New Approaches and Analytical Tools for Studying Mercury in the Gulf of Mexico: Sources and Transformations

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OVERVIEW OF PRESENTATION

- Introduction
  - Why the continued interest in mercury?
  - Overview of our research
- New Analytical Tools
  - Stable isotope tracers*
  - Isotopic composition/fractionation
- Overview of Hg issues in the Gulf of Mexico
Why the interest in mercury?

Dispersion and long-range transport through the atmosphere

Wet and Dry Deposition

Terrestrial and Aquatic Ecosystems

Mercury Methylation

MeHg Entry into the Food Web

Bioaccumulation and Biomagnification

Human Exposure

Wildlife Exposure

Effects brain function, memory, behavior

Not decreasing despite emission controls

Gulf Coast residents have higher consumption of marine fish

Source: UNEP, Global Hg Assessment, 2013
Increasing levels of Hg in the Biosphere

Roos-Barraclough, et al., 2003

Increasing Mercury Accumulation Rate (AR) in Arctic Peat Bog

UNEP, 2008
Minamata Convention on Mercury

- Legally-binding global treaty (>100 nations) focused on reducing Hg pollution.
- U.S. signed on November 6th 2013.

Atmospheric Hg Monitoring

Speciation in Natural Waters and Gulf of Mexico sediments

Our Research

Sediment

100 km

N

Oxford, MS
New Directions in Environmental Hg Studies

Stable Isotope Isotopic Fingerprinting & Fractionation Studies

- Example: Enriched isotope of Hg(II) is injected altering natural ratios of Hg isotopes
- Sample is incubated allowing methylation to occur naturally
- Amount of tracer incorporated into MeHg is used to calculate methylation rate.
- MeHg, labeled with a different Hg isotope, keeps track of competing de-methylation
New Directions in Environmental Hg Studies

Isotopic Fingerprinting & Fractionation Studies

- Different sources of Hg have different isotopic compositions
- High precision isotope ratios are measured with MC-ICPMS
- Different physical-chemical processes alter the isotopic compositions
- Mass-dependent & mass-independent fractionation
- Probe into reaction pathways and history of Hg

Tracing Mercury Contamination Sources in Sediments Using Mercury Isotope Compositions

Mercury Isotopic Evidence for Multiple Mercury Sources in Coal from the Illinois Basin

Mass-Dependent and -Independent Fractionation of Hg Isotopes by Photoreduction in Aquatic Systems
Why measure Hg methylation potentials in sediment?

- Much Hg methylation in aquatic systems occurs in sediments
- Often inferred from ancillary data – often better to measure it directly…
- MeHg concentration in water and biota can relate to methylation rates, but not always
- To understand geochemical controls affecting production and distribution of MeHg in aquatic ecosystems
- Why potentials?
  - Assume spike has same speciation as ambient Hg(II)
  - Must equilibrate with site water
Hg methylation in the sediments

- Mediated by SRB
- Methylation occurs in cells via B12 and other mechanisms
- Inorganic Hg speciation determines uptake rates
Analytical Considerations

• Must measure both MeHg and Hg$^{+2}$, plus evaluate the kinetics of methylation and demethylation

\[ (↑) \text{Hg}^0 \leftrightarrow \text{Hg}^{+2} \leftrightarrow \text{MMHg} \leftrightarrow \text{DMHg} \ (↑) \]

• Compromise between ability to detect changes and maintain realistic microbial and geochemical conditions
  – Equilibrate with bottom or pore water to attain natural speciation
  – Keep spike levels low to minimize increase in Hg bioavailability

• First step?
### Hg Isotopes Abundance (%)

<table>
<thead>
<tr>
<th>Mass #</th>
<th>Natural</th>
<th>Enriched</th>
</tr>
</thead>
<tbody>
<tr>
<td>196</td>
<td>0.015</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>198</td>
<td>9.97</td>
<td>1.2</td>
</tr>
<tr>
<td>199</td>
<td>16.87</td>
<td><strong>91.09</strong></td>
</tr>
<tr>
<td>200</td>
<td>23.1</td>
<td>4.22</td>
</tr>
<tr>
<td>201</td>
<td>13.18</td>
<td>0.92</td>
</tr>
<tr>
<td>202</td>
<td>29.6</td>
<td>1.89</td>
</tr>
<tr>
<td>204</td>
<td>6.87</td>
<td>0.68</td>
</tr>
</tbody>
</table>

How do we produce isotopically labeled Hg?

\[
{^{201}\text{HgO}} + 2 \text{HCl} \rightarrow {^{201}\text{HgCl}_2} + \text{H}_2\text{O}
\]

\[
{^{201}\text{HgCl}_2} + \text{Me-Co} \rightarrow \text{Me}^{201}\text{Hg}^+
\]
Enriched Stable Isotope Tracers

How can we accurately measure MeHg levels & methylation rates when species transform? **Monitor 3 isotopes: ICPMS is mandatory!**

- $^{199}\text{Hg}$ = newly produced MeHg from inorganic tracer
- $^{200}\text{MeHg}$ = demethylation of MeHg tracer
- $^{201}$ = changes in MeHg levels derived from Hg originally present

**Spike isotope ratio:**

\[
\frac{^{201}\text{Hg}}{^{202}\text{Hg}} = 6.53 \text{ (natural ratio = 0.44)}
\]

**Intensity (x10^3 cps)**

Retention time (min)
Sample Core Collection

Inject core with enriched isotope spikes ($^{199}$MeHg, $^{200}$Hg$^{+2}$) equilibrated with site water for double tracer study

