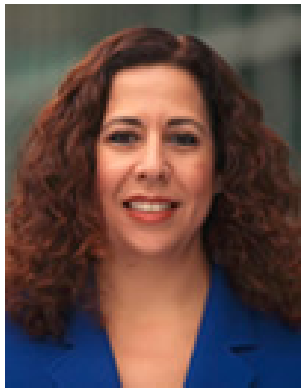
New Tools for Improving the Management of Contaminated Sediment Sites

Dr. Philip Gschwend, MIT
Dr. Bart Chadwick, SPAWAR Systems Center Pacific

SERDP DOD • EPA • DOE | ESTCP

Welcome and Introductions

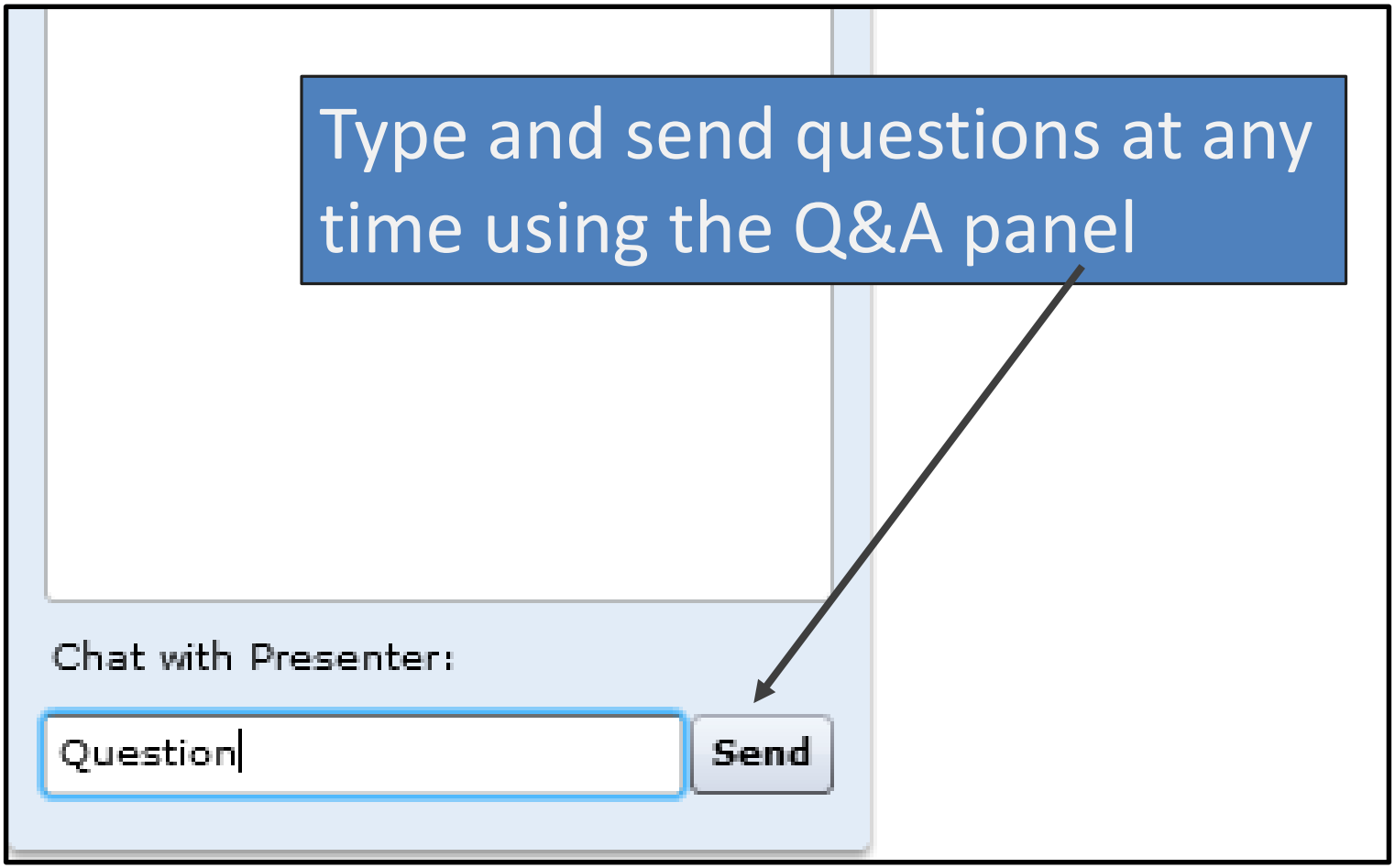
Rula Deeb, Ph.D.
Webinar Coordinator



Webinar Agenda

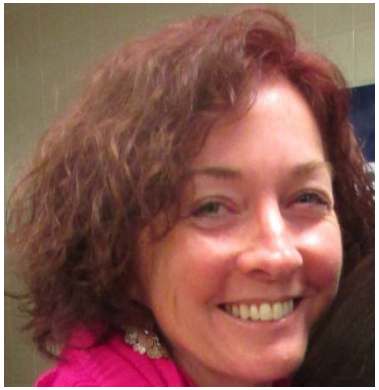
- Webinar Overview and ReadyTalk Instructions
  Dr. Rula Deeb, Geosyntec (5 minutes)
- Overview of SERDP and ESTCP, and webinar series goals
  Dr. Andrea Leeson, SERDP and ESTCP (5 minutes)
- PE Passive Sampling for Assessing Contaminated Sediments
  Dr. Phil Gschwend, MIT (30 minutes + Q&A)
- An In-Situ Friction-Sound Probe for Mapping Particle Size at Contaminated Sediment Sites
  Dr. Bart Chadwick, SPAWAR Systems Center Pacific (30 minutes + Q&A)
- Final Q&A session

How to Ask Questions Using ReadyTalk



SERDP and ESTCP Overview

Andrea Leeson, Ph.D.
Deputy Director



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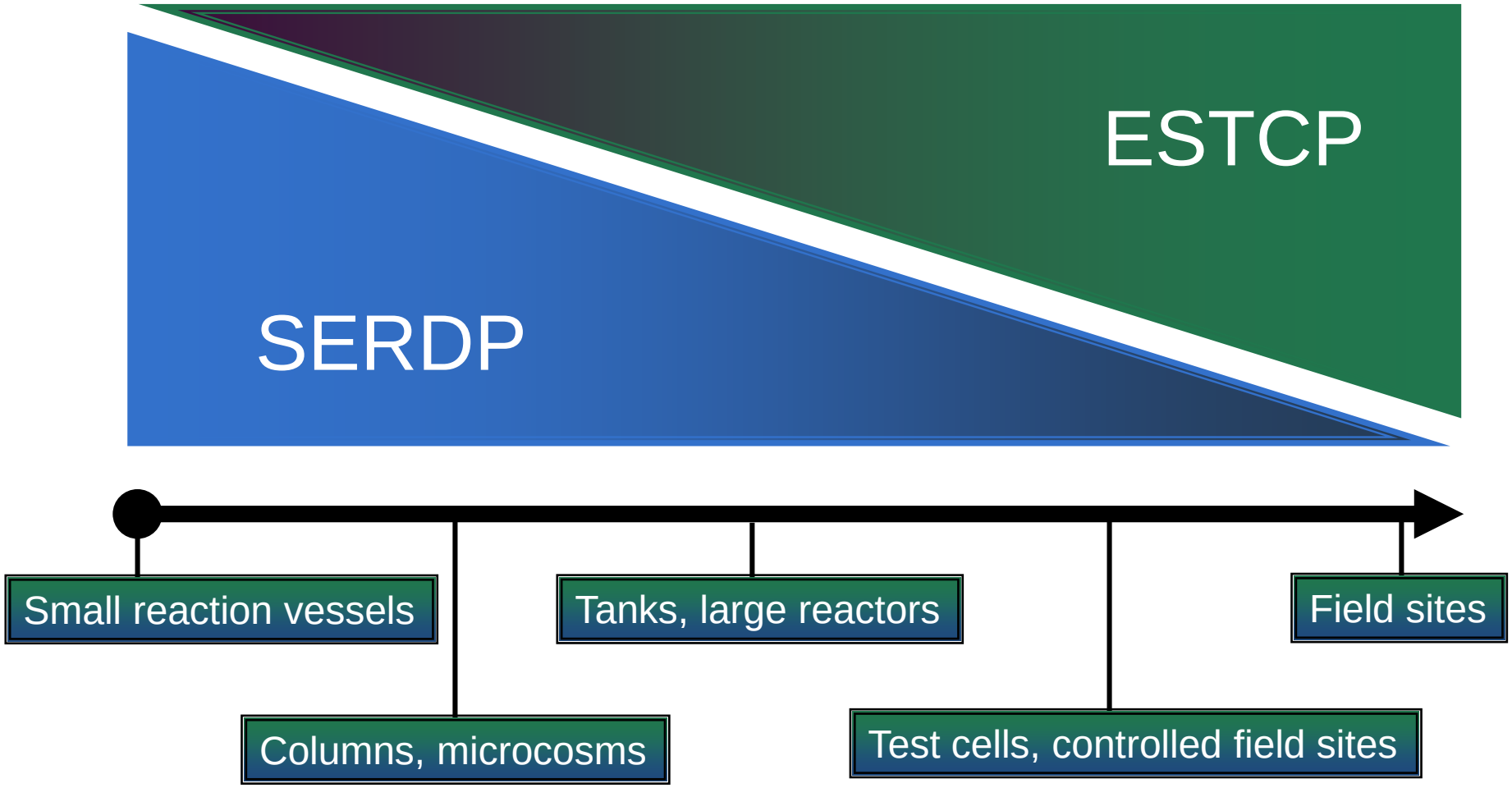
SERDP

- Strategic Environmental Research and Development Program
- Established by Congress in FY 1991
  - DoD, DOE and EPA partnership
- SERDP is a requirements driven program which identifies high-priority environmental science and technology investment opportunities that address DoD requirements
  - Advanced technology development to address near term needs
  - Fundamental research to impact real world environmental management

ESTCP

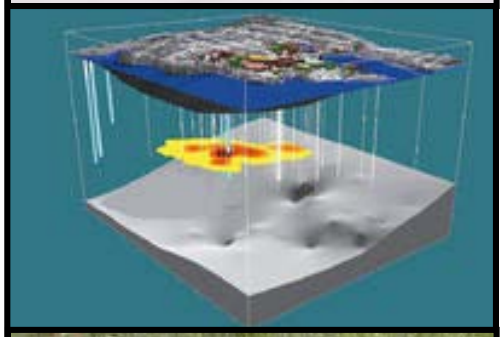
- Environmental Security Technology Certification Program
- Demonstrate innovative cost-effective environmental and energy technologies
  - Capitalize on past investments
  - Transition technology out of the lab
- Promote implementation
  - Facilitate regulatory acceptance

Scales of Research



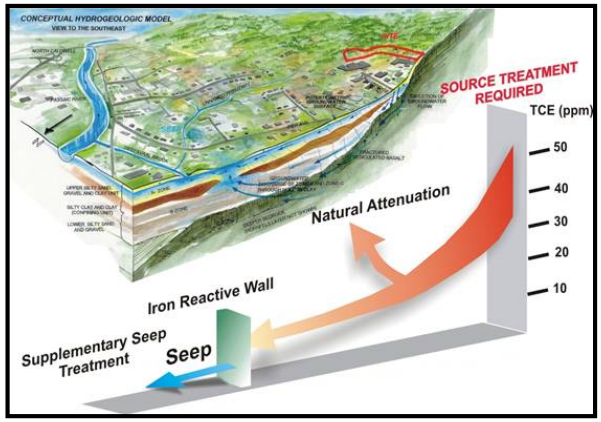
Program Areas

1. Energy and Water
2. Environmental Restoration
3. Munitions Response
4. Resource Conservation and Climate Change
5. Weapons Systems and Platforms



Environmental Restoration

- Major focus areas
  - Contaminated groundwater
  - Contaminants on ranges
  - Contaminated sediments
  - Wastewater treatment
  - Risk assessment



SERDP and ESTCP Launch a Webinar Series

DATE	WEBINARS AND PRESENTERS
December 4, 2014	**The Roles Efficient Tar Management and Rotary Kiln Gasification for Base Camps as Options for Waste to Energy** ▪ Leigh Knowlton, U.S. Army Natick Soldier Research Development and Engineering Center ▪ Mr. Patrick Scott (Lockheed Martin) ▪ Mr. Steven Cosper (U.S. Army Engineer Research and Development Center, Construction Engineering Research Laboratory)
December 18, 2014	**Energy Audits: From Clipboard to Cloud** ▪ Oliver Davis (concept3D, Inc.) ▪ Cara Brill (FirstFuel)
January 8, 2015	**DNAPL Source Zone Management** ▪ Dr. Paul Johnson (Arizona State University) ▪ Dr. Charles Newell (GSI Environmental)
January 22, 2015	**Sustainable Materials** ▪ Dr. Andrew Guenthner (Air Force Research Laboratory, Aerospace Systems Directorate) ▪ Dr. Benjamin Harvey (Naval Air Warfare Center, Weapons Division) ▪ Dr. John La Scala (U.S. Army Research Laboratory)

http://serdp-estcp.org/Tools-and-Training/Webinar-Series

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PE Passive Sampling for Assessing Contaminated Sediments

Dr. Phil Gschwend
MIT

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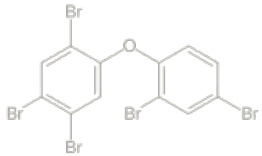
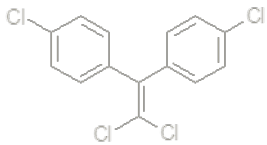
PE Passive Sampling for Assessing Contaminated Sediments

ESTCP Project Number: ER-0915

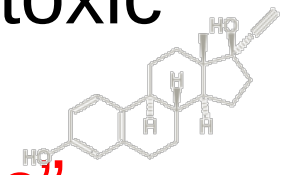
Phil Gschwend, Massachusetts Institute of Technology

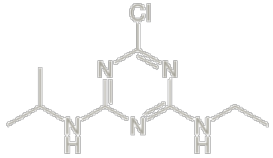
The Problem



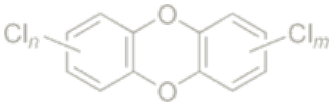


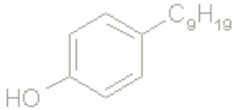
- Diverse organic pollutants
- Many persistent, bioaccumulative, and toxic (PBT)
- Many "hydrophobic" => "sedimentophilic"

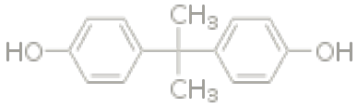




- For the USA, EPA says: "Approximately <u>10%</u> of the sediment ....sufficiently contaminated to pose potential <u>risks to fish and to humans and wildlife</u> who eat fish"

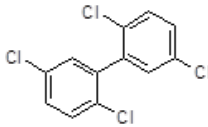




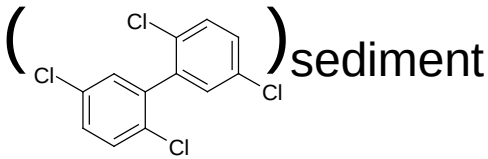


The Problem (Continued)

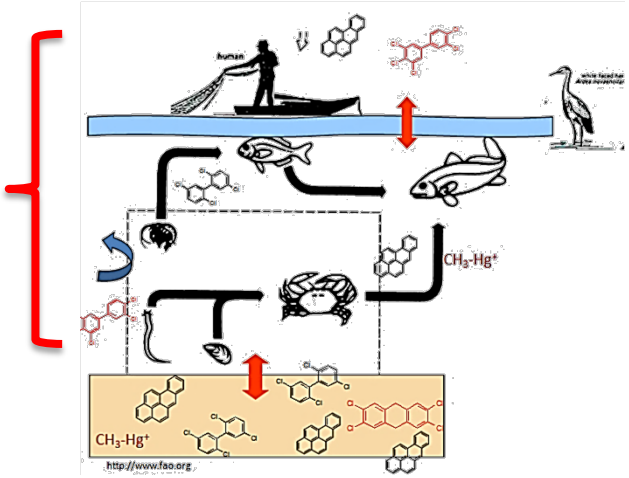
- Risks often based on levels in fish and shellfish



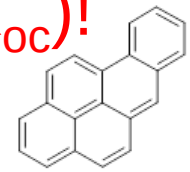
- Models (e.g., BSAF & FWMs) used to predict these biota body burdens



?



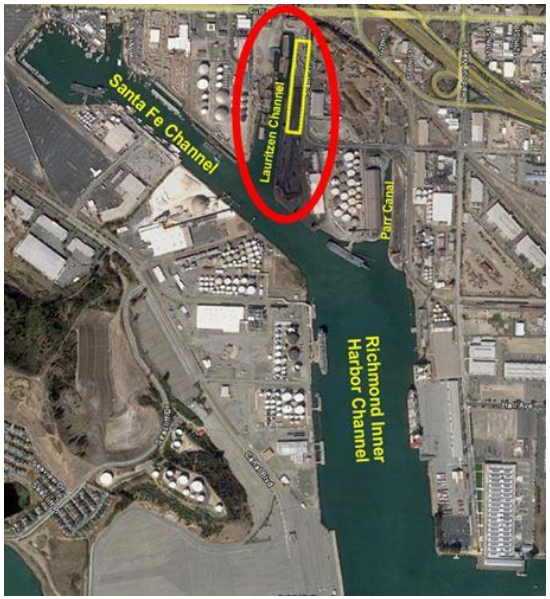
- However, model results are "suspect" if driven by inaccurate exposure information ($C_{porewater}$ from $C_{sediment}/f_{oc}K_{oc}$)!

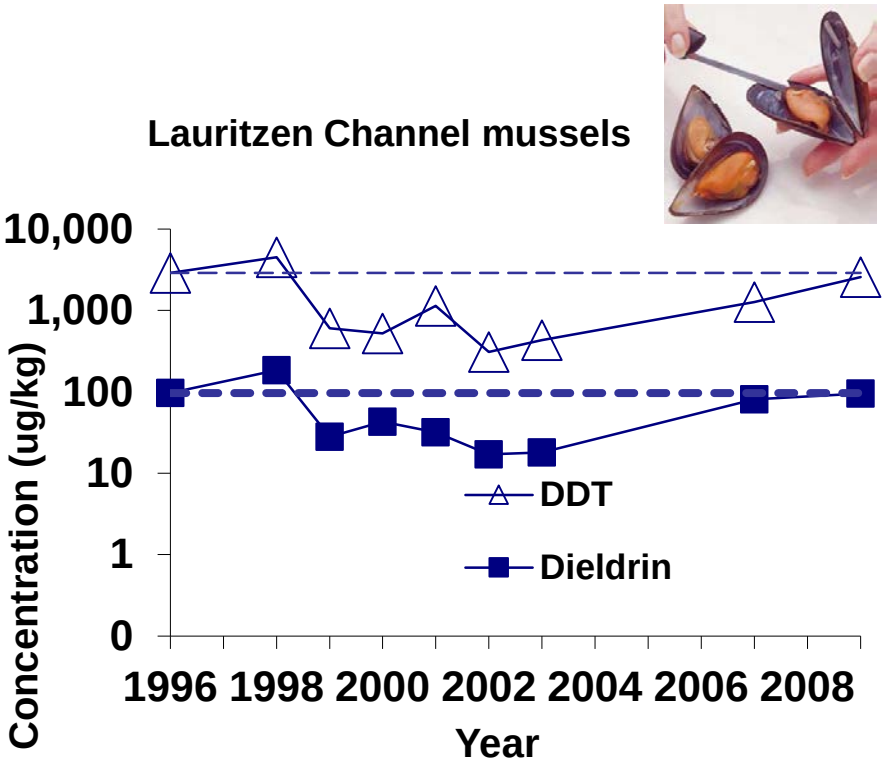


Problem: Cleanups expensive & often unsuccessful

- e.g., DDTs and dieldrin in Richmond, CA

completed in 1997. Approximately 107,000 tons of sediment were removed from the waterways and transported to disposal facilities. After



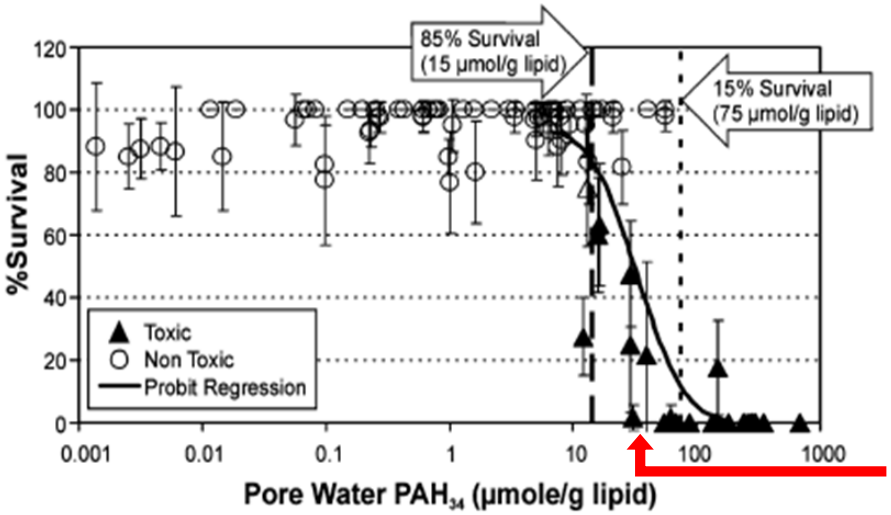


- Need a better way to identify source(s)

(Tamara Frank, E2 Consulting Engineers)

Background

- Pore water concentrations: best metric to assess sources and exposures in sediments
- With porewater, also know organisms at equilibrium



Hawthorne et al., 2007

~1% PAH saturation in lipids

Expected to be toxic!!!

