Fundamentals of Passive Sampler Use at Superfund Sites

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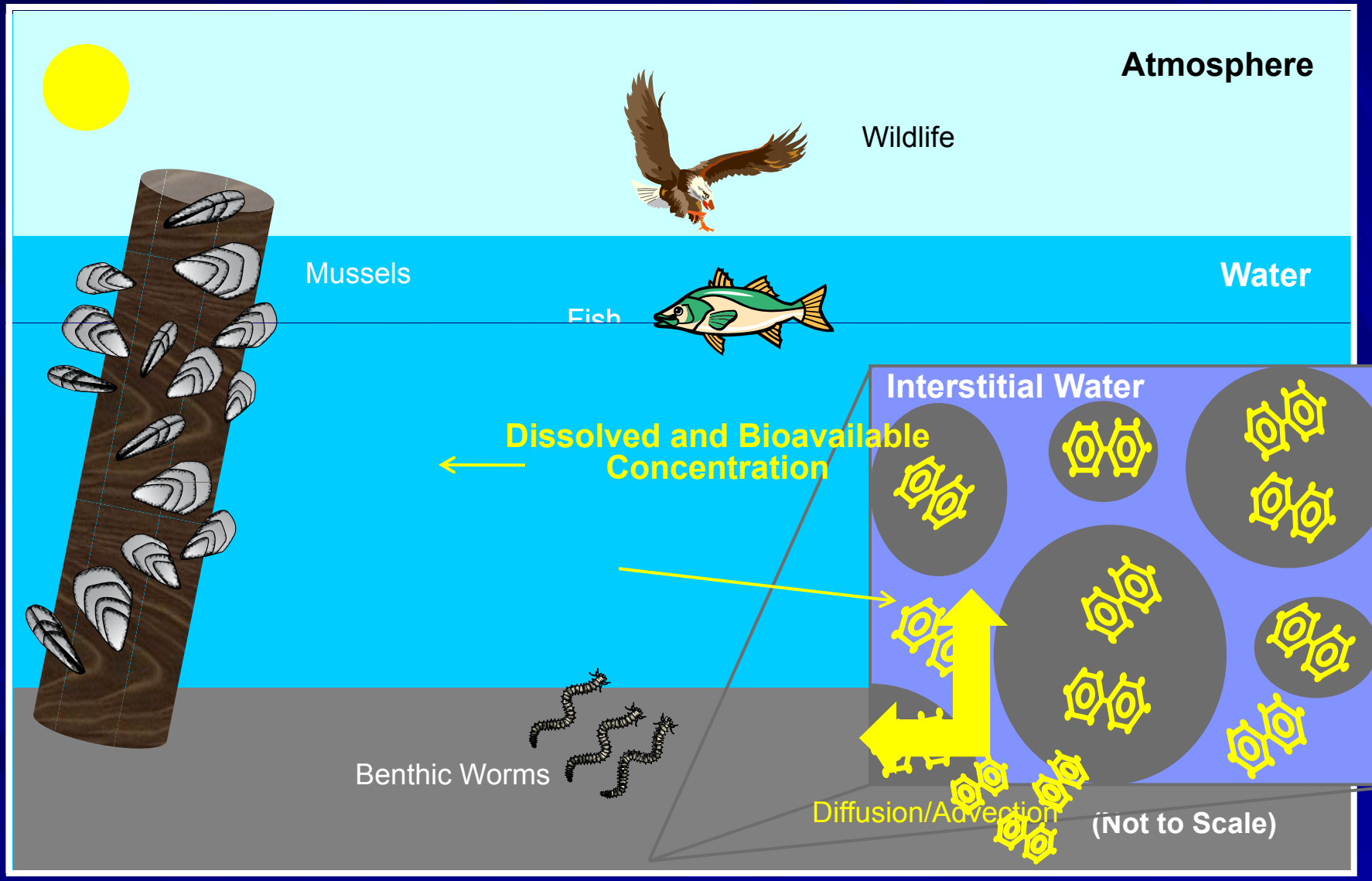
Outline

- Introduction to passive samplers
- What information can passive samplers provide
- Characteristics of passive samplers
  - Types of passive samplers
  - Passive sampler deployment
  - Passive sampler costs
  - Passive sampler theory
  - Technical issues using passive samplers
- Passive sampler application at a Superfund site
- Summary

Conceptual Model of Relationship Between Contaminated Sediments and Aquatic Life



Introduction

- How to determine or measure dissolved and bioavailable concentrations in the water column and interstitial waters?
- Why not use conventional sampling methods? Some problems:
  - Water Column
    - Logistically and technically difficult to collect large volumes of surface water and extract
    - Several artifacts including losses to filters and contamination by colloids reduce accuracy of analysis
    - Analytical detection limits are often not sufficiently low
  - Interstitial Water
    - Centrifuge or squeeze interstitial water
    - Similar artifacts as water column
    - Collecting large volumes of interstitial waters is challenging
- Are there other sampling methods for collecting and measuring dissolved and bioavailable contaminants?

Introduction

- Passive samplers
  - Since late 1980s or so
  - Consist of an organic phase (i.e., simple organic film or polymer) which accumulates contaminants from the dissolved phase
    - Semi-permeable membrane devices (SPMDs)
    - Solid phase micro-extraction (SPME)
    - Polyethylene devices (PEDs)
    - Polyoxymethylene (POM)

Introduction

- Types of contaminants sampled
  - Organic compounds
    - Low water solubility
    - Highly hydrophobic, lipiphillic and bioaccumulating (medium to large K_{OW}s)
  - Many legacy contaminants (e.g., PCBs, PAHs, DDTs, Dieldrin)
  - Metals
- Passive samplers behave like aquatic organisms
  - Accumulate contaminants from the dissolved phase
  - Concentrate contaminants into the polymer like animals accumulate contaminants into their lipids (analytically useful)

What information can passive samplers provide at a Superfund site?