Incubate, section and lyophilize

MeHg

Extract/Distill
Ethylate, purge and trap, GC-ICPMS

Total-Hg

Microwave Digest
[O] with BrCl; [R] with SnCl$_2$
Hg$^0$→ICPMS. Or DMA-ICPMS

Tracer calculations for $K_m$ and $K_{dm}$


varies widely but net production ~0.2 µg/kg/day
Hg Methylation Potentials in Sky Lake Sediment: Preliminary Data

![Graph showing Hg methylation potentials in Sky Lake sediment across different seasons. The graph compares open water and swamp conditions.](image-url)
Land vulnerable to sea level rise along the Gulf Coast*: land loss and new wetlands

*Titus and Richman, *Climate Research* 2001, 18, 205.*

**Mailman et al. *Sci Tot Environ* 2006, 368, 224.*
Mercury in GoM (GoM Alliance, 2013)

- Gulf coasters consume ~3x seafood/person as national ave.
  - At-risk: Pregnant women, young children, recreational and subsistence fishers
- Commercial harvest 2x > recreational, and distributed nationally
- Natural variability of Hg levels among fish
  - Biological factors: Age is “master” variable but size, diet, metabolic rate, assimilation and elimination rates, growth rate, community structure…
- Geographic variability in Hg levels in seafood
  - Source variability (atm. deposition, watershed delivery)
  - Transport and transformation processes (partitioning to particles and sediments, biodilution, methylation rates)
- Where is MeHg produced from inorganic GoM
  - Imported: atmosphere, adjacent watersheds, Atlantic Ocean
  - Estuarine sediments: High biological production, shallow water depths/ flushing
  - Coastal and Open Gulf sediments: but no methylation rate measurements
- Uptake into the food chain
  - Phytoplankton: high surface to volume ratio; other important primary producers
- Research Needs and Approaches
  - *Paucity of MeHg measurements limits ability to assess sources, etc.
Research Group
Support and Collaborators

- Alan Shiller and Davin Wallace, U. Southern Mississippi
- Joel Blum, University of Michigan
- Mike Beiser, Mississippi Dept. of Environmental Quality
- Keith Meals, Mississippi Dept. of Fisheries and Parks
- Ken Sleeper, Mississippi Mineral Resources Institute
- Daniel Wren, National Sedimentation Laboratory (USDA)
- Gregg Davidson, University of Mississippi
Thank You!

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DON'T MOVE, or I'll fill you full of 98% lead, 1% antimony, 0.75% silver, 200 parts per million nickel, trace amounts of cobalt, and other components below their respective detection limits!

Wait a minute! Are those values CERTIFIED?!

Analytical Chemists in the Wild West
Extra Slides
ICP-MS Facility at Ole Miss

Double Focusing ICP-MS

Desolvating nebulizer

Laser ablation unit (213 nm)

Autosampler enclosure
Why monitor Hg in the Atmosphere?

Emission Inventory*

Modeling*

Atmospheric Monitoring*

Understanding & Decisions:
- Deposition to Region*
- Inputs to ecosystem models
- Sources and Trends*
- Future emission scenarios

Modeling required to help interpret measurements and estimate source-receptor relationships

Monitoring required to develop models and to evaluate their accuracy
Mercury in fish from Enid, Sardis and Grenada Lakes: concentrations, trends, and risk assessment
add lake statistics: lake area and watershed area

202 fish
Piggyback study

Used with permission MDEQ

THE UNIVERSITY OF MISSISSIPPI
Hg increased with fish trophic level

Hg (wet weight ng/g)

Average Fish Concentration

- FH: Flathead catfish
- Crappie: White crappie
- LMB: Largemouth bass
- CC: Channel catfish
- BC: Blue catfish
- GS: Gizzard shad

Grenada: 199, 469, 369, 312, 222, 44
Sardis: 147, 214, 269, 56, 32, 6
Enid: 147, 109, 109, 109, 109, 109

The University of Mississippi
Estimating Dry Deposition of Hg using Surrogate Surfaces

- **Passive sampler:** cation exchange membrane
- While it does not simulate heterogeneity of natural surfaces, they do provide a physical means for estimating temporal trends and spatial variability of GOM dry deposition
  - \( D = \frac{(S - B)}{A} / T \)
  - **D** = Deposition Flux in ng/m\(^3\)/hr
  - **S** = Sample; **B** = Blank; **A** = Area; **T** = Time
  - 2 weeks: mean of 115 ng Hg vs 9 ng in blanks

Membrane: Unsupported (bi-directional) negatively charged polyethersulfone (PES) (Pall Corp.)
Reservoir Study Summary & Recommendations

- PBM is a major factor driving the distribution of Hg
- A large proportion of the Hg entering the lakes occur in storm events
- Agriculture runoff likely contributes the most Hg

Recommendations
- Measures to reduce soil erosion would help to limit Hg loading the lakes
- Prevent disruptions to wetlands that alter oxygen levels (e.g. eutrophication, flooding)
- Re-assess Hg levels in fish at least every decade
- Limit intake of large predatory fish.
Hg levels, speciation, and isotopic composition in sediment from a cold seep in the northern GoM

Cizdziel et al. (2013)
Background

- Hydrocarbons support a diverse chemisynthetic community.
- Conditions that potentially favor methylation
- Cold seep sediment may have 2 sources of Hg
Purpose of this Pilot Study

- Are there differences in Hg levels between cold seep and background sites?
- Are cold seeps significant sources of MeHg to the marine ecosystem?

- significant differences would warrant further study
Deep Water Sample Sites

Figures provided by MMRI
Sampling

Box core

Polycarbonate tubes
Levels of Mercury in Environmental and Biological Samples and Techniques Used to Measure It

- **PPM**
  - DMA, CVAAS

- **PPB**
  - ICPMS

- **PPT**
  - CVAFS

- **PPQ**

Source: US EPA