

Passive Sampling Techniques:

Measuring Hydrophobic Organic Contaminants in
Sediment Porewater and Surface Water

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<http://www.epa.gov/superfund/health/conmedia/sediment/index.htm>



Talk Outline

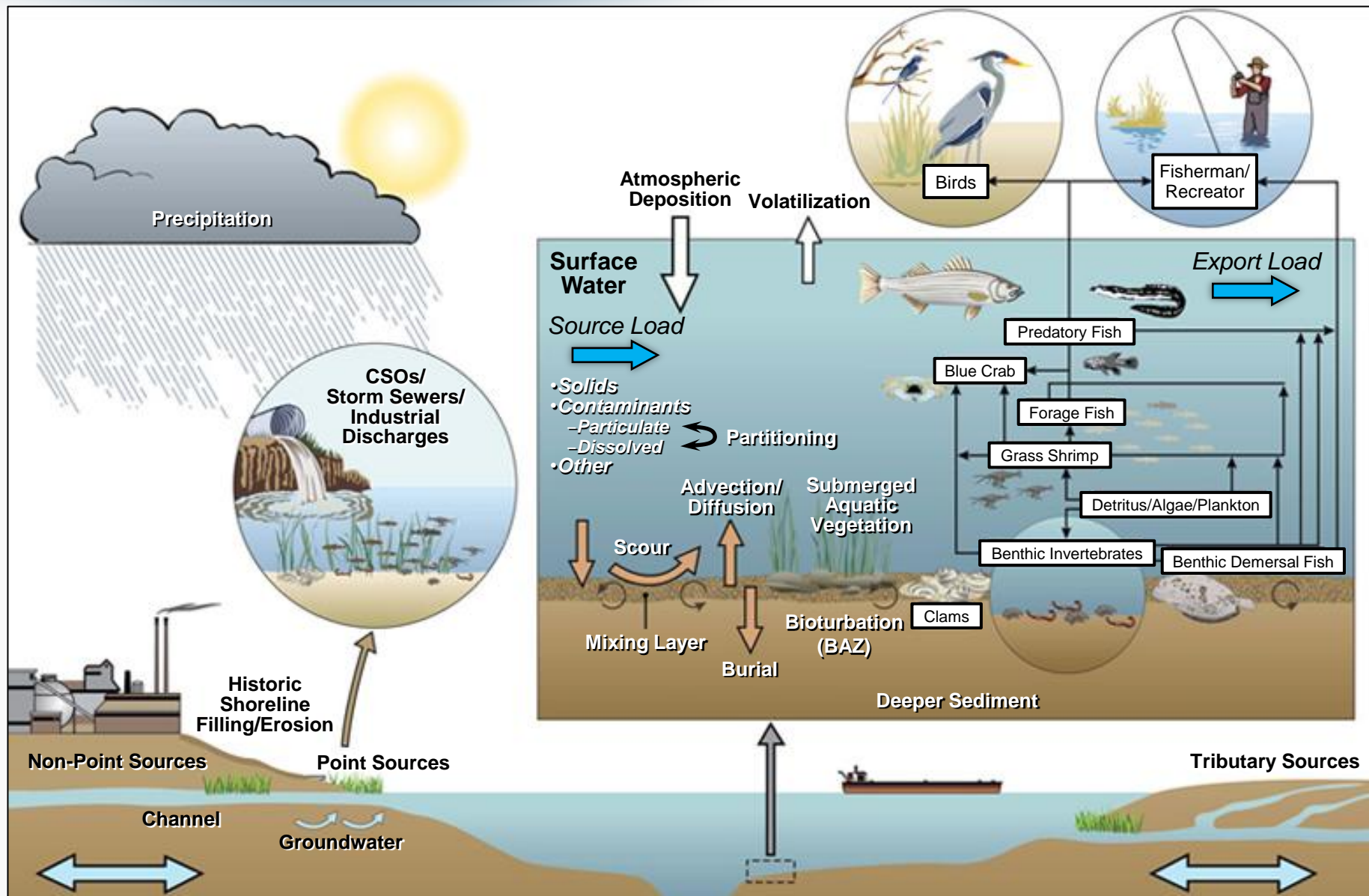
I. Introduction

- a) A CSM for sediment sites
- b) Traditional vs Passive Sampling
- c) Passive Sampling Fundamentals

II. Field Deployment & Laboratory Analysis

III. Benefits and Limitations of Passive Samplers

IV. A Superfund Case Study





Traditional Sampling

1. Bulk Sediment Concentrations

- Analysis is fast, simple, and well established.
- Generally used to establish Action Levels, Cleanup Levels, etc.
- Poorly correlated with sediment toxicity and bioaccumulation tests or risk exposure.

2. Equilibrium Partitioning- ($f_{oc}K_{oc}$)

- Improved relationship to toxicity and bioaccumulation tests.
- Does not account for multiple types of OC or competitive sorption of DOC and other contaminants.
- Literature values of K_{oc} can vary over 2 orders of magnitude.



Traditional Sampling

3. Surface Water

- Requires large volumes of water.
- Water must be filtered.
- Requires a correction for the presence of dissolved organic carbon (DOC).

4. Porewater

- Difficult to obtain significant volume of water.
- Water must be separated from the sediment particles.
- Requires a correction for the presence of DOC.

