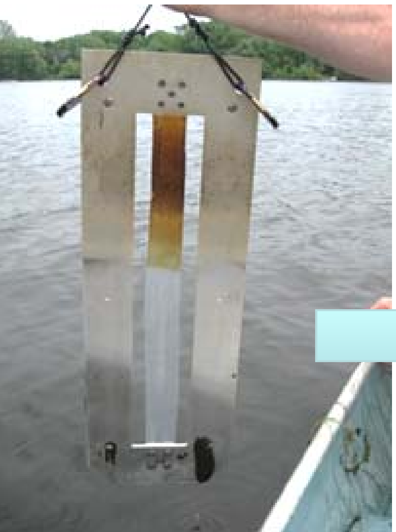
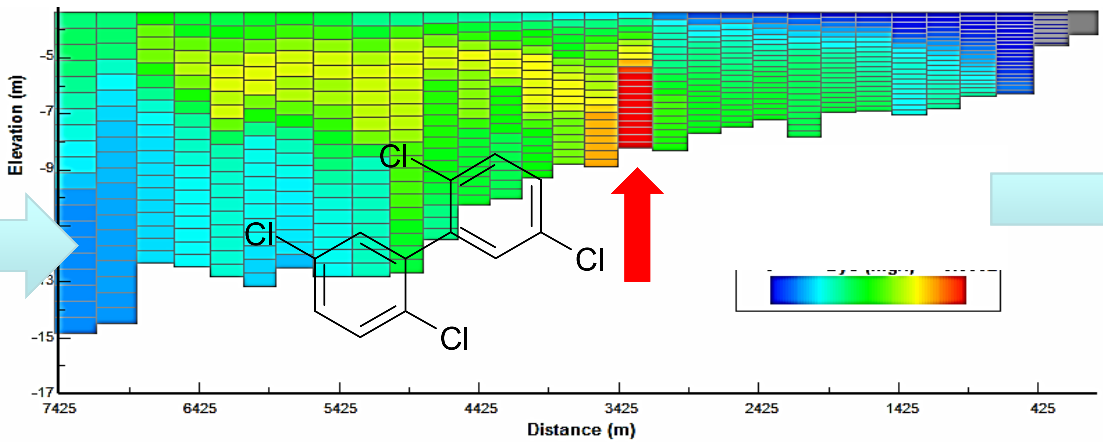
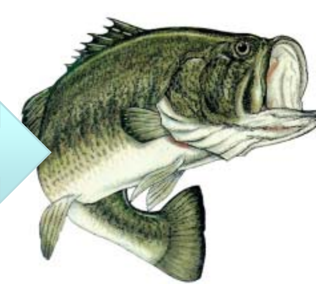
Combining Mass Balance Modeling with Passive Sampling at Contaminated Sediment Sites to Evaluate PCB Sources and Food Web Exposures

Philip Gschwend & Eric Adams, MIT
Mandy Michalsen, ACoE, and
Katherine von Stackelberg, NEK Assoc & HSPH

Federal Remediation Technologies Roundtable
May 11, 2016

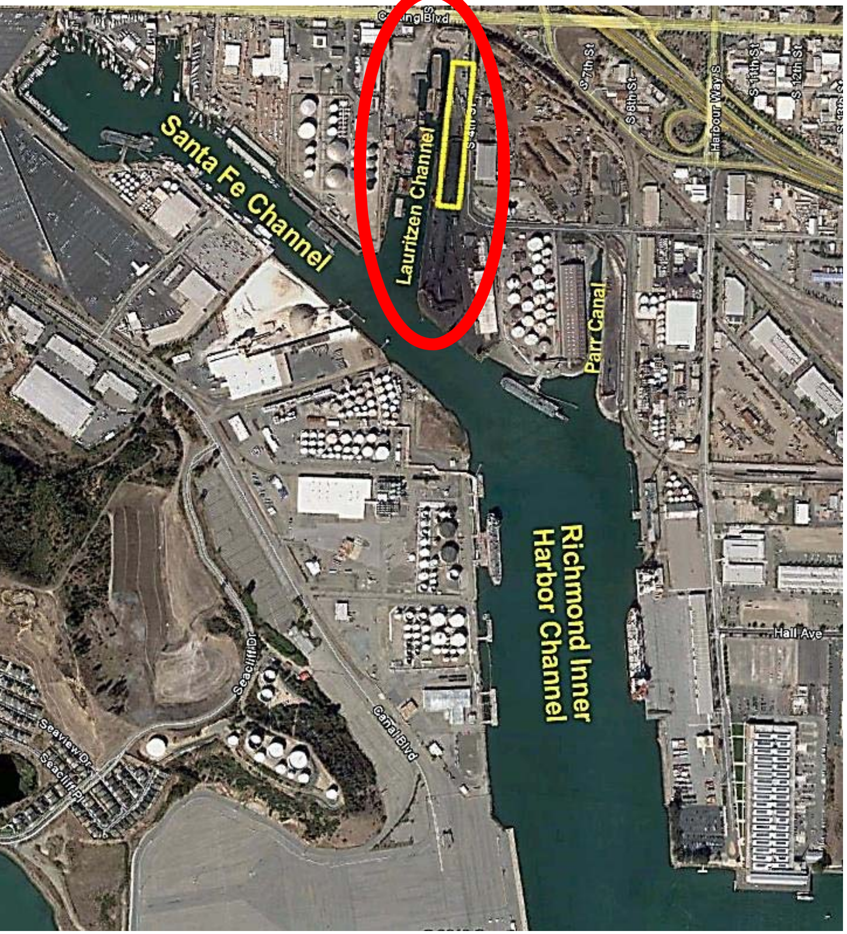






Bkgd: some "clean ups" don't work based on food web!

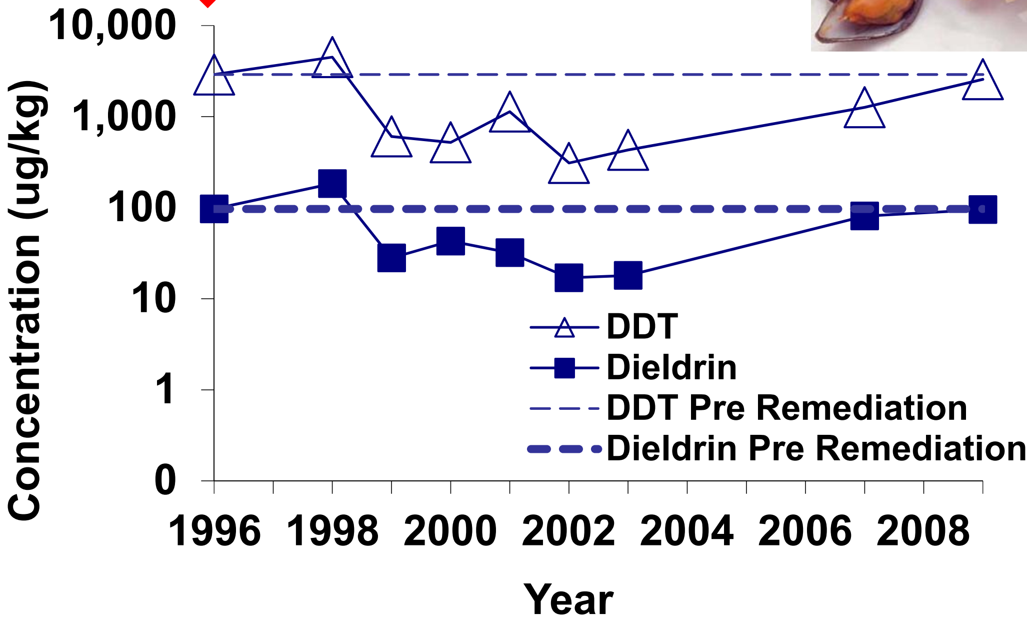
e.g., DDT



107,000 tons of sediment were removed from the waterways and transported to disposal facilities.

mussel tissue concentrations

Tamara Frank E2 Consulting Engineers)



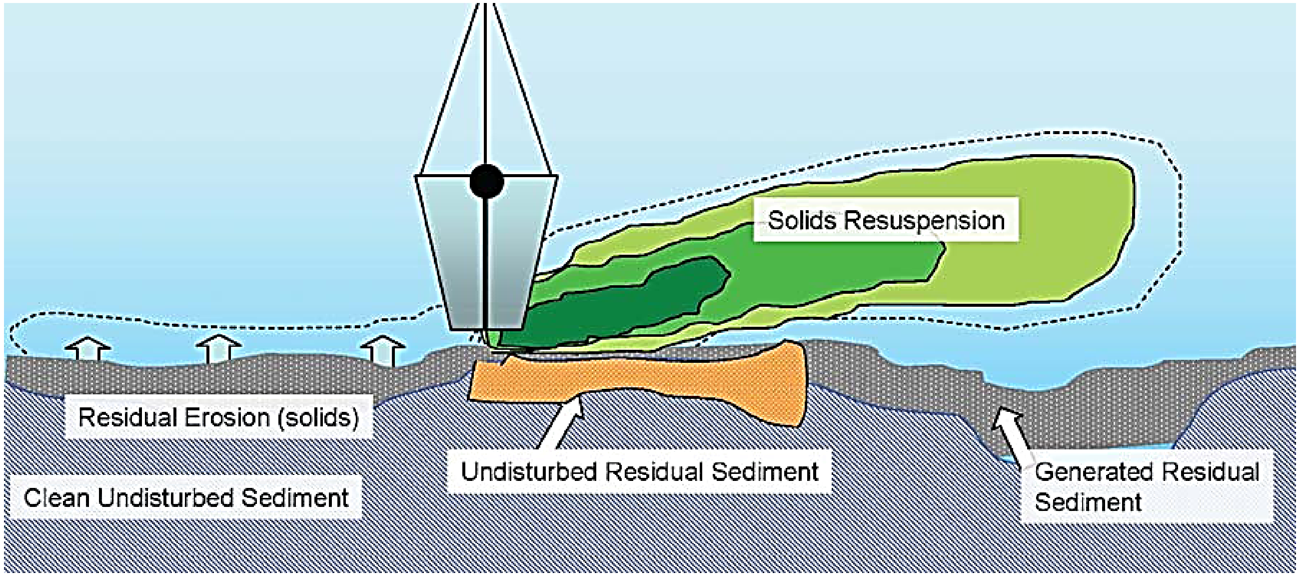
=> **missed sources?**

Bkgd: Sediments not always biggest source!

...for completed dredging projects...

post-dredging residual levels ...**often greater than the cleanup levels**

(Bridges et al., 2008)



other **source(s)** can lead to re-contamination.

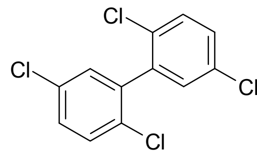
e.g. point sources 10/20, runoff 8/20, residual sediment 8/20; other 3/20

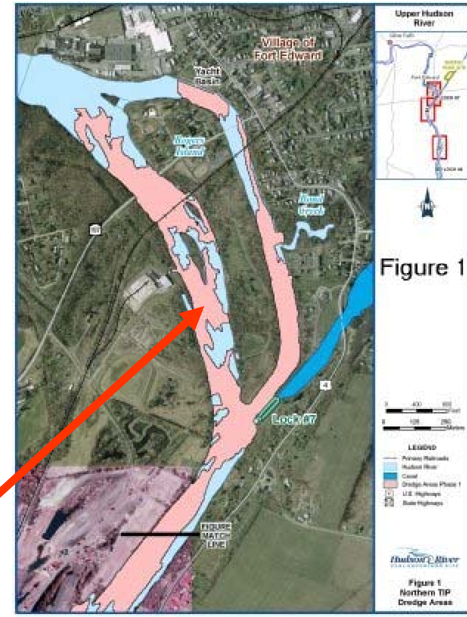
(Nadeau & Skaggs 2006)

Bkgd: Large $$$$$$$

e.g., PCB clean up in the Hudson River

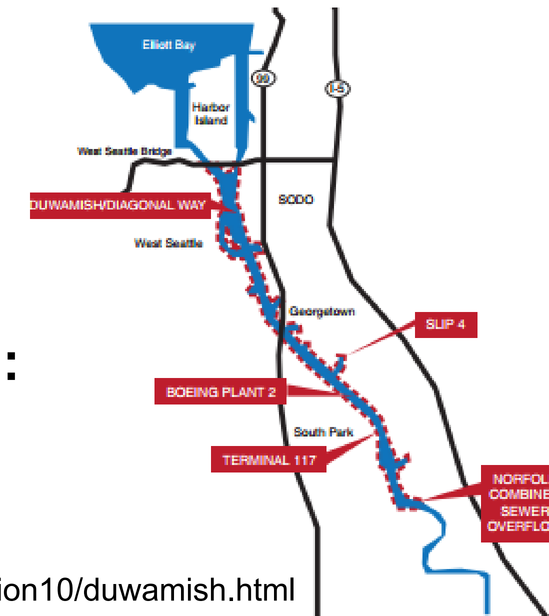
www.physorg.com/news164877380.html





cost ~$700 million

Copyright 2007 by United Press International

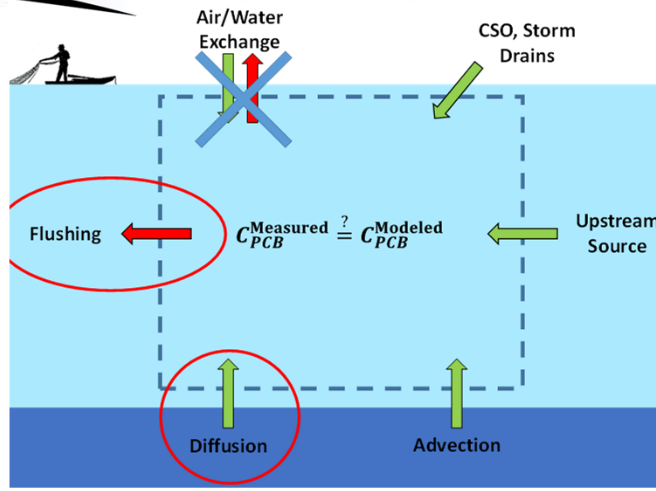


likewise for Lower Duwamish Waterway, ROD (2014):

"Total estimated net present value costs for the Selected Remedy are $342 million…"

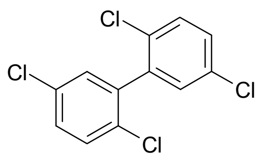
www.epa.gov/region10/duwamish.html

Objectives

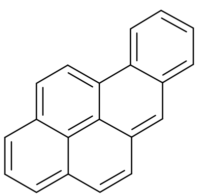


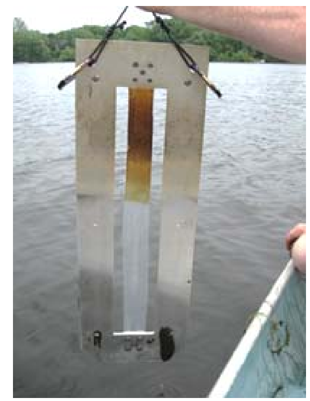
i. **Mass Balance Model (MBM)**

=> do MBM estimated conc's match measures?

