Biogeochemistry of mercury in boreal wetlands with emphasis on methylation and demethylation processes

1) Background: Sources and sinks of methyl mercury (MeHg)
2) Budgets and transformations of Hg and MeHg in eight boreal Swedish wetlands
3) Synthesis: Factors in control of MeHg net production and degradation in wetlands
4) Conclusions
5) Discussion

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Background
Sources and sinks of MeHg
Biogeochemical processes
Annual mass balance budgets for MeHg in boreal wetlands

MeHg wetland yields (g/km²)

- St. Louis et al., 2004

Locations and data sources:
- Riparian Adirondack: Selvendiran et al., 2008
- Riparian/first order Svartberget: Lee et al., 1995
- Riparian/first order Allequash: Krabbenhoft, 1995
- Valley-bottom 1, ELA: St. Louis et al., 1996
- Valley-bottom 2, ELA: St. Louis et al., 2004
- Riverine, ELA: Driscoll et al., 1998
- Basin, ELA: Driscoll et al., 1998
- Riverine postflood, ELA: Driscoll et al., 1998
- Beaver meadow, Adirondack: New York: Driscoll et al., 1989
- Beaver pond, NY: Driscoll et al., 1998
- Riverine postflood, ELA: Driscoll et al., 1998
Conclusions from large-scale manipulations

The concentration of MeHg in soil and sediment is a net result of simultaneously ongoing methylation and demethylation processes.

The amount and quality of organic substrate (electron donor) control the net methylation.
## Sinks for MeHg: Uplands and lakes

### MeHg yield (net output) $g \text{ km}^{-2} \text{ yr}^{-1}$

<table>
<thead>
<tr>
<th>Location</th>
<th>MeHg yield</th>
<th>Output as % of input</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lake 240, Ontario (drainage lake)</td>
<td>-0.13</td>
<td>30%</td>
</tr>
<tr>
<td>Devils lake, Wisconsin (drainage lake)</td>
<td>-0.083</td>
<td>89%</td>
</tr>
<tr>
<td>Ängessjön, Sweden (drainage lake)</td>
<td>-0.30</td>
<td>64%</td>
</tr>
<tr>
<td>Upland (0% wetland)</td>
<td>-0.03</td>
<td></td>
</tr>
</tbody>
</table>

### Estimates of input, output and internal processes in lakes

<table>
<thead>
<tr>
<th>Location</th>
<th>% of input</th>
<th>% of output</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lake 240 1-yr period</td>
<td>stream input 23%</td>
<td>stream outflow 22%</td>
</tr>
<tr>
<td></td>
<td>wet deposition 3%</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>internal methylation &gt;73%</strong></td>
<td><strong>photodegradation 78%</strong></td>
</tr>
<tr>
<td>Devils lake (May 30-Aug 19)</td>
<td>wetland runoff 7.8%</td>
<td>stream &amp; GW outflow 7%</td>
</tr>
<tr>
<td></td>
<td>wet deposition 1.4%</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>internal methylation 90%</strong></td>
<td><strong>degradation/burial 93%</strong></td>
</tr>
<tr>
<td>Spring lake, Minnesota seepage lake</td>
<td>runoff 4.9%</td>
<td>burial 12%</td>
</tr>
<tr>
<td>(March –Nov)</td>
<td>wet deposition 9.8%</td>
<td>uptake by fish 28%</td>
</tr>
<tr>
<td></td>
<td><strong>internal methylation 82%</strong></td>
<td><strong>photodegradation 60%</strong></td>
</tr>
</tbody>
</table>

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1 Sellers et al., LimnolOceanogr 2001; 2 Watras et al., ES&T 2005; 3 Skyllberg et al. in prep.; 4 Hines & Brezonik, Biogeochem. 2007; 5 St Louis et al., ES&T 1996
Reduction

\[ \text{Hg}^0(g) \]

Methylation (SRB, IRB)

\[ \text{Hg}^{\text{II}} \text{X}_2 \Leftrightarrow \text{Hg-S-NOM} \]

Demethylation reactions

Biotic Oxidative Hg(II)

\[ \text{CO}_2 \]

Biotic Reductive Hg(II)

\[ \text{CH}_4 \]

Abiotic photo-degradation

\[ \text{Hg}^0(g) \]

\[ \text{CH}_3\text{HgX} \Leftrightarrow \text{NOM-S-CH}_3\text{Hg} \]

\[ X = \text{HS}^-, \text{RS}^- \text{ (thiol), polysulfides?} \]

Xenobiotica

Biomagnification

Fish

Zooplankton

Phytoplankton Bacteria
MeHg net formation/degradation experiments

First order kinetics:

\[
d[\text{MeHg}]/dt = k_m[\text{Hg(II)}] - k_d[\text{MeHg}]
\]

- \( k_m \) methylation rate constant (d\(^{-1}\))
- \( k_d \) demethylation rate constant (d\(^{-1}\))

