Passive Sampling Methods for Managing Contaminated Sediments - A November 2012 SETAC Workshop

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Passive Sampling Methods for Managing Contaminated Sediments - A November 2012 SETAC Workshop

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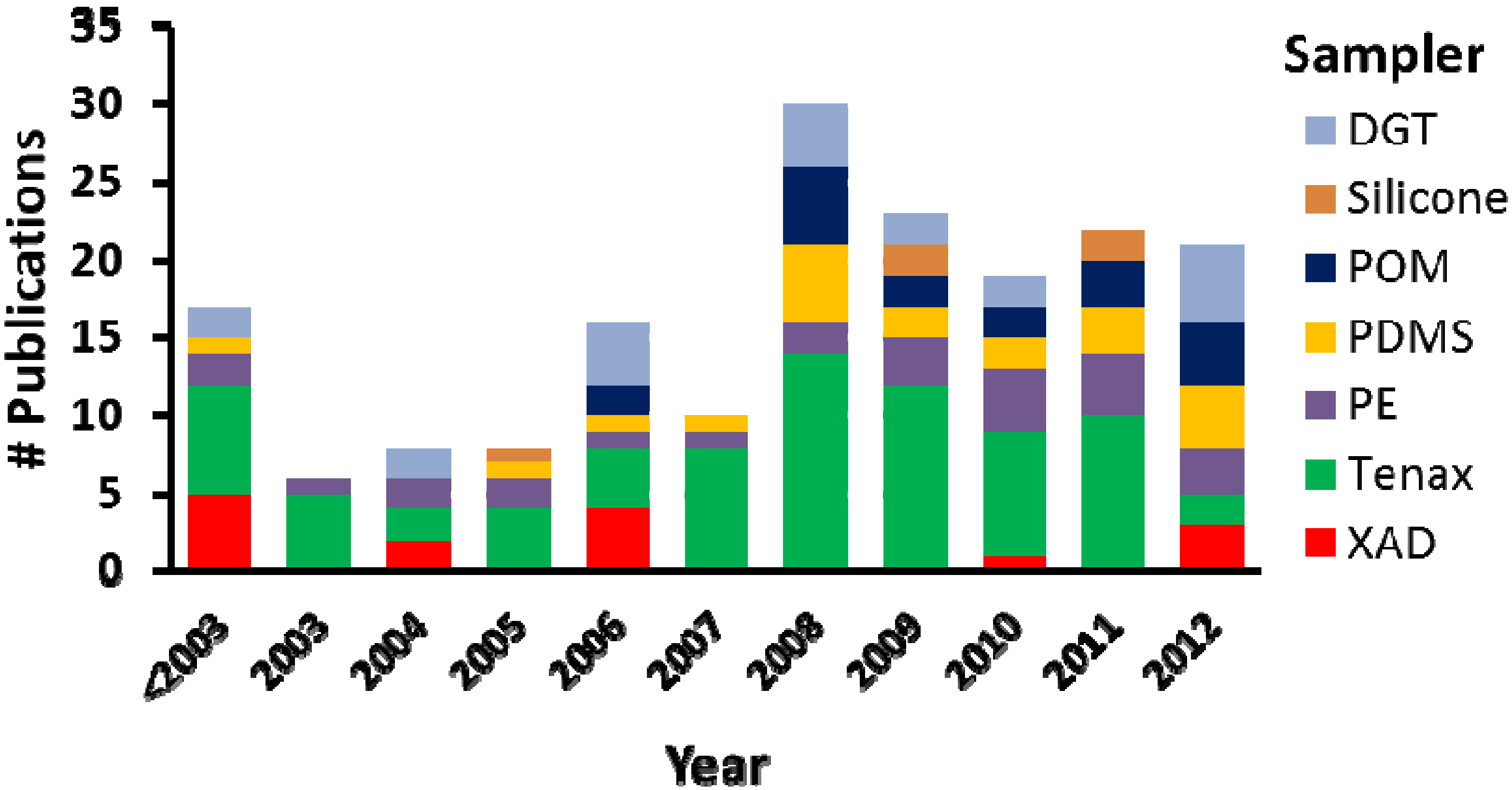
Background

