Role of Sulfate on Wild Rice Health

Governor's Task Force on Wild Rice

Meeting 2

October 11, 2018

Presenters

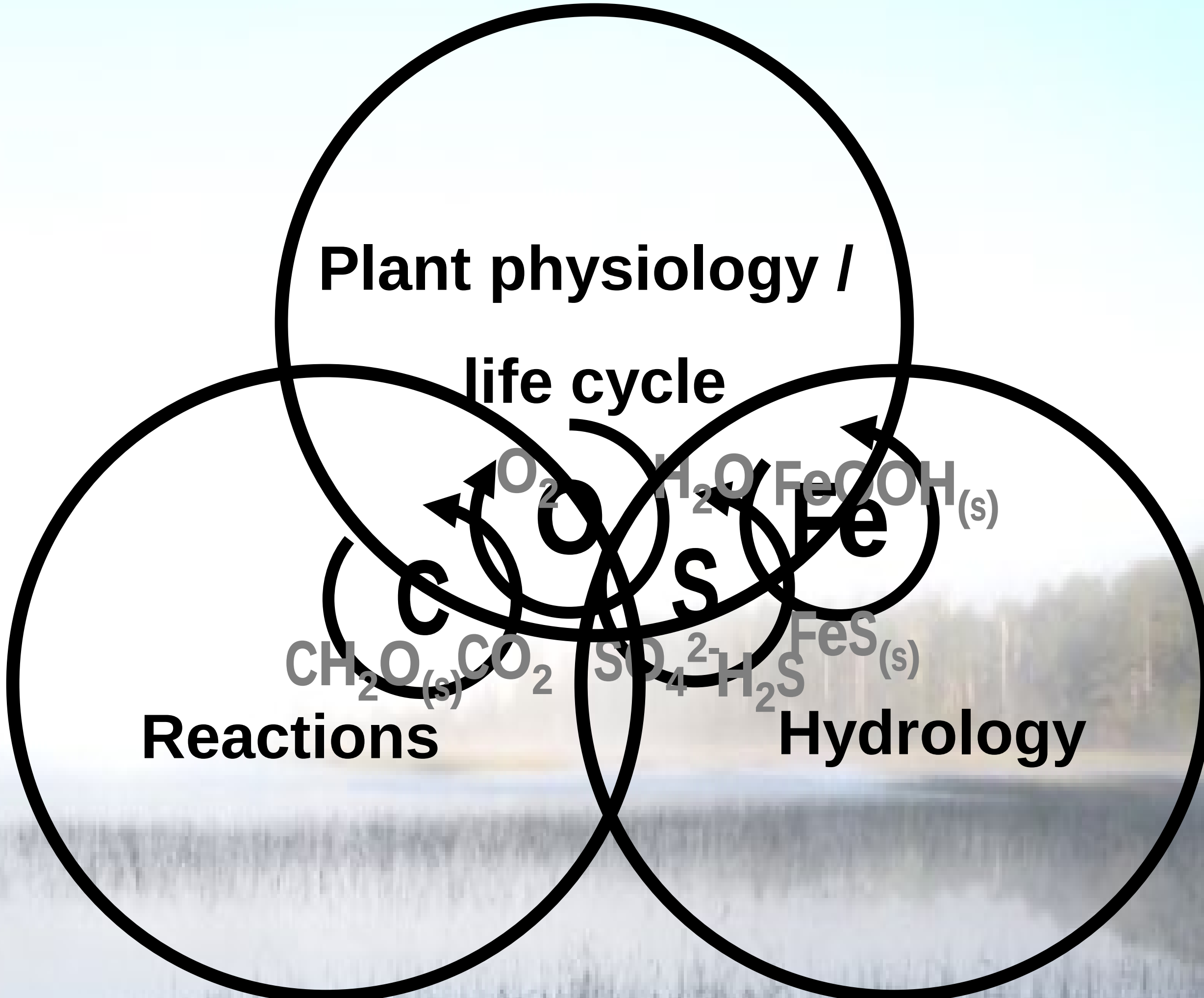
§ Ed Swain, Research Scientist, Minnesota Pollution Control Agency

§ Mike Hansel, Principle Emeritus, Senior Chemical Engineer, Barr Engineering (retired)

§ Dr. Nate Johnson, Professor, University of Minnesota Duluth

- Wild rice (*Zizania palustris*) is an annual aquatic plant that grows in lakes and rivers of north-central North America.
- Wild rice populations are sensitive to chemical/physical/biological processes including…
  - Competing vegetation
  - Water clarity
  - Waterfowl predation
  - Water level fluctuations
  - Water chemistry

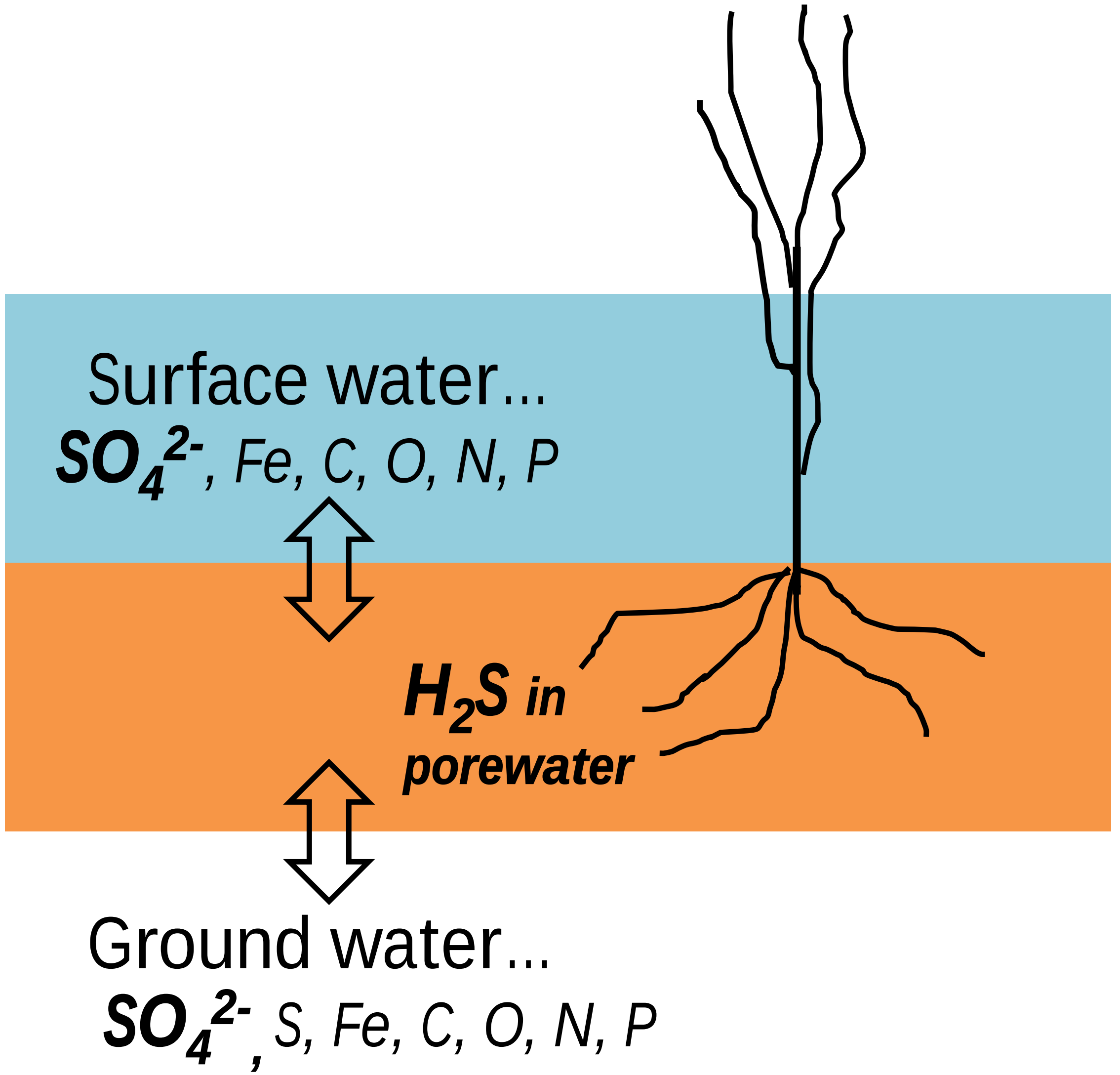
Our presentation today concerns only how **water chemistry** (sulfur in particular) affects wild rice.



A **combination of factors** impact **which chemicals are present** in sediment where wild rice grows.

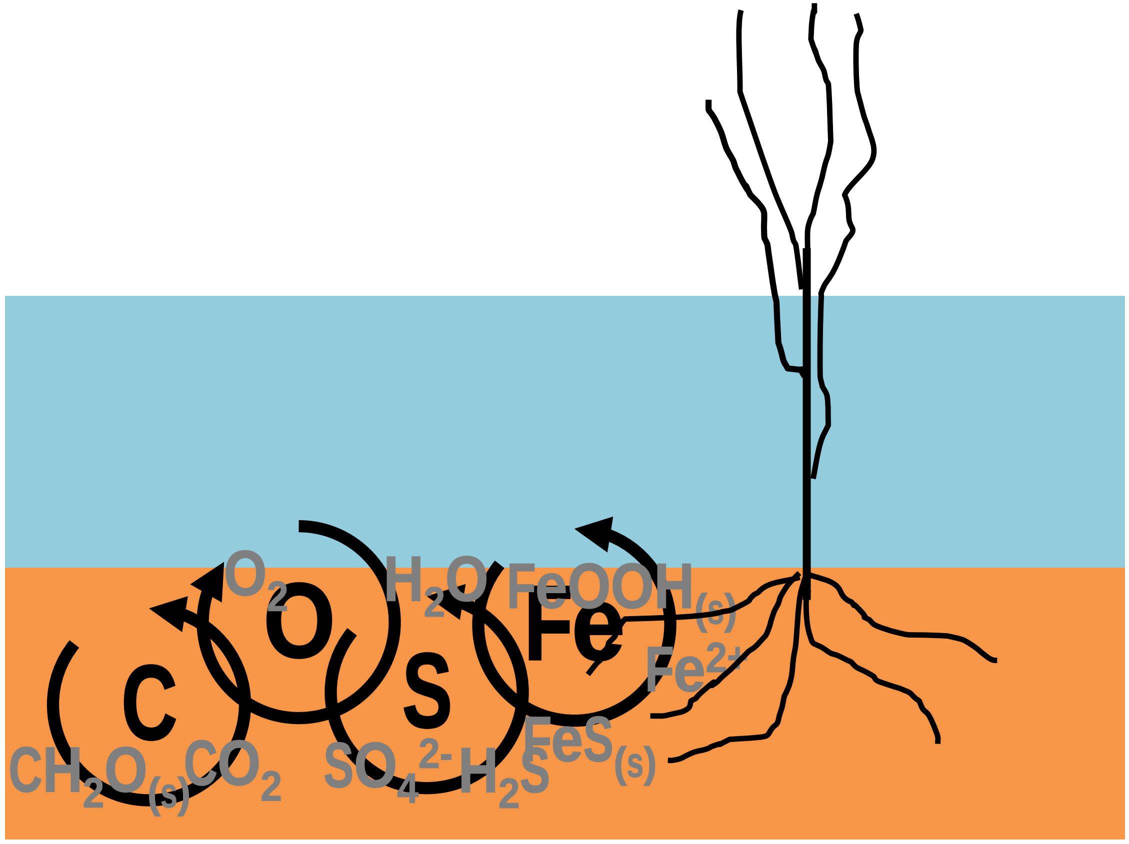
Hydrology matters:

- *How are **chemicals transported** to the rice rooting zone in different hydrologic scenarios?* experimental vs. natural; rivers vs. lakes; ground water vs. surface water



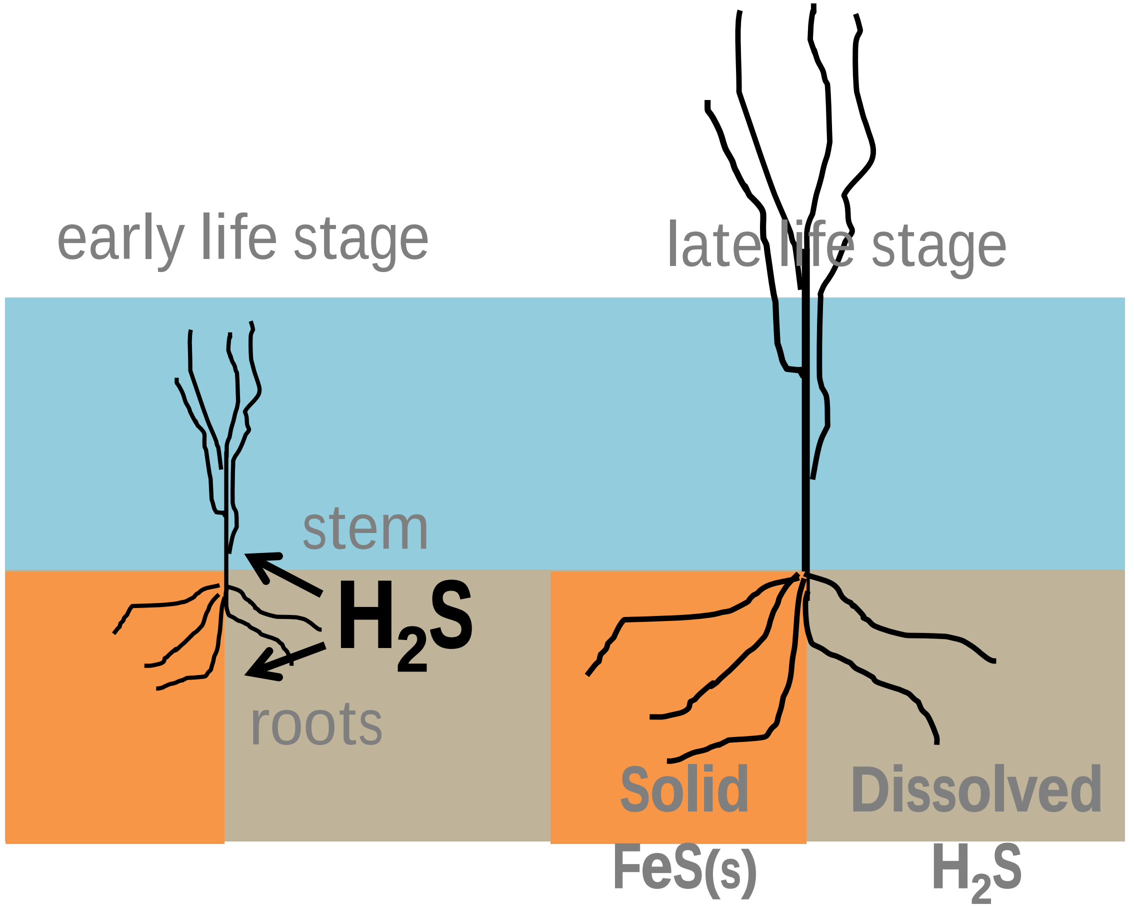
Sediment reactions matter:

- *How do **chemicals change form and combine with each other** to create conditions toxic to wild rice?* bacteria, solid vs. porewater, balance of inputs among S, C, Fe, O.



