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Data Usability Considerations in the Passive Sampling of Porewater

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CH2M Hill

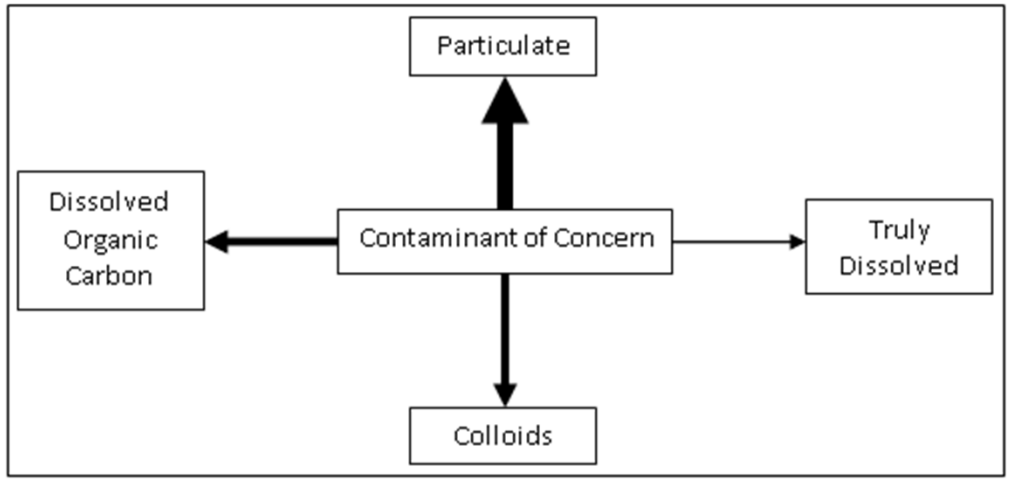
Agenda

- Porewater Considerations
  - Why it matters
  - Methods to collect porewater
- Passive Sampling of Hydrophobic Organic Compounds (HOCs)
- Passive Sampling Data Usability
- Discussion

Porewater Considerations

Why Are Porewater Concentrations Important?

- Many of the organic constituents of concern (CoCs) are hydrophobic and are likely to be sediment bound.
- Hydrophobic organic compounds (HOCs) in the interstitial water, or porewater, are at equilibrium with the sediment.
- The porewater concentrations represent the truly dissolved portion (C_{free}) of CoCs at a sediment site.
- C_{free} is predictive of the bioavailability of HOCs.



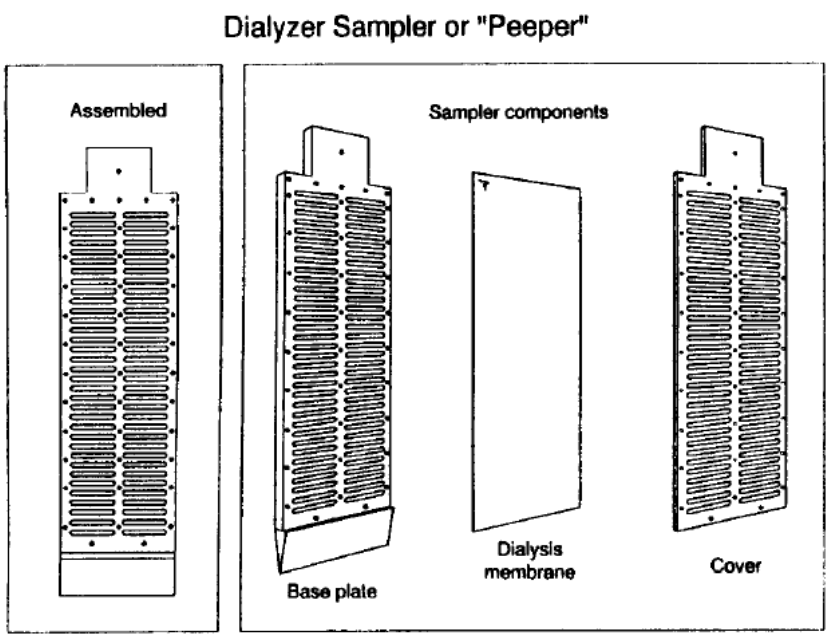
How Can We Determine Porewater Concentrations?

