WaterLegacy
Protecting Minnesota's waters and the communities who rely on them

# Comments on Wild Rice Sulfate Standard Studies and MPCA Draft Analysis of these Studies

WaterLegacy is a Minnesota non-profit organization formed to protect Minnesota water resources and the communities that rely on them. Along with the comments below, we have submitted Comments and Proposed Charge Questions for the Wild Rice Sulfate Standard Studies peer review.

WaterLegacy appreciates the work done by the Minnesota Pollution Control Agency (MPCA) in its June 2014 *Analysis of the Wild Rice Sulfate Standard Study: Draft for Scientific Peer Review* (MPCA Draft Analysis) to summarize the wild rice sulfate research. However, our review of the research identifies several important omissions in the MPCA Draft Analysis and areas where the MPCA appears to overstate or inaccurately characterize the research findings. These areas of concern are highlighted in the discussion below.

Our Comments here, like those on the Charge Questions, reflect the study objectives set by the Minnesota Legislature: to determine whether the existing sulfate standard of 10 milligrams per liter in waters producing wild rice is appropriate and whether there should be a temporal or seasonal limitation to the application of the sulfate standard. WaterLegacy notes that official decision-makers in the upcoming rulemaking process will assume that the peer review committee has examined all pertinent data and issues related to these underlying policy questions.

Field Studies

WaterLegacy believes that data should have been supplied from the initial and subsequent Field Survey sampling showing the prevalence of wild rice in low and high sulfate waters. The rarity of finding wild rice in high sulfate waters is significant in itself as well as a factor that should be considered in analyzing Field Survey correlations.

The MPCA Draft Analysis cites 2008 Minnesota Department of Natural Resources (MDNR) surveys showing wild rice is rarely found in higher sulfate waters. (MPCA Draft Analysis, p. 9, lines (ll) 231-233). The Draft Analysis does not directly state that Field Surveys in the MPCA Wild Rice Sulfate Standard Studies also rarely found wild rice beds in waters with more than 10 milligrams per liter (mg/L) of sulfates.[1] This ecological finding is obliquely referenced in the statements, "After the 2011 season, MPCA identified a need to identify and sample sites with elevated sulfate concentrations (above 10 mg/L) that conceivably could host wild rice based on suitable wild rice habitat." (*Id*., p. 17, ll 429-431) and, "If wild rice habitats had been sampled probabilistically, most of the sites would have had very low sulfate concentrations and little would have been learned about the effect of elevated sulfate." (*Id*., p. 21, ll 497-498).

Even with Field Surveys intentionally biased to find wild rice in high sulfate locations, it appears that the vast majority of wild rice beds in lakes were found in waters with sulfate below 10 mg/L and very few wild rice beds were found in any waters with sulfate above 20-50 mg/L. (*Id.*, p. 35, Figure 15).

The Draft Analysis did note the large difference in the 75th percentile of sulfate in lakes used for the MPCA's wild rice Field Survey and the sulfate levels in MDNR wild rice lakes. MPCA wild rice Field Survey

---

[1] Characterization of Field Surveys made in personal communication with Amy Myrbo, July 2, 2014.

lakes have *more than three times* the sulfate of Minnesota wild rice lakes as a whole. (*Id*., p. 21, ll 505-513). No stream or river data was provided for a similar comparison.

WaterLegacy does not disagree with MPCA that a biased sample was more efficient to determine under what circumstances wild rice might survive elevated sulfate. However, regulatory limits must protect a resource in its natural environment, so results based on biased sampling must be viewed with caution. WaterLegacy believes that the implications of intentionally biased sampling should be explicitly discussed in terms of the way in which Field Survey data may or may not predict impacts of sulfate and sulfide wild rice under prevalent rather than anomalous conditions.

<u>Hydroponic Experiments</u>
WaterLegacy appreciates that, despite their short-term and limited scope, hydroponic experiments may be useful to confirm the toxic effects of chemicals. However, the converse is not necessarily true. Even if a chemical or a tested concentration of a chemical is not toxic after a few days in a test tube, this doesn't prove that the chemical or concentration would not be toxic in the natural environment.

The Hydroponic Experiments performed on wild rice under MPCA auspices lasted 11 days and measured rates of germination or the growth (as measured by plant length and dry weight change) of emergent seedlings. (MPCA Draft Analysis, p. 13). What we find striking about these results is that, even under the very limited conditions of the hydroponic environment and the few endpoints studied, sulfide was found to have significant effects on seedling growth at 309 micrograms per liter (µg/L) of sulfides. (*Id*., p. 15).

However, these data are insufficient to demonstrate that sulfide below 300 µg/L or even below 134 µg/L is not also toxic to wild rice, as suggested in the MPCA Draft Analysis. (*Id*., pp. 15-16). The limitations of wild rice survival in the hydroponic environment prevented assessment of adverse effects of lower sulfide levels at different parts of the wild rice life cycle or over a longer duration.

The insufficiency of hydroponic testing to postulate a level below which sulfide would not be toxic to wild rice is underscored by the Field Survey data. As explained in the Draft Analysis, the Field Survey data demonstrated wild rice sensitivity to sulfide at any concentration above *75 µg/L*: "69 to 80% of the sites had wild rice present above the presence threshold when porewater sulfide was less than 75 µg/L, and b) a more-or-less continuous decline in the percent of sites with wild rice present occurred above 75 µg/L." (*Id.*, p. 36, l. 821 to p. 37, l. 823). Unless a more-or-less continuous decline in the presence of wild rice is desirable, sulfide levels above 75 µg/L should be deemed levels of concern.

<u>Mesocosm Experiments</u>
WaterLegacy believes the Mesocosm Experiments provide critical evidence to demonstrate the adverse effects of increased sulfates on wild rice under more natural conditions and between generations.