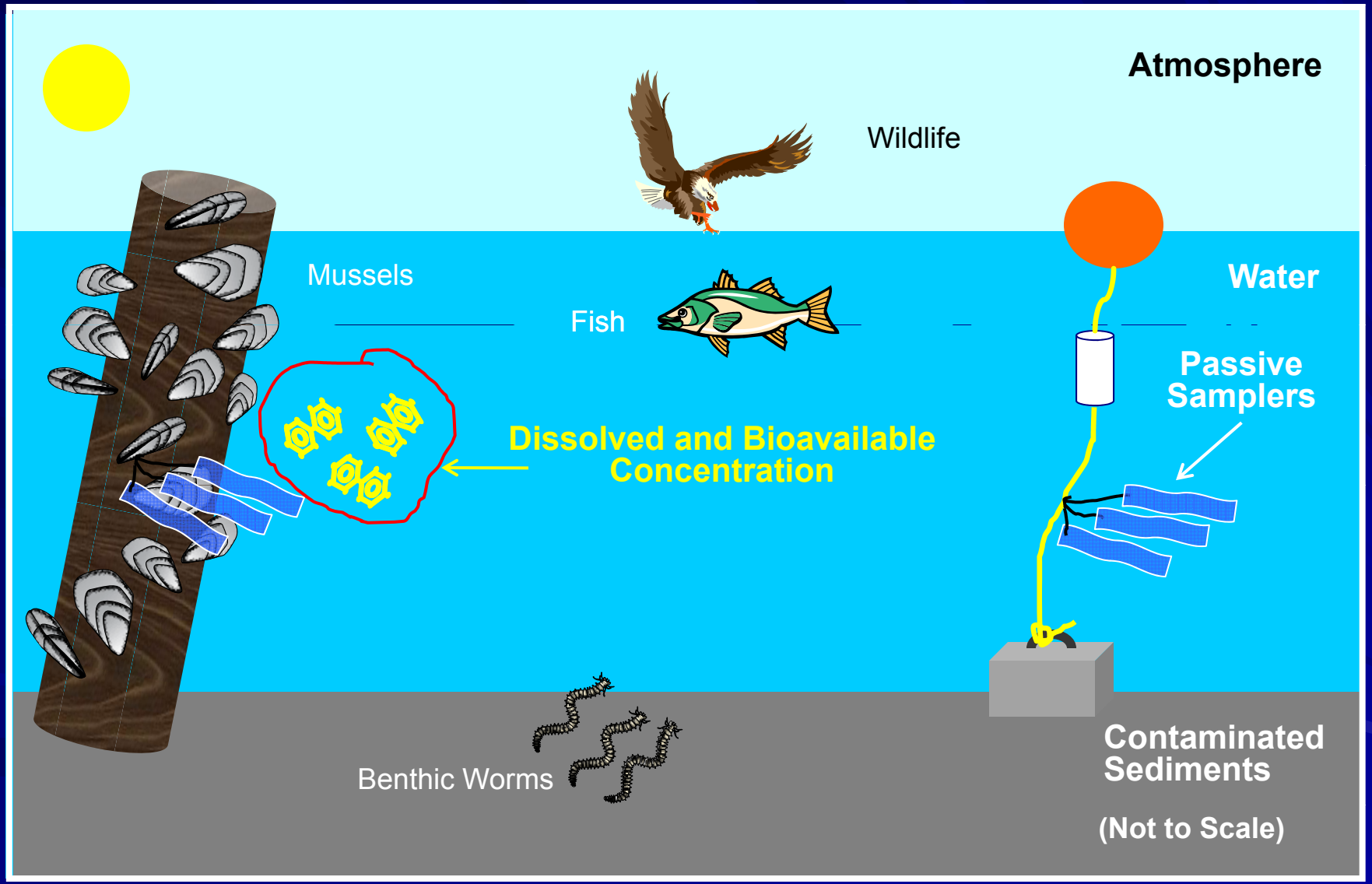
(1) Dissolved and bioavailable water column and interstitial water concentrations of many legacy chemicals

- Compare to Water Quality Criteria (WQC) or other standards or toxicity data

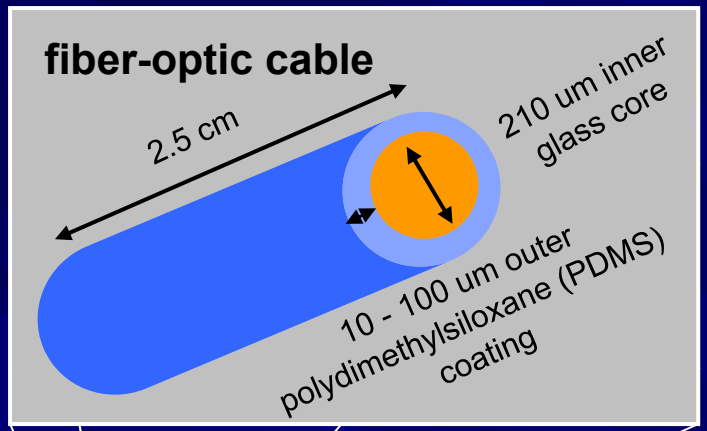
(2) Accumulated concentrations of many legacy chemicals

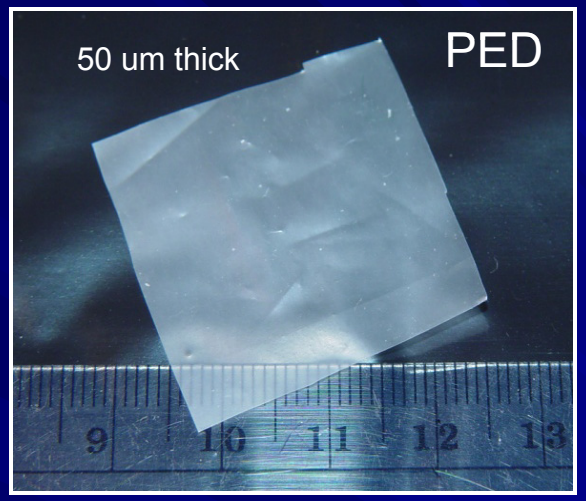
- **E**mulate uptake by aquatic organisms
- Serve as surrogates for biomonitoring organisms
  - Especially in situations where mussels or fish cannot be used (e.g., low dissolved oxygen, toxicity, low/high temperature constraints)

Conceptual Model of Relationship Between Contaminated Sediments and Aquatic Life

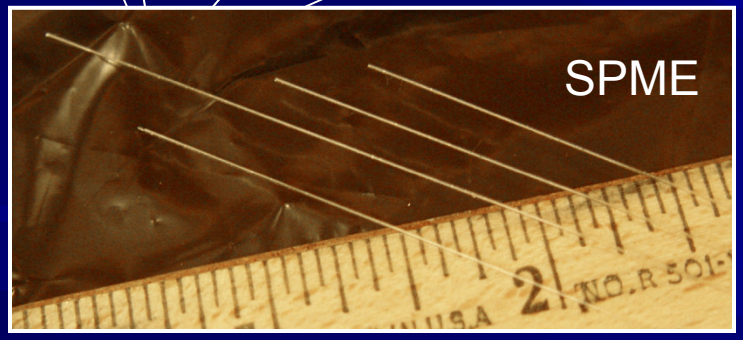


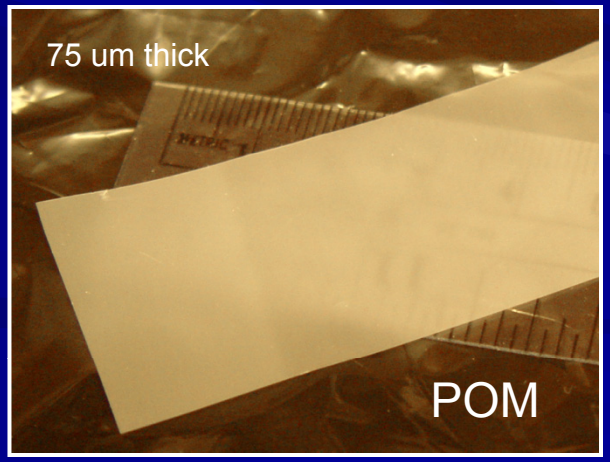
Types of Passive Samplers





SPMD (polyethylene tubing containing triolien)