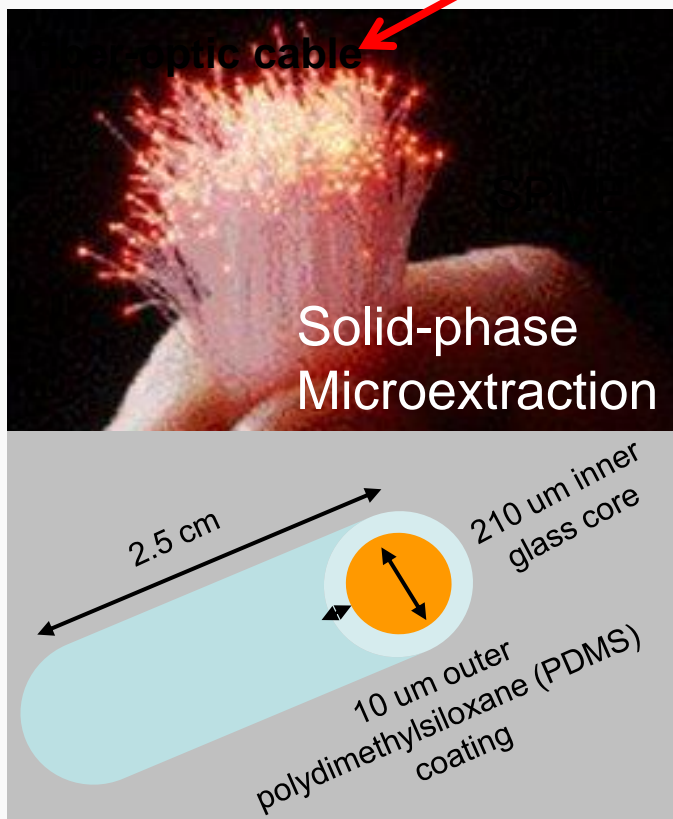
Key Message: traditional sampling methods have logistical challenges, high detection limits, and much uncertainty.



Types of Surface Water/Sediment Porewater Samplers

- For Hydrophobic Organic Contaminants (HOCs)
 - Solid-phase microextraction (SPME)
 - Polyethylene (PE)
 - Polyoxymethylene (POM)
 - Ethylvinylacetate (EVA)
 - Silicone Rubber (SR)
- For Metals
 - Peepers
 - Diffusion Gel Thin Film Device (DGT)
 - Gellyfish
 - Metal-chelating media

SPME, PE, & POM





What information do you get from passive samplers?

1. The Freely Dissolved Concentration of the HOC

- It involves the following calculation (the partitioning coefficient must be known):

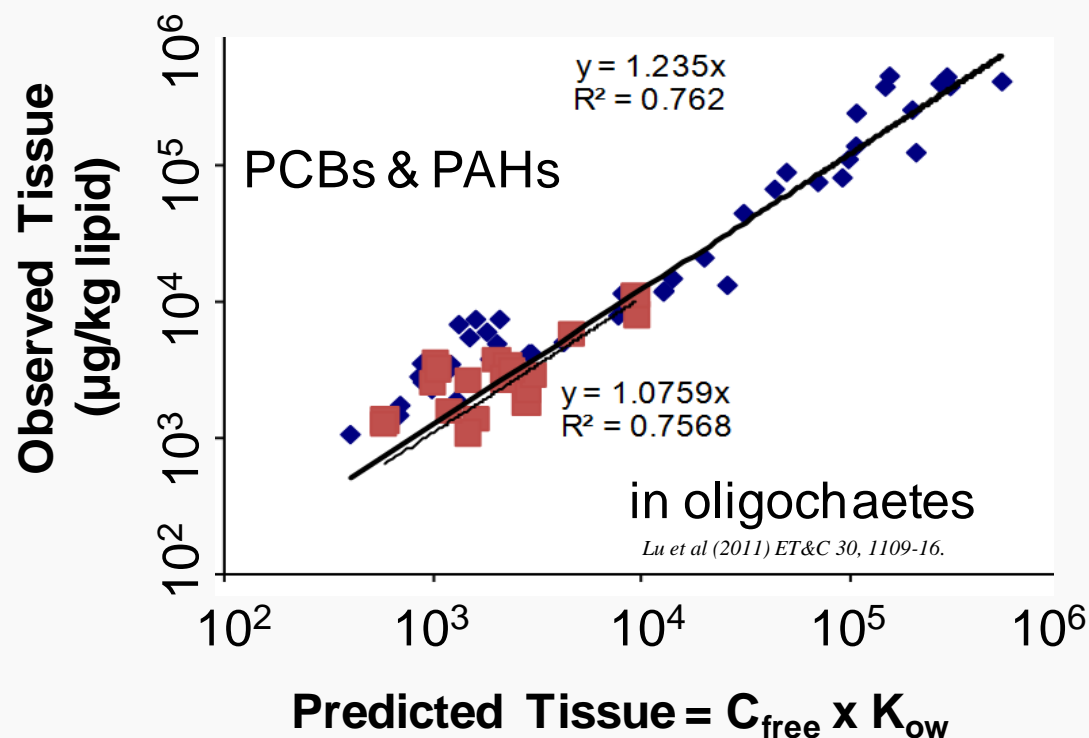
$$\text{Freely Dissolved Concentration (C}_{iw}\text{)} = \frac{\text{Passive Sampler Sorbed Concentration (C}_{iPS}\text{)}}{\text{Passive Sampler – Water Partitioning Coefficient (K}_{iPS}\text{)}}$$

Key Message: This method is more accurate than the traditional methods, but it depends on having an accurate K_{iPS} value.

