

**Comments on MPCA's Proposed Permanent Rules  
Relating to Wild Rice Sulfate Standard and Wild Rice  
Waters**

***In the Matter of Amendment of the sulfate water quality  
standard applicable to wild rice and identification of wild  
rice waters. Minn. R. chapters 7050 and 7053***

***(MN Revisor No. RD 4324A)***

***Office of Administrative Hearings Docket***

***No. OAH 80-9003-34519***

Submitted On Behalf of Iron Mining Association of Minnesota by:  
Michael J. Hansel  
Principle Emeritus

November 21, 2017



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# 1.0 Introduction and Overview

My name is Michael J. Hansel. I am a Principal Emeritus at Barr Engineering Co. I hold both a BS and MS in Chemical Engineering, and am a registered Professional Engineer in the state of Minnesota. I have over 40 years' experience in environmental engineering, working for the MPCA, the petroleum, power and mining industries as well as a consultant.

I have participated in Water Quality rulemakings since 1973, and have worked on wild rice issues since 2009. I participated (as an observer) in the MPCA's Advisory Committee. I was the chief drafter of the Minnesota Chamber of Commerce comments to the Advisory Committee and the MPCA throughout that process. I was a coauthor on Fort et al 2014<sup>1</sup> and Fort et al 2017<sup>2</sup> publications.

The proposed beneficial use of "wild rice waters"<sup>3</sup> protected "use of the grain of wild rice as a food source for wildlife and humans"<sup>45</sup> is uniquely Minnesotan. There is no federal beneficial use protecting wild rice, nor are there any other states which protect this particularly beneficial use.<sup>6</sup>

As such, MPCA cannot rely solely upon US Environmental Protection Agency (US EPA) rules or guidance. Instead, it must rely on Minnesota Law and state-of-the-art toxicology to determine what is needed to protect this beneficial use.

Minnesota law specifically directs the MPCA to review and revise the sulfate standard for wild rice in 2011, providing in part:

"(a) Upon completion of the research referenced in paragraph (d), the commissioner of the Pollution Control Agency shall initiate a process to amend Minnesota Rules, chapter 7050. The amended rule shall:

- (1) Address water quality standards for waters containing natural beds of wild rice, as well as for irrigation waters used for production of wild rice;
- (2) Designate each body of water, or specific portion thereof, to which wild rice water quality standards apply; and
- (3) Designate the specific times of year during which the standard applies.

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<sup>1</sup> Reference (1)

<sup>2</sup> Reference (10)

<sup>3</sup> Proposed Minn. R. 7050.0130, Subp.6.b. 2017, MPCA, MN Revisor No. RD4324A Line 1.23 – 1.24

<sup>4</sup> Proposed Minn. R. 7050.0224, Subp. 5. A. MN Revisor No. RD4324A Line 7.18-7.19

<sup>5</sup> See also MPCA Statement of Need and Reasonableness (SONAR), 2017 at Section 6. C.1. at page 33-34

<sup>6</sup> Some Native American Tribes in Minnesota have wild rice rules which are, for the most part, consistent with the current rule.

Nothing in this paragraph shall prevent the Pollution Control Agency from applying the narrative standard for all class 2 waters established in Minnesota Rules, part 7050.0150, subpart 3.”<sup>7</sup>

Using monies provided by the Legislature, MPCA conducted the following experiments to determine the toxicity of sulfate to wild rice plants:

- Hydroponic sulfate toxicity experiments
- Hydroponic sulfide toxicity experiments
- Outdoor container experiments
- Field Surveys of wild rice habitats <sup>8</sup>

In addition, the Minnesota Chamber of Commerce (Chamber) commissioned Fort Environmental Labs to conduct hydroponic sulfate and sulfide toxicity studies, to confirm and/or correct the work done by MPCA and its contractors. Finally, MPCA relied upon published literature in its deliberations.

MPCA relied upon these “multiple lines of evidence” to determine a “protective” concentration of sulfide in the porewater of wild rice beds. The MPCA, assuming that sulfate in the water column is the source of sulfide found in sediment porewater, then uses statistical methods to derive, via back-calculation, a “protective” concentration of sulfate in the overlying water column.

*“Ultimately, multiple lines of evidence, derived from field studies, outdoor container studies, and laboratory hydroponic studies, support the MPCA’s decision that the protective level of sulfide for wild rice is 120 µg/L.”<sup>9</sup>*

MPCA used a “weight-of-evidence” approach to “weight” or favor certain lines of evidence over other lines of evidence.

*“EPA has consistently recommended “a ‘weight-of-evidence’ approach that considers all relevant information and its quality, consistent with the level of effort and complexity of detail appropriate in establishing and refining water quality standards.” Information can be found in EPA’s document entitled *Weight of Evidence in Ecological Assessment*.”<sup>1011</sup>*

And

See also “Figure 3. Estimates of protective sulfide concentrations for biological endpoints from hydroponic studies, outdoor container studies, and field data, based on EC10 estimates, change-

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<sup>7</sup> Laws of Minnesota, 2011 First Special Session, ch.2, article 4, section 32. See also the MPCA’s Statement of Need and Reasonableness, Section 2.F, page 21 and following.

<sup>8</sup> Chapter 1.A of reference (2). page 4

<sup>9</sup> Section 6.E.2 of reference (3), page 67

<sup>10</sup> Id.

<sup>11</sup> Reference (11)

point analysis, and visual examination of trends. (TSD)” and especially the footnote to that figure: *“Estimates marked with an asterisk (\*) received less weight in the weighing of multiple lines of evidence due to limitations of the experiment or analysis. See TSD (Exhibit 1) for further discussion.”*<sup>12</sup>

And

See also “Table 1-8. Estimates of protective sulfide concentrations for wild rice from hydroponic studies, outdoor container studies, and field data, based on change-point analysis, EC10 estimates, and visual identification of a decrease in a graph of the proportion of field sites with wild rice present.” and especially the footnote to that table: *“Estimates identified in the text as deserving less weight in the weighing of multiple lines of evidence.”*<sup>13</sup>

MPCA proposes to set a “protective” sulfate concentration in the overlying water column of wild rice waters, calculated from the “protective” sulfide concentration in pore water, as ameliorated by concentrations of iron in the sediment. The proposed water quality standard is:

*“A. The standards in items B and C apply to wild rice waters identified in part 7.18 7050.0471 to protect the use of the grain of wild rice as a food source for wildlife and humans. The numeric sulfate standard for wild rice is designed to maintain sulfide concentrations in pore water at 120 micrograms per liter or less. The commissioner must maintain all numeric sulfate standards for wild rice waters on a public Web site.”*<sup>14</sup>

And

“(1) the calculated sulfate standard, expressed as milligrams of sulfate ion 7.26 per liter (mg SO<sub>4</sub><sup>2-</sup>/L), is determined by the following equation:

$$\text{Calculated sulfate standard} = 0.0000121 \times \text{iron}^{1.923} / \text{organic carbon}^{1.197} \text{”}^{15}$$

## 1.1 Deletion of the current standard is needed and reasonable

MPCA proposes to delete the current standard of 10 mg/L<sup>16</sup>; this proposal is needed and reasonable and fully supported by the multiple lines of evidence.

## 1.2 The proposed new water quality standard is unneeded and unreasonable

The proposed new water quality standard is **unneeded** and **unreasonable** because:

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<sup>12</sup> Reference (2)

<sup>13</sup> Chapter 1.C. of reference (2) page 33

<sup>14</sup> Reference (15) , per Minnesota Reviser RD4324A, Proposed Minn. R. 7050.0224, Subp. 5. B.1.

<sup>15</sup> Id., Subp. 5. B.1.

<sup>16</sup> Id., Subp. 2



- 
- MPCA, though alerted by their own peer review panel, misconceptualized the hydrogeological conditions under which sulfate is delivered to sediment beds. This flawed conceptual model led to the following issues which pervade their analysis:
    - Unreasonably assuming that chemical diffusion of sulfate from an overlying water column to the sediment porewater is a process favored in these environments; and
    - Unreasonably excluding important controlling variables, such as the concentrations of iron and sulfate in groundwater, from field survey data collection.
  - MPCA's model and key hypothesis are incorrect and are not supported out by the multiple lines of evidence;
  - In considering the evidence, MPCA improperly weighted the multiple lines of evidence by:
    - Unreasonably excluding or discounting peer-reviewed published science that represents the state of the art in determining toxicity of chemicals to organisms;
    - Unreasonably relying too heavily upon non-peer-reviewed, unpublished science and analyses ;
    - Unreasonably failing to take into account other wild rice stressors, and ascribed all deleterious effects on wild rice to sulfide alone.

The MPCA never states (or proves) that the proposed "protective" porewater sulfide and water column sulfate are needed. MPCA's Statement of Need and Reasonableness (SONAR) lists only the following "needs" for the proposed rules:

*"2. Statement of General Need*

*A. Need to protect the wild rice resource*

*B. Need to revise the standard to reflect current scientific understanding of sulfate/sulfide*

*C. Need to clarify the wild rice beneficial use and where it applies*

*D. Need to clarify the application of the sulfate standard*

*E. Need for a process to address wild rice waters identified in the future*

*F. Need to address legislative mandates to undertake rulemaking*

*G. Need to make supporting changes to Minnesota rules to facilitate development and implementation of effluent limits<sup>17</sup>*

Indeed, MPCA devotes only 2 paragraphs as to the need to revise the numeric standard, a total of 234 words, with absolutely **zero** discussion as to the need for a “protective” porewater sulfide and “protective” water column sulfate standard. While MPCA devotes much of the SONAR to discussion of the alleged reasonableness of the proposed standard, it gives short shrift as to the need for such a standard, and especially the need for the particular “protective” level of porewater sulfide and water column sulfate it proposes.

Each of the MPCA’s hypothetical model and the multiple lines of evidence used to support that model are reviewed in these comments, clearly demonstrating that:

- MPCA’s conceptual model does not correspond to natural conditions on wild rice waters;
- MPCA’s hypothesis is not supported by the evidence; and
- MPCA unreasonably weighted the multiple lines of evidence; discounting sound science and unreasonably relying on questionable science and analyses.

Because of the MPCA’s flawed analysis, discounting and reliance, the proposed “protective” level of sulfide and “protective” level of sulfate is unreasonable. Based on the MPCA’s and other research, there is no need to regulate sulfate or sulfide to the levels proposed, because wild rice is not affected by sulfate or sulfide at those levels, only at much higher levels. And, even if a need can be shown, the proposed “protective” porewater sulfide and water column sulfate levels are unreasonable.

### **1.3 US EPA Guidance requires the use of controlled testing to determine toxicity**

MPCA’s initial research followed the state-of-the-art toxicity testing performed on aquatic organisms to determine whether individual substances, such as sulfate, are toxic to those organisms. US EPA has multiple publications, and relies upon other publications, to develop water quality criterion and to guide states in their development of such criterion.<sup>18</sup> These include:

- Organisms and Their Uses <sup>19</sup>

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<sup>17</sup> Section 2 of reference (3), pages 19-22.