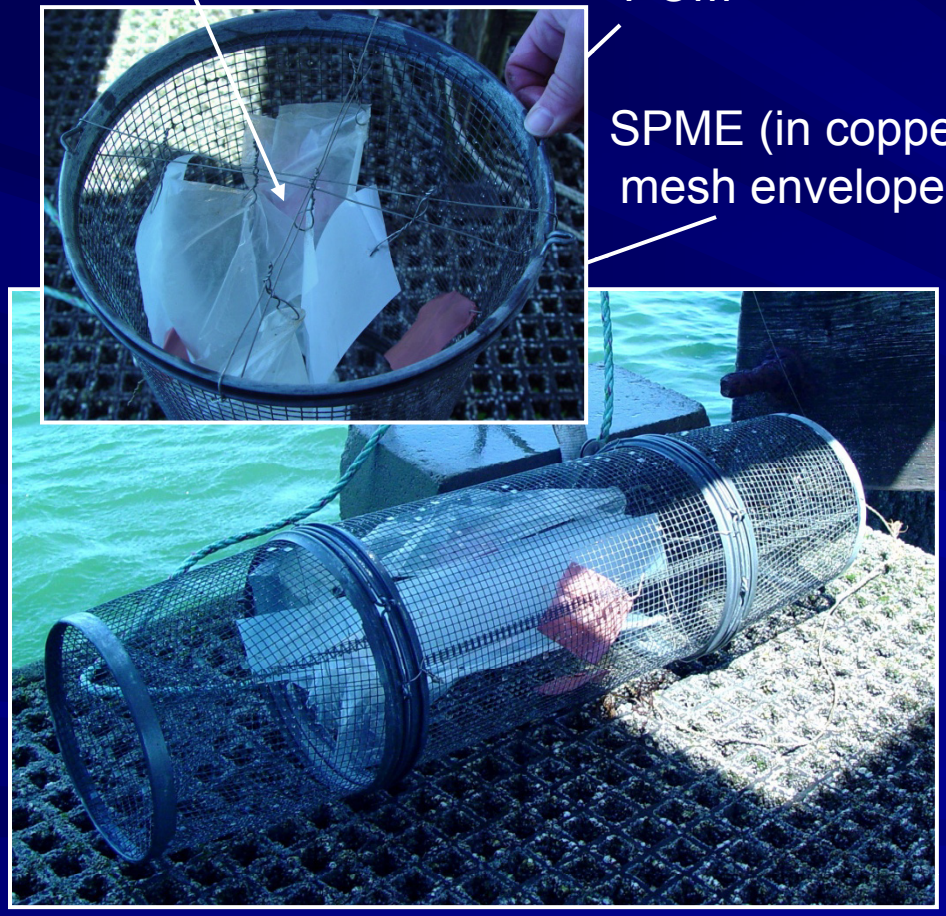
Passive Sampler Deployment

Water Column

PED

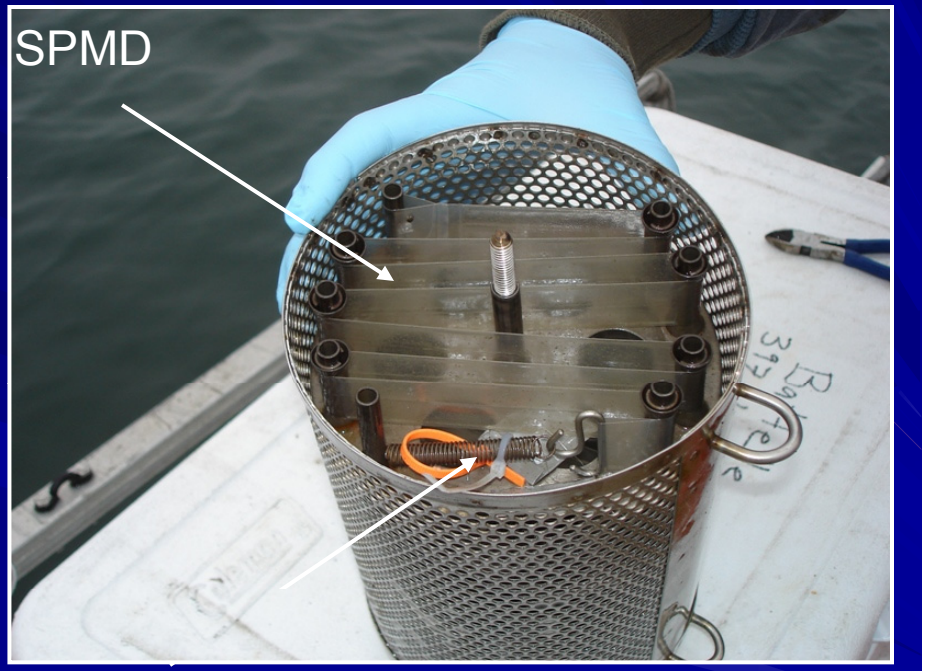
POM

SPME (in copper mesh envelope)



(NHEERL & Brown U)

SPMD



SPME (in stainless steel mesh cover)