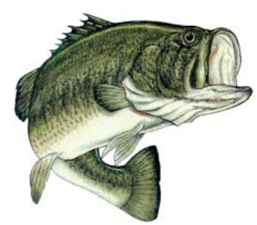


ii. **Passive Sampler methods to ID hypothesized sources and "drive" the Mass Balance Model**

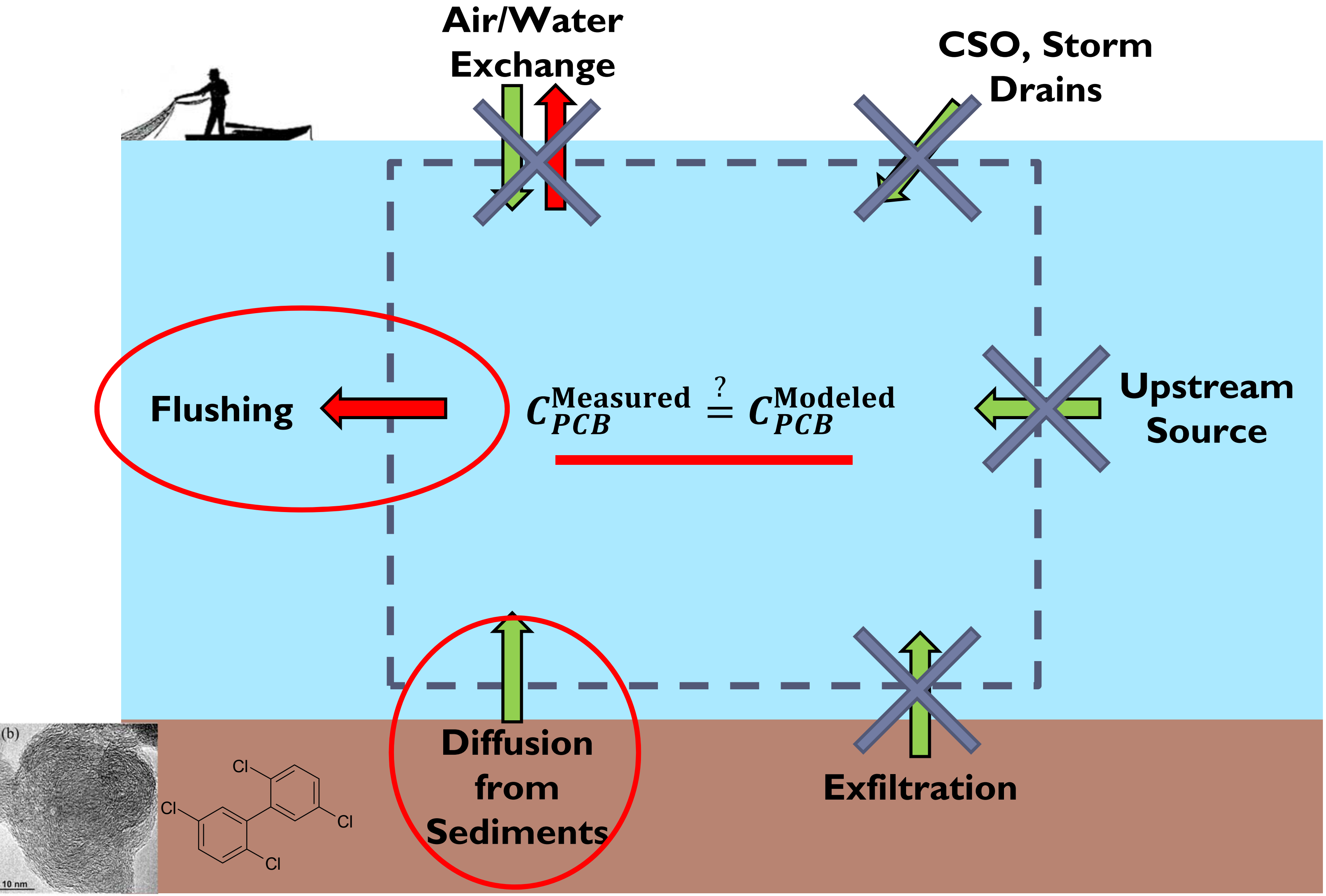




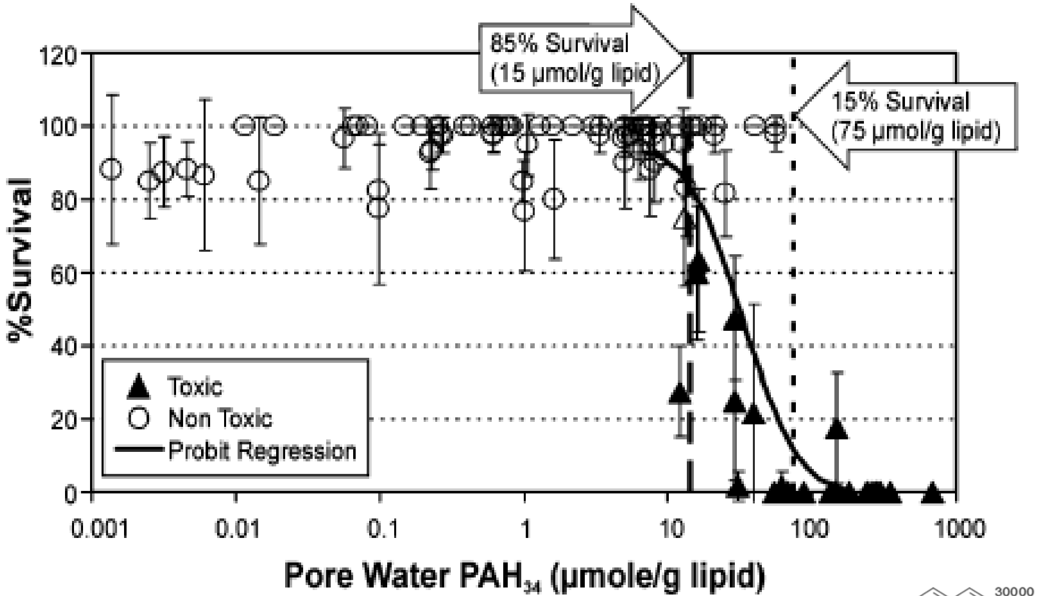
iii. **integrate with Food Web Model (FWM) using MBM description of exposure field, is FWM biouptake consistent with measured body burdens?**



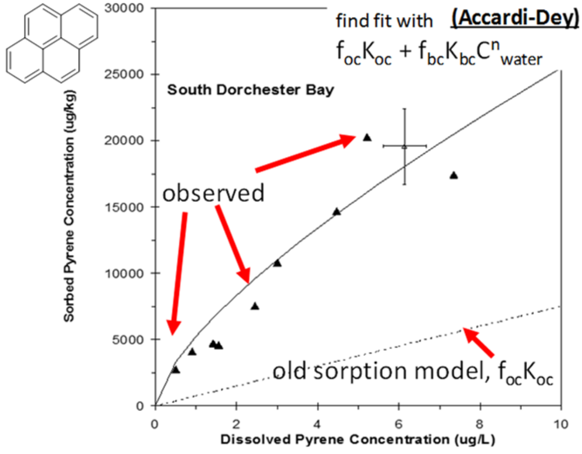
Approach: Start "Simple"



Bkgd: know mobility & tox' "freely dissolved conc's"
=> need water column AND porewater conc's

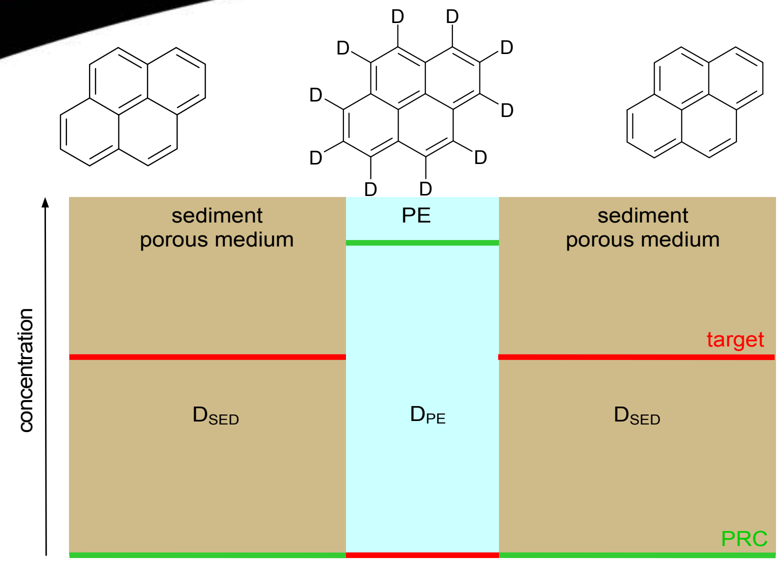


Hawthorne et al. (2007)

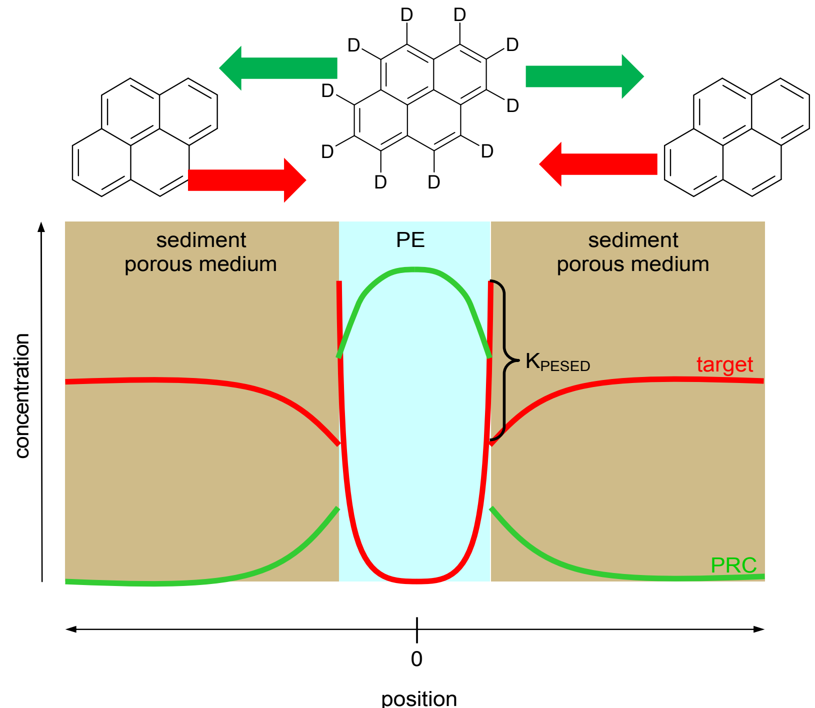


Bkgd: use PE to get conc's

Fernandez et al. 2009, Apell & Gschwend, 2014



at time = 0
with PRCs



at later time

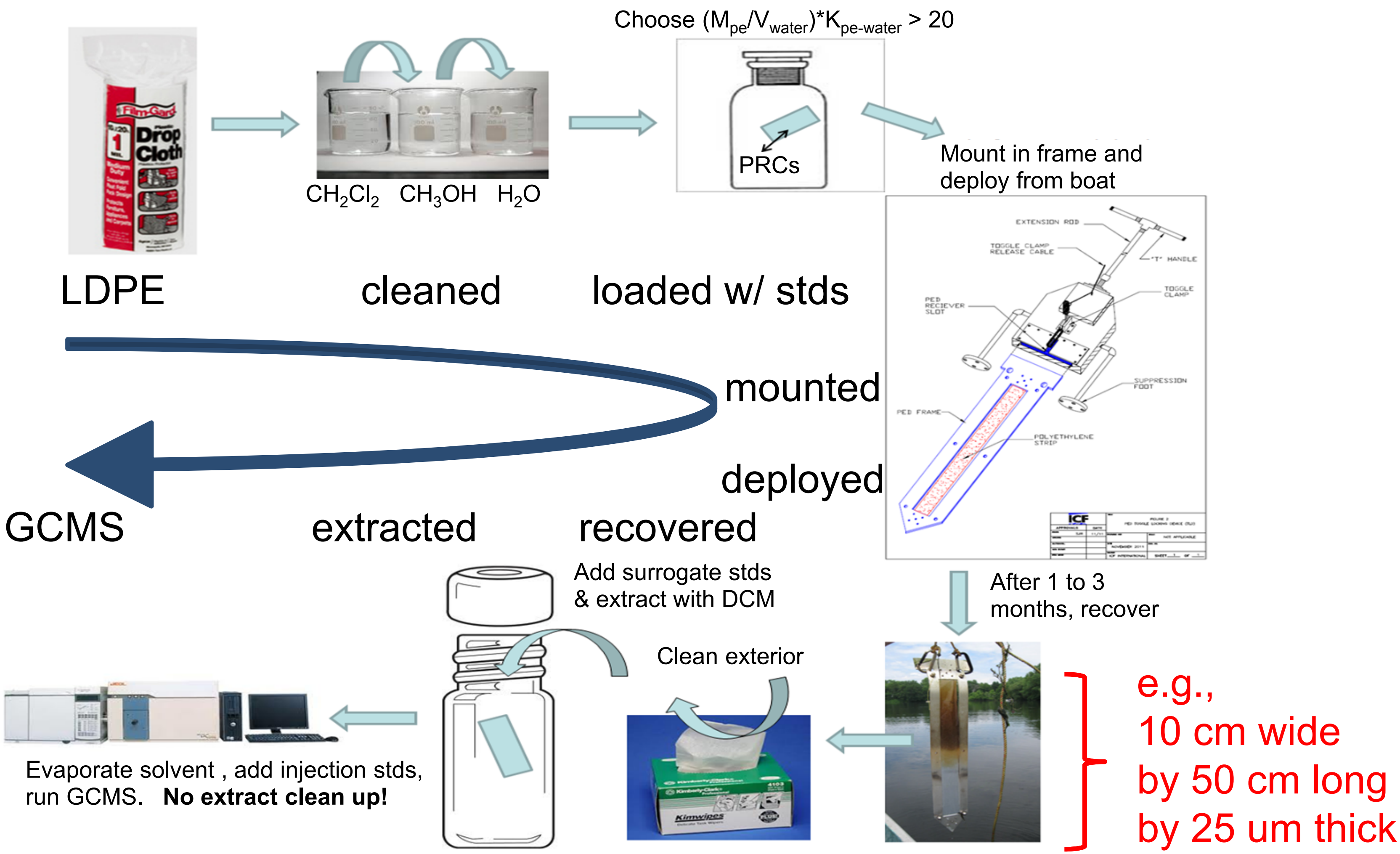
use **loss of PRCs** to calculate fractional approaches to equilibration (function of site & compound)