- \([\text{Hg(II)}]\) concentration of Hg(II) bioavailable to SRB, IRB
- \([\text{MeHg}]\) concentration of MeHg available for demethylation

As long as \([\text{Hg(II)}]\) and \([\text{MeHg}]\) are unknown, natural rates cannot be calculated and we have to settle with qualitative comparisons of values on \( k_m, k_d \) and the \( k_m/k_d \) ratio among sites.
**Determination of $k_m$ and $k_d$ using Hg stable isotope tracers in incubation studies**

\[
\begin{align*}
^{196}\text{Hg}^{2+} & \xrightarrow{k_m} \text{CH}_3^{^{196}\text{Hg}} \\
\text{CH}_3^{^{198}\text{Hg}} & \xrightarrow{k_d} ^{198}\text{Hg}^{2+}
\end{align*}
\]

- **Sample**
  - Incubation: 20 °C, 48h, dark, N₂
  - Homogenisation
  - Equilibration

- **Extraction**
  - H₂SO₄/CuSO₄/KBr

- **Clean-up**
  - H₂O-extract
  - CH₂Cl₂

- **NaB(C₂H₅)₄ derivatisation**
  - Hg²⁺ → Hg(C₂H₅)₂
  - CH₃Hg⁺ → CH₃HgC₂H₅

- **GC-ICPMS analysis**
Budgets and transformations of Hg and MeHg in eight boreal Swedish wetlands

Results reported in


Tjerngren et al., In Review
Budgets and transformations of Hg and MeHg in eight boreal Swedish wetlands

All wetlands selected had a history of artificial drainage and they were subjected to restoration measures by land owners.

1) Input-output mass balances for MeHg, $\text{Hg}_{\text{inorg}}$, $\text{SO}_4$, DOC and Cl during four calendar years: 2007-2010.

2) Determination of MeHg production and degradation rates in the wetland soils by isotope addition incubation experiments.
Group I – Northern wetlands

Nutrient poor
*Sphagnum/Carex* peatlands
C/N 28-37, pH 4.3-4.8

Riparian zone

Dystrophic lake-peatland

Open fen
Group II – Nutrient gradient

Upstream bog/fen (LDNA)

Downstream fen (LDNB)

Intermediate nutrient status: *Sphagnum* dominated bog grading into a *Carex* and broad-leaved grasses dominated fen

C/N 21-34, pH 4.6-5.1
Group III – Southern wetlands

Alnus swamp

Nutrient rich wetlands with herbs and broad-leaf grasses
C/N 14-21, pH 5.6-5.8

Artificial wetland

Mesotrophic lake - peatland
## Division of the eight wetlands into three nutrient groups

<table>
<thead>
<tr>
<th>Wetland area ha (%)</th>
<th>Northern nutrient poor</th>
<th>Nutrient gradient</th>
<th>Southern nutrient rich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Riparian zone wetland</td>
<td>Open fen</td>
<td>Dystrophic lake-peatland</td>
</tr>
<tr>
<td>Wetland area ha (%)</td>
<td>2.0 (4.2)</td>
<td>8.4 (7.0)</td>
<td>26 (26)</td>
</tr>
<tr>
<td>Vegetation</td>
<td>Acidophilic Polytricum/Sphagnum/Carex</td>
<td>Sphagnum Calluna</td>
<td>Carex Grasses</td>
</tr>
<tr>
<td>pH soil pore water</td>
<td>4.3±0.1</td>
<td>4.6±0.1</td>
<td>4.8±0.1</td>
</tr>
<tr>
<td>C/N soil</td>
<td>28±1.2</td>
<td>36±4.3</td>
<td>37±2.4</td>
</tr>
<tr>
<td>Tsum &gt;5°C</td>
<td>1950</td>
<td>1950</td>
<td>1950</td>
</tr>
<tr>
<td>SUVA$_{254nm}$ outlet</td>
<td>4.7±0.1</td>
<td>4.2±0.1</td>
<td>4.0±0.1</td>
</tr>
<tr>
<td>Fe$_{tot}$ (µM) outlet</td>
<td>34±2</td>
<td>24±3</td>
<td>15±1</td>
</tr>
<tr>
<td>SO$_4$ (µM) outlet</td>
<td>6.9±0.6</td>
<td>16</td>
<td>10±0.7</td>
</tr>
<tr>
<td>S(-II) (µM) soil pore water</td>
<td>&lt;1.0</td>
<td>~3.0</td>
<td>~5.0</td>
</tr>
</tbody>
</table>
Results
Incubation studies of wetland soils
Methylation & demethylation rate constants

![Graph showing methylation and demethylation rates for different environments.]