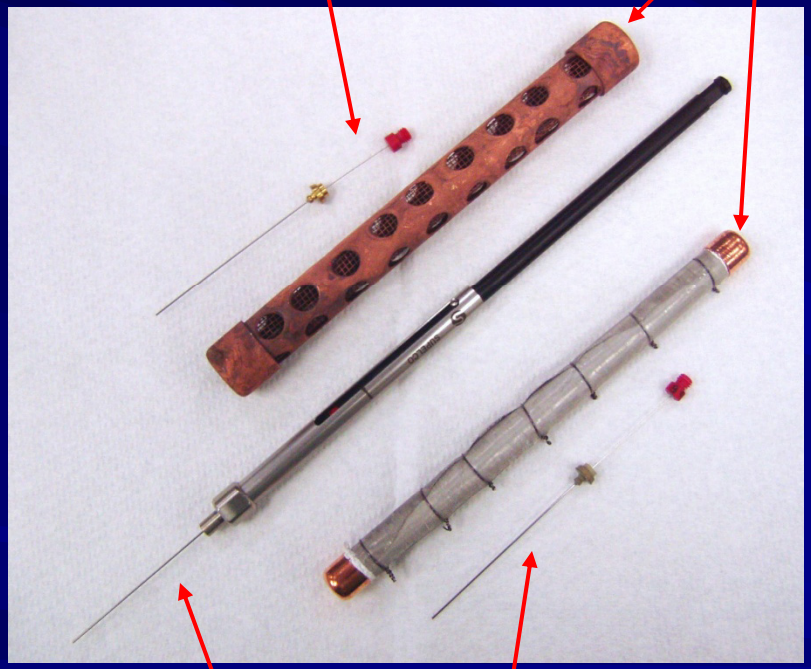
(NRMRL & Battelle)

Passive Sampler Deployment

Sediment

SPME (in protective syringe)

Copper tubing housing



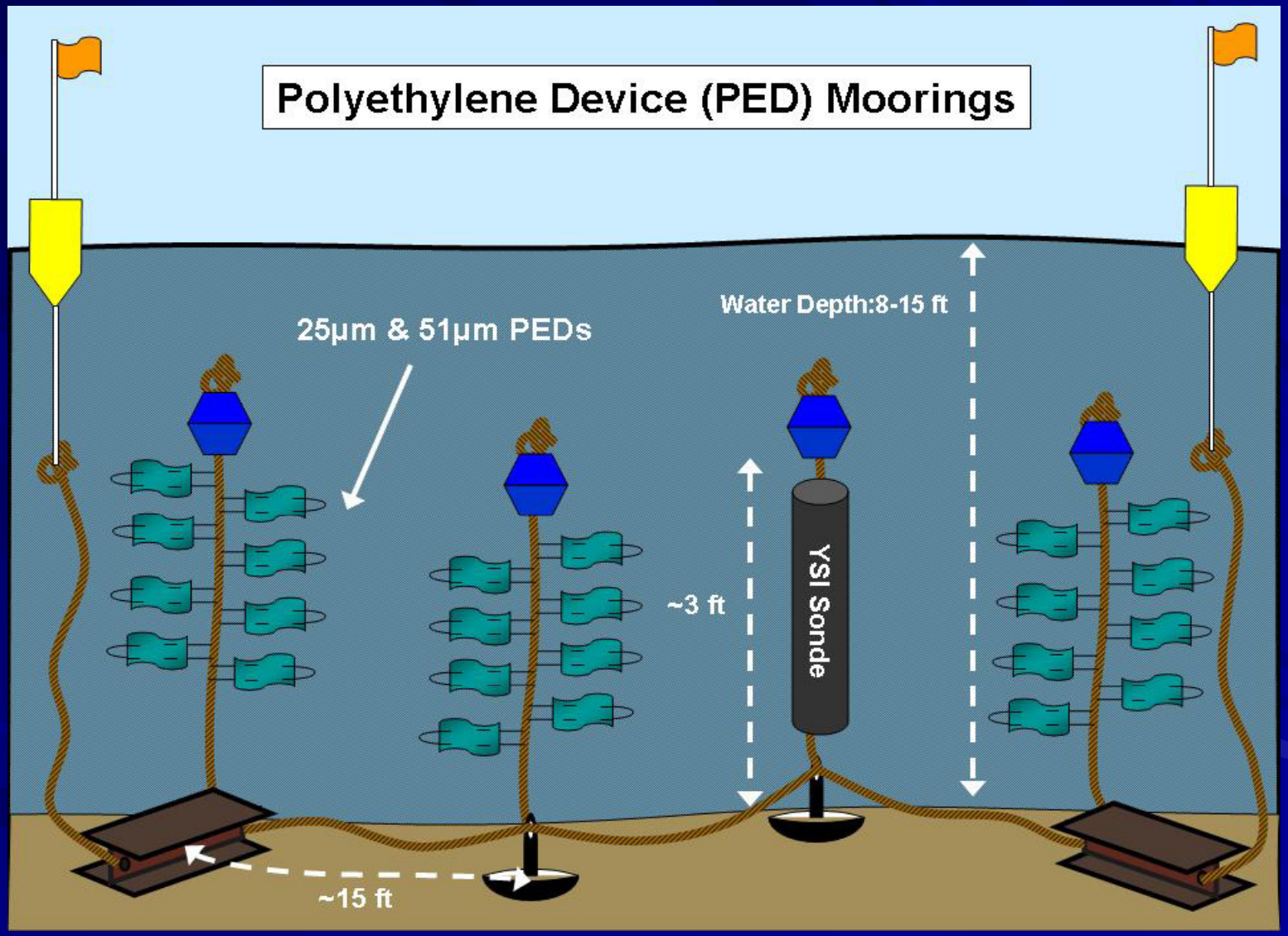
(SCCWRP)

SPME (in protective syringe)

(MIT)

PED (in aluminum frame)