<sup>18</sup> US EPA distinguishes between water quality “standards” and water quality “criterion” as follows: “Water quality standards are regulations that include designated uses and water quality criteria to protect those uses. The criteria adopted and incorporated into the standards are the allowable concentrations of pollutants in State, Territory and authorized Tribal waters. These standards, which include water quality criteria, are adopted by the State, Territory or authorized Tribe and reviewed and approved or disapproved by EPA.” See “Relationship between Water Quality Criteria and Water Quality Standards” US EPA at <https://www.epa.gov/standards-water-body-health/relationship-between-water-quality-criteria-and-water-quality-standards> . Thus, the numerical “protective” porewater sulfide and water column sulfate “standards” as proposed by the MPCA are actually criteria under US EPA nomenclature.

<sup>19</sup> Reference (4)

- Water Quality Standards Handbook - Chapter 3: Water Quality Criteria<sup>20</sup>
- Standard Guide for Conducting Acute Toxicity Tests on Test Materials with Fishes, Macroinvertebrates, and Amphibians<sup>21</sup>
- Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms<sup>22</sup>
- Ecological Effects Test Guidelines<sup>23</sup>
- Selection of Water Quality Criteria in State Water Quality Standards <sup>24</sup>
- Technical Support Document for Water Quality-Based Toxics Control <sup>25</sup>
- Guidelines for Deriving Numerical National Water Quality Criteria for the Protection Of Aquatic Sulfate is not toxic to wild rice

Interestingly, MPCA only cites one of these publications: "Technical Support Document for Water Quality Based Toxics Control". It is clear that MPCA did not follow US EPA guidance on the development of water quality criteria, including the only one cited by them. Instead, MPCA seems to have embarked on a "voyage of discovery" to find some way to tie sulfate in the water column to alleged impacts to wild rice from sulfide in porewater, e.g. in the rooting zone. For example, even from the earliest parts of the process, the MPCA had unreasonably, and against a general and basic understanding of hydrogeology, implicated sulfate in the water column as the source of sulfide in the rooting zone: the 2014 Summary Report of the Meeting Peer Review MPCA's *Draft Analysis of the Wild Rice Sulfate Standard Study* contains this response from the MPCA to the technical reviewers: "MPCA was operating on the hypothesis that sulfate was diffusing down from the surface water into the sediment". While MPCA has determined that there may be a correlation between porewater sulfide concentration and wild rice growth, MPCA has not demonstrated how sulfide impacts wild rice, or how sulfate in the water column is the exclusive source of sulfate which gives rise to increased sulfide in the porewater.

US EPA's guidance and practice is to use hydroponic testing to determine the level at which specific chemicals impact biological organisms in water.

"If it were feasible, a freshwater (or saltwater) numerical aquatic life national criterion\* for a material should be determined by conducting field tests on a wide variety of unpolluted bodies of fresh (or salt) water. It would be necessary to add various amounts of the material to each body of water in order to determine the highest concentration that would not cause any unacceptable

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<sup>20</sup> Reference (5)

<sup>21</sup> Reference (12)

<sup>22</sup> Reference (6)

<sup>23</sup> Reference (7)

<sup>24</sup> Reference (8)

<sup>25</sup> Reference (9)

long-term or short-term effect on the aquatic organisms or their uses. The lowest of these highest concentrations would become the freshwater (or saltwater) national aquatic life water quality criterion for that material, unless one or more of the lowest concentrations were judged to be outliers. Because it is **not** feasible to determine national criteria by conducting such field tests, these Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses (hereafter referred to as the National Guidelines) describe an objective, internally consistent, appropriate, and feasible way of deriving national criteria, which are intended to provide the same level of protection as the infeasible field testing approach described above.<sup>26</sup>

And

"In each of two or more treatments, test organisms of one species are maintained for 2 to 8 days in one or more test chambers. In each of the one or more control treatments, the organisms are maintained in dilution water to which no test material has been added in order to provide (1) a measure of the acceptability of the test by giving an indication of the quality of the test organisms and the suitability of the dilution water, test conditions, handling procedures, and so forth, and (2) the basis for interpreting data obtained from the other treatments. In each of the one or more other treatments, the organisms are maintained in dilution water to which a selected concentration of test material has been added. Data concerning effects on the organisms in each test chamber are usually obtained periodically during the test and analyzed to determine LC50s, EC50s, or IC50s for various lengths of exposure."<sup>27</sup>

In fact, most of the water quality criteria were developed based upon some sort of hydroponic testing.<sup>28</sup> The reason for this is simple – it allows investigators to determine most precisely the level at which a specific chemical is toxic to aquatic life. US EPA notes in its guidance:

"In addition, aquatic organisms in field situations might be stressed by diseases, parasites, predators, other pollutants, contaminated or insufficient food, and fluctuating and extreme conditions of flow, water quality, and temperature."<sup>29</sup>

Indeed, the literature on restoration of wild rice notes many of the stressors (e.g. fluctuating water conditions, predators, parasites) are important to the proper growth of wild rice.<sup>30</sup> MPCA also noted that several of these factors are statistically significant in their own field studies (e.g. fluctuating water levels, other pollutants).<sup>31</sup> About which, more anon.

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<sup>26</sup> Reference (4)

<sup>27</sup> Reference (12)

<sup>28</sup> Review of US EPA water quality criteria, including "Quality Criteria for Water, 1986 and National Recommended Water Quality Criteria (reference (45)).

<sup>29</sup> Reference (4)

<sup>30</sup> Reference (40), (41), Chapter 12 (Chapter 12: Wild Rice Community Restoration) of Reference (42), Reference (43)

<sup>31</sup> See Table 1-5 of reference (2). The 12 field variables that are significantly correlated with the presence/absence of wild rice, as determined through binary logistic regression,

## 2.0 Sulfate is not toxic to wild rice (at concentrations observed in Minnesota Wild Rice waters)

Two state-of-the-art scientific studies clearly demonstrate that sulfate is not toxic at concentrations observed in Minnesota wild rice waters. These studies were conducted in a laboratory where physical conditions were tightly controlled (e.g. temperature, light levels, periods of darkness). Chemical parameters of all other compounds were also strictly controlled, so that only sulfate concentrations varied. Biological parameters were also tightly controlled, with no competition from other competitive or invasive species and no disease parasites. Negative controls – where the wild rice is exposed to zero (or near zero) sulfate concentrations was grown under the same conditions as the exposed wild rice. One of the two, Fort et al<sup>32</sup>, also used a positive control – where wild rice was exposed to a known toxicant, to be sure that the wild rice was not resistant to chemical toxicants. The Fort et al study also followed Good Laboratory Practices<sup>33</sup>, an internationally recognized standard “to ensure the generation of high quality and reliable test data”.

Dr. Pastor et al conducted a state-of-the-art controlled toxicity test, and concludes:

*“Sulfate exposure concentrations of 0, 10, 50, 100, 400, and 1600 mg SO<sub>4</sub>/L did not affect germination success, mesocotyl lengths, or the masses of the stem plus leaf (if any) and roots (P > 0.10 for each test).”<sup>34</sup>*

Because Dr. Pastor et al struggled early on to grow wild rice in the laboratory, the Chamber commissioned Fort Environmental Labs to conduct similar hydroponic toxicity tests. Fort et al concluded:

*“In summary, sulfate concentrations below 5000 mg/L did not adversely affect early-life stage wild rice during a 21-d [ay] period, and effects at 5000 mg/L sulfate were attributable to conductivity-related stress rather than sulfate toxicity in 2 of 4 end points.”<sup>35</sup>*

There is excellent agreement between Dr. Pastor et al and Fort Labs et al that sulfate is not toxic to wild rice at concentrations seen in Minnesota waters. Dr. Myrbo found the highest concentration of sulfate in wild rice waters to be well under either the 1,600 mg/L sulfate found by Dr. Pastor and the 5,000 mg/L found by Fort Labs et al. The primary differences between the two studies is that Fort Labs et al tested higher concentrations than did Pastor et al, and also tested sodium chloride to determine that the toxic effects of sulfate were not due to sulfate per se, but due to salt related stress (conductivity related stress).

The toxic sulfate levels determined by both Pastor et al and Fort et al, using standard toxicological testing, are more than 1,000 times the current standard of 10 mg/L. It is also interesting that the toxic sulfate levels determined by both Pastor et al and Fort et al, using standard toxicological testing, are more than

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<sup>32</sup> Reference (1)

<sup>33</sup> See OECD webpage at <http://www.oecd.org/chemicalsafety/testing/good-laboratory-practiceglp.htm>

<sup>34</sup> Reference (13)

<sup>35</sup> Reference (1)

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1,000 times the median sulfate concentration in streams (17 mg/L) and lakes (3 mg/L).<sup>36</sup> Those same levels are more than double the highest level measured by Myrbo et al. – 838 mg/L at Second Creek.<sup>37</sup>

Based on these controlled sulfate hydroponic experiments, there is absolutely no scientific support for the current standard of 10 mg/L sulfate in the water column. Nor is there any scientific support for the notion that sulfate is toxic to wild rice at concentrations observed in Minnesota wild rice waters. Therefore, the current standard of 10 mg/L sulfate<sup>38</sup> (proposed Minn. R. 7050.0224, Subp.2) should be struck as MPCA proposes; there is ample evidence of the need for and reasonableness of its elimination.

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<sup>36</sup> Chapter 1.A. of reference (2), page 7.

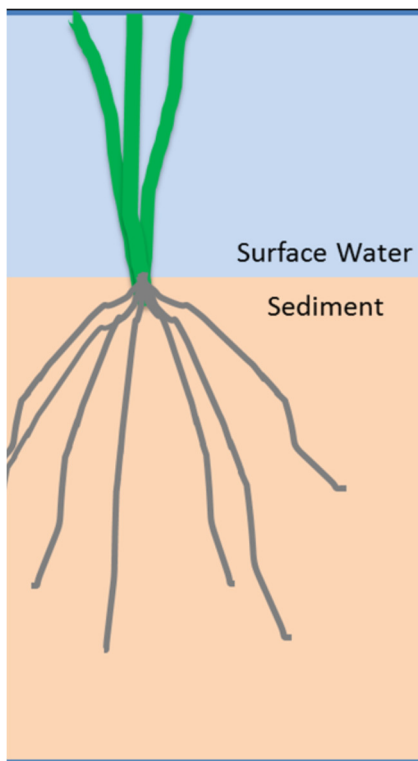
<sup>37</sup> Raw data from reference (14)

<sup>38</sup> Reference (15) per Minnesota Reviser RD4324A, Proposed Minn. R. 7050.0224, Subp. 2

### 3.0 Sulfide is not toxic to wild rice (at concentrations observed in Minnesota Wild Rice Waters)

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It may be instructive to be reminded of what a wild rice plant looks like, and how it grows. At the end of a growing season, unharvested wild rice seeds fall to the sediment in the wild rice water, and spend the winter in or on the sediment. Because wild rice seeds are so light, they do not penetrate very far into the sediment – a matter of a few centimeters, if at all. The seeds overwinter in or on the sediment, and when the overlying water warms in the spring, the seeds sprout. The seed sprouts a mesocotyl (the first leaf and bit of stem) and roots. The shoot extends up through the water and spreads leaves out on the surface of the water – the “floating leaf” stage of growth. Eventually the shoot extends above the water, where additional leaves and flowers form, and seeds are pollinated and set. See the figure below.<sup>39</sup>



As can be seen, the only parts of the wild rice plants that reside in or on the sediment are:

- The seed
- The roots

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<sup>39</sup> Table 1-7 of reference (2). page 42

- The mesocotyl

The only processes which operate in or on the sediment are:

- Sprouting
- Mesocotyl growth
- Root growth

All other processes occur above the sediment, either in the water or in the air above the water. Those processes above the sediment are exposed to oxygen – either oxygen in the air or oxygen dissolved in the water. Because of the presence of oxygen, sulfide does not exist in any appreciable amount – it is almost immediately oxidized to sulfate. Thus the only portions of the wild rice plant which could be exposed to sulfide are the seeds, the roots and the early mesocotyl growth.

