Modeling the Effects of Sulfate Loading and Methylmercury Production in the Everglades

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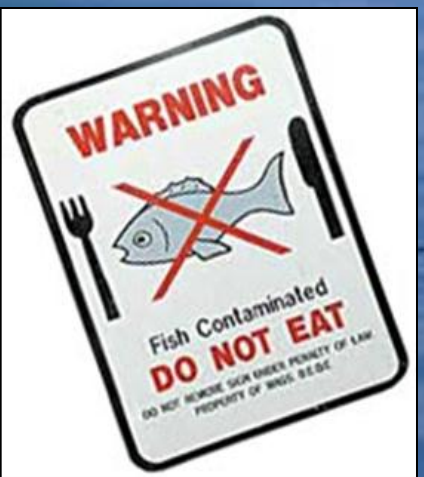

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Sulfur Loading to the Everglades

- **Excess sulfate has been observed in the freshwater Everglades by USGS, EPA, SFWMD, and others**

- **Background levels of sulfate in the ecosystem are estimated as < 1 mg/L and some areas far removed from anthropogenic sources have sulfate levels as low as 0.05 mg/L**

- **60% of the freshwater Everglades has sulfate concentrations exceeding background; average sulfate concentrations at marsh sites adjacent to canal or STA discharges are >60 mg/L**

- **There is a general decrease in sulfate from north to south across the Everglades; highest concentrations occur in canals within the Everglades Agricultural Area (EAA)**

- **Changes in the movement of canal water accompanying restoration is changing where sulfate loading to the ecosystem occurs – however, levels of sulfate in canals has not changed appreciably in the past 15 years**

- **Distributions of sulfide and organic S in soil parallel those for sulfate**

Sulfate Distributions In Surface Water

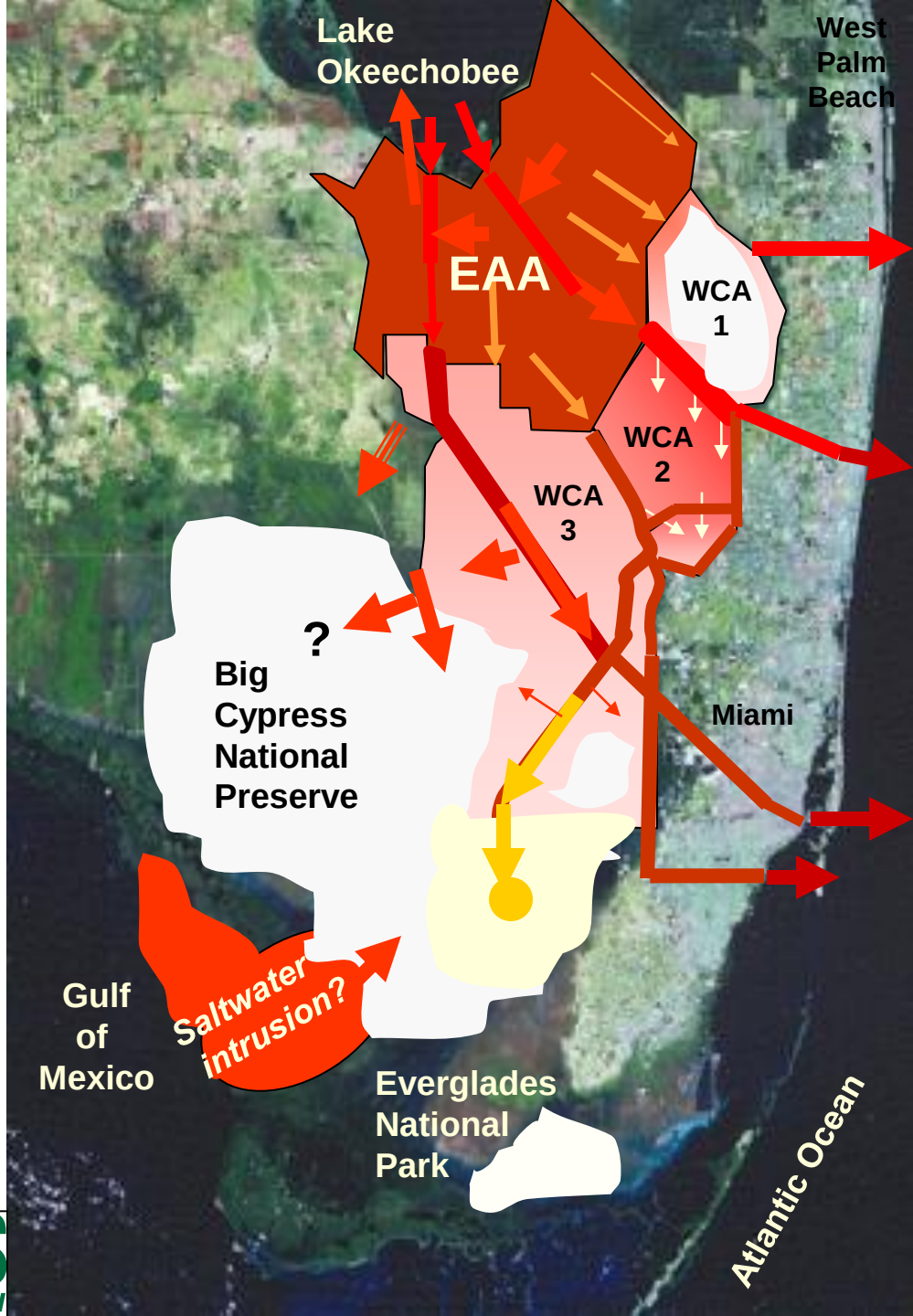
> 50 mg/L

~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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Impacts of Sulfur Loading
Why is This Important to Everglades Restoration

- **Sulfate stimulates microbial sulfate reduction; fundamentally alters microbial community structure in impacted areas**

- **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**

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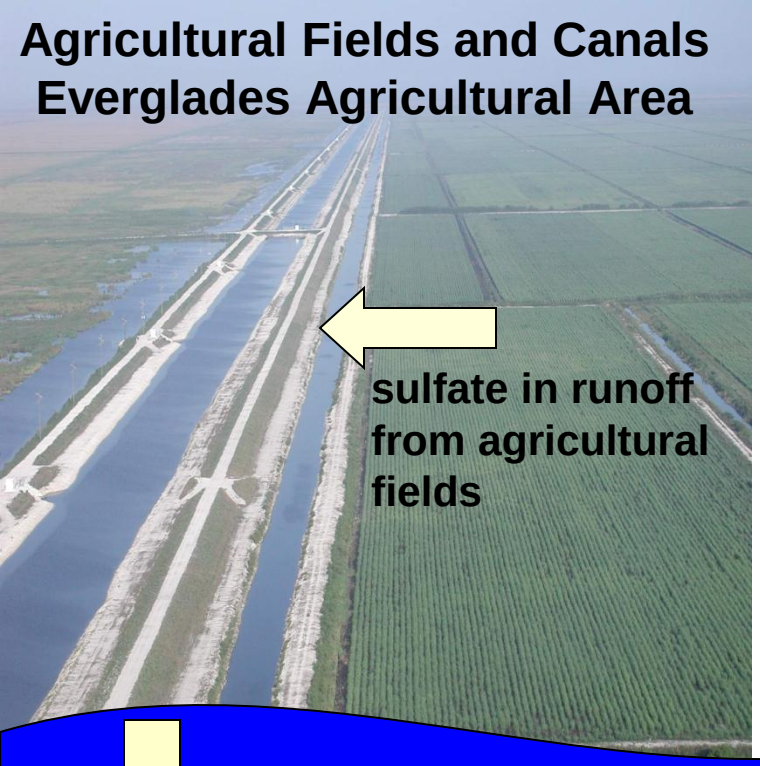
Linking Sulfate and Methylmercury in the Florida Everglades



