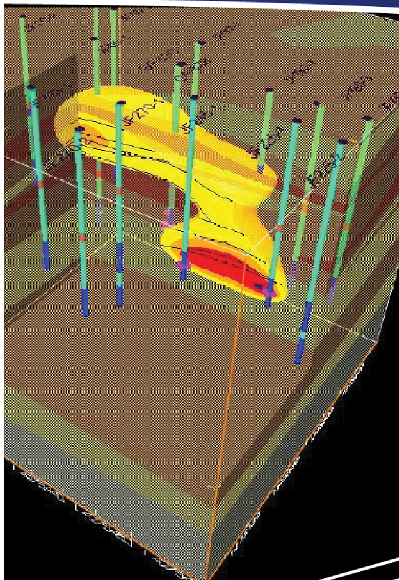

Porewater Concentrations & Bioavailability

Passive Sampling Methods for Managing Contaminated Sediments: Risk Assessment & Management

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EPA United States Environmental Protection Agency

23rd Annual NARPM Training Program

Issues decision makers must face

- Perception that any contamination left behind when bioavailability information is incorporated into cleanup decisions is bad.
- Many promising new technologies that evaluate bioaccessibility/bioavailability of contaminants within the abiotic media, or may act as indicators (or surrogates) of biouptake
- Sediment amendments as an in situ remedial option

Technical Challenges

- 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 (uncertainty!)**
  - **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**

Regulatory “Acceptance” of PSMs…

- They are accepted…by some
- 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:
  - Limited understanding of 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**

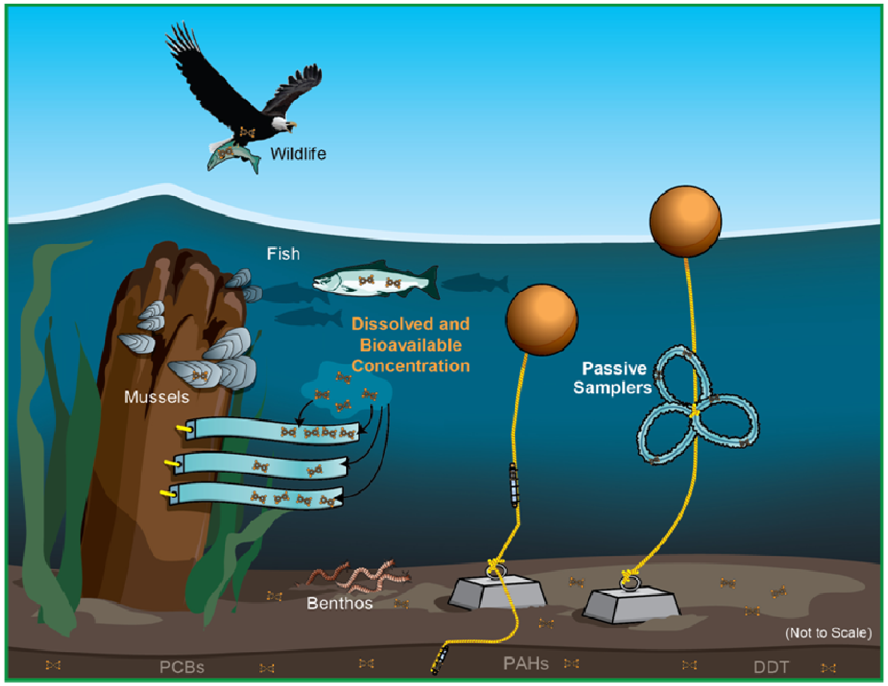
Sediment Assessment & Monitoring Sheet (SAMS) #3

United States Environmental Protection Agency

Office of Superfund Remediation and Technology Innovation
and
Office of Research and Development

Sediment Assessment and Monitoring Sheet (SAMS) # 3

Guidelines for Using Passive Samplers to Monitor Organic Contaminants at Superfund Sediment Sites



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RECENT IEAM PAPER

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Passive Sampling Methods for Contaminated Sediments: Risk Assessment and Management

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- Freely dissolved concentration (C_{free}) of a hydrophobic organic contaminant in sediment is a better predictor of bioavailability than total concentration in bulk sediment.
- PSMs that target C_{free} reduce uncertainty in site investigations by characterizing spatial and temporal contaminant trends, source contributions, calibrating models, and improving weight-of-evidence based decision frameworks.
- PSMs can help delineate sediment management zones, assess remedy effectiveness, and evaluate risk reduction following management action.
- C_{free} can be used to better inform risk management decision making.

What are the current and projected future management applications for PSMs in assessing and managing risk associated with contaminated sediments?

PODCAST http://onlinelibrary.wiley.com/journal/10.1002/%28ISSN%291551-3793/homepage/ieam_podcast_15.htm

Applications of PSMs and C_{free} 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
- Defining remedial zones, options, and designs
  - Optimize design based on measured C_{free} relative to risk based concentrations and specific pathways
- Evaluating remedial options and design
  - In situ treatment, capping and dredging designs are informed by desorption and activity-based PSMs

Applications of PSMs and C_{free} in Context of Sediment Management

- 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
- Use in ambient monitoring programs to reduce the need to collect and process sediment and water samples
- Provide data to assist in managing exposures associated with multiple sources

