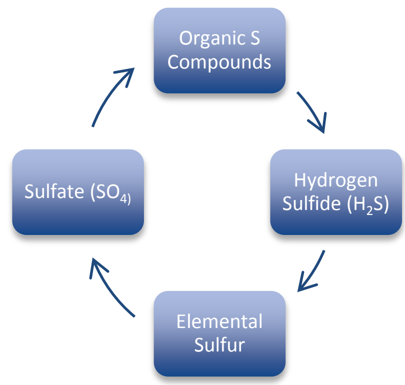
Minnesota Pollution Control Agency

Minnesota's Wild Rice Sulfate Standard

CLEAN WATER LAND & LEGACY AMENDMENT

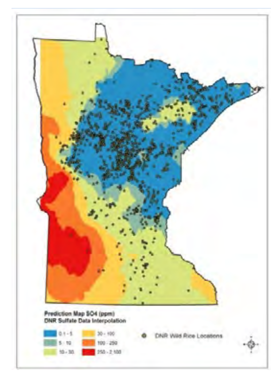
Sulfate in the Environment

- Commonly found in air and water
- Created by sulfur reacting with oxygen in land and water
- Micronutrient at low levels
- Can cause impacts at elevated levels
  —Wild rice more sensitive than humans



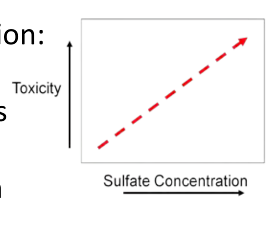
Wild Rice Sulfate Standard

- Studies found correlation between lower sulfate and wild rice
- Sulfate standard adopted in 1973 to protect wild rice
  — "10mg/L, applicable to water used for the production of wild rice during periods when the rice may be susceptible to damage by high sulfate levels:"



Wild Rice Standards Study

- Goal: Enhance understanding of the effects of sulfate on wild rice; inform standards evaluation
- Key avenues of Investigation:
  -- Field survey
  -- Laboratory experiments
  --Container experiments
- Any standard modification will be based on multiple information sources



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Wild Rice Standards Study Plan (2012-2013)

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Clarify the Meaning of "Water Used for Production of Wild Rice"

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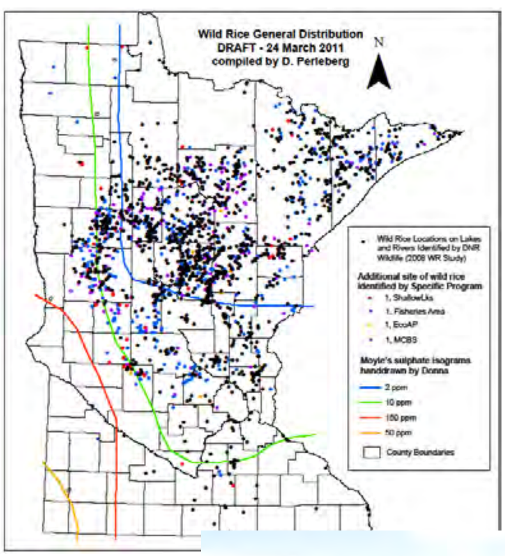
Minnesota Rules Chapter 7050 Class 4A water quality standard:

Sulfates (SO4) 10 mg/L, applicable to water used for production of wild rice during periods when the rice may be susceptible to damage by high sulfate levels.

Background:

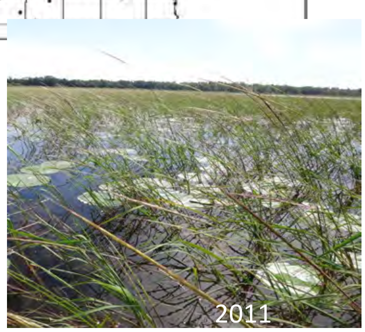
- Wild rice sulfate standard first adopted in 1973; originally proposed in draft rule to have applied to all Minnesota surface waters.
- As a result of public hearing input, applicability of the sulfate standard narrowed to "water used for production of wild rice" – no specific list of waters identified at the time.
- Some wild rice waters listed in Minn. R. 7050.0470, subp. 1, but absent a specific listing in Minn. R. 7050.0470, MPCA staff determines waters used for production of wild rice on a case-by-case basis.
- The Minnesota Legislature directed the MPCA to establish criteria for naturally occurring wild rice waters and the "*criteria shall include, but not be limited to, history of wild rice harvests, minimum acreage, and wild rice density.*" (Laws of Minnesota 2011, 1st Special Session, Chapter 2, Article 4, Section32)



Where does the wild rice sulfate standard apply?

- The case-by-case determinations rely heavily on existing wild rice inventories and field survey observations performed by the MDNR, MPCA, USFWS, 1854 Treaty Authority, and Tribal Governments.
- November 28, 1975 to the present is the time period that will be used to determine an existing wild rice use of the water.

Little Round Lake, Becker Co.



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Proposed Criteria Being Considered for Defining a "Water Used for Production of Wild Rice"

The Minnesota Legislature enacted a law in 2011 specifying that before designating naturally occurring wild rice waters that are "subject to a standard… the commissioner of the Pollution Control Agency shall establish criteria … [that] shall include, but not be limited to, **history of wild rice harvest, minimum acreage, and wild rice density**." (emphasis added)

q Minimum Acreage / Minimum Density

§ Lakes and wetlands - one acre (cumulative lake-wide total); two wild rice stems per square meter density.

§ Rivers and streams - 0.1 acre (cumulative coverage per river mile); two wild rice stems per square meter density.

q Wild Rice Harvest Information

§ Wild rice harvest information by humans will be considered in the evaluation but lack of any such information will not preclude a water from being listed as a water used for production of wild rice.

Density Example: Raymond Lake, Stearns Co. August 2, 2012.