use that result, to extrapolate target uptake to $\mathbf{C_{pe}(\infty)}$

$$\Rightarrow \quad C_{water} = C_{pe}(\infty) \, / \, K_{pew}$$

Bkgd: PE Methods

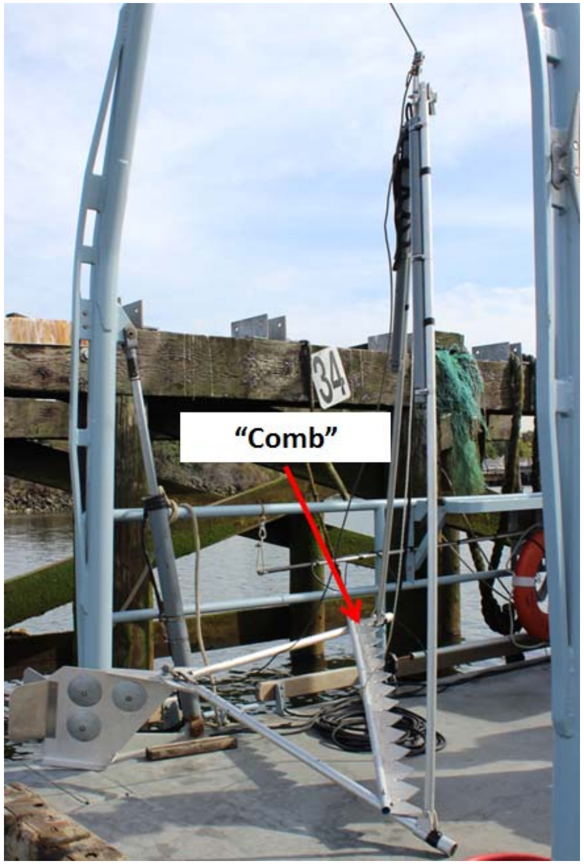
Gschwend et al. 2012



Can deploy via divers, but also from vessels

deployment
all depths
~10 min

Bill Jaworski
Marine Sampling Systems Inc



recovery system
from boat

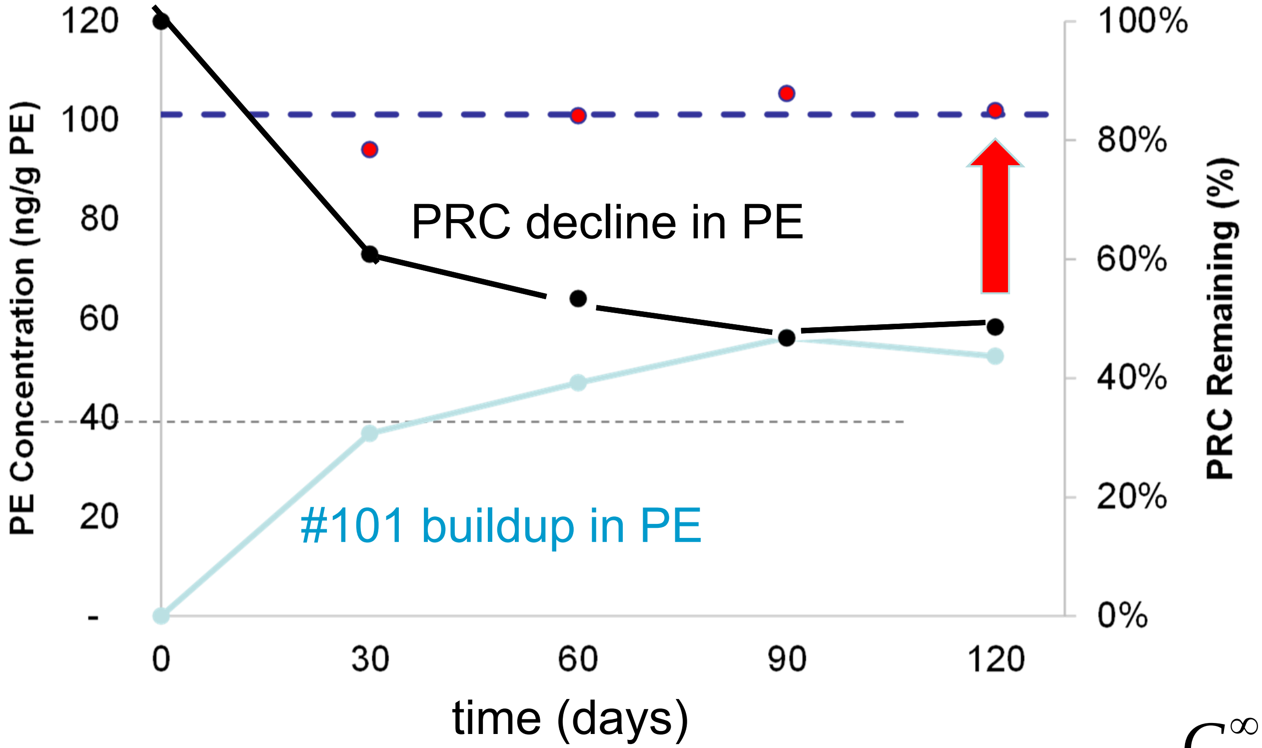
bed & water
samplers

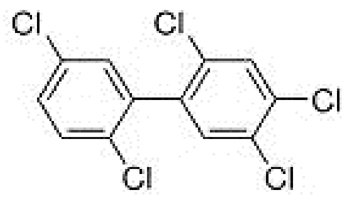
PE sheets 10 cm wide by 60 cm long by 25 um thick

Bkgd: Use PRCs to Find C^{∞}_{PE} (lab tests)

(Apell and Gschwend 2014)

with PCB-contaminated lake sediments





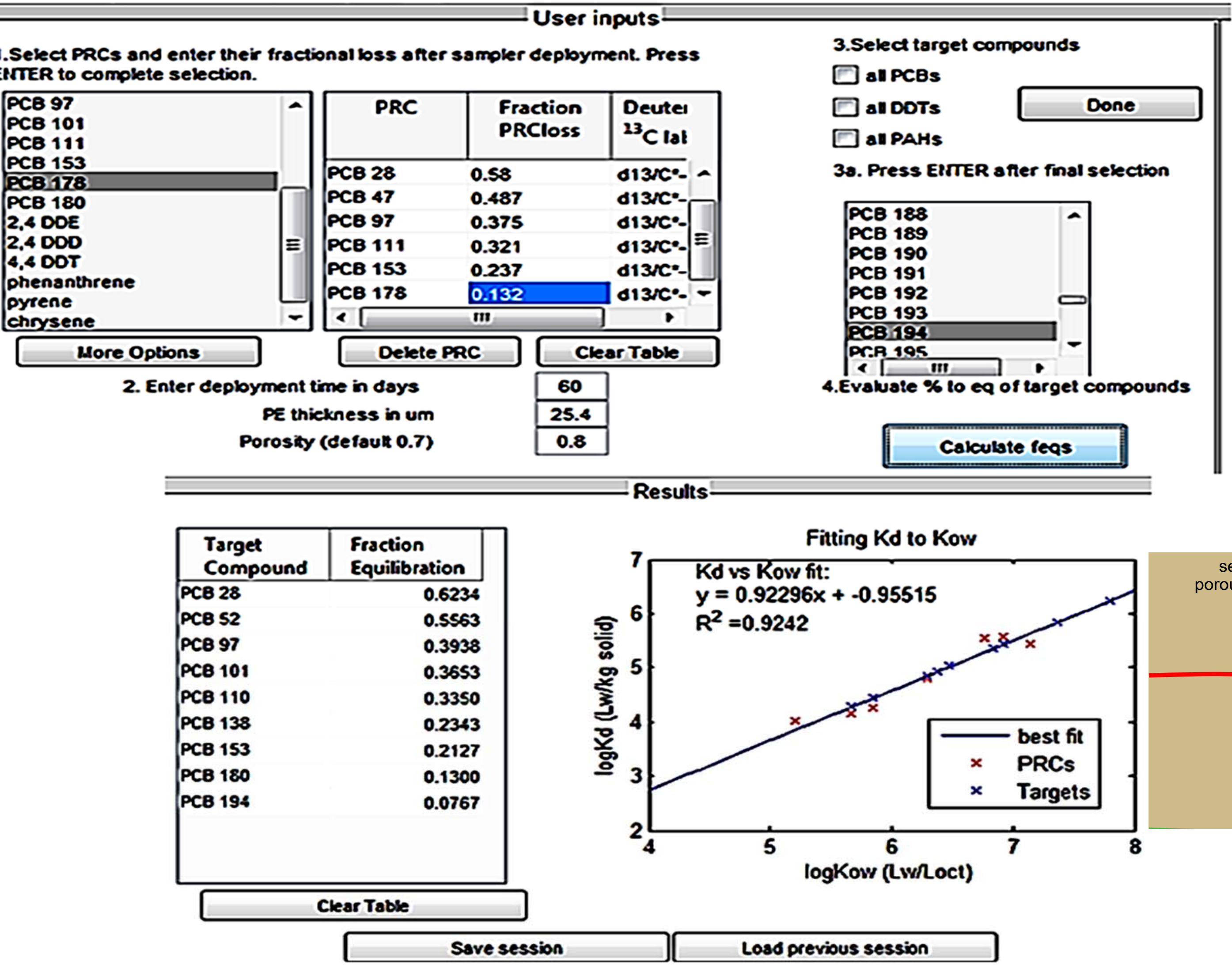
PCB #101

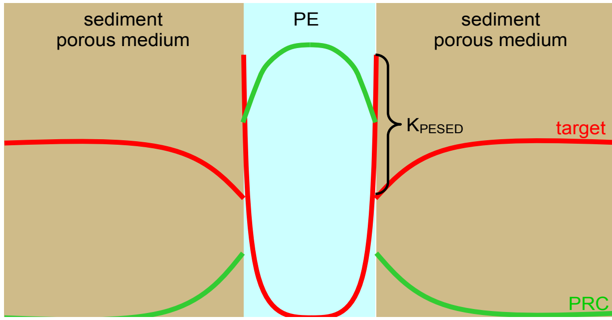
$$C^{\infty}_{PE} / K_{PE-water} = C_{porewater}$$

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

Graphic User Interface allows users to process own C^{∞}_{pe}

(Tcaciuc et al.)

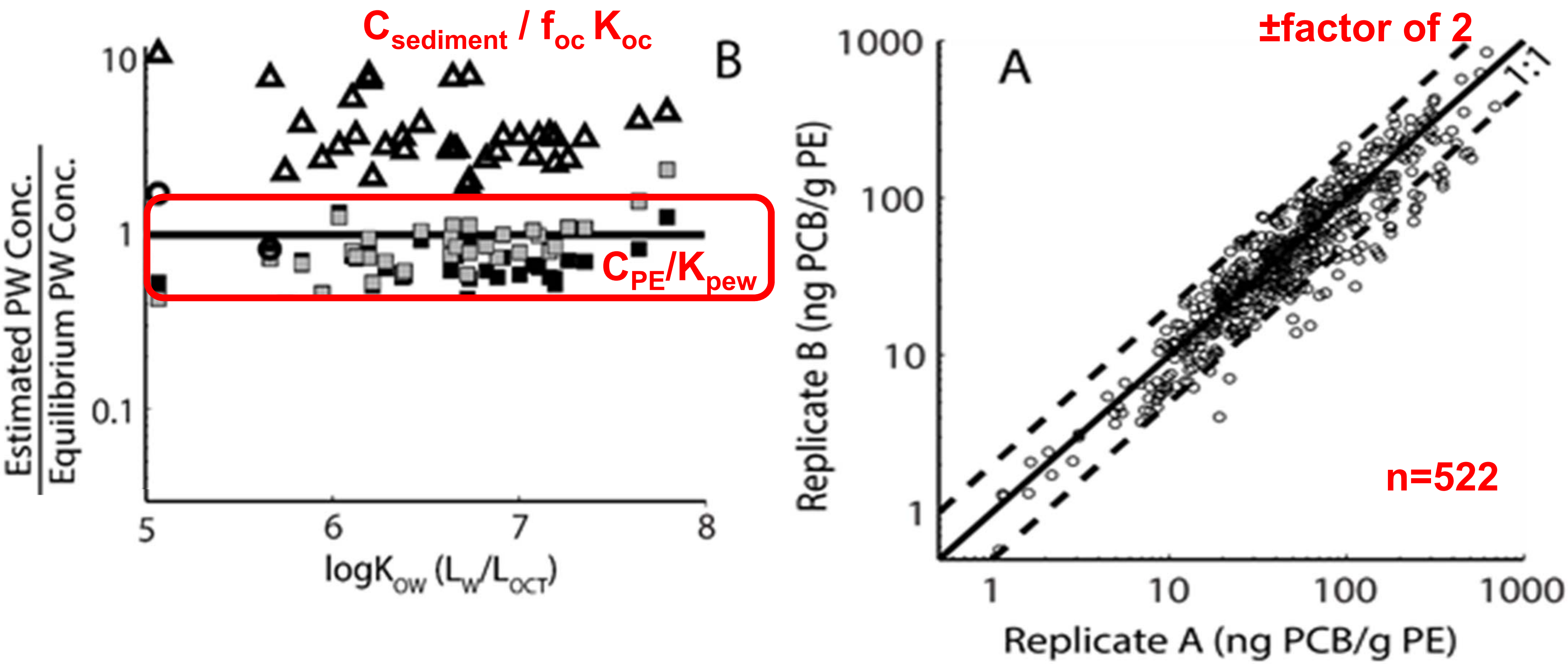




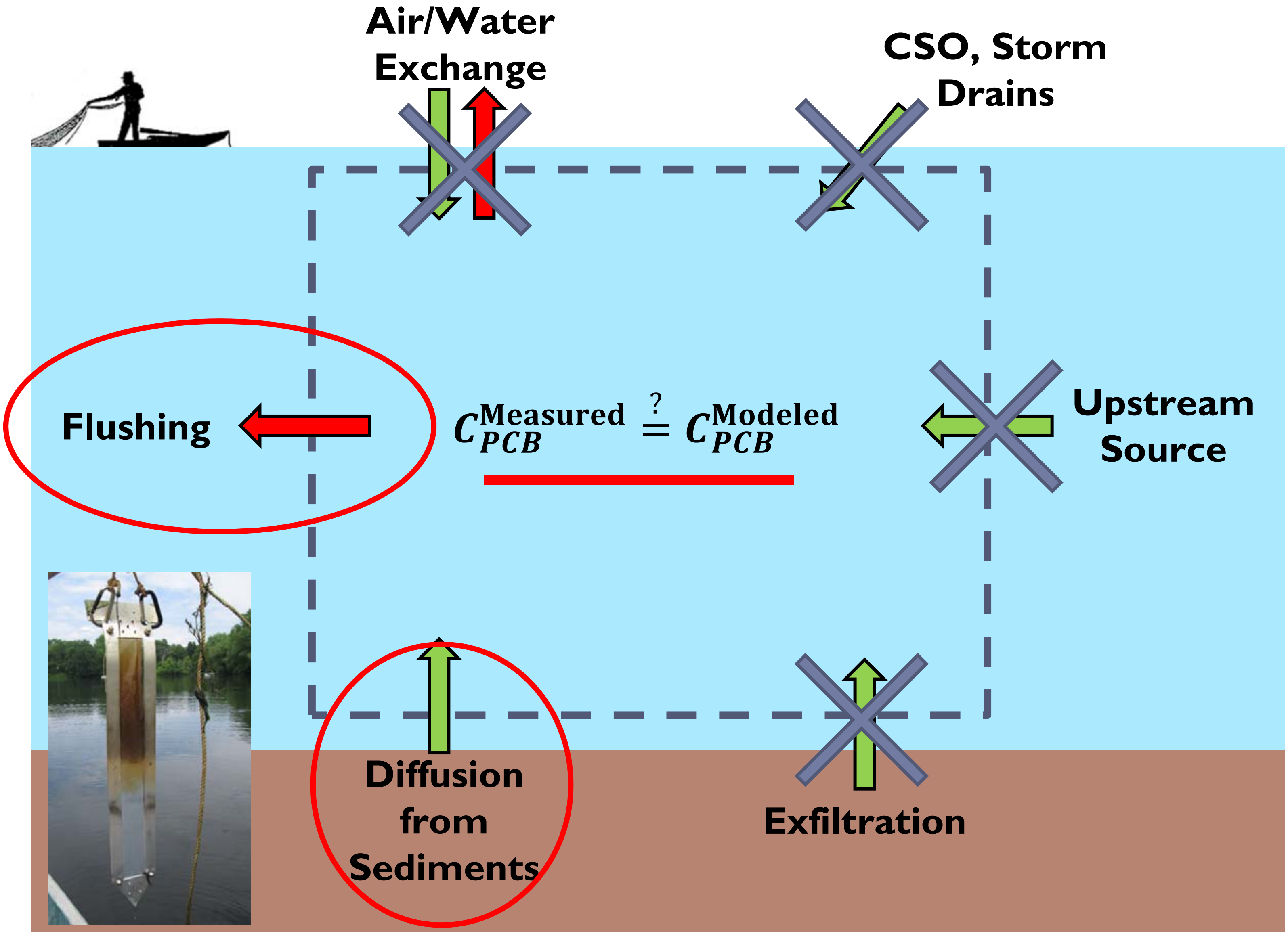
https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Sediments/ER-200915 **=> User Manual & Matlab**

Accuracy and Precision *in situ* in the LDW (Apell)