Plant physiology/toxicity/life cycle matters:

- *Where and when are **rice plants sensitive** to sulfide?* Which portion of the plant (roots, stem, leaves)? Which portion of the annual life cycle is sensitive? How are successive generations impacted by sulfide?



Goals

- Present state of science
- Identify areas where interpretations differ or experiments/observations are inconclusive
- Identify knowledge gaps in state of science
- Discuss next steps, moving forward

No expectation of full resolution or complete consensus: building blocks for shared understanding

Introduction, points of agreement, and recent research on mechanisms

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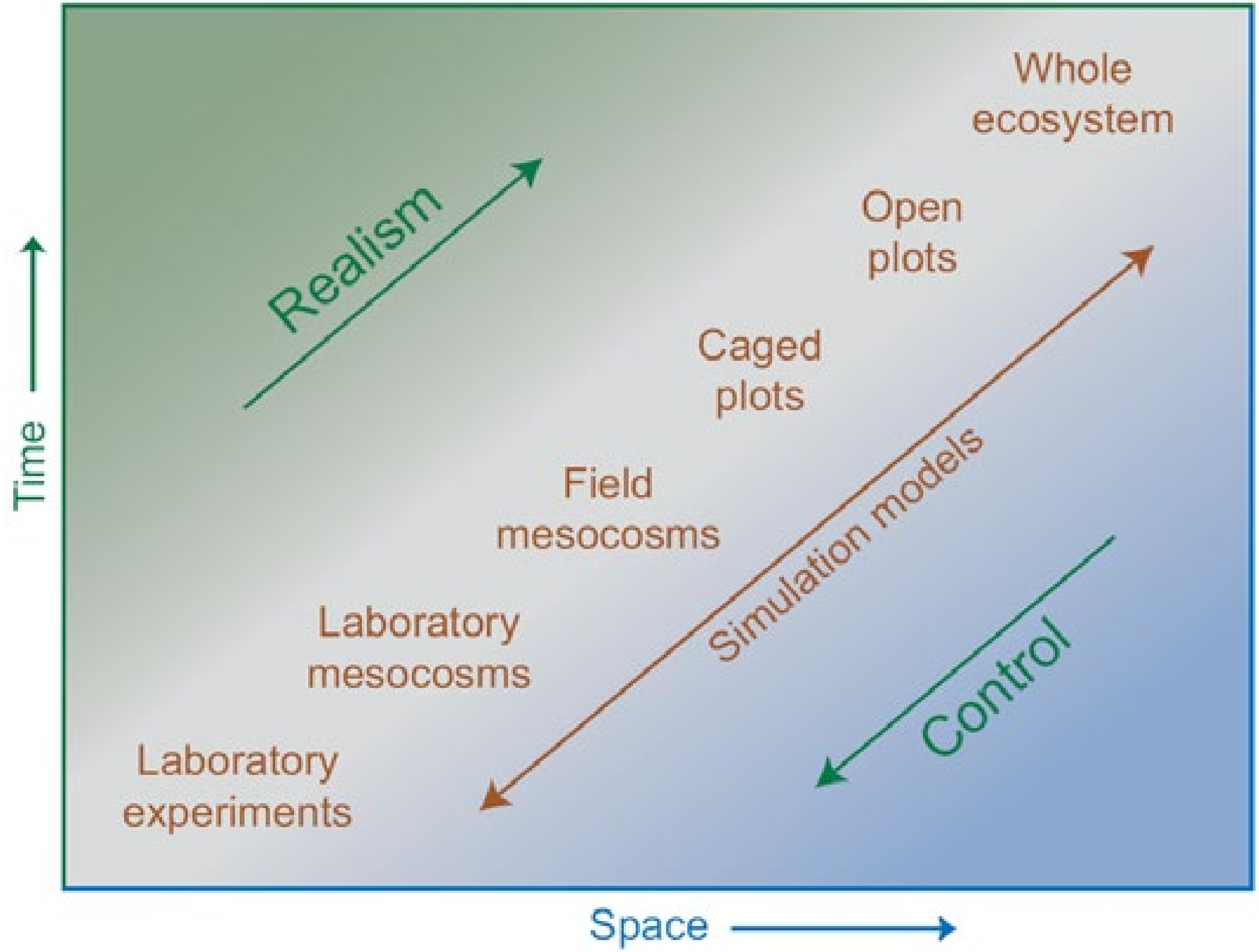
Nate Johnson
Associate Professor of Civil Engineering
University of Minnesota Duluth

What is known?

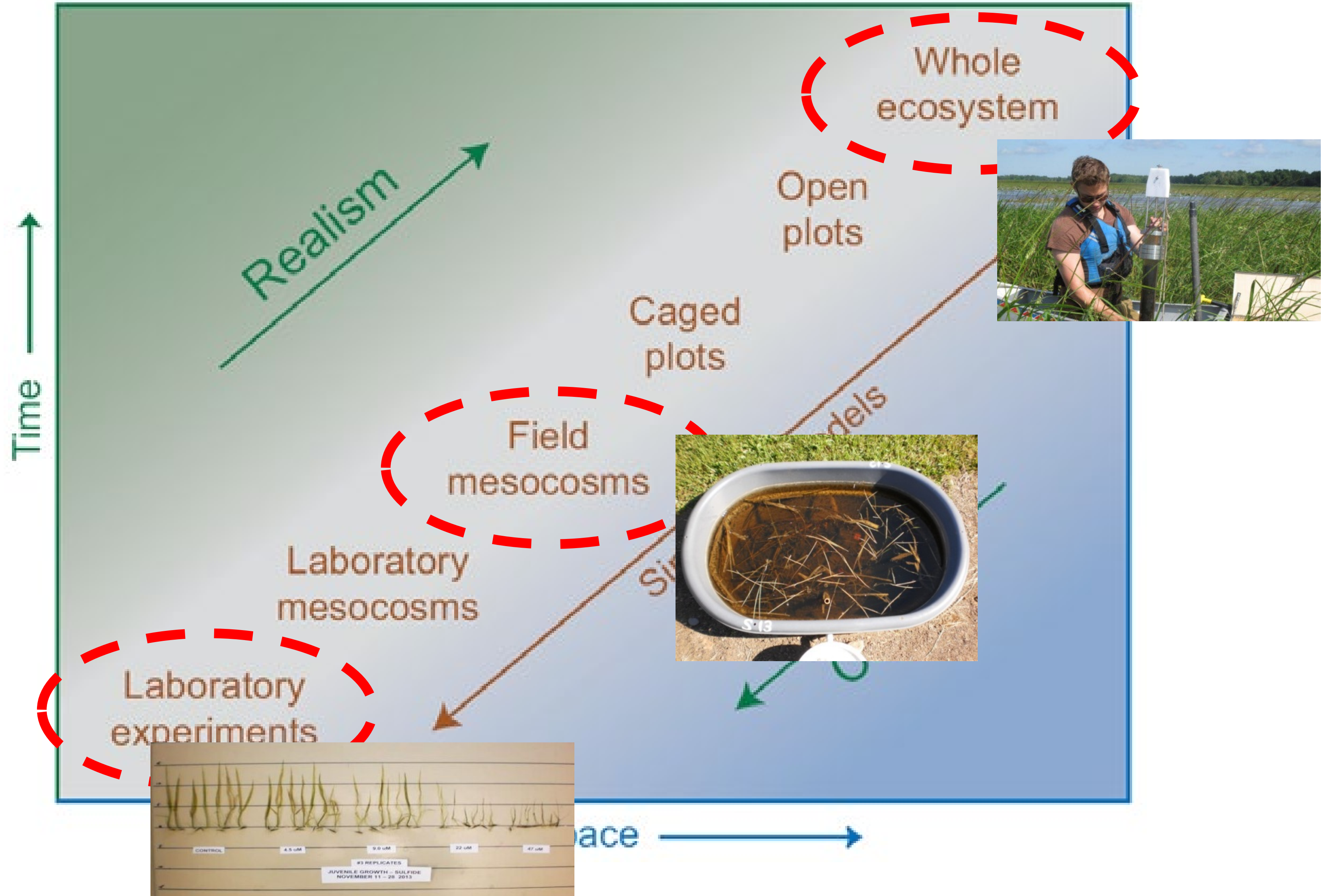
- Some historic knowledge: Moyle 1947 – *no large stands of wild rice found in waters containing more than 10 mg/L sulfate*
- Literature for studies based on other plants (not much study on wild rice)
- Much knowledge gained from recent studies commissioned by legislature through MPCA and other follow-up studies

Tradeoff between experimental control and realism



From: Petersen & Kemp, The role of enclosed experimental ecosystems ("mesocosms") in ocean science

Recent wild rice studies encompass a range of experimental/observational scales



Modified from: Petersen & Kemp, The role of enclosed experimental ecosystems ("mesocosms") in ocean science

What is (generally) agreed upon?

Form of sulfur (reactions)

- Sulfate (in surface water or ground water) is essentially not toxic at concentrations seen in MN Wild Rice waters
- Elevated porewater sulfide is potentially toxic
- In some cases, sulfate can be converted to sulfide in sediment; *(notable exceptions when groundwater "upwelling" is important)*
- Control of sulfate from dischargers would be very expensive

What is (generally) agreed upon?

How does sulfur get to rice (hydrology)

- Both groundwater and surface water can input chemicals to rice rooting zone *(discussion to follow)*
- Contributions of groundwater are not well-characterized; difficult in light of natural variability

What is (generally) agreed upon?

<u>Where/when is rice sensitive to sulfide (toxicity/ecology)</u>

- Some concentration of sulfide is toxic to wild rice *<u>(discussion to follow)</u>*
- Most sensitive life stage is not known; juvenile survival and seed production both impacted
- Chronic impacts (sulfate-induced or other factors, e.g. water level, water clarity, predation, etc.) can cause slow decline in populations

Recent UMD research on wild rice

- Working at scales between lab and field mesocosms

- Studying mechanisms of how sulfide interacts with rice roots in sediment, especially over course of wild rice annual life cycle
- Combination of Fe, C, S additions to mesocosms

Recent UMD findings

- Sulfide impacts different stages of rice growth: juvenile survival, plant reproduction
- Cumulative impacts matter (over time); plant populations and chemical accumulation
- Near-root geochemistry may be decoupled from porewater chemistry à
  plant / geochemistry feedbacks
- Iron additions partly ameliorates impact of SO_4 in mesocosms; not completely, especially at early life stage

MPCA's scientific research on the role of sulfate on wild rice

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Ed Swain
Minnesota Pollution Control Agency

MPCA's Research on Wild Rice

- 2011 legislature provided funds to re-evaluate the existing sulfate standard of 10 mg/L.
- MPCA's mandate is to identify a numeric standard that is protective of wild rice.
  - EPA suggests that protection of a species can be achieved at toxin concentrations that have a 10% negative impact (an EC_{10}).
- Use multiple lines of evidence to identify a protective concentration.

