Sediment Bioavailability Assessment Using Passive Porewater Samplers

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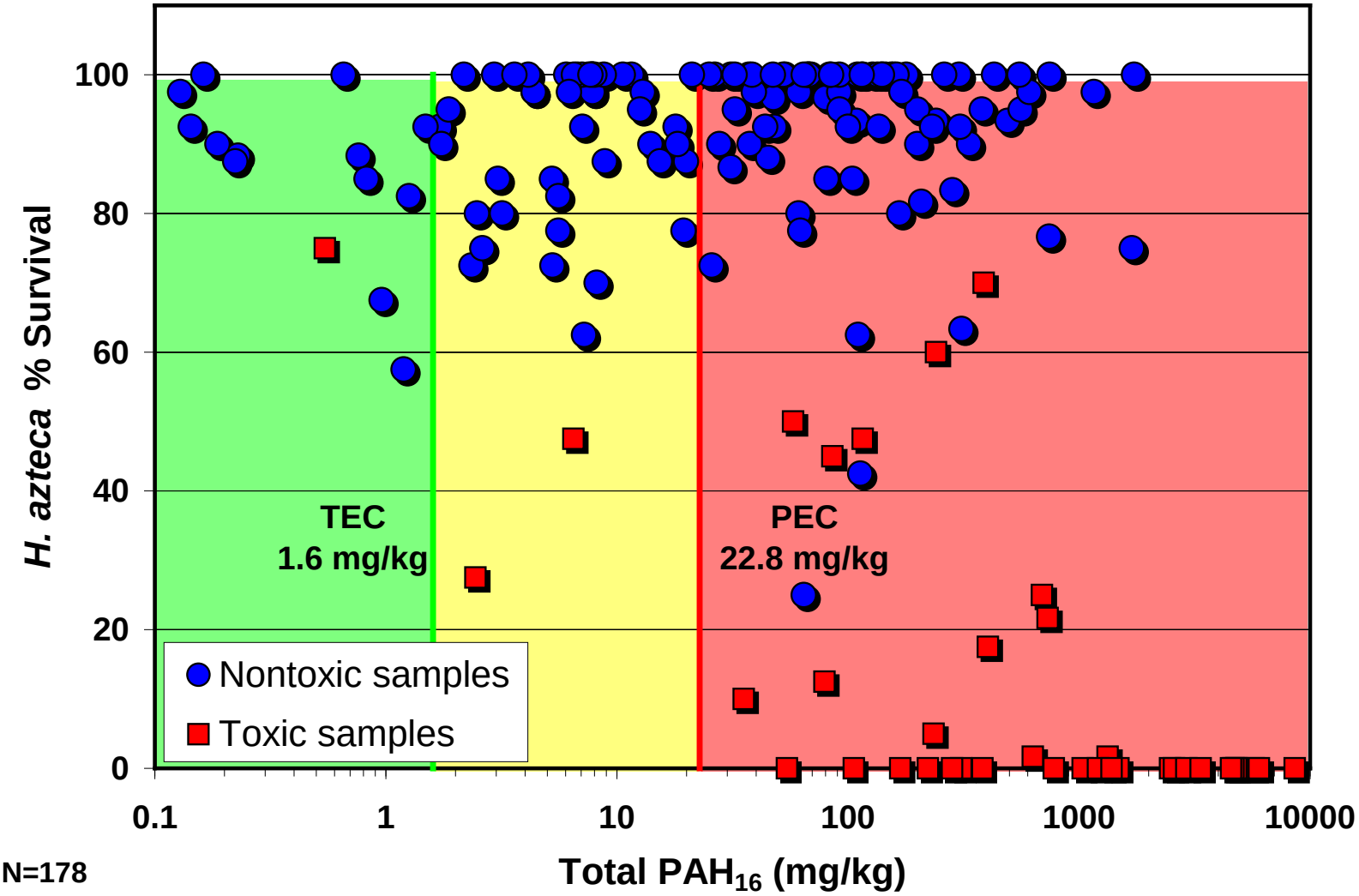
Bulk Sediment Concentrations Are Poor Predictors of Toxicity



Source: Survey To Characterize PAH Toxicity and Bioavailability at MGP and Al Smelter Sites, accomplished by Alcoa and SCBA. http://www.nws.usace.army.mil/PublicMenu/documents/DMMO/FINAL_2006_SMARM_minutes.pdf

Estimating Bioavailability from Bulk Sediment Has Limitations

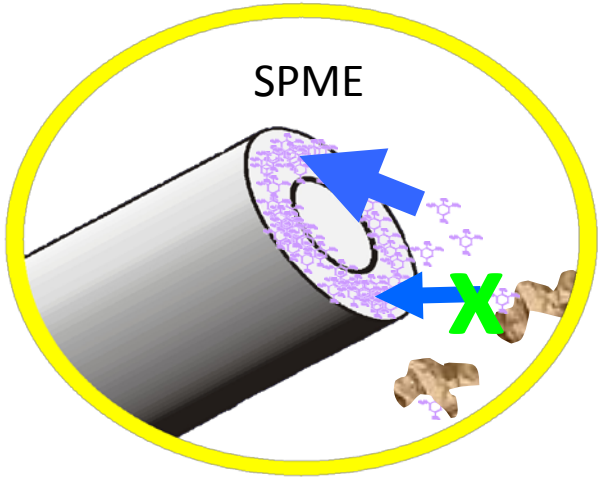
- Prediction of toxicity – from EPA (2003) and EPA (2007):
  - Use Equilibrium Partitioning (EqP) to determine concentration
  - Calculate the ratios of individual PAHs to their Final Chronic Values ("Toxicity Units", TU)
  - Add these to determine ΣTU
  - Compare to a ΣTU of 1.0 – the probable effect level using the narcosis model
- Caveats:
  - EqP overestimates toxicity by 100x.
  - Also, "black carbon" adjusted EqP tends to under predict toxicity (Gschwend, et al. 2010)

http://www.itrcweb.org/contseds-bioavailability/

Measuring Porewater Contaminants

- Solid Phase MicroExtraction (SPME)
  - Sorbent Polymer: PDMS (poly-dimethylsiloxane)
    - Thickness of glass core: 114-108 µm
    - Thickness of PDMS coating: 30-31 µm
    - Volume of coating: 13.55 (±0.02) µL PDMS per meter of fiber
  - ng/L detection with 1 cm resolution

http://www.caee.utexas.edu/reiblegroup/reible-materials/PassiveSamplingofPorewaterfortheIn-situAssessment.pdf



- Polyethylene (PE) Sampler
  - Sorbent Polymer: Polyethlyene (PE)
  - Thickness of PE: ~ 51 µm
  - ng/L detection with 1 cm resolution

http://www.clu-in.org/download/contaminantfocus/sediments/sediment-er-1496-fr.pdf

