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

Acid Rain

Sea Spray

Dry Deposition

Surface Runoff

Agriculture
Mine drainage
Urban runoff
Industrial runoff

Saltwater Intrusion
Sealevel Rise

Groundwater

Sulfate Distributions In Surface Water

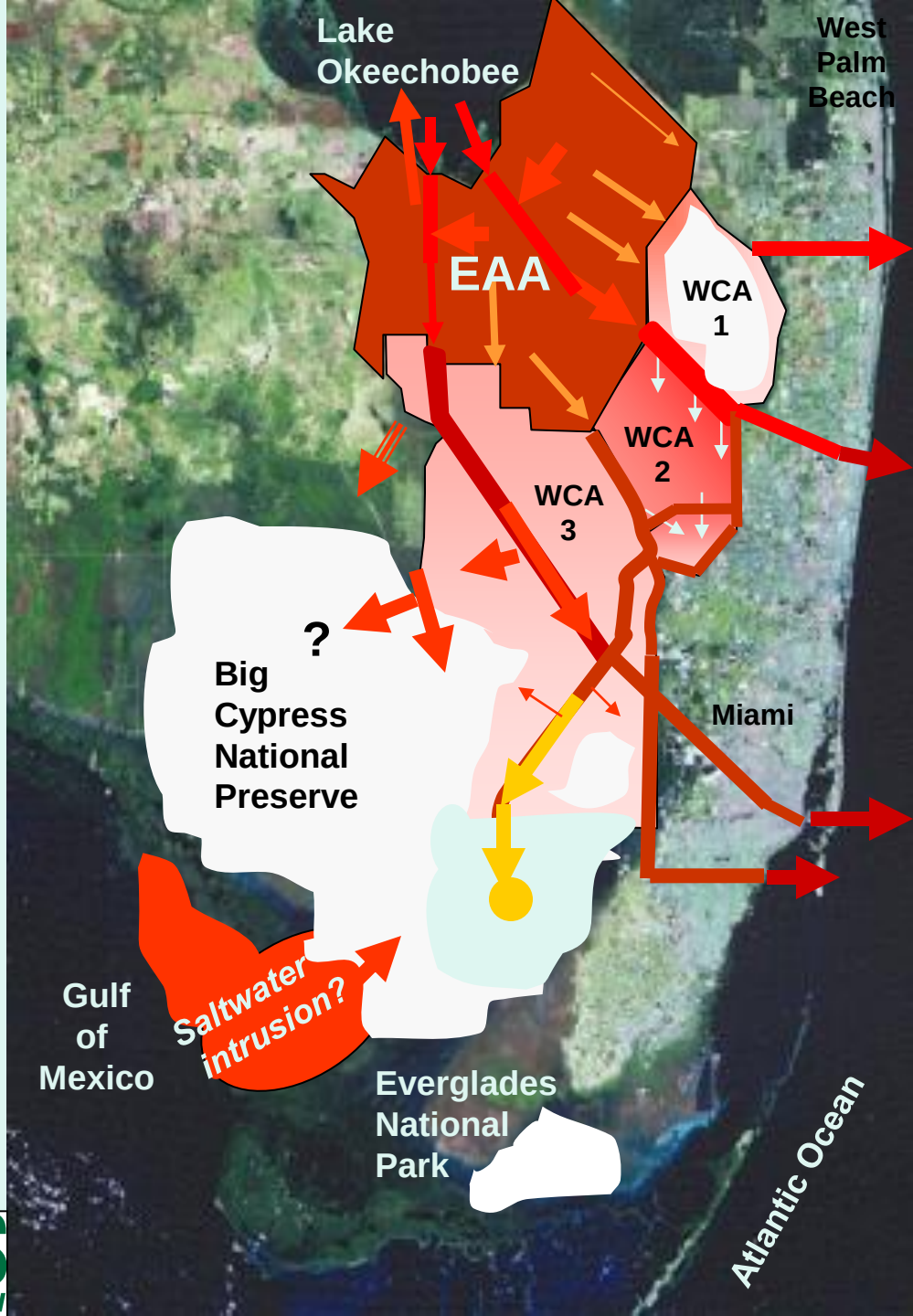
> 50 mg/L

~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



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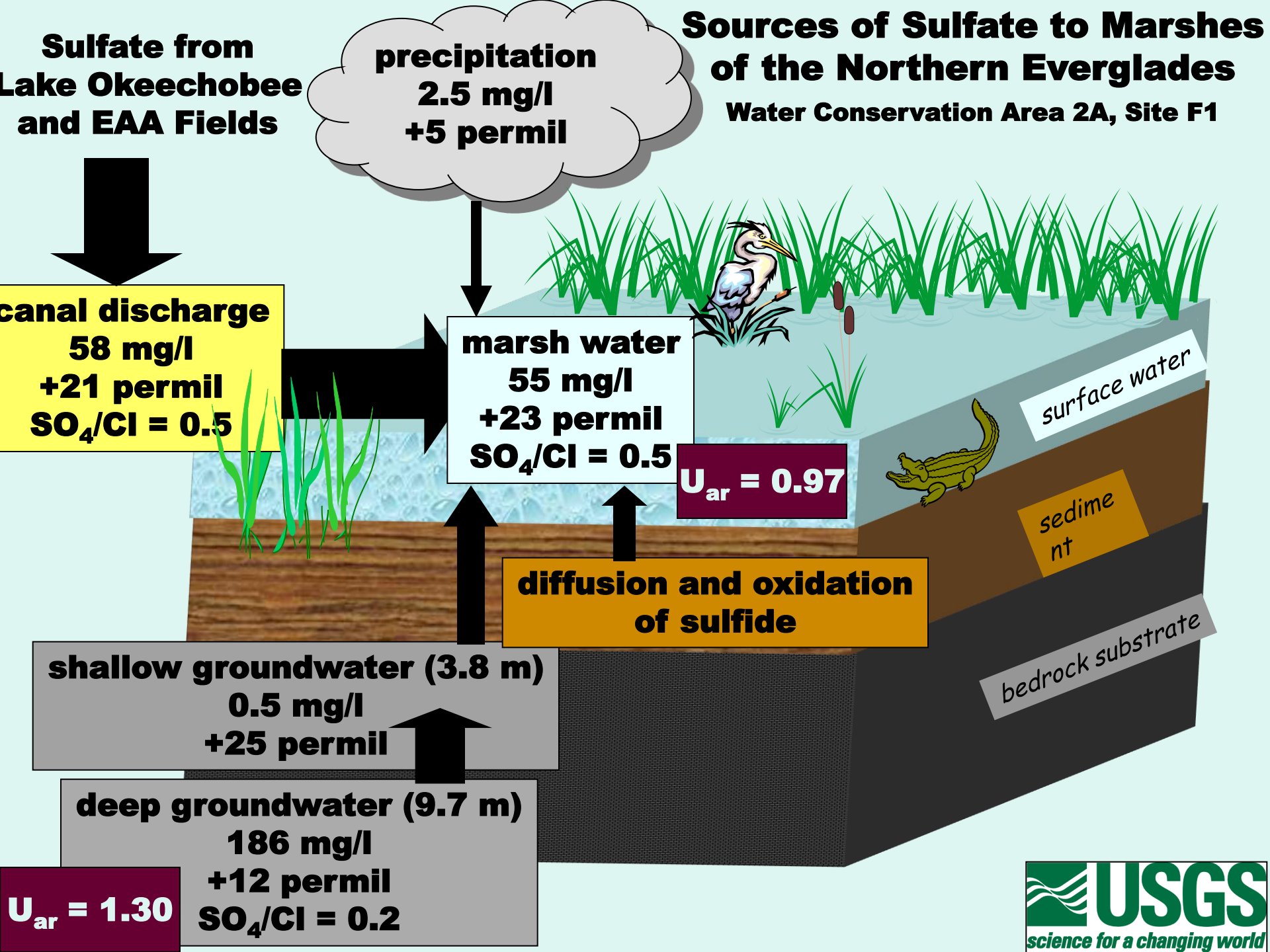
Sources of Sulfate to Marshes of the Northern Everglades