Hg^{2+}

mercury from distant sources

rainfall

Hg^{2+}

sulfate from canals

Everglades Marsh

SURFACE WATER

SOIL

sulfate-reducing bacteria

sulfate

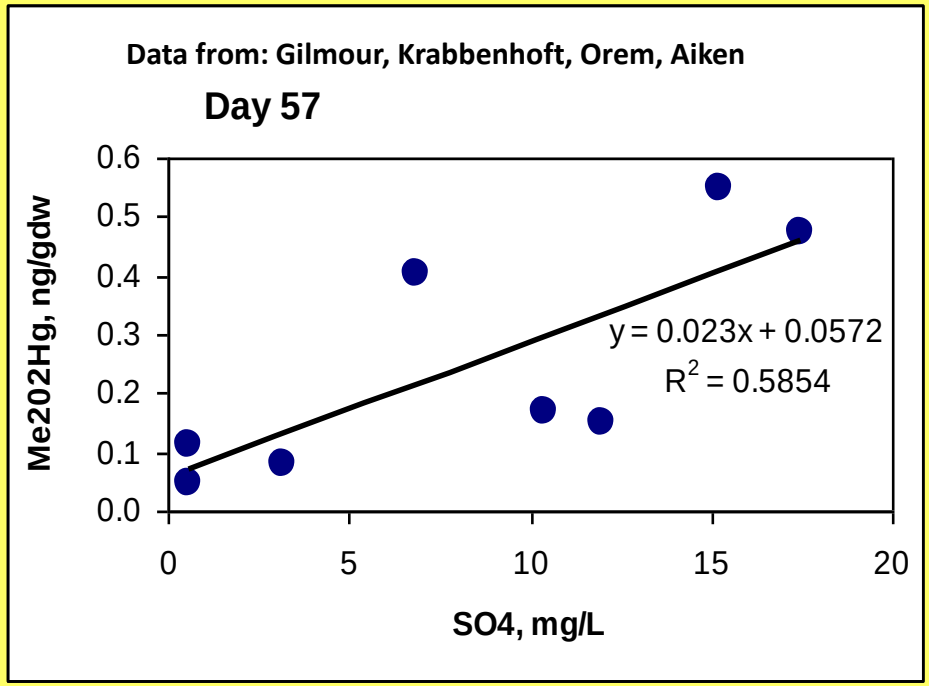
Hg^{2+}

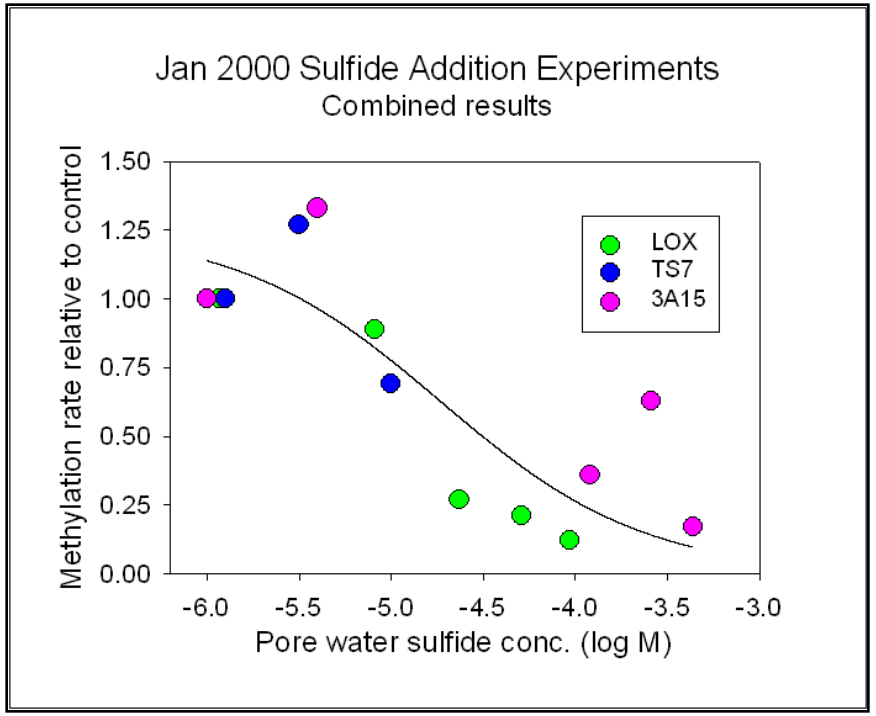
sulfide

methylmercury

bioaccumulation of methylmercury

Sulfate/Sulfide and MeHg – Mesocosm Studies





-Add sulfate to Everglades soil and MeHg production increases; confirmed at 5 different fieldsites and lab experiments

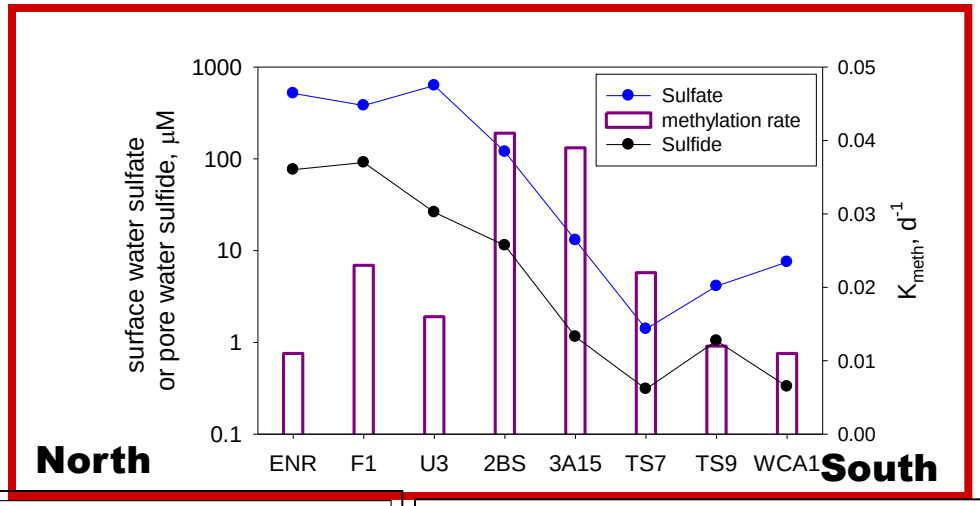
-Linear relationship between sulfate and MeHg production through 20 mg/L