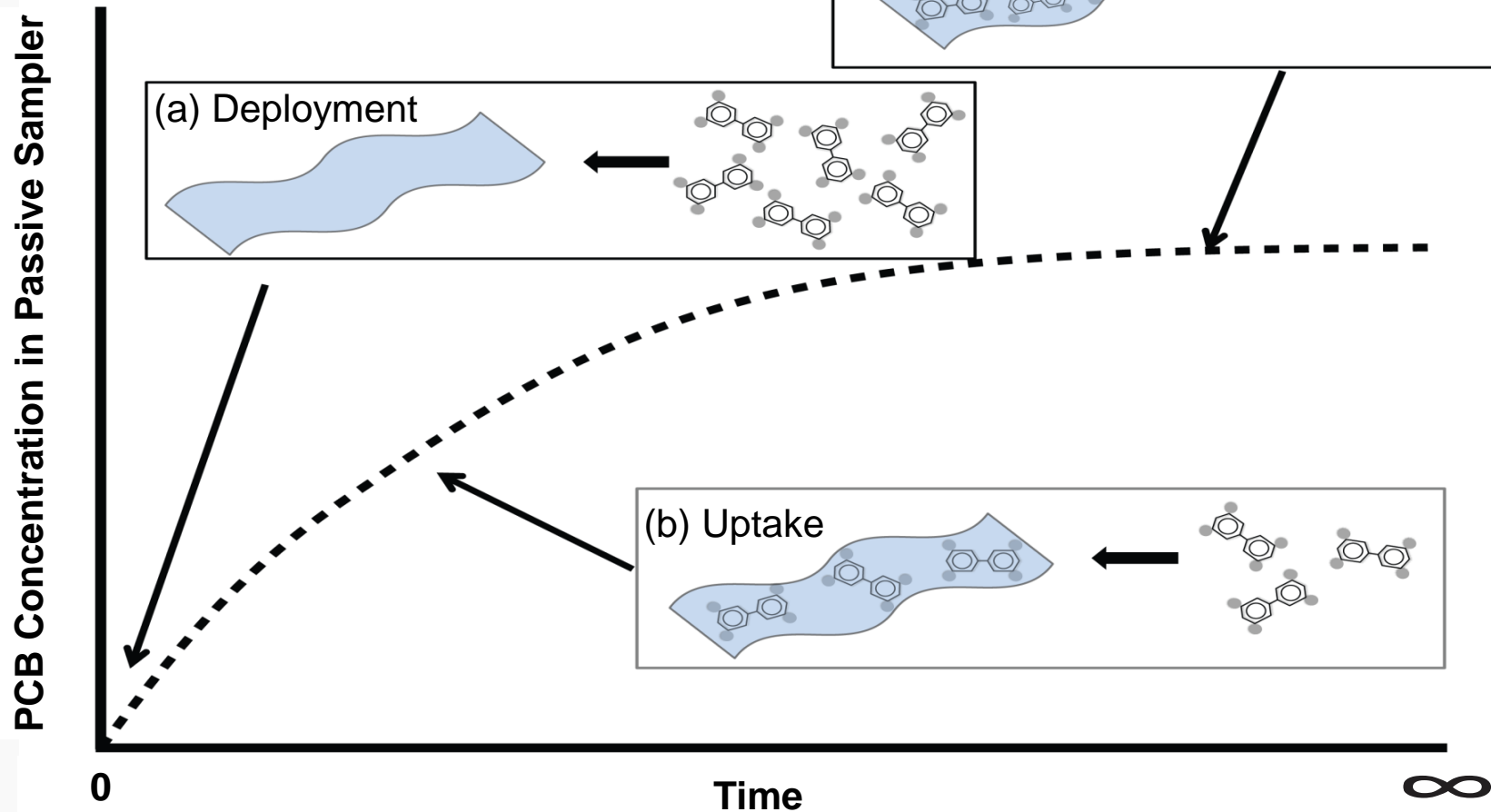


What information do you get from passive samplers? (cont.)

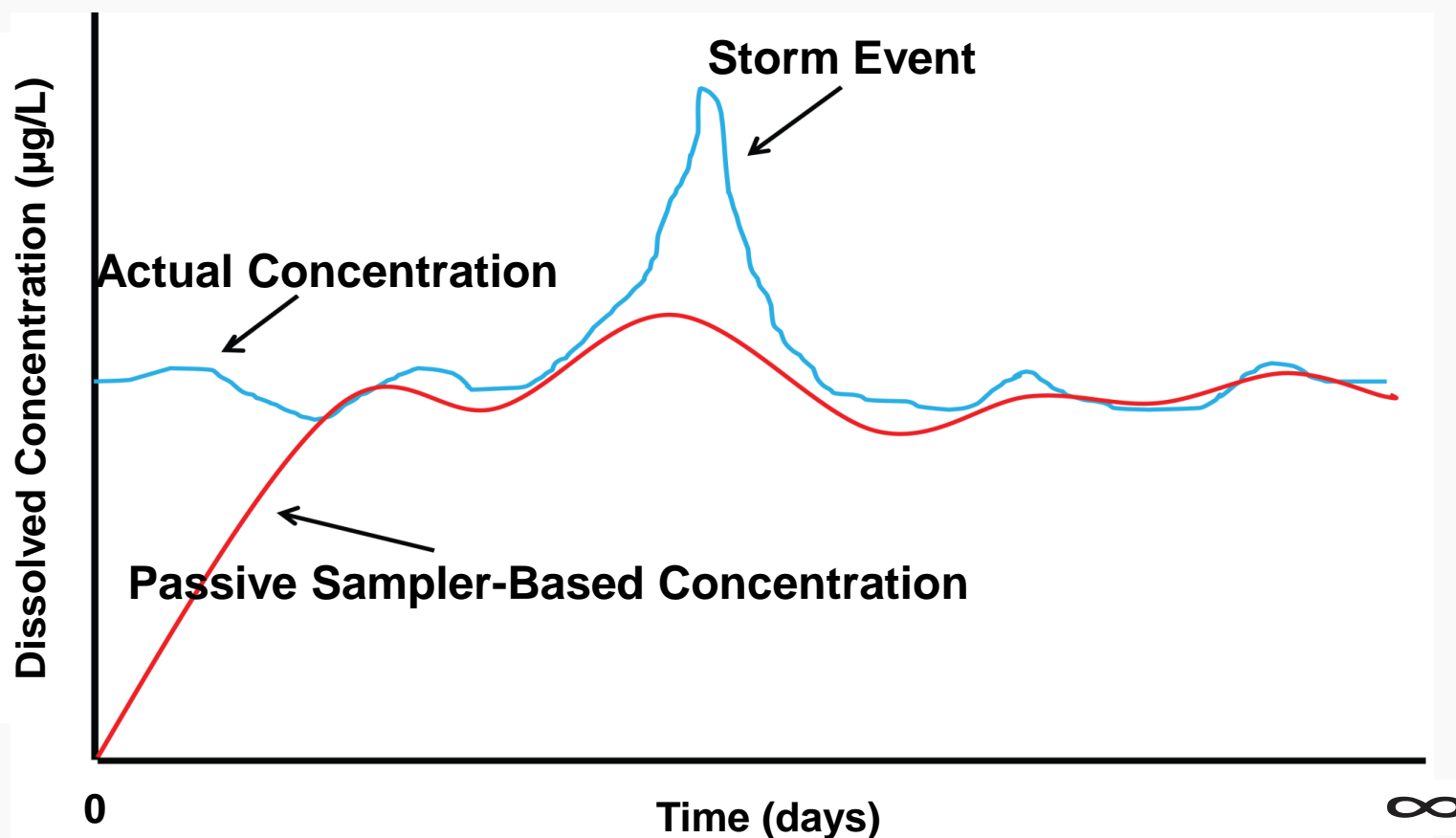
- “Biomimicry?” —
No, but...



