
# Welcome to the CLU-IN Internet Seminar

Superfund Research Program Sediment Bioavailability Assays - Kick-off Webinar Featuring New Research Projects

*Sponsored by:* NIEHS Superfund Research Program

Delivered: May 7, 2012, 3:00 PM - 5:00 PM, EDT (19:00-21:00 GMT)

*Instructors:*

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*Upal Ghosh, University of Maryland Baltimore County Campus (ughosh@umbc.edu)*
*Michael Unger, Virginia Institute of Marine Science (munger@vims.edu)*

*Moderator:*

*Heather Henry, Program Administrator for the Superfund Research Program at the National Institute of Environmental Health Sciences (NIEHS)*

*Visit the Clean Up Information Network online at* www.cluin.org

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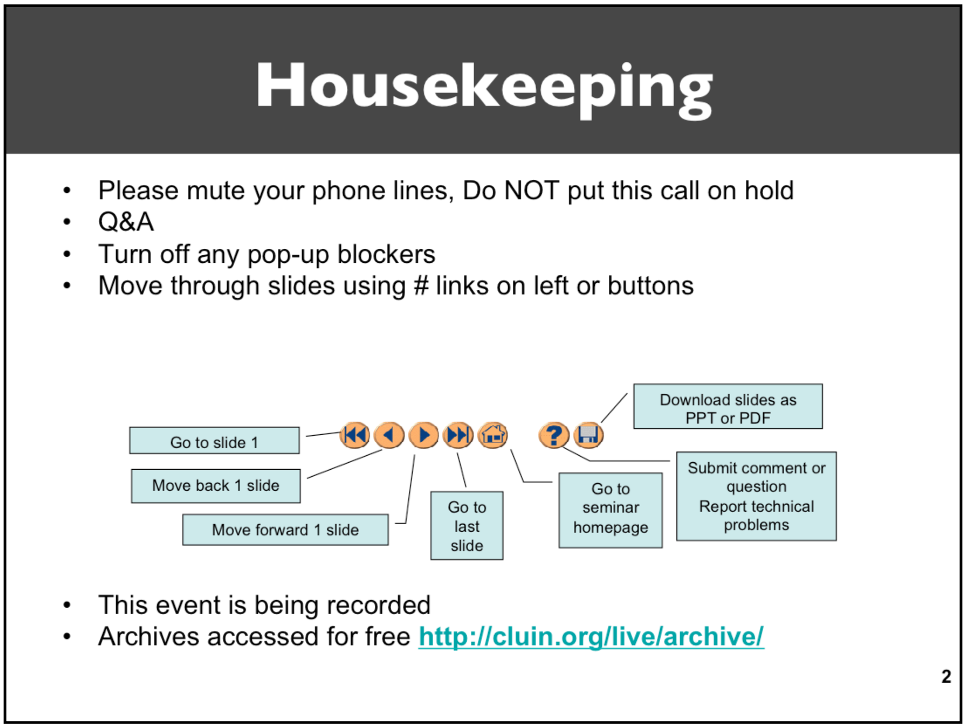


Although I'm sure that some of you have these rules memorized from previous CLU-IN events, let's run through them quickly for our new participants.

Please mute your phone lines during the seminar to minimize disruption and background noise. If you do not have a mute button, press *6 to mute #6 to unmute your lines at anytime. Also, please do NOT put this call on hold as this may bring delightful, but unwanted background music over the lines and interupt the seminar.

You should note that throughout the seminar, we will ask for your feedback. You do not need to wait for Q&A breaks to ask questions or provide comments. To submit comments/questions and report technical problems, please use the ? Icon at the top of your screen. You can move forward/ backward in the slides by using the single arrow buttons (left moves back 1 slide, right moves advances 1 slide). The double arrowed buttons will take you to 1st and last slides respectively. You may also advance to any slide using the numbered links that appear on the left side of your screen. The button with a house icon will take you back to main seminar page which displays our agenda, speaker information, links to the slides and additional resources. Lastly, the button with a computer disc can be used to download and save today's presentation materials.

With that, please move to slide 3.

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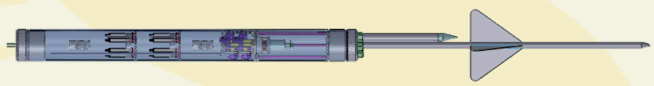
# *In Situ* Sampling Tool for Assessing Bioavailability (IS2B)



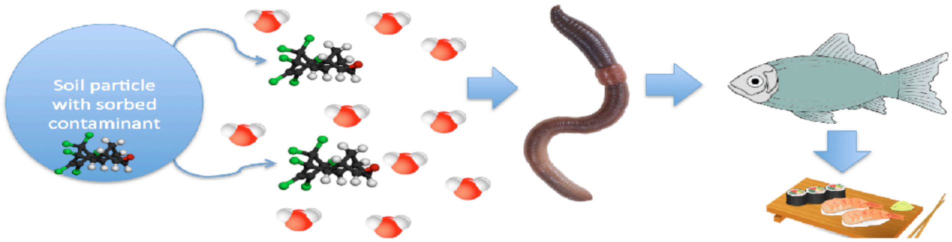

Rolf U. Halden
Sam Supowit
Isaac Roll
Nancy Denslow
Viet Dang
Kevin Kroll

UF UNIVERSITY of FLORIDA The Foundation for The Gator Nation

Srp Superfund Research Program

ASU ARIZONA STATE UNIVERSITY

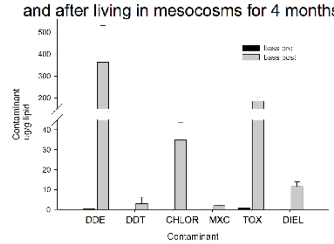
# Can Bioavailability be Assessed Without Analyzing Exposed Organisms?




