Application of Passive Sampling for Measuring Dissolved Concentrations (C_{free}) of Organic Contaminants in the Water Column at Three U.S. EPA Marine Superfund Sites

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Outline

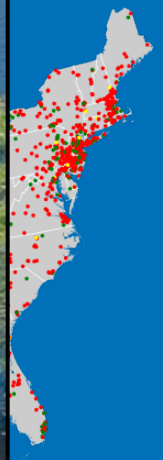
- Background
  - Superfund Program
  - Passive sampling
- Objectives
- Materials and Methods
  - Study sites
  - Passive samplers
- Results
- Summary

Background

- Contaminated sediments recognized as a serious source of risk in United States
  - National Research Council (2001, 2003) report 70% coastal ecosystems negatively affected (e.g., 2,800 fish advisories (i.e., fish unsafe to consume))
- Risk "Drivers"
  - Human health (i.e., cancer and non-cancer effects)
  - Ecological effects (i.e., toxicity, bioaccumulation)
    - Need to evaluate contaminant bioavailability to properly assess ecological risk
- Superfund Program
  - Empowers U.S. EPA to clean-up contaminated sites and compel responsible parties to perform cleanups or reimburse the government for EPA-lead cleanups
- Passive Sampling
  - Technology more accurately evaluates contaminant bioavailability improving site ecological risk assessments and decision-making

Hudson River (NY, USA) Superfund Site

(Removal of 2 x 10^6 m^3 PCB contaminated sediments)



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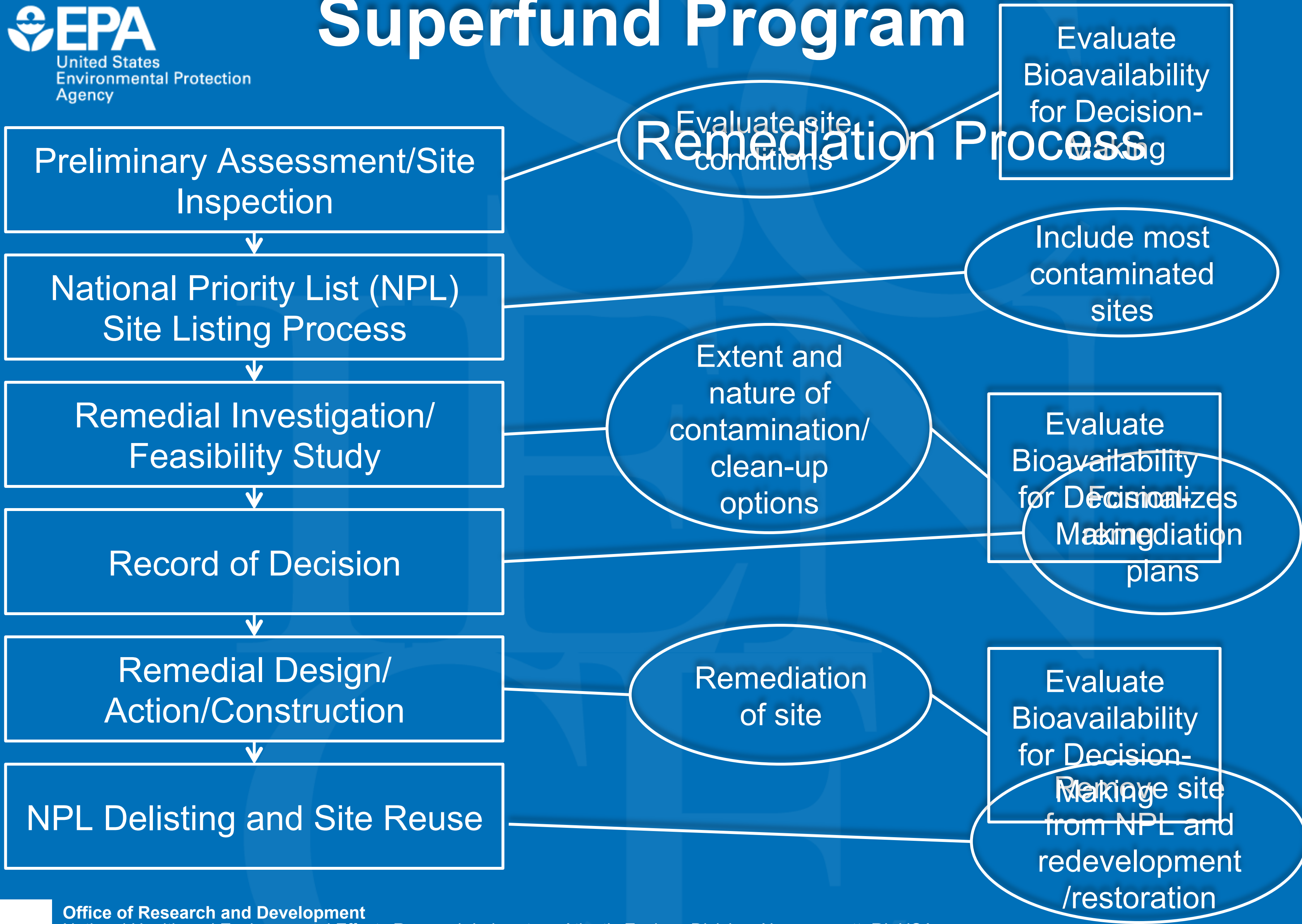
Superfund Program

Remediation Process



Passive Sampling

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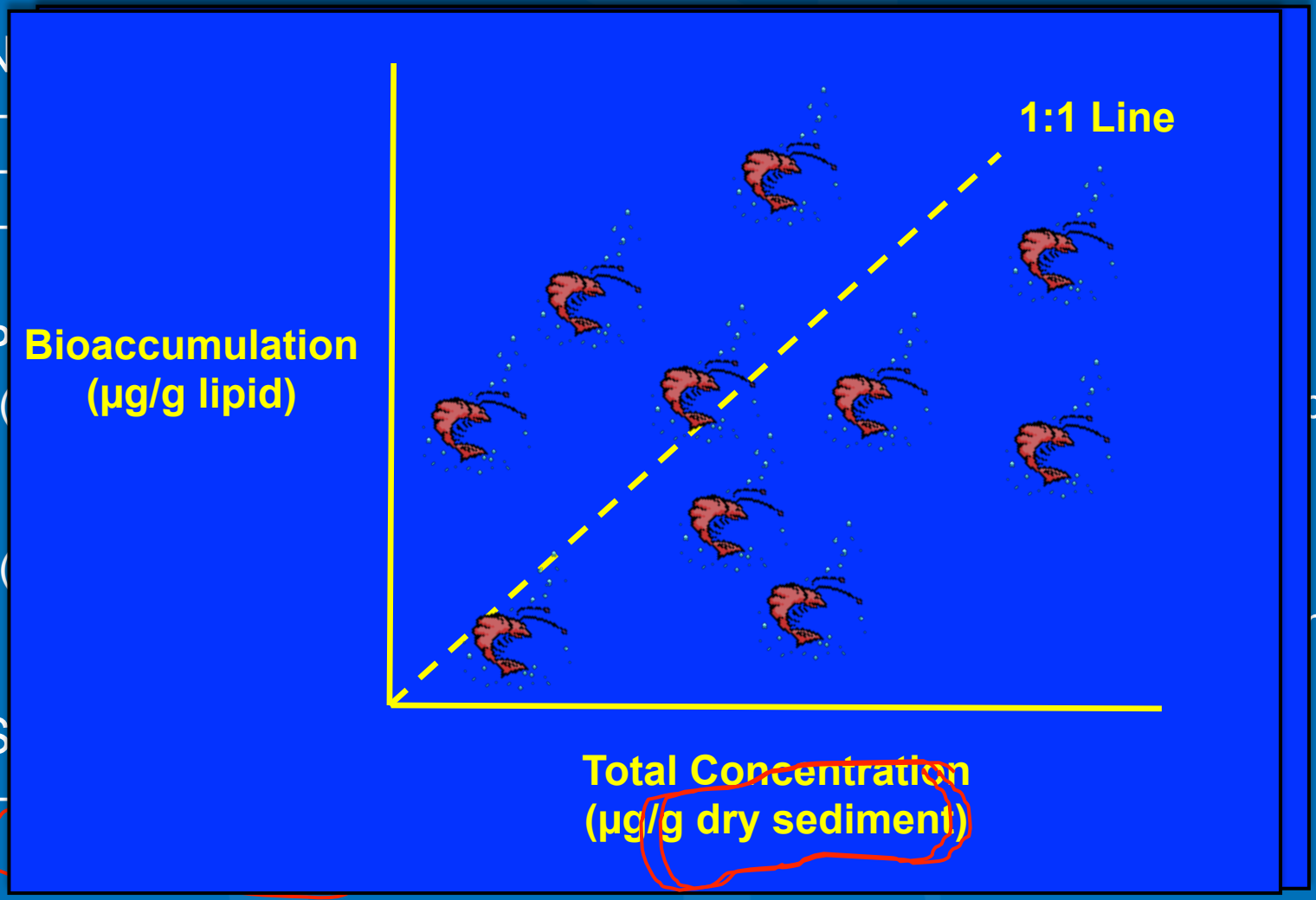

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Passive Sampling: Types

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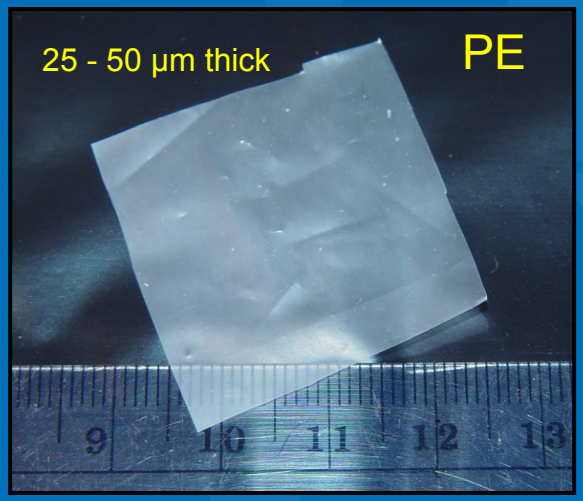
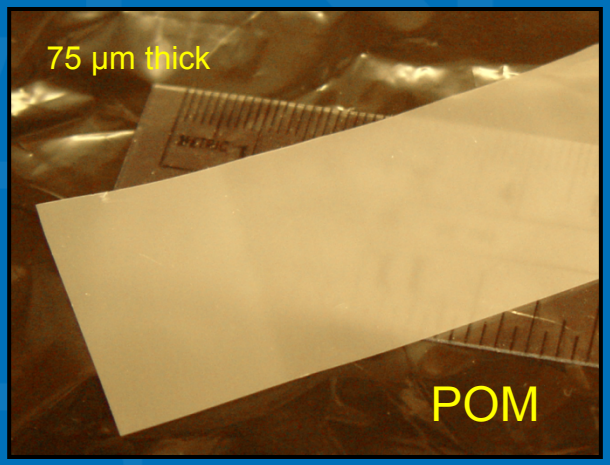
Polyethylene (PE)