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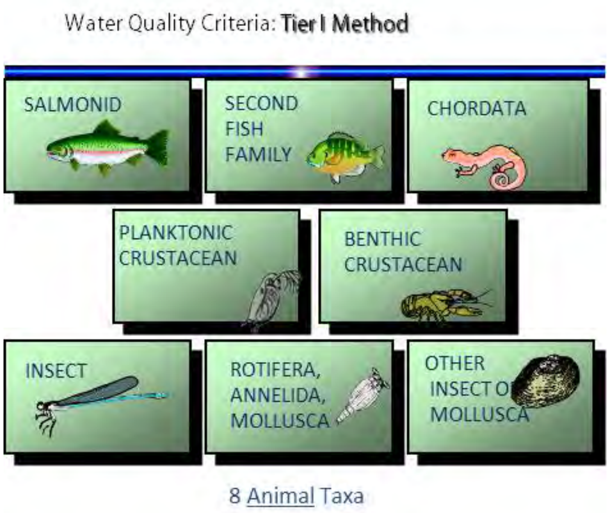
Developing and Revising Minnesota Water Quality Standards for Protection of Aquatic Life and Wild Rice

Minnesota Pollution Control Agency

Water quality standards comprise:

- Criteria values that are protective of aquatic life and human uses of aquatic resources
- Designated use for aquatic resources
- Nondegradation policy of those aquatic resources



How water quality criteria are developed:

- EPA "Tier I" methods provide guidelines for criteria development
- Considers best science on toxic effects to animals (8 taxa)
- Calculates water quality criteria value to protect whole aquatic community
- Recommends appropriate interpretation for final criteria values
- Includes consideration of important native species – Plant and Animal

Wild Rice Studies

Goal is to obtain information that will be useful in evaluating Minnesota's current water quality standard for protection of wild rice. Any modification of the standard would be based on multiple data sources including:

- Experimental/study results
- Field data
- Historical information
- Relevant scientific literature

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Laboratory Toxicity Tests Using Wild Rice

Efforts by the MPCA to gather information about sulfate effects on Wild Rice concluded that laboratory toxicity tests would be important

How will toxicity tests help inform us?

- Study protocol emphasized need for laboratory studies to:
- Inform about effects of sulfate and sulfide on wild rice
- Develop better understanding of magnitude of toxicity
- Investigate key aspects of how wild rice is affected

How is it done?
Methods Used for Performing Toxicity Tests will:

- Examine effects at multiple growth stages of wild rice
- Use hydroponic exposures as feasible
- Establish measurement endpoints for growth of wild rice

What more needs to be done?

- Perform tests with sulfide
- Complete methods for seedling test
- Examine possible effects of cationic ratio in solutions

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Laboratory Toxicity Tests Using Wild Rice

Draft Test Methods Completed

Germination Test

- Conditioned seed used to start test
- Growth endpoints of % germination and length
- Exposure solutions renewed every 2-3 days
- Range finder tests with sulfate completed

Post-germination Test

- Sprouted seeds used to start test
- Growth endpoints of survival, weight and length
- Exposure solutions renewed every 2-3 days
- Range finder tests with sulfate completed

In Development

Seedling Test

- Plants 4-5 weeks old used to start test
- Growth endpoints of survival, weight and length
- Test may be performed with plants growing in substrate

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Field Survey

LacCore
LacCore.org
National Lacustrine Core Facility

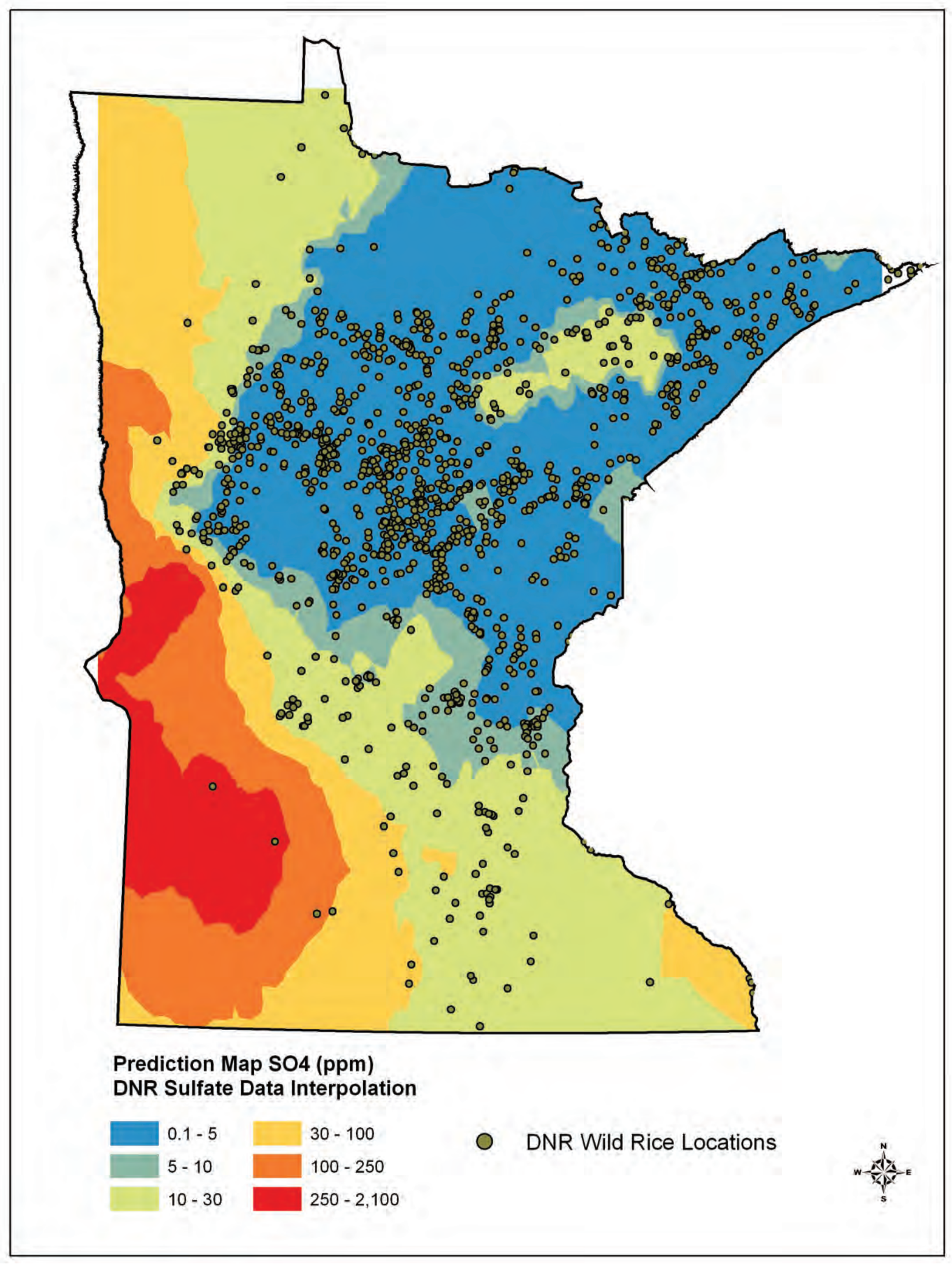
NSF

University of Minnesota
Driven to Discover[SM]

