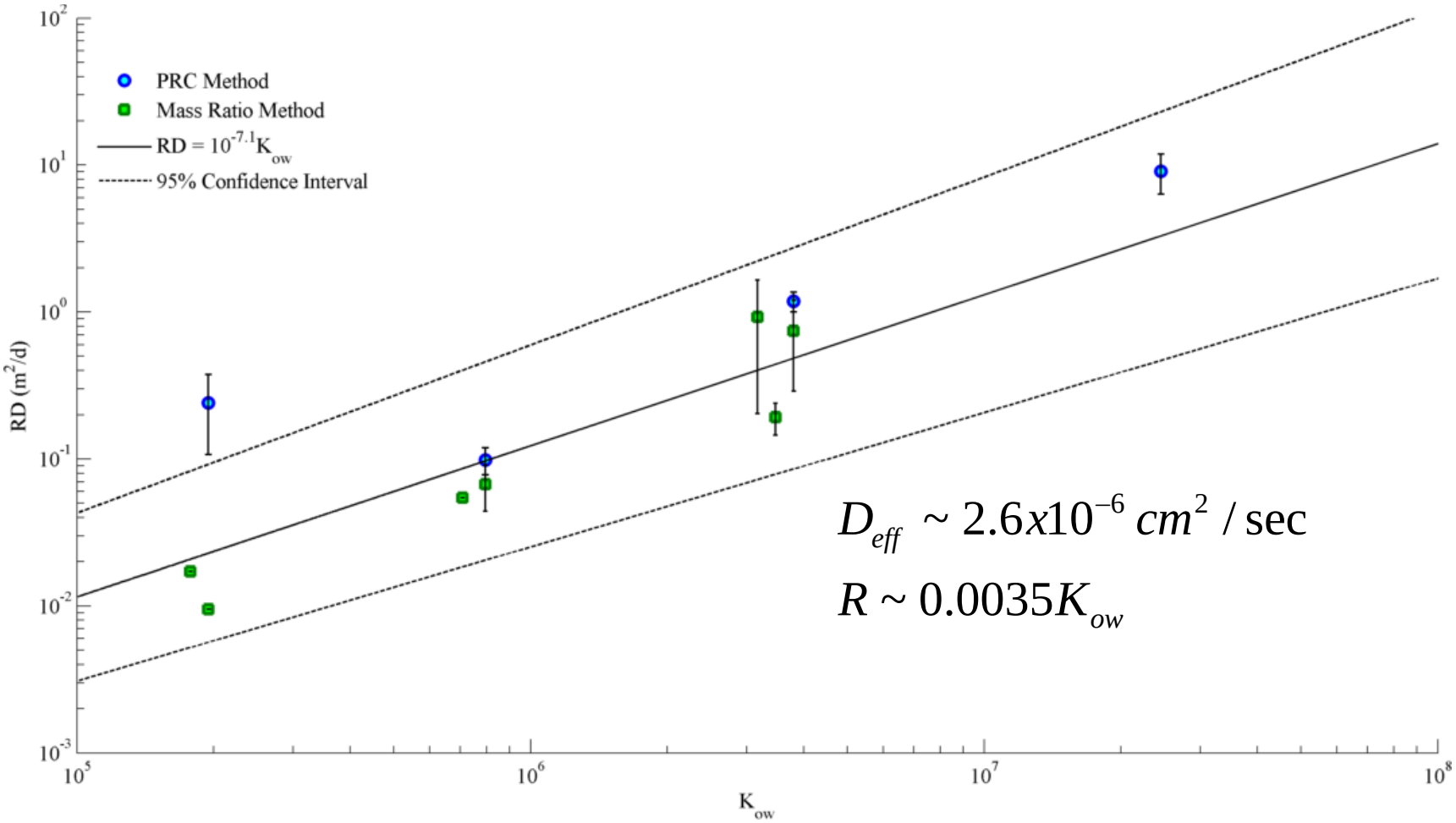
α - ratio of sorption on polymer to "displaced sediment"