MPCA's contractors conducted similar state-of-the-art controlled tests for the toxicity of sulfide. When Dr. Pastor began his hydroponic sulfide studies, he attempted to imitate the natural process, sprouting and growing seeds in a jar containing anaerobic solutions with varying concentrations of sulfide, and allowing the shoots to grow through a sealed lid so that the plant (above the mesocotyl) was in air.<sup>40</sup>

Unfortunately, Dr. Pastor was not able to grow wild rice in this manner, and so changed the experiment such that the entire plant, from sprouting seeds to 10 to 11 day's growth, was sealed inside a container, with the entire plant exposed to anaerobic conditions with varying concentrations of sulfide.

The Peer Review Panel had serious concerns about Dr. Pastor's hydroponic study, and recommended that "If these experiments can be repeated, the panel recommends the following approach:

- Use of **a split design**, in which there is a root compartment separated from the shoot. This allows **anaerobic conditions in the root zone to be maintained** and exposure of the root (but not shoots) to the experimental sulfide concentrations.
- Use of an **experimental period of 14 or 21 days**, which is standard in ecotoxicology for aquatic macrophytes. Response measurements should be collected at regular intervals.
- To the extent possible, **use of the same biological endpoints** in the laboratory study as used in the outdoor container and field studies. Decisions on biological endpoints for all the field and laboratory studies in turn will feed into the modeling approaches that can be used. This should be part of the conceptual framework and design for the overall Study and will allow better integration of the study components.

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<sup>40</sup> Meeting of MPCA Advisory Committee, 2012. Duluth, MN



- **A larger sample size.** A power analysis should be done to determine the number of replicates and treatment levels needed.
- We anticipate that **a minimum of six exposure concentrations** should be used, with several treatment levels bracketing the current water quality standard.
- **Maintaining the exposure concentrations throughout the experimental period.** This will be easier if roots are separated from shoots."<sup>41</sup> (Emphasis added)

The Peer Review Panel was chosen by a contractor to the MPCA, and included international experts on wild rice and rice production.<sup>42</sup> At the time, MPCA indicated that it would rely upon the opinions of these experts in weighting the multiple lines of evidence.

However, the MPCA and Dr. Pastor chose not to repeat the experiment, or to implement the recommendations of the Peer Review Panel. The Chamber engaged Fort Environmental Labs to undertake a further hydroponic study on the toxic effects of sulfide. At that point, the MPCA had revised its hypothesis: that the "that sulfide concentration is a function of the level of sulfate in the overlying water, and the concentrations of carbon and iron in the sediment."<sup>43</sup> Accordingly, Fort Labs also varied the amount of iron and organic carbon along with sulfide in the experiment.

The results of the Fort Labs study found that at Day 10, with no additional iron, emergence of seedlings was most affected by sulfide, but the lowest observed effects concentration (LOEC) was 3.2 mg/L sulfide.<sup>44</sup>

*"Increasing Fe concentrations reduced the toxic effects of sulfide to wild rice,"<sup>45</sup> with day 10 LOEC for emergence of seedlings rising to 7.8 mg/L sulfide.*

MPCA effectively dismisses the Fort Lab study:

*"However, under natural conditions, 21-day old wild rice plants would not have access to the atmosphere because the stems would not yet have elongated sufficiently to reach the water surface. Therefore, it is unlikely that 3-week old plants would have access to sufficient oxygen to detoxify such high levels of sulfide. ... the [Fort et al] is not given great weight among the multiple lines of evidence."<sup>46</sup>*

**MPCA's essential rejection of the Fort et al sulfide hydroponic study is not reasonable.** First, Fort Labs followed as nearly as possible the recommendations of the Peer Review Panel. Second, the Fort Labs study followed Good Laboratory practices and was certified as such. Third, the Fort Labs study followed

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<sup>41</sup> Reference (16)

<sup>42</sup> Reference (16)

<sup>43</sup> Section 1.B of reference (3). page 12

<sup>44</sup> Reference (10)

<sup>45</sup> Id.

<sup>46</sup> Section 6.E.2 of reference (3). page 71

US EPA guidance for conduct of toxicity testing for the purpose of developing water quality criterion and standards.

While the wild rice plants would not have access to the atmosphere in a natural setting, they would have access to both oxygenated water (e.g., the water above the sediment) and sunlight (allowing the plants to photosynthesize, producing oxygen). It is well documented that aquatic macrophytes can supply oxygen to the root system.<sup>47</sup> Indeed, Dr. Pastor found that in his sulfide hydroponic studies:

*"Because the plants were photosynthesizing and producing oxygen, the sulfide concentration declined during these two–three day periods."<sup>48</sup>*

Because 10 and 21 day old seedlings in the wild **would** have had access to oxygen, or could have produced their own oxygen, it is unreasonable for the MPCA to effectively dismiss the Fort et al studies. The Fort et al studies remain scientifically valid, have been peer reviewed and published, and MPCA unreasonably rejected their findings.

Interestingly, despite the fundamental flaws in Dr. Pastor's sulfide hydroponic studies, he found similar results for those parts of the plant which are in contact with the sediment:

*"Sulfide concentrations of 0, 96, 320, 960, and 2880 µg/L did **not** affect **germination success of seeds, mesocotyl masses, or mesocotyl lengths** ( $P > 0.10$  for each test)."<sup>49</sup> (Emphasis added)*

And

*"**Root lengths were only weakly depressed with increasing sulfide concentration** ( $P < 0.10$ )."<sup>50</sup> (Emphasis added)*

Thus, based on the hydroponic tests conducted by Pastor et al and Fort Labs et al, sulfide is not toxic "in the root zone" or "in the sediment" to those parts of the wild rice plant that lives there, at concentrations of 2,800 µg/L to 3,200 µg/L – hundreds of times more than the "protective" level of sulfide proposed by the MPCA – 120 µg/L. These levels are more than 50 times the median concentration determined during the field surveys conducted by Myrbo as well. Setting aside the two outlier lakes (which had sulfide concentrations more than 10 times higher than any other water body surveyed), these levels are nearly double the sulfide concentration found in wild rice waters.

Based on these controlled sulfate hydroponic experiments, there is absolutely no scientific support for the proposed "protective" sulfide standard of 120 µg/L sulfide pore water<sup>51</sup>. Nor is there any scientific support for the notion that sulfide is toxic to wild rice at concentrations observed in Minnesota wild rice waters.

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<sup>47</sup> Reference (25)

<sup>48</sup> Reference (13)

<sup>49</sup> Id at 1.

<sup>50</sup> Id

<sup>51</sup> Reference (15), per Minnesota Reviser RD4324A, Proposed Minn. R. 7050.0224, Subp. 5.A

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Therefore, MPCA has not demonstrated the need for or reasonableness of the proposed “protective” sulfide standard of 120 µg/L sulfide in the porewater<sup>52</sup>.

Based on these state-of-the-art controlled sulfide hydroponic experiments, the need for and reasonableness of the proposed “protective” sulfate standard:

Calculated sulfate standard =  $0.0000121 \times \text{iron}^{1.923} / \text{organic carbon}^{1.197}$ <sup>53</sup>, has not been demonstrated.

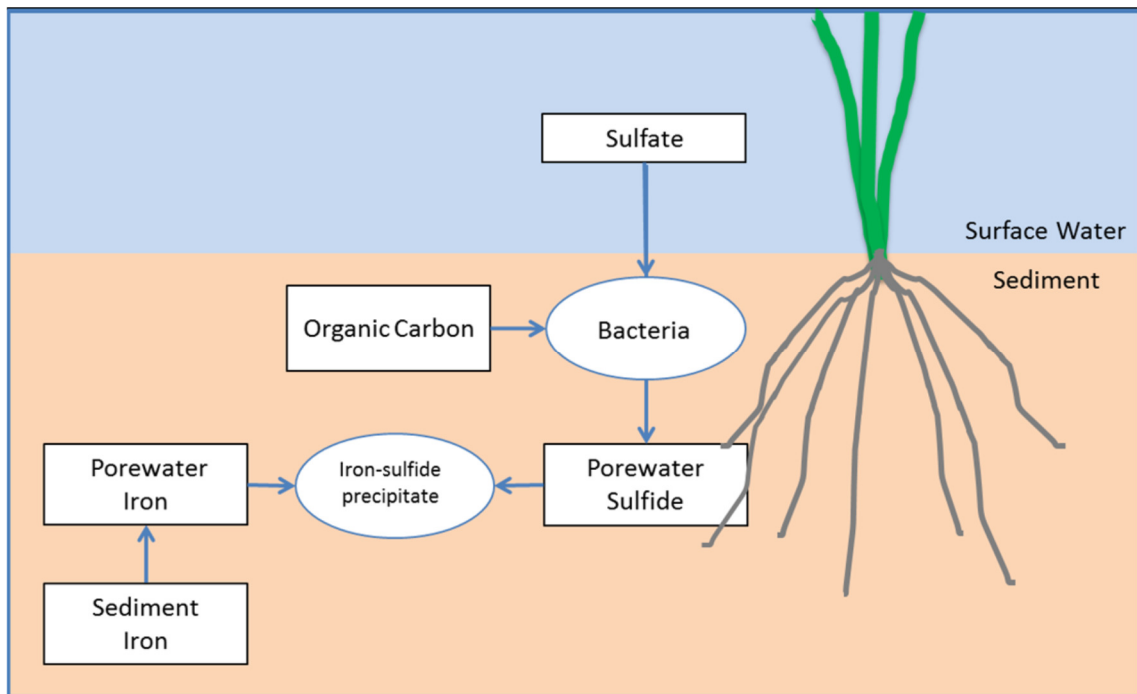
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<sup>52</sup> Id.