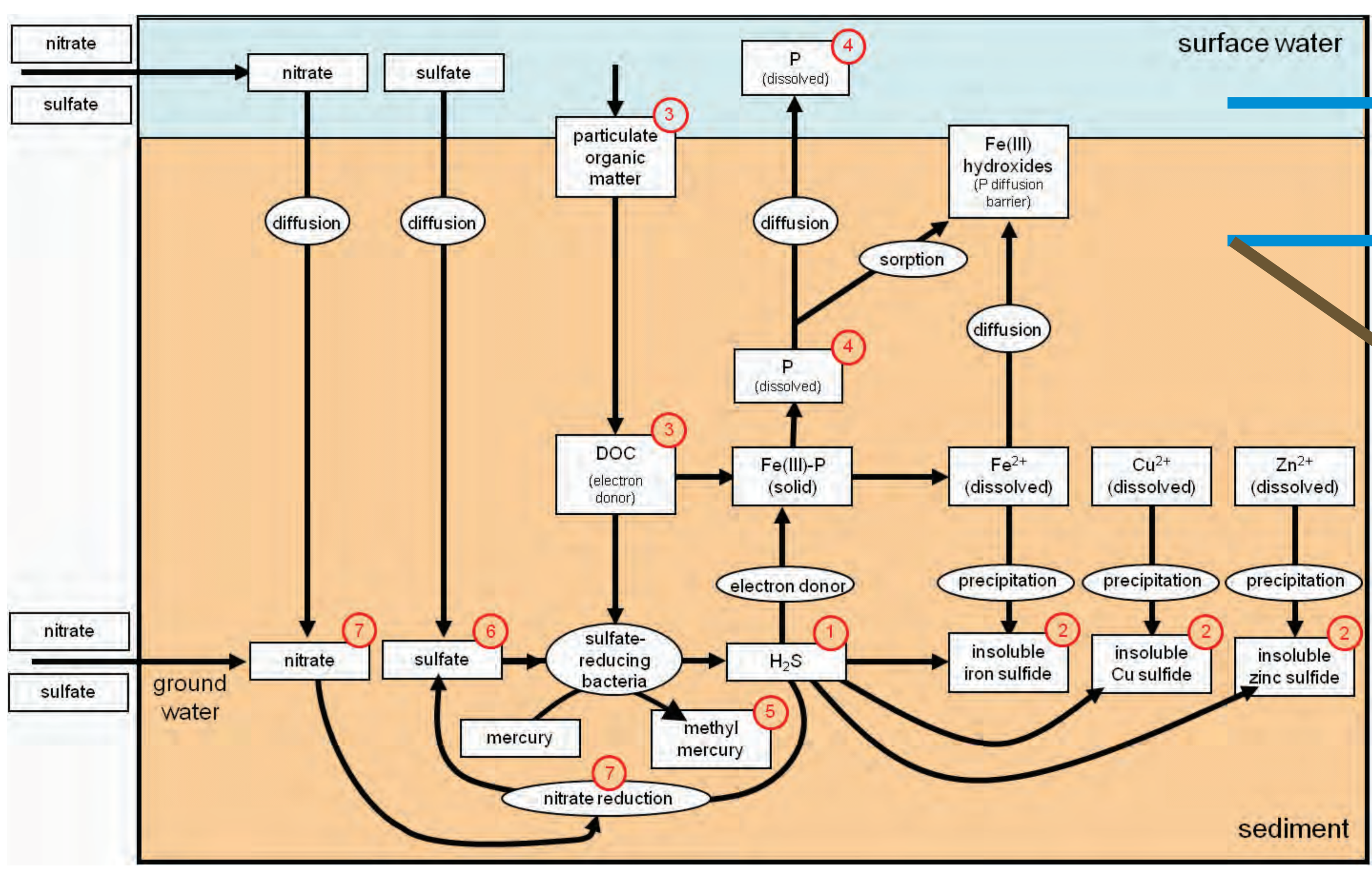
CLEAN WATER LAND & LEGACY AMENDMENT

Amy Myrbo
LacCore, Department of Earth Sciences
University of Minnesota - Twin Cities

Wild rice waters in Minnesota overlain on contours of sulfate



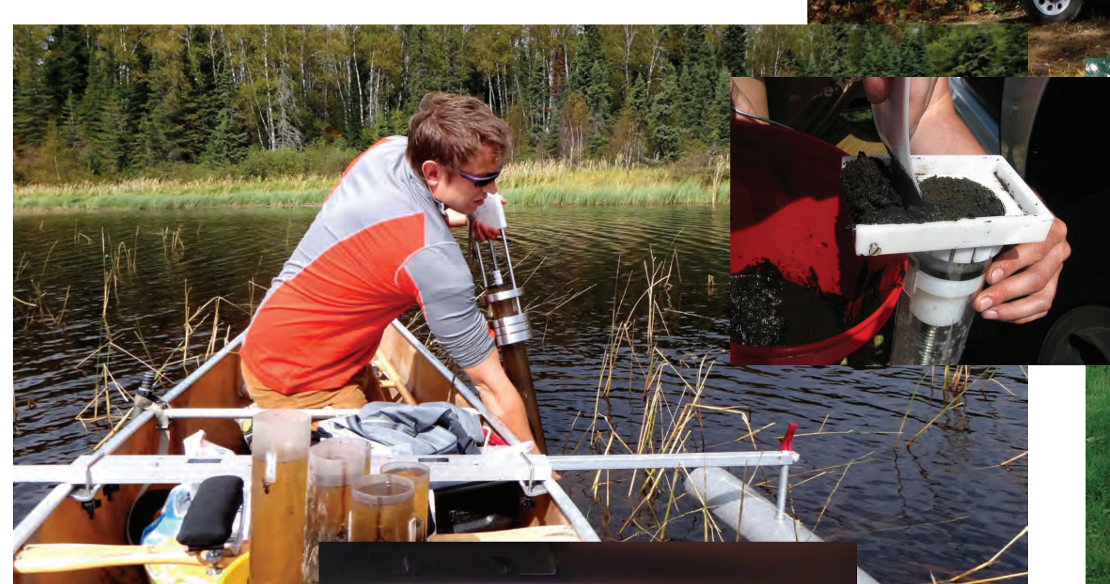
* Two-person teams
* Two field crews operating simultaneously, full time
* Two months (July 22-Sept 21, 2012)
* 112 sites sampled in 2012
* Over 14,000 miles driven
* 52 sites in 2011