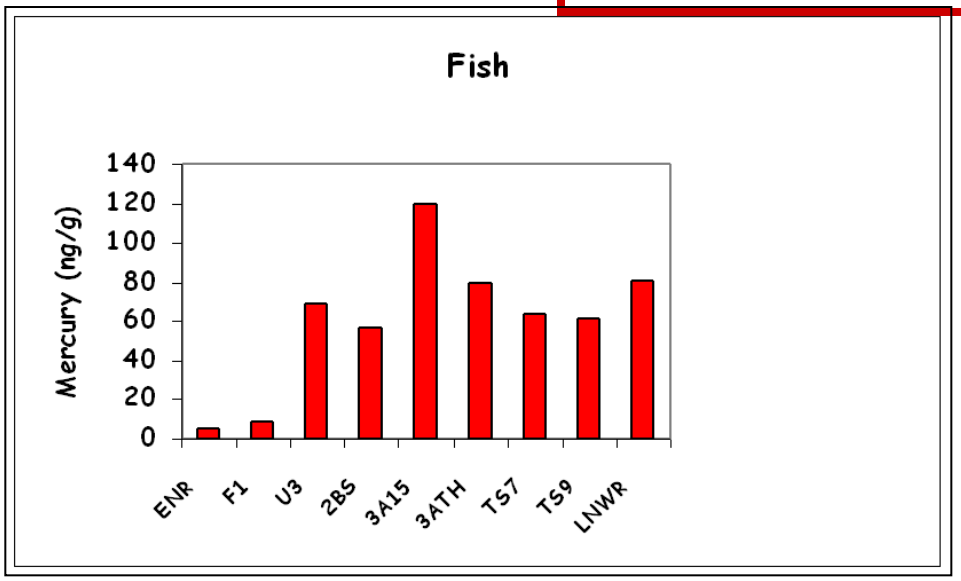
-Sulfide inhibits methylation at 10-100 μM (0.3-3 mg/L); Field distributions, experimental studies in cores and in cultures are all consistent

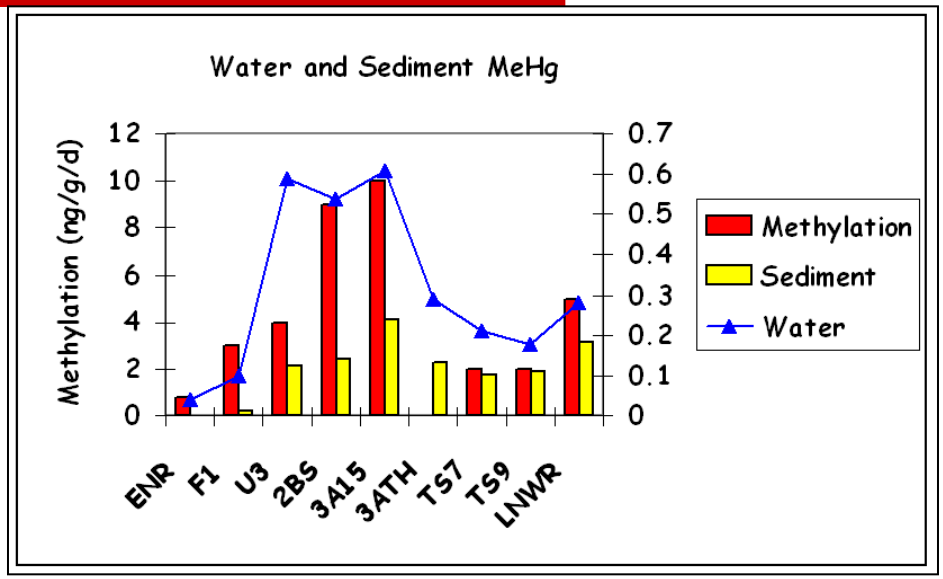
Trends in Sulfur and MeHg Across the Ecosystem

-Highest sulfate/sulfide in north near source (agricultural runoff)

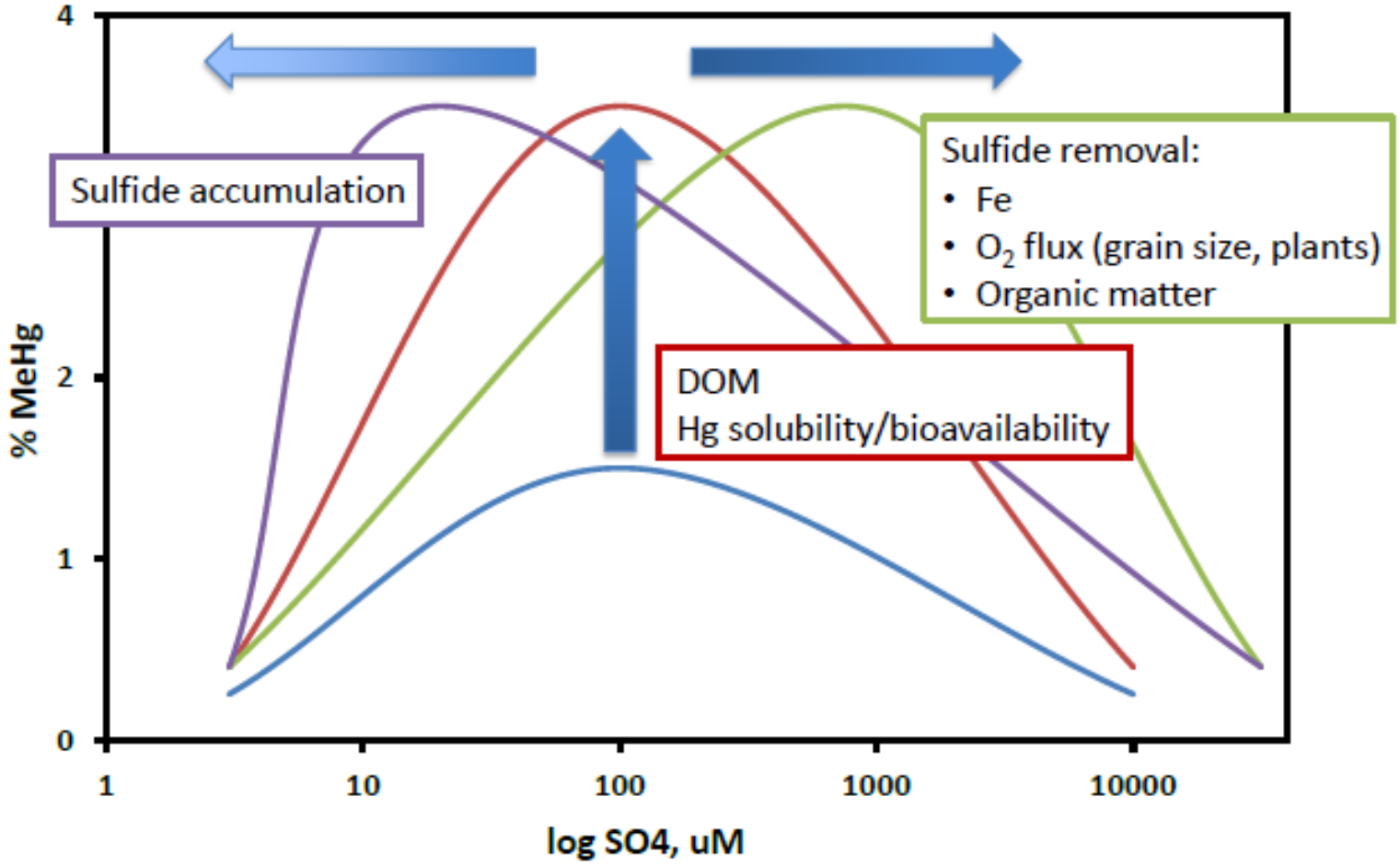
-MeHg peaks in middle "Goldilocks Area" where sulfate and sulfide levels are just right (sulfate stimulation vs. sulfide inhibition)







Conceptual diagram of the relationship between sulfate concentration and MeHg accumulation



Research Needs

Because of the level of sulfate contamination and its myriad impacts (especially methylmercury production and bioaccumulation) there is a need for land and water managers to understand how changes in water management accompanying restoration will impact sulfate loading to the ecosystem and resulting impacts.