- Management of contaminated sediments includes source and institutional controls, remediation, and evaluating effectiveness of selected management actions
- Contaminant analyses for bulk or whole sediment are used to support decision-making; however…
  - Poor predictor of exposure and subsequent risk since contaminant bioavailability ignored
  - EqP models to predict freely dissolved concentrations in sediment pore water a step forward but do not account for sorption and sequestration processes
- 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

Use of PSMs for Contaminated Sediments

Search query: "sediment" + "bioavailability" + "sampler"



http://wcs.webofknowledge.com

What Do We Mean by Passive Sampling Methods?

- **PSMs broadly defined as:**

  Techniques that quantify bioavailability based on the diffusion and subsequent partitioning of contaminants from sediment to a reference sampling phase ("passive sampler")

  - **Rely on the concept of chemical activity which aims at determination of freely dissolved concentrations (C_{free}) in interstitial (pore) water**

Focus at the workshop on chemical-activity based PSMs that target reliable measurement of C_{free} for hydrophobic organic contaminants (HOCs)

Desorption not considered (concentration that can be rapidly desorbed from the sediment using a commercial sorbent that serves as an infinite sink [e.g., Tenax beads or XAD resin])

Variety of PSM Phases and Configurations

Passive Sampling Phase or Media	Configuration	Target Analytes
Polydimethylsiloxane	Coated fiber, vial	HOCs
Polyethylene (PE)	Film/sheet, tube	HOCs
Polyoxymethylene (POM)	Film/sheet	HOCs
Ethylvinylacetate	Coated vial	HOCs
Silicone rubber	Sheet, Ring	HOCs
Gels (e.g., DGT)	Thin film “DGT”	Metals
Resin impregnated polyacrylamide gel	“Gellyfish”	Metals
Metal-chelating media	Disk/membrane	Metals
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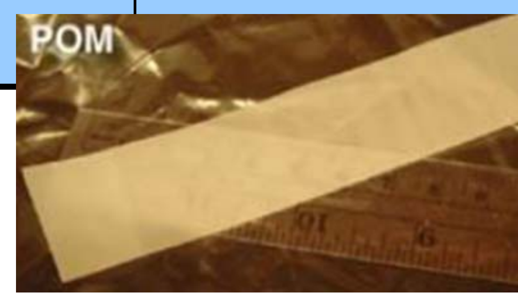
Solid phase microextraction



… So Why Aren't PSMs More Widely Used?

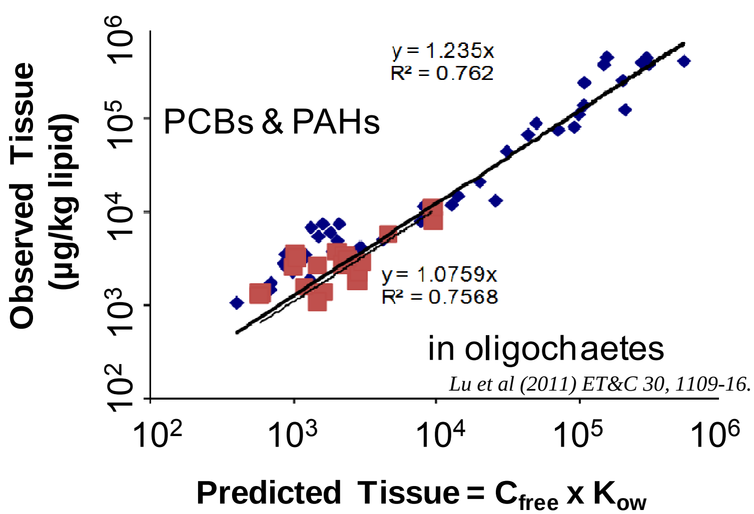
- **Key barriers to regulatory acceptance and use include:**
  - **Failure of practitioners and decision-makers to understand the advantages and limitations of these chemical-based approaches over traditional analytical methods**
  - **Confusion regarding the plethora of different methods and formats 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 versus benefit**