Results

Input-output budget calculations
Element budgets

Wetland yield (g/km²) = (mass_{Output} – mass_{Input}) / wetland area

\[ \text{MeHg}_{\text{Output}} \ (\text{mass}) = V_{\text{Outlet}} \times [\text{MeHg}]_{\text{Outlet}} \]

\[ \text{MeHg}_{\text{Input}} = (V_{\text{Inlet}} \times [\text{MeHg}]_{\text{Inlet}}) + (V_{\text{Soil runoff}} \times [\text{MeHg}]_{\text{Soil water}}) + (V_{\text{Precipitation}} \times [\text{MeHg}]_{\text{Precipitation}}) \]
“riparian” and wetlands receiving water from a mixture of acid peatlands and surface soil discharge.

“basin wetlands” receiving deeper soil water from upland soils and slightly richer peatlands

Large-scale "flooded peatlands"

MeHg wetland yields

Alnus swamp significant sink!
MeHg catchment exports related to %MeHg and $k_m/k_d$ in wetland soils average 2007-2009 (2008)

**Graphs:****

1. **%MeHg vs. MeHg export (g/km²):**
   - Data points for different sites (SKM, SRD, KSN, LDNA, LDNB, GTN, GDL, EHT).
   - Linear regression equations:
     - $y = 0.0271x + 0.0417$ with $R^2 = 0.73$.
     - $y = 0.4368x + 0.0385$ with $R^2 = 0.57$.

2. **$k_m/k_d$ vs. MeHg export (g/km²):**
   - Data points for different %MeHg soil values.
   - Linear regression equations:
     - $y = 0.0271x + 0.0417$ with $R^2 = 0.73$.
     - $y = 0.4368x + 0.0385$ with $R^2 = 0.57$.

**Table:****

<table>
<thead>
<tr>
<th>Site</th>
<th>pH</th>
<th>C/N</th>
</tr>
</thead>
<tbody>
<tr>
<td>SKM</td>
<td>4.3</td>
<td>28</td>
</tr>
<tr>
<td>SRD</td>
<td>4.6</td>
<td>36</td>
</tr>
<tr>
<td>KSN</td>
<td>4.8</td>
<td>37</td>
</tr>
<tr>
<td>LDNA</td>
<td>4.6</td>
<td>34</td>
</tr>
<tr>
<td>LDNB</td>
<td>5.1</td>
<td>21</td>
</tr>
<tr>
<td>GTN</td>
<td>5.6</td>
<td>19</td>
</tr>
<tr>
<td>GDL</td>
<td>5.8</td>
<td>21</td>
</tr>
<tr>
<td>EHT</td>
<td>5.7</td>
<td>14</td>
</tr>
</tbody>
</table>

MeHg wetland yields related to %MeHg and $k_m/k_d$ in wetland soils

How can we explain the pattern of MeHg net production in relation to nutrient status of wetlands?

Conceptual model of MeHg net production

<table>
<thead>
<tr>
<th>Wetland nutrient status</th>
<th>Methylation rate</th>
<th>Demethylation rate</th>
<th>Net MeHg production rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH, Fe, SO$_4^{2-}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SUVA, C/N</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

What is limiting methylation rates at intermediate nutrient status?

Specific types of SRB/IRB are strong methylators.

And they may be limited by:
1) Electron donors (LMM OA)
2) Electron acceptors (Fe, SO$_4$)
3) Bioavailability of Hg for methylation
4) Micronutrients (e.g. Co)?

Abiotic demethylation?

If biotic (oxidative) demethylation is a general process taken care of by many different groups of bacteria, the demethylation rate may follow a general increase in bacterial activity with improved conditions for growth (increased nutrient status and e-donor quality).
Time for questions!
Results
Alder swamp – a sink for MeHg
**Alnus swamp, Edshult – a significant sink for MeHg**

<table>
<thead>
<tr>
<th>Year</th>
<th>Hg$_{\text{inorg}}$ yield</th>
<th>% yield</th>
<th>MeHg yield</th>
<th>% yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>2007</td>
<td>-53</td>
<td>-6</td>
<td>-62</td>
<td>-58</td>
</tr>
<tr>
<td>2008</td>
<td>-99</td>
<td>-14</td>
<td>-35</td>
<td>-38</td>
</tr>
<tr>
<td>2009</td>
<td>-76</td>
<td>-21</td>
<td>-17</td>
<td>-44</td>
</tr>
<tr>
<td>2010</td>
<td>-116</td>
<td>-17</td>
<td>-17</td>
<td>-29</td>
</tr>
</tbody>
</table>
Studies in September 2008 indicate that MeHg loss is due to demethylation processes in the soil, which is increasingly expressed with distance from the Alnus swamp inlet.

Further studies are in progress to identify the type of process (biotic/abiotic) and which type of bacteria that may be involved in biotic demethylation.
Conclusions wetlands

Methylation
Net production of MeHg

Northern mixed poor bog/fens and dystrophic lake

Southern bog-fen Sphagnum-Carex peatland

Southern nutrient rich peatland/ mesotrophic lake

Alnus swamp situated downstream methylation hot-spot

"Hot-spots" demethylation high nutrient status

"Hot-spots" methylation intermediate nutrient status

pH 4.3-4.8

pH 5.5-6.0

Nutrient status
C/N

Demethylation

40