Polyethylene (PE) Sampler

Porewater Sampler Demonstration, Lower Duwamish Waterway Superfund Site, EPA Region 10

http://yosemite.epa.gov/r10/cleanup.nsf/sites/lduwamish

Polyethylene (PE) Porewater Sampler Field Demonstration Objectives

- Do the measured C_{pw} PCBs at five sites representative of the Lower Duwamish Waterway compare well to values estimated using equilibrium partitioning

$$C_{pw} = C_{sed} / (f_{oc} * K_{ow})$$

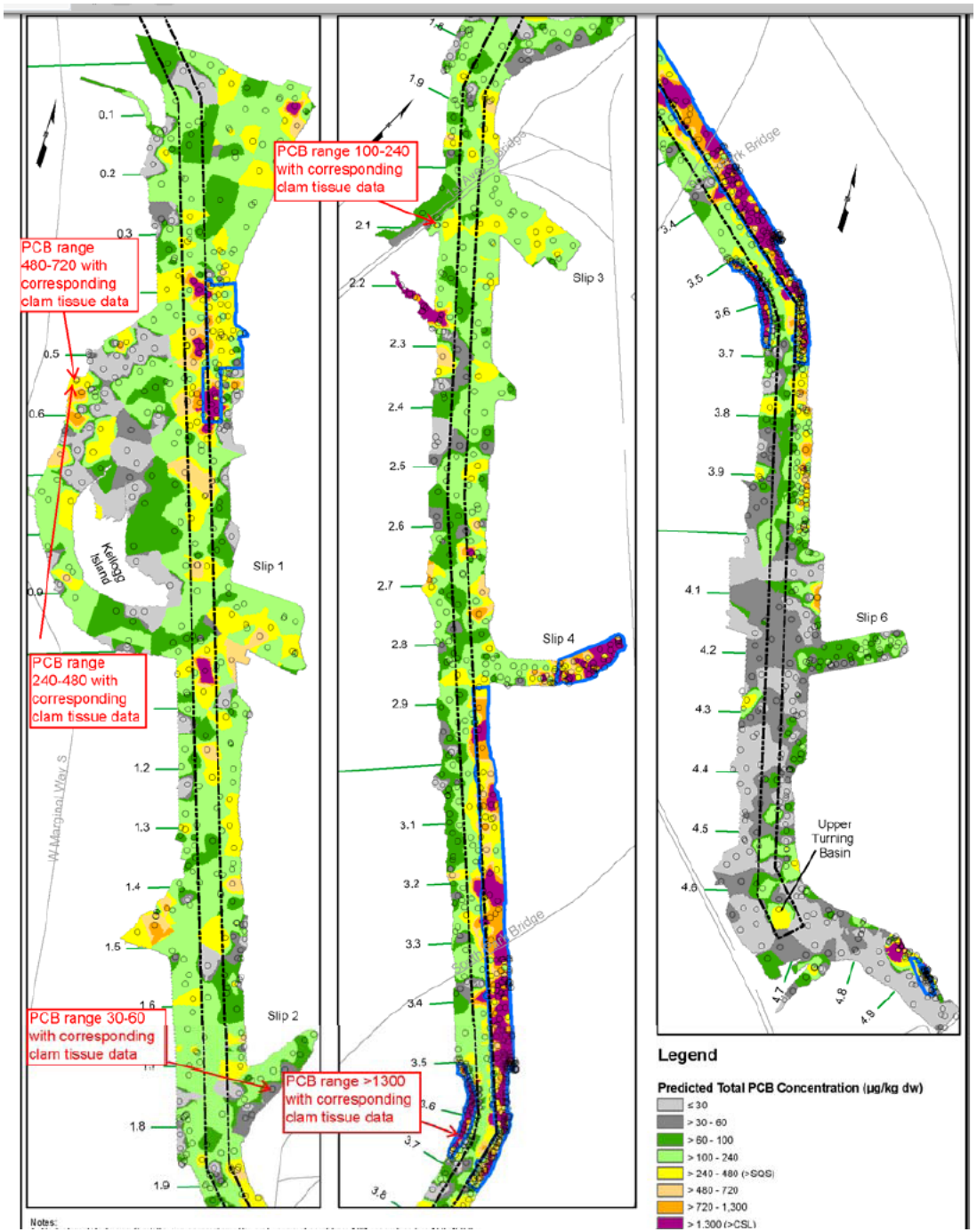
- Do measured C_{pw} PCB porewater concentrations compare well to values estimated using black carbon adjusted estimate below?

$$C_{pw} \approx C_{sed} / K_d \approx C_{sed} / (f_{oc} * K_{oc} + f_{bc} * K_{bc} * C_{pw}^{n-1})$$

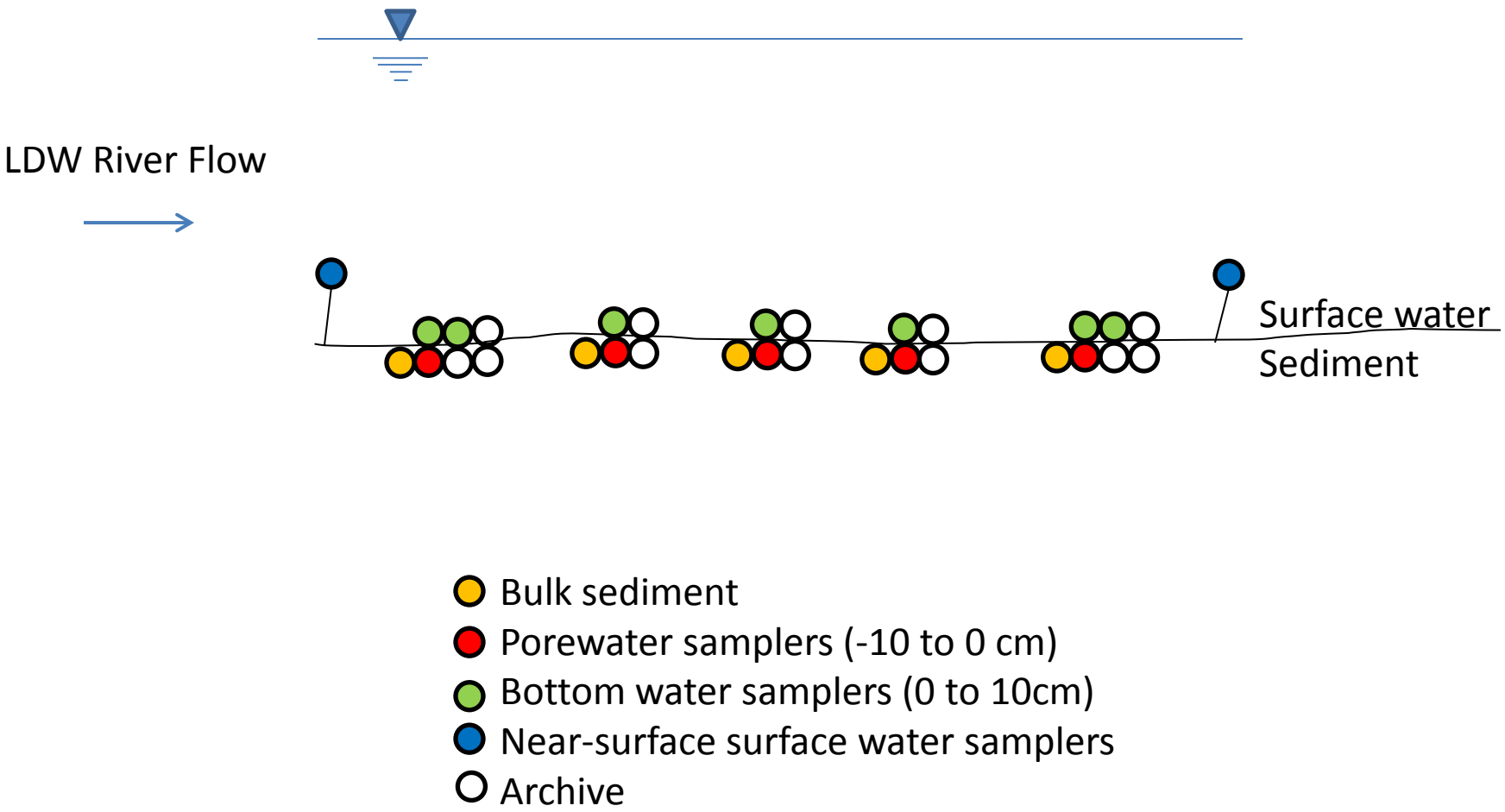
K_{bc} is fraction of sediment OC which is black carbon