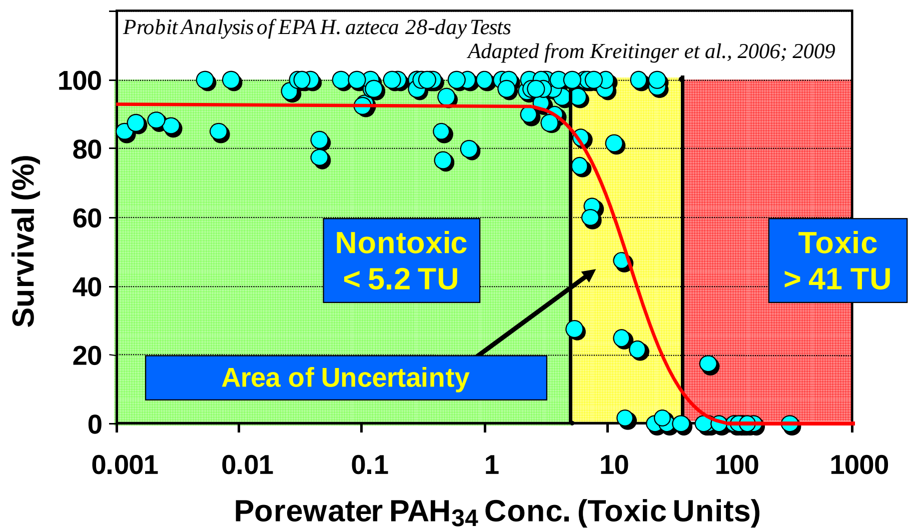
Purpose, Scope, and Goals of Workshop

- **Promote understanding of PSMs**
- **Provide consensus recommendations for increased use in contaminated sediment management process / decisions**
- **Six papers in review in IEAM:**
  - Passive Sampling in Contaminated Sediment Assessment**: Building Consensus to Improve Decision-Making**
  - Passive Sampling Methods for Contaminated Sediments**: State of the Science for Organic Contaminants**
  - **“”: State of the Science for Metals**
  - **“”: Scientific Rationale Supporting Use of Freely Dissolved Concentrations**
  - **“”: Practical Guidance for Selection, Calibration and Implementation**
  - **“”: Risk Assessment and Management**

State of the Science

- **Generally accepted that C_{free} provides more relevant exposure metric than total or bulk sediment chemistry**
- **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**

State of the Science (cont'd)

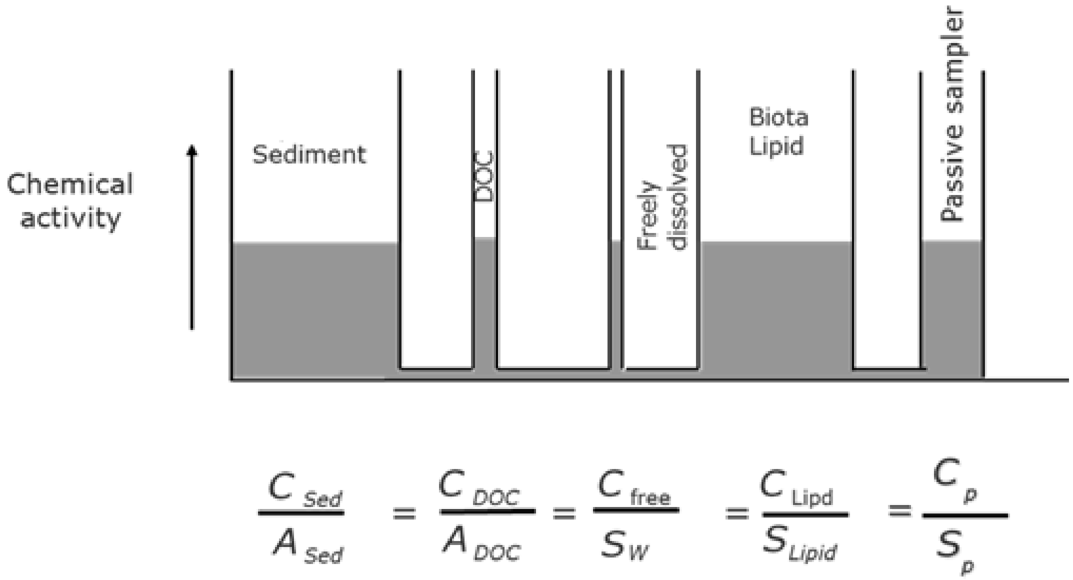
- **Metals (including metalloids and non-metals)**
  - Literature on PSMs for sediment-associated metals is less established than for organics
  - Metal speciation renders PSM measurements more challenging to interpret and relate to endpoints of concern, e.g., bioaccumulation
    - Linkage to geochemical speciation models needed
  - Additional data showing benefits compared with and in addition to conventional risk assessment needed
    - Limited number of studies demonstrating PSM utility

