DISTRIBUTION OF MERCURY SPECIES IN THE EVERGLADES: A GEOCHEMICAL PERSPECTIVE AND IMPLICATIONS ON MERCURY BIOACCUMULATION

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Mercury Cycling in the Everglades

(Liu et al, 2009)
Inorganic Mercury (iHg) Speciation and Hg Cycling

Water

Floc

Soil

Periphyton

Hg$^{2+}$

MeHg

Hg$^{2+}$

Hg(OH)$_2$, Hg(OH)$_3^-$

HgS$_2^{2-}$, Hg(HS)$_2$

HgCl$^+$, HgCl$_2$

Hg-DOM...

Hg$^{2+}$

MeHg

Hydrology
Geochemistry
Microbiology

Hydrology Geochemistry Microbiology
Objective

Understand how geochemical factors regulate speciation of inorganic Hg and subsequently influence Hg cycling in the Everglades.
Geochemical Modeling of Hg Speciation

❖ Geochemical Model
  ❑ PHREEQC  (Parkhurst and Appelo, 2013)

❖ Data Sources
  ❑ Everglades Regional Environmental Monitoring and Assessment Program (R-EMAP)
  ❑ USGS ACME
  ❑ SFWMD DBHYDRO
A long list of parameters

- Surface: DO, Cond., pH, Temp., Secchi Depth, Turbidity, TOC, Eh, depth, $S^2-$, APA.
- Water: TP, TKN, $NH_3$, $NO_{2+3}$, $SO_4$, Cl, Dissolved: $SO_4$, $NH_4$, $NO_{2-3}$, $PO_4$
- Porewater: TP, TN, $SO_4$, $S^2-$, Anions (Cl, $NO_{2-3}$, SRP)
- Soil: Bulk Density, TP, AFDW, Type, Thickness, $SO_4$, Mineral Content, APA.
- Floc: Bulk Density, TP, AFDW, Type, Thickness, $SO_4$, Mineral Content, APA.
- Periphyton: THg, MeHg
- Mosquitofish: THg, length, weight, sex, food habits

(Scheidt and Kalla, 2007)
Data Sources

2005 R-EMAP

Dataset:
THg, MeHg, Biogeochemical parameters

Sampling stations:
109 in dry season
119 in wet season

[S²⁻] > 0.02 mg/L
18 in dry season
21 in wet season

USGS ACME
SFWMD DBHYDRO
Model Input

- Physicochemical Parameters
  - pH
  - Redox Potential
  - Hg Binding Ligands
    - Cl\(^-\), Br\(^-\), SO\(_4\)^{2-}\...

- Hg-DOM Complexation

- Hg-Sulfide Complexation
Hg-DOM Complexation

- **Binding Sites**
  - Thiol Groups (RS\(^{-}\))
  - Oxygen Functional Groups (RO\(^{-}\))

- \[ \text{Hg(OH)}_2 + \text{RSH}^{n-} + \text{H}^+ = \text{RSHg}^{(n-1)-} + 2\text{H}_2\text{O} \]

  \[ \text{Log } K = 20.8 \quad (\text{Skyllberg, 2008}) \]

- **Determination of RS\(^{-}\) Concentrations**

  \[ [\text{RS}^{-}] = 0.00017[D\text{OC}] \quad (\text{Benoit et al., 2001}) \]

<table>
<thead>
<tr>
<th>Everglades DOM Isolates</th>
<th>Molecular Weight</th>
<th>Carbon Content (%)</th>
<th>Reduced S Fraction (mol/mol DOM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrophobic</td>
<td>1031</td>
<td>52.2</td>
<td>0.12</td>
</tr>
<tr>
<td>Hydrophilic</td>
<td>862</td>
<td>49.3</td>
<td>0.05</td>
</tr>
</tbody>
</table>
Hg-Sulfide Complexation

**Database:**

\[
\text{Hg(OH)}_2 + 2\text{HS}^- = \text{HgS}_2^{2-} + 2\text{H}_2\text{O} \quad \text{Log K}=31.24
\]

\[
\text{Hg(OH)}_2 + 2\text{HS}^- + 2\text{H}^+ = \text{Hg(HS)}_2 + 2\text{H}_2\text{O} \quad \text{Log K}=43.82
\]

**Complementary:**

\[
\text{Hg(OH)}_2 + \text{H}^+ + 2\text{HS}^- = \text{HgHS}_2^- + 2\text{H}_2\text{O} \quad \text{Log K}=38.10
\]

\[
\text{Hg(OH)}_2 + \text{H}^+ + \text{HS}^- = \text{HgHSOH} + \text{H}_2\text{O} \quad \text{Log K}=22.70
\]

**Sulfide Concentrations**

- \( \geq 0.02 \text{ mg/L} \)
- \(< 0.02 \text{ mg/L} \)
  - 0.00000032 mg/L (0.00001 µM)
  - 0 mg/L

(Skyllberg, 2008)
### Hg species in Everglades Surface Water ([S²⁻] > 0.02 mg/L)