n is the Freundlich exponent (0.7) to account for nonlinearity

PE Deployment Locations in Lower Duwamish Waterway



Sampling/Analysis Program Schematic



PE Sampler Visuals

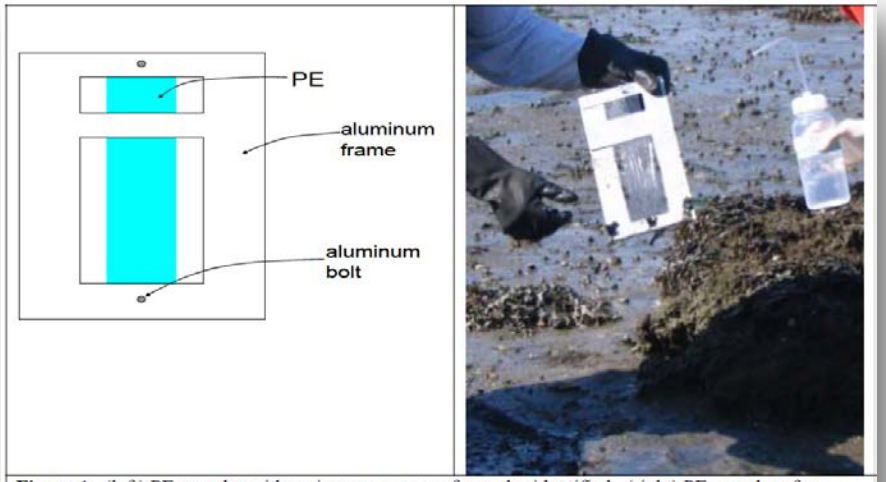
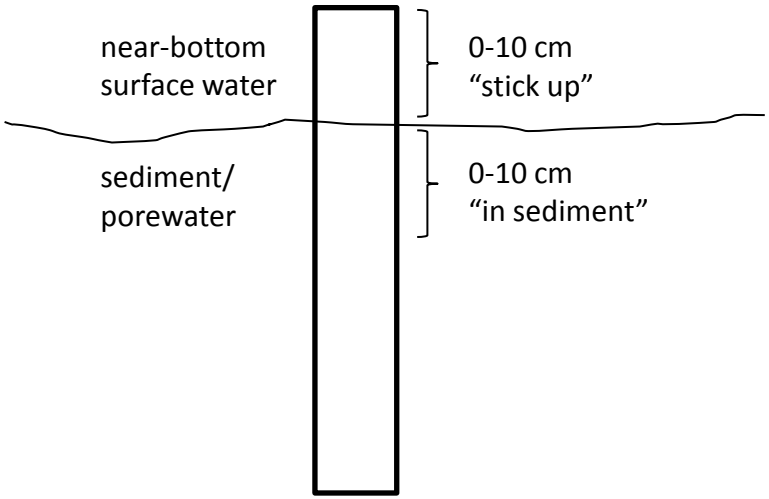
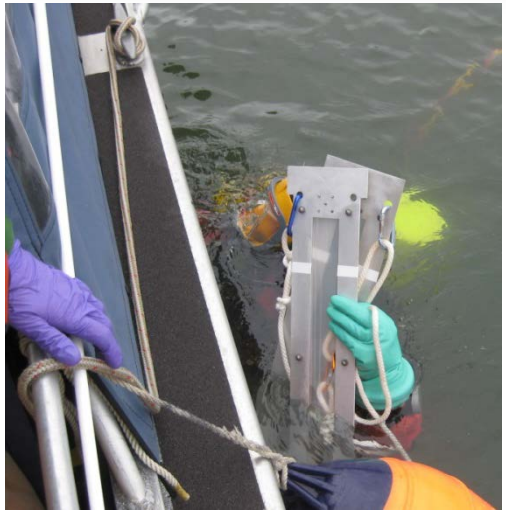


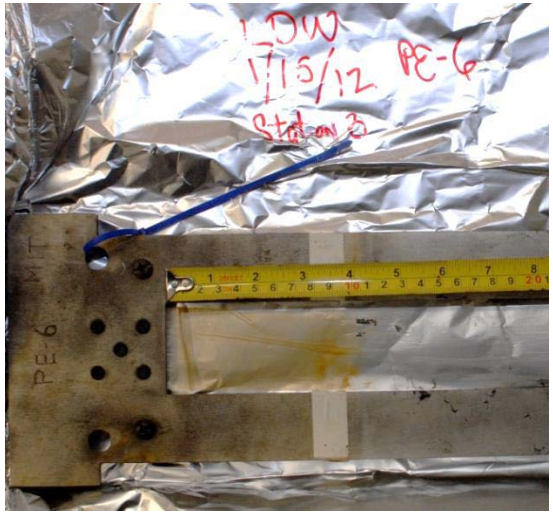
Figure 1. (left) PE sampler with main components of sampler identified. (right) PE sampler after recovery from a mudflat at low tide being rinsed with distilled water.

Conceptual In-Place PED Sampler with Collection Intervals Identified in LDW Project



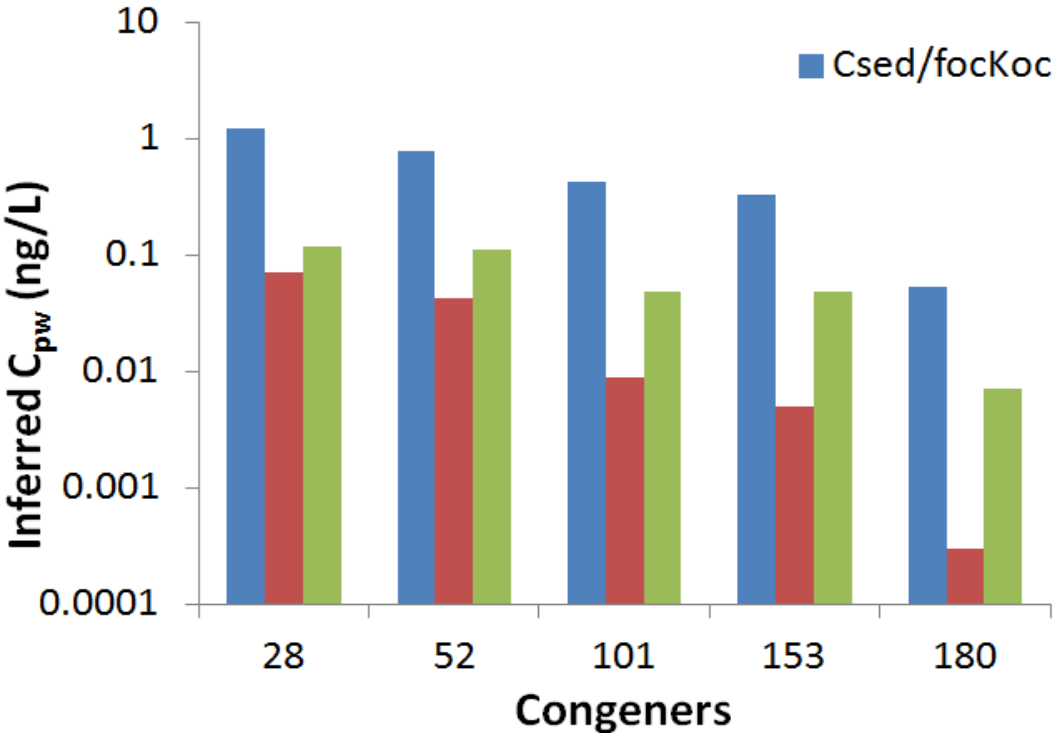


Passive sampler retrieval by divers in Lower Duwamish Waterway



Post-retrieval processing of passive samplers in on-shore laboratory

Results by Key Congeners



Comparison of PW concentrations of individual PCB conger sets estimated by sediment concentration divided (1) f_{oc}*k_{oc} (**blue**), (2) estimate of the sorption coefficient expressed as funciton of f_{oc} and f_{bc} (**red**), and (3) PE concentrations divided by K_{pew} (**green**)