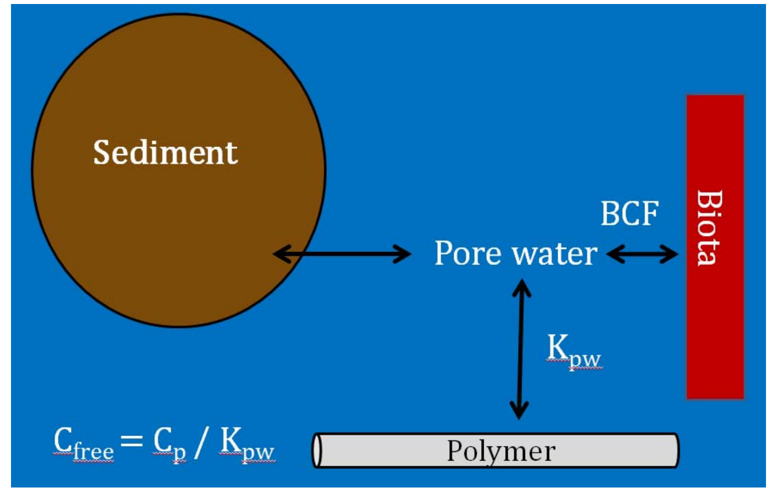
MORE WORK WITH METALS IS NEEDED !

Scientific Rationale and Theoretical Considerations

- **Consensus view that chemical activity is superior to bulk or "total" concentration in describing bioavailability of HOCs and metals in sediments**
- **Recognized that translating activity-based measurements into C_{free} in the interstitial water will facilitate improved communication and acceptance of PSM data**
- **At thermodynamic equilibrium, the chemical activity across environmental compartments is by definition equal**
  - **C_{free} is a proxy for activity in pore water and is directly related to concentration in the passive sampler**

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 = S_p / S_w (S = solubility in phase)**

Thus, C_{free} not measured directly; depends on accurate K_{pw} values

Scientific Rationale and Theoretical Considerations (cont'd)

For successful use of PSMs to estimate C_{free} two critical conditions must be met:

1. **Attainment of equilibrium (or near-equilibrium)**
2. **PSMs should not deplete local concentration of the target contaminant (thereby disrupting the pool available for exchange across compartments)**

In the absence of equilibrium (or near-equilibrium), correction using performance reference compounds (PRCs) may be possible – assuming reliable, validated methods for such correction available

Practical Guidance for Application in Laboratory and Field Settings

- **Agreed that several PSMs ready for application**
- **Developed 5 key guiding principles for selection, preparation, implementation, and validation of PSMs**