## Organochlorine Pesticides

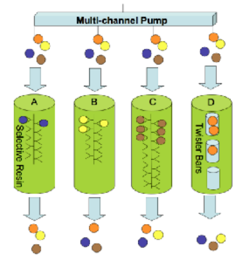
- Most uses banned for decades
- Ecologically persistent
- High rate of use in Florida
- Aquatic sediment contamination
- ENDOCRINE DISRUPTORS

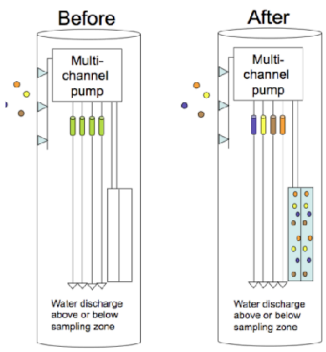
Contaminants in largemouth bass before and after living in mesocosms for 4 months

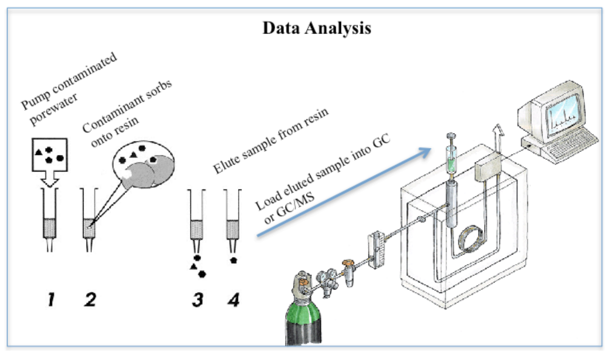


# Approach: Performing SPE In Situ

Solid phase extraction (SPE) resins ($C_{18}$ etc.) are charged in situ in a sampler that actively concentrates analytes from porewater using a peristaltic pump and slow flow rates.



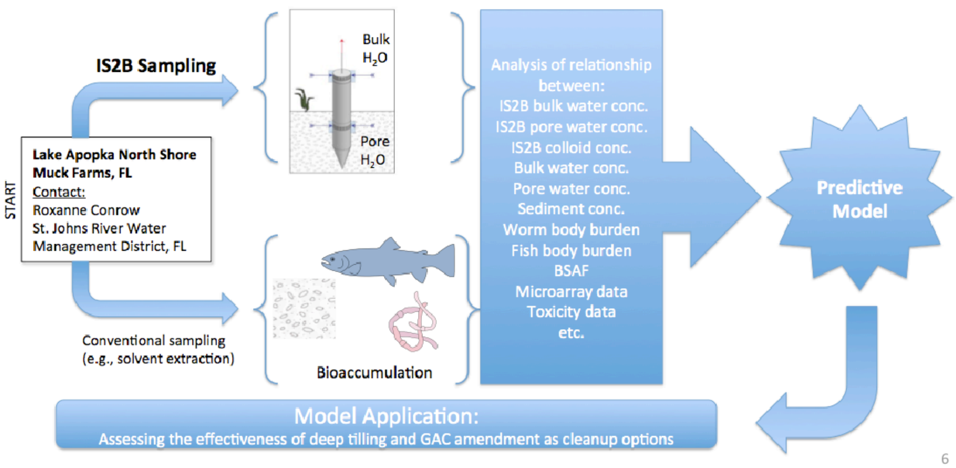




Halden, R. U. and I. B. Roll. Devices and Methods for the Determination of the Bioavailability of Pollutants. Provisional Patent Application, ASU, 2011.

# Project Overview

**Goal:** create an empirical model that relates sediment/bulk-water toxicant levels to their associated adverse effects in animals (worms/fish), so that a simple physical measurement of both concentrations can inform on the bioavailability and toxicity of sediment-borne pollutants.