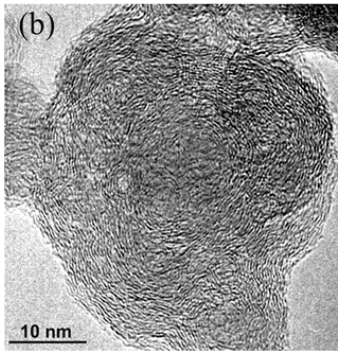
Background

- Reduce bioavailability if compounds BC sorbed

e.g., *Mya arenaria* (soft-shelled clam)

OC sorbs

and Black Carbon sorbs



decrease fraction dissolved in pore water?

C_{biota} proportional to $C_{porewater}$

Background

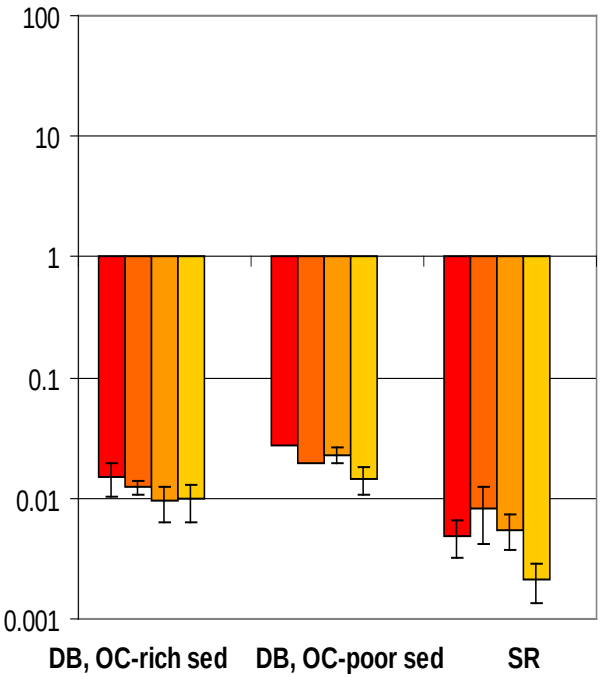
Bioaccumulation predictions more accurate with OC and BC!

- "Old way"

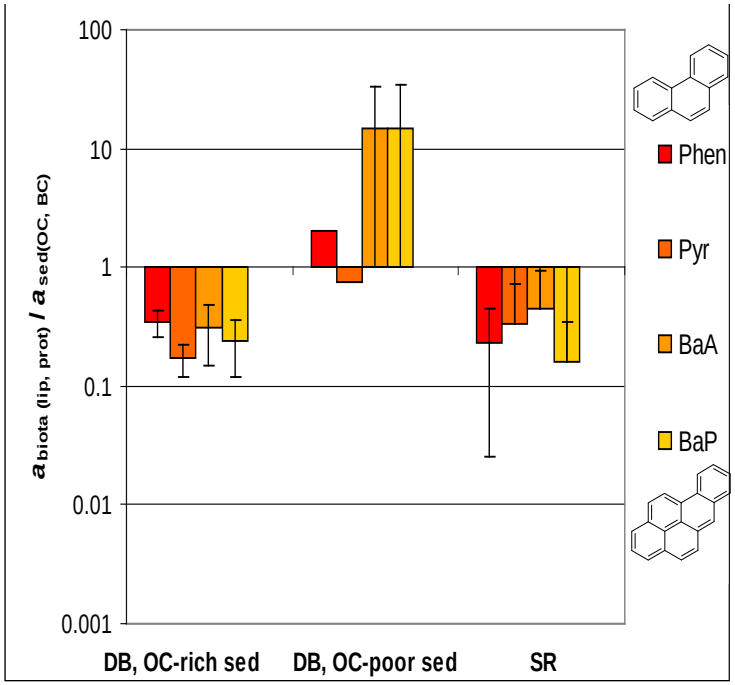
w/ $C_{water} = C_{sed}/(f_{oc}K_{oc})$

- "New" BC-inclusive way

w/ $C_{water} = C_{sed}/(f_{oc}K_{oc} + f_{BC}K_{BC}C_w^{n-1})$



observed in clam divided by predicted in clam

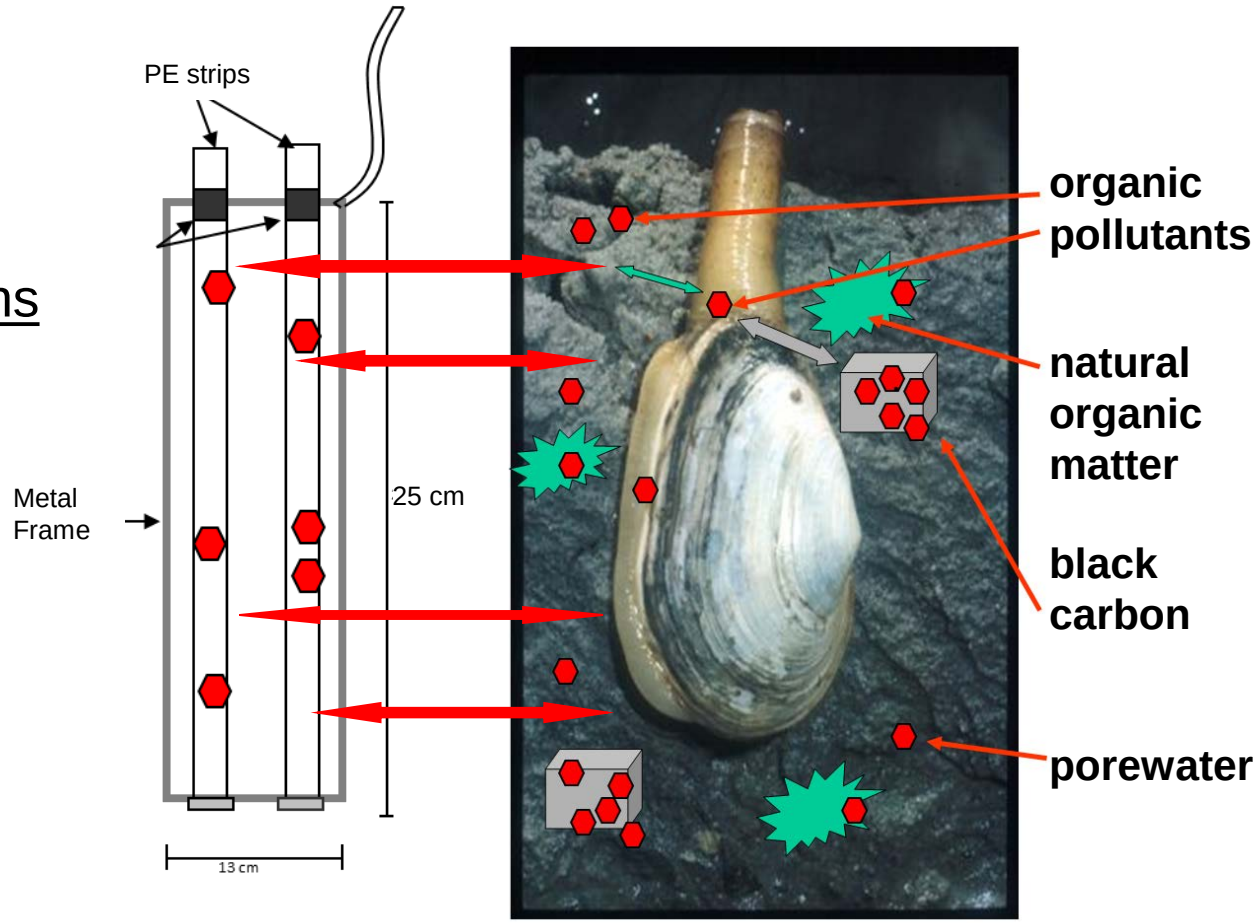


PE Approach

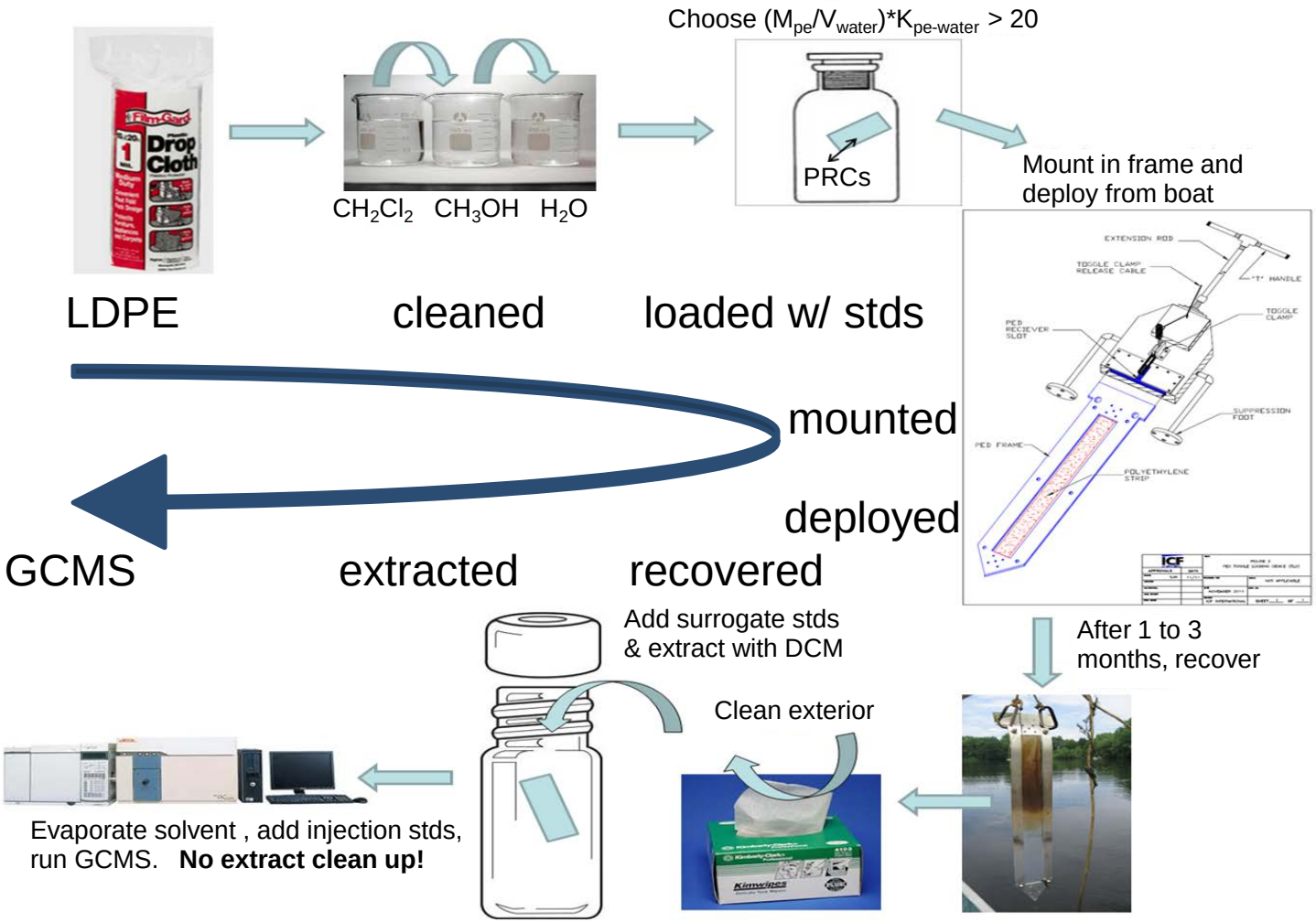
- Use polymer to equilibrate with sediment

Accumulate contaminants proportional to <u>porewater concentrations</u>

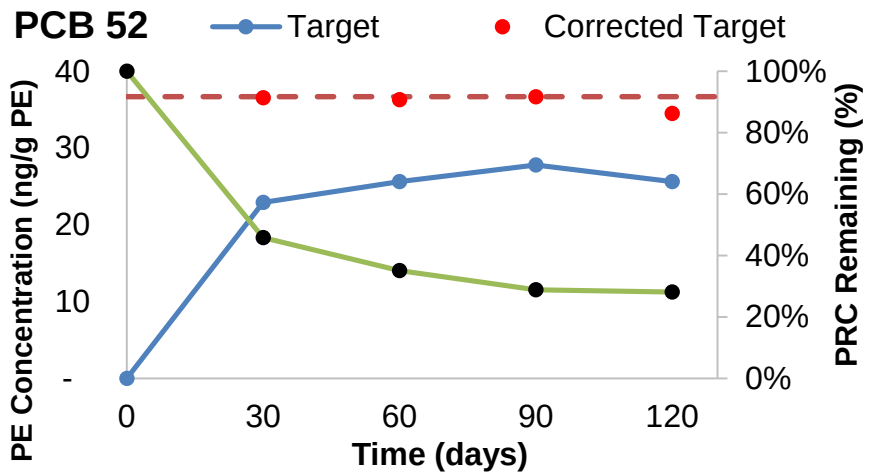
$$C_{PE} = K_{PEwater} * C_{porewater}$$



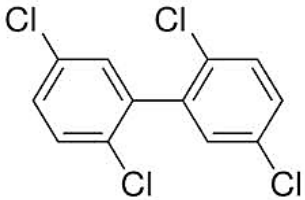
PE Methods


Choose $(M_{pe}/V_{water})*K_{pe\text{-}water} > 20$
CH_2Cl_2 CH_3OH H_2O
PRCs
Mount in frame and deploy from boat
LDPE
cleaned
loaded w/ stds
mounted
deployed
GCMS
extracted
recovered
Add surrogate stds & extract with DCM
Clean exterior
After 1 to 3 months, recover
Evaporate solvent , add injection stds, run GCMS. **No extract clean up!**

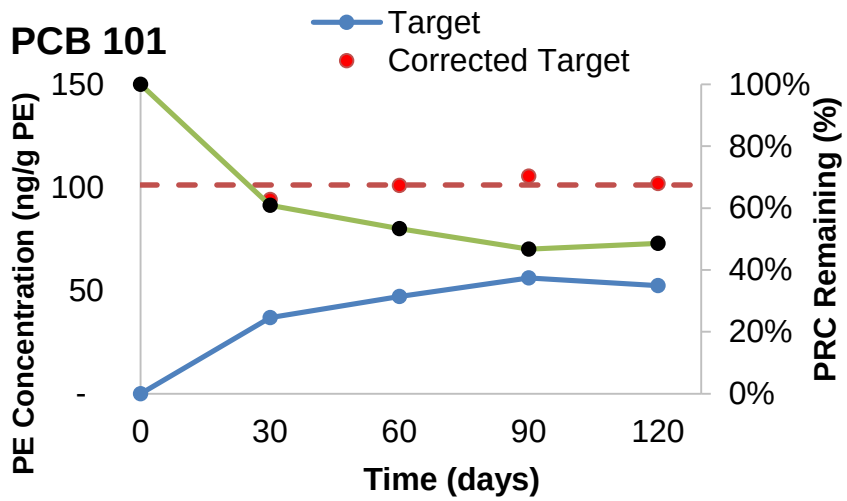
Data Processing: Use PRCs to Find C^{∞}_{PE}



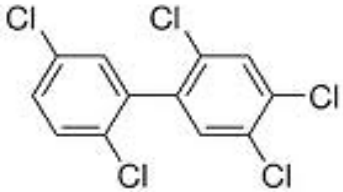
PCB 52						
Day	0	30	60	90	120	Equilibrated
	100%	46%	35%	29%	28%	0%
Target (ng/g)	-	23	26	28	26	
Corrected (ng/g)	-	37	36	37	35	37



$$C^{\infty}_{PE} / K_{pe\text{-}w} = C_{porewater}$$

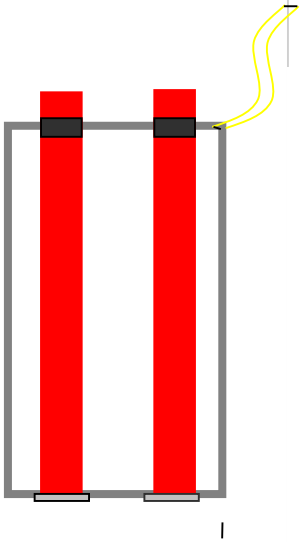


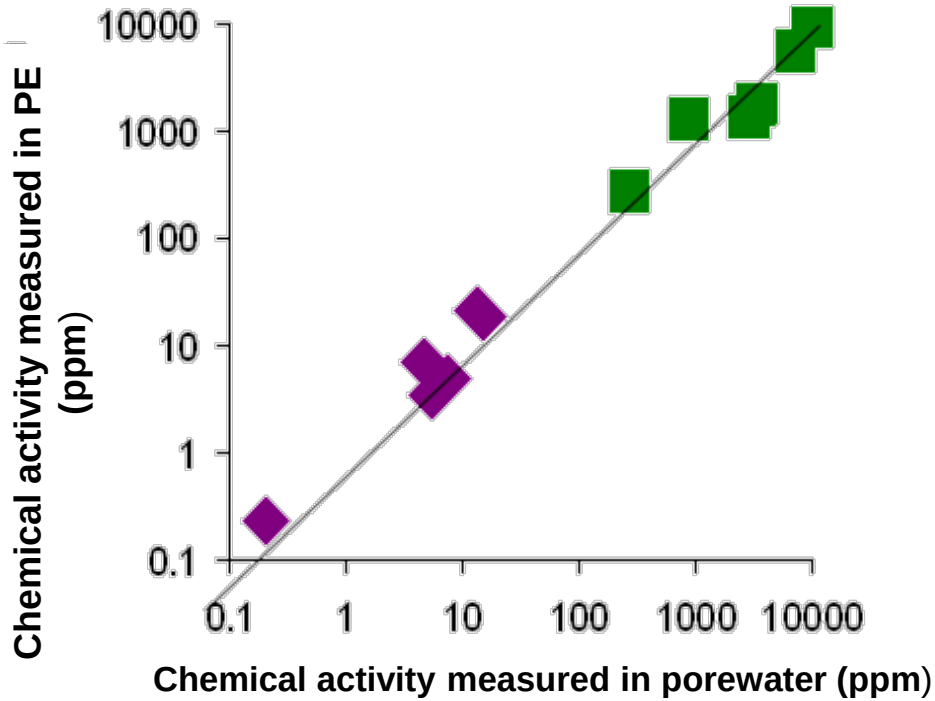
PCB 101						
Day	0	30	60	90	120	Equilibrated
PRC Remaining	100%	61%	53%	47%	49%	0%
Target (ng/g)	-	37	47	56	52	
Corrected (ng/g)	-	94	101	105	102	101