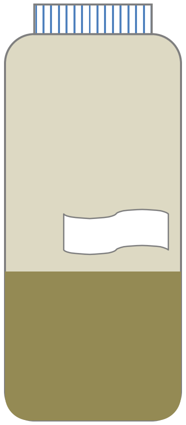
1. Define question(s) posed by managers to be addressed by measurement of C_{free} using PSMs

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 (cont'd)

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



Other Considerations

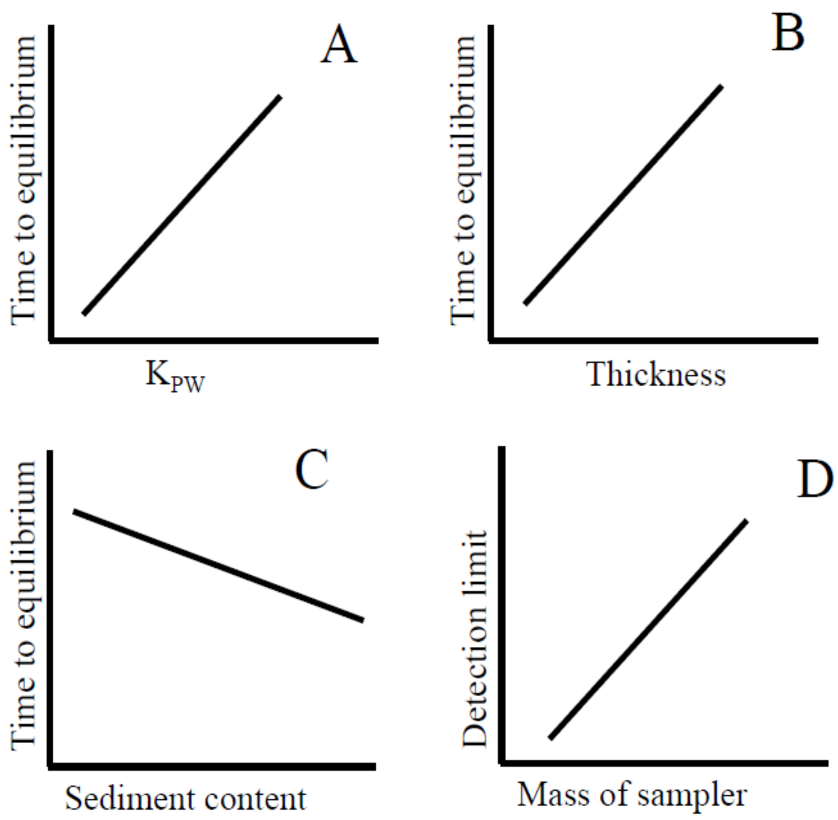
- Site accessibility / security
- Time / Cost
- Level of expertise required
- Regulatory considerations
- Importance of spatial resolution (heterogeneity, grab vs. fine scale)
- Temporal resolution

Guiding Principles (cont'd)

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

Technical Considerations

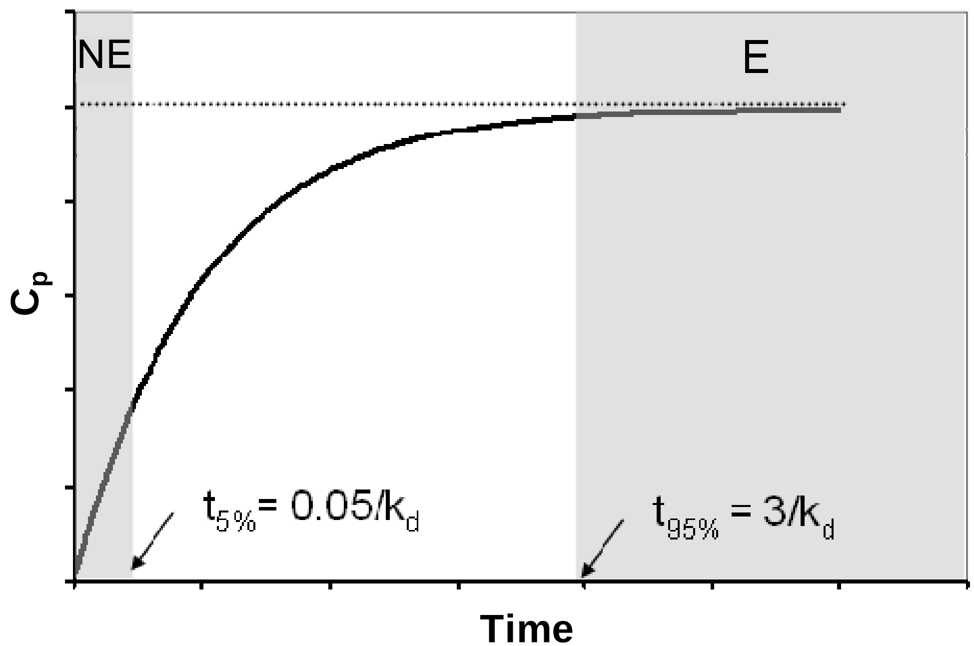
- Target analytes (magnitude of K_{ow}, organic/inorganic)
- Physicochemical conditions
- Time for deployment
- Performance specifications (sensitivity, accuracy, precision)
- Optimum phase / medium
- Commercial availability



