Methods of Sulfur Analysis in Wetlands, and Applications to Studies of Mercury Biogeochemistry

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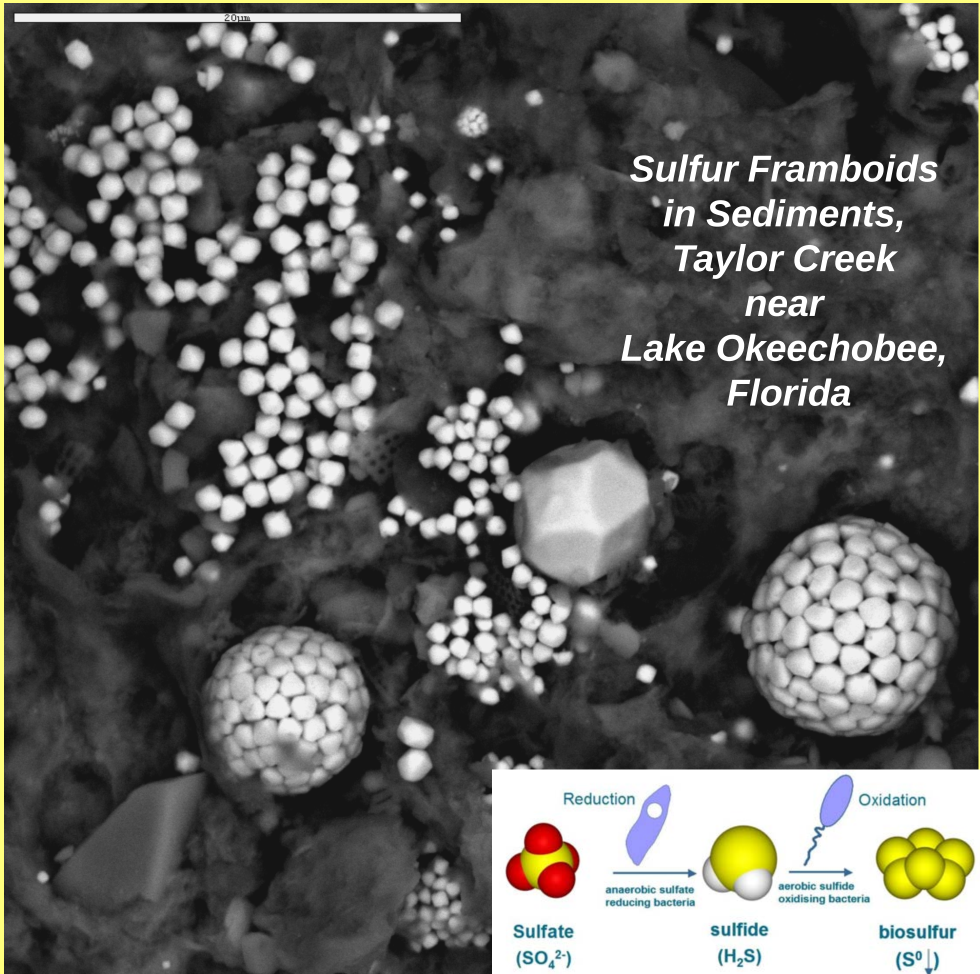
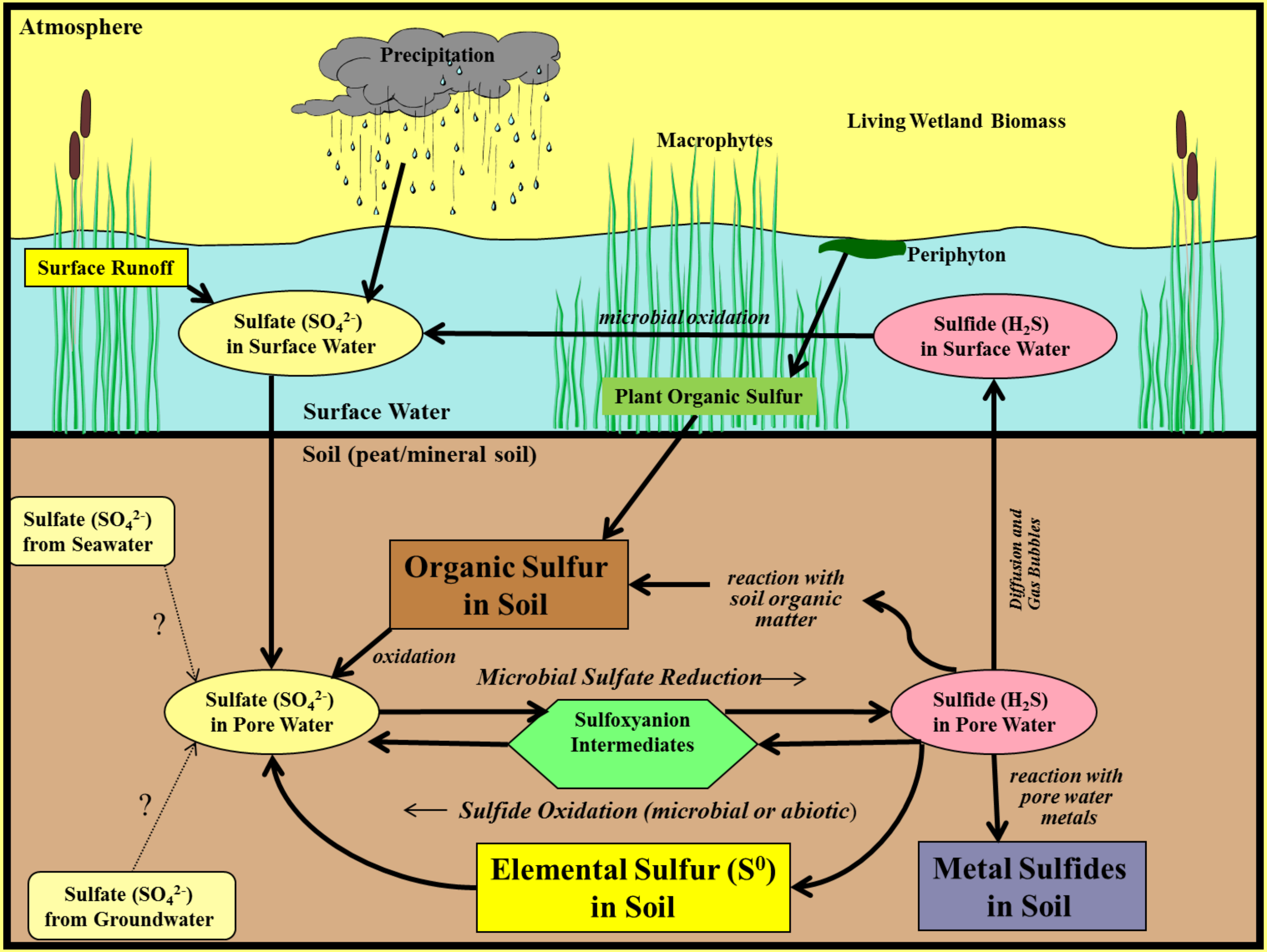