PDMS PRC Model

- Cylindrical geometry more rapid approach to equilibrium



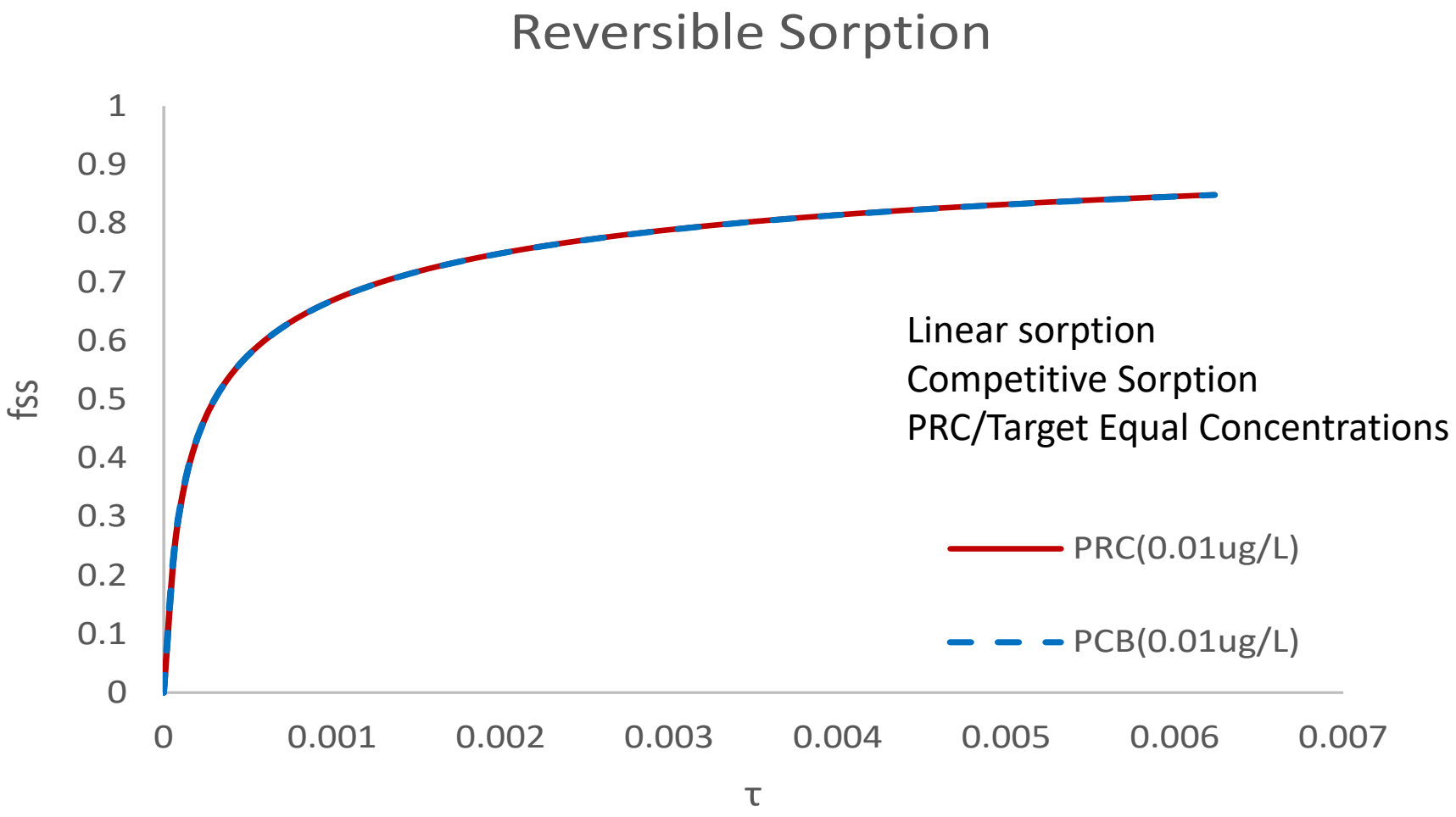
Field measurement of kinetics



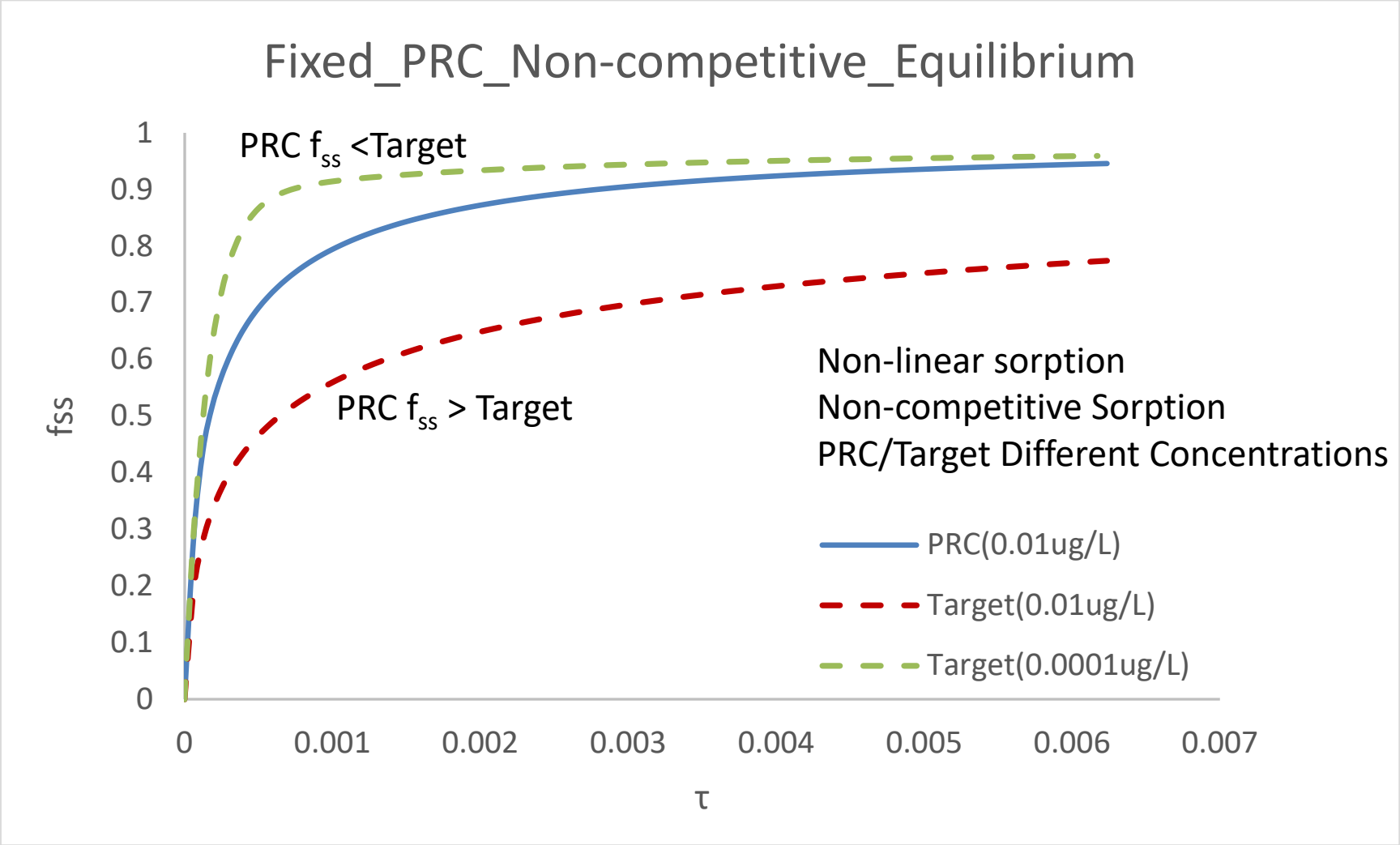