Water Conservation Area 2A, Site F1



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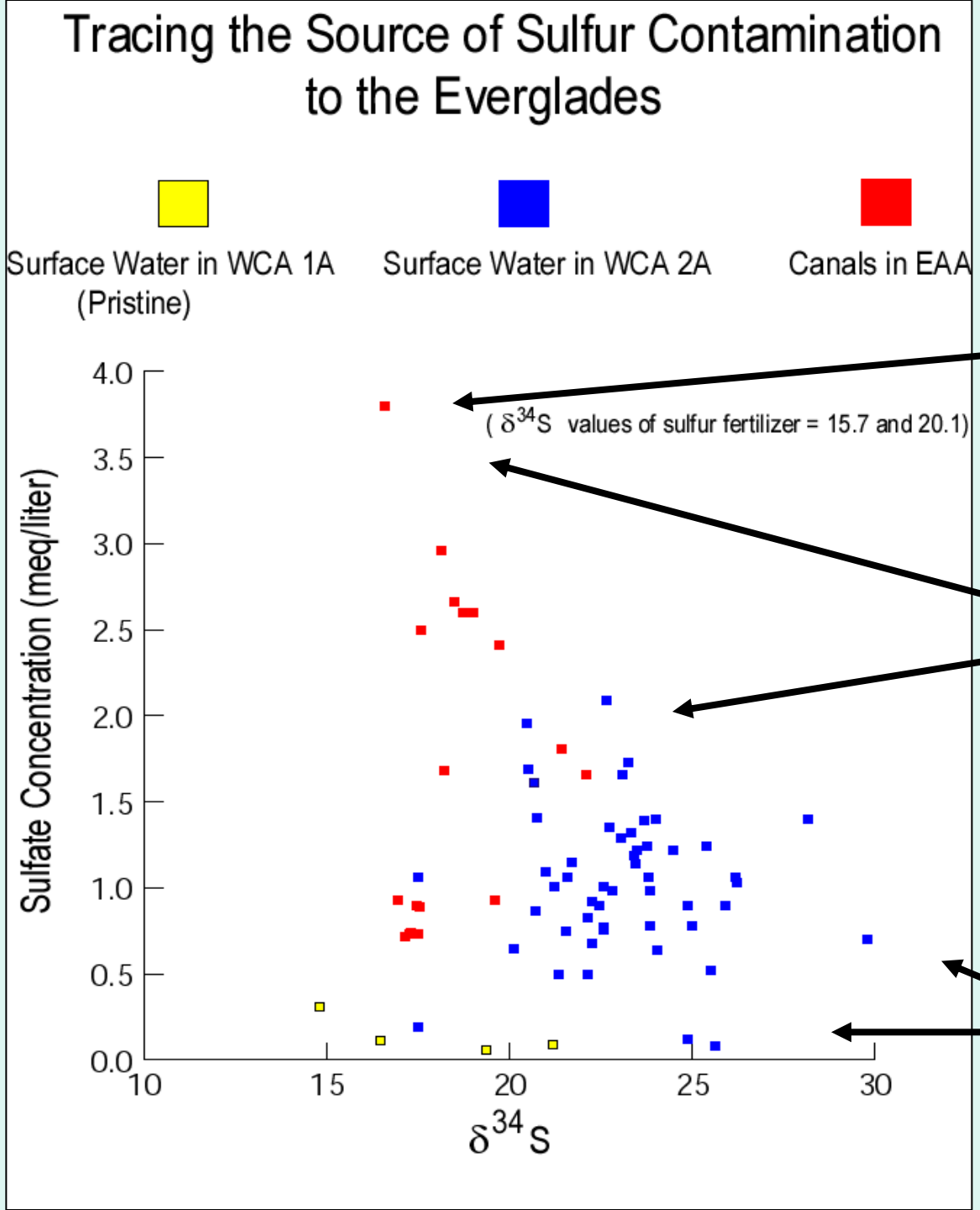
Tracing the Source of Sulfur Contamination to the Everglades



