Application of Passive Sampling for Measuring Dissolved Concentrations ($C_{\text{free}}$) 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 $2 \times 10^6 \text{ m}^3$
PCB contaminated sediments)
Superfund Program

Remediation Process

- Evaluate site conditions
  - Include most contaminated sites

Extent and nature of contamination/ clean-up options

- Evaluate Bioavailability for Decision-Making
- Evaluate Bioavailability for Decision-Making
- Evaluate Bioavailability for Decision-Making

Remediation of site

- Remediation of site from NPL and redevelopment/restoration

Record of Decision

- Remedial Design/Action/Construction

NPL Delisting and Site Reuse

- Remedial Investigation/Feasibility Study

National Priority List (NPL) Site Listing Process

- Preliminary Assessment/Site Inspection
Passive Sampling

• New environmental sampling technology
  - Scientifically-robust (i.e., dissolved concentrations sampled ($C_{\text{free}}$))
  - Possibly less expensive
  - Relatively simple

• Provide two types of information
  1. Dissolved contaminant concentrations in water around passive sampler ($C_{\text{free}}$)
     - Surrogate for bioavailable concentrations
     - Porewater (Interstitial Water) and Water column
  2. Concentration of contaminants in passive sampler
     - Evidence of correlation with bioaccumulation by aquatic organisms

• Superfund Program
  - Considered a better tool for performing evaluations of contaminant bioavailability at Superfund sites

![Graph showing Bioaccumulation (µg/g lipid) vs. Total Concentration (µg/g dry sediment)](image-url)
Passive Sampling: Types

Polyethylene (PE)

- 25 - 50 µm thick

Polyoxymethylene (POM)

- 75 µm thick
Passive Sampling: Types

Solid Phase Microextraction (SPME)

- fiber-optic cable
- 2.5 cm length
- 210 um inner glass core
- 10 - 100 um outer polydimethylsiloxane (PDMS) coating

SPME

Semi-Permeable Membrane Device (SPMD)

- Cross-section SPMD
- 2.5 cm length
- triolien layer
- 50 - 95 um thick polyethylene shell containing synthetic lipid triolien

Not Used in Sediments
Passive Sampling: Configurations

Water Column

- PE
- POM
- SPME (in copper mesh envelope)
- Stainless steel ring
- Minnow trap

(NHEERL & Brown U)

(NHEERL & MIT)
Passive Sampling: Deployment

Water Column Deployments

- Buoy connected to anchor line
- PE or POM deployed on wire loops
- Sediment Bed (Not to Scale)

- Buoy connected to anchor line
- PE or POM deployed in fish trap
- Sediment Bed (Not to Scale)

- Buoy connected to anchor line
- SPMEs deployed in copper tubing
- Sediment Bed (Not to Scale)
Passive Sampling: Configurations

Porewater

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

SPME (inside stainless steel tube)

PE or POM (in aluminum frame)

(Texas Tech U)
Passive Sampling: Deployment

Porewater Deployments

- Buoy
- Marker Line
- Passive samplers (e.g., PE or POM) deployed in aluminum frame
- Sediment Bed
- Passive samplers (e.g., SPME) deployed in stainless steel rod
- Passive samplers (e.g., SPME) deployed in copper tubing

Office of Research and Development
National Health and Environmental Effects Research Laboratory, Atlantic Ecology Division, Narragansett, RI, USA
National Environmental Monitoring Conference, 13-17 July 2015, Chicago, IL, USA
Passive Sampling: Principles

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

Polyethylene

Polyoxymethylene

Polydimethylsiloxane

Atom Key:
Black = Carbon
Red = Oxygen
Grey = Silicon

PCB molecule (green = chlorine)
Passive Sampling: Principles

Initial concentration of PCBs in passive sampler = 0 ng/g

PCB molecule (C_{free} form)

Water Column or Porewater

Passive Sampler (e.g., PE, POM, SPME)
Passive Sampling: Principles

Equilibrium Sampling

![Diagram showing Equilibrium Sampling](image)

\[ C_{\text{free}} = \frac{C_{\text{Sampler}}}{K_{\text{Sampler-free}}} \]

where,

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

Dissolved and Bioavailable Concentration (C_{\text{free}})

Deployment Time (days)
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 ($C_{\text{free}}$) for decision-making
Materials and Methods: Basics

- **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

New Bedford Harbor

Palos Verdes Shelf

Blue Whale Naval Station

PCBs

PAHs

PBDEs

PCBs

National Environmental Monitoring Conference, 13-17 July 2015, Chicago, IL, USA
M & M: Passive Samplers

New Bedford Harbor

Semi-Permeable Membrane Device (SPMD) & Solid Phase Micro Extraction (SPME) Moorings

Polyethylene Device (PED) Moorings

SPMD

SPME

LDPE
M & M: Passive Samplers

Pre-deployment current meter array

Palos Verdes Shelf

Post-deployment current meter array

LDPE passive sampler
M & M: Passive Samplers

Naval Station Newport

Subsurface flotation

Extended minnow trap containing

Anchor

LDPE and POM

Naval Station Newport
Results: New Bedford Harbor

Total PCBs $C_{\text{free}}$

- **NBH2**
  - 2x
  - $C_{\text{free}}$ (ng/L)
  - 23
  - * *

- **NBH4**
  - 3x
  - $C_{\text{free}}$ (ng/L)
  - * * * * * * * * * *
  - 75

**Graphs**:
- LDPE
- SPME
- SPMD
- Total water

- **Upper New Bedford Harbor**
- **Lower New Bedford Harbor**
Results: Palos Verdes Shelf

Total PCBs $C_{\text{free}}$

- **LDPE**

Most contaminated sediments

Southern California Eddy

Sources: ESRI, GOECO, NOAA, National Geographic, DeLorme, NAVTEQ, & other contributors.
Results: Naval Station Newport

Total PCBs

C_{\text{free}}

LDPE

POM

Results for NSN4:

- C_{\text{free}} (pg/L): 18x
- Total PCBs: *

Results for NSN2:

- C_{\text{free}} (pg/L): *
- Total PCBs: *

Results for NSN3:

- C_{\text{free}} (pg/L): *
- Total PCBs: *

Results for NSN1:

- C_{\text{free}} (pg/L): *
- Total PCBs: *
Results: Naval Station Newport

Total PAHs & Total PBDEs

\[ C_{\text{free}} = \frac{\text{Total PAHs}}{\text{Total PBDEs}} \]

**C_{\text{free}}**

- **LDPE**
- **POM**

**Results:** Naval Station Newport

**Total PAHs = 1.3x**

**Total PBDEs = 1.2x**
Summary

• Passive sampling provided valuable information about contaminant water column $C_{\text{free}}$, 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
Thank you