$$D_{eff} \sim 2.6x10^{-6}\ cm^2 / \sec$$

$$R \sim 0.0035K_{ow}$$

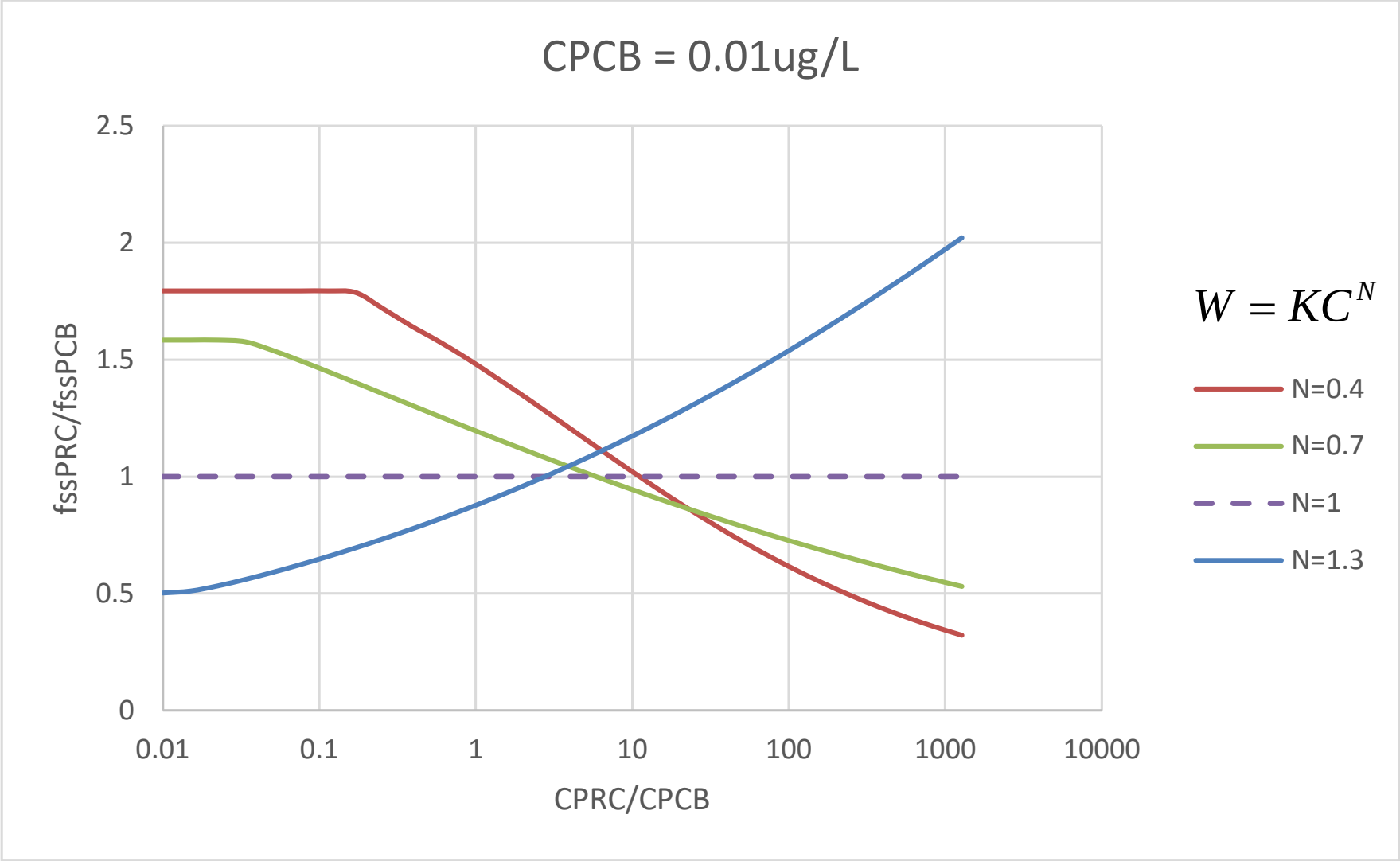
Reversible Sorption Cases
PRC behave as expected



