Implementation of Solid Phase Microextraction (SPME) Polydimethylsiloxane (PDMS) Fibers for in situ Performance Evaluation of Remediation Efforts at Contaminated Sediment Sites

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Research Drivers

SETAC Technical Workshop
“Guidance on Passive Sampling Methods to Improve Management of Contaminated Sediments”
November 2012

“Peer-reviewed publications of more case study examples where PSMs have been used in site assessments and management decisions”
(Ghosh et al., 2014)

“Further development of the non-equilibrium PSMs in the field and further validation of PRC use in static sediment environments”
(Ghosh et al., 2014)

QA/QC strategies to correct for key interferences
(i.e. evaporative loss and DOM)

Routine use in the field as an in-situ technology for evaluating remedial performance
THE BIG PICTURE

Can we accurately quantify $C_{\downarrow \text{free}}$ using PSMs?
And use the information to make assessments concerning remediation goals?

Water Column

Modified Henry Sampler containing PDMS Rod

Sediment Cap
The Importance of $C_{\downarrow{free}}$

Aqueous concentration of chemicals not bound to particulate matter, colloids, or dissolved organic carbon

- Proportional to chemical activity (Reichenberg and Mayer, 2009)
- Better indicator of potential risk
- Direct assessor of:
  - fate & transport of contaminants between sediment porewater and surface water
  - bioavailability & toxicity of contaminants to benthic organisms (Lu et al., 2011)
- Sediment Quality Guidelines (SQGs) derived using Equilibrium Partitioning (EqP) Theory estimate $C_{\downarrow{free}}$ from $C_{\downarrow{total}}$ (bulk solids) and assumed partitioning to water ($K_{\downarrow{d}}$) (Mayer et al., 2014)
  - Misrepresentation of risk
  - Passive sampling methods accurately determine $C_{\downarrow{free}}$
Passive Sampling Methods

Ex-situ

- Best to understand \( C_{\text{free}} \) equilibrium condition
  - Partitioning
  - Toxicity
  - Bioaccumulation
- Reproducibility & typical experiment control

In-situ

- Best to understand \( C_{\text{free}} \) field condition
  - Groundwater intrusion
  - Currents
  - Gradients & flux
  - Bioturbation

Sources:
Jahnke et al., 2012
Huckins et al., 2002
Reible and Lotufo, 2012
Gschwend et al., 2012
Oen et al., 2011
Common Passive Sampling Materials for HOCs

- **Polyethylene (PE)**
  - Thin rectangular sheets- High volume, good surface area to volume ratio, moderate internal diffusion rates, marginal in situ feasibility

- **Polyoxymethylene (POM)**
  - Molded thermoplastic- High volume, fair surface area to volume ratio, slow internal diffusion rates, marginal in situ feasibility

- **Polydimethylsiloxane (PDMS)**
  - Thin coating on glass fibers- Moderate volume, good surface area to volume ratio, high internal diffusion rates, good in situ feasibility
  - Hydrophobic surface after crosslinked and polymerized
  - Potential to absorb hydrophobic contaminants

Images from USEPA, 2012
At equilibrium: $C_{\text{free}} = C_{\text{polymer}} / K_{pw}$

Non-equilibrium: $C_{\text{free}} = C_{\text{polymer}} / f_{ss} K_{pw}$
Modeling Contaminant Uptake: Governing Equations

Transport within the PSM (DRM & IRM)

\[ \frac{\partial C_{\downarrow PSD}}{\partial t} = D_{\downarrow PSD} \frac{\partial^2 C_{\downarrow PSD}}{\partial x^2} \]

Transport to the PSM from the sediment (DRM & ERM)

\[ R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \]

Internal Resistance Model (Huckins et al., 2006)

- transport to PSM from sediment is ignored: \[ C_{\downarrow PSD} (x=L) = K_{\downarrow PSD} C \]
- Exact solution from analogous heat transport problem (Carslaw and Jaeger, 1959)
- For \( t > t_{\text{internal}} \approx 0.848L^2 / D_{\downarrow PSD} \), transport resistance externally dominated

Dual Resistance Model (Fernandez et al., 2009)

- Diffusion-based internal & external transport
- Semi-exact solution using numerical inversion of the LaPlace transform
- Bulky & often can be simplified

External Resistance Model (Lampert et al., in review)

- Exact solution from analogous heat transport problem (Carslaw and Jaeger, 1959)
- Single unknown parameter RD which is a function of the transport and sorption-related retardation in the surrounding porous media
Relative Importance of Internal & External Transport

\[ \frac{t_{\text{external}}}{t_{\text{internal}}} = 36.1 K^{1.2} PSD^{1.2} \]

\[ \frac{D_{\text{PSD}}}{RD} = 36.1 \]