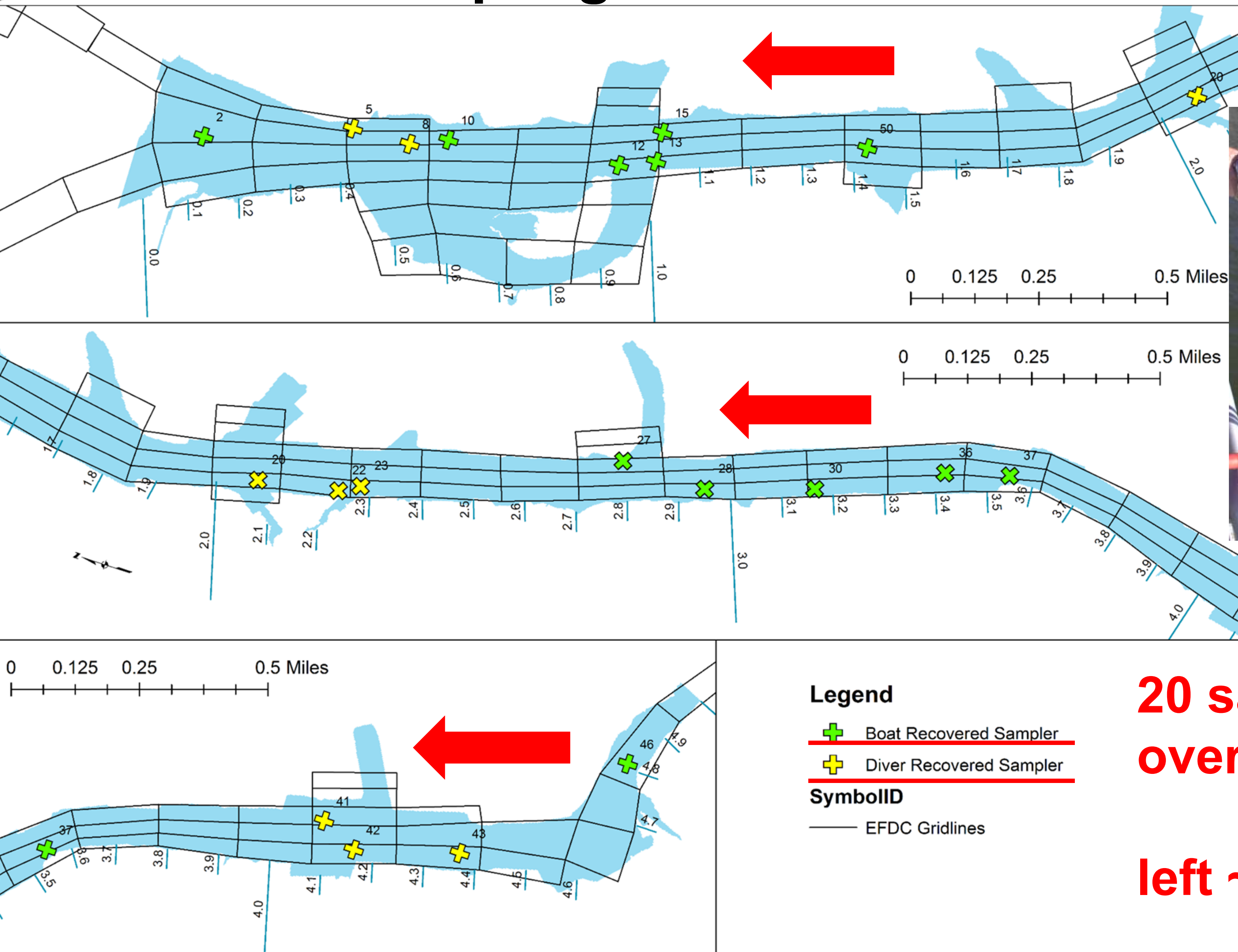
(Nov 2012-Jan 2013)



Field Approach: Start "Simple"
(are sediments main source now?)



LDW sampling summer-fall 2014

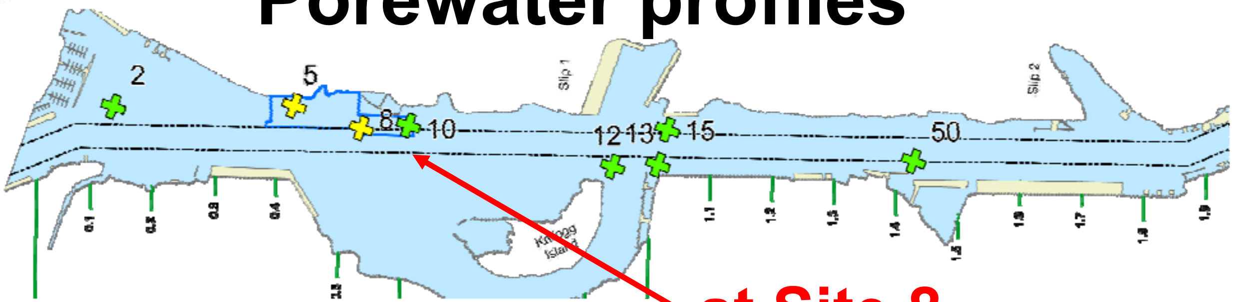


20 samplers over 4.5 miles

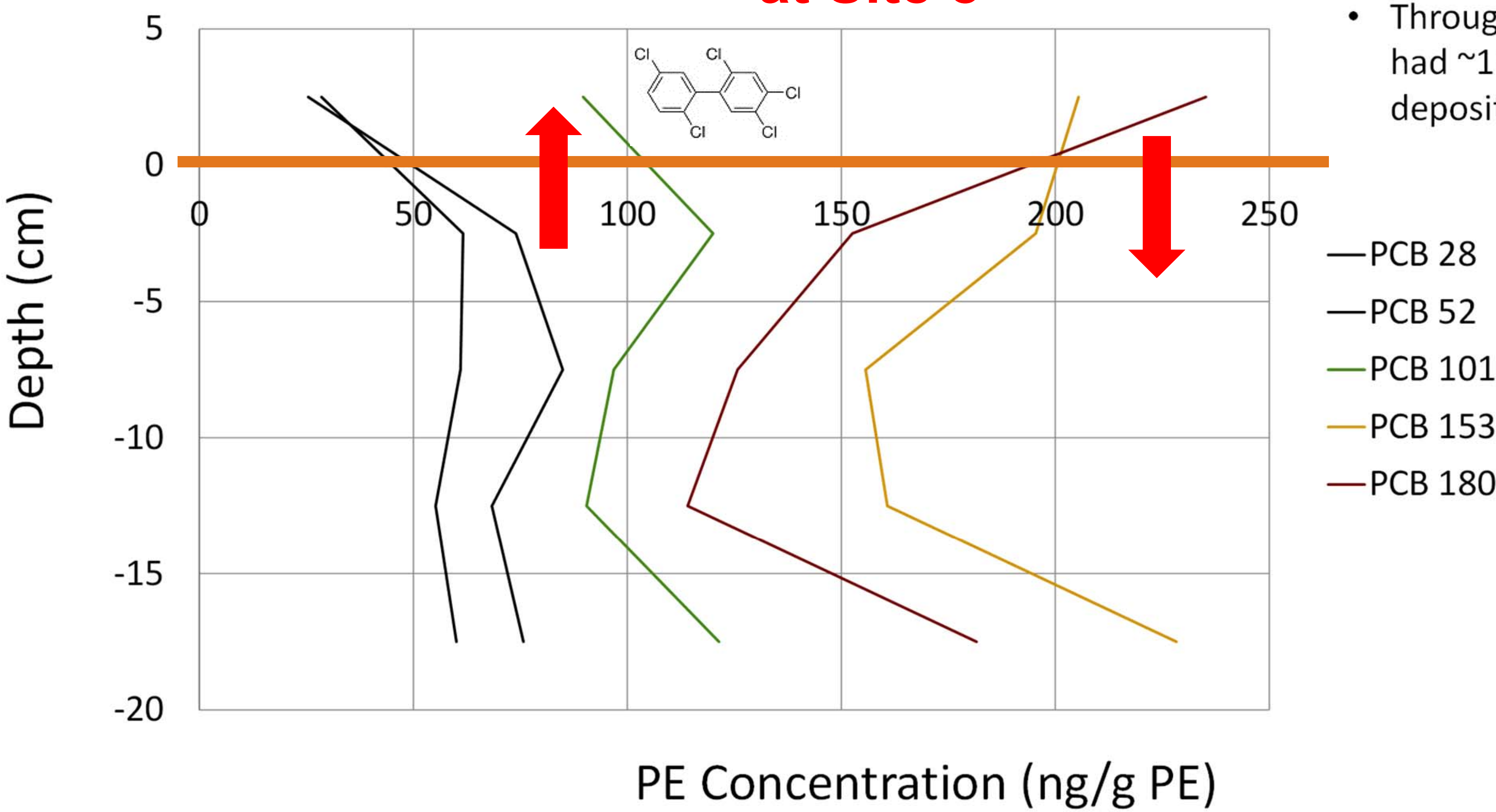
left ~2 mos.

Porewater profiles

(Apell)

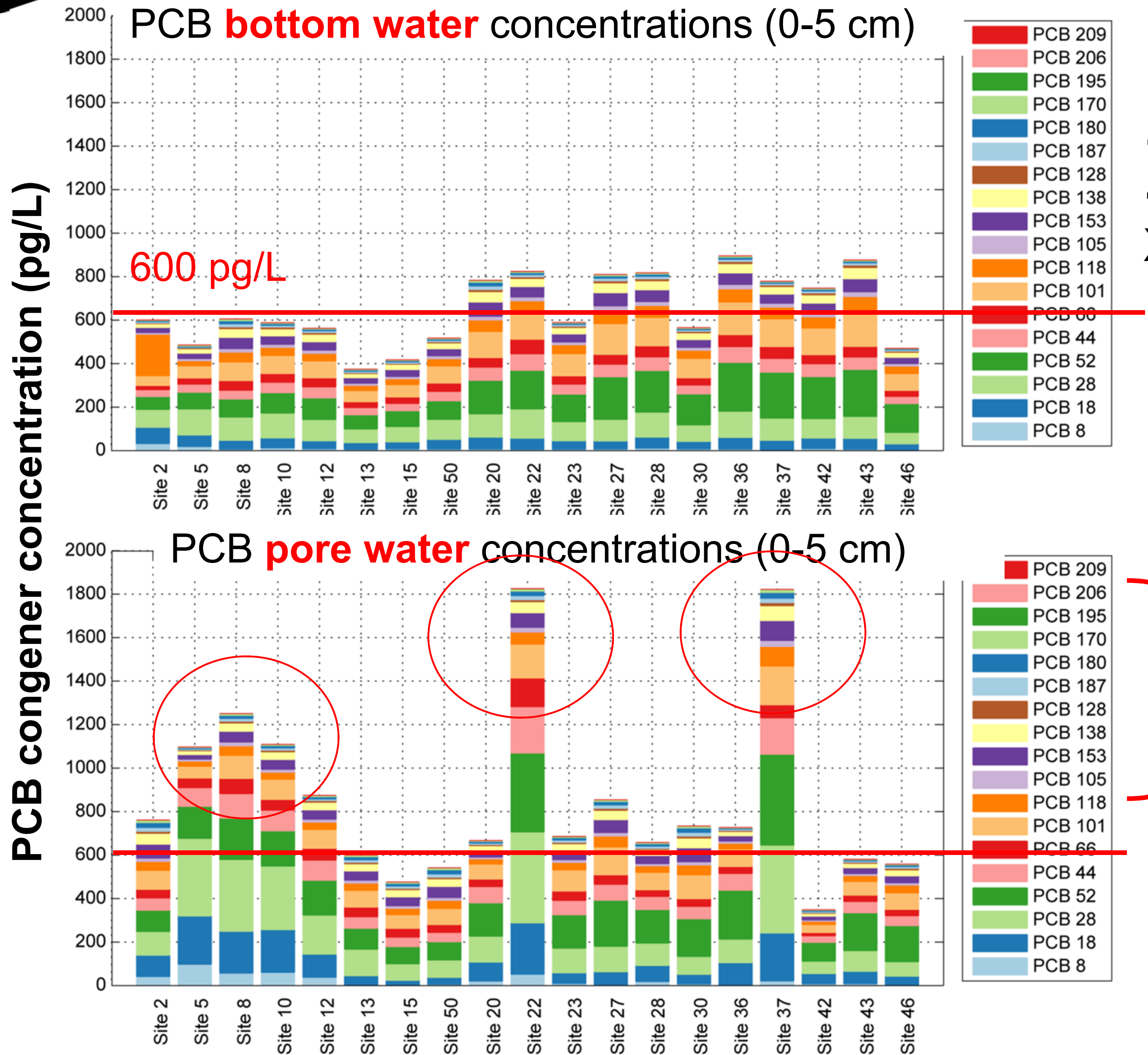


- Downriver (north)
- Through a cap that had ~10 cm deposited over it



LDW sampling

(Apell et al.)

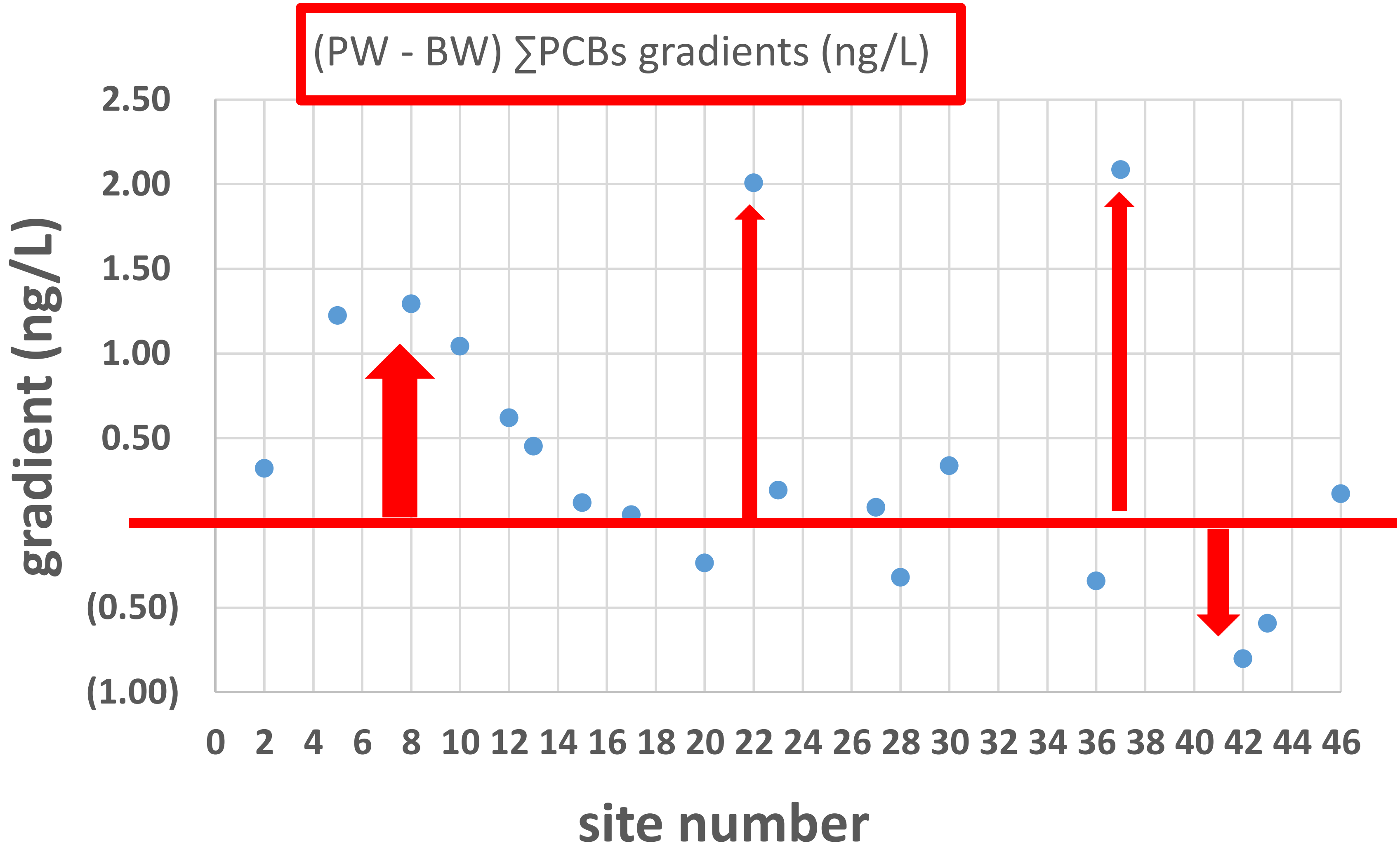


$\sum$"NOAA 18"

x 2 ≈ **1.4 ng/L**

see some "hotspots" factor of 2

Results => bed-water gradients



Results: Boundary Layer with ADCP

(Prendergast)