The MPCA Draft Analysis noted that seedling emergence from sediment decreased significantly ($p < 0.01$) with increased sulfate levels, that survival of those seedlings that remained after thinning declined with increasing sulfate concentration, and that, even with poor overall seedling survival in the 2013 season, the trend of less survival with increasing sulfate test concentration remained. (MPCA Draft Analysis, p. 30, ll. 647-651).

The Draft Analysis found "the proportion of viable seeds (those determined to be able to germinate and grow) from each plant remained relatively constant during all three years in the controls (55 – 60%) but decreased to 48% in 2011, 40% in 2012, and 31% in 2013 at the 300 mg $SO_4$/L treatment level. These decreases were statistically significant for all three years." (*Id*., p. 27, ll. 637-640). Seed weights also remained constant in the control tanks, but progressively decreased in high sulfate treatments. As compared to the controls seed weights in the 300 mg $SO_4$/L treatment level decreased by 12% in 2011, 21% in 2012, and 50% in 2013. (*Id*., p. 27, ll 631-634).

In addition to demonstrating several endpoints where varying sulfate in surface water affected wild rice, the Mesocosm Experiments showed how wild rice populations could be impaired over time, as seed viability and seed weights progressively decrease.

In the Mesocosm Experiments, increasing the independent variable of surface water sulfate resulted in increased porewater sulfide. (*Id*., p. 30, ll 665-667). Median porewater sulfide concentrations in the control mesocosms were 68 µg/L – below the 75 µg/L level at which wild rice prevalence decreased in the Field Surveys. As sulfate concentrations were increased to 50, 100, 150 and 300 mg/L, the mesocosms yielded median sulfide porewater levels of 138, 190, 265 and 778 µg/L respectively. (*Id*., p. 37, ll 840-843), raising porewater sulfide above levels found in Field Surveys and hydroponic tests to impair wild rice.

Sediment Incubation Studies

WaterLegacy is troubled by MPCA's failure to provided peer reviewers with the findings from the Sediment Incubation Studies. These studies were undertaken to evaluate whether there should be seasonal limitations on the application of the wild rice sulfate standard or whether the standard should be applied year-round. This question was directed by the Legislature and is particularly salient in light of a recent permit issued by the MPCA to allow unlimited discharge of sulfates upstream of wild rice waters from September through March.[2]

The MPCA Draft Analysis summarized findings that sulfate movement into sediments and reduction to sulfides occurred 49% faster in the warmer temperature of 23°C as compared to the colder temperature of 4.5°C. (MPCA Draft Analysis, p. 34, ll728-729). This summary is accurate and pertinent.

However, the MPCA omitted from its Draft Analysis the more significant Study results demonstrating that, under cold conditions, of 3,800 micrograms per centimeter squared (µg/cm2) total sulfate that fluxed into sediment during the 80-day loading phase, 3,000 µg/cm2 reacted to form sulfide. (Will DeRocher, Nathan W. Johnson, *Temperature Dependent Diffusion Rates of Sulfate in Aquatic Sediments*, Report Dec. 31, 2013, pp. 30, 33). From this data, Mr. DeRocher and Dr. Johnson concluded, "regardless of adjustments of diffusion and reaction rates to field conditions, a great majority of the sulfate that diffuses into sediments during an ~80 day loading phase is likely to be reduced to sulfide in either warm or cold conditions." (*Id*., p. 35) Thus, "over an 80 day sulfate loading phase, a vast majority of the sulfate added to sediment reacts to form sulfide, even at 4°C when biological rates are slower." (*Id*., p. 38)

Mr. DeRocher and Dr. Johnson further explained how their findings addressed the study question pertaining to seasonal sulfate loading and sulfide formation:

> Elevated sulfate levels in the porewaters provide favorable conditions for sulfate reducing bacteria that, over time, could produce sulfide in excess of the iron availability in a system and

[2] Mesabi Nugget, NPDES/SDS permit MN0067687, approved Oct. 23, 2012.

> result in an accumulation of dissolved sulfide in pore fluids (Johnson 2014). Sufficient quantities of dissolved sulfide could have detrimental effects on aquatic vegetation and organisms. This study provided both a physical and mathematical model to describe the porewater sulfate response to seasonal sulfate loading into surface water under different temperatures. These results will help to answer the question of how much sulfate diffuses into, and reacts within sediment, as a function of temperature and inform management decisions regarding the timing of sulfate release to natural waterways. (*Id*., p. 38)

WaterLegacy asks that peer review evaluate the Sediment Incubation Studies along with other study results to review whether there is a scientific basis for seasonal application of the wild rice standard.

<u>Sulfate Standard and Sulfide Toxicity</u>
WaterLegacy requests peer review of data from the Field Surveys to answer the primary wild rice sulfate study question: whether the existing 10 mg/L sulfate limit is appropriate and sufficient to protect natural beds of wild rice.

The MPCA's presentation to the Wild Rice Advisory Committee on April 16, 2014*, Wild Rice Sulfate Standard Study: Summary of Preliminary Analysis,* contained the regression analysis attached as Exhibit A. WaterLegacy's scientific advisors believe this slide, which was not included in the MPCA's Draft Analysis, should be reviewed to evaluate the appropriateness of the existing wild rice sulfate standard.

WaterLegacy's advisors explain that the regression analysis in Exhibit A indicates that sulfide levels in sediments may reach levels toxic to wild rice where surface water sulfate is below 10 mg/L. Even if the threshold of concern for porewater sulfide were as high as 300 μg/L, under a surface water sulfate of 10 mg/L, wild rice would be protected only approximately 80% of the time. Reviewing this data, our advisors have expressed the concern that the 10 mg/L standard may not be protective enough of wild rice and have suggested that a sulfate limit of 6 mg/L might be needed to protect wild rice in the natural environment.