Design, scale and temporal considerations

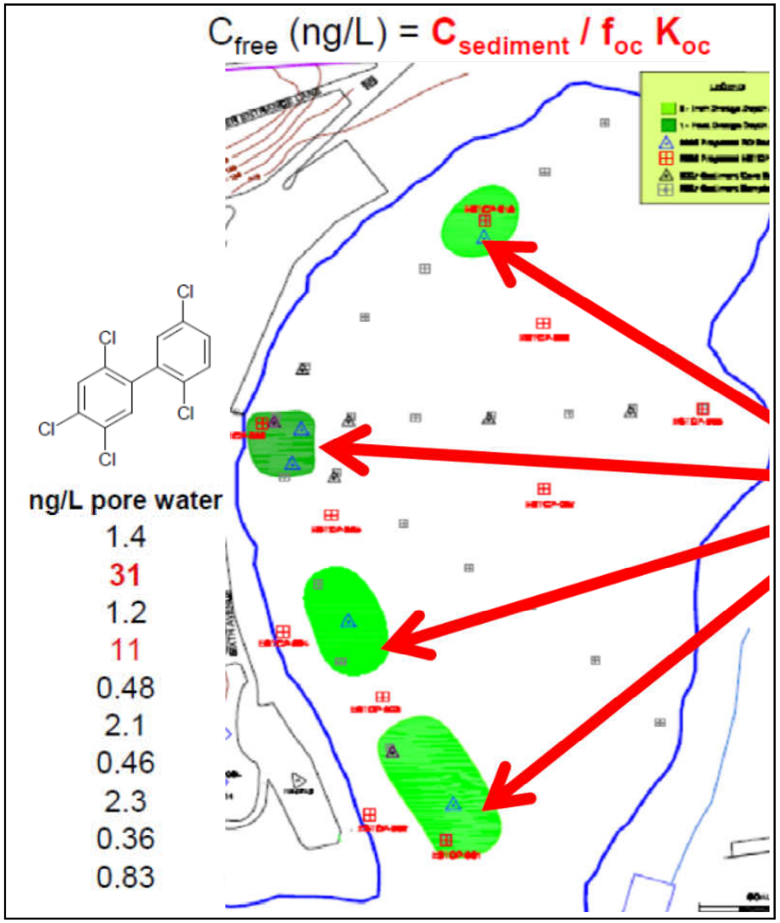
- Question-driven (DQOs): Exposure? risk? remedy effectiveness?
- Scale for application of PSMs?
  - Large: Estimate contribution of land based sources to urban water bodies
  - Small: Evaluate impacts to organisms living in the sediment
- Consideration of horizontal and vertical heterogeneity of sediment characteristics and contaminant distribution
- In-situ / ex-situ deployments and adequacy of data for decisions

Investigation/Site Characterisation

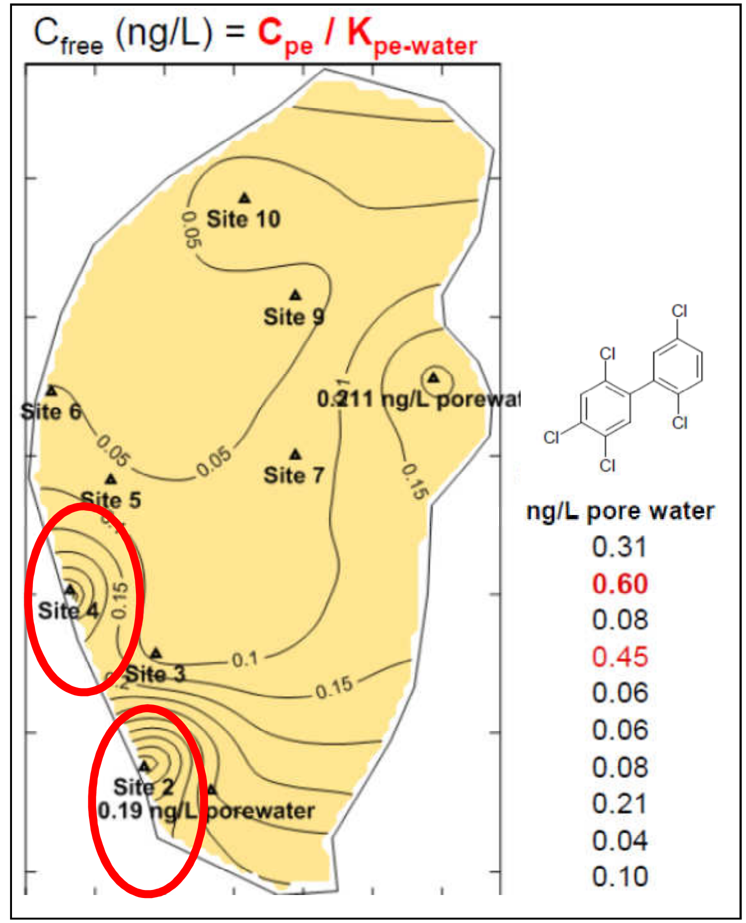
- Ambient monitoring - Role of C_{free} measurement
  - Compliance checking or identify new sources
    - Results generally used for source and emission control and landscape and water body management
- Source identification/pathways:
  - Indicate contaminant sources and relevant exposure pathways
  - Provide data on contaminant desorption and release from both bedded and suspended particles into the dissolved phase
- C_{free} can be used to map sediment areas of concern
  - Mapping more relevant to bioavailability, risk, mobility
  - Can be linked to site remedial goals and used to support the development of remedial footprints (action areas)

Mapping to Establish Remediation Footprints/Zones

Current common practice - C_{sed}



Future practice – C_{free} ?

