Passive Sampling to Quantify Bioavailable PCB Concentrations

Presented by

Eli Patmont, Masakazu Kanematsu, Dimitri Vlassopoulos, and Jim Redwine

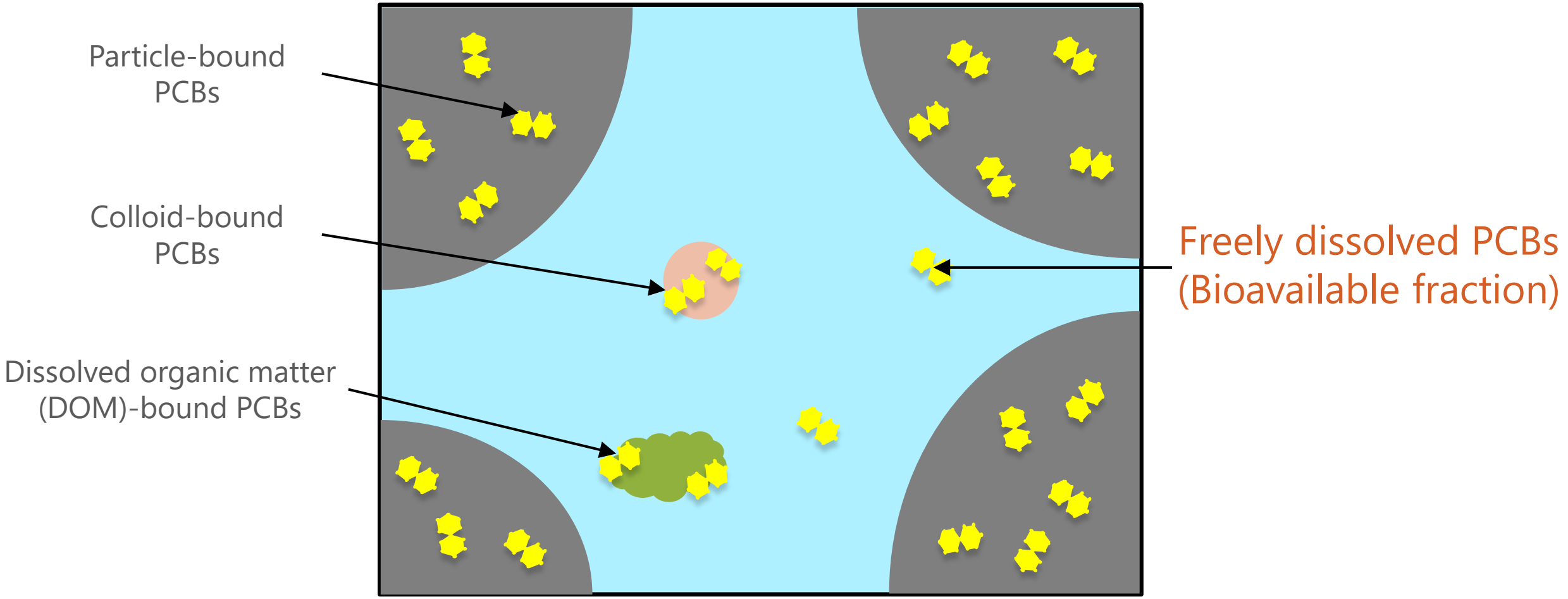
April 11, 2024

ANCHOR QEA

Overview

- What is passive sampling?
- How passive samplers work
- Advantages and limitations of passive sampling
- Types of passive samplers
- In situ and ex situ deployment
- What can we do with passive sampling?

Bioavailable PCB Concentration in Aqueous Media



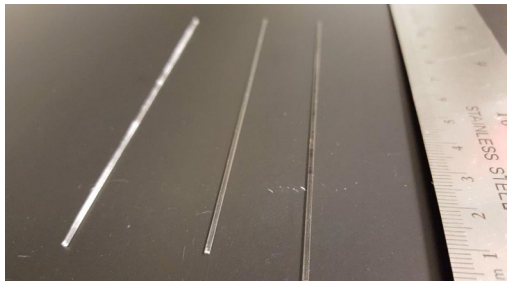
ANCHOR QEA

Challenges in Conventional Active Sampling

- Impact on sample matrix
- Large sample volume requirement
- Sample processing
- “Snap shot” measurement
- Detection limits
- Interference with dissolved organic matter
- Waste generation during extraction and concentration