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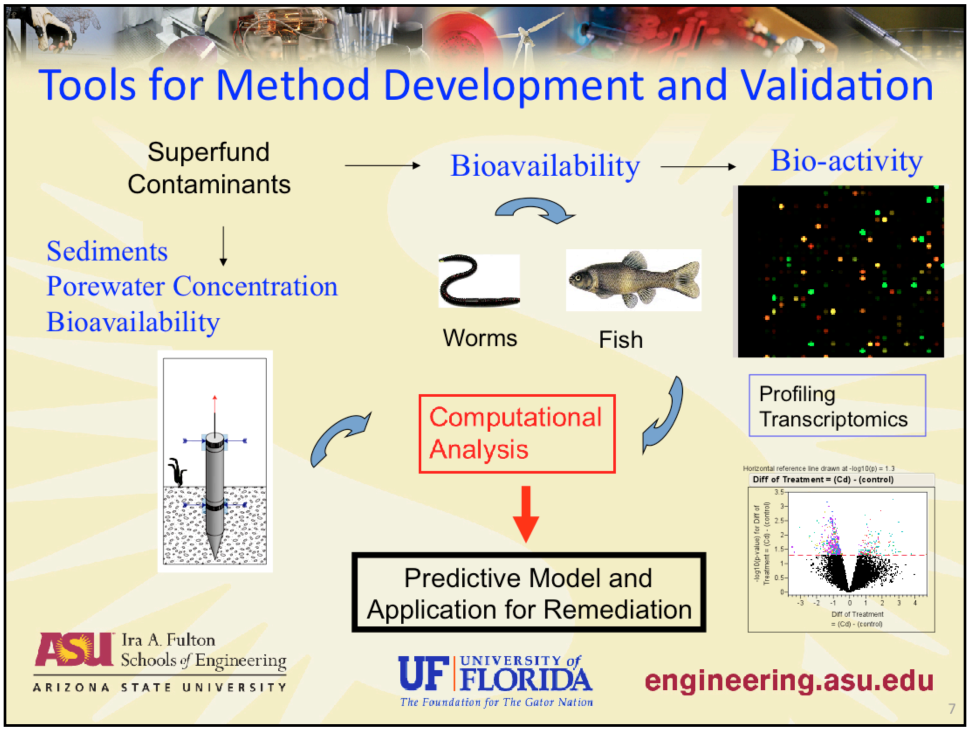
Tools for Method Development and Validation
Superfund Contaminants
Bioavailability
Bio-activity
Sediments
Porewater Concentration
Bioavailability
Worms
Fish
Profiling Transcriptomics
Computational Analysis
Predictive Model and Application for Remediation
Diff of Treatment = (Cd) - (control)
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# Remediation Effectiveness for Mining Sites: Hysteresis and Metal Mixture Effects

*Principal Investigators*

James Ranville, Christopher Higgins — Colorado School of Mines

James Shine — Harvard School of Public Health

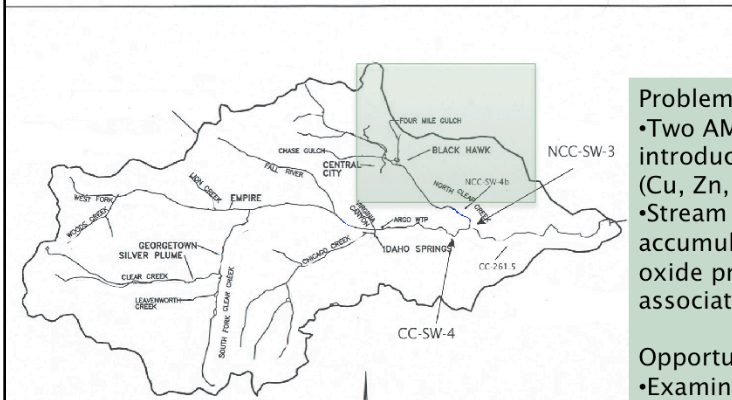
William Clements — Colorado State University

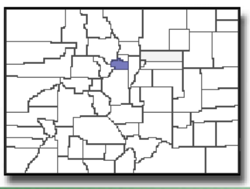
Joseph Meyer — Arcadis

*Site Collaborator*

Mike Holmes — USEPA Region VIII

## Field Study: Blackhawk/Central City Superfund Site



Problem:
- Two AMD sources introduce dissolved metals (Cu, Zn, Cd)
- Stream sediments have accumulated Fe, Al, Mn oxide precipitates and associated metals

Opportunity:
- Examine the recovery of the stream following restoration (late 2013)

Research Approach
- laboratory/mesocosm/in-stream experiments & field observations

