Managing Aquatic Mercury Pollution: Strategies to Quantify Mercury Biomethylation Potential in Sediments

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R01ES024344
Methylmercury: the driver of risk at Hg-contaminated sites

- Mercury biomagnifies in aquatic food webs as monomethylmercury (MeHg)
- MeHg is produced by anaerobic microorganisms
Management of Mercury-Contaminated sites

Onondaga Lake (NY)
cleanup estimate: ~$500 million

East Fork Poplar Creek (Tennessee)
cleanup estimate: ~$3 billion

Penobscot River estuary (Maine)
cleanup estimate: >$130 million
Management of Mercury-Contaminated sites

Benchmarks for Site Assessment

Challenges:
• Total Hg content is a poor predictor of risk
• Current water quality standard: MeHg in fish

Needs:
• More functional shorter-term target for watershed management & remediation (e.g., Biomethylation potential of Hg)

Why do we need a model to predict Hg methylation potential?
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Total Hg Methylation Risk Profile

- High %MeHg (d[MeHg]/dt)
  - HgS contaminated tidal marsh
  - Mesohaline marsh
- Moderate %MeHg
  - Cinnabar mine drainage
  - Hg(0) discharge in low order stream
- Low %MeHg (d[MeHg]/dt)
  - Low Hg bioavailability

Impacts of Remediation Activities and Other Perturbations

- Activated carbon amendment
  - Wetland creation, flooding, sea level rise, sulfate deposition
- Water column aeration
  - Site A (original status)
    - E.g. upland, unsat’d soil

Hg Bioavailability

Productivity of Hg-methylating microbes

- Low
  - High
- High
  - Low
Methods for Quantifying Mercury Biomethylation Potential

The conventional approach: Equilibrium speciation

### Dissolved

- Weakly complexed: Hg(OH)$_2$, HgCl$_2$, HgCl$_3^-$
- Strongly complexed: Hg(HS)$_x$, Hg-DOM

### Particulate

- Mineral phase: HgS$_{(s)}$
- Sorbent: Organic matter FeS$_{(s)}$

$K_{sp}$ or $K_d$

### Bioavailable

Hg-methylating microbes:
- All have the HgcA and HgcB proteins
- Ubiquitous in anaerobic niches (sulfate reducers, Fe reducers, methanogens)

### Equilibrium Equations

\[
Hg^{2+} + xHS^- \leftrightarrow Hg(HS)_x^{2-x}
\]

\[
K_{Hg(HS)x}
\]

\[
Hg^{2+} + \text{DOM} \leftrightarrow Hg-\text{DOM}
\]

\[
K_{HgDOM}
\]

Parks et al. 2013 Science

Gilmour et al. 2013 ES&T
Hg speciation in benthic settings

Sediment porewater of a freshwater lake

Most of the mercury in porewater is bound to particles
Bioavailability of Mercury for Methylation: An Alternative Approach

Inorganic Hg is primarily associated with particles

Rates of these reactions at microbial interfaces determine bioavailability

Aiken et al., ES&T 2011
Methods to Quantify Hg Bioavailability

Thiol-based selective extraction

Glutathione (GSH) Extraction

Add GSH (1 mM)

end-over-end mix anaerobic for 30 min

Quantify Hg in <0.2 μm fraction

Ticknor et al., Env Engr Sci (2015)
Methods to Quantify Hg Bioavailability

Diffusive Gradient in Thin-film (DGT) samplers

**Conventional approach:** derive a ‘truly dissolved’ concentration

\[
\frac{m}{C_b} = \frac{D \times A}{\Delta g} \times t
\]

Hg uptake into DGT:

**Our approach:**

- Mass of Hg uptake \( m \)  \( \propto \) reactive Hg fraction

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**Diagram details:**
- Polypropylene cover
- 0.45-µm membrane filter
- Agarose diffusion layer
- Thiolated silica resin layer
- Polypropylene support base
- Area \( A \)
- Dissolved Hg in bulk solution, \( C_b \)
- Sediment or surface water
- Hg concentration
- Thiolated resin interface
- Soluble Hg concentration in DGT agarose diffusion layer
- Depth
- Mass of Hg uptake
- Reactive Hg fraction
Testing Methods of Quantifying Hg Methylation Potential