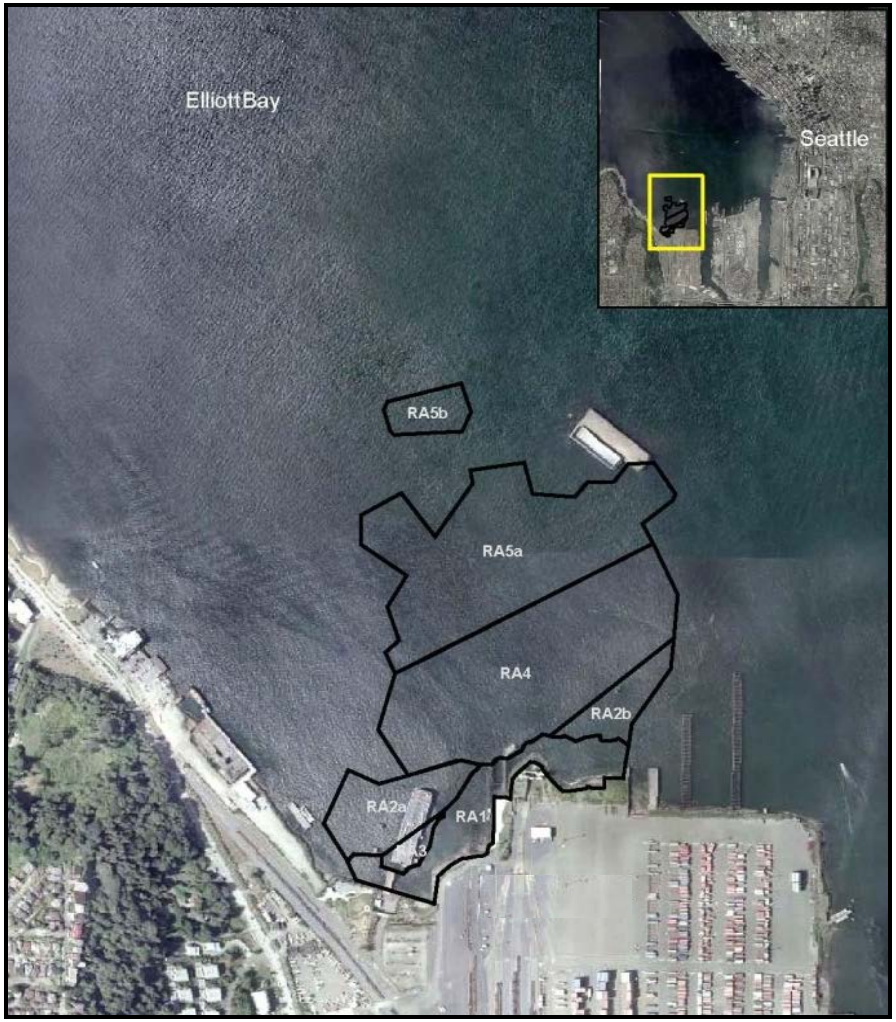
→ Traditional Equilibrium Partitioning overestimates C_{pw} by about 7 times

→Using an EqP adjustment with standard black carbon K_{bc} underestimates the observed C_{pw} by 3-4 times

→The predominant form of black carbon is coal/coke derived

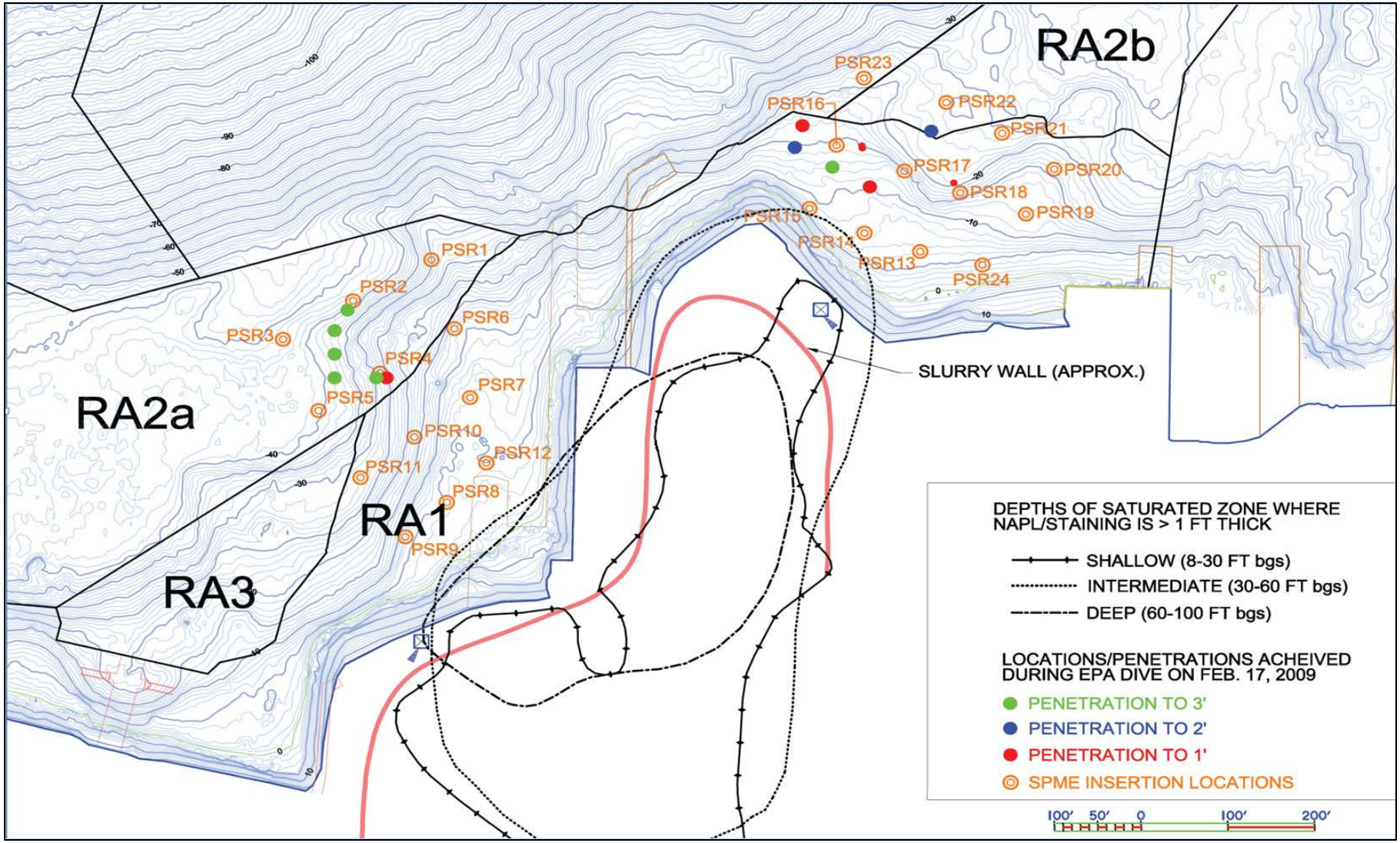
Pacific Sound Resources (PSR) Superfund Site, EPA Region 10