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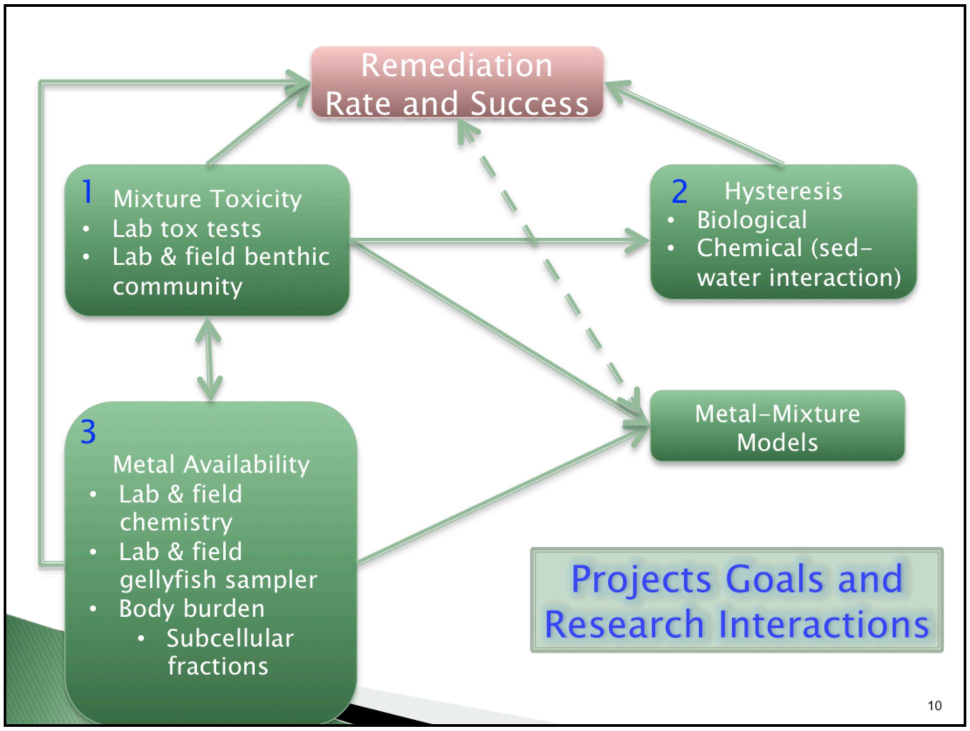
Remediation
Rate and Success
1 Mixture Toxicity
• Lab tox tests
• Lab & field benthic community
2 Hysteresis
• Biological
• Chemical (sed-water interaction)
Metal-Mixture Models
3
Metal Availability
• Lab & field chemistry
• Lab & field gellyfish sampler
• Body burden
• Subcellular fractions
Projects Goals and Research Interactions
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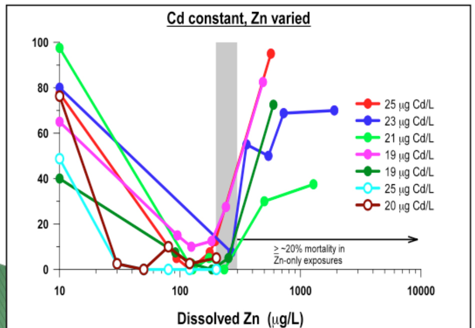
- Metals are regulated on an individual basis but usually occur in mixtures in aquatic systems
- Metal-mixture toxicity can be:
  - additive
  - less-than-additive
  - more-than-additive

1 Mixture Toxicity
- Lab tox tests
- Lab & field benthic community




Addition of low levels of Zn reduces Cd toxicity to D. magna

Concentrations of individual dissolved metals might not be good predictors of mixture toxicity

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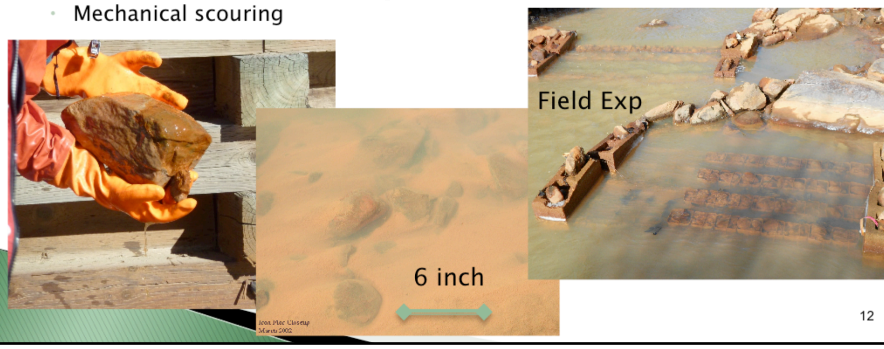
2 Hysteresis

- Biological
- Chemical (sed-water interaction)

- Physical and Chemical Aspects of Stream Sediments
  - Sediments can be loosely deposited flocs or armored coating on rocks
  - These forms of metal-containing sediments may be removed at different rates and by different processes
    - Desorption
    - Dissolution
    - Mechanical scouring

- There may be a delay (hysteresis) in recovery following remediation
- Different degrees of chemical and biological hysteresis may result for different metals

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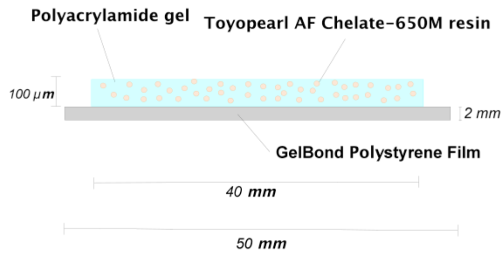


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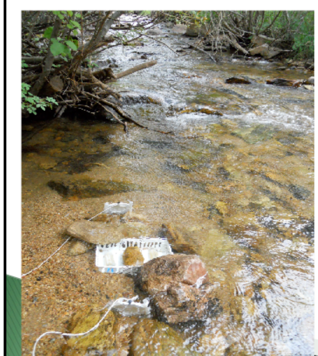
Metal Availability

- Lab & field chemistry
- Lab & field gellyfish sampler
- Body burden
  - Subcellular fractions



Gellyfish:

-Iminodiacetate (IDA) metal-binding resin held within a polyacrylamide wafer equilibrates with free metal ions

-Calculate free metal-ion concentrations in surrounding solution ($Cu^{2+}$, $Ni^{2+}$, $Cd^{2+}$, $Pb^{2+}$, $Zn^{2+}$); can account/correct for competitive metal-metal interactions

-Test whether Gellyfish results correlate with instream invertebrate community responses

$\Rightarrow$ will help explain bioavailability mechanisms

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# COMBINING BIOAVAILABILITY ASSAYS WITH MODELING TO PREDICT PCBS IN FISH AFTER REMEDIATION