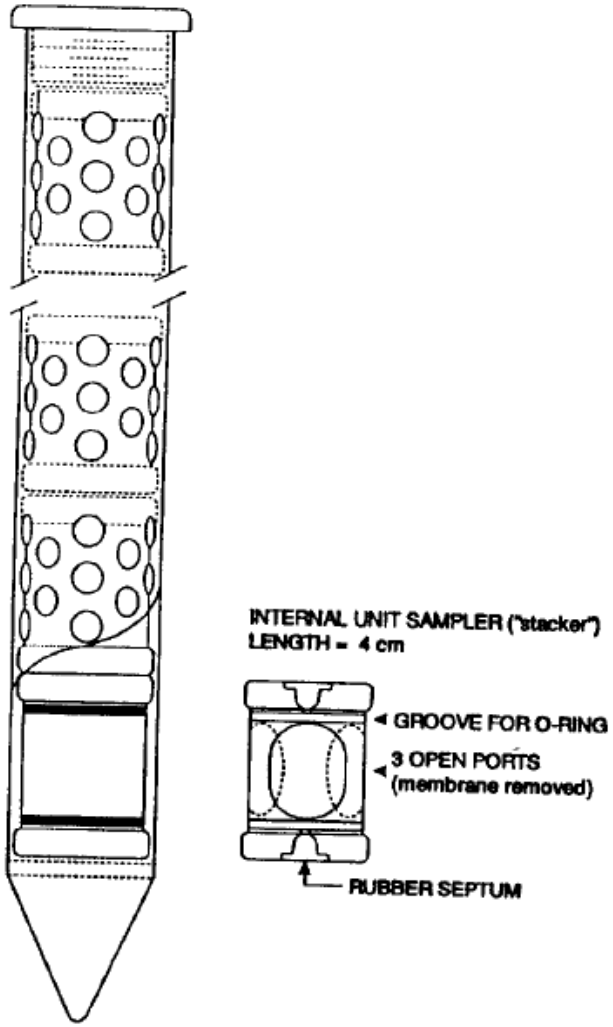
- Bulk sample collection and estimation
  - Collect a bulk sediment sample
  - Determine Contaminants of Concern (CoCs)
  - Determine Organic Carbon (Total, Black)
  - Estimate Bioavailable Concentrations
- *Ex Situ* collection of porewater:
  - Collect a large volume of sediment
  - Physically separate porewater and sediment via centrifugation or pressing

Ex situ Porewater Collection Concerns

How Can We Determine Porewater Concentrations?

- *In Situ* collection of porewater:
  - Diffusion Type (Peeper) Sampler
  - Suction methods
  - Limited volumes typically collected



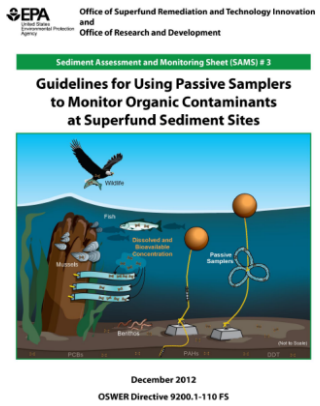


Images from Methods for Collection, Storage, and Manipulation of Sediments for Chemical and Toxicological Analyses – Contaminated Sediments in Water, Chapter 6, USEPA, October 2001

Passive Sampling of HOCs from Sediment

Passive Sampling Background

- Use of passive sampling first proposed in the 1980s
- Research started during the1990s (over 100 papers published)
- Variety of materials for passive sampling have been investigated:
  - Research has been split almost equally between films (PE, POM) and fibers (PDMS)
- Can be performed either *in situ* or *ex situ*.
- Samples may be collected from:
  - Water column,
  - Sediment porewater,
  - Air
- In 2012 US EPA published “Guidelines for Using Passive Samplers to Monitor Organic Contaminants at Superfund Sediment Sites”