<sup>53</sup> Reference (15), per Minnesota Reviser RD4324A, Proposed Minn. R. 7050.0224, Subp. 5. B.1.

## 4.0 MPCA's Conceptual Model and Key Hypothesis do not correspond to natural conditions

MPCA has developed and relied upon a model of how wild rice interacts with the environment in wild rice waters. This model is summarized in Figure 1-7 of the Technical Support Document<sup>54</sup> (TSD), reproduced below:



Source: Figure 1-7 of reference (1)

### Conceptual model of the primary variables affecting the relationship between surface water sulfate and porewater sulfide. .

This conceptual model underwent much scrutiny by the Peer Review Panel (PRP) which the MPCA employed during the development of this rule. On the issue of the utility of the field survey data, which the MPCA heavily relies on in developing the proposed standard. The PRP asked specifically for clarification about groundwater:

*"Did MPCA consider how sulfate loadings from groundwater may influence sulfate and sulfide concentrations in surface waters and sediment porewaters?"*

<sup>54</sup> Reference (2)

**MPCA Response:** *MPCA recognized that groundwater movements into or out of surface waters may influence surface water and sediment porewater concentrations of sulfate and sulfide, but did not have a reliable method of assessing groundwater movement, especially for sulfate and sulfide.*<sup>55</sup>

Setting aside the fact that reliable methods, including seepage meters, groundwater wells, and robust modeling methods have been developed and used by hydrologists for decades<sup>56</sup>, the MPCA's analysis has yet to address sulfate in groundwater and its likely control of both the concentrations of sulfide in sediment porewater and sulfate in the surface water column.

This is the heart of the problem: in northern Minnesota, groundwater is constantly, and nearly everywhere, discharging to streams and lakes because groundwater water table elevations are higher than adjacent surface water levels, leading to hydraulic pressure that favors this discharge<sup>57</sup>. Coupled with the fact that this groundwater carries with it 1-100 mg/L sulfate in this region<sup>58</sup>, it is likely that groundwater is the dominant control on porewater sulfate and sulfide concentrations, and, to a large degree, also likely controls sulfate concentrations in the surface water column.

A recent study by the Minnesota Department of Natural Resources (MDNR) explicitly states that while point discharges "are the dominant source of sulfate to sites downstream from them, it appears that the background sulfate. . .has the largest influence" on sediment porewater chemistry, and the conversion of sulfate to sulfide (Berndt et al., 2016). "This is because point sourced sulfate is transported generally under oxidized conditions and is not flushed through riparian sediments in a gaining stream watershed system."<sup>59</sup>

In stark contrast, MPCA's conceptual model relies on sulfate delivery **to the sediment bed from the overlying water column through chemical diffusion**; nowhere does MPCA demonstrate that this mechanism is reasonable. The MPCA also neglects the groundwater contributions of dissolved iron.

The MPCA model gives rise to the following oversights and interpretive errors in the MPCA's analysis:

- Because of the "a prior assumption" assumption and untested hypothesis about the source of sulfate in the sediment porewater, MPCA neglected to collect pertinent information on groundwater quality and groundwater advection rates during the field survey. Although the PRP specifically pointed out the oversight, MPCA continued to neglect to collect the reasonably needed data. Even though these data were not collected, they cannot be ruled out as dominant factors controlling the chemistry of the sediment porewater (e.g. nutrients, iron and other metals). Most hydrologists would recognize that groundwater is the dominant control<sup>60</sup>.

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<sup>55</sup> Reference (16), page 15.

<sup>56</sup> Reference (18)

<sup>57</sup> Reference (19)

<sup>58</sup> Reference (20)

<sup>59</sup> Reference (17), pages 74-79

<sup>60</sup> Linking soil- and stream-water chemistry based on a riparian flow-concentration integration model. Reference (21).

- Because those data were not collected, they were not included in statistical analysis such as the regression analyses or the structural equation modelling that resulted in the proposed equation. Therefore, the analysis does not include a likely controlling factor - a “lurking” third factor that controls both the dependent and independent variables in the study.

So, the MPCA’s supposition that a tenuous correlation between water column sulfate and porewater sulfide indicates that the “equation works 80% of the time” is problematic. The tenuous correlation found by MPCA may simply reflect two factors that are controlled by the underlying (and unmeasured) influence of groundwater.

Under MPCA’s conceptual model, and in the resulting proposed equation-based sulfate standard, **sulfate migrates via diffusion only from the overlying water column** where it is converted by microorganisms in the sediment to sulfide, using organic carbon from the sediment. **There are no other sources of sulfate** which can move into the sediment, and no other sources of organic carbon that can move into the sediment.

Similarly, under MPCA’s model, **organic carbon only moves from the sediment to the porewater**. **There are no other sources of dissolved organic carbon**. And, under MPCA’s model, **iron only moves from the sediment to the porewater** and reacts with sulfide to precipitate the sulfide and make it unavailable to interact with wild rice or other biota. **There are no other sources of iron** which can move into the porewater and interact with sulfide.

This model gives rise to MPCA’s key hypothesis regarding the impact of sulfate on wild rice:

*“MPCA staff had a hypothesis, stated in the study protocol informed by researchers, tribes and stakeholders, (Exhibit 7) that **sulfate exerts negative effects on wild rice** when it is converted to hydrogen sulfide, which is much more toxic than sulfate. In mucky low-oxygen environments, such as those favored by wild rice (which roots in the sediment of aquatic habitats), the respiration of sulfate reducing bacteria in the sediment converts **sulfate diffusing into the sediment from the overlying water into hydrogen sulfide in the sediment porewater**.”*

*“The sulfide concentration in the porewater, the water in the sediment between solid particles, is key because it is the porewater that is in contact with the roots of wild rice. The wild rice study and research supported the MPCA staff’s hypothesis, showing that the pollutant that harms wild rice is sulfide in the sediment porewater.”<sup>61</sup> (Emphasis added)*

Neither MPCA’s conceptual model nor key hypothesis is a reasonable depiction of the natural conditions in wild rice waters. They were specifically called into question by the technical peer review panel, who explicitly identified that the field study “requires addressing the full hydrological system (supply by surface water and groundwater)”. the conceptual model used by the MPCA is not borne out in the general

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<sup>61</sup> Reference (3)

understanding of the hydrologic cycle, in decades of research on Minnesota lakes and rivers by USGS and other researchers, or by recent research published by the Minnesota DNR<sup>62</sup>.

#### 4.1 MPCA's Conceptual Model of wild rice waters as “bathtubs” does not reflect natural conditions

In natural wild rice beds (both in streams and lakes), groundwater flows into sediment porewater, generally from the area of high hydraulic head (the groundwater) to the area of low hydraulic head (the surface water body).<sup>63</sup> MPCA acknowledges that wild rice appears to be associated with areas of groundwater inflow:

*“Wild rice is in a group of emergent plant species that had a mild statistical association with groundwater inflow areas of lakes”<sup>6465</sup>*

In fact, the reference cited by the MPCA in its TSD goes further:

*“Emergent and isoetid (Adams 1985) species **may be the most likely to be influenced by groundwater flow**. Both plant types were not well represented in this study. Emergent species are found in shallow water where groundwater flow is often the strongest (McBride and Pfannkuch 1975) and they are dependent on roots for nitrogen and phosphorus, whereas many submersed species can obtain nutrients from the water column if they are more abundant in the water than in the underlying sediment.” (NB: wild rice is an emergent aquatic macrophytes) (Emphasis added)*

And

*“This study showed a group of emergent species including *Pontederia cordata*, *Eleocharis palustris*, *Sagittaria graminea*, *Carex aquatilis*, *Typha latifolia*, and ***Zizania spp.*** [e.g. **wild rice**] that was mildly associated with shallow water, groundwater inflow areas.”<sup>66</sup> (Emphasis and insert added)*

Unfortunately, the MPCA treats their dataset as if wild rice waters are essentially “bathtubs” with no interaction between groundwater and surface water, and no interaction between groundwater and sediment and porewater. Thus, MPCA’s model ignores the important role of groundwater in bringing nutrients and sulfate into the sediment and porewater. It is unlikely that sulfate from the surface water is the primary source for the formation of sulfide.

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<sup>62</sup> Reference (17)

<sup>63</sup> Reference (18).

<sup>64</sup> Table 1-6 of reference (2), page 26.;

<sup>65</sup> Reference (22)

<sup>66</sup> Reference (22)

In fact, this scenario almost never exists, because water bodies dominantly “gain” water from groundwater in this region. Groundwater is well known to interact with sediment porewater. There is strong evidence of groundwater interaction with the water column (surface water) and sediment and porewater.<sup>67</sup>

## 4.2 Literature demonstrates that groundwater interacts with sediment and wild rice

One of the references cited by Nichols and Shaw<sup>68</sup> describes the interaction between groundwater and wild rice waters:

*“The mutual exchange of water between lakes and contiguous permeable ground-water bodies, which are thin relative to the diameter of the lakes, was modeled digitally. **A significant rate of seepage was found to extend only a relatively short distance from shore, thus forming a narrow band around the lake's perimeter.** This near-shore concentration of seepage is an effect only of the geometry of the ground-water flow system, which is governed by the geometry of the body of permeable material, the spatial distribution of permeability within it, and the form of the water table. Near-shore seepage occurs independently of the presence of fine-grained, low permeability sedimentary bottom materials in the central part of the lake. Digital modeling indicates that the velocity of seepage generally decreases at an exponential rate as a function of distance from shore. **Field measurements of seepage rates through the bottom of Lake Sallie, west-central Minnesota, confirm the model results by demonstrating that both the near-shore seepage band and the exponential decrease in seepage velocity actually exist.**”<sup>69</sup>*  
(Emphasis added)

The “near-shore seepage band” is precisely where wild rice grows. A recent publication by Berndt et al. (2016) reaches similar conclusions.

*“**. stream segments along the flow path mostly gain water from the surrounding landscape.** The hydraulic gradient is, therefore, well poised to produce and transport chemicals . . . to the river, but water [in the water column] is not well poised hydrologically to interact with riparian sediments.”<sup>70</sup>* (Emphasis added)

Thus, MPCA’s model is fundamentally flawed, because it unreasonably implicates the water column as the source of sulfate. It ignores the important role of groundwater in bringing nutrients and sulfate into the sediment and porewater.