- if $\boxed{\textbf{Flux} = - D_{water}\ (C_{porewater} - C_{bottom\ water}) / \delta_{boundary\ layer}}$

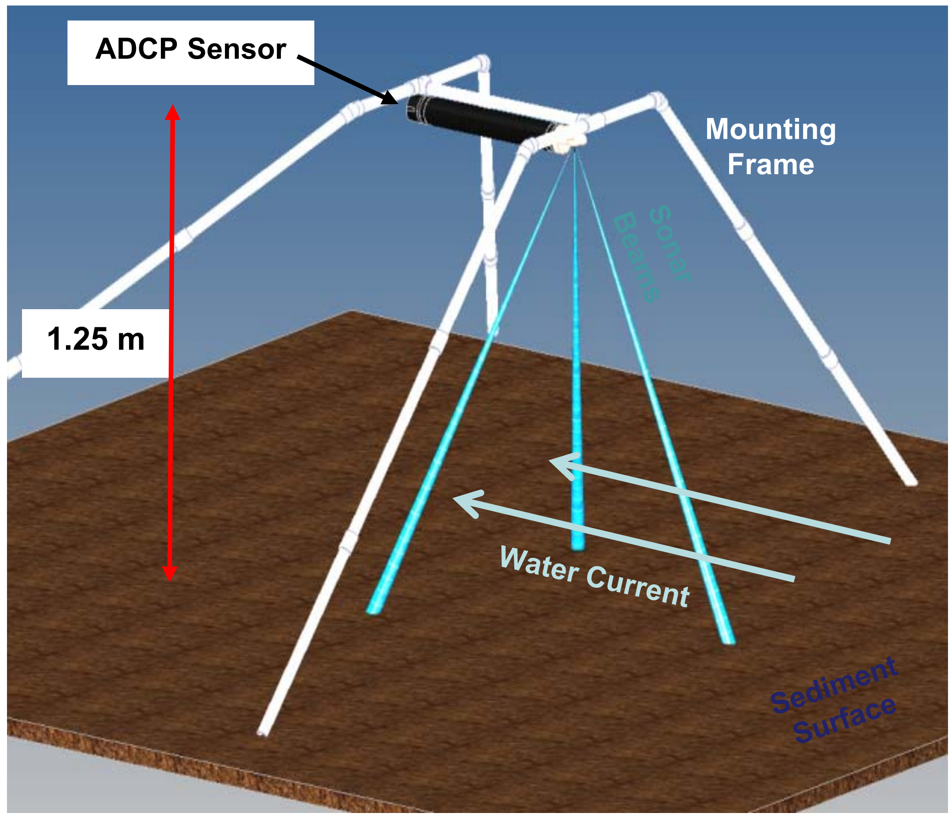
  need $\delta_{boundary\ layer}$

- downward-facing ADCP

  deployed on river bottom

- **Eight locations**

  15 minute intervals

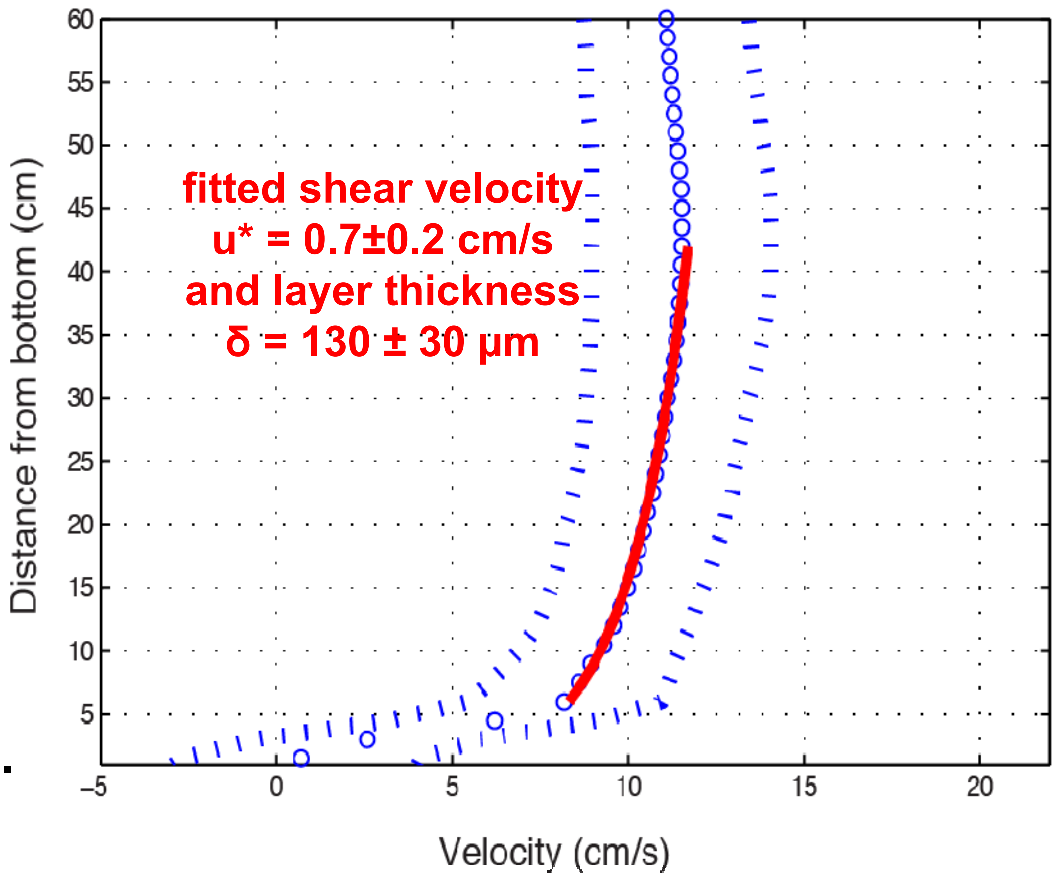


Results: Boundary Layer with ADCP

(Prendergast)

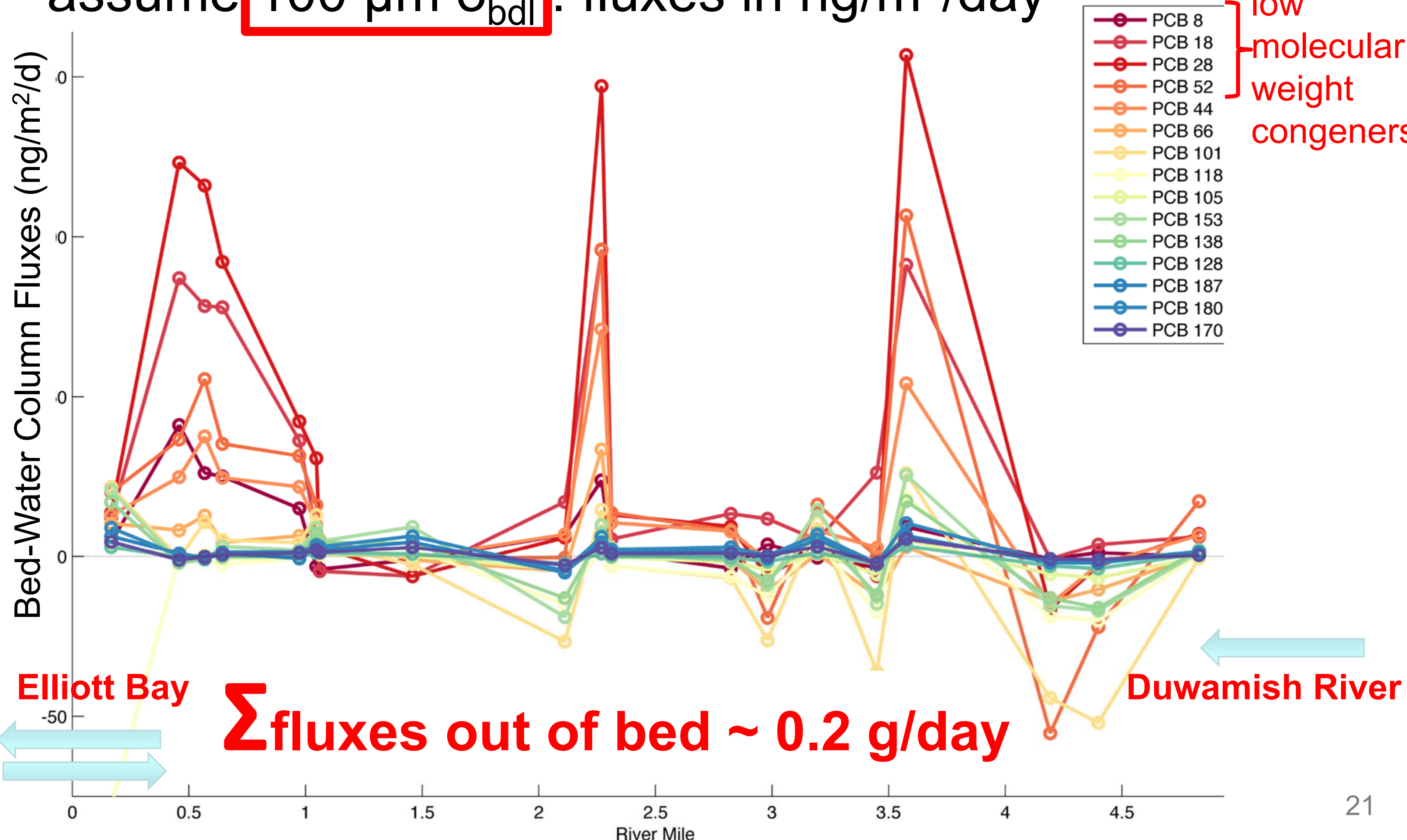
- **Eight locations**
  water boundary range
  50-250 µm
  varying as expected with current/tide

- results lower than 2009 EFDC model-calibrated value of **400 µm**.



Estim' Diffusive Fluxes

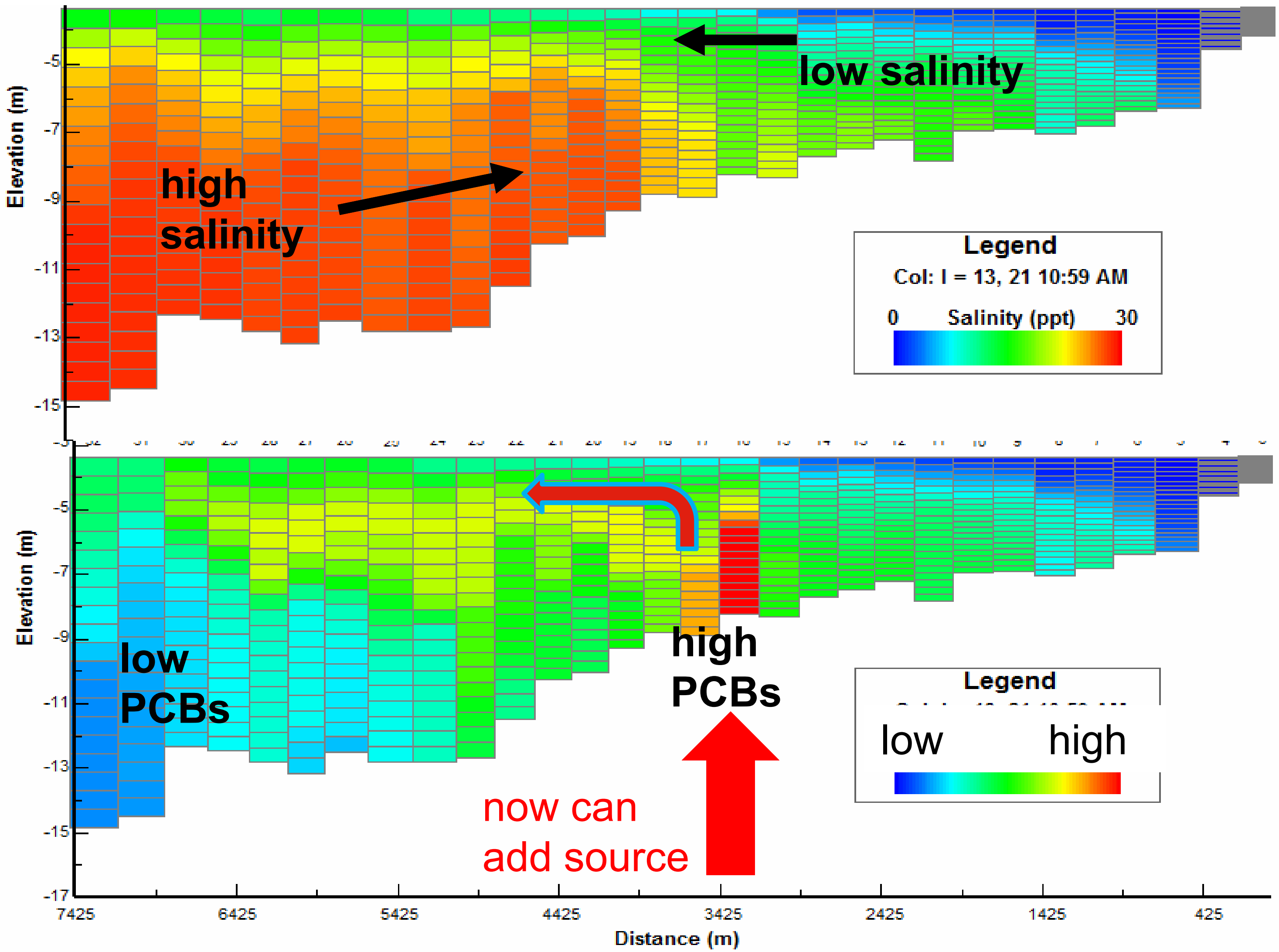
assume $\boxed{100\ \mu m\ \delta_{bdl}}$: fluxes in $ng/m^2/day$



Σfluxes out of bed ~ 0.2 g/day

MBM modeling with EFDC (Adams and Predergast)