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

Sediment Assessment and Monitoring Sheet (SAMS) # 3

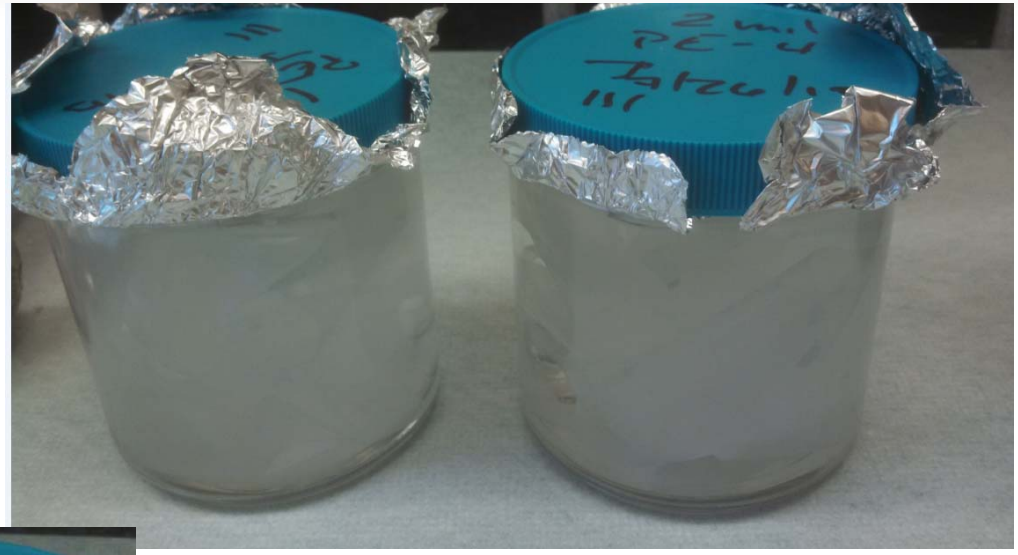
Guidelines for Using Passive Samplers to Monitor Organic Contaminants at Superfund Sediment Sites

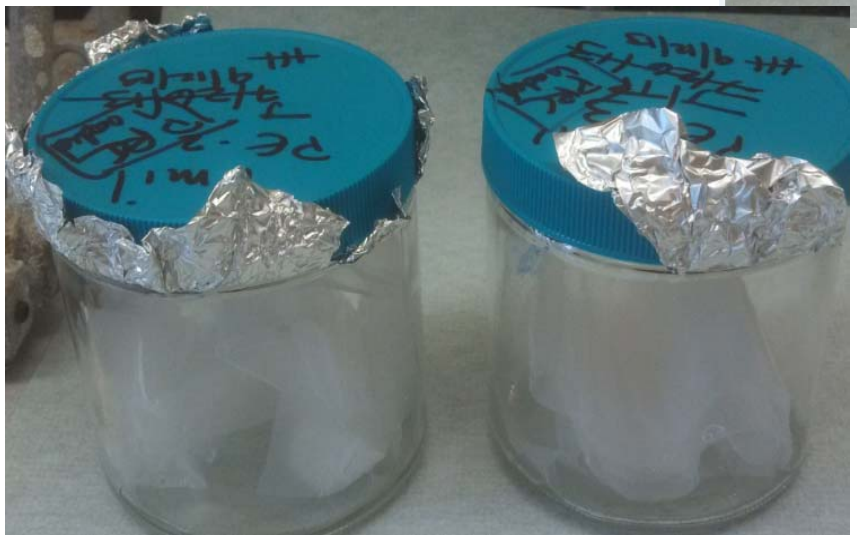
December 2012

OSWER Directive 9200.1-110 FS

Polyethylene Preparation

- Preparation:
  - Determine type, size, amount of material needed
  - Clean material



