Passive Sampling Techniques:
Measuring Hydrophobic Organic Contaminants in Sediment Porewater and Surface Water

Matt Lambert
U.S. Environmental Protection Agency, Office of Superfund Remediation and Technology Innovation, Science Policy Branch

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

Solid-phase Microextraction

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

Polyoxymethylene

Polyethylene
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…

Observed Tissue (µg/kg lipid) vs Predicted Tissue = $C_{free} \times K_{ow}$

PCBs & PAHs

in oligochaetes

How does it work?

(a) Deployment

(b) Uptake

(c) Equilibrium
Time Averaged Sample

- Actual Concentration
- Passive Sampler-Based Concentration
- Storm Event
Cost Estimate for Different Types of Sampling

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

<table>
<thead>
<tr>
<th>Type of Sample</th>
<th>Materials ($)</th>
<th>Chemical Analysis ($)</th>
<th>Total ($)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (5 L by conventional method)</td>
<td>&lt;5</td>
<td>525</td>
<td>530</td>
</tr>
<tr>
<td>Semi-permeable Membrane Device (SPMD)</td>
<td>505</td>
<td>400</td>
<td>905</td>
</tr>
<tr>
<td>Polyethylene (PE)</td>
<td>~5</td>
<td>375</td>
<td>380</td>
</tr>
<tr>
<td>Polyoxymethylene (POM)</td>
<td>~50</td>
<td>375</td>
<td>425</td>
</tr>
<tr>
<td>Solid Phase Micro-extraction (SPME)</td>
<td>~35</td>
<td>275</td>
<td>310</td>
</tr>
</tbody>
</table>
Deployment Methods: Surface Water

Polyethylene Device (PED) Moorings

Water Depth: 8-15 ft

25 µm & 51 µm PEDs

~3 ft

YSI Sonde

~15 ft
Deployment Methods: Sediment Porewater

Passive samplers (e.g., SPME) deployed in copper tubing
Passive samplers (e.g., PE or POM) deployed in stainless steel rod
Passive samplers (e.g., PE or POM) deployed in aluminum frame

PE & Frame
SPME & Casing
POM
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
Performance Reference Compounds (PRCs)

Measured HOC

PRC

HOC Concentration (ng/mL Passive Sampler)

Deployment Time (days)

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)

Sediments – PEs & POMs (flux platform deployment)
Sediment Monitoring Platform in Place
Passive Sampler-based Total Dissolved PCBs versus Ambient Water Quality Criteria (AWQC) (prior to remediation)

Station

B1 B2 B3A B3B B5 B6A B6B

Concentration (pg/L, ppQ)

0 60 200 400 600 800 1000

Aquatic Life AWQC

Human Health AWQC

30,000

PCBs Prior to Remediation
In Situ Sediment Core Analysis: SPME
**In Situ Sediment Core Analysis (cont.): SPME**

124B1-WC

**Estimated MU, o-E, p-E (ng/L)**

- **p,p’-DDMU**
- **o,p’-DDE**
- **p,p’-DDE**
- **MDL-MU**
- **MDL-oE**
- **MDL-pE**
- **124B1sed**

147B4-WC

**Estimated MU, o-E, p-E (ng/L)**

- **p,p’-DDMU**
- **o,p’-DDE**
- **p,p’-DDE**
- **MDL-MU**
- **MDL-oE**
- **MDL-pE**
- **147B4sed**
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
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