# Wild Rice Sulfate Standard – Summary of Findings and Preliminary Recommendations Legislative Briefing Document; February, 2014

## Background:

In 2011, the Minnesota Legislature appropriated funding and directed the Minnesota Pollution Control Agency (MPCA) to conduct research on the effects of sulfate and other substances on the growth of wild rice. This research was intended to inform an evaluation of the existing wild rice sulfate standard. In 1973, the MPCA adopted and the U.S. Environmental Protection Agency (USEPA) approved that standard to protect the beneficial use of "water used for production of wild rice" during periods when the rice "may be susceptible to damage by high sulfate levels." (Minn. R. 7050.0224, subpart 2).

Following the development of a detailed research protocol in 2011, in 2012 the MPCA contracted with groups of scientists at the University of Minnesota Duluth and Twin Cities to undertake a Wild Rice Sulfate Standards Study. The Study's main hypothesis is that wild rice is impacted by sulfate via the conversion of sulfate to sulfide in the rooting zone of the plants. Data collection was completed in December 2013 and is documented in individual reports from the researchers (see Table 1 for a summary of Study components).

During January and February 2014, MPCA staff integrated the study results; analyzed the data as a whole; gained input from the Wild Rice Standards Study Advisory Committee; and reviewed existing monitoring data, other relevant scientific studies/information, and the original basis for the wild rice sulfate standard to develop findings and preliminary recommendations regarding the standard. In evaluating the existing sulfate standard, the MPCA has the responsibility of demonstrating that any recommended changes to the standard have a scientific basis and would protect the beneficial use of "water used for production of wild rice."

## Findings and Preliminary Recommendations Regarding the Wild Rice Sulfate Standard

#### **Key Findings:**

- 1. **Sulfate is not directly toxic to wild rice**. Both the MPCA Study and the research commissioned by the Minnesota Chamber of Commerce support this conclusion. However, sulfate in the surface water can be converted by bacteria to sulfide in the rooting zone of wild rice (see Figure 1).
- 2. **Sulfide** is **toxic to wild rice.** The MPCA Study demonstrated that elevated sulfide concentrations were toxic to wild rice seedlings. Hydroponic experiment data showed deleterious effects of sulfide on seedling plant growth when sulfide exceeded the range of 150 to 300  $\mu$ g/L.
- 3. Sulfide in the sediment is affected by the amount of sulfate in the water column, and the amount of iron in the sediment. Data from a majority of the field sampling sites show that the range of 150 to 300 μg/L sulfide in the sediment relates to a water column concentration of sulfate between 4.3 and 16.2 mg/L. This range illustrates that conditions at some of the field sites are more effective than others at converting sulfate to sulfide, in part due to the availability of iron in the sediment (see Figure 1).

# **Preliminary Conclusions and Recommendations:**

- 1. The 10 mg/L sulfate standard is needed and reasonable to protect wild rice production from sulfate-driven sulfide toxicity. The MPCA will also consider including a sediment sulfide concentration as a component of this water quality standard, in the range of 150 to 300 µg/L sulfide.
- 2. The 10 mg/L wild rice sulfate standard should continue to apply to both lakes and streams. Analysis of the field data does not support placing lakes and streams into separate subclasses. Iron availability, not water body type, appears to be a key controlling factor in the concentration of sulfide.
- 3. **Site-specific standards are expected for some waters**. Considerable data suggest that in some cases the development of a site-specific standard would be protective of wild rice production. This is most likely to

occur in waters where the sediment iron is elevated and therefore a higher sulfate water column concentration may not result in a sulfide sediment concentration above 150 to 300  $\mu$ g/L. There are also data to suggest that a site-specific standard lower than 10 mg/L may be needed for waters where sulfate is more efficiently converted to sulfide.

