Polyethylene Passive Samplers for Quantifying Dissolved Hydrophobic Organic Contaminants in Aquatic Environments

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Outline

• Introduction & Motivation
• Hydrophobic Organic Contaminants & Regulatory Concern
• Partitioning and Time to Equilibrium
• PED Field Measurements: Boston Harbor
• PED & SPME Laboratory Measurements
• Pyrethroids
• Conclusions
Introduction & Motivation: Dissolved Phase & Passive Samplers

**Freely Dissolved Phase**

- This freely dissolved fraction is of interest as it is the bioavailable fraction (does not include DOM-bound fraction)

- **Low concentrations make it difficult to measure chemicals!**

**Passive Samplers**

- Mussel Watch

- Semipermeable Membrane Devices (SPMDs)

- Solid Phase Microextraction (SPMEs)

- **Polyethylene Devices (PEDs):** Passive samplers used to measure the activity or fugacity of HOCs in the environment based on the partitioning of HOCs between polyethylene & water.
Hydrophobic Organic Contaminants (HOCs)

Polycyclic Aromatic Hydrocarbons (PAHs)
- sources:
  - combustion of fossil fuels and wood (non-point source)
  - oil spills (point source)
- toxic, carcinogenic, & mutagenic

Polychlorinated Biphenyls (PCBs)
- manufactured in the U.S. between 1929 & 1979 as insulating fluids in transformers and capacitors (tradename: Arochlor)
- estimated that General Electric released between 200,000 to 1.3 million pounds of PCBs into the Hudson River between the 1940’s and 1977 (EPA, 2000)
- toxic (neurological, developmental, reproductive problems) and carcinogenic
Hydrophobic Organic Contaminants (HOCs)

Dichloro-Diphenyl-Trichloroethane (DDT) and Metabolites (DDE, DDD)

- insecticide used during WWII and after
- banned in the US in 1972—now world-wide (with exception for vector control—India & China)
- estimated that Montrose Chemical released (via Joint Power Pollution Control Plant) 1700 tons of DDT from the late 1950s to early 1970s on Palos Verdes shelf
- toxic, thinning of eggshells

Chlorinated Pesticides

- chlordane and heptachlor
- insecticide banned in U.S. in 1988
Hydrophobic Organic Contaminants (HOCs)

Pyrethroids

• current-use synthetic insecticides

• uses for agricultural crops, nurseries, urban structures and landscaping, home/garden

• In 2004, 1.4 million lbs sold in California (Spurlock & Lee, 2008)

• acute toxicity to aquatic organisms ($LC_{50} = 0.4 \mu g/L; Daphnia magna$)
Regulatory & Environmental Concerns

- PAHs, PCBs, DDT, chlordane are all contaminants of concern
  - California’s 303(d) List of Impaired Water Bodies
  - Total Maximum Daily Loads

- Pyrethroids emerging contaminants of concern

- Ballona Creek Estuary TMDL recommends improved water quality methods
  - Current MDLs are 0.05 μg/L to 0.1 μg/L for PAHs, PCBs, and pesticide
  - PEDs allow for MDLs ranging from 0.04 pg/L (PCB 180) to 0.015 ng/L (phenanthrene)

- Contaminants in the freely dissolved fraction are the bioavailable fraction are most closely correlated to chemical toxicity
PEDs: Polyethylene Devices

Strip of low-density polyethylene
2.5 cm wide, 43 cm long, & 25, 51, or 70 μm thick
Equilibrium Partitioning

\[ K_{PEW} = \frac{C_{PE}}{C_{W}} \]

For pyrene, 
\[ K_{PEW} = 100,000 \, (\text{mol/kg}_{PE})/(\text{mol/L}_{W}) \] so

100,000 mols/ 1 mol/
1 kg plastic 1 L water

where \( K_{PEW} \) is the equilibrium polyethylene-water partitioning coefficient,
\( C_{PE} \) is the chemical concentration in the polyethylene, and
\( C_{W} \) is the chemical concentration in the water.
Time to equilibrium (i.e., $k_{\text{exchange}}$)

$$C_{W\infty} = \frac{C_{PET}}{(1 - e^{-k_et}) \cdot K_{PEW}}$$

where $C_{W\infty}$ is the chemical concentration in the water at equilibrium, $C_{PET}$ is the chemical concentration in the polyethylene at time $t$, $k_e$ is the exchange rate coefficient and $K_{PEW}$ is the equilibrium polyethylene-water partitioning coefficient.
Time to Equilibrium Dependent on Percentage of Solute Finally Taken up by Sampler

