Application and Use of Passive Samplers for Monitoring Organic Contaminants at Superfund Sediment Sites

CLU-IN

26 August 2013

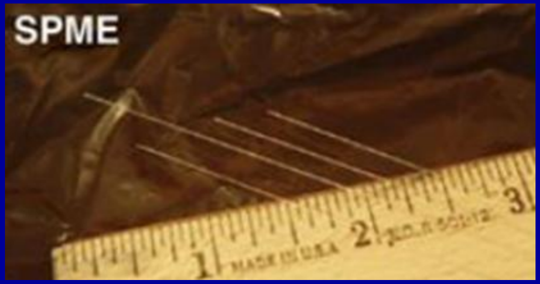
Contaminated Site Clean-Up Information

Background

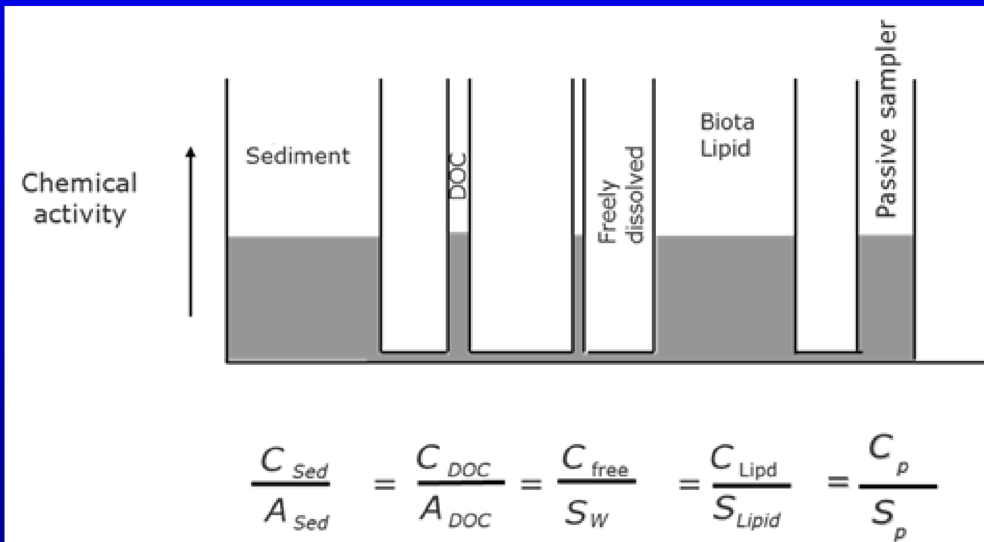
- Management of contaminated sediments includes source and institutional controls, remediation, and evaluating effectiveness of selected management actions
- Contaminant analyses for bulk or whole sediment often serve as a critical LOE used to support decision-making
  - **Often provide a poor predictor of exposure and subsequent risk since contaminant bioavailability is ignored**
  - **EqP models were developed to predict freely dissolved concentrations in sediment porewater…BUT WITH LIMITATIONS**
- Driven partly by cost of remedial decisions, these challenges have led to advances in use of passive sampling methods (PSMs)
  - Goal: **quantify bioavailability of contaminants in sediments**

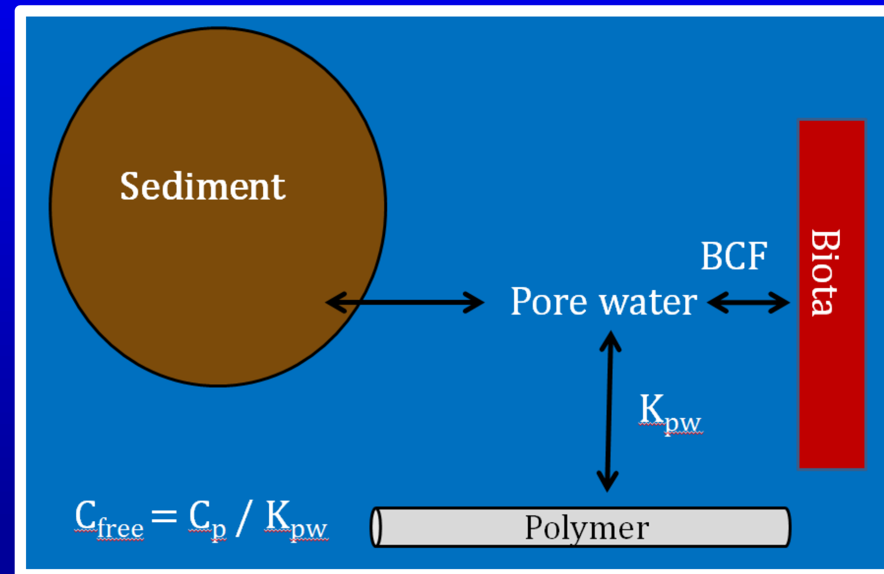
Variety of PSM phases and configurations