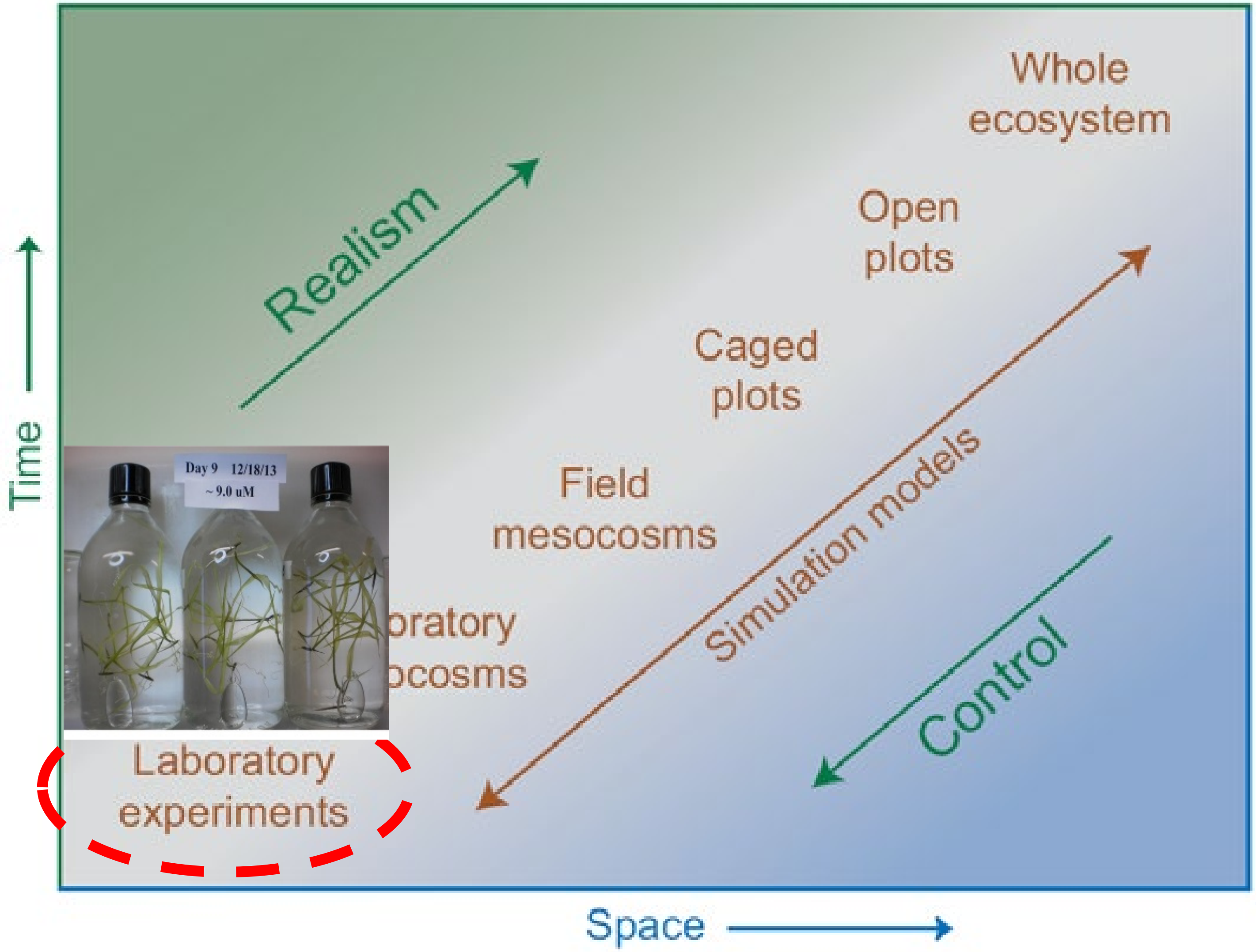
Significant peer-reviewed publications

1. **Myrbo** et al. 2017. Sulfide generated by sulfate reduction is a primary controller of the occurrence of wild rice (*Zizania palustris*) in shallow aquatic ecosystems.
2. **Myrbo** et al. 2017. Increase in nutrients, mercury, and methylmercury as a consequence of elevated sulfate reduction to sulfide in experimental wetland mesocosms.
3. **Pastor** et al. 2017. Effects of sulfate and sulfide on the life cycle of *Zizania palustris* in hydroponic and mesocosm experiments.
4. **Pollman** et al. 2017. The evolution of sulfide in shallow aquatic ecosystem sediments: An analysis of the roles of sulfate, organic carbon, and iron and feedback constraints using structural equation modeling.
5. **Fort** et al. 2014. Toxicity of sulfate and chloride to early life stages of wild rice (*Zizania palustris*).
6. **Fort** et al. 2017. Toxicity of sulfide to early life stages of wild rice (*Zizania palustris*).
7. **Ng** et al. 2017. Modeling hydrologic controls on sulfur processes in sulfate-impacted wetland and stream sediments. .
8. **LaFond-Hudson** et al. 2018. Iron sulfide formation on root surfaces controlled by the life cycle of wild rice (*Zizania palustris*).
9. **Lamers** et al. 2013. Sulfide as a soil phytotoxin—a review.

Key findings from research

- Sulfate is not toxic to wild rice.
- Sulfide in sediment porewater exerts significant control over wild rice presence and density across Minnesota.
- Porewater sulfide is usually derived from sulfate in the surface water.
- Porewater sulfide levels are controlled equally by surface water sulfate, sediment iron, and sediment organic carbon levels.
- A small proportion of surveyed sites (6%) develop less sulfide than expected, and therefore would be candidates for a site-specific sulfate standard (as provided for in the Clean Water Act).

Recent wild rice studies encompass a range of experimental/observational scales



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Hydroponic Experiments Yield Protective (EC10) Concentrations (Pastor, Fort)

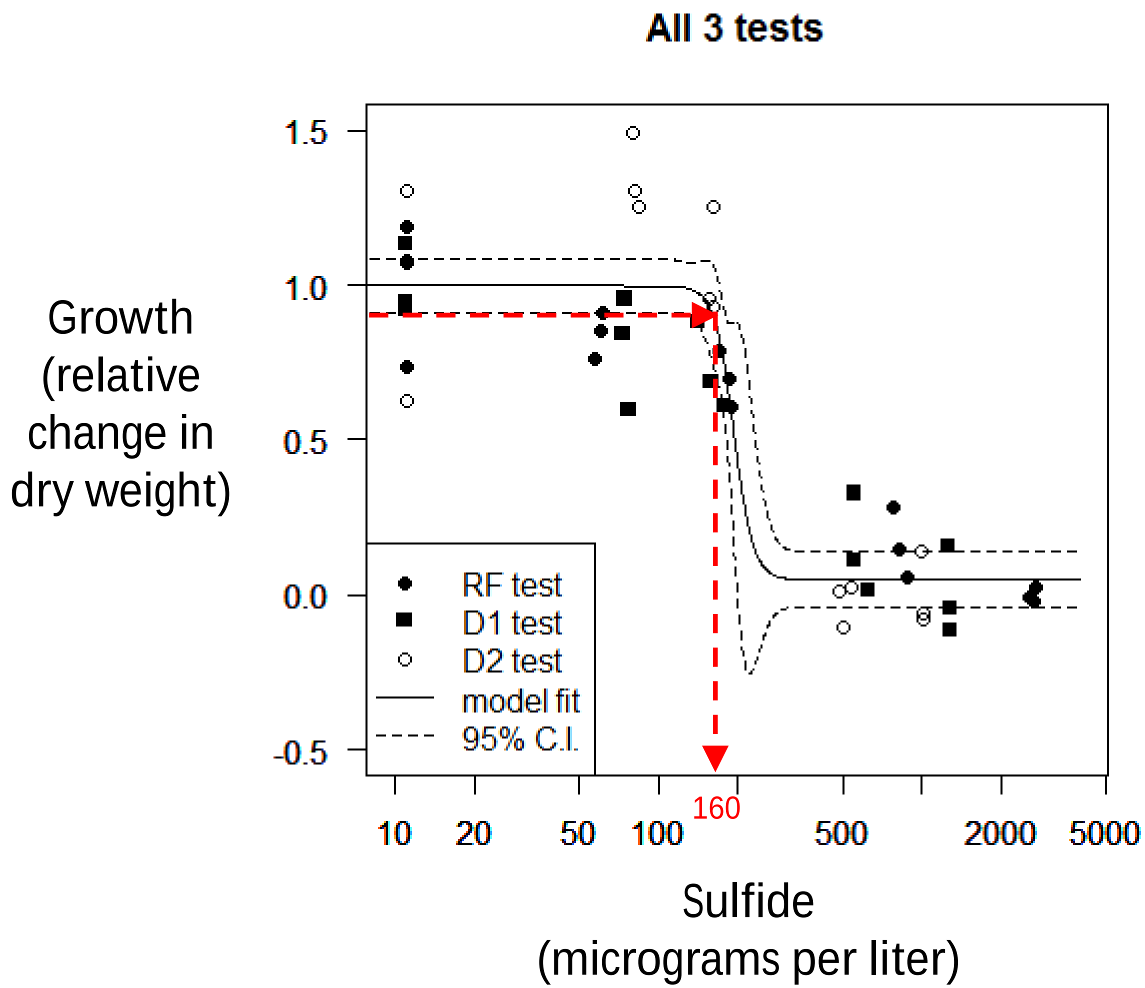
Pastor et al. bottles

EC_{10} Values (µg/L)

299 (mean initial concentration)

160 (time-weighted arithmetic mean)

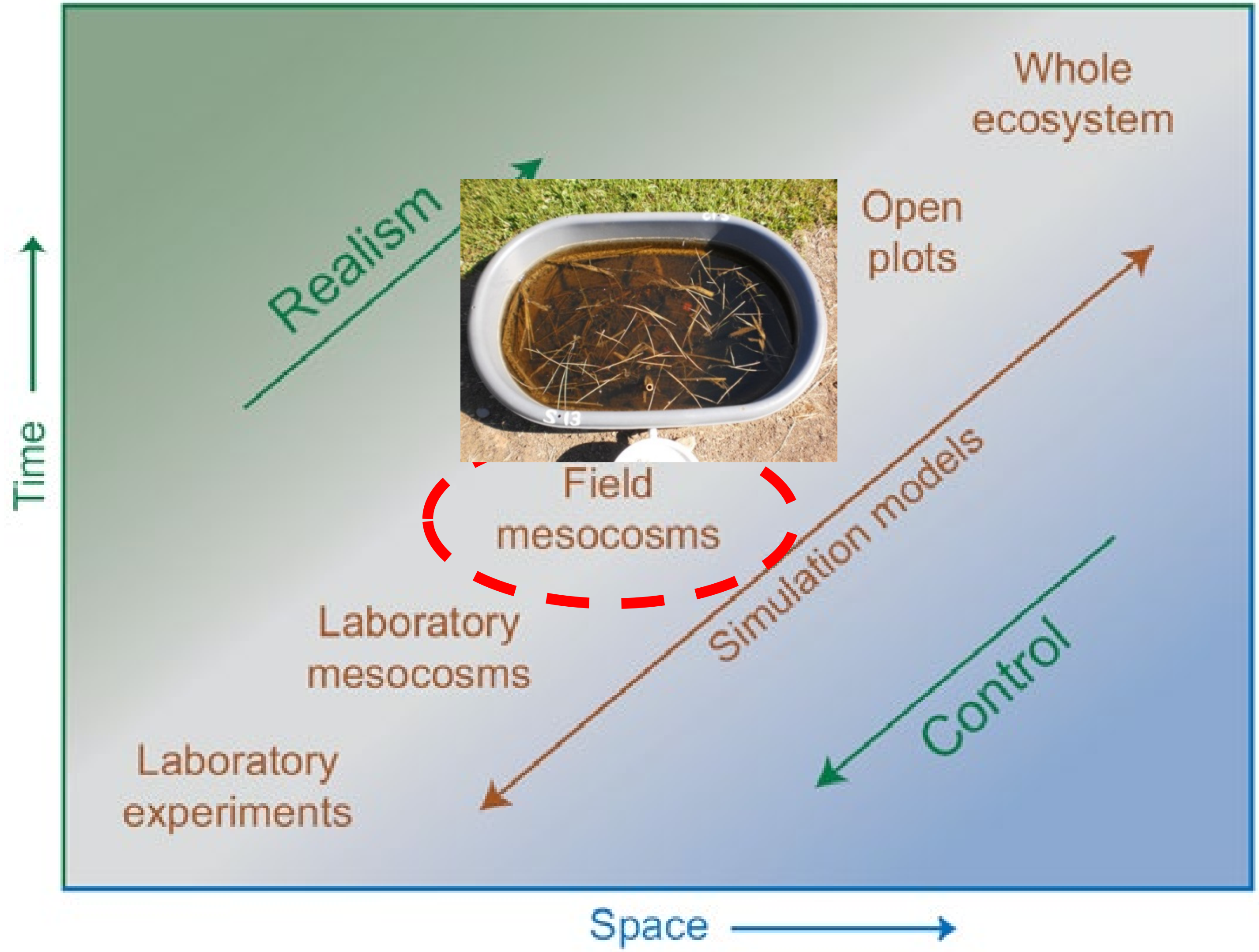
71 (time-weighted geometric mean)



Conclusions from Hydroponic Experiments

- Sulfate not toxic at observed surface water concentrations.
- Sulfide toxic at some observed pore water concentrations, depending on experimental set-up.

Recent wild rice studies encompass a range of experimental/observational scales



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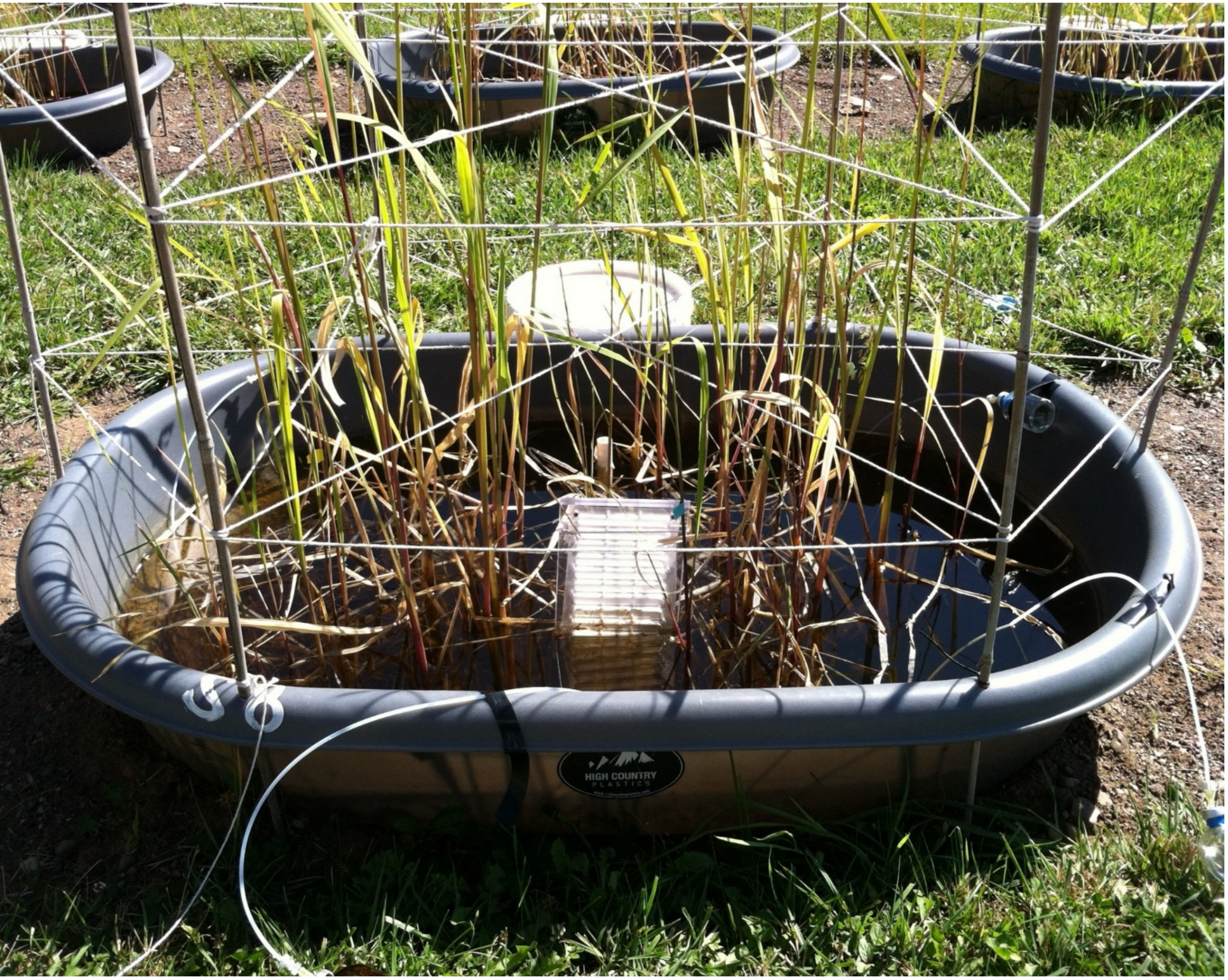
Outdoor Mesocosms tell us how sulfate turns into sulfide, and how that affects wild rice (Pastor)



