Methylmercury Dynamics in Streams and Wetlands in Illinois and Indiana: Applications of a Novel Analytical Method

Illinois Water 2008

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- Illinois Water Resources Center (Piasa Creek).
- National Great Rivers Research and Education Center (Piasa Creek).
Acknowledgments: Support/Collaborators

- Low-cost use of field research facilities and lodging at Indiana Dunes National Lakeshore. Research coordinator Joy Marburger.
- Fish sample collection and wetland survey site collection by Dr. Thomas Simon (NFWS) and Jim Smith (IDEP).
- Total Hg in sediments (Filippelli, IUPUI)
- Analysis of anions and DOC in Prof. Mark David’s laboratory.
Why Methylmercury?

- CH$_3$Hg$^+$ is more strongly bioaccumulated in aquatic food webs than inorganic Hg$^{2+}$.

- Hg in fish is almost entirely CH$_3$Hg$^+$.

- CH$_3$Hg$^+$ is $>$95% absorbed during digestion by humans, versus $\sim$10% for Hg$^{2+}$.

- CH$_3$Hg$^+$ is more toxic than inorganic Hg$^{2+}$.
# Forms of Mercury in the Environment

<table>
<thead>
<tr>
<th>Form of Hg</th>
<th>Abbreviation</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elemental</td>
<td>Hg\textsuperscript{0}</td>
<td>Gas, pure liquid, dissolved</td>
</tr>
<tr>
<td>Divalent (mercuric)</td>
<td>Hg\textsuperscript{II} or Hg\textsuperscript{2+}</td>
<td>Dissolved ionic species</td>
</tr>
<tr>
<td>Methyl</td>
<td>CH\textsubscript{3}Hg\textsuperscript{+} or MeHg</td>
<td>Organometallic compound, dissolved ionic species</td>
</tr>
<tr>
<td>Dimethyl</td>
<td>(CH\textsubscript{3})\textsubscript{2}Hg</td>
<td>Organometallic compound, Gas or dissolved</td>
</tr>
</tbody>
</table>
# Measuring MeHg in the Environment

<table>
<thead>
<tr>
<th>Environmental Medium</th>
<th>Total Hg Concentrations</th>
<th>Fraction of Total Hg Present as Methyl-Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet deposition</td>
<td>10-100 ppt</td>
<td>Low</td>
</tr>
<tr>
<td>Typical surface water – atmospheric source</td>
<td>0.5-5 ppt</td>
<td>5-20% oxic; Up to 100% anoxic</td>
</tr>
<tr>
<td>Contaminated Water</td>
<td>&gt;10 ppt</td>
<td>0.5%</td>
</tr>
<tr>
<td>Sediments</td>
<td>0.1-10 ppm</td>
<td>0.1-5%</td>
</tr>
<tr>
<td>Fish and biota</td>
<td>0.1-3 ppm</td>
<td>&gt;90%</td>
</tr>
</tbody>
</table>

ppt = parts per trillion; ppm = parts per million
Total Mercury in Wet Deposition

Total Mercury Wet Deposition, 2006

National Atmospheric Deposition Program/Mercury Deposition Network
Calculated Hg in 14-in Largemouth Bass
National Descriptive Model for Mercury in Fish (USGS)
Calculated Hg in 14-in Largemouth Bass

National Descriptive Model for Mercury in Fish (USGS)
Schematic Showing Wetlands and Link to Stream MeHg
Methylation of MeHg

Fig 1. Hg is transported in streams both in dissolved form and adsorbed to particles. When bacterial reduction processes in sediments are active enough that sulfate reduction occurs, dissolved Hg(SH)_2 species form, releasing Hg^{II} from sediment particles. These neutral Hg-complexes are bioavailable to the sulfate reducing bacteria (SRB) that carry out the methylation reaction. When metal oxides are not abundant in surface sediments, MeHg can diffuse back into the streamwater, where it is absorbed by aquatic plant life and then transferred efficiently between trophic levels of the aquatic food web. Demethylation of MeHg also occurs in oxic water and sediments (not depicted here).
Methylmercury in Illinois

- Illinois has a statewide consumption advisory on predatory fish (bass, etc.).
- Illinois has several site-specific advisories.
- Relatively little study of Hg compared to states in the Upper Midwest or Indiana.
What makes Illinois uniquely low in Hg?

- Not known yet.
  - Too few data?
  - Low methylation (wetlands drained)?
  - Nitrate inhibition?
  - Reduction/volatilization due to high pH’s?
  - Low bioavailability?
  - Food web structure?