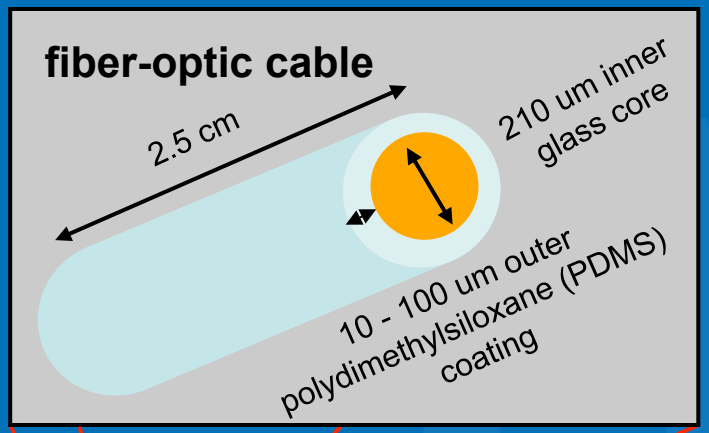


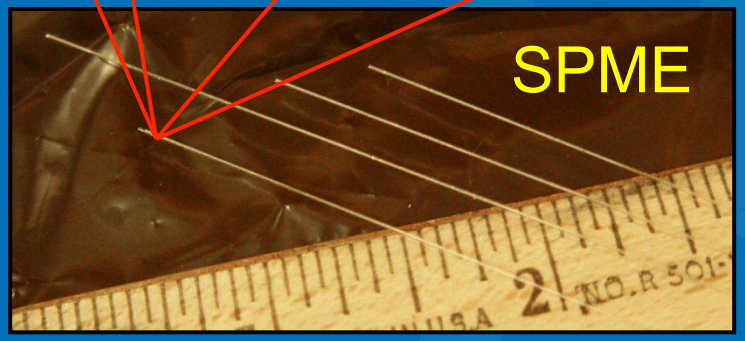
Polyoxymethylene (POM)



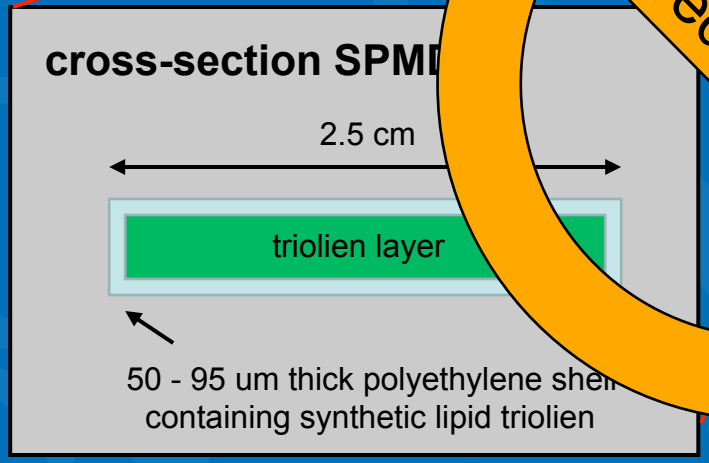
Passive Sampling: Types

United States Environmental Protection Agency





Solid Phase Microextraction (SPME)



Semi-Permeable Membrane Device (SPMD)

Passive Sampling: Configurations

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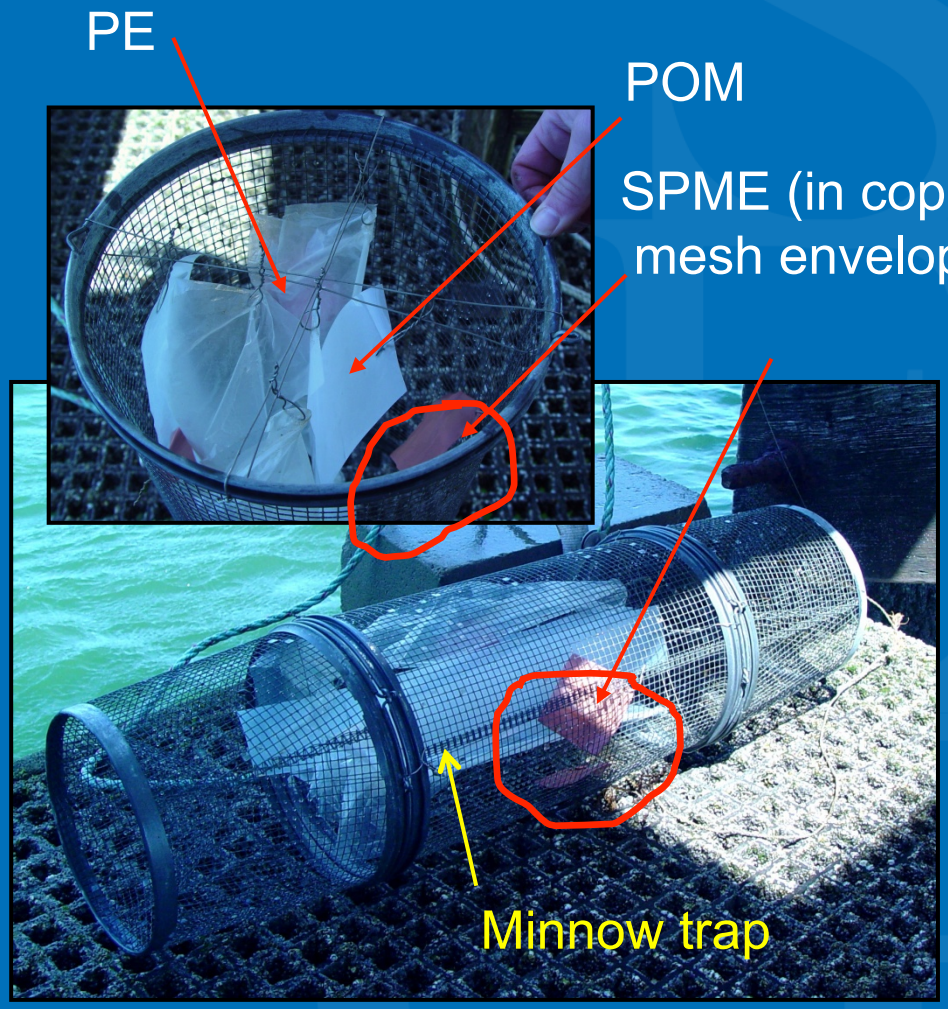
Water Column



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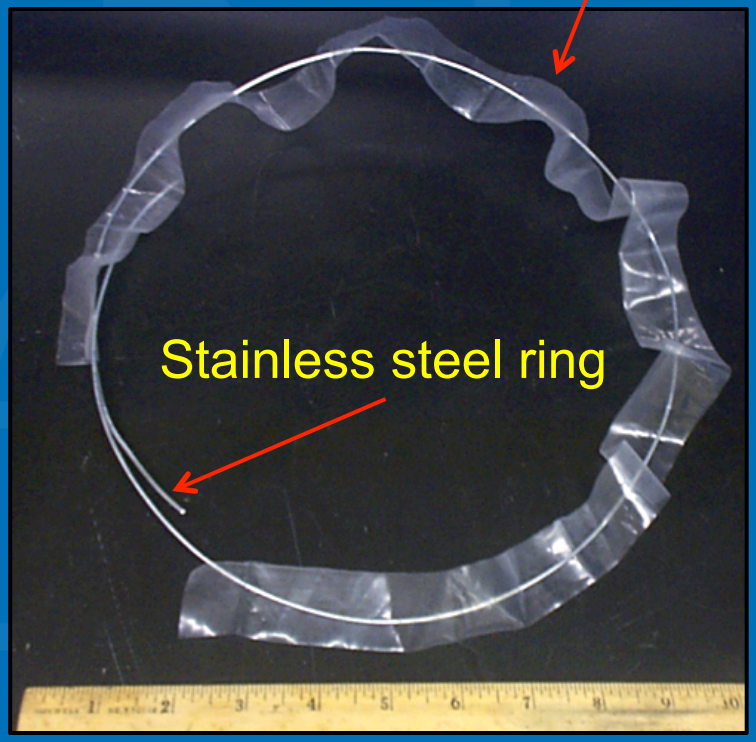
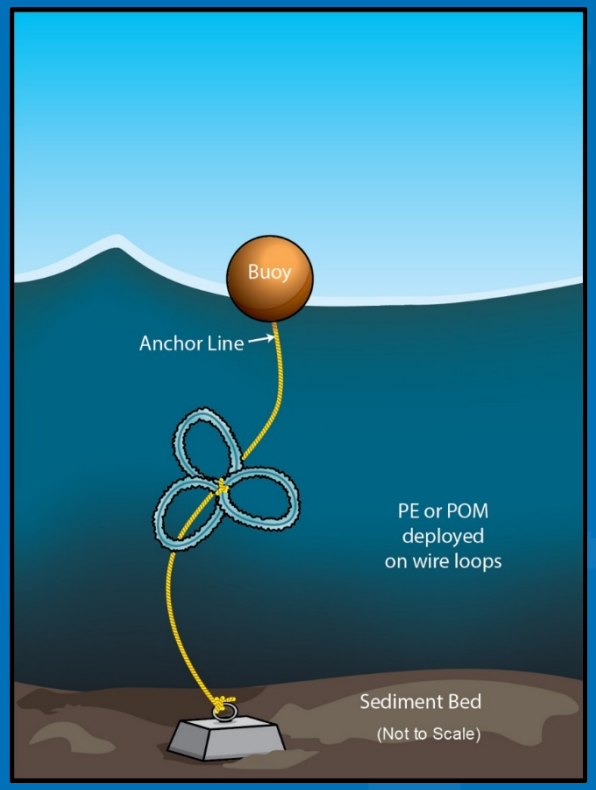


