Proposal

Minnesota Pollution Control Agency, March 24, 2015

Protecting wild rice from excess sulfate

What is the issue?

Wild rice growth is negatively affected by excess sulfate, a naturally occurring chemical that can also be found in discharges from mining operations, municipal wastewater treatment plants, and industrial facilities. Minnesota adopted a wild rice sulfate standard in 1973 to protect wild rice from excess sulfate, but recent questions have prompted a review of the standard and additional research into the effects of sulfate on wild rice.

Why is it important?

Wild rice is an important cultural and economic resource in Minnesota. It provides income to those who harvest and market wild rice, and is food for waterfowl. But the cost to businesses and communities of limiting sulfate discharges can be significant. It's critical that the standard to protect wild rice be based on the best available science, and that there is flexibility in implementation to help address cost concerns.

Key findings and draft recommendations

- Sulfate is converted to sulfide by bacteria in the sediment in which wild rice is rooted. Sulfide's toxicity to animals and plants, including wild rice, varies with its concentration. As sulfide levels in the sediment increase, the likely presence of wild rice decreases. The MPCA is currently recommending a sulfide concentration threshold of 0.165 milligrams per liter (mg/L; 165 micrograms per liter) as protective of wild rice.
- Some variables, especially iron and organic carbon in the sediment, affect the amount of sulfide produced from sulfate. So while sulfate may negatively affect wild rice, **no single level of sulfate can be protective of wild rice in all water bodies**. Sulfate is converted to sulfide in each water body differently depending on the concentrations of iron and organic carbon.
- An equation that accounts for the iron and organic carbon variability in sediment among water bodies can calculate a protective sulfate concentration for a water body that allows wild rice growth and self-perpetuation. The equation to calculate the proper sulfate concentration:

$$\textbf{Sulfate} = \textbf{0.0000136} \times \textbf{Organic Carbon}^{-1.410} \times \textbf{Iron}^{1.956}$$

The MPCA proposes determining protective sulfate concentrations for each wild rice water by collecting sediment samples and measuring iron and organic carbon concentrations in wild rice stands, and then entering iron and carbon sampling data into the equation above to get a protective sulfate value.

Wild rice waters: The standard will apply in lakes, streams, and wetlands that are wild rice waters. MPCA has compiled a draft list of wild rice waters, along with a process to add waters to the list over time. The agency proposes that a sulfate standard is not needed to protect commercial rice paddies.

About this study

In 2012, the MPCA contracted with scientists at the University of Minnesota's Duluth and Twin Cities campuses to conduct a study of the relationship between sulfate, sulfide, and wild rice with field surveys, laboratory experiments, and outdoor container experiments. In early 2014, MPCA integrated and analyzed the data, got input from the study's advisory committee, and developed a draft analysis that was subjected to scientific peer review in summer 2014. The analysis was then refined based on the peer reviewers' recommendations.

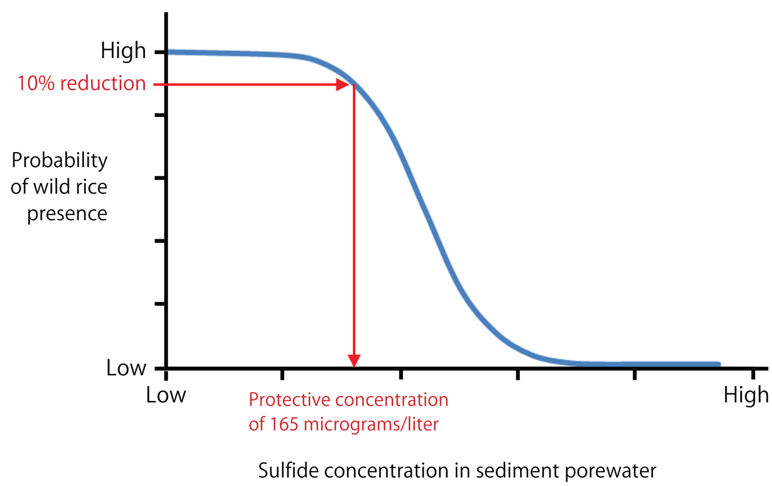
Detailed scientific findings

The following provides details on the relationships between wild rice, sulfate, sulfide, iron, and organic carbon, and the proposed approach to protecting wild rice from sulfide impacts due to elevated sulfate.

1) The recommended sulfide concentration

The sulfide concentration in water contained in the sediment (known as sediment porewater) is the measure that will govern the ultimate protective sulfate concentration. The MPCA is recommending a sulfide concentration threshold of 0.165 mg/L (165 micrograms per liter). In the field survey data, this concentration corresponds to the sulfide porewater level at which a 10% reduction in the probability that wild rice would be observed at a site. (Field data best characterizes the conditions under which wild rice populations are self-perpetuating over many generations. The laboratory and outdoor container results, which did not examine multiple generations, are compatible with the field data.)