Problematic PRC Cases

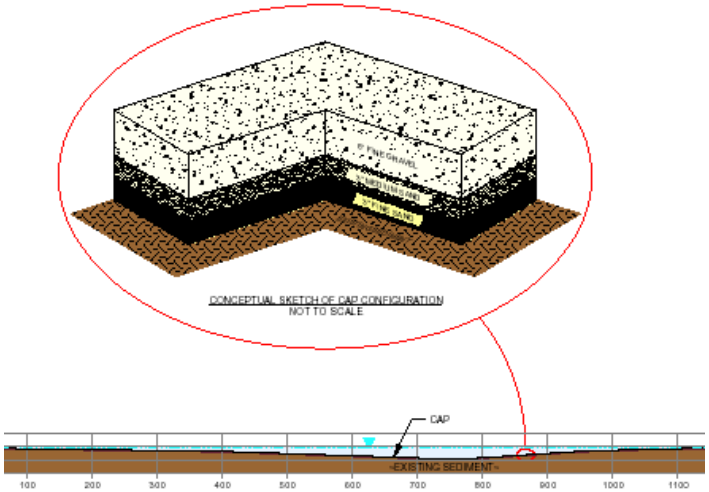


General f_{ss} Behavior from PRCs



In-Situ Management Approaches to Reduce Mobility and Availability

- **Amendment addition directly to sediments**
  - ✓ Sorbing or reactive amendments
- **Conventional (sand/sediment) capping**
- **Thin layer capping**
  - ✓ Sand or other inert material
  - ✓ Amended thin layer
- **Amended isolation capping**
  - ✓ Sorbing amendments
  - ✓ Active management approaches (e.g. redox control systems)