Uptake by a plane sheet from a stirred solution where

\[ D \text{ is the diffusion coefficient, } t \text{ is time, and } l \text{ is one-half of the sheet thickness} \]

Numbers on curves indicate the percentage of solute finally taken up by the sheet (Crank, 1975)

Pyrene: Time for 50% Equilibrium
Lab: 1.7 hrs
Field: 43 hrs
PEDs: Time for Equilibrium in Closed Lab Experiment

(Adams et al, 2007)
PEDs: Measured $K_{PEW}$s as a function of $K_{OW}$

$$y = 1.13x - 0.86$$

$R^2 = 0.89$

(Adams et al, 2007)
**PEDs: Temperature and Salinity Corrections**

- Excess Enthalpy of Solution, $H_s^e$ can be used to correct for temperature differences

- Setchenow constant, $K_s$ can be used to correct for salinity effects (open triangle and square)

\[
y = 12x + 7.3 \\
R^2 = 0.71
\]

\[
y = 29x - 0.24 \\
R^2 = 0.97
\]

\[
y = 18x + 2.3 \\
R^2 = 0.98
\]

(Adams et al., 2007)
Spiked vs. PE-Deduced Dissolved Concentrations in Seawater

- Seawater samples with known HOC concentration
- Pre-added deuterated reference compounds added
- Sampling for 2 days (non-equilibrium)
- k-exchange used to correct for time to equilibrium

<table>
<thead>
<tr>
<th>Test</th>
<th>HOC</th>
<th>Spiking concentration (ng/L)</th>
<th>PED-measured concentration (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spring</td>
<td>Phenanthrene</td>
<td>450 ± 50</td>
<td>410 ± 70</td>
</tr>
<tr>
<td></td>
<td>Fluoranthene</td>
<td>500 ± 60</td>
<td>450 ± 140</td>
</tr>
<tr>
<td>Summer</td>
<td>Phenanthrene</td>
<td>450 ± 50</td>
<td>340 ± 120</td>
</tr>
<tr>
<td></td>
<td>Fluoranthene</td>
<td>500 ± 60</td>
<td>730 ± 260</td>
</tr>
</tbody>
</table>

(Adams et al., 2007)
Boston Harbor Field Measurements

- Two Sites: Near Charles River and Airport
- 15 days in December (2 & 3°C; 33 psu; POC = 0.2 mg/L)
- Total Water: (One point in time) vs. PED (Time-averaged)
## Boston Harbor Dissolved Concentrations:
### Total Water Extracts vs. PEDs

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Location</th>
<th>Total water extracts (ng/L)</th>
<th>Estimated dissolved fraction</th>
<th>PED extracts (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>phenanthrene</td>
<td>Airport</td>
<td>8</td>
<td>0.99</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>near Charles River</td>
<td>10</td>
<td>0.99</td>
<td>10</td>
</tr>
<tr>
<td>pyrene</td>
<td>Airport</td>
<td>7</td>
<td>0.98</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>near Charles River</td>
<td>8</td>
<td>0.98</td>
<td>2</td>
</tr>
<tr>
<td>PCB # 52</td>
<td>Airport</td>
<td>&lt; 0.03</td>
<td>0.93</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>near Charles River</td>
<td>&lt; 0.02</td>
<td>0.94</td>
<td>0.06</td>
</tr>
</tbody>
</table>
Ongoing Research

**PED & SPME Laboratory and Field Sampling (Sayre et al., in prep)**

- **Quantifying** PAHs, PCBs, and chlorinated pesticides (e.g., DDT, chlordane) in laboratory and field

**Pyrethroids in Ballona Creek Estuary (Lao et al., 2008)**

- Using PEDs to measure 8 pyrethroids in Ballona Creek Estuary
### PED and SPME Estimated Method Detection Limits