Passive Sampling Phase or Media	Configuration	Target Analytes
Polydimethylsiloxane (PDMS)	Coated fiber, vial	HOCs
Polyethylene (PE)	Film/sheet, tube	HOCs
Polyoxymethylene (POM)	Film/sheet	HOCs
Ethylvinylacetate (EVA)	Coated vial	HOCs
Silicone rubber (SR)	Sheet, Ring	HOCs
Gels (e.g., DGT)	Thin film "DGT"	Metals
Resin impregnated polyacrylamide gel	"Gellyfish"	Metals
Metal-chelating media	Disk/membrane	Metals
Water-filled equilibration cell	"Peeper"	Metals



C_{free} estimates from PSMs





- Measure the equilibrated polymer concentration (C_p)
- $C_{free} = C_p / K_{pw}$

where K_{pw} is the substance-specific polymer-water partition coefficient

Regulatory "Acceptance" …

- They are accepted
- Are being used at several sites, mostly to revise the Conceptual Site Model
- Is no formal Superfund acceptance process
- If passive samplers helps remedial project managers (RPMs) answer key site questions, they will be used:
  - Is there a risk, what are the key exposure pathways?
  - What combination of dredging, capping, MNR?
  - What are the risk-based goals and sediment cleanup levels?
  - How to determine remedy effectiveness?
  - Does the remedy meet performance targets and RAOs ?

… So why aren't PSMs more widely used?

- Key barriers to more regulatory acceptance and use include:
  - Failure of practitioners and decision makers to understand the advantages and limitations of these chemical-based approaches over traditional analytical methods
  - Confusion regarding the plethora of different methods and formats that are increasingly reported in the literature
- **Lack of consensus on:**
  - Technical guidance for PSM selection and standardization
  - Use in regulatory decision-making contexts
- Limited experience in use and analysis of PSMs by commercial laboratories
- **Uncertainty over cost vs. benefit**

Technical Guidance on Bioavailability & Bioaccessibility Measurements Using Passive Sampling Methods and Partitioning-Based Approaches for Management of Contaminated Sediments

Summary of a SETAC Workshop

Rachel Adams
Ian Allan
Mayumi Allinson
Kim Anderson
Sabine Apitz
Chris Beegan
Todd Bridges
Steven Brown
Robert Burgess
John Cargill
Peter Campbell
Peter Chapman*
Yongju Choi
Beate Escher*
Will Gala

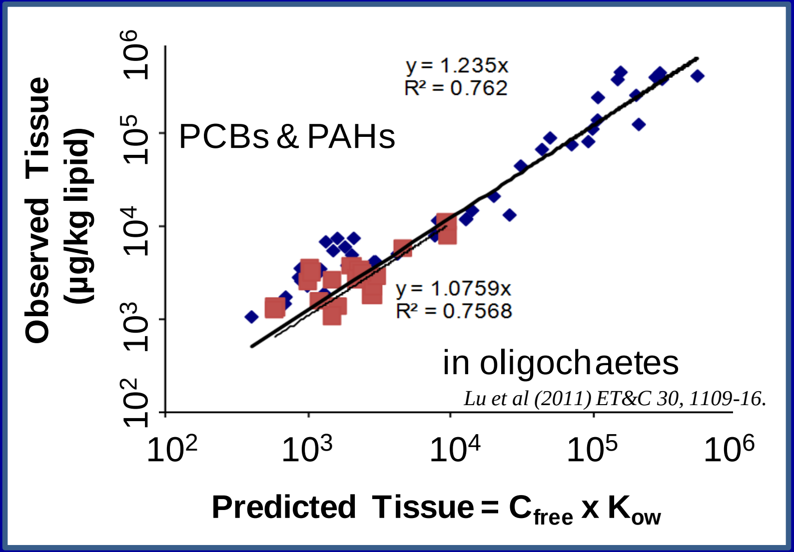
Jay Gan
Upal Ghosh*
Frank Gobas
Todd Gouin
Marc Greenberg*
Phillip Gschwend
Amanda Harwood
Steven Hawthorne
Paul Helm
Michiel Jonker
Susan Kane-Driscoll*
Peter Landrum*
Huizhen Li
Michael Lydy*
Keith Maruya*

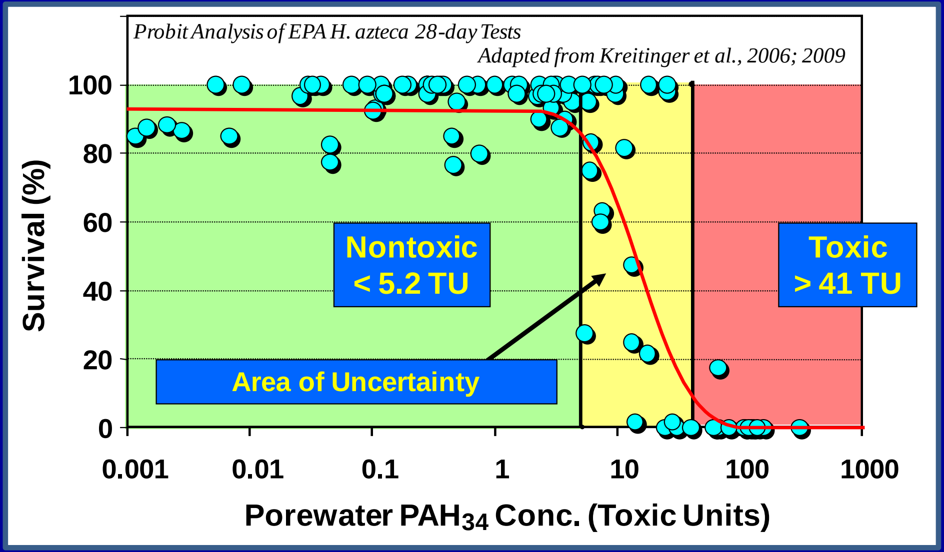
Philipp Mayer*
Charles Menzie
Megan McCulloch
Julie Mondon
Munro Mortimer
Jochen Mueller
Amy Oen
Thomas Parkerton*
Willie Peijnenburg*
Danny Reible
James Shine
Foppe Smedes
Jing You
Gesine Witt
Eddy Zeng*

