Florida Department of Environmental Protection

Limiting Factors in Mercury Methylation Hotspot Development: The Tangled Web

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GEER 2017

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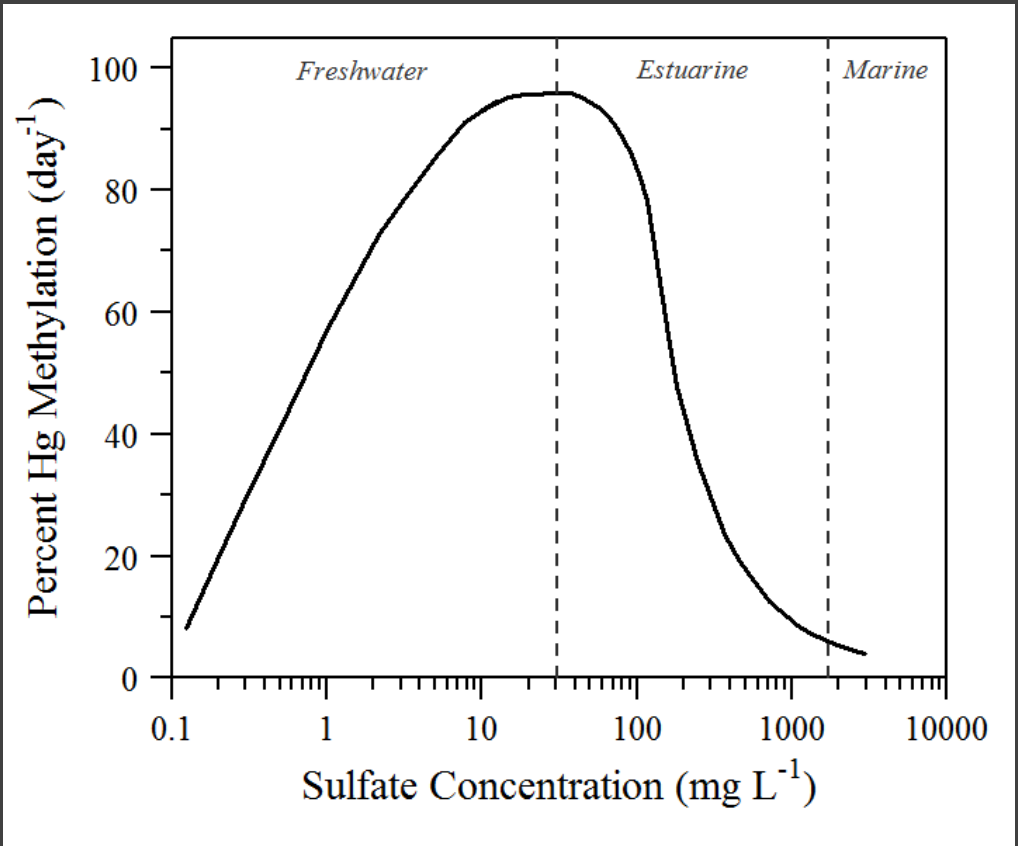
Mercury in the Everglades

- Atmospheric deposition is the dominant delivery mechanism of Hg to the Everglades ecosystem
- Elevated Hg concentrations in fish and other biota were first observed within the Everglades in the early 1970's
- Highly spatially-variable elevated Hg concentrations continue to be observed in fish within the Everglades ecosystem
- Mercury is converted to the more toxic and bioavailable methyl-mercury (MeHg) through microbial processes
- Once Hg is methylated, uptake by biota is rapid where it enters the food-chain or trophic continuum

Unimodal Sulfur-Mercury Relationship



- Hypothetical relationship between mercury methylation potential in sediment versus surface water sulfate concentrations hypothesized by Gilmour and Henry (1991).
- Partially explained fish Hg in acid-impacted lacustrine lakes

Gilmour CC, Henry EA (1991) Mercury methylation in aquatic systems affected by acid deposition. Environmental pollution 71:131–169.

Unimodal Sulfur-Mercury Relationship

- Unimodal relationship referred to the "Goldilocks area" in common and some technical literature.
- Gilmour and Henry (1991) explicitly laid out the limitations to the hypothesized relationship based on available data at the time.
  - *"…the optimal level would probably vary from system to system and even site to site as a function of other factors affect sediment sulfate-reduction rates such as temperature, sediment porosity and organic carbon availability."*
  - *"Iron and hence FeS, levels in sediment should also affect this relationship…"*
- Eventually the hypothetical S-Hg relationship was transposed to the Everglades Ecosystem in a effort to explain Hg bioaccumulation in the Everglades.

"Goldilocks and the Three Bears"
Illustration by Arthur Rackham

Gilmour CC, Henry EA (1991) Mercury methylation in aquatic systems affected by acid deposition. Environmental pollution 71:131–169.