Research needs include:

- **Accurate mass balance models of sulfate sources, including agricultural, soil oxidation, atmospheric, ASR, groundwater, and other sources.**
- **Determine if sulfate is the major form of S entering the ecosystem, or if dissolved organic S and particulate S are also important**
- **Modeling of sulfate as it moves along canals or in sheet flow across the wetland landscape is needed to understand sulfate loading at various locations; especially as more sulfate-contaminated water is moved to sensitive areas like Everglades National Park**
- **Modeling of the impacts of various levels of sulfate loading on methylmercury production taking into account variations from location to location**

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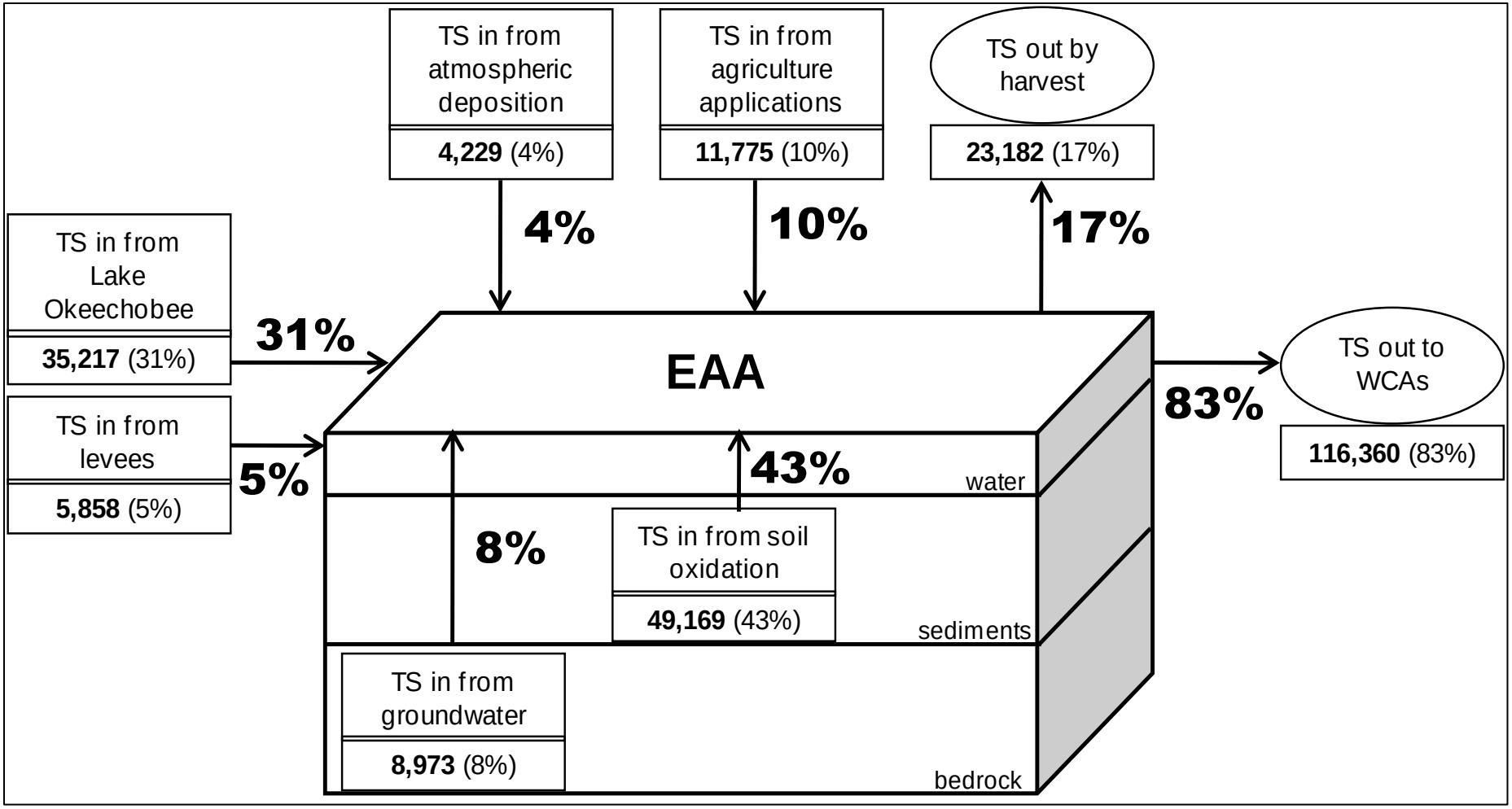
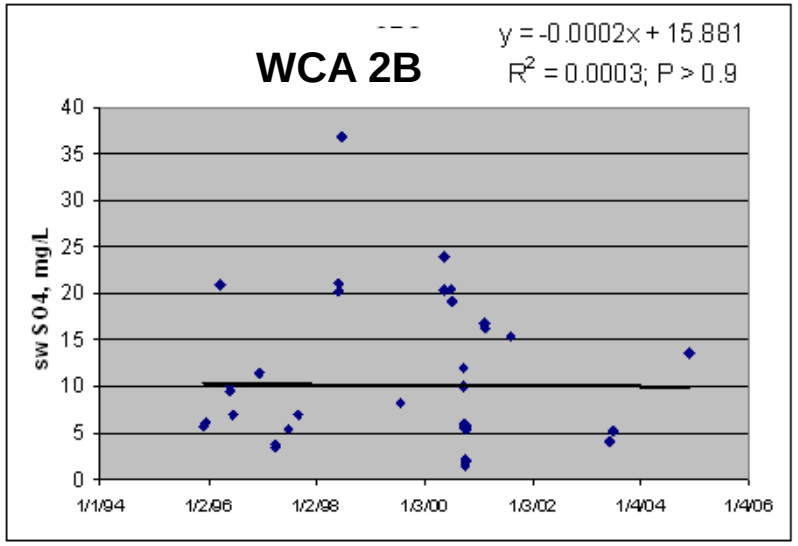
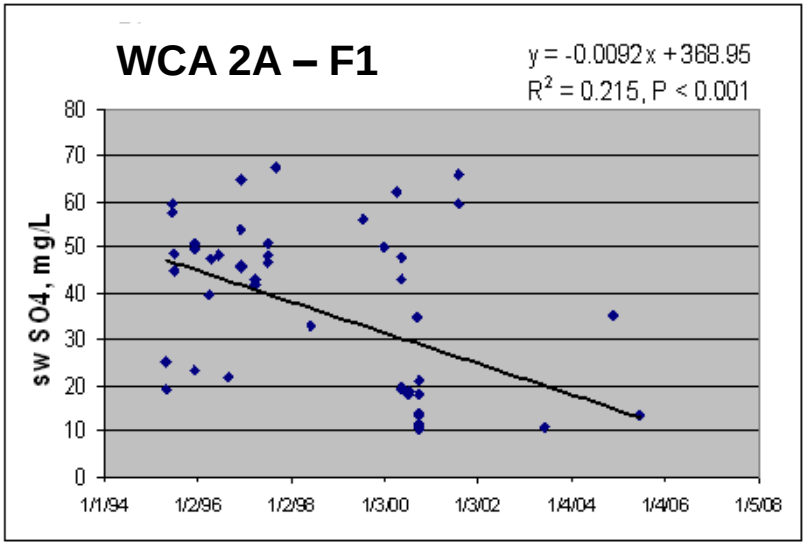
Sulfur Mass Balance of EAA