http://www.setac.org/resource/resmgr/publications_and_resources/executivesummarypassivesampl.pdf

State of the Science

- Generally accepted that C_{free} provides more relevant exposure metric than total or bulk sediment conc
- Hydrophobic organic compounds (HOCs)
  - Significant literature available detailing calibration and application of PSMs in sediment assessment (>100 papers)
  - Estimates of C_{free} from PSMs shown to better predict measurement endpoints e.g. sediment bioaccumulation and toxicity



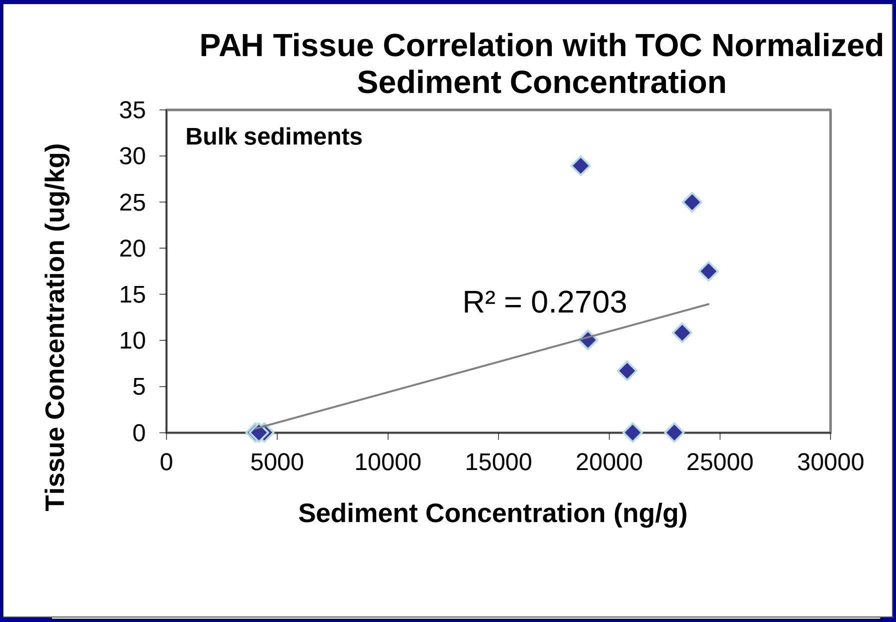


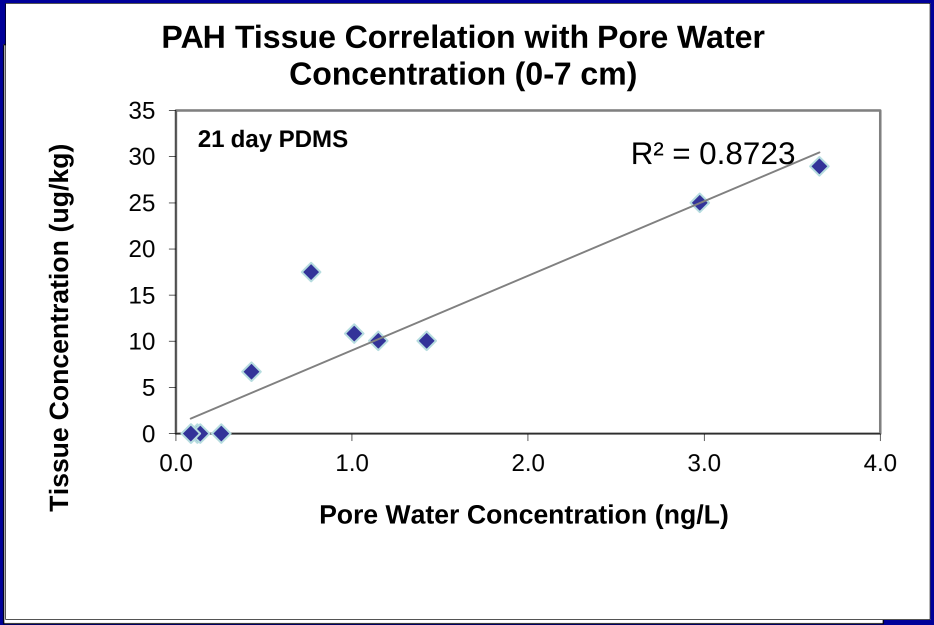
  - Wide range of calibration parameters have been published for the various polymers and/or configurations of PSMs