The Biogeochemistry of Sulfur in Wetlands

- Many Chemical Forms and Oxidation States
- Dissolved and Solid Phase
- Biologically-mediated and non-biological chemical reactions



Importance of Sulfur in Wetlands

- **Sulfate drives microbial sulfate reduction, an important anaerobic process in many wetlands; role in CARBON CYCLING and MERCURY METHYLATION**

- **Sulfide (major endproduct of microbial sulfate reduction) is toxic and highly reactive:**
  - **-toxic to vascular plants and animals**
  - **-sulfide highly reactive with metals; control on metal speciation**
  - **-sulfide reacts with organic matter to form organic sulfur species**

Sampling and Analytical Considerations

- **Many different sulfur species requiring many types of analytical approaches; soild phase, dissolved, and gaseous forms of sulfur**

- **Many sulfur species are redox sensitive; require precautions to avoid oxidation and loss of constituents (e.g. anoxic conditions, stabilization in the field)**

Major Sources of Sulfur to Freshwater Wetlands

Wet Deposition

Sea Spray

Dry Deposition

Surface Runoff

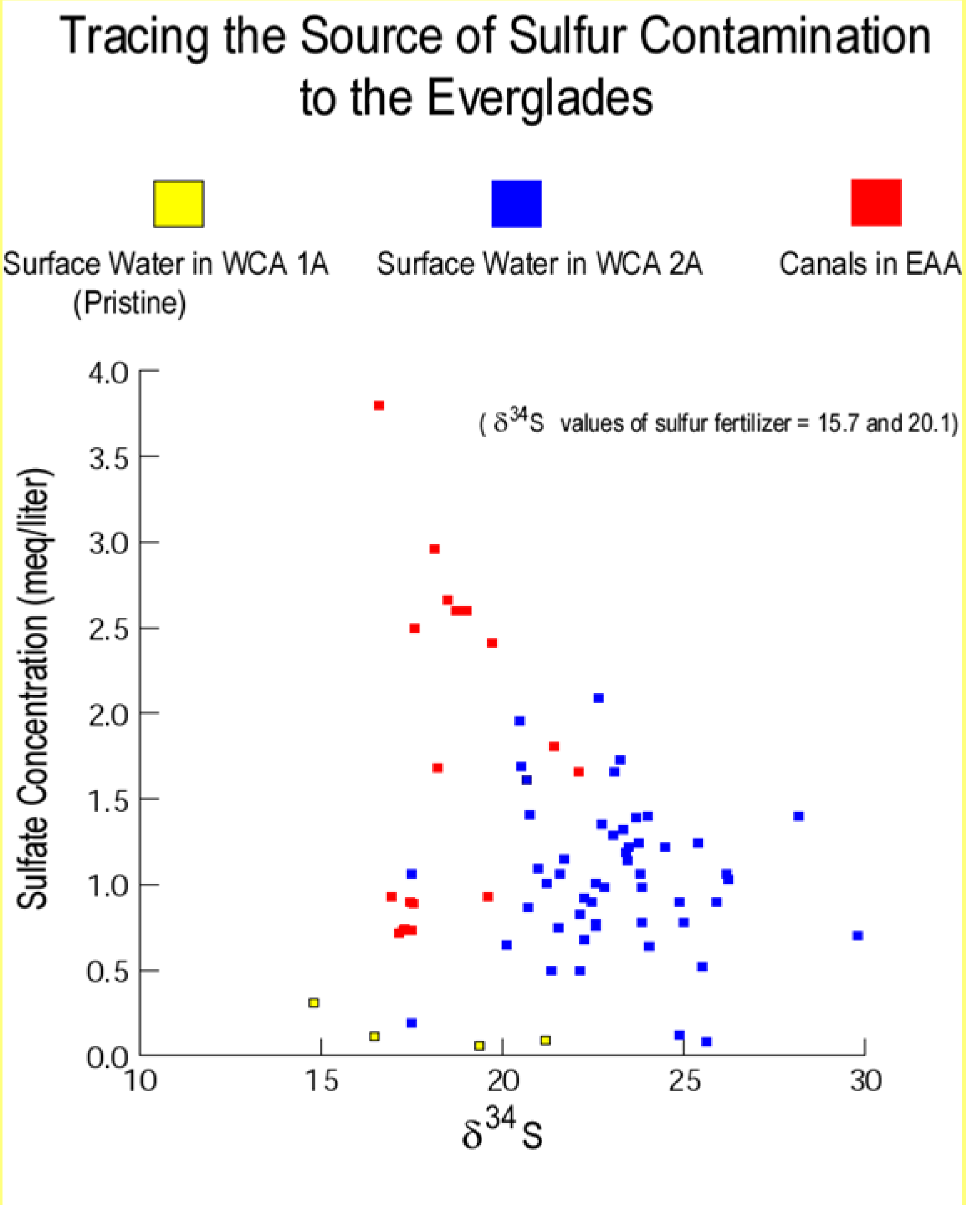
Agriculture
Mine drainage
Urban runoff
Industrial runoff

Saltwater Intrusion
Sealevel Rise

Groundwater

Tracing Sources of Sulfur to Wetlands Using Stable Isotopes

<u>Method</u>:
-Isolation and precipitation of sulfur species
-Analysis using an IRMS