Pastor et al. grew wild rice for 3 years in 5 levels of sulfate:

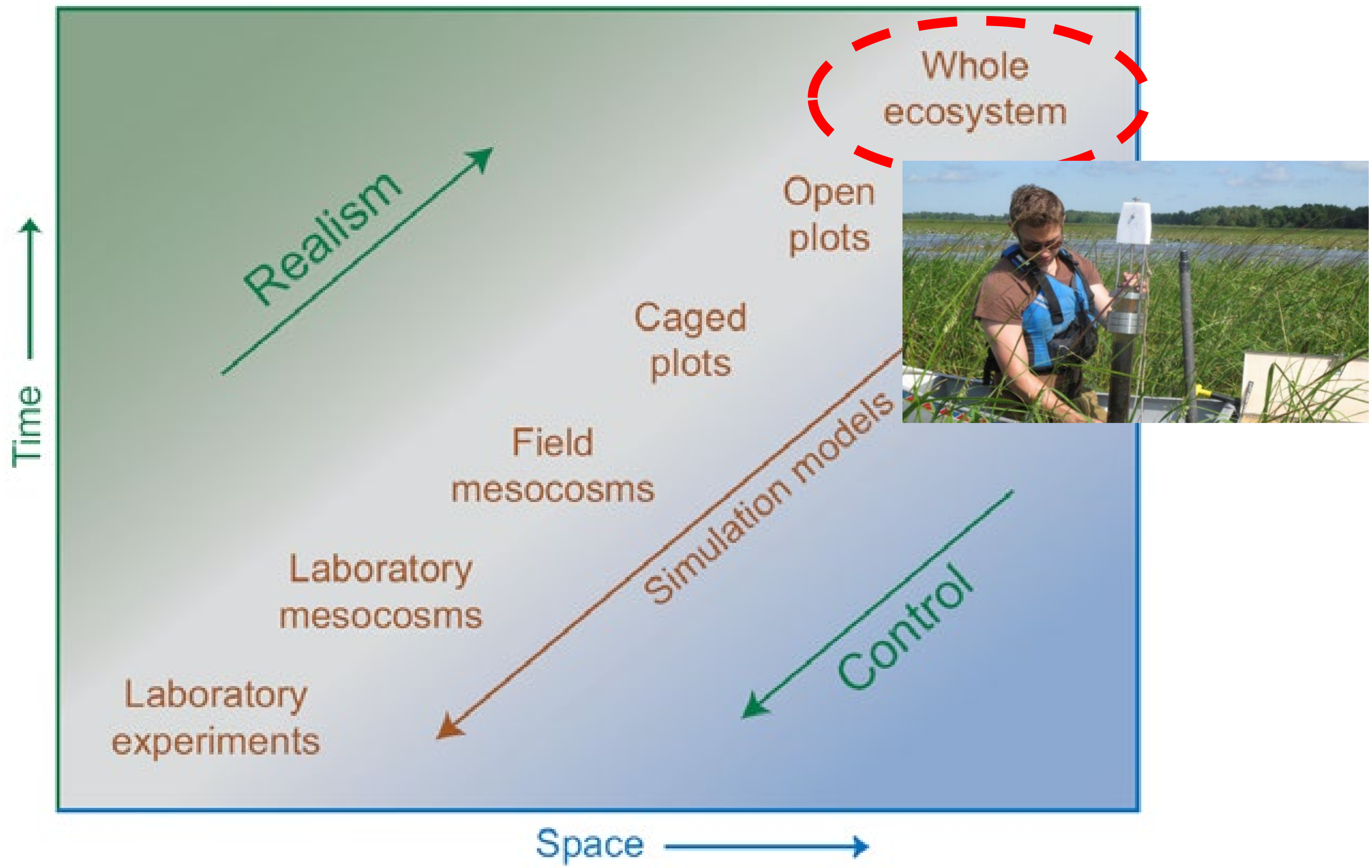
control, 50, 100, 150, 300 mg/L

(6 tubs per treatment)

Conclusions from outdoor experiments in tubs

- More sulfate in surface water produces more porewater sulfide.
- Wild rice seedling emergence, seedling survival, biomass growth, viable seed production, and seed mass all declined with increasing sulfate additions and hence increasing porewater sulfide.

Recent wild rice studies encompass a range of experimental/observational scales



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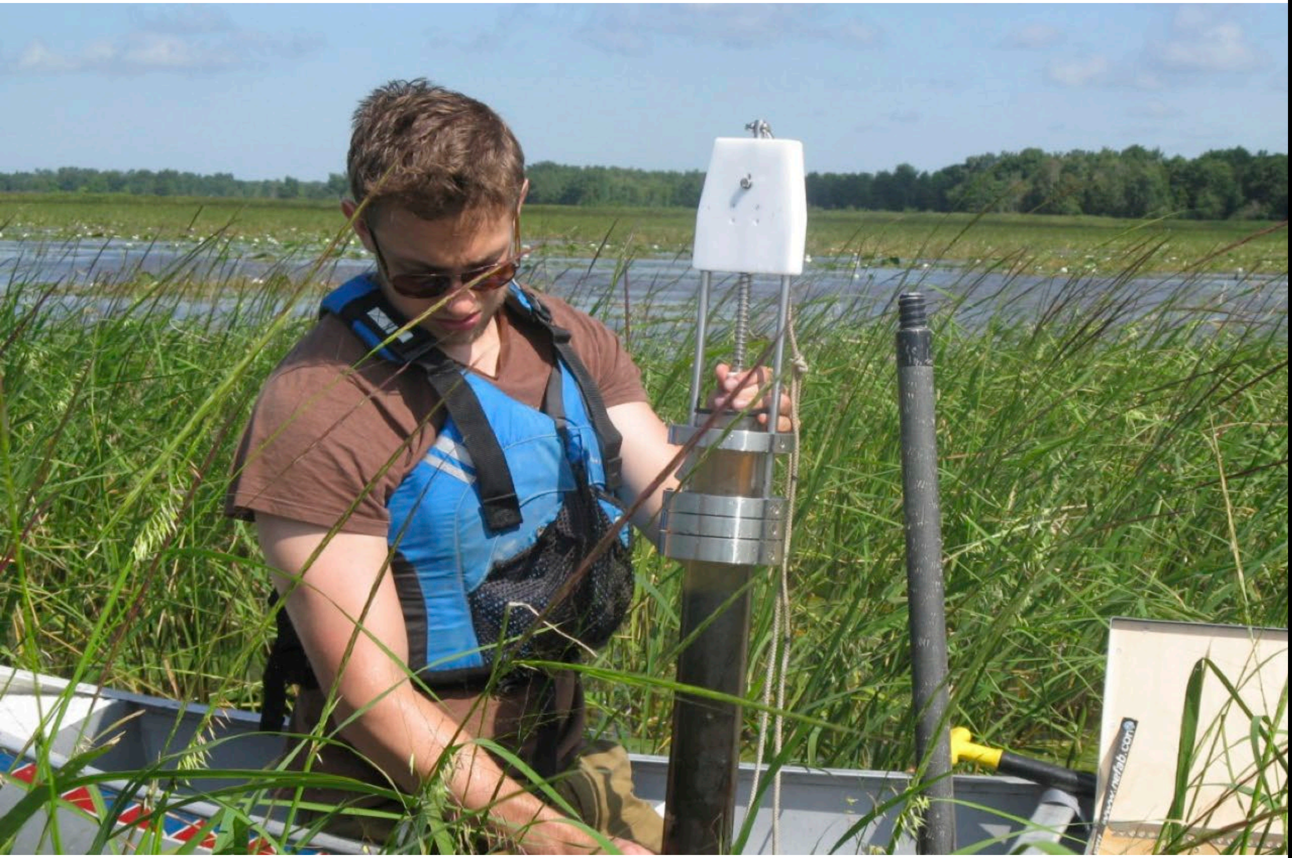
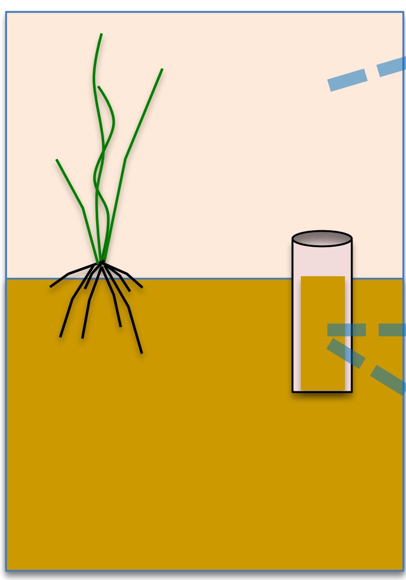
Wild Rice Field Survey (Mybro)



Wild Rice Field Survey



Surface water
- Na, K, Mg, Ca, Fe
- SO4, Cl
- Alkalinity, pH, conductivity, Total P, Total N, Ammonia, Nitrate + Nitrite, transparency

Bulk Sediment Chemistry
- Acid-Volatile Sulfide
- Total carbon, phosphorus, nitrogen, sulfur
- Phosphorus fractionation
- Simultaneously-Extracted Metals:
  Fe, Cu, Zn, Co, Ni, Mn, Mo, Se, As, B

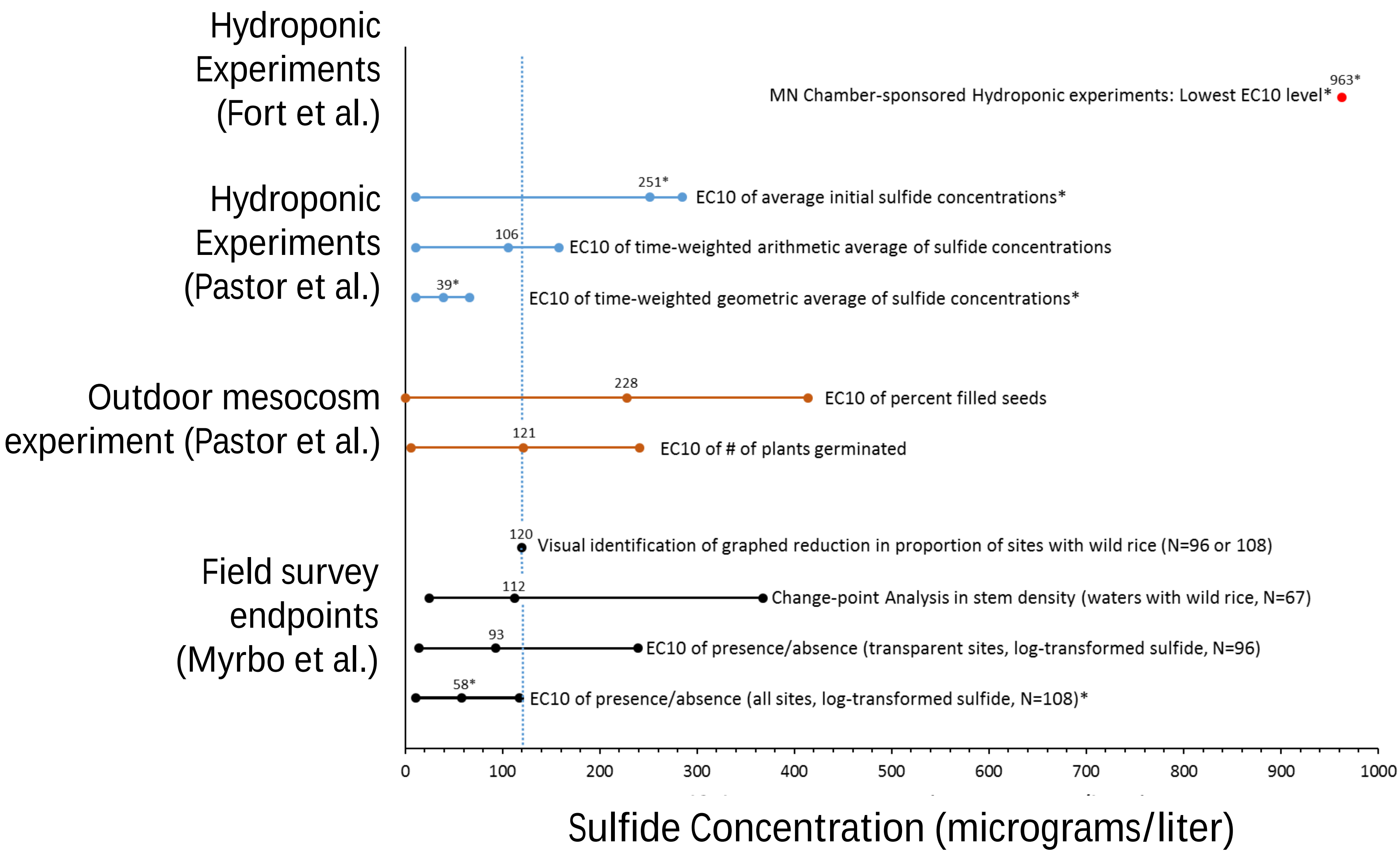
Porewater
- Sulfide
- Na, K, Mg, Ca,
- SO_4, Cl
- Total P, Total N, Silica
- Ammonia, Nitrate + Nitrite
- DOC (dissolved organic carbon)
- Fe, Cu, Zn, Co, Ni, Mn, Mo, Se, As, B

Other Sediment Properties
- Water
- organic matter
- carbonate content
- Organic grain size
- Wild rice phytolith presence/absence