MPCA appears to acknowledge that groundwater flow can be significant, when it authorizes an alternate standard (see proposed rule MN Rules 7050.0224, Subp. 5. B.2:

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<sup>67</sup> Reference (17)

<sup>68</sup> Reference (22)

<sup>69</sup> Reference (22)

<sup>70</sup> Reference (17)



*“(2) The commissioner may establish an alternate sulfate standard for a wild rice water when the ambient sulfate concentration is above the calculated sulfate standard and data demonstrates that sulfide concentrations in pore water are 120 micrograms per liter or less. Data must be gathered using the procedures specified in Sampling and Analytical Methods for Wild Rice Waters, which is incorporated by reference in item E. The alternate sulfate standard established must be either the annual average sulfate concentration in the ambient water or a level of sulfate the commissioner has determined will maintain the sulfide concentrations in pore water at or below 120 micrograms per liter.”<sup>71</sup>*

The SONAR states that the commissioner may develop an alternate standard, and notes that groundwater influence is the reason for the need for and reasonableness of the provision. At page 14 of the SONAR:

*“As an alternative to the equation-derived numeric standard, the proposed rule allows the commissioner to establish an alternate standard based on the actual amount of sulfide in the sediment porewater. The equation-based numeric standard is designed for the vast majority of water bodies, where changes in the porewater sulfide concentration is proportional to changes in sulfate in surface water. An alternate standard may be appropriate **when the sulfide in the sediment porewater is being controlled by sulfate in the groundwater**, rather than surface water.”<sup>72</sup>(Emphasis added)*

At page 33:

*“The proposal establishes a process for developing an alternate standard where evidence exists that porewater sulfide is at or below 120 µg /L without reference to surface water sulfate levels (**as when groundwater is a heavy influence on sediment porewater**).<sup>73</sup> (Emphasis added)*

At pages 89 to 91 of the SONAR, MPCA is clear why the alternate standard is needed and reasonable:

*“A water body that consistently exhibits porewater sulfide less than 120 µg/L when the equation predicts sulfide greater than 120 µg/L is **most likely experiencing the upward movement of groundwater through the sediment**.<sup>74</sup> (Emphasis added)*

And

*“The ability to set an alternate standard responds to concerns about false positives (where surface water sulfate above the calculated standard does not elevate porewater sulfide) that **potentially could cause investment in sulfate control that is not needed to protect wild rice**. The MPCA is aware of sites where the relationships established by the equation do not hold true; that is, where*

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<sup>71</sup> Proposed Permanent Rules Relating to Wild Rice Sulfate Standard and Wild Rice Waters MN State Revisor No. RD 4324A, lines 8.18 to 8.25

<sup>72</sup> Reference (3)

<sup>73</sup> Id

<sup>74</sup> Id

sulfate does not convert to expected levels of sulfide based on the equation. **This is usually due to circumstances specific to the water body, such as groundwater flow that counteracts the diffusion of surface water sulfate into the sediment.**<sup>75</sup> (Emphasis added)

And

*“False positives may also be the result of the **failure of a waterbody to conform to the conceptual model** upon which the equation is based.”<sup>76</sup> (Emphasis added)*

We respectfully suggest that the failure is more likely of the conceptual model and hypothesis, not the water body.

The technical support document (TSD) attempts to provide the evidence that the MPCA’s model is correct, reasonable and needed. However, it is essentially a tautology. MPCA argues that because certain waters don’t fit the model (e.g. exhibit “false positives”), the model is correct and the waters that don’t fit the model (because groundwater inflow to the sediment prevents the formation of sulfide at levels which have the potential to harm wild rice) are “outliers”. Indeed, MPCA presents only one measurement to demonstrate that this occurs; a measurement of Second Creek (see Yourd, 2017)<sup>77</sup>. Those measurements showed that porewater sulfide was lower than the “protective” level of 120 µg/L, “porewater sulfide was less than 120 µg/L in each case despite relatively high sulfate concentrations (303 to 838 mg/L; sulfate was not measured for one of the samplings).”<sup>78</sup>

MPCA makes other admissions in the TSD regarding groundwater flow being an important consideration in the geochemistry of porewater – one that is not reflected in the MPCA’s model. For example, on page 1, MPCA admits:

*“Sulfate is a natural chemical **commonly found in** surface and **groundwater.**” (Emphasis added)*

*In Table 1-1 (under outdoor container experiment column), MPCA admits that the container study has the following limitations:*

*“Eventual steady states with various sulfate loads may not mimic the environment, **since there is no loading of other key constituents, such as iron, from groundwater** or the watershed.” (Emphasis added)*

And under the Sediment incubation laboratory experiment column, MPCA admits the groundwater is a key missing component

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<sup>75</sup> Id.

<sup>76</sup> Id.

<sup>77</sup> Reference (36)

<sup>78</sup> Reference (2), page 69

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*"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."* (Emphasis added)

On page 23

*"However, **one exception may be sites with upwelling groundwater; it has been reported that such sites may be favorable habitat for wild rice** (Table 1-6). **Consistent upward groundwater flow would break the usual relationship between sulfate in surface water and sulfide in porewater, because sulfate would be less likely to move downwards into the sediment when groundwater is moving upwards. Therefore, at some sites the sulfate concentration of the groundwater may be more important than the surface water in controlling the production of porewater sulfide**, but statistical analysis shows that at most sites porewater sulfide is a function of surface water sulfate (Pollman et al., in press). ... Even if this were not the case, the **possibility that groundwater, rather than surface water, controls porewater sulfide in a specific wild rice bed does not negate the validity of the empirically observed, statistically significant, relationship between surface water sulfate, sediment iron, sediment TOC, and porewater sulfide as a general matter** (Part D of this chapter, below; Pollman et al., in press)." (Emphasis added)*

In other words, groundwater "upwelling" through the sediment has been observed as a critical component in the growth of wild rice. Yet, despite the measurements of multiple lakes in Wisconsin and multiple streams and lakes in Minnesota, MPCA holds that the model is still "valid" because of the MPCA's and Dr. Pollman's statistical analysis.

In Table 1-6 on page 26, MPCA admits that it has made no measurements of groundwater flow in the field surveys, and that upward groundwater flow would invalidate the model:

*"**No information was collected on groundwater movement at the field sites. Upward flow would break the usual relationship** between surface water sulfate and sulfide, because sulfate would be less likely to move downwards into the sediment when groundwater is moving upwards." (Emphasis added)*

Not only does groundwater movement through the sediment prevent chemical diffusion of surface water (and associated sulfate) into the sediment, but groundwater also brings with it other chemicals which participate in the reaction to form or prevent the formation of sulfide. On page 53 of the TSD:

*"For instance, an isolated bay of a wild rice water could plausibly have **low sediment iron concentrations because the local watershed is poor in iron or there is no emergent groundwater rich in iron** (Maranger et al., 2006)." (Emphasis added)*

At page 67 of the TSD, MPCA admits that sulfate will not move from the water column into the sediment when groundwater is moving into the sediment:

*"False positives were consistently observed in four of the waterbodies. These four waterbodies consistently had porewater sulfide below 120 µg/L, despite predicted sulfide concentrations above that threshold (Table 2-1). Wild rice was growing in all four of the waterbodies. The most reasonable explanation for unexpectedly low porewater sulfide in these waterbodies is that **surface water sulfate was not penetrating downward into the sediment because of upwelling groundwater.**" (Emphasis added)*

On page 69 of the TSD, the MPCA admits that the model is based upon assumption, not evidence, not measurements:

*"**The model is based on the assumption that** porewater sulfide is produced by bacteria in the sediment that are utilizing **sulfate transported from the surface water downwards into the sediment.** However, **there may be wild rice waters where groundwater actively moves upward through the sediment, in which case sulfate in surface water would not play a major role in the production of sulfide.** In such cases, ambient sulfate in surface water in comparison to the calculated sulfate standard can produce false positives, depending on the sediment concentrations of organic carbon and extractable iron. **Wild rice waters with upwelling groundwater might be most often encountered in gaining streams, which receive water from groundwater, and some lakes that receive groundwater.** The interaction of groundwater and surface waters is complicated, and is a function of multiple variables such as the texture and depth of soils, topography, and even seasonal growth of plants that transpire large amounts of groundwater, such as willows (Fetter, 2001). (Emphasis added)*

Most water bodies (both streams and lakes) in Minnesota (except southeast Minnesota) are gaining. In Table 2-1 of the TSD MPCA notes multiple reasons why the model is incorrect, yet treats these:

*"Waterbodies are clustered into three categories in an effort to understand why false positives were produced: 1) Four waterbodies for which **the likely explanation is that groundwater was upwelling through the sediment,** so that the sites were not accurately modeled by the proposed equation; 2) Four waterbodies for which the likely explanation is random error because sulfate level is only slightly greater than the calculated protective concentration; and 3) **Six waterbodies,** each of which were sampled at least three times, **that exhibited inconsistent behavior,** which might be resolved with more extensive sampling. (CPSC120 = Calculated Protective Sulfate Concentration associated with a protective sulfide concentration of 120 µg/L)".*

Note that there are 15 such lakes, of the 67 lakes which MPCA sampled which actually contained wild rice. Thus, 22% of the wild rice waters don't behave as the model suggests, which caused the MPCA to include an "alternate" standard, which is not found in any other Minnesota water quality standard or US EPA water quality criterion:

*"The commissioner may establish an alternate sulfate standard for a wild rice water when the ambient sulfate concentration is above the calculated sulfate standard and data demonstrates that sulfide concentrations in pore water are 120 micrograms per liter or less. Data must be gathered*

using the procedures specified in *Sampling and Analytical Methods for Wild Rice Waters*, which is incorporated by reference in item E. The alternate sulfate standard established must be either the annual average sulfate concentration in the ambient water or a level of sulfate the commissioner has determined will maintain the sulfide concentrations in pore water at or below 120 micrograms per liter.”<sup>79</sup>

Pollman et al also note the fact that groundwater discharge is “important” for replenishment of iron and other substances:

“This is an extension of the fact that sediment Fe must be present for dissolved Fe(II) concentrations to develop in the porewater, **unless an alternative source of dissolved Fe(II) such as via shallow groundwater discharge is important**, ref: Appelo, C. A. J. and H. Postma (2010), *Geochemistry, groundwater and pollution*. Second edition. CRC Press, Boca Raton, FL. 649 pp.”<sup>80</sup> (Emphasis added)

Berndt et al found that this was exactly the case in the St. Louis River system in northeastern Minnesota.

“It was found that peaks in measured methylmercury (MeHg), total mercury (THg), **dissolved organic carbon (DOC), and dissolved iron (Fe) concentrations correspond to periods in time when modeled recharge was dominated by active groundwater throughout the watershed.**

“Taken together, the data and flow model imply that MeHg is released into groundwater that recharges the river through riparian sediments following periods of elevated summer rainfall. The measured sulfate concentrations at the upstream site reached minimum concentrations of approximately 1 mg/L just as MeHg reached its peak, **suggesting that reduction of sulfate from non-point sources exerts an important influence** on MeHg concentrations at this site. While mines are the dominant source of sulfate to sites downstream from them, **it appears that the background sulfate which is present at only 1-6 mg/L, has the largest influence** on MeHg concentrations. This is because **point sourced sulfate is transported generally under oxidized conditions and is not flushed through riparian sediments in a gaining stream** watershed system. (Emphasis added)

“According to these models, **groundwater that enters a river in its headwater regions attains much of its chemistry by reaction with riparian sediments, the last substrate with which it is in contact prior to becoming part of the surface water flowage.** Thus, a comparison of measured chemistry to HSPF modeling results can help to determine the degree to which similar processes might help to account for the chemistry of water in mine-impacted portions of the St. Louis River.” (Emphasis added)

“CAG [concentration in active groundwater] values close to 1.0 throughout the region indicate that **active groundwater was the overwhelmingly dominant source of water input during most**

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<sup>79</sup> Reference (15), per Minnesota Reviser RD4324A, Proposed Minn. R. 7050.0224, Subp. 5. B.1.