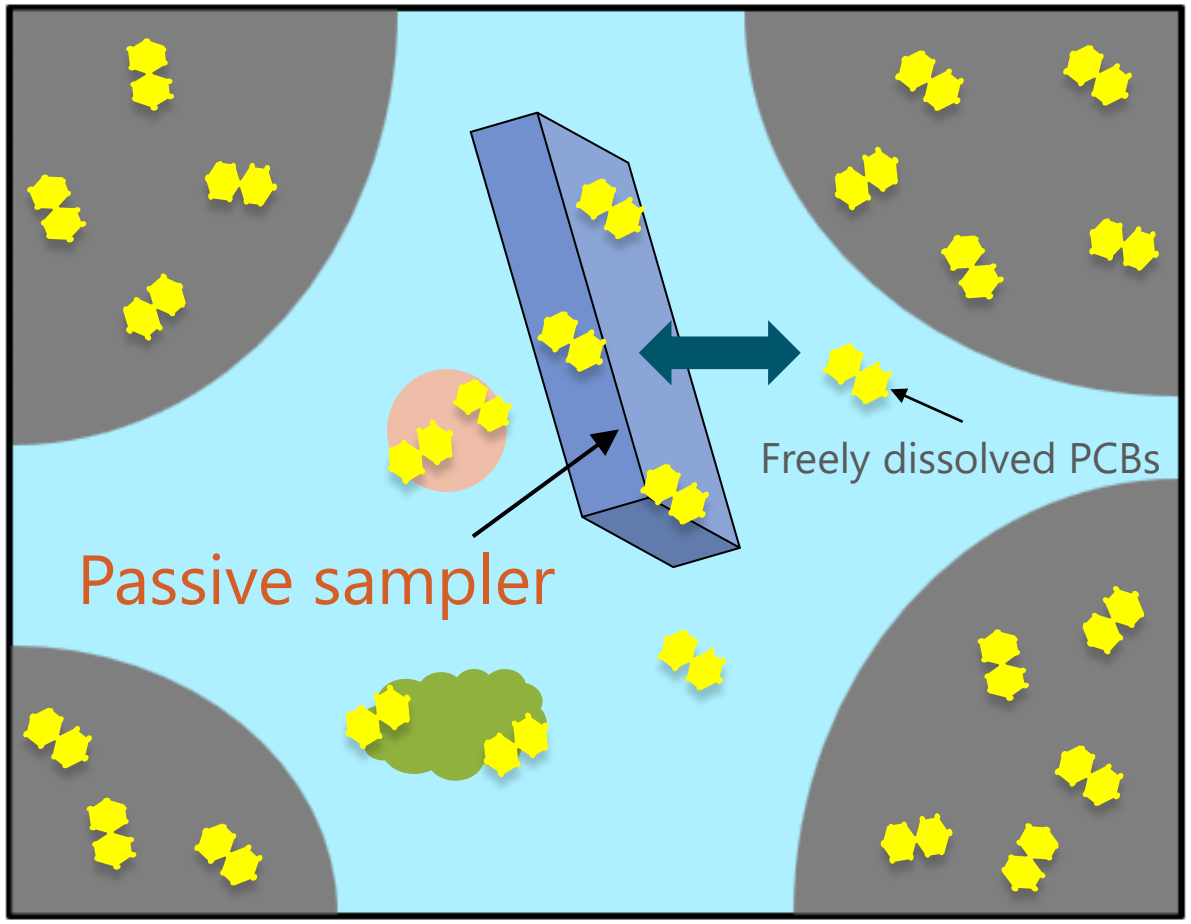
Passive Sampling

- What is passive sampling?
  - Defined in contrast to conventional active sampling
  - No active transport of aqueous media induced by pumping or purging
- Passive samplers
  - There are many different passive samplers for different target analytes
  - Polymeric sampling devices work for hydrophobic organic compounds such as PCBs
    - Low-density polyethylene
    - Solid-phase microextraction (SPME) fiber



ANCHOR QEA

How Passive Samplers Work?



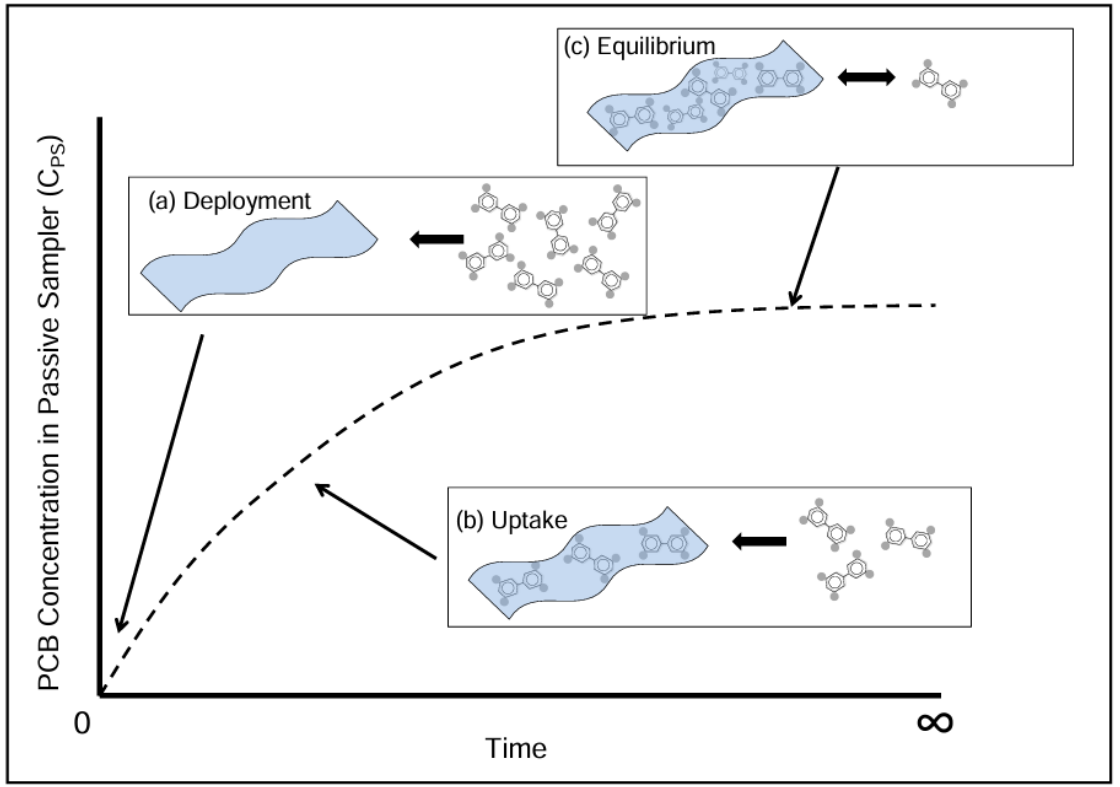
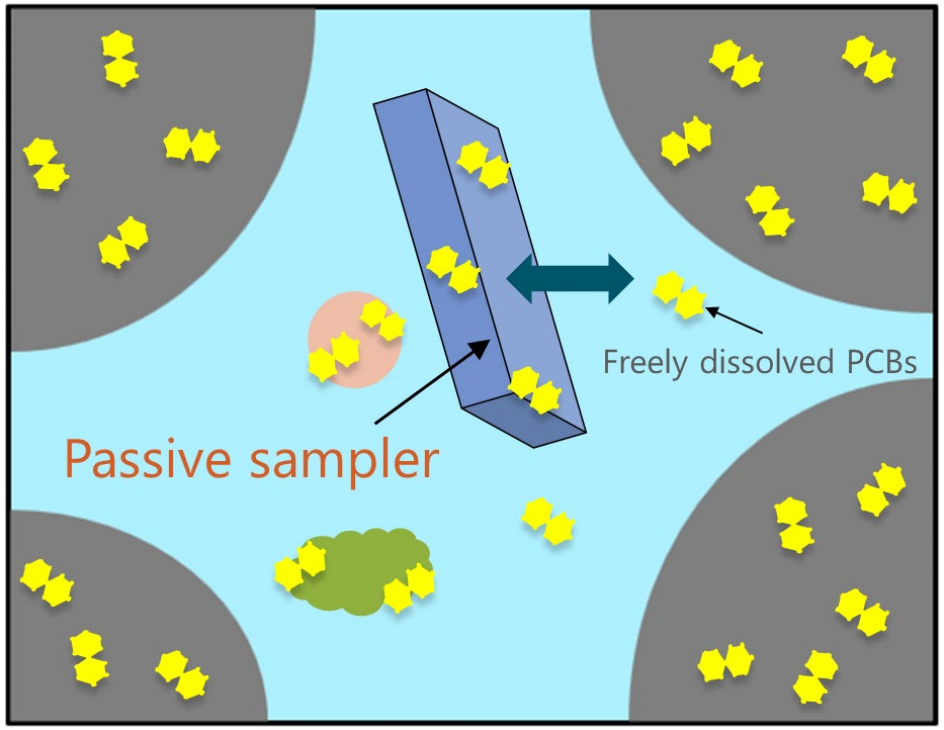


Figure 1-6. Cartoon showing the three stages of passive sampler operation: (a) deployment, (b) uptake (or kinetic), and (c) equilibrium. The blue forms represent passive samplers, and the small icons are PCB molecules (from U.S. EPA 2012b).