Tissues & Integration of Passive Samplers

Example: Naval Station San Diego

- **Good** correlation between *Musculista* tissue and SPME-derived pore water concentrations for PAHs
- **Weak** correlation between TOC-normalized bulk sediment concentration and tissue concentration
- Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene



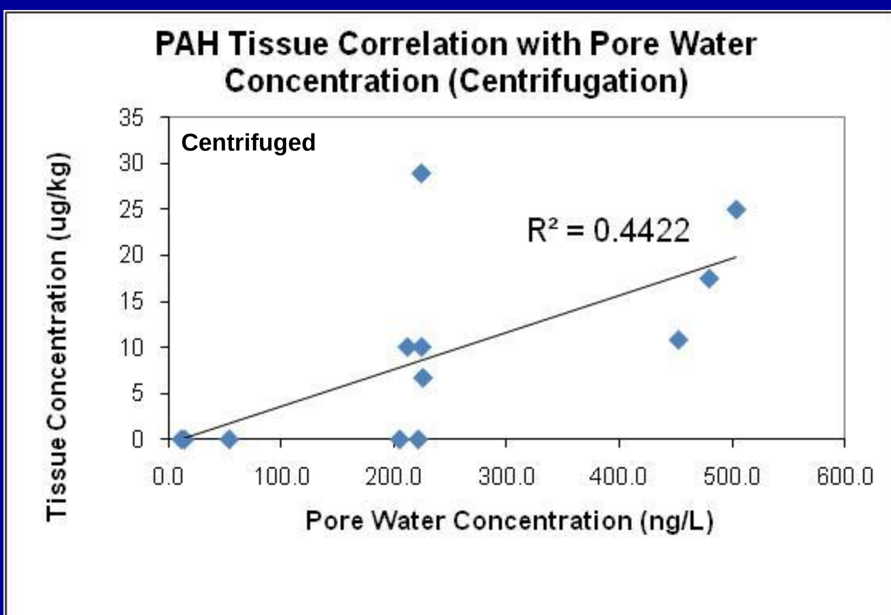


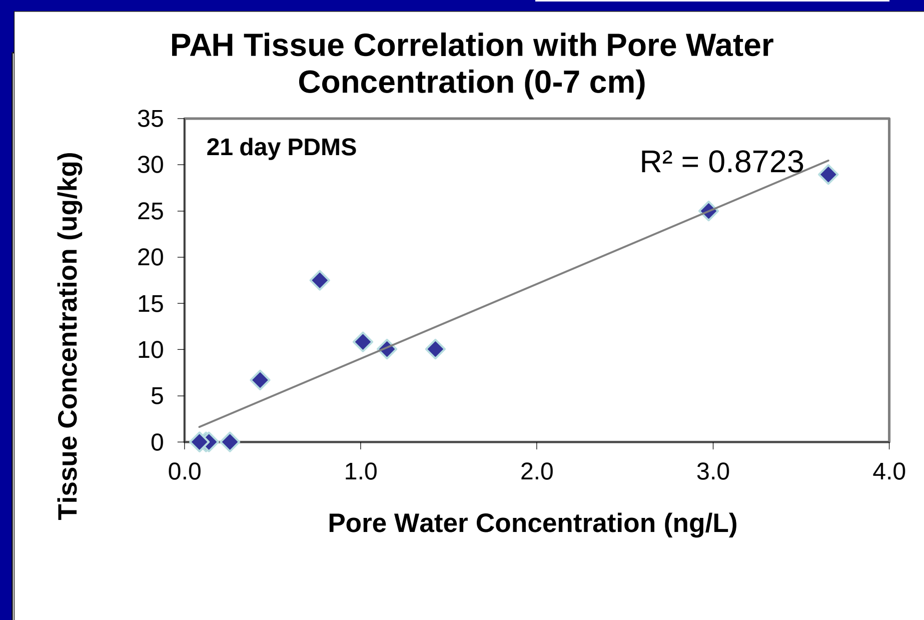
Tissues & Integration of Passive Samplers

Example: Naval Station San Diego

- **Good** correlation between *Musculista* tissue and SPME-derived pore water concentrations for PAHs
- **Centrifugation slightly improved predictability over bulk sediments, but still disturbs samples and can confuse relationships between porewater and bioaccumulation**

DoD EPA DOE SERDP





Potential Application in Laboratory & Field Settings

- Consensus that several PSMs ready for application
- Consider 5 key guiding principles for selection, preparation, implementation and validation of PSMs

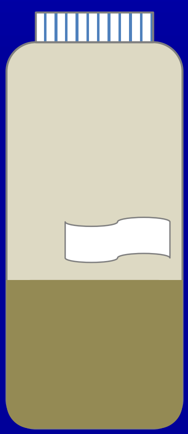
1. **Define question(s) posed by managers to be addressed by measurement of C_{free} using PSMs**

Endpoints addressed by PSMs

- Sediment toxicity
- Benthic organism bioaccumulation
- Transport (*i.e.*, direction of flux, gradients)
- Spatial extent delineation
- Site-specific K_{OC}
- Model calibration / verification