\( \sigma = 0.001 \)
\( \sigma = 0.1 \)
\( \sigma = 0.01 \)
\( \sigma = 1 \)
\( \sigma = 0.027 \)
\( \sigma = 10 \)
for 30 µm PDMS layer

\[
\frac{t_{\text{external}}}{t_{\text{internal}}} = 36.1 K^{1/2} \downarrow \frac{PSD}{PSD/rd} = 36.1 \sigma
\]

\[
\tau = \left\{
\begin{array}{c}
\log \ \text{t = 0.5 hour} \\
\text{t = 1 day} \\
\text{t = 7 days}
\end{array}
\right.
\]

<table>
<thead>
<tr>
<th></th>
<th>-log</th>
<th>t = 0.5 hour</th>
<th>t = 1 day</th>
<th>t = 7 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>NAP</td>
<td>9.95</td>
<td>225</td>
<td>11000</td>
<td>75400</td>
</tr>
<tr>
<td>DB(a,h)A</td>
<td>11.35</td>
<td>9</td>
<td>430</td>
<td>3000</td>
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</tbody>
</table>

\[
\sigma = 0.001
\]

\[
\sigma = 10
\]

\[
\tau_{\text{DB(a,h)A}} \downarrow \quad t = 0.5 \text{ hr}
\]

Off the plot!

DRM & ERM are converged @ t = 0.5 hr!

\[
\tau_{\text{NAP}} \downarrow \quad t = 0.5 \text{ hr}
\]
for 30 µm PE sheet

<table>
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<tr>
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<th>(-\log)</th>
<th>(t = 0.5) hour</th>
<th>(t = 1) day</th>
<th>(t = 7) days</th>
</tr>
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<tbody>
<tr>
<td>NAP</td>
<td>11.76</td>
<td>3.5</td>
<td>170</td>
<td>1170</td>
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<tr>
<td>DB(a,h)A</td>
<td>15.5</td>
<td>0.001</td>
<td>0.03</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Slower kinetics

\(\tau_{DB(a,h)A}\)  
\(t = 0.5\) hr 
\(\sigma = 0.001\)

\(\tau_{NAP}\)  
\(t = 0.5\) hr 
\(\sigma = 10\)

Steady State Fraction

Dimensionless Time (\(\tau\))

<table>
<thead>
<tr>
<th>IRM</th>
<th>DRM</th>
<th>ERM</th>
</tr>
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</table>
% error when neglecting internal mass resistance

\[ \tau \downarrow \mathcal{D} \mathcal{B} (a, h) \]
\[ A_{\text{PDMS}} \]
\[ t = 0.5 \text{ hr} \]
\[ \tau \downarrow \mathcal{D} \mathcal{B} (a, h) \]
\[ A_{\text{PE}} \]
\[ t = 7 \text{ days} \]
\[ \tau \downarrow \mathcal{D} \mathcal{B} (a, h) \]
\[ A_{\text{PE}} \]
\[ t = 1 \text{ day} \]

DRM necessary when using PE
But we have a simple & still robust solution for PDMS using ERM

\[ C_{\downarrow \text{PDMS}}(t) = K_{\downarrow \text{PDMS}} - w C_{\downarrow \text{pw}} \left[ 1 - \exp \left( \frac{R_D t}{L^2 K_{\downarrow \text{fw}}} \right) \right] \text{erfc} \left( \sqrt{\frac{R_D t}{L K_{\downarrow \text{fw}}}} \right) \]
Modeling Contaminant Uptake

\[ C↓1060/1000 \mu m \quad v C↓230/210 \mu m \]

\[ C↓t=7 \text{ days} \quad v C↓t=30 \text{ days} \]

\[ RD = \beta K↓ow \uparrow \alpha \]

Internal Resistance Model
Dual Resistance Model
External Resistance Model

\[ f↓ss = [1 - \exp\left(\frac{RDt}{L↑2} K↓fw↑2\right)] \text{erfc}\left(\frac{\sqrt{RDt}}{LKW}\right) \]

Absolute Porewater Concentrations
\[ C↓free = C↓PSM / K↓fw f↓ss \]

Comparable to Environmental Criteria

Magnitude of Diffusive Flux
\[ R\partial C↓pw / \partial t = D\partial↑2 C↓pw / \partial z↑2 \]

\[ J = -\frac{RD}{\rho↓b f↓oc} K↓oc \frac{dC}{dz} \]

Or for highly hydrophobic contaminants,
At equilibrium: $C_{\text{free}} = C_{\text{polymer}} / K_{\text{pw}}$

Non-equilibrium: $C_{\text{free}} = C_{\text{polymer}} / f_{\text{ss}} K_{\text{pw}}$

**Remediation Evaluation**
Vertical Profiles, Comparison with WQC, Comparison with Surface Water

**Fate & Transport**
Chemical Activity
Migration Potential, Flux

**Toxicity & Bioaccumulation**
Passive Sampling for Performance Assessment

- Provides measure of the reduction of availability and transport in in-situ treatments and sediment caps
- Potentially provides indication of migration deep within cap
- Moves away from typical performance evaluations based upon implementation metrics and physical characteristics not focused on exposure and risk
- Overcomes problems of bulk solid measurement
  - Conventional sand caps do not sorb contaminants
  - Caps (or in-situ treatments) work by sorbing contaminants and reducing availability
  - In either case, bulk solids largely irrelevant
Demonstration of in situ SPME PDMS methods for monitoring remediation efforts

