Sulfate as a Contaminant in Freshwater Ecosystems: Sources, Impacts and Mitigation

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Acknowledgments

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Major Sources of Sulfur to Freshwater Wetlands

- Sea Spray
- Dry Deposition

- Surface Runoff
  - Agriculture
  - Mine drainage
  - Urban runoff
  - Industrial runoff

- Saltwater Intrusion
- Sealevel Rise

- Groundwater

- Acid Rain

- Fire and Drought
Sulfate Distributions In Surface Water

- > 50 mg/L
- ~10-50 mg/L
- ~1-10 mg/L
- <1.0 mg/L

Sulfate moves from the EAA and Lake Okeechobee down canals and is discharged into the Everglades through water control structures and breaches in levees.
Sources of Sulfate to Marshes of the Northern Everglades
Water Conservation Area 2A, Site F1

- Precipitation:
  - 2.5 mg/l
  - +5 permil

- Canal discharge:
  - 58 mg/l
  - +21 permil
  - $\text{SO}_4/\text{Cl} = 0.5$

- Marsh water:
  - 55 mg/l
  - +23 permil
  - $\text{SO}_4/\text{Cl} = 0.5$

- Shallow groundwater (3.8 m):
  - 0.5 mg/l
  - +25 permil

- Deep groundwater (9.7 m):
  - 186 mg/l
  - +12 permil
  - $\text{SO}_4/\text{Cl} = 0.2$

- U$_{ar}$ = 0.97

Sulfate from Lake Okeechobee and EAA Fields

Diffusion and oxidation of sulfide

U$_{ar}$ = 1.30
At low sulfate concentrations, S isotope values span a broad range, indicating multiple sources. As sulfate concentrations increase, a trend line in the S isotope values emerges, indicating that a single source is dominating. The S isotope trend line converges on a value of about +16 per mil. Agricultural sulfur used in the EAA has a similar S isotope value. As sulfate concentrations increase, a trend line in the S isotope values emerges, indicating that a single source is dominating. At low sulfate concentrations, S isotope values span a broad range, indicating multiple sources.
Everglades – Fire and Drought/Rewet Cycles Effects on Sulfur and Mercury Biogeochemistry

- Oxidation of organic soil by fire or drought converts reduced sulfur species (organic sulfur and metalsulfides) to sulfate, and releases soil bound mercury and DOC

- After rewet, sulfate is remobilized into water, stimulating microbial sulfate reduction and mercury methylation

- Large amounts of methylmercury may be produced before sulfate is depleted and/or sulfide levels buildup to levels that inhibit methylation

- Effect observed in field studies in the Everglades, in STAs routinely dried down and rewet, and confirmed experimentally in laboratory microcosm experiments
Sulfur Impacts on Freshwater Wetlands

- Sulfate promotes methylation of mercury to its most toxic and bioaccumulative form: methylmercury

- Sulfide is toxic to plants and animals

- Sulfate promotes release of nutrients from sediments (internal eutrophication)

- Sulfide binds metal ions and sequesters them in soils as metal sulfides

- Sulfate enhances biodegradation of organic soils
Linking Sulfate and Methylmercury in the Florida Everglades

Agricultural Fields and Canals
Everglades Agricultural Area

sulfate from canals

sulfate in runoff from agricultural fields

Hg$^{2+}$

mercury from distant sources

rainfall

Everglades Marsh

sulfate-reducing bacteria

Hg$^{2+}$

SURFACE WATER

SOIL

bioaccumulation of methylmercury

sulfate

sulfate-reducing bacteria

methylmercury
Sulfate-MeHg Response

High SO$_4$  \[ \begin{aligned} &\text{Sulfide Inhibition Zone} \\
&\text{Goldilocks Zone} \quad \text{“Just Right”} \\
&\text{Sulfate Limitation Zone} \end{aligned} \]

Low SO$_4$

MeHg

sw sulfate, mg/L

<table>
<thead>
<tr>
<th>High SO$_4$</th>
<th>Low SO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$&gt;$ 50</td>
<td>0</td>
</tr>
<tr>
<td>10-20</td>
<td>0</td>
</tr>
</tbody>
</table>

pw sulfide, mg/L

| > 5       | 0.2-0.3     |
| 0         | 0           |
Relationship Between Sulfate and MeHg

