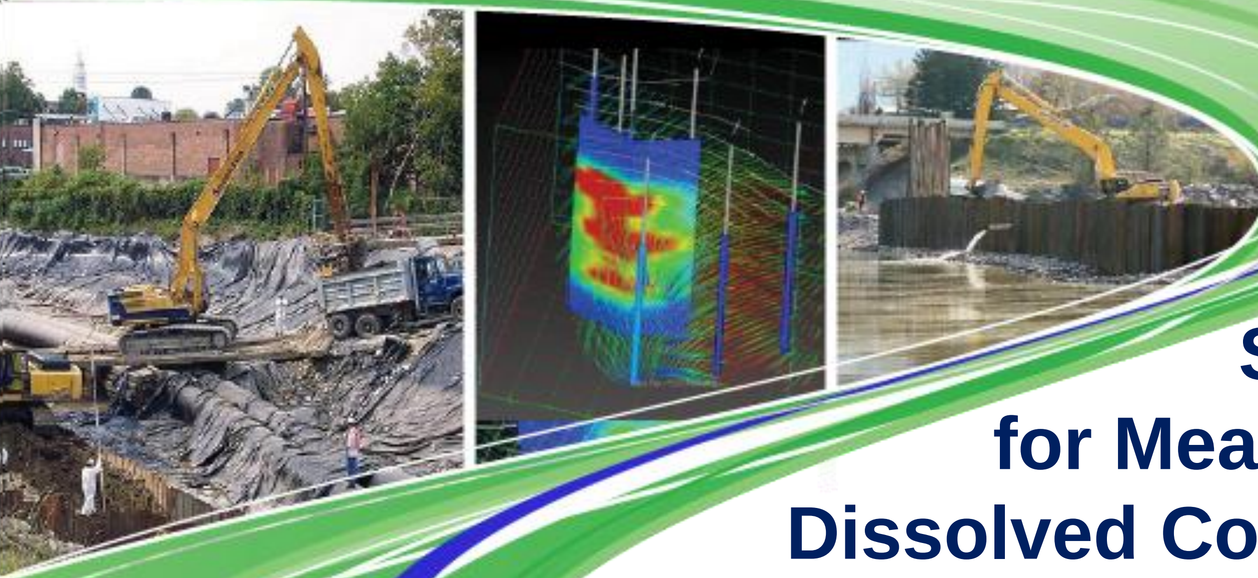


Passive Sampling for Measuring Freely Dissolved Contaminants in Sediments: *Basics, Principles & Applications*

Robert M Burgess

U.S. EPA ORD NHEERL

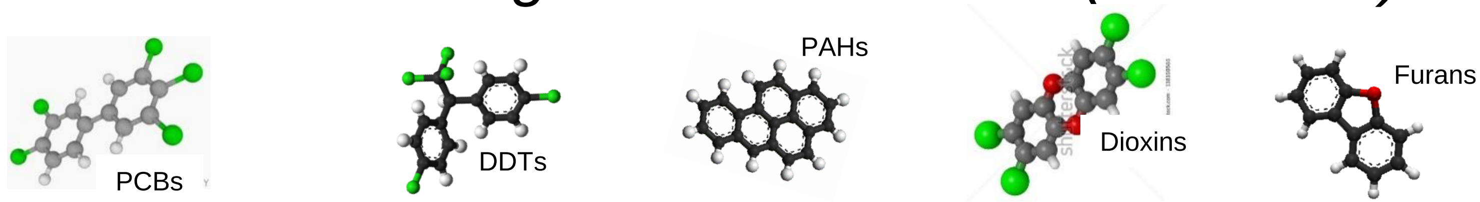
Atlantic Ecology Division

Narragansett, RI, USA

OUTLINE

- Why use passive sampling methods (PSM) and what they tell us
- Why do we care about the freely dissolved concentration (C_{free})
- Types of PSM and how they work
- Preparing, deploying, recovering, and storing PSM
- Analyzing PSM data
- Evaluating PSM applications
- Summary

- *Focus on nonionic organic contaminants (no metals)*



WHY USE PASSIVE SAMPLING METHODS (PSM) AND WHAT THEY TELL US

√ (1) Freely dissolved concentrations (C_{free}) of contaminants of concern (COC) in water around passive sampler

- Surrogate for bioavailable concentrations of COC
- Media
  - Porewater (Interstitial Water)
  - Water column
- Compare to Water Quality Criteria (WQC), other water quality standards, sediment guidelines or water-only toxicity data

√ (2) Concentration of COCs in passive sampler

- Evidence of correlation with bioaccumulation by aquatic organisms
- Serve as surrogates for biomonitoring organisms
  - Benthic and water column organisms
  - Especially in situations where mussels or fish cannot be used (e.g., low dissolved oxygen, toxicity, low/high temperature constraints (ice))

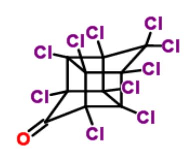
WHY DO WE CARE ABOUT THE FREELY DISSOLVED CONCENTRATION (C_{FREE})?

- For benthic organisms: What media is an effective surrogate for exposure to bioavailable chemicals?
  - Sediment?
  - Food?
  - Water column?
  - Pore Water = Freely dissolved?

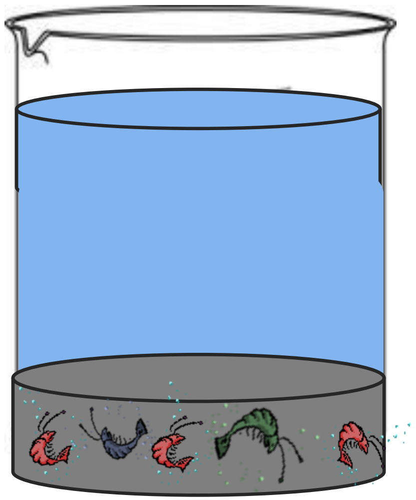
=

Chironomus tentans

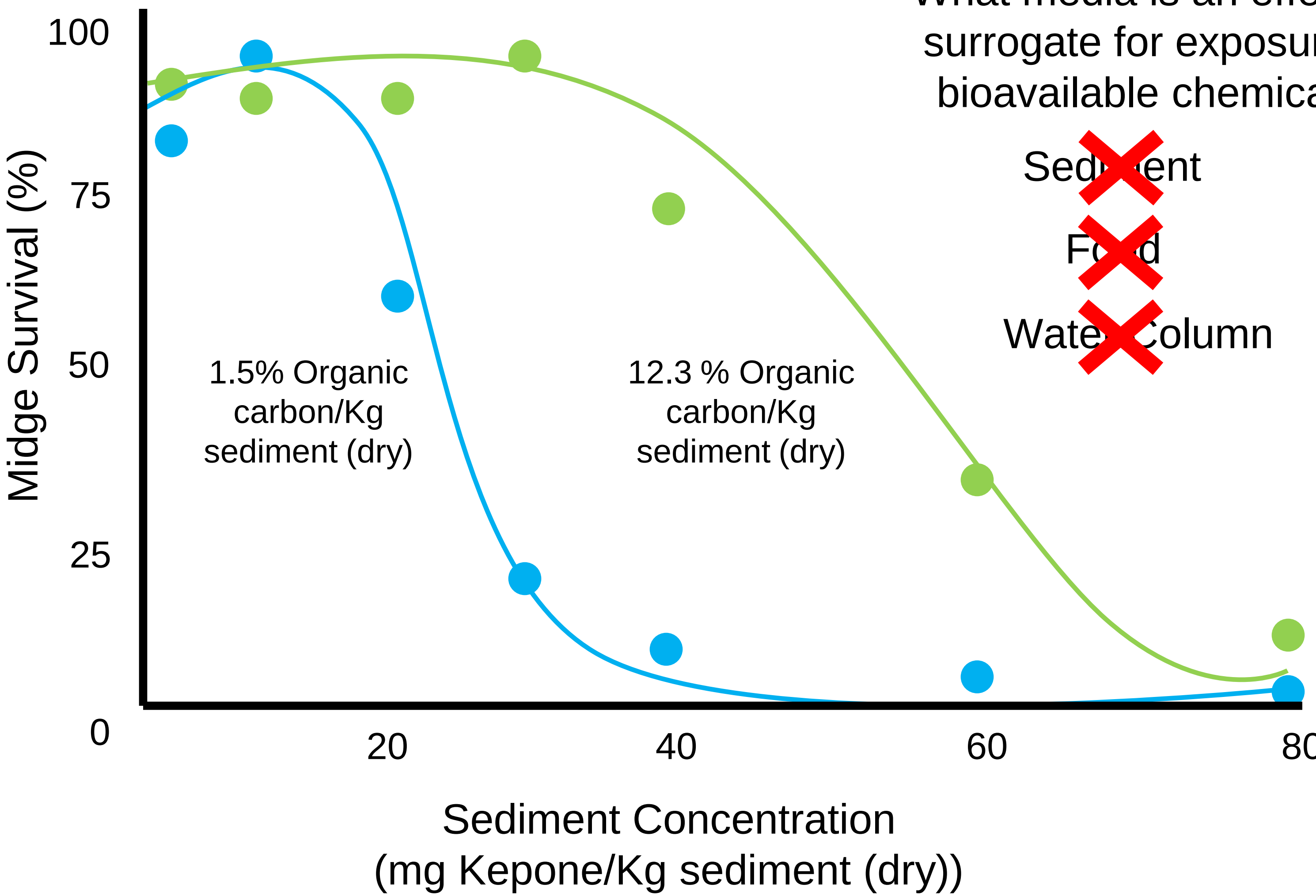
- Adams et al. (1985) addressed this question
  - Two Kepone-amended sediments (same levels)
    - 1.5% and 12.3% Sediment organic carbon
  - Freshwater midge (*Chironomus tentans*)
  - Flow-through and static 14 day exposures
  - Acute and chronic (growth) endpoints
  - Exposure-response relationships
    - Survival and growth versus exposure



Kepone



WHY DO WE CARE ABOUT THE FREELY DISSOLVED CONCENTRATION (C_{FREE})?



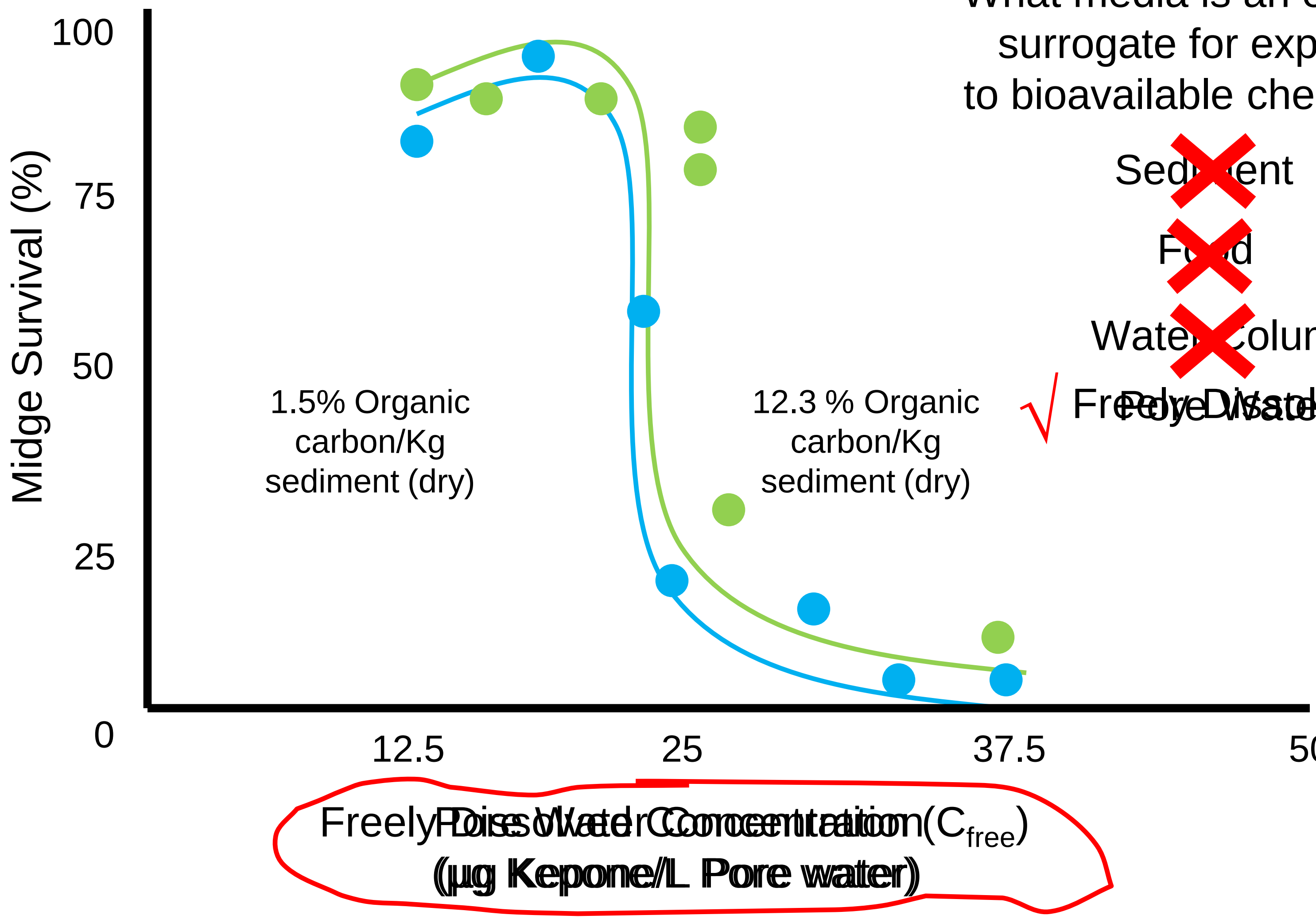
What media is an effective surrogate for exposure to bioavailable chemicals?

~~Sediment~~

~~Food~~

~~Water Column~~

WHY DO WE CARE ABOUT THE FREELY DISSOLVED CONCENTRATION (C_{FREE})?



What media is an effective surrogate for exposure to bioavailable chemicals?