In the field survey of 112 natural lakes, wetlands, streams, and rivers, wild rice was observed less frequently as the sulfide concentration increased. A line was fit to the data, allowing the calculation of the sulfide concentration that corresponds to a 10% reduction in the probability that wild rice would be observed at any given site.



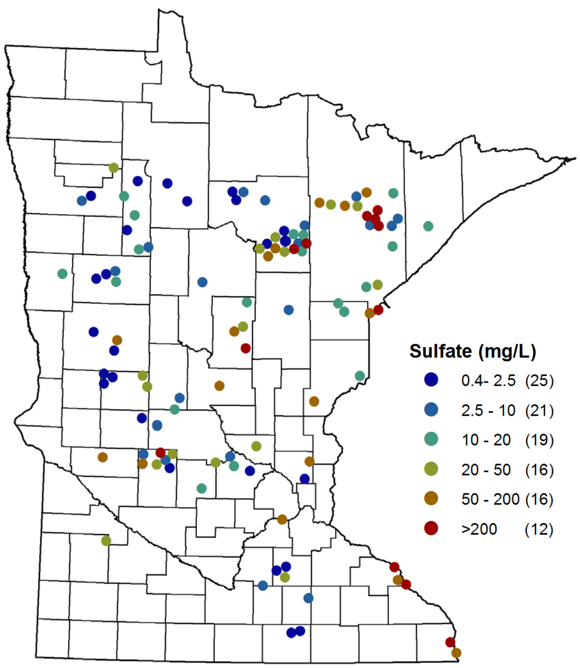
2) The conversion of sulfate to sulfide

Sulfide found in the sediment porewater of lakes, streams, and wetlands is primarily generated from sulfate diffused into the sediment from overlying water. The relationship between elevated sulfate in a water body and sulfide impacts on wild rice is primarily affected by:

> **Organic carbon:** The rate of conversion of sulfate to sulfide by bacteria in the sediment varies from one waterbody to the next, primarily due to different levels of total organic carbon in the sediment; total organic carbon is the food for the sulfide-producing bacteria. Higher levels of organic carbon in the sediment can lead to more sulfide being produced from sulfate in the overlying water.

Iron: If iron is available in the sediment, it can interact with the sulfide and form a solid that does not affect wild rice. The concentration of iron in sediment is difficult to predict, so must be measured at each site. Higher levels of iron in the sediment can lead to less sulfide being available to impact the wild rice.

For more, see graphics in accompanying "Protecting wild rice from too much sulfate" document (and online at www.pca.state.mn.us/yp3h36h).



Protective sulfate concentrations for the lakes and streams in the MPCA field survey, calculated with Equation 1. Numbers in parentheses are the number of sites in the indicated sulfate range.

3) Using a structural equation model

Encouraged by the study's peer reviewers, the MPCA developed a structural equation model (SEM) to predict the sulfide concentration in sediment porewater based on the concentrations of surface water sulfate, sediment iron, and sediment organic carbon observed at each site. It is assumed that the concentrations of these variables are stable over the long term. SEM is appropriate for modeling processes that involve indirect effects and feedback between variables like dissolved iron and sulfide. The model predicts that a given concentration of sulfate can produce different concentrations of sulfide depending on the concentrations of iron and total organic carbon in the sediment at a given site.

4) Calculation of sulfate concentration protective of wild rice

The concentration of sulfate that would be protective of wild rice at a site can be calculated using this equation from the MPCA's model:

$$\textit{Sulfate} = 0.0000136 \times \textit{Organic Carbon}^{-1.410} \times \textit{Iron}^{1.956}$$
(Equation 1)

Sediment organic carbon and sediment iron data from a wild rice water must be entered into the equation to get the protective concentration of sulfate. Calculating the appropriate sulfate level based on iron and total organic carbon measurements is a more appropriate approach than relying on a single sulfate concentration as a protective threshold for all sites.

5) No single sulfate value would be protective of wild rice at all sites

The range in protective sulfate concentrations can be illustrated by calculating the sulfate thresholds for the sites sampled during the MPCA wild rice field survey. For instance, a sulfate level of 10 mg/L would be protective of wild rice for 58% of the sites in the field survey (that is, the resulting sulfide concentration is predicted to be less than 165 micrograms per liter). However, for 42% of the sites, porewater sulfide concentrations are predicted to be greater than 165 micrograms per liter at a sulfate concentration of 10 mg/L in the overlying water, and the wild rice populations in those waters would be more likely to decline over time. Even a sulfate value as low as 2.5 mg/L would leave some vulnerable sites unprotected, while sites naturally high in iron and low in organic carbon would be protected at sulfate concentrations higher than 200 mg/L.

6) Commercial wild rice paddies

Water-environment management in paddies likely produces sediment conditions that are rarely seen in natural wild rice waters. In particular, sediment dewatering from July to September may oxidize the sediment, and the use of nitrogen fertilizer increases primary production significantly over natural waters. Both of these may reduce the production of sulfide from sulfate, or the impact of sulfide on plants. Therefore, MPCA proposes that a sulfate standard is not needed for commercial wild rice paddies. Data from commercial wild rice paddies were not used to calibrate the model and develop the equation discussed above.