Guiding Principles (con't)

2. Determine pros/cons of ex-situ (bring sediment sample back to lab) versus in-situ application of PSMs



Other Considerations

- Site accessibility / security
- Time / Cost
- Level of expertise required
- Regulatory considerations
- Importance of spatial resolution

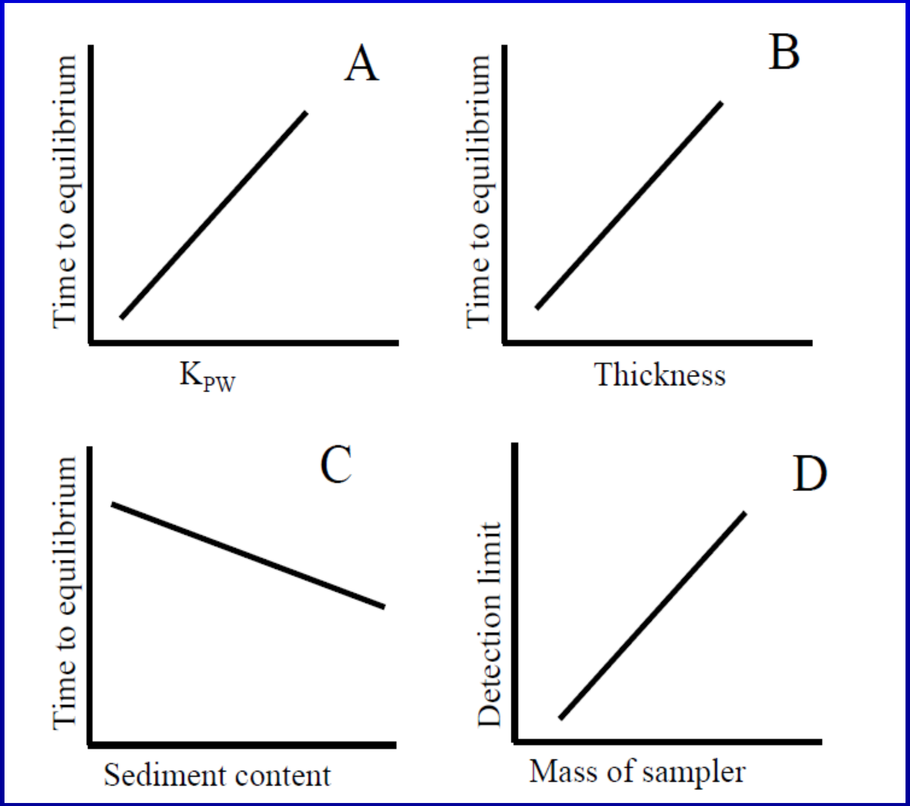
  (heterogeneity; grab vs. fine scale)
- Temporal resolution

Guiding Principles (con't)

3. Perform trade-off of key considerations to select the most appropriate PSM(s)

Technical Considerations

- Target analytes (magnitude of K_{ow}, organic/inorganic)
- Physicochemical conditions
- Time for deployment
- Performance specs (sensitivity, accuracy, precision)
- Commercial availability



4. Establish QA/QC guidelines for project

Guiding Principles (con't)

5. **Quantify PSM measurement uncertainty and propagate through the risk assessment**

PSMs uses in sediment assessments and decision frameworks

- Nature and Extent
- Flux measurements
- Evaluating remedial options
- Exposure and risk assessment
- Use in tiered assessment approaches

The uncertainty associated with C_{free} measurements using PSMs is expected to be only a fraction of the uncertainty associated with the status quo

Fate, Transport and Exposure Processes

- Characterizing exposure under current and future conditions
  - Mass movement vs phase movement
  - Getting from contaminant mass distribution to exposure point concentrations and dose
  - Projecting the effects of remedial actions