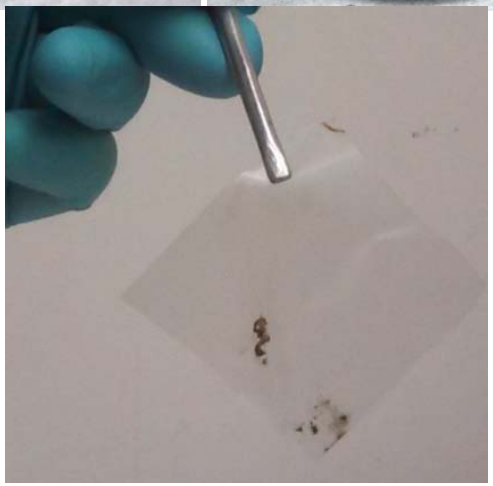


  - Load devices with performance recovery compounds (PRCs)
  - Send to the field or deploy in the lab

Passive Sampler Exposure

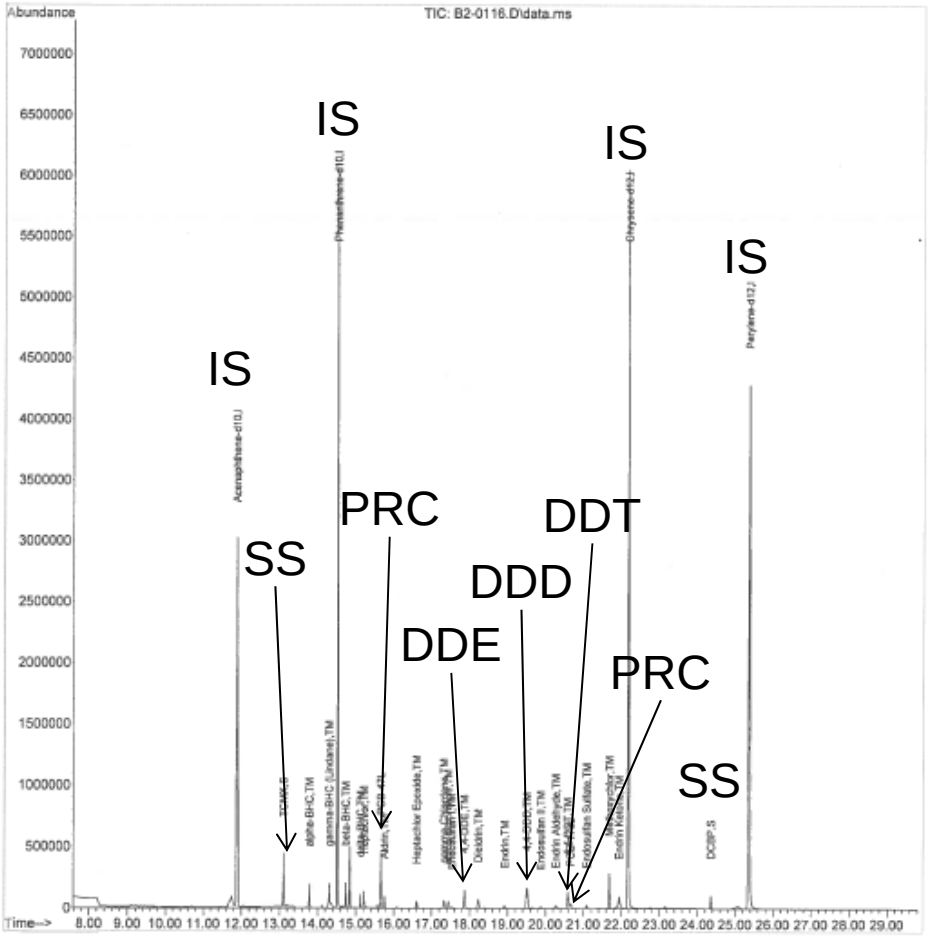
- Exposure:

