Passive Sampling Approaches for Contaminated Sediment Management

session chair: Phil Gschwend, MIT

with Kees Booij, Royal Netherlands Institute for Sea Research

Loretta Fernandez, US EPA- Narragansett

Keith Maruya, Southern California Coastal Water Research Project

Upal Ghosh, Univ. of Maryland Baltimore County

Steve Ells, EPA Office of Superfund Remediation and Technology Innovation
Passive Sampling Approaches for Contaminated Sediment Management

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Approved for public release; distribution unlimited

Passive Sampling Approaches for Contaminated Sediment Management

GOALS FOR TODAY’S SESSION:

1. acquaint you with diverse methods we call “passive sampling”

2. convince you to say, “I could do that!”

3. inform you so you can help site managers

4. enable your use of passive sampling to:
   assess sites (exposures)
   gain info’ needed to design remedial strategies
   improve long term monitoring efforts
“The Problem”

• have diverse array of organic chemicals in use

• many are persistent

• many are toxic

• many are “hydrophobic” => “sedimentophilic”
### Chemicals and Sediments of Concern

<table>
<thead>
<tr>
<th>Site</th>
<th>Primary Chemicals of Concern</th>
<th>Volume of Dredged Sediment (cy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bayou Bonfouca, LA</td>
<td>PAHs</td>
<td>170,000</td>
</tr>
<tr>
<td>Lavaca Bay, TX</td>
<td>Hg</td>
<td>80,000</td>
</tr>
<tr>
<td>Black River, OH</td>
<td>PAHs</td>
<td>45,000-60,000</td>
</tr>
<tr>
<td>Outboard Marine Corp., Waukegan Harbor, IL</td>
<td>PCBs</td>
<td>38,000</td>
</tr>
<tr>
<td>Commencement Bay–Head of Hylebos, Tacoma, WA</td>
<td>PCBs, As, PAHs</td>
<td>419,000</td>
</tr>
<tr>
<td>Duwamish Diagonal, Seattle, WA</td>
<td>PCBs</td>
<td>66,000</td>
</tr>
<tr>
<td>Puget Sound Naval Shipyard, Bremerton, WA</td>
<td>PCBs</td>
<td>225,000</td>
</tr>
<tr>
<td>Harbor Island–Lockheed, Seattle, WA</td>
<td>PCBs, PAHs, Hg, Pb, As, Cu, Zn, tributyltin</td>
<td>70,000</td>
</tr>
<tr>
<td>Harbor Island–Todd, Seattle, WA</td>
<td>As, Pb, Zn, Cu, PAHs, PCBs, tributyltin, Hg</td>
<td>220,000</td>
</tr>
<tr>
<td>Cumberland Bay, NY</td>
<td>PCBs</td>
<td>195,000</td>
</tr>
<tr>
<td>Dupont, Christina River, DE</td>
<td>Zn, Pb, Cd</td>
<td>11,000</td>
</tr>
<tr>
<td>Lower Fox River (SMU 56/57), WI</td>
<td>PCBs</td>
<td>82,000</td>
</tr>
<tr>
<td>Ketchikan Pulp Company, Ward Cove, AK</td>
<td>4-methyl phenol; ammonia</td>
<td>8,700</td>
</tr>
<tr>
<td>Newport Naval Complex–McCallister Landfill, RI</td>
<td>PAHs, PCBs</td>
<td>34,000</td>
</tr>
<tr>
<td>GM Central Foundry, St. Lawrence River, NY</td>
<td>PCBs</td>
<td>14,000</td>
</tr>
<tr>
<td>Grasse River, NY remedial options pilot study (ROPS)</td>
<td>PCBs</td>
<td>30,000</td>
</tr>
<tr>
<td>Lake Jarnsjon, Sweden</td>
<td>PCBs</td>
<td>196,000</td>
</tr>
</tbody>
</table>
Where are the beds hazardous?

US Environmental Protection Agency

Approximately 10 percent of the sediment underlying the nation’s surface water is sufficiently contaminated to pose potential risks to fish and to humans and wildlife who eat fish.
Hazard Assessment “Paradigm”

(source(s))

exposures

Dose/Response

risk/hazard

(exposure)(potency) = risk of “bad” effect
=> decide if “acceptable”

& less obvious legacies

air we breath

water we drink

food we eat

…

not so “hard”

emcom.ca/science/dose.shtml
Problem: how does contaminated sediment pose risks?

can we “map” unhealthy exposure paths?

Passive Samplers!

http://www.fao.org
Sediments are mix of solids, colloidal suspension, and solution(s)

Hunters Point (SF Bay) sediment: where are the PAHs & PCBs?

(basis of EPA “Benchmarks”)

typically have \( C_{\text{sed}} \), so

need \( C_{\text{sed}} / f_{oc}K_{oc} = C_{\text{pore water}} \)

if \( > C_{\text{water criteria}} \)

then bed is unacceptable,

but... is this right \( K_d \)?

or is there another way to get \( C_{\text{pore water}} \)?