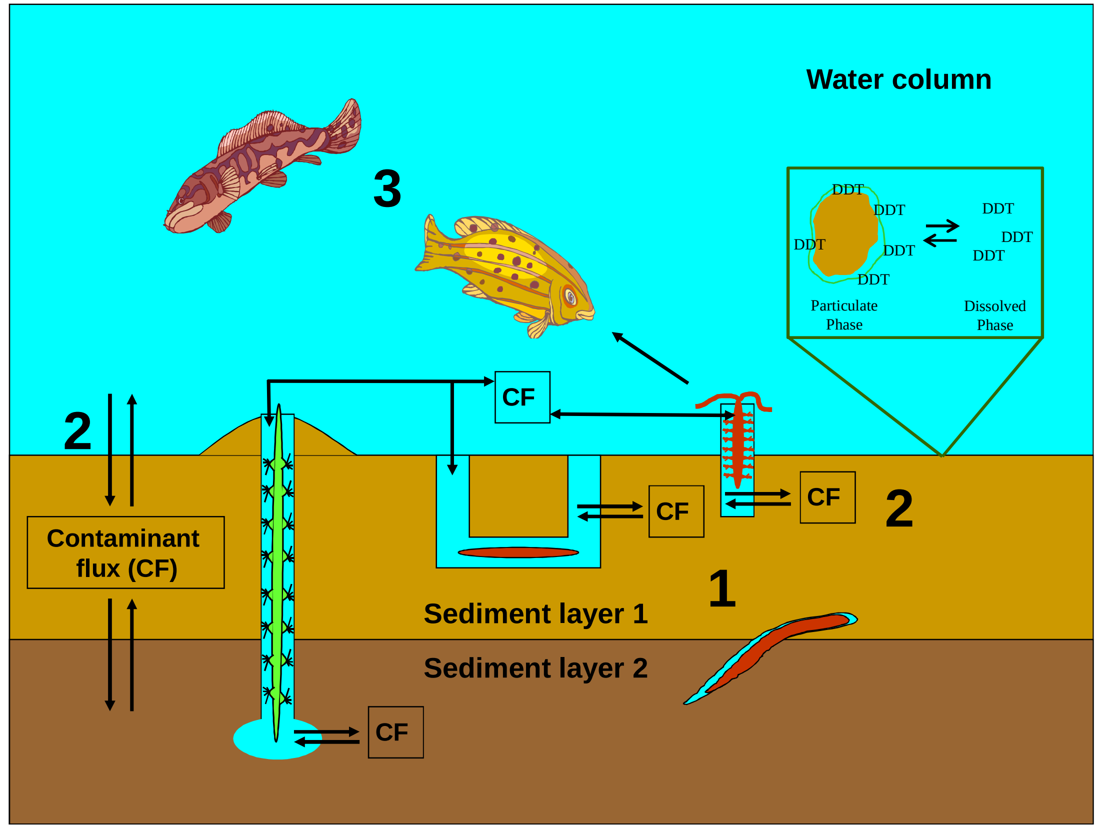


- Green areas based on sediment concentrations (C_{sed})
- Red circles based on C_{free} from PSM (*note higher PW conc nearshore*)

Potential Risk Management Applications

- C_{free} **gives managers 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



Ex-situ or in-situ application of PSMs to measure C_{free} relative to these pathways will reduce uncertainty in risk assessment and subsequent risk management decisions