Distributional data across Everglades’ sites

- MeHg production increases w/ SO₄ up to at least 100 µM (10 mg/L)
- Methylation declines at porewater sulfide above ~ 20 µM (0.6 mg/L)
Relationship Between Sulfate and MeHg – Mesocosm Studies

- Add sulfate to Everglades soil and MeHg production increases (confirmed at 5 different sites)

- Linear relationship between sulfate and MeHg production through 20 mg/L

- Sulfide inhibition above 20 mg/L sulfate

- Results confirmed by field, laboratory, and mesocosm data

Data from: Gilmour, Krabbenhoft, Orem, Aiken

- Day 57

y = 0.023x + 0.0572

R² = 0.5854

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Data from: Gilmour, Krabbenhoft, Orem, Aiken
**Sulfide Toxicity and Macrophyte Growth**
Li, Mendelssohn, Chen, and Orem
Freshwater Biology, 2010

- *Cladium* oxidized zone only at root tips; *Typha* oxidized zone all along root axis.

Development of oxidized haloes around roots of *Typha* (A) and *Cladium* (B) immersed in a reduced methylene blue-agar medium.

- *Sawgrass* (*Cladium*) more sensitive to sulfide toxicity than cattail (*Typha*) sulfide levels >9 ppm

![Graph showing Pn (µmol CO₂ m⁻² s⁻¹) vs Sulfide Concentration (mM)]

- Oxidized zone all along root axis for *Typha*
- Oxidized zone only at root tips for *Cladium*

(Chabbi, McKee, Mendelssohn 2000)

- Sulfide Toxicity and Macrophyte Growth
  - *Sawgrass* (*Cladium*) more sensitive to sulfide toxicity than cattail (*Typha*) sulfide levels >9 ppm

![Graph showing Pn (µmol CO₂ m⁻² s⁻¹) vs Sulfide Concentration (mM)]

*Cladium* and *Typha* are compared for their response to sulfide levels in a medium.

- Reduced (no halo) zones are noted for both species.
- Oxidized (halo) zones are observed for both species, but with distinct differences in distribution.

(Chabbi, McKee, Mendelssohn 2000)
Copper-Nickel Sulfide Mining in Minnesota and Sulfide Toxicity to Wild Rice In Freshwater Wetlands

Effects on Wild Rice:
healthy roots (left) and roots with sulfidic black discoloration (right)

Symptoms of Sulfide Toxicity in Macrophytes:
- interveinal chlorosis of emerging leaves
- black, poorly developed root system
- increased occurrence of diseases

Mining of Sulfide Ores

oxidation to sulfate
discharge of sulfate to natural waters
Internal Eutrophication from Sulfate Contamination of Freshwater Wetlands

**SURFACE WATER**

**SOIL**

- FePO$_4$(s) + H$_2$S $\rightarrow$ FeS$_2$(s) (Fe$_2$S$_3$(s))
- microbial sulfate reduction
- organic soil biodegradation

**Porewater**

- PO$_4^{3-}$
- SO$_4^{2-}$
- DOC
- NH$_4^+$

stimulation of anaerobic microbial activity
syntrophy
Sulfate Stimulation of Internal Eutrophication
- degradation of organic matter in soils
- enhanced release of nutrients into surface and pore water
- enhanced release of dissolved organic matter (DOC and DON) into surface and pore water
Sulfate Contamination of Freshwater Wetlands: Mitigation Strategies

- Reduce sulfur loading at source
  - BMPs for agricultural sources
  - Emission regulations for acid rain
  - Reduce or mitigate mine drainage at source
  - Avoid wet/dry cycles leading to internal sulfate sources

- Avoid direct discharges of contaminated water to sensitive wetland areas
  - Use buffer wetlands to protect more sensitive areas

- Sulfate Mitigation
  - Redesign existing Stormwater Treatment Areas (STAs) to improve sulfate removal
  - Pass contaminated water through limestone and feldspar as an initial removal process
  - Consider use of large anaerobic bioreactors
  - Use of permeable reactive barriers for sulfate removal
  - Reverse osmosis desalination
Decreasing sulfate loading in central Everglades resulted in rapid decline in methylmercury production and levels of methylmercury in fish in <3 years.
Questions?