- Retrieval

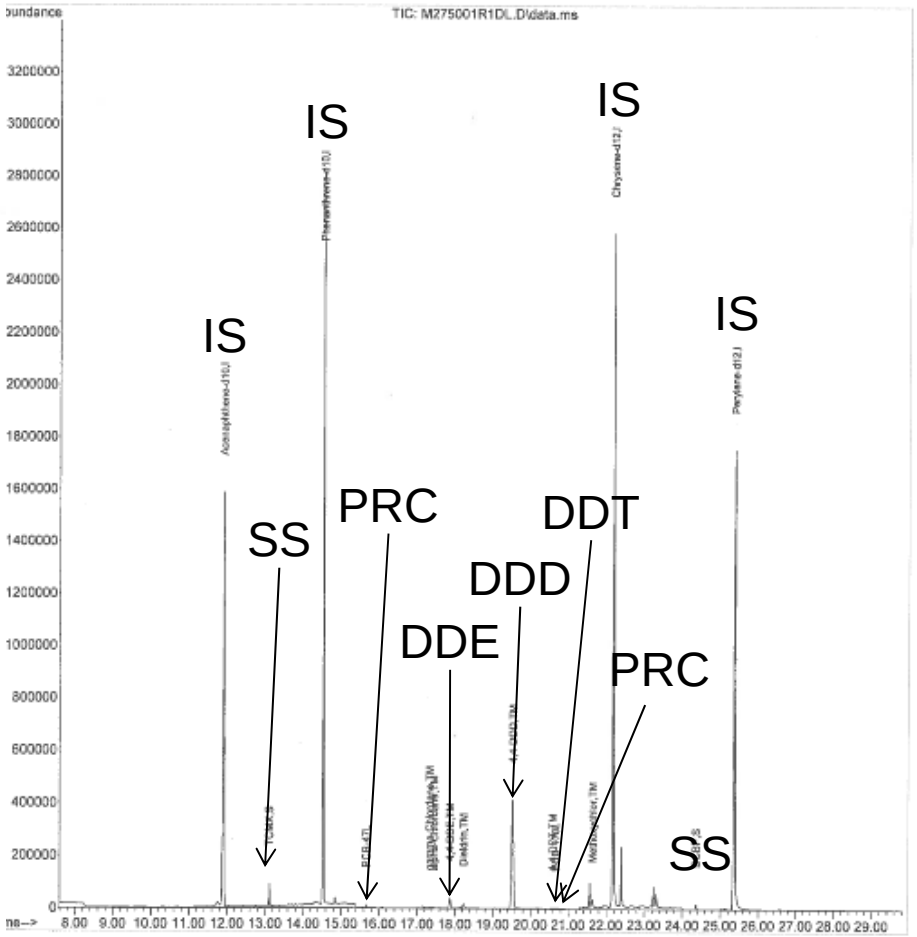


Passive Sampler Analysis

Laboratory Control Sample



Passive Sampler Extract



Passive Sampling Data Usability Considerations

Parameters that Influence Passive Sampling

- Considerations for selecting a passive sampling device (PSD) include:
  - The material should be non-depletive and allow for equilibrium to be approached
  - The material needs to be absorptive for HOCs
  - The partitioning coefficients for the HOCs in the exposure system (polymer-water) need to be known, or be estimated
  - Required detection limits need to be determined to appropriately size the PSD to be deployed
- Other considerations that may be site specific include:
  - Biofouling
  - NAPL fouling
  - Tidal influences

In-situ v. Ex-situ

In-situ Deployment

- Potential to identify site characteristics that may not otherwise be determined:
  - Re-suspension of sediments
  - Additional sources of HOCs
- Ability to measure gradients:
  - Vertical profiles
  - Flux from sediment to water
  - Temporal variation
- Longer deployments needed
- Equilibrium endpoint more difficult to judge
- Multiple field events needed

Ex-situ Deployment

- Snapshot of concentrations based on date of sediment collection
- Easier to control parameters
- Shorter time to reach equilibrium due to ability to mix/agitate samples
- Easier to perform time series to determine equilibrium state
- Lower costs