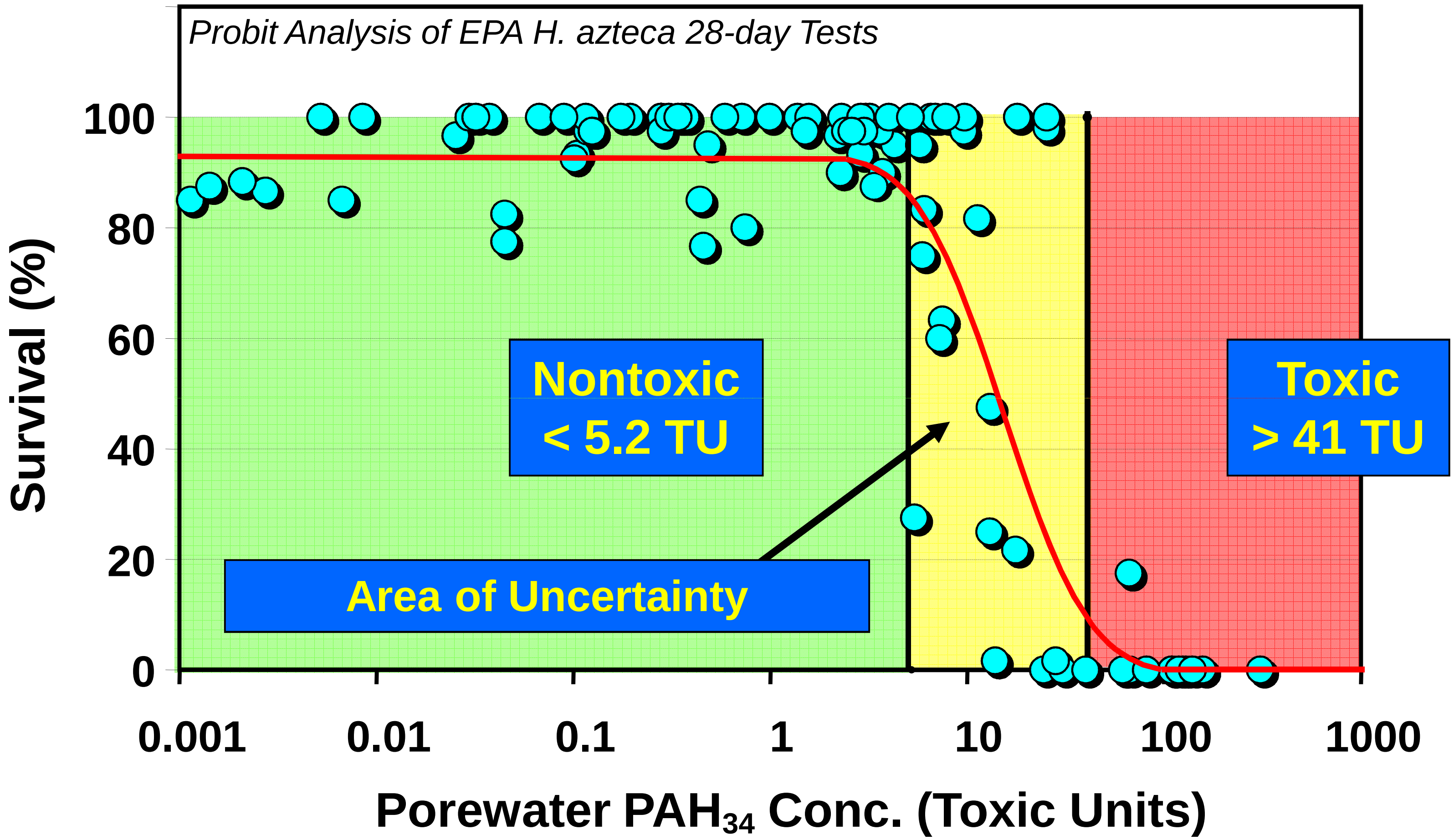
Screening-Level Risk Assessment

- **Pore water is often assumed to be the primary ecological risk-driving pathway, and relying on C_{free} over bulk sediment is expected to improve accuracy of site characterization & COC identification**
  - Incorporate PSM data in site characterization sampling design as additional LOE to reduce uncertainty in exposure/risk assessment.
  - Just as bulk sediment data can be compared to SQGs, C_{free} can be compared to water quality benchmarks, however,… caution (only within SLRA).

Baseline Risk Assessment

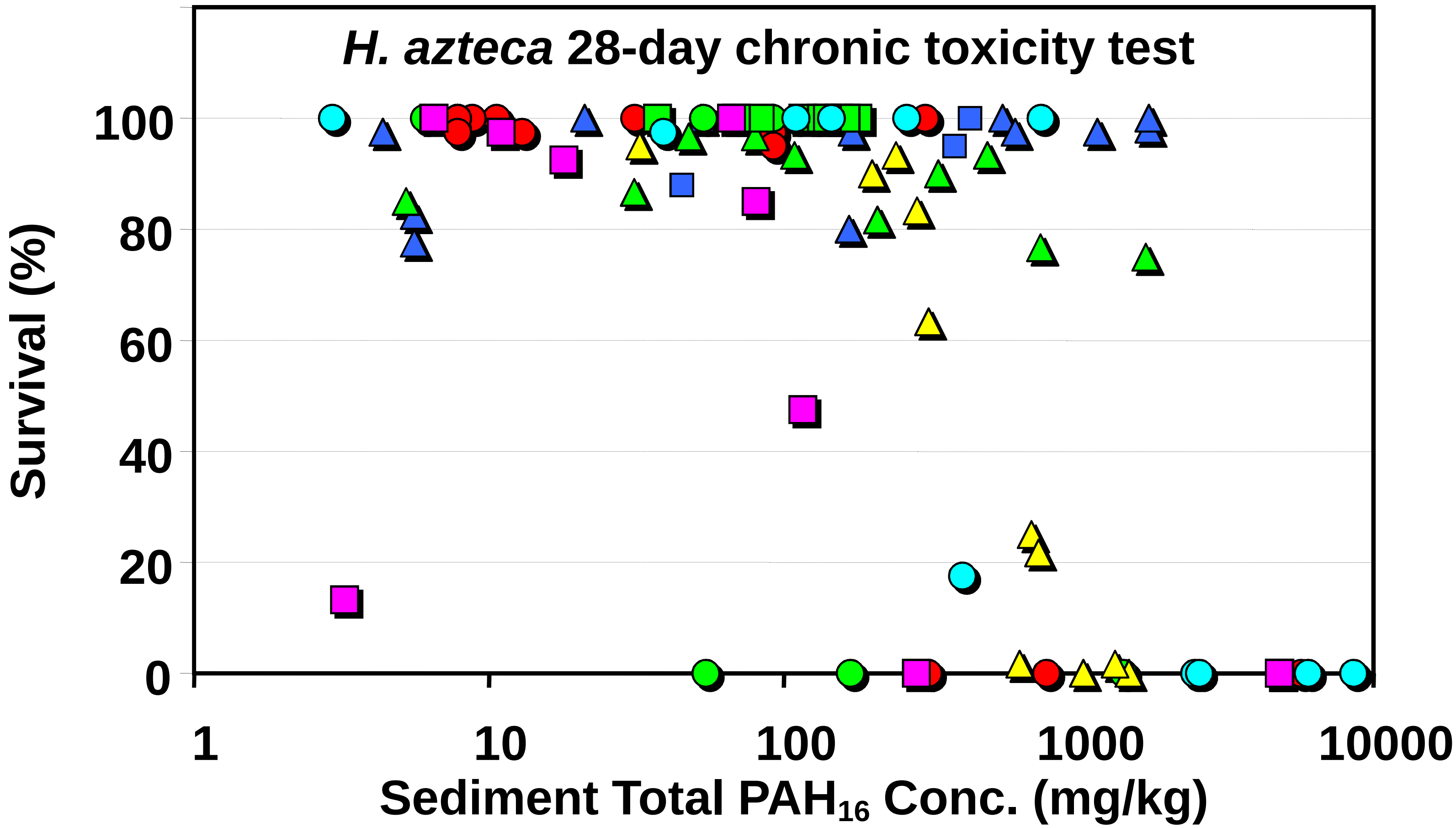
- **C_{free} can be used to derive concentration-response curves for benthos, inform food-chain modeling, and improve ecological and human health risk assessment.**
  - Can develop C_{free}-based dose metric to reduce uncertainty in risk assessment for the benthos.
  - Can use C_{free} to estimate bioaccumulation potential and tissue concentrations for comparison to tissue residue effects benchmarks (e.g., TRVs) and used in trophic transfer modeling.
  - Can improve exposure assessment (reduce uncertainty) associated with human health RA via fish consumption.