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Log $K_{OW}$ (Lw/L$_{octanol}$)</th>
<th>Log $K_f$ (100 μm) (Lw/L$_{fiber}$)</th>
<th>Log $K_{PEW}^f$ (51 μm) (Lw/kg$_{PE}$)</th>
<th>Method Detection Limit (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenanthrene</td>
<td>4.52$^a$</td>
<td>3.90$^c$</td>
<td>4.33</td>
<td>5.1</td>
</tr>
<tr>
<td>Pyrene</td>
<td>5.00$^a$</td>
<td>4.86$^d$</td>
<td>5.02</td>
<td>0.56</td>
</tr>
<tr>
<td>Benzo[a]pyrene</td>
<td>6.35$^a$</td>
<td>5.82$^c$</td>
<td>6.61</td>
<td>0.06</td>
</tr>
<tr>
<td>PCB 52</td>
<td>6.17$^b$</td>
<td>5.52$^c$</td>
<td>5.51</td>
<td>0.12</td>
</tr>
<tr>
<td>PCB101</td>
<td>6.65$^b$</td>
<td>5.61$^e$</td>
<td>6.16</td>
<td>0.10</td>
</tr>
<tr>
<td>PCB153</td>
<td>7.09$^b$</td>
<td>6.45$^c$</td>
<td>6.71</td>
<td>0.014</td>
</tr>
<tr>
<td>PCB180</td>
<td>7.21$^b$</td>
<td>6.54$^c$</td>
<td>6.91</td>
<td>0.012</td>
</tr>
<tr>
<td>cis-Chlordane</td>
<td>6.22</td>
<td>5.37$^c$</td>
<td>5.53</td>
<td>0.17</td>
</tr>
<tr>
<td>DDE</td>
<td>6.96</td>
<td>5.68$^c$</td>
<td>6.25</td>
<td>0.028</td>
</tr>
</tbody>
</table>

$^a$Sangster, 1989; $^b$Ruelle, 2000; $^c$Maruya et al, 2009; $^d$Doong & Chong, 2000; $^e$Zeng et al., 2005; $^f$Sayre et al, in prep.
Laboratory PED & SPME Comparisons

- Four 20-L carboys with PE and SPME in triplicate
- Dissolved concentrations over 4 orders of magnitude
- MDL for 2 g PE below that of SPME
- Two PE-measured concentrations at MDL diverged from LLE

SPME: slope = 0.91
\((n = 24; R^2 = 0.81)\)

PE: slope = 1.1
\((n = 34; R^2 = 0.90)\)

(Sayre et al., in prep)
Pyrethroids in Ballona Creek Estuary

PEDs deployed in Ballona Creek Estuary to measure 8 target pyrethroids

PE deployed for 23 days (sites 1-6)

In situ pump with XAD resin deployed at site 5 (4 days)

Estimated Method Detection Limits for target pyrethroids

<table>
<thead>
<tr>
<th>Compound</th>
<th>MDL ng/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bifenthrin</td>
<td>0.0003</td>
</tr>
<tr>
<td>Fenpropathrin</td>
<td>0.0028</td>
</tr>
<tr>
<td>Lamda-Cyhalothrin</td>
<td>0.0001</td>
</tr>
<tr>
<td>Cis-Permethrin</td>
<td>0.0161</td>
</tr>
<tr>
<td>Trans-Permethrin</td>
<td>0.0224</td>
</tr>
<tr>
<td>Cyfluthrin</td>
<td>0.0107</td>
</tr>
<tr>
<td>Cypermethrin</td>
<td>0.0027</td>
</tr>
<tr>
<td>Esfensvalerate</td>
<td>0.0150</td>
</tr>
<tr>
<td>Deltamethrin</td>
<td>0.0022</td>
</tr>
<tr>
<td>Average</td>
<td>0.0080</td>
</tr>
</tbody>
</table>

Sampling sites for PE Deployment in Ballona Creek Estuary (Sept.- Oct. 2007)

(Lao et al., 2008)
Pyrethroids in Ballona Creek Estuary

- Freely dissolved pyrethroids measured 0.5 m below water surface and 0.5 m above creek bottom
- Cis-permethrin ranging from 0.1 – 0.3 ng/L
- Bifenthrin ranging from 0.01 ng/L – 0.07 ng/L

(Lao et al., 2008)
Dissolved bifenthrin concentrations increase with increasing distance from ocean

(Lao et al., 2008)
Pyrethroids in Ballona Creek Estuary

PED-measured vs. XAD-measured at Site 5 in Ballona Creek

- In situ pump 1.5 m from surface pumping 944 L used to measure dissolved conc.
- Strong correlation with PE-measured dissolved concentration

(Lao et al., 2008)
Conclusions

• PEDs are useful devices for the measurement of freely dissolved HOCs in the water column
• Time-averaged, in situ
• Simple extraction and clean-up procedure
• Equilibrium on order of days to weeks
• Reference compounds can be used to correct for non-equilibrium cases
• Temperature and salinity effects can be corrected
• Low detection limits (sub pg/L); increase in mass of PED will further lower DL
• Good agreement with LLE and SPME
• Field Measurements for pyrethroids at pg/L concentrations
Acknowledgments

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