ANCHOR QEA

Equilibrium Partitioning

$$C_W = \frac{C_P}{K_{P-W}}$$



C_W: Freely dissolved PCB concentration in aqueous media

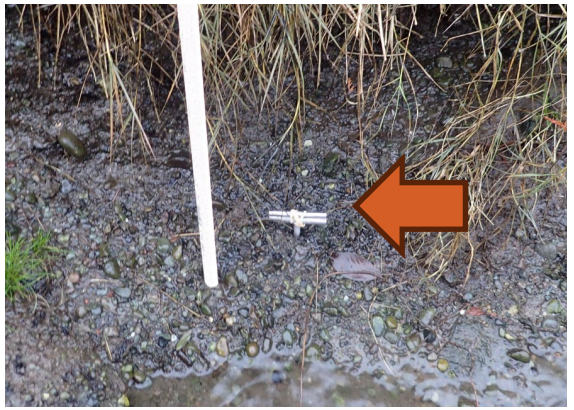
C_P: PCB concentration in passive sampler

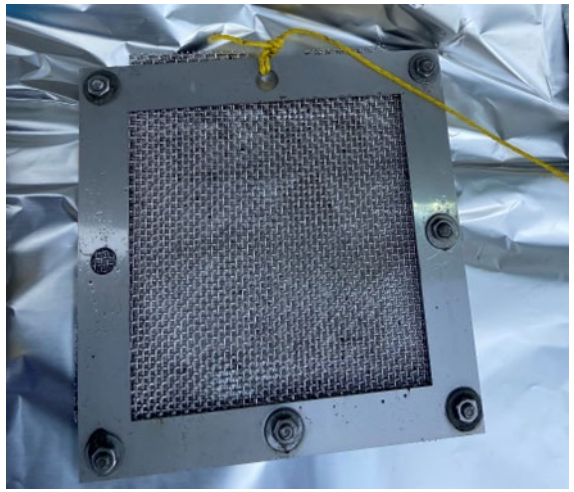
K_{P-W}: Polymer-water partition coefficient for PCB

ANCHOR QEA

Advantages of Passive Sampling

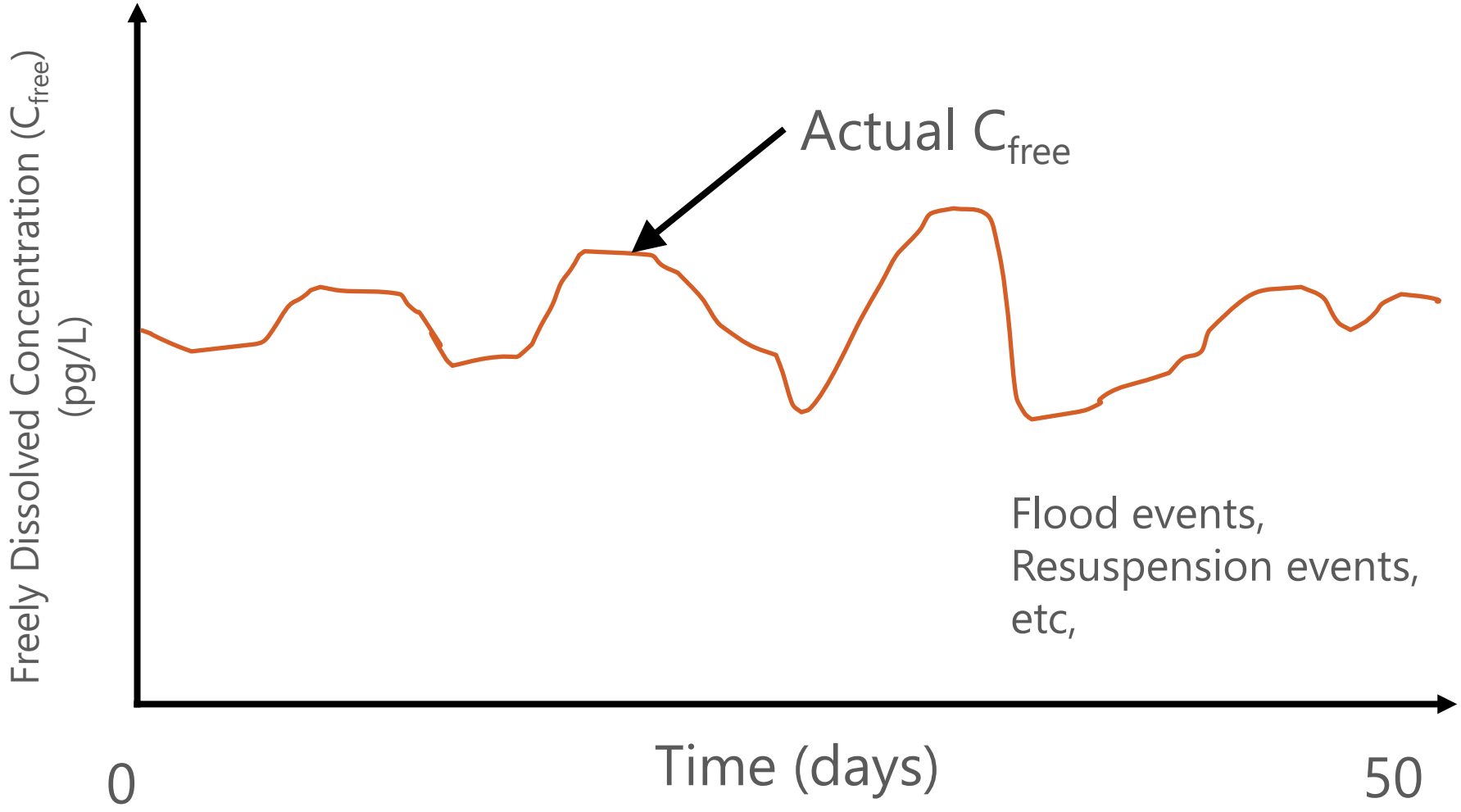
- Minimal impact on sample matrix
- Measurement of freely dissolved concentration
- Easier sample handling compared to active sampling
- Combines water sampling, extraction, concentration
- Measures “time-averaged” concentration
- Low detection limits
- No interference with dissolved organic matter
- High-resolution profiling





ANCHOR QEA

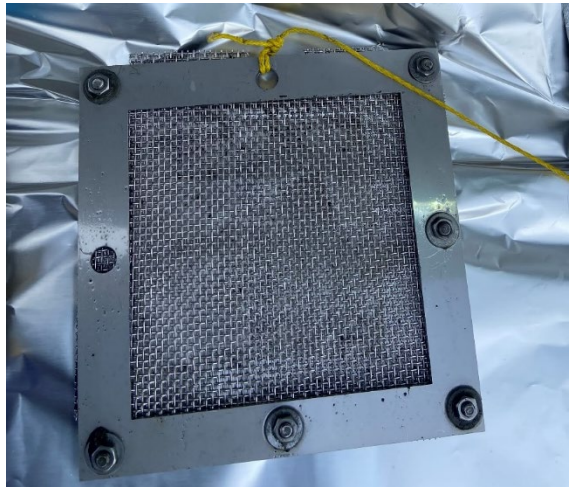
"Time-Averaged" Concentration

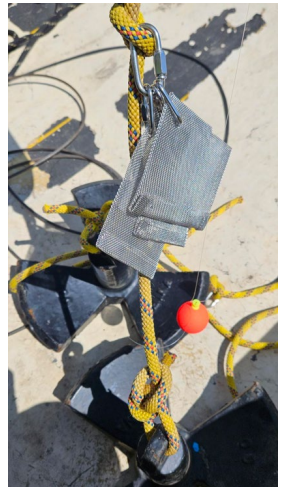


ANCHOR QEA

Types of Passive Sampling Devices

- Low-Density Polyethylene (LDPE)
  - Easy to cut into different sizes
  - A very thin (typically 2-mil) sheet
  - Inexpensive material
  - Loaded on a stainless-steel mesh sleeve for in situ deployment