Enhanced Predictability by Measuring Dissolved [PAH] in Porewater



Adapted from Kreitinger et al., 2006; 2009

Poor Relationship Between the bulk Total PAH_{16} and Toxicity

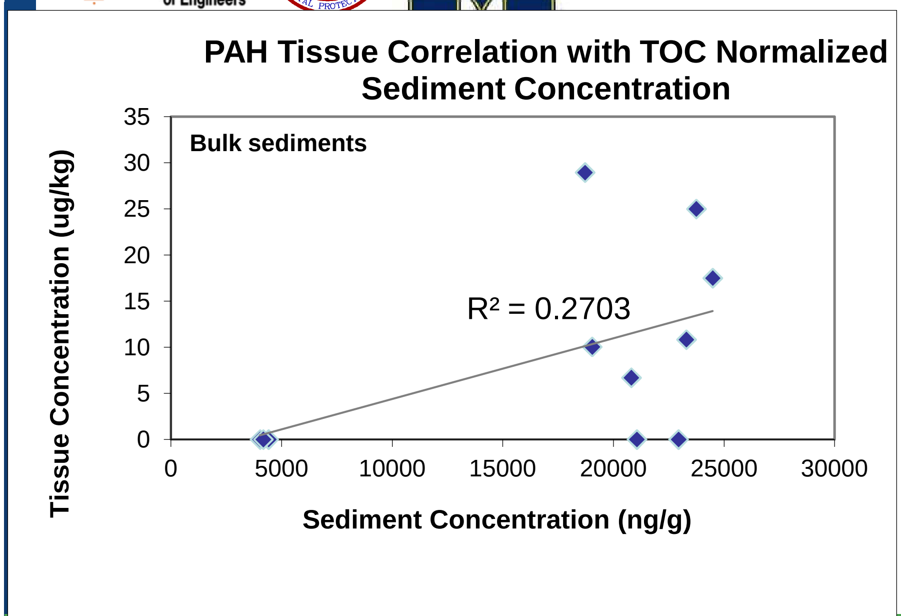


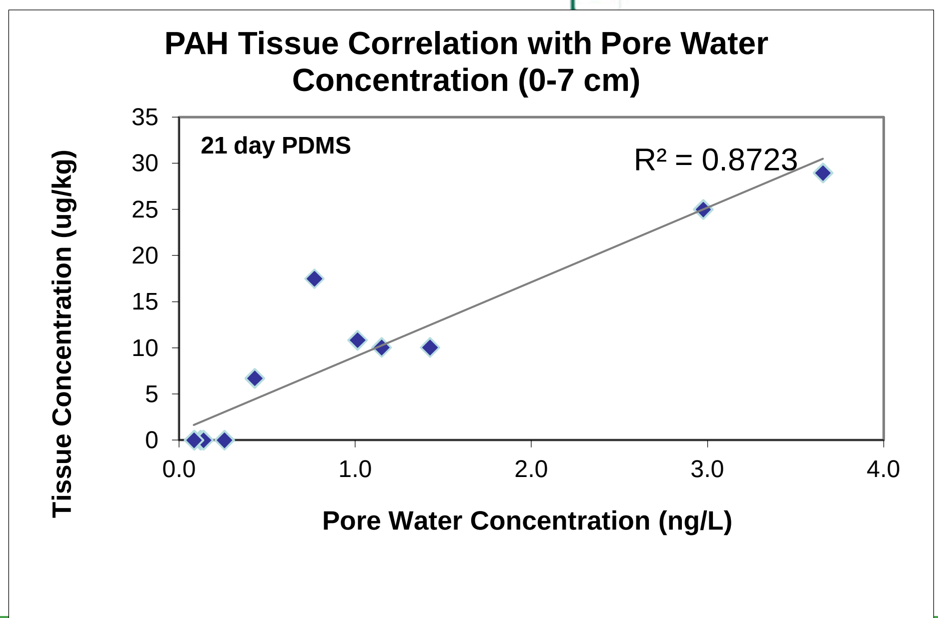
Adapted from Kreitinger et al., 2006; 2009