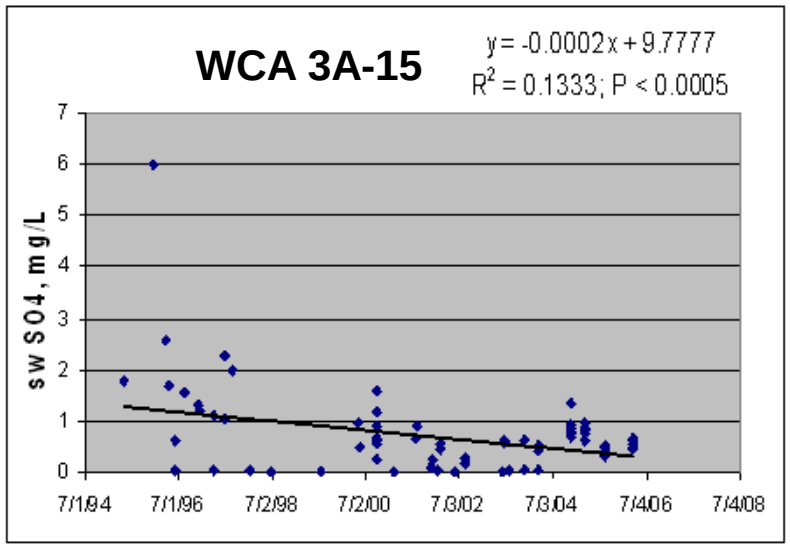
Corrales J., Naja G.M., Dziuba C., Rivero R.G., and Orem W., 2011, Sulfate threshold target to control methylmercury levels in wetland ecosystems. Sci. Tot. Environ. 409: 2156-2162.

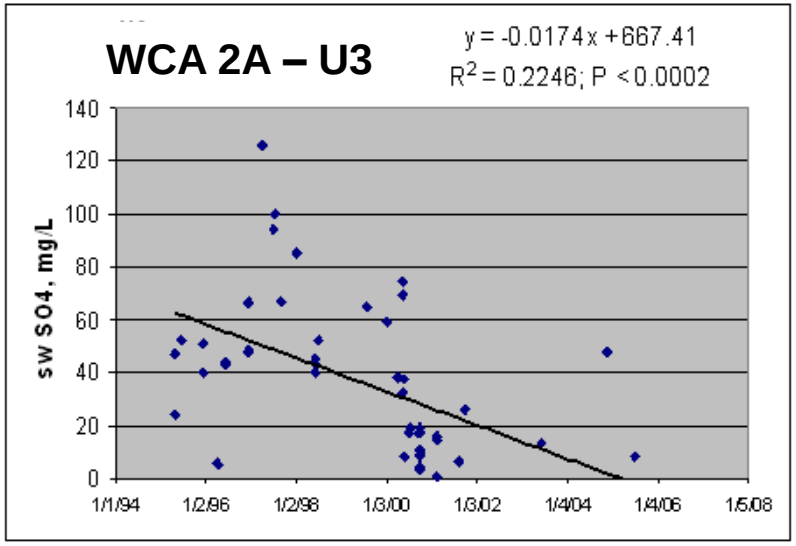


Another Variable – Sulfate Loading is Changing at Different Locations as Restoration Proceeds

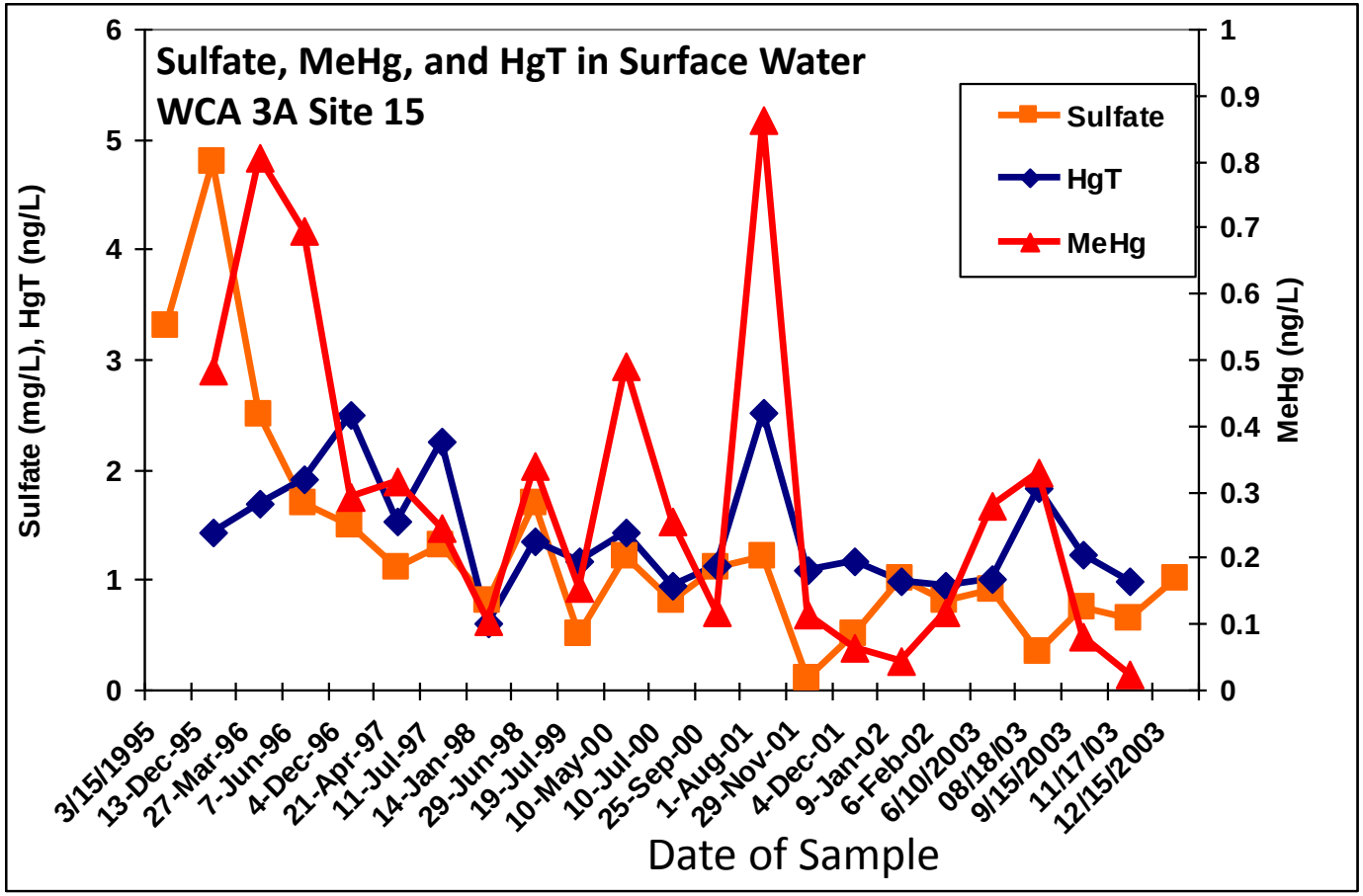








What Happens to MeHg Production in the Everglades if Sulfate Contamination is Reduced??