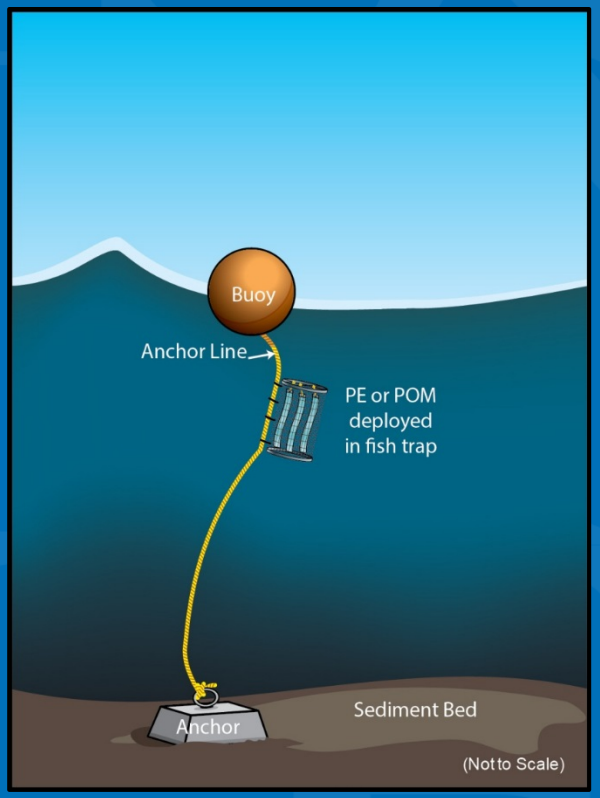
(NHEERL & MIT)

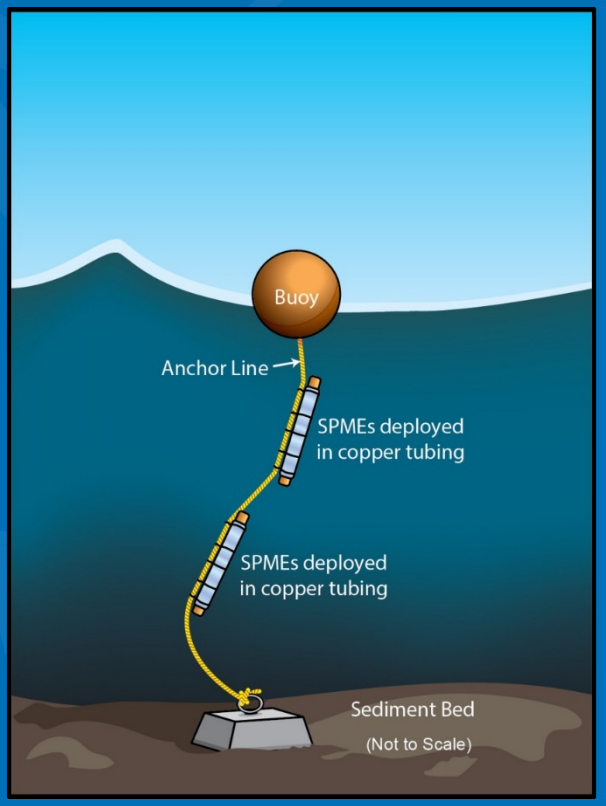
Passive Sampling: Deployment

United States Environmental Protection Agency

Water Column Deployments







Passive Sampling: Configurations

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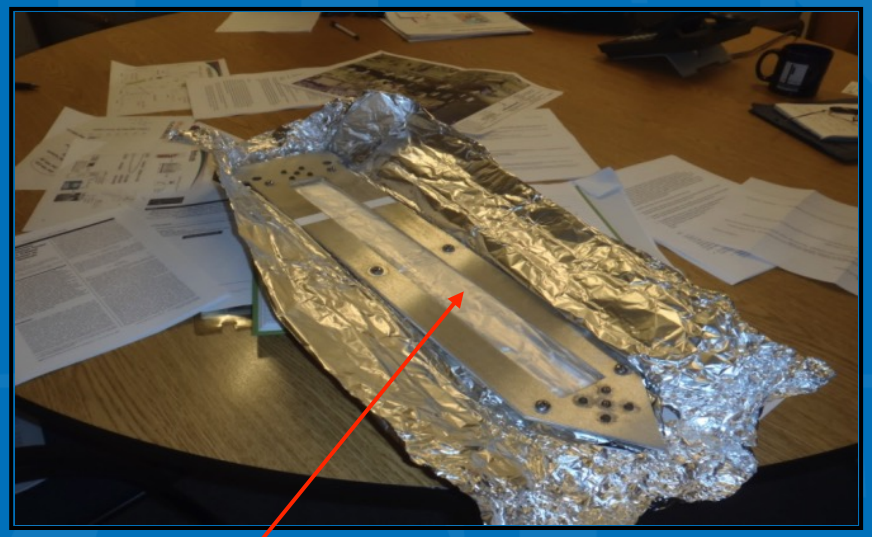
Porewater

SPME (in protective syringe in copper tubing housing surrounded with stainless steel mesh)

(SCCWRP)



(MIT)

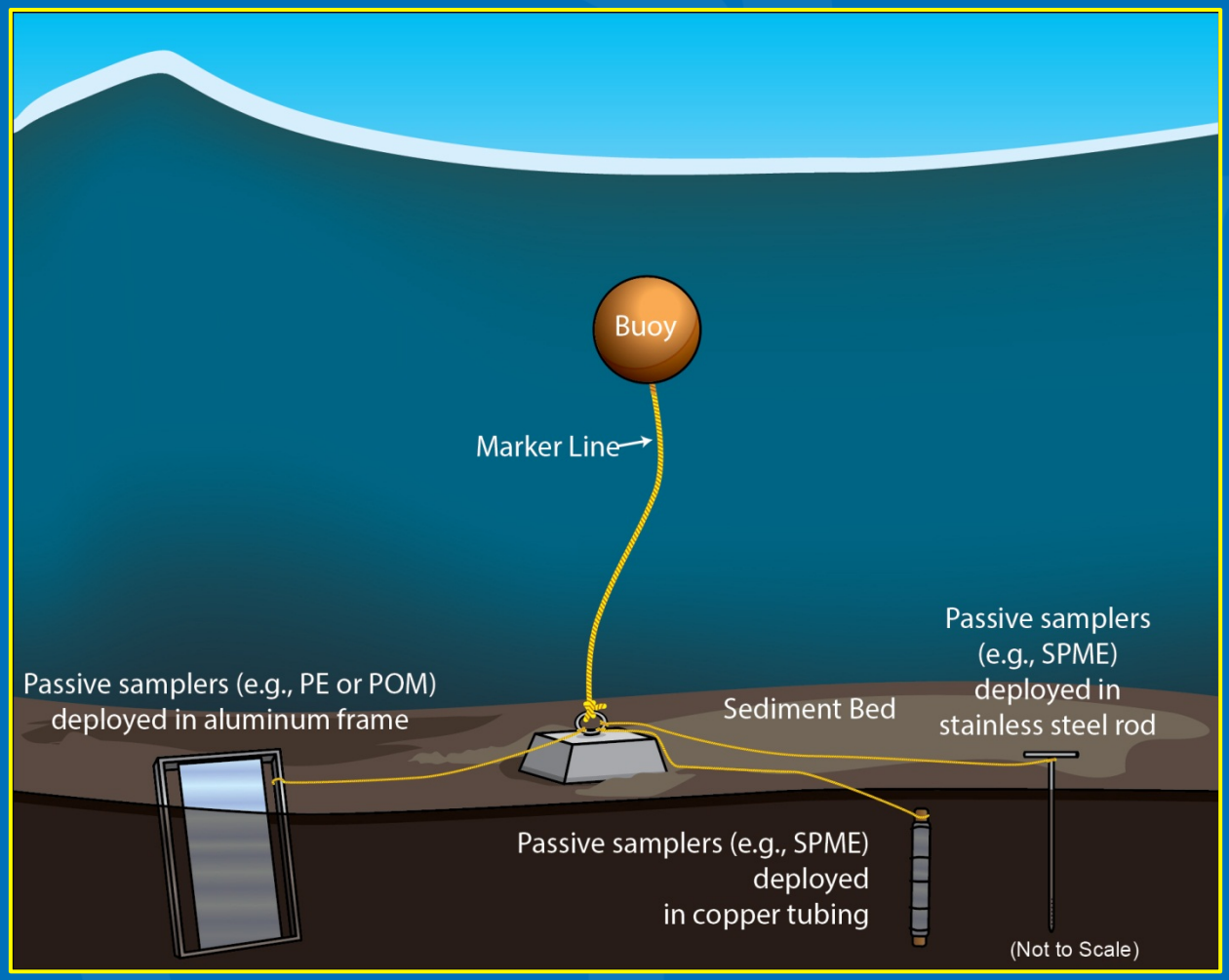
PE or POM (in aluminum frame)

SPME (inside stainless steel tube)

(Texas Tech U)