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

Experimental Dry/Rewet Setup

Desiccated Peat

Background Photo: Fire in Northern WCA 3 – 1999

Sulfur Impacts on Freshwater Wetlands

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

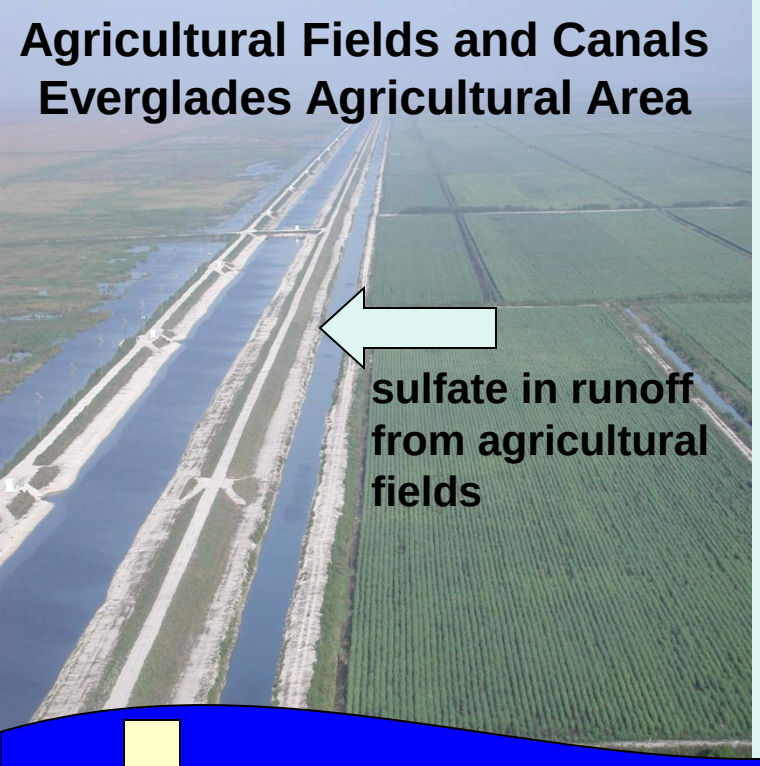
- **Sulfide is toxic to plants and animals**