Passive Sampler Deployment



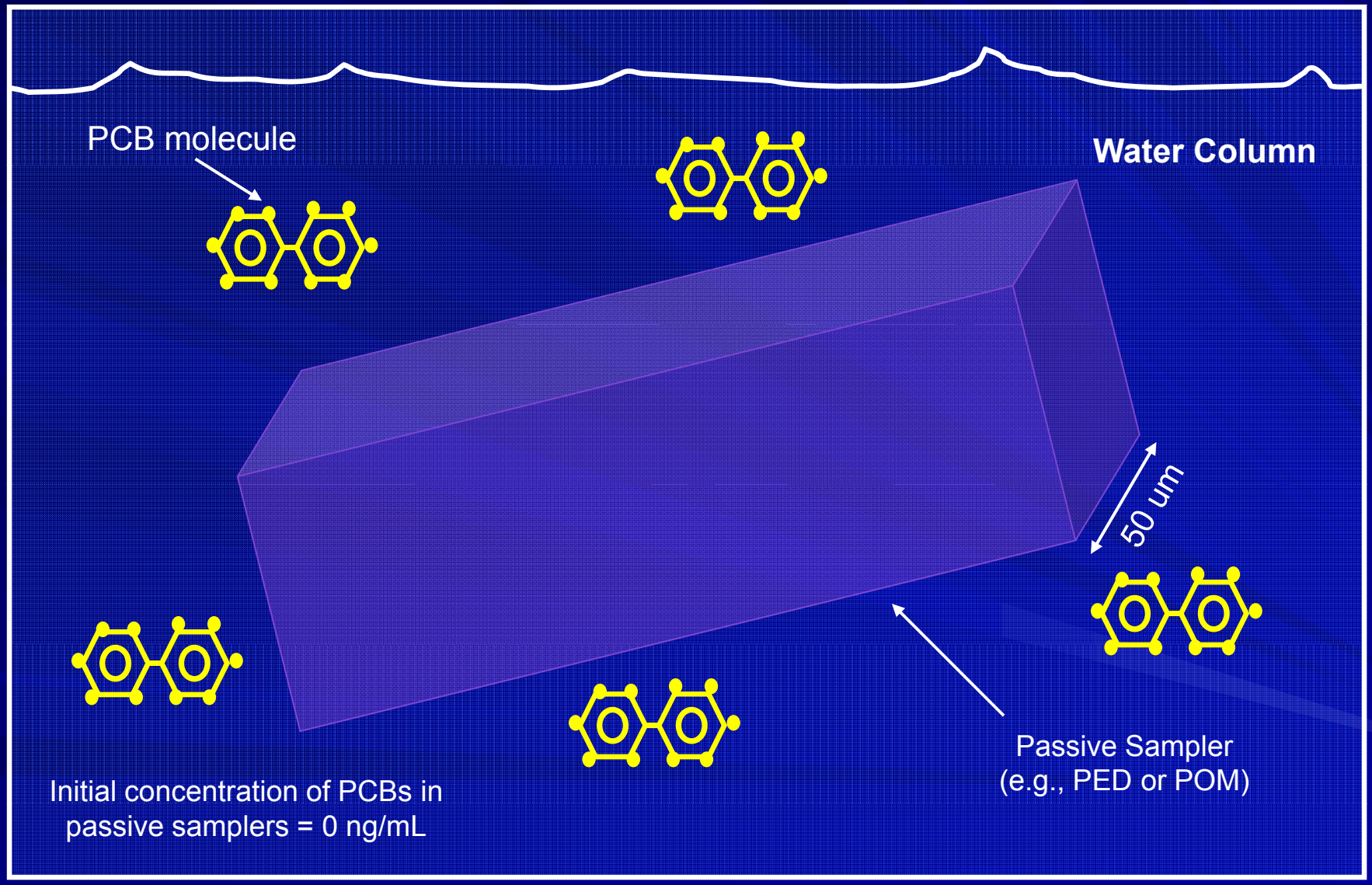
Passive Sampler Costs ($/sampler)[a,b]

Type	Materials (samplers and deployment equipment)	Preparation (dialysis)	Chemical Analyses	Total
Water (5 L)	<5	-	525	530
SPMD	350	115	350	815
SPME	~35	-	275	~310
PED	~15	-	375	~390
POM	~50	-	375	~425

[a] 2011 Battelle costs (L Lefkovitz, Duxbury, MA, USA)

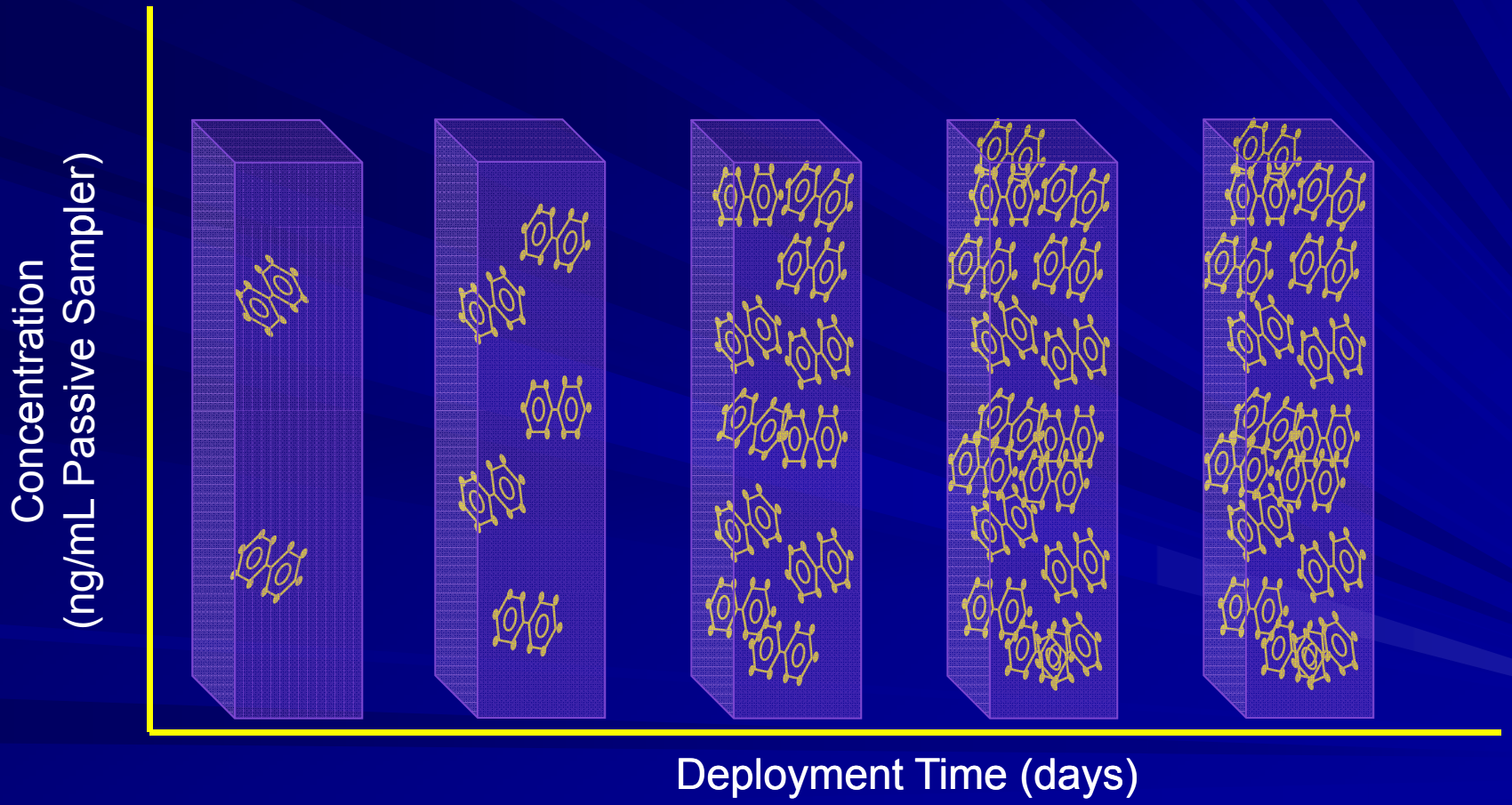
[b] Assume 10 - 20 samples, GC/MS analysis of NOAA PCB list (20 congeners)

