Mercury & Methyl Mercury in Great Salt Lake: Overview & Analysis

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Presentation Outline

• Introduction
  – Mercury & Mercury Cycle
  – Concerns
• Research Objectives
• Methods
  – Sampling Methods & Analysis
• Results & Discussions
• Summary
Introduction

Elemental Hg(0)

Inorganic Hg(I)/(II) → Organic

Oxidation/Reduction
Methylation
Demethylation

Human & Ecological Consequences

Ecosystem Transport

Emissions & Speciation

Atmospheric Transport & Depositions

Biological Uptake & Release
Concerns & Consequences

- Persistent Bioaccumulative Toxin (PBT)
- Ecological effects
  - Bioaccumulation & magnification
- Human health concerns
  - Potent neurotoxin
  - RfD for MeHg: 0.1 µg/kg-day
  - Acute LD$_{50}$ (Body weight of 70-kg human)
    - Inorganic: 14-57 mg/kg
    - Organic: 20-60 mg/kg (MeHg)
Mercury Concerns in Great Salt Lake (GSL) Watershed

• 2003 USGS finds Hg levels in GSL water, among highest ever measured

• Mercury sources
  – Hg in GSL likely not new
  – Natural/Anthropogenic

• 2005 USGS finds elevated Hg in brine shrimp, grebe livers from GSL

• 2005 DOH, DWR and DEQ, consumption advisories for fish and water fowl in Utah

• Great Salt Lake Ecosystem Program
  – Selenium (Se) Standard
  – Wetlands assessment plan
  – Mercury analysis
Research Objectives

- Synoptic sampling & analysis of mercury, in water column & sediments from Farmington Bay (FB), Utah Lake and Jordan River
- Analyze the fate of mercury entering municipal waste water treatment plants (WWTP), emptying into Jordan River
- To evaluate the rate of mercury methylation in the sediments from the Turpin unit of FB
- And, to investigate the ecology of sulfate reducers possibly participating in mercury methylation of the sediments
Methodology

• Cold Vapor Atomic Florescence Spectrometry (CVAFS)
• Reference methods 1630 and 1631 of EPA Hg Analysis
• Methyl mercury in sediments extraction using Liquid-Liquid Extraction (LLE) (Nicolas S. Bloom et al., 1997)

Sampling Strategies

• Water Column
  o EPA 1669 Clean Sampling Techniques
  o Preservation
• Sediments
  o Core Sampler
  o Processing & Storage

Analysis Aspects

• Quality Control parameters
  o Blanks
  o Calibration Standards
  o Certified Reference Materials
Mercury Analyzer Setup

Instrument setup

Distillation unit

Cold Vapor Atomic Florecente Spectrometer (CVAFS)
Total Mercury Analysis

Calibration Curve

\[ y = 10233x - 159935 \]

\[ R^2 = 0.9998 \]

Peak Area

Analyzed Conc. (pg)

Conc. (pg)
Methyl Mercury Analysis

Calibration Curve

- $y = 140.44x - 510.14$
- $R^2 = 0.9995$

- Concentration...
Sampling Locations
Methylation Rate Analysis Setup

Sediment Sample → Aliquot → Blank, Control, 6Hr Sample, 12Hr Sample

Frozen in Liquid N₂ & stored ≤-20 °C

Hg (II) → MeHg

\[ K_{\text{METH}} = \frac{[\text{MeHg}]}{[\text{Hg (II)}]} \times t \]

Where,
\[ K_{\text{METH}}: \text{Kinetic Rate Constant (Time}^{-1}) \]

Time: Days
Sulfate Reducers Diversity Analysis

1. DNA Extraction
2. Gene Amplification
3. Phylogenetic Analysis

- PCR
- Phylogenetic Analysis
- Cloning & Sequencing

Genomic DNA Extraction
Unv. Primers
Grp. Specific Primers

Clones on growth media spiked with kanamycin

Phylogenetic Analysis
Compare sequences with other similar 16S rRNA sequences of Sulfate Reducers
### Water Column

<table>
<thead>
<tr>
<th>Site</th>
<th>THg (ng/L)</th>
<th>MeHg (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FB1</td>
<td>18.65 ± 4.32</td>
<td>1.69 ± 0.007</td>
</tr>
<tr>
<td>FB2</td>
<td>5.56 ± 1.36</td>
<td>0.87 ± 0.268</td>
</tr>
<tr>
<td>FB3</td>
<td>26.30 ± 1.70</td>
<td>0.51 ± 0.006</td>
</tr>
<tr>
<td>FB4</td>
<td>15.45 ± 0.92</td>
<td>1.57 ± 0.702</td>
</tr>
<tr>
<td>FB5</td>
<td>29.25 ± 4.45</td>
<td>3.71 ± 0.594</td>
</tr>
<tr>
<td>FB6</td>
<td>29.90 ± 4.38</td>
<td>0.62 ± 0.017</td>
</tr>
</tbody>
</table>