WaterLegacy believes the Draft Analysis and peer review process should consider the evidence of a decline in wild rice prevalence with porewater sulfide exceeding 75 μg/L discussed previously and the relation between sulfate and sulfide levels in the Field Surveys reflected in Exhibit A to inform whether the existing 10 mg/L sulfate limit is appropriate or sufficient to protect wild rice.

<u>Iron Mitigation Hypothesis</u>
The MPCA's discussion of the relationship between sulfate, iron and sulfide overstates the evidence that iron, in fact, mitigates the effects of sulfate and sulfide on the presence and growth of wild rice.

Although some text in the Draft Analysis (MPCA Draft Analysis, p. 45, ll 1076-1077) suggests that additional research is needed to account for the role of iron, the MPCA disregards this caution in concluding that iron in sediments removes sulfide from solution "and from potential harm to wild rice," (*Id*., p. 51, ll 1204-1207) and that "wild rice abundance is not diminished when iron concentrations are high in the porewater, but is diminished when sulfide concentrations are high and iron is low." (*Id*., p. 52, ll 1232-1233).

From the limited evidence in the Wild Rice Sulfate Standard Studies, the MPCA suggests that an equation derived from Field Survey can be employed, if the iron concentration of the sediment solid phase is known, “to predict the potential employed to predict the potential maximum sulfide concentration that would be produced from a given concentration of sulfate in surface water” (*Id*., p. 52, ll 1258-1260). The MPCA further suggests that this “prediction” can be applied where a “site has the capacity to consume more sulfide” to assess whether increasing sulfate concentrations should or should not be viewed with caution. (*Id*., p. 52, ll 1260-1267).

WaterLegacy believes the MPCA Draft Analysis oversimplifies the relationships between sulfate and sulfide in the presence of iron. Attempting to predict sulfide concentrations in the natural environment from iron content of sediment is premature, and any assumption that such predictions can determine the ability of wild rice to thrive in high sulfate environments is scientifically unsubstantiated.

Although there are some interesting correlations pertaining to iron in the Wild Rice Sulfate Standard Studies, there are no experiments varying iron concentrations in sediments and measuring the levels of sulfide produced when a given concentration of sulfate is supplied in surface water. There are no experiments co-varying sulfate and iron concentrations and evaluating wild rice biological endpoints to determine whether iron mitigates effects of sulfide on wild rice and, if so, to what degree and under what conditions. Unrepresentative Field Survey correlations in stream and river environments are insufficient to demonstrate causal or protective relationships. There has been no analysis of biological effects of plaque formation on wild rice roots in the presence of iron and sulfide, and no analysis of rooting zone chemistry to determine to what degree sulfides remain sequestered in the presence of iron or cycle in and out of porewater in a natural environment.

No Hydroponic Experiments tested any aspect of the iron hypothesis.

The Mesocosm Experiments showed diminished iron in porewater with increased sulfate concentrations in surface water, (*Id*., p. 31, Figure 12). However, there was no evidence in the Mesocosm Experiments that iron mitigated the formation of porewater sulfide or mitigated adverse impacts of the sulfate treatments on the growth of wild rice.

Field Survey correlations are insufficient to support the assertion that iron mitigates adverse effects of sulfate and sulfide on wild rice abundance in a natural environment. As discussed previously, any conclusions regarding wild rice survival in the natural environment should be tempered by the knowledge that sampling was intentionally biased to find sites where wild rice was present despite high surface water sulfate. Caution is also required because lakes, streams and rivers in the Field Survey have dissimilar findings.

First, although the MPCA Draft Analysis characterizes the data sets as “lakes” and “streams,” the category of “streams” actually includes rivers as well as streams, including several sites along the St. Louis River and the Mississippi River. Only a small number of streams and rivers were actually sampled – 6 or 8 water bodies in total.[3]

The Draft Analysis acknowledges that data from streams, rivers and lakes is different, noting that the median sulfate concentrations at sites in which wild rice occurs in streams and rivers in the 2012-2013 Field Survey (14.2 mg/L) is *more than five times higher* than in Field Survey lakes (2.5 mg/L). (MPCA Draft

[3] Personal communication with Ms. Myrbo, July 2, 2014. See also MPCA, Draft Analysis, p. 25, Table 6.

Analysis, p. 22, l 544 to p. 23, l 546). In addition, this median sulfate level for the 23 stream and river sites sampled during the 2012-2013 Field Survey was *nearly six times higher* than the median value for the eight stream sites with wild rice sampled during the 2011 Pilot Survey (2.4 mg/L). As the MPCA noted, this discrepancy "calls into question the assumption that the data from the streams sites sampled during the 2012-2013 Field Survey truly represents the population of stream sites where wild rice grows in Minnesota." (*Id*., p. 23, ll 546-550).

To postulate that porewater iron permits wild rice survival despite high sulfate waters, the MPCA has conflated dissimilar data from lakes, streams and rivers. The Draft Analysis shows wild rice presence in higher sulfate waters almost entirely in streams and rivers, not in lakes, whether or not high levels of iron are present. (*Id*., p. 35, Figure 15). In lakes, wild rice is absent (<1% coverage) in many high iron sites, (*Id*., p. 35, Figure 15 and p. 36, Figure 16). For streams and rivers, on the other hand, irrespective of iron levels, there are few data points where wild rice is absent. (*Id*.) If dissimilar data from lakes, rivers and streams were not combined, it is unlikely that any correlations could be drawn between iron levels and wild rice presence.

WaterLegacy is concerned that the MPCA's hypothesis that iron mitigates impacts of sulfate and sulfide on natural wild rice is based on several layers of conjecture. The Draft Analysis suggests that iron in sediments serves as an available reservoir that removes sulfide from solution. (*Id*., p. 44, ll 1049-1055). However, the United States Geological Survey (USGS) measure of iron in soil and sediment "is not predictive of the iron metrics used in this study." (*Id*., p. 48, ll 1141-1142).