<sup>80</sup> Reference (39)

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**periods from April through July. Overland surface runoff and interflow waters were common immediately following large rain events, but these were flushed quickly downstream by more persistent, longer lasting recharge from active groundwater flow.**

(Emphasis and parenthetical added)

*"Calculated transit times for groundwater-derived components were generally 10 days or less at all sites from April through July." (E.g. the early growing season for wild rice)*

*"Active groundwater tracer concentrations calculated for each of the sampling points approached unity during periods when elevated methylmercury concentrations were found, **signifying the importance of groundwater recharge** in the MeHg generating process in this river. Although three major rain events early in the growing season led to pronounced but briefly elevated simulated tracer concentrations for interflow and **surface water runoff, these components were diluted and washed quickly downstream by groundwater recharge** when elevated MeHg concentrations were found in the river (Figs. 3 and 4)."<sup>81</sup> (Emphasis added)*

The fact is that groundwater provides much of the flow into wild rice waters, carries with it many nutrients, including dissolved sulfate and iron, and controls the chemistry of porewater in riparian environments. MPCA cannot ignore either the flow or, as will be seen below, the chemistry that accompanies the flow.

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<sup>81</sup> Reference (17)

## 5.0 MPCA's key Hypothesis is not supported by the multiple lines of evidence

In a nutshell, MPCA's key hypothesis is that:

***The source of sulfate is the water column.*** Sulfate from the water column migrates via chemical diffusion into the sediment and porewater. There, microbes convert sulfate to sulfide, using organic carbon in the porewater. ***The source of the organic carbon is the sediment.*** The ***sulfide***, rather than sulfide, ***is the compound which is toxic to wild rice*** because "it is the porewater that is in contact with the roots of wild rice".<sup>82</sup> Iron reacts with the sulfide, providing some amelioration of the sulfide toxicity. ***The source of the sulfide is the sediment.*** Iron may ameliorate the toxicity of sulfide by precipitation it out of the porewater. ***The source of the iron is the sediment.***

Note that a **hypothesis** is not a fact or even a scientific theory:

"A **supposition** or proposed explanation **made on the basis of limited evidence** as a **starting point** for further investigation.<sup>83</sup> (Emphasis added)

Berndt et al were studying the formation of methyl mercury (MeHg) in the St. Louis River. While not directly related to wild rice, the same processes are in place – sulfate is reduced to sulfide, using dissolved organic carbon, to form methyl mercury in the porewater. The formation of methyl mercury involves the same chemical and biological reactions in the sediment and porewater as does the formation of sulfide which can impact wild rice.

The work of Berndt et al suggests that, regarding sulfate from surface water interacting with sediment and porewater:

***"sulfate from mines [point discharges] may have had relatively little opportunity to interact with reduced sediments.***<sup>84</sup> (Emphasis and brackets added)

*"Two factors make it difficult for sulfate from the mines to impact MeHg in the rivers. First, the sulfate from mines is introduced largely as point sources at the ends of a relatively few tributaries and, thus, is limited geographically from interacting with riparian sediments in the great majority of the region. Second, even **in the streams it flows through, it may be hydrologically excluded from reacting with riparian sediments that have the reduced conditions** needed to promote methylation. The St. Louis River watershed receives, on average, approximately 8 inches more precipitation than is evaporated or transpired, and thus stream segments along the flow path mostly gain water from the surrounding landscape. **The hydraulic gradient, is therefore, well poised to***

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<sup>82</sup> Reference (2)

<sup>83</sup> Google dictionary at: [https://www.google.com/search?sourceid=navclient&aq=&oq=hypothesis&ie=UTF-8&rlz=1T4IAGV\\_enUS652US653&q=hypothesis&gs\\_l=hp...0i131i3j0i0131j41.0.0.0.1735.....0.LLx4jMLLz4k](https://www.google.com/search?sourceid=navclient&aq=&oq=hypothesis&ie=UTF-8&rlz=1T4IAGV_enUS652US653&q=hypothesis&gs_l=hp...0i131i3j0i0131j41.0.0.0.1735.....0.LLx4jMLLz4k)

<sup>84</sup> Reference (17)

***produce and transport chemicals like DOC and MeHg to the river, but water derived from mines is not well poised hydrologically to interact with riparian sediments where DOC and MeHg are likely to be produced.*** This does not mean that sulfate introduced as point sources from mines or municipalities will never impact zones of active mercury methylation, but it does imply that instances may be rare in a mining region that receives more rainfall than can evaporate or transpire from the landscape.<sup>85</sup> (Emphasis added)

And

***“However, the great majority of the mining sulfate added to streams apparently has little measureable impact on stream chemistry because opportunities are rare for the sulfate added as a point source to flow onto landscapes, through reduced soils, and back out into openly flowing waters.”***<sup>86</sup> (Emphasis added)

Ng et al also found that, except for flooding conditions, groundwater upwelling prevented influx of surface water.

***“At our study site, very high concentrations of  $SO_2^{-4}$  from mining-derived surface water (2.8 to 10.3 mM) penetrates deeper into sediments under down welling flood conditions, while lower concentrations in the up-gradient groundwater buffer against the influx of surface water during upwelling conditions.”***<sup>87</sup>

Thus, it is **unlikely** that sulfate from the water column is the main source for sulfide formation in the porewater. It is also **likely** that iron and dissolved carbon are migrating to the porewater, not from dissolution of the sediment (MPCA's primary source), but are being transported to the sediment, porewater, and ultimately, to the surface water body, via the groundwater flow into the wild rice water. MPCA presents no evidence that sulfate from the water column is the only source for conversion to sulfide in the porewater. It merely makes a policy decision, in the form of the hypothesis, that such is the fact.

In short, MPCA's hypothesis remains a “supposition” or “proposed explanation” – one that is not supported by a general understanding of what controls the chemistry of porewater. The hypothesis has led to a statistical analysis that lacks characterization of a potential controlling factor – groundwater quality. If the quality of groundwater controls porewater sulfide, instead of surface water sulfate (as assumed by the MPCA), this source may exist completely independent of surface water concentrations. It cannot be ruled out with the existing dataset. The likelihood, based on the work of Berndt et al., 2016 – that groundwater, rather than surface water, controls porewater sulfide in a wild rice bed means that controlling sulfate concentrations in overlying surface water may be ineffective in mitigating the effects of porewater sulfide. It means that changing surface water sulfate concentrations may not affect

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<sup>85</sup> Id.

<sup>86</sup> Id.

<sup>87</sup> Reference (37), page 18



concentrations of porewater sulfide **at all**. The lack of characterization, or inclusion of groundwater quality in this analysis leads to a proposed equation that is analogous to blaming increased incidents of drowning on ice cream consumption. This is unreasonable. MPCA's Unreasonable Weighting of Multiple Lines of Evidence

As noted above, MPCA relied primarily upon the following research which it commissioned to determine the toxicity of sulfate to wild rice plants:

- Controlled sulfate and sulfide toxicity experiments
- Outdoor container experiments
- Field Surveys of wild rice habitats <sup>88</sup>

However, MPCA unreasonably ignored research commissioned by the Chamber as well as other literature, giving all considerably less weight in its weighting of the multiple lines of evidence.

While MPCA concedes that sulfate in and of itself is not toxic to wild rice, MPCA next developed a hypothesis that sulfide in the rooting zone of wild rice was the toxicant which impacted wild rice, and that sulfate from the overlying porewater, diffusing into the rooting zone, was the primary source of that sulfide.

*"MPCA staff had a **hypothesis**, ... that sulfate exerts negative effects on wild rice when it is converted to hydrogen sulfide, which is much more toxic than sulfate. ... the respiration of sulfate reducing bacteria in the sediment converts sulfate diffusing into the sediment from the overlying water into hydrogen sulfide in the sediment porewater."<sup>89</sup>*

*"The sulfide concentration in the porewater, the water in the sediment between solid particles, is key because it is the porewater that is in contact with the roots of wild rice. The wild rice study and research supported the MPCA staff's hypothesis, showing that **the pollutant that harms wild rice is sulfide in the sediment porewater**."<sup>90</sup> (Emphasis added)*

MPCA's multiple lines of evidence do not prove MPCA's hypothesis; at best they demonstrate a correlation between sulfide and wild rice presence or absence. At worst, they demonstrate that a protective level of sulfide is much higher than proposed by the MPCA. Further, the MPCA has not resolved the conflicts between the findings of the hydroponic tests with the other studies it conducted. As such, it is unreasonable to propose such a low protective level, as will be seen.

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<sup>88</sup> Chapter 1.A. of reference (2), page 4

<sup>89</sup> Section E.1. of reference (3), page 65

<sup>90</sup> Id

## 5.1 State-of-the-Art Controlled sulfate & sulfide toxicity experiments

MPCA effectively dismisses the very studies which represent the state-of-the art in toxicity testing, and the best controlled experiments. Pastor et al and Fort et al state-of-the-art controlled hydroponic studies clearly demonstrated that sulfate is not toxic to wild rice at concentrations observed in Minnesota wild rice waters. The studies also show that sulfide in the rooting zone (e.g. sediment and porewater) is not toxic to wild rice at concentrations observed in Minnesota wild rice waters. See above.

However, MPCA completely disregards the controlled, state-of-the-art toxicity testing for sulfate on wild rice, and effectively dismisses the Fort et al study on the toxicity of sulfide, despite the fact that it followed the recommendations of MPCA's Peer Review Panel. MPCA incorrectly calculates the toxicity of sulfide on the entire plant from Pastor et al, including those portions of the plant which are not and would never be exposed to anaerobic conditions or sulfide. MPCA disregarded the recommendations of its own Peer Review Panel, and did not require Pastor et al to perform new controlled sulfide toxicity tests, but incorrectly and unreasonably relied upon the flawed studies. MPCA appears to have purposely misinterpreted those tests, ignoring the results of the Fort et al tests and the recommendations of the peer review study.

Therefore, MPCA unreasonably relied upon the Pastor et al controlled sulfide toxicity tests (hydroponic tests) in, for example, Figure 1-2 of the TSD<sup>91</sup>, and elsewhere throughout the SONAR and TSD.

## 5.2 Outdoor Container studies were seriously flawed and cannot be reasonably relied upon.

The MPCA unreasonably relied upon the data generated by Dr. Pastor et al in his outdoor container study. There are serious flaws in the outdoor container studies, because of which the MPCA should have not relied as heavily as it did in developing protective sulfide and sulfate levels.

