DGT as a Field Sampling Tool for Porewater Mercury and Methylmercury

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Outline

• Porewater sampling techniques
• DGT Theory and Background
• DGT Field Applications
  – Time-Integrated Sampling
  – Measuring Remedy Effectiveness
  – Mercury Behavior in River Banks and Sediments
Mercury Conceptual Model

- Dissolved mercury is available to microbes for methylation
- Bulk solid mercury is not a good measure for methylation potential of the system
- To reduce methylation, control solid phase sorption or aqueous speciation
Porewater Sampling Techniques

• Active sampling techniques
  – Centrifugation and Filtration
  – Displacement
  – Direct water sampling (Henry sampler)

• Passive sampling techniques
  – Diffusive gradient in thin films (DGT)

  • Advantages
    • Minimal disturbance
      – No suspension of particles
      – Maintain redox conditions
    • Flexible Placement
    • Vertical Resolution
Henry Sampler Porewater

• Henry Sampler- Conventional porewater sampler

<table>
<thead>
<tr>
<th>Location</th>
<th>THg Unfiltered (ng/L)</th>
<th>THg Filtered (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2300</td>
<td>1</td>
</tr>
<tr>
<td>B</td>
<td>310,000</td>
<td>301</td>
</tr>
<tr>
<td>C</td>
<td>72,000</td>
<td>2.5</td>
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</table>

• Conventional porewater samples filtered <0.1% of unfiltered
  – Compared to 10-60% in surface water
DGT Background

• Davison & Zhang – Lancaster, UK
• Based on Fick’s 1st Law of Diffusion
  – Measures flux, not an equilibrium device
  \[ J = -D \frac{\partial \phi}{\partial x} \quad \rightarrow \quad J = \frac{DC_b}{\Delta g} \quad \rightarrow \quad C_b = \frac{M\Delta g}{DtA} \]

• Diffusion of metal = to that in pure water
DGT in sediments

• DGT theory also applicable to sediments
  – Difference is solid phase influence

• *Pseudo* steady state achieved in ~ day deployments times
DGT for Hg/MeHg Measurement

- Resin
  - 3-mercaptlypropyl functionalized silica gel resin
  - Acrylamide gel base

- Diffusion layer
  - Agarose gel

- Filter Layer
  - 0.45 µm polysulfone
DGT Fabrication Procedure

- DGT are fabricated at Texas Tech
- Deployed in sediment/water for ~2 days
- Analysis performed at Texas Tech
  - Depth profilers sectioned at 1-2cm intervals
  - Resin split for TotHg/MeHg
  - TotHg resin is eluted in HCl and analyzed by EPA 1631
  - MeHg resin is eluted in HCl/Thioreau and analyzed by EPA 1630
South River Background

- Legacy mercury contamination from industrial source
- Large amount of traditional sampling
  - Biota, sediments, soils, surface water, groundwater
- Goal was to use diffuse gradient in gel-thin film (DGT) samplers to measure surface water and in-situ porewater mercury and methylmercury
Time Integrated Sampling

- Concentration calculated is an average over the deployment time
  - Can capture variations over sampling interval
Water Column Sampling

- Autosampler and DGT deployed in a river for 48 hours
- Autosampler measured an average concentration of 13.9 ng/L
- DGT Measured an average concentration of 15.3 ng/L
Measuring Remedy Effectiveness

• Goal of remediation is to lower mercury levels in biota

• Sediment amendment does this by lowering the amount of available mercury through sorption

• DGT allow for a chemical measurement of remedy effect instead of just endpoints
Biochar Sediment Amendment

- Pilot site was a 2-year floodplain pond, adjacent to the South River, Virginia, USA
- Pond was divided and Biochar amendment was applied to one side
Sampling

- DGT sampling was conducted at 0, 4, 16 weeks and ~10 months
  - 3 amended and 3 control locations
  - 18 samples from each sampling event
- Conventional Sampling performed in parallel
  - Included surface water, sediment porewater (Henry samplers), bulk sediment and biota
  - Analyzed for TotHg and MeHg
DGT Sampling

- Data from sediment porewater 0-4 cm
- Higher concentrations in area to be amended initially
- Decrease at surface over time in amended
- Control approximately constant

% Reduction in Total Mercury

<table>
<thead>
<tr>
<th>Treatment</th>
<th>SE1</th>
<th>SE2</th>
<th>SE3</th>
</tr>
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<tbody>
<tr>
<td>Control</td>
<td>-</td>
<td>.23</td>
<td>.28</td>
</tr>
<tr>
<td>Amended</td>
<td>-</td>
<td>.80</td>
<td>.53</td>
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</table>
Conventional Sampling

- Filtered porewater data is significantly lower than DGT
  - Very close to filtered surface water
- Porewater collected with Henry samplers
  - Dilution of porewater samples?

![Graph of Filtered Surface Water](chart1.png)

![Graph of DGT Pore Water](chart2.png)

![Graph of Filtered Pore Water](chart3.png)
Mercury Behavior in River Banks and Sediments

- Terrestrial soil is a major source of mercury to the river
  - River banks are interface

- More accurate measurements in channel and bank sediments
  - Improve understanding of how banks and sediments influence mercury cycling in the river
Site Conceptual Model

Baseline Data

- DGT Field Sampling Conducted 2010-2014
- Three areas of the river were sampled
  - Source area, upstream, downstream
- Consistent results 2010-2012
  - Always sampled at baseline flow
May 2013 Flood Event

• Sampling event occurred during a high flow event (~3000 cfs)
  - DGTs deployed just after the high flow crested
  - Measured mercury behavior in banks during declining stage
May/July 2013 Data

May 2013 – Declining Stage

July 2013 – Baseline Flow

May 2013 DGT Total Mercury (ng/L)

July 2013 DGT Total Mercury (ng/L)
May/July 2013 Data

2013 DGT Total Mercury (ng/L)

- Depth (cm)
- 20000 40000 60000 80000 100000 120000 140000
- July
- May
May 2014 Sampling

- Sampling conducted at baseline flow and declining stage, ~3 days apart
- Peak flow ~1000 cfs
- DGT samplers deployed during both flow regimes
May 2014 Data

Baseline flow

Declining Stage

May 2014 Total Mercury DGT (ppt) vs. Depth (cm)
Mercury Behavior in River Banks and Sediments

- DGT able to capture major differences in mercury behavior
  - Large concentration range
- DGT able to give vertical resolution
  - Not bulk sample
- Small sampler size allow placement in difficult sampling environments
Conclusions

• DGT can effectively measure low and high level mercury concentrations
  – PDL: 10 ng/L, depending on sampling parameters
  – Wide range of concentrations can be measured with same samplers, but can tailored for specific ranges

• More direct chemical measurement that sampling biota
  – Important for understanding remediation mechanisms

• DGT samplers give flexibility in sampling
  – Vertical resolution in a narrow space

• Related Talk: Validation of Diffusive Gradient in Thin-films Technique for Mercury and Methylmercury
  – Thursday, 11am. Dr. Ariette Schierz
Acknowledgements

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• South River Science Team

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