Elliott Bay September – Spring Tide – Low Tide **Duwamish River**



freshwater outflow near surface

high salinity at bottom near Bay

relative **PCB** concentration

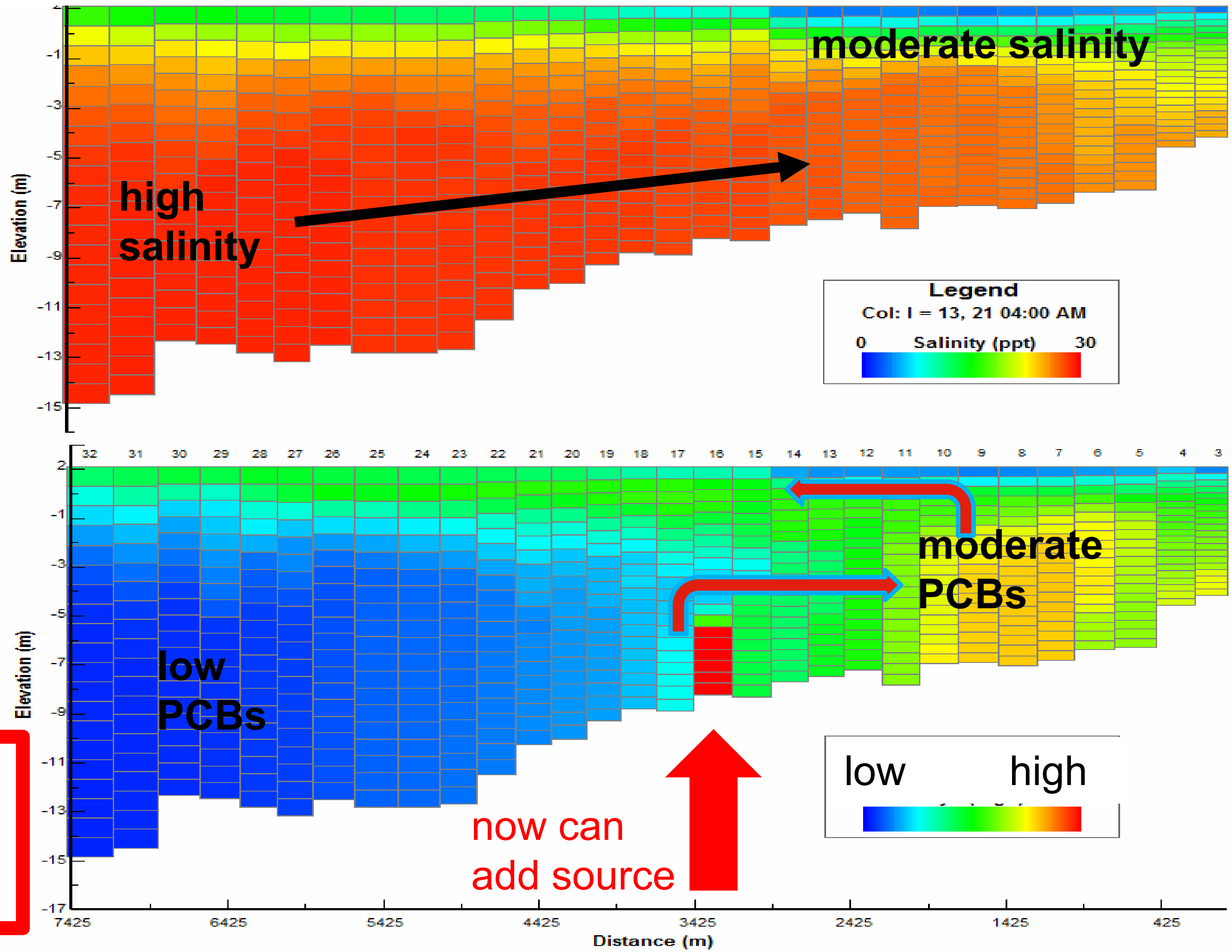
=> FWM exposure field in space

MBM modeling with EFDC (Adams and Predergast)

Elliott Bay September – Spring Tide – High Tide Duwamish River

higher salinity

(and much deeper)



relative PCB concentration

Key: Res' Time ~ 4 d

Putting in all together

Prendergast, Apell, et al.

1. average porewater-bottom water gradient was 400 pg ∑PCBs/L (N=19)

   assuming water-side controlled diffusive exchange (D_{water} = 4E-6 cm^2/s)
   (with a boundary layer thickness 0.01 cm)

   computed flux: 1.5E-16 g∑PCBs /cm^2/s

LDW bottom area (8000 m x 200 m) about 1.6×10^{10} cm^2

   so total flux from the bed sediments about **0.2 g/day**

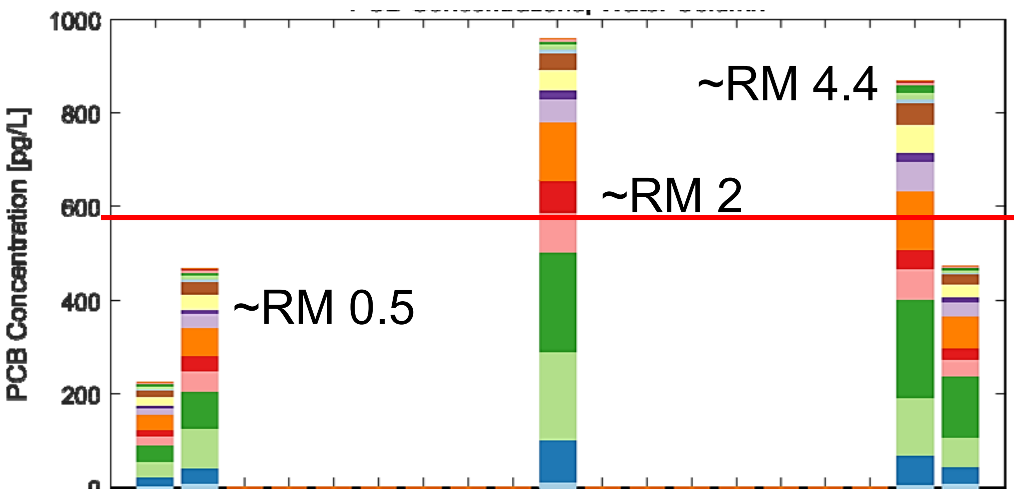
2. the EFDC suggests a hydraulic residence time of about **~4 days** in LDW estuary

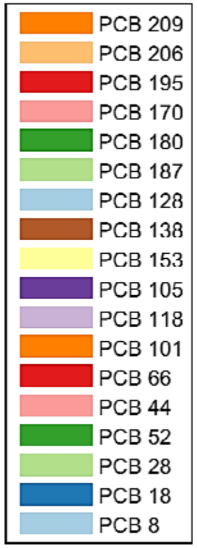
3. implies accumulate about **0.8 g ∑PCBs** at steady state in LDW

PE Water Column Sampling for PCBs (Apell)

water column

conc's (pg/L)





NOAA 18 averages about 600 pg/L

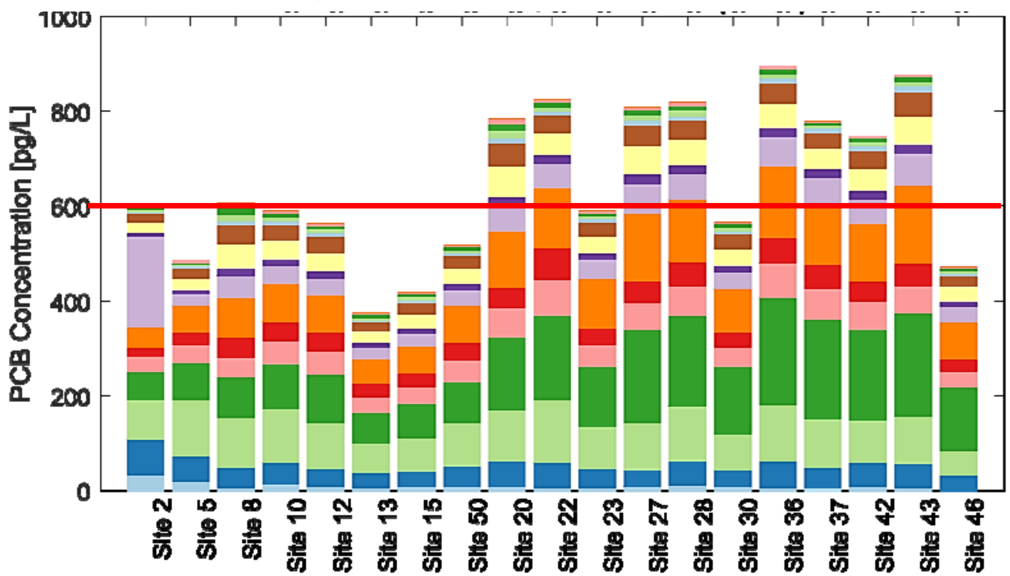
x2

∑PCBs ≈ 1.2 ng/L

<= Elliott Bay <= Duwamish River

bottom water

conc's (pg/L)



~600 pg/L

Putting in all together

Prendergast, Apell, et al.

1. total flux from the bed sediments about **0.2 g/day**

2. the EFDC suggests a hydraulic residence time of about **~4 days** in LDW estuary

3. fluxes => accumulate about **0.8 g ∑PCBs** at steady state in LDW

---

4. using PE samplers in LDW water, "NOAA Status and Trend 18 PCBs" x 2

= about **1.2 ng/L**

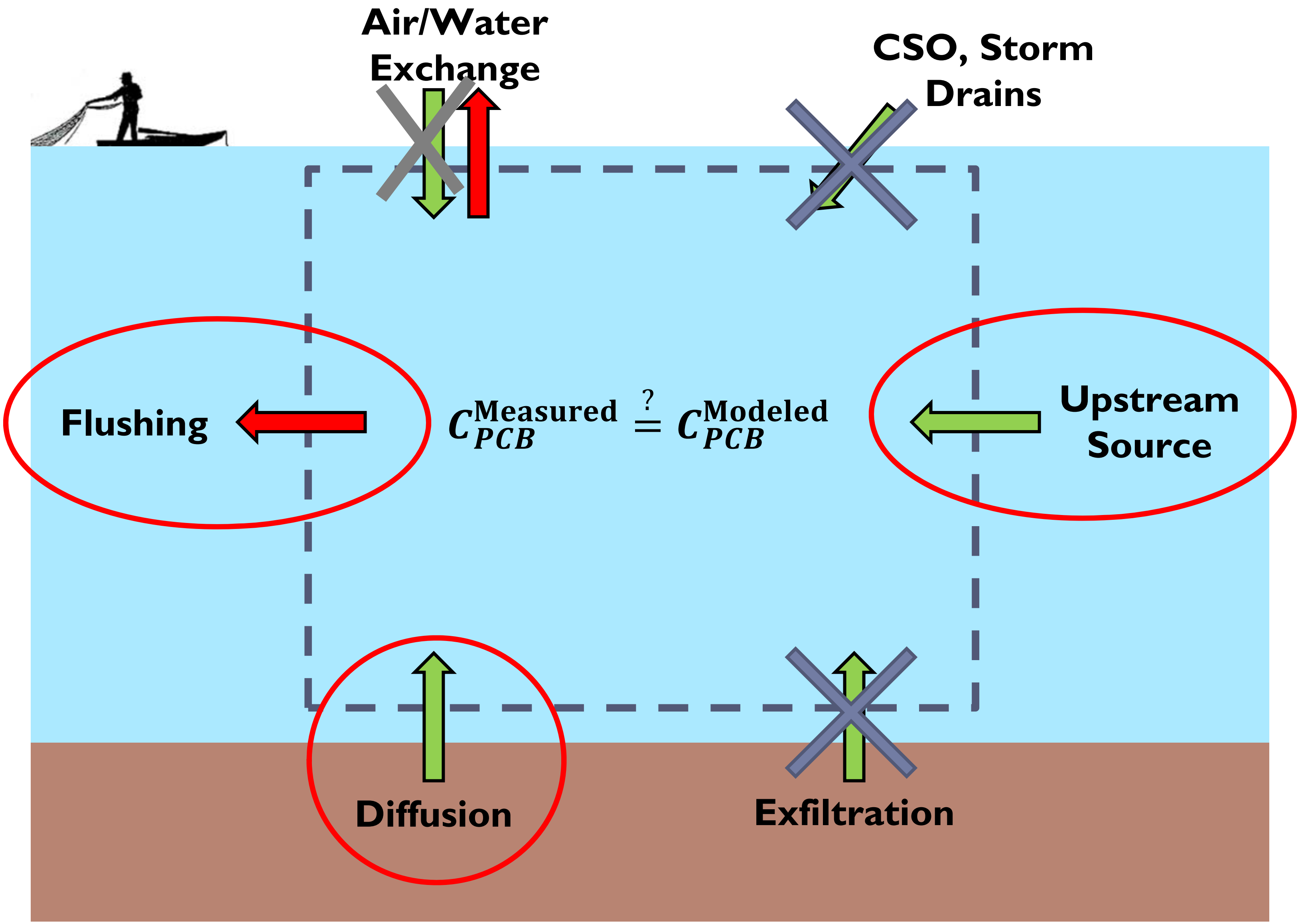
LDW volume is about 1.6×10^{10} L, so total PCB load in water is about **20 g ∑PCBs**

---

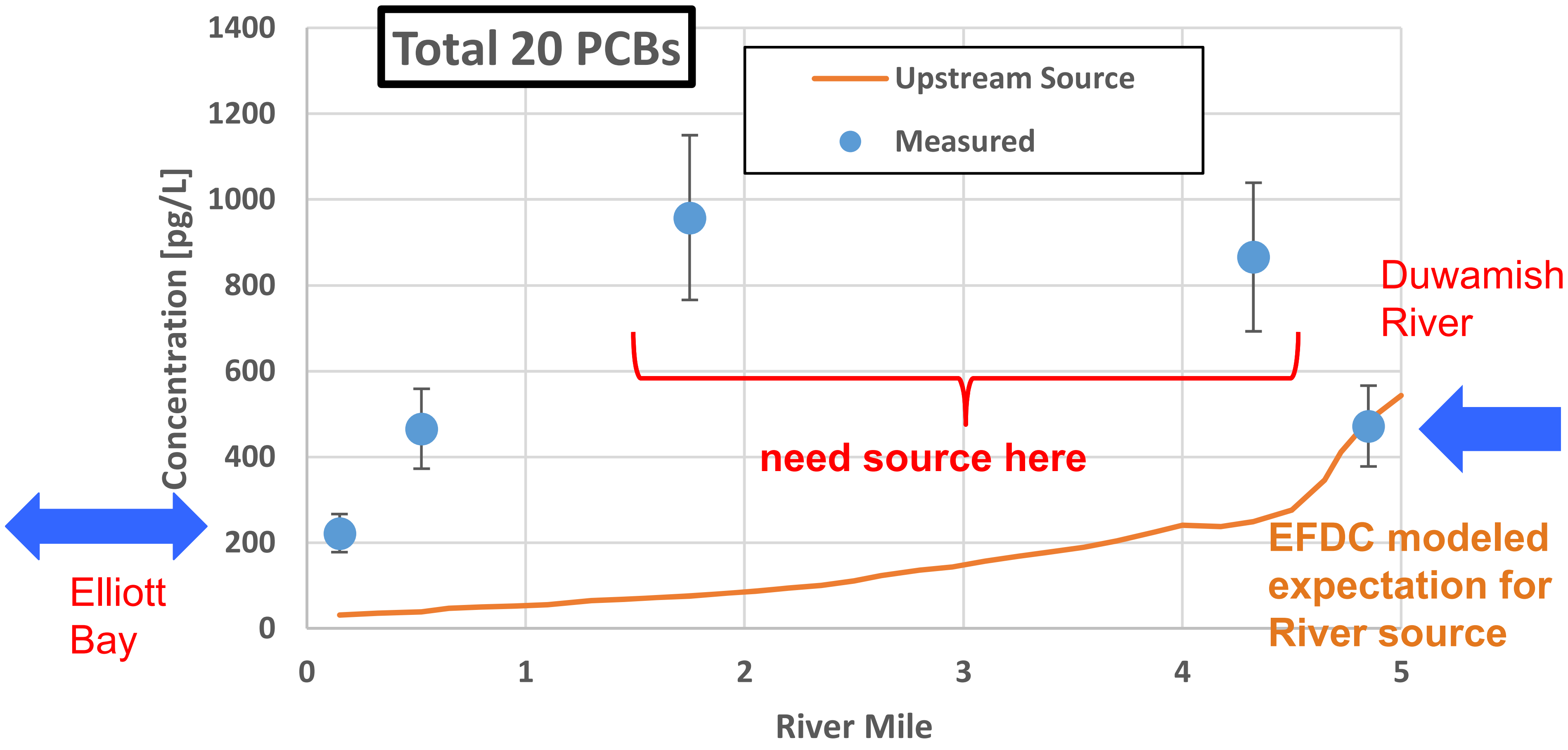
5. with 4-day residence time, implies have input of PCBs **5 g/day!**

Sediment diffusive fluxes ~20-30 times less!