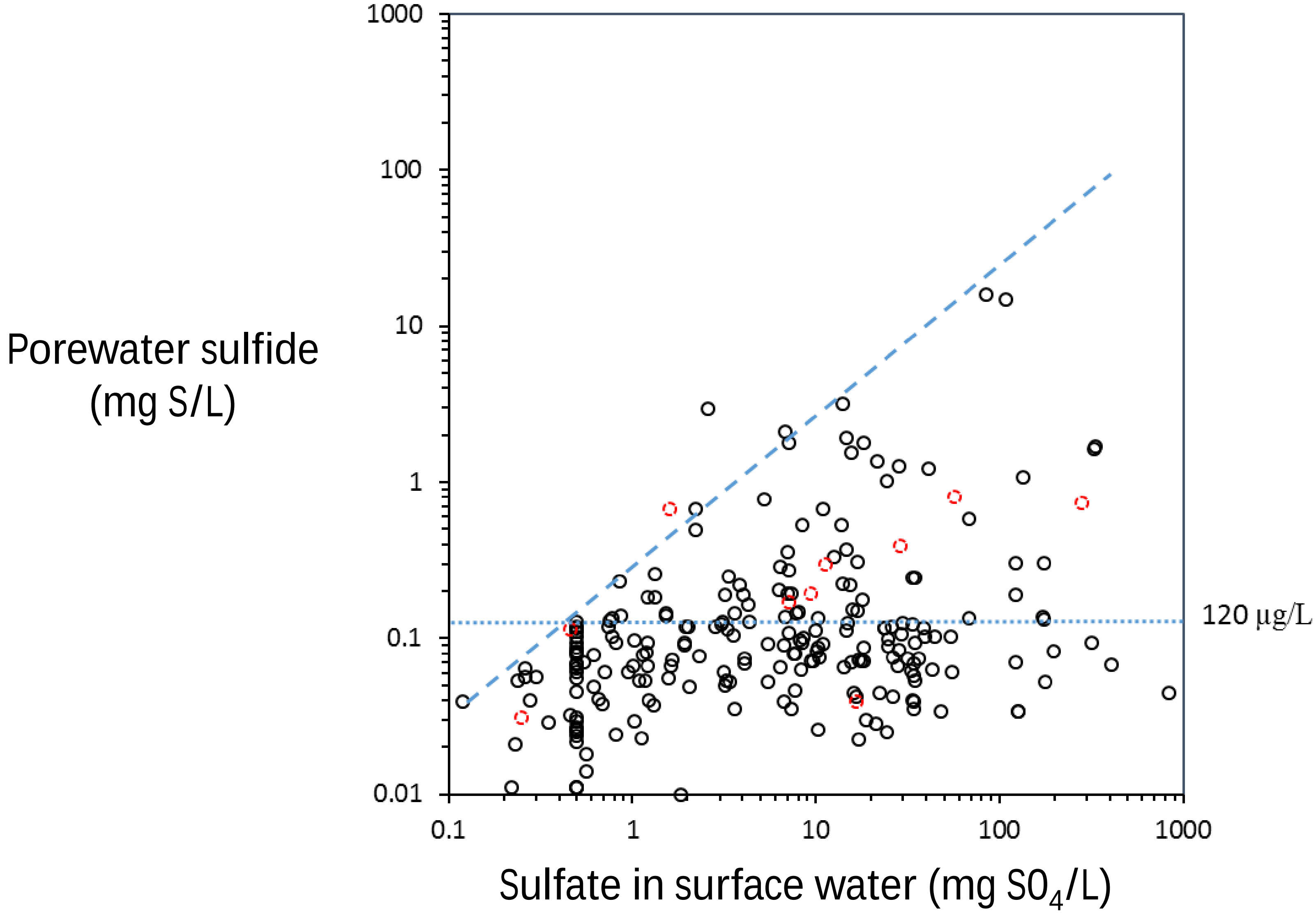
Statistical analysis identified three variables that control wild rice (Myrbo et al. 2017)

- Porewater sulfide
  - Probability of wild rice presence declines
  - Probability of dense wild rice declines
- Water transparency
  - Wild rice needs light to get to the water surface, where it can get more light & much more oxygen.
- Water temperature
  - Colder is better

Multiple Lines of Evidence

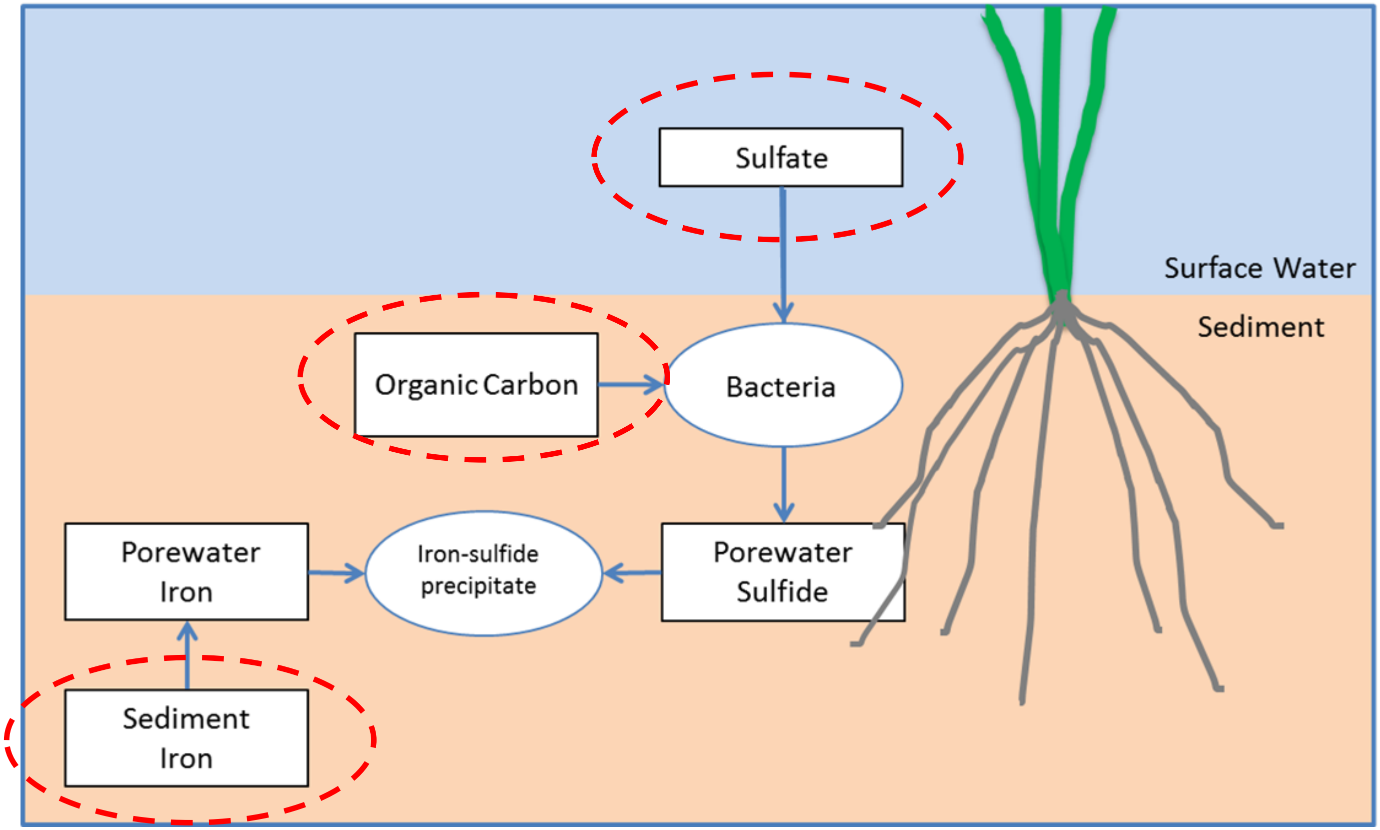


Even though sulfide comes from sulfate, there is a poor relationship between them

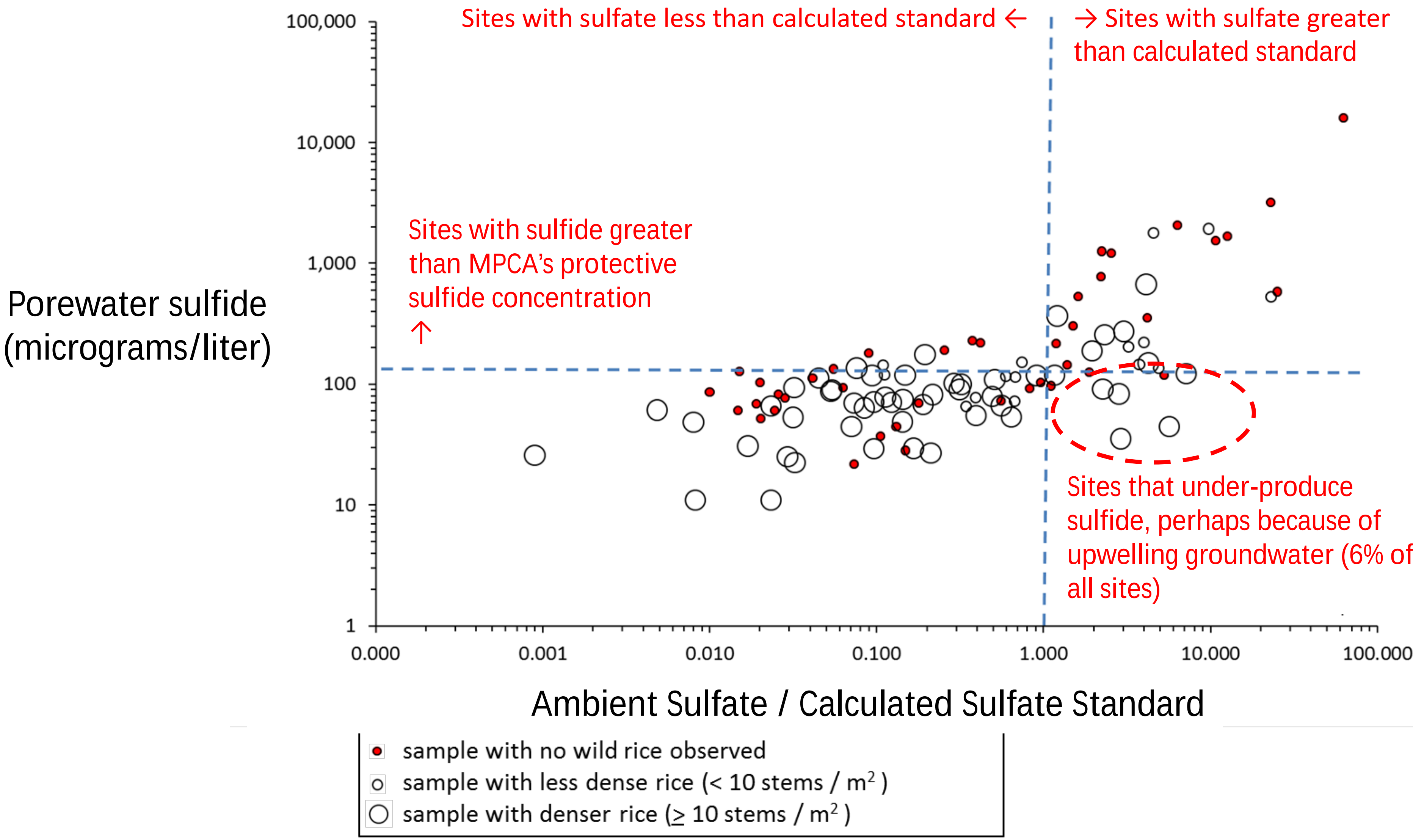


Porewater sulfide is controlled equally by three variables

- Sulfate in surface water
- Iron in sediment
- Organic carbon in sediment



Outliers from the proposed MPCA equation



MN business point of view

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Mike Hansel
Principal Emeritus, Senior Chemical Engineer (retired) Barr Engineering

MN Business Point of View

- Only industry is currently challenged by the existing 10 mg sulfate/L standard
  - Only mines and 1 power plant have sulfate standards to protect wild rice
  - Only mines have been required to monitor wild rice presence and health downstream
- Cost to comply with 10 mg sulfate/L standard for industries will be OTOO $10- 100 MM/site (NPV)!

Groundwater

- Groundwater is a much bigger factor than has been previously been acknowledged
  - NE MN groundwater: high iron, low sulfate
  - SW MN groundwater: high sulfate, low iron (glaciers)
- Groundwater interaction with wild rice waters is not well understood, particularly for individual wild rice waters
  - e.g. lakes vs. headwater streams

Life Stage and Affected Parts

- Most organisms are most affected by toxic chemicals in the early life stages
  - US EPA guidance requires testing on neonates and juveniles
- MN Business believes that germination and mesocotyl growth are most affected
  - Other plant parts are not in contact with anoxic sediment or sulfide
  - Once wild rice produces “green” parts, photosynthesis produces oxygen which can offset toxicity of sulfide

Life Stage and Affected Parts

- Most experiments assumed that sulfate and sulfide are acute toxicants
- Some very recent experiments (LaFond-Hudson et al, September 2018), suggest that sulfate/sulfide may act as chronic toxicants
- More research needed to determine the mode of action of sulfate/sulfide toxicity.

Sulfide Toxicity

- While sulfide can be toxic to wild rice, the level at which sulfide is toxic is in dispute
- MN Business believes that sulfide may be toxic only above 3,200 µg/l, based on standard toxicity testing exposing only the germinating seed and mesocotyl
- In the presence of iron, sulfide may be toxic only above 7,800 µg/L (Fort et al 2017)
- Very few wild rice waters have concentrations of sulfide in porewater above that level
- Therefore, sulfide may not be the controlling factor in wild rice presence and health.

