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.

<table>
<thead>
<tr>
<th>Main Purpose</th>
<th>Field Survey</th>
<th>Laboratory Hydroponic Experiments</th>
<th>Outdoor Container Experiments</th>
<th>Collection and Analysis of Rooting Zone Depth Profiles</th>
<th>Sediment Incubation Laboratory Experiments</th>
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<tbody>
<tr>
<td><strong>Sulfate (SO₄)</strong></td>
<td>Expand understanding of environmental conditions correlated with presence/absence of wild rice.</td>
<td>Evaluate effects of sulfate on wild rice seed germination and growth of sprouts.</td>
<td>Evaluate effects of sulfide on wild rice seed germination and growth of sprouts.</td>
<td>Characterize sulfate, sulfide, and iron in the rooting zone of wild rice container experiments and field sites.</td>
<td>Evaluate effect of temperature on movement of sulfate into and out of underlying sediment.</td>
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<td><strong>Endpoints</strong></td>
<td>Concentrations of chemicals in surface water &amp; rooting zone (e.g. SO₄ &amp; H₂S vs. wild rice occurrence).</td>
<td>Controlled dose-response experiment. Controlled exposure to known concentrations of SO₄.</td>
<td>Controlled dose-response experiment. Controlled exposure to known concentrations of H₂S.</td>
<td>Controlled dose-response experiment. Includes natural sediment matrix as rooting environment. Involves entire growth cycle, multiple years.</td>
<td>Provides additional data to understand and interpret container experiments and field sites.</td>
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<td><strong>Key Strengths</strong></td>
<td>Most reflective of actual environmental conditions. Multiple wild rice stands and breadth of characteristics sampled.</td>
<td>Controlled dose-response experiment. Controlled exposure to known concentrations of SO₄.</td>
<td>Controlled dose-response experiment. Controlled exposure to known concentrations of H₂S.</td>
<td>Controlled dose-response experiment. Includes natural sediment matrix as rooting environment. Involves entire growth cycle, multiple years.</td>
<td>Controlled experiment with natural sediment and water.</td>
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<td><strong>Key Limitations</strong></td>
<td>Least controlled. Annual visit for most sites, 3x/year for a subset. Not definitive on cause and effect.</td>
<td>Only evaluates early growth stages. Leading hypothesis is that sulfate is converted to sulfide, which is directly toxic.</td>
<td>Only evaluates early growth stages. Unable to simultaneously keep roots anaerobic &amp; shoots aerobic.</td>
<td>Full effect of sulfate may take longer than several years to realize. No groundwater movement.</td>
<td>Utility lies in the integration of this data with the other Study components, not in this data set alone.</td>
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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 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](http://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_JuvenileSeeder_Growth_Response_to_Sulfate_SOP.pdf
   Appendix3_Germination_Response_to_Sulfide_SOP.pdf
   Appendix4_JuvenileSeeder_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
   LacCore_dataexport_finalreport.xls

_Sediment_Incubation_Experiments
   Temperature_Dependent_Diffusion_Rates_of_Sulfate_in_Aquatic_Sediments_final.pdf
   UMDCE_Lab_Microcosm_MPCA_SulfateStudy_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