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

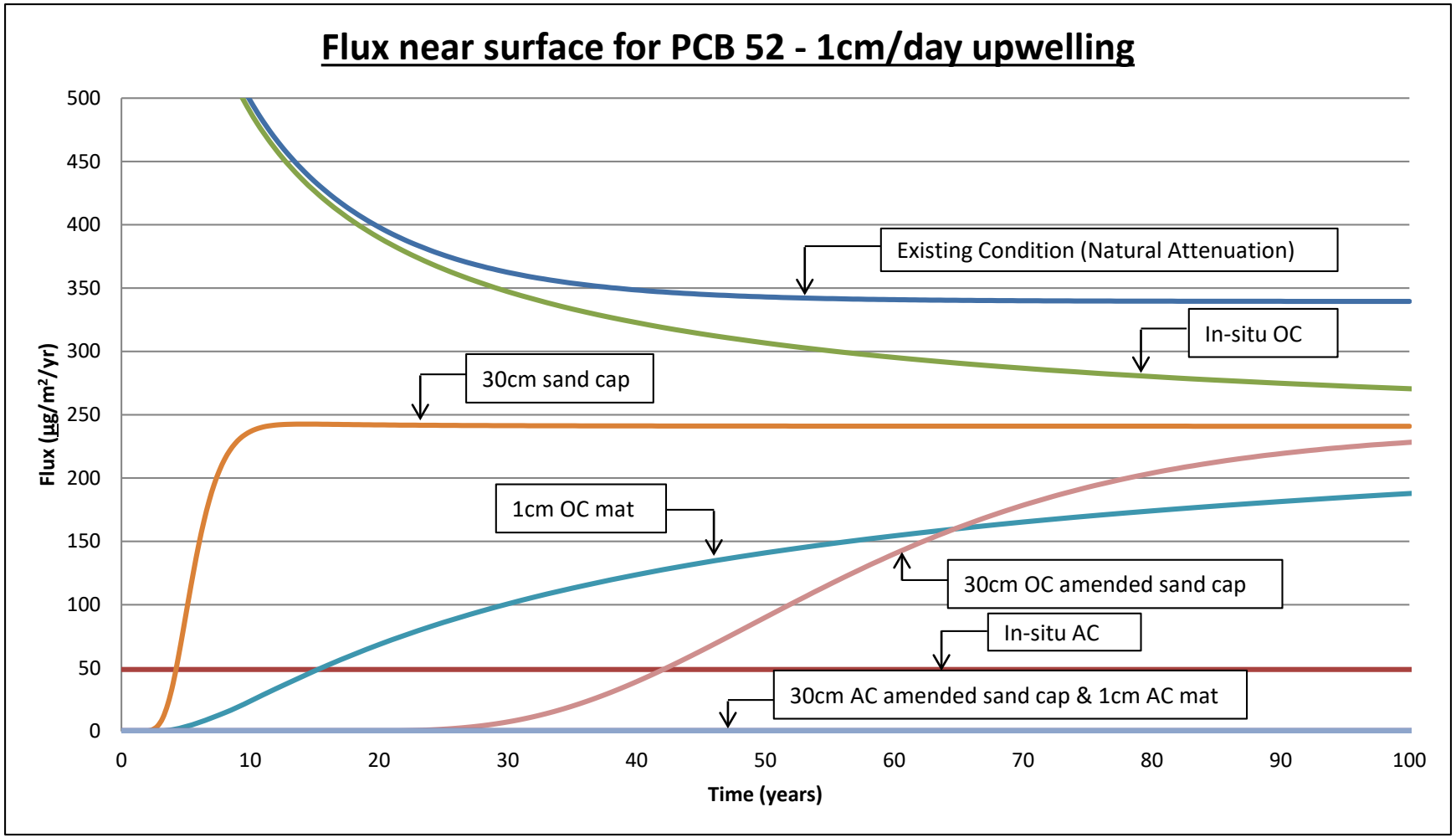
Speculative

Model

- **CapSim**
  - ✓ Widely used tool to model sediment-water exchange and design sediment remedies
  - ✓ Processes
    - **Advection, diffusion, dispersion, reaction, sorption**
    - **Multiple reactive species, linked reactions, arbitrary order**
    - **Linear & non-linear sorption and sorption kinetics**
    - **Bioturbation, Deposition, Consolidation**
    - **Multiple sediment layers and mixtures**
  - ✓ Used to model performance of Hunter's Point AC treatment
    - **AC mixing due to bioturbation**
    - **Kinetics of sorption onto AC**
  - ✓ Used to explore PRC and contaminant behavior during passive sampling