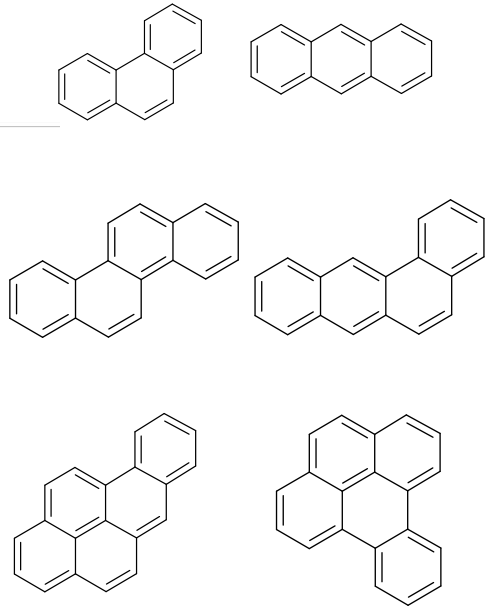


Accuracy Test

- With sediments in lab: PE vs. pore water
  - Island End (green squares)
  - Dorchester Bay (purple diamonds)





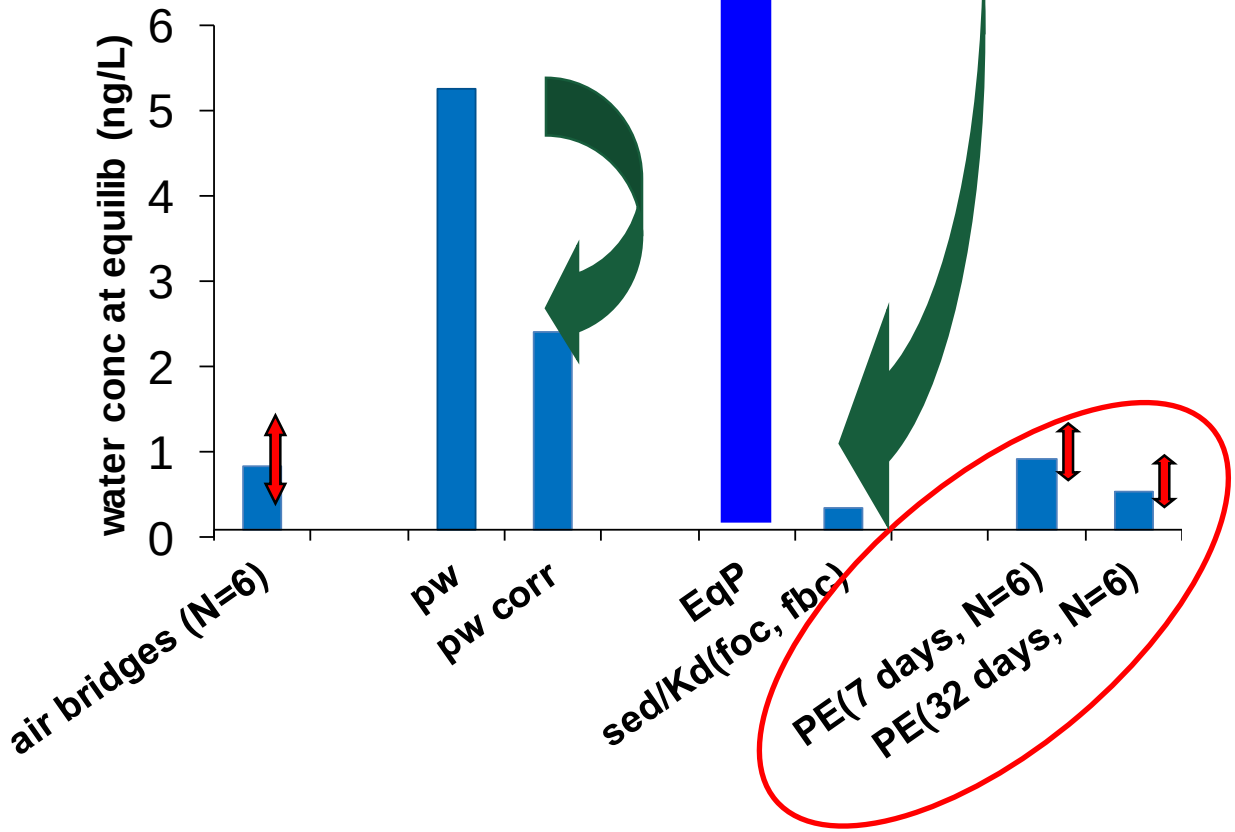


Accuracy Test

Compare to other methods

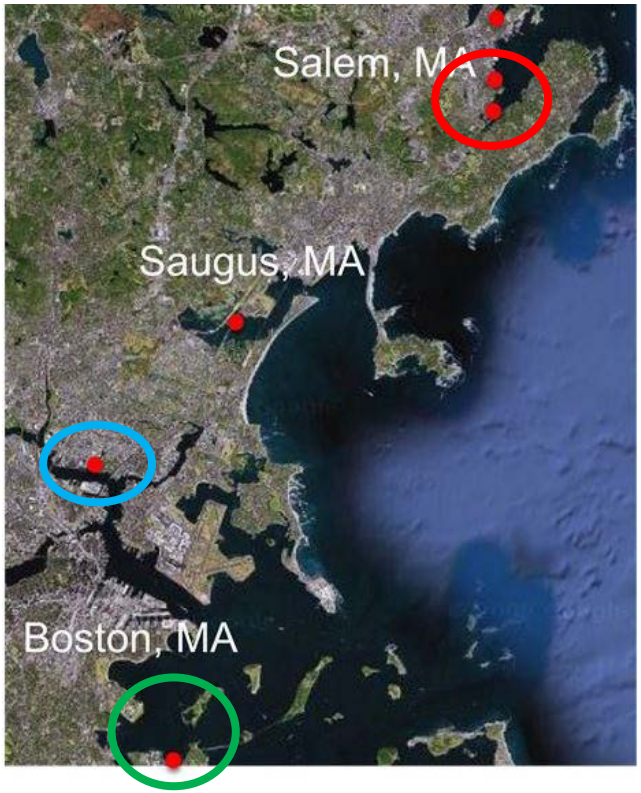
32 ng/L

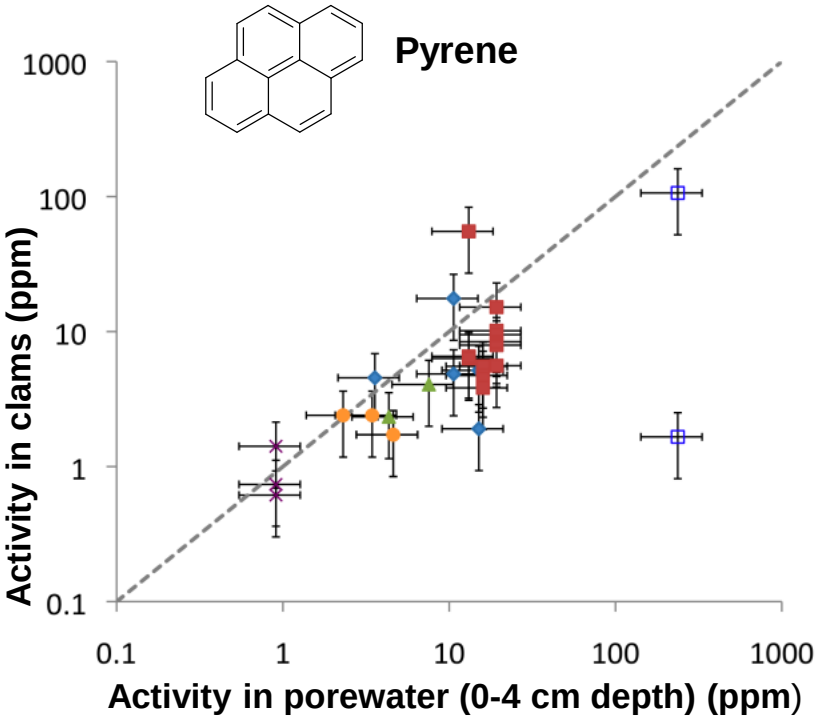
Hunters Point & PCBs



Case Study #1

- PAH biouptake from coastal sediments





<u>activity in porewater =</u> $C_{porewater} / C_{water}^{sat} = (C_{PE} / K_{PE\text{-}water}) / C_{water}^{sat}$

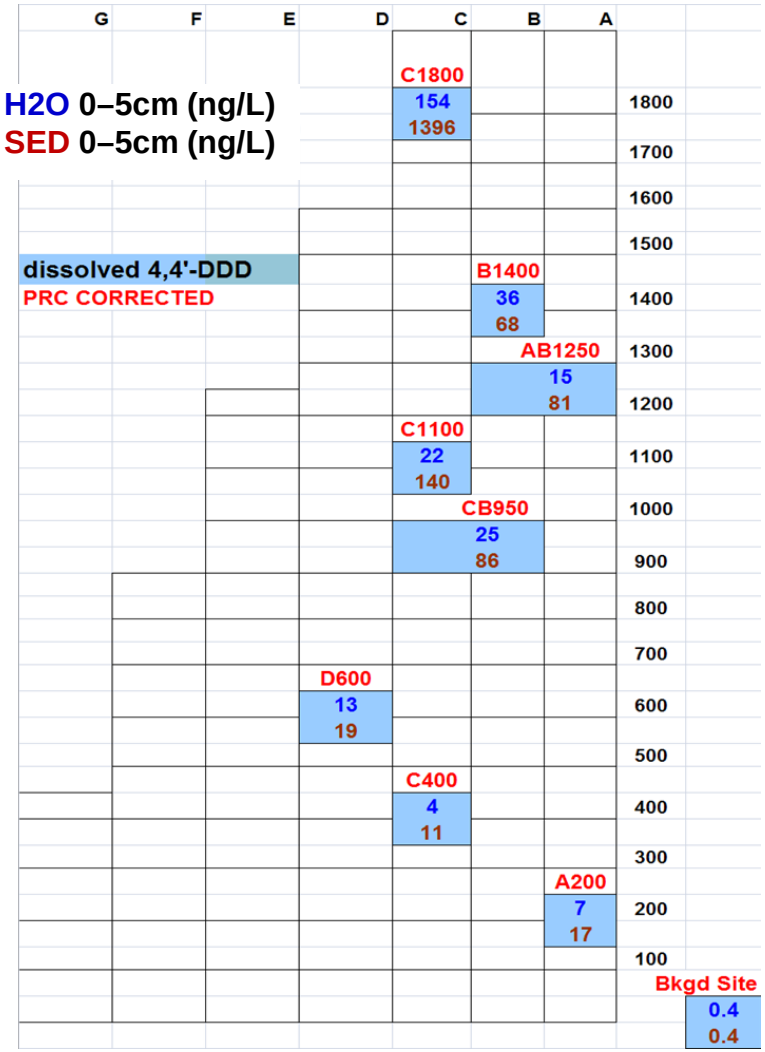
<u>activity in clam</u> = $(C_{lipid} / f_{lipid} K_{lipid\ water}) / C_{water}^{sat}$

Case Study #2

- DDTs in a harbor
  1. Test “conceptual model”
     - Main source = diffusion from bed
  2. Test substitution
     - Passive samplers for biomonitors (mussels)

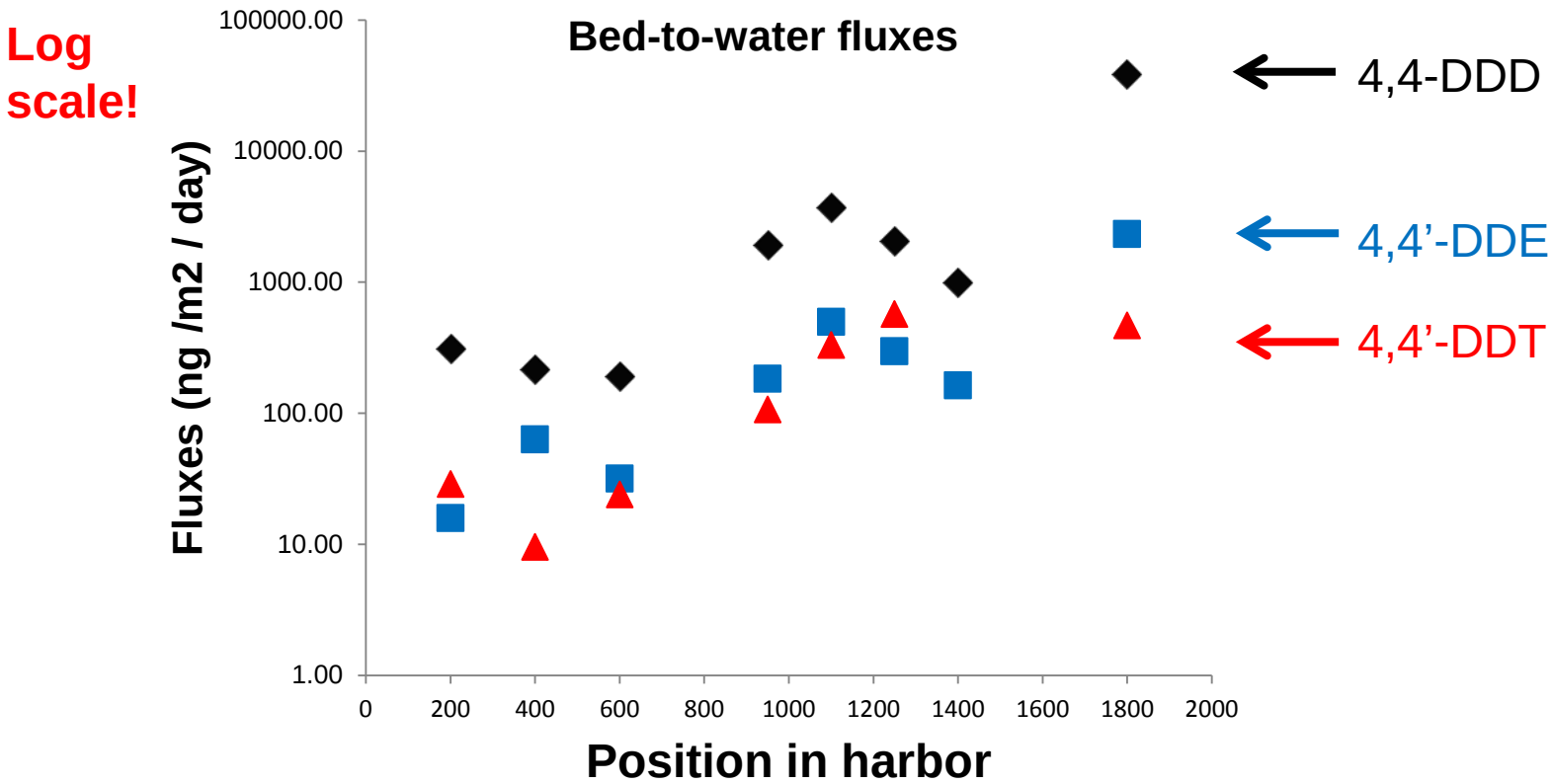
Bottom Water vs. Porewater

- Map bottom water and porewater concentrations
  - Strong gradient down channel
  - Higher C_{pw} than bkgd site
  - Every station has pw > bw =>bed-to-water fluxes



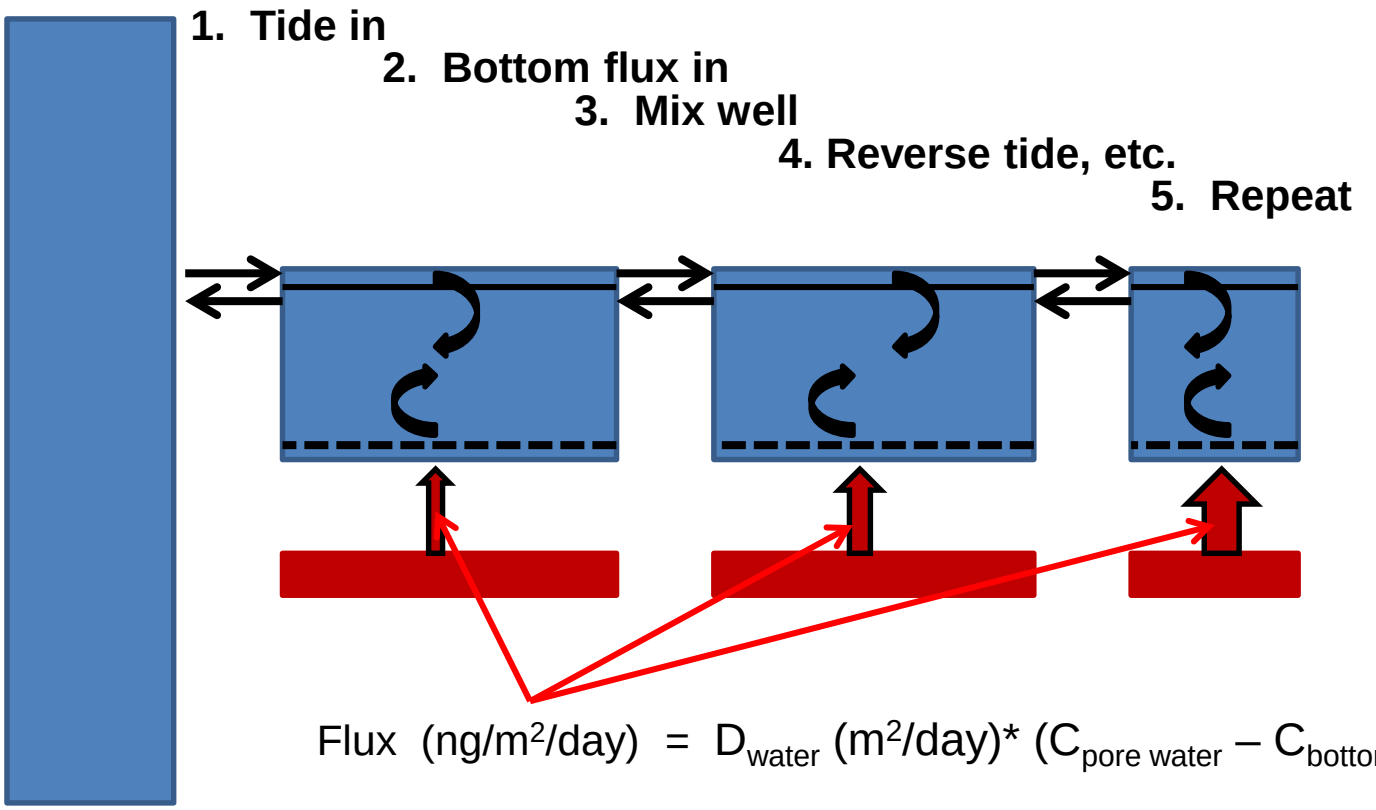
Use Passive Sampling Data

- Bed-to-water column fluxes (ng/m^2/day)



Surface Water Concentrations

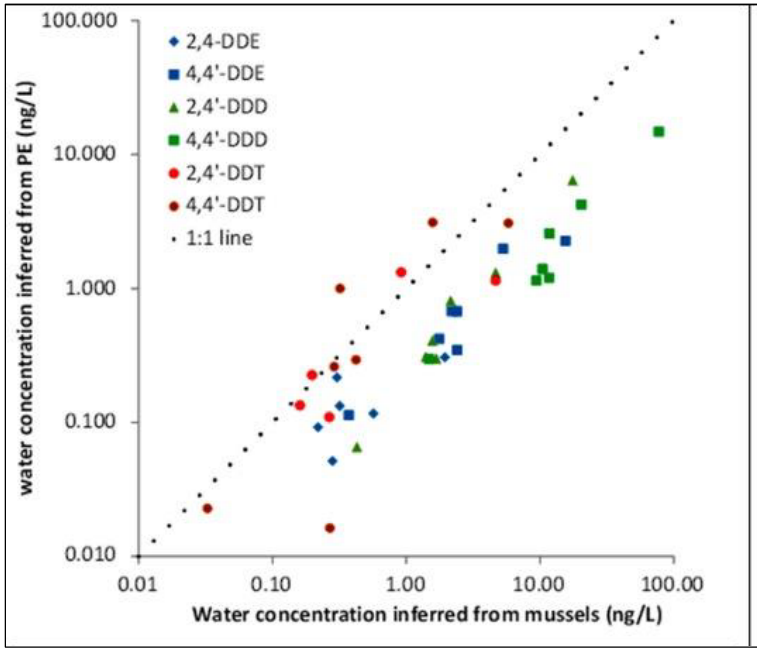
- Use fluxes in mass balance model to estimate surface water concentrations

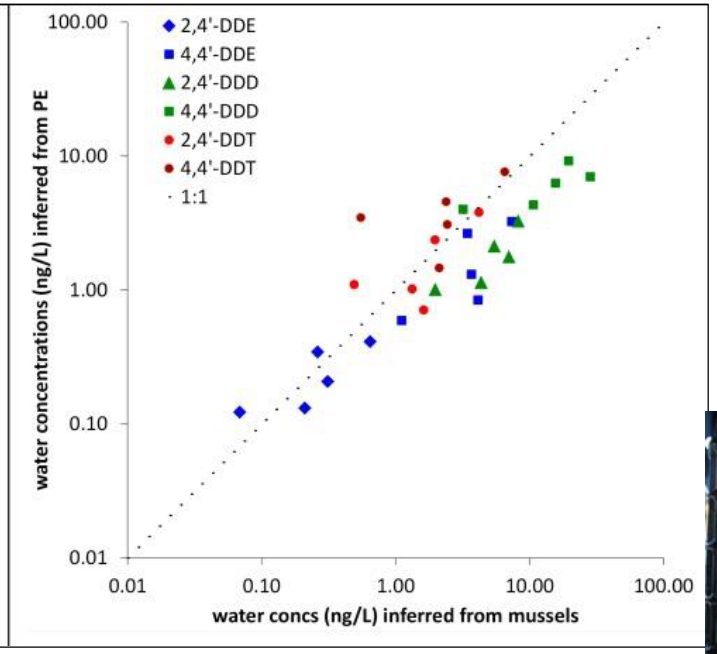


$$\text{Flux } (ng/m^2/day) = \frac{D_{water}\ (m^2/day) * (C_{pore\ water} - C_{bottom\ water})\ (ng/m^3)}{\text{boundary layer thickness } (m)}$$

Water Column Concentrations

- Use PE passive samplers (and mussels) to measure water column concentrations





- See good correspondence to mussels

Water Column Concentrations

- Do fluxes from sediments explain water column concentrations?