- **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



Hg^{2+}

mercury from distant sources

rainfall

Hg^{2+}

sulfate from canals

Everglades Marsh

SURFACE WATER

SOIL

sulfate-reducing bacteria

sulfate

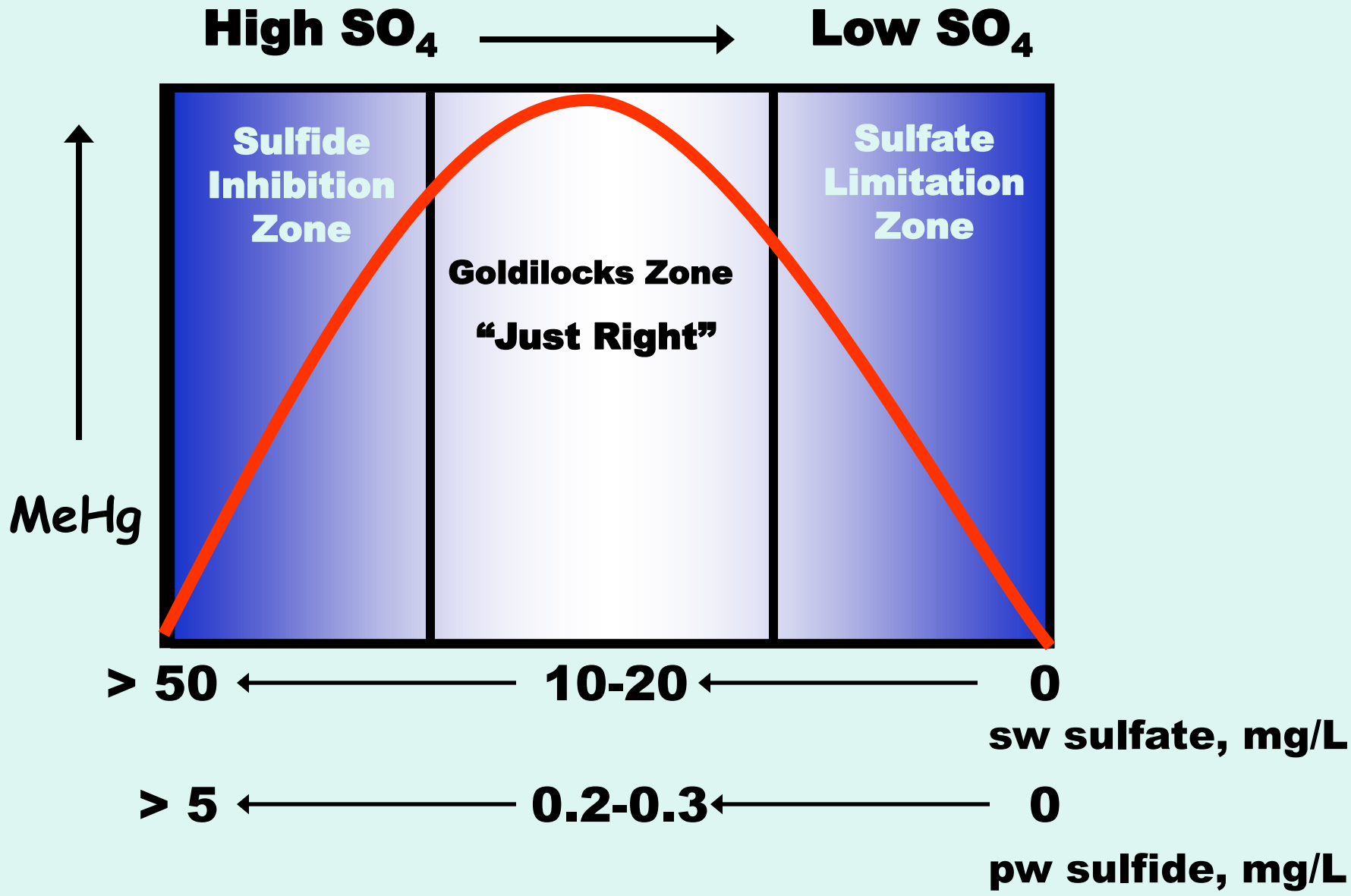
Hg^{2+}

sulfide

methylmercury

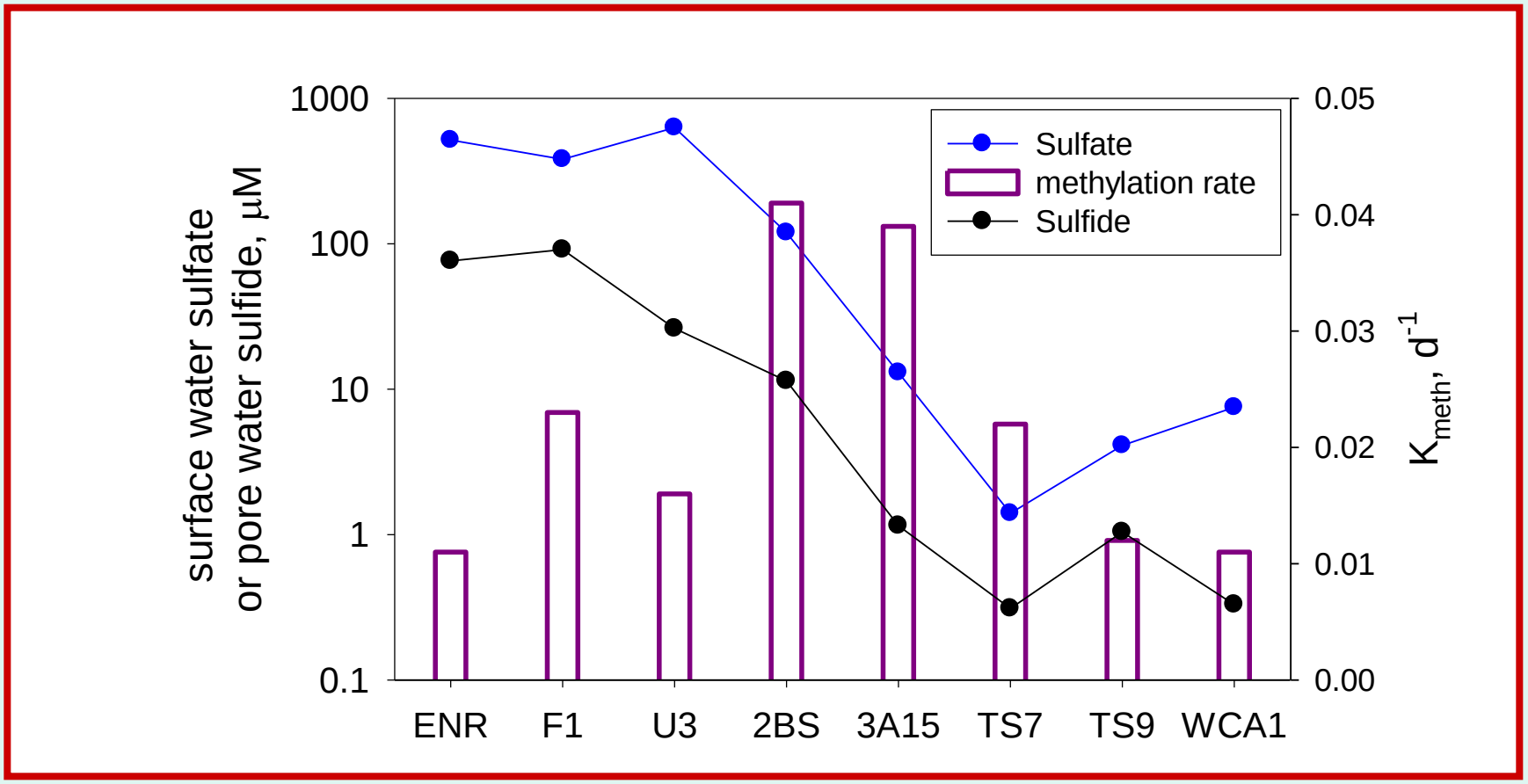
bioaccumulation of methylmercury

Sulfate-MeHg Response



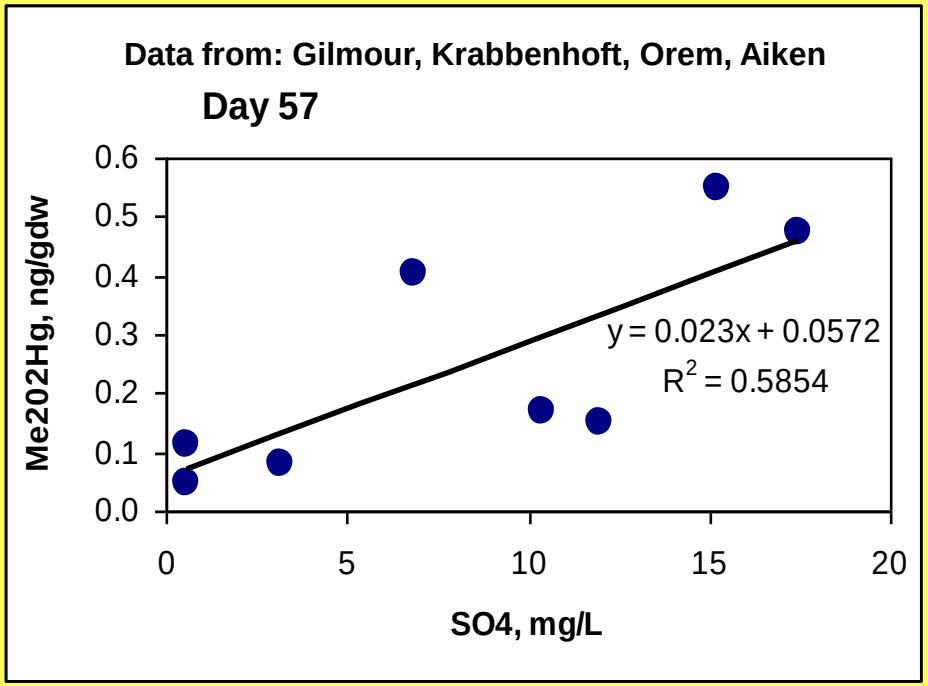
Relationship Between Sulfate and MeHg

Distributional data across Everglades' sites



- **MeHg production increases w/ SO_4 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