Passive Sampler Theory

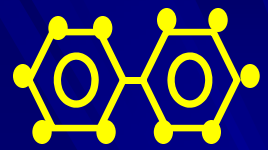


Passive Sampler Theory

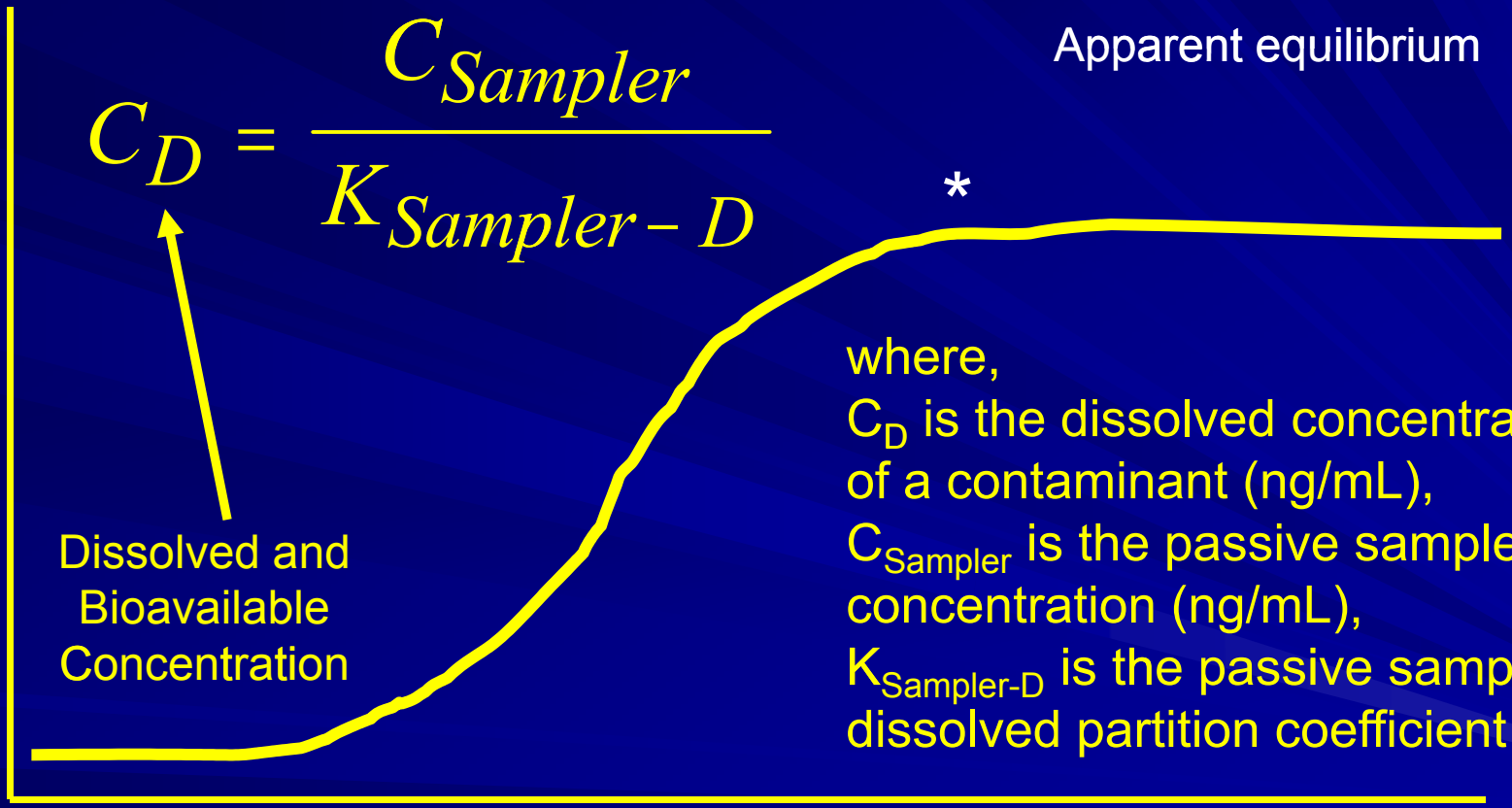
Equilibrium Sampling



Passive Sampler Theory



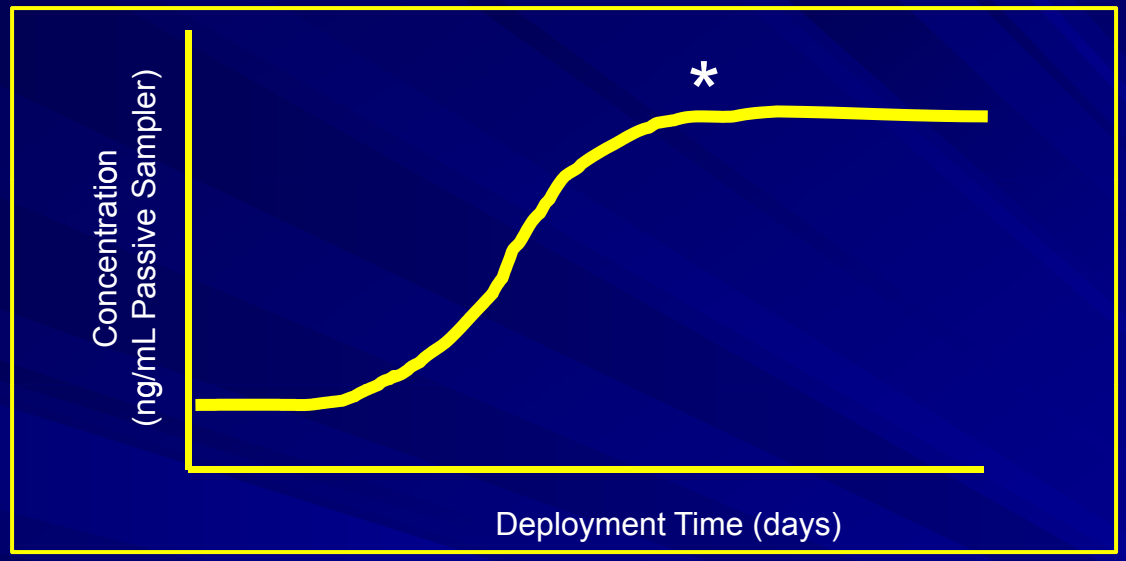
$$C_D = \frac{C_{Sampler}}{K_{Sampler-D}}$$



where,
C_D is the dissolved concentration of a contaminant (ng/mL),
$C_{Sampler}$ is the passive sampler concentration (ng/mL),
$K_{Sampler-D}$ is the passive sampler-dissolved partition coefficient