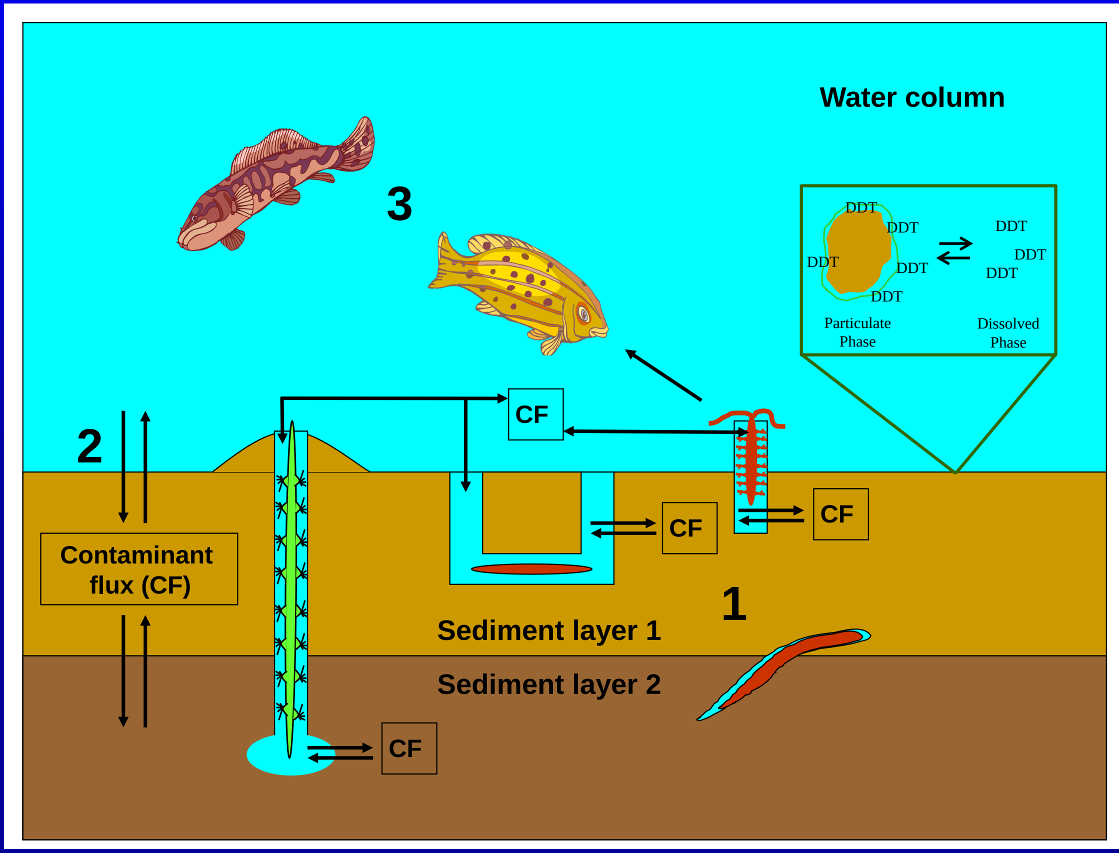
Modeling

- PSDs are source of input parameters for models:
  - Contaminant mass-balance
  - Sediment and contaminant transport
  - Exposure and Dose-Response
  - Bioaccumulation
  - Engineering design
  - Risk/site recovery projection

Potential Risk Management Applications

- **C_{free} gives managers a better predictor of bioavailability for 3 key exposure pathways:**

1. Direct exposure to inverts. (tox, bioaccum)
2. Flux from sediments to overlying water column
3. Exposures in water column



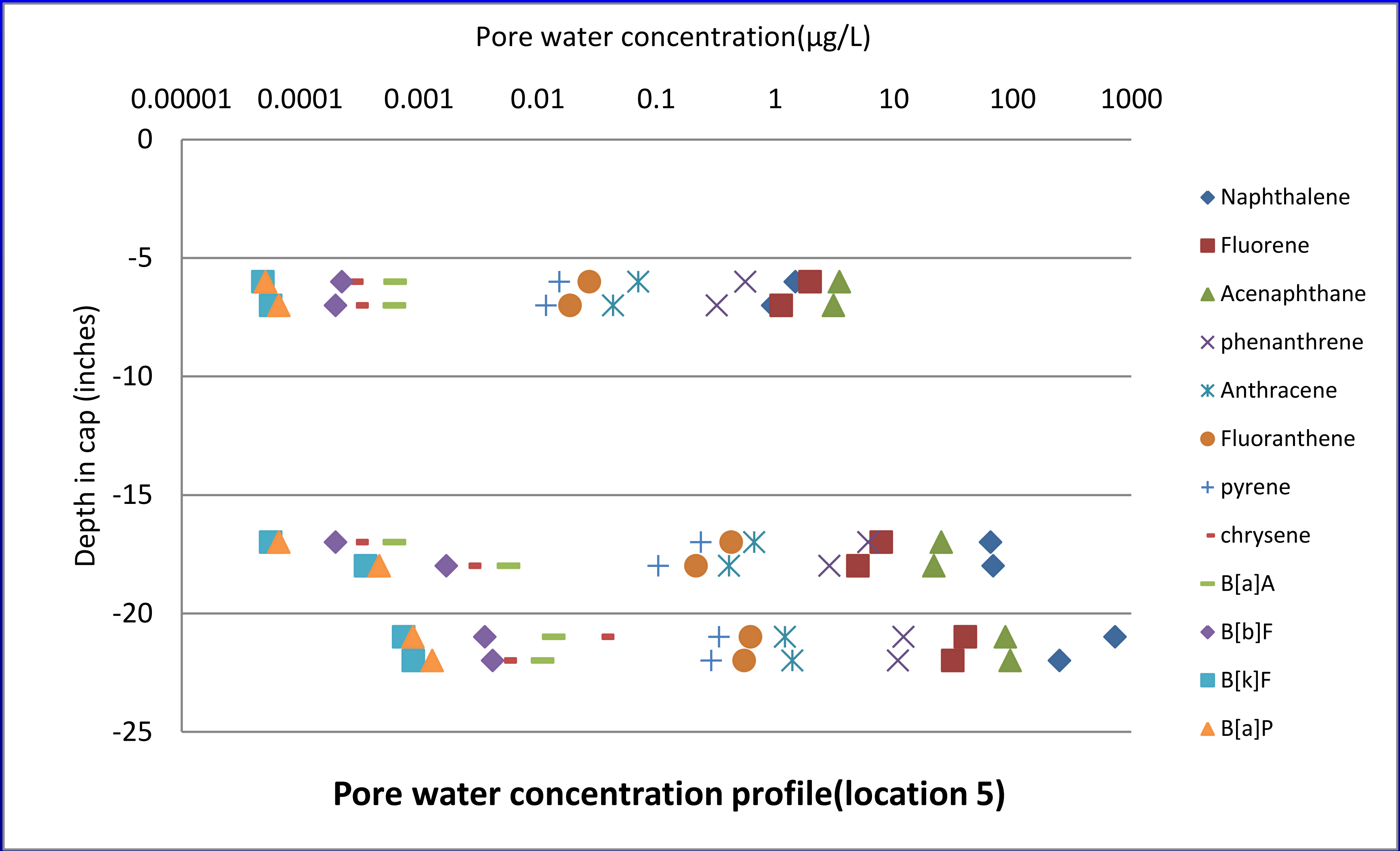
Measurements of C_{free} with PSMs can reduce uncertainty in risk assessment and subsequent risk management decisions