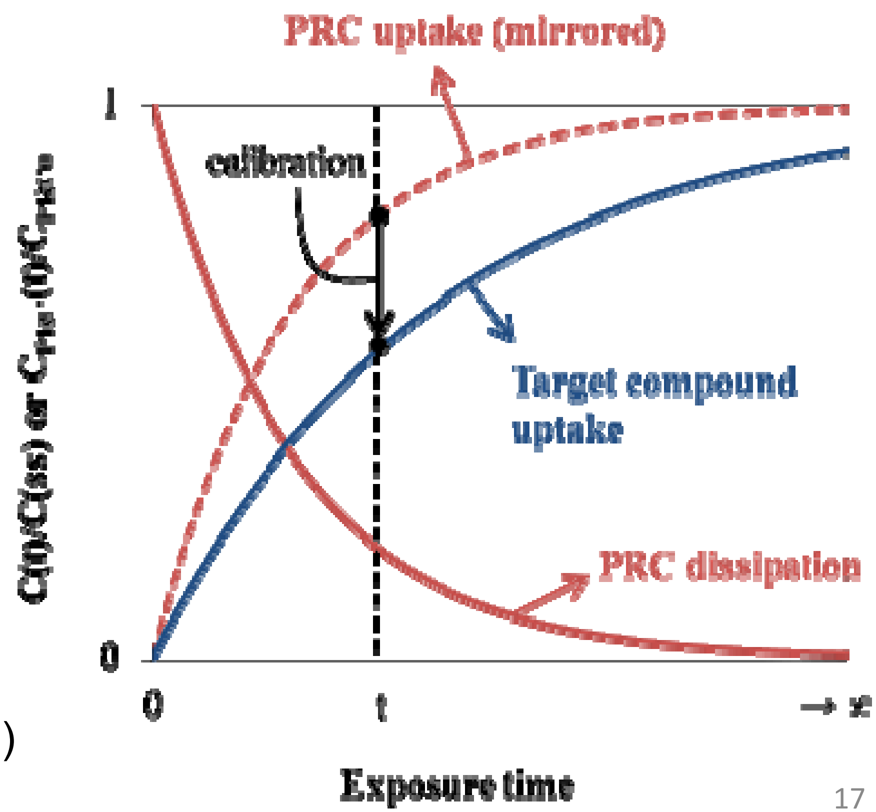
Guiding Principles (cont'd)

4. Establish QA/QC guidelines

- **Selection and use of appropriate pre-calibration parameters (e.g., K_{pw} values and potential temperature/salinity corrections)**
- **Provisions to ensure attainment of equilibrium or, alternatively, for correction to an equilibrium condition**
- **Non-depletive conditions**



NE = Non-Equilibrium sampling (linear uptake phase)
E = Equilibrium sampling (steady-state phase)