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

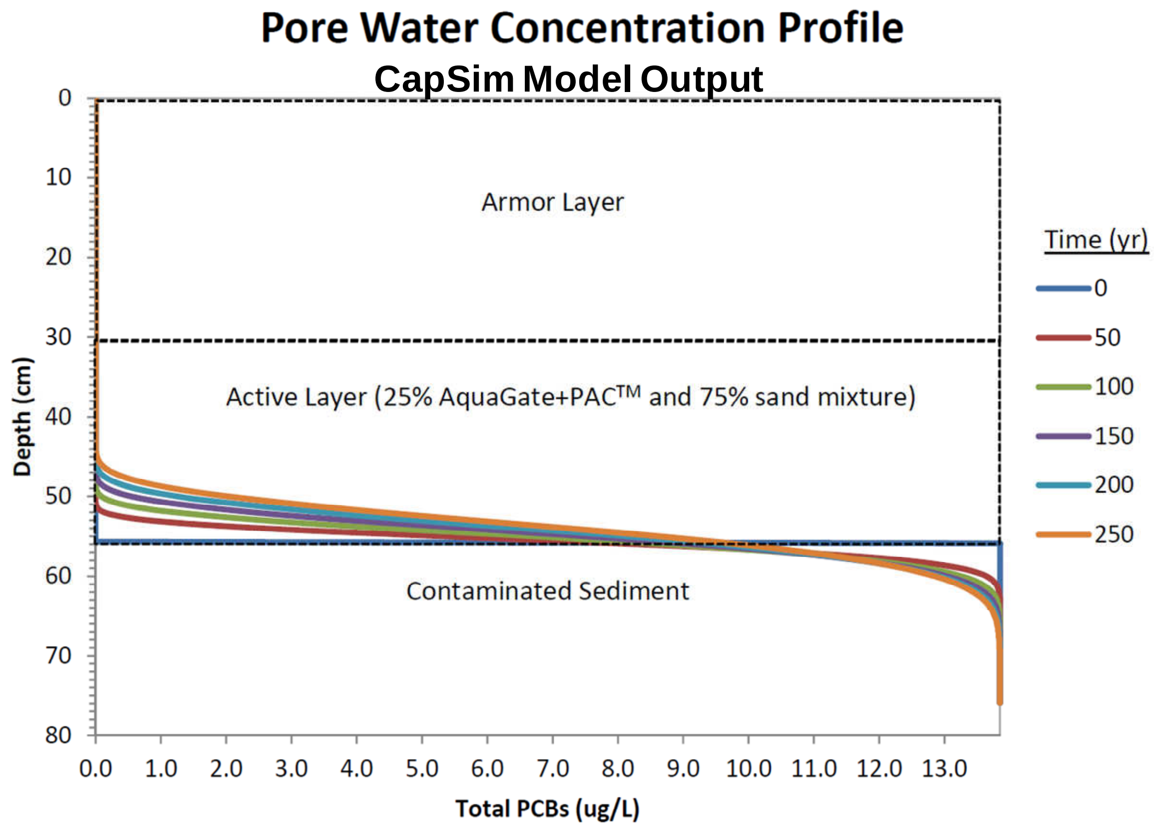


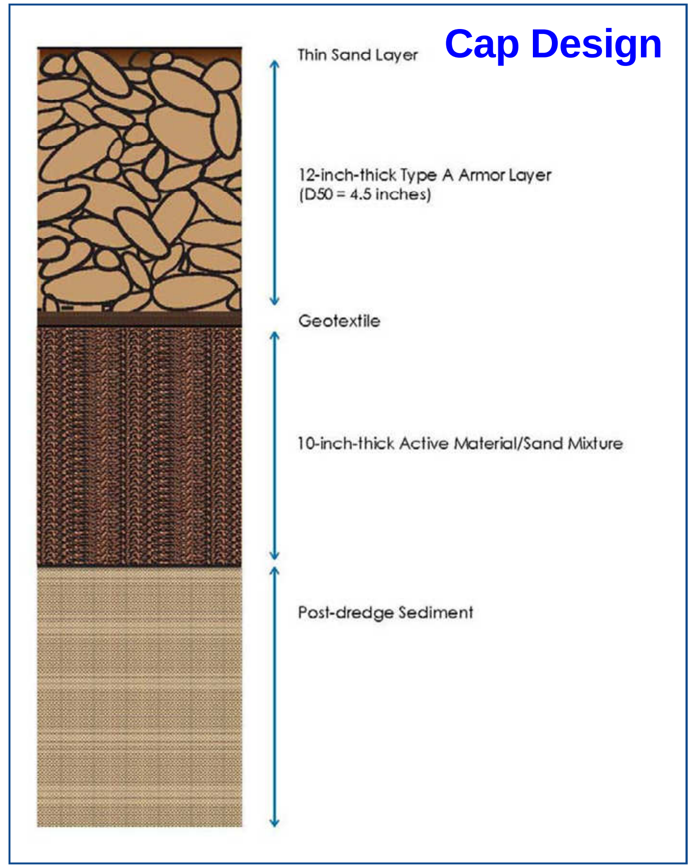


Modeling

- PSMs and C_{free} measurements are source of input parameters for models:
  - Contaminant mass-balance
  - Sediment and contaminant transport
  - Exposure and Dose-Response
  - Bioaccumulation
  - Risk/site recovery projection
  - Engineering design

C_{free} in evaluating remedial options or cap design





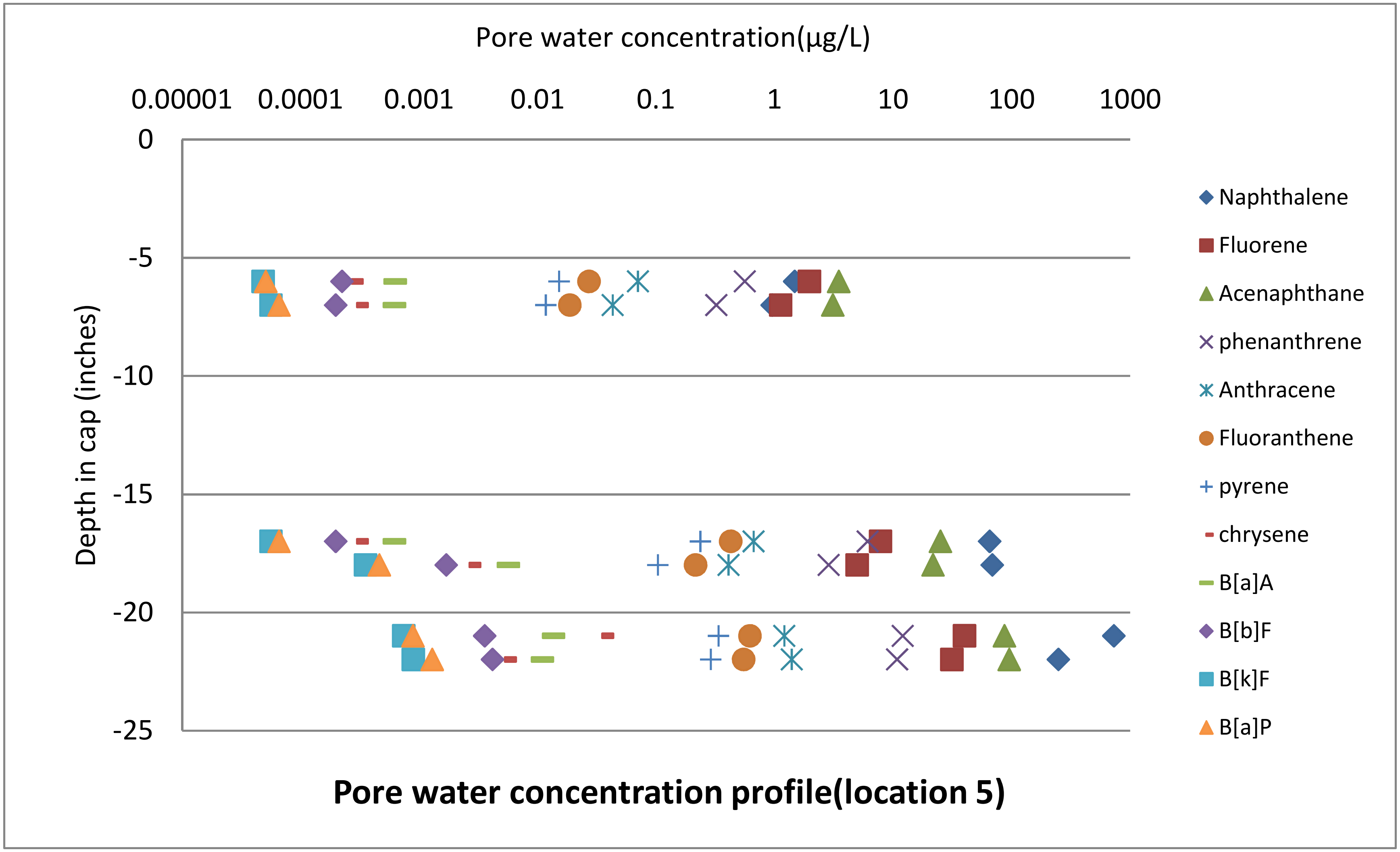
- Pore water concentration is a critical parameter in the CapSim model
- Can design so contaminant concentrations in the BAZ of the cap do not exceed concentrations that would cause toxicity to benthic invertebrates colonizing the surface layer of the cap