Changes in sulfate, MeHg, and HgT at a site in the central Everglades (WCA 3A-15) from 1995 to 2003

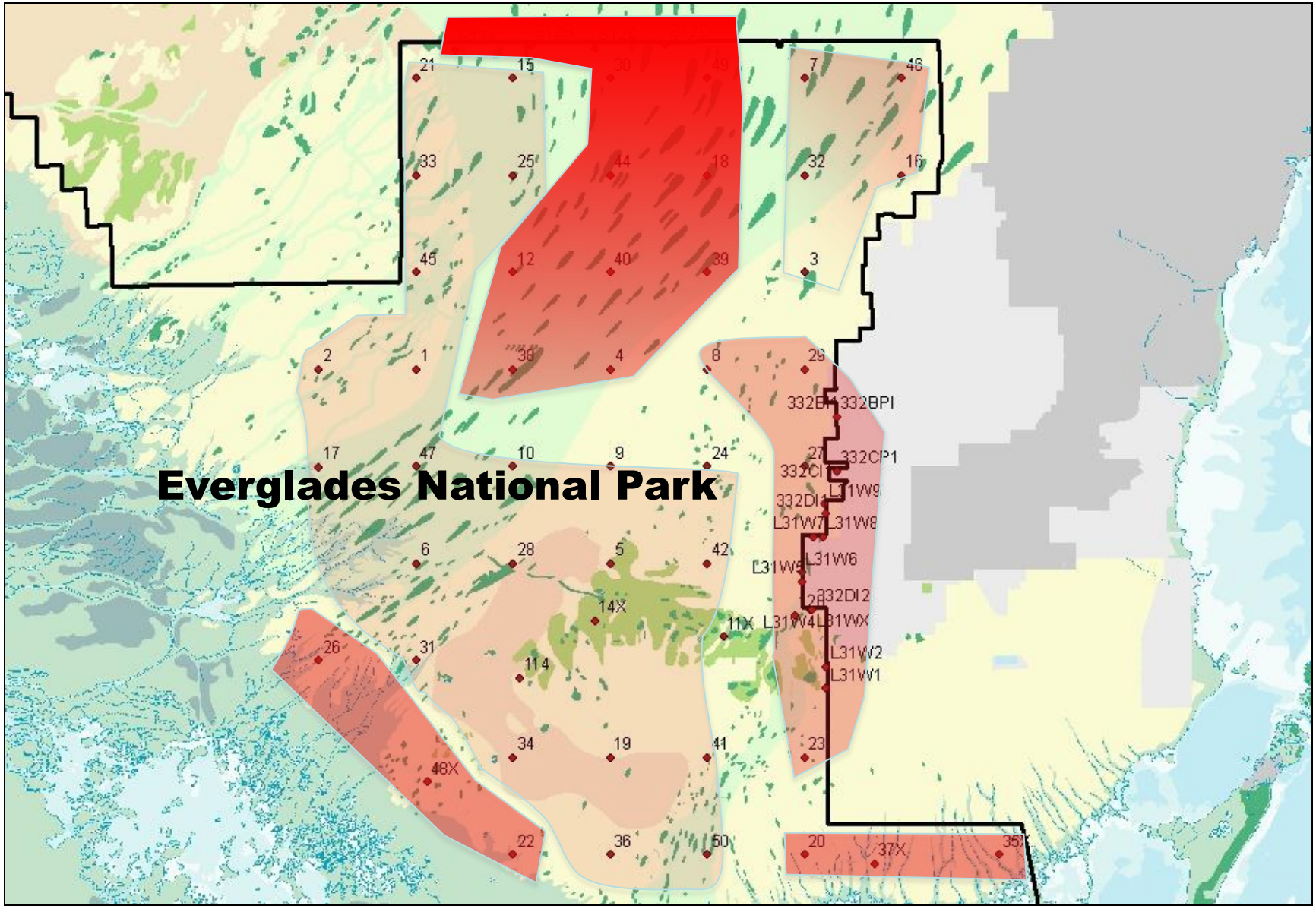
-Former MeHg hotspot showed dramatic decline in MeHg over time

-Decline not correlated to declines in Hg deposition at this site

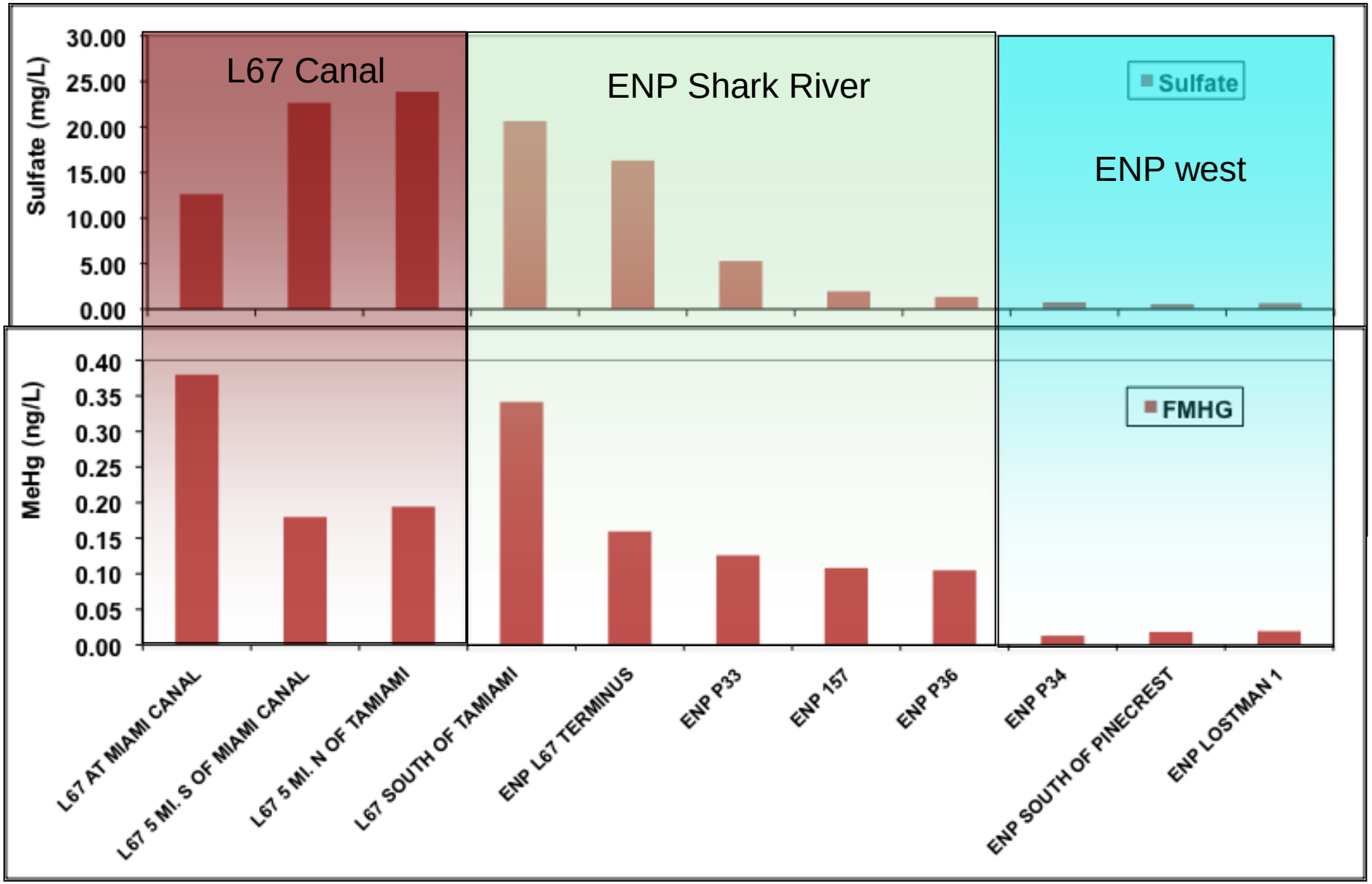
-Decline closely linked to decline in sulfate at site

-Illustrates fast response of ecosystem to declines in sulfate w/r to MeHg production and biopaccumulation

