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

Atmosphere

Wildlife

Water

Mussels

Fish

Interstitial Water

Dissolved and Bioavailable Concentration

Benthic Worms

Diffusion/Advection

(Not to Scale)

U.S. EPA NARPM 2011
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, lipophilic and bioaccumulating (medium to large $K_{ow}$)
      - 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
   - Emulate 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

- Atmosphere
- Water
- Passive Samplers
- Contaminated Sediments (Not to Scale)

Diagram includes:
- Mussels
- Fish
- Benthic Worms
- Dissolved and Bioavailable Concentration
- Eagles

The diagram illustrates the flow of contaminants from contaminated sediments through water to aquatic life and ultimately to wildlife.
Types of Passive Samplers

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

- SPME
  - 75 um thick

- PED
  - 50 um thick

- POM
  - 75 um thick

- SPMD (polyethylene tubing containing triolien)
  - 70 – 95 um thick
  - 2.5 cm
  - 0.25 m

U.S. EPA NARPM 2011
Passive Sampler Deployment

**Water Column**

- PED
- POM
- SPME (in copper mesh envelope)
- SPMD
- SPME (in stainless steel mesh cover)

(NHEERL & Brown U)

(NRMRL & Battelle)

U.S. EPA NARPM 2011
Passive Sampler Deployment

Sediment

- SPME (in protective syringe)
- Copper tubing housing
- PED (in aluminum frame)

U.S. EPA NARPM 2011
Passive Sampler Deployment

Polyethylene Device (PED) Moorings

- 25μm & 51μm PEDs
- Water Depth: 3-15 ft
- ~3 ft
- ~15 ft

U.S. EPA NARPM 2011
## Passive Sampler Costs ($/sampler)\textsuperscript{a,b}

<table>
<thead>
<tr>
<th>Type</th>
<th>Materials (samplers and deployment equipment)</th>
<th>Preparation (dialysis)</th>
<th>Chemical Analyses</th>
<th>Total</th>
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<tbody>
<tr>
<td>Water (5 L)</td>
<td>&lt;5</td>
<td>-</td>
<td>525</td>
<td>530</td>
</tr>
<tr>
<td>SPMD</td>
<td>350</td>
<td>115</td>
<td>350</td>
<td>815</td>
</tr>
<tr>
<td>SPME</td>
<td>~35</td>
<td>-</td>
<td>275</td>
<td>~310</td>
</tr>
<tr>
<td>PED</td>
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<td>-</td>
<td>375</td>
<td>~390</td>
</tr>
<tr>
<td>POM</td>
<td>~50</td>
<td>-</td>
<td>375</td>
<td>~425</td>
</tr>
</tbody>
</table>

\textsuperscript{a} 2011 Battelle costs (L Lefkovitz, Duxbury, MA, USA)

\textsuperscript{b} Assume 10 - 20 samples, GC/MS analysis of NOAA PCB list (20 congeners)
Water Column

PCB molecule

Passive Sampler (e.g., PED or POM)

Initial concentration of PCBs in passive samplers = 0 ng/mL

Passive Sampler Theory
Passive Sampler Theory

Equilibrium Sampling

Deployment Time (days)

Concentration (ng/mL Passive Sampler)
Passive Sampler Theory

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

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

Apparent equilibrium
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 bioaccumulation

- Critical for determining how to interpret passive sampler data

- Data on passive sampler accumulation to animal bioaccumulation

- Solution: Generate general linear models

Animal Concentration (ng/g) = \alpha + \beta \times \text{PED Concentration (ng/mL)}

\text{PED Concentration (ng/mL)} = \frac{100000}{\text{Mussels}}

\text{Correlation Coefficient: } r^2 = 0.88

1:1 Line

U.S. EPA NARPM 2011
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)

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

Passive Sampler-based Total Dissolved PCBs versus AWQC (prior to remediation)

Aquatic Life
AWQC

Human Health
AWQC

Concentration (pg/L)

Station

B1  B2  B3A  B3B  B5  B6A  B6B
Passive Sampler Application
SAMS guidance document in preparation for using 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