How does it work?



Time Averaged Sample





Cost Estimate for Different Types of Sampling

- Cost estimates provided courtesy of an independent laboratory in dollars per sample

Type of Sample	Materials (\$)	Chemical Analysis (\$)	Total (\$)
Water (5 L by conventional method)	<5	525	530
Semi-permeable Membrane Device (SPMD)	505	400	905
Polyethylene (PE)	~5	375	380
Polyoxymethylene (POM)	~50	375	425
Solid Phase Micro-extraction (SPME)	~35	275	310

Deployment Methods: Surface Water

Polyethylene Device (PED) Moorings

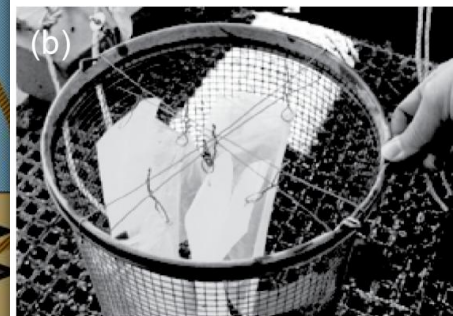
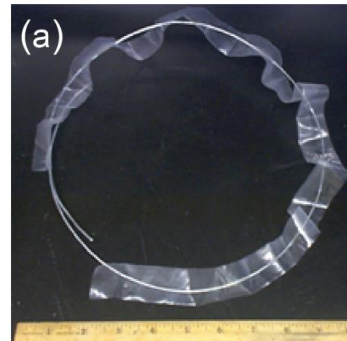
25 μ m & 51 μ m PEDs