Passive Sampling: Deployment

Porewater Deployments



Passive Sampling: Principles

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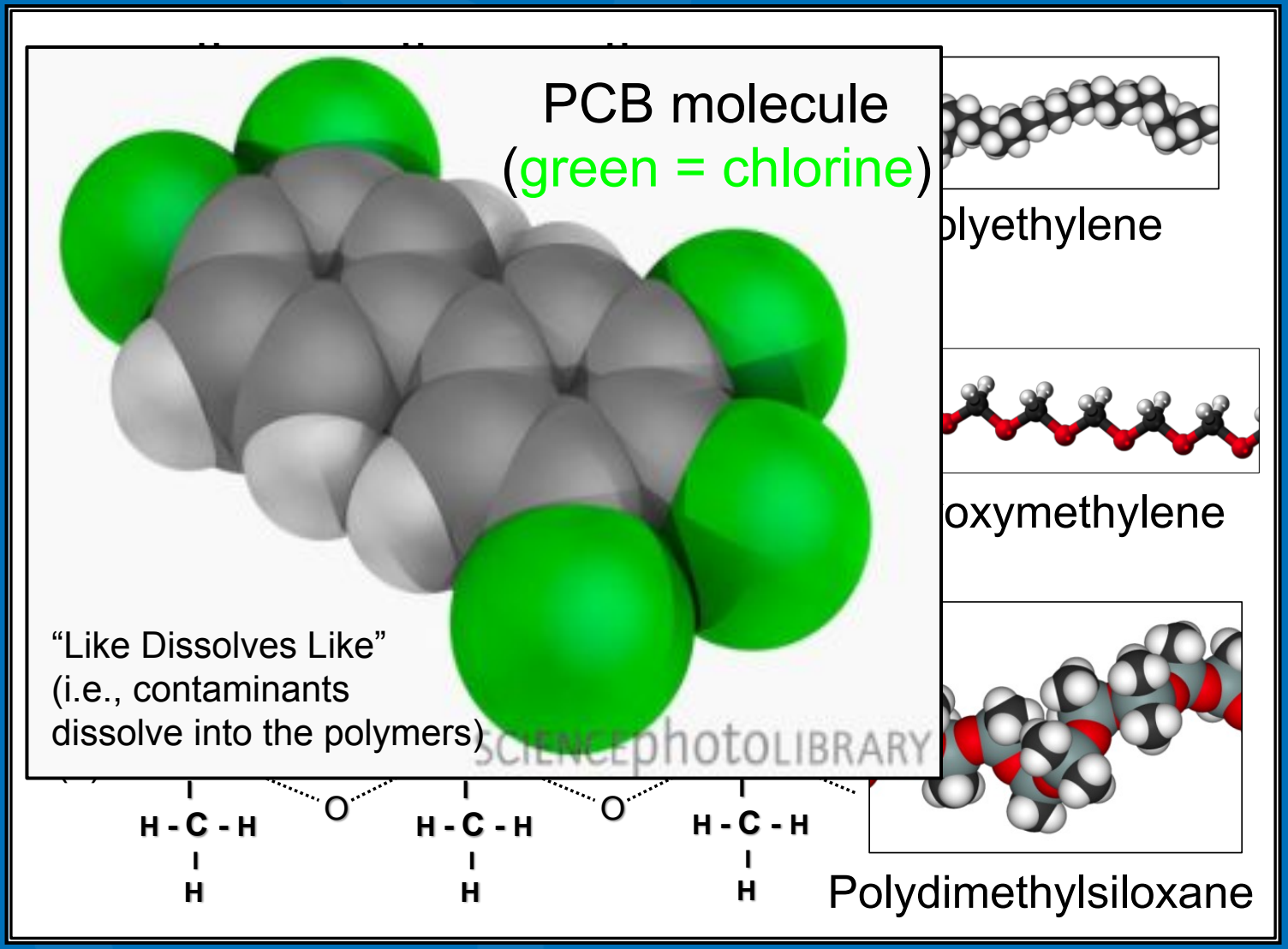
Atom Key:

Black = Carbon

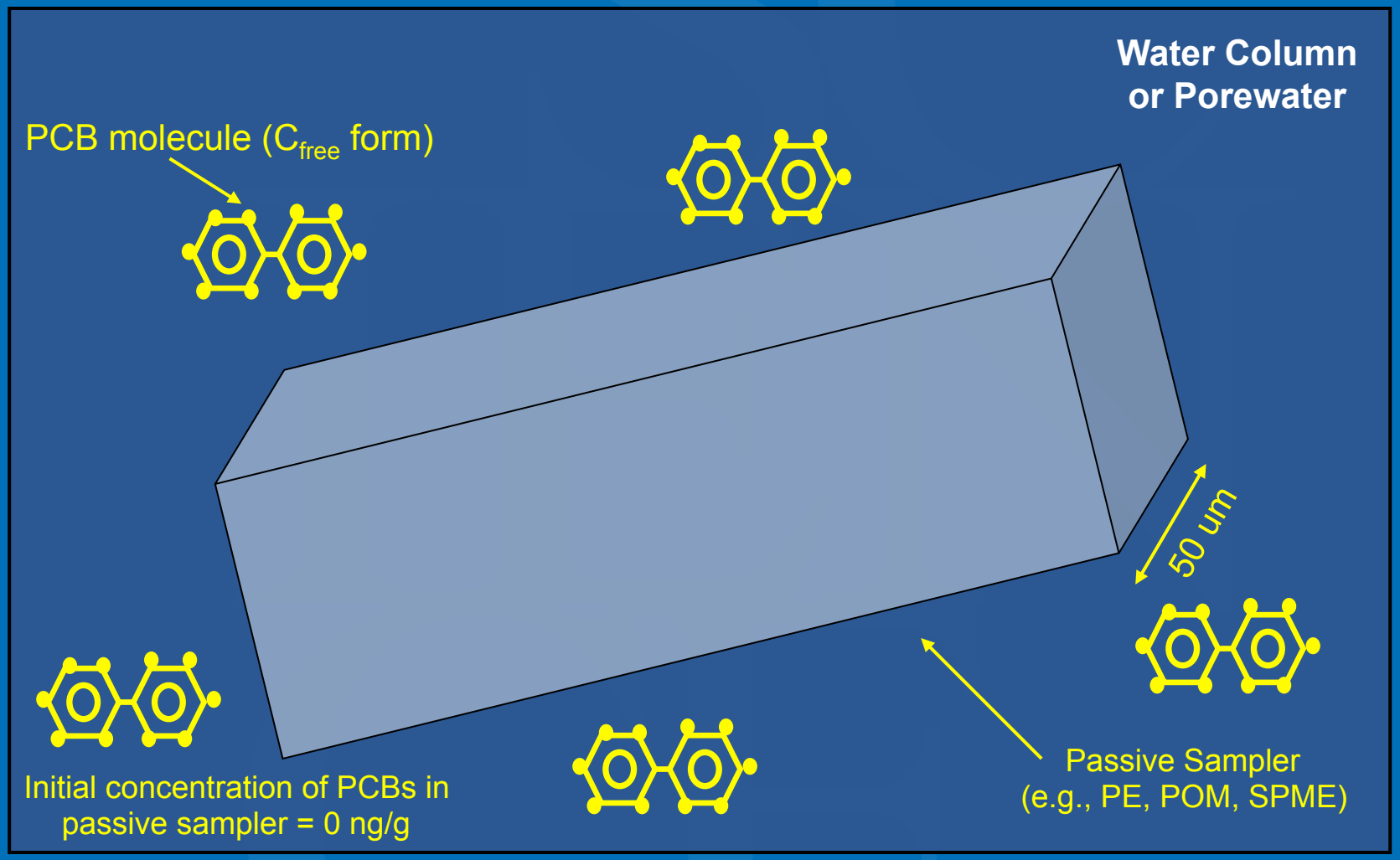
Red = Oxygen

Grey = Silicon



Passive Sampling: Principles

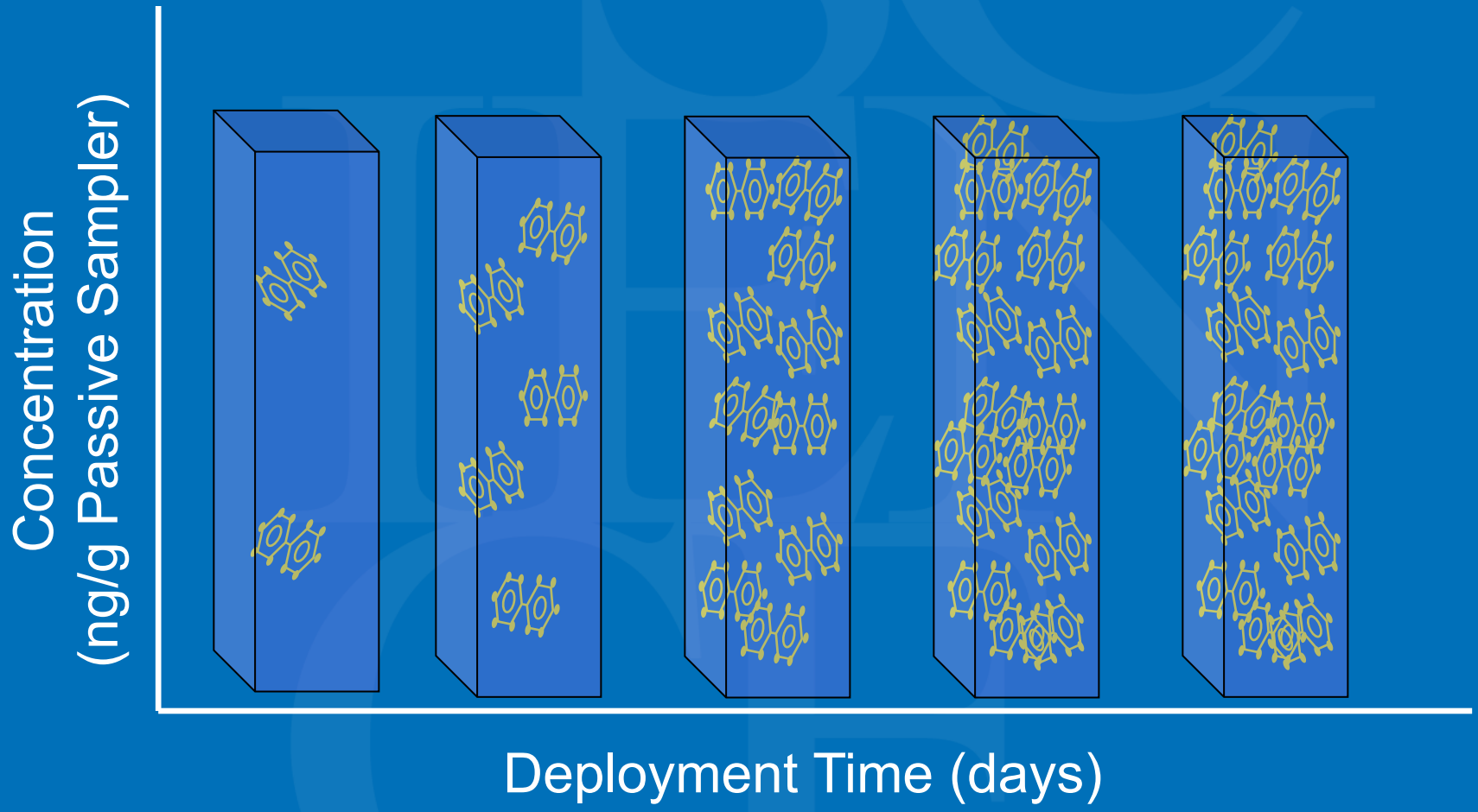
United States Environmental Protection Agency