Unimodal Sulfur-Mercury Relationship

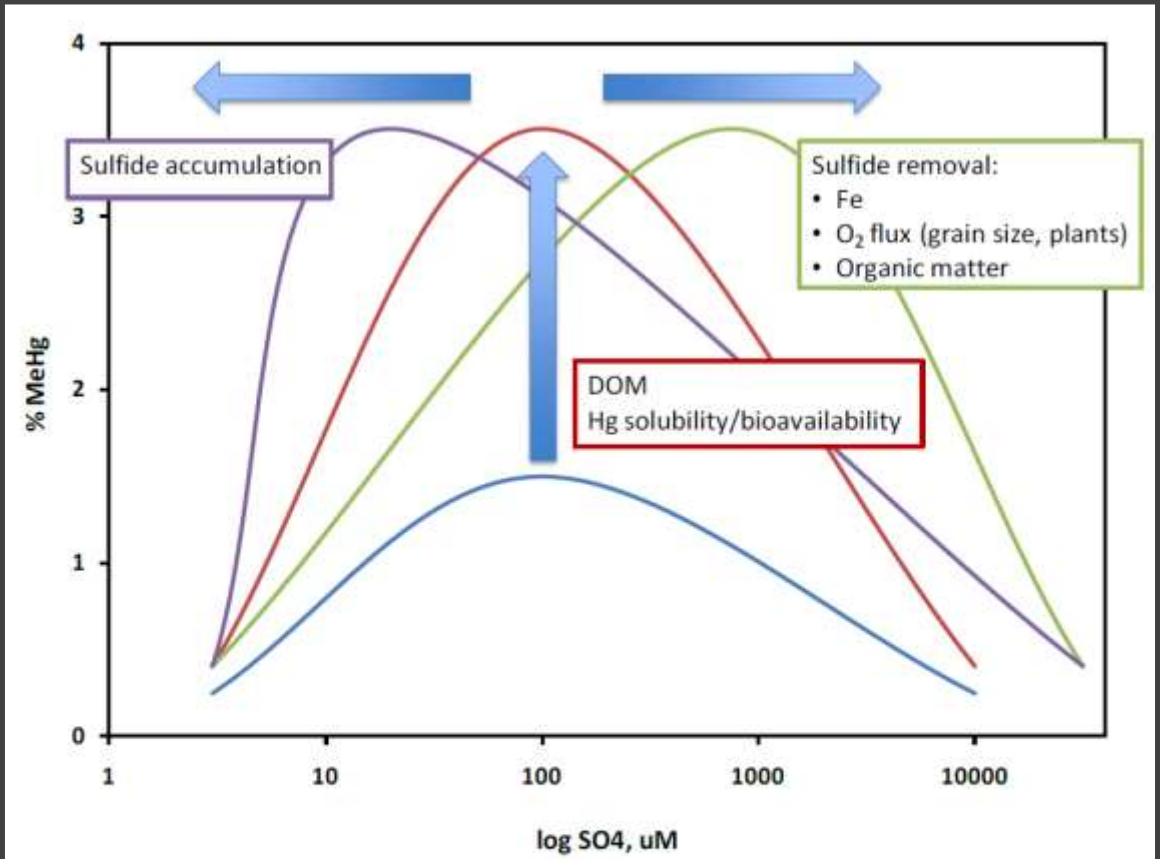
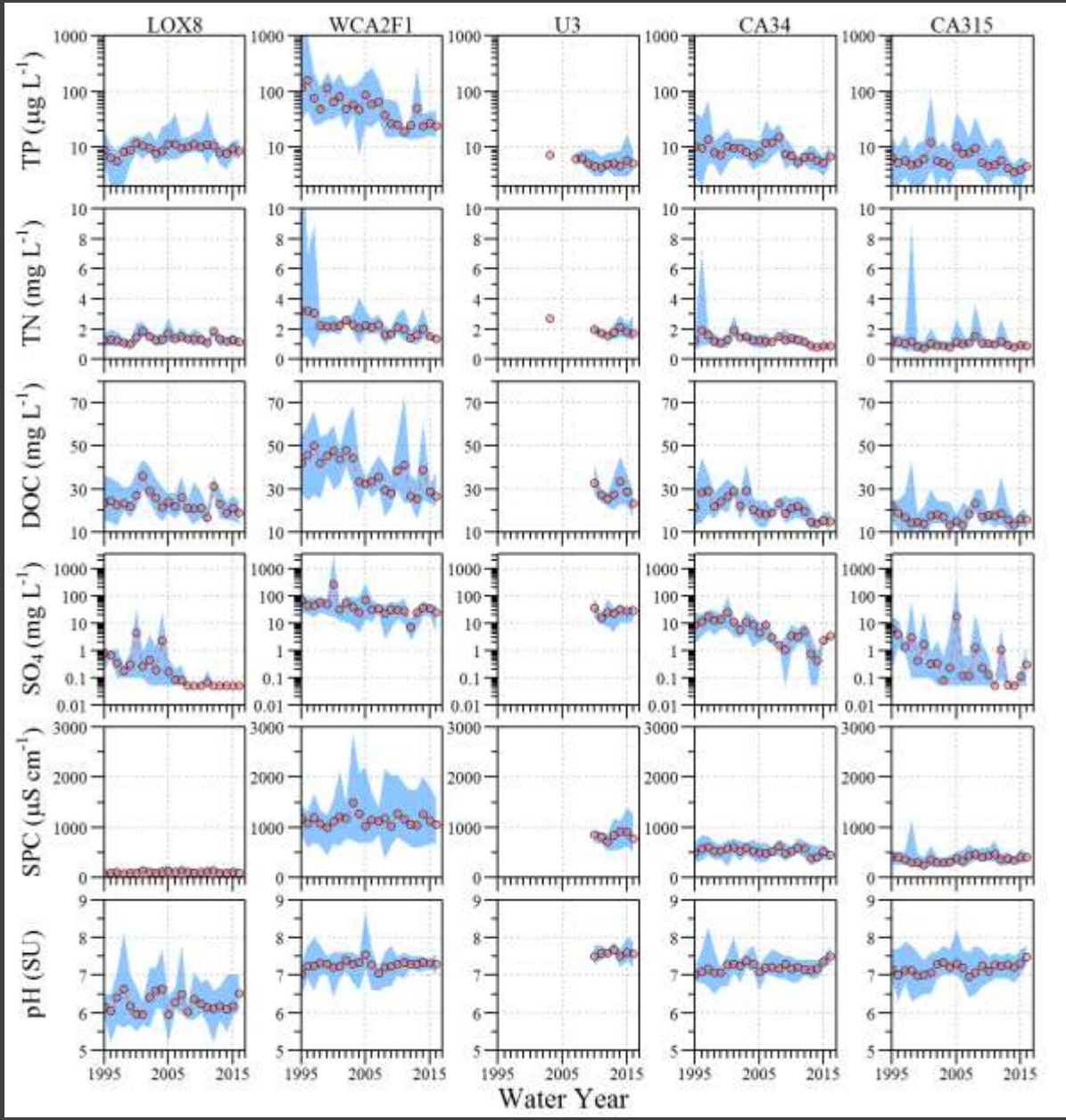
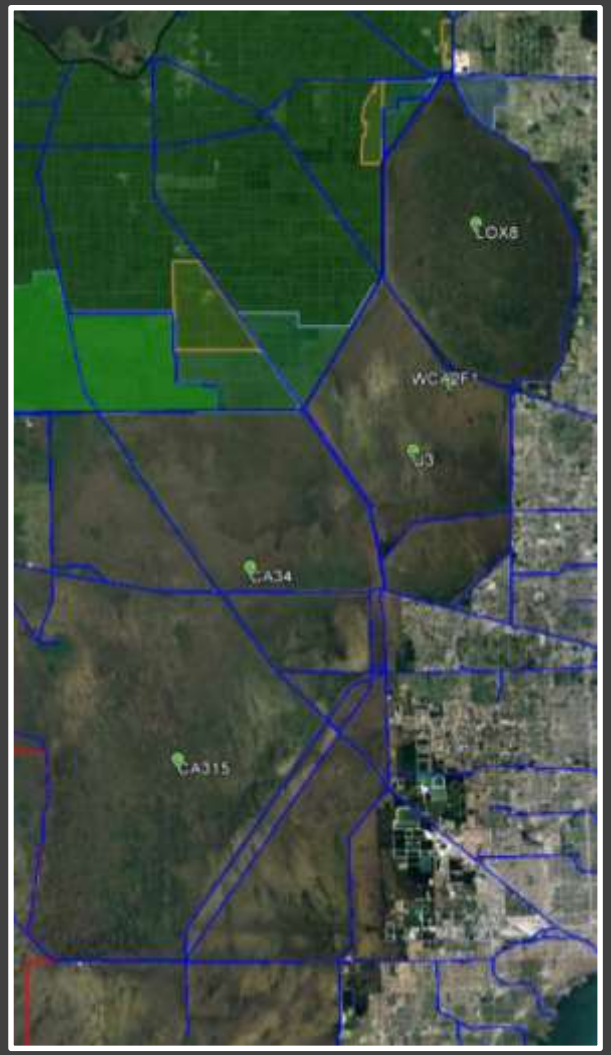


Figure 2. Conceptual diagram of the relationship between sulfate concentration and MeHg accumulation. Experimental sulfate amendment studies suggest that on average, the optimum sulfate concentration for MeHg production is about 100 µM. However, the amount of sulfide that accumulates in response to sulfate reduction can shift that optimum left of right (horizontal arrows). Additionally, the magnitude of net MeHg production (vertical arrow) changes with DOM-driven bioavailability of Hg for uptake and methylation by bacteria.