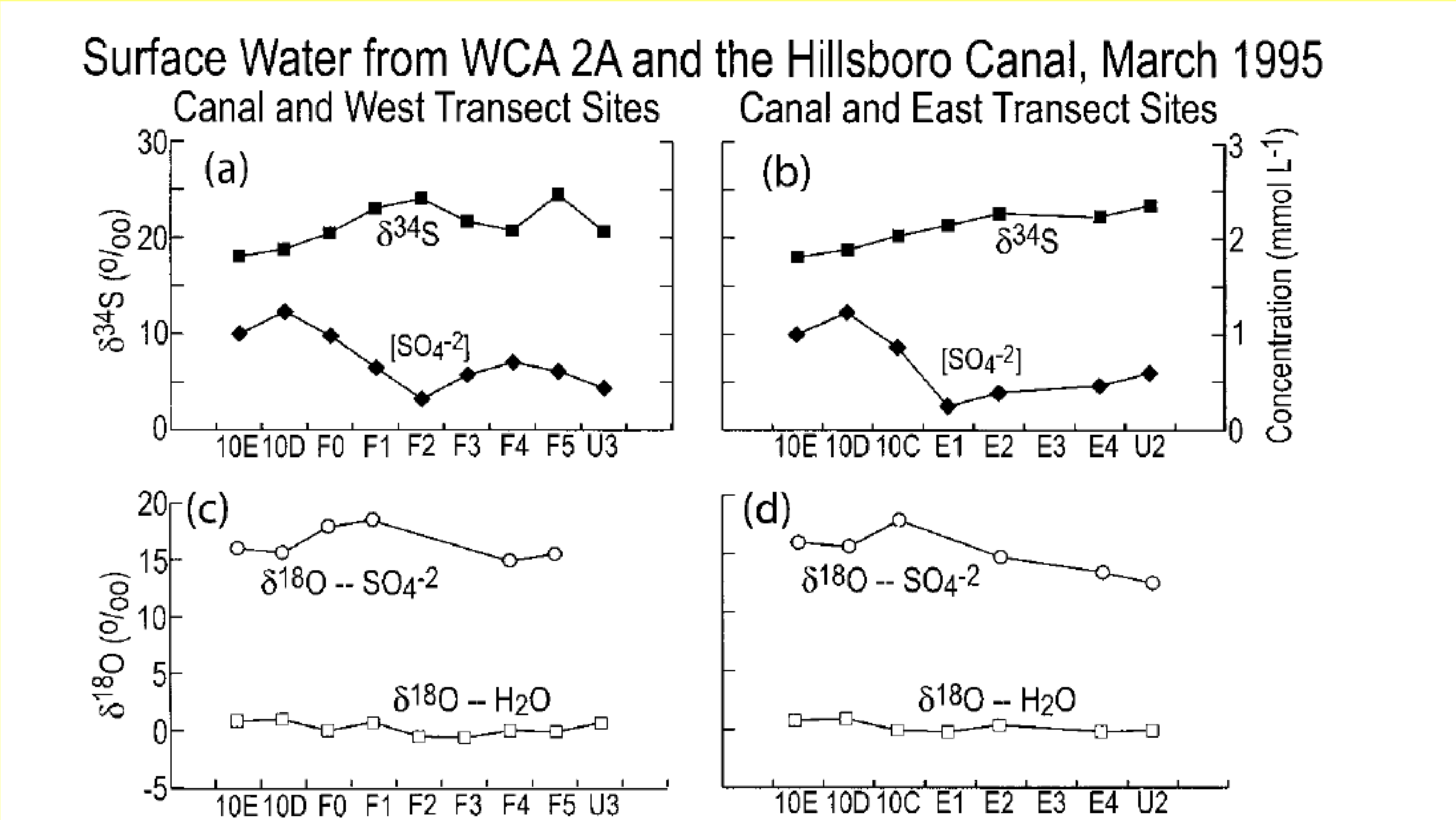


●The S isotope trend line converges on a value of about +16 per mil. Agricultural sulfur used in the EAA has a similar S isotope value.

●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

Use of Sulfur and Oxygen Isotopes of Sulfate to Trace Redox Processes



Direction of flow across marsh

- **Sulfate concentration decreases and $\delta^{34}S$ decreases across marsh due to fractionation from microbial sulfate reduction**
- **At end of transect $\delta^{18}O$ trends toward $\delta^{18}O$ of water due to sulfide oxidation**

Sulfite and Thiosulfate

- Intermediates in the microbial reduction of sulfate to sulfide
- Role in wetland biogeochemistry is poorly understood

Analysis:

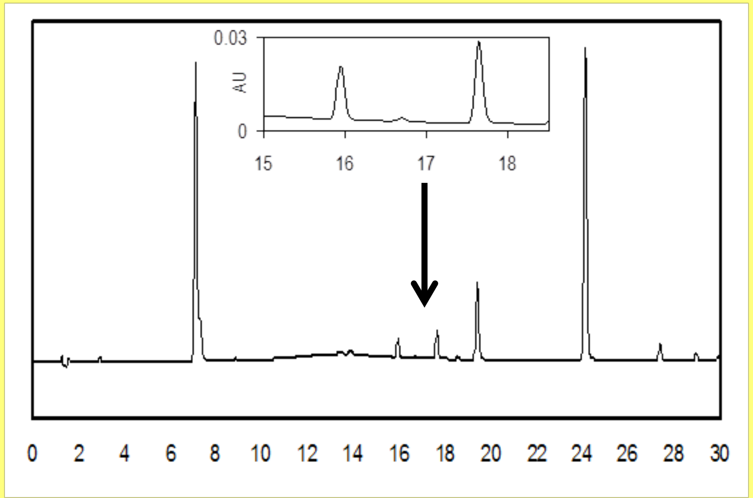
-derivatization in the field with 2,2'-dithiobis(5-nitropyridine) ("DTNP")