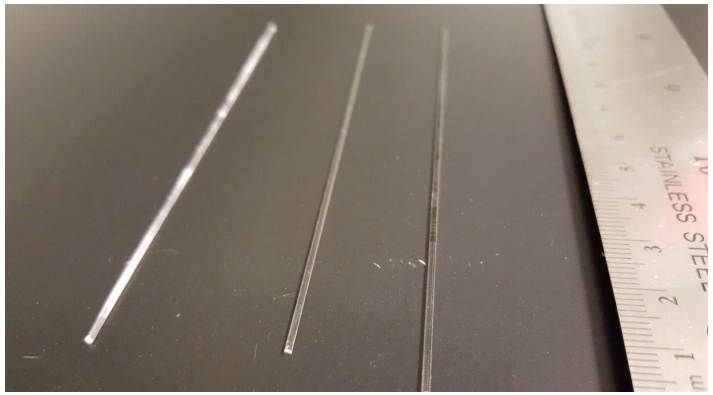


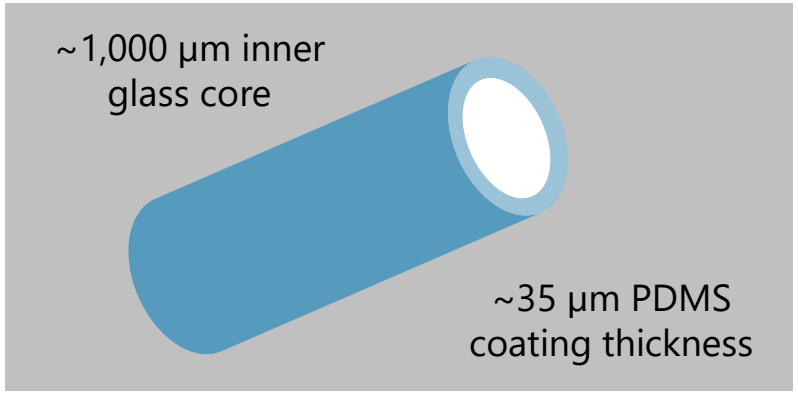


ANCHOR QEA

Types of Passive Sampling Devices (cont.)

- Solid-phase microextraction (SPME) fiber
  - Polydimethylsiloxane (PDMS) coated glass fiber
  - Originally developed in the 90s as a solvent-free method for preparation of samples for measurement in an analytical laboratory
  - Easy to cut into different lengths
  - Loaded on a stainless-steel push-point sampler for in situ deployment





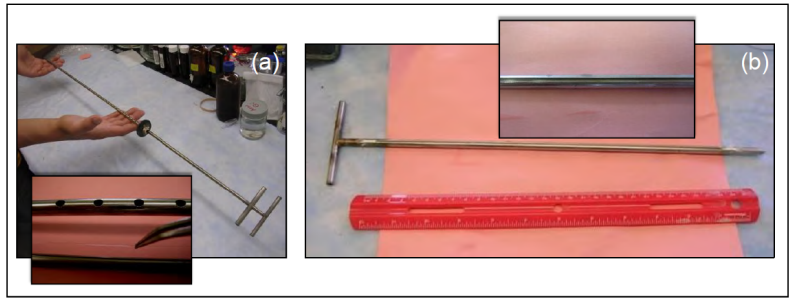


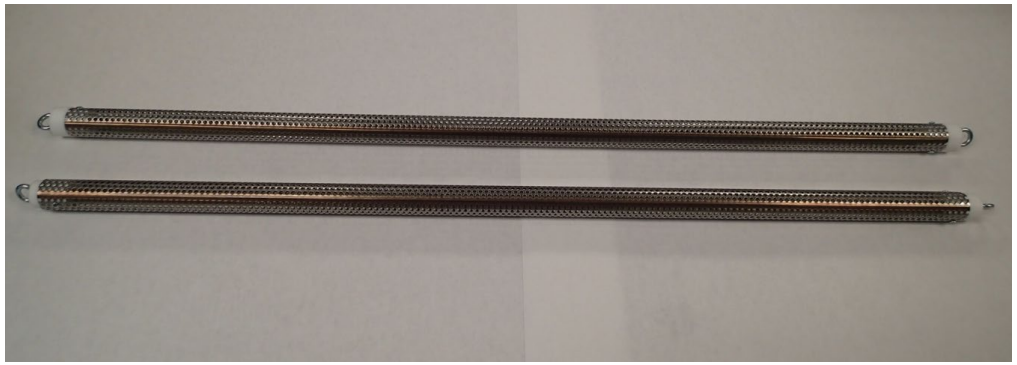
Figure 3-3. Shielded and unshielded holders forPDMS coated SPME fibers with insets showing the SPME fiber for *in situ* deployments: (a) shielded modified push point type sampler with perforations and marker washer (91 cm in length) and (b) unshielded holder (36 cm in length).

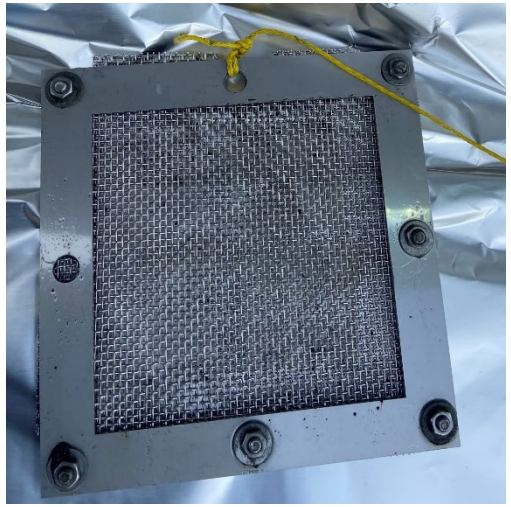
USEPA (2017)