<table>
<thead>
<tr>
<th>Station</th>
<th>Hg mol/L</th>
<th>HgS²⁻ mol/L</th>
<th>HgHS⁻ mol/L</th>
<th>Hg(HS)₂ mol/L</th>
<th>HgHSOH mol/L</th>
<th>RSHg⁽ⁿ⁻¹⁾ mol/L</th>
<th>HgCl₂ mol/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>1.45E-11</td>
<td>1.20E-11</td>
<td>2.39E-12</td>
<td>4.43E-14</td>
<td>1.70E-21</td>
<td>1.94E-22</td>
<td>3.44E-29</td>
</tr>
<tr>
<td>35</td>
<td>9.97E-12</td>
<td>8.04E-12</td>
<td>1.90E-12</td>
<td>3.48E-14</td>
<td>2.81E-22</td>
<td>5.42E-24</td>
<td>4.19E-33</td>
</tr>
<tr>
<td>40</td>
<td>1.70E-11</td>
<td>1.11E-11</td>
<td>5.67E-12</td>
<td>2.23E-13</td>
<td>2.30E-21</td>
<td>1.15E-22</td>
<td>9.01E-32</td>
</tr>
<tr>
<td>64</td>
<td>8.97E-12</td>
<td>4.28E-12</td>
<td>4.36E-12</td>
<td>3.36E-13</td>
<td>1.18E-21</td>
<td>4.49E-23</td>
<td>3.43E-32</td>
</tr>
<tr>
<td>72</td>
<td>6.48E-12</td>
<td>4.67E-12</td>
<td>1.76E-12</td>
<td>5.10E-14</td>
<td>1.22E-21</td>
<td>1.16E-22</td>
<td>1.29E-31</td>
</tr>
<tr>
<td>74</td>
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<td>4.48E-32</td>
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<tr>
<td>76</td>
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<td>2.53E-12</td>
<td>5.48E-14</td>
<td>1.73E-21</td>
<td>1.17E-22</td>
<td>5.20E-32</td>
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<tr>
<td>86</td>
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<td>3.17E-12</td>
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<td>2.83E-21</td>
<td>2.53E-22</td>
<td>2.88E-31</td>
</tr>
<tr>
<td>96</td>
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<td>9.24E-12</td>
<td>1.70E-12</td>
<td>2.49E-14</td>
<td>1.39E-21</td>
<td>2.16E-22</td>
<td>2.56E-31</td>
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<tr>
<td>97</td>
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<td>7.91E-12</td>
<td>2.14E-13</td>
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<td>2.43E-31</td>
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<tr>
<td>100</td>
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<td>2.43E-12</td>
<td>4.48E-14</td>
<td>1.31E-21</td>
<td>1.34E-22</td>
<td>1.66E-31</td>
</tr>
<tr>
<td>110</td>
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<td>3.28E-12</td>
<td>2.78E-14</td>
<td>2.31E-22</td>
<td>5.12E-24</td>
<td>6.31E-33</td>
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<tr>
<td>117</td>
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<td>7.43E-12</td>
<td>1.78E-11</td>
<td>1.67E-19</td>
<td>7.16E-19</td>
<td>7.12E-27</td>
</tr>
<tr>
<td>118</td>
<td>1.65E-11</td>
<td>9.33E-12</td>
<td>6.75E-12</td>
<td>3.74E-13</td>
<td>7.93E-21</td>
<td>1.10E-21</td>
<td>1.39E-30</td>
</tr>
<tr>
<td>120</td>
<td>3.29E-11</td>
<td>9.97E-13</td>
<td>1.49E-11</td>
<td>1.70E-11</td>
<td>1.43E-19</td>
<td>2.65E-19</td>
<td>3.03E-27</td>
</tr>
<tr>
<td>121</td>
<td>7.98E-12</td>
<td>3.34E-12</td>
<td>4.23E-12</td>
<td>4.08E-13</td>
<td>2.68E-21</td>
<td>2.49E-22</td>
<td>3.67E-31</td>
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<td>350</td>
<td>2.24E-11</td>
<td>1.96E-11</td>
<td>2.78E-12</td>
<td>3.20E-14</td>
<td>3.38E-22</td>
<td>1.10E-23</td>
<td>2.40E-32</td>
</tr>
</tbody>
</table>

**Sample model output**
HgS$_2^{2-}$, HgHS$_2^-$, and Hg(HS)$_2$ are major species.
Relative Distribution of iHg Species
(Assuming \([S^{2-}] = 0.00000032\ mg/L\))

RSHg\((n-1)\)- and Hg-sulfide complexes are major species.
Relation of iHg Species with MeHg
([S\textsuperscript{2-}] > 0.02 mg/L)