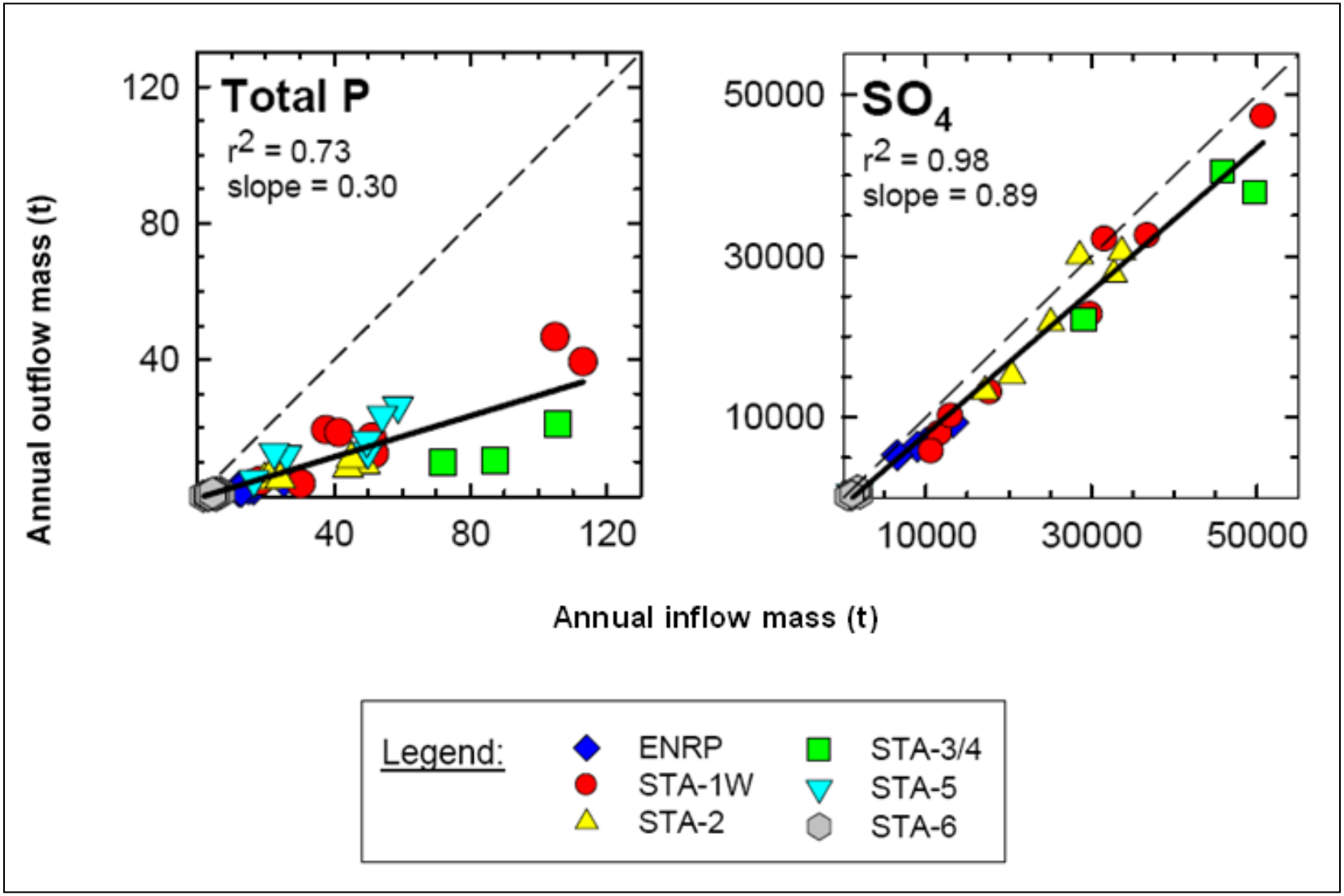
What Happens When Sulfate Levels Increase in A Region of the Everglades?



Sulfate Loading to Northern ENP Correlates with Increased Methylmercury Production

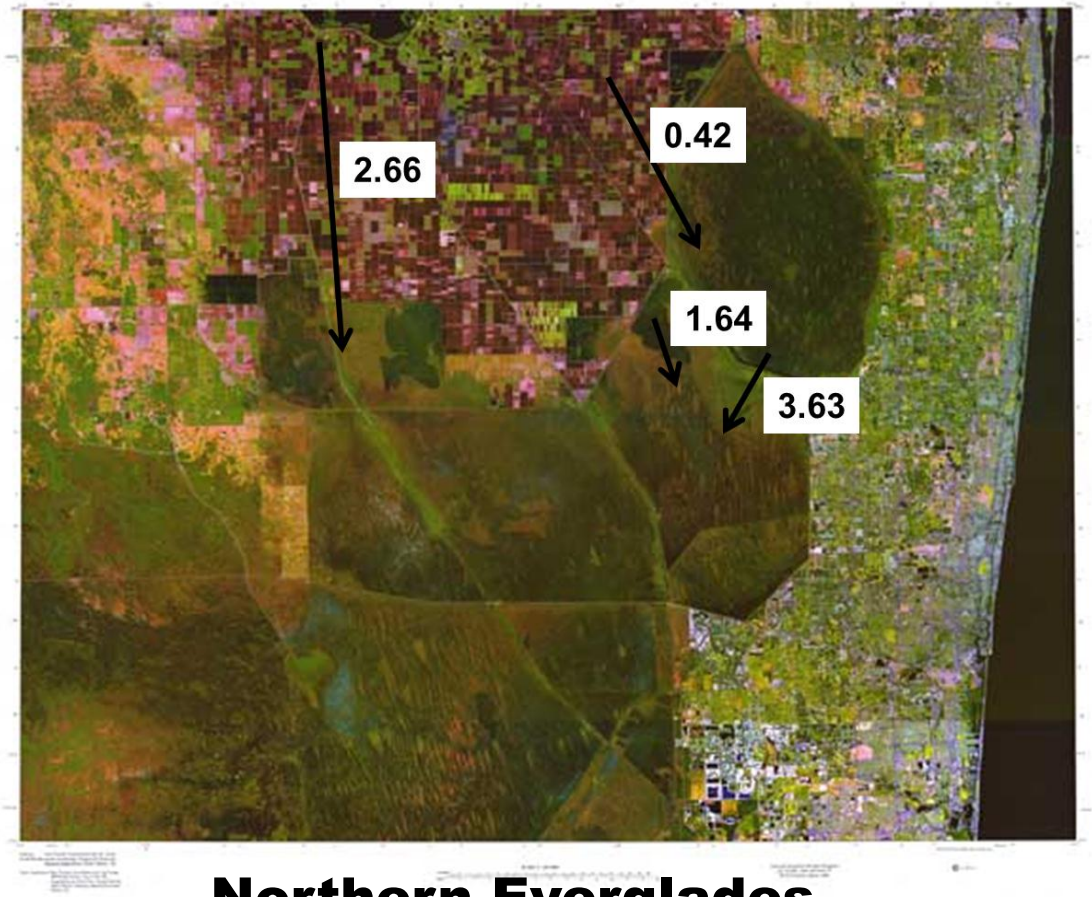


Sulfate is Removed and Sequestered By the Marsh But Much More Slowly Than Phosphorus