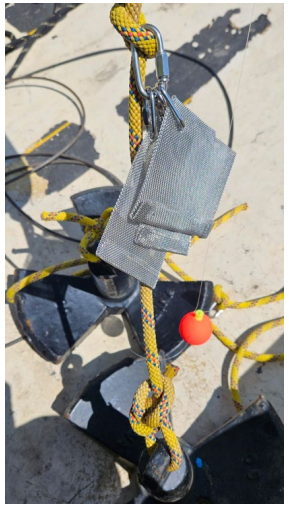
ANCHOR QEA

In Situ Passive Sampling for Different Aqueous Media

- Sediment porewater
- Surface water
- Groundwater

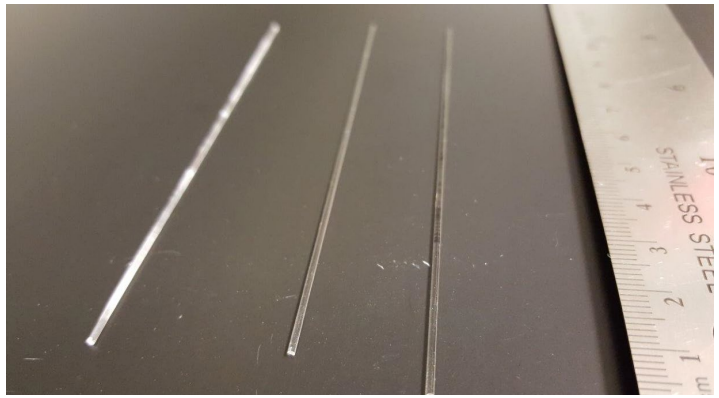


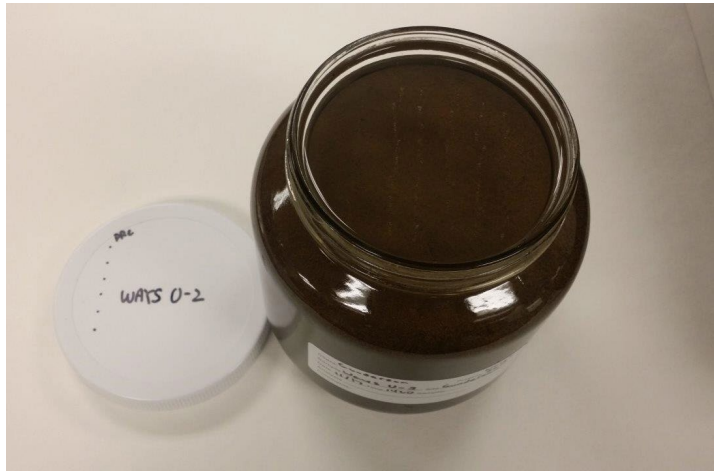


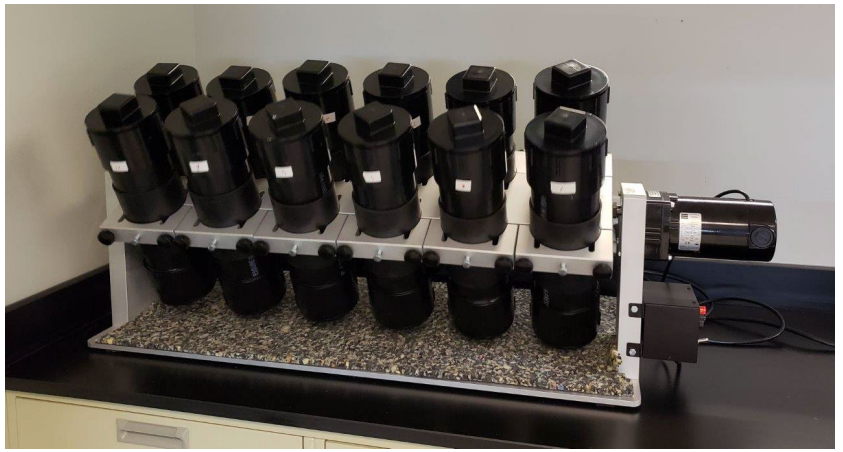


ANCHOR QEA

Ex Situ Passive Sampling (Sediment Porewater)

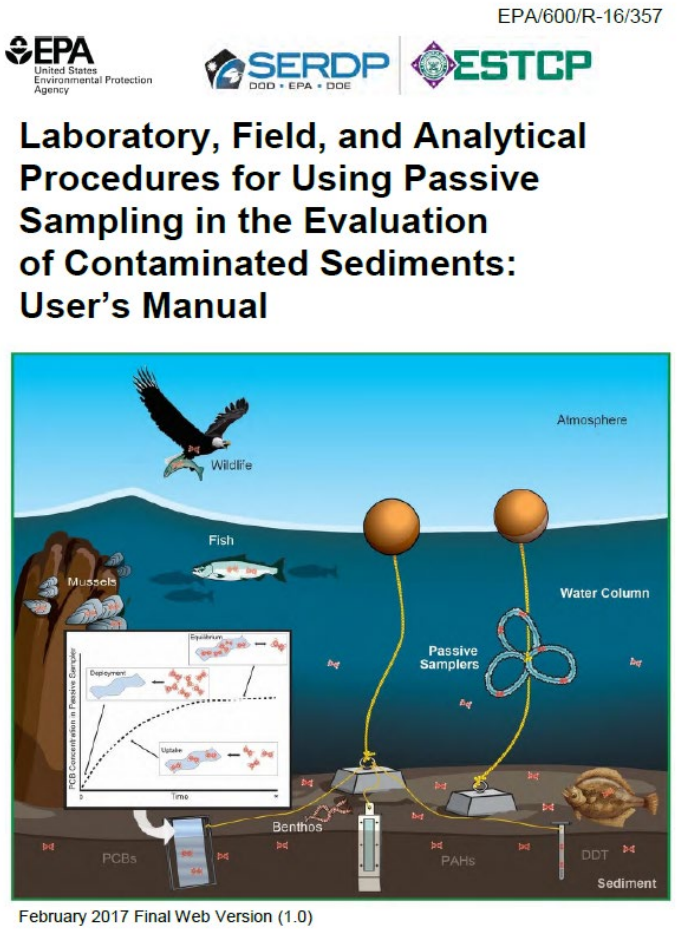






Regulatory Acceptance of Passive Sampling

- EPA has published multiple guidance documents on passive sampling
- Passive sampling has been used for a number of environmental remediation projects
- ITRC has convened a team to review and update its original passive sampling guidance published in 2004-2007
  - Expected to be updated in December 2024