Wild Rice Protection

- MN Business believes that protection of wild rice should take into account **all** known factors which could affect wild rice
- MN Business notes that single species protection plans in Minnesota typically involve management plans specific to regions of the state or even specific water bodies. E.g.:
  - Walleye in Mille Lacs Lake
  - Gray Wolves in NE MN
  - White tail deer

Wild Rice Protection

- Wildlife management plans encompass **<u>all</u>** known factors affecting the presence and health of the species
  - Takings and possession limits
  - Disease control
  - Habitat improvement
- Wild Rice protection should similarly encompass **<u>all</u>** known factors

Summary, final thoughts, questions

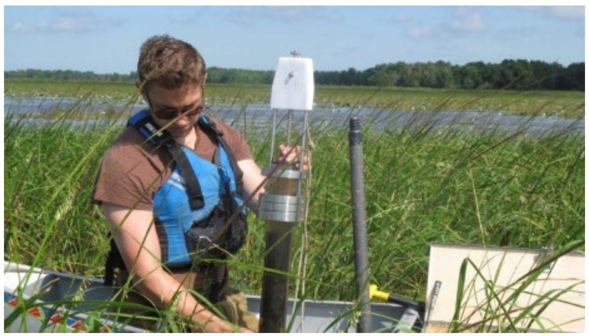
Panel & Task Force

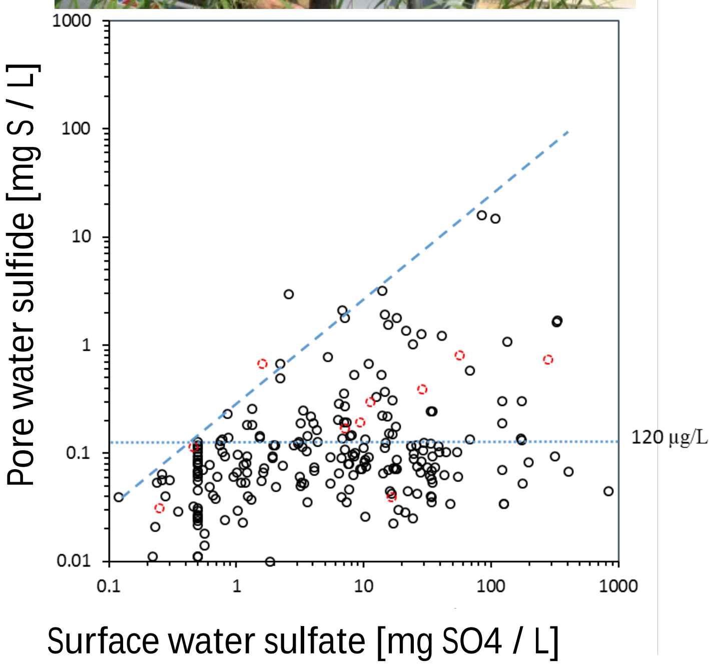
Extra Johnson slides follow

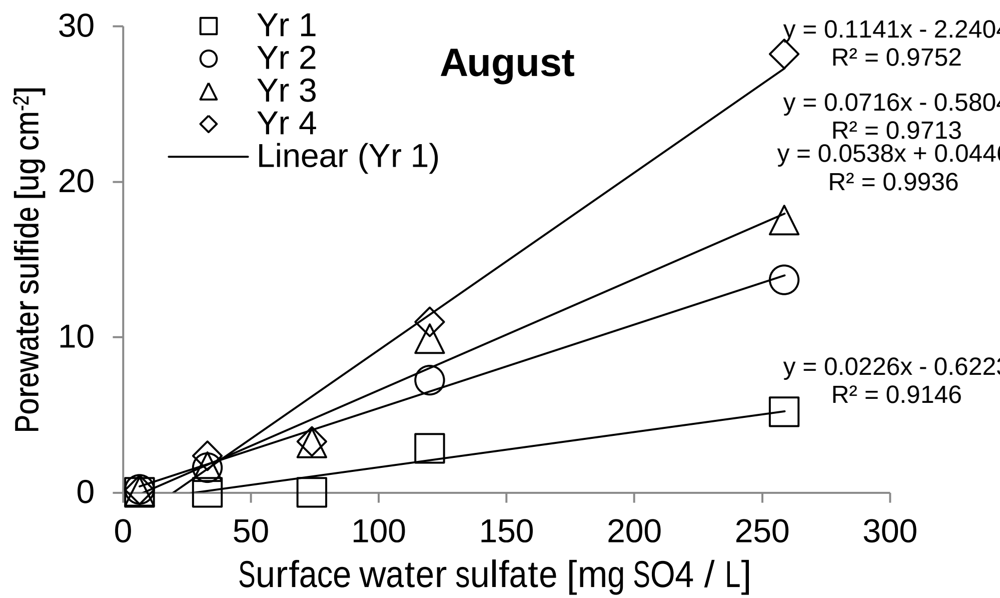
Two relationships involved in quantifying sulfate impacts to rice

- Surface water sulfate à rooting-zone sulfide
  - Messy relationship in field data, clear trend in mesocosms
  - Reactions matter: allowed reactions to occur in mesocosms, (but for only one combination of Fe, C, O and everything else)
- Rooting-zone sulfide à plant effects
  - Isolated rooting-zone sulfide from other factors in lab studies (tight control)
  - Measured rooting zone sulfide in-situ (with other elements, Fe, S, C, O, etc.) for both mesocosm, field observations

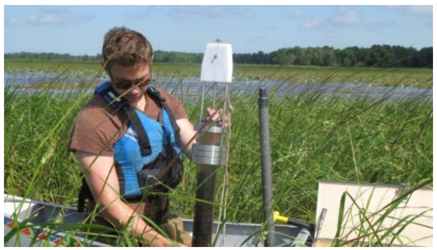
- Rooting-zone sulfide – related to surface water sulfate

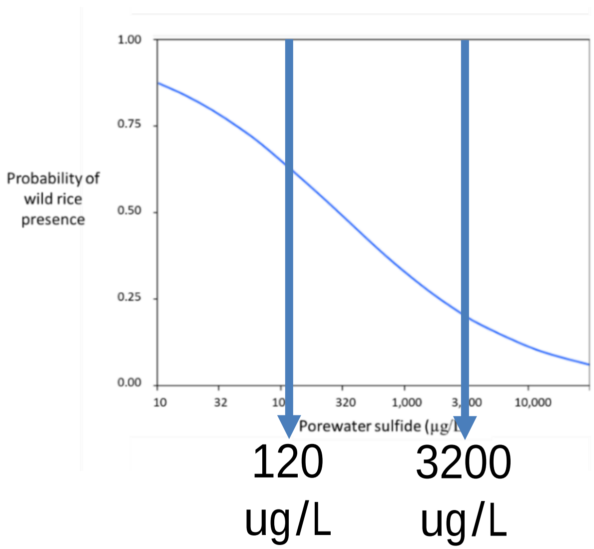


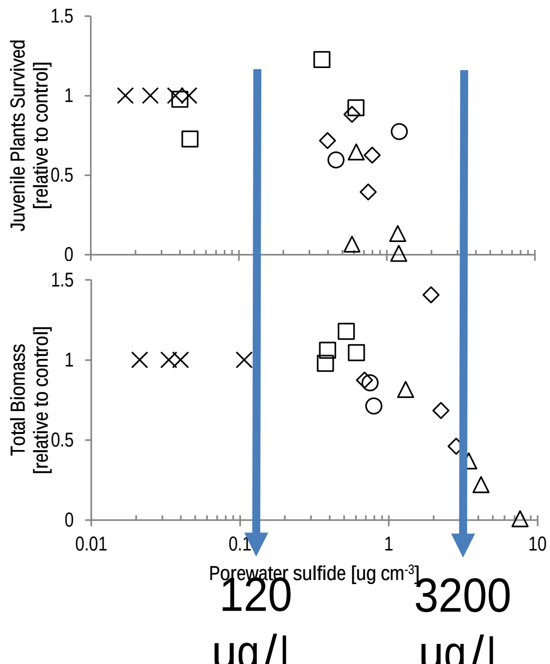


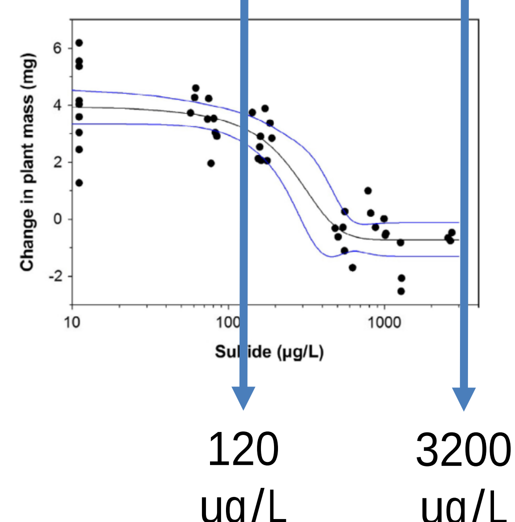


- Rooting-zone sulfide – related to plant effects







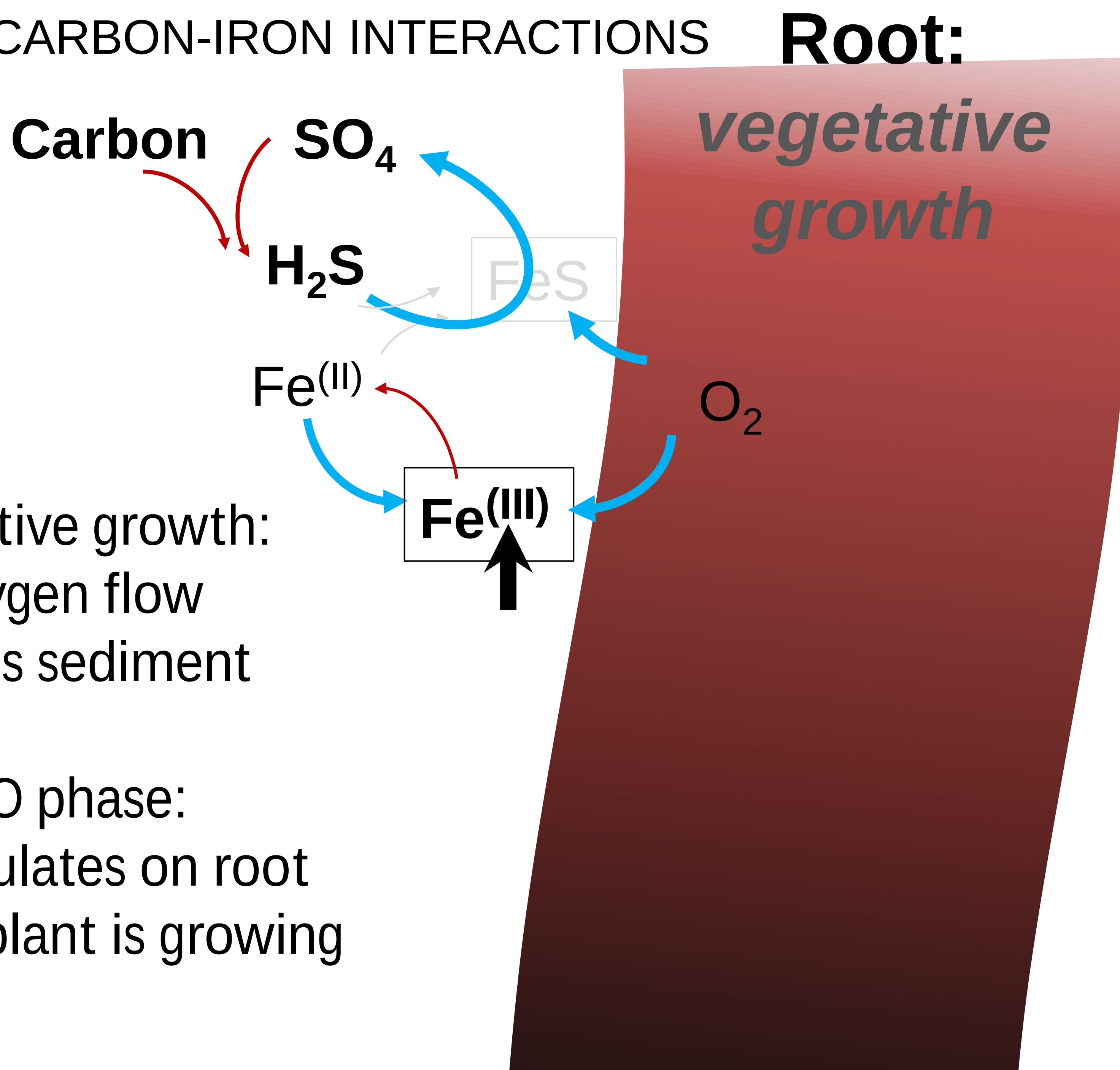


Porewater sulfide à wild rice effects

- Relating porewater sulfide to plant health/reproduction is the state of practice based on established research: borne out in hydroponics, mesocosms, and field observations

- Recent studies show that there are additional (near-rooting zone) nuances that result in seasonal and life-stage variations in the sensitivity of rice to sulfide...