### Sediments

<table>
<thead>
<tr>
<th>Site</th>
<th>THg (µg/Kg)</th>
<th>MeHg (µg/Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>51.90 ± 17.89</td>
<td>0.11 ± 0.02</td>
</tr>
<tr>
<td>S2</td>
<td>78.07 ± 5.03</td>
<td>0.86 ± 0.65</td>
</tr>
<tr>
<td>S3</td>
<td>51.43 ± 13.83</td>
<td>0.07 ± 0.01</td>
</tr>
</tbody>
</table>
## Utah Lake Mercury Analysis

### Water Column

<table>
<thead>
<tr>
<th>Site</th>
<th>THg (ng/L)</th>
<th>MeHg (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UL1</td>
<td>4.05 ± 0.21</td>
<td>0.054 ± 0.0450</td>
</tr>
<tr>
<td>UL2</td>
<td>2.33 ± 0.30</td>
<td>0.053 ± 0.0024</td>
</tr>
<tr>
<td>UL3</td>
<td>2.94 ± 0.45</td>
<td>0.025 ± 0.0195</td>
</tr>
<tr>
<td>UL4</td>
<td>2.65 ± 0.45</td>
<td>0.771 ± 0.0103</td>
</tr>
<tr>
<td>UL5</td>
<td>1.80 ± 0.57</td>
<td>0.059 ± 0.0315</td>
</tr>
<tr>
<td>JR (U)</td>
<td>19.95 ± 0.78</td>
<td>0.18 ± 0.08</td>
</tr>
<tr>
<td>JR (L)</td>
<td>26.9 ± 0.57</td>
<td>0.64 ± 0.072</td>
</tr>
</tbody>
</table>

### Sediments

<table>
<thead>
<tr>
<th>Site</th>
<th>THg (µg/Kg)</th>
<th>MeHg (µg/Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UL1</td>
<td>47.00 ± 2.12</td>
<td>0.0083 ± 0.004</td>
</tr>
<tr>
<td>UL2</td>
<td>23.6 ± 4.95</td>
<td>0.0456 ± 0.027</td>
</tr>
<tr>
<td>UL3</td>
<td>19.85 ± 1.63</td>
<td>0.2805 ± 0.057</td>
</tr>
<tr>
<td>UL4</td>
<td>21.95 ± 0.92</td>
<td>0.0094 ± 0.010</td>
</tr>
<tr>
<td>UL5</td>
<td>23.25 ± 3.23</td>
<td>0.0147 ± 0.019</td>
</tr>
<tr>
<td>JR (U)</td>
<td>18.50 ± 0.28</td>
<td>0.021 ± 0.00</td>
</tr>
<tr>
<td>JR (L)</td>
<td>79.05 ± 29.63</td>
<td>0.147 ± 0.023</td>
</tr>
</tbody>
</table>

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[Map of Utah Lake and the Jordan River]
### WWTP’s Mercury Analysis

<table>
<thead>
<tr>
<th>POTW's</th>
<th>Influent (ng/L)</th>
<th>Effluent (ng/L)</th>
<th>Bio-Solids (µg/Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>THg</td>
<td>MeHg</td>
<td>THg</td>
</tr>
<tr>
<td>NDSD</td>
<td>52.35 ± 1.77</td>
<td>0.967 ± 0.16</td>
<td>6.87 ± 4.34</td>
</tr>
<tr>
<td>CDSD</td>
<td>83.55 ± 9.97</td>
<td>1.55 ± 0.431</td>
<td>6.99 ± 3.12</td>
</tr>
<tr>
<td>SDSD (S)</td>
<td>95.65 ± 7.57</td>
<td>1.57 ± 0.651</td>
<td>8.68 ± 1.25</td>
</tr>
<tr>
<td>CVWRF</td>
<td>153 ± 11.32</td>
<td>1.165 ± 0.092</td>
<td>4.5 ± 2.79</td>
</tr>
<tr>
<td>SVWRF</td>
<td>190 ± 14.14</td>
<td>1.61 ± 0.678</td>
<td>11.5 ± 5.66</td>
</tr>
</tbody>
</table>

- Mercury Sources & Fate
- Bio-Solids
Methylation Rate Studies

- Comparative Study
- Factors affecting methylation
- What next?
  - Correlating methylation with biota mercury accumulation

<table>
<thead>
<tr>
<th>Sediment Sites</th>
<th>$K_{\text{METH}}$ (Day$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.0302</td>
</tr>
<tr>
<td>S2</td>
<td>0.0120</td>
</tr>
<tr>
<td>S3</td>
<td>0.0210</td>
</tr>
<tr>
<td>Average</td>
<td>$0.021 \pm 0.0091$</td>
</tr>
</tbody>
</table>
Microbial Diversity Established

(Total Number of Clones = 35)