Measured water concs (pg/L) using PE (PRC corr'd) in fall 2013			Modelled water concs (pg/L) 2, 1, 0.5, 0.1 mm bbls	Model/Measure	Modelled water concs (pg/L) 10, 10, 0.1, 0.1 mm bbls	Model/Measure
	section 4					
4,4'-DDE			1660		2155	
4,4'-DDD			14708		13771	
4,4'-DDT			516		872	
	section 3					
4,4'-DDE	620		1229	1.98	2069	3.34
4,4'-DDD	5100		7564	1.48	12349	2.42
4,4'-DDT	290		432	1.49	855	2.95
	section 2					
4,4'-DDE	6600	2300	1040	0.23	1953	0.44
4,4'-DDD	35000	13000	4519	0.19	11151	0.46
4,4'-DDT	9600	7200	396	0.05	812	0.10
	section 1					
4,4'-DDE	2000	2700	821	0.35	1109	0.47
4,4'-DDD	4200	8500	2366	0.37	4467	0.70
4,4'-DDT	3100	4200	313	0.09	444	0.12

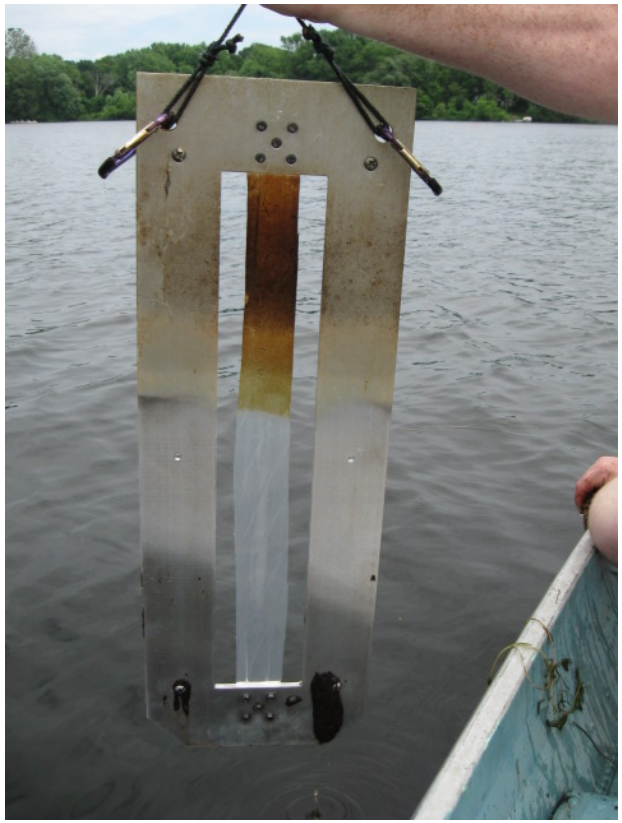
Too high

Too low

Need mid-channel input!

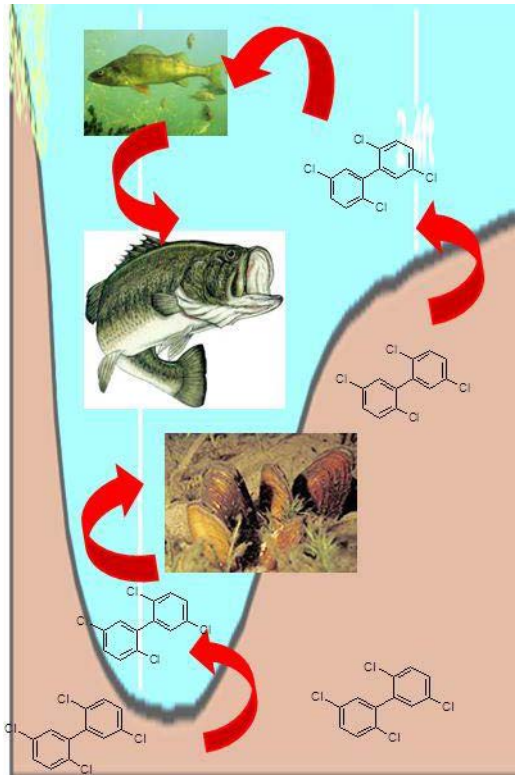
Case Study #3

- PCBs in a lake sediment
  1. Food web understanding
     - $C_{porewater}$
  2. Mapping contamination
     - $C_{sediment}$ vs. $C_{porewater}$
  3. Environ' system operation
     - Infiltration?

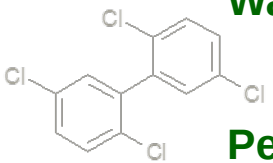


Case Study 3: PCBs in Lake Cochituate

- Typical risk assessment uses C_{water} and $C_{sediment}$



PCB #52 in finfish & shellfish living near PCB-contaminated lake sediments



Medium	Conc's
Water	non-detect
Perch	16 µg/kg
Bass	3 µg/kg
Mussels	7 µg/kg
Sediment	23 µg/kg

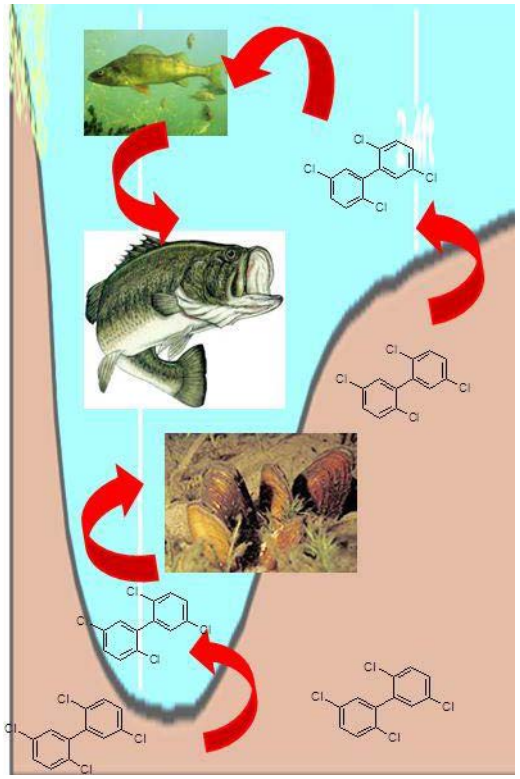
$?C_w/f_{lip}K_{lip}$

$?C_{sed}/f_{oc}K_{oc}$

Can do better with passive sampler data!

Case Study 3: PCBs in Lake Cochituate

- With PE, can relate water, pore water, organisms

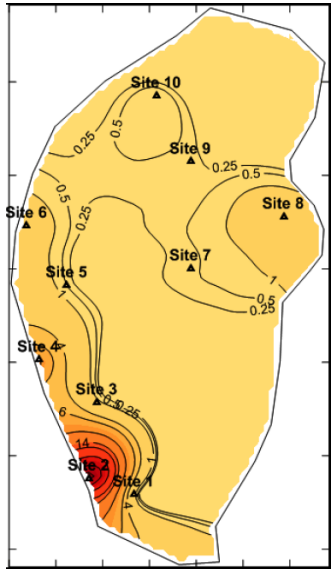


PCB #52	BEFORE Conc's	AFTER w/ PE SAMPLING eval' using "equil'd water conc"
Water	no detect	10 pg/L (via LDPE)
		w/ $C_{biota}/f_{lip}K_{lipw}$
Perch	16 ug/kg	9 pg/L
Bass	2.5 ug/kg	60 pg/L
Mussels	7.2 ug/kg	30 pg/L
Sediment	23 ug/kg	
w/ $K_d = f_{oc}K_{oc}$		5000 pg/$L_{porewater}$
via LDPE		400 pg/$L_{porewater}$

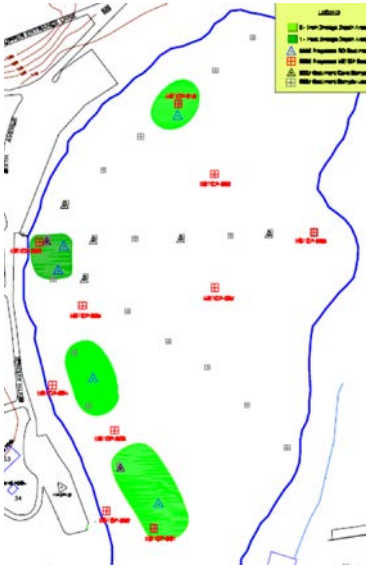
Contamination Mapping with $C_{porewater}$

- PCB congener (#101) concentrations (ng/L) using:

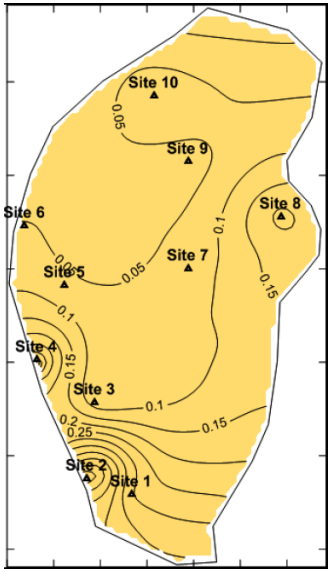
Sediment Data ($C_{sed}/f_{oc}K_{oc}$)



vs (C_{sed} basis)



PE data (*ex situ*) (C_{PE}/K_{PEw})

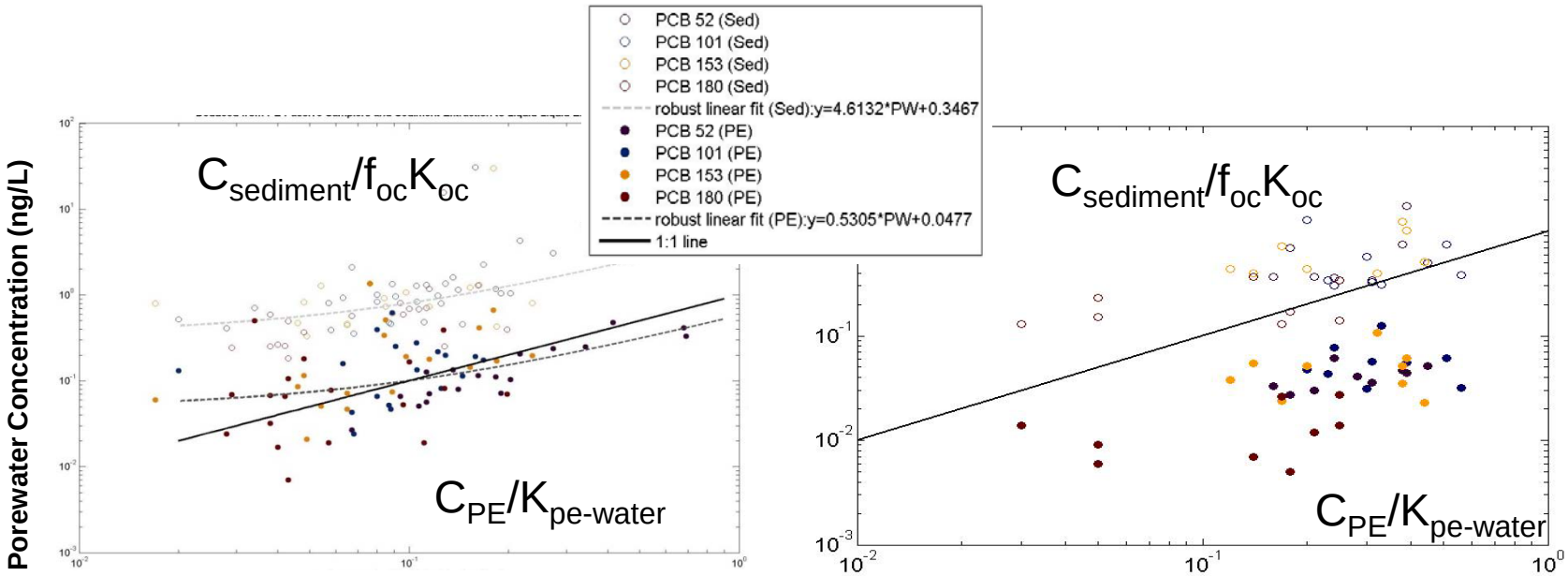


- Porewater conc's: $C_{sedimen}t / f_{oc}K_{oc}$ averages 20x higher than $C_{pe} / K_{pe\text{-}w}$
- Based on PE sampling, hotspots located near shore…sandy areas not previously sampled!

Ex Situ vs. *In Situ* PE Sampling

(E. Follett and J. Apell)

- *Ex Situ* PE (incubated in lab)
- *In Situ* PE (incubated in field)



Analysis of isolated pore water

Analysis of isolated pore water

Lower C_{PE}/K_{pew} for *in situ* than *ex situ*

=> Suspect Flushing

Cost Assessment (w/ ICF International)

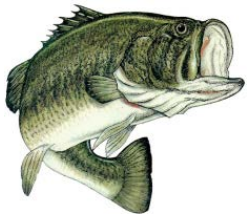
- 12 PE samplers vs. 12 (Ponar) sediment samplers

Cost Element	Ponar Dredge Sampling Technique Cost	PE Sampling Technique Cost	% Difference
Expendable Items	$169	$37	128%
Non-Expendable Items	$960	$948	1%
Field Labor	$1,530	$1,240	21%
Sample Shipment	$243	$104	80%
Total Field Cost	**$2,902**	**$2,330**	**22%**
Total Analytical Cost	**$10,080**	**$11,022**	**-9%**
Totals	**$12,982**	**$13,352**	**-3%**

- Note: assumes contract lab charges same for PE analysis as sediment analysis

Summary

1. Passive samplers yield more accurate porewater concentration data than estimates using $C_{sediment}/f_{oc}K_{oc}$
2. Passive samplers are good for mapping data ➡ enable "risk" assessment
3. Passive samplers enable bed-to-water flux estimates ➡ mass balances
4. Passive samplers: easy to use and safe



For additional information, please visit:
<https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Sediments/ER-200915>

Speaker Contacts:

email: pmgschwe@mit.edu

phone number: 617-253-1638

Extra Slides

Background

- $C_{sediment}/f_{oc}K_{oc}$ doesn't get pore water right!

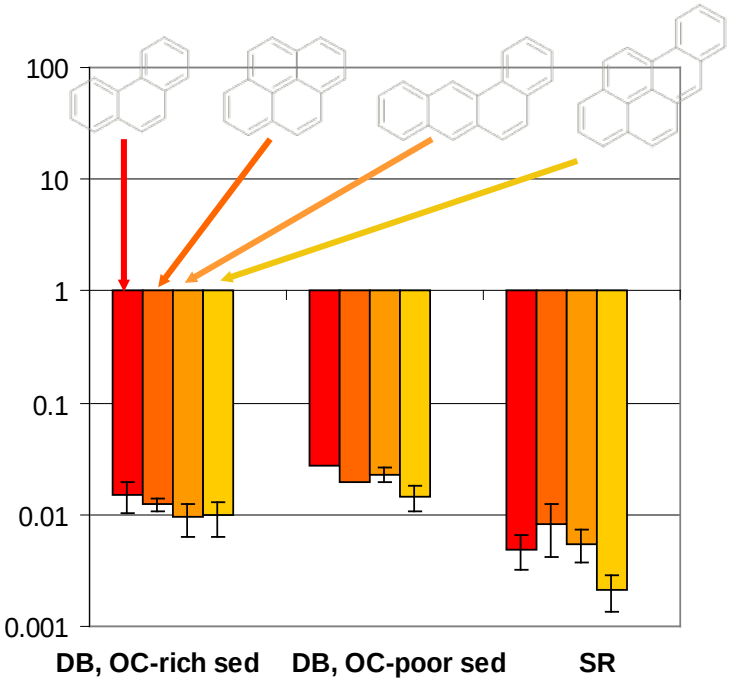
$C_{clam} = (f_{lip}K_{lip\text{-}w})$ **$C_{porewater}$** with **$C_{porewater}$** from $C_{sediment}/f_{oc}K_{oc}$