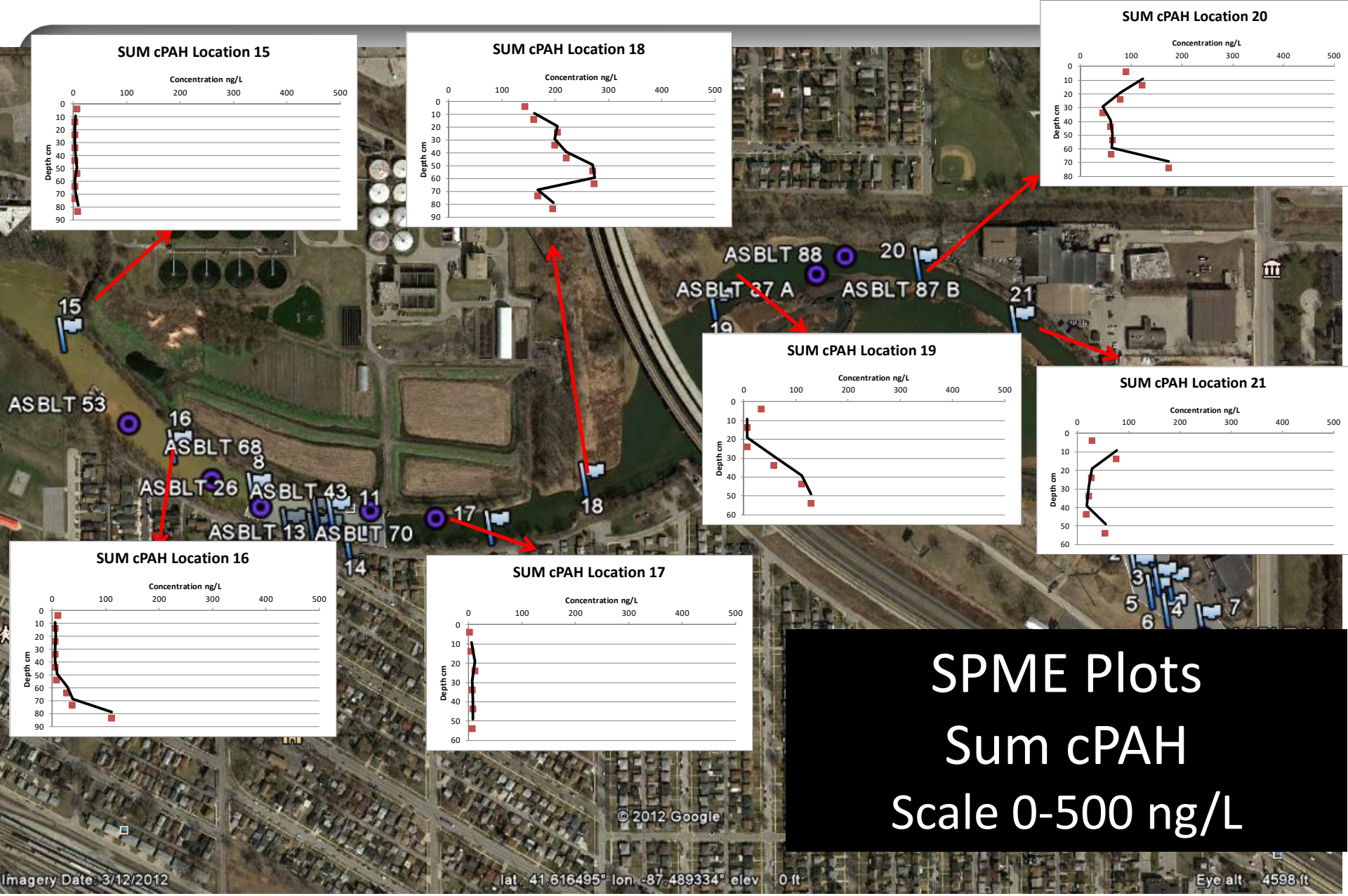
- **http://www.depts.ttu.edu/ceweb/groups/reiblesgroup/**