-isolation (same day) on solid phase (C18) cartridges

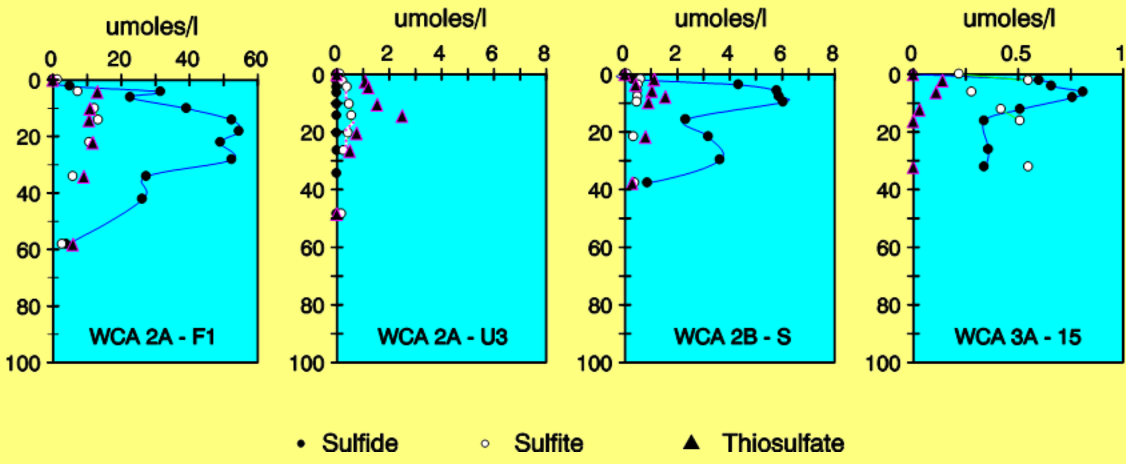
-store cartridges at 5 °C for up to 2 weeks

-analysis after elution of analytes with methanol from cartridge by HPLC/UV-Vis/MS using Waters Nova-Pak C-18 3.9 x 150 mm reversed-phase column or equivalent.