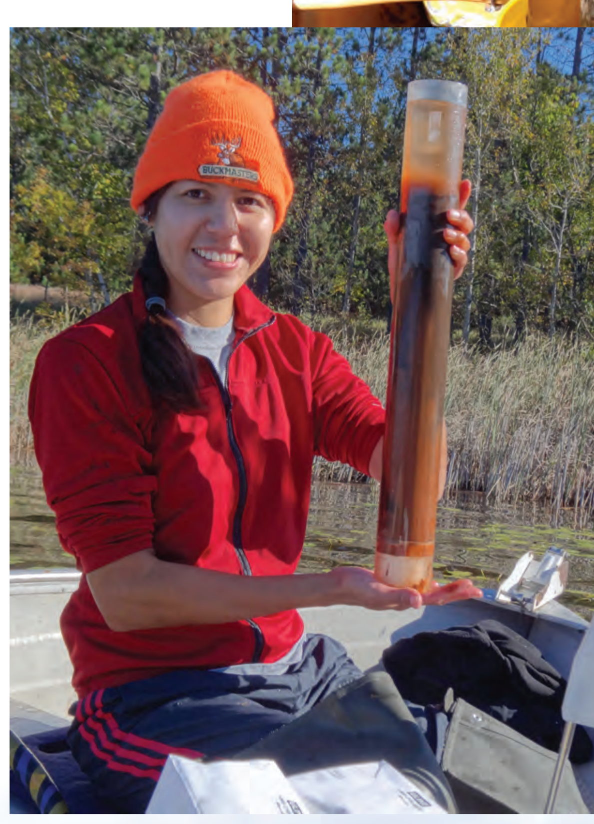


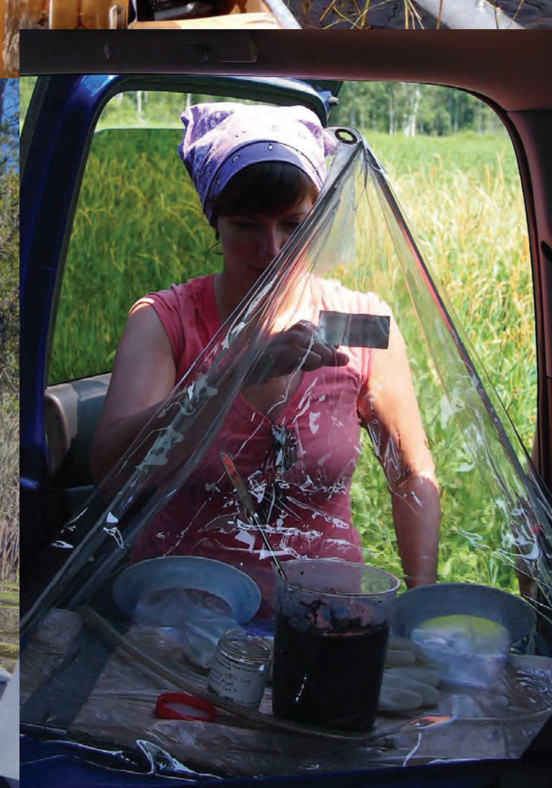
surface water

pore water

sediment







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Field Survey

Amy Myrbo