Applications of PSMs in Context of Sediment Management

- Use in site investigations and risk assessment *(these studies form the technical basis of a clean-up decision)*
  - Pore water concentration estimates
  - Moving toward use of PSM measurements as dose metric
  - Indicator of bioaccumulation and/or bioavailability

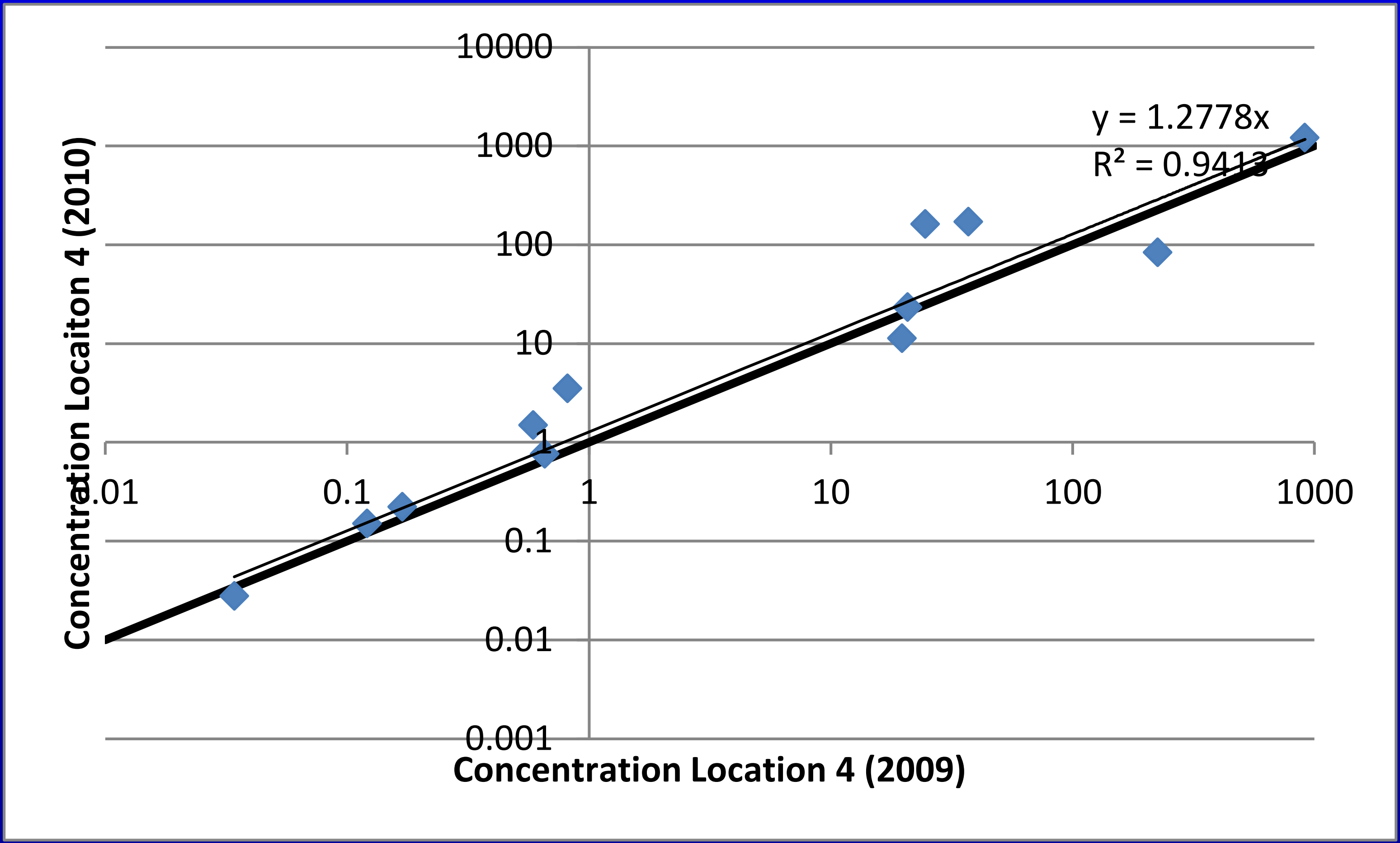
- Use in remedial effectiveness monitoring
  - Surface and pore water concentrations—bioavailability trends
  - Sediment cap and amendment performance
  - Surrogate for benthic organism bioaccumulation
  - Indicator for fish bioaccumulation