~~Sediment~~

~~Food~~

~~Water Column~~

√ Freely Dissolved

Pore Water

WHY USE PASSIVE SAMPLING METHODS (PSM) AND WHAT THEY TELL US

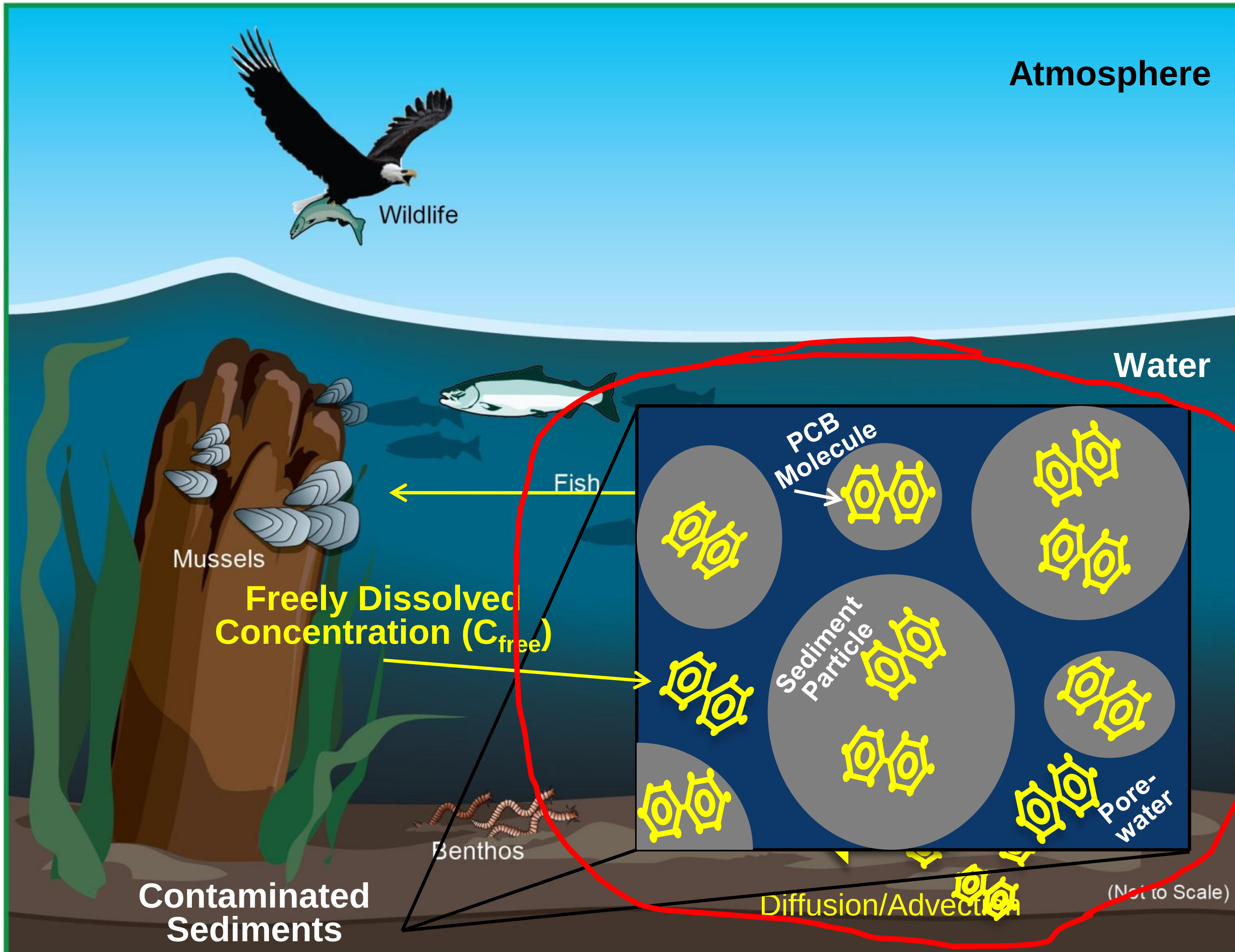
- Measuring freely dissolved concentrations (C_{free}) in the pore waters and water column

  - Why not continue to use conventional sampling methods? Some problems:

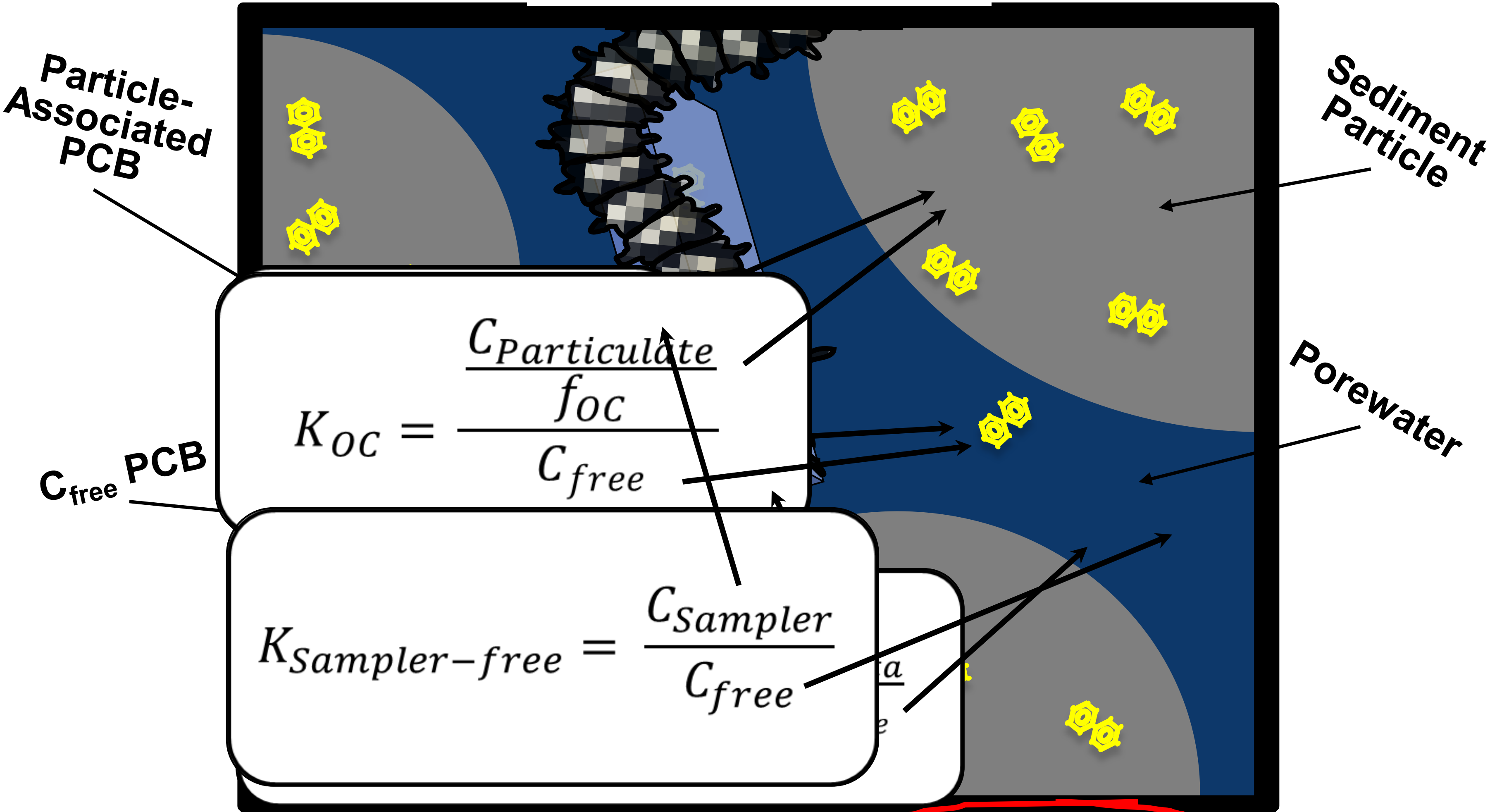
Is there another sampling method for measuring the freely dissolved concentrations (C_{free}) of contaminants?

  - √ Pore Water
    - Centrifugation or squeezing pore water results in limited volumes
    - Several artifacts including losses to filters and surfaces and contamination by colloids and small particles reduce accuracy of analysis
    - Collecting large volumes of pore waters is logistically challenging, scientifically dodgy and generally expensive
  - √ Water Column
    - Logistically and technically difficult to collect and extract large volumes of surface water
    - Same artifacts as pore water collection
    - Analytical detection limits are often not sufficiently low