Passive Sampling: Principles

United States Environmental Protection Agency

Equilibrium Sampling



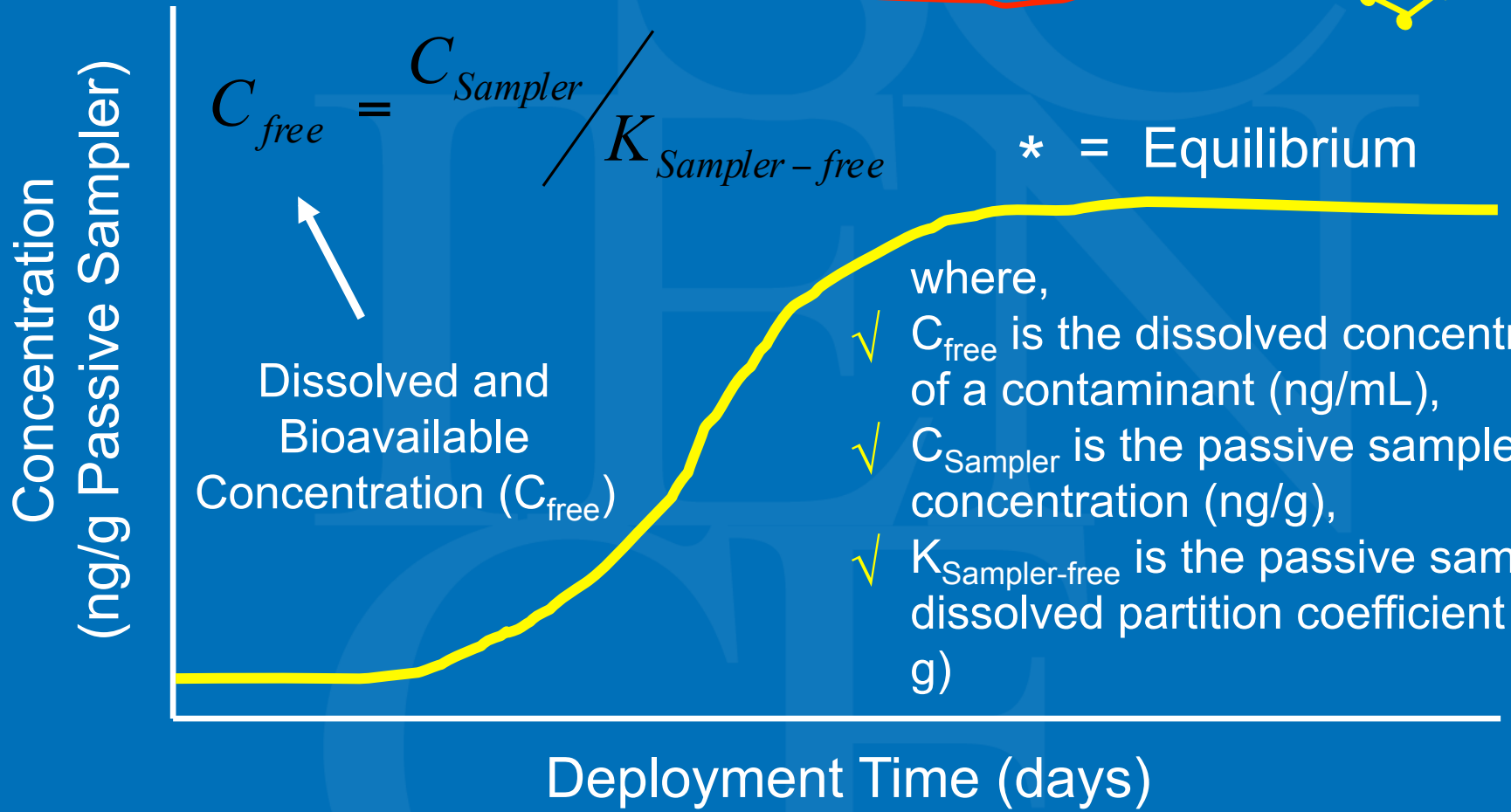
Passive Sampling: Principles

United States Environmental Protection Agency

Equilibrium Sampling

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

* = Equilibrium



where,

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

Objectives

- Investigate the use of passive samplers at three U.S. EPA Superfund sites
  - Compare the performance of four types of passive samplers
  - Background concentrations (e.g., before remediation)
  - Feasibility of using passive samplers
- Overall: Demonstrate the usefulness of passive sampling for evaluating bioavailable concentrations (C_{free}) for decision-making

Materials and Methods: Basics

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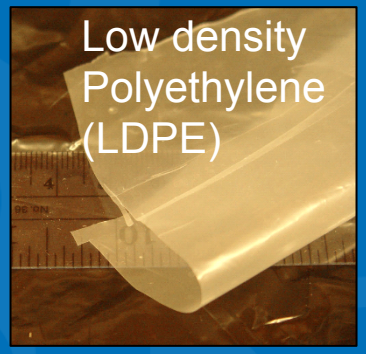
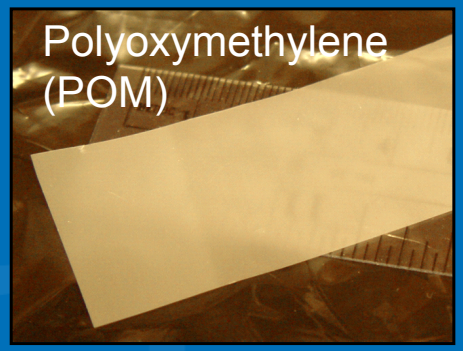
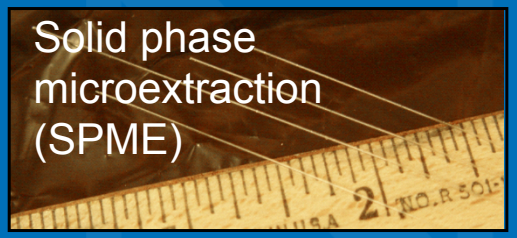
- Passive Samplers
  - Low density polyethylene (LDPE)
  - Polyoxymethylene (POM)
  - Solid phase microextraction (SPME)
  - Semi-permeable membrane devices (SPMD)
- Deployments
  - Water column
  - One meter above sediment surface (Palos Verdes Shelf: 1.2 – 5.2 m)
  - 21 to 29 days (Palos Verdes Shelf: 86 – 145 days)
  - Total Water (New Bedford Harbor)
- C_{free} Calculations
  - Deployed performance reference compounds (PRCs)
  - First order approach