Materials & Methods

• Modified Henry Sampler

• PDMS sorbent fiber
  Selective for non-polar compounds
  ≤ ng/L detection with 1 cm resolution
West Branch Grand Calumet River & Roxana Marsh

• COCs: PAHs, PCBs, pesticides & metals
• Remediation Activities: Sediment removal (~235,000 cu. yds in WBGCR and ~150,000 cu. yds in Roxana Marsh) & capping with sand/gravel
• Monitoring Activities: SPME porewater/surface water sampling & sediment cores (EPA)

“…appears picturesque, but the river sediment is highly contaminated.” (USEPA, 2009)
Expected Profiles
Clean cap layer (low concentrations), sharp increase in concentration below the cap layer

“Snapshot in time”
Loc 9: Defined Cap Layer

Cap Boundary Measurements provided by USEPA
Loc 13: Highest Observed Concentration Levels (NAPL Present)

- **Anthracene Concentration (ng/L)**
  - MDL = 0.33 ng/L
  - WQC = 40,000,000 ng/L
  - Baseline
  - 2013
  - Gravel Layer Lower Boundary
  - Sand Layer Lower Boundary

- **Benzo(a)anthracene Concentration (ng/L)**
  - MDL = 0.04 ng/L
  - WQC = 18 ng/L
  - Baseline
  - 2013
  - Gravel Layer Lower Boundary
  - Sand Layer Lower Boundary

- **Benzo(a)pyrene Concentration (ng/L)**
  - MDL = 0.02 ng/L
  - WQC = 18 ng/L
  - Baseline
  - 2013
  - Gravel Layer Lower Boundary
  - Sand Layer Lower Boundary
**Loc 19: Surface Recontamination**

**Anthracene Concentration (ng/L)**
- Baseline
- 2013
- MDL = 0.33 ng/L
- WQC = 40,000,000 ng/L
- Gravel Layer Lower Boundary
- Sand Layer Lower Boundary

**Pyrene Concentration (ng/L)**
- Baseline
- 2013
- MDL = 0.16 ng/L
- WQC = 4,000,000 ng/L
- Gravel Layer Lower Boundary
- Sand Layer Lower Boundary

**Benzo(a)pyrene Concentration (ng/L)**
- Baseline
- 2013
- MDL = 0.02 ng/L
- WQC = 18 ng/L
- Gravel Layer Lower Boundary
- Sand Layer Lower Boundary
Wyckoff/Eagle Harbor

- COCs: PAHs, PCP, organics, creosote, and heavy metals
- Remediation Activities: Capping and source control
- Monitoring Activities (2011): SPME porewater sampling and grab samples/cores (USACE)

[Images: Creosote pool and Wood treatment facility off Bainbridge Island]
The effective organic carbon partition coefficient

\[ K_{oc} = \frac{W_{ss}/C_{pw}}{f_{oc}} \]

- “Measured” \( K_{oc} \sim 2x \) estimated \( K_{oc} \) using literature values (Baker et al., 2007)
- Deviation between measured and bulk-solid predictions of porewater concentrations are consistent with aged contaminants and strongly solid-associated contaminants.

Primary advantages of directly measuring porewater concentrations with SPME:
- No assumption of 100% availability
- No dependence of theoretical estimate of \( K_{oc} \)

Relationship determined from the upper 10 cm of twelve sampling locations at Eagle Harbor where grab samples and SPME samples overlapped. The orange solid line represents the best fit relationship of the field data (slope = 1.15, \( r^2 = 0.88 \)). The black solid line represents the relationship determined by Baker et al.\(^{28}\) between \( \log K_{oc} \) and \( \log K_{ow} \).

Thomas et al., 2014
Assessing PAH Bioavailability

21-day bioaccumulation experiment using bivalve mytilida *Musculista senhousia* and 210/230 µm PDMS fiber

Bulk solids (even carbon normalized) - a weaker indicator of bioaccumulation potential than porewater concentrations
Key Points about SPME PDMS Profiling

- **Porewater concentration**
  - More sensitive indicator of migration in caps than bulk sediment concentration
    - Sensitive indicator of in-situ mixing processes
    - Can also indicate performance of in-situ treatment
    - Correlates with contaminant availability and bioaccumulation

- **Polymer sorbents**
  - Effective measures of in-situ porewater concentrations
    - No assumptions of $K_{loc}$ or 100% availability
  - Note- detection limits and time to equilibrium strong function of hydrophobicity
    - Tracks bioaccumulation
    - dominated by more highly hydrophobic compounds
    - May not track narcosis
    - dominated by lower hydrophobicity compounds
Thank you, USACE & USEPA
Especially, Paul Schroeder, Karl Gustavson, Marc Mills, Amy Mucha, and Heather Williams

Any Questions?

Thank you for your attention!
References noted in presentation