LacCore, Department of Earth Sciences
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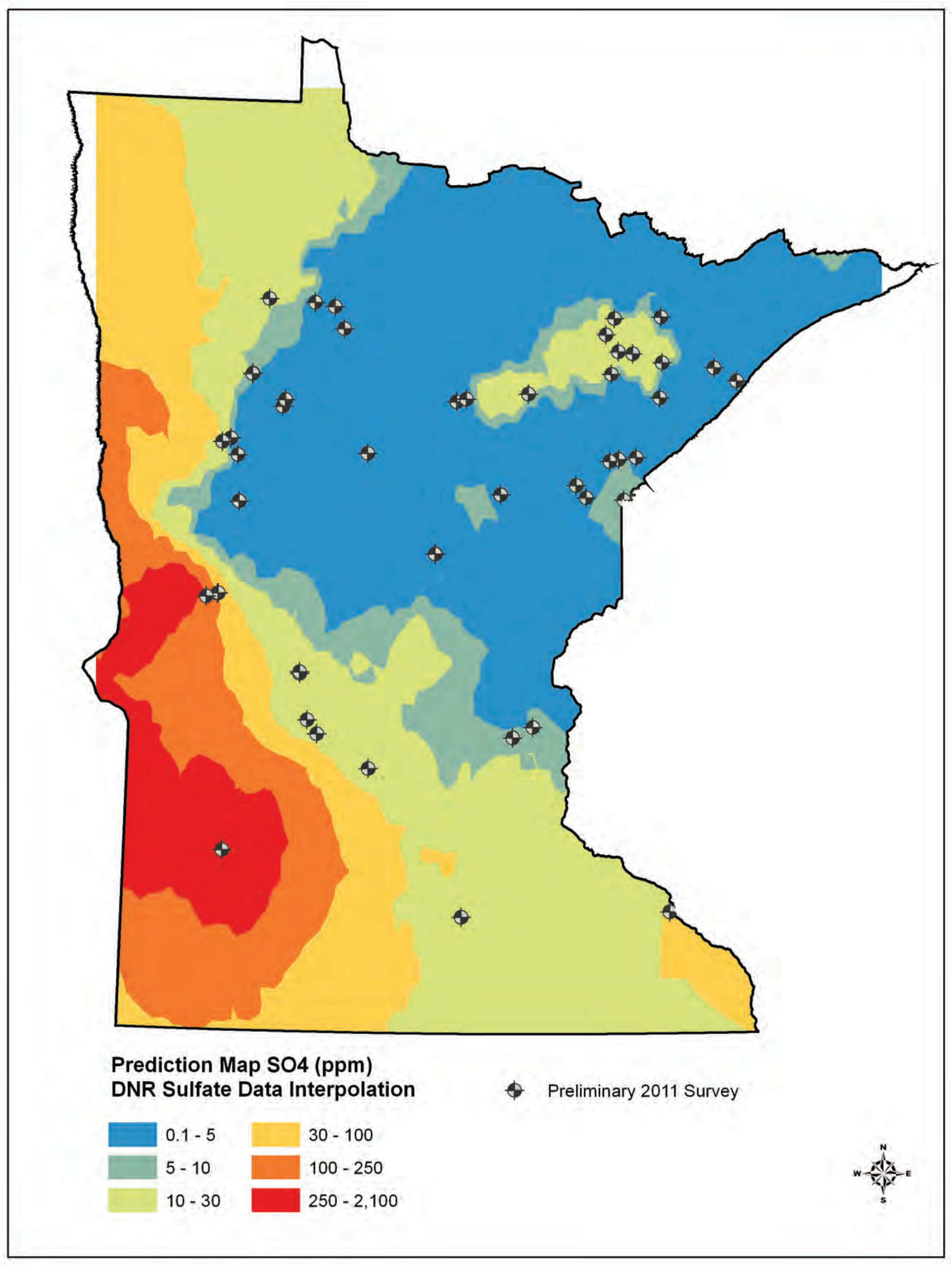
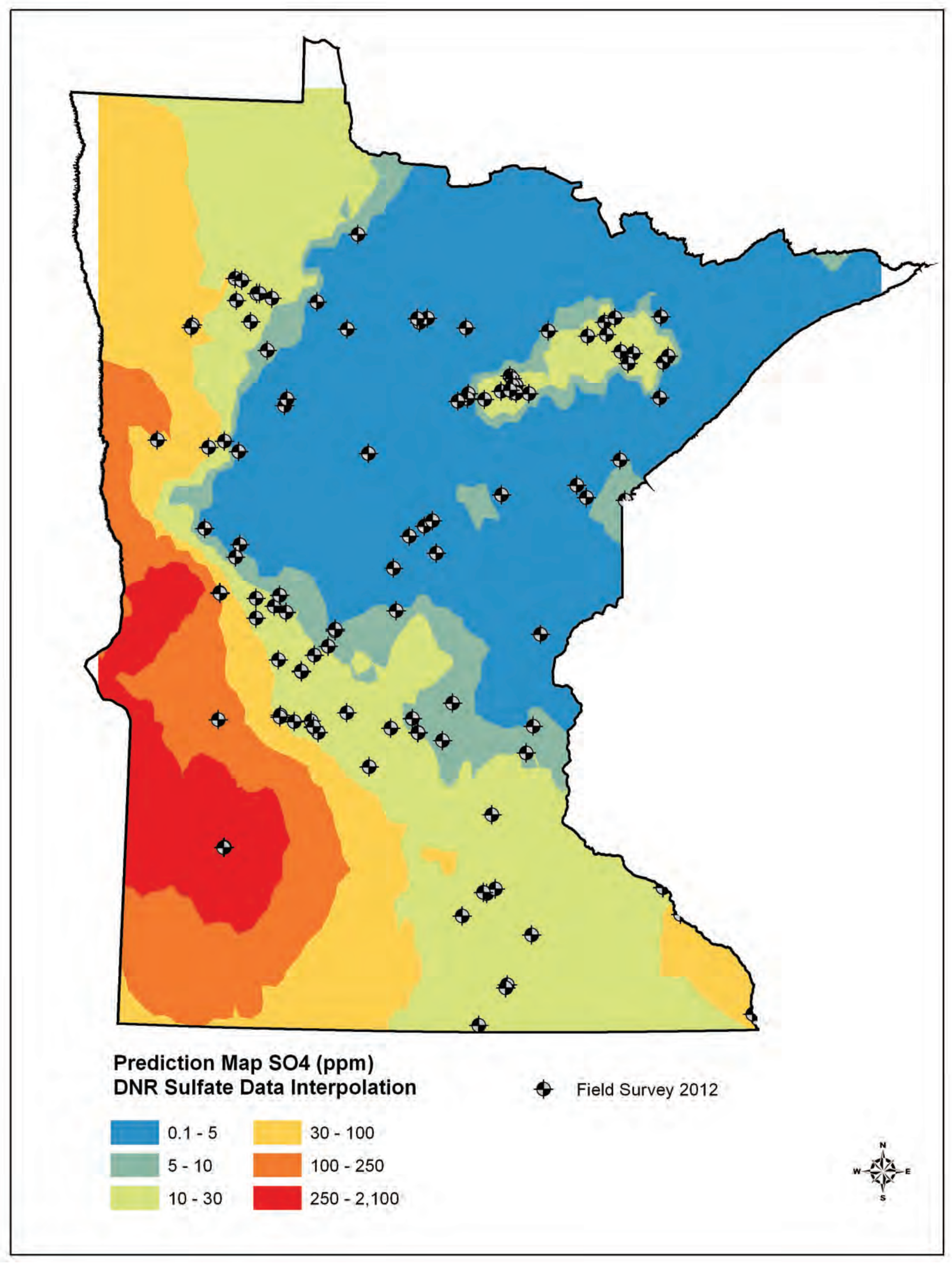
Driven to Discover℠
Clean Water Land & Legacy Amendment