Ratios

Measure in clam

Divided by

Predicted in clam



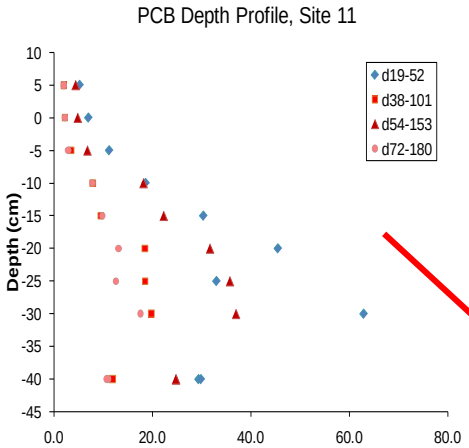
Sampling stations

- **Over-estimate bioavailability by ~ 100x**

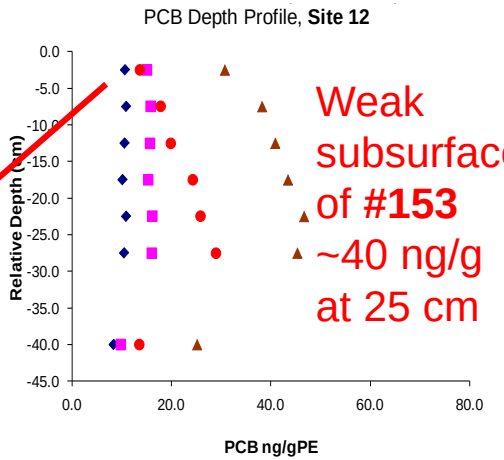
Lohmann et al., 2004

In Situ Sampling: Dec 2010 – Apr 2011

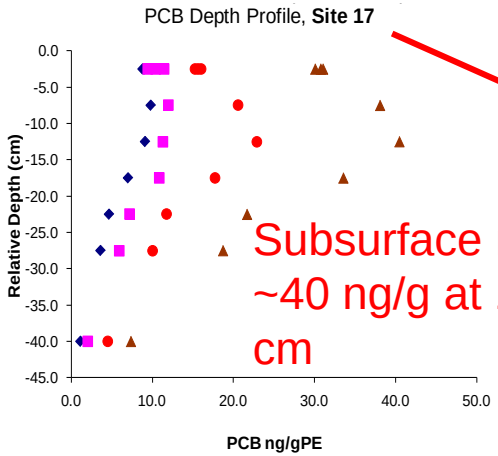
- Depths of contamination



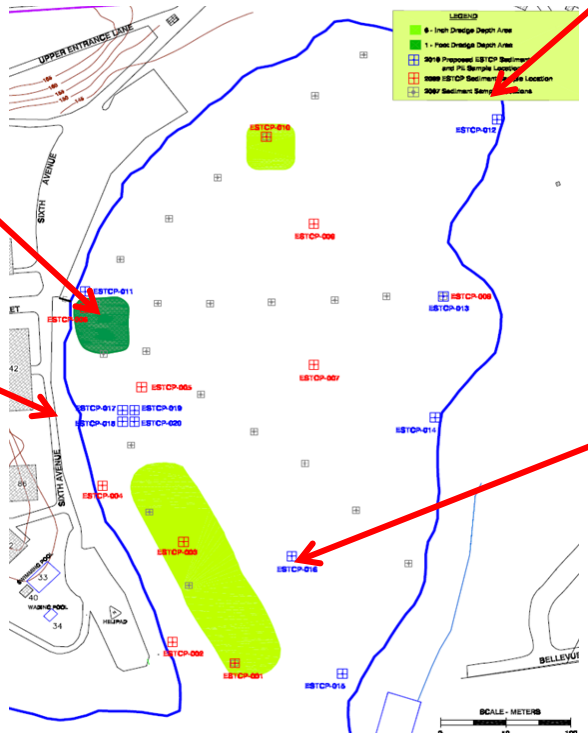
Strong subsurface max of #**52** at 30 cm

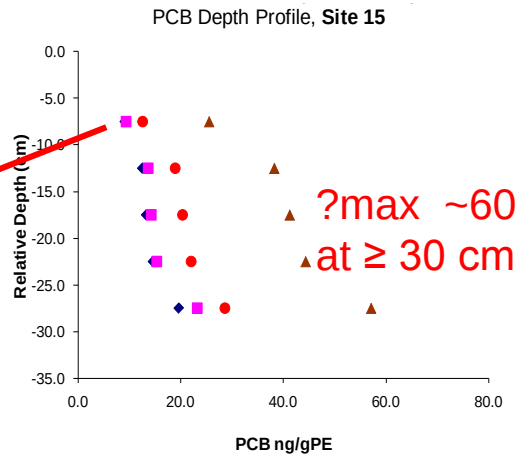


Weak subsurface max of #**153** ~40 ng/g at 25 cm



Subsurface max ~40 ng/g at 15 cm

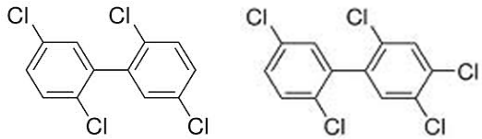


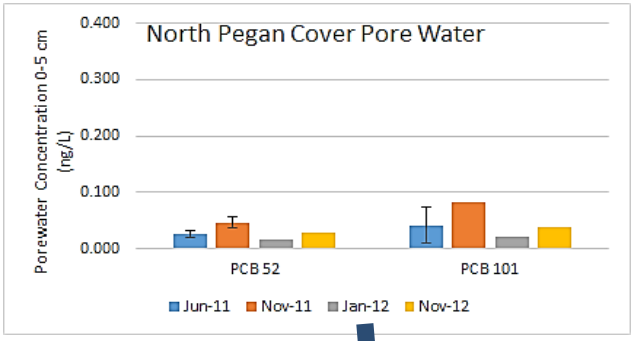


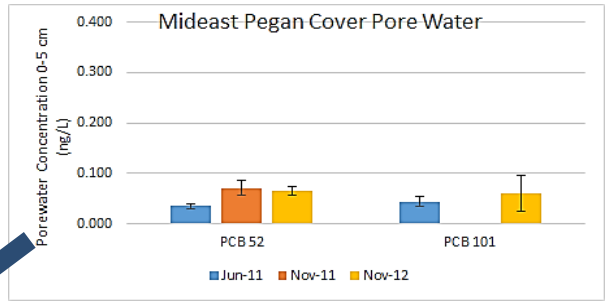
?max ~60 ng/g at ≥ 30 cm

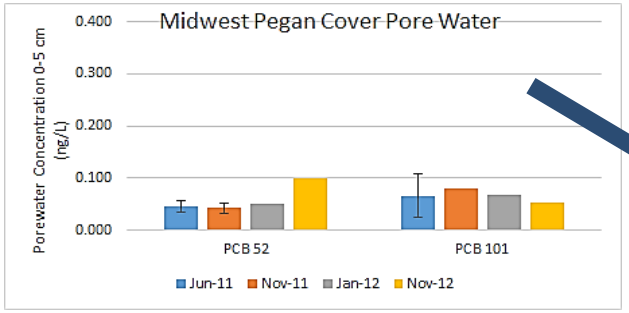
Monitoring

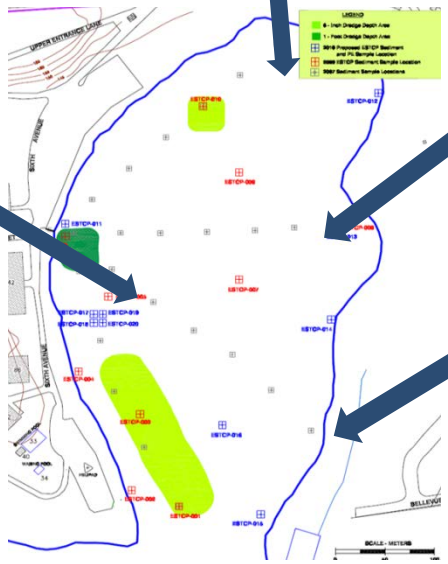
- Post-dredging/capping June 2011, Nov 2011 (5 mos), Jan 2012 (7 mos), Nov 2012 (15 mos)

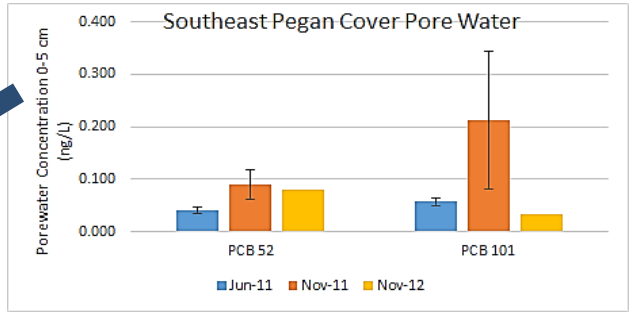






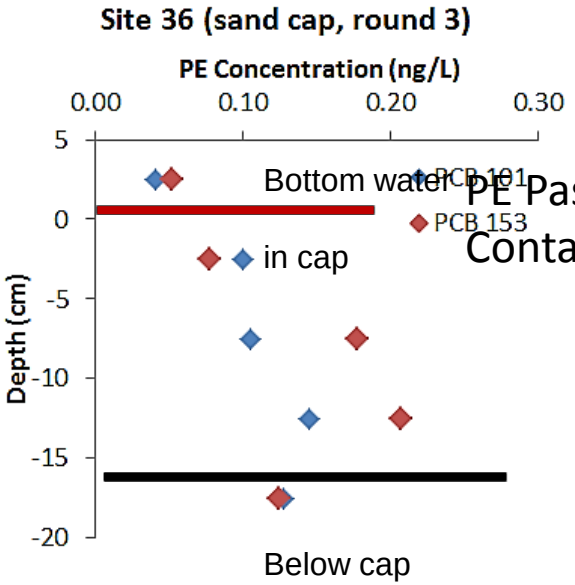




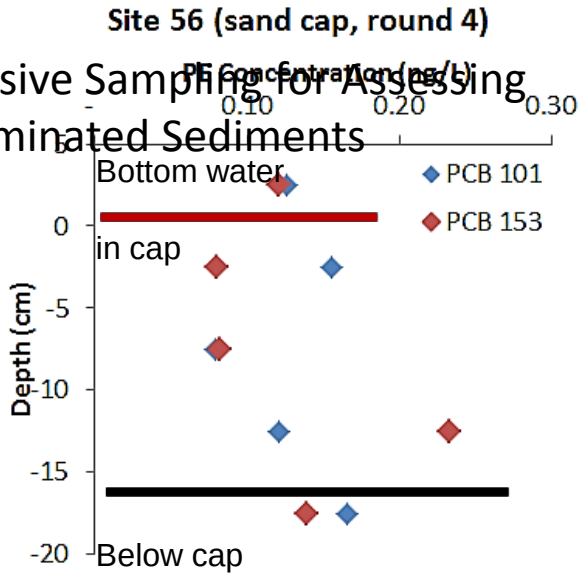


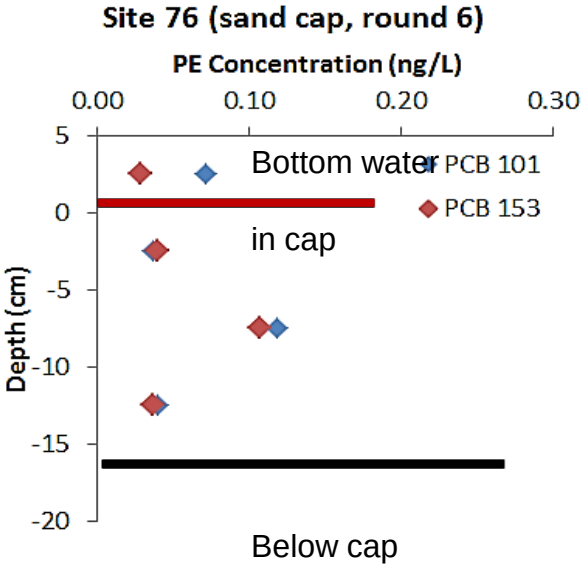
Monitoring

- Profiles through the cap



PE Passive Sampling for Assessing Contaminated Sediments

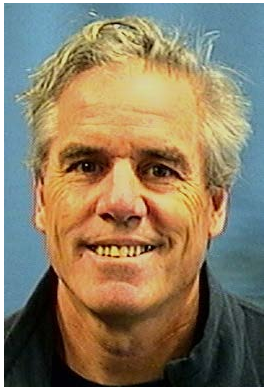




Q&A Session 1

An In-Situ Friction-Sound Probe for Mapping Particle Size at Contaminated Sediment Sites

Dr. Bart Chadwick
SPAWAR Systems Center Pacific



SERDP DOD • EPA • DOE | ESTCP

An In-Situ Friction-Sound Probe for Mapping Particle Size at Contaminated Sediment Sites

SERDP/ESTCP ER-200919

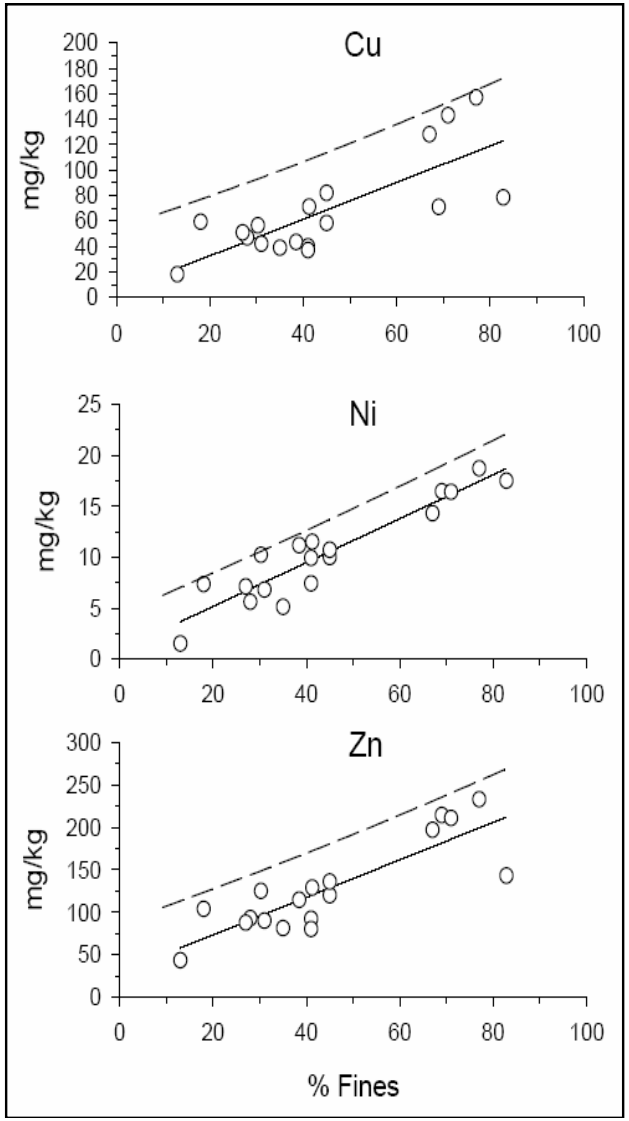
Bart Chadwick, SPAWAR Systems Center Pacific

Webinar Agenda

- Technology background
- Technology description
- Lab results
- Field application at DoD sites
- Conclusions

Technology Background

- DoD has a broad range of contaminated sediment sites
- Contamination in sediments partitions to fine grained particles
- Groundwater discharge of contaminants associated with course grained, permeable sediments
- Potential zones of contamination and groundwater discharge zones often readily identified by grain size analysis



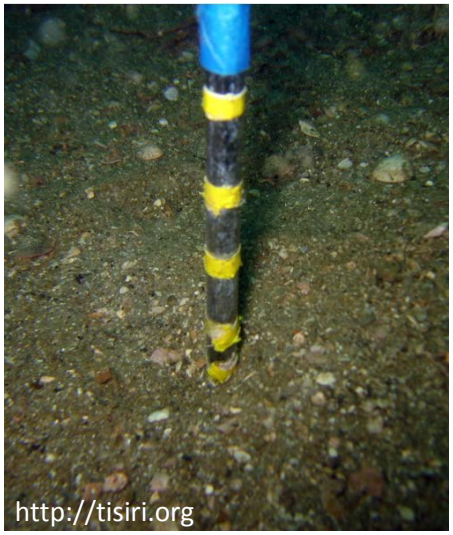
(SCCWRP & Navy, 2005)

Technology Background

- Traditional methods
  - Collect grabs or cores
  - Analyze by sieving and/or settling
- Requires field collection, manipulation, handling, shipping, and analysis
- Time consuming, costly and precludes adaptive sampling

Technology Background

- Low-tech sediment probing
  - Hand push small diameter rod into sediment
- Determine sediment type and thickness
- Based on qualitative “feel” and resistance
- Similar results from Trident Probe surveys



Technology Background

- Friction sound generated by motion of probe through the sediment
- Friction-sound intensity (I) is a function of the total displaced probe material

$$I \propto RL$$

where R is the particle radius and L is the length of the groove

- Friction sound intensity thus related to grain size and push velocity (Koomans, 2000)

From Koomans, 2000

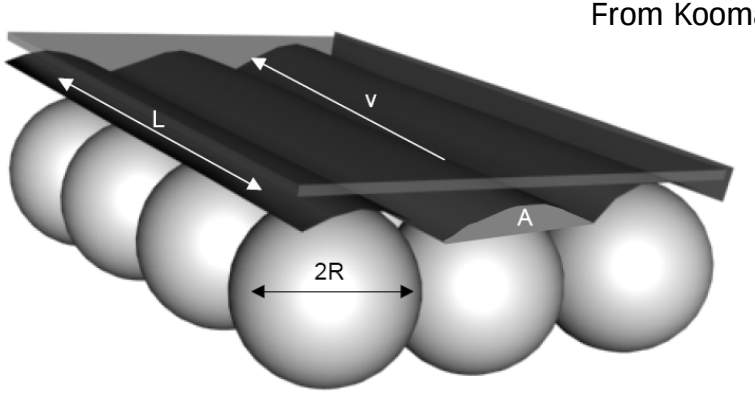
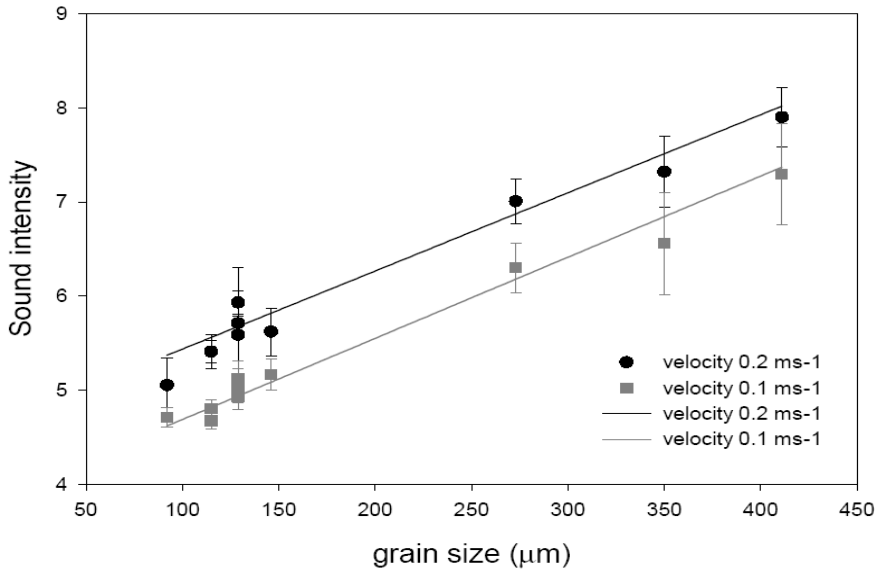
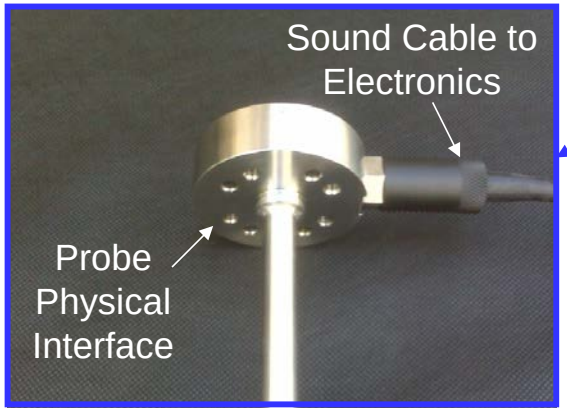


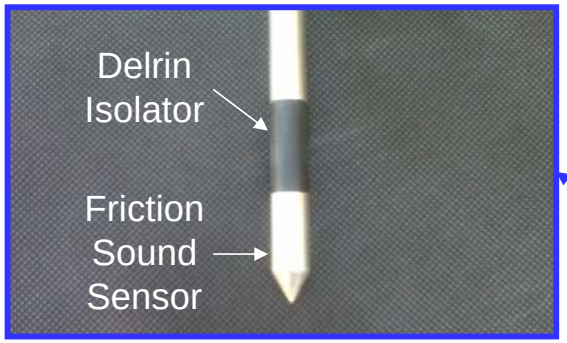
Figure 4.7: Schematic presentation of a parallel grooves, formed when a plate moves over sediment grains.