The MPCA proposes that, where ferrous iron is present, "sulfide immediately reacts with iron and precipitates, removing the sulfide from solution and from potential harm to wild rice." (*Id*., p. 51, ll 1206-1207). However, Mesocosm Experiments show high sulfide with sulfate treatments, even when sediments had high iron levels and control iron exceeded 10,000 µg/L. (*Id*., p. 31, Figure 12). Dr. Johnson's data on Sandy Lake and Second Creek suggests a build up of sulfide as the growing season progressed, even approaching or exceeding the high levels of sulfide (~300 µg/L or 9.35 micromoles/L) found to be toxic in hydroponic experiments. (Johnson, *Response of Rooting Zone Geochemistry to Experimental Manipulation of Sulfate Levels in Wild Rice Mesocosms*, Dec. 31, 2013, see Figures B1-B3, pp. 38, 40, 42). Iron and sulfides may or may not reach a steady state in the natural environment, and sulfides may both precipitate from and re-enter solution, affecting porewater concentrations and wild rice.

Given the lack of experimental evidence, the mesocosm and field data suggesting sulfide may reach toxic levels despite the presence of iron, and the inconsistencies and unrepresentative nature of Field Survey findings of wild rice presence in high sulfate waters, there is insufficient scientific support to predict either sulfide or wild rice presence in natural systems as a function of iron in sediments.

MPCA's selection of an hypothesis from the literature that iron coatings on the roots of wild rice are benign (p. 52, ll 1223-1232) also seems to be wishful thinking, not objective analysis. The cited literature pertains to iron hydroxide on white rice, rather than the iron sulfides believed to coat the roots of wild rice when sulfate concentrations are elevated and iron is present. (*See* Pastor, *Effects of Enhanced Sulfate Concentrations on Wild Rice Populations: Results from a Mesocosm Experiment*, Report December 31, 2013, pp. 11-12). In addition to the salutary hypothesis selected by the MPCA, some published literature suggests that, at high levels, iron may itself become a toxicant to plants in wetland sediments. (*See* van der Welle et al., *Detoxifying Toxicants: Interactions between Sulfide and Iron*

*Toxicity in Freshwater Wetlands*, Environ. Tox. and Chem., 2006, 25(6): 1592–1597.) Additional research would also be needed to determine whether the plaque coating wild rice roots in the presence of iron and sulfide is benign or whether it impedes nutrient uptake or results in other adverse effects.

Mercury Methylation

WaterLegacy would also caution that sulfate discharge has adverse impacts beyond the effects of sulfide on wild rice. The MPCA has long expressed concern that sulfate discharge to water increases mercury methylation and adverse impacts to health and the environment. (MPCA, *Strategy to Address Indirect Effects of Elevated Sulfate on Methylmercury Production and Phosphorus Availability*, Oct. 19, 2006), attached as Exhibit B). Despite this history, the MPCA rejected the opportunity to measure mercury or methylmercury as part of the Wild Rice Sulfate Standard Studies. As a result, no information is available on the degree to which mercury and methylmercury in surface water, porewater or the aquatic food chain vary in relationship to sulfate, sulfide or iron.

Recent research suggests that a substantial portion of the biological potential for mercury methylation in freshwater systems may be attributable to iron-reducing bacteria, rather than sulfate-reducing bacteria. (*See e.g.*, Fleming et al., *Mercury Methylation from Unexpected Sources: Molybdate-Inhibited Freshwater Sediments and an Iron-Reducing Bacterium*, Appl. Environ. Microbiol., Jan. 2006; 72(1): 457–464; Kerin et al., *Mercury Methylation by Dissimilatory Iron-Reducing Bacteria,* Appl. Environ. Microbiol., Dec. 2006: 72(12): 7919–7921; Yu et al., *Contribution of Coexisting Sulfate and Iron Reducing Bacteria to Methylmercury Production in Freshwater River Sediments*, Environ. Sci. Technol., Mar. 6, 2012: 46(5): 2684-2691).

WaterLegacy and the health and scientific professionals with whom we collaborate are concerned about mercury methylation in waters downstream of sulfate discharge. We believe that, before iron or any other variable can be considered as a site-specific mitigative factor for sulfate discharge adverse impacts, much more analysis must be done – not only of the relationship of iron in sediments to wild rice but of the relationships between sulfate, sulfide and iron in sediments to mercury methylation risks.