- Why care?
  - Anticipate changes.
UIUC Method for Methylmercury Analysis

Mercury-thiourea complex ion chromatography for mercury speciation analysis (Shade and Hudson, ES&T 2005).

- A radically-different method for analyzing methylmercury.
- Liquid chromatography vs. gas chromatography.
- Uses CVAFS detection, so sensitivity is comparable to standard method.
**pH-Modulated Thiol-Thione Switch**

After Laws (1970)

- **pH > 3:** Adsorption Favored
- **pH < 2:** Desorption Favored
Hg$^{2+}$ and CH$_3$Hg$^+$ Thiourea Complexes

MeHg$^+$

\[
\begin{array}{c}
\text{Hg} \\
\text{C=S} \\
\text{Hg} \\
\end{array}
\]

Hg$^{2+}$

\[
\begin{array}{c}
\text{Hg} \\
\text{C=S} \\
\text{C=S} \\
\end{array}
\]
## A Full Suite of Methods for MeHg Analysis

<table>
<thead>
<tr>
<th></th>
<th>Method 1630</th>
<th>New Method</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sample Preparation</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biota</td>
<td>Acid Digestion / Solvent Extraction</td>
<td>Acid Digestion / Solvent Extraction;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Eluant Leaching</td>
</tr>
<tr>
<td>Sediments</td>
<td>Acid Digestion / Solvent Extraction; Distillation</td>
<td>Acid Digestion / Solvent Extraction</td>
</tr>
<tr>
<td>Water</td>
<td>Distillation</td>
<td>TU-Catalyzed Solid Phase Extraction</td>
</tr>
<tr>
<td><strong>Concentration</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ethylate &amp; Purge / Trap on Tenax</td>
<td>Buffer pH / Trap on Thiol Resin</td>
</tr>
<tr>
<td><strong>Species Separation</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gas Chromatography</td>
<td>Ion Chromatography</td>
</tr>
<tr>
<td></td>
<td>MeHgEt and Hg(Et)$_2$</td>
<td>MeHgTU$^+$ and Hg(TU)$_4^{2+}$</td>
</tr>
<tr>
<td><strong>Detection</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Generate Hg$^0$ and Quantify by Atomic Fluorescence Spectrometry</td>
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</tr>
</tbody>
</table>
Validation of Sediment and Biota Sample Preparations

Shade (2008)

Vermillion et al. (in prep)
Dissolved Mercury Speciation Analysis

Extremely challenging (and hence expensive) because:

1) Mercury occurs at very low concentrations, i.e., low parts per trillion or (ng/L).

2) MeHg, which typically makes up 5-20% of total, is the most toxicologically-important species.

3) HgII and MeHg can be strongly bound by ligands in the water, including thiols in DOM and HS\(^-\) making it difficult to separate from Sample matrix.
Thiourea-catalyzed solid phase extraction of dissolved methylmercury

Vermillion and Hudson (Analytical and Bioanalytical Chemistry 2007)
Pre-Concentration of MeHg from Water

$K_{\text{MeHgBr}} = 10^{5.2}$

$K_{\text{MeHgTU}} = 10^{11.8}$
Methylmercury in Piasa Creek Watershed
(Near Alton, IL)

Main loading likely is current deposition.
DOC Control of Mercury Transport

\[ y = 0.8671x - 0.4343 \]
\[ R^2 = 0.2958 \]

\[ y = 0.1012x - 0.0191 \]
\[ R^2 = 0.3366 \]
MeHg versus UV Absorbance

\[ y = 0.7093x + 0.0462 \]

\[ R^2 = 0.5654 \]
DOC Control of MeHg Transport

\[ y = 0.1552x \]
\[ R^2 = 0.7445 \]

\[ y = 0.0247x \]
\[ R^2 = 0.7867 \]
Total versus Methyl Mercury

\[ y = 0.1779x - 0.0182 \]

\[ R^2 = 0.9286 \]
Methylmercury and Land Use in Piasa Creek Watershed
Methylmercury in Biota (June 2007)

![Graph showing methylmercury levels in biota]
Test of DGT Methylmercury Probes

![Graph showing the comparison of DGT methylmercury to biota methylmercury for different biota species. The x-axis represents DGT methylmercury (ng/L), and the y-axis represents biota methylmercury (ppm). The graph includes data points for Darter, Crayfish, and Progomphus.]
MeHg Bioconcentration Factors