Technical Approach: Add Upstream



Upstream Source? (Apell, Prendergast)



SERDP
DOD • EPA • DOE

Option: Bed-Water Fluxes Inc' Due to Bio-irrigation

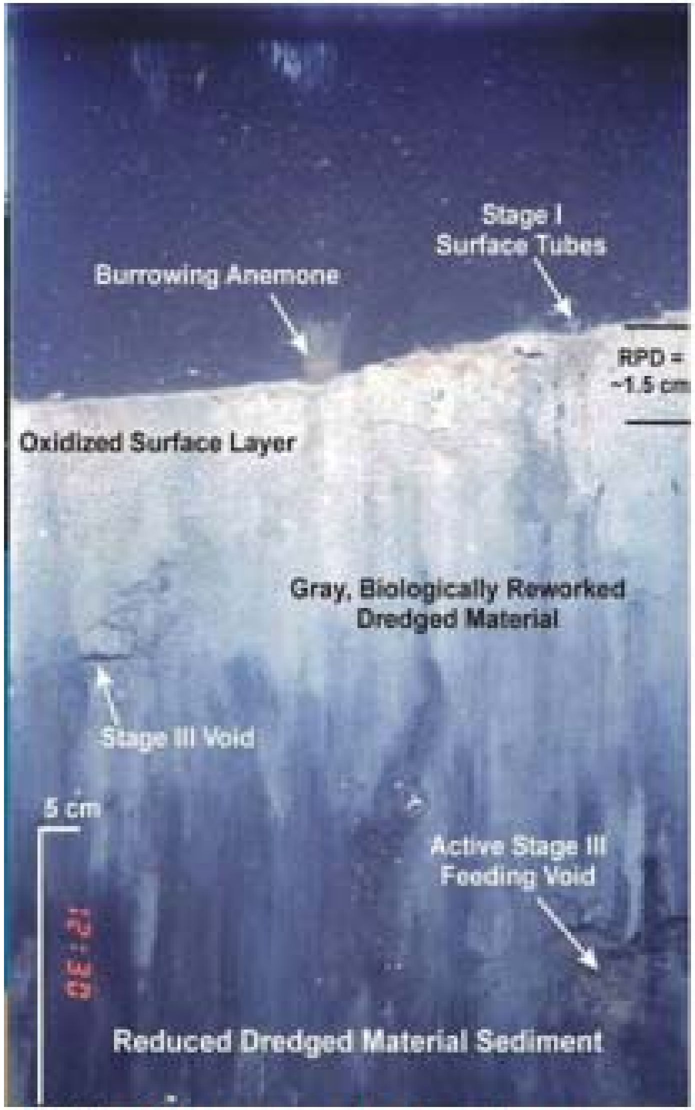
WASHINGTON STATE
DEPARTMENT OF
ECOLOGY

Using Sediment Profile Imaging (SPI) to Evaluate Sediment Quality at Two Cleanup Sites in Puget Sound

Part I – Lower Duwamish Waterway

July 2007

Publication No. 07-03-025

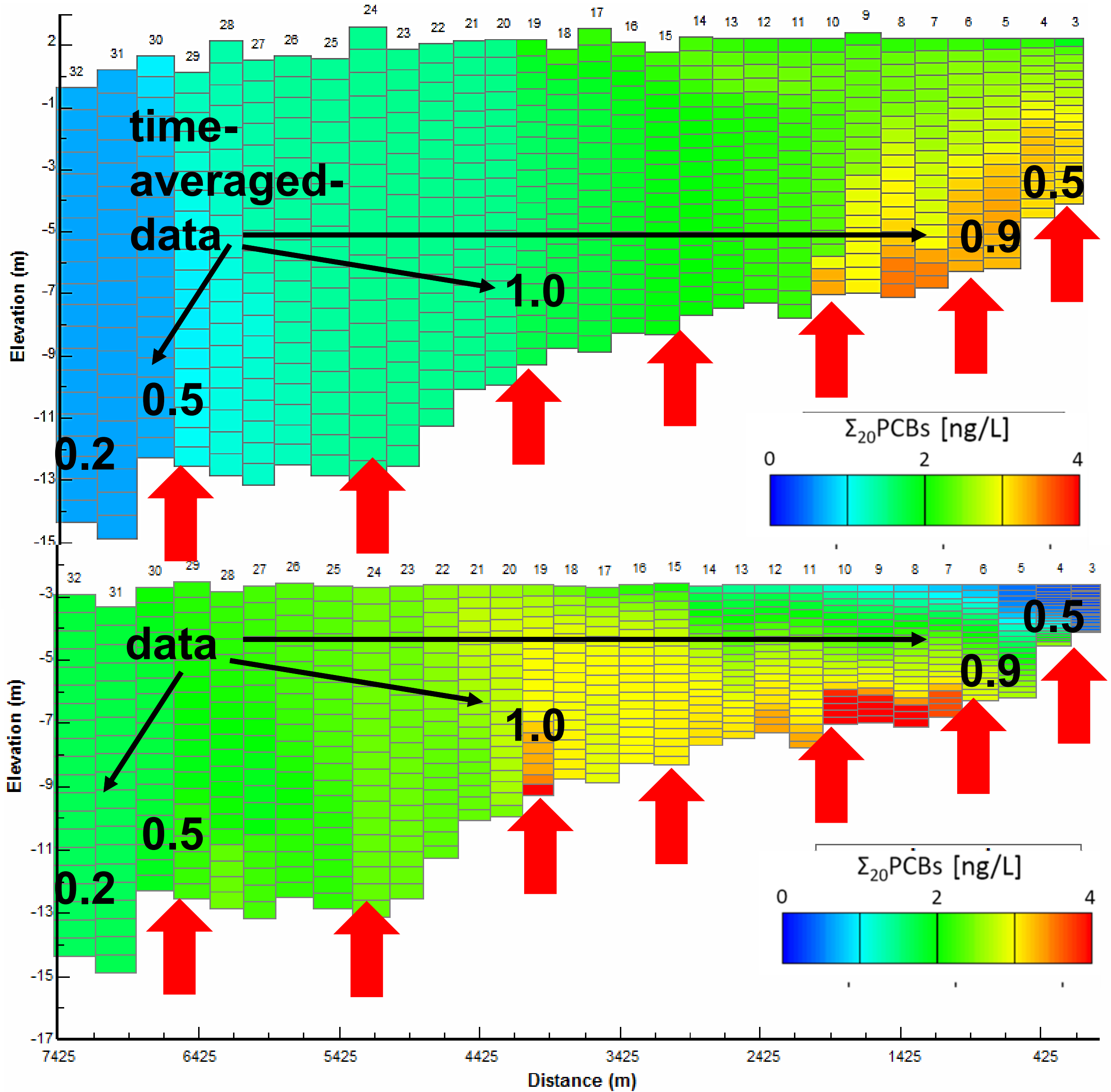


Germano and Associates

Option: Bioturbation Enhanced what would water-column look like?

SERDP DOD • EPA • DOE

(Prendergast)



High Tide

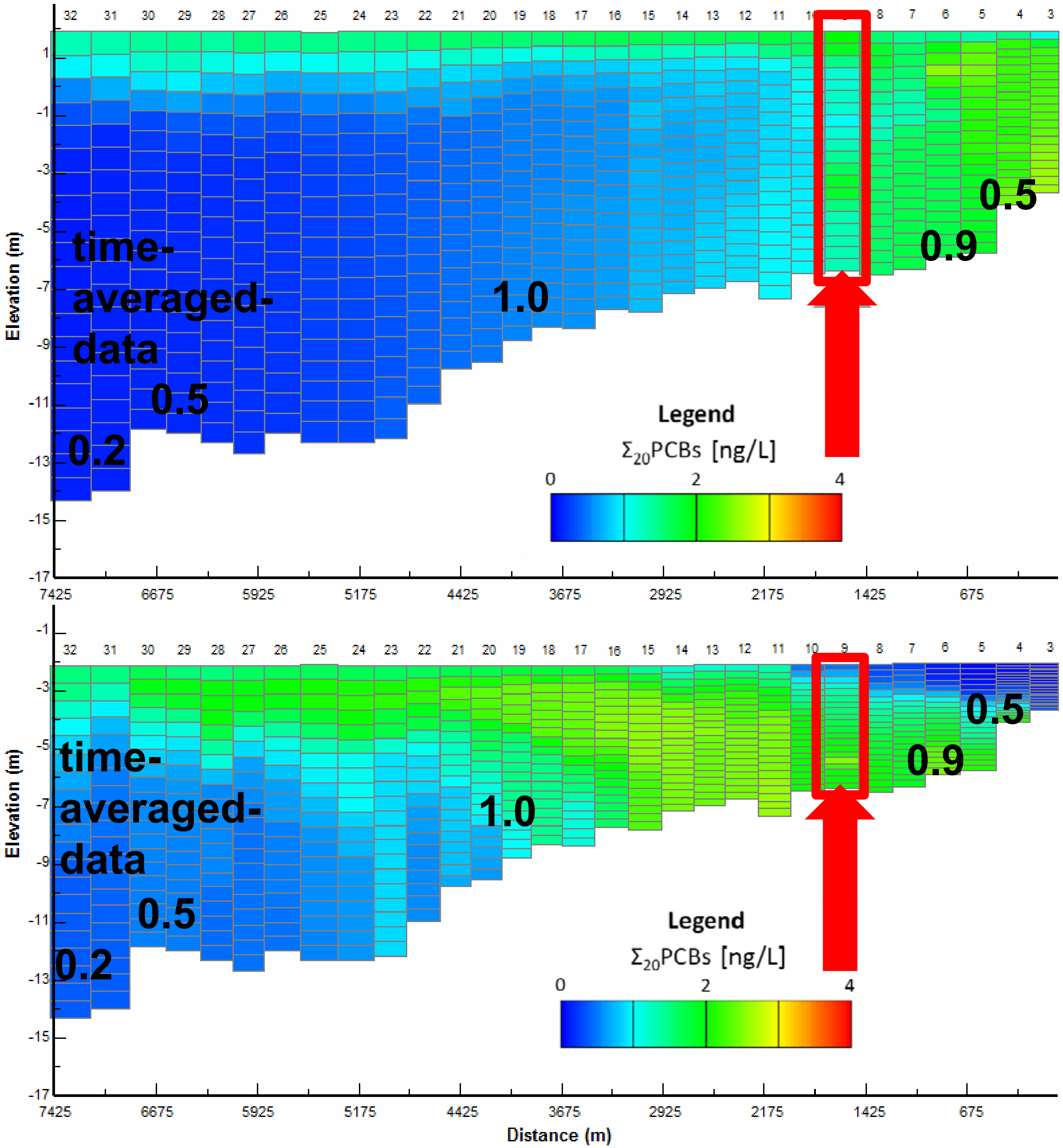
Bed => Water Input at 4 g/day throughout LDW

Low Tide

=> measures too low for that source?

Option: Resuspension & Desorption?

Option: Local Resuspension Source



(Prendergast)

High Tide

Bed => Water Input at only RM 3.5 adding 4 g/d Throughout Water Column

Low Tide

=> not too bad

Option: Outfall sources into LDW surface?

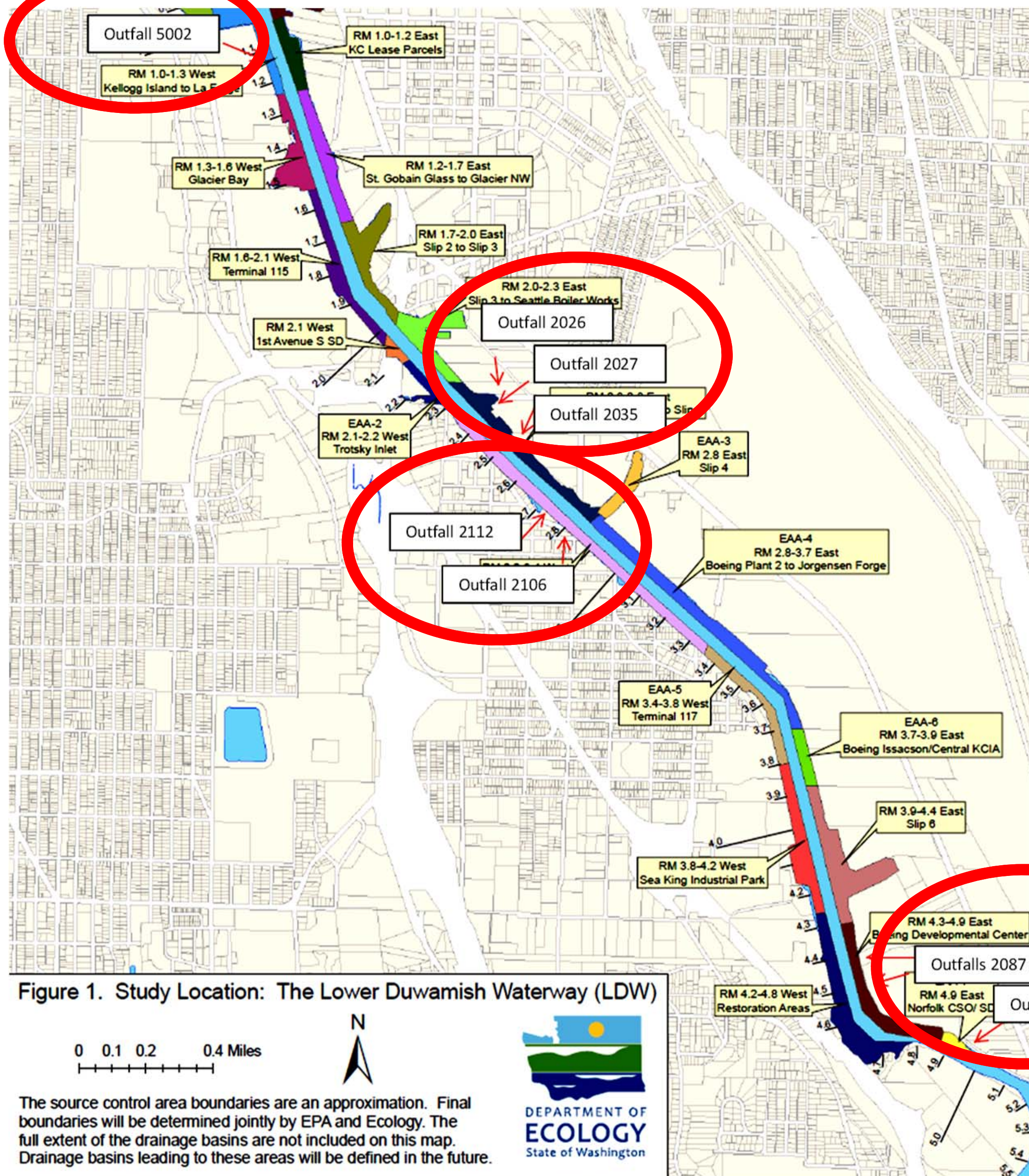
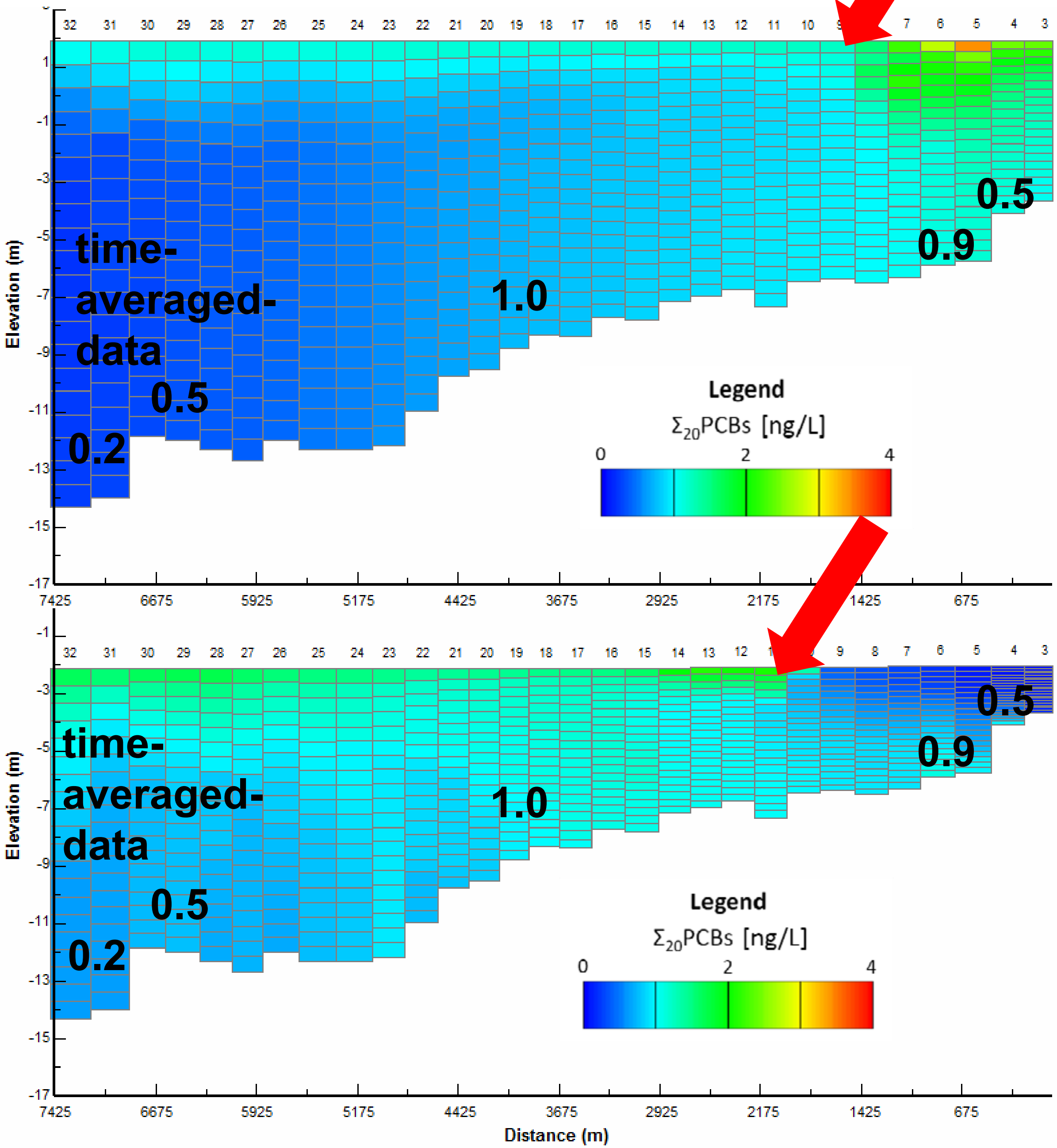