WHY USE PSM AND WHAT THEY TELL US

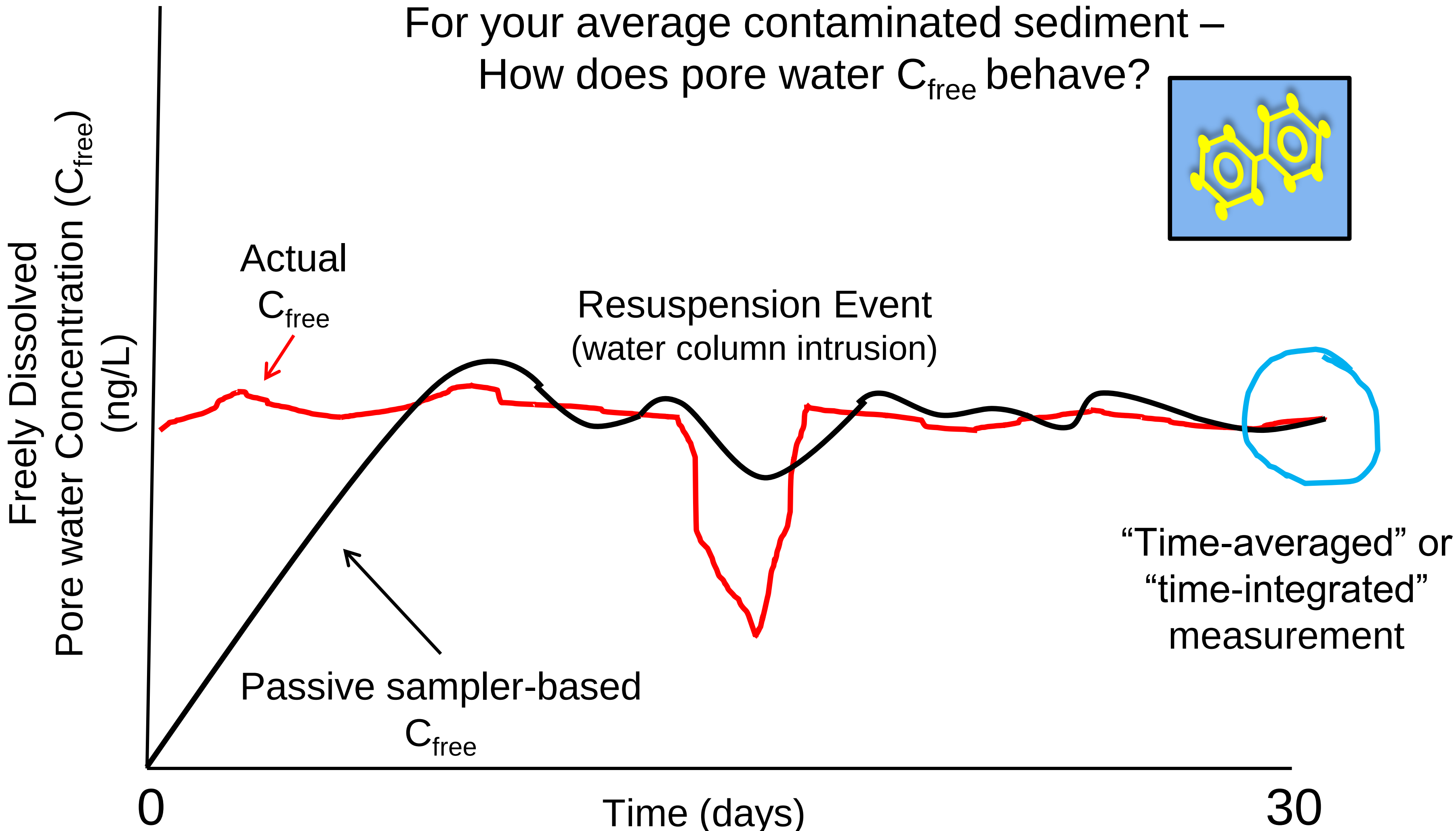


WHY USE PSM AND WHAT THEY TELL US

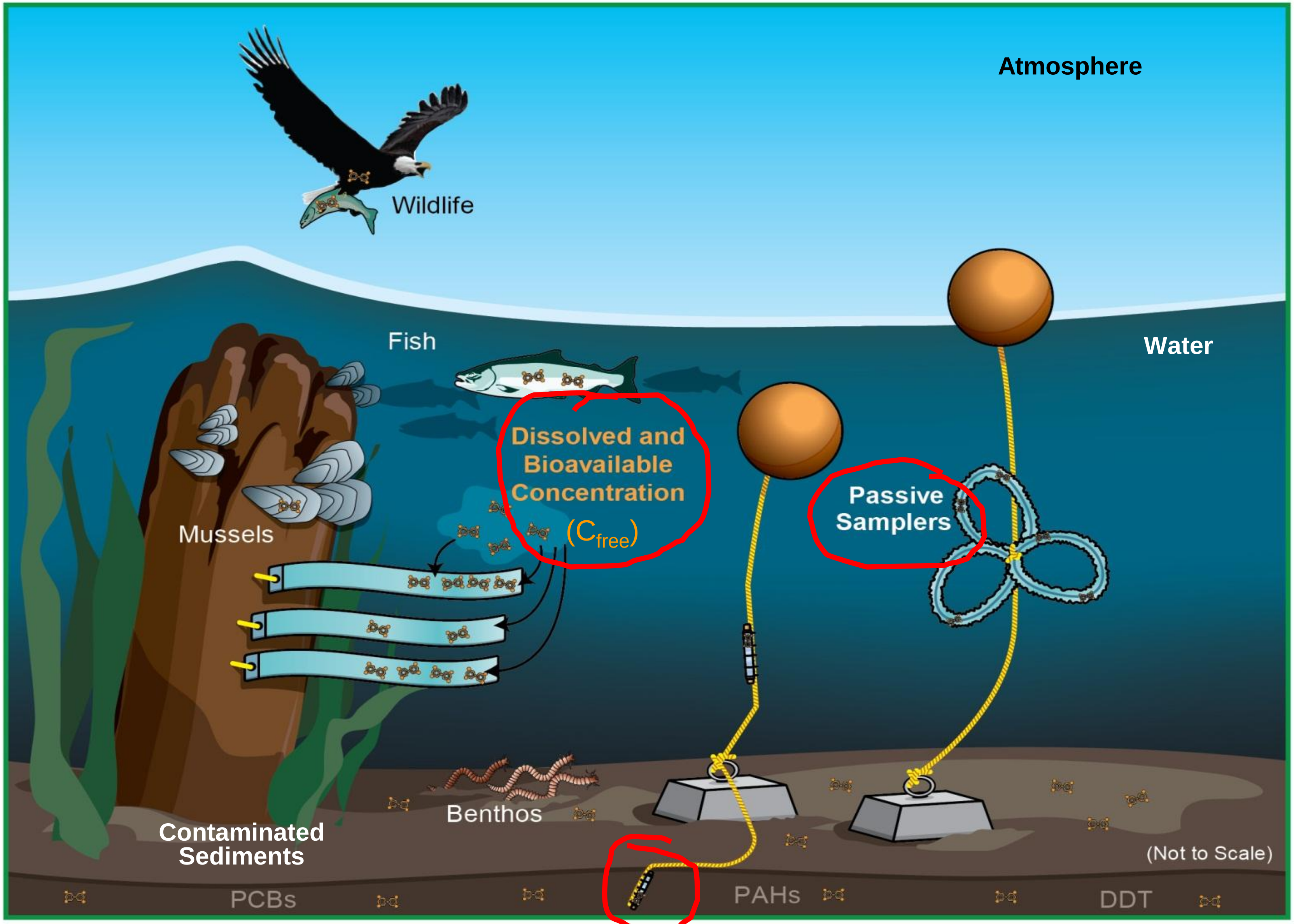


In equilibrium systems… there is equilibrium partitioning and there are partition coefficients

WHY USE PSM AND WHAT THEY TELL US

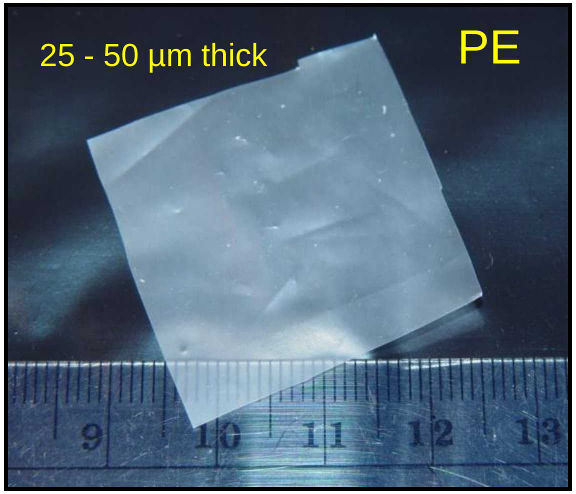


TYPES OF PSM AND HOW THEY WORK

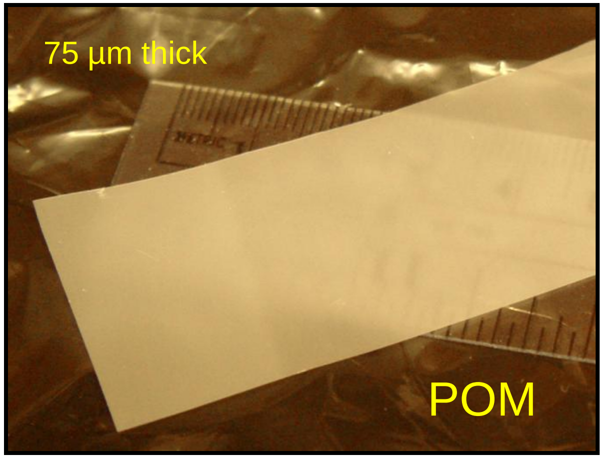


TYPES OF PSM AND HOW THEY WORK

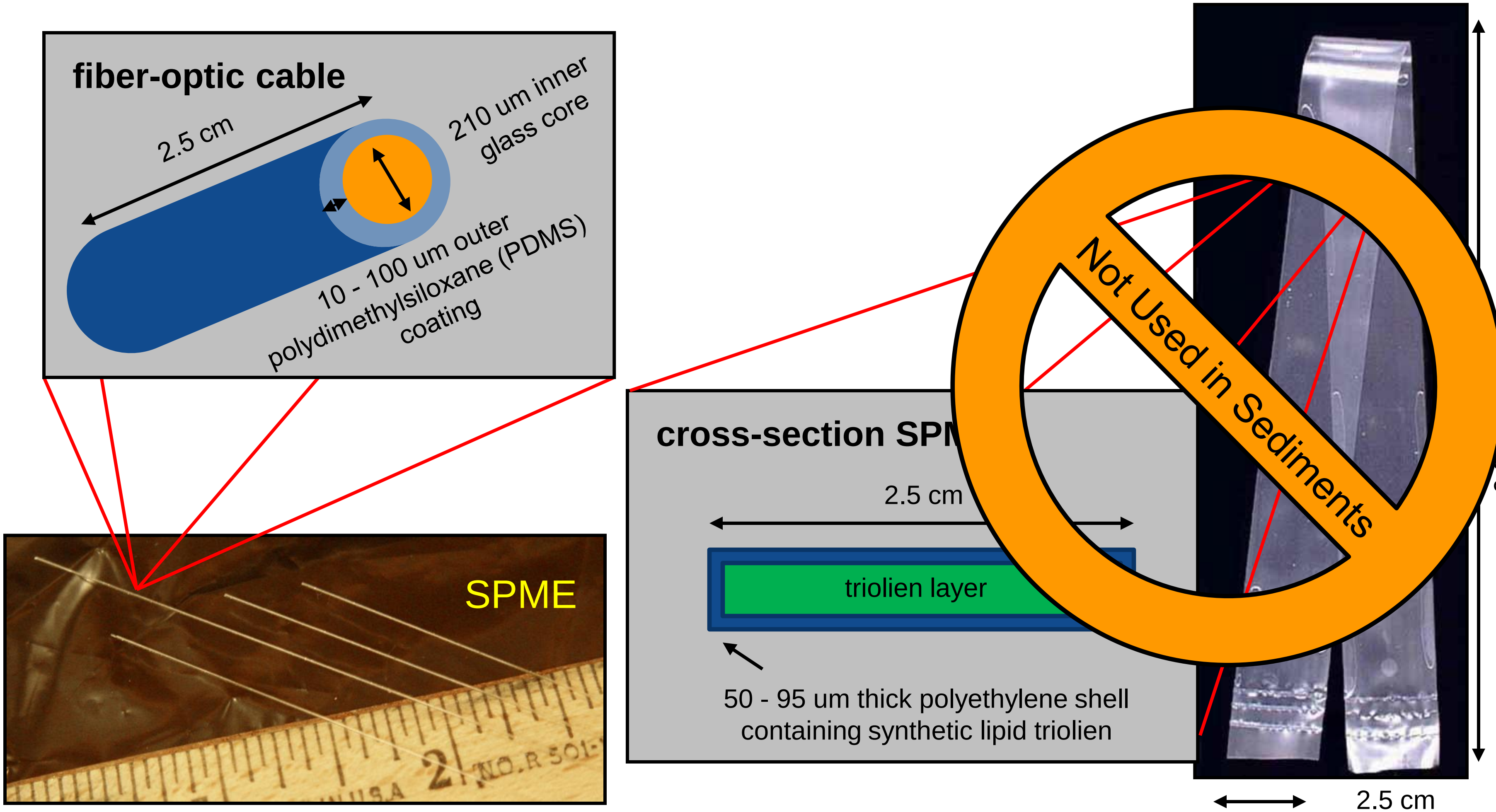
Polyethylene (PE)



Polyoxymethylene (POM)



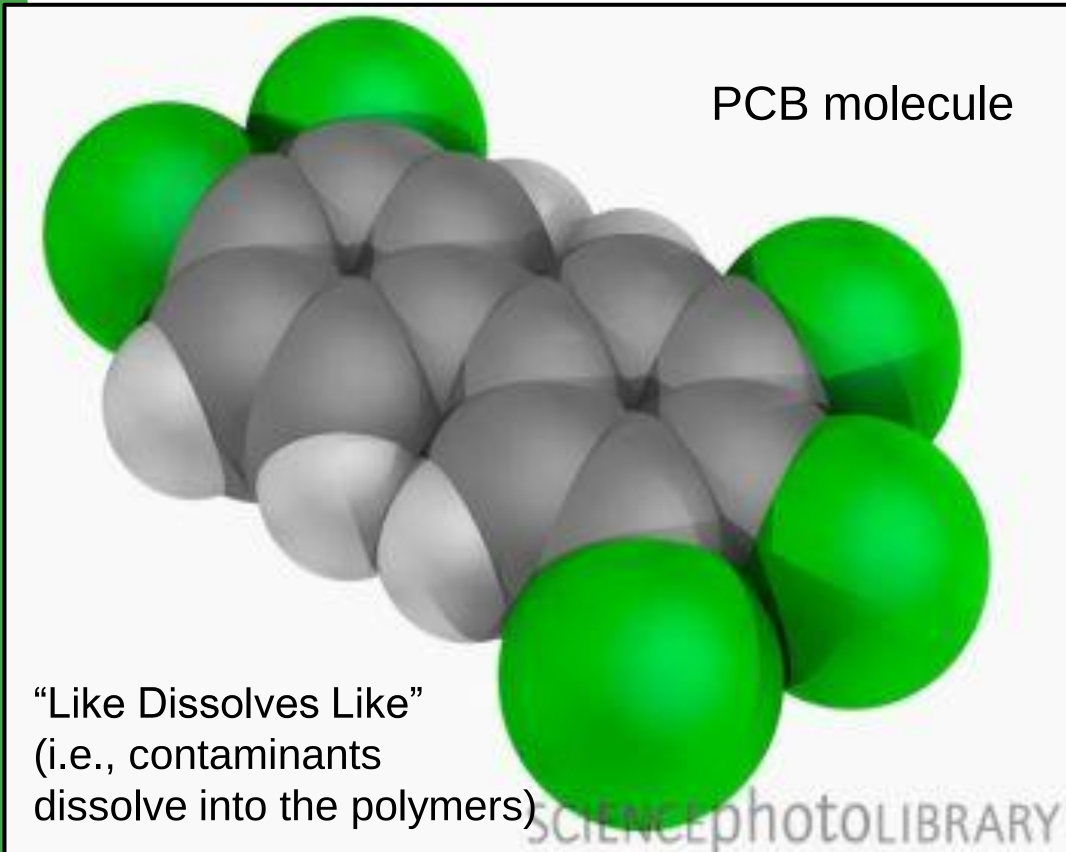
TYPES OF PSM AND HOW THEY WORK



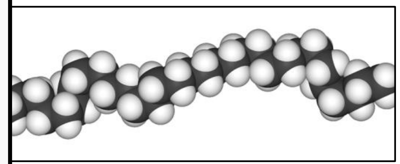
Solid Phase Microextraction (SPME)

Semi-Permeable Membrane Device (SPMD)

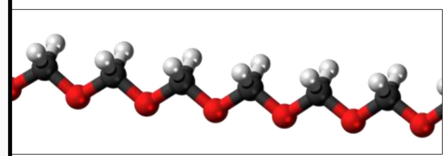
TYPES OF PSM AND HOW THEY WORK



"Like Dissolves Like"
(i.e., contaminants
dissolve into the polymers)

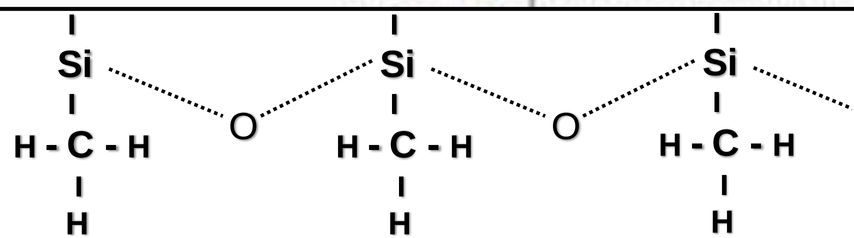


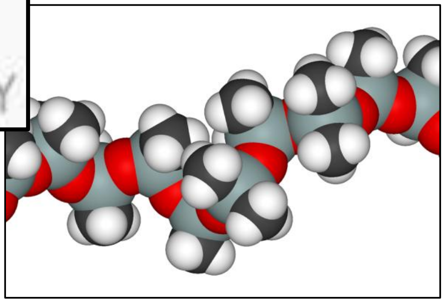
Polyethylene



Polyoxymethylene

(c)





Polydimethylsiloxane

Atom Key:

White = Hydrogen

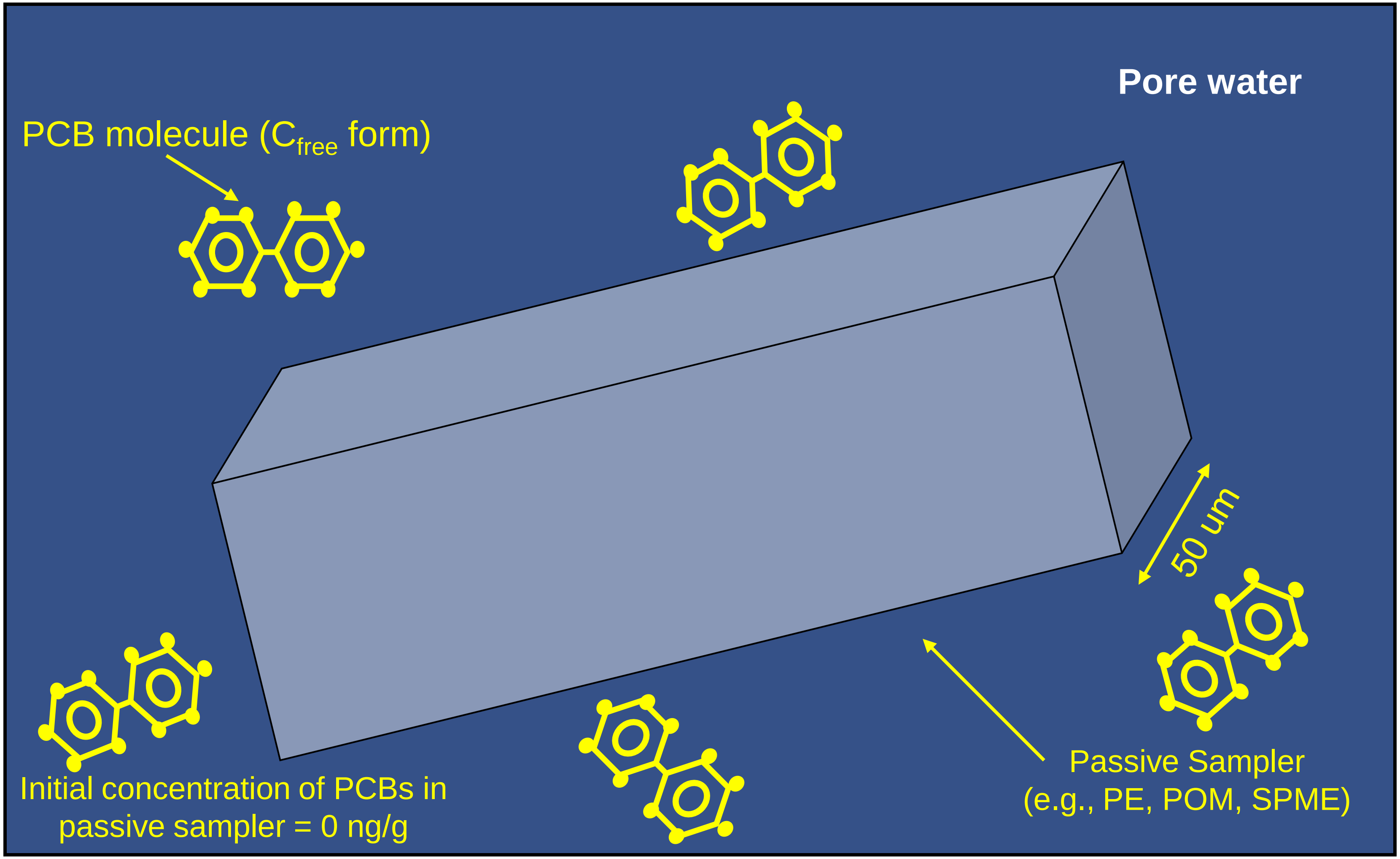
Black = Carbon

Red = Oxygen

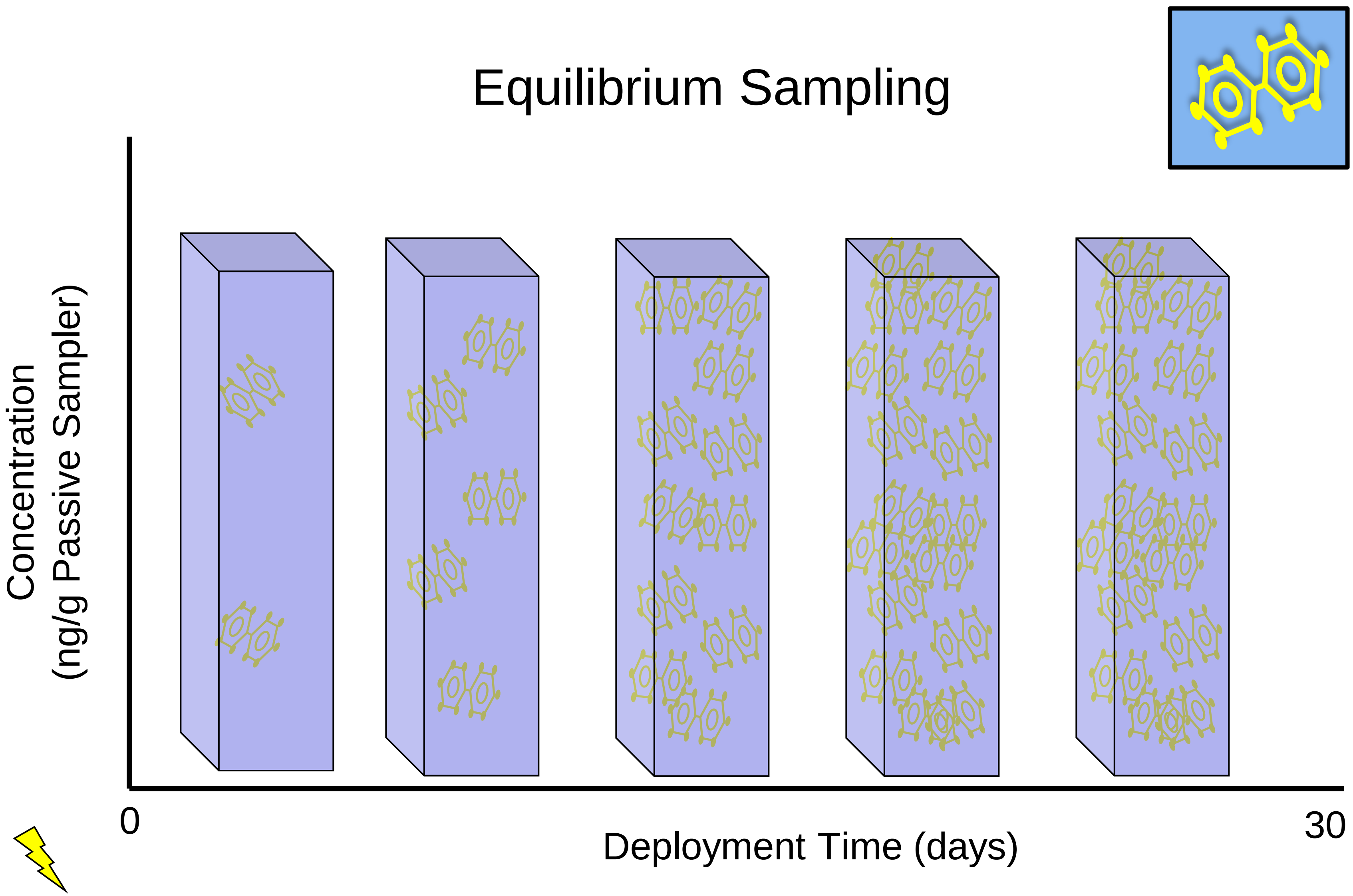
Grey = Silicon

Green = Chlorine

TYPES OF PSM AND HOW THEY WORK

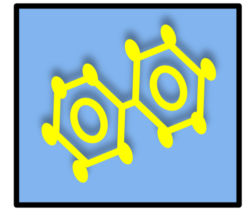


TYPES OF PSM AND HOW THEY WORK

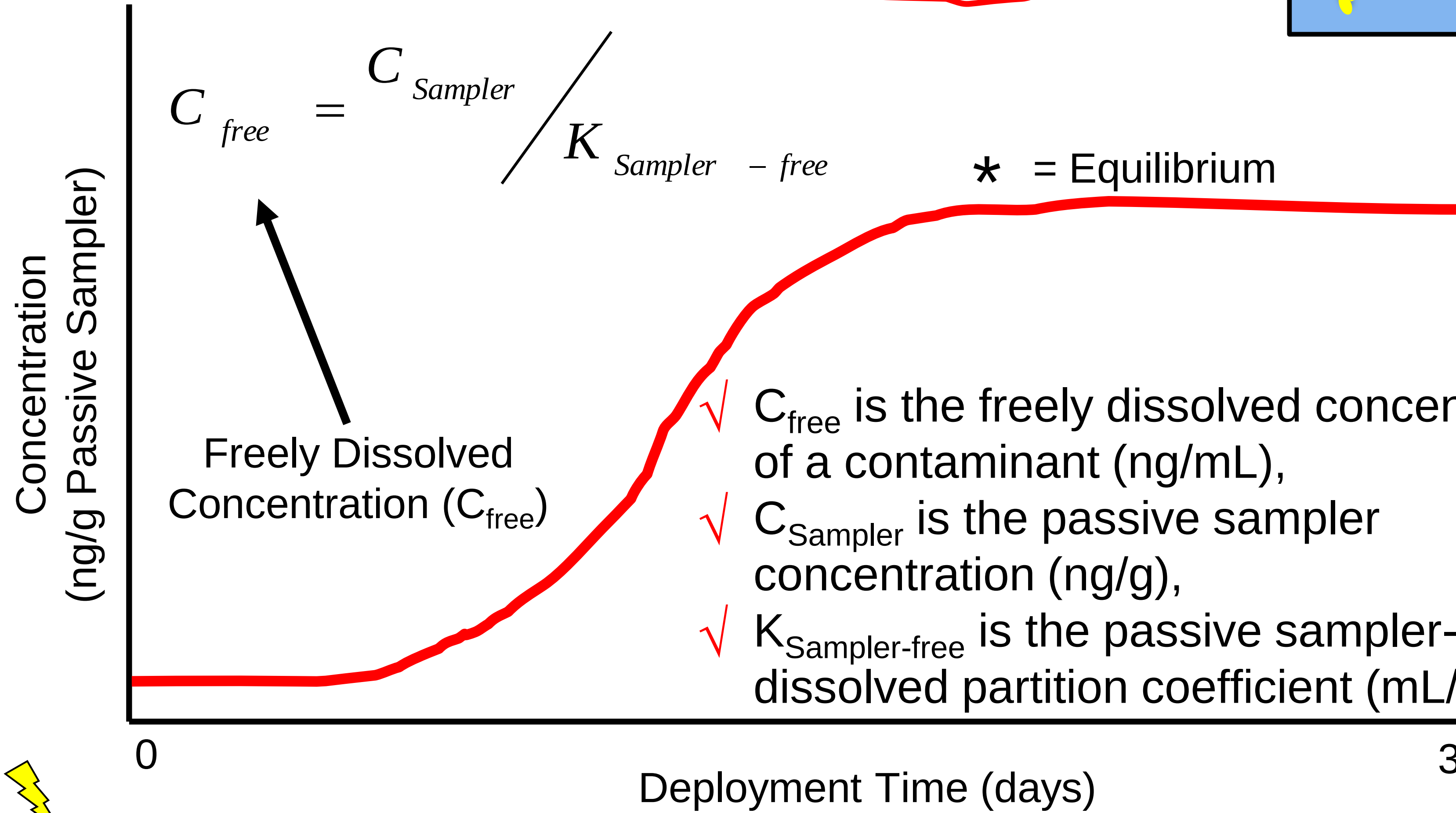


TYPES OF PSM AND HOW THEY WORK

Equilibrium Sampling



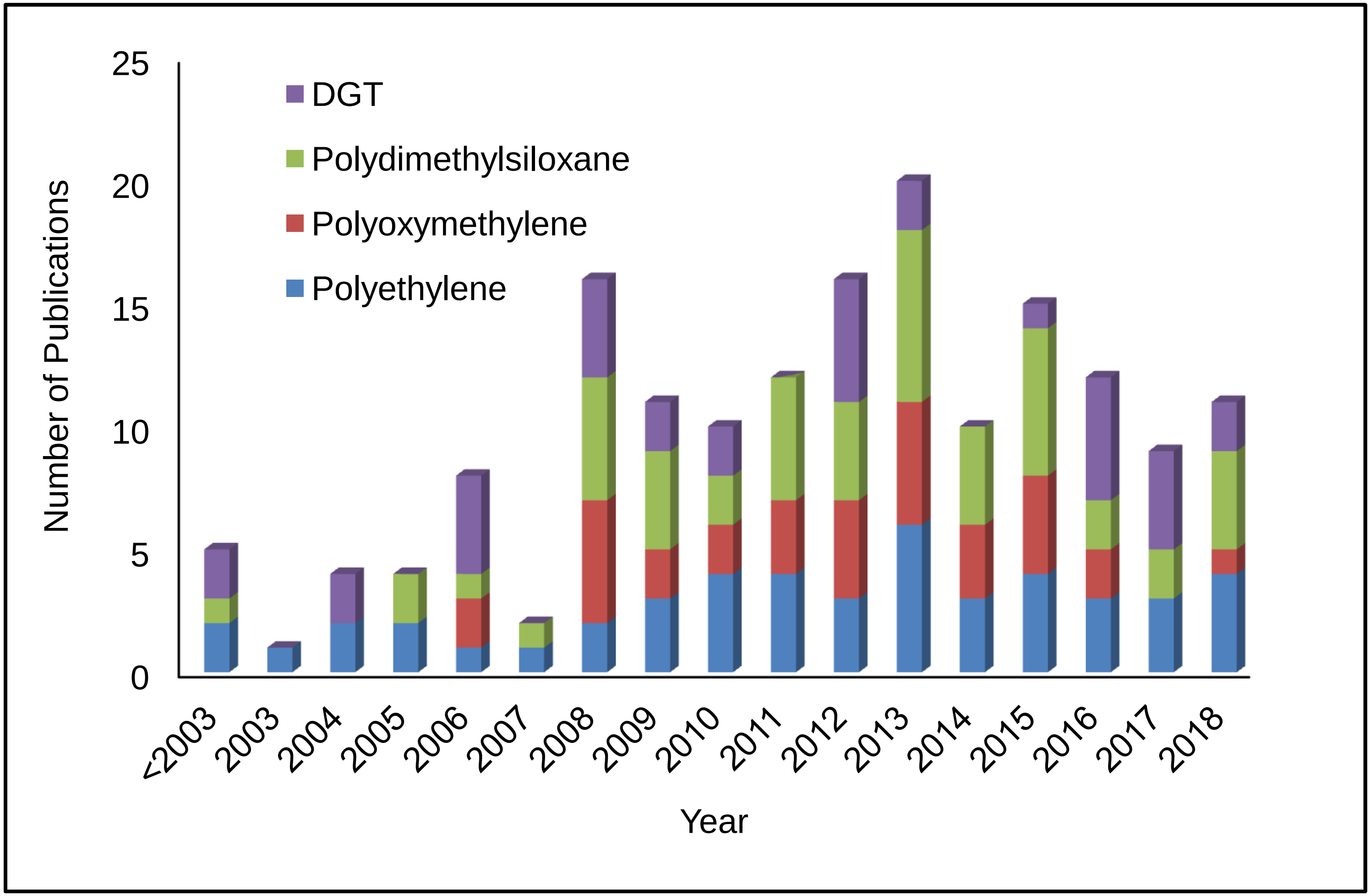
$$C_{free} = C_{Sampler} / K_{Sampler-free}$$