Technical Issues using Passive Samplers

- Establishing when equilibrium occurs

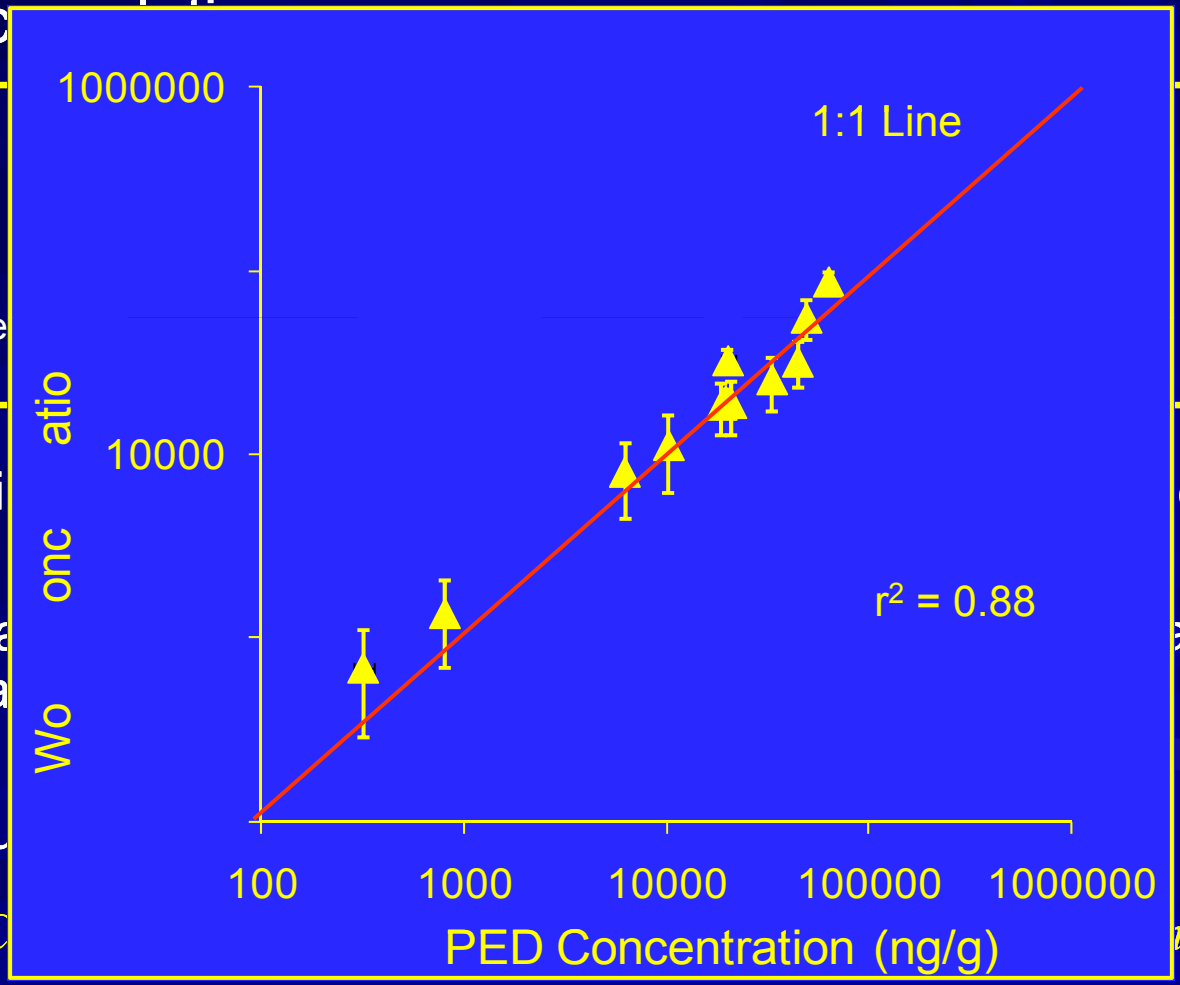


  - Unless deployment time series data is available (i.e., $$$)
  - Challenge in all monitoring (including biomonitoring)
    - Often assume 28 days is sufficient
  - Solution: Use of performance reference compounds (PRCs) to establish equilibrium

    SPMDs, PED, POM

Technical Issues using Passive Samplers

- Relating passive sampler accumulation to animal bioacc



Passive

– Criti ... er data

– Data ... animal bioa

– Solu

Animal C ... *(ng / mL)*

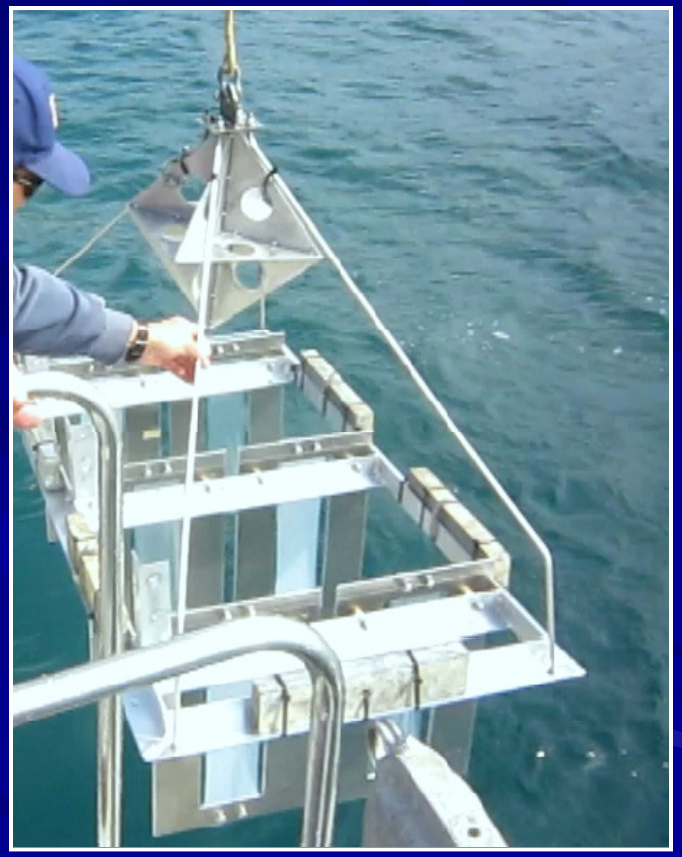
Passive Sampler Application

- Palos Verdes Superfund Site
  - Water Column and Sediment Deployments
    - Los Angeles (CA)
    - Carmen White (RPM)
    - Deep water marine site (60 m)
    - DDTs & PCBs
    - Seven water column stations and five sediment stations
  - Objectives
    - Determine water column concentrations of contaminants resulting from remediation activity (before, during, after)
    - Determine magnitude of flux of contaminants into the water column from sediments
    - Compare different types of passive samplers (PED, POM, SPME)

