Wild Rice Sulfate Study

Summary and next steps

In 2010, the Minnesota Pollution Control Agency (MPCA) initiated a multi-year effort to clarify implementation of the state's wild rice sulfate standard. Based on a review of available information, the MPCA determined that additional studies were needed to evaluate the effects of sulfate on wild rice production. In 2011 the Minnesota Legislature provided direction, and funding from the Clean Water, Land and Legacy Amendment, to gather this additional information.

Study information

The goal of the Wild Rice Sulfate Standard Study is to enhance understanding of the effects of sulfate on wild rice and to inform a decision as to whether a revision of the wild rice sulfate standard is warranted. The Study consists of parallel research efforts (Study components) conducted by groups of scientists at the University of Minnesota Duluth and Twin Cities under contract with the MPCA.

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. Each of the Study components has a specific purpose and associated strengths and limitations, as noted in Table 1. The Study was designed so individual components together will provide a better understanding of the effects of sulfate on wild rice. The Study components are:

- **Field survey of wild rice habitats** to investigate physical and chemical conditions correlated with the presence or absence of wild rice, including sulfate in surface water and sulfide in the rooting zone
- **Controlled laboratory hydroponic experiments** to determine the effect of elevated sulfate and sulfide on early stages of wild rice growth and development
- **Outdoor container experiments using natural sediments** to determine the response of wild rice to a range of sulfate concentrations in the surface water, and associated sulfide in the rooting zone, across the growing season
- **Collection and analysis of rooting zone depth profiles** of dissolved chemicals at wild rice container experiments and field sites to characterize sulfate, sulfide, and iron
- **Sediment incubation laboratory experiments** to explore the difference ambient temperature has on the rate that elevated sulfate concentrations in water enter underlying sediment and convert to sulfide, and to what degree sulfate is later released back into the overlying water

Some of the reports include information about the sulfate or sulfide concentration(s) at which effects on wild rice were observed; however, it would be premature to conclude that those concentrations are directly comparable to the wild rice sulfate standard. Each Study component uses a different approach to examine how sulfate might affect wild rice. The results of each component must be analyzed and integrated with the other components before any recommendations can be made about the standard.

Data collection was completed in December 2013 and is documented in individual reports from the researchers. Some lab analysis will occur during January 2014 and be added to the report(s) when complete. During January and February 2014, MPCA staff will integrate the results; analyze the data as a whole; and review existing monitoring data, other relevant scientific studies/information, and the original basis for the wild rice sulfate standard to determine if a change to the standard is warranted and, if so, what it should be. The MPCA will release preliminary recommendations by the end of February 2014.

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_4)	Sulfide (H_2S)			
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_4 & H_2S 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_4, iron, H_2S, & 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_4.	Controlled dose-response experiment. Controlled exposure to known concentrations of H_2S.	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.

Summary of Study Components

The Study researchers provided reports and the associated data for each of the Study components. Appendix A lists the reports and data files associated with each of the Study components, all of which are available on the MPCA's FTP site at ftp://files.pca.state.mn.us/pub/tmp/wildRice. The reports include general conclusions from each component, but do not integrate the data and information across the Study components. The following paragraphs briefly summarize each Study component and highlight the MPCA's next steps and considerations in analyzing and integrating the Study components.

Field Survey of Wild Rice Habitats

The purpose of the field survey was to expand understanding of environmental conditions correlated with the presence and absence of wild rice. This included investigating both the water quality of the overlying water and the sediment characteristics of water bodies with and without the presence of wild rice. The data are valuable because the field survey collected and analyzed a wide range of environmental characteristics *in situ* (i.e. in the "natural" environment). However, they are limited because it is hard to determine the direct cause and effect mechanism of any observed correlations.