- √ C_{free} is the freely dissolved concentration of a contaminant (ng/mL),
- √ $C_{Sampler}$ is the passive sampler concentration (ng/g),
- √ $K_{Sampler\text{-}free}$ is the passive sampler-dissolved partition coefficient (mL/g)

TYPES OF PSM AND HOW THEY WORK

- Number of peer-reviewed publications by PSM

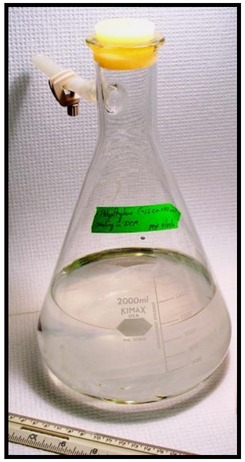


TYPES OF PSM AND HOW THEY WORK

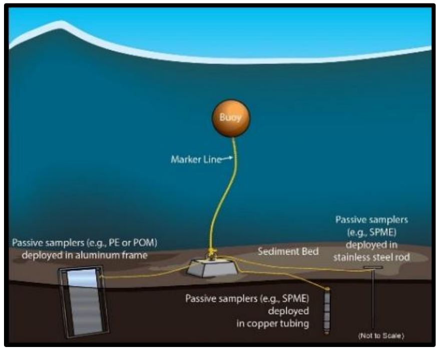
- Superfund sites where PSMs have been used (Updated 2 November 2017):
  - Allegany Ballistics Laboratory (Region 3)
  - Aniston PCB (Region 4)
  - Berry's Creek (Region 2)
  - Brodhead Creek (Region 3)
  - Columbia Slough (Region 10)
  - Dover Gas Light (Region 3)
  - Diamond Alkali (Region 2)
  - Grand Calumet (GLNPO-Region 5)
  - Grasse River (Region 2)
  - Lake Hartwell (Region 4)
  - Lower Duwamish Waterway (Region 10)
  - Manistique River (Region 5)
  - McCormick and Baxter (Region 10)
  - Metal Bank (Region 3)
  - MW Manufacturing (Region 3)
  - Naval Station Newport (Region 1)
  - New Bedford Harbor (Region 1)
  - Ordot Landfill (Region 9)
  - Pacific Sound Resources (Region 10)
  - Palos Verdes Shelf (Region 9)
  - Portland Harbor (Region 10)
  - San Jacinto Waste Pits (Region 6)
  - Tennessee Products (Region 4)
  - United Heckathorn (Region 9) √
  - Whitmoyer Laboratories (Region 3)
  - Wyckoff (Region 10)

PREPARING, DEPLOYING, RECOVERING, AND STORING PSM

Passive Sampler (PE or POM)

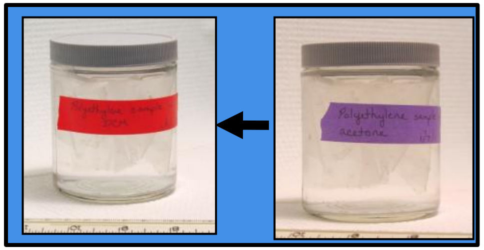


(1) Solvent Cleaning (~24 hours)

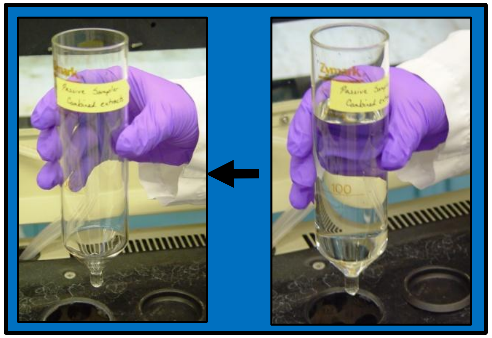


(2) Deployment and Recovery (~ 30 days)

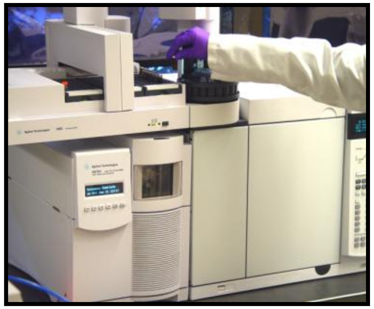
(3) Storage (-4 ˚C wrapped in foil)



(4) Solvent Extraction (48 hours)



(5) Volume reduction (~ 1 hour)



(6) GC/MS Analysis and Data Interpretation

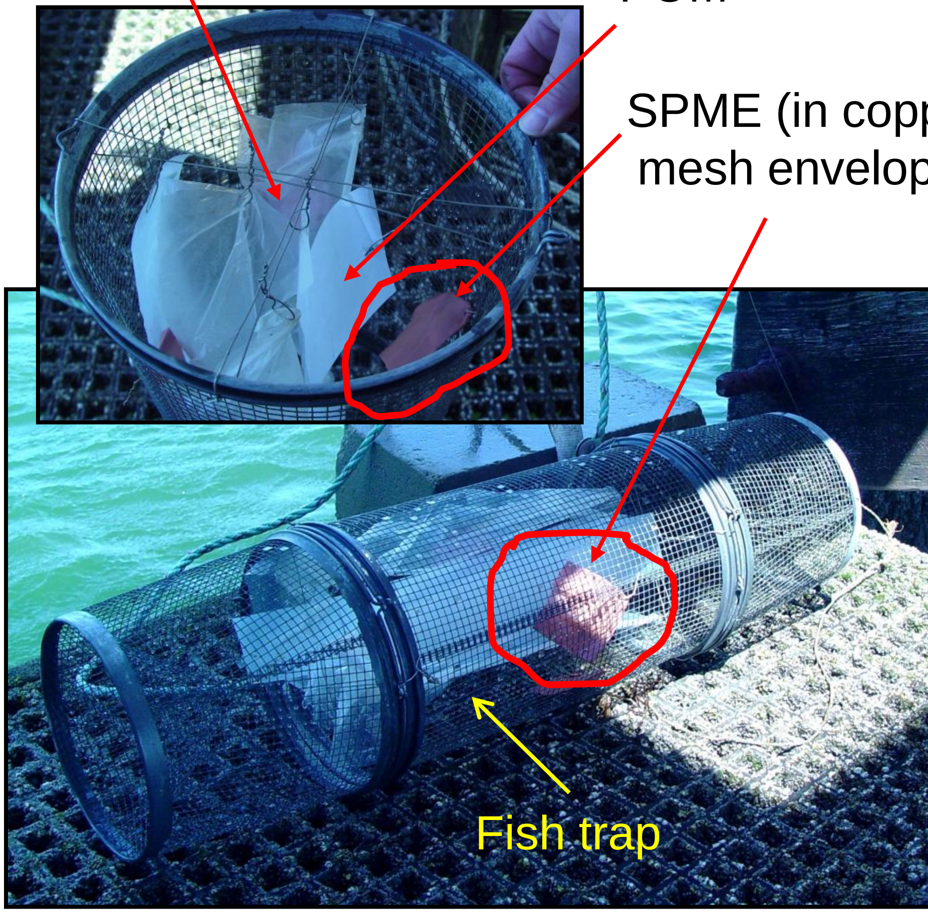
PREPARING, DEPLOYING, RECOVERING, AND STORING PSM

Water Column Deployment

PE

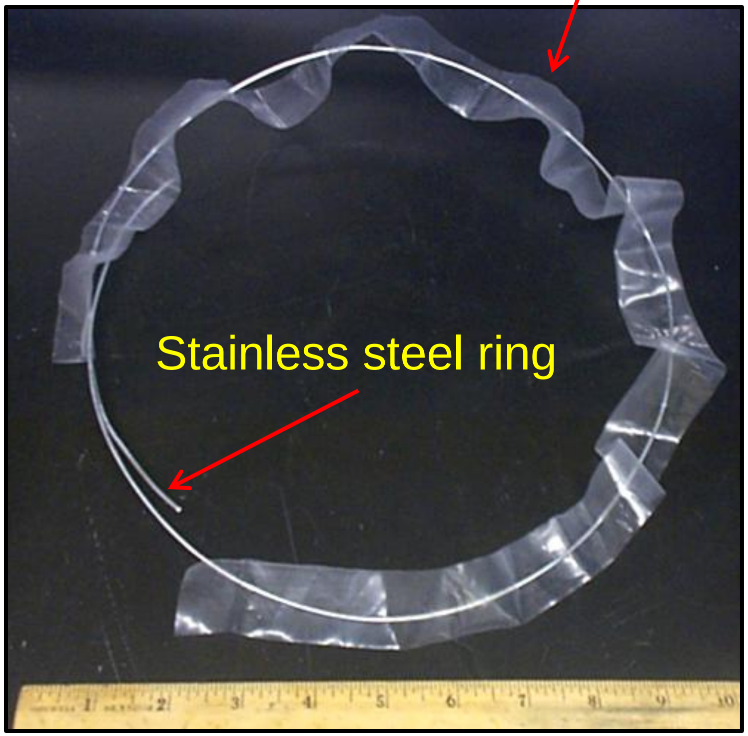
POM

SPME (in copper mesh envelope)



(NHEERL & Brown U)

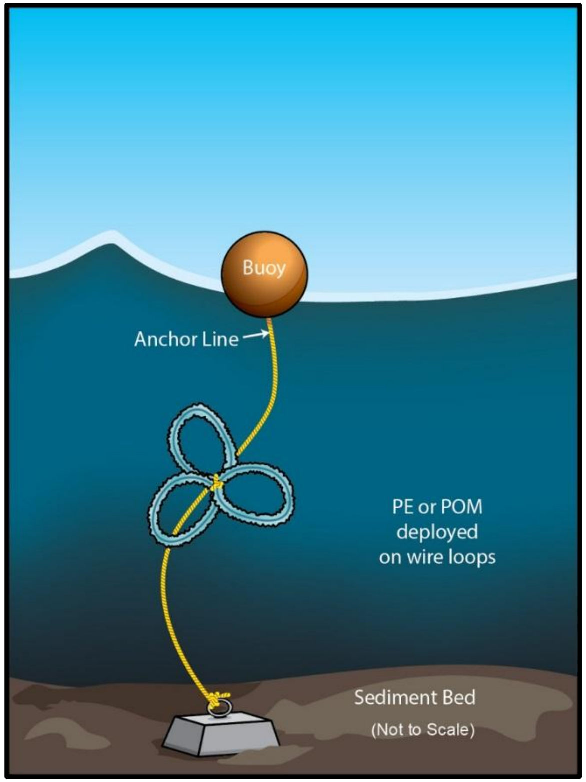
PE

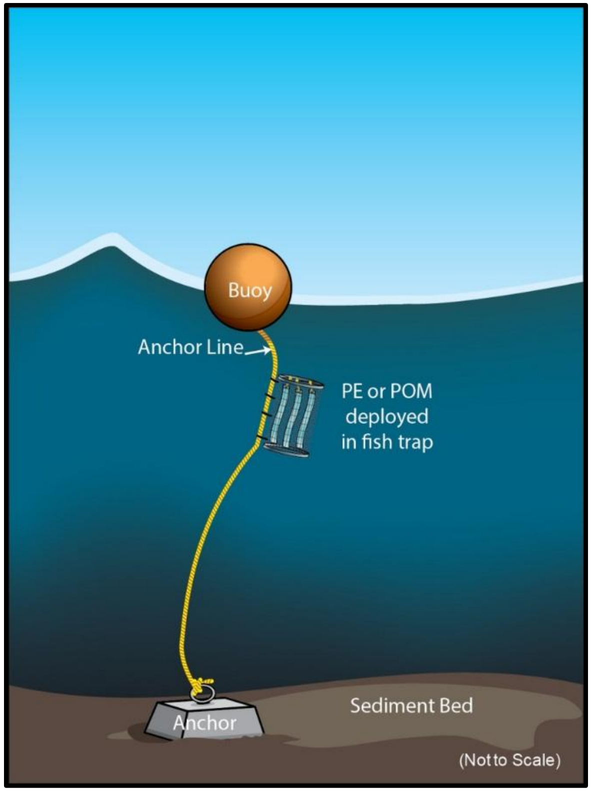


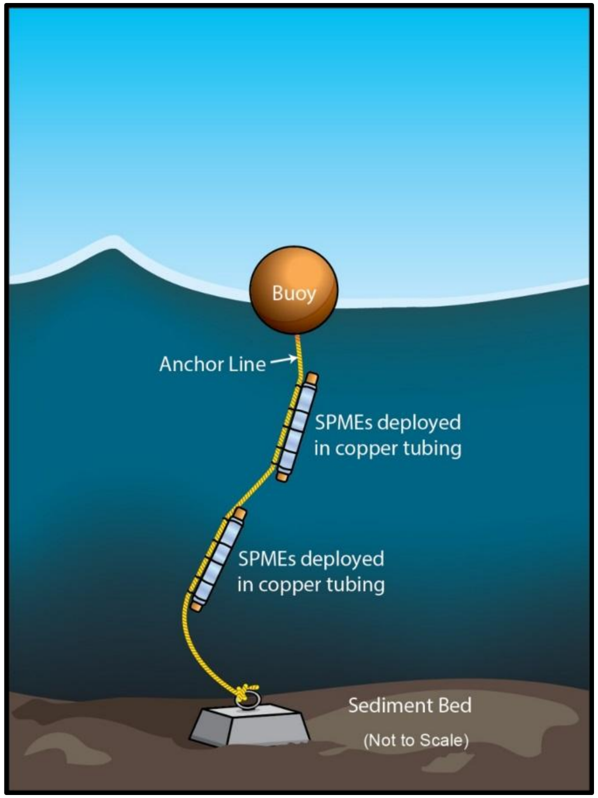
(NHEERL & MIT)