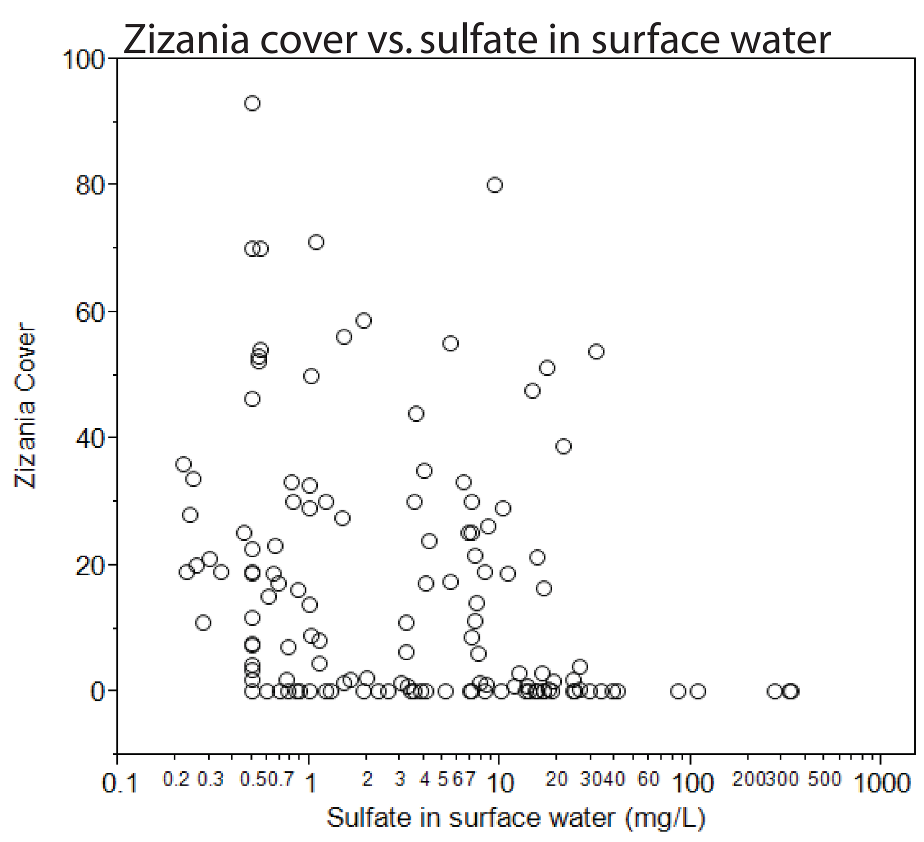
Sites sampled in 2011



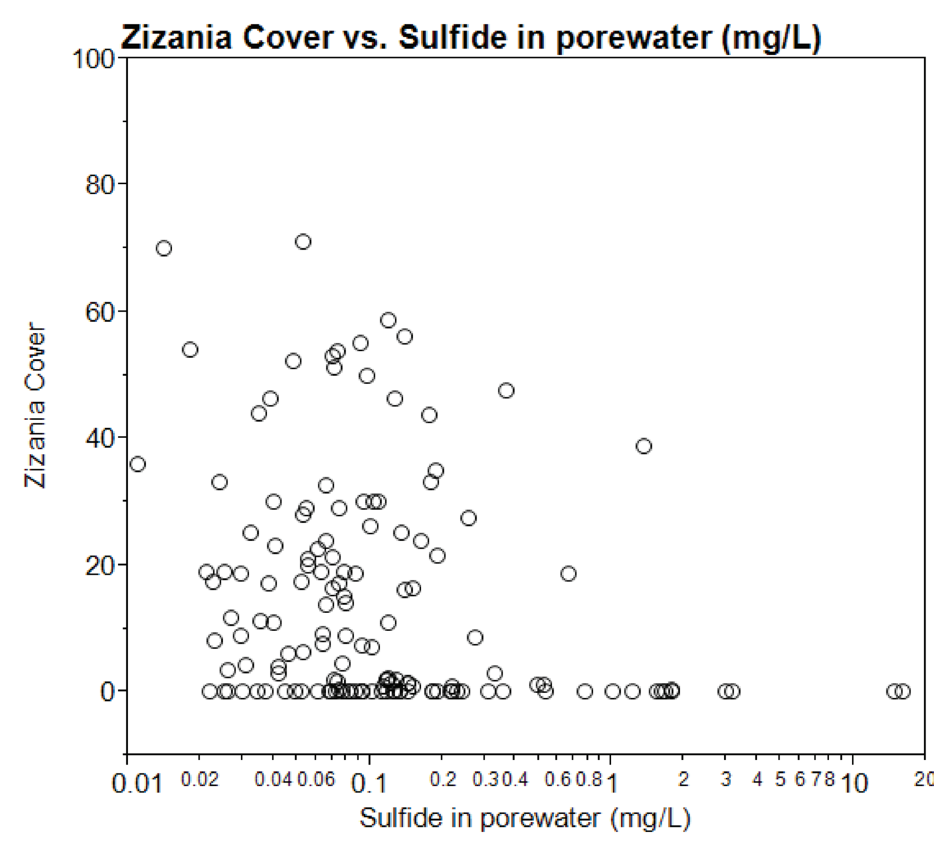
Sites sampled in 2012

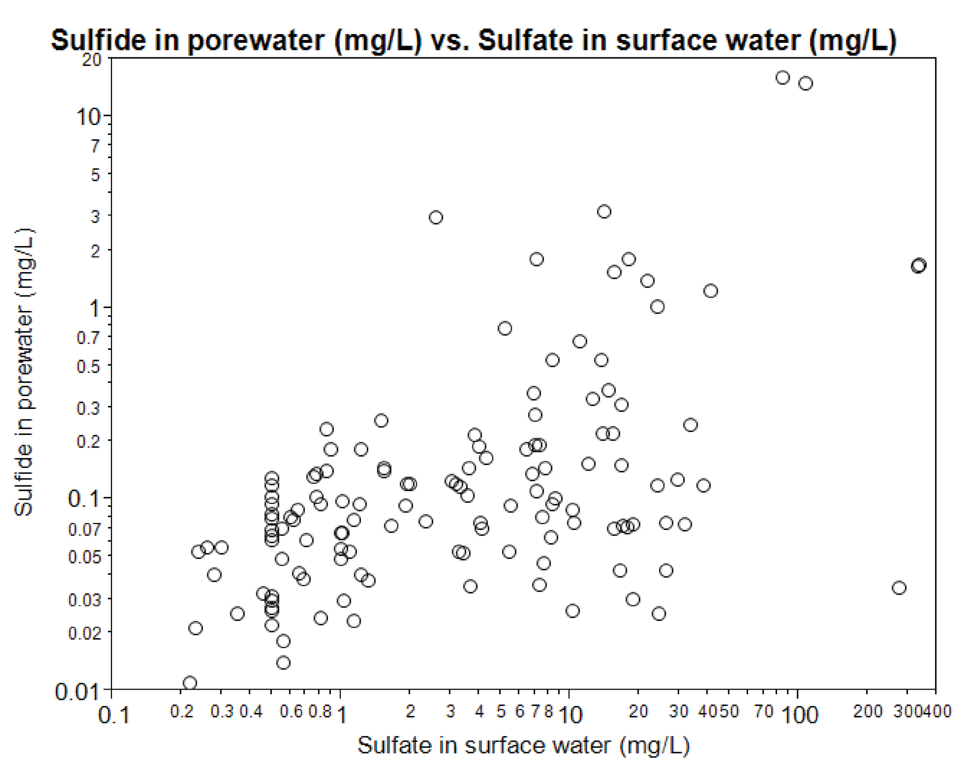


Wild rice was absent in waters above ~30 ppm sulfate

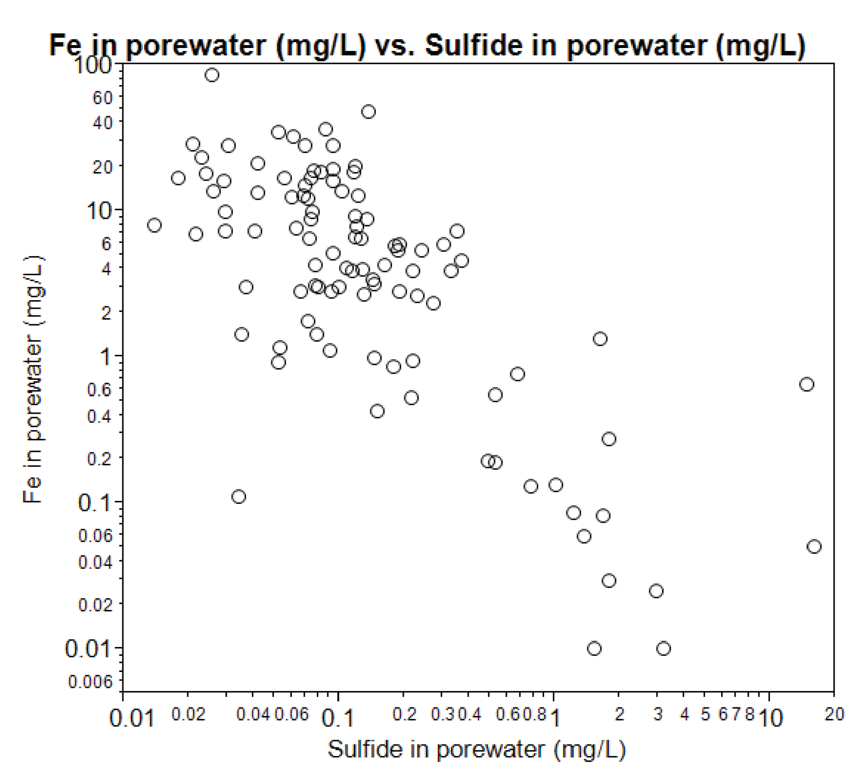


Sulfide in porewater is negatively correlated with wild rice abundance





High sulfate in the water is correlated with high sulfide in the porewater



Iron and sulfur in porewater are negatively correlated (because they react to form pyrite, FeS_2)

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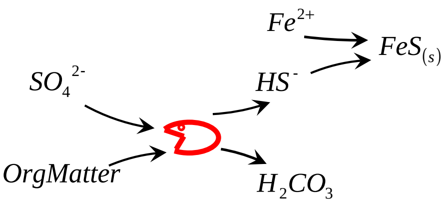