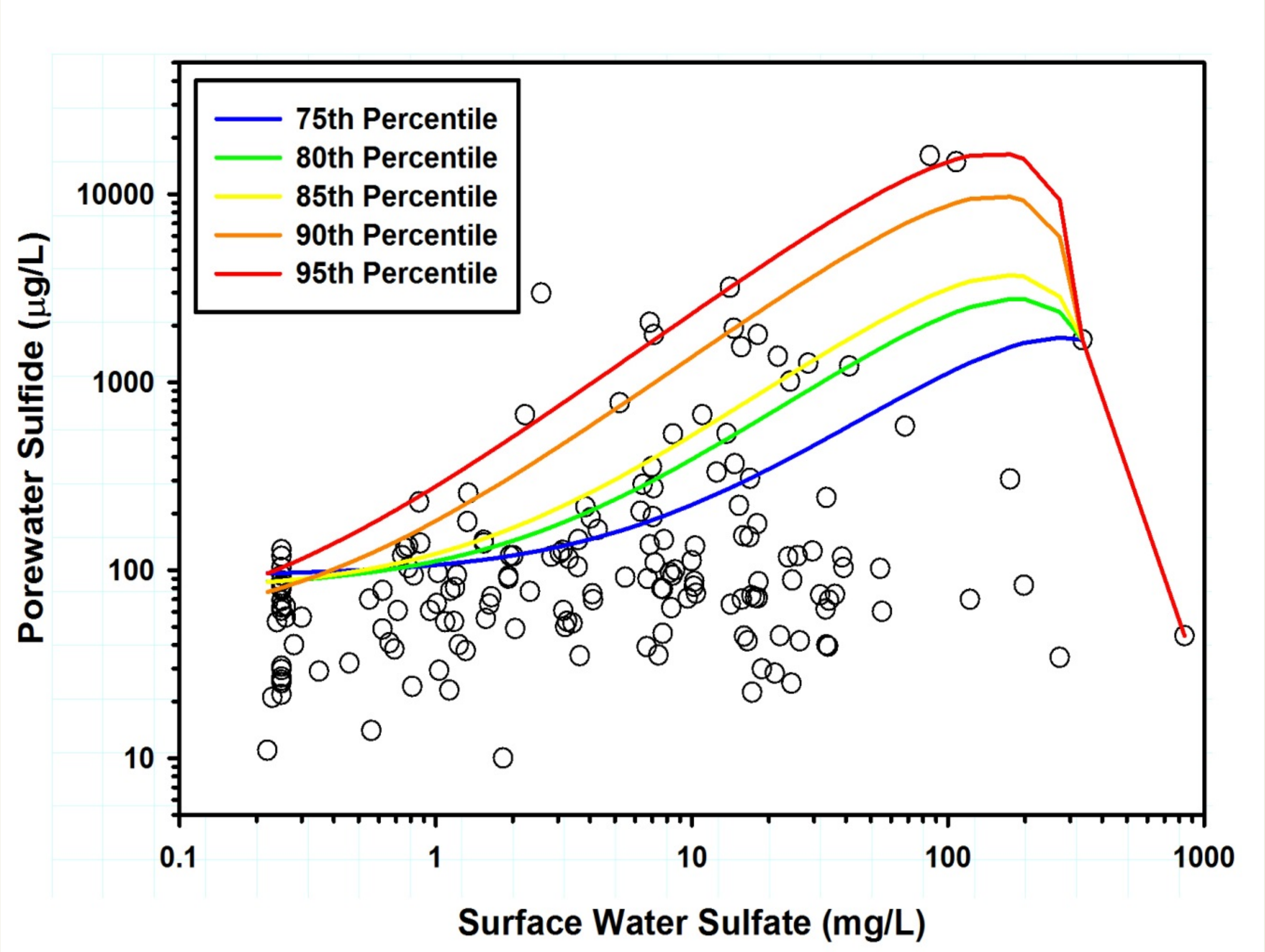
Conclusion

Based on the foregoing discussion of the Wild Rice Sulfate Standard Studies, WaterLegacy believes that the data shows the existing 10 mg/L sulfate standard should be preserved, if not reduced to 6 mg/L in order to protect natural beds of wild rice. The threshold of concern for sulfide porewater is exceeded between 150 and 300 µg/L, and may be as low as 75 µg/L in the natural environment. There is no scientific basis to restrict the temporal application of the wild rice sulfate standard and insufficient scientific evidence to propose that iron may mitigate sulfate impacts in any site-specific application.

Respectfully submitted, DATE: July 8, 2014

Paula Maccabee, Esq.
JUST CHANGE LAW OFFICES
1961 Selby Ave.
St. Paul MN 55104
phone: 651-646-8890
cell: 651-775-7128
email: pmaccabee@justchangelaw.com
Advocacy Director/Counsel for WaterLegacy

# 5. Quantile regression of sulfide on sulfate is a useful way to translate sulfide levels to surface water sulfate



*Final 10/19/06*

# MPCA Strategy to Address Indirect Effects of Elevated Sulfate on Methylmercury Production and Phosphorus Availability

**Summary:** Although there is evidence that elevated sulfate loading can increase methylmercury production and phosphorus mobilization, it is premature to develop specific sulfate concentration limits or other regulatory responses based on these effects. The deleterious effects of sulfate may be restricted to certain areas of the state, certain background sulfate concentrations, or other environmental controlling factors. These factors will be explored in a multi-year data collection effort combined with ongoing data analysis. It is anticipated that sensitive areas of the state will be identified and appropriate controls on sulfate discharges will be developed if necessary. The primary focus of the strategy is to pursue research to further understand impacts from sulfate on methylmercury production and phosphorus mobilization and to use the research to guide the future need for additional requirements or controls in environmental review and NPDES permits. This strategy was approved by the MPCA Risk Managers on August 28, 2006 and the MPCA WQ Policy Forum on October 19, 2006.

**Problem Statement:** Research indicates a correlation between sulfate loading and methylmercury (MeHg) production and phosphorus (P) mobilization under certain conditions. Many waters of the state are impaired as a result of MeHg in fish tissues and excess nutrients. MPCA staff need to better understand the relationship between sulfate concentration and MeHg production/P mobilization so that appropriate responses, if necessary, can be developed. Sulfate is a common constituent in domestic and industrial wastewaters. Additional information is needed so that the MPCA can develop a permitting strategy for existing, expanding and new domestic and industrial process wastewater discharges. The strategy must reflect varying MeHg production and P availability under differing environmental conditions.

## MPCA Actions to Monitor & Evaluate Sulfate Impacts

MPCA staff will evaluate the following hypotheses over three to five years.

1) Elevated sulfate discharge into low-sulfate receiving waters significantly increases MeHg concentrations (as percent of total mercury) and P concentrations.
2) Elevated sulfate discharge into high-sulfate receiving waters has no significant effect on MeHg concentrations (as percent of total mercury) and P concentrations.
3) Elevated sulfate discharge into low-sulfate waters has greater effect on P concentrations when the iron to P ratio is low in the sediments of the receiving water.