**Upal Ghosh and Hilda F. Khoei**

**Dept. of Chemical, Biochemical, and Environmental Engineering, UMBC**

**Allen Place and Aaron Watson**

**Institute of Marine and Environmental Technology, UMCES**

**John Connolly**

**Anchor QEA**

SRP Webinar for Sediment Bioavailability May 7 2012

UMBC · IMET Institute of Marine & Environmental Technology · ANCHOR QEA

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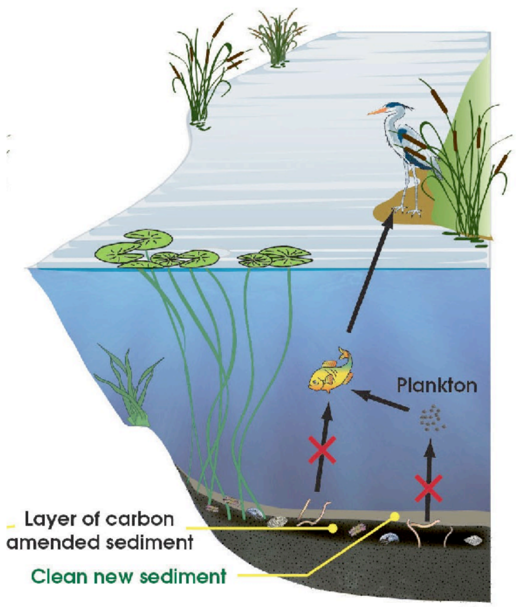
# ASSESSING REMEDIATION EFFECTIVENESS




Our recent work has demonstrated that activated carbon amended to surficial sediments reduces contaminant exposure to food chain through:

•Reduced bioaccumulation in benthic organisms

•Reduced flux into water column and uptake in the pelagic food web.

- **Evaluation of in-situ remedy requires measurement of exposure pathways**
- **Traditional measurement of residual surface concentration not useful in assessing bioavailability reduction**

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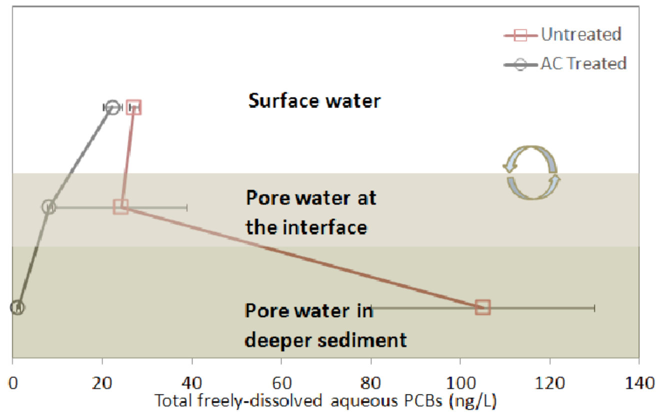
## PASSIVE SAMPLERS USEFUL IN ASSESSING EXPOSURE

Bioavailability measurements useful when they can be used to measure exposure pathways

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## RESEARCH AIMS

**Specific aim 1**: Develop the fundamental basis of passive sampling.
Approach: Using a combination of thin sectioning and micro-scale analytical techniques quantify PCB diffusion in and out of common polymers used for measurement.

**Specific aim 2**: Use passive sampling to measure bioavailability processes and uptake in fish.
Approach: Perform laboratory aquaria studies to assess uptake in a pelagic and benthic feeding fish for treated and untreated PCB impacted sediment.

**Specific aim 3**: Incorporate passive sampling inputs to PCB fate and bioaccumulation model.
Approach: Model PCB exposure to:1) interpret results from the mesocosm exposure experiments, and 2) use these results and field observations to explore the efficacy of in situ remediation on PCB accumulation in fish

# FIRST SET OF LABORATORY EXPOSURE EXPERIMENTS


Treatments: clean sediment, PCB impacted sediment, PCB impacted sediment-AC treated
Replicate aquaria with passive samplers in water column and sediment
Two species of fish: a pelagic feeder and a benthic feeder
Uptake in algae, daphnia, and oligochaetes
Sediment Source: Grasse River NY

# ACKNOWLEDGEMENTS

Students: Hilda Fadei Khoei (UMBC), Aaron Watson (IMET)

Source of funding: NIEHS Superfund Research Program

Source of PCB-impacted sediments: Grasse River, NY.  Larry McShea Alcoa.

## A real-time antibody-based field assay to predict contaminant bioavailability in sediments

PIs: Michael Unger, Stephen Kaattari, Wolfgang Vogelbein
Virginia Institute of Marine Science, College of William & Mary, Gloucester Point, VA
Collaborator: Josef Rieger, The Elizabeth River Project, Portsmouth, VA

Bioaccumulation models are needed

- •Analysis of biota expensive/ time consuming
- •Variability can hinder model predictions
- •Real-time analysis of the bioavailable component is needed

For this NIEHS-SRP project we will evaluate, refine and validate a quantitative, monoclonal antibody (mAb)-based sensor to measure polycyclic aromatic hydrocarbons (PAH) in sediment-associated water as a rapid predictor of PAH bioaccumulation in the oyster.

