Decrease in Net Mercury Methylation Following an Iron Amendment to Wetland Microcosms

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How to Reduce MeHg Uptake?
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We propose a “bottom-up” approach: Limit the bioavailability of inorganic Hg to methylators to reduce methylmercury production.
Hg Speciation in Wetland Sediments

- In anoxic sediments, sulfide influences mercury speciation
  - Cinnabar \((\text{HgS}_\text{(s)})\)
    \[
    \text{HgS}_\text{(s)} + \text{H}^+ \rightleftharpoons \text{Hg}^{2+} + \text{HS}^-
    \]
- Excess \(\text{HS}^-\) enhances apparent solubility of \(\text{HgS}_\text{(s)}\) via formation of dissolved species
  - \(\text{Hg}^{2+} + \text{HS}^- \rightleftharpoons \text{HgHS}^+\)
  - \(\text{Hg}^{2+} + \text{HS}^- \rightleftharpoons \text{HgS}^0 + \text{H}^+\)
  - \(\text{Hg}^{2+} + 2\text{HS}^- \rightleftharpoons \text{Hg(HS)}_2^0\)
  - \(\text{Hg}^{2+} + 2\text{HS}^- \rightleftharpoons \text{HgS}_2\text{H}^- + \text{H}^+\)
  - \(\text{Hg}^{2+} + 2\text{HS}^- \rightleftharpoons \text{HgS}_2^{2-} + 2\text{H}^+\)
- \(\text{Hg(HS)}_2^0\) and \(\text{HgS}^0\) are bioavailable forms
Fe(II) Affects Hg-Bioavailability

• Fe(II) decreases HS\(^-\) concentrations via formation of FeS\(_{(s)}\)

• As HS\(^-\) decreases, dissolved Hg also decreases

\[
\text{HgS}_{(s)} \leftrightarrow \text{HgS}^0 \\
\text{HgS}_{(s)} + \text{HS}^- + \text{H}^+ \leftrightarrow \text{Hg(HS)}^0_2
\]
Previous Research

Two previously published studies demonstrated the potential effectiveness of iron amendment in anoxic batch reactors.

Microcosm Experiment

• Objectives:
  – To test the efficacy of Fe amendment in more realistic system
    • Includes native bacteria (sulfate and iron reducers)
    • Includes complex geochemical parameters found in wetland sediments (ie, Fe-S minerals, NOM, etc...)
    • Includes biogeochemical stratification and heterogeneity
  – Determine effective dose
  – Evaluate duration of effect
  – Evaluate Fe-S mineral formation and aging
Microcosm Experiment

Gambinini Marsh

Map from Google Earth

Photo of people working in a field and a laboratory setting with microcosm experiments.
Microcosm Dosing & Operation

• Operated for 17 weeks following Fe addition
• No Hg added to microcosms
• Kept under simulated daily tidal & light cycle in the lab
  – 2 high tides/day
  – Each high tide lasted 3 hrs, water depth ~1.5cm

• Iron added as FeCO$_3(s)$ via subsurface injection
• Four dosing levels (n=3):
  – Control: No Fe added
  – Low Dose: 180 g-Fe/m$^2$
  – Medium Dose: 360 g-Fe/m$^2$
  – High Dose: 720 g-Fe/m$^2$
Comparison of Iron Dosing

This study

CH$_4$ red’n. rice paddies
(Jäckel et al. 2005)

HS$^-$ red’n. seagrass
(Ruiz-Halpern et al. 2008)

HS$^-$ red’n. seagrass
(Holmer et al. 2005)

P control wetlands
(Ann et al. 1999)
Effect on Sulfate
Effect on Porewater Sulfide
Effect on Inorganic Mercury
Effect on Methylmercury
Sediment Cores

• Sediment cores taken at end of experiment
• Top 10-cm sectioned at 1-cm resolution
• Evaluated for:
  – Reduced sulfur speciation
    • Acid-volatile sulfur (AVS)
    • Chromium reducible sulfur (CRS, pyritic fraction)
  – Will be analyzed for total mercury and methylmercury
AVS in Sediment Cores
CRS in Sediment Cores
Conclusions

• Iron addition reduced porewater sulfide at all three amendment levels
• MeHg concentrations in surface water were decreased for the Medium and High doses
• Potentially enhanced MeHg production at Low iron dose
• Evidence of enhanced AVS & pyrite formation in amended sediments
Next Steps

- Evaluate role of plants (pickleweed) in microcosm experiment
- Field experiments to address:
  - Efficacy under field conditions
  - Long term duration
  - Application method
  - Different marsh elevations & vegetation types
  - Unintended consequences
- Results are promising so far, but further research is needed to determine if this will be an appropriate method
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