Environmental Analysis and Outcomes Division will coordinate the following activities to evaluate the above hypotheses and support eventual changes in the environmental review and permitting practices:

1) Continued research at Wetland 6 in the Marcell Experimental Forest north of Grand Rapids;
2) Milestone Monitoring – permanently add sulfate, TOC, total mercury, and MeHg to the MPCA's ambient water quality monitoring sites; (In FY07 Milestones did include THg, MeHg, sulfate, and TOC, through use of the Mercury Trends allotment).

3) Continue to track and participate in the research of national / international work groups;
4) Compile and map existing surface water sulfate concentration data in Minnesota;
5) Compile and map existing effluent sulfate concentration data in Minnesota;
6) Compile and map existing stormwater sulfate concentration data in Minnesota (if few data have been collected, consider obtaining representative data);
7) Fish Consumption Advisory Monitoring - Work with DNR and MDH to collect fish for mercury analysis of fish tissue at a subset of sites where environmental data is being collected on water or sediments;
8) Implement the Environmental Review and NPDES Permitting actions (below) Regional, Municipal and Industrial Divisions will lead as appropriate; and
9) Compile data from the above activities and complete an evaluation of the hypotheses.

## Environmental Review and NPDES Permitting

While research shows a relationship between sulfate concentration and MeHg production/P mobilization, there is currently insufficient information to reach firm conclusions on whether specific point source (non-stormwater) discharges containing sulfate may impact water quality or cause/contribute to water quality impairments. The following information will guide the development of programmatic direction and procedures to address sulfate discharges. This approach includes 1) further characterization of the problem, 2) development of interim permitting and environmental review procedures, 3) research of sulfate impacts from point source dischargers, and 4) annual incorporation of new knowledge into the permitting and environmental review procedures. Prior to development of the interim procedures, NPDES permit writers and environmental review staff will need to manage projects on a case-by-case basis. They will use the current knowledge (as outlined below and in Appendix A) and work with the program supervisor and Ed Swain to assess and respond to the environmental risk from sulfate discharges.

### Environmental Review

If a new or expanding domestic or industrial process wastewater discharge triggers environmental review for a wastewater-related threshold (not a non-wastewater related threshold) or if wet air controls that contribute sulfate to a wastewater stream are proposed the impact from sulfate must be evaluated in the environmental review document. The environmental review should include available data on projected effluent design flow rate, sulfate concentration, and sulfate load as well as best estimates of receiving water flow rate (7Q10 and other statistics) and concentrations of sulfate, mercury, MeHg, iron, ortho-P, total P, and, as a measure of organic matter in the water, TOC and/or DOC. If receiving water flow was measured concurrently with water sampling, flow data should also be included. The environmental review must also include available data on the organic matter, mercury, iron, and P content of the sediments of receiving waters and lakes or impoundments downstream. It is understood that available data may be limited. To the extent possible, qualitative discussion of downstream conditions and mitigative options should also be included.

**NPDES Permitting**

If a new, expanding or existing domestic or industrial wastewater discharge for "high risk" situations is encountered, 1) the need for effluent and/or receiving water monitoring for sulfate, mercury, MeHg, iron, ortho-P and/or total P should be considered; and 2) if research or other information supports a likely impact from sulfate in a specific situation an evaluation of the treatment technologies and pollution prevention opportunities should be included with the permit application. Existing discharges will be addressed at the time of reissuance. A guidance for project proposers and NPDES permit writers will be developed by June 2007 to explain the procedures for addressing sulfate discharges. In the interim, permit writers will work with the program supervisor and Ed Swain to assess and respond to the environmental risk from sulfate discharges.

Currently, high-risk situations may include:

- Discharge of elevated sulfate concentrations into high-organic aquatic environments (e.g., wetlands that drain to fisheries, lakes with organic sediment, rivers with slow-moving back waters, ponds where rising water might inundate vegetation).
- Discharge of elevated sulfate into low-sulfate waters (< 40 ppm or so) where sulfate may be a limiting factor in the activity of sulfate-reducing bacteria (SRB).
- Discharge of elevated sulfate into streams with fluctuating water levels and bordering wetlands. Rising water levels would introduce sulfate into the high-organic wetland matrix, followed by falling water levels that hydraulically deliver elevated MeHg and/or phosphate to the stream.
- Discharge of elevated sulfate to waters that flow to a lake or impoundment downstream that may thermally stratify even temporarily in the summer or be cut off from the atmosphere from ice cover in the winter. Either stratification or ice cover can produce anoxic water, in which sulfate can be converted to sulfide, potentially enhancing both mercury methylation and phosphate release.

Conditions that decrease the risk that elevated sulfate loading may enhance mercury methylation:

- Discharge of elevated sulfate to waters with high background sulfate (>100 ppm or so), including downstream waters.
- Discharge of elevated sulfate to highly oxygenated, turbulent waters with low-organic sediment and no adjacent riparian or lacustrine wetlands, and none downstream.

**Research Impacts of Sulfate from Domestic and Industrial Process Wastewater Discharges**

MPCA staff will pursue funding to study specific impacts from domestic and industrial process wastewater discharges of sulfate on MeHg production and P availability in receiving waters. The study (or series of smaller studies) will include site-specific evaluations at facilities representing the various high risk situations identified in "Environmental Review and NPDES Permitting" above. This work may include effluent and receiving water monitoring for sulfate, mercury, MeHg, iron, ortho-P, total P, and supporting parameters that may reveal biogeochemical mechanisms, such as DOC, pH, oxygen, nitrate, and potassium. The work will include an evaluation of the data to determine whether domestic and industrial process wastewater discharges are impacting receiving waters during any time of the year with a particular focus on the summer months. Some of the study work may need to be contracted out to a research entity (i.e. UMD, NRRI, U of M St. Anthony, U of Toronto). Funding sources may include Legislative Initiative, CW Legacy Act, GLNPO, salary savings, or other related project savings.