- Site Background
  - Wood Treatment Operation 1909-1994
  - Upland area unit
    25 acres
  - Marine sediment unit
    58 acres
  - Remedial action included dredging, capping and institutional controls and upland source control measures
- Study Objectives
  - Measure near-surface porewater concentrations
    - *Exceedance of surface water quality criteria?*
  - Measure porewater concentrations with depth in the sediment cap
    - *Concentration gradients indicate contaminant migration through cap?*

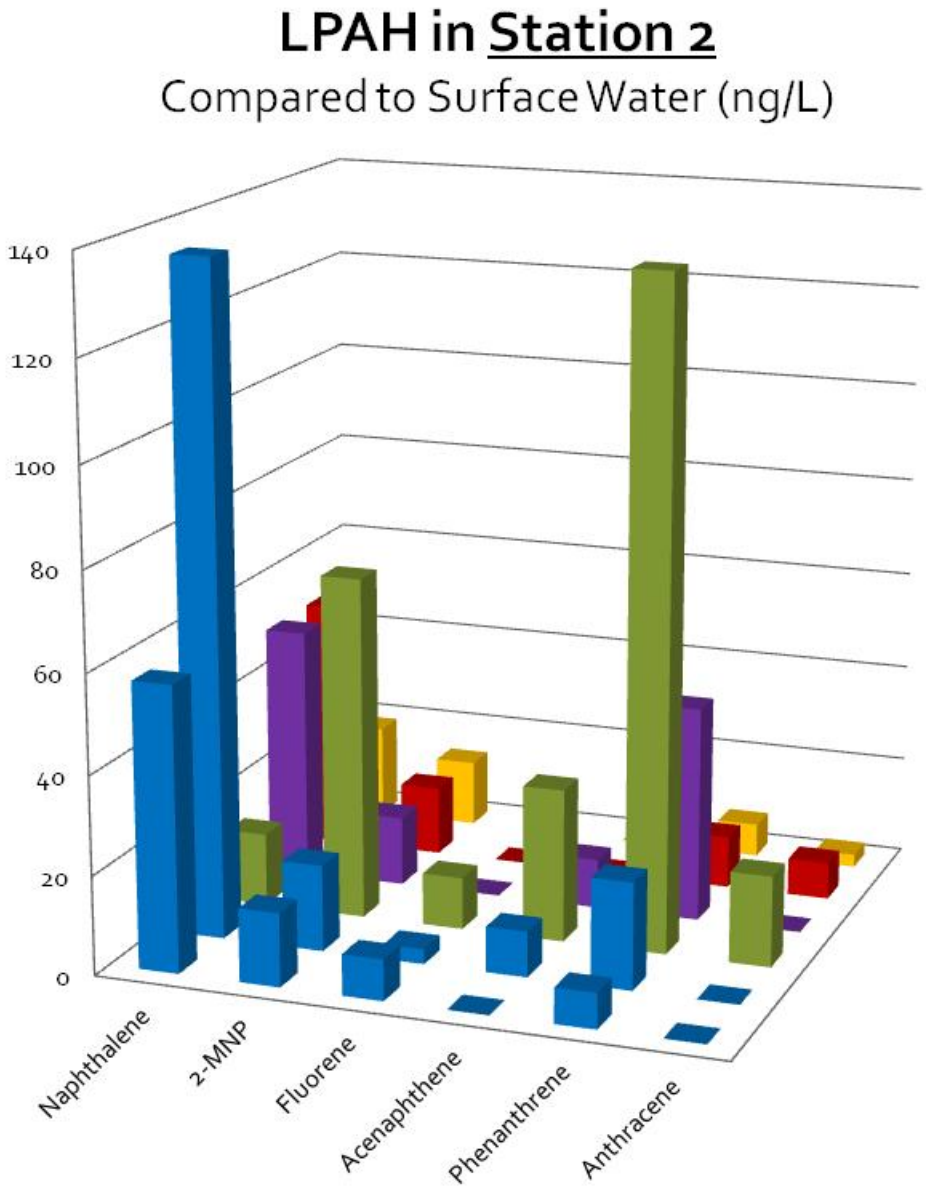


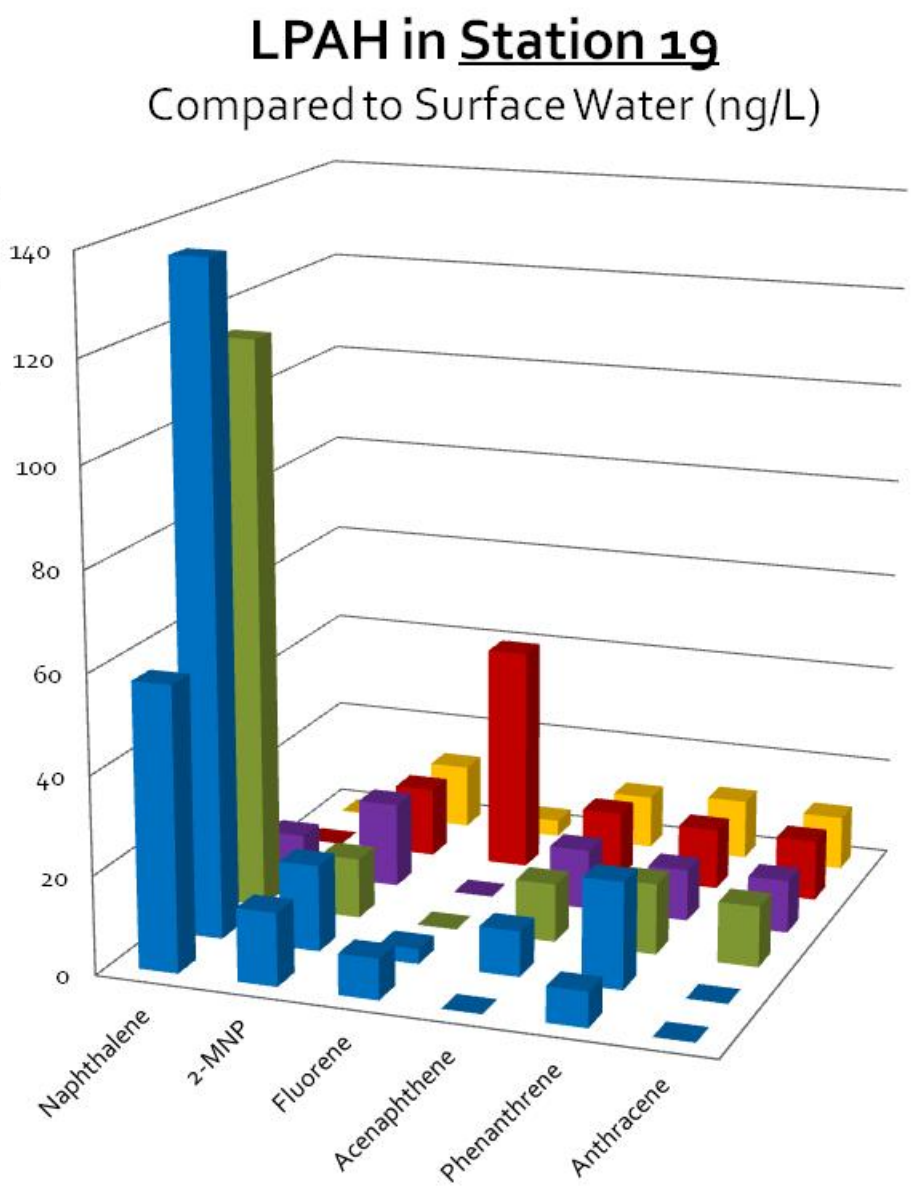
Solid-Phase Microextraction (SPME)