Modified from: Vaughn & Greenberg, SETAC 2013.

Remedy Effectiveness Monitoring

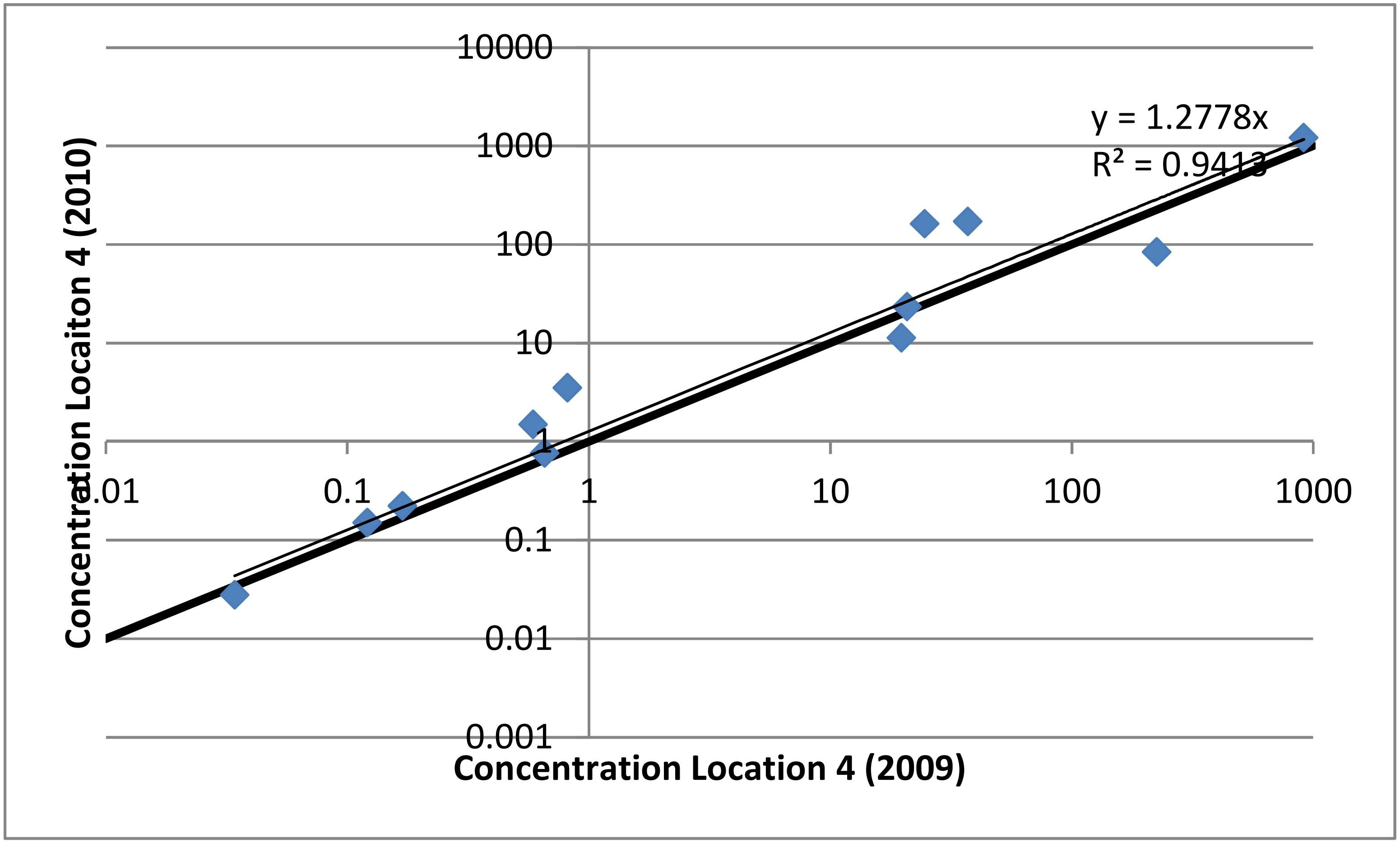
- Use C_{free} to evaluate whether risk reduction objectives have been achieved, or are being achieved over time
  - RAOs exist for "…reduce bioavailable concentrations of sediment contaminants…
- PSMs applicable to assessing long-term remediation success across different remedial strategies
  - Dredging followed by backfill
  - Capping
  - Monitored natural recovery
  - C_{free} in sediment that is slated for disposal or beneficial reuse after management actions such as maintenance dredging