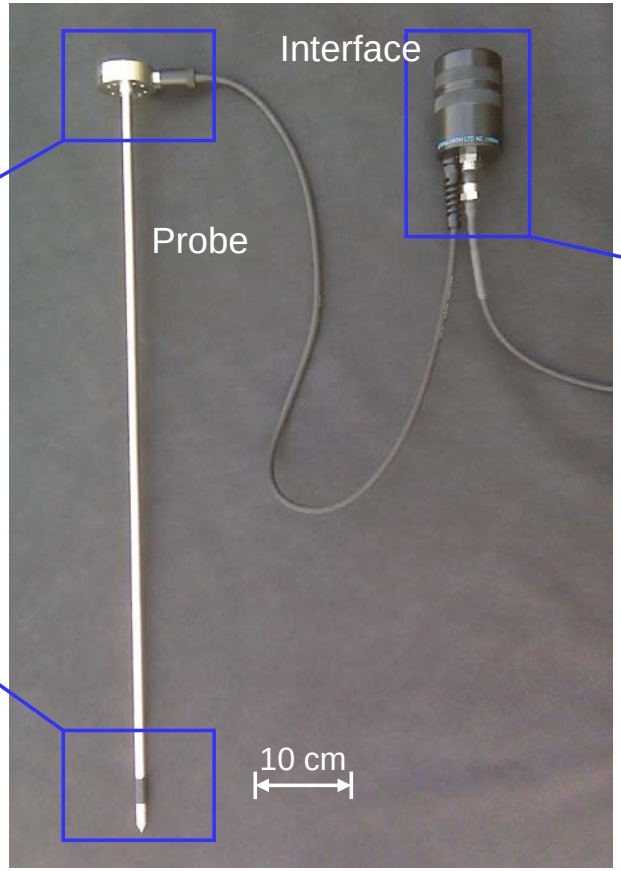


Technology Description – Probe

- Commercial prototype friction sound probe (Sed-FSP)
- Isolated microphone in tip of probe picks up friction sound
- Signal is filtered (~2KHz) and sound amplitude is recorded







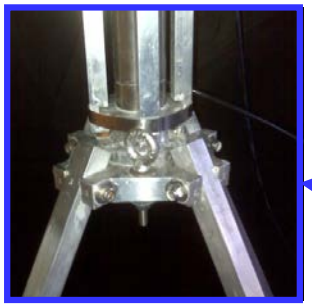
Electronics Interface

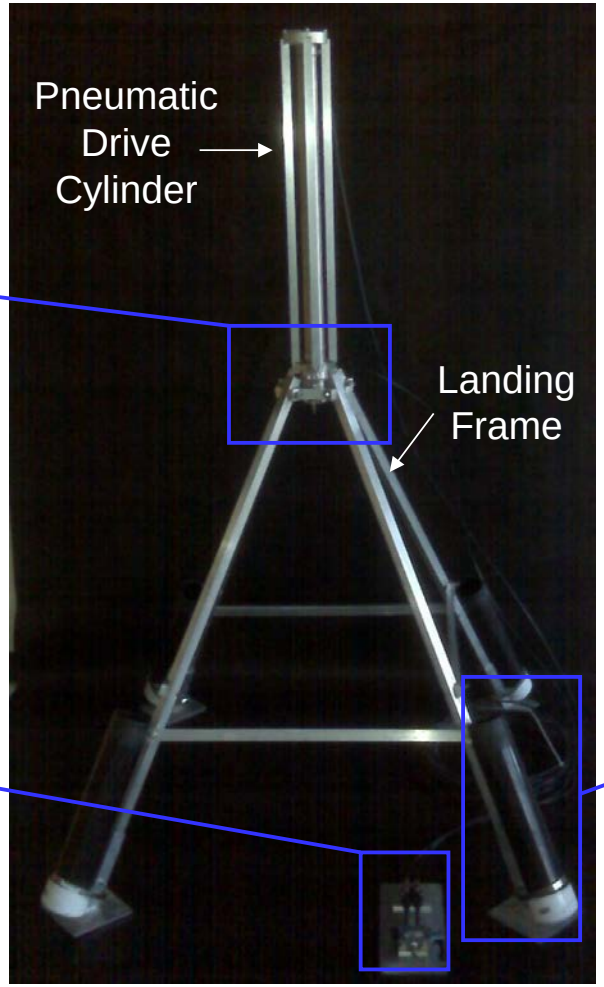
Software Interface

Technology Description – Drive System

- Pneumatic drive pushes the probe into the sediment
- Provides controlled, constant velocity push

Collapsible Frame





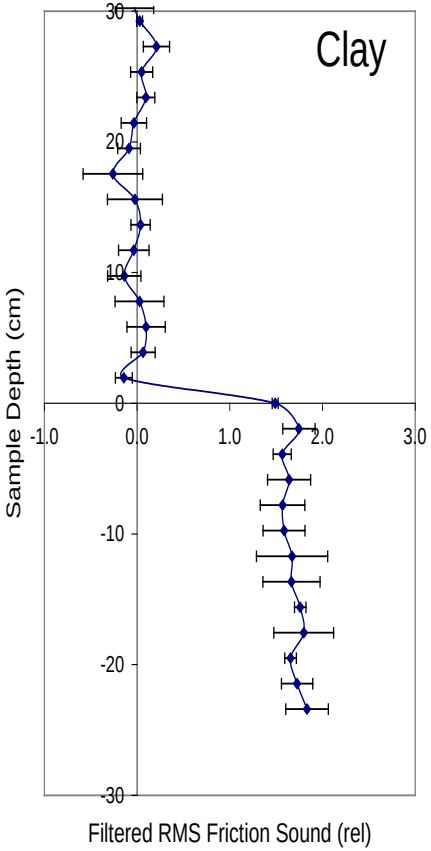
Isolation Bobbins

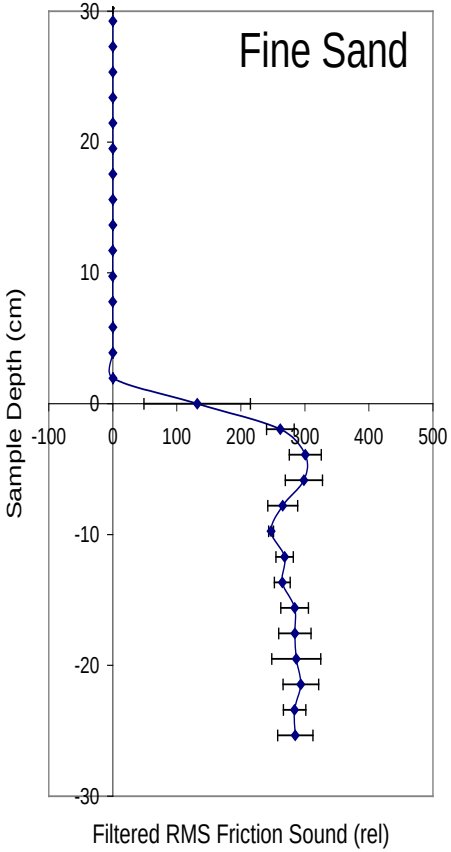
Control System

Reaction Weight Canisters

Lab Testing – Standard Sediments

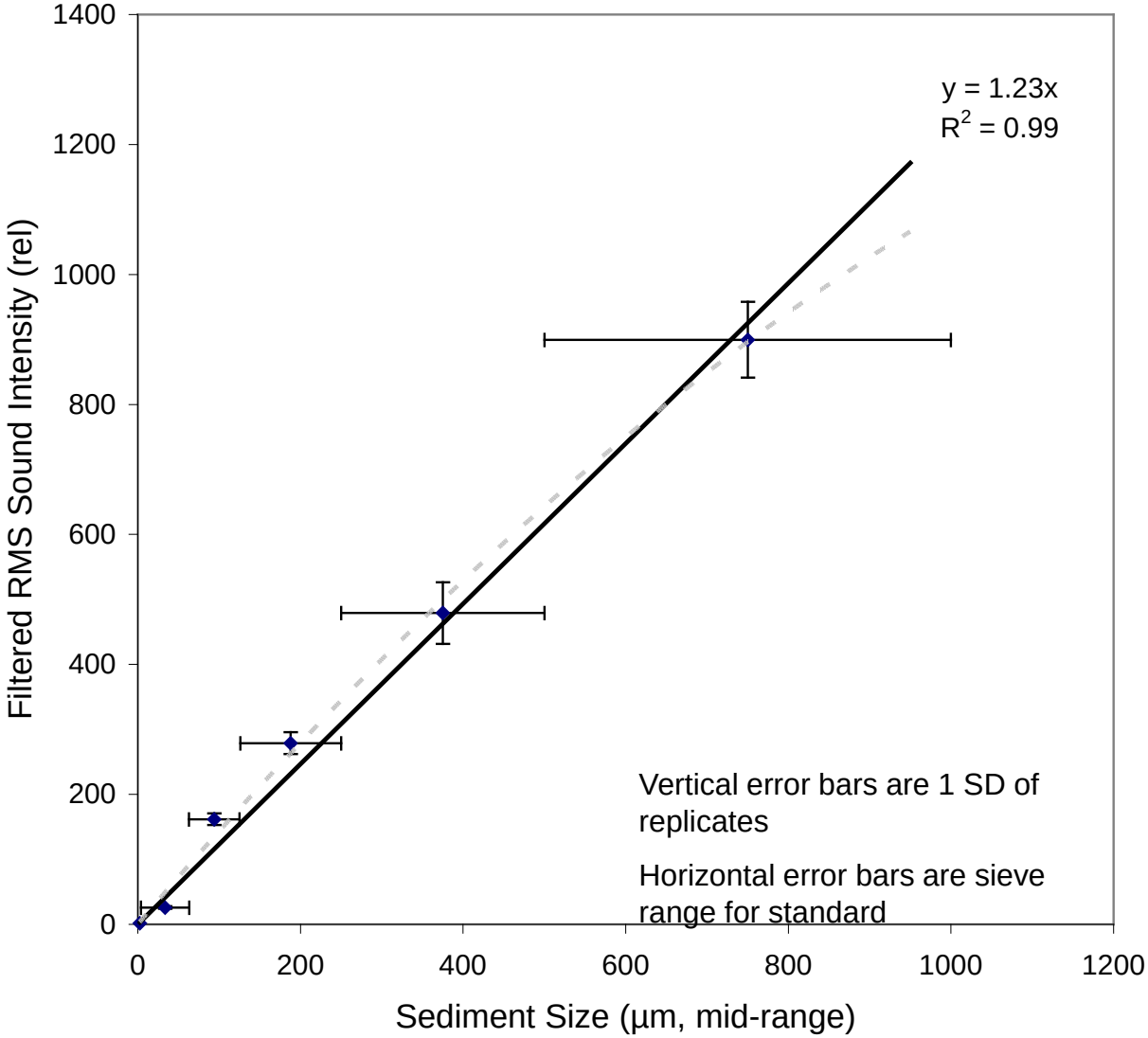
- Probe mounted to test rig on the wall
- ~25 cm push in 5 gallon buckets
- Replicate probe push in 6 standard sediments





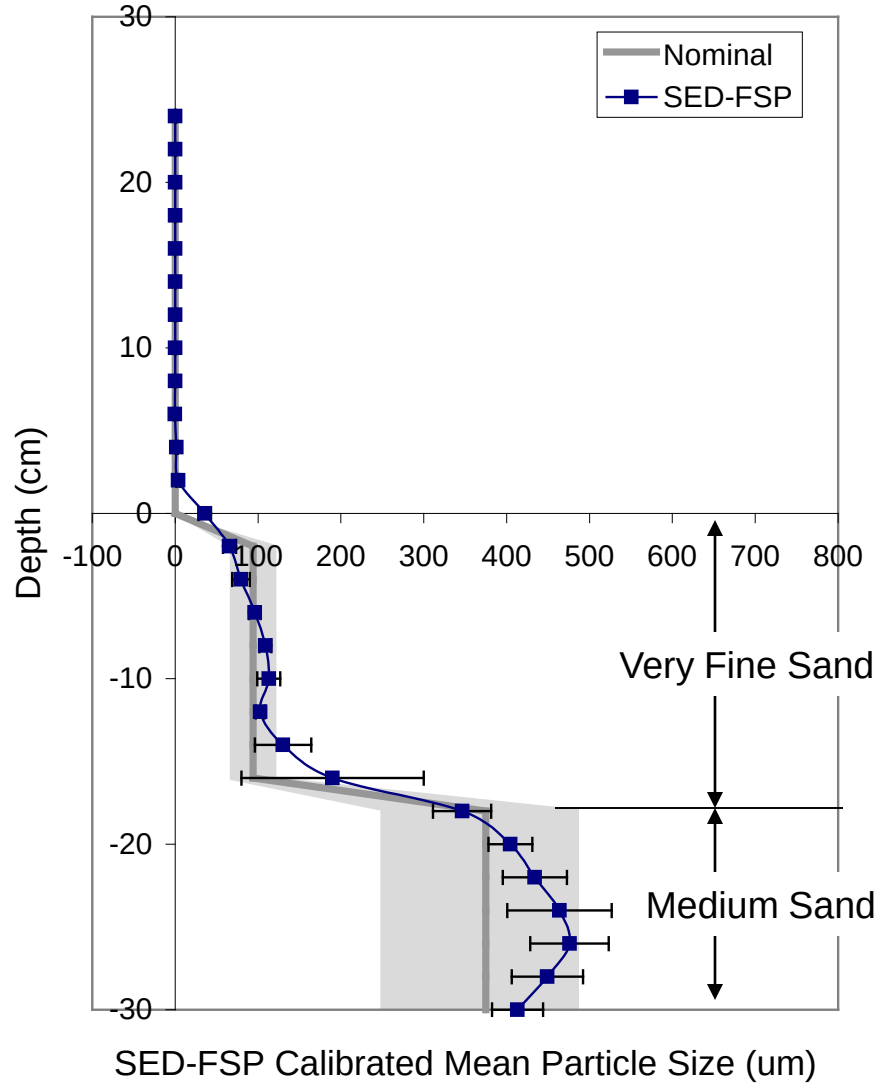
Lab Testing – Standard Sediments

- Expected increase in friction sound with particle size
- Clay to coarse sand range
- Near linear response over 3 orders of magnitude in size



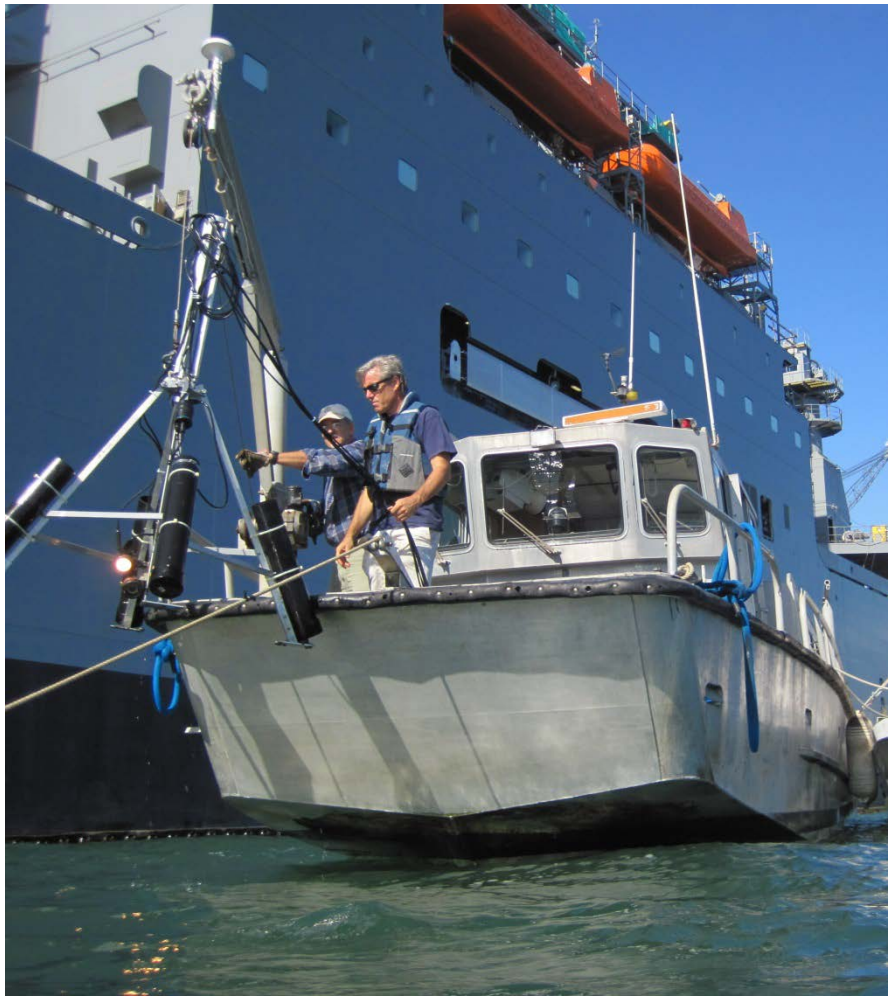
Lab Testing – Vertical Profiling

- Two layer stratified standard samples
- Replicate pushes through the upper layer and into underlying
- Calibrated based on standards relationship



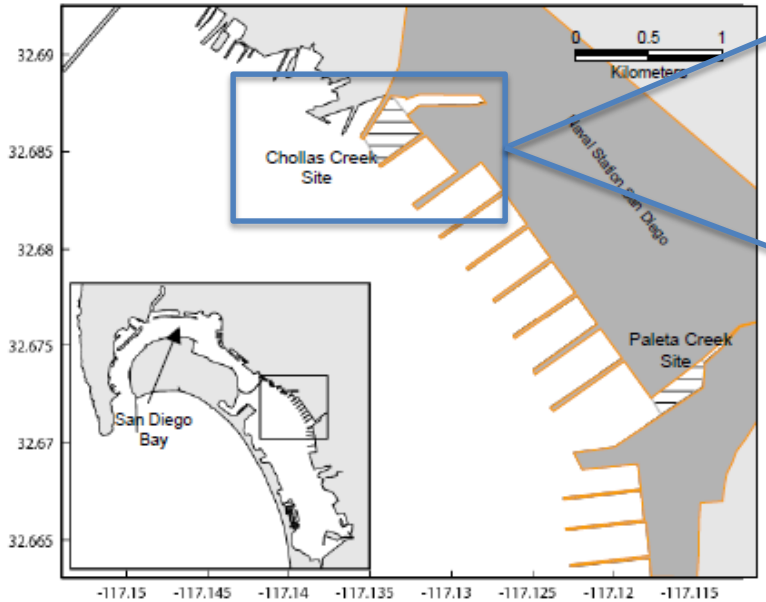
Field Demonstrations

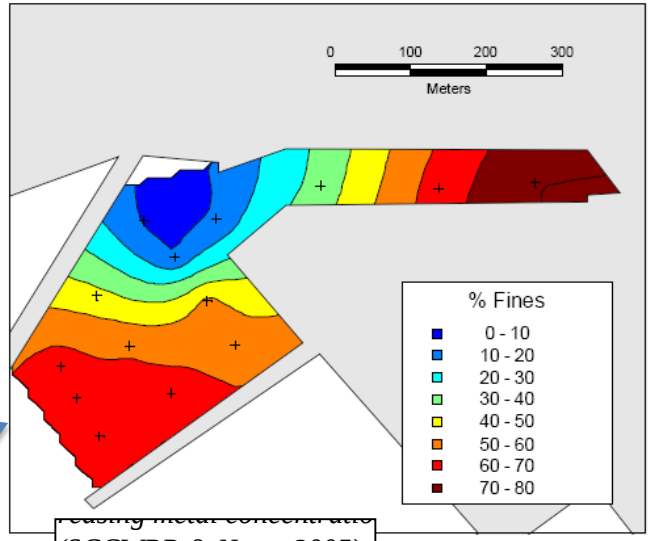
- Naval Base San Diego
  - Chollas Creek contaminated sediment TMDL site
- Naval Base Coronado
  - Site 9 groundwater VOC discharge to surface water
- Washington Navy Yard
  - Anacostia River pilot thin layer capping site



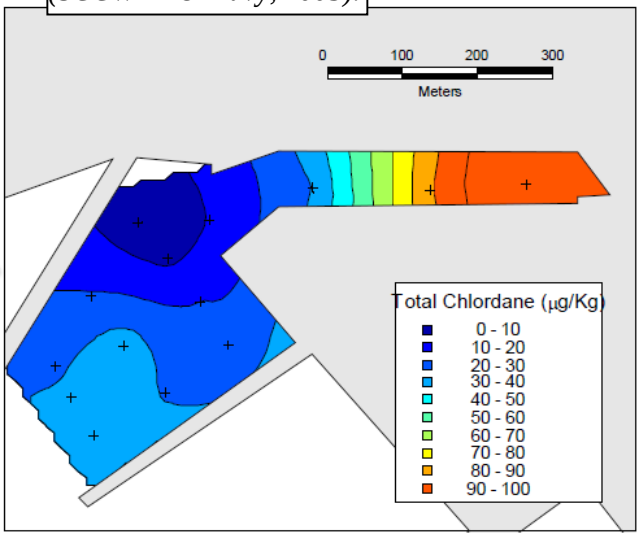
Field Demo – NBSD Chollas Creek

- Contaminated sediment site at mouth of urban creek in San Diego Bay
- Ongoing TMDL characterization studies
- Primary drivers are pesticides, also metals and PAHs
- Contamination zones related to fines distribution – physical effects





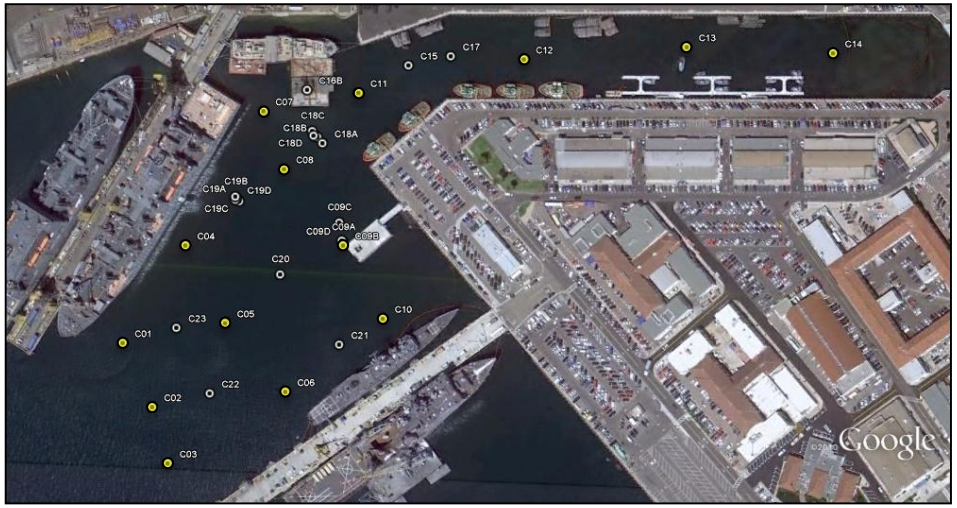
(SCCWRP & Navy, 2005).