In situ v. Ex situ Deployment

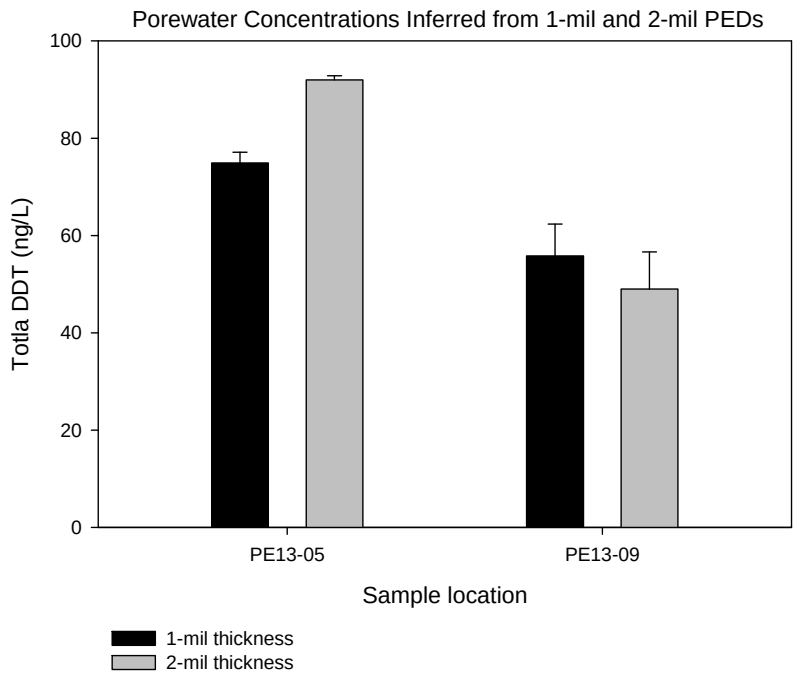
- Samples for e*x situ* PSD deployment were collected at adjacent locations to the placement of the *in situ* PSDs
- Same exposure duration was used for both *Ex situ* and *In situ* deployment

	DDx Conc (ng/L)	
Sample Location	*In situ* Primary Lab	*Ex situ* CH2M HILL ASL
A	149	92[a]/74.9[b]
B	260/168*	49[a]/55.8[b]
C	12	11.5
D	12	6.18

* Sample B duplicate at Primary laboratory
[a] 2 mil PE sheeting
[b] 1 mil PE sheeting

Equilibrium

- The ability to predict bioavailability of HOCs is dependent on reaching, or nearing, equilibrium of the passive sampler with the sediment and porewater
- The time to reach equilibrium will vary based on the K_{pw} of each HOC and can be several months
- Equilibrium may be evaluated by:
  - Conducting a time-series of PSDs
  - Deploy different Area-Volume PSD configurations
  - Use of Performance Reference Compounds (PRCs)



Average and standard deviation of three replicates are shown.

Performance Reference Compounds

- Selecting appropriate PRCs
  - PRCs should be similar compounds to HOCs
  - Loaded at a concentration similar to site HOC concentrations
  - Often isotopically labeled analogs of HOC
    - Use of Mass Spectrometry for analysis to separate and identify the PRC
  - May be a compound that is similar to the HOC but not expected at site
- Two methods for loading PRCs are currently used
    - Spiked water: long exposure time (~2 months), highly efficient
    - Spiked Methanol/Water: shorter exposure time (~ 1wk), less efficient
  - Check PRC concentration in passive sampler before deploying
- PRC loss from PSD is expected to be at the same rate as uptake of HOCs
  - Provides ability to correct for non-equilibrium state
  - Fouling of PSD should impact PRC loss at the same rate as HOC uptake

Partitioning Coefficients

- Use of the correct partitioning coefficients is critical to the proper calculation of inferred porewater concentrations
  - PRC loading calculations require K_{ow} values to be determined or estimated.
  - To convert data from PSD concentrations to inferred porewater concentrations K_{pw} is required
    - K_{pw} have been determined for some compounds
    - Calculations exist for compounds without existing K_{pw} values based on K_{ow}

Conclusions

- PSDs add another line of evidence to investigations at contaminated sediment sites
- The use of PSDs to determine C_{free} may have fewer sources of uncertainty that previously used methods for collecting and analyzing porewater
- Several parameters must be carefully considered before deploying PSDs
  - *In situ* v. *Ex situ*
  - Polymer type
  - Deployment parameters
  - Equilibrium

Discussion

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