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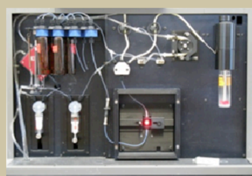
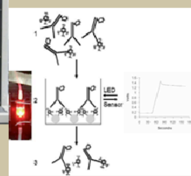
Measuring contaminant uptake in biota is time consuming and expensive so models have been developed to predict contaminant fate and disposition. However, temporal variability and heterogeneity of natural and remediated habitats make it difficult to apply models to reliably predict bioaccumulation for risk assessments. Recent advances in biosensor technology now allows near real-time measurement of contaminants in the field at sub part per billion concentrations that should provide good prediction of bioaccumulation.

# Antibody Biosensor Technology

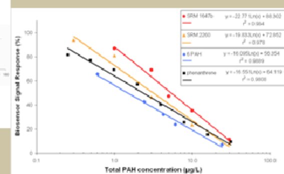


Sāpidyne Instruments Inc.

**KinExA Inline Sensor**
Fluorescence detection, rapid (minutes), small sample volume (1mL)

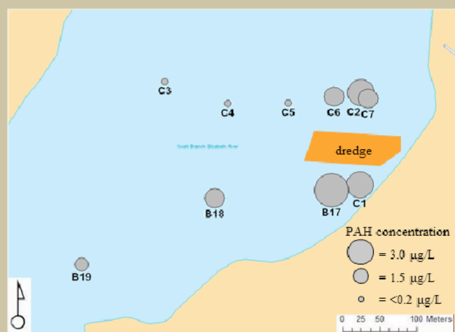


PAH selective antibody (Spier et al, 2009, Anal. Biochem.)

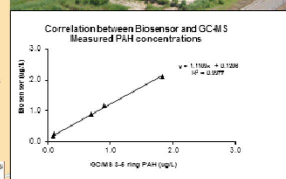



Sensitive (sub-ppb) and precise

Antibodies can be selected for various targets (ie. 3-5 rings)




Field tested during Elizabeth River sediment remediation efforts




Good correlation with GC-MS results (Spier et al, 2011, Environ. Chem. Tox.)

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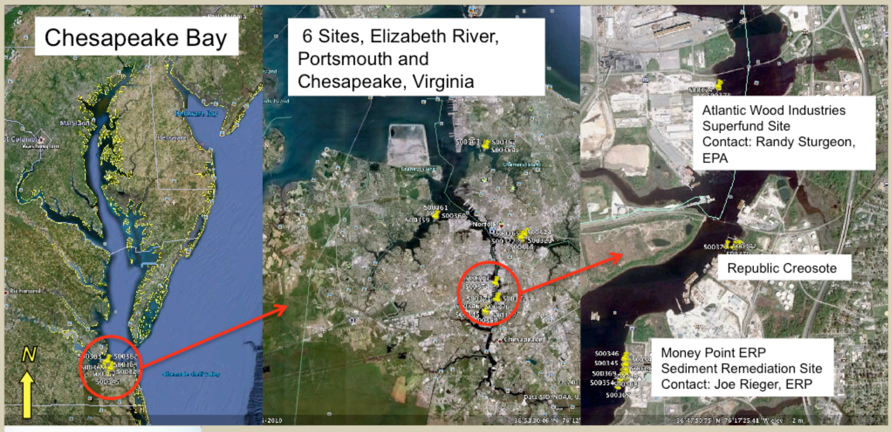
**Aim 1. Conduct on-site PAH measurements of water using a rapid, cost-effective real-time biosensor and test its ability to predict tissue burdens in oysters from PAH-contaminated environments.**




Six sites with wide range of PAH contamination: Reference sites and Superfund clean-up of creosote contaminated sediment

Measure PAH in water and pore water by Biosensor and GC-MS measurement of PAH in water, pore water, sediment and oyster tissues (natives and transplants)

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**Aim 2. Conduct controlled laboratory dosing of oysters to validate the biosensor as an effective predictor of oyster tissue burdens as a strict function of dose (concentration, time).**

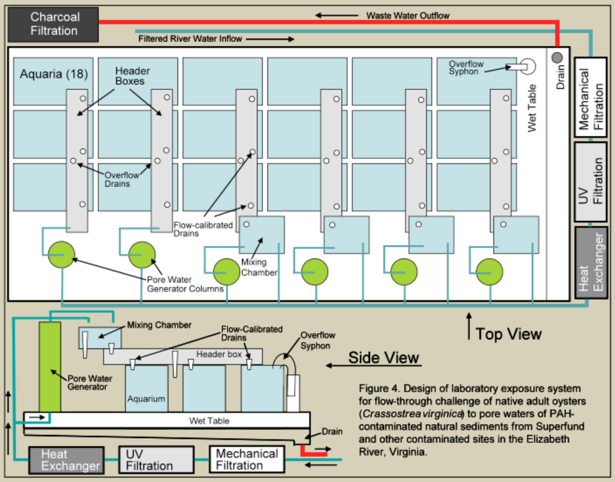


Figure 4. Design of laboratory exposure system for flow-through challenge of native adult oysters (*Crassostrea virginica*) to pore waters of PAH-contaminated natural sediments from Superfund and other contaminated sites in the Elizabeth River, Virginia.