PREPARING, DEPLOYING, RECOVERING, AND STORING PSM

Water Column Deployment







PREPARING, DEPLOYING, RECOVERING, AND STORING PSM

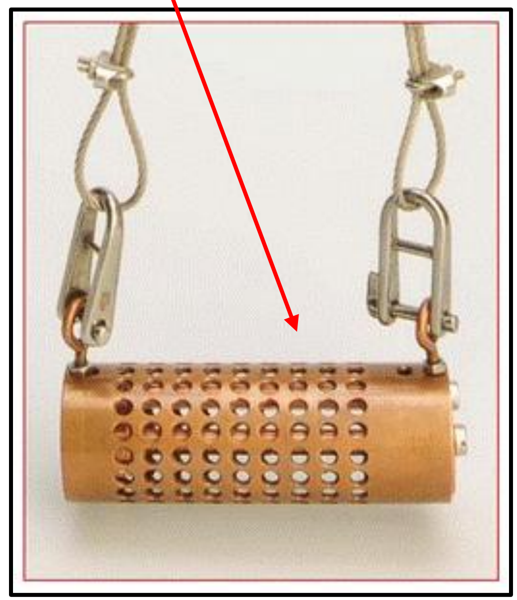
Pore water Deployment

SPME (in protective syringe)

Copper tubing housing

SPME (inside stainless steel tube)

(SCCWRP)



(Technical U Denmark)

(Texas Tech U)

SPME (in protective syringe)

PREPARING, DEPLOYING, RECOVERING, AND STORING PSM

Pore water Deployment

(MIT)

PE or POM (in aluminum frame)

(MIT)

PE or POM (in aluminum frame)

PREPARING, DEPLOYING, RECOVERING, AND STORING PSM

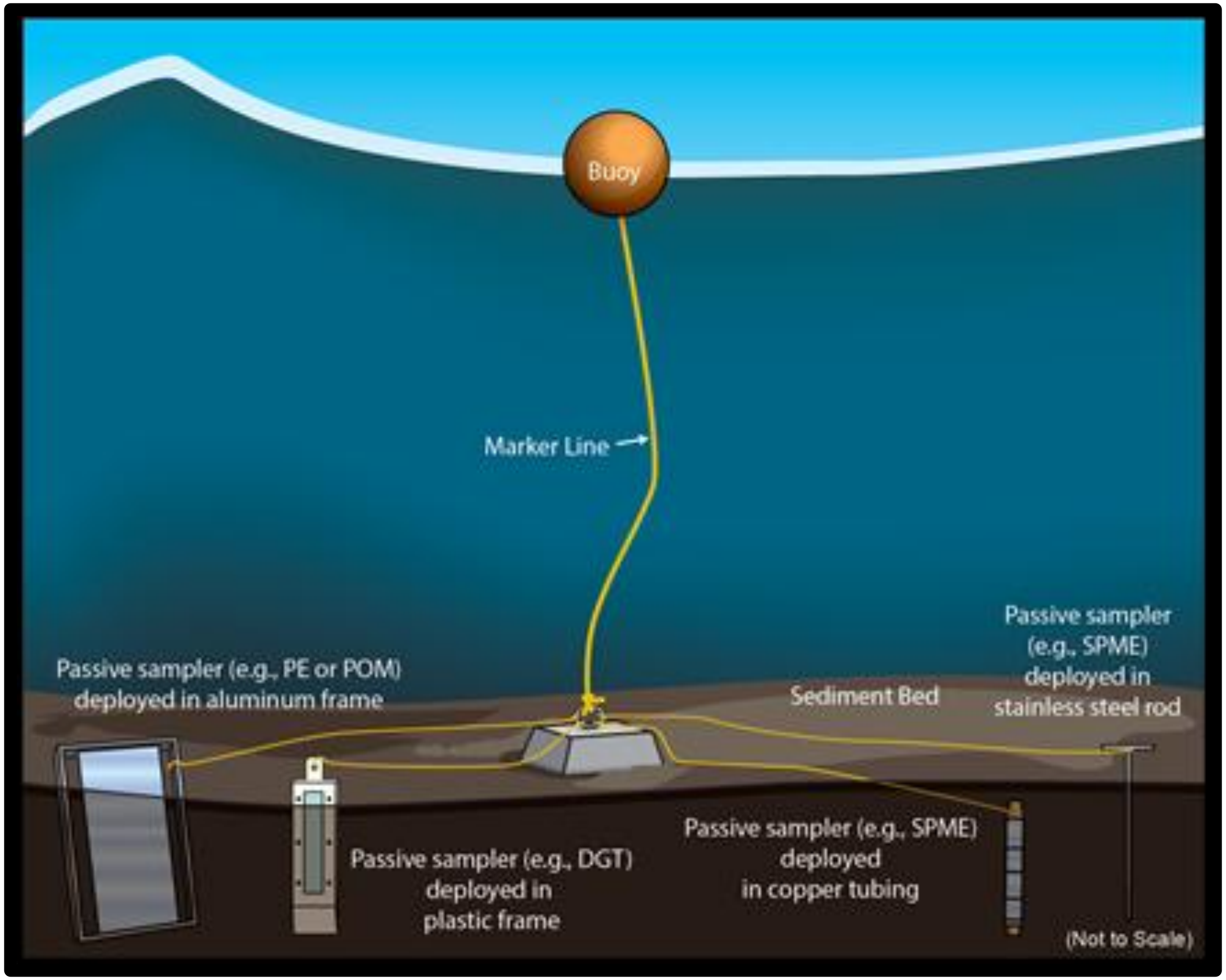
Pore water Deployment

POM
(in wire mesh enclosure)

(U Maryland Baltimore County)

PREPARING, DEPLOYING, RECOVERING, AND STORING PSM

Pore water Deployment



PREPARING, DEPLOYING, RECOVERING, AND STORING PASSIVE SAMPLERS

Pore water Deployment

(MIT & Region 9)

OSRTI's Environmental Response Team Dive Team & Region 10's Dive Team have extensive experience deploying and recovering passive samplers – cost-effective resource

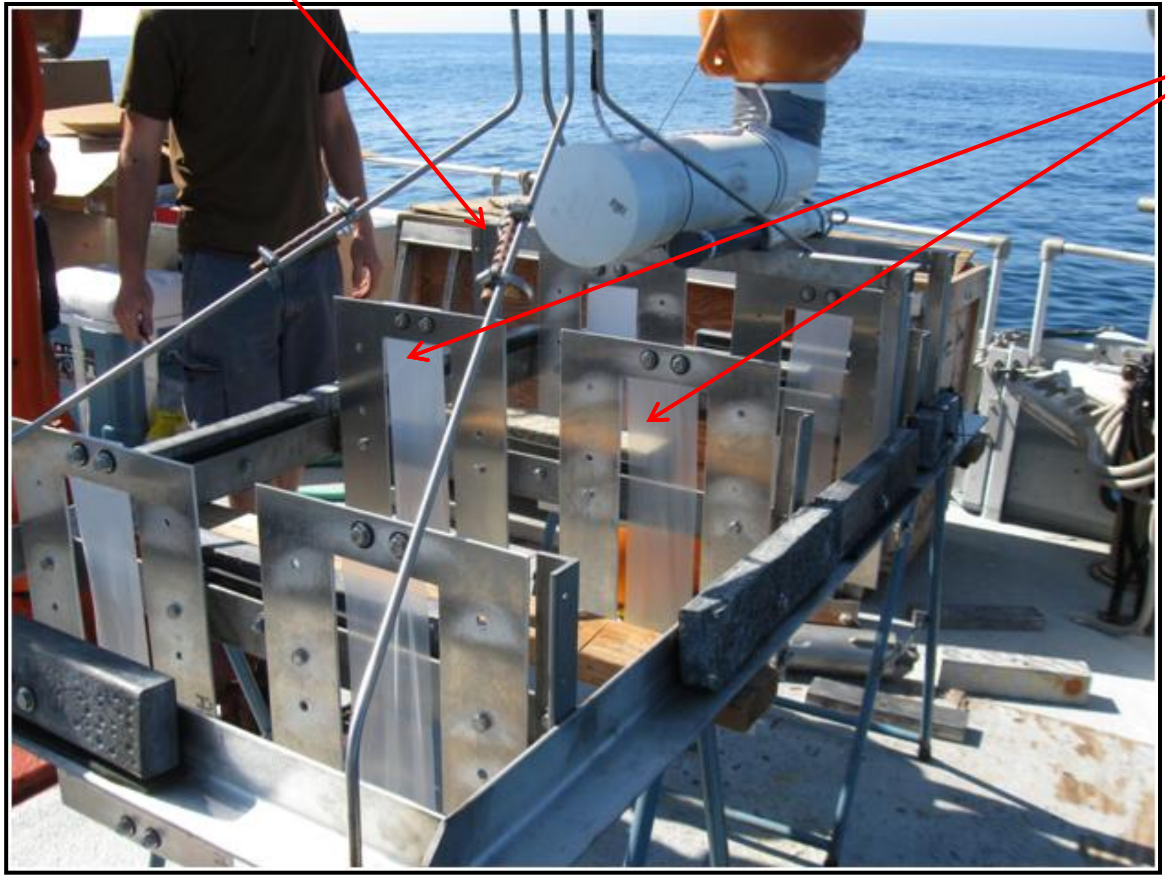
PREPARING, DEPLOYING, RECOVERING, AND STORING PSM

Porewater Deployment

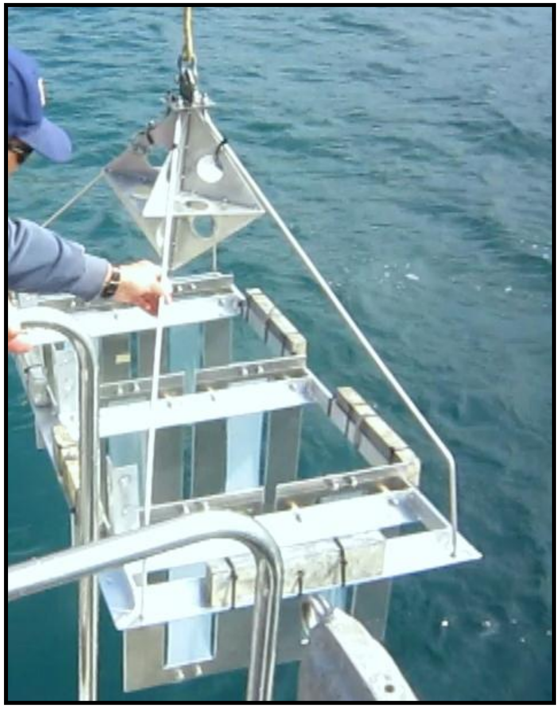
(Palos Verdes Shelf Superfund Site)

SPME in copper tubing

PE and POM
(in aluminum frames)



(NHEERL)



(NHEERL)

ANALYZING PSM DATA

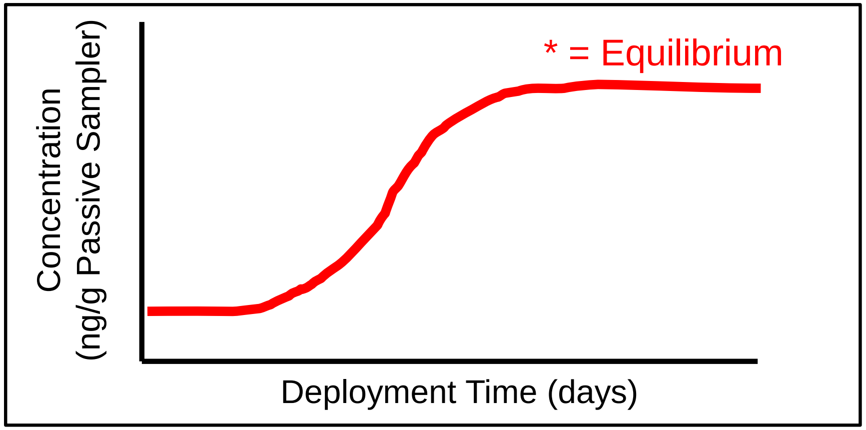
- Raw data (from the analytical laboratory)
  - Measured concentration of contaminants in the passive sampler ($C_{Sampler}$)
    - Units
      - ng/g sampler
      - ng/mL sampler (convert to µg/g sampler by dividing by the passive sampler density (e.g., PE = 0.92 g/mL))