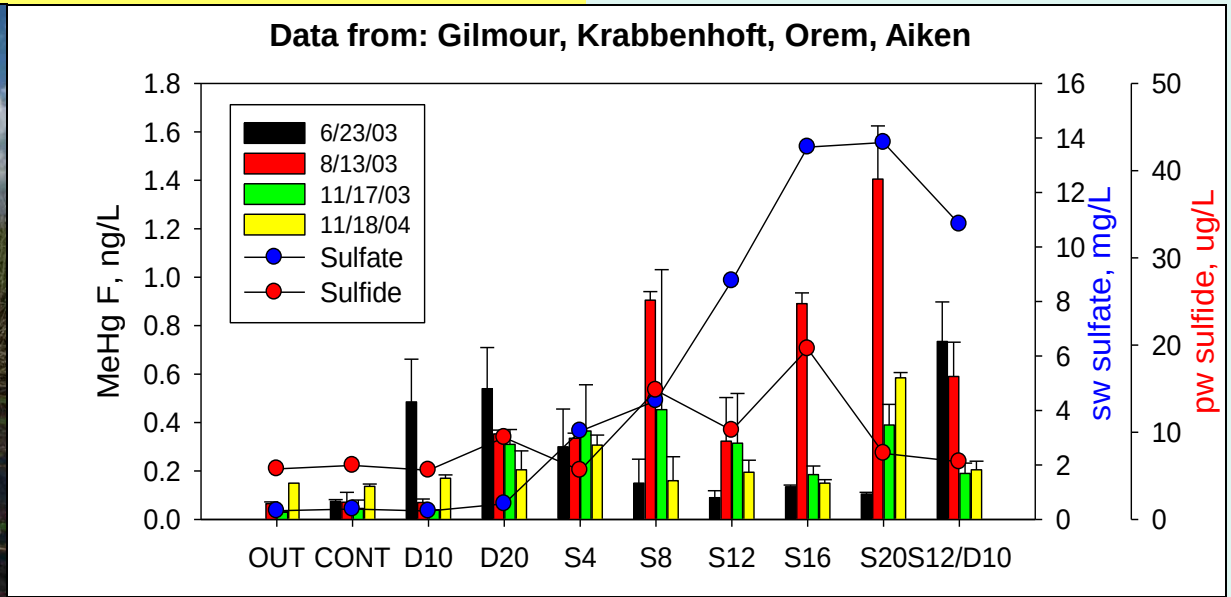


-Add sulfate to Everglades soil and MeHg production increases (confirmed at 5 different sites)

-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



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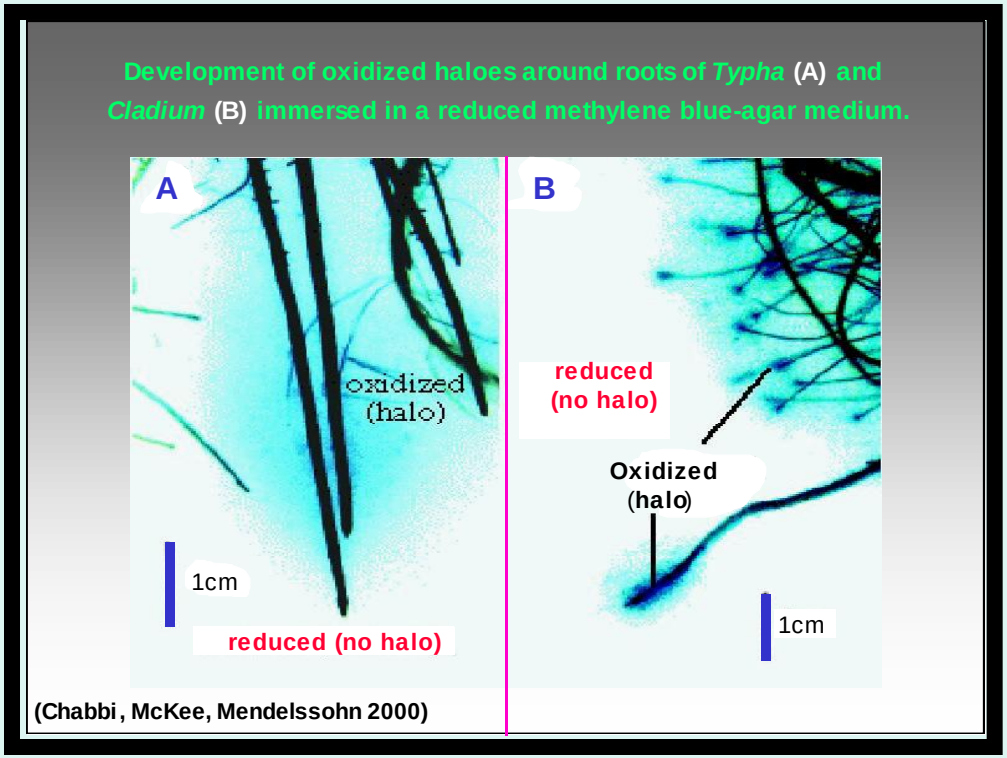
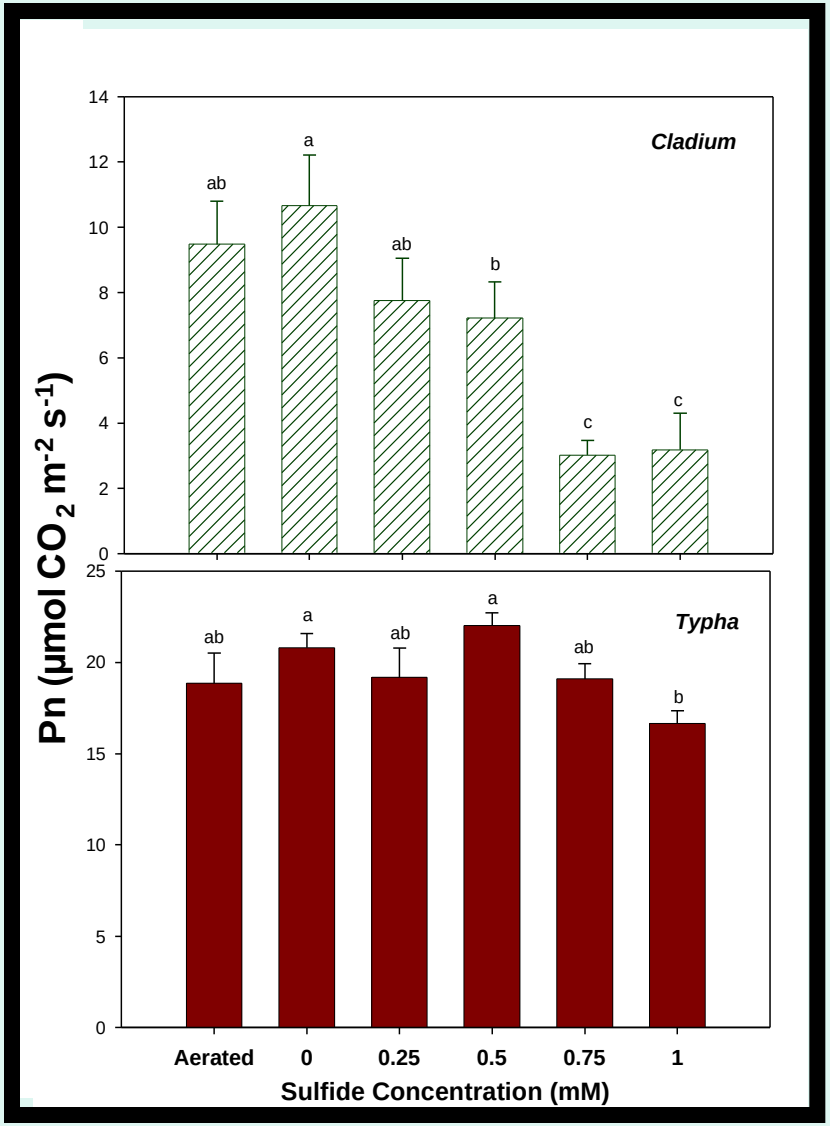
Sulfide Toxicity and Macrophyte Growth