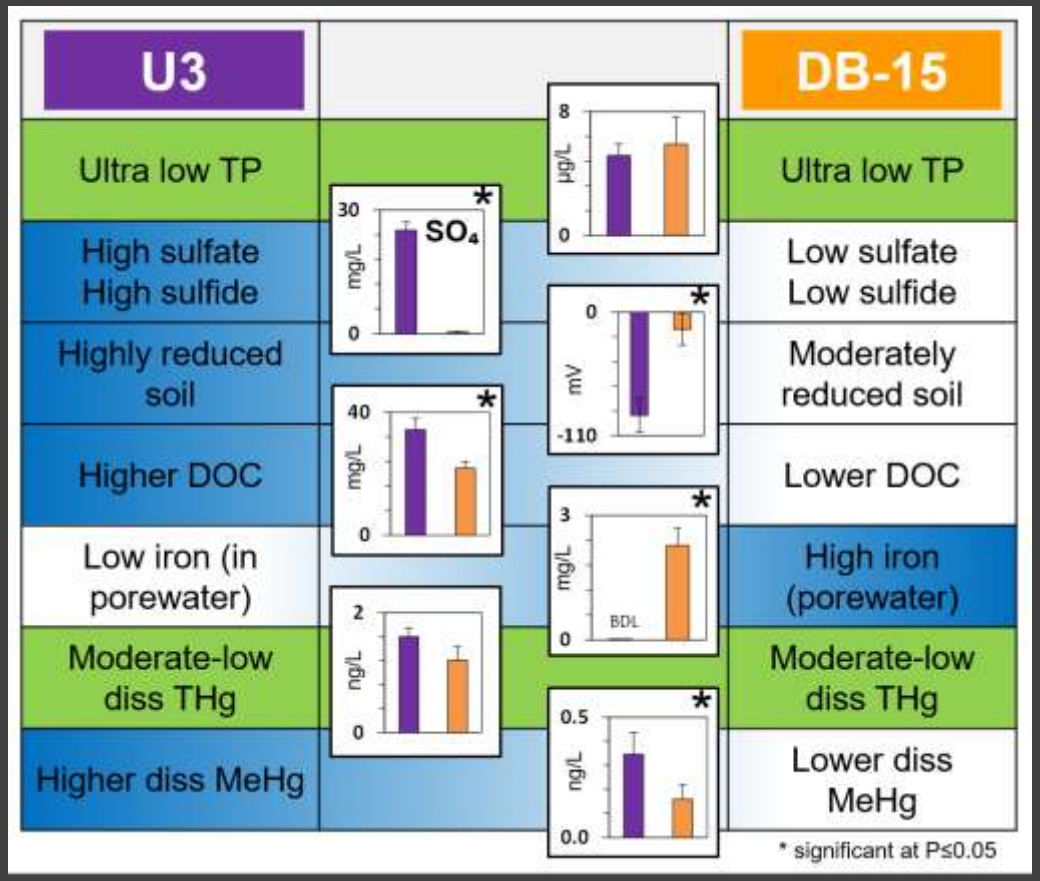
Gilmour CC (2011) A review of the literature on the impact of sulfate on methylmercury in sediments and soils. Florida Department of Environmental Protection, Tallahassee, FL