Water Depth: 8-15 ft

~3 ft

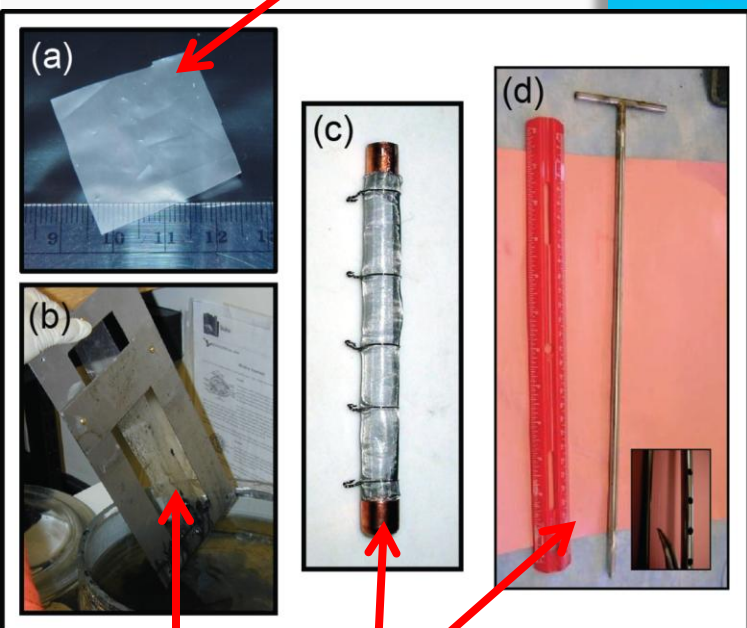
YSI Sonde

~15 ft



Deployment Methods: Sediment Porewater

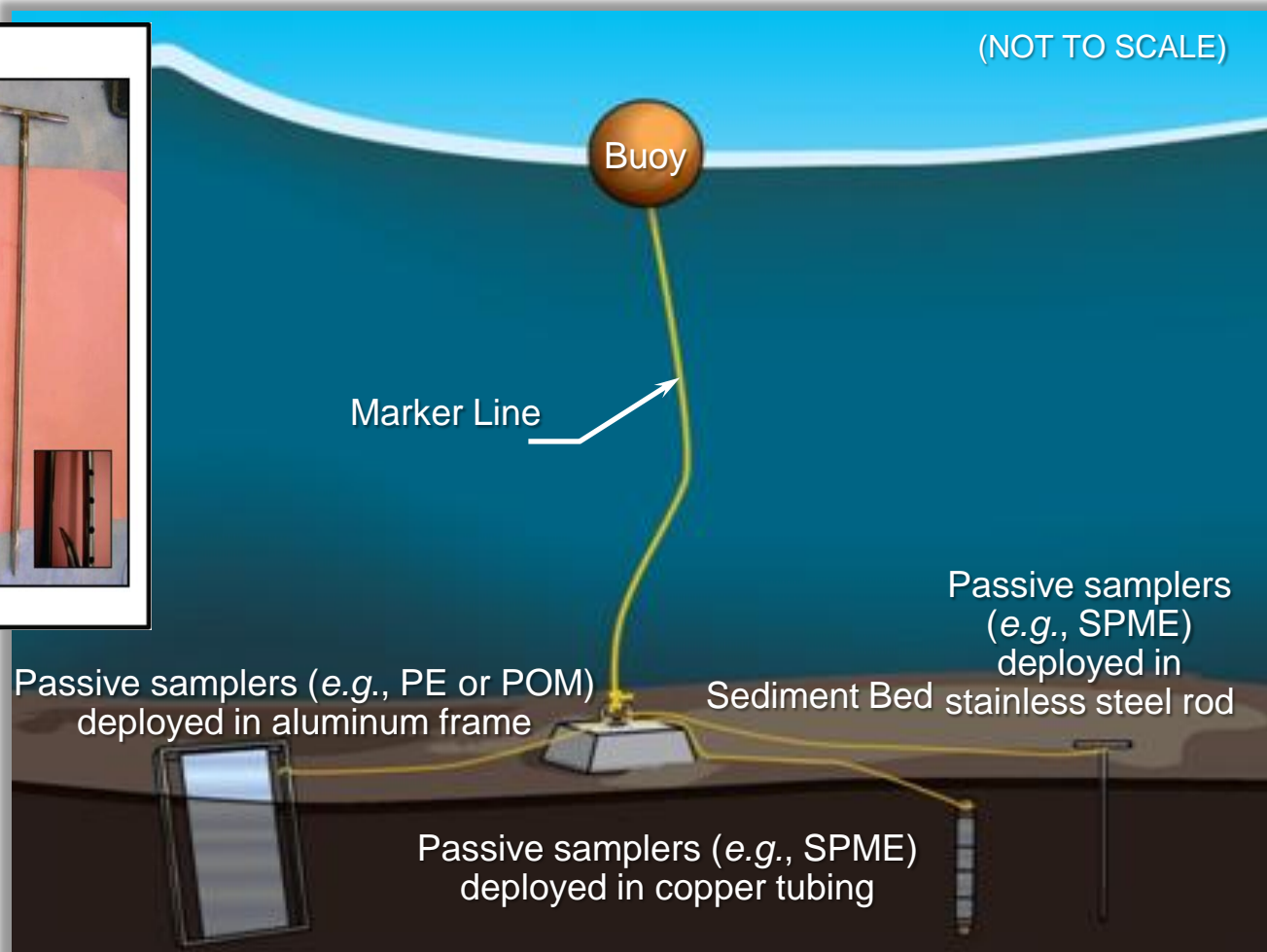
POM



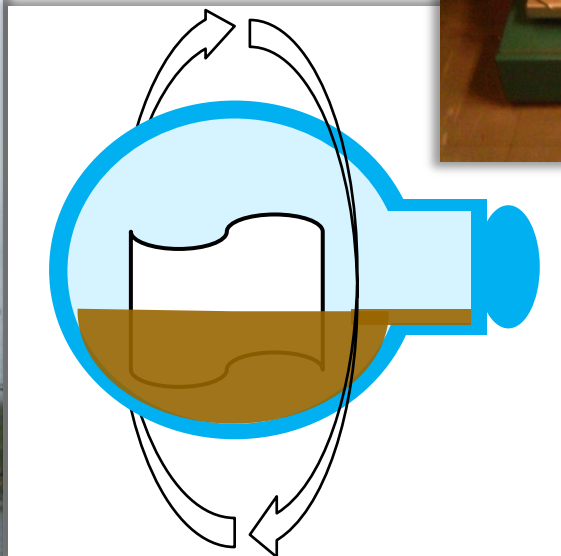
PE & Frame

SPME & Casing

(NOT TO SCALE)



Deployment Methods: Sediment Porewater (cont.)