Unlike the state-of-the-art controlled hydroponic tests conducted by Pastor et al and Fort et al, the outdoor container studies were much less well controlled. In direct contradiction to US EPA guidance, Pastor et al did not renew the solutions in the outdoor containers, resulting in depletion of iron, and perhaps nutrients and other compounds necessary for the growth and health of wild rice.

- Other serious flaws in the outdoor container study are:
- In 2013, 72 to 84% the control plants, for reasons unrelated to sulfate or sulfide concentrations;
- In the years following 2013, less than 30% of the plants survived, resulting in insufficient numbers for reasonable statistical analysis; and

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<sup>91</sup> Chapter 1.C. of reference (2), page 34.

- Dr. Pastor et al failed to measure the initial concentrations of sulfide, iron, other nutrients and other parameters in the water, porewater and sediment, which could have resulted in depletion of iron and nutrients in the containers, which may have skewed the results of the studies.

The MPCA does not resolve the discrepancies between the results of the Fort et al controlled sulfate and sulfide toxicity testing, the Pastor et al controlled sulfate and (properly interpreted) sulfide toxicity testing and the uncontrolled outdoor container studies. These are significant as will be seen.

The Chamber noted these primary concerns with the outdoor container study in its 2014 Technical Analysis<sup>92,93</sup>

*... it is not possible to know initial container conditions, including baseline sediment, porewater, and surface water physical conditions and chemical concentrations. Second, the containers are hydrologically isolated, preventing infusion of groundwater carrying iron or other constituents (e.g., plant micronutrients) that would be present in the natural environment. Nutrient depletion may also have occurred over time (without replenishment). Finally, in 2013, Dr. Pastor reported significant seedling mortality following thinning. As discussed by Dr. Pastor, seedling mortality may have been influenced by removal of five plants per tank in years 2011 and 2012 (one sixth of the population) resulting in depletion of the seed bank for future population growth.<sup>94</sup> In 2013, decreases in total plant biomass were not significantly correlated with increases in sulfate concentration.*

The 2013 data are particularly troublesome because many of the plants, including the controls, died. "In 2013, significant seedling mortality in all tanks after thinning but before the floating leaf stage precluded this sampling of individual plants".<sup>95</sup> The Chamber noted these deficiencies in its 2014 technical analysis and it bears repeating here.<sup>96</sup>

Unlike the hydroponic experiments conducted by Chamber and Fort Labs, no test acceptability criteria were established to determine whether the test data were acceptable. Therefore, these tests cannot be relied upon in determining or corroborating the level of sulfide which is protective of wild rice. In Dr. Pastor's other hydroponic toxicity experiments on sulfates, the following test acceptability criteria are established:

*Tests were deemed acceptable if:*

- 1. At least 90% of control juvenile seedlings were living at test termination;*
- 2. Mesocotyl length of juvenile seedlings from control exposures were at least 5.0 cm at the end of the 10 day duration of growth; and*

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<sup>92</sup> Reference (24).

<sup>93</sup> Reference (47)

<sup>94</sup> Reference (25)

<sup>95</sup> Id.

<sup>96</sup> Reference (24).

3. Control juvenile seedlings did not indicate any visible phytotoxic or developmental symptoms at any time during the test and the controls grew. See Appendix 2 for more details.<sup>97</sup>

Dr. Pastor’s sulfide hydroponic experiments had similar test acceptability criteria:

*Tests were deemed acceptable using the same criteria as described above for the tests of sulfate on germination. See Appendix 3 for more details.*<sup>98</sup>

The Fort Environmental Labs study applied more rigorous test acceptability criteria (Table 5):<sup>99</sup>

**Table 5 Fort Labs Hydroponic Studies Acceptability Criteria**

<b>Criterion</b>	<b>Acceptable Limits</b>	<b>Criterion passed? (d 21 value, if applicable)</b>
Control activation	95%	95%
Control mesocotyl emergence	≥30%	≥30%
Control survival	≥90%	≥90%
Positive control (BA) phytotoxicity	≥80%	≥80%
pH	6-7.5 in all replicates of control and treatments	6.5-7.0 in all replicates of control and treatments
Water temperature	21° ± 2°C (day), and nightly, 12 ± 2°C (night) in all replicates of control and treatments	21° ± 2°C (day), and nightly, 12 ± 2°C (night) in all replicates of control and treatments
Sulfate concentration	Inter-replicate CV ≤20% for control and treatments for individual measurement set (Study Day 0, 10, and 21)	Inter-replicate CV ≤20% for control and treatments based on TWA concentration and ≤35% 24-hour sulfide loss based on TWA concentration

No test acceptability criteria were established for the outdoor container studies.<sup>100</sup> Significant but undefined mortality occurred in 2013 across all concentrations, including controls. High mortality is indicative of a test system unable to support healthy plants absent the presence of the test variables (i.e., increased sulfide). In laboratories with established Quality Control and Quality Assurance programs, including laboratories which conduct Good Laboratory Practices studies whose data are used in regulatory applications, the results would subsequently be rejected as unreliable, especially given the poor rate of control survival (i.e., 15 percent in 2013). Under no circumstances should a test design that resulted in 85% control mortality be used to inform what might constitute a protective level of any potential

<sup>97</sup> Reference (26).

<sup>98</sup> Id.

<sup>99</sup> Reference (47).

<sup>100</sup> Reference (25).

pollutant. Although not directly applicable, an attempt was made to compare the results of the outdoor container study to the test acceptability criteria for the hydroponics study. That comparison is provided in Table 6.<sup>101</sup>

**Table 6 Outdoor Container Study Acceptability Criteria<sup>102</sup>**

<b>Hydroponic Experiment Acceptability Criteria</b>	<b>Outdoor Container Study – Criteria Passed?</b>
At least 90% of control juvenile seedlings were living at test termination	Fail – less than 15% of control seedlings survived
Length of juvenile seedlings from control exposures were at least 5.0 cm at the end of the 10 day duration of growth;	Passed. Initial seedling stem and leaf length was 6.1, 6.6 and 6.8 cm. Final control seedling stem and leaf length were 10.1, 11.4 and 12.9 cm
Control juvenile seedlings did not indicate any visible phytotoxic or developmental symptoms at any time during the test and the controls grew.	Passed in part, unknown in part. Control seedlings grew (see above). Phytotoxic or developmental symptoms of controls were not reported.

Based on Dr. Pastor’s criteria for the hydroponic experiments, the outdoor container studies do not pass all test acceptability criteria.

It is important to note that control mortality at these levels (85%) represents a stressed population of wild rice, and the impact from any added stressors are likely to be greatly exaggerated compared to a healthy population of wild rice.

Because the 2013 “crop” was so poor, there were ramifications for the 2014 and 2015 years. No changes were made to the outdoor containers following the across-the-board mortality in 2013. Pastor et al note:

“The rate of decline in seedling survival with amended sulfate was twice as high in 2014 and 2015 than in 2012 and 2013.”<sup>103</sup>

This is hardly surprising, and it cannot be determined whether the trend begun in 2011 continues, or whether the decline in seedling survival is due to the unknown factors that caused the across-the-board mortality observed in 2013. Although Pastor et al opine:

“We believe this early season mortality was due to a record cold and late spring in northern Minnesota in April and May of 2013; ice stayed on lakes an average of 3 weeks later than the median ice-out date (data available online).”<sup>104</sup>

While this may have been the case, it may also have been due to depletion of any number of parameters (e.g. iron, nutrients) which affected wild rice plants in the control containers as well as the treated

<sup>101</sup> Reference (26)

<sup>102</sup> Id.

<sup>103</sup> Reference (1)

<sup>104</sup> Id.

containers. It may have been disease, or another parameter that was not measured. It is impossible to tell, and the outdoor container studies should have been given no weight, given the across-the-board mortality observed.

Myrbo et al admit as much:

“This experiment was not an accurate long-term mimic of the consequences of increased SO<sub>4</sub> loading on net porewater sulfide concentrations, because the external supply of Fe was cut off at the inception of the experiment. With no loading of Fe, **the continued production of sulfide could eventually consume all available Fe, allowing sulfide levels to exceed those observed in a natural system at equivalent surface water SO<sub>4</sub> concentrations.** This mesocosm experiment provides evidence for just such a process. The experiment was continued for two years after the synoptic sampling presented here. In August 2015 porewater sulfide was much greater than had been observed in 2013, and disproportionately so in the highest SO<sub>4</sub> treatment. Between the 2013 and 2015, porewater sulfide increased in the control SO<sub>4</sub> treatment (about 7 mg SO<sub>4</sub> L<sup>-1</sup>) from a median value of 68 µg L<sup>-1</sup> in 2013 to 116 µg L<sup>-1</sup> in 2015, a 1.7x increase. Porewater sulfide in the highest treatment (nominally 300 mg SO<sub>4</sub> L<sup>-1</sup>, Table 3) increased from a median value of 808 in 2013 to 9,350 µg L<sup>-1</sup> in 2015, an 11x increase [Pastor et al., 2017]. In a survey of 108 Minnesota waterbodies, only two exceeded a porewater sulfide level of 3,200 µg L<sup>-1</sup> [Myrbo et al., submitted].<sup>105</sup> (Emphasis added)

Myrbo also advises caution in using the results of the outdoor container studies:

“Although **caution should be used in extrapolating the results of the mesocosms to natural systems with continuous carbon and iron loads,** the results presented here clearly demonstrate the consequences of increased SO<sub>4</sub> concentrations that enhance MSR-driven mineralization of organic matter, as well as the impact of elevated sulfide on wild rice [Pastor et al., 2017].”<sup>106</sup> (Emphasis added)

The test design did not include regular changing of the solutions in the containers, as suggested in US EPA guidance. While some rainwater and groundwater was added to the system,<sup>107</sup> the tests were essentially static tests. ASTM international and US EPA recommend that static tests be limited to no longer than 96 hours<sup>108</sup>, and if test water is to be renewed, it should be renewed “once every 24 h, either by transferring the organisms from one test chamber to another or by replacing nearly all the test solution.”<sup>109</sup>

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<sup>105</sup> Reference (38)

<sup>106</sup> Id

<sup>107</sup> Id at 24

<sup>108</sup> Reference (12)

<sup>109</sup> Id.

Thus, the outdoor container tests conducted by Pastor et al did not follow US EPA guidance, and should be given considerably less weight.

While the water levels were maintained by intermittent additions of well water or precipitation, no additional nutrients or sulfate was added, and the water quality was infrequently monitored. This well water is ground water from an aquifer which does not have the same chemical composition as shallow groundwater that would be in contact with water bodies in nature. Without nutrient and iron-infused recharge, this experimental design more closely resembles a seasonal pond or pothole, where wild rice may not grow or grow as well as in a natural setting. The test design likely stressed the entire wild rice population and made the results questionable. Conditions with no groundwater infusion, and no inflow or outflow carrying additional nutrients are important constraints that confounded results. Given these confounding results, the outdoor container tests should not be relied upon in revising the water quality standards.