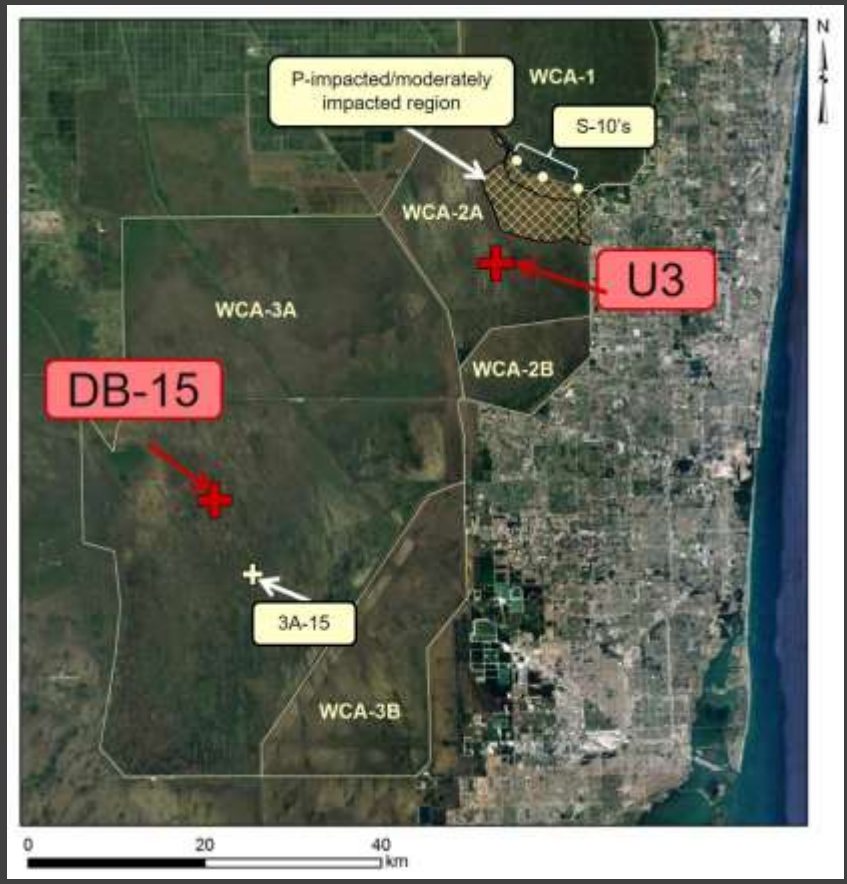
Water Quality Variability





Water Year Minimum, Arithmetic Mean, and Maximum

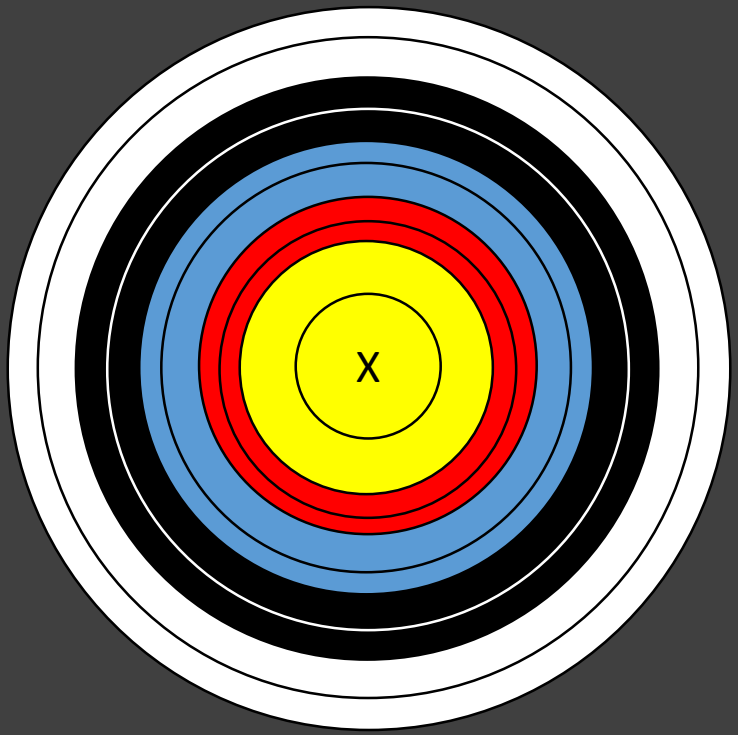




Period of Record
DB-15: 2011 – 2015
U3: 2010 - 2015

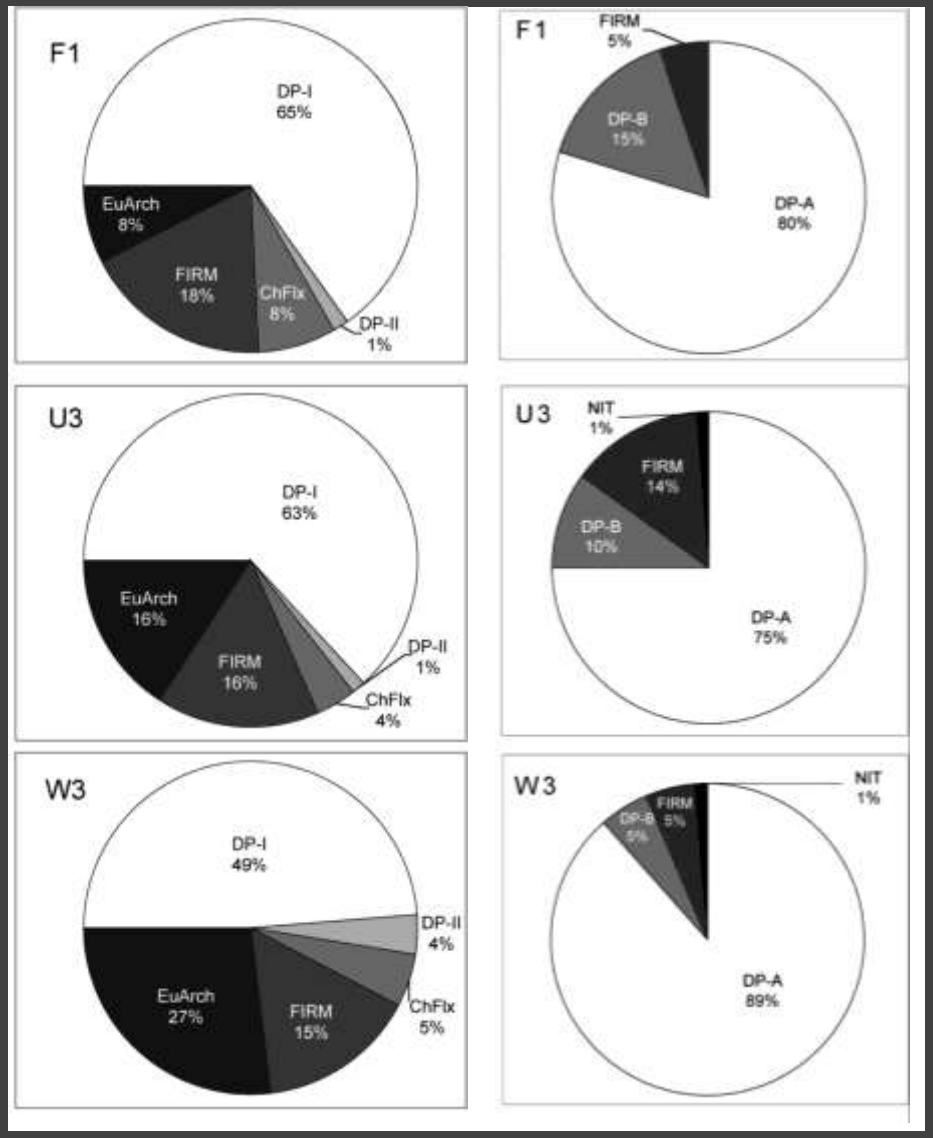
Dierberg et al. (2016) Contrasting Biogeochemical Conditions at Two Everglades Locations with Historically Elevated Mosqitofish (*Gambusia holbrooki*) Mercury Concentrations. 7th SETAC World Congress/ 37th Annual SETAC North American Meeting.

Moving Target!!