Field Demo

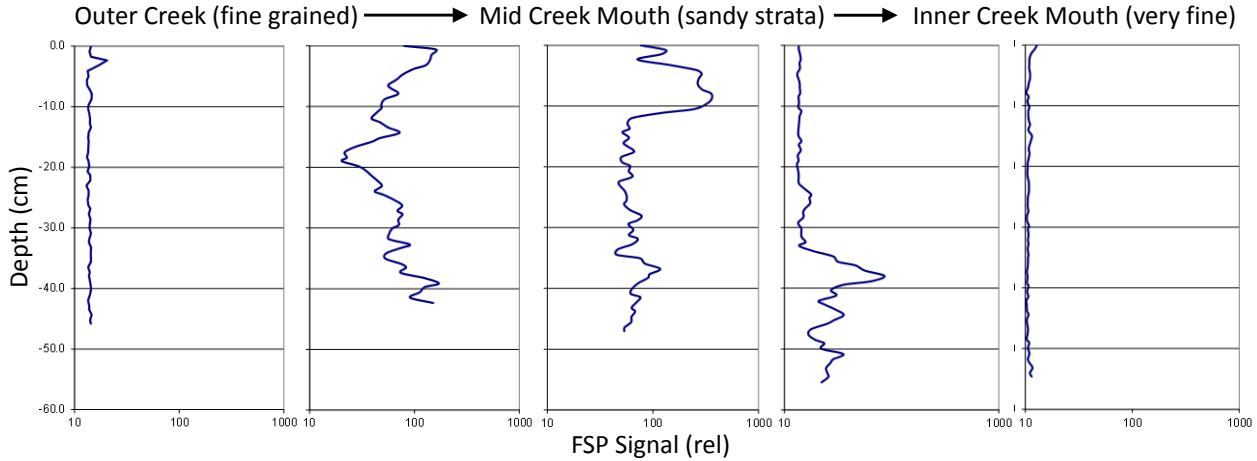
NBSD Chollas Creek

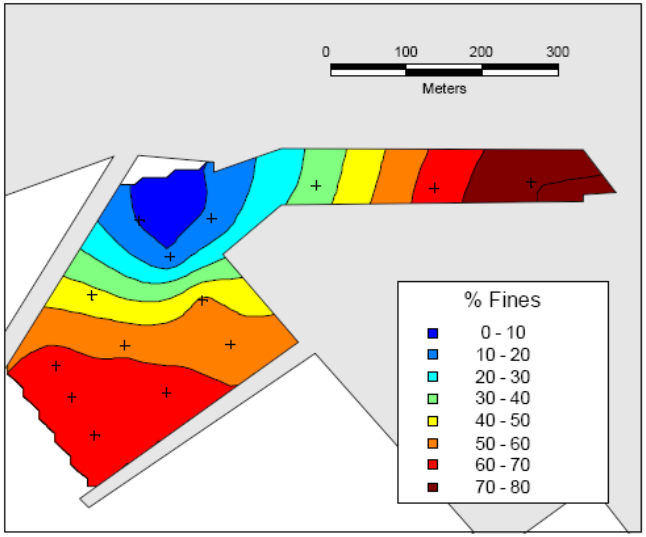
- Re-occupy original 14 TMDL + 9 intermediate stations
- FSP profiles to ~20” bgs
- Cores collected directly adjacent to push location
- Top 6” of cores homogenized and subsampled for PSD analysis
- FSP data averaged over top 6” of profile and compared to PSD results



Field Demo – NBSD Chollas Creek

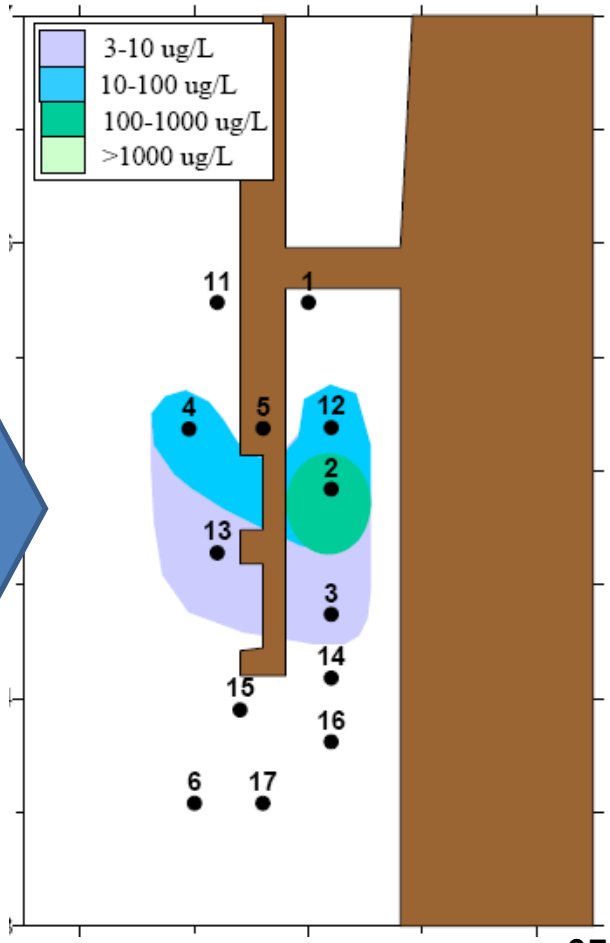
- Clear variations across site
- Site-specific calibration
- Comparable to historical (2001) data





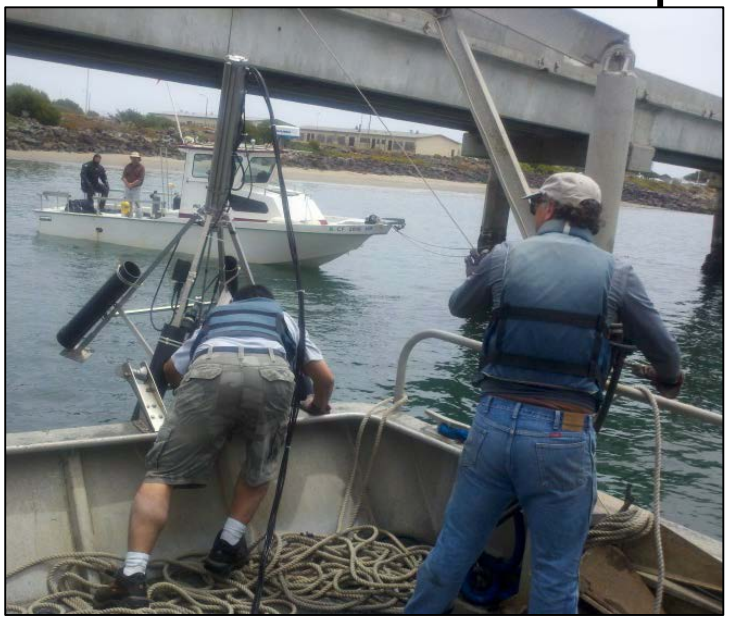
Field Demonstration – NBC Site 9

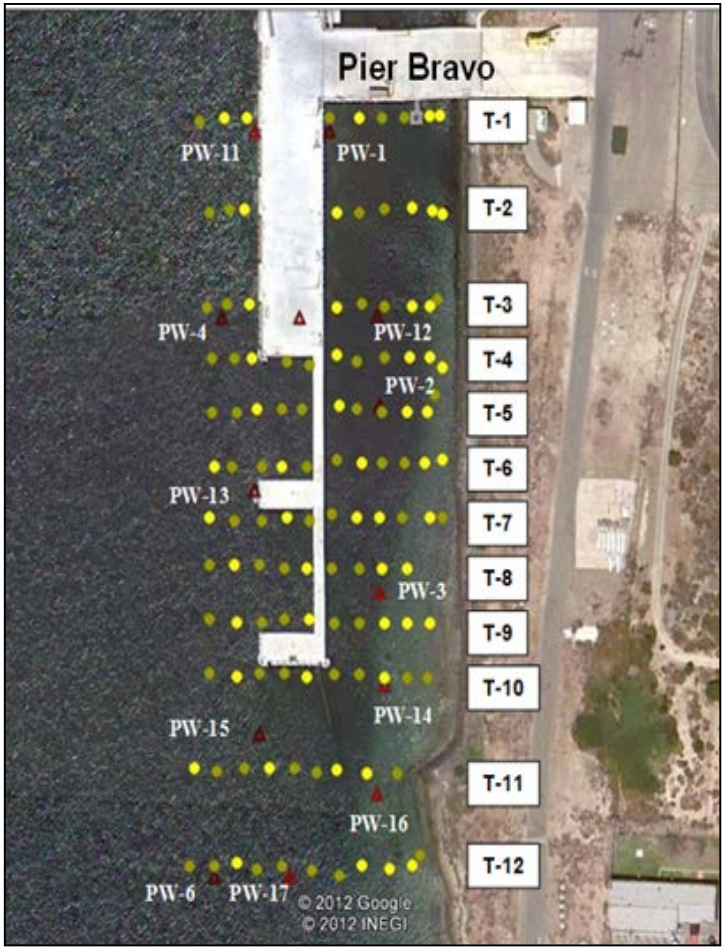
- Groundwater-surface water interaction (GSI) site
- VOCs potentially discharging to San Diego Bay
- Identify potential GSI pathways based on coarse-grained permeable sediments



Field Demonstration – NBC Site 9

- SED-FSP profiles collected at 116 stations
- Validation cores collected at 27 stations with replicates at three locations
- Profiles averaged over 6” strata to create four depth maps

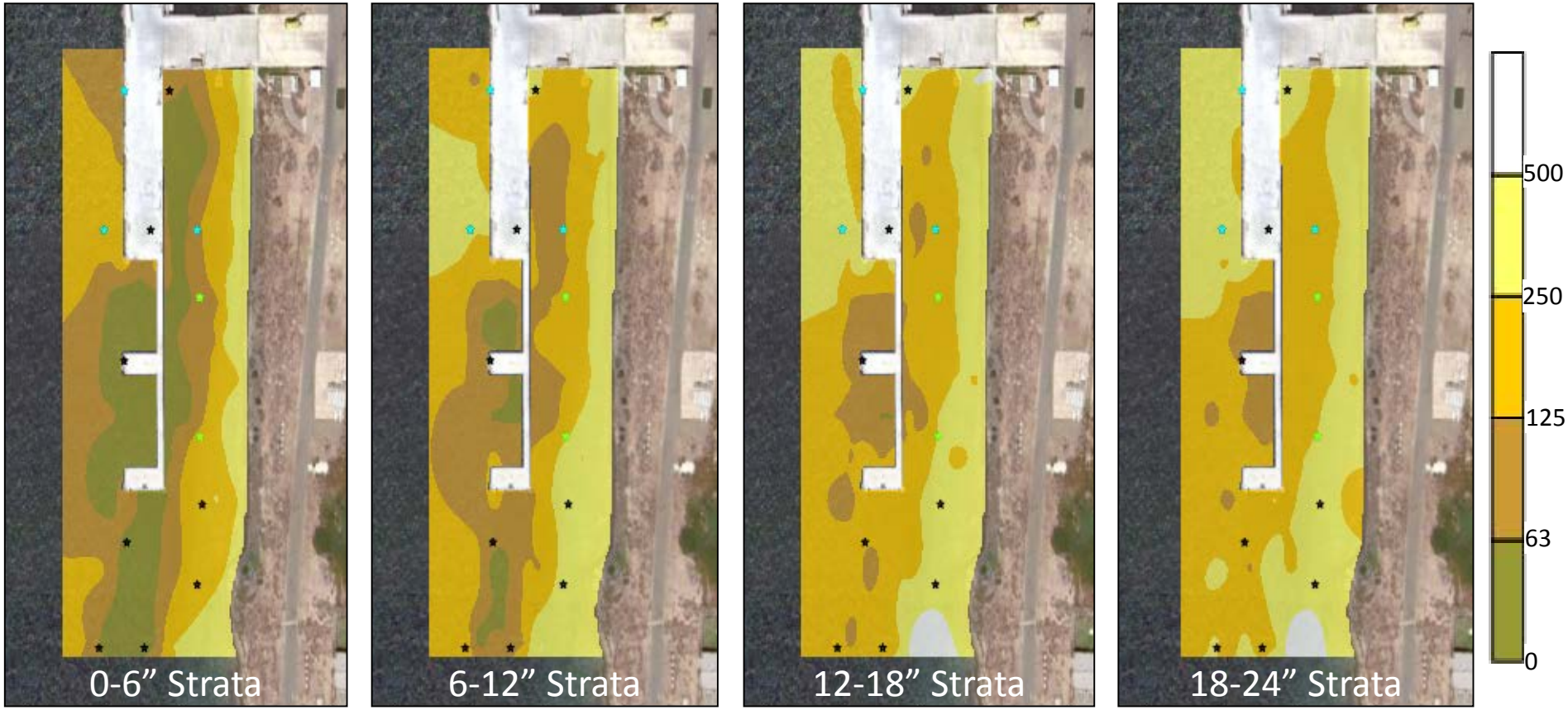




Field Demonstration – NBC Site 9

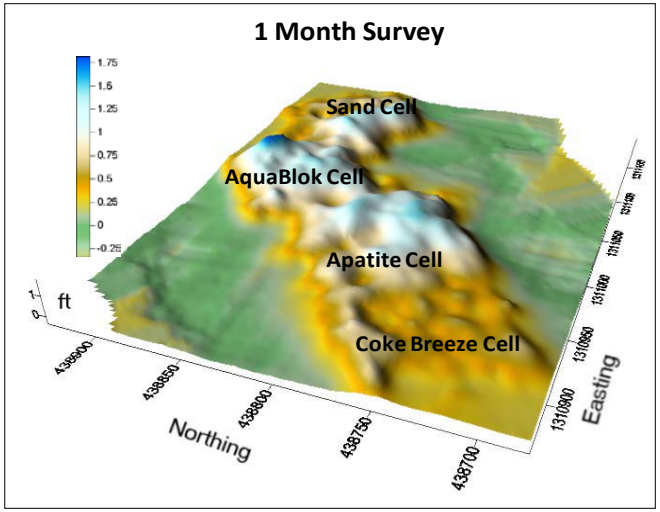
- Results show fine-grained sediments at surface and near pier
- Suggest preferential GSI discharge pathways inshore and offshore of pier

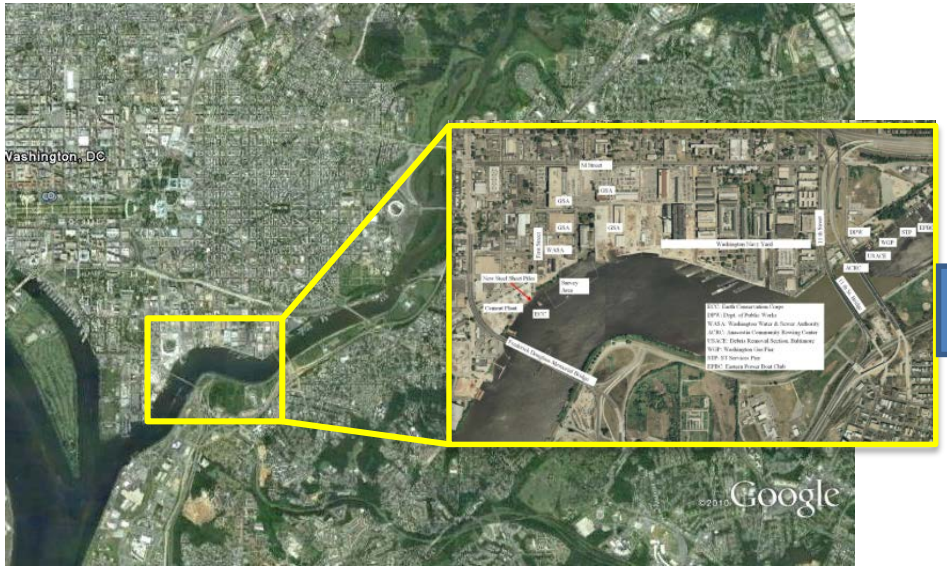
Calibrated Mean Particle Size (um)

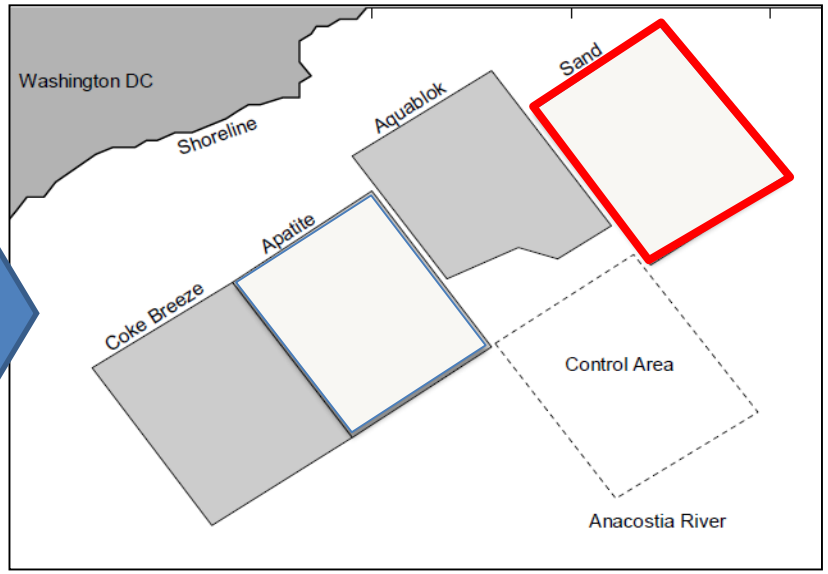


Field Demo – Anacostia Pilot Cap

- Reactive capping test site, includes reactive, sand and control caps
- Profile through sand cap
- Characterize cap thickness and mixing of cap material