Example Porewater Profiles



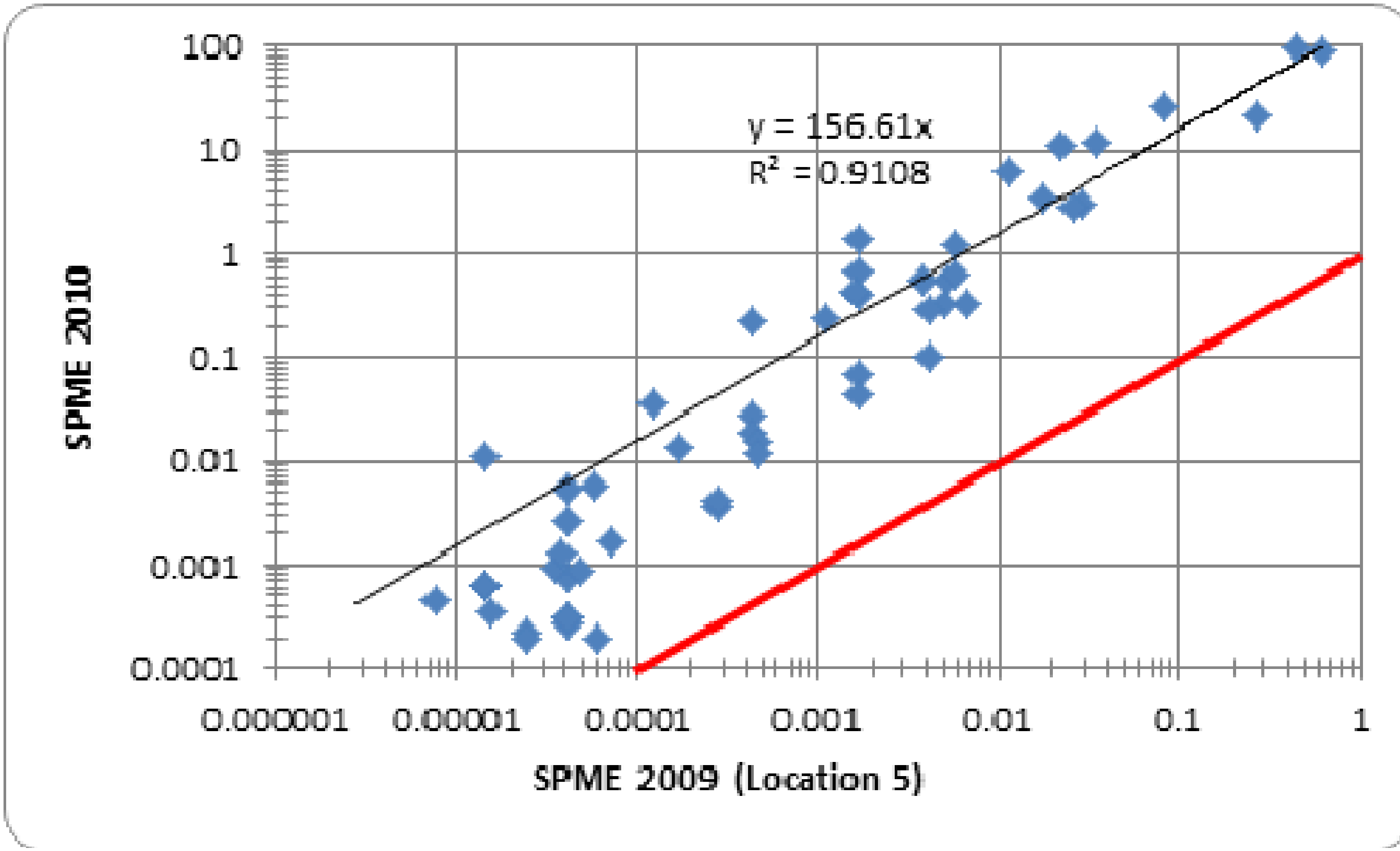
Site Year to Year Comparison

Site 1



Site Year to Year Comparison

Site 1



PSMs as Indicators for Fish Tissue Monitoring

- Use combined evidence from passive sampler trend monitoring of surface water and porewater to determine when fish tissue evaluations would be appropriate
  - for assessing whether remedial targets for fish tissue are achieved, or
  - whether fish consumption advisories should be set, maintained, or relaxed
- This approach reduces need for regular and destructive sampling of live indigenous organisms.
- This approach would also reduce costs by minimizing the need for biota collection, sample preparation, extraction, cleanup, and analyses.

Capstone concepts: *Advantages PSMs provide*

- Can measure C_{free} gradients *(environ. & field relevance)*
  - Vertical profile of the sediment, at the sed-water interface, and between the sediment and overlying water column
  - Time-integrated concentrations
  - Gain insights into the direction and magnitude of diffusive flux of contaminants and thus improve the conceptual site model

- C_{free} reduces uncertainty because we gain an increased understanding of bioavailable concentrations

Capstone concepts (con't):
Advantages PSMs provide

- Improved accuracy in how we represent the EPCs in sediments, pore water, and surface water
- Simpler, less disruptive sampling approach than 'conventional' techniques (*which can be misleading*)
- Some passive samplers (e.g, SPMEs), can be direct injected into analytical instruments (*minimize sample prep time & solvents*)

Summary of Risk Assessment & Management Applications

- Improvements from using passive samplers for C_{free} determinations and data collection:
  - Ambient, compliance, long-term 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

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