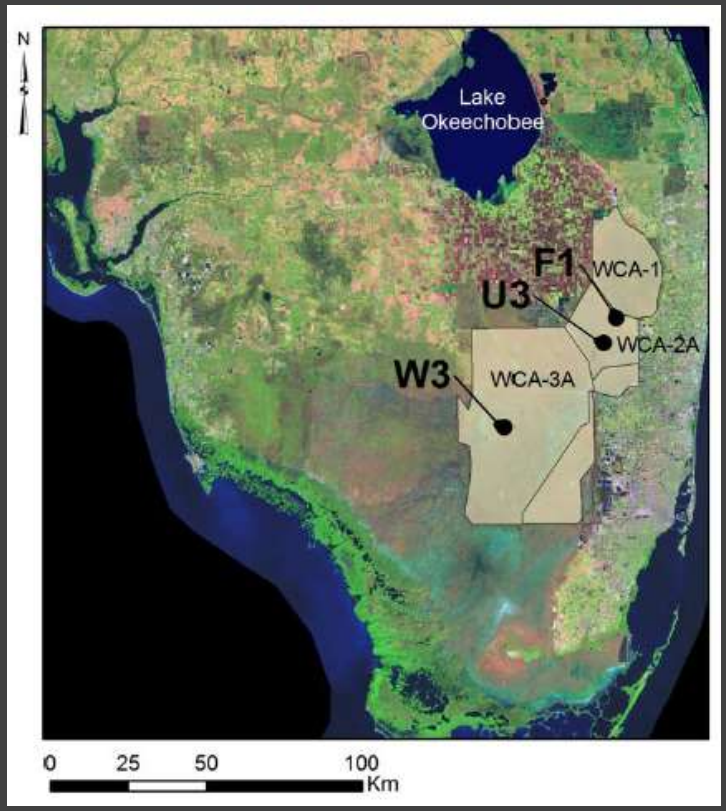


Microbial Diversity

hgcA dsrB



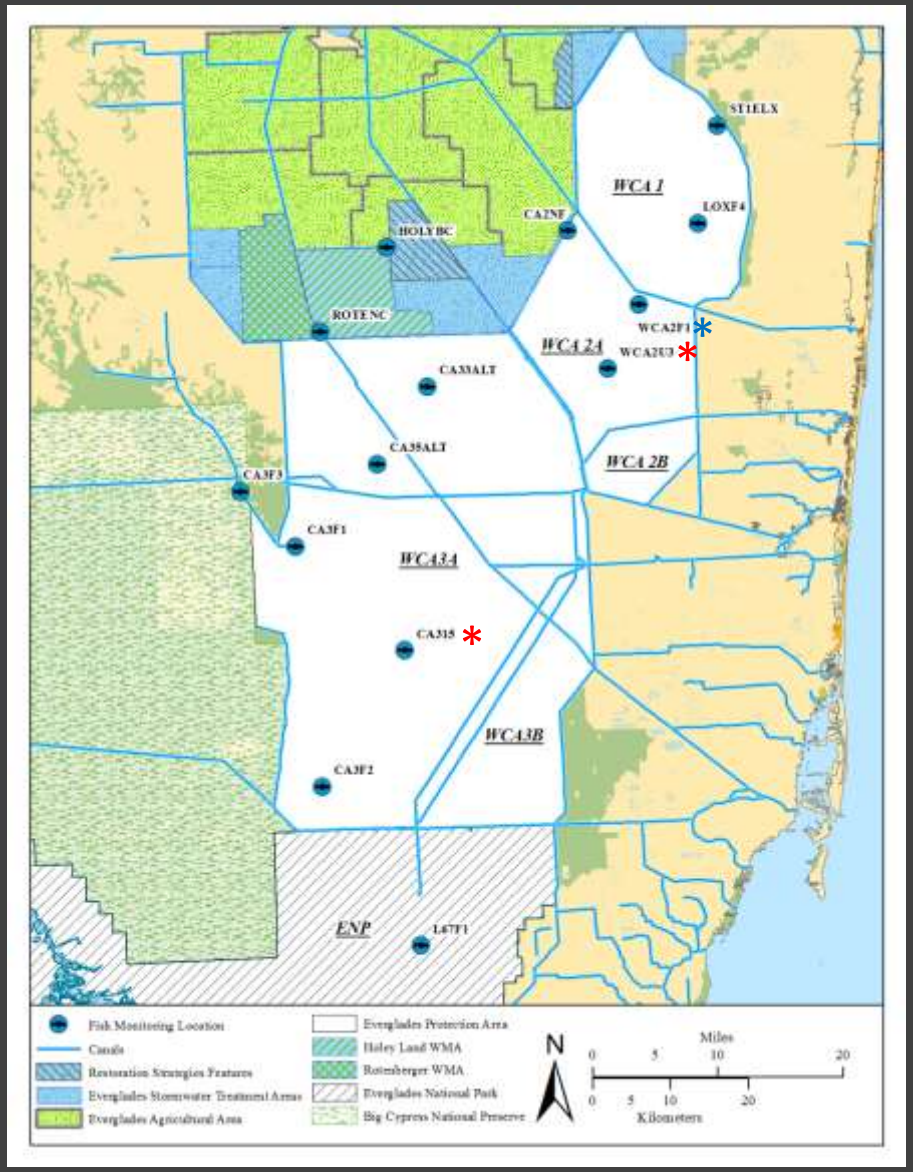
Phylogenetic distribution

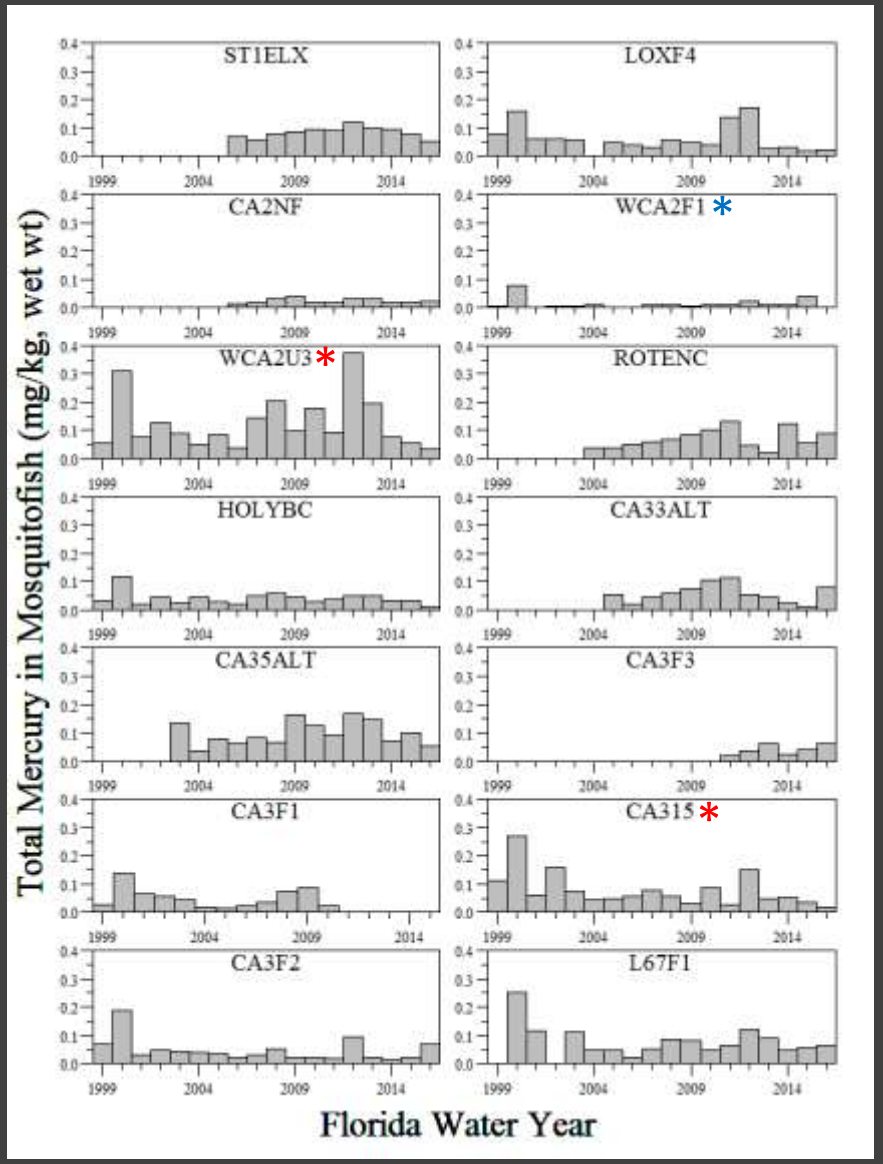


- Syntrophs are the predominate group controlling methylation of Hg in low-sulfate areas.
- Therefore the control of sulfur (as sulfate) alone would not eliminate Hg methylation.