<table>
<thead>
<tr>
<th>MeHg</th>
<th>Surface water iHg species</th>
<th>HgS\textsubscript{2}\textsuperscript{2-}</th>
<th>HgHS\textsubscript{2}\textsuperscript{-}</th>
<th>Hg(HS)\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dry</td>
<td>Wet</td>
<td>Dry</td>
<td>Wet</td>
</tr>
<tr>
<td>Surface water</td>
<td>0.88**</td>
<td>0.39</td>
<td>0.08</td>
<td>0.53**</td>
</tr>
<tr>
<td></td>
<td>(18)</td>
<td>(21)</td>
<td>(18)</td>
<td>(21)</td>
</tr>
<tr>
<td>Epiphytic periphyton</td>
<td>0.9*</td>
<td>0.11</td>
<td>0.9*</td>
<td>0.32</td>
</tr>
<tr>
<td>Floc</td>
<td>0.50*</td>
<td>-0.10</td>
<td>0.18</td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td>(16)</td>
<td>(17)</td>
<td>(16)</td>
<td>(17)</td>
</tr>
<tr>
<td>Soil</td>
<td>-0.22</td>
<td>0.13</td>
<td>0.67**</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>(18)</td>
<td>(21)</td>
<td>(18)</td>
<td>(21)</td>
</tr>
</tbody>
</table>

** Significant correlations at p < 0.001 level;  
* Significant correlations at p < 0.05 level
## Relation of iHg Species with MeHg

(Assuming $[S^{2-}] = 0.00000032$ mg/L)

<table>
<thead>
<tr>
<th>MeHg</th>
<th>Surface water iHg species</th>
<th>Surface water iHg species</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\text{HgS}_2^{2-}$</td>
<td>$\text{HgHS}_2^{-}$</td>
</tr>
<tr>
<td></td>
<td>Dry</td>
<td>Wet</td>
</tr>
<tr>
<td>Surface water</td>
<td>0.27 (51)</td>
<td>-0.12 (92)</td>
</tr>
<tr>
<td>Floating mat periphyton</td>
<td>0.09 (6)</td>
<td>-0.10 (16)</td>
</tr>
<tr>
<td>Epiphytic periphyton</td>
<td>0.34 (17)</td>
<td>-0.12 (64)</td>
</tr>
<tr>
<td>Floc</td>
<td>0.26 (50)</td>
<td>-0.25 (71)</td>
</tr>
<tr>
<td>Soil</td>
<td>0.07 (51)</td>
<td>0.30** (91)</td>
</tr>
</tbody>
</table>

** Significant correlations at $p < 0.001$ level;
* Significant correlations at $p < 0.05$ level
Relation of iHg Species with MeHg
(Assuming $[S^{2-}] = 0$ mg/L)

<table>
<thead>
<tr>
<th>MeHg</th>
<th>iHg species in surface water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RSHg^{(n-1)}-</td>
</tr>
<tr>
<td></td>
<td>Dry</td>
</tr>
<tr>
<td>Surface water</td>
<td>0.45** (51)</td>
</tr>
<tr>
<td>Floating mat periphyton</td>
<td>-0.14 (6)</td>
</tr>
<tr>
<td>Epiphytic periphyton</td>
<td>0.34 (17)</td>
</tr>
<tr>
<td>Floc</td>
<td>0.23 (50)</td>
</tr>
<tr>
<td>Soil</td>
<td>0.31* (51)</td>
</tr>
</tbody>
</table>

** Significant correlations at p < 0.001 level;
* Significant correlations at p < 0.05 level
## Hg speciation and mosquitofish Hg

<table>
<thead>
<tr>
<th>Sulfide concentrations</th>
<th>Hg species in surface water</th>
<th>Hg in mosquitofish</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Dry season</td>
</tr>
<tr>
<td>[S] &gt; 0.02 mg/L</td>
<td>HgS(_2)^{2-})</td>
<td>0.47 (16)</td>
</tr>
<tr>
<td></td>
<td>HgHS(_2)^{-})</td>
<td>-0.16 (16)</td>
</tr>
<tr>
<td></td>
<td>Hg(HS)(_2)</td>
<td>-0.29 (16)</td>
</tr>
<tr>
<td>[S] = 0.00000032 mg/L</td>
<td>RSHg(^{(n-1)})^{-}</td>
<td>0.06 (39)</td>
</tr>
<tr>
<td></td>
<td>HgS(_2)^{2-})</td>
<td>0.02 (39)</td>
</tr>
<tr>
<td></td>
<td>HgHS(_2)^{-})</td>
<td>0.18 (39)</td>
</tr>
<tr>
<td></td>
<td>Hg(HS)(_2)</td>
<td>0.06 (39)</td>
</tr>
<tr>
<td>[S] = 0 mg/L</td>
<td>RSHg(^{(n-1)})^{-}</td>
<td>0.08 (39)</td>
</tr>
</tbody>
</table>
Summary

• Sulfide and DOM dominate iHg speciation in Everglades surface water.

• Distribution of iHg species have implications on Hg methylation and bioaccumulation, but more studies are needed.
Next Step…

- Porewater and bottom water
- DOM quality variations
- More accurate sulfide concentration
- MeHg speciation
Acknowledgements

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• EPA Region 4
• National Park Service
• Army Corps of Engineers
• Florida Department of Environmental Protection