<table>
<thead>
<tr>
<th>Group</th>
<th>Class</th>
<th>Order</th>
<th>Family</th>
<th>No. of Clones</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Alphaproteobacteria</td>
<td>Caulobacterales</td>
<td>Caulobacteraceae</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>Betaproteobacteria</td>
<td>Rhodocyclales</td>
<td>Rhodocyclaceae</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>Deltaproteobacteria</td>
<td>Desulfobacterales</td>
<td>Desulfobacteraceae</td>
<td>19</td>
</tr>
<tr>
<td>4</td>
<td>Clostridia</td>
<td>Clostridiales</td>
<td>Lachnospiraceae</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>Sphingobacteria</td>
<td>Sphingobacterales</td>
<td>Flexibacteraceae</td>
<td>4</td>
</tr>
</tbody>
</table>

Bacteria identified from 16S rDNA sequencing of the clones from Farmington Bay using RDP Database

- Family *Desulfobacteraceae*
  - Acetate Utilizing Members
  - Genus’ *Desulfovibacter* & *Desulfonema*
Summary

• Established sampling and analysis methods
• Higher mercury levels associated with FB and wetlands in comparison to Utah Lake and Upper Jordan River
• The rates of mercury methylation and the phylogenetic diversity of sulfate reducers in the sediments of the FB wetlands were established
• Broader implications of understanding the control of methyl mercury and developing remediation strategies.
Acknowledgements

• Utah DWQ and Central Davis Sewer District for funding Farmington Bay work
• Mr. Leland Myers, Manager, & team, Central Davis County Sewer District
• Dr. Theron Miller, Jordan River/FB Water Quality Council
• Mr. Ken Burgener, Lab Director, North Davis Sewer District
Questions?

Thank You!
Other Research Findings

• Michael R. Conover, 2009
  – “Elevated Se & Hg concentrations in Sea Gulls nesting on GSL, did not appear to impaired gulls’ health or reproductive ability”

• Mae Gustin, 2008
  – “Higher Hg in brine shrimps from summer to fall”
  – “No direct or regional Hg source to lake”
Why is Mercury of concern???

- Ease of methylation
- Bacteria mediated conversions
- MeHg is lipophilic

<table>
<thead>
<tr>
<th>Physical &amp; Chemical Conditions</th>
<th>Qualitative influence on methylation (sediments)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low DO</td>
<td>Enhanced</td>
</tr>
<tr>
<td>Decreased pH</td>
<td>Decreased</td>
</tr>
<tr>
<td>Increased salinity</td>
<td>Decreased</td>
</tr>
<tr>
<td>Increased nutrients</td>
<td>Enhanced</td>
</tr>
<tr>
<td>Increased temp.</td>
<td>Enhanced</td>
</tr>
<tr>
<td>Increased sulfide/sulfate conc.</td>
<td>Enhanced</td>
</tr>
</tbody>
</table>
Bioenergetics

• Anoxic/AAnaerobic Microbial Metabolism
  – Fermentative
  – Sulfate/Nitrate/Carbonate Reduction

• Sulfate Reducers
  – $4(\text{AH}_2) + \text{SO}_4^{2-} + \text{H}^+ \rightarrow 4\text{A} + \text{HS}^- + 4\text{H}_2\text{O}$
  – Dissimilatory Sulfate Reduction

• Metabolic Process/Groups
  – Incomplete Oxidizers
    Lactate $\rightarrow$ Pyruvate $\rightarrow$ Acetate + CO$_2$
  – Complete Oxidizers
LACTATE → PYRUVATE → ACETATE

ACETYL-CoA PATHWAY IN COMPLETE OXIDIZING SRB STRAINS
Mercury Remediation Processes

- Remediation Processes
  - Dig and Dump
  - Pump and treat ex situ
  - In situ low-cost techniques
- Sorption & Precipitation
  - SRB’s are use as a source of $\text{H}_2\text{S}$ for ppt. as $\text{HgS}$
- Demethylation Process
  - Mer Operon
  - Narrow Spectrum and Broad Spectrum
Disperse Mercury (non-point source)

Probable Bioaccumulation

Yes

Assess Exposure Pathways (consumption, inhalation)

No

Management and Monitoring

Mercury Remediation
Source: Jennifer Hinton-Mercury Contaminated Sites: A Review
Figure 2 - Appropriate Responses to Point Source Mercury Contamination

Probable or Proven Bioaccumulation?

YES \rightarrow Containment Measures

NO \rightarrow Management & Monitoring

Removal Feasible or Needed?

YES \rightarrow Treatment Feasible?

NO \rightarrow Landfill

YES \rightarrow Removal & Treat

In-Situ Treatment Techniques

- Soil Vapour Extraction
- Reactive Walls
- In-situ Leaching
- Chemical Immobilization
- Water Interceptors
- Phytoremediation
- Wetlands

Containment & Covering

- Inert Covers
- Reactive Covers

Physical Separation
- Hydrometallurgical
- Thermal