Li, Mendelssohn, Chen, and Orem
Freshwater Biology, 2010

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



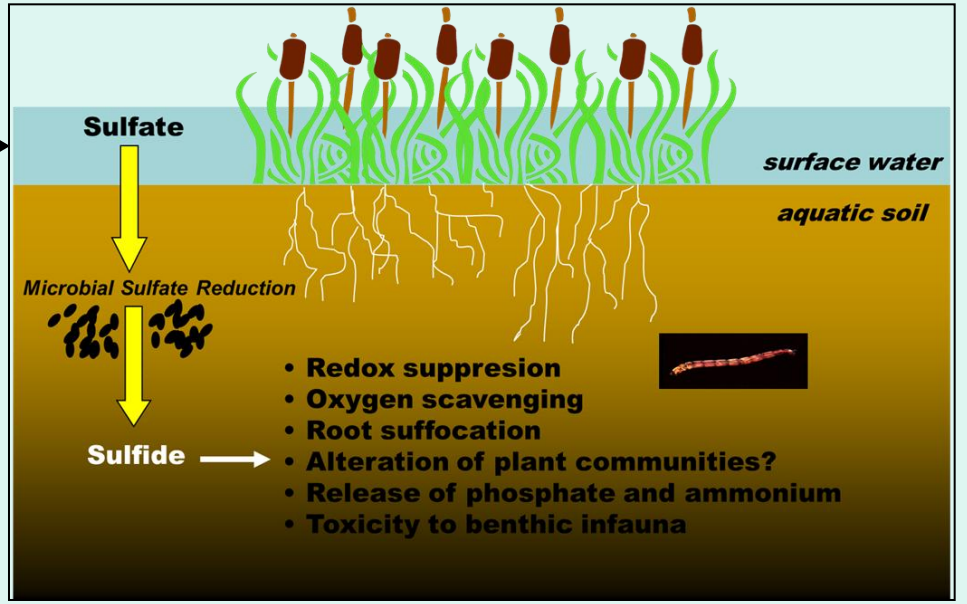
- **Sawgrass (Cladium) more sensitiveto to sulfide toxicity than cattail (Typha) sulfide levels >9 ppm**



Copper-Nickel Sulfide Mining in Minnesota and Sulfide Toxicity to Wild Rice In Freshwater Wetlands