SPME Fiber Field Demonstration at PSR

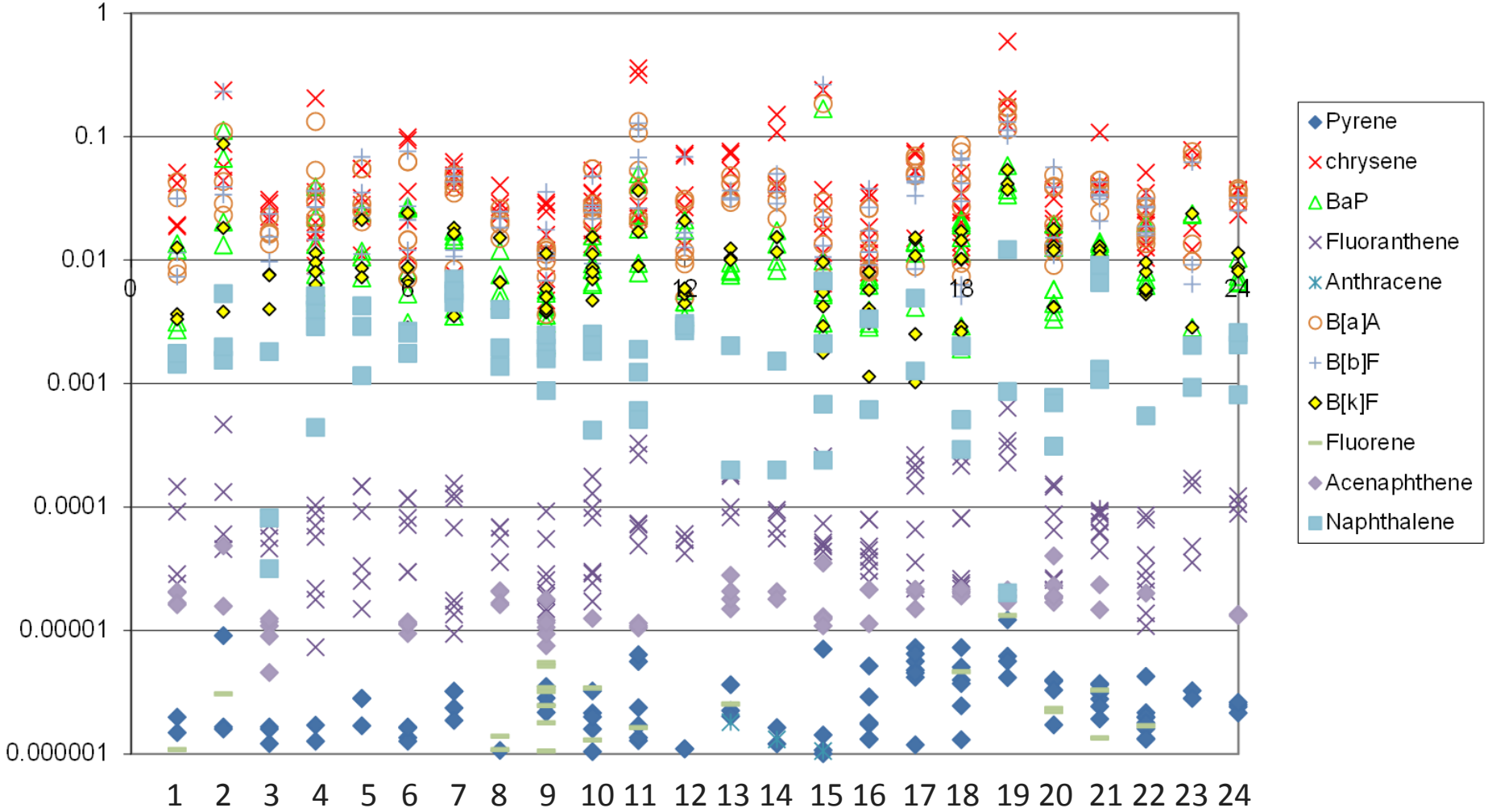


SPME Fiber Results





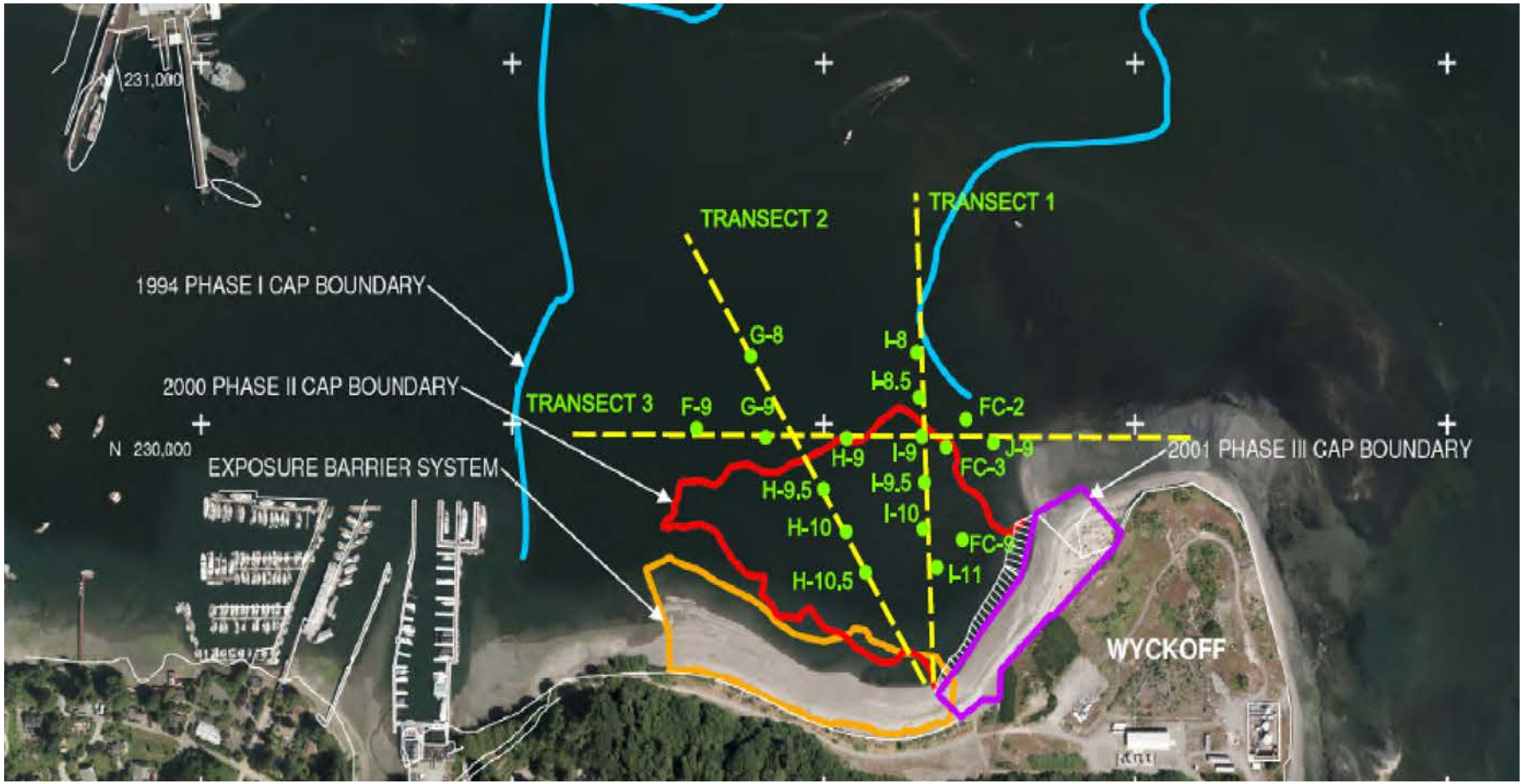
SPME Fiber Results



SPME Porewater Sampler Demonstration at Wyckoff/Eagle Harbor Superfund Site, EPA Region 10