Simulated Remedy Performance



SPME Stations (flags) & As-Built Cores (circles)
SPMEs Deployed 6/2012 & 9/2013

Roxana Marsh – Grand Calumet River, Hammond, IN

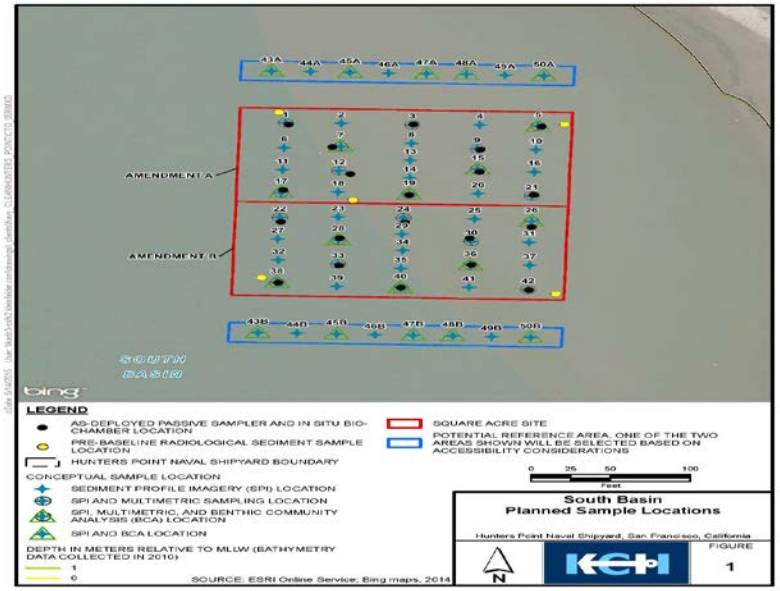


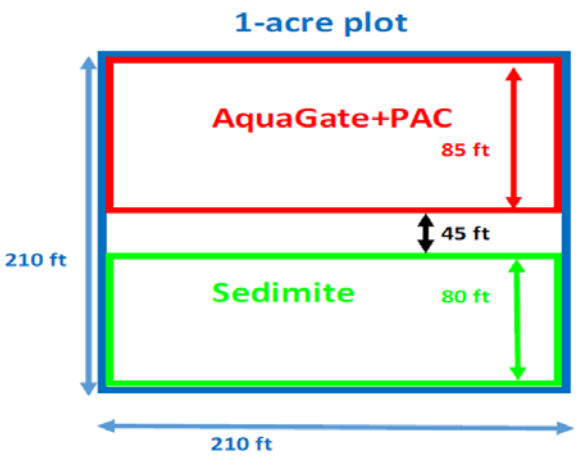
SPME Plots
Sum cPAH
Scale 0-500 ng/L

Hunter’s Point Shipyard

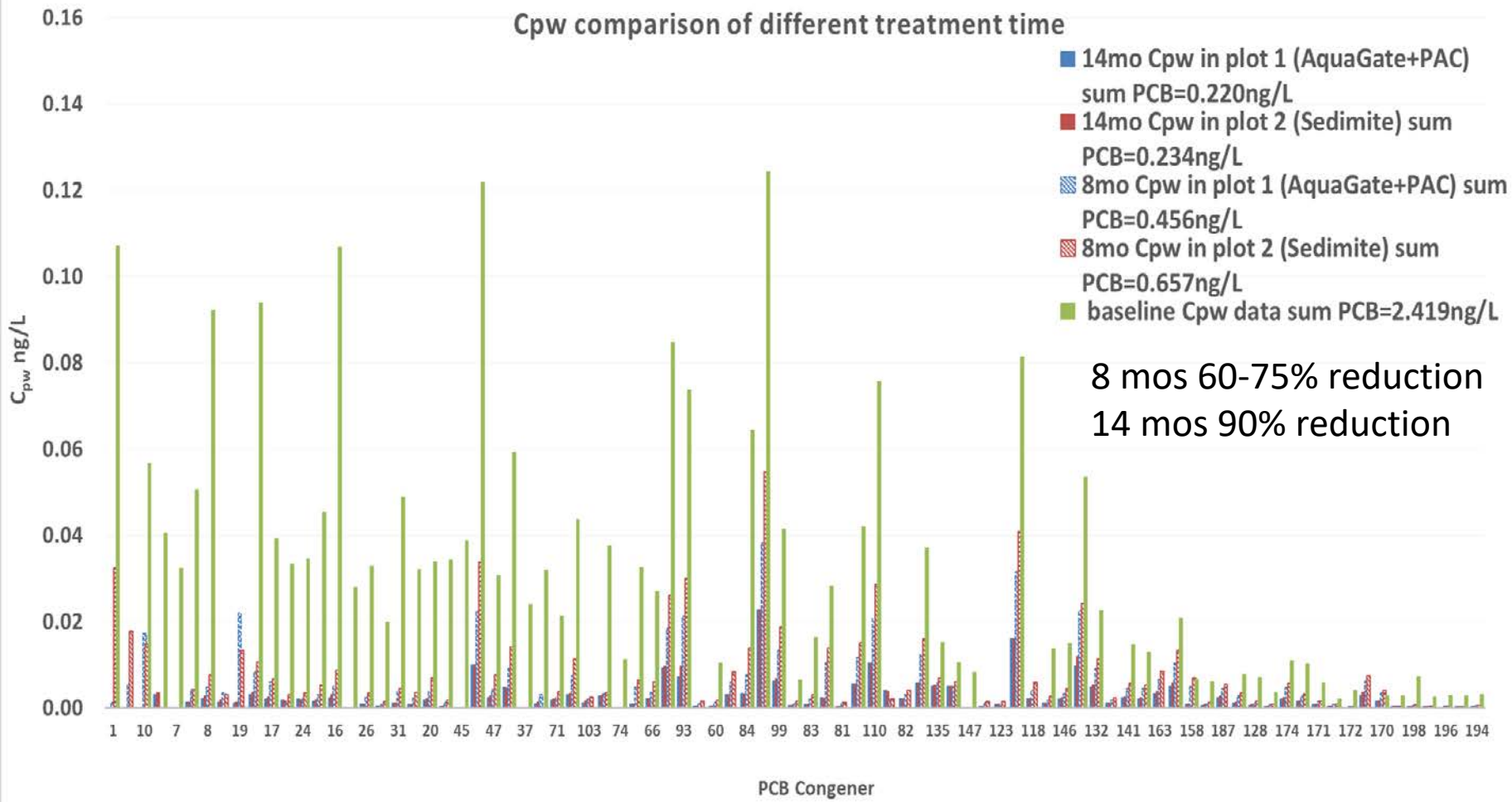
Large shielded sampler- 36”