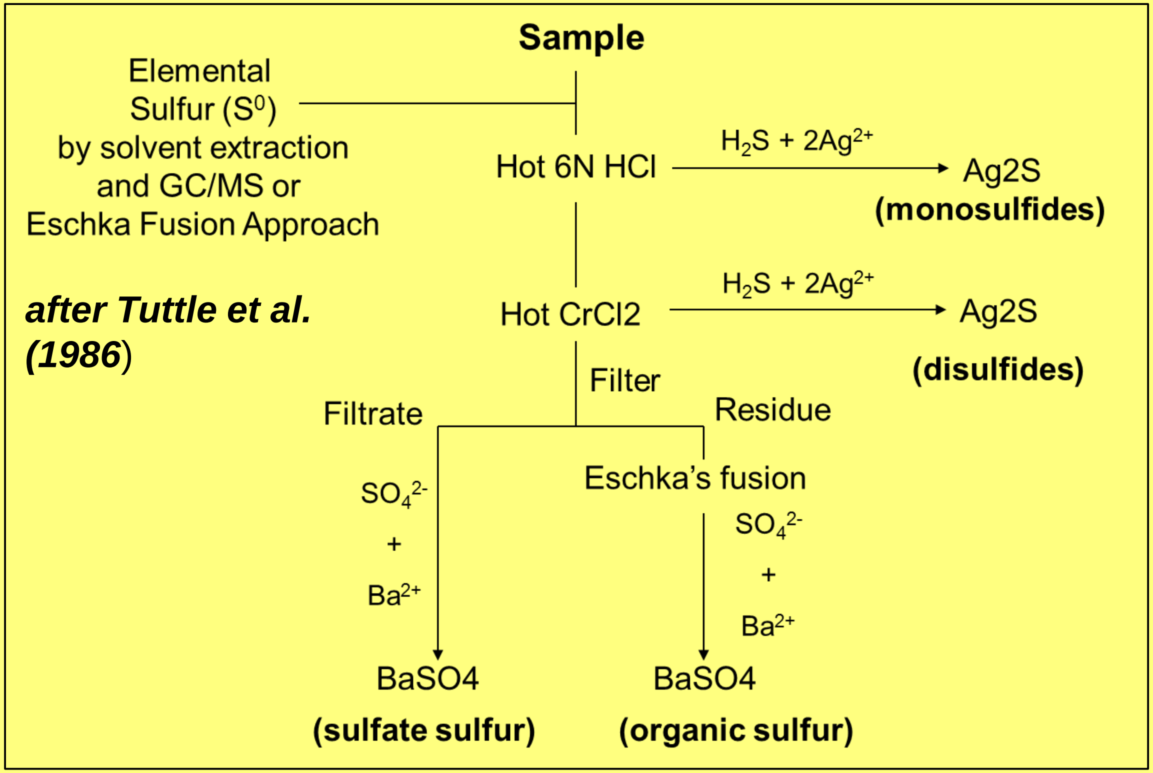
Sample Chromatogram

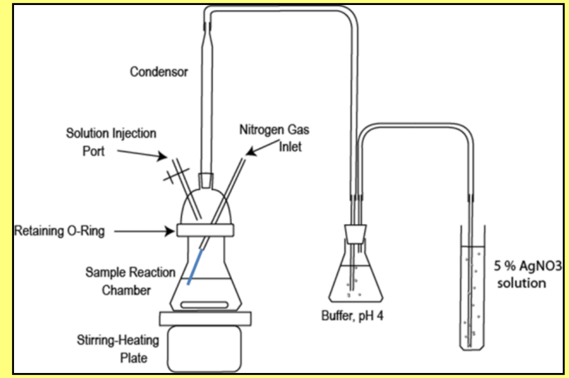


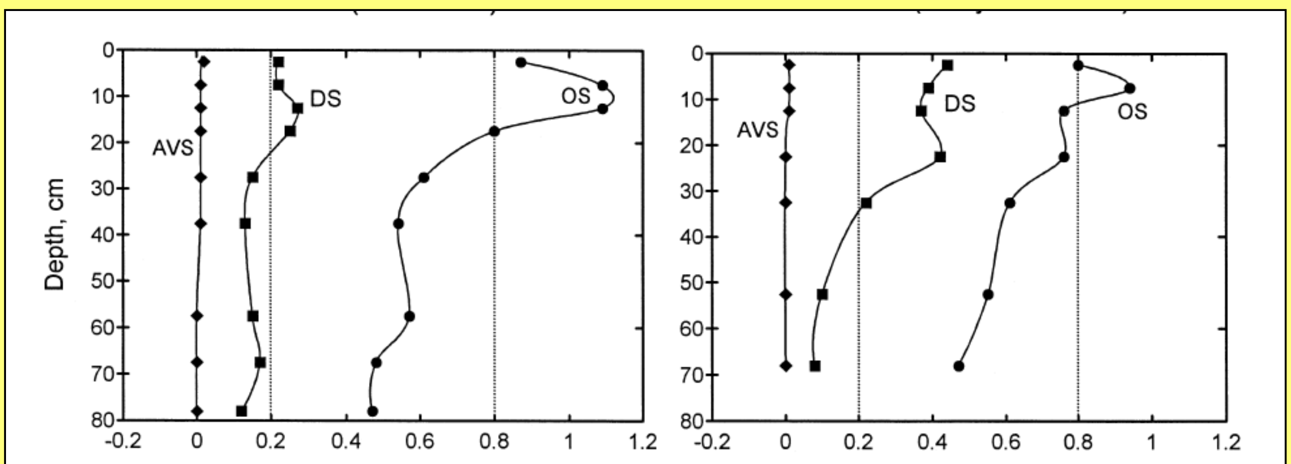
Sulfide, Sulfite, Thiosulfate Data
Everglades Pore Water – SEP 2000