PAH contaminated sediments collected in the field will be used to generate pore water solutions to dose oysters with a range of PAH concentrations and distributions to evaluate bioaccumulation

These exposures will assess biosensor performance at predicting PAH bioaccumulation under controlled laboratory conditions

The system will also be used to evaluate sediment remediation techniques and how they alter PAH concentrations in the aqueous phase and how that alters bioavailability

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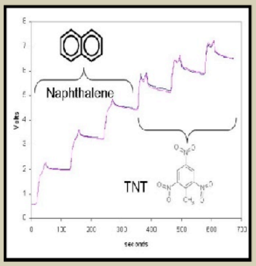
**Aim 3. Extend current Biosensor capabilities via development of a bi- or multi-analyte biosensor that permits rapid, combined monitoring of different PAH classes within a single site.**




Preliminary work has shown that our biosensor platform can be adapted to use more than one antibody to quantify multiple analytes in a sample

Based on the results of our field and laboratory evaluations, a repertoire of PAH antibodies will be incorporated to improve the biosensor prediction capabilities for specific PAH or groups of PAH

**Summary-The three specific aims of this project are designed to help us understand how:**

• PAH concentrations measured by antibody detection in the aqueous phase can predict the biologically available fraction of the total contaminant pool in sediments

• Sediment characteristics and remediation approaches influence the bioavailability and steady state bioaccumulation of PAH from the aqueous phase

•Additional antibody specificities can be used in combination to better predict contaminant bioavailability to aquatic organisms.

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# Use of Stable Isotopes in Bioavailability Assessment

PI: Jay Gan, University of California, Riverside
Co-PI: Dan Schlenk, UC Riverside
Collaborators: K. Maruya, SCCWRP, CA
Joe Gully, LA Sanitation District

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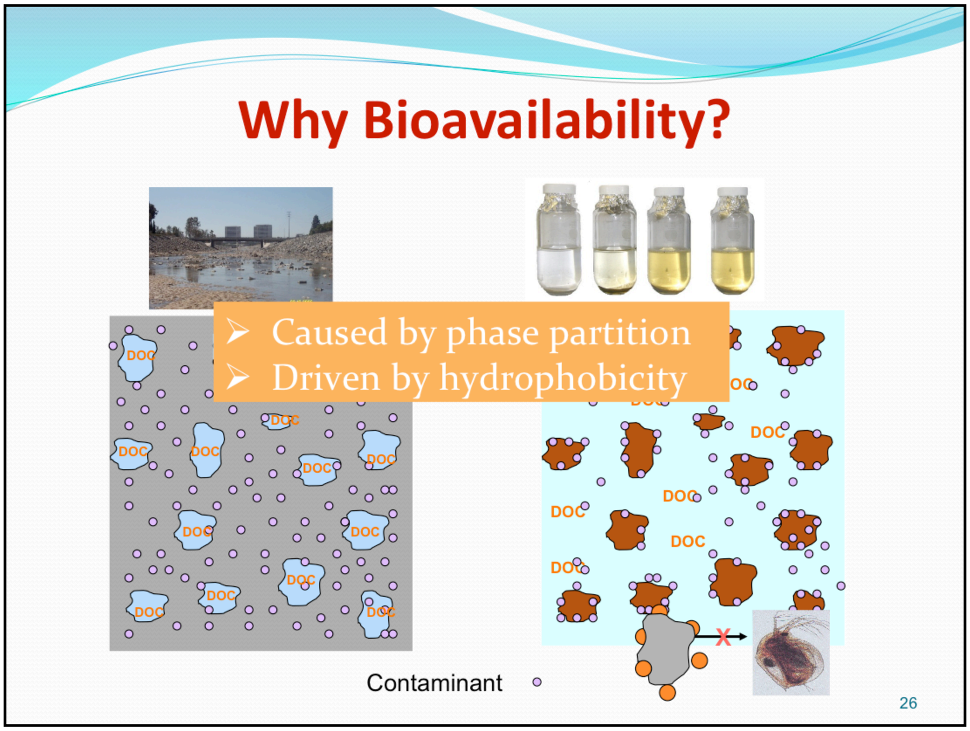
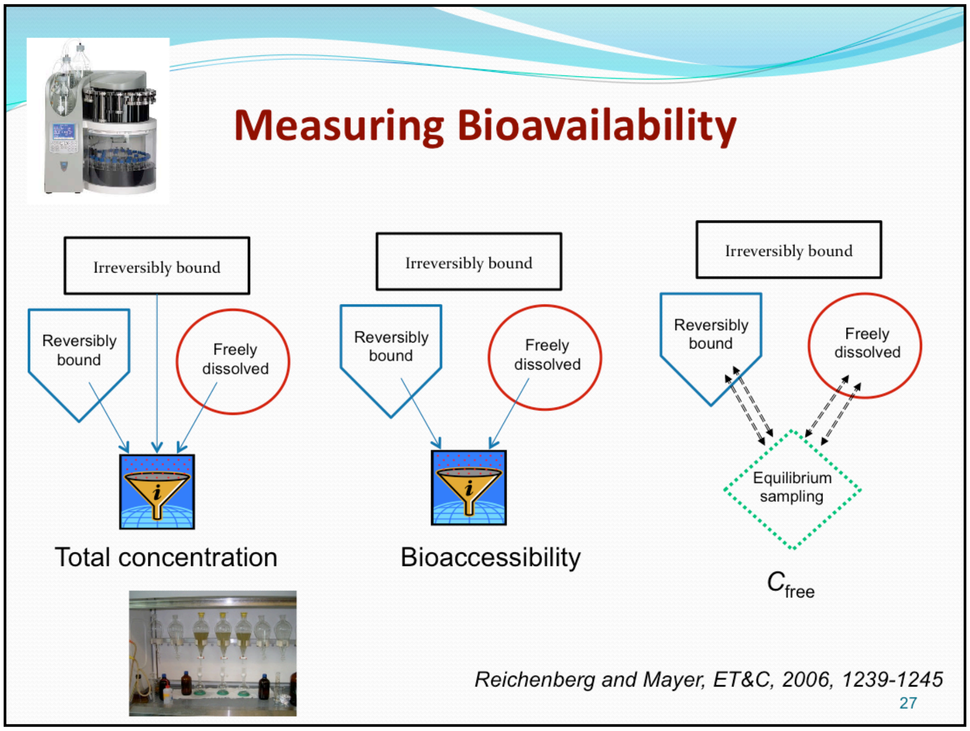