**Dissolved Organic Carbon (mg/L)**

- **Progomphus**
  - \( y = -0.0699x + 1.219 \)
  - \( R^2 = 0.4364 \)
- **Darter**
  - \( y = -0.2711x + 3.9142 \)
  - \( R^2 = 0.3749 \)
- **Crayfish**
  - \( y = -0.103x + 1.0286 \)
  - \( R^2 = 0.6897 \)

**Chloride (mg/L)**

- **Progomphus**
  - \( y = 0.1593x - 0.7785 \)
  - \( R^2 = 0.4157 \)
- **Darter**
  - \( y = 0.0578x - 0.5336 \)
  - \( R^2 = 0.9545 \)

\[ \text{MeHg-DOM + Cl}^- \rightarrow \text{MeHgCl}^0 + \text{DOM} \]
Methylmercury in Grand Calumet Watershed

- Driven by legacy pollution and current deposition?
Steel Mills in Gary, IN
Dissolved Methylmercury

Grand Calumet Wetland Survey - July 2006

Dissolved Methylmercury (ng/L) vs. Dissolved Organic Carbon (mg/L)

R² = 0.501
Dissolved Methylmercury

Grand Calumet Wetland Survey - July 2006

Dissolved Methylmercury (ng/L) vs. pH

R² = 0.369
MeHg in Sediments of Grand Calumet

![Graphs showing the relationship between MeHg in sediments and dissolved MeHg in porewater.](image)

- **Graph 1:** Correlation between Mercury Species in Sediments (ng/g-dw) and Sediment Organic Matter (%LOI).
- **Graph 2:** Correlation between Dissolved MeHg and THg in Porewater (ng/L) and Sediment MeHg (ng/g-dw).
MeHg in Grand Calumet Fish
(NDMMF Modeled 10-in Yellow Perch)
Validation of Method

Comparison to Distillation/Ethylation Results
- Trent University (Hintelmann Lab)
- USGS NAWQA samples (WDML)

All standard QA/QC results are excellent.
- Replicate RSD ~5%
- Blank is non-detectable
- Tests for artifact formation yield negative results
Comparison with Trent University

Distillation/Ethylation with Isotope Dilution and ICP-MS Detection
Lake 658: Experimental Lakes Area, Ontario

![Graph showing dissolved oxygen and mercury levels in Lake 658.](image-url)
UIUC-Trent University Intercomparison

![Graph showing the ratio of MeHg concentrations measured by D/E-ID relative to TU-SPE (Percent). The graph compares Oxic systems and Sulfidic systems.](image-url)
Pre-Concentration of MeHg from Water

Separation from Sample Matrix

Distillation
- \( \text{H}_2\text{SO}_4 \)
- \( \text{KBr} \)

Preserved Sample

Ethylation
- Acetate
- \( \text{NaBE}_{14} \)

Purge & Trap

Concentration / Loading

Chromatography / Quantitation

GC

ICP-MS

CVNFS

Distillation Residue
MeHg in Fract

CRc

CRa'

PWA

Whole Sample
TU
DBID

Distillation Fractions
Residue (TU-SPE)
Distillate (DE)
Whole Sample versus Distillation Fractions

\[ y = 0.988x \]

\[ R^2 = 0.988 \]
Intercomparison with USGS WDML

Note: MeHg results for suspended sediments are not significantly different.
Intercomparison with USGS-Wisconsin Lab at NAWQA Sites

A) New York-Fishing Brook

B) South Carolina-McTier Creek
Why do the methods yield different results?

- Distillation does not completely recover MeHg from samples.
  - Hypothesize the existence of a very stable, non-volatile MeHg species. Perhaps MeHg is bound to sulfide-containing nanoparticles.

- Artifactual MeHg formation?
  - All tests to date indicate not a factor.
  - Chemical process of TU-SPE indicate not likely.
  - Most sensitive test still needed.
Conclusions

• There has been relatively little study of Hg biogeochemistry in Illinois.

• Methylmercury in some streams (Piasa Creek) occurs at significant concentrations and Hg levels in fish are substantial.

• The new UIUC analytical method should help reduce costs of MeHg analysis for environmental studies.

• The improved capability to measure dissolved MeHg should lead to a more precise and accurate understanding of MeHg production and transport in the environment.

• Consideration needs to be given to how attempts to mitigate nitrate pollution affect MeHg production in streams, wetlands, and bioreactors.