Speciation of Sulfur in Wetland Soils



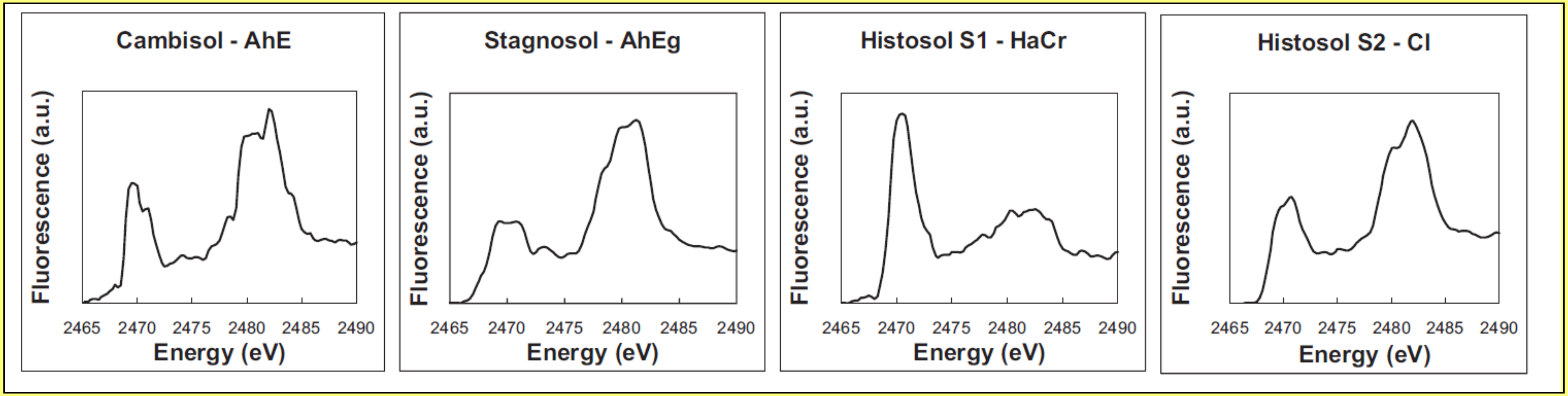




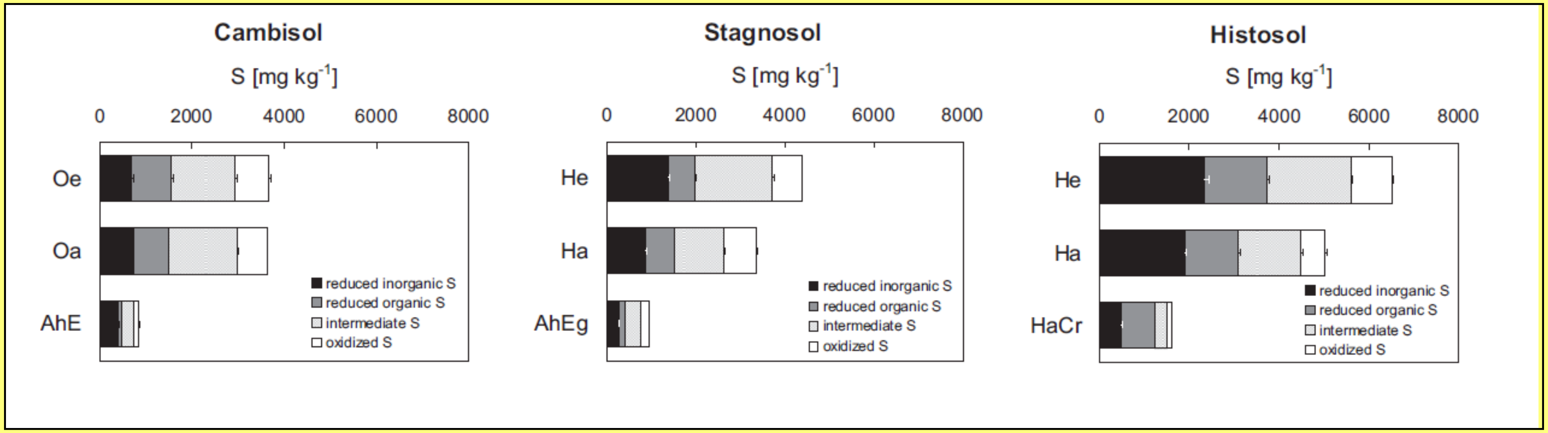
Speciation of Sulfur in Wetland Soils

Sulfur K-edge XANES

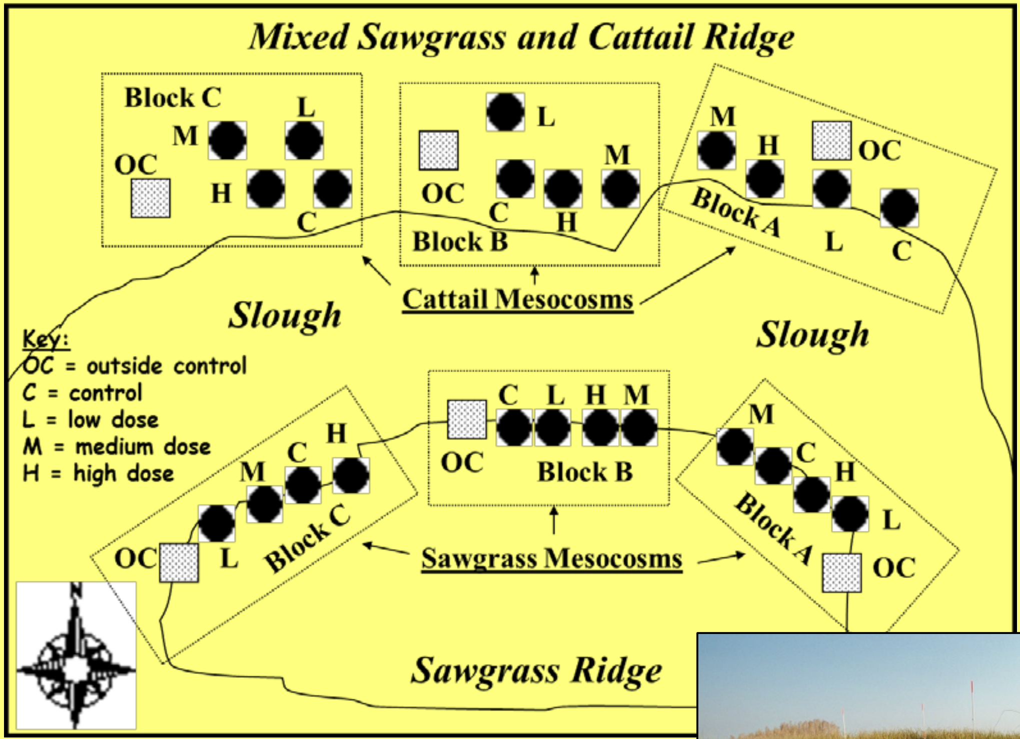
Prietzel et al. (2009). Plant Nutr. Soil Sci. 172, 393–409

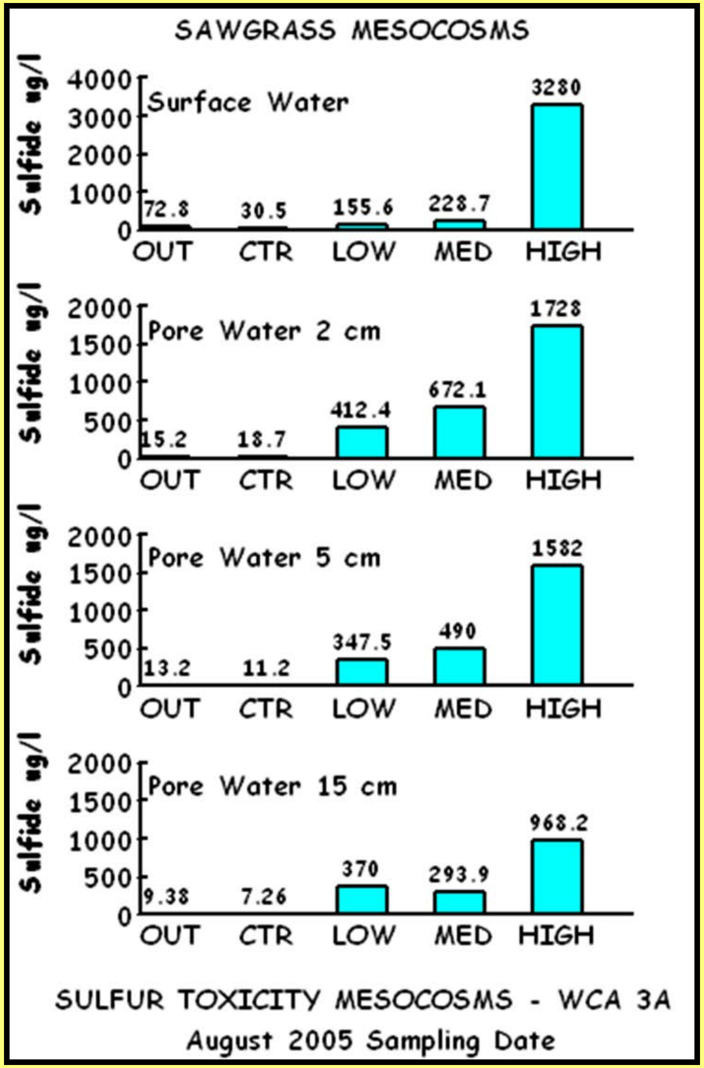


Peaks at various energies represent different S species (2469–2472 eV: inorganic sulfide, 2473 eV: organic sulfide, 2476 eV: sulfoxide; 2479 eV: sulfite; 2480 eV: sulfone; 2481 eV: sulfonate; 2482–2483 eV: ester sulfate and sulfate).