Small unshielded sampler- 14”





Comparison of Pre and Post Cpw



8 mos 60-75% reduction
14 mos 90% reduction

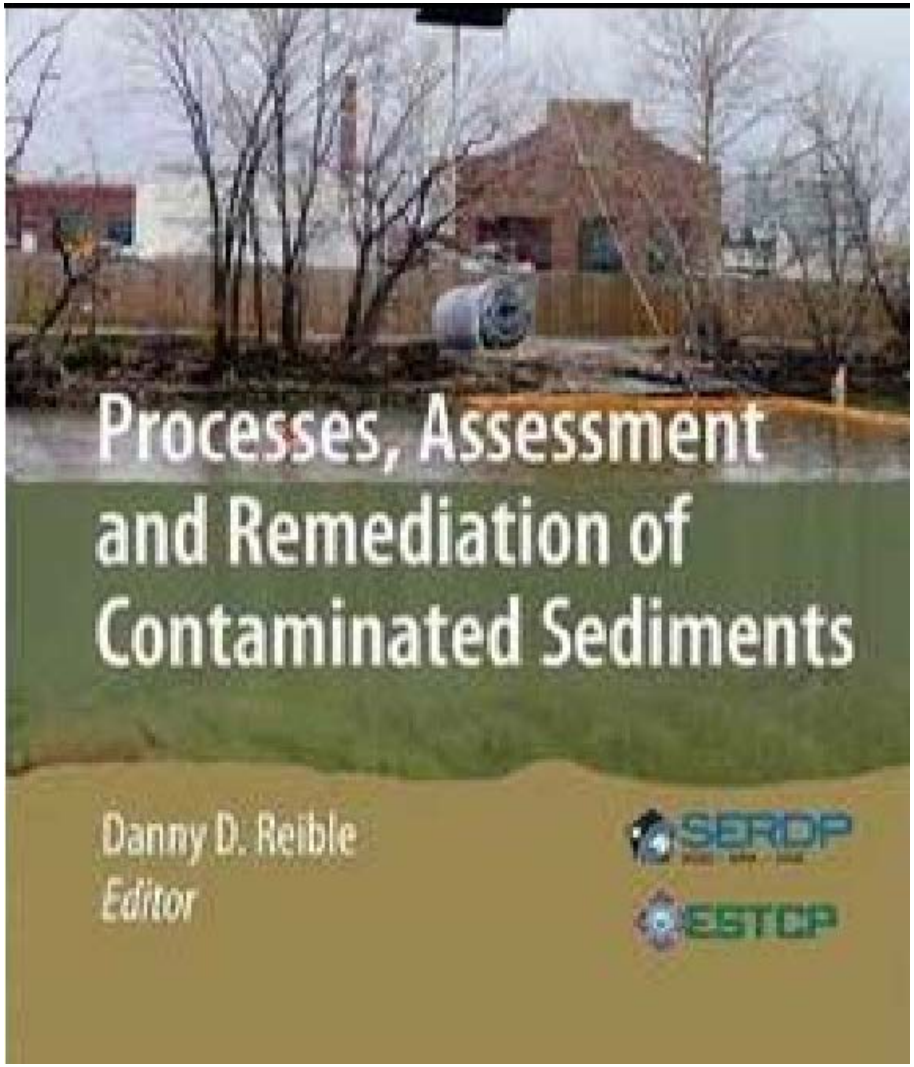
Summary

- **Growing emphasis on *in situ* remedies that emphasize reducing contaminant mobility and availability**
- **Growing use of porewater to measure mobile and available fraction and assess remedy performance using passive sampling**
- **Passive sampling shows activated carbon placement and reworking into sediment to be effective as a cap or *in situ* treatment**
- **Passive sampling poses challenges in its interpretation and use**
  - ✓ Slows its transition to routine use to monitor sediments and remedies

Understanding the processes influencing contaminant fate and behavior

Assessing the resulting exposure and risks

Implementing appropriate remedies



Acknowledgements

Current Funding

- DoD SERDP/ESTCP
- Department of Homeland Security
- US Navy
- Maddox Research Foundation
- National Science Foundation
- Chevron
- DuPont
- Alcoa
- ExxonMobil
- Electric Power Research Institute
- Tierra Solutions
- Haley & Aldrich
- TetraTech
- Cabot
- State of Oregon
- Canadian Ministry of Environment and Climate Change

Department of Homeland Security
Critical Infrastructure Resilience Institute

Live Long and Prosper