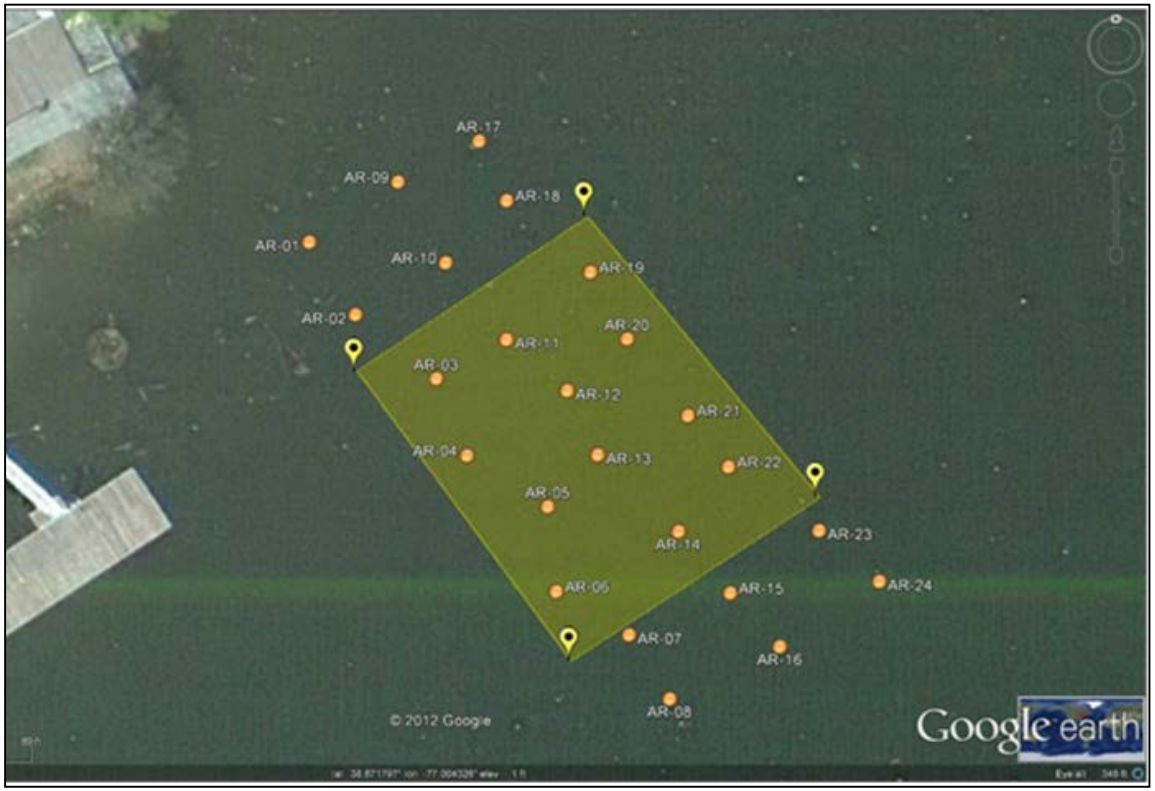






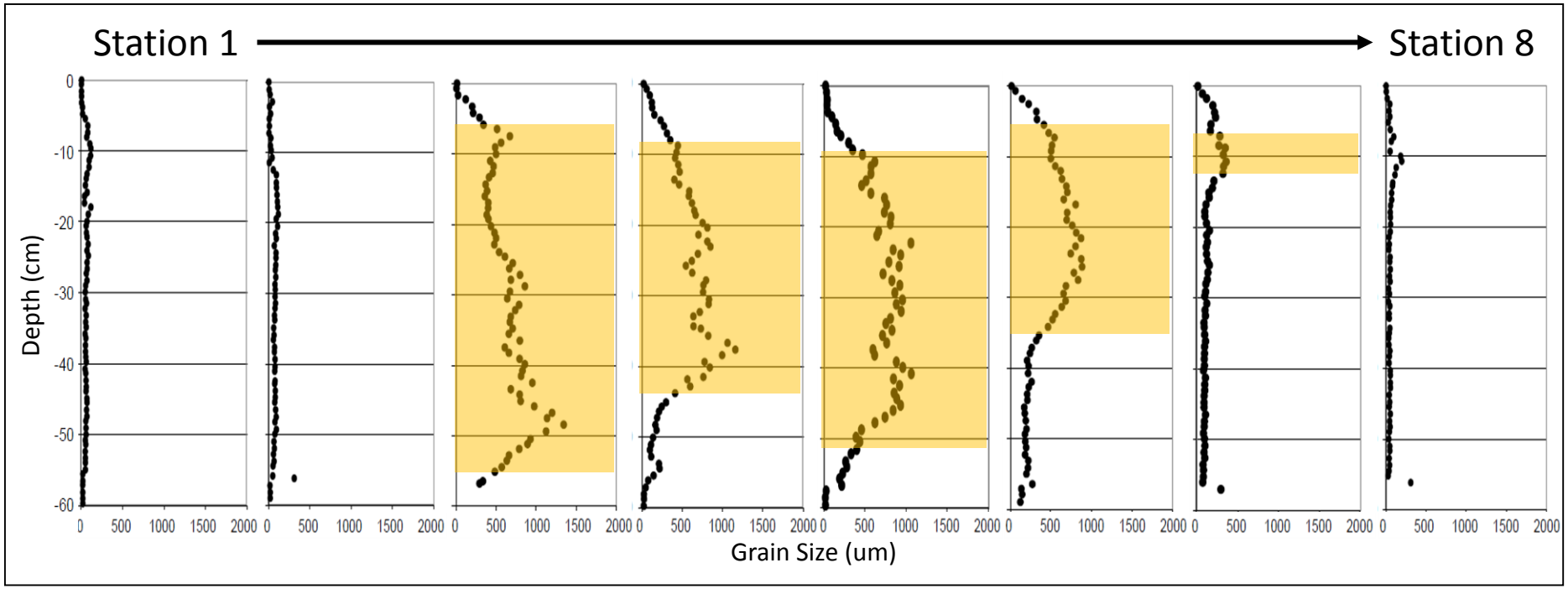
Field Demo – Anacostia Pilot Cap

- SED-FSP profiles collected at 24 stations including 12 on-cap and 12 off-cap
- Validation cores collected at 11 on-cap and 2 off cap locations
- Cores were segmented a regular intervals for analysis



Field Demo – Anacostia Pilot Cap

- Results clearly show the presence and thickness of the sand cap
- Minimal cap material detected in off cap locations
- Illustrates mixed layers and new deposition

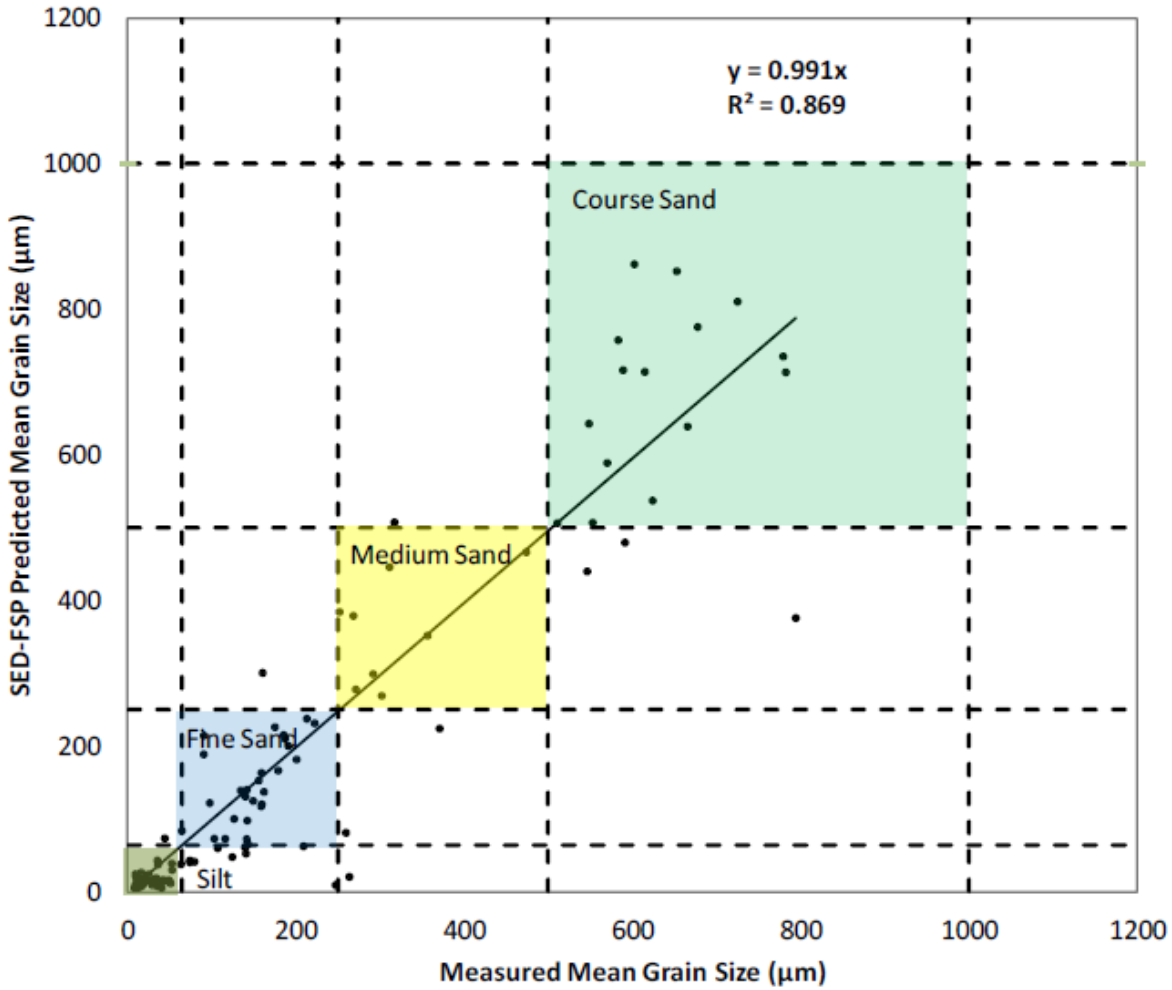


Field Demo – Anacostia Pilot Cap

- Demonstrates capability to rapidly map cap thickness for thin-layer caps

FSP Performance

- Results combined across three demonstrations
- Incorporate site-specific calibration
- Spanned silt and sand range, no field samples in clay range



FSP Performance

- FSP performance met targets for reliability, efficiency and specificity
  - Reliability = % correct out of total
  - Efficiency = % correct out of total predicted for that class
  - Specificity = % correct out of total stations in that class

Target Criteria	Measured Criteria				
	Description			No. Stations	Result
Reliability - 80%	Reliability		Correctly predicted stations.	103	92%
			Total stations.	112	
Efficiency - 80%	Efficiency	Silt	Correctly predicted silt stations.	39	85%
			Total predicted silt stations.	46	
		Sand	Correctly predicted sand stations.	64	97%
			Total predicted sand stations.	66	
Specificity - 80%	Specificity	Silt	Correctly predicted silt stations.	39	95%
			Total silt stations. (ASTM)	41	
		Sand	Correctly predicted sand stations.	64	90%
			Total sand stations. (ASTM)	71	

Conclusions

- The Sediment Friction Sound Probe is a new technology for screening particle size
- Provides a capability for rapid, in-situ mapping and profiling of mean particle size
- Enables rapid screening of potential contaminated sediment zones and preferential groundwater discharge zones
- Enables detailed evaluation of cap thickness, mixing and new deposition
- Addresses the DoD defined need for:

  "… rapid, inexpensive, and standardized assessment tools to measure the rates and magnitude of the fundamental contaminant fate and transport processes in order to adequately develop and refine a conceptual site model."

For additional information, please visit:
https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Sediments/ER-200919

Speaker Contact:
bart.chadwick@navy.mil; 619-553-5333

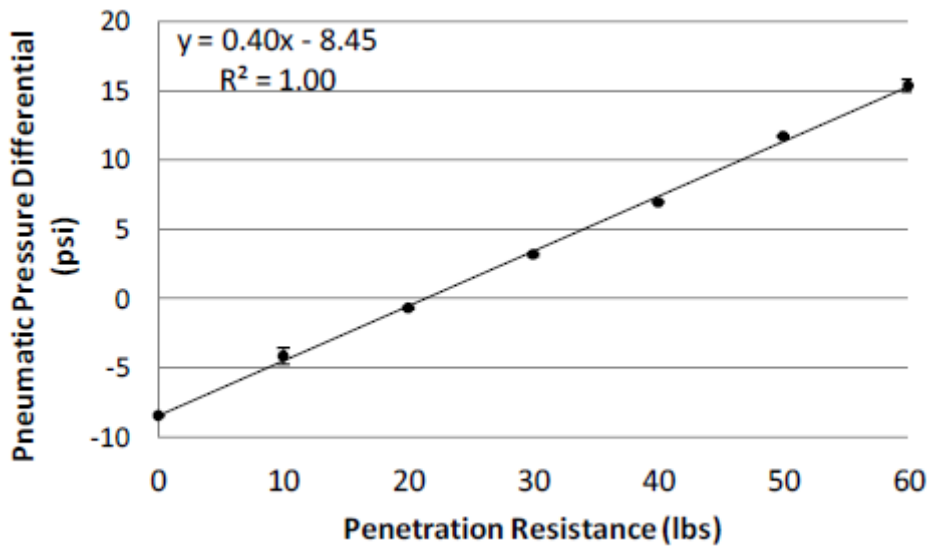
Backup Slides

Cost Summary

Estimate of Initial Cost for Capital and Ancillary Equipment			
Item			Initial Cost
SED-FSP			$ 5,000
Ancillary - Air Compressor/Supply			$ 500
Ancillary - Field Computer			$ 500
Ancillary - Drive System			$ 4,000
		Total SED-FSP	$ 10,000
Equipment Replacement Cost Estimate			
Inflation Rate	*4%*		
	Years of Use		
	0	5	10
SED-FSP & Ancillary Replacement	$ 10,000	$ 12,000	$ 14,000
Estimated Rental Rate Including Inflation and Maintenance			
Maintenance Rate	*5%*		
SED-FSP & Ancillary		Years of use	
	Uses/year	5	10
	10	$ 252	$ 147
	20	$ 126	$ 74
	30	$ 84	$ 49
	40	$ 63	$ 37
	50	$ 50	$ 29
Estimated Rental Rates (per/day)			
SED-FSP			$ 50
Ancillary - Air Compressor/Supply			$ 25
Ancillary - Field Computer			$ 25
Ancillary - Drive System			$ 50
		Total SED-FSP	**$ 150**

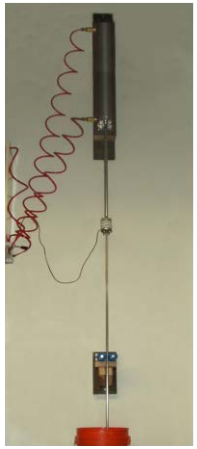
Push Resistance

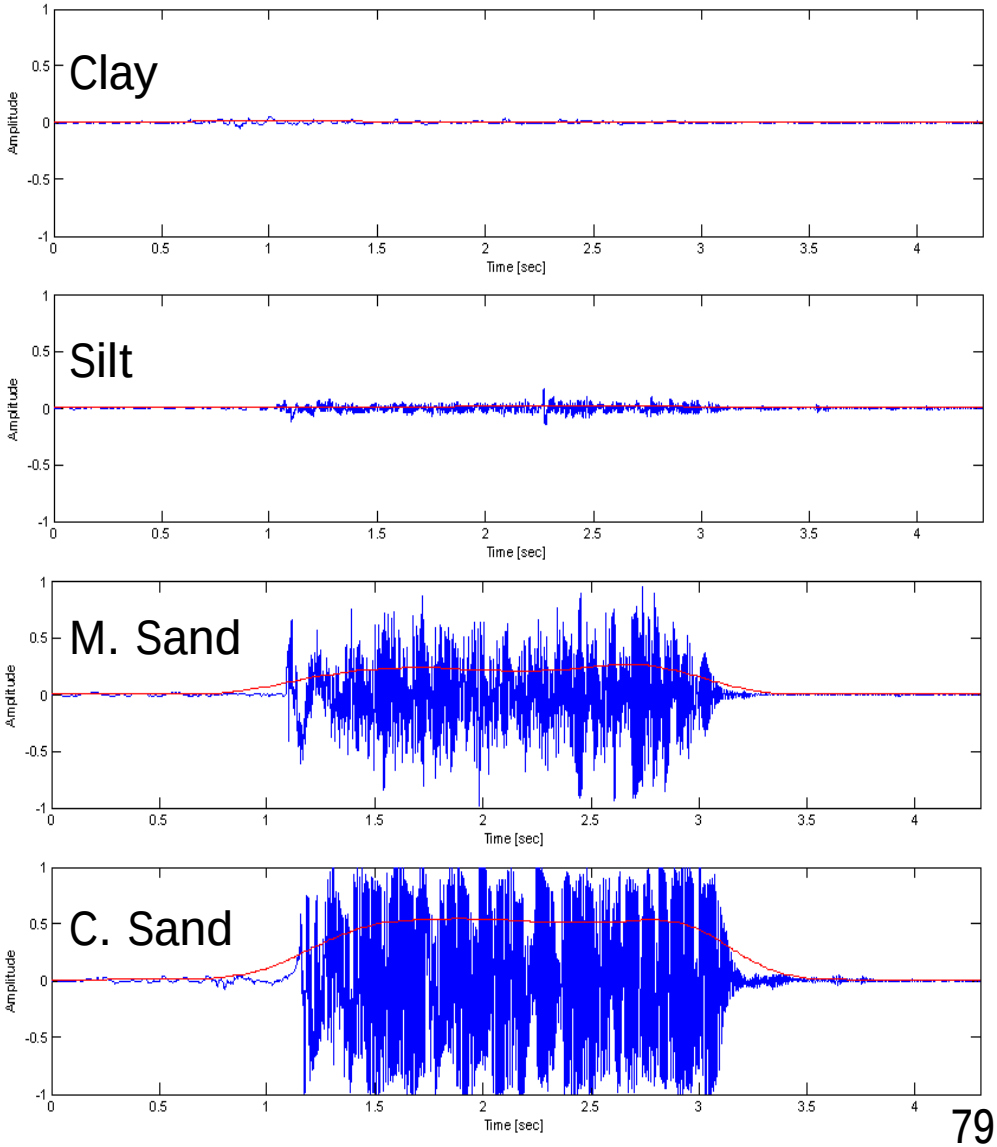
- Added feature at end of project
- Still needs refinement
- Provides insight into effects of compaction



Sounds of Sediment

- Laboratory push tests in different sediments
- Amplitude varies with particle size
- Frequency spectra may bring additional insight
- Sounds recorded for representative pushes





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  - Brian Gordon/Len Sinfield: NBSD Chollas Creek
  - Michael Pound: NBC Site 9

References

- Southern California Coastal Water Research Project (SCCWRP) and US Navy, 2005. Sediment assessment study for the mouths of Chollas and Paleta Creeks, San Diego, Phase I Final Report, A joint study funded by the San Diego Regional Water Quality Control Board and Commander Navy Region Southwest
- Koomans, R.L. 2000. Sand in motion - Effects of density and grain size, PhD Thesis, University of Groningen, Netherlands

Q&A Session 2

The next webinar is on December 4

The Roles Efficient Tar Management and Rotary Kiln Gasification for Base Camps as Options for Waste to Energy

http://www.serdp-estcp.org/Tools-and-Training/Webinar-Series/12-04-2014

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Survey Reminder

Please take a moment to complete the survey that will pop up on your screen when the webinar ends

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