- Site Background
  - Wood treatment operation
  - Added to NPL in 1987
  - COCs include PAHs, PCP and metals
  - Remedial actions included capping ~ 70 acres with clean sediment in addition to upland source control measures
- SPME Study Objectives
  - Measure near-surface porewater concentrations
    - *Exceedance of surface water quality criteria?*
  - Measure porewater concentrations with depth in the sediment cap
    - *Concentration gradients indicate contaminant migration through cap?*
  - Compare colocated bulk sediment and porewater results
    - *Would the two methods support different conclusions if used alone?*

SPME Fiber Field Demonstration at Wyckoff/Eagle Harbor

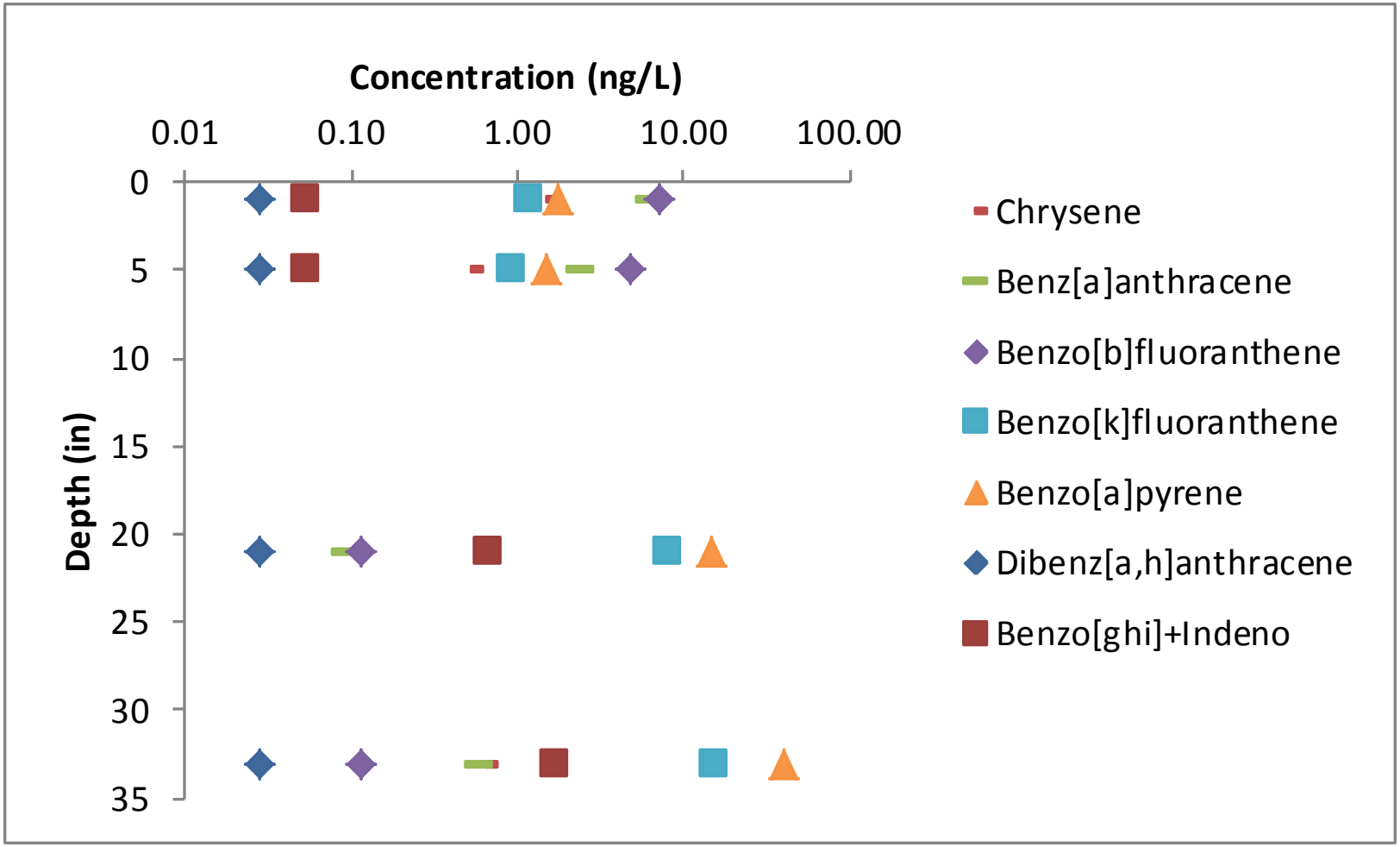


Corrections for Steady State

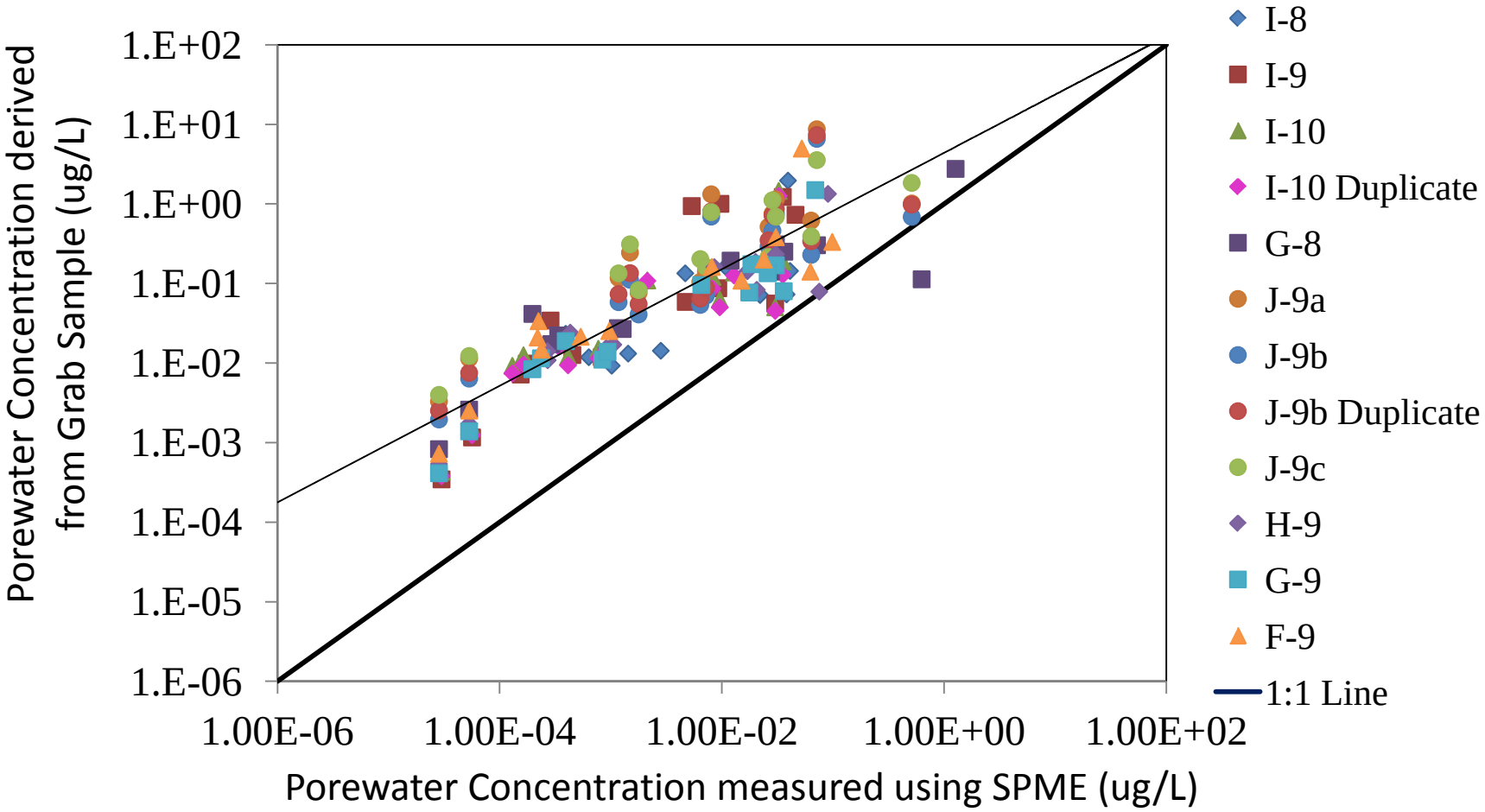
- Deuterated PAHs are ideal performance reference compounds (Gschwend et al. 2009)
  - fluoranthene-d10
    chrysene-d12
    benzo[b]fluoranthene -d12
    and
    dibenz[a,h]anthracene -d14