Guiding Principles (cont'd)

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

PSMs uses in sediment assessments and decision frameworks

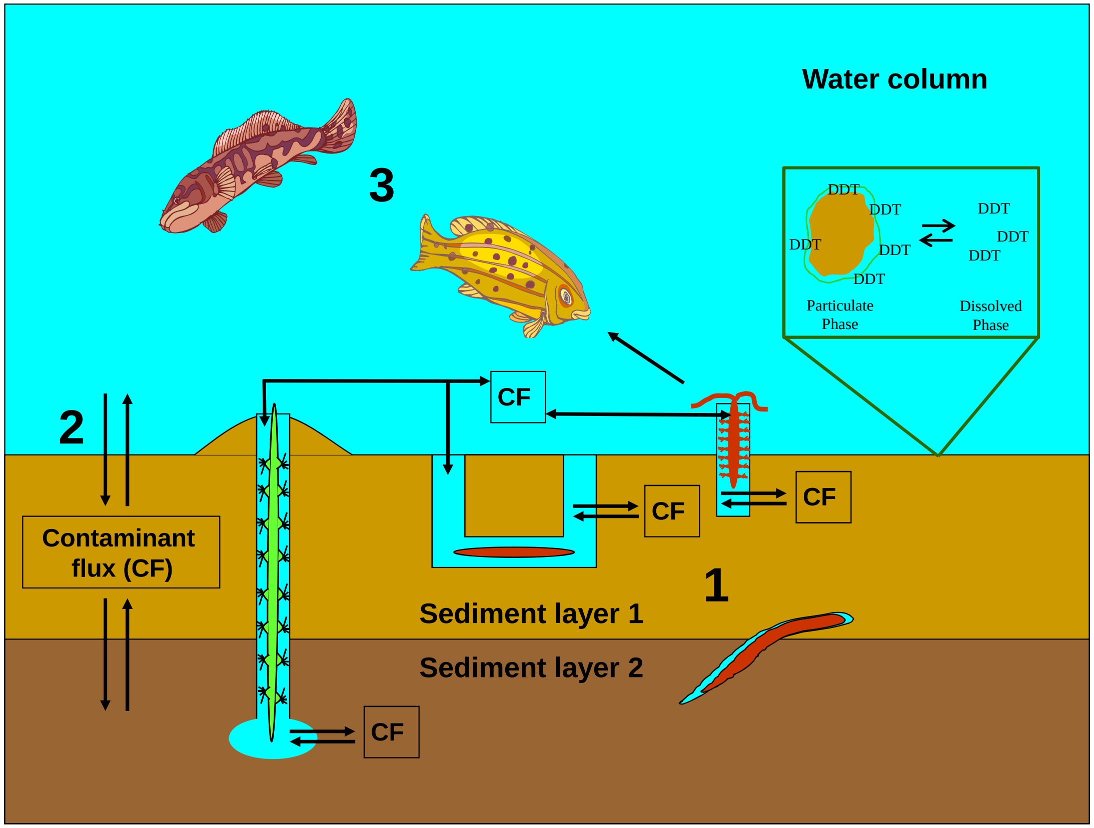
- Nature and extent
- Flux measurements
- Evaluating remedial options
- Exposure and risk assessment
- Use in tiered assessment approaches

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

Risk Management Applications

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

  1. Direct exposure to biota (toxicity, bioaccumulation)
  2. Flux from sediments to overlying water column
  3. Exposures in water column