Why Bioavailability?
Caused by phase partition
Driven by hydrophobicity
DOC
Contaminant
26


Measuring Bioavailability
Irreversibly bound
Reversibly bound
Freely dissolved
Total concentration
Irreversibly bound
Reversibly bound
Freely dissolved
Bioaccessibility
Irreversibly bound
Reversibly bound
Freely dissolved
Equilibrium sampling
$C_{free}$
Reichenberg and Mayer, ET&C, 2006, 1239-1245
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# Current Methods and Limitations

**Bioaccessibility**

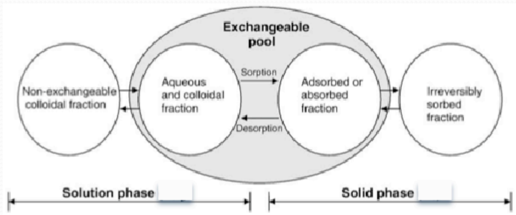
- Partially depletive
  - Mild solvent extraction
  - Gut fluid extraction
  - Cyclodextrin extraction
  - Tenax adsorption extraction

## Limitations

- Mild solvent extraction
  - Varies with solvent strength
  - Influenced by extraction time or conditions
- Tenax, HPCD
  - Multi-step extractions
  - Tedious
  - Impractical

# Isotope Exchange/Dilution

- HOC in a soil (or sediment) ($C_t$) is distributed in different forms:




$$C_{\text{total}} = (D \times C_{\text{w}}) + C_{\text{e}} + C_{\text{n}}$$

$E$

$$E = \frac{C_w}{C_w^*} \times C^*$$

$C_{\text{w}}$ = soluble (isotopically dilutable)
$C_{\text{e}}$ = reversible sorbed (isotopically exchangeable)
$C_{\text{n}}$= irreversible fixed (non-isotopically exchangeable)

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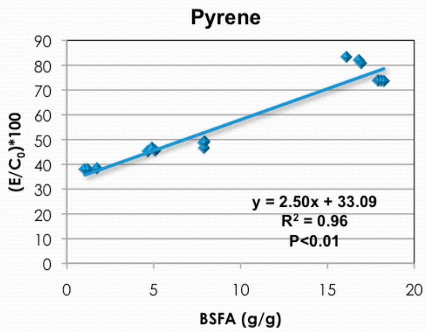
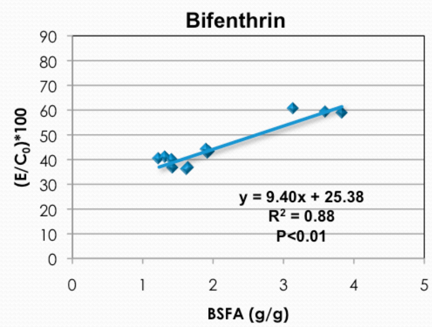
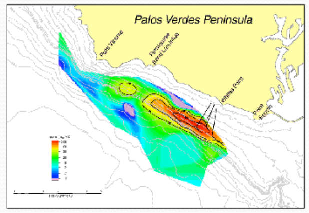
# *E* Predicts Bioaccumulation

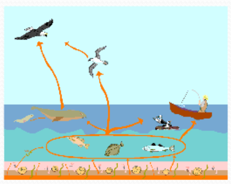



- **Feasibility**:
  - Labeled compounds commonly available, at low cost
  - GC-MS commonly available in labs
  - No safety concerns

# Palos Verdes Superfund Site

**Method application:**

- Palos Verdes Shelf
- Sediments severely contaminated with DDT, PCBs
- Scheduled for capping in 2012-2013
- In collaboration with LA County Sanitation District (Mr. J. Gully) and SCCRWP (Dr. K. Maruya)

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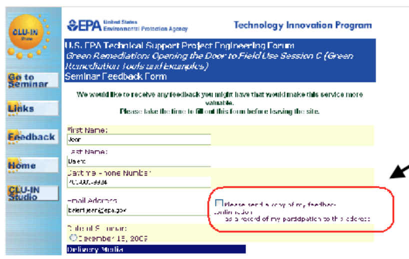
# Resources & Feedback

- To view a complete list of resources for this seminar, please visit the **Additional Resources**
- Please complete the **Feedback Form** to help ensure events like this are offered in the future

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