M & M: Study Sites

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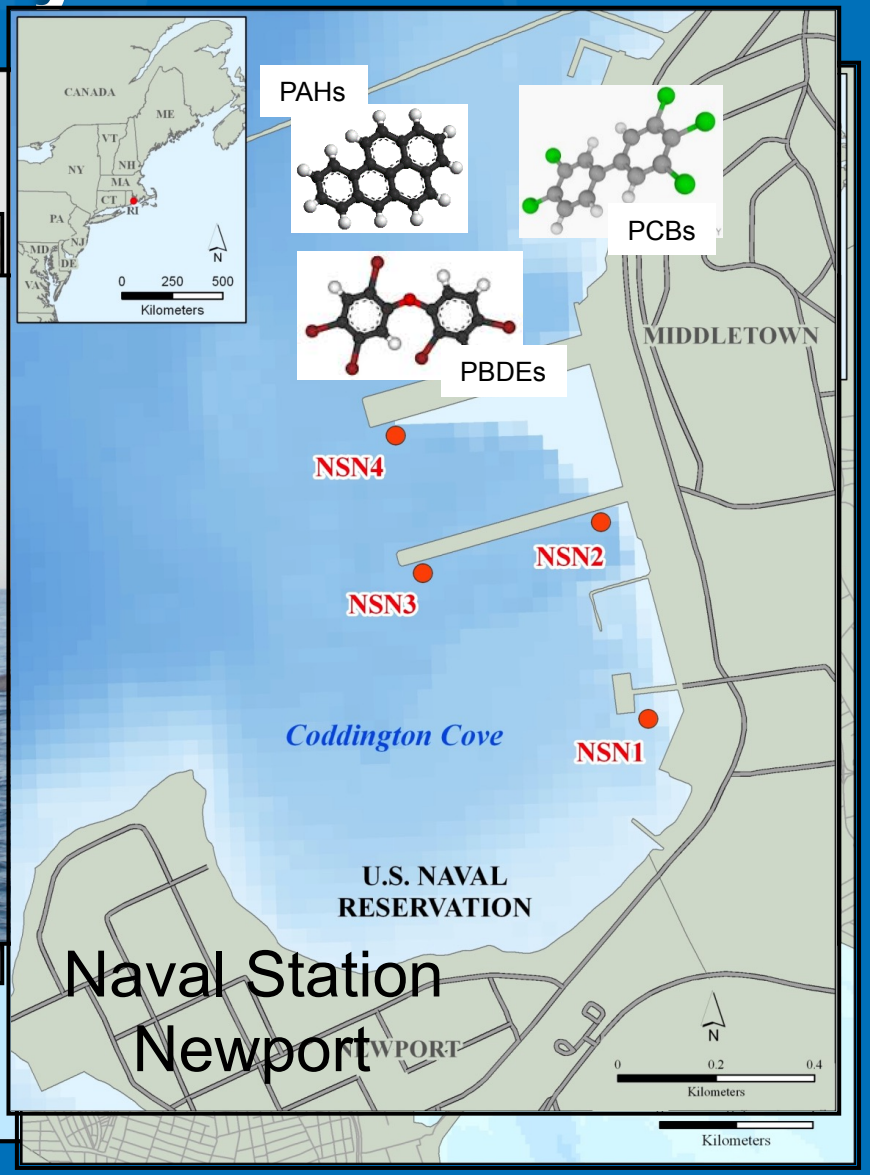
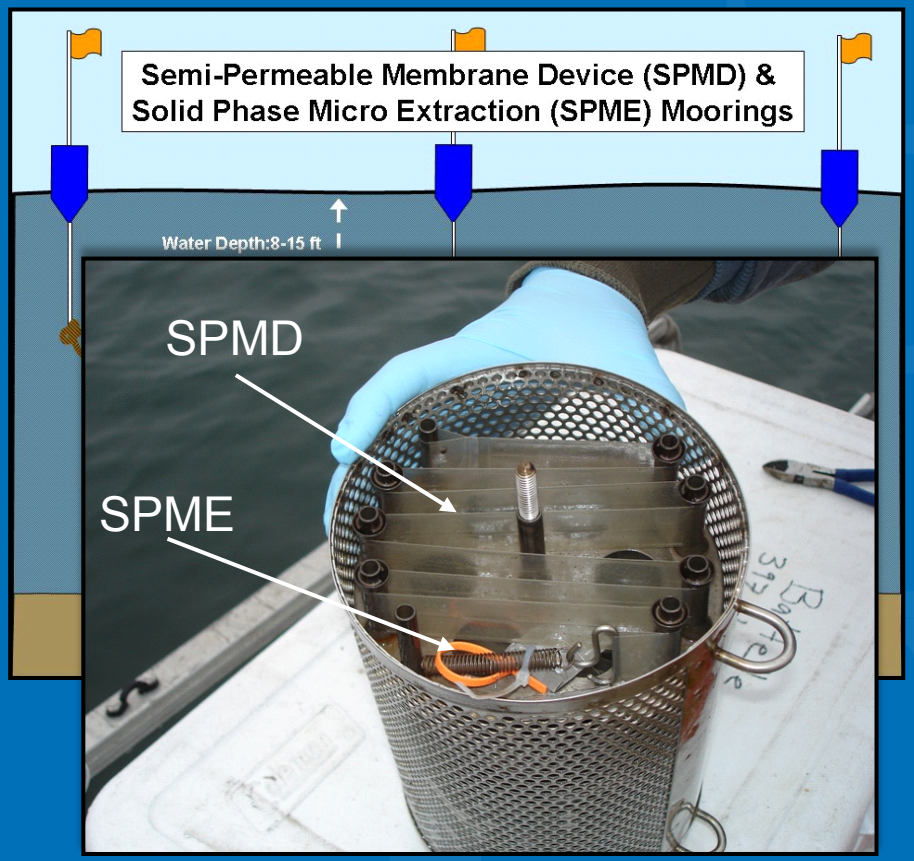
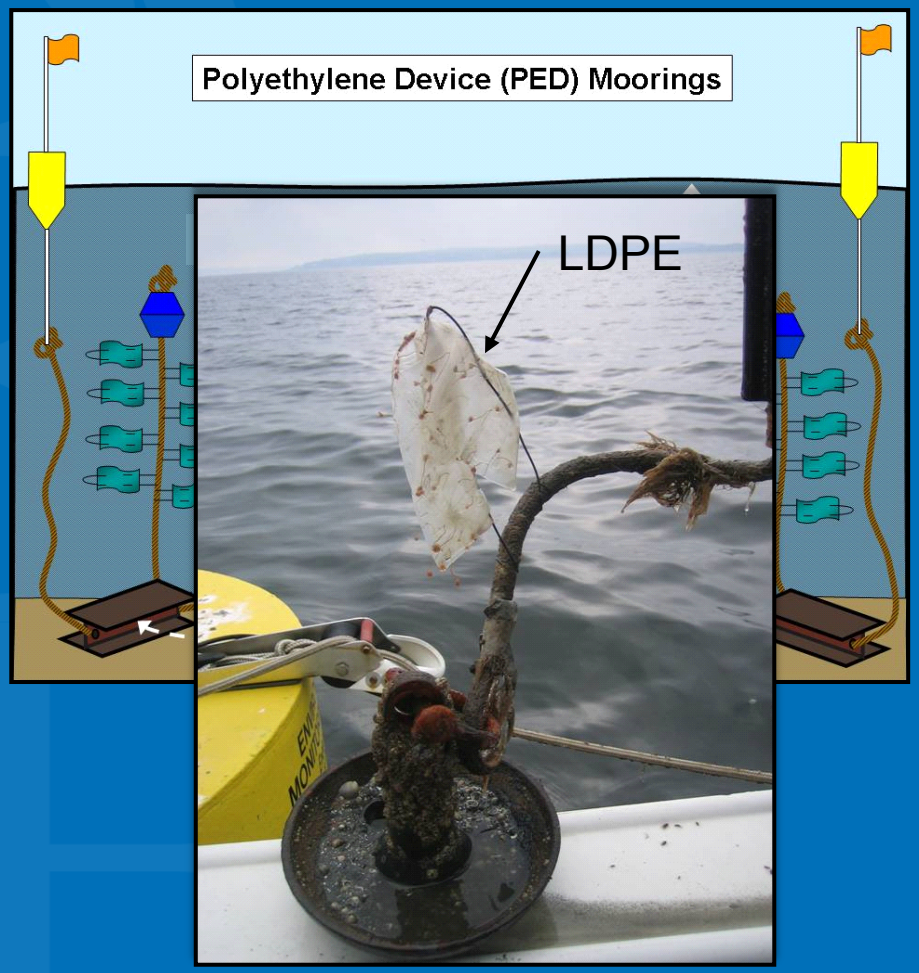