Bae et al. (2014) Syntrophs dominate sequences associated with the mercury-methylating gene hgcA in the Water Conservation Areas of the Florida Everglades. Applied and Environmental Microbiology

Mercury in Everglades Biota





Julian et al. (*2017*) Chapter 3B: Mercury and Sulfur Environmental Assessment for the Everglades. 2017 South Florida Environmental Report

Cattail

- Occur in eutrophic (high TP) areas
- Dominant in non-Hotspot locations
- Higher biomass/litterfall relative to sawgrass (estimated at 3.4 - 4.9 kg m^{-2} yr^{-1})
- Hg flux throughfall is less than sawgrass (0.13 μg m^{-2} yr^{-1})

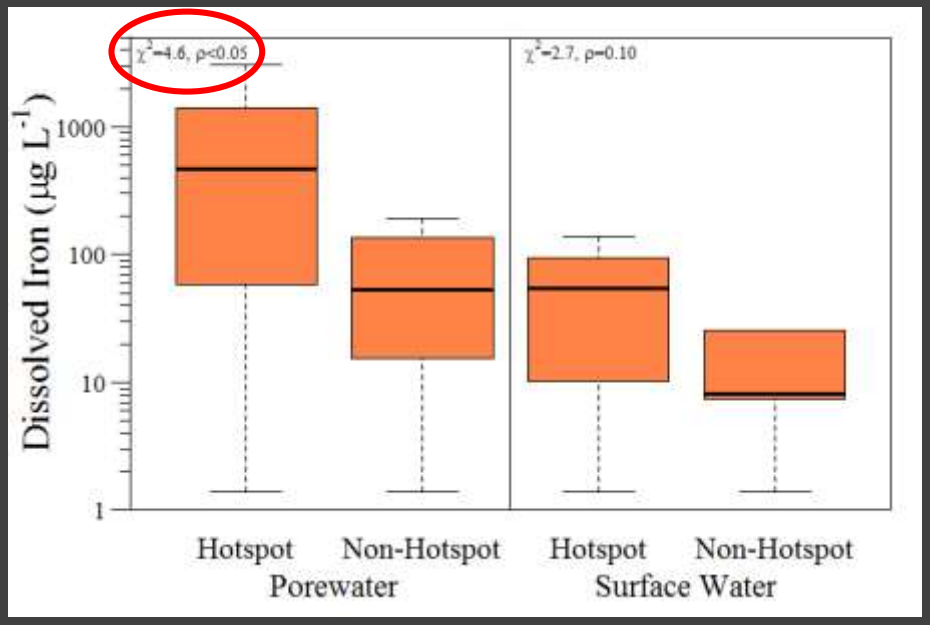
Sawgrass

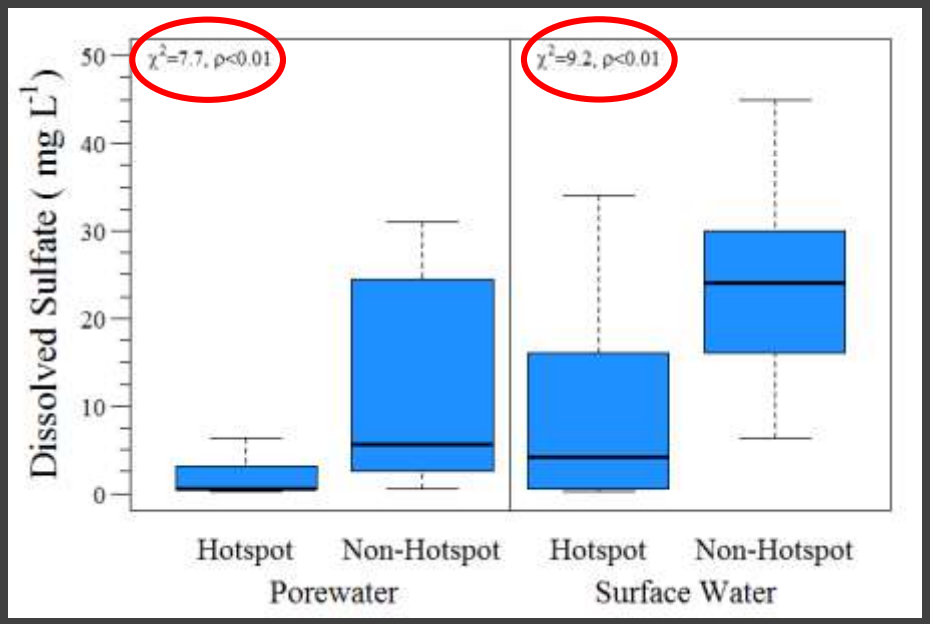
- Occur in oligotrophic (low TP) areas
- Dominant in Hotspot locations
- Lower biomass/litterfall relative to cattail (estimated at 0.2 - 0.7 kg m^{-2} yr^{-1})
- Hg flux throughfall is greater than cattail (0.33 μg m^{-2} yr^{-1})

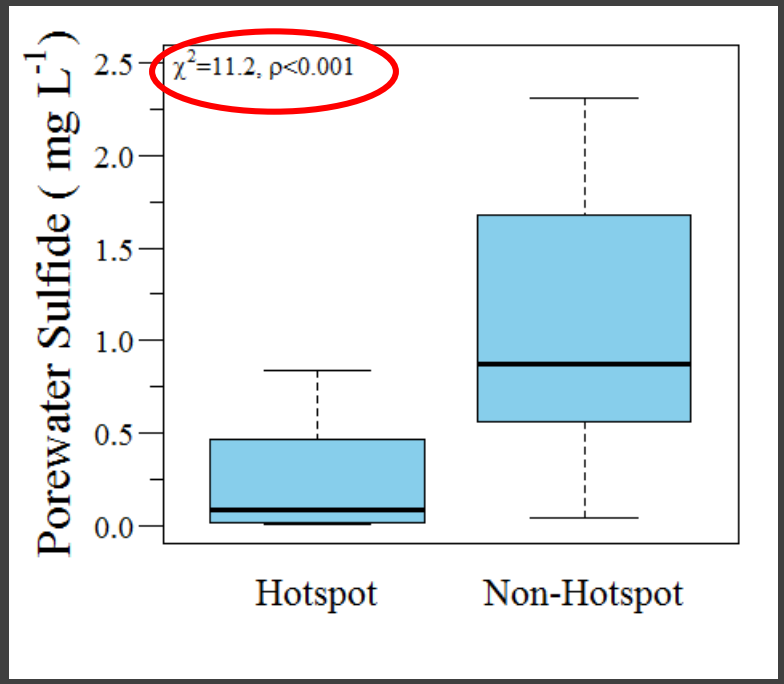
Differences in Lignocellulose index observed between Hotspot and non-Hotspot stations

Julian et al. (*2016).* Mercury stoichiometric relationship in a subtropical peatland. Water, Air and Soil Pollution. 227(12)