It appears that the tanks were nutrient deficient including iron and perhaps other limiting trace metal nutrients. As discussed by Dr. Johnson, in hydrologically isolated outdoor containers without the delivery of iron, it is likely that sulfide would build up.<sup>110</sup> Without the benefit of measurements of initial conditions and data from previous years' experiments, no one can analyze the 2013 results. Similarly, without the benefits of measurements of initial conditions, no one can determine whether sulfide build up (unprecipitated by iron) that occurred or other substances (or lack of other substances) affected the test organisms. It may be that the third year of testing (2013) was a part of the normal life cycle of wild rice. Dr. Pastor notes (reference (2)):

*Delays in the release of nitrogen from these litters in subsequent years may be responsible for the population oscillations of 3-5 year periods often seen in wild populations (Pastor and Walker 2006, Walker et al. 2010, Hildebrandt et al. 2012).*

The Great Lakes Indian Fish and Wildlife Commission also notes, based upon years of observations of wild rice;

*Rice abundance can vary widely from year to year, especially on the most "lake-like" beds. The rule-of-thumb for lake beds: A typical four year period will include a bumper year, two fair years, and a bust year.<sup>111</sup>*

The results between 2013 and 2015 may have been simply part of the natural low-density cycle of wild rice, caused, perhaps, by delays in release of nutrients from the litter.

Based on all of these considerations, outdoor container study should not be relied upon to inform or develop water quality regulations.

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<sup>110</sup> Reference (39)

<sup>111</sup> Reference (28)

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The Peer Review Panel also expressed criticism about the outdoor container studies (Reference (11)). The panel had the following recommendations regarding the outdoor container studies:

- The performance of wild rice and water quality conditions in the controls need to be **compared to that expected under natural conditions** in order to validate the test systems themselves.
- Clarity regarding the measured responses should be improved; for example, when, how, and why responses occurred should be described in the report.
- Plant responses as they relate **to measured, not nominal, sulfate concentrations** should be described and modeled.
- The demographic data should be used to develop a population model in order to understand factors influencing population persistence, within the limits of the study conducted. This should help elucidate whether specific measured responses can be linked to population persistence, which could inform assessment endpoints for field monitoring.
- Plant responses as they relate to measured porewater sulfide concentrations should be modeled, similar to what is recommended above.
- If possible, the **mesocosm study should be repeated** with an **effective control for sulfate**, and with **more treatment levels bracketing the current water quality standard**. This could be achieved by reducing replication, but should be done with caution following power analysis.
- Other, more powerful statistical approaches, for example, mixed-level (hierarchical) modeling, should be explored when analyzing the totality of the dataset.
- **Rooting zone profiles should be incorporated** into the interpretation of plant response data. (Emphasis added)

Given the serious flaws in the outdoor container data and corresponding Peer Review Panel criticisms, the MPCA cannot reasonably rely upon the results to corroborate a “protective” sulfide” or “protective sulfate” level.

MPCA does not reconcile the differences between the “protective” sulfide levels determined from the hydroponic studies and the outdoor container studies. In Figure 1.2 of the Technical Support Document, MPCA provides the following EC10 values:



Study/Experiment	EC10 Value (µg/L)
Pastor et al hydroponic (avg. Initial concentration) *	251
Pastor et al hydroponic (time weighted arithmetic avg)	106
Pastor et al hydroponic (time weighted geometric avg) <sup>(1)</sup>	39
Fort et al hydroponic (lowest EC10 level) <sup>(1)</sup>	936

(1) Estimates marked with an asterisk (\*) are identified in the text as deserving less weight in the weighing of multiple lines of evidence. <sup>112</sup>

If in fact the MPCA had looked at the effect of sulfide **in the rooting zone** from Pastor et al, as discussed above, a 4<sup>th</sup> EC10 value could be calculated:

Study/Experiment	EC10 Value (µg/L)
Pastor et al hydroponic (avg. Initial concentration) *	251
Pastor et al hydroponic (time weighted arithmetic avg)	106
Pastor et al hydroponic (time weighted geometric avg) *	39
Pastor et al hydroponic (effects in rooting zone only) <sup>(1)</sup>	819
Fort et al hydroponic (lowest EC10 level) <sup>(1)</sup>	936

(1) Estimates marked with an asterisk (\*) are identified in the text as deserving less weight in the weighing of multiple lines of evidence. <sup>113</sup>

While MPCA cites the Peer Review Panel comments as the reason to reject the average initial concentration value of 251 µg/L (because sulfide levels fell throughout the experiment because the growth solution was not renewed, per US EPA guidance), the MPCA does not calculate the impact on those parts of the wild rice plant in the rooting zone and expected to be exposed to sulfide. Again the results of the Pastor et al hydroponic studies, when reasonably focused on those parts of the plant that are in the rooting zone and the Fort et al hydroponic studies show good agreement. MPCA does not resolve the very large discrepancies between the results of the controlled hydroponic studies and the outdoor container or field survey studies.

MPCA makes the policy decision that the Fort et al studies are “deserving less weight, even though that study followed all of the recommendations of the Peer Review Panel (not just the one which the MPCA made a policy decision to use), and which followed the US EPA guidance on conduct of toxicity testing, and which met the standards for Good Laboratory practices.

MPCA made the policy decision:

*“under natural conditions 21-day old wild rice plants would not have access to the atmosphere because the seeds germinate in water that is much deeper than 1 cm, and the stems would not yet have elongated sufficiently to reach the water surface.”<sup>114</sup>*

<sup>112</sup> Chapter 1.C. of reference (2), page 32.

<sup>113</sup> Chapter 1.C. of reference (2), page 32.

<sup>114</sup> Chapter 1.C. of reference (2), page 38

In fact, a careful review of the methods used by Fort et al, shows that a consistent anaerobic condition was made up to the water level (by bubbling nitrogen gas through the growth medium, resulting in a well-mixed medium and maintaining a much more constant level of sulfide than did Pastor et al. MPCA also makes the policy decision to ignore the fact that once the wild rice plant rises above the sediment, there is sufficient oxygen dissolved in the water:

*"... the availability of oxygen in water (a maximum of about 10 ppm)"<sup>115</sup>*

MPCA also makes the policy decision to ignore the fact that the plant will photosynthesize while underwater and produce oxygen by themselves:

*"Because the plants were photosynthesizing and producing oxygen, the sulfide concentration declined during these two-three day periods."<sup>116</sup>*

Thus, MPCA unreasonably rejects the Fort et al sulfide hydroponic studies, misinterprets the Pastor et al sulfide hydroponic studies, and does not reconcile the fact that there is nearly a factor of 10 difference between these studies and the other studies on which the MPCA relies.

### **5.3 Field Surveys were seriously confounded**

MPCA relies most heavily on the field surveys to determine a "protective" concentration of sulfide in the porewater, and the "protective" concentration of sulfate in the water column. Three of the six studies which MPCA fully relied upon (and did not make the policy decision that the others were "deserving less weight"). Yet the field surveys contain serious flaws, which make it unreasonable for the MPCA to so heavily rely upon them.

Unlike the state-of-the-art controlled hydroponic studies, the field surveys are entirely uncontrolled. The wild rice growing in the wild rice waters (and non-wild rice waters) surveyed were subject to weather and all of the other stressors which can affect the presence and density of wild rice (the only two biological parameters that the MPCA measured for wild rice). MPCA acknowledges that several of these other stressors are "statistically significant", yet does nothing to separate their effects from the effects of sulfide. Instead, MPCA ascribes all ill effects on wild rice to sulfide and sulfate alone.

Other major flaws include the following:

- MPCA unreasonably used data from non-wild rice waters to determine "protective" levels of sulfide and sulfate
  - MPCA admitted as much during Dr. Swain's testimony at the first of several hearings on the proposed rule:

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<sup>115</sup> Id.

<sup>116</sup> Reference (13)

*"The point of the equation is to relate sulfate to sulfide given the amount of iron and carbon at a particular site. And it's a chemical relationship, it doesn't matter whether there's wild rice there or not. So, in calculating the equation, we include sites with no wild rice because it's the chemistry that we're performing statistics on."<sup>117</sup>*

And

*"The error rates we've been discussing are how accurately the sulfide concentration is predicted and has nothing to do with wild rice presence and absence, I agree."<sup>118</sup>*

- MPCA ignores other stressors of wild rice, several of which the MPCA determined were statistically significant, in determining the sulfide and sulfide alone impacts the growth and density of wild rice
- MPCA does not prove its hypothesis, in that there is no causal determination that sulfide in the porewater (e.g. the rooting zone) impacts the presence and density of wild rice
- MPCA does not resolve the inconsistencies between the results of the hydroponic studies (where only sulfide or sulfate are stressing the wild rice) and the field surveys, where multiple stressors are operating on the wild rice.

### 5.3.1 Use of non-wild rice waters to determine “protective” levels of sulfide and sulfate

MPCA claims that waters that contain white water lilies (*Nymphaea odorata*) and yellow water lilies (*Nuphar lutea*) indicate that wild rice “would most likely grow”:

***“When the field crews could not find wild rice in a waterbody, they sampled the water and sediment at a location where wild rice would most likely be growing if it were to grow in that waterbody. These “non-wild rice” sampling locations were usually identified by the presence of either white or yellow waterlilies. The presence of waterlilies is taken to indicate that the habitat is similar to the habitat required by wild rice, because waterlilies and wild rice frequently co-occur (Pillsbury and McGuire, 2009). In addition, in an analysis of 1,753 MDNR aquatic plant surveys from shallow Minnesota lakes, the odds of finding wild rice where there are water lilies are 27 times the odds of finding wild rice where there are no water lilies, with a 95% confidence interval of 20-36 times. This high odds ratio is strong evidence that wild rice and waterlilies share many habitat requirements, although it appears that waterlilies may have a higher tolerance to elevated sulfide concentrations.”<sup>119</sup> (Emphasis added)***

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<sup>117</sup> Transcript, State Of Minnesota Office Of Administrative Hearings For The Minnesota Pollution Control Agency MPCA Proposed Amendment Of The Sulfate Water Quality Standard Applicable To Wild Rice And Identification Of Wild Rice Waters OAH Docket No. 80-9003-34519, Revisor No. RD4324A, Kirby Kennedy & Associates, wq-rule4-15y, Page 148 Lines 15 to 23,

<sup>118</sup> Id at Page 152 Lines 22 to 25

<sup>119</sup> Chapter 1.A. of reference (2), page 8.

Note that MPCA cites only two supporting pieces of information. One of them – “an analysis of 1,753 MDNR aquatic plant surveys from shallow Minnesota lakes”<sup>120</sup> – appears to be an unpublished analysis of unpublished data. MPCA provides no citation to either. This is clearly not