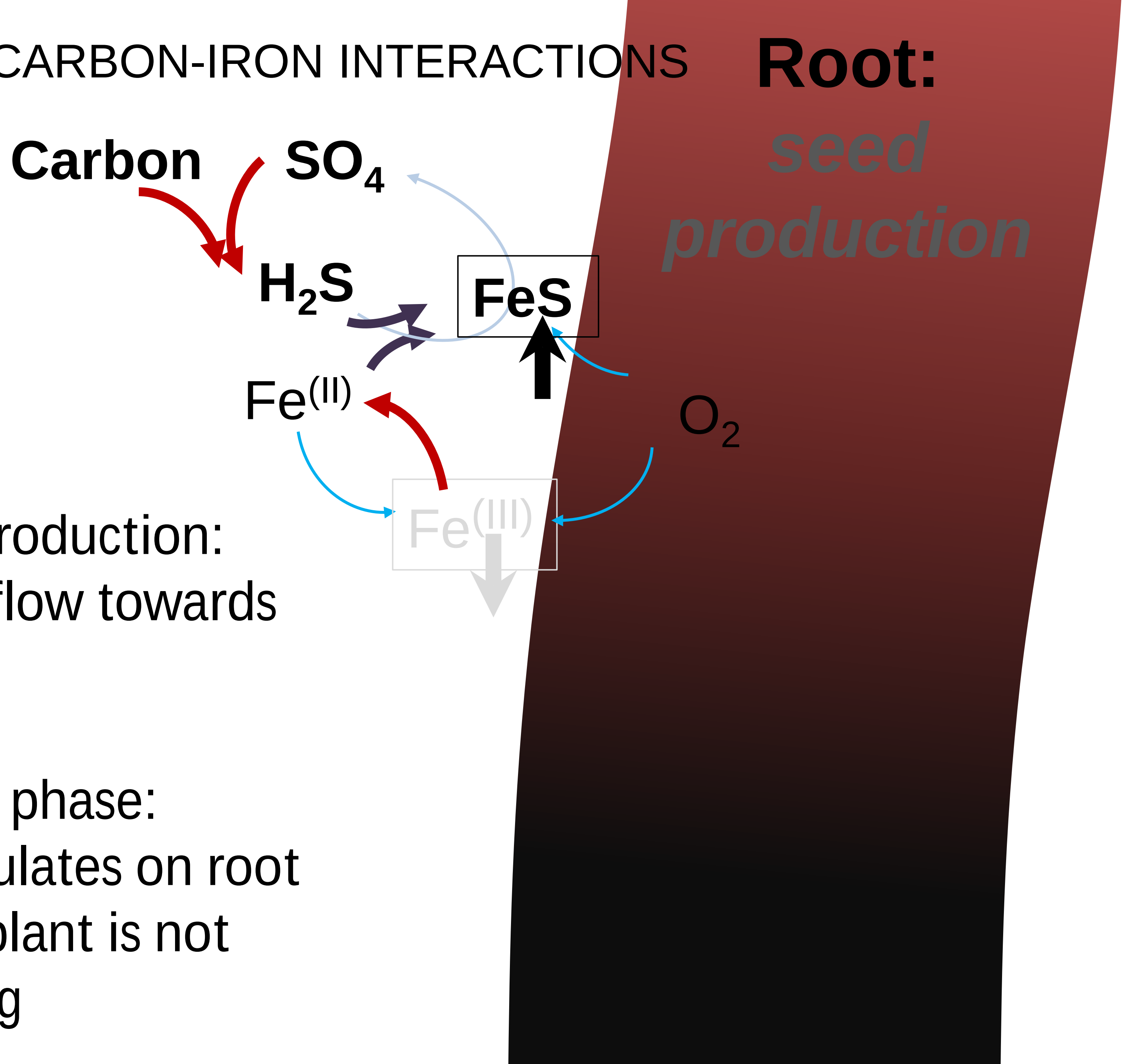
SULFATE-CARBON-IRON INTERACTIONS



1. Vegetative growth: net oxygen flow towards sediment

2. Fe(III)-O phase: accumulates on root when plant is growing

SULFATE-CARBON-IRON INTERACTIONS



1. Seed production: net e- flow towards root

2. Fe(II)-S phase: accumulates on root when plant is not growing

Extra MPCA slides follow

MBLR Equations

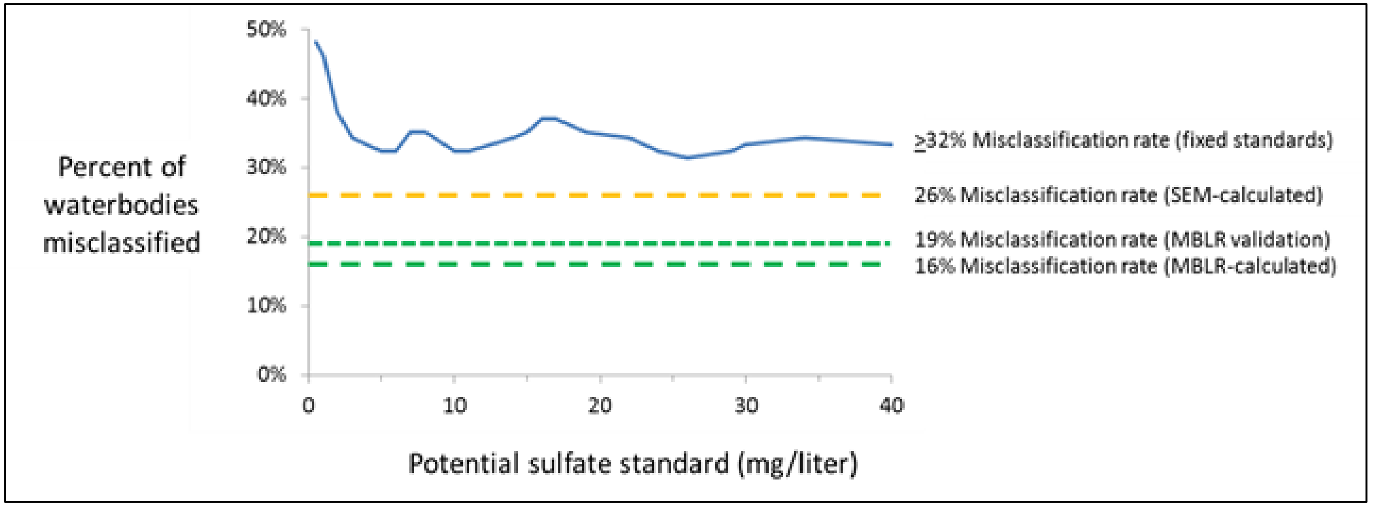
$$\text{MBLR120 Sulfate} = 0.0000121 \times \text{TOC}^{-1.197} \times \text{TEFe}^{1.923}$$

where sulfate is expressed as mg/L, Total Organic Carbon (TOC) as percent dry weight, and Total Extractable Iron (TEFe) as mg/kg

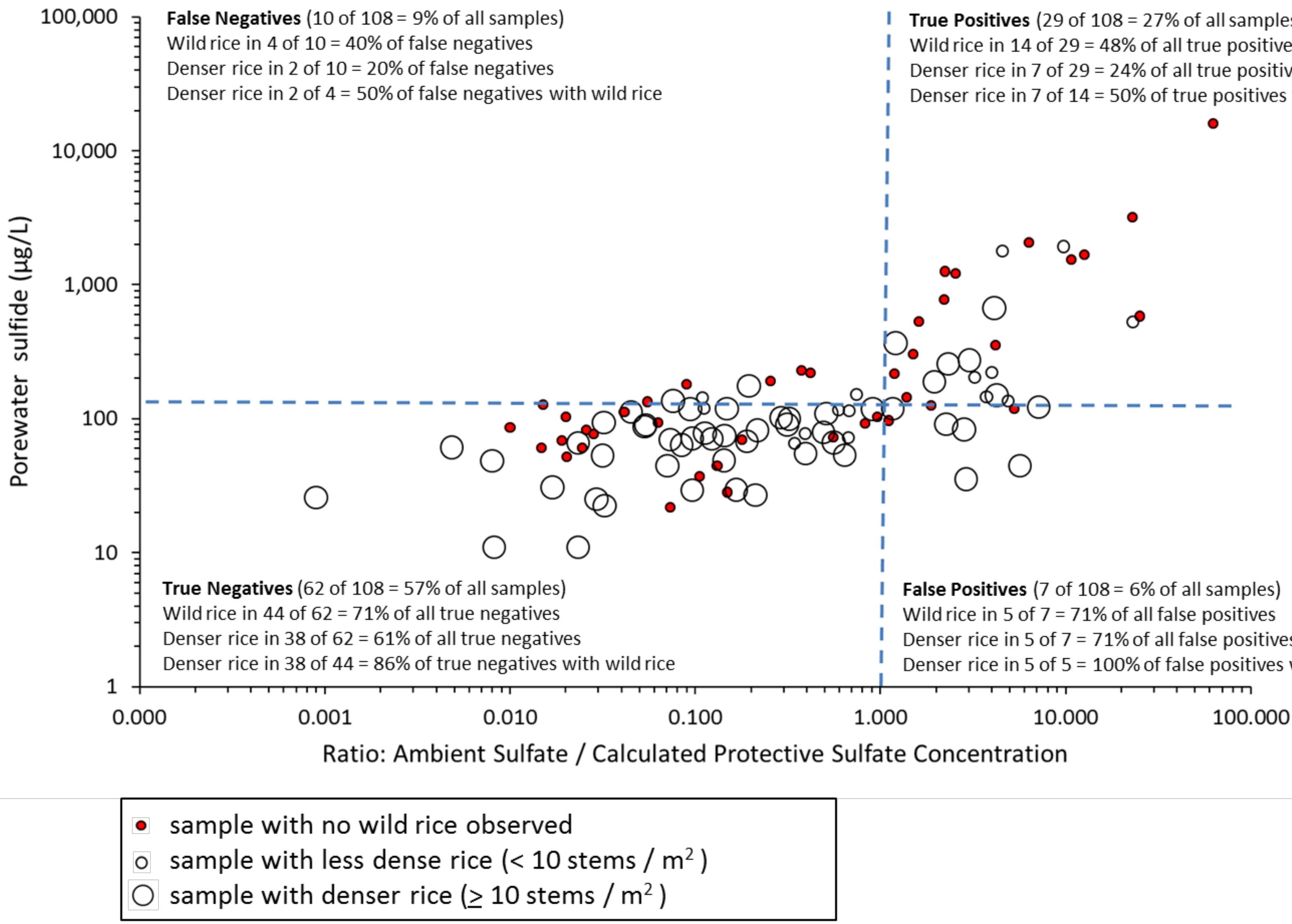
Study Site	State ID	Sediment Total Organic Carbon (%)	Sediment Iron (µg/g)	MBLR-Calculated Sulfate (mg/L)
Little Round Lake	03-0302	27.5	3,069	1.2
Elk Lake	15-0010	10.2	8,480	27
Rice Lake	18-0053	35.6	50,389	186

Equation-Based; "Fixed" Standard: Considerations

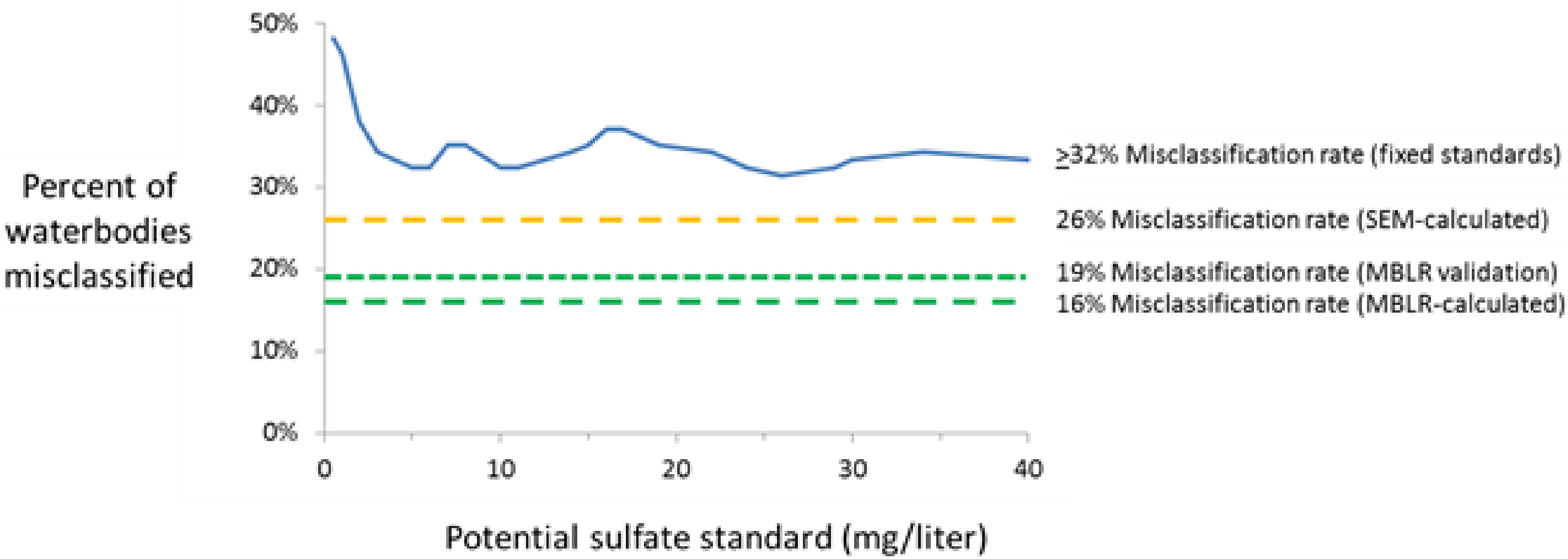
- Many commenters expressed concern with equation approach
- Equation-based standards are not new, but are less common
- Enhanced precision ó additional data collection



Accuracy of the MPCA's proposed equation (Myrbo's 108 field sites)