Experimental Methods for Examining Sulfur Biogeochemistry of Wetlands: Mesocosms





Sulfide response to addition of sulfate to mesocosms

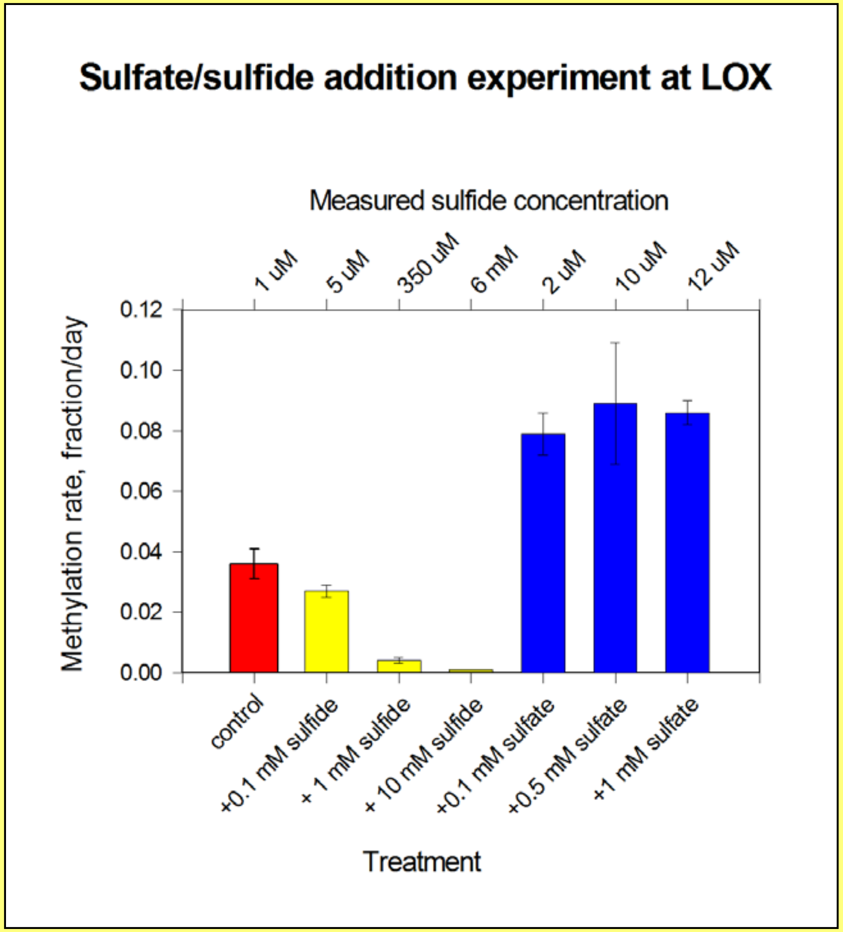
Mesocosm Study

-Isolates parts of marsh for Experiments

-Communicates with outside through base, but exchange is slow

-Randomized block design

Experimental Methods for Examining Sulfur Biogeochemistry of Wetlands: Microcosms



- **Addition of sulfate to the culture increased MeHg production relative to the control.**

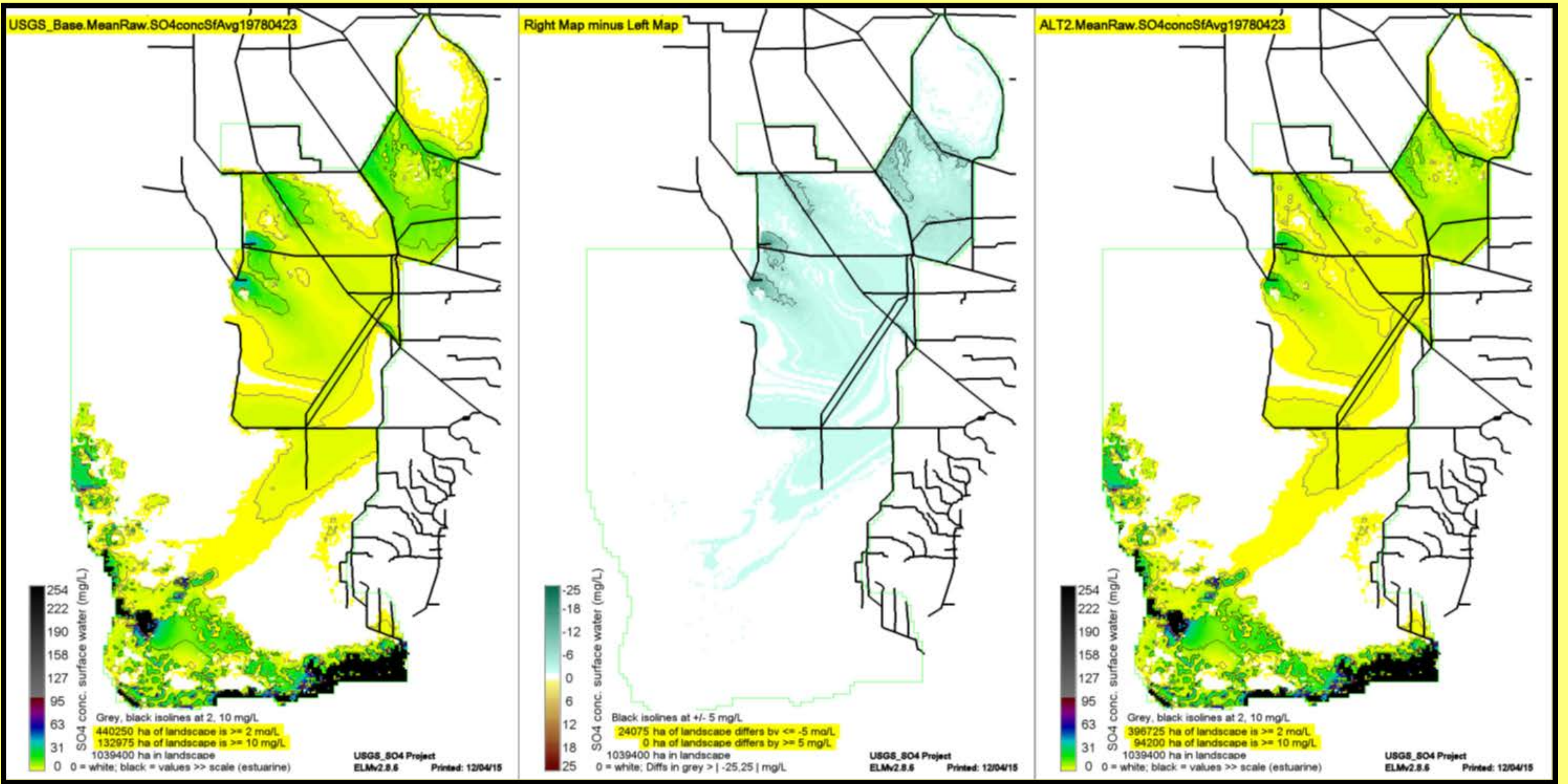
- **Addition of sulfide to the culture decreased MeHg production relative to the control.**

Modeling of Sulfur in Wetlands

●**Existing landscape models can be used as a base to construct sulfur models with the addition of specialty modules that describe movement of sulfur species.**

Sulfate Concentration (mg/L)