Passive Samplers!
commonly find overestimated biouptake predictions (Lohmann et al 2004)

i.e., bioavailability proportional to $C_{\text{pore water}}$

so $C_{\text{pore water}} = C_{\text{sediment}}/f_{oc}K_{oc}$

observed in clam

divided by

predicted in clam

using

$C_{\text{pore water}}$
as above
And commonly over-estimate toxicity with measures of PAHs in sediments (McDonough et al., 2010)

\[ \frac{\sum \left( \frac{C_{\text{sediment}}}{f_{oc} K_{oc}} \right)}{C_{\text{final chronic water concentration}}} \]

nontoxic cases

toxic cases

too high if \( f_{oc} K_{oc} \) too low
Approach 2: add polymeric phase to equilibrate with sediment phases

polymeric sampler inserted into multi-phase environment

absorbs in relation to chemical activity or

\[ C_{\text{pore water}} = \frac{C_{PE}}{K_{PE\text{water}}} \]
This “passive sampling” solution:
advantages

directly reveal “available” concentrations (activities)
can us in field deployments without mixing
facilitates contaminant analyses
cost-effective

historically

mussels
sediment

SPMDs

SPME (PDMS)

LDPE, POM, others for water &

Farrington et al 1983  Huckins et al 1993  Pawliszyn group 1992
Passive Sampling Approaches for Contaminated Sediment Management

FANTASTIC GROUP OF SPEAKERS!!

1. Phil Gschwend (MIT)
   “Passive sampling in sediments: We can finally get the story right!”

2. Kees Booij (Royal Netherlands Institute for Sea Research)
   “Passive sampling of nonpolar compounds in sediments”

3. Loretta Fernandez (US EPA-Narragansett, RI)
   “Using a diffusive mass transfer model to interpret contaminant uptake by polymeric passive samplers from environmental porous media?”

4. Keith Maruya (Southern California Coastal Water Research Project)
   “Passive sampling devices (PSDs) to improve sediment quality assessment”

5. Upal Ghosh (University of Maryland, Baltimore County)
   “Application of passive samplers to monitor remediation progress”

   “Increasing regulatory acceptance of passive samplers”
this morning’s first speaker...

1. is still waiting for the Red Sox to invite him to a spring training try out!

2. fun guy...skilled athlete...brilliant scholar!

3. never shy about asking questions...

4. gives terrifying final exams(!)

5. & is generally useless in the field ...

   etc. etc. etc.

and today he joins us to talk about:

**Passive sampling in sediments: We can finally get the story right!**
<table>
<thead>
<tr>
<th>START</th>
<th>END</th>
<th>TOPIC/TITLE</th>
<th>SPEAKER</th>
<th>ORGANIZATION</th>
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<tbody>
<tr>
<td>8:30 AM</td>
<td>8:40 AM</td>
<td>Welcome &amp; Introduction by Session Chair</td>
<td>Philip Gschwend</td>
<td>Massachusetts Institute of Technology</td>
</tr>
<tr>
<td>8:40 AM</td>
<td>9:10 AM</td>
<td>KEYNOTE: Passive Sampling in Sediments: We Can Finally Get the Story Right!</td>
<td>Philip Gschwend</td>
<td></td>
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<tr>
<td>9:10 AM</td>
<td>9:35 AM</td>
<td>Passive Sampling of Nonpolar Compounds in Sediments</td>
<td>Kees Booij</td>
<td>Royal Netherlands Institute for Sea Research</td>
</tr>
<tr>
<td>9:35 AM</td>
<td>10:00 AM</td>
<td>Using A Diffusive Mass Transfer Model to Interpret Contaminant Uptake by Polymeric Passive Samplers from Environmental Porous Media</td>
<td>Loretta Fernandez</td>
<td>U.S. Environmental Protection Agency – Office of Research and Development</td>
</tr>
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<td>10:00 AM</td>
<td>10:20 AM</td>
<td><strong>Break</strong></td>
<td></td>
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<tr>
<td>10:20 AM</td>
<td>10:45 AM</td>
<td>Passive Sampling Devices (PSDs) to Improve Sediment Quality Assessment</td>
<td>Keith Maruya</td>
<td>Southern California Coastal Water Research Project</td>
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<tr>
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<td>11:10 AM</td>
<td>Application of Passive Samplers to Monitor Remediation Progress</td>
<td>Upal Ghosh</td>
<td>University of Maryland Baltimore County</td>
</tr>
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<td>11:10 AM</td>
<td>11:35 AM</td>
<td>Increasing Regulatory Acceptance of Passive Samplers</td>
<td>Stephen Ells</td>
<td>U.S. Environmental Protection Agency – Office of Superfund Remediation and Technology Innovation</td>
</tr>
<tr>
<td>11:35 AM</td>
<td>11:45 AM</td>
<td><strong>Discussion/Wrap-Up</strong></td>
<td>Philip Gschwend</td>
<td></td>
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</table>
1. Toxicity is related to chemical activity (Hutchinson et al. 1980)

$C_{50%_{\text{water}}}$ (uM)

water concentration that slows photosynthesis by factor of 2

Clamydomonas: ave $C_{50%_{\text{water}}}/\text{Sol’y} = 0.35$

water solubility (uM)
Toxicity and measures of PAHs in sediments (McDonough et al., 2010)

\[ \sum [PAH_{pore\text{ water}}] / [\text{final chronic water concentration}] \]

where

\[ [PAH_{pore\text{ water}}] = [PAH_{sediment}] / (f_{oc} K_{oc}) \]

or

\[ [PAH_{sediment}] / (f_{oc} K_{oc} + f_{BC} K_{BC} PAH_{pw}^{-0.3}) \]

move data “left”

100% of toxic
17% of nontoxic

43% of toxic
97% of nontoxic

do we have \( K_{BC} \) and \( n \) right?

100% of toxic
71% of nontoxic