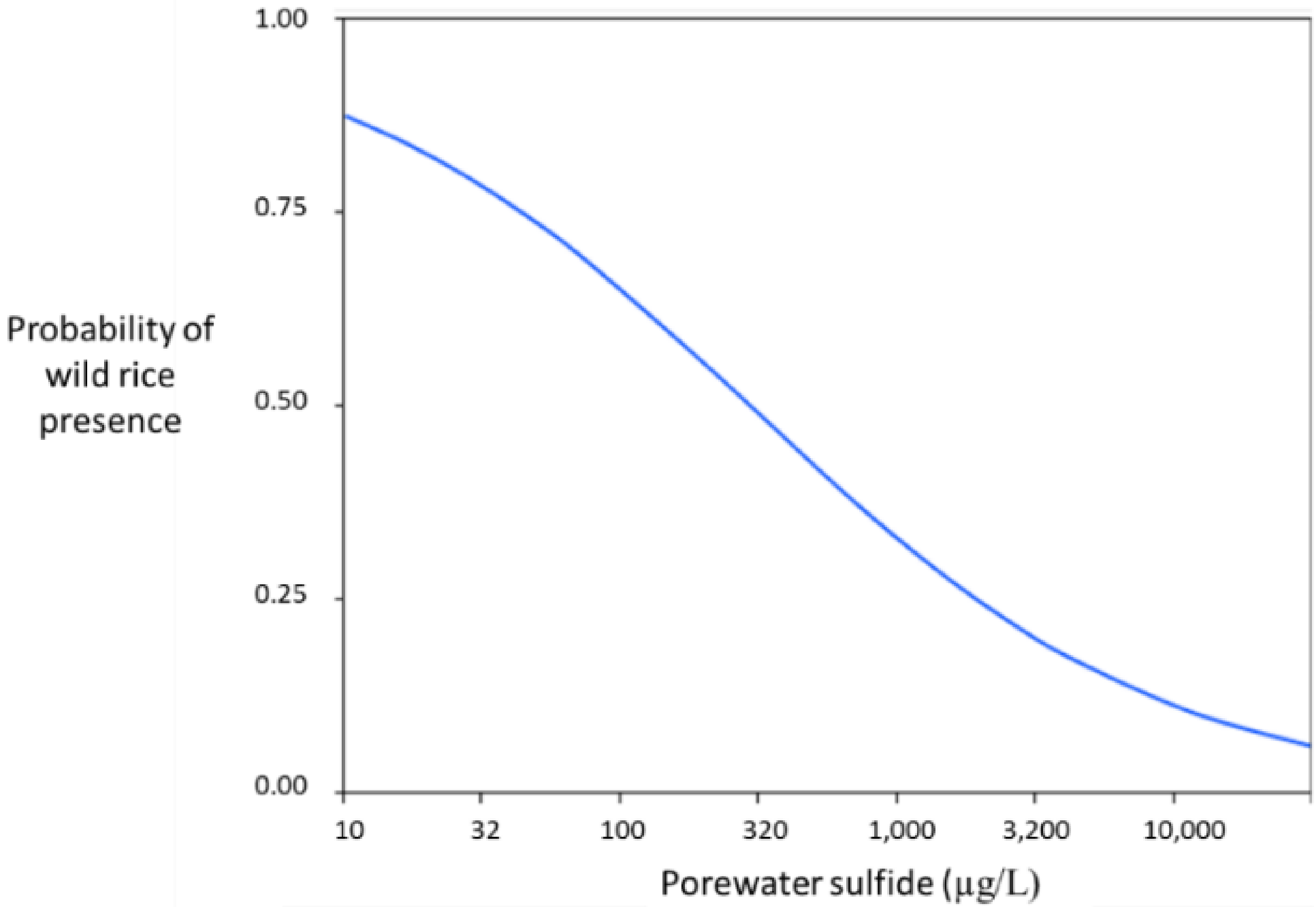
Percent of waterbodies misclassified



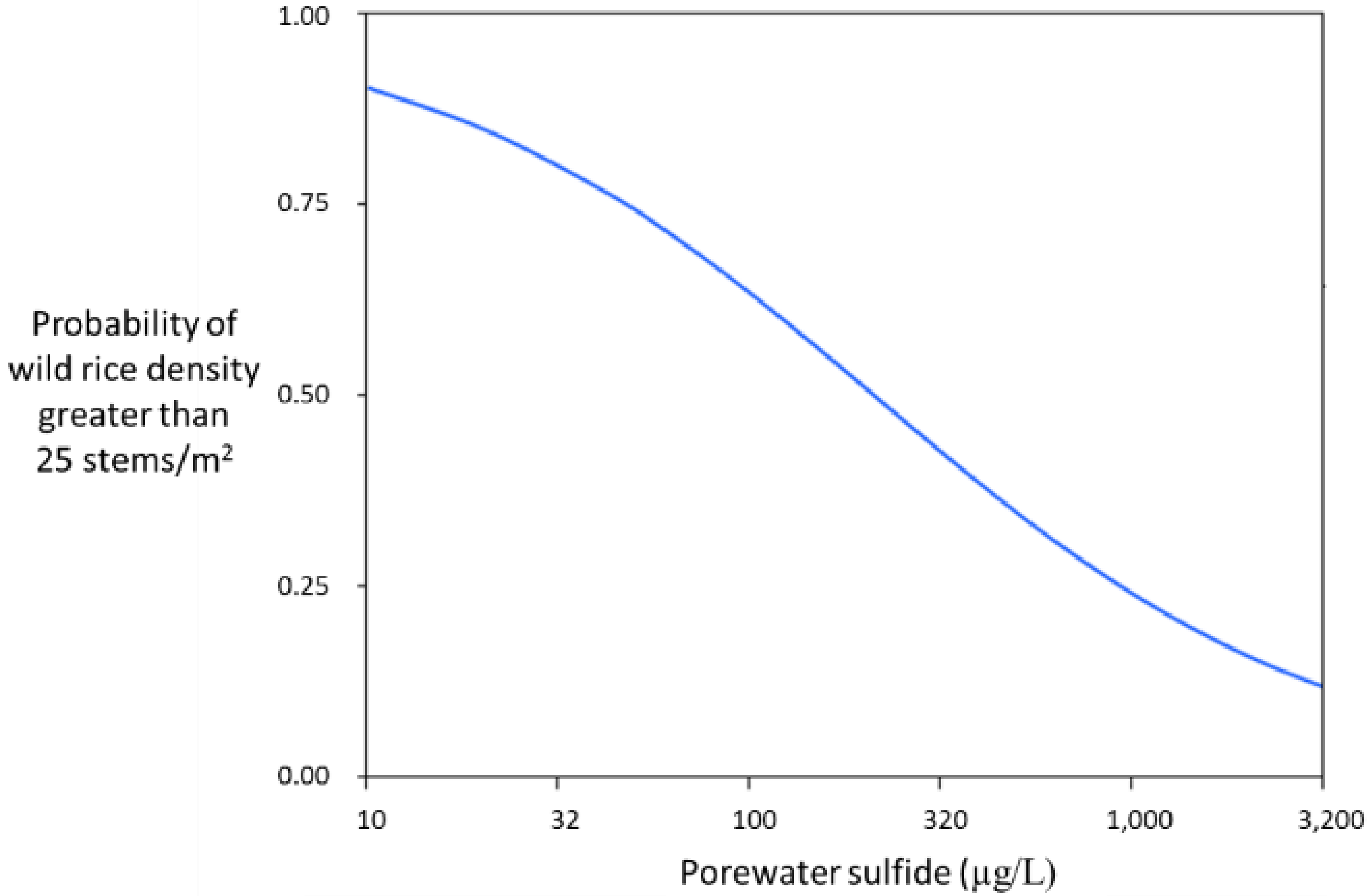
Field survey of lakes & streams (Amy Myrbo)

- 108 different lakes and streams sampled for surface water, sediment porewater, & sediment.
- 67 of 108 waterbodies had wild rice.
- When field crew couldn’t find wild rice, sediment was sampled at waterlilies, since they often co-occur with wild rice.
- Sampling sites with and without the species of interest is a standard method in conservation biology to discover what variables control favorable habitat (via binary logistic regression).
- 65 variables measured at each site.

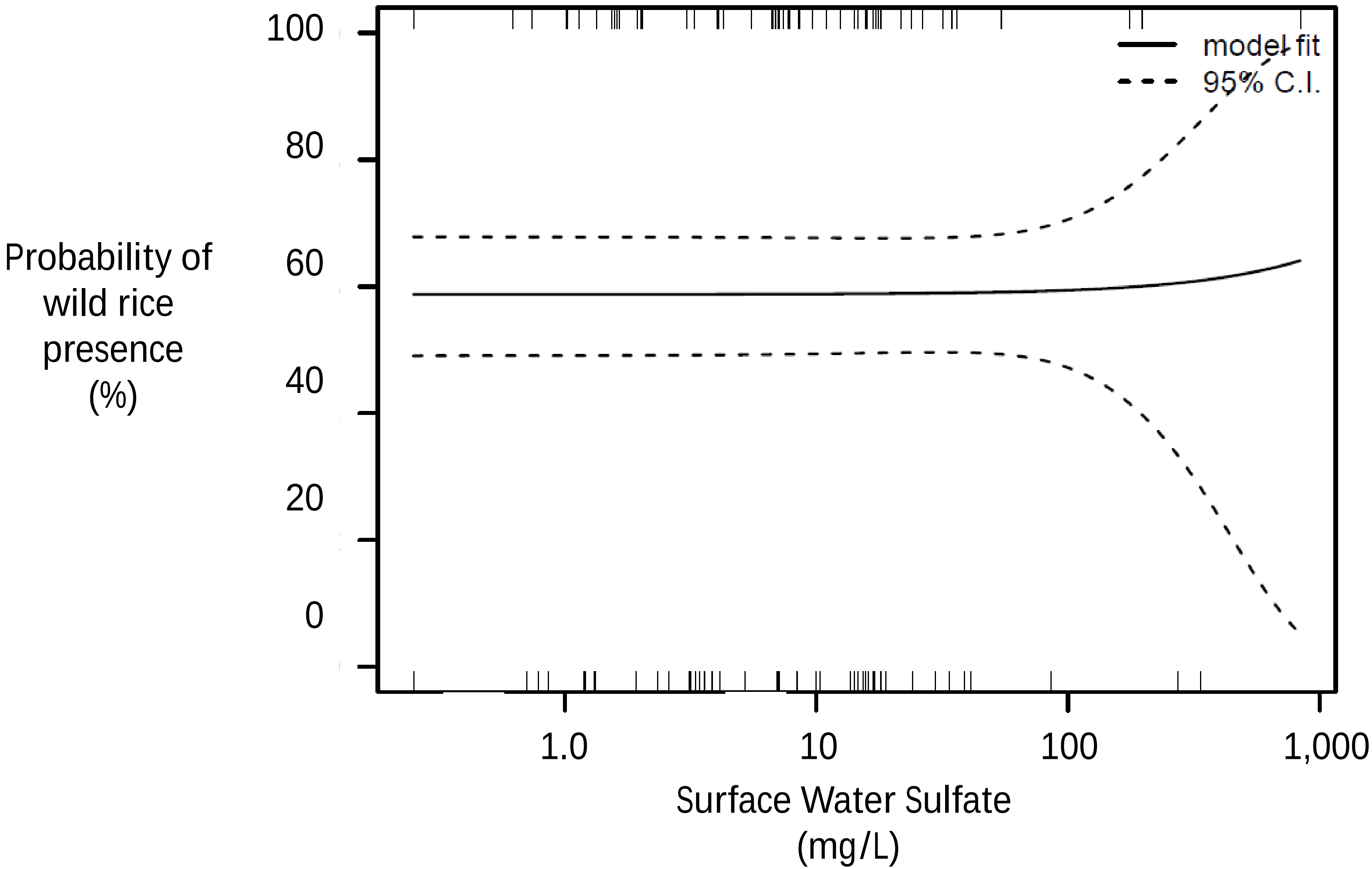
Probability that wild rice is present declines as porewater sulfide increases



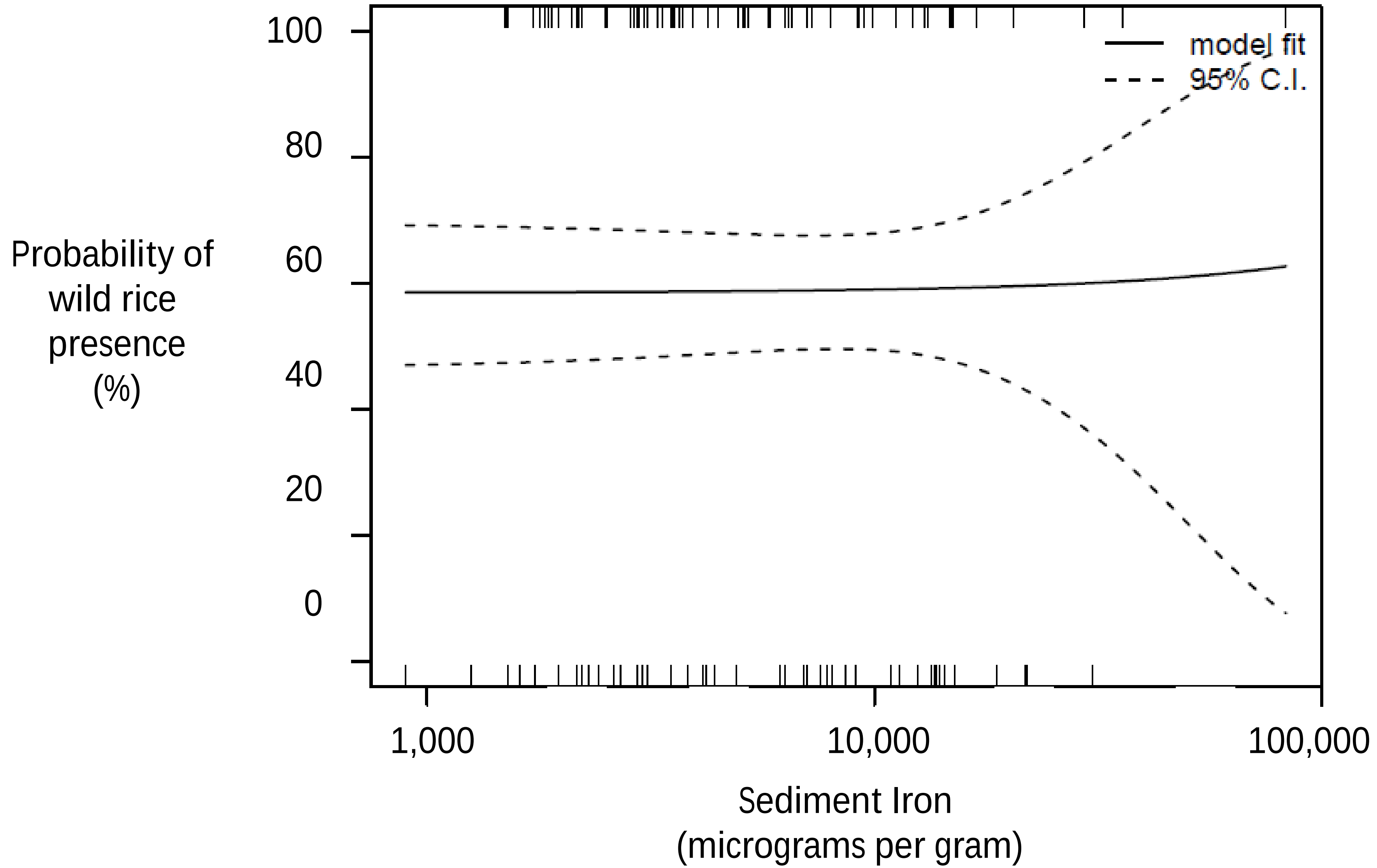
Probability that wild rice is dense declines as porewater sulfide increases



So porewater sulfide can only be predicted by considering all 3 variables simultaneously



Probability of wild rice presence as a function of sediment iron



Probability of wild rice presence as a function of Sediment Total Organic Carbon