Passive Sampler Application

Deployments

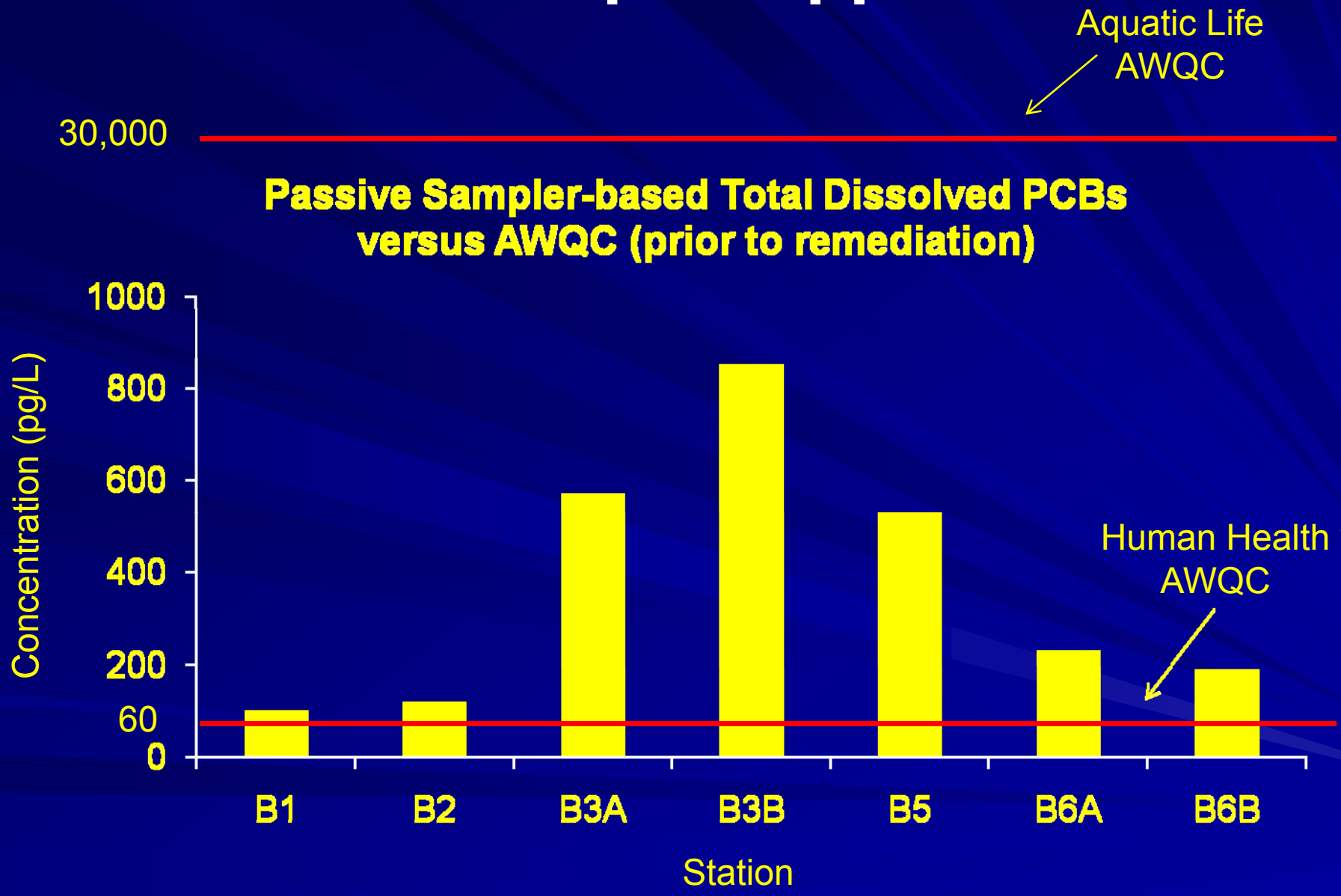
Water Column – PEDs
(flow meter deployment)



LACSD

Sediments – PEDs, POMs & SPME
(flux platform deployment)

Passive Sampler Application



Passive Sampler Application

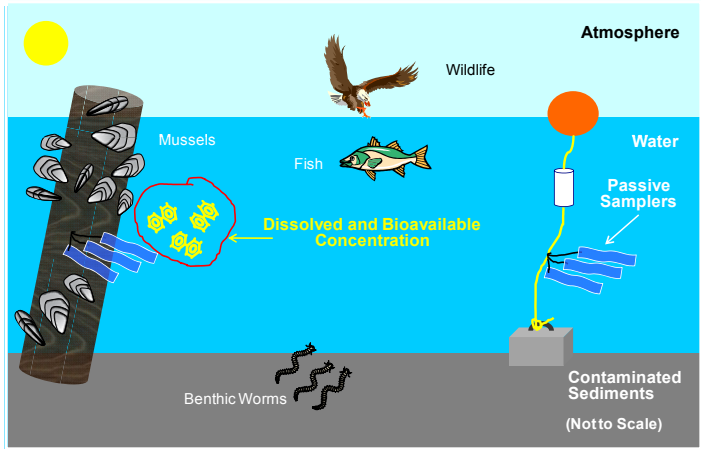
Passive Sampler Application

SAMS guidance document in preparation for using passive samplers at Superfund sites

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

Sediment Assessment and Monitoring Sheet (SAMS)

Guidance for the Application of Passive Samplers at Superfund Sites



OSWER Directive 9200.1-96FS

February 2012

Summary

- Passive sampling a scientifically sound and cost-effective approach for monitoring contaminant concentrations in the water column and sediment interstitial waters
- Passive samplers provide information on:
  - Dissolved and bioavailable concentrations of contaminants
  - Sampler uptake may serve as a surrogate for animal bioaccumulation
- Applications include:
  - Monitoring water column concentrations before, during and after remediation
  - Determining sources of contaminants released from sediments to the water column (e.g., site model development)
  - SAMS guidance document in preparation