- Calculate contaminant freely dissolved concentration (C_{free}) (ng/mL):

$$C_{free} = C_{Sampler} / K_{Sampler-free}$$

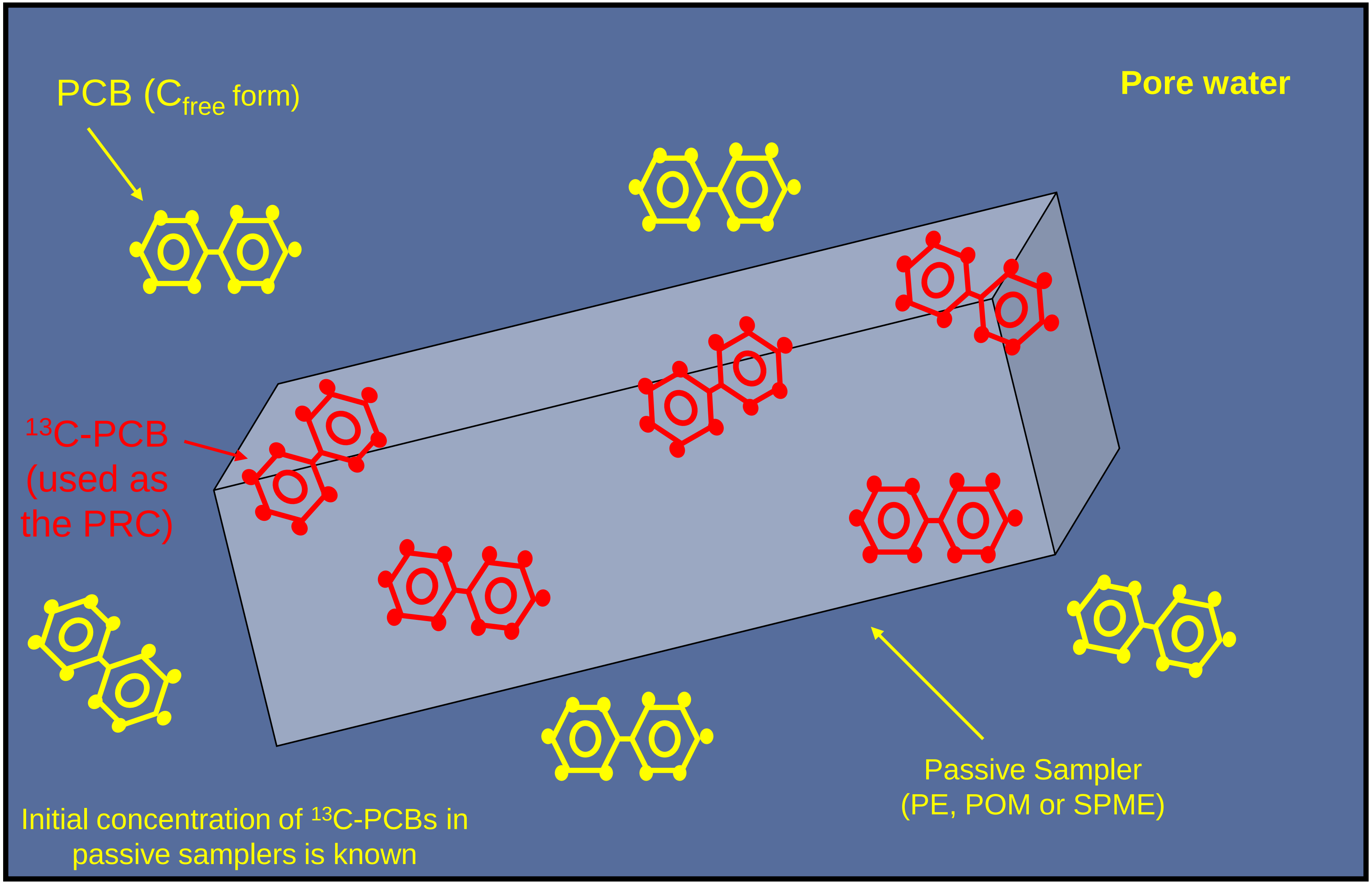
ANALYZING PSM DATA

- Establishing when equilibrium between the contaminants and passive sampler occurs

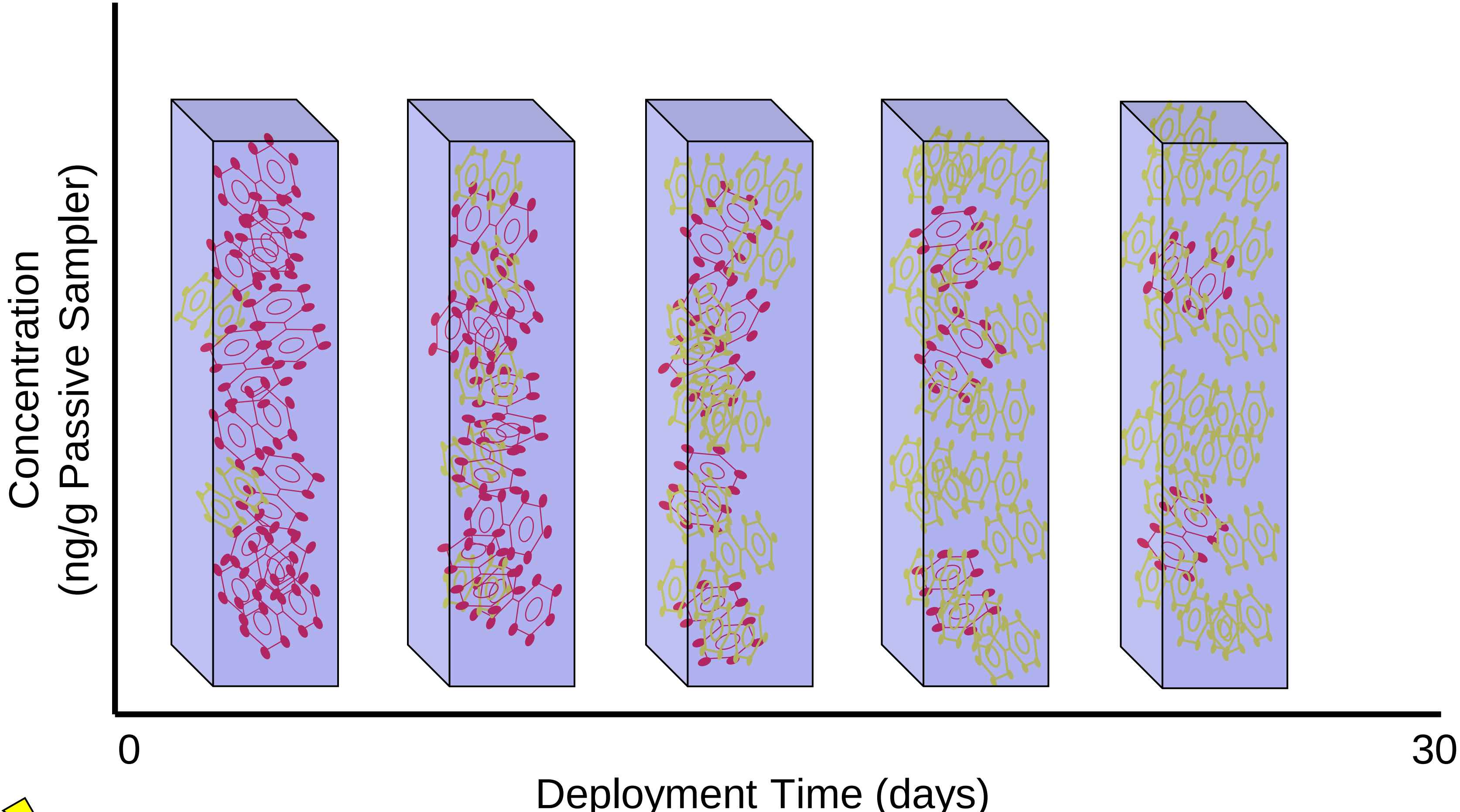


- Challenge in all monitoring (including biomonitoring)
- Potentially expensive to determine (i.e., extra samples = $$$)
  - Perform time series (e.g., collect PSM weekly for 30 days)
  - Compare different thicknesses of PSM
- One approach: Performance Reference Compounds (PRCs) loaded into the passive sampler to predict equilibrium
  - PRC is a chemical that behaves like the target COC

ANALYZING PSM DATA



ANALYZING PSM DATA



ANALYZING PSM DATA

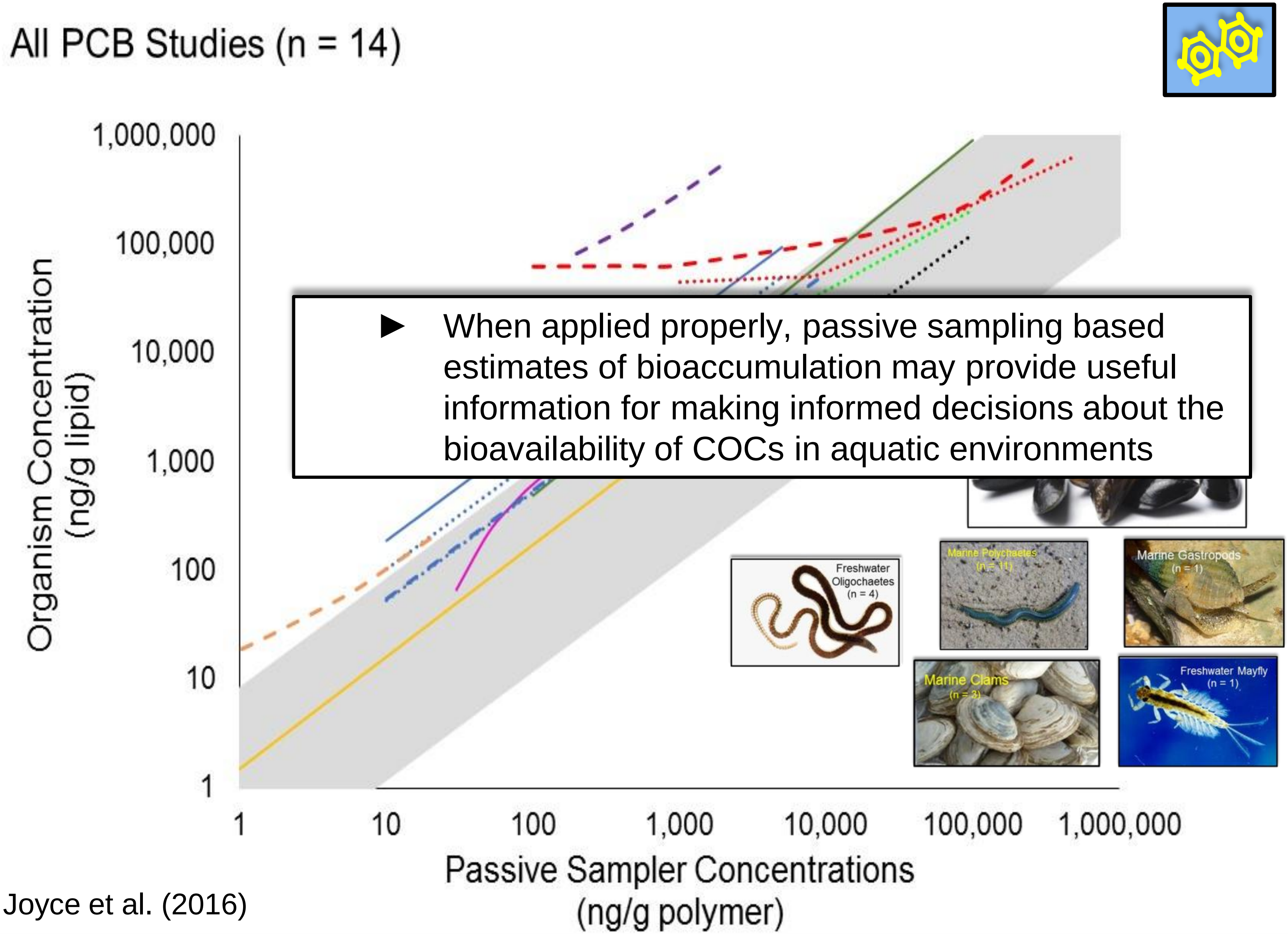
Two other methods:

- Diffusion-based
  - Rate of PRC diffusion through polymer is used to determine magnitude of disequilibrium correction for target contaminants

- Exchange rate-based
  - PRC data used to calculate disequilibrium-corrected exchange rates for target contaminants

- Both methods are very calculation intensive and are available on computer-based graphical-user interfaces (GUIs) or spreadsheets
  - GUIs available on-line
    - Superfund website
    - SERDP/ESTCP websites

EVALUATING PSM APPLICATIONS

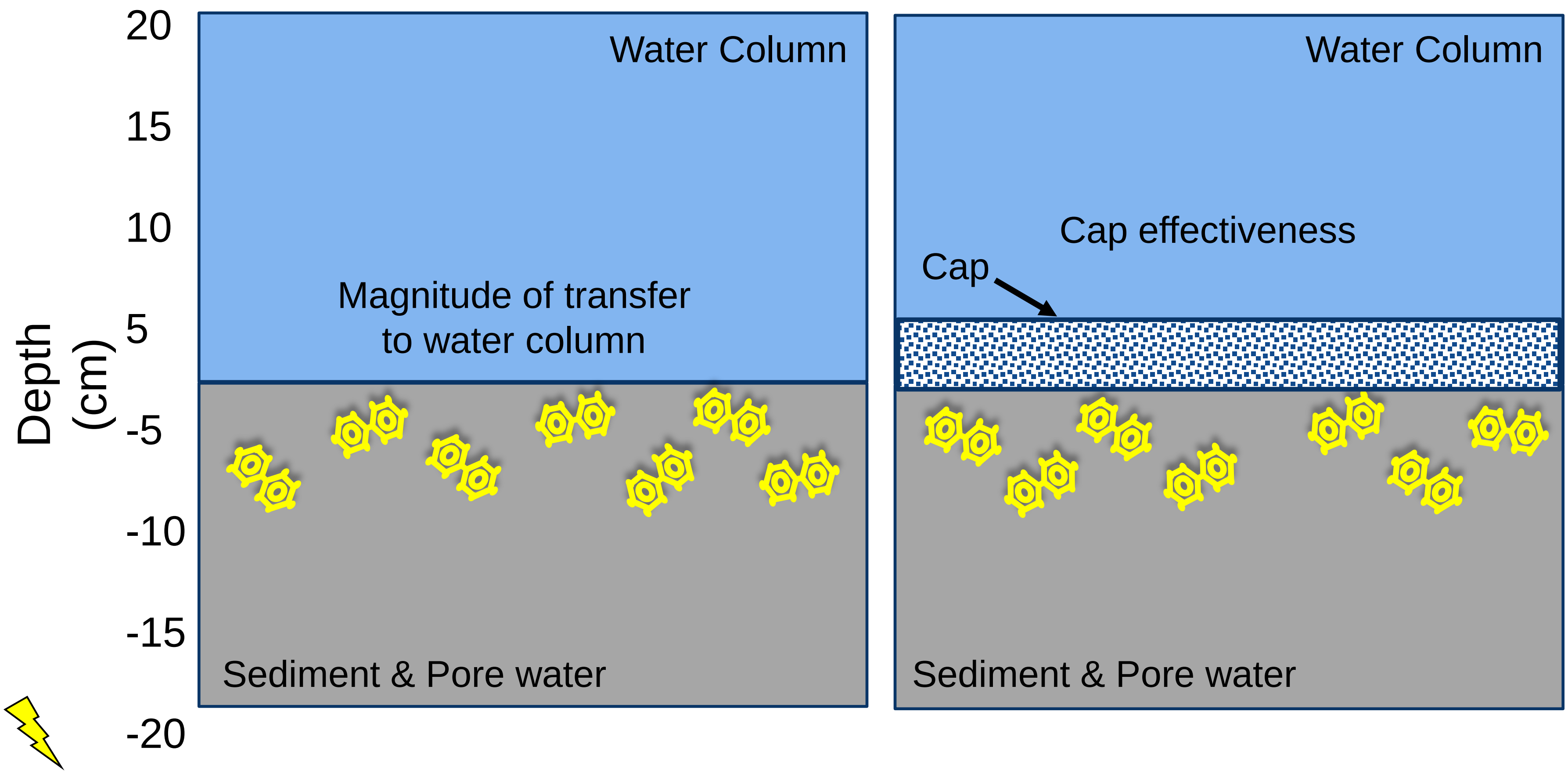


- When applied properly, passive sampling based estimates of bioaccumulation may provide useful information for making informed decisions about the bioavailability of COCs in aquatic environments