Figure 1. Study Location: The Lower Duwamish Waterway (LDW)

The source control area boundaries are an approximation. Final boundaries will be determined jointly by EPA and Ecology. The full extent of the drainage basins are not included on this map. Drainage basins leading to these areas will be defined in the future.

Option: Outfall Sources

(Prendergast)



High Tide

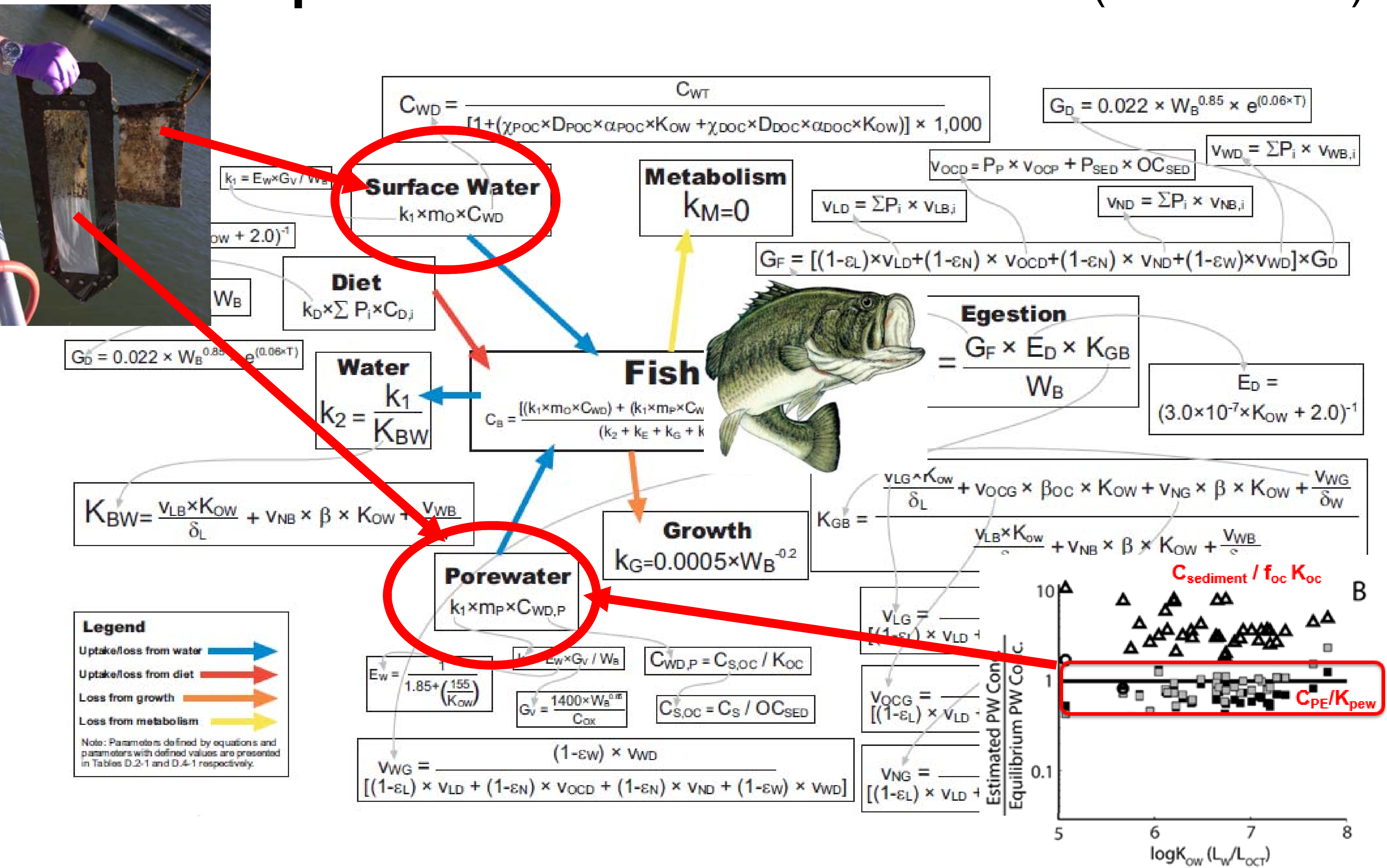
Bed => Water Input at Surface near RM 3.5 adding 4 g/d

Low Tide

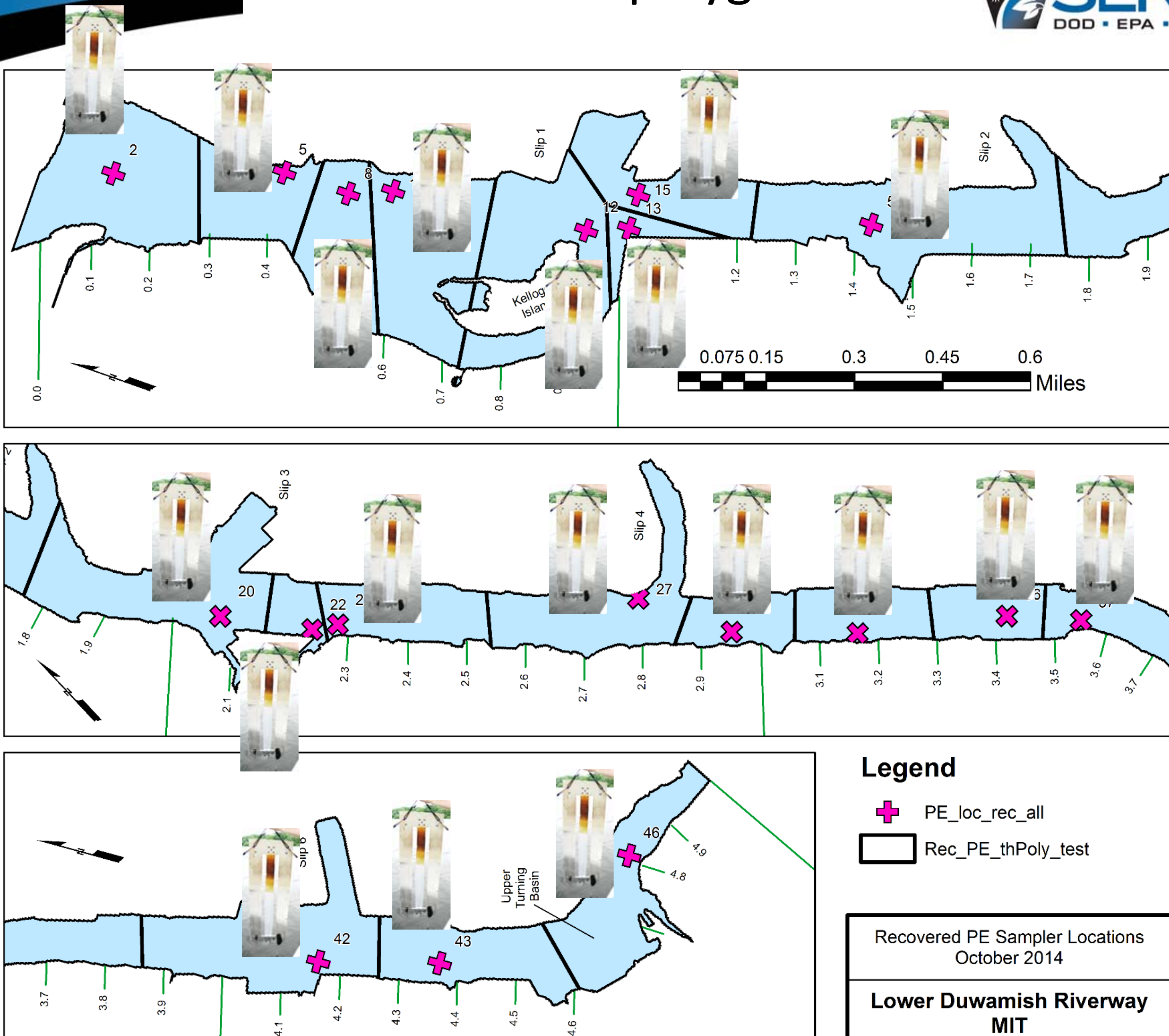
=> need surface water data

SERDP
DOD • EPA • DOE

Exposures => Food Web Model (after Gobas)

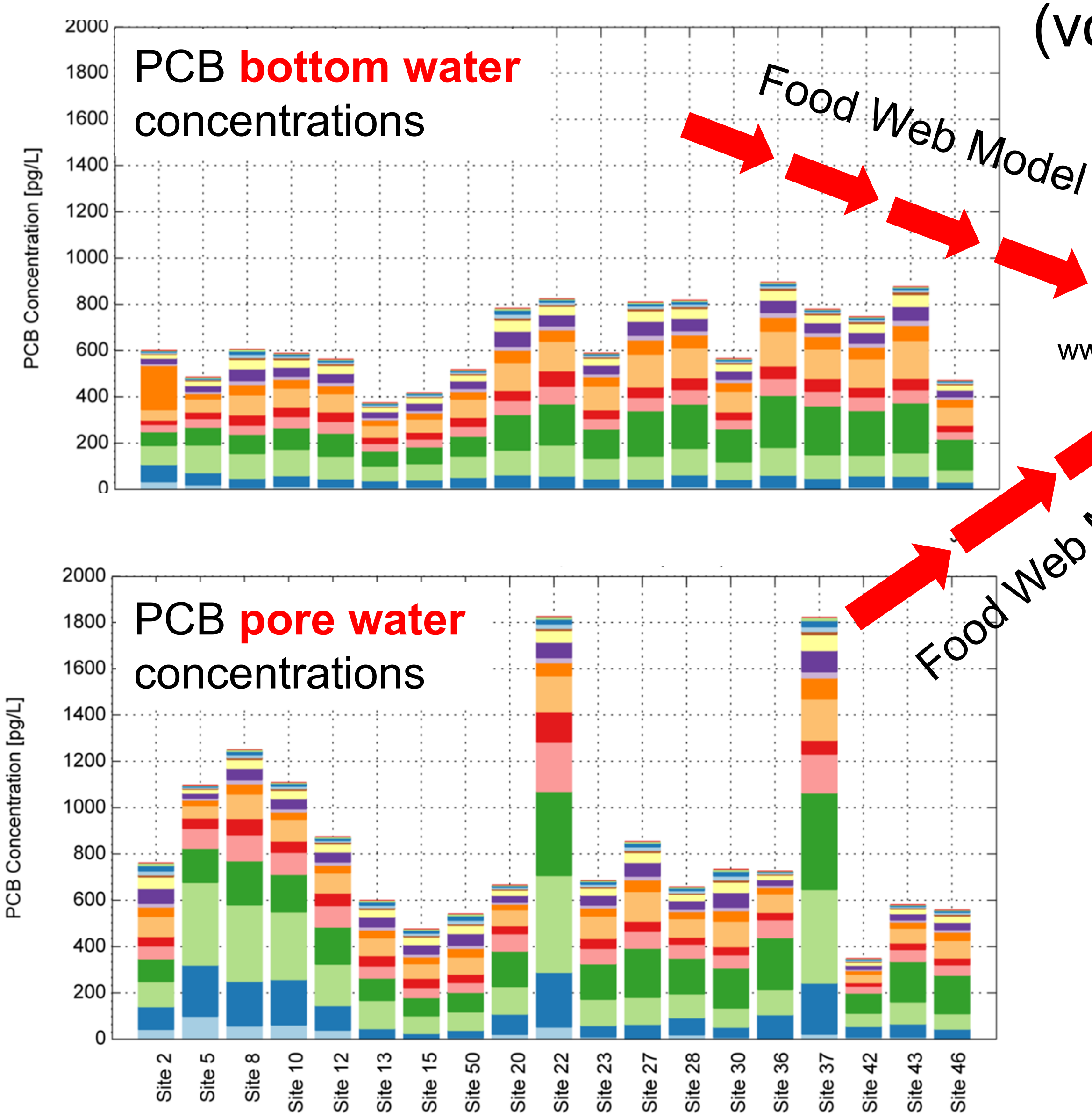


FWM: Thiessen polygons



PCB congeners concs in water and porewater for FWM

(von Stackelberg & Apell)

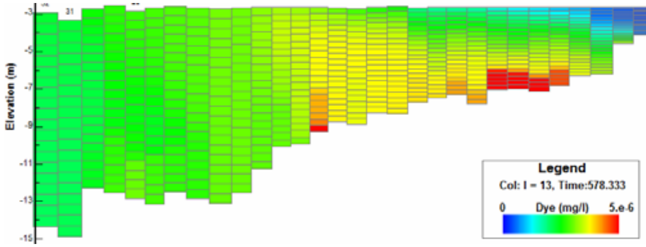


www.seattleweekly.com

Summary

1. PE passive samplers => water and porewater concentrations
   (at sub parts per trillion levels! averaged over weeks)

2. Mass balance modeling integrates water data,
   "points" to most important sources (guide remediation)
   provides "exposure field" in space and time



3. Food web modeling should translate the exposure field to
   quantify risks (decisions)

Acknowledgments

SERDP/ESTCP/US ACoE for funding

Kristen Kerns (ACoE)
Dan Prendergast (MIT)
Fidele Bingwa (MIT)
Rose Wang (Tufts)
Jenn Apell (MIT)
John MacFarlane (MIT)
Megan Burke (MIT)

Tim Thompson (SEE)
Earl Hayter (ACoE)
Dave Michalsen (ACoE)
EPA Divers (Sean Sheldrake et al.)
Bill Jaworski (Marine Sampling)
Analytical Resources Inc.