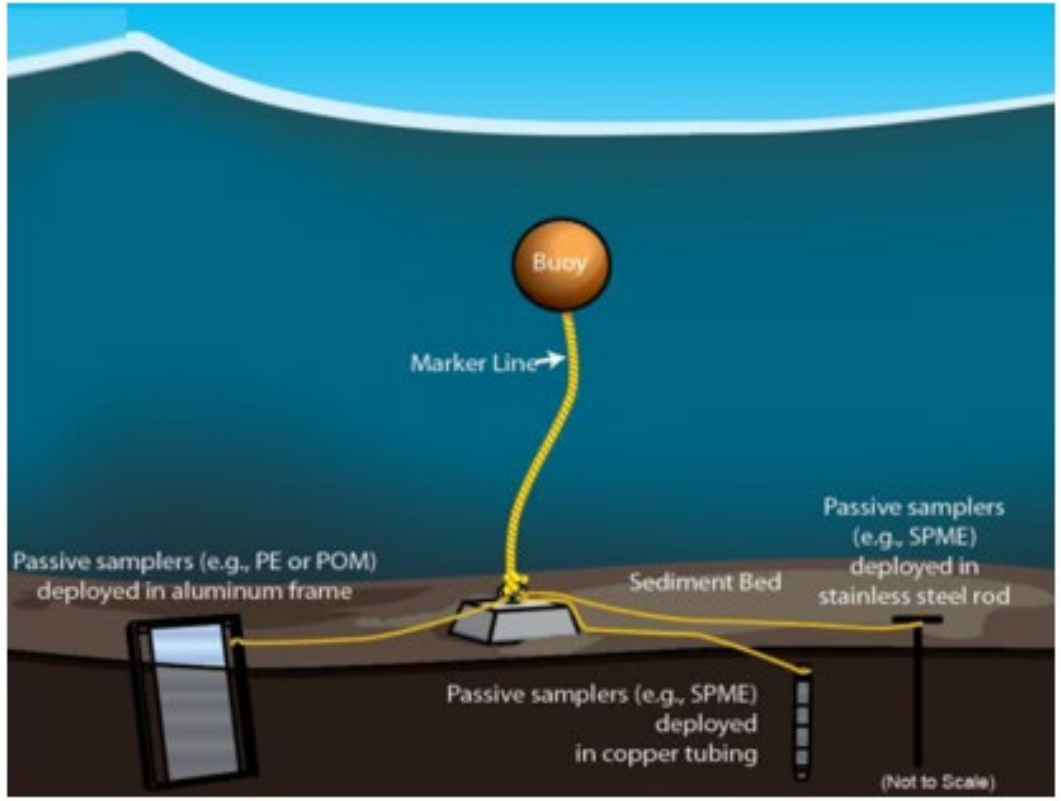
ANCHOR QEA

Passive Sampling for Decision Making

- Identification of monitored natural recovery as a feasible option
- Increased confidence in fate and transport modeling
  - May avoid an over-engineered remedy or indicate need for additional engineering
  - May allow for the use of more habitat-friendly remediation technologies (i.e., in situ treatment, thin layer covers, etc.)
  - Characterization of current and future conditions
- Cost savings either in construction or over the lifetime of the project

Site-Specific Evaluation with Passive Samplers

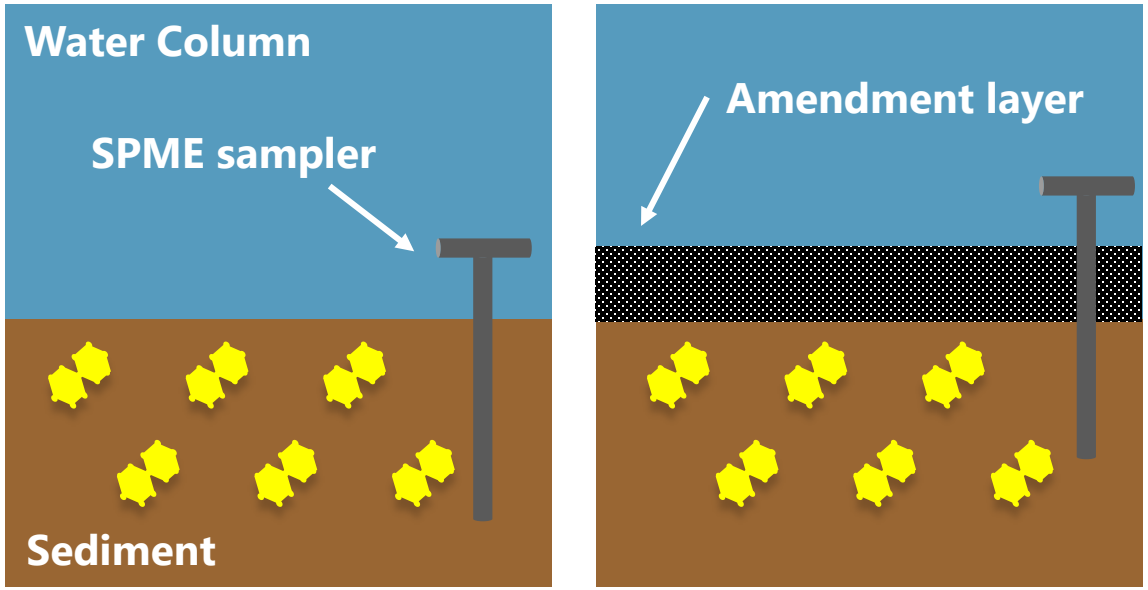
- Assess PCB flux through sediment layers or amendment layer into overlying water
- Assess site-specific partition coefficients
  - Partition coefficients define equilibrium partitioning
  - Literature-based partition coefficients may not be appropriate for a specific site

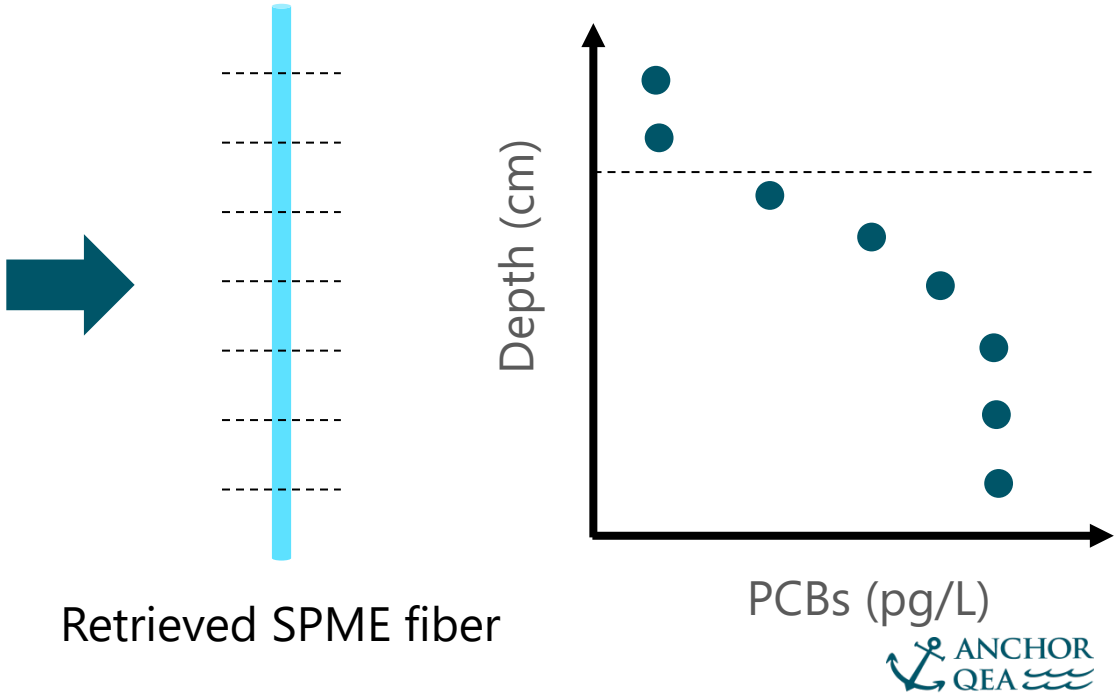


ANCHOR QEA

Determining PCB Concentration Profile and Flux

- Passive sampling can be used to measure PCB flux between sediments and water column
- High-resolution profiling
- Selection of remediation Approach