Baseline (Current Conditions)	Difference Map Model minus Baseline	Model (33% reduction) Mean Results

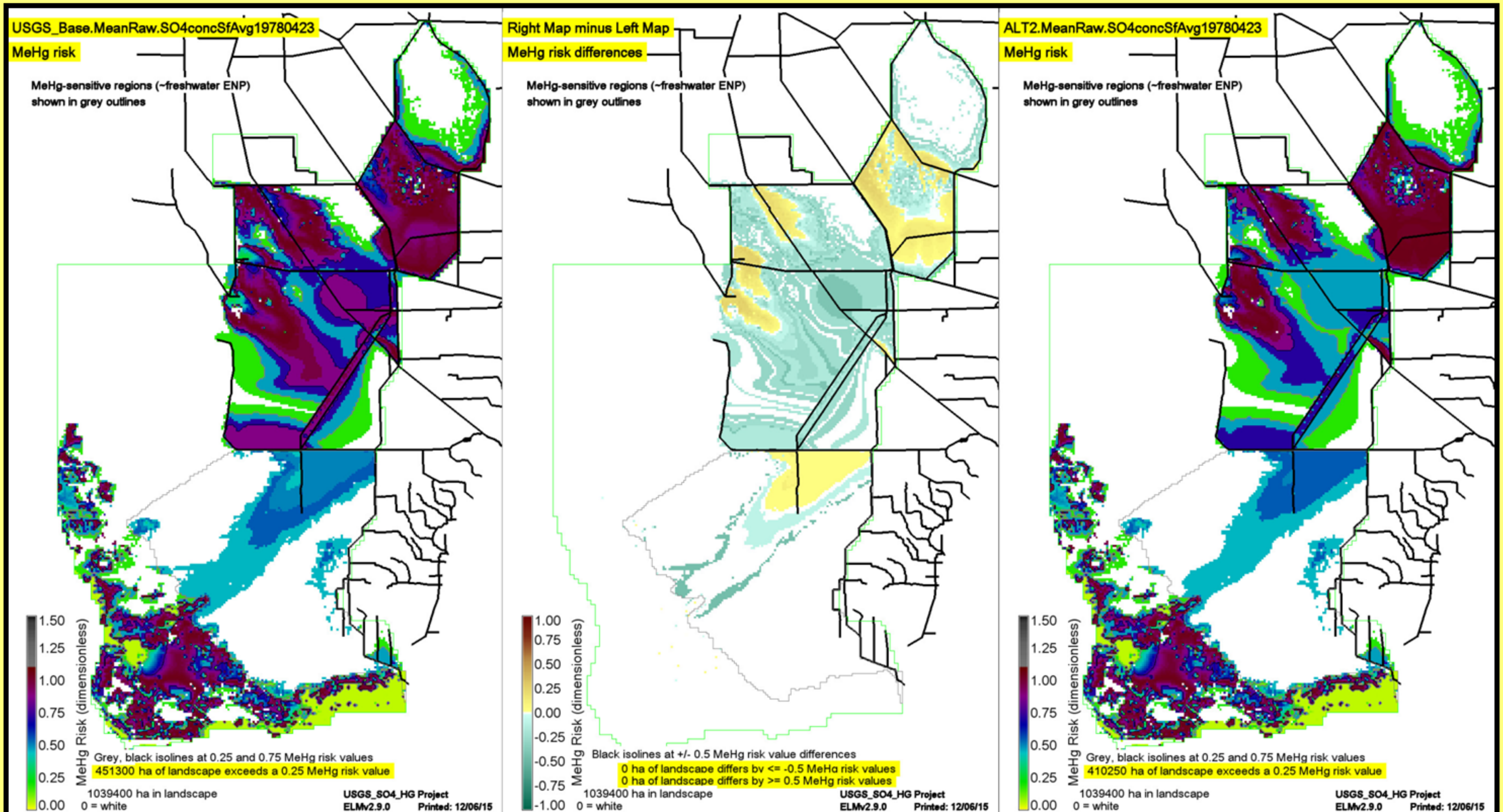


Modeling of Sulfur in Wetlands

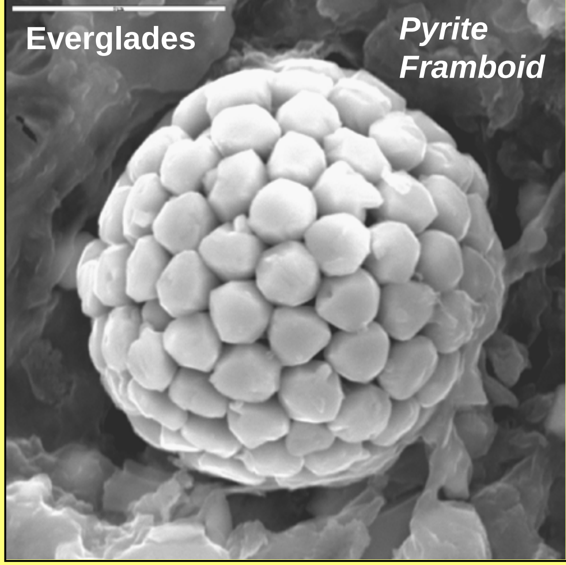
- Addition of a module relating sulfur and methyl mercury

MeHg Risk (Dimensionless)

Baseline (Current Conditions) | **Difference Map Model minus Baseline** | **Model (33% reduction) Mean Results**



Conclusions



●Sulfur biogeochemistry in wetlands is complex, with many forms and redox states (+6 to -4) present

●Much of the complexity is driven by microbial processes, especially microbial sulfate reduction

●Biogeochemical processes in wetlands affected by sulfur include carbon and nutrient cycling, trace metal speciation and solubility, and mercury methylation

●Stable isotope analysis of sulfur species is an important for examining sources Of sulfur to wetland ecosystems, and in following biogeochemical processes

●Analytical methods employed in sulfur species analysis include colorimetric, electrochemical, chromatographic, spectroscopic, and wet chemical methods

●Experimental methods employing field mesocosms and laboratory microcosms allows manipulation of isolated portions of the wetland to examine biogeochemical processes involving sulfur and other elements

●Modeling of sulfur biogeochemistry can provide important insights that drive additional field and experimental studies