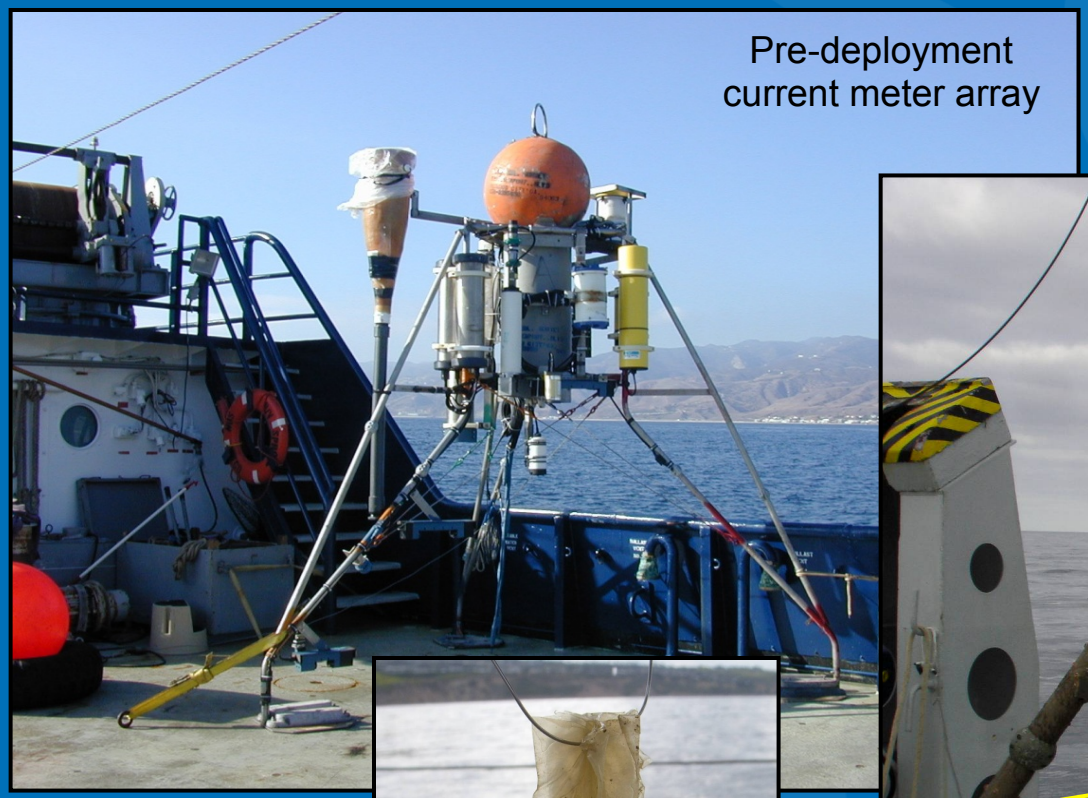
M & M: Passive Samplers

New Bedford Harbor





M & M: Passive Samplers



Palos Verdes Shelf

LDPE
passive sampler

M & M: Passive Samplers

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Naval Station Newport

Results: New Bedford Harbor

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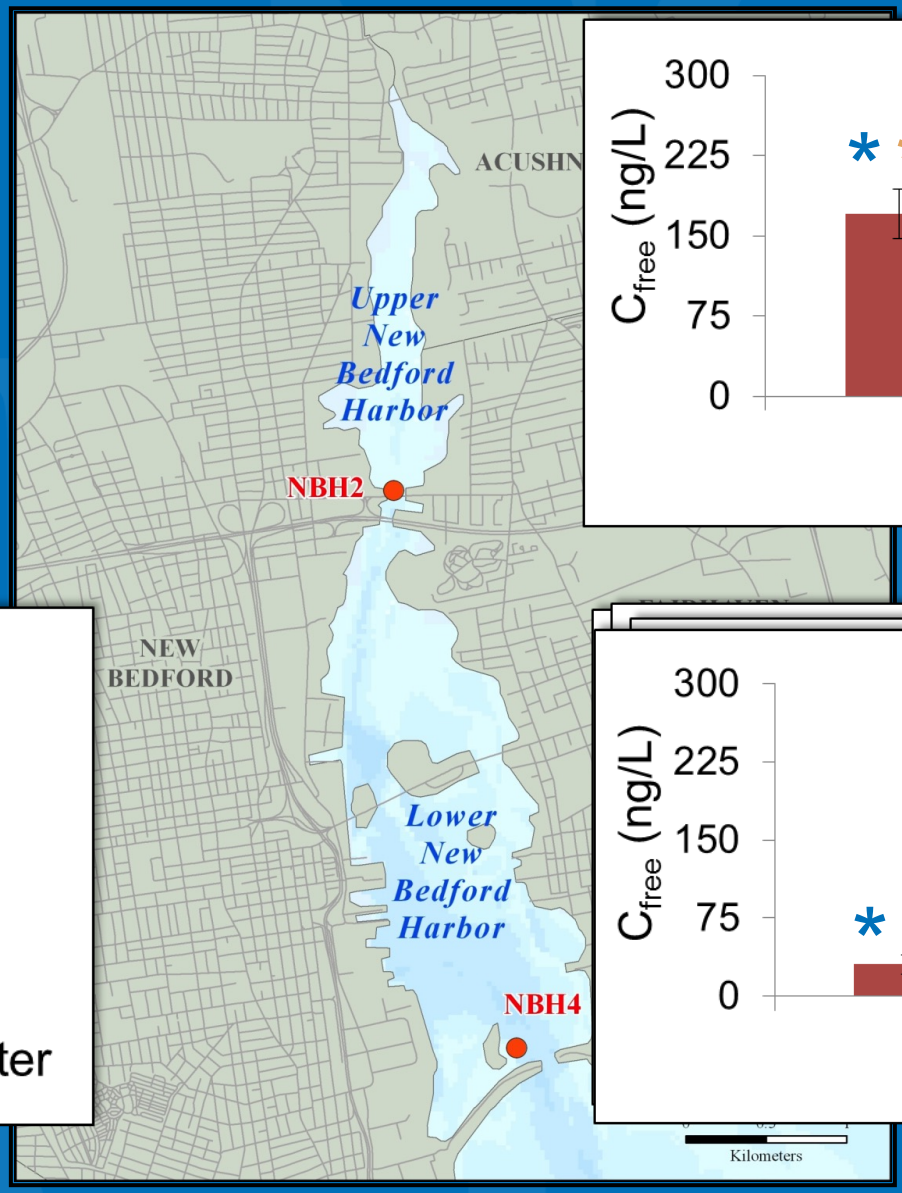
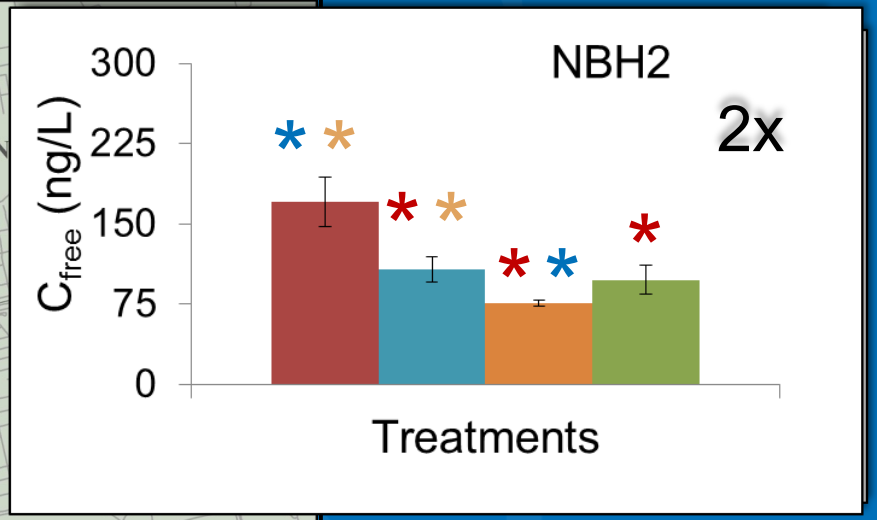
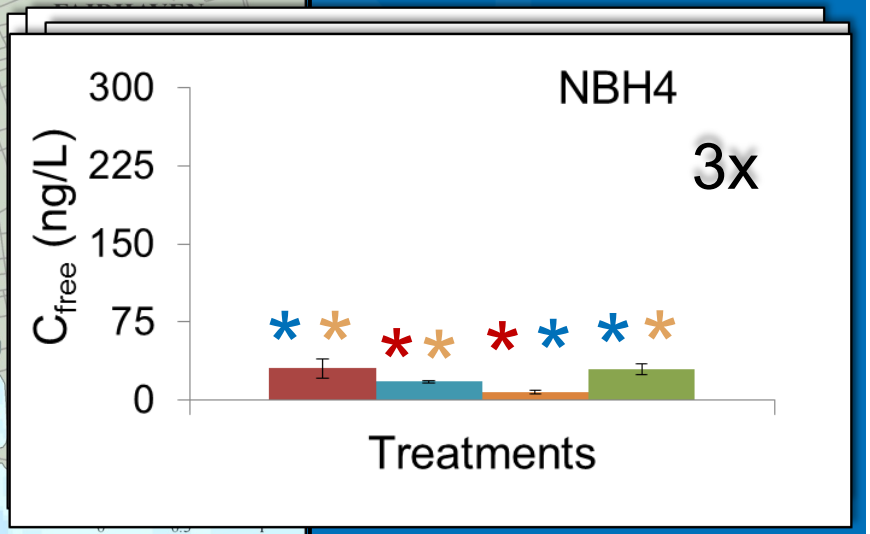
Total PCBs C_{free}



- LDPE
- SPME
- SPMD
- Total water





Results: Palos Verdes Shelf

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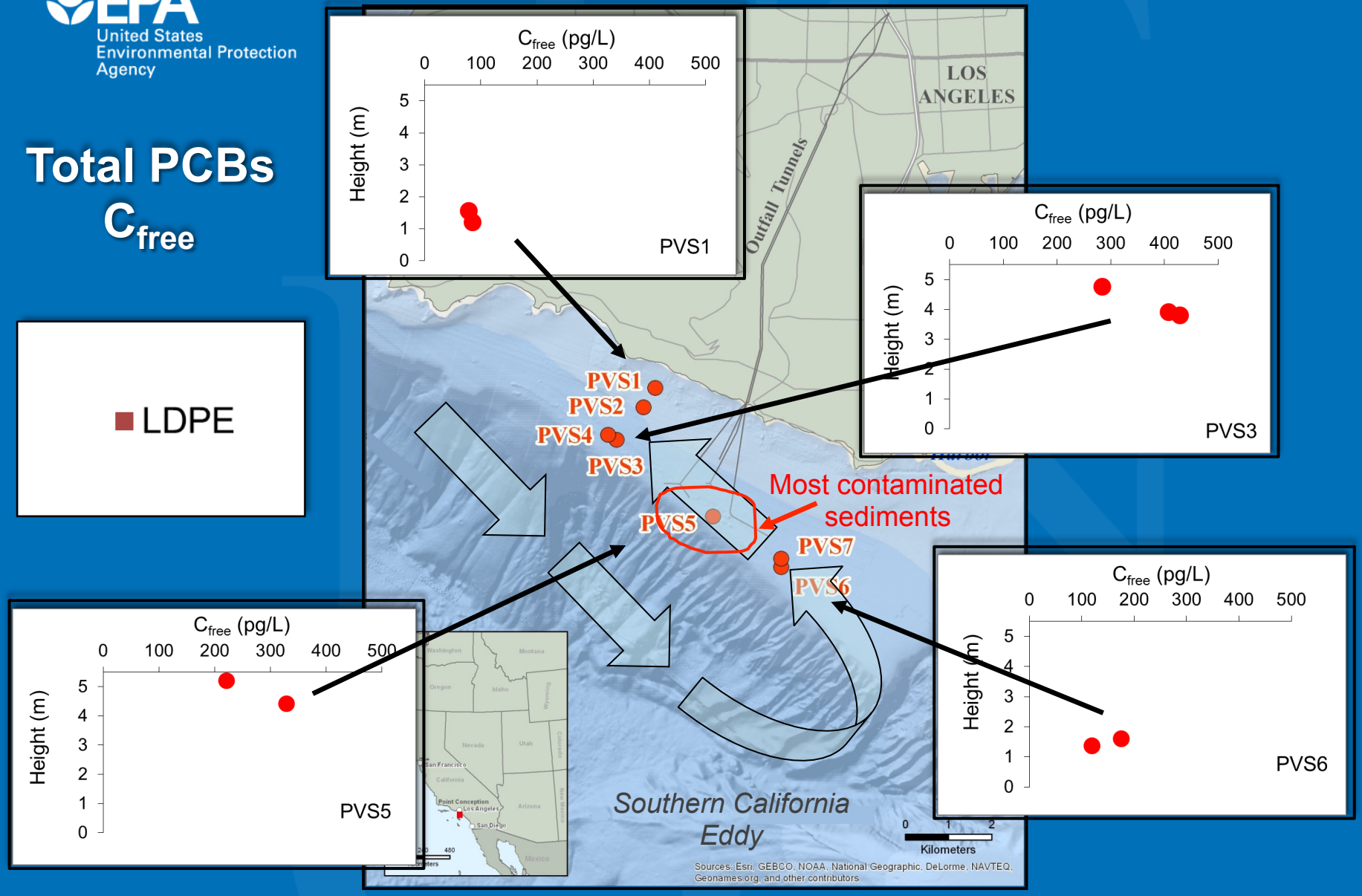
Total PCBs C_{free}

