Porewater and Bioavailability at Contaminated Sediment Sites

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Outline

◆ Problem definition
◆ Porewater, bioavailability, and exposures
◆ Passive samplers for porewater assessment
◆ Passive sampler applications and environments
◆ Recommendations for use
Sediment Remediation

- Conducted to decrease risk to consumers of fish.
- Conducted to decrease risk to benthos.
There is a complex relationship between sediment and biota contamination.

...influenced by concentration, bioavailability, fish diet, behavior, movement, etc.

Magar et al. 2009
All sediments aren’t created equal… they vary in potential to drive contaminant uptake.

- wood
- lignite
- charcoal
- coke

Gosh 2003

Magar et al. 2009
Terms

◆ Porewater (interstitial water)
  ▪ Water residing in the pore space of sediments.

U.S. Geological Survey


◆ Bioavailability
  ▪ The individual physical, chemical, and biological interactions that determine exposure of organisms to chemicals associated with soils and sediments.
Bioavailability Driving Exposures and Effects

- “Only a portion of the sediment-bound contamination is bioavailable, and there is no simple way of determining the available fraction through the use of extractants”
- “For several kinds of pollutants the interstitial water fraction has been shown to be most available to the benthos” (Swartz and Lee, 1980)

**Figure 6.** Conceptual model for accumulation of sediment-associated contaminants.

Landrum 1989, ES&T 23:588
Bioavailability Driving Exposures and Effects

- Lack of concordance between toxicity and bioaccumulation and contaminant concentrations in bulk sediment.
Using EqP with lit. Koc and sediment PAH-34 *grossly* over-predicts mortality, and does not separate toxic from non-toxic sediments.

![Graph showing H. azteca survival vs. U.S. EPA ESB TU34 (BSfTOC method)](image)

*Courtesy of Steve Hawthorne, Univ North Dakota*
The two carbon (Koc/Kbc) model and sediment PAH-34 *grossly* under-predicts mortality, and does not separate toxic from non-toxic sediments.

$log\ K_{BC}=0.6997\ log\ K_{ow} + 2.822$, Koelmans, 2006

Courtesy of Steve Hawthorne, Univ North Dakota
Measured freely-dissolved PAH-34 greatly improve mortality predictions, while still being conservative.

Courtesy of Steve Hawthorne, Univ North Dakota
PCB-18 (2,2',4) Log Kow: 5.24

Compared to Koc of:

a) Traffic soot
b) Oil soot
c) Wood soot
d) Coal soot
e) Coal
f) Charcoal
g) Flyash
h) Activated carbon
i) Graphite

Jonker and Koelmans. 2002
Variation in Contaminant Partitioning

Hawthorne et al. 2011
Porewater Sampling

◆ Importance long recognized.
  ▪ Variety of techniques: squeezing, centrifugation, leaching, filtering, direct sampling
  ▪ Issues
    • sampling altering chemistry
    • including DOC- and POC-associated contaminants
  ▪ Need to measure freely-dissolved fraction
    ➢ More detail in Mark Cantwell’s Presentation

Sayles et al. 1976
Passive Samplers

• Accumulate freely-dissolved organic contaminants from surrounding water into a solid phase.
• Contaminant concentrations of the samplers are measured.
• Circumvent problems associated with colloids, rapid- and slow-desorbing contaminants, and accounting for carbon content and variation.
Diversity of Passive Samplers

**SPME**
solid phase microextraction

**PED**
polyethylene device

**SPMD**
semi-permeable membrane devices

**POM**
polyoxymethylene samplers
Prediction of Dissolved Concentration

“Equilibrium” Sampling

\[ C_{\text{dissolved}} = \frac{C_{\text{passive sampler}}}{K_{\text{passive sampler/water}}} \]
Quantification of Dissolved Concentration

"Depletive" Sampling

SPME Fiber

~1.5 mL porewater

Courtesy of Joseph Kreitinger, USACE
Water Column Contaminant Analysis
<table>
<thead>
<tr>
<th>Area</th>
<th>Total DDx (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>North Harbor</td>
<td>0.2</td>
</tr>
<tr>
<td>South Harbor</td>
<td>1.5</td>
</tr>
<tr>
<td>Nearshore (SF-12)</td>
<td>Not recovered</td>
</tr>
</tbody>
</table>

Conventional Sampling was Non-detect

◆ “Freely dissolved” DDx concentration in surface water.

- Nature and Extent
- Relative Contamination
- Exposure Assessment
- Inclusion in food web modeling
Use of Passive Samplers in Cap Performance Monitoring

In-situ SPME Samplers and Associated Cores

D. Reible, Texas Tech University
PAH Profiles through Isolation Cap

- Cap profile shows performance as expected (isolation)
PAH Profiles through Isolation Cap

- Evidence of recontamination

![Graph showing PAH Profiles through Isolation Cap](image)
Use of Passive Samplers in Cap Performance Monitoring

Freely-dissolved PAH profiles through cap:
- Nature and extent
- Changes over time
- Cap performance
- Recontamination
- Source ID

D. Reible, Texas Tech University
Surrogates for Aquatic Organisms?

Aquatic organisms vary in their interaction with the environment and physiology

- Gradient from sessile to highly mobile
- Large differences in food preference and feeding behavior
- Gradient from poor metabolizes (e.g., mussels) to efficient biotransformers (e.g., fish from contaminated environments)
Benthic Invertebrate Feeding Strategies

Rhoads 1974
Variability in Bioaccumulation Potential

- Comparison of PCB uptake among organisms with different feeding strategies.
- All organisms exposed to the same PCB-contaminated sediment.
Where Porewater/Bioavailability Assessments are Useful?

◆ Where bulk sediment concentrations aren’t sufficient.
◆ To define
  ▪ Nature and Extent of Contamination
  ▪ Concentration-Toxicity Relationships
  ▪ Definining Exposure Concentrations
    • “Truly-dissolved” pore- or surface-water
    • Flux from sediment bed
  ▪ Remedial Effectiveness Evaluations
Questions

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