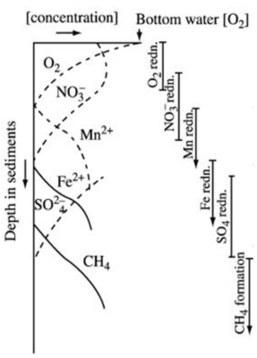
Porewater Measurements in Wild Rice Microcosms during Summer/Fall 2012

Nathan Johnson, Joseph Sternberg

University of Minnesota Duluth – Department of Civil Engineering

This study was funded by the University of Minnesota Undergraduate Research Opportunities program





Background:

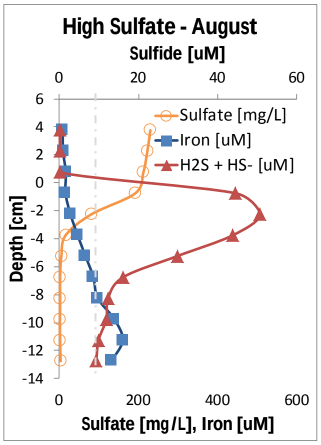
- Sulfate can be transformed to sulfide in anoxic sediment environments via biological processes
- Iron in sediments acts to remove hydrogen sulfide (H_2S), a suspected agent for adverse effects in wild rice

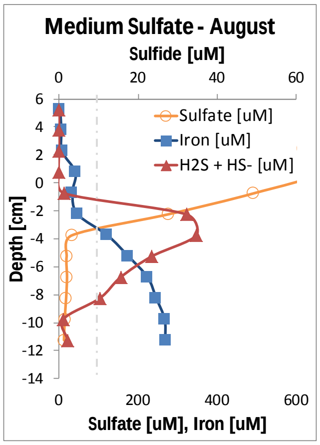
Methods:

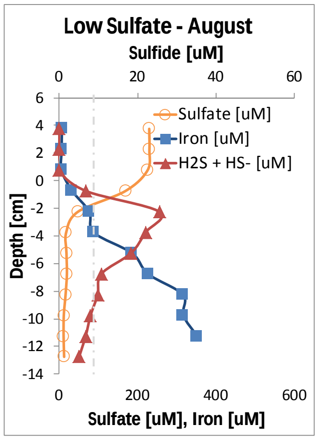
- Small volume samples were non-destructively collected from wild rice microcosms amended with varying amounts of sulfate in the overlying water (10, 50, 150, 300mg/L)
- High resolution (1.5cm) equilibrium samplers (peepers) provided measurements of depth-dependent pore water geochemistry
- Samplers were deployed (2-3wks) in June, August, and October 2012; samples analyzed for dissolved sulfate, sulfide, iron, and pH

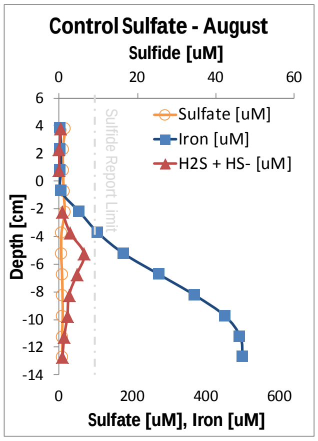
Preliminary Results:

Example Depth profiles Aug 2012

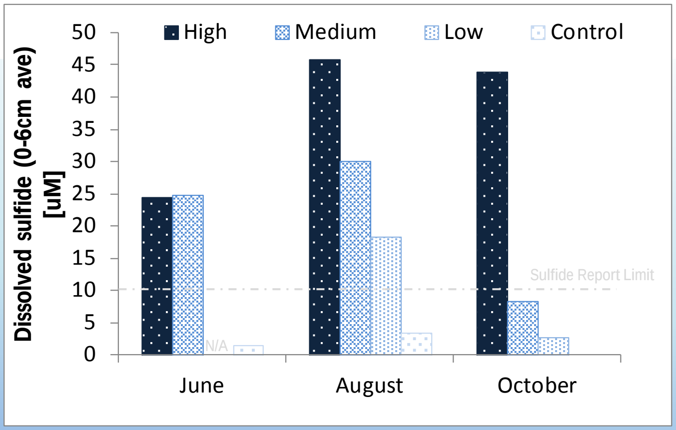








Pore water sulfide summary



- Sulfate depleted in the top 3-8cm of porewaters regardless of overlying water sulfate amendment concentration
- Sulfide above reporting limit of 10uM observed in the porewaters of high, medium and low sulfate amendments between 0-8cm sediment depth during August 2012
- Lower dissolved iron in porewaters of sulfate amended sediment suggests consumption via iron sulfide precipitation

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Temperature dependent sulfate diffusion and reaction – lab studies

Nathan Johnson, Will DeRocher
University of Minnesota Duluth – Department of Civil Engineering

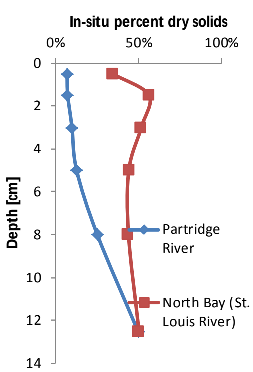
Background:

- Sulfate can be transported to sediment porewaters from the overlying water via diffusion and react to form sulfide in anoxic sediment.
- Temperature affects both rates of sulfate diffusion and sulfate reaction, though the effect on reaction is more pronounced

Methods:

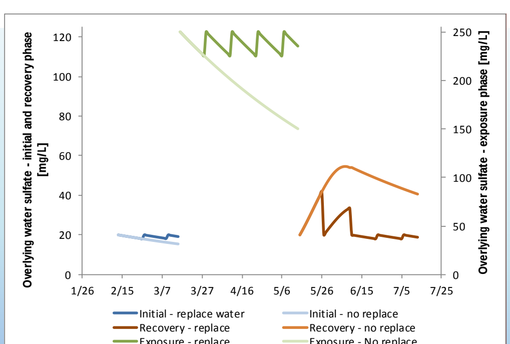
- Homogonized sediment from top 10cm collected (through ice) from two contrasting sites (high and low organic) and replicate (3) microcosms will be incubated at 5º C and 21º C.
- All microcosms will be exposed to three experimental phases: 1 month equilibration phase (in-situ sulfate in overlying water), a 2 month "sulfate loading" phase (~250mg/L sulfate) and a 2 month "recovery" phase (return to in-situ sulfate)

Experimental procedures:



- Slow stream of air bubbles to keep the overlying water well mixed and oxidized
- Overlying water monitored to quantify sulfate flux into sediment
- Porewater samples will be occasionally extracted for analysis of sulfate; inert tracer included in overlying water to quantify effective diffusion
- Destructive sampling at the end of lab experiments will quantify solid phase sulfides

Experimental phases:



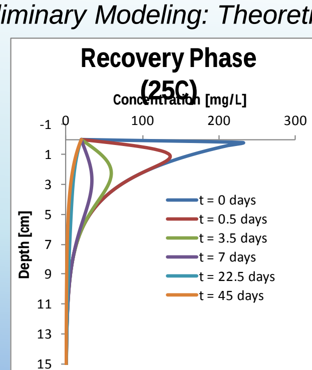
Expected timeline for three experimental phases. Two parallel sets of experiments will occur: 5ºC and 21ºC.

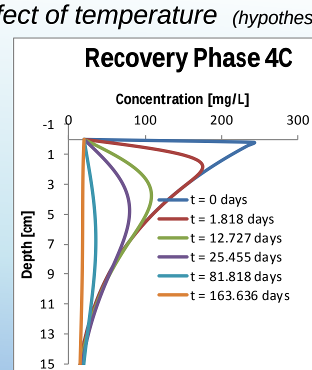
Modeling procedures:

- Time dependent reactive-transport model calibrated to observations

$$C(x) = C_0 e^{-\left(\sqrt{\frac{k}{D}}\right)x} \qquad D_w]_T = D_w]_0 + 0.2125x10^{-6} * T \qquad k]_T = k]_{25} Q_{10}^{\left(\frac{T-25}{10}\right)}$$

Preliminary Modeling: Theoretical effect of temperature (hypothesis to be tested)





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