Sample calculations

To illustrate the calculation of protective sulfate concentrations, Equation 1 was applied to three MPCA study site locations: Little Round Lake, Elk Lake, and Rice Lake. These sites are in minimally disturbed lakesheds, and have widely varying protective sulfate concentrations (see the table below). Note that these examples are for illustrative purposes only.

Study site	Total organic carbon in sediment (%)	Extractable iron in sedment (µg/g)	Protective sulfate concentration (mg/L)
Little Round Lake	27.5	3,069	0.8
Elk Lake	10.2	8,480	25
Rice Lake	35.6	50,389	140

Sediment sample considerations

Protecting wild rice waters from elevated sulfate depends on collecting iron and organic carbon sediment data where the wild rice is growing. Prior to formally proposing changes to the existing wild rice sulfate standard through rulemaking, the MPCA intends to define the number of organic carbon and iron sediment samples needed for a body of water to adequately calculate a protective sulfate value. Protocols to collect and analyze sediment samples are being prepared and will be made available on the MPCA web site and included in a technical support document prior to formal rulemaking.

Wild rice waters: Where the standard applies

The 2011 Minnesota Legislature directed the MPCA to identify the specific surface waters "to which the wild rice water quality standards apply." The agency has compiled a draft list of wild rice waters — identified on a map on the MPCA web site (www.pca.state.mn.us/r6wxpf9) — and developed criteria and a process to add waters to the list over time. MPCA intends to complete rulemaking to list wild rice waters, and proposes to replace the existing rule language "water used for the production of wild rice" with the phrase "wild rice waters," to better describe the beneficial use the standard is intended to protect.

The draft list of 1,300 wild rice waters was developed using information from various wild rice inventories. MPCA also sought and received input from the Minnesota Department of Natural Resources and Minnesota Indian Tribes. Acreage, density, and the importance of wild rice to humans and waterfowl were considered when developing the proposed approach for identifying wild rice waters. The agency also consulted wild rice harvester and field survey databases, and responses to a 2013 formal call-for-data by the MPCA. The information resources used by MPCA to formulate the draft list of wild rice waters are described on the MPCA web site (www.pca.state.mn.us/r6wxpf9).

Updating the wild rice waters list

A comprehensive inventory of Minnesota's natural wild rice stands does not exist; MPCA recognizes that the wild rice waters list will need periodic updates as new information becomes available. After the initial rulemaking to identify wild rice waters, MPCA intends to consider adding waters approximately every five years. New waters will have to meet the following proposed definition of "wild rice water":

> *"Wild rice water" means a surface water of the state that contains a self-perpetuating population of wild rice plants, either currently present or that have been present in the given waterbody since November 28, 1975. The self-perpetuating wild rice population must be represented by a minimum of 8,000 wild rice stems over the surface of a lake, wetland, or reservoir waterbody, or a minimum of 800 wild rice stems over a river-mile reach for a riverine waterbody. Waters designated as wild rice waters are specifically listed as such in Minn. R. 7050.0470 and are identified with the symbol [WR] preceding the name of the waterbody.*

To provide some context to the proposed definition of wild rice waters, 8,000 stems in a lake roughly equate to two stems per square meter over one acre. Seed from 8,000 stems has the potential to feed approximately 12 ducks during a one week migratory stop.

Standard implementation considerations

MPCA intends to move ahead with rulemaking beginning in 2015 to refine the existing wild rice sulfate water quality standard to reflect the most up-to-date science, and to identify wild rice waters. Prior to rulemaking, the MPCA will consider how to use the new understanding of the relationship between sulfate, sulfide, total organic carbon, iron, and wild rice to inform regulatory decisions, to more precisely protect wild rice waters from potential sulfate impacts, and better ensure efficient and effective use of resources.

MPCA will engage with interested stakeholders to discuss:

- the proposed approach for revising the sulfate standard
- approaches to monitor for wild rice and sediment conditions
- the new science as it relates to regulatory decisions

Toward that end, MPCA will schedule meetings with Minnesota Tribes, the Wild Rice Standards Advisory Committee, and EPA in April and May of 2015 to further describe and get input on the proposed approach. MPCA also welcomes opportunities to meet with other interested parties about this proposal.

The agency will continue to refine the proposal based on feedback and any new information received. At the same time, MPCA technical staff will continue to develop the more detailed technical documentation needed for the formal rulemaking proposal. We will also be developing the data collection protocol for gathering the information needed to calculate a protective level of sulfate. Field data collected this summer will help to inform those details.

We anticipate having a formal rulemaking package, including draft rule language and the detailed Statement of Need and Reasonableness, ready for discussion in late summer or early fall of 2015. The rulemaking process will include multiple opportunities for informal and formal public comment, and is expected to last approximately two years. We will consider any new data and input during this process.