oxidation to sulfate

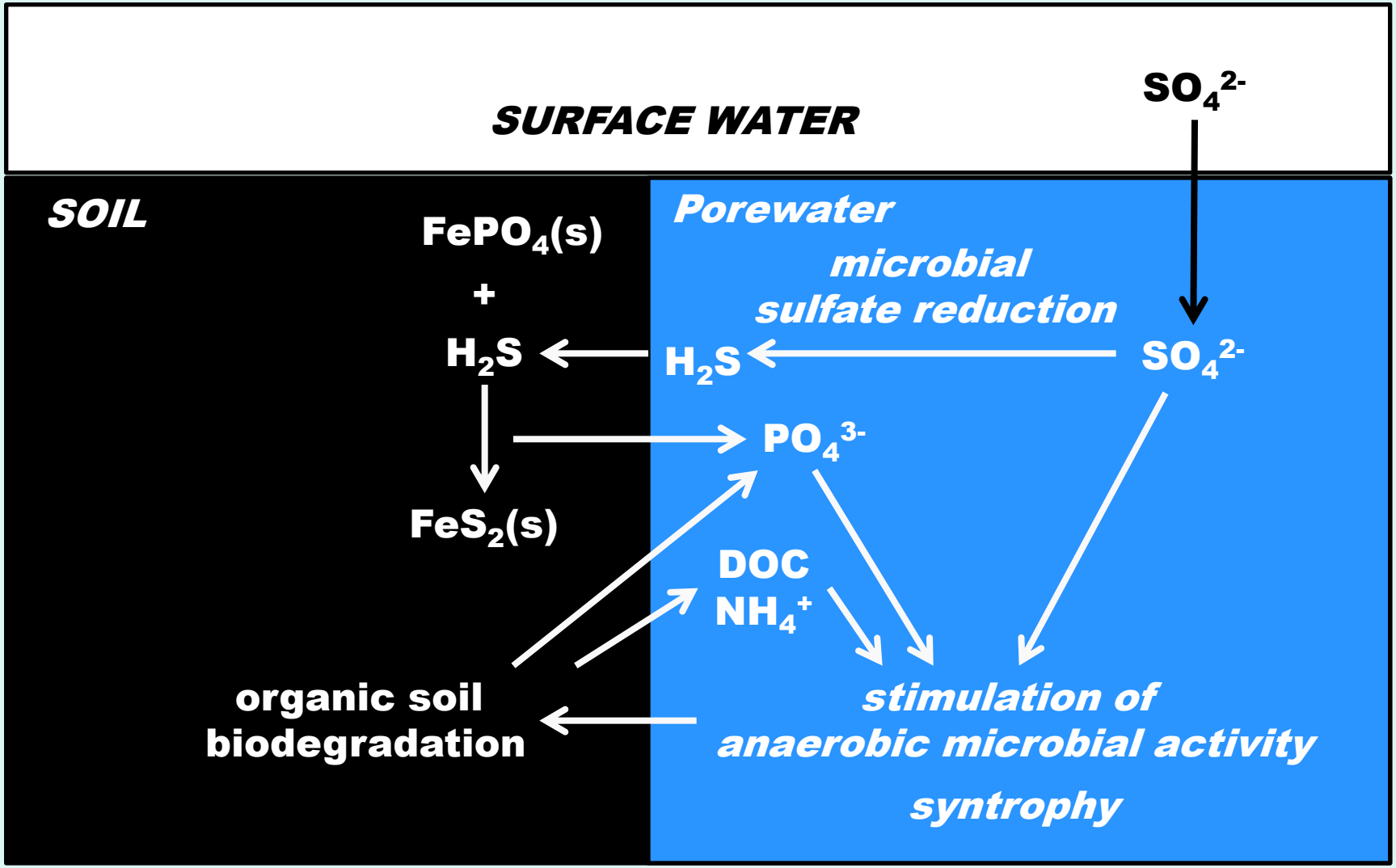
discharge of sulfate to natural waters



Symptons of Sulfide Toxicity in Macrophytes

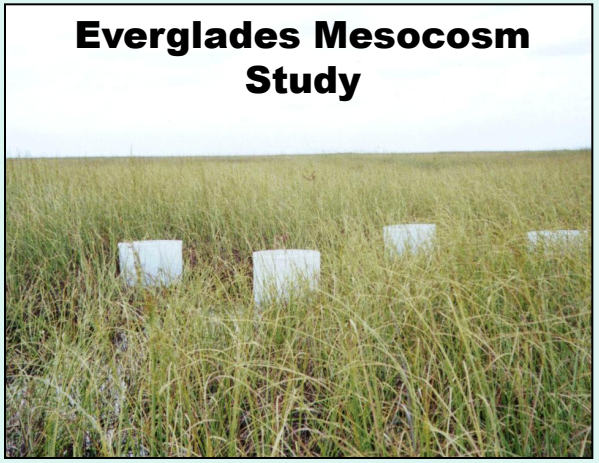
-interveinal chlorosis of emerging leaves
-black, poorly developed root system
-increased occurrence of diseases

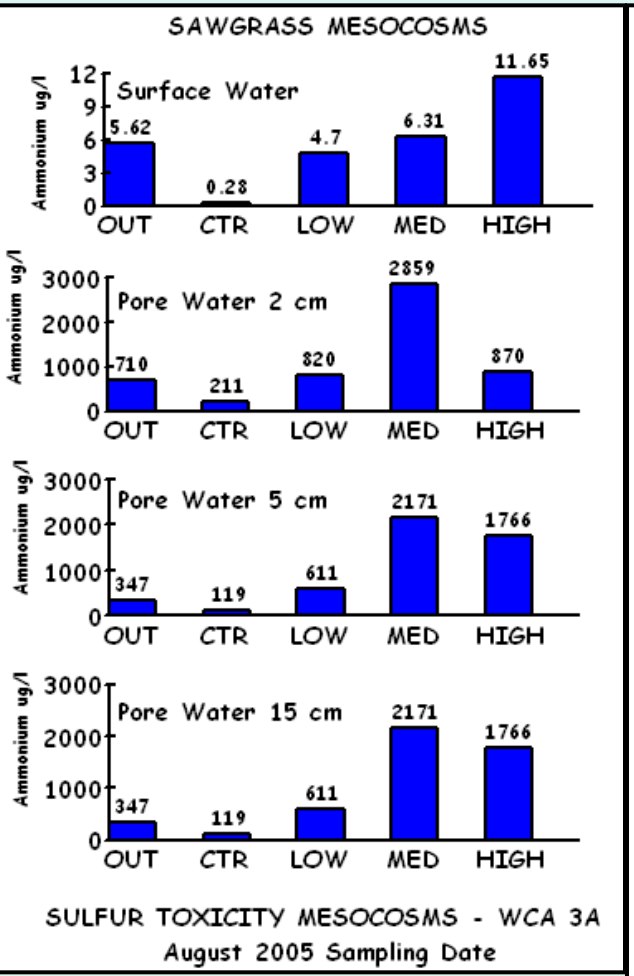
Internal Eutrophication from Sulfate Contamination of Freshwater Wetlands