**Action Items / Resource Needs**

1) Risk Managers need to select an EAO Division representative to coordinate the overall Sulfate Strategy **by August 28, 2006**. Action Complete: Marvin Hora will be overall coordinator.

2) Sulfate Strategy Coordinator (Marvin Hora) will work with the appropriate managers to recommend staff team members to develop guidance documents described in the Environmental Review and NPDES Permitting action items below **by September 25, 2006**. Recommendation: Team should include Ed Swain, Jeff Stollenwerk, Deb Lindlief, Dana Vanderbosch, Bruce Wilson and a GIS specialist (see MPCA Actions 4 & 5 above).

3) Water Policy Team reviews and approves the Sulfate Strategy including staff assignments **by October 31, 2006**. Jeff Stollenwerk will coordinate.

4) EAO staff should develop funding requests, detailed plans and funding applications, RFPs and conduct study oversight necessary to complete research on impacts of sulfate from domestic and industrial process wastewater discharges. **Ed Swain - Ongoing.**

5) The Sulfate ER/NPDES Permitting staff team (from item 2 above) further defines and characterizes high-risk situations/criteria and develops interim procedures for environmental review and NPDES permitting activities. This action should be completed **by February 28, 2007**. Estimated time commitment – 40 to 80 hours for each team member.

6) The Sulfate ER/NPDES Permitting staff team (from item 2 above) develops brief guidance for project proposers and MPCA staff that provides background on the sulfate issue and factors that will need to be evaluated as part of the environmental review and/or permit process. Guidance should also address permitting projects that do not require environmental review. The team should develop procedure documents that will be included in the program manual for the environmental review and the NPDES Permit Writers' Manual. This document will provide background on the sulfate issue and issues that will need to be evaluated as part of the environmental review and/or permit process. These actions should be completed and presented to the WQ Policy Forum for review and approval **by June 29, 2007**. Estimated time commitment – 30 to 40 hours for each team member.

7) If necessary, revise the Illuminated EAW document and NPDES permit application to include background on the sulfate issue and issues that will need to be evaluated as part of the environmental review and NPDES permitting. These actions should be completed **by July 31, 2007.** ER Staff, Permit Staff and EAO staff – 10 hours each.

8) Complete technical review of environmental review submittals and NPDES permit applications. Develop responses to comments on specific projects. **Timeline is project-specific.** Environmental Review, Municipal/Industrial engineers and permit writers lead, and EAO staff support – workload could vary greatly.

9) Review research findings and if necessary incorporate into permitting and environmental review procedures. Sulfate ER/NPDES Permitting staff team (from item 2 above) 10 to 20 hours – **Annually.**

10) Provide technical assistance to permit writers regarding high-risk case-specific monitoring requirements and information protocols for targeted facilities or facility types. – EAO staff **as needed** – 40 to 80 hours per year.

11) Update agency managers on policy development needs, including needs to revise the sulfate standard - Strategy Coordinator **– Annually.**

**Attachment A**

**MPCA Strategy**
**to Address Indirect Effects of Elevated Sulfate on**
**Methylmercury Production and Phosphorus Availability**

**Technical Background**

Sulfur naturally cycles in aquatic systems between sulfate and sulfide, depending on multiple factors, including oxygen availability, hydrologic fluctuations, and organic matter degradation. Sulfate is a relatively inert chemical species, but its conversion to sulfide has a number of undesirable indirect effects that this strategy ultimately seeks to minimize. Under certain as-yet undefined environmental conditions, additional sulfate may enhance MeHg production and the availability of P for algal growth. The mechanisms associated with enhanced MeHg production and P availability are different, but are both associated with the tendency during decay of organic matter for natural bacteria to convert sulfate to sulfide after oxygen is depleted. This group of bacteria is called sulfate-reducing bacteria (SRB).

The initial tasks of the strategy involve collecting and interpreting data so that defensible quantitative permitting limits on sulfate discharge can be established. For instance, aquatic systems that are naturally elevated in sulfate due to local geological sources may not be sensitive to moderate increases in sulfate concentration. Other environmental attributes may make some systems more or less sensitive to added sulfate, including existence of wetlands and background dissolved iron concentrations.

Elevated sulfate can enhance MeHg production because SRBs are known to convert inorganic mercury (which is widely available due to atmospheric pollution) to MeHg, the only form that accumulates in fish. When the availability of sulfate controls the activity of SRBs, then additional sulfate may cause additional fish contamination. Recent research (Jeremiason et al. 2006) has documented increased MeHg production through increased sulfate concentrations in a wetland environment. SRBs produce MeHg when certain environmental factors coincide: low oxygen and adequate levels of bioavailable inorganic mercury, sulfate, and decaying organic matter. High organic matter can, of course, cause low oxygen because other bacteria will consume available oxygen in the first phases of organic matter degradation. SRBs are most active in aquatic systems because water decreases atmospheric oxygen availability and maintains a moist environment in which bacteria can thrive. SRB production of MeHg can be constrained by low mercury, low sulfate, low organic matter, or high oxygen. There is also a hypothesis that continued production of sulfide by SRBs can produce negative feedback by reducing mercury availability through the formation of sulfide-mercury chemical bonds. However, it is not clear how to model such negative feedback, and the production of sulfide is not necessarily permanent, as sulfide can oxidize back to sulfate. So, at this point, trying to maintain high sulfide does not seem like a viable strategy. However, data collection will provide empirical information on this hypothesis.