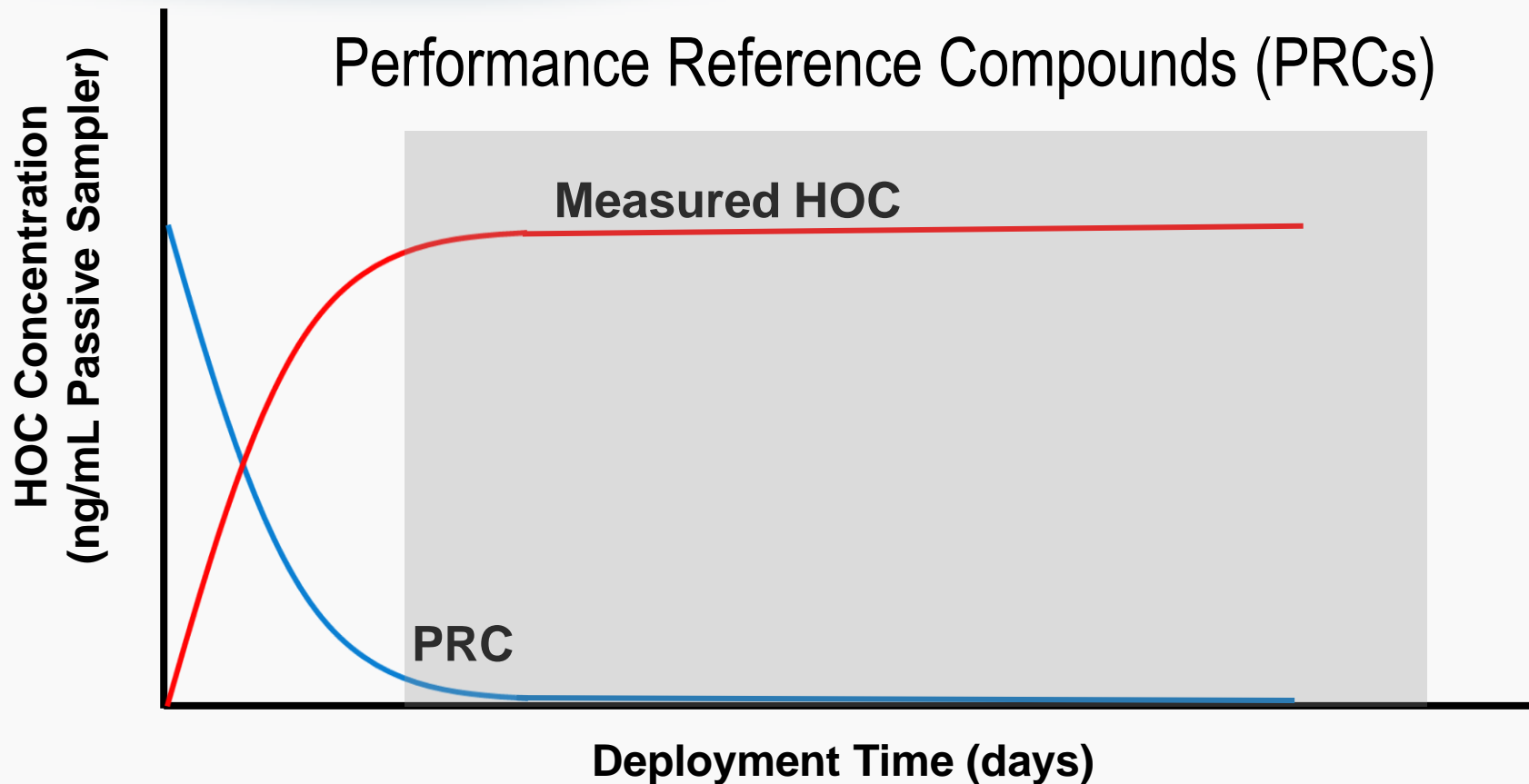
Deployment Time

The time to equilibrium is affected by

1. the polymer thickness,
2. the temperature and salinity of the water,
3. advection of water adjacent to the polymer, and
4. algal growth (biofouling) on the sampler.

**The sampler must be at equilibrium
in order to make accurate measurements**

- Unless you know how “close” to equilibrium the sampler is



Key Message: PRCs are an important QA/QC step.



Sample Extraction and Analysis

- HOCs are typically extracted from passive samplers using solvents at room temperature for 24 – 48 hrs
 - Soxhlet Extractors or Accelerated Solvent Extractors are not necessary
 - SPMEs can be inserted directly into a GC without any extraction or cleanup
 - Fewer cleanup steps are necessary relative to sediment, water, or tissue extractions
- Sample analysis uses the same methods as traditional samples

Key Message: Passive samplers generally use fewer chemicals and are easier to prepare for analysis, making them a sustainable, green remediation technology



Passive Sampling Method Limitations

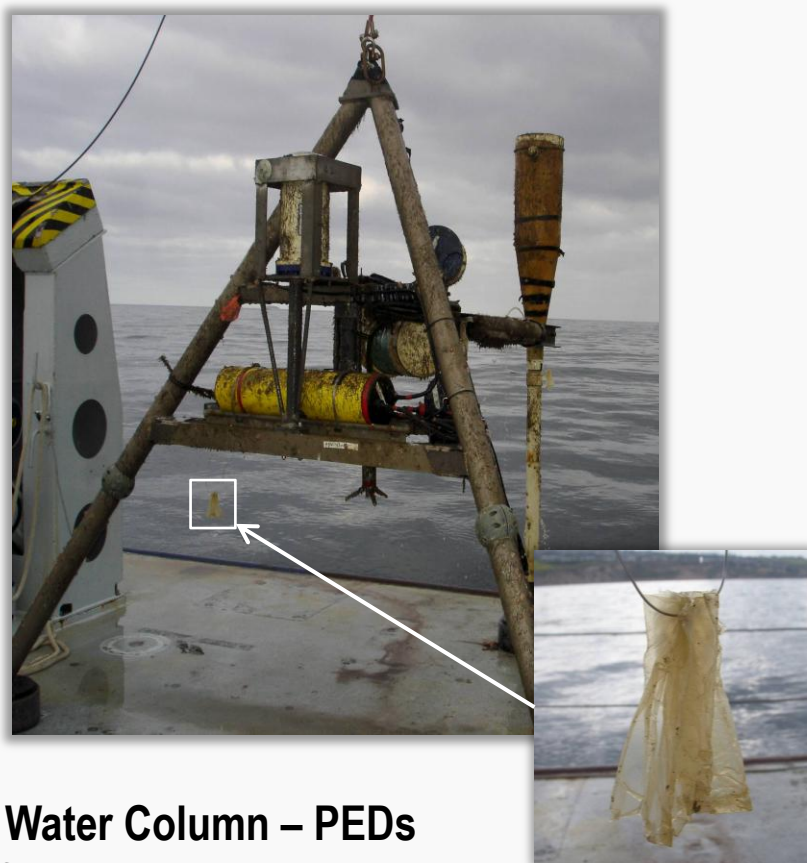
- There is no standardized method to use, which creates two primary hurdles:
 1. Regulatory acceptance – to date, the use of passive samplers has been negotiated between the parties involved at each site and typically a pilot study to demonstrate the acceptability of the technology has been required
 2. Lack of consensus on partitioning values
 3. There is a small pool of commercial laboratories with the required experience
- Uncertainty over their use in the decision-making process

Pales Verdes Shelf Case Study

- Deep water marine site (~60m)
- COCs – PCBs, DDT & breakdown products
- Montrose Chemical Corporation discharged to local sewers from 1947 to 1983
- Two passive sampler studies have been done at this site:
 - Water column and *in situ* porewater monitoring
 - *Ex situ* sediment core analysis

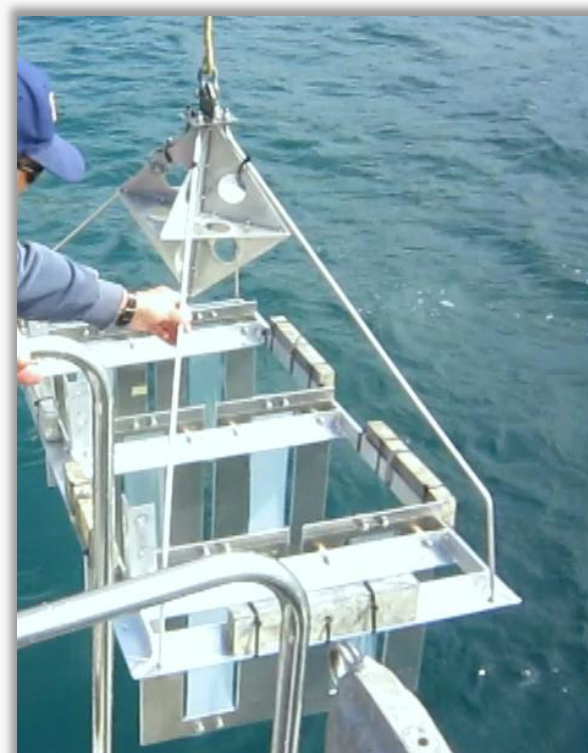


Deployment of Monitoring Stations



**Water Column – PEDs
(flow meter deployment)**

5/7/2013



**Sediments – PEs & POMs
(flux platform deployment)**

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Sediment Monitoring Platform in Place