Diffusive Gradient in Thin-Films (DGT) passive samplers

Glutathione (GSH) Selective Extraction

Method testing: sediment microcosms

Added Hg: (100-200 ng g⁻¹ dw per species)
- dissolved ²⁰⁴Hg-nitrate
- dissolved ¹⁹⁶Hg-humic
- ¹⁹⁹Hg adsorbed to FeS
- humic-coated nano-²⁰⁰HgS

sediment slurry with DGT
(sample origin: tidal marsh, freshwater lake)

Quantify over time:
- MeHg from each isotopic endmember
- Hg on DGTs
- GSH-extractable Hg fraction
- hgcA gene copy number and microbial community composition
Testing Methods of Quantifying Hg Methylation Potential

Methylation of Hg added to slurries

Type of Hg added:
- $^{204}$Hg$^{2+}$
- $^{199}$Hg-FeS
- $^{196}$Hg-humic
- nano-$^{200}$HgS

Uptake of total Hg in DGTs

Hg uptake in DGTs correlates with MeHg production

Net MeHg production:
- correlated with uptake on the DGT sampler
- did not correlate with the <0.45 µm or the GSH-extractable fraction

Hg uptake in DGTs correlates with MeHg production

Freshwater Lake
Sediment Slurry
with 1 mM pyruvate

Type of Hg added:
- $^{204}\text{Hg}^{2+}$
- $^{199}\text{Hg}$-FeS
- $^{196}\text{Hg}$-humic
- nano-$^{200}\text{Hg}$S

GSH-extractable fraction

Filter-passing fraction

DGT Sampler

$\text{MeHg (\% of total Hg)}$

$\text{Time (days)}$

$\text{Hg on DGT resin (% of THg)}$

$\text{Filter-passing Hg (% of THg)}$

$\text{GSH-Extractable Hg (% of THg)}$

$\text{MeHg (\% of THg)}$
Comparing the Hg-Methylating Microbial Communities

**Mesohaline Slurry**

Difference because of abundance of *hgcAB*+ microbes?

**Freshwater Slurry**

Geochemical vs. Microbiome Controls on Mercury Methylation

Inorganic Hg Speciation in anaerobic settings

- amorphous, hydrated nanostructured weakly sorbed
- well-crystalline macrostructured strongly sorbed

Bioavailable Hg

- Polymerization & Sorption: Sulfide, NOM

Biogenic sulfide, organic carbon, redox gradients

Anaerobic Microbiome

MeHg

- microbial community composition
  - hgcAB+ Firmicute
  - hgcAB+ methanogen
  - hgcAB+ α-Proteobact.

Geochemical vs. Microbiome Controls on Mercury Methylation

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Comparing the Hg-Methylating Microbial Communities

**Mesohaline Slurry**

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**Freshwater Slurry**

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</table>

**qPCR hgcA genes**

- **Deltaproteobacteria**
- **Archaea**

**Diversity and abundance of methylators from DNA-based approaches**

- **hgcA+ Deltaproteobacteria**
- **hgcA+ methanogenic Archaea**

Next Steps

Can DGTs work in the real world?
Next Steps

Can DGTs work in the real world?

Outdoor freshwater wetland mesocosms.

Added Hg:
- dissolved $^{202}$Hg$^{2+}$
- dissolved $^{201}$Hg-humic
- $^{199}$Hg adsorbed to FeS
- nano-$^{200}$HgS

![Graph](image)

-meHg in sediment (ng g$^{-1}$)

Inorganic Hg flux into DGT (ng Hg m$^{-2}$ h$^{-1}$)

- mesocosm 1
- mesocosm 2
- mesocosm 3
Next Steps

Model for Hg Methylation Potential

A possible simplification.....

Semi-Mechanistic Model

\[
\frac{d[MeHg]}{dt} = k_m[\text{bioavailable Hg flux}] - k_d[MeHg]
\]

\[
k_m = f(hgC_{\delta-\text{proteobact}}, hgC_{\text{archaea}}, hgC_{\text{firmicutes}})
\]

\[\text{[bioavailable Hg]} = f(Hg \text{ uptake rate in DGT})\]
Summary

Mercury: Strategies to Quantify Methylation Potential in the Environment

- Needs for site management & remediation: functional measures of MeHg production potential

- Hg bioavailability for methylation: Controlled by reactivity of Hg-S-NOM phases at microbial interfaces

- Quantifying MeHg potential in ecosystems:
  1. Hg bioavailability (Hg uptake rate in DGTs)
  2. Productivity of the methylating microbiome \((hgcA\) gene expression?)

Additional questions are welcome!
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References