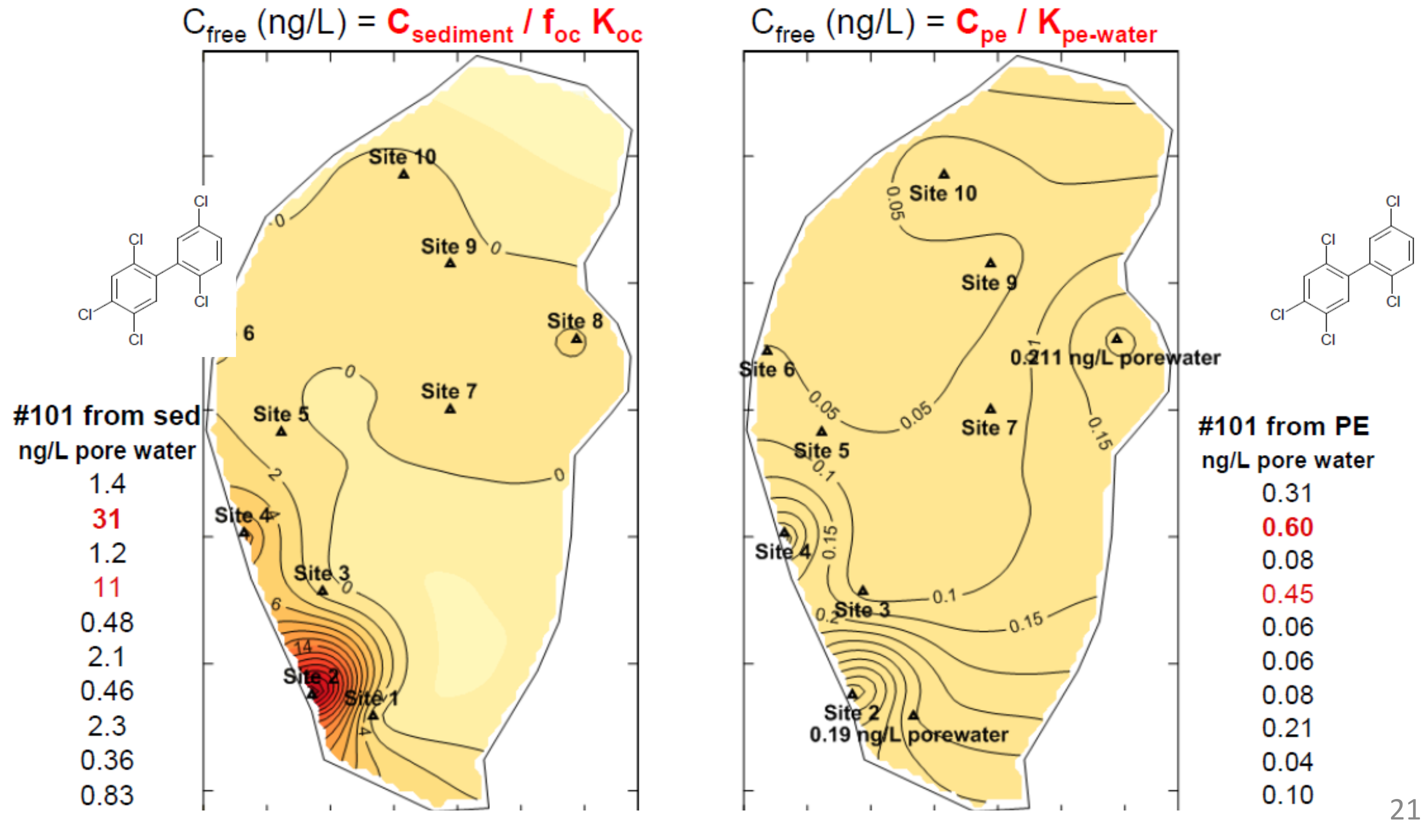
Measurements of C_{free} with PSMs can reduce uncertainty in risk assessment and subsequent risk management decisions

Risk Management Applications (cont'd)

- **Improvements to management applications utilizing C_{free} determinations and data:**
  - Ambient or compliance monitoring programs
  - Identifying contaminant sources
  - Dose metric to develop exposure concentration-response relationships—*can inform development of cleanup goals*
  - 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

Communication and Outreach

- Consensus guidance needed (scientific/technical and regulatory)
- Training opportunities for PSM users
- Key stakeholders should be engaged at sites where PSMs are being considered by technical teams
- Case study presentations showing value in decisions



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