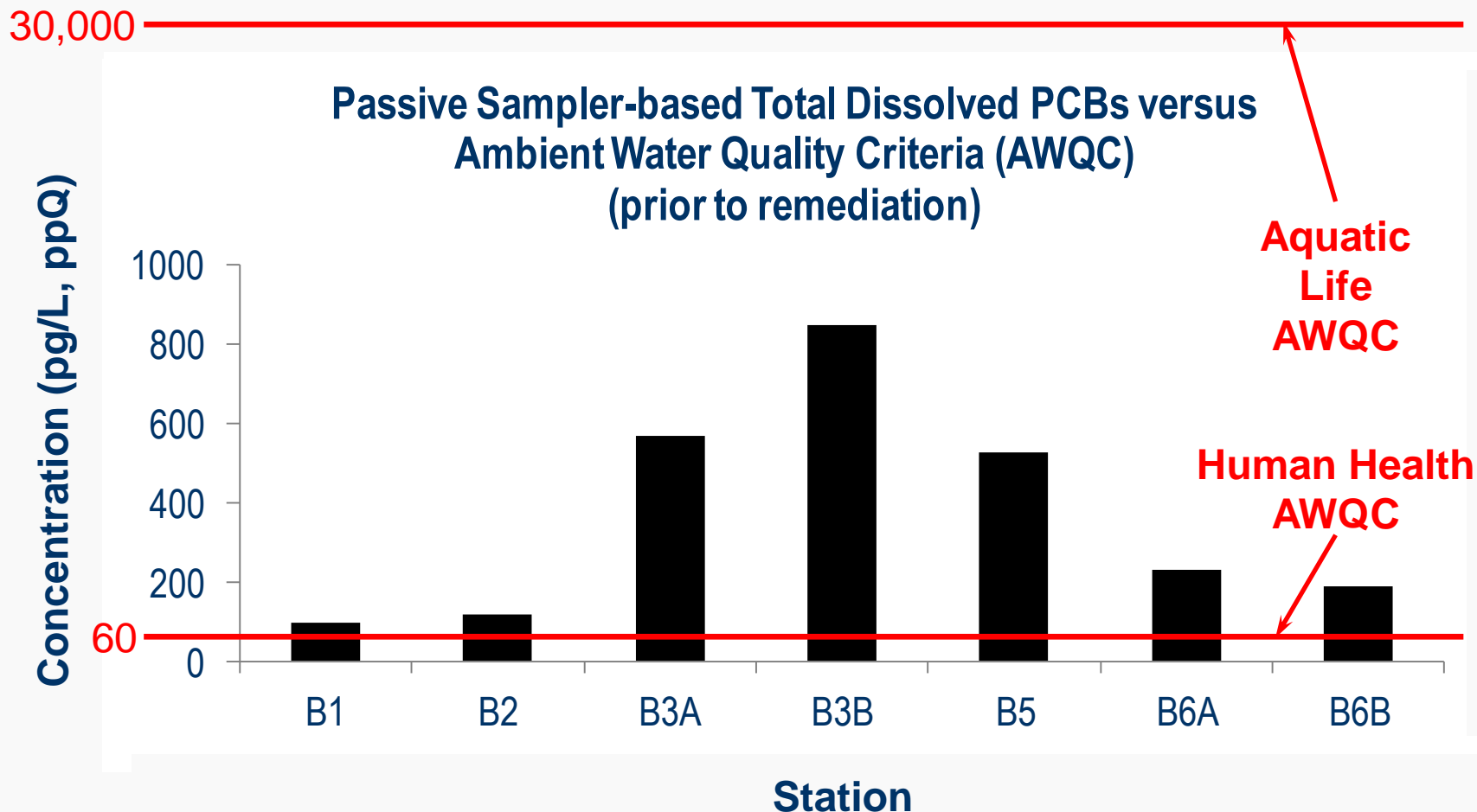
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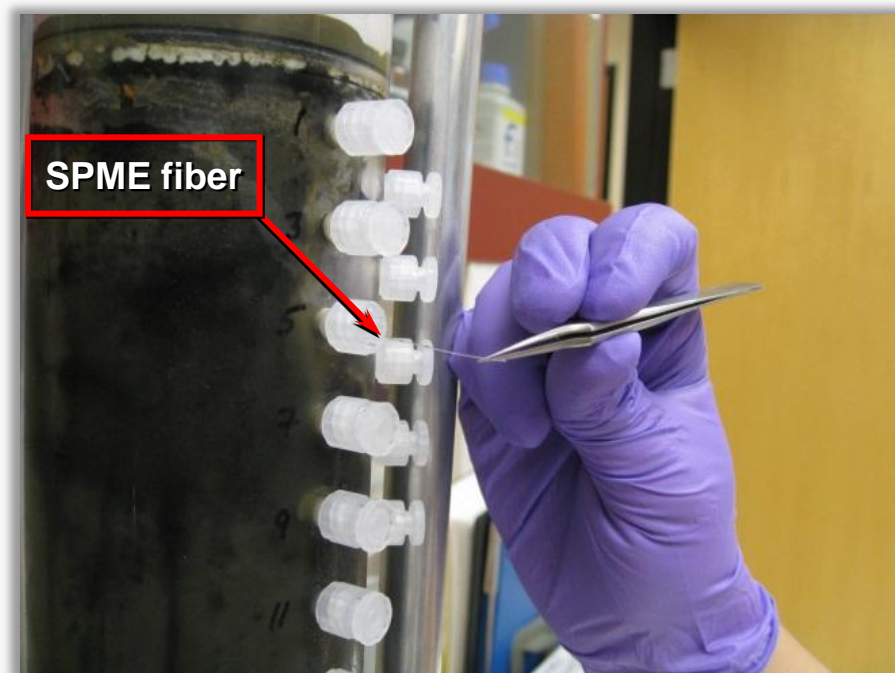
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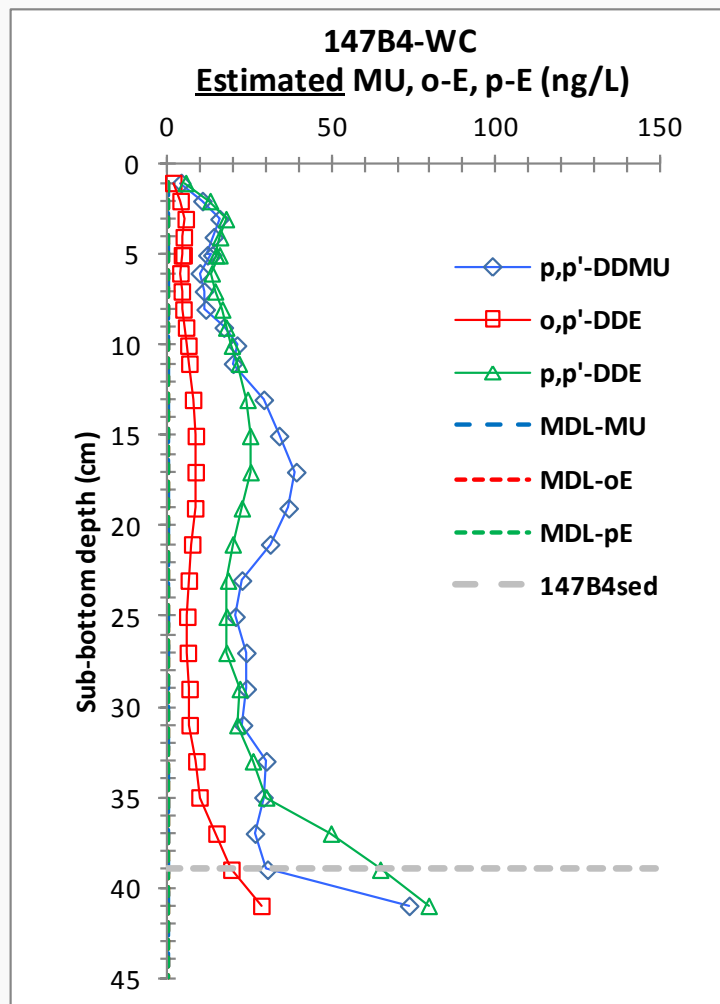
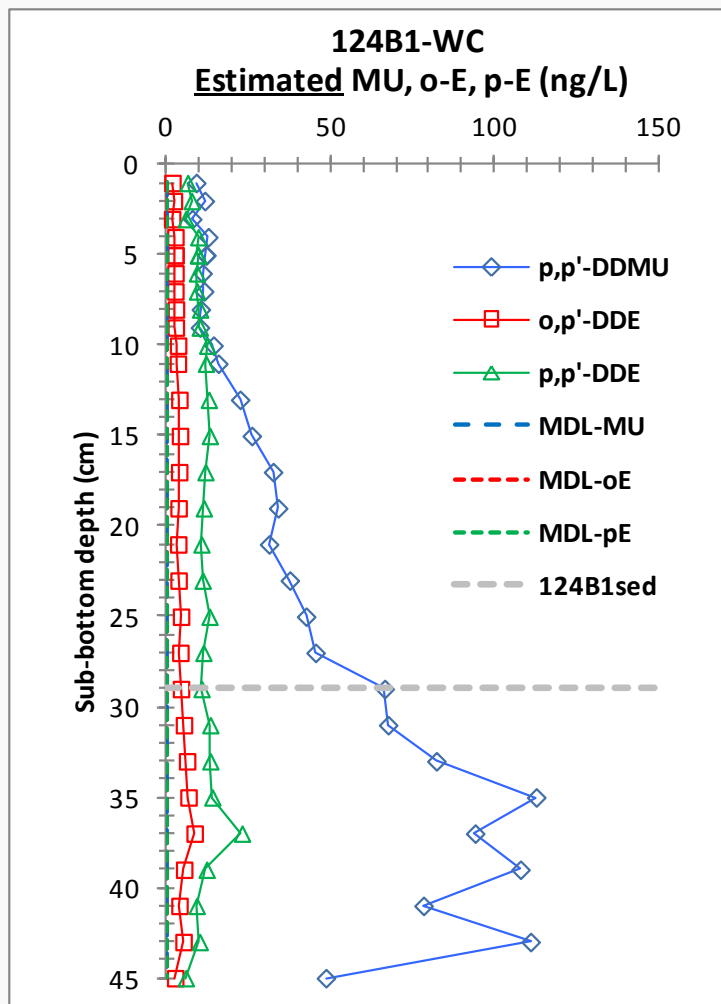
PCBs Prior to Remediation



In Situ Sediment Core Analysis: SPME



In Situ Sediment Core Analysis (cont.): SPME





Lessons Learned- Perspectives from the Principle Investigators and RPM

- PE, POM, & SPME are extremely sensitive
- *In situ* equilibration of PE & POM is feasible in deep water
- High spatial resolution in cores is possible because small size of SPME,
 - but this small size resulted in higher detection limits (ppt in the SPME vs ppq in the PE and POM)
- Relatively long equilibration times are required for HOCs; PRCs are necessary!

Key Message: Passive Sampling is an important tool being used at this site to better understand the link between sediment concentrations and fish tissue concentrations.



Take-Home Points –

- **Passive sampling is a significant improvement over traditional methods, though not a perfect method**
 - a. Better detection limits, less sample variability
 - b. Better able to explain toxicity and bioaccumulation results
 - c. They're cheaper
 - d. Long deployment times



Acknowledgements

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