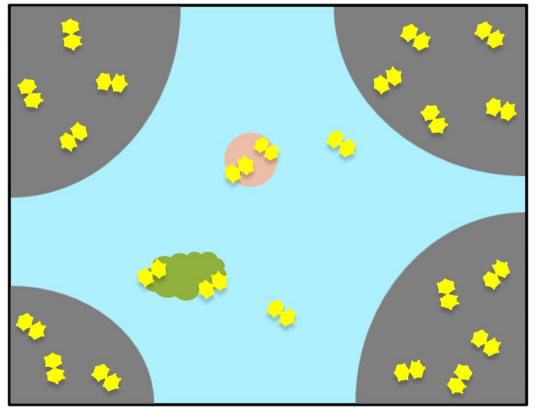




Retrieved SPME fiber

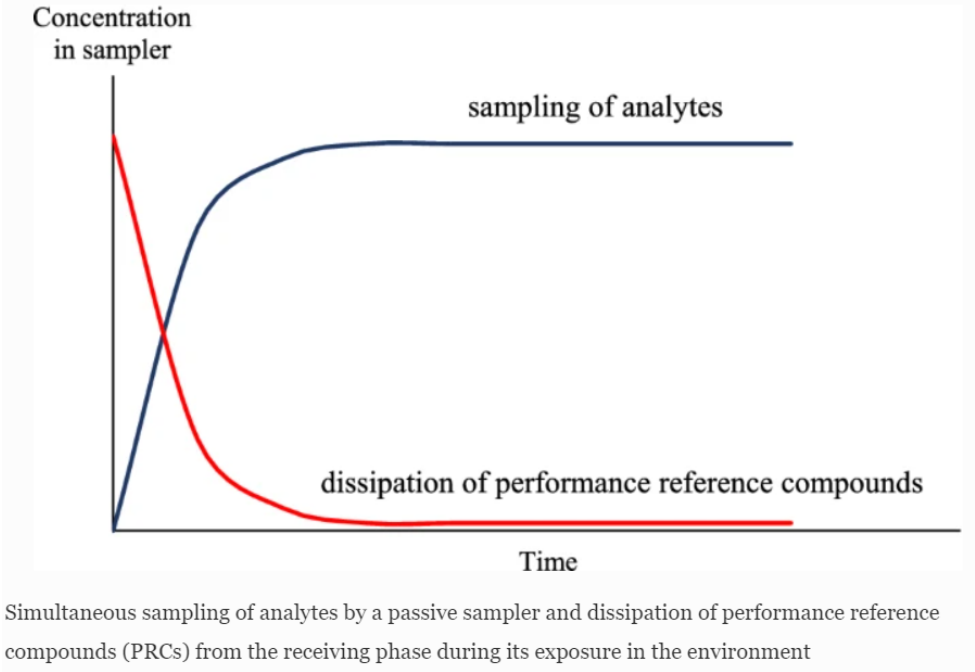
Limitations of Passive Sampling

- Unable to directly address the transport associated with suspended and colloidal particles
- Not applicable for less hydrophobic organic compounds (e.g., log K_{OW} < 4)
- Difficult to reach equilibrium for more hydrophobic organic compounds (including highly chlorinated PCB congeners)
- Sampler deployment is difficult in deep waters
- Interference with non-aqueous phase liquids (NAPLs)



Correction of Disequilibrium

- Performance reference compounds (PRCs): isotope-labeled target analytes spiked on passive samplers prior to deployment



Simultaneous sampling of analytes by a passive sampler and dissipation of performance reference compounds (PRCs) from the receiving phase during its exposure in the environment

From Godlewska et al., 2021

$$C_W = \frac{C_P}{K_{P-W} \times f_e}$$

C_W: Freely dissolved PCB concentration in aqueous media

C_P: PCB concentration in passive sampler

$K_{P\text{-}W}$: Polymer-water partition coefficient for PCB

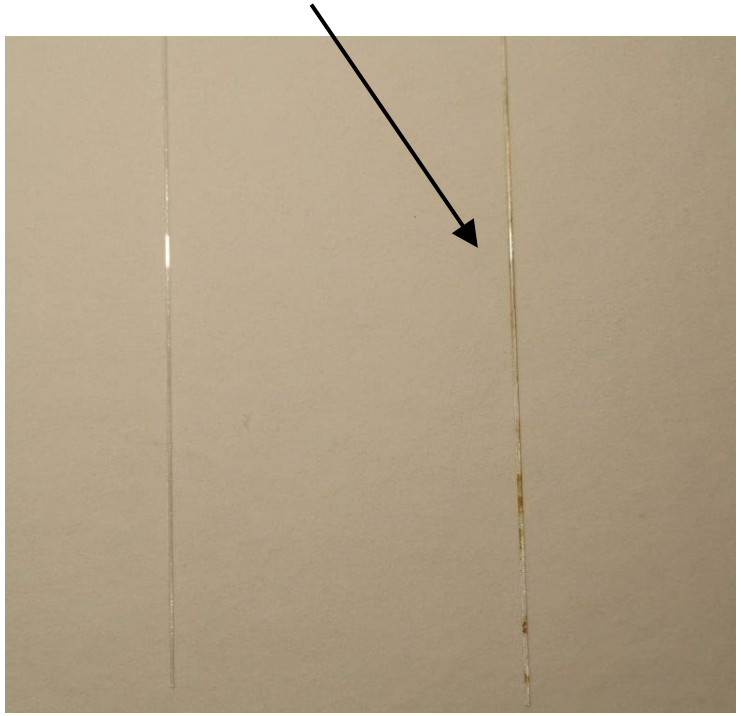
f_e: Fraction of equilibrium

ANCHOR QEA

NAPL Fouling on Passive Samplers

- NAPL coating can exaggerate freely dissolved concentrations
- Once coated, it is difficult wipe off NAPL