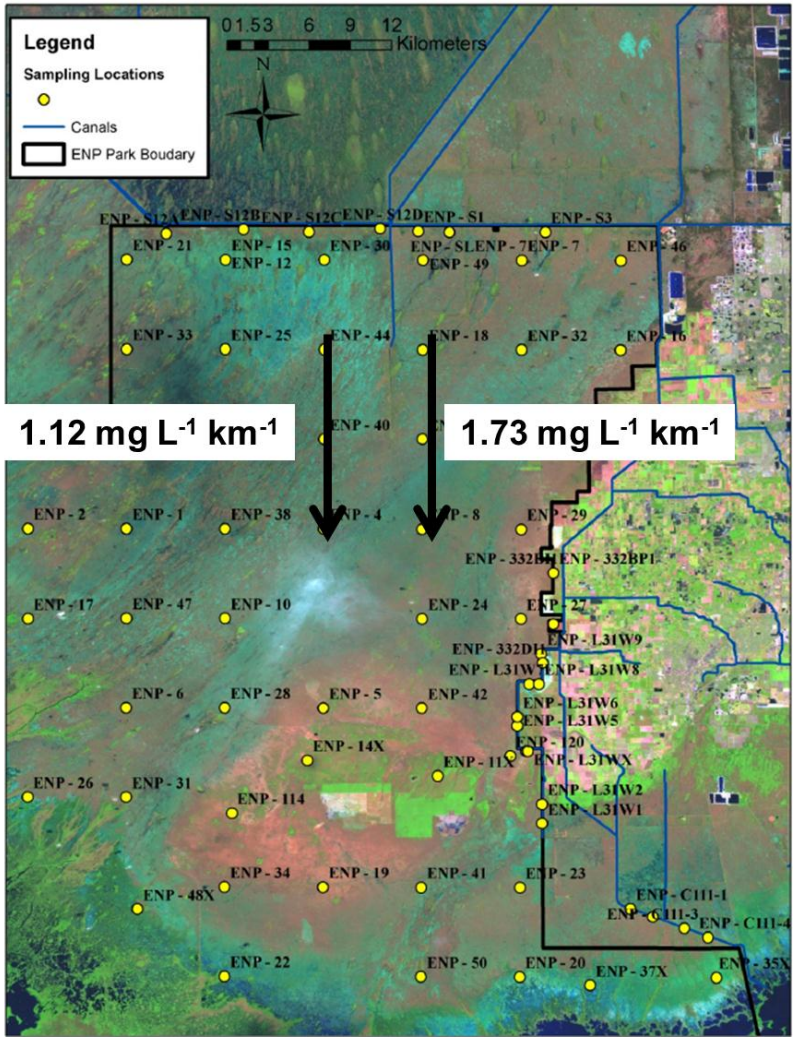


Rates of Sulfate Removal by Overland Sheet Flow mg L^{-1} km^{-1}

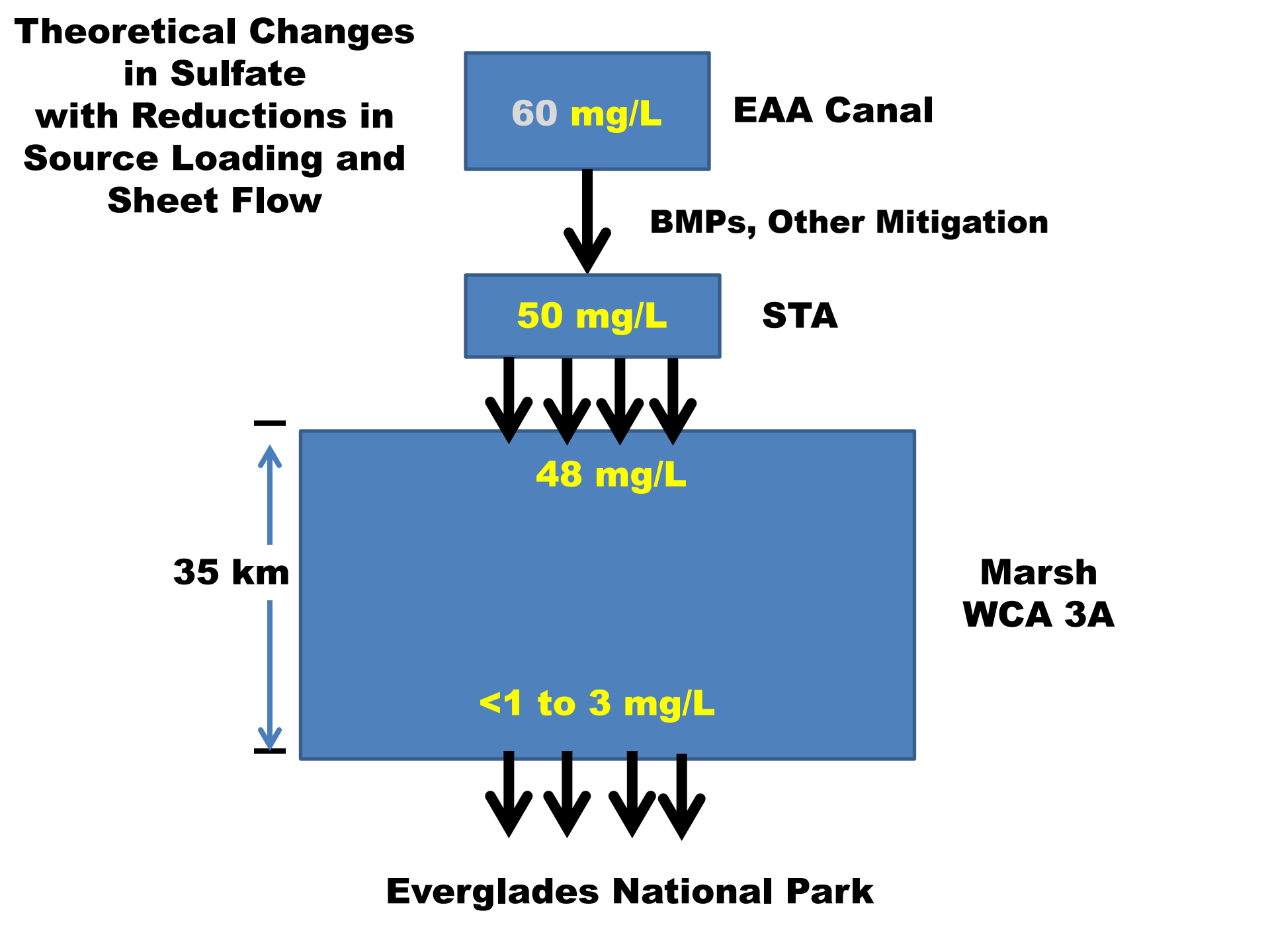
-Sulfate reduction and sequestration
-dilution



Northern Everglades



Everglades National Park


Theoretical Changes in Sulfate with Reductions in Source Loading and Sheet Flow
60 mg/L
EAA Canal
BMPs, Other Mitigation
50 mg/L
STA
48 mg/L
35 km
Marsh
WCA 3A
<1 to 3 mg/L
Everglades National Park

Conclusions

- Sulfate contamination is a key water quality issue facing Everglades restoration

- Sulfate is one of the principal drivers of methylmercury production within the ecosystem, but the biogeochemistry of the sulfur/methylmercury linkage is complex

- Both the loading and distribution of sulfate are important in determining where methylmercury production is highest

- Accurate sulfur mass balance models are needed to determine sulfur sources and design mitigation strategies

- Models addressing where sulfate loading occurs, and how sulfate-laden canal water moves across the marshes are needed to examine where methylmercury production will occur, and protect sensitive areas

- Slow sheet flow over extensive areas of marsh can effectively remove sulfate and sequester it in organic soils