Compound	logKow	Correction Factor for 1000/1071µm fiber	Correction Factor for 1000/1060 µm fiber
Naphthalene	3.37	0.90	0.91
Acenaphthene	3.92	0.84	0.87
Fluorene	4.18	0.81	0.84
Anthracene	4.54	0.76	0.79
Phenanthrene	4.57	0.75	0.79
Pyrene	5.18	0.64	0.68
Fluoranthene	5.22	0.63	0.67
Benzo[b]fluroanthene	5.8	0.51	0.56
Chrysene	5.86	0.50	0.54
Benz[a]anthracene	5.91	0.49	0.53
Benzo[k]fluroanthene	6	0.47	0.51
Benzo[a]pyrene	6.04	0.46	0.50
Benzo[ghi]perylene +Indeno(1,2,3-cd)pyrene	6.5	0.36	0.41
Dibenz[a,h]anthracene	6.75	0.32	0.36

Concentration Depth Profiles Allow Assessment of Through-Cap Migration



Bulk Sediment Estimated Porewater vs. Measured Porewater



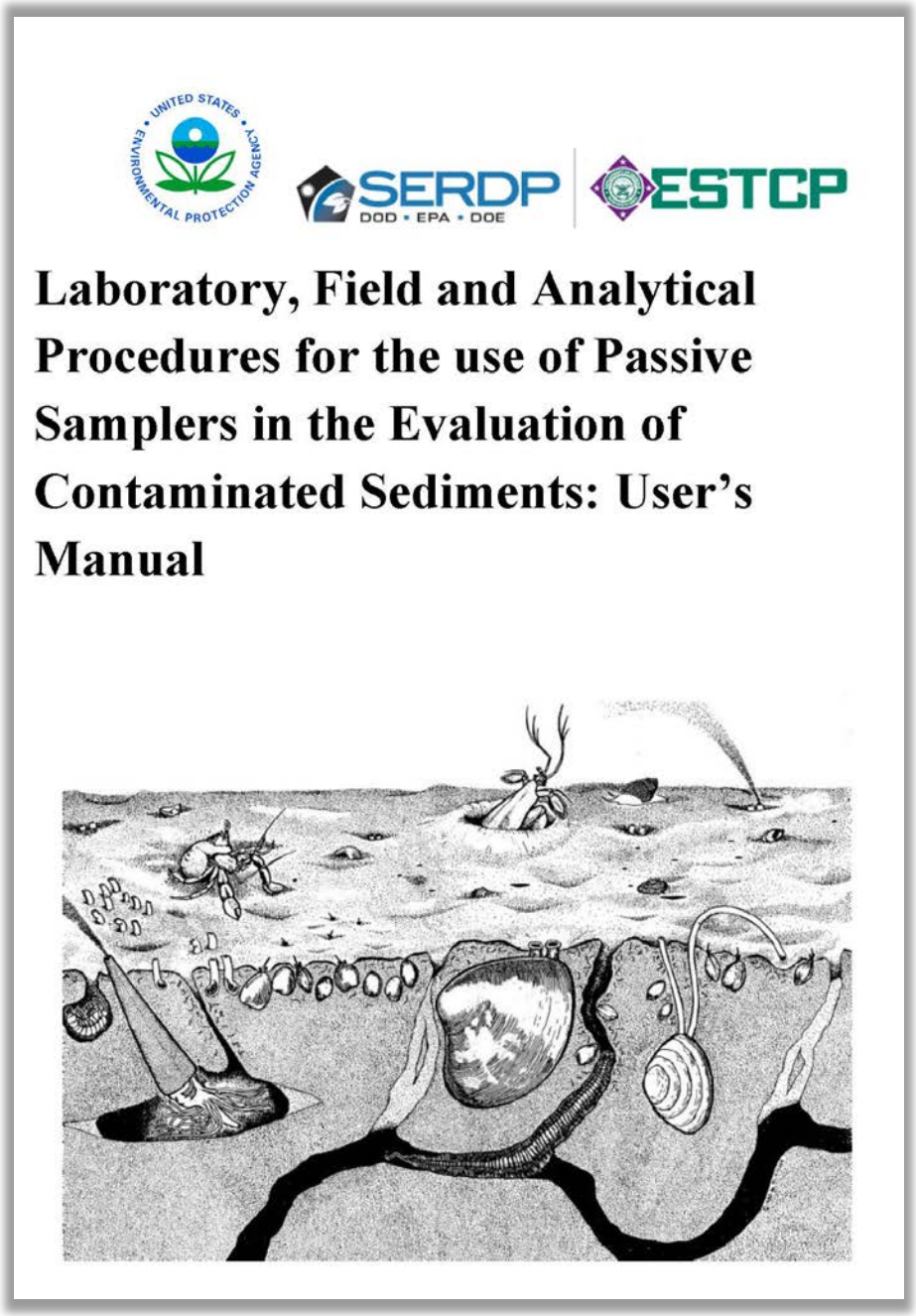
Take Home Messages

- Benefits of direct porewater measure
  - Better proxy for bioavailability
  - Deployable in near surface sediment/surface water column
  - cm-level depth resolution and ng/L DLs allow assessment of concentration gradients/migration potential
  - Not cost prohibitive compared to bulk sediment analysis, though commercial laboratories offering passive porewater samplers/analysis is limited
- Ideal approach for monitoring activated carbon-amended sediments

  (Gidley et al. *Environ. Sci. Technol.* 2012, 46, 5032–5039)

Standard Methods and Laboratories

- EPA and SERDP/ESTCP Guidance Document
- Accredited Labs
  - Axys (BC)
  - ALS
  - Pace Analytical
  - Test America



Contact for User's Manual:

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