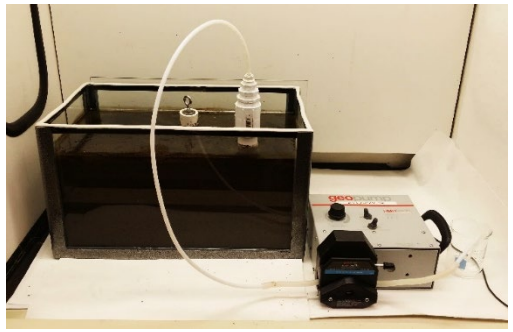
NAPL coating on a SPME fiber

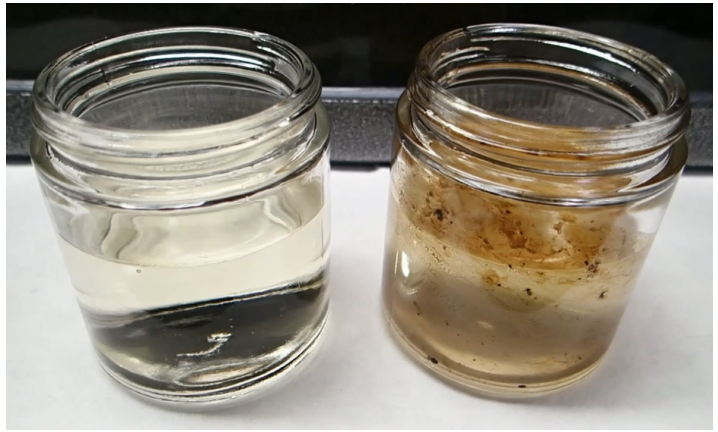


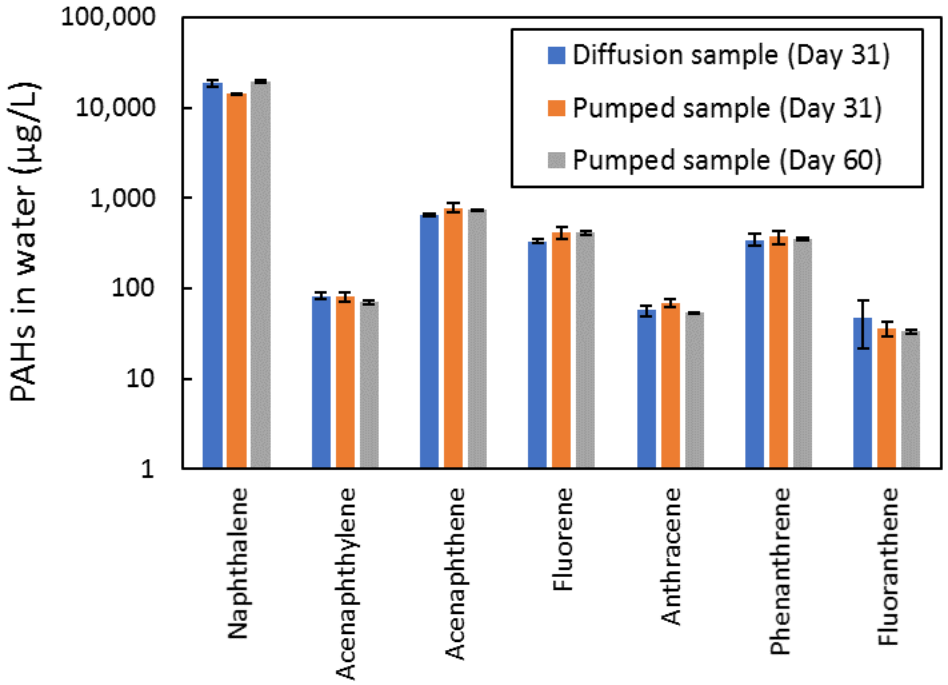
ANCHOR QEA

Ceramic Diffusion Sampler

- Ceramic diffusion sampler can exclude NAPL from aqueous media
- Work for both passive sampling and active sampling



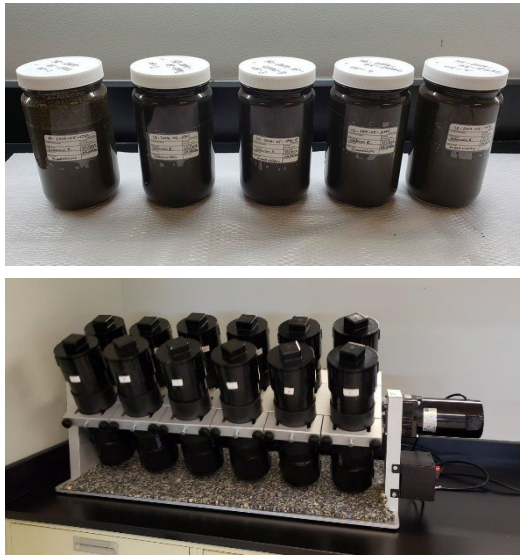


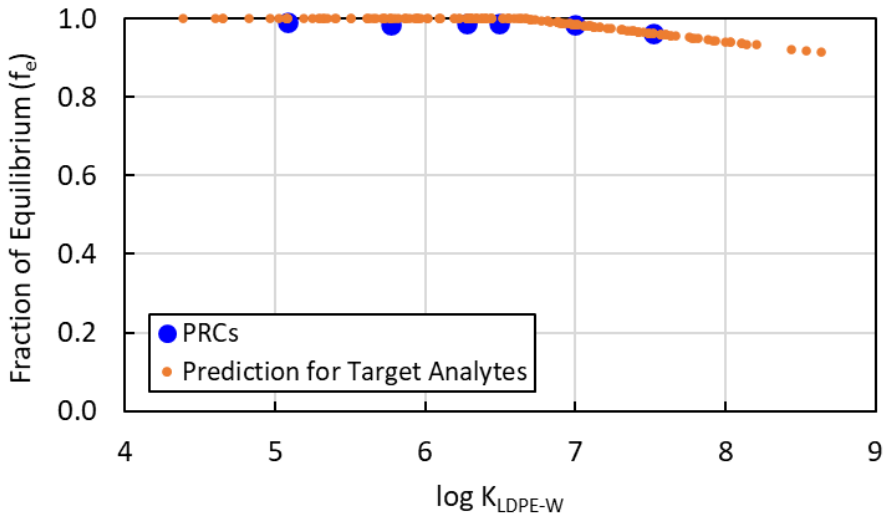


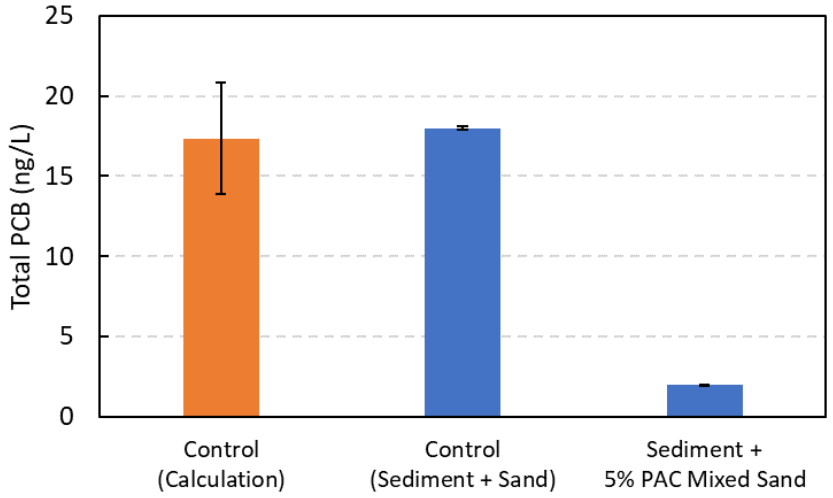
ANCHOR QEA

Case Study

- To assess the effectiveness of powdered activated carbon (PAC) to reduce freely dissolved PCB concentrations in sediment porewater
- Ex situ LDPE deployment in sediment slurry jars







ANCHOR QEA

Questions?