- 4. MPCA will continue to explore if the sulfate standard is needed to protect paddy-grown wild rice production. The Study data do not suggest that paddy-grown wild rice is less susceptible to impacts from elevated sulfide. However, the land- and water-management activities associated with paddy wild rice production likely reduce the potential for sulfide production in the sediment.
- 5. MPCA does not currently have a recommendation regarding the "period of susceptibility" of wild rice to sulfate effects, but will continue to analyze data to further explore this question. The sediment incubation experiment data show that sulfate can be converted to sulfide in both warm and cold conditions, and that sediment sulfide concentrations decrease once sulfate concentrations in the overlying water decrease. This is a complex interaction and more data analysis is needed before recommendations can be developed about this important question; any recommendation may also need to consider site-specific factors that affect this question.
- 6. Consideration should be given to changing the use class of the wild rice sulfate standard: The MPCA is considering moving the wild rice sulfate standard from Class 4 where it currently resides to Class 2 and creating a new subclass to clarify that the wild rice sulfate standard is designed to protect the growth of wild rice grains for consumption by humans and wildlife. The MPCA is also considering revising the term "water used for production of wild rice." The MPCA has received comments asserting this wording is not the best descriptor for natural stands of wild rice that provide benefits to humans and wildlife.

## **Next Steps**

- In late March, MPCA will meet with the Wild Rice Sulfate Standards Advisory Committee and Minnesota
  Tribes in separate meetings to get their feedback on the MPCA's Findings and Preliminary
  Recommendations. MPCA will also continue to seek feedback from USEPA and the Study researchers.
- MPCA technical staff will continue to develop and assemble material for a technical support document
  that will be used in wild rice rulemaking. Further analysis of results and data from the outdoor container
  experiments and sediment incubation study will also continue. MPCA will, as appropriate, refine the
  recommendations based on the input received and this continued analysis.
- The MPCA is also contracting for expert scientific review of the wild rice study reports and specific aspects of the MPCA's preliminary recommendations and rationale about whether a change to the current 10 mg/L wild rice sulfate standard is warranted, and the nature of the change. The expert review panel will likely be convened in late spring 2014, and will include the opportunity for interested stakeholders/members of the public to address the panel.
- In a parallel effort MPCA is working to develop factors that will help identify specific waterbodies as "water used for production of wild rice." These factors will be used in case-by-case determinations and to inform rulemaking to identify specific waterbodies as "water used for production of wild rice" in Minnesota Rules Chapter 7050. The goal is to put these factors on public notice for a 30-day public comment period in March 2014. Comments received will be used to help refine the factors.
- Any proposed change to the wild rice standard would be adopted into Minnesota's water quality standard rule (Minnesota Rules Chapter 7050) in accordance with the requirements of the Minnesota Administrative Procedures Act and would require the approval of the USEPA. MPCA is targeting fall 2014 for having the rule package ready for public notice and comment.

#### Considerations

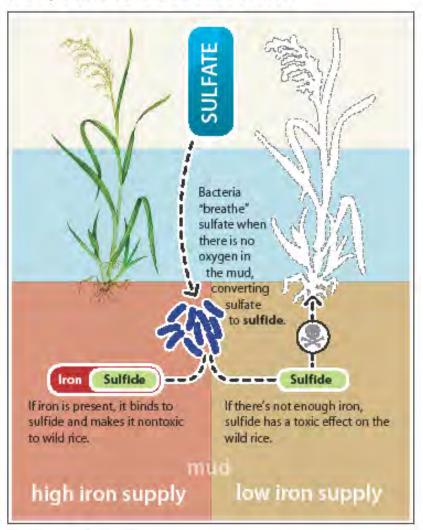
- As a result of the Wild Rice Sulfate Standard Study and other data collection efforts, MPCA now has a much better understanding of the relationship between wild rice presence and absence, sulfate in the water column, and sulfide and iron in sediment porewater. This includes a reinforcement of the hypothesis that sulfate is not directly toxic to wild rice, but is converted to sulfide, which is toxic to wild rice (this is supported by the hydroponics and field data).
  - This enhanced understanding is very important because it helps explain why a subset of
    waterbodies have elevated sulfate concentrations and apparently healthy wild rice stands, when
    most waterbodies that have successful wild rice beds have relatively low sulfate concentrations.
  - This enhanced understanding which MPCA did not have prior to the study will be invaluable
    in implementing the wild rice sulfate standard. This will be particularly valuable in evaluating the
    need for site-specific standards and developing such standards.
- Any changes to the current wild rice sulfate standard will take some time to implement. The Clean Water
  Act requires implementation of the existing standard while any proposed changes are going through the
  administrative process and USEPA approval.
- The MPCA wastewater permitting approach for the current wild rice sulfate standard is as follows:
  - Where elevated discharge sulfate levels are suspected but no sulfate data are available, discharge monitoring requirements are being added to NPDES permits as they come up for reissuance every five years.
  - If discharge data collected during the five year permit cycle indicate a potential to violate the sulfate standard for wild rice, and it is determined that a water used for production of wild rice may be affected by the discharge, a discharge limit will be added to the permit upon reissuance.
  - If discharge limits cannot be met immediately a schedule of compliance will be included in the permit to allow for steps such as evaluation of treatment technologies, design, procurement of funds, and construction.
  - The compliance schedule will contain a requirement that the facility either demonstrate compliance with the limit as soon as possible or submit a variance request with the application for permit reissuance.
    - It is important to note that the sulfate discharge limit included in a permit may not be identical to the wild rice sulfate standard. When setting discharge limits, MPCA factors in variables such as dilution in the receiving water and distance between the discharge point and the water used for production of wild rice. The discharge limit is set such that the standard is achieved at the water used for production.
  - Note that in accordance with federal law, compliance schedules and variances are typically not allowed for new dischargers, which must meet the effluent limit upon commencement of operations.
  - Implementation of the existing standard does not preclude permitted facilities from requesting a site specific wild rice sulfate standard. The MPCA can employ the knowledge gained about site-specific standards immediately, where conditions indicate that such a standard likely is needed. MPCA is exploring options for addressing site-specific standards requests efficiently.