LDPE



Results: Naval Station Newport

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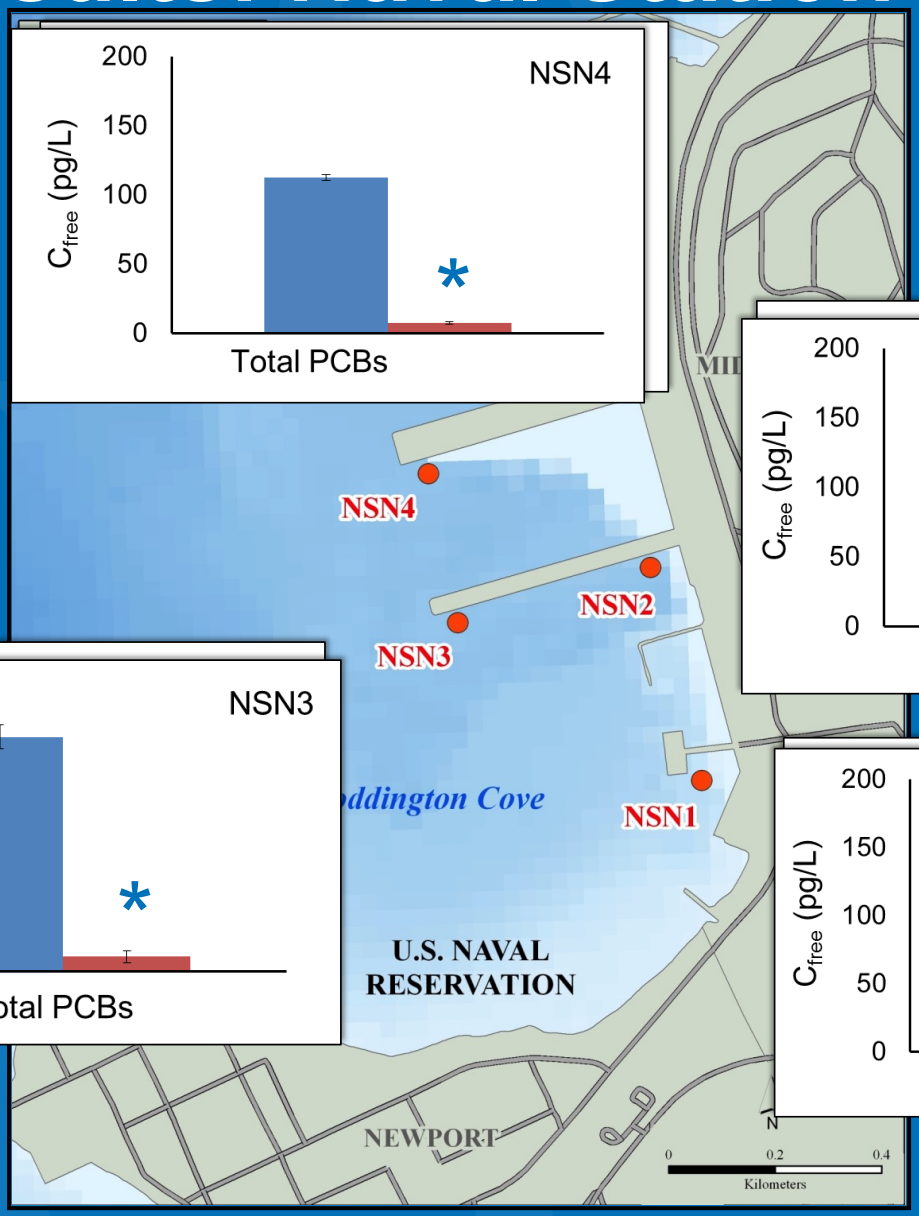
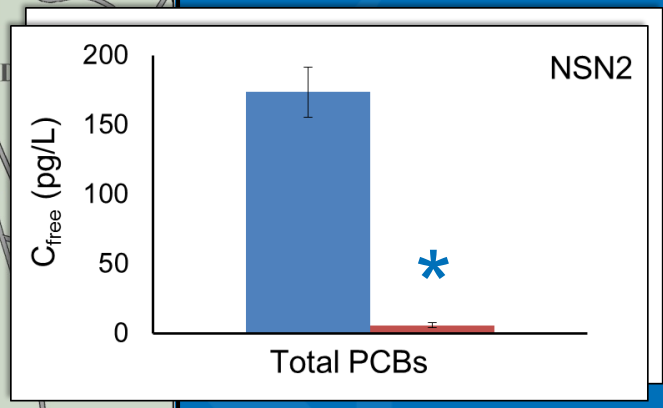
Total PCBs C_{free}

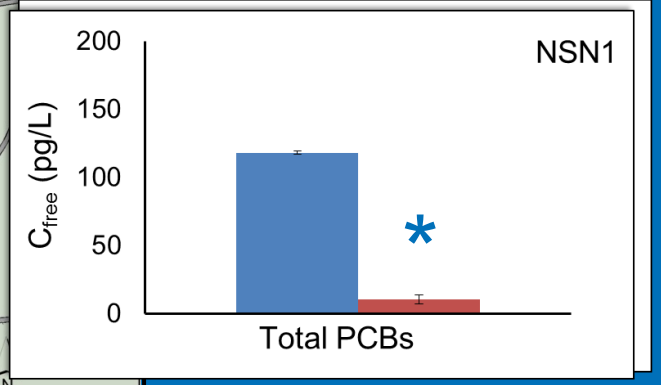
LDPE

POM

18x







Results: Naval Station Newport

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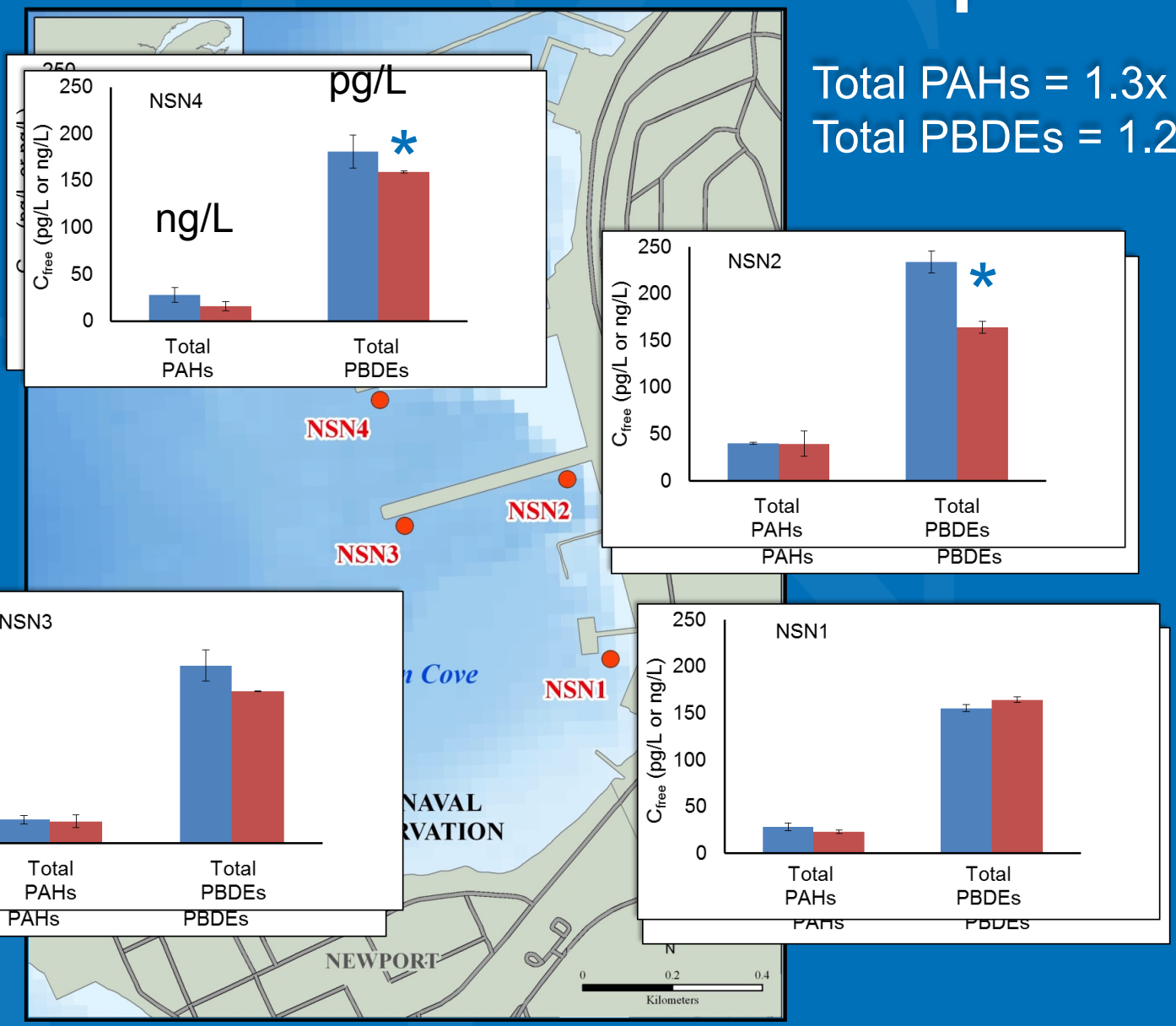
Total PAHs & Total PBDEs C_{free}

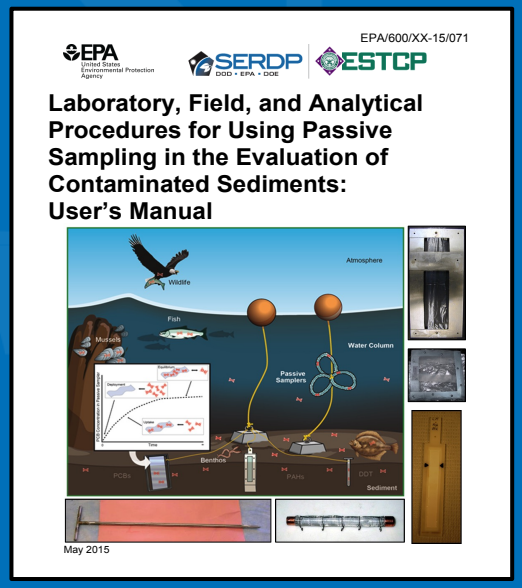
- LDPE
- POM

Total PAHs = 1.3x
Total PBDEs = 1.2x



Summary

- Passive sampling provided valuable information about contaminant water column C_{free}, a surrogate measure of bioavailability, at three Superfund sites
  - Background concentrations (All sites)
  - Feasibility of using passive sampling routinely (Palos Verdes Shelf)
  - Comparison of passive sampler performance (New Bedford Harbor & Naval Station Newport)
- Encouraging remedial project managers at Superfund sites to use passive sampling for evaluating contaminant bioavailability
  - Guidance document in preparation



Summary

- Guidance Document
  - Collaboration between Strategic Environmental Research and Development Program (SERDP), Environmental Security and Technology Certification Program (ESTCP), and U.S. Environmental Protection Agency
  - Intended to assist in developing standard operating procedures (SOPs)
  - Topics covered
    - Laboratory and field procedures for POM, SPME and LDPE
    - Use of performance reference compounds (PRCs)
    - Analytical procedures and quality assurance
    - Data analysis
    - References
  - Available early 2016

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Thank you