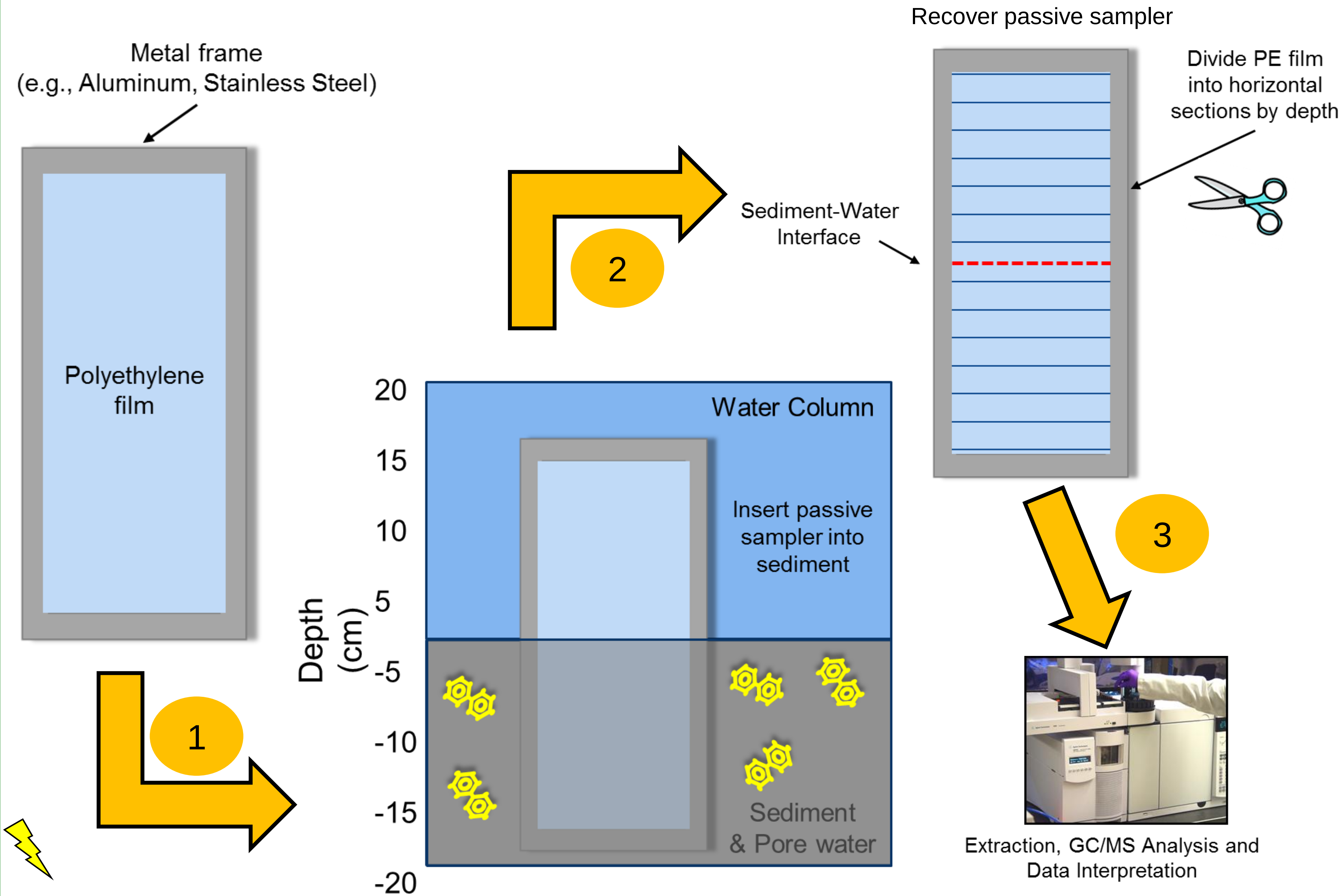
Joyce et al. (2016)

EVALUATING PSM APPLICATIONS

- Determining COC Flux
  - Using PSM to measure transport of COCs between sediments and water column

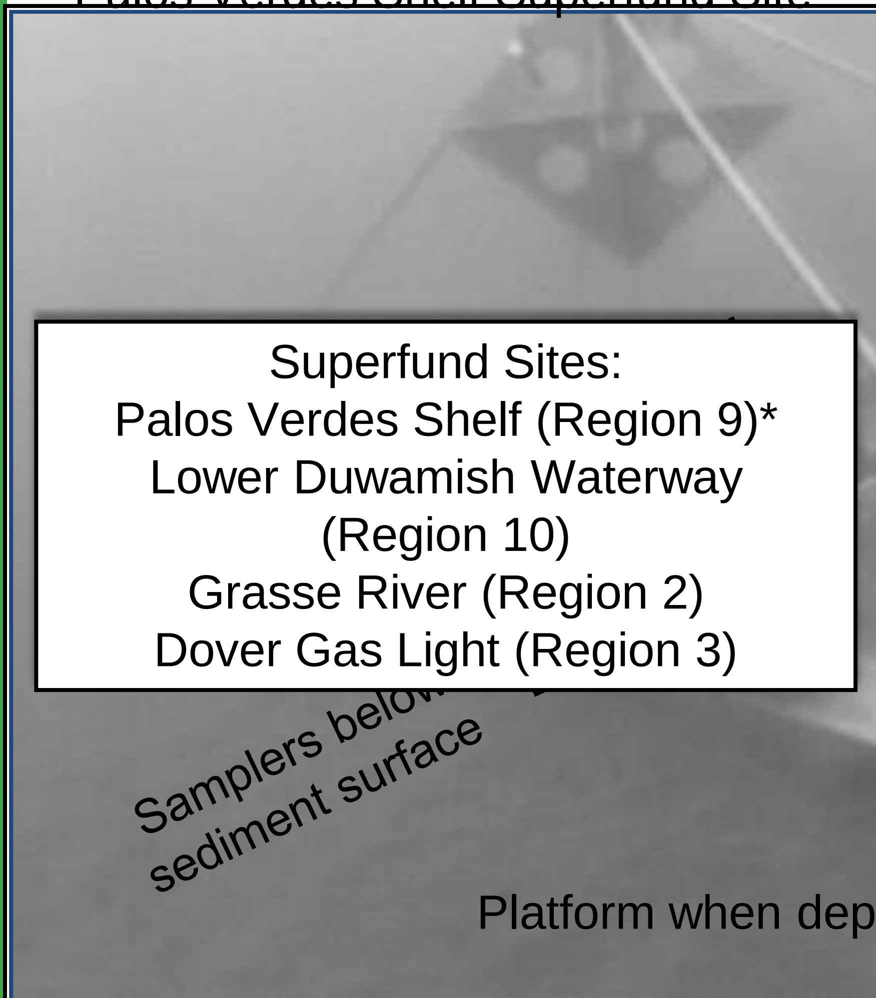


EVALUATING PSM APPLICATIONS

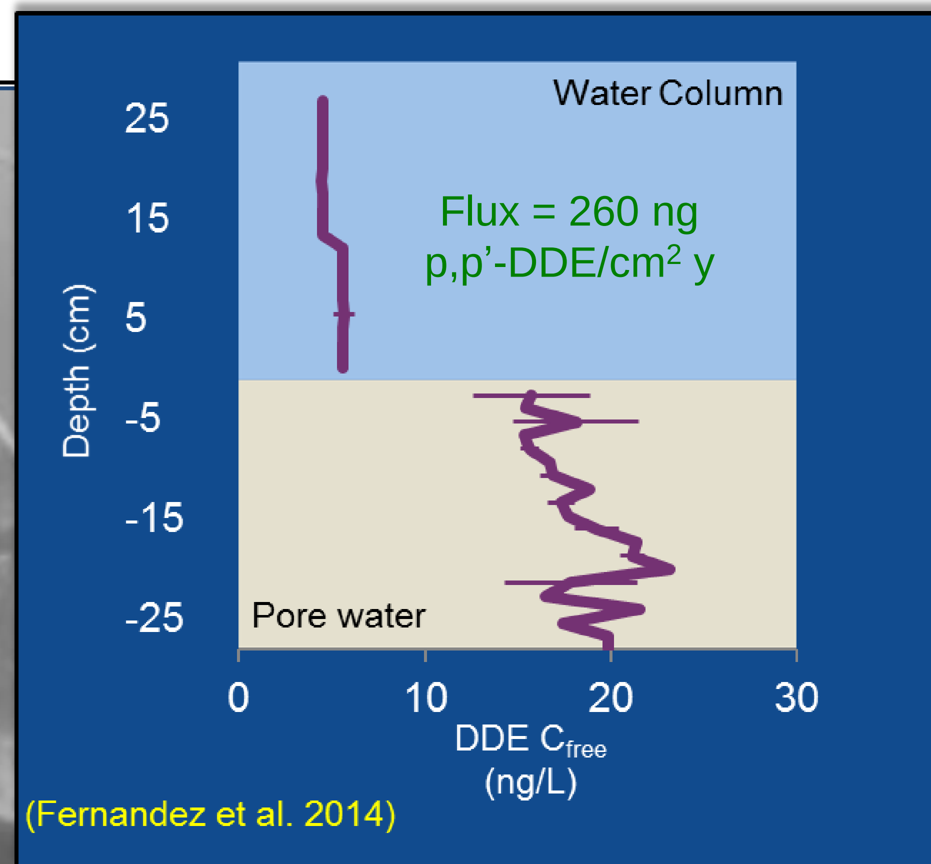


EVALUATING PSM APPLICATIONS

Palos Verdes Shelf Superfund Site



Superfund Sites:
Palos Verdes Shelf (Region 9)*
Lower Duwamish Waterway (Region 10)
Grasse River (Region 2)
Dover Gas Light (Region 3)



EVALUATING PSM APPLICATIONS

◆ Developing Pore Water Remedial Goals (PWRGs)

- PWRGs are values intended to protect organisms living in and on the sediments from direct toxicity from sediment contaminants
- Two basic elements:
  - Method for measuring or inferring the freely dissolved concentration (C_{free}) of contaminant in pore water
  - Threshold chemical concentration that delineates acceptable and unacceptable toxicological exposures
- Basic quantitative form:

Derived from Passive Sampling

$$PWRG = \frac{C_{free}\ (\mu g/L)}{Threshold\ Chemical\ Concentration\ (\mu g/L)}$$

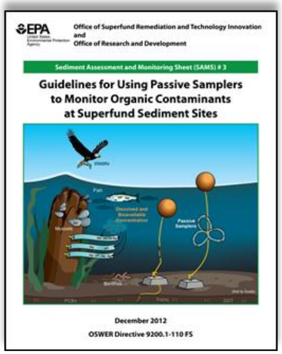
SUMMARY

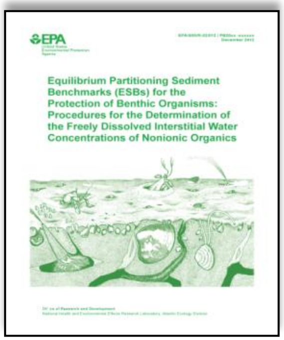
- Passive sampling provides data on:
  - √ Freely dissolved concentrations (C_{free}) of COCs
    - Effective surrogate for bioavailable contaminant concentrations
  - Concentration of COCs in the passive sampler
- Approach operates based on the well-understood principles of equilibrium partitioning and sampling
- Preparation, deployment, recovery and storage are no more complicated than current contaminant sampling methods
  - √ Possibly greater scientifically-robustness, logistically simpler, and more cost-effective
- Applications
  - √ Assessing COC bioavailability
  - Measuring COC fluxes
  - Developing Pore Water Remedial Goals (PWRGs)

SUMMARY

◆ Useful documents

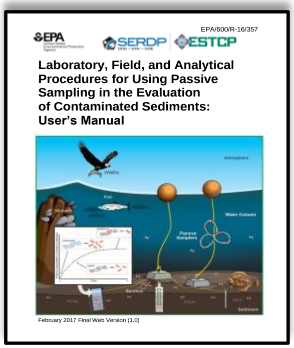
- https://semspub.epa.gov/work/HQ/175405.pdf (2012)



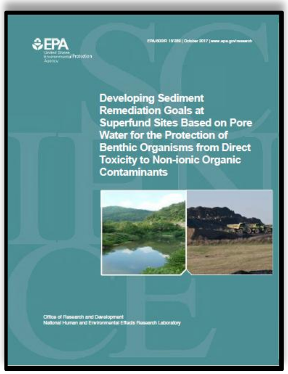


- http://www.epa.gov/nheerl/download_files/publications/ RB%20ESB%202012final_2.pdf (2012)

- Society of Environmental Toxicology and Chemistry journal: *Integrated Environmental Assessment and Management* 2014 Series (Six papers on passive sampling) (2014)



- https://semspub.epa.gov/work/HQ/100000146.pdf (2017)



- https://semspub.epa.gov/work/HQ/100000539.pdf (2017)