Elevated sulfate can enhance P availability because of an indirect effect of sulfide production. When aquatic systems become anoxic (common in both hypolimnia and wetlands) there is a tendency for enhanced P release from sediment to the water. While anoxic, iron oxides become soluble, which causes the dissolution of phosphate that had co-precipitated with the iron during an oxygenated phase. The phosphate will largely re-precipitate with the iron when the water is oxygenated, unless the iron to phosphate ratio is too low. During anoxia, sulfide may be produced, which has the unfortunate ability to form a precipitate with the dissolved iron—unfortunate because elevated levels of sulfide can decrease the amount of iron that is available to co-precipitate the P. If the P is not precipitated upon oxygenation (either turnover of a lake or hydraulic movement in a wetland), then the additional P will likely stimulate algal growth above the historical range for that waterbody (Caraco et al. 1993).

Both of these indirect effects of elevated sulfate are difficult to model in a quantitative manner. One impediment is that the conversion to sulfide may be downstream from the site of sulfate discharge because the required combination of low oxygen and elevated organic matter may not occur immediately below the discharge. Sulfate conversion may occur when water flows laterally into adjacent wetlands or when the water reaches an impoundment or lake deep enough to have a hypolimnion. Enhanced loading of P and MeHg would occur when the anoxic water mixes back into surface water. This mixing would occur in a lake when the hypolimnion mixes with the epilimnion, and in rivers with lateral wetlands during a falling hydrograph.

Sulfate comes from a variety of sources. Generally, natural background sources result from marine rock and glacial till containing some marine rock such as limestone or shale. Surface water and ground water in the granitic Canadian Shield area is expected to have relatively low sulfate concentrations while waters in other parts of the state are expected to have relatively higher sulfate concentrations. Anthropogenic sources include air deposition (typically less than 1 mg/l) and domestic and industrial wastewater discharges. Wastewater sulfate concentrations can be elevated above surface water concentrations simply because of use of high-sulfate groundwater. In addition, sulfate may be elevated in wastewater by concentration through evaporation, capture of sulfur compounds by air pollution control equipment, or various industrial processes (e.g. lime addition in taconite production).

It is important to minimize the effect of sulfate on MeHg and P because Minnesota's water quality is threatened by these chemicals state-wide. Federal NPDES permitting regulations prohibit the authorization of wastewater discharges that may cause or contribute to water quality impairments. Numerous water bodies in the state are listed as impaired because the MeHg concentrations in fish tissues make the fish unsuitable for frequent human consumption. Similarly, numerous water bodies are impaired because of excess P concentrations.

Treatment technologies for sulfate removal from wastewaters are limited. Reverse osmosis and evaporation are energy intensive and generally considered infeasible. A new treatment technology, submerged packed bed, has shown potential but there is an unevaluated risk of MeHg production within the treatment system. Land application or rapid infiltration basins may be effective but must be evaluated on a case-by-case basis.

While research indicates a strong correlation between sulfate loading and MeHg production in a sulfate-poor wetland, the factors that control MeHg production and P release in other surface waters are not documented. The research results do not, however, tell us how aquatic systems higher in sulfate react to increased sulfate loading. We have not reached a sufficient level of confidence with our understanding of the controlling factors such that firm effluent limitations based on these phenomena can be established. Therefore, a permitting strategy will need regulatory and study/monitoring components to reflect our varying levels of understanding of MeHg production under differing environmental scenarios. MeHg study and control is further complicated by the lack of a standard EPA analytical method and limited commercial laboratories that are prepared to conduct MeHg analyses. EPA has developed Draft Method 1630 (January 2001) for MeHg analyses. The draft method can be found at:

*Final 10/19/06*

http://www.epa.gov/nerleerd/108Complete.pdf#search=%22mercury%20method%20methyl%201630%20site%3Aepa.gov%22
and
http://www.brooksrand.com/FileLib/1630.pdf

MPCA staff have used Frontier Geosciences in Seattle, WA for recent analyses. It is anticipated that the MDH lab, and possibly other labs in Minnesota, would gear-up to run Draft Method 1630 if demand for this work increased.

**Notes: [since this note does not seem to be referred to anywhere, perhaps it should be moved up into the text.—otherwise, it is not contributing to the appendix]**

1) As a general rule, the order of depletion of electron acceptors during bacterial metabolism in aquatic systems is $O_2$, $NO_3$, $Fe_2O_3$, $MnO_2$, then $SO_4$. SRBs are known to produce MeHg and it is thought that iron-reducing bacteria may also methylate mercury under certain conditions. In any given environmental setting, it is not easy to determine which bacteria are dominating degradation of organic matter. To achieve an understanding of biogeochemical mechanisms of the effects of elevated sulfate, it may be desirable to measure a number of parameters, including sulfate, total mercury, MeHg, iron, ortho-P, total P, and supporting parameters such as DOC, pH, oxygen, nitrate, and potassium (for an example of the utility of measuring this suite of parameters, see Balogh et al. 2004). For instance, elevated nitrate or oxidized iron could negate the effect of elevated sulfate because the bacterial community likely finds it energetically advantageous to consume either of those two chemicals as electron acceptors before consuming sulfate. Without information on nitrate and iron, the effect of elevated sulfate may appear to be inexplicably unpredictable. Potassium data may be useful in a different way—elevated potassium can be an indicator of a hydraulic source area in decaying organic matter such as a wetland. When potassium is correlated over time with DOC, MeHg, and P, then the weight of evidence tends toward wetlands as the source area for all of the materials.

**Literature Cited:**

Balogh, S.J., Y. Nollet, and E.B. Swain. 2004. Redox Chemistry in Minnesota Streams during Episodes of Increased Methylmercury Discharge. Environmental Science & Technology. 38:4921-4927.

Caraco, N.F., J. J. Cole, and G. E. Likens. Sulfate control of phosphorus availability in lakes. Hydrobiologia. 253:275-280.

Jeremiason et al. 2006. Sulfate addition increases methylmercury production in an experimental wetland. Environmental Science & Technology. 40:3800-3806.