Minimal statistical analyses of the data are completed to date because laboratory analyses are still ongoing and the data have yet to be fully merged into a comprehensive database. Key activities to be completed by the MPCA in January and February include:

- Complete the merger of the field and laboratory data
- Develop summary statistics, and complete correlation and regression analysis of the variables
- Identify any patterns or differences in the data sets from the lake, stream and paddy rice sites
- Relate field water chemistry and sediment statistics to wild rice presence and absence

Controlled Laboratory Hydroponic Experiments

This involved evaluating the effects of sulfate and sulfide on wild rice seed germination and growth of sprouts in a laboratory setting. The data are valuable because the controlled laboratory setting allowed researchers to vary the concentration of a single parameter – in this case sulfate or sulfide – and measure any effect on the plants, thereby establishing a dose-response relationship. The laboratory experiments were limited as the wild rice proved very difficult to grow beyond the seedling stage in the laboratory. Consequently experiments were only conducted on early stages of wild rice germination and growth.

Over the next two months, MPCA research scientists will be further verifying and analyzing the experimental results, as follows:

- Review the data and statistical analyses for sulfate and sulfide; complete additional statistical analysis as needed to further evaluate the effects of sulfate and sulfide on seeds and sprouts

Outdoor Container Experiments

Container experiments were conducted to evaluate effects of sulfate on wild rice plants over the full growing cycle of the plants. Because of previous work done at the experimental research station where this Study component was conducted, the researchers observed wild rice over three years of sulfate additions. During the third year (2013) sulfide measurements were made in the sediments of these experiments.

The container experiments represent another type of dose-response experiment against which the laboratory results and field survey data can be compared. The container experiments are more representative of natural conditions in that the plants are growing in lake sediment. However, they have the limitation of being less controlled than the laboratory experiments and are still not a completely "natural" system as compared to data from the field survey. For example, the outdoor containers did not lose or gain any water to or from groundwater. This provided control to the experiment but did not fully mimic conditions in natural wild rice beds, where groundwater could be supplying chemicals that alter the effect of sulfate in the overlying surface water or sulfide in the sediments.

During January and February, MPCA analysis of the container experiment results will include:

- Review the data and statistical analysis; complete additional statistical analysis as needed to further analyze and describe the effect of elevated sulfate and sulfide on wild rice
- Compare the sulfate concentrations (calculated and measured) to the rooting-zone depth profile data, to examine the relationship between sulfate in the water column and sulfide in sediments
- Examine the cumulative effect of added sulfate over the three years, and the relationship between the sulfate doses and the accumulation of sulfide in the sediment

Collection and Analysis of Rooting Zone Depth Profiles

This Study component involved detailed analysis of the sediment at field survey sites and the container experiments to provide detailed information about the sediment and porewater chemistry (particularly sulfate, sulfide, and iron) of the wild rice rooting zone. The purpose of this effort was to provide data to help interpret the results of the field survey and container experiments. As noted in the summaries above, during January and February the data from this Study component will be evaluated with the water quality data from the field sites and container experiments to help understand what the wild rice roots are being exposed to, and also inform the understanding of how iron may mitigate the effects of sulfide production in the rooting zone of the sediment.

Sediment Incubation Laboratory Experiments

This Study component enhanced the understanding of the effect of temperature on movement of sulfate into and out of underlying sediment. The experiment was conducted in the laboratory with sediment and water collected from two sites in northeastern Minnesota, but did not include any wild rice or other rooted aquatic plant growth. While the experiment was not conducted using a flow-through design, water column mixing was part of the experimental method so this was not a completely static incubation. MPCA will review the data from this Study component to help inform the MPCA's recommendations about the current wild rice sulfate standard, particularly the "period during which the rice may be susceptible to damage by high sulfate levels."

Data integration and development of preliminary recommendations about the Wild Rice Sulfate Standard

During January and February 2014, MPCA staff will analyze the data and integrate the information gained from each Study component to inform recommendations regarding whether a revision of the wild rice sulfate standard is warranted and if so, what changes are needed. In addition to the further analysis identified above for each Study component, data integration efforts will include:

- Comparing the data from the hydroponic and outdoor container experiments to further describe:
    - The effect of sulfate on wild rice
    - The effect of sulfide on wild rice

  Note: To inform the wild rice sulfate standard review, an important aspect of this analysis will be determining what concentrations of sulfate and sulfide are *protective* of wild rice, which may be different than the concentrations at which effects are observed in the study results.