Table 1. Purpose, strengths, and limitations of Study components.

	Field Survey	Laboratory Hydroponic Experiments		Outdoor Container Experiments	Collection and Analysis of Rooting Zone Depth Profiles	Sediment Incubation Laboratory Experiments
		Sulfate (SO <sub>4</sub> )	Sulfide (H₂S)			
Main Purpose	Expand understanding of environmental conditions correlated with presence/ absence of wild rice.	Evaluate effects of sulfate on wild rice seed germination and growth of sprouts.	Evaluate effects of sulfide on wild rice seed germination and growth of sprouts.	Evaluate effects of sulfate on wild rice plants over full life cycle, and multiple years.	Characterize sulfate, sulfide, and iron in the rooting zone of wild rice container experiments and field sites.	Evaluate effect of temperature on movement of sulfate into and out of underlying sediment.
Endpoints	Concentrations of chemicals in surface water & rooting zone (e.g. SO <sub>4</sub> & H <sub>2</sub> S vs. wild rice occurrence).	Growth of wild rice sprouts (biomass, root & shoot elongation). Germination rate of seeds.	Growth of wild rice sprouts (biomass, root & shoot elongation). Germination rate of seeds.	Growth of wild rice (biomass, plus number & weight of seeds). Sulfide concentrations in rooting zone.	Concentrations of sulfate, sulfide and iron in porewater.	Sulfate concentrations in overlying water over time; SO <sub>4</sub> , iron, H <sub>2</sub> S, & anion tracers in sediment porewater. Simple model.
Key Strengths	Most reflective of actual environmental conditions. Multiple wild rice stands and breadth of characteristics sampled.	Controlled dose-response experiment. Controlled exposure to known concentrations of SO <sub>4</sub> .	Controlled dose-response experiment. Controlled exposure to known concentrations of H <sub>2</sub> S.	Controlled dose-response experiment. Includes natural sediment matrix as rooting environment. Involves entire growth cycle, multiple years.	Provides additional data to understand and interpret container experiments and field sites.	Controlled experiment with natural sediment and water.
Key Limitations	Least controlled. Annual visit for most sites, 3x/year for a subset. Not definitive on cause and effect.	Only evaluates early growth stages. Leading hypothesis is that sulfate is converted to sulfide, which is directly toxic.	Only evaluates early growth stages. Unable to simultaneously keep roots anaerobic & shoots aerobic.	Full effect of sulfate may take longer than several years to realize. No groundwater movement.	Utility lies in the integration of this data with the other Study components, not in this data set alone.	Provides preliminary assessment of sediment from two sites that may inform but is not fully transferrable to other sites. No groundwater movement. No wild rice plants grown.

Figure 1. The relationship of sulfate, sulfide and iron in surface water and sediment.

# When the mud has a good supply of iron, sulfate does less harm



#### The iron-sulfide battle

The amount of iron and sulfide are dynamic and one affects the other. If enough new iron is flowing into the mud (e.g. via groundwater), then even a lake or stream with high sulfate levels can support wild rice. On the other hand, enough sulfate can overwhelm the supply of iron and make sulfide levels toxic.