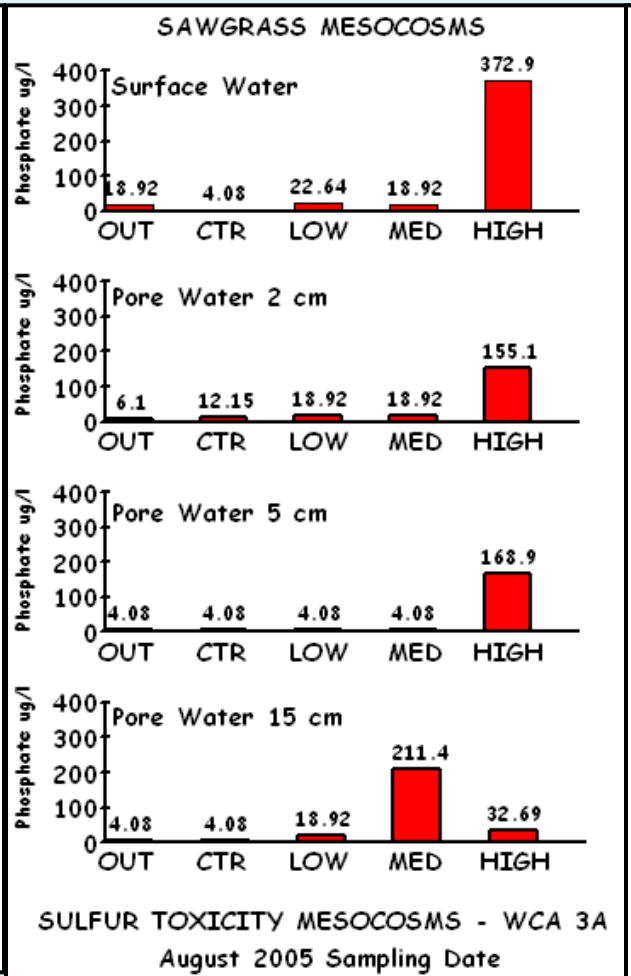


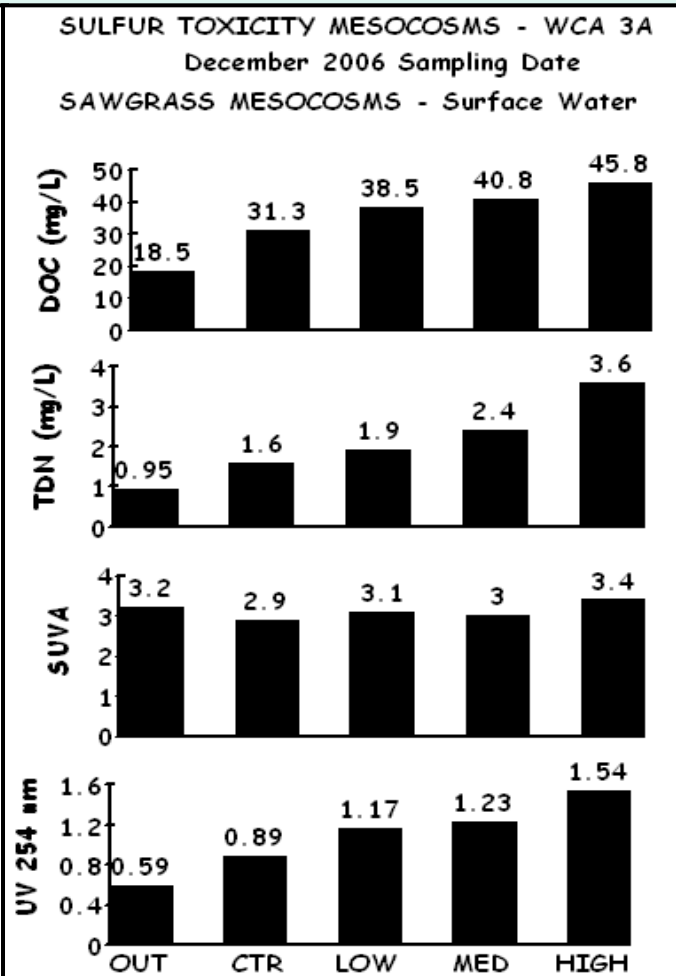
Sulfate Stimulation of Internal Eutrophication

-degradation of organic matter in soils
-enhanced release of nutrients into surface and pore water
-enhanced release of disolved organic matter (DOC and DON) into surface and pore water









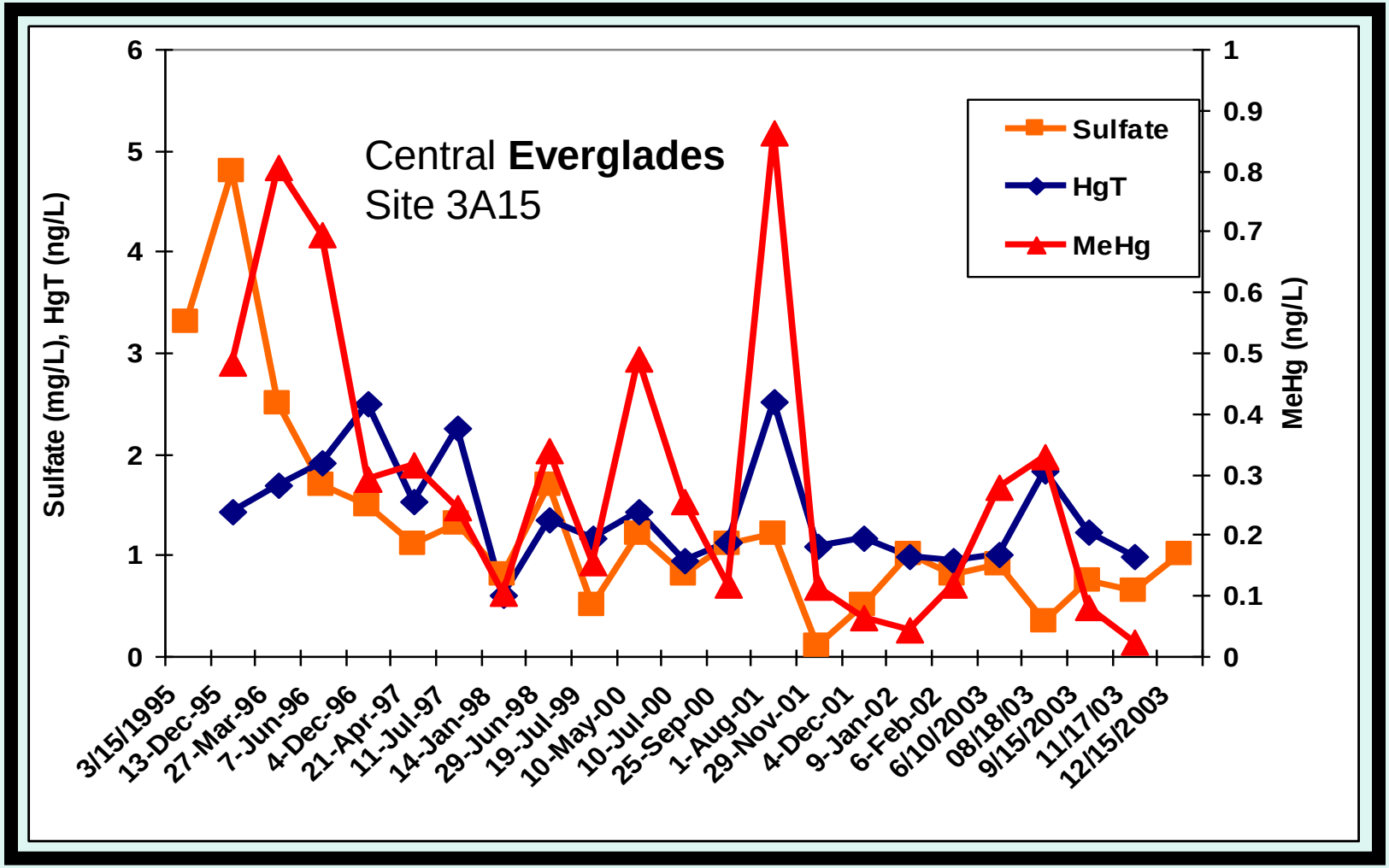
Sulfate Contamination of Freshwater Wetlands: Mitigation Strategies

- 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
  - -Redeisgn 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

Response of Wetlands to Reduction in Sulfate Loading can be Rapid



Decreasing sulfate loading in central Everglades resulted in rapid decline in methylmercury production and levels of methylmercury in fish in <3 years

Questions?