- Integrating the laboratory experimental data with the field survey data to identify any patterns in wild rice impacts and water quality variables in the laboratory and field setting

- Comparing the data from the field survey, outdoor container experiments, and sediment incubation laboratory experiments to evaluate:
    - The relationship between sulfate in the overlying water and sulfide in the sediment
    - The role of iron in removing sulfide from solution and mitigating the production of sulfide
    - The time-course of net sulfide production after sulfate has been added to overlying water, given that there may be loss of sulfide through various mechanisms. For example, iron may remove sulfide from solution

MPCA staff will release their analysis in the form of preliminary recommendations regarding the wild rice sulfate standard, and accompanying reasoning, by the end of February 2014. Those recommendations will include:

- Does the scientific evidence indicate that the standard should go up or down and, if so, generally by how much?
- Should there be a different standard for lakes/wetlands, or streams, or paddy rice?
- What more can be said about the "period when the rice may be susceptible to high sulfate"?

Additional details, including a technical support document, will follow.

Opportunities for Public Input and Comment

The MPCA will share its preliminary recommendations with the Wild Rice Standards Study Advisory Committee for their input and feedback. Also, there may be an expert panel review of the study results and preliminary recommendations in spring 2014.

Any proposed change to the wild rice sulfate standard would be adopted into Minnesota's water quality standards rule (Minnesota Rules Chapter 7050) in accordance with the requirements of the Minnesota Administrative Procedures Act and would require the approval of the U.S. Environmental Protection Agency.

Contact information

For more information visit www.pca.state.mn.us/ktqh1083.

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Appendix A

The following is a list of the folders (bold) and individual files that comprise the MPCA Wild Rice Standards Study on the MPCA's FTP site at ftp://files.pca.state.mn.us/pub/tmp/wildRice.

_Wild_Rice_Study_Summary

WildRice_summarydoc_Jan2014.docx

Literature_List

Wild_Rice_Literature_Holdings.pdf

Laboratory_Hydroponics_Experiments

Pastor_Hydroponics_Experiment_Report.pdf
Appendix1_Germination_Response_to_Sulfate_SOP.pdf
Appendix2_Juvenile_Seedling_Growth_Response_to_Sulfate_SOP.pdf
Appendix3_ Germination_Response_to_Sulfide_SOP.pdf
Appendix4_ Juvenile_Seedling_Growth_Response_to_Sulfide_SOP.pdf
Appendix5_ Effects_of_Sulfate_on_Germination.xls
Appendix6_Effects_of_Sulfate on Juvenile Growth.xls
Appendix7_ Effects_of_Sulfide_on_Germination.xls
Appendix8_Rangefinder_Test_of_Effects_of_Sulfide_on_Juvenile_Growth.xls
Appendix9_Definitive_Tests_of_Effects_of_Sulfide_on_Juvenile_Growth_Trial 1.xls
Appendix10_Definitive_Tests_of_Effects_of_Sulfide_on_Juvenile_Growth_Trial 2.xls

Outdoor_Container_Experiments

Pastor_Mesocosm_report.pdf
Appendix1_Water_chemistry_of_mesocosms.xls
Appendix2_Mesocosm_Plant_Data.xls

2011_2012_2013_Field_Surveys

Myrbo_Final_Report_on_2011_2012_2013_Field_Surveys_20131231.pdf
LacCore_dataexport_finalreport.xls

Sediment_Incubation_Experiments

Temperature_Dependent_Diffusion_Rates_of_Sulfate_in_Aquatic_Sediments_final.pdf
UMDCE_Lab_Microcosm_MPCA_SufateStudy_Summary_of_Surfacewater_samples.xlsx
UMDCE _Lab_ Microcosm _SulfateStudy_PorewaterBromide.xlsx
UMDCE_Lab_Microcosm_SulfateStudy_PorewaterFluoride.xlsx
UMDCE_Lab_Microcosm_SulfateStudy_PorewaterSulfate.xlsx
Note: Data for pore water iron, sulfide, and pH will follow

Collection_and_Analysis_of_Rooting_Zone_Depth_Profiles

Sulfate_Manipulation_Rooting_Zone_Geochemistry_final.pdf
Porewater_Metals _Cu Zn Fe_at_Mesocosms_by_ICP-MS-final_wParamID.xlsx
MPCA_Wild_Rice_Pore_Water_2013_12_31.accb