Example Profiles



Site Year to Year Comparison

Site 1



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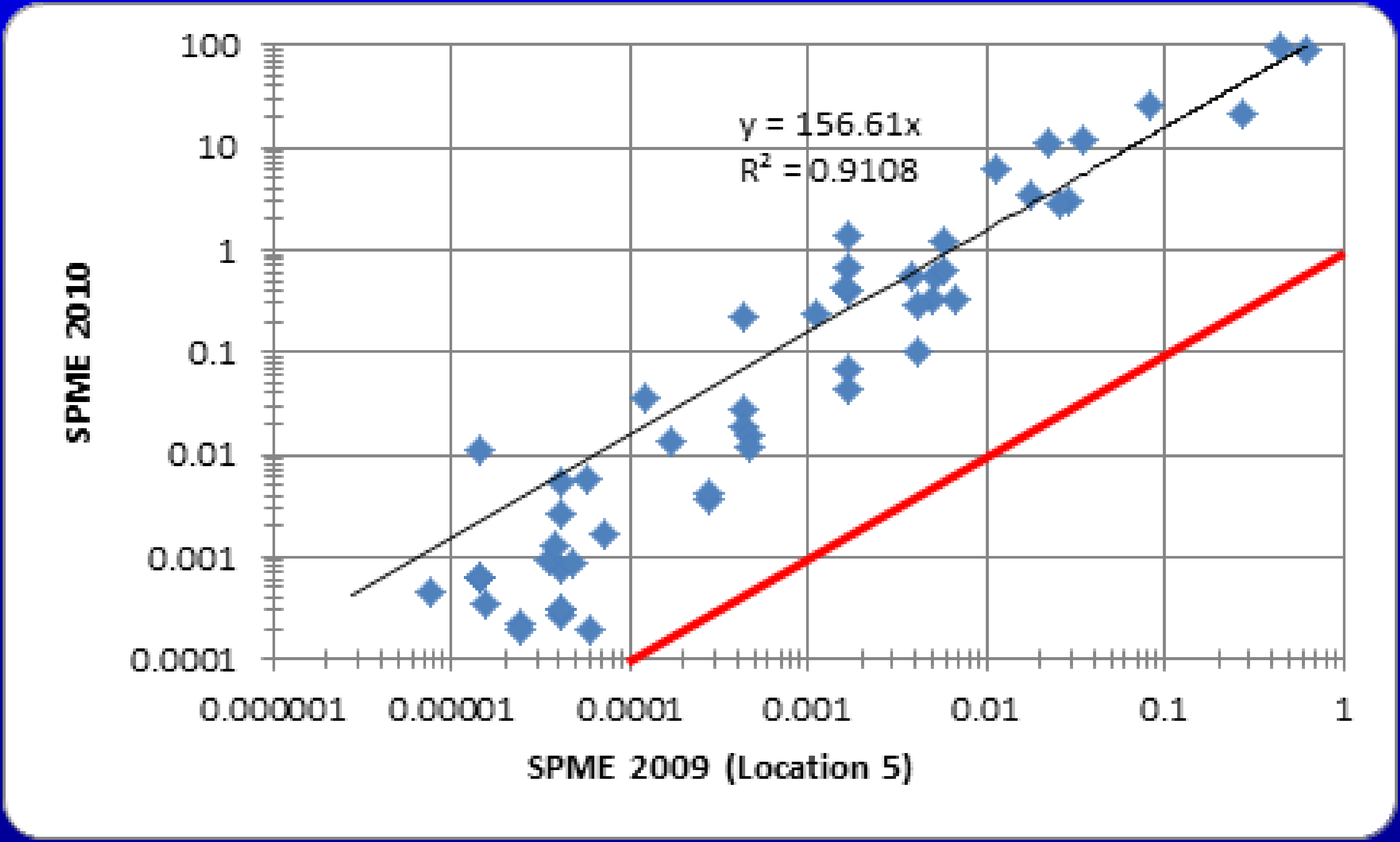

Summary of Potential Assessment & Risk Management Applications

- Improvements from using passive samplers for C_{free} determinations and data collection—increase certainty:
  - Ambient or compliance monitoring programs
  - Quantifying spatial and temporal trends in bioavailable contaminants
  - Identifying contaminant sources
  - Dose metric to develop exposure concentration-response relationships
  - Understanding of risk zones based on likelihood of effects
  - Modeling (input parameters or verification data)
  - Evaluating remedial options and designs
  - Short- and long-term monitoring of chemical bioavailability
  - Evaluating results of sediment treatment, disposal, or beneficial reuse following management actions
  - Evaluating remedy effectiveness

Thank you for your attention today