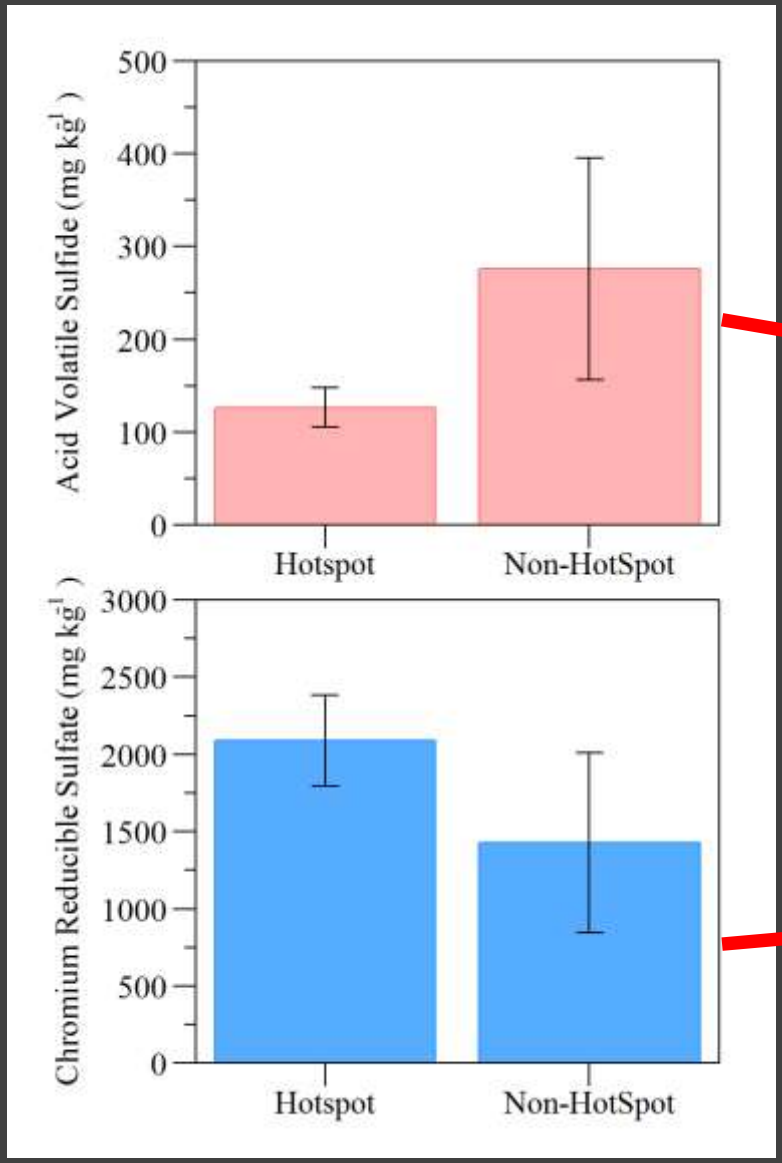
Other Biogeochemical Drivers

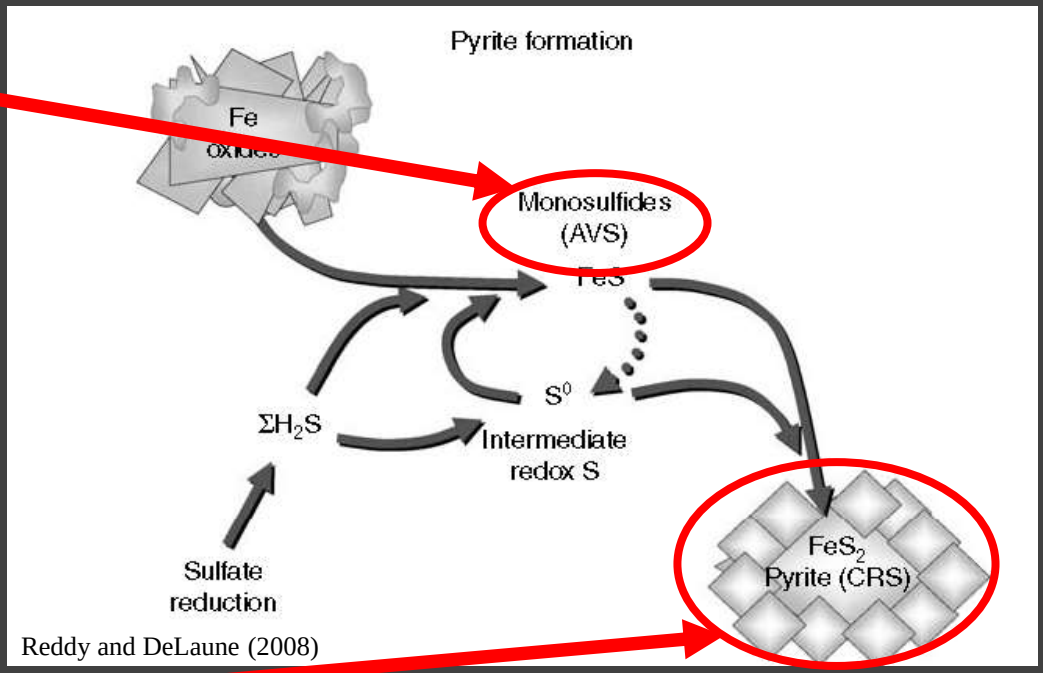






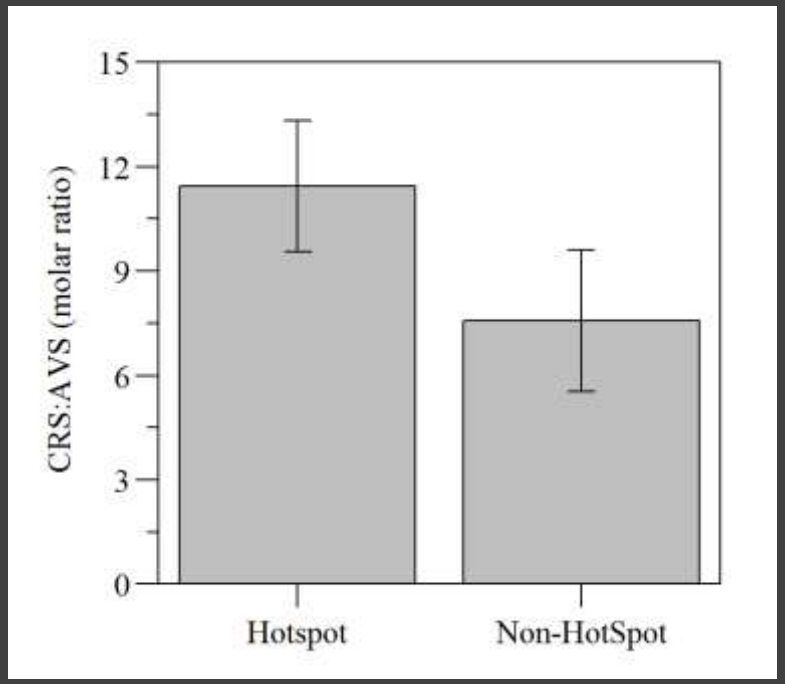
Other Biogeochemical Drivers



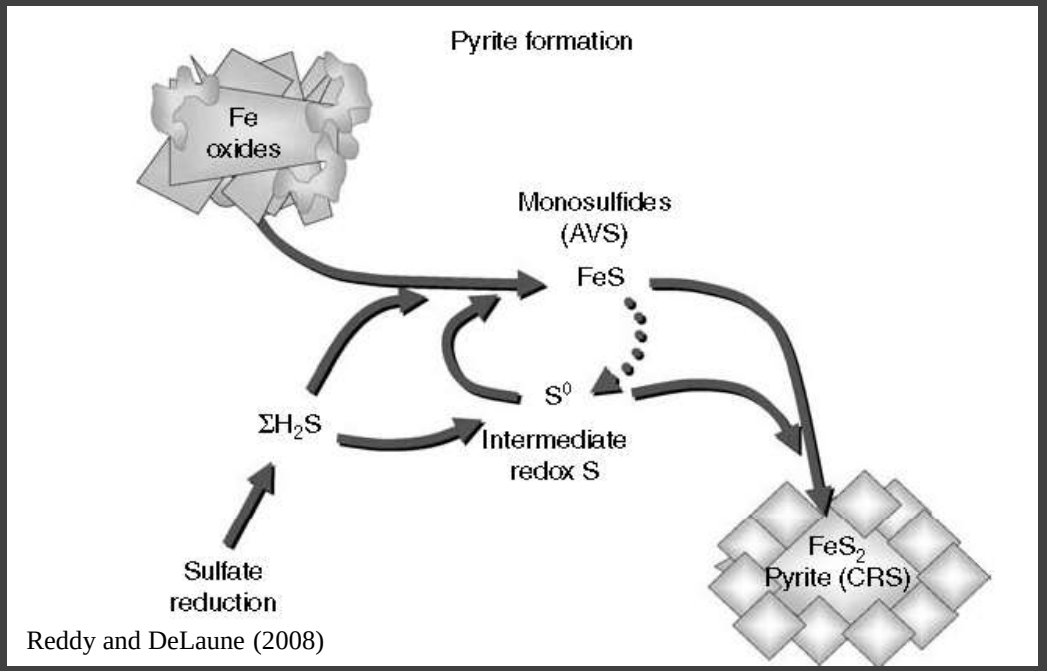


Reddy and DeLaune (2008)

Other Biogeochemical Drivers

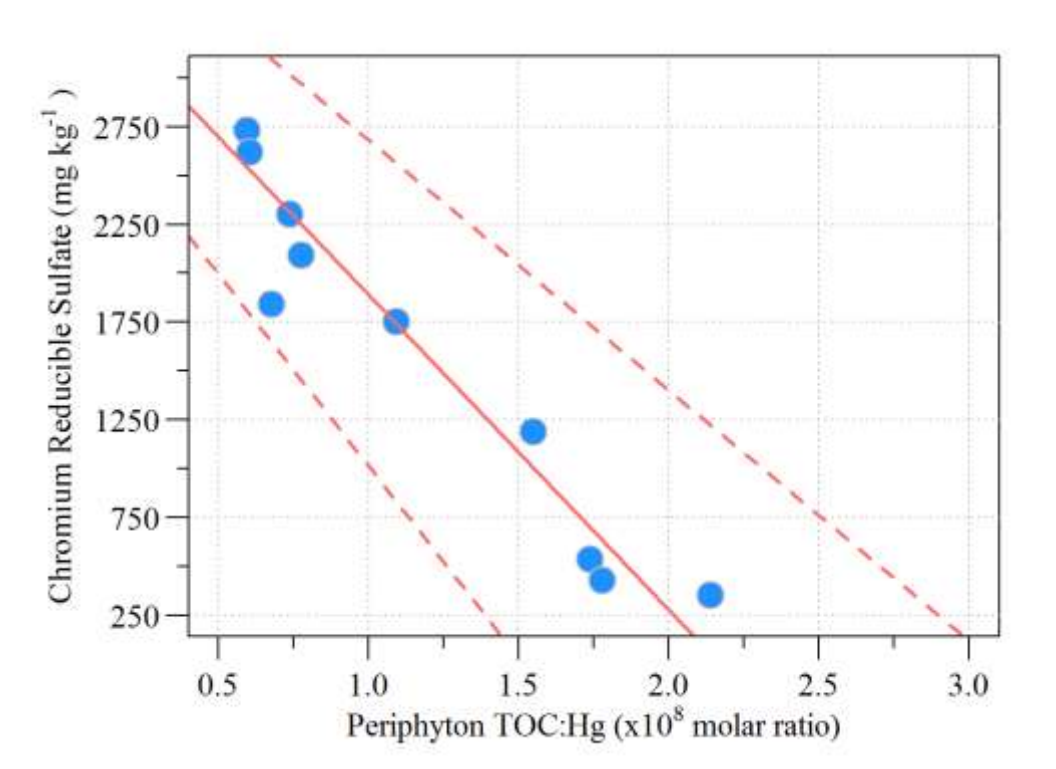


FeS_2:FeS molar ratio



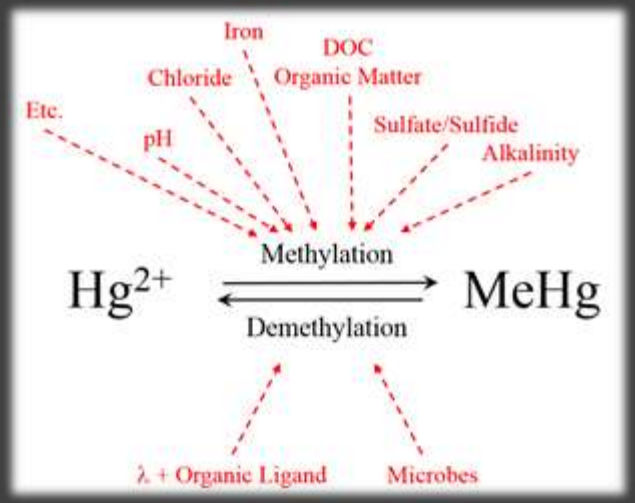
Reddy and DeLaune (2008)

- Differences in Fe and S dynamics — Chemical
- Influences formation of pyrite (and other minerals) — Geological
- Could influence microbial dynamics — Biological
- ***Implications in Hg dynamics***



- Periphyton Hg relative to some metric of biomass.
- CRS and Periphyton TOC:Hg in negatively correlated.
  - Spearman Correlation: $r = -0.96$, $\rho < 0.001$
- Interaction of Fe and S could:
  1. Reduce the availability of THg for further biogeochemical reactions.
  2. Inhibit Hg methylation.
  3. Stimulate Hg demethylation.

Complexities of the Mercury interactions



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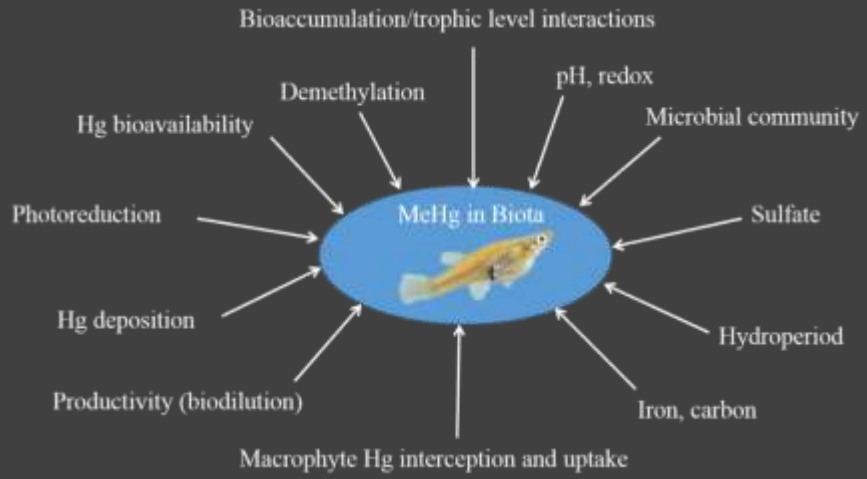

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Hydrology

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Vegetation Dynamic

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Habitat (Species Specific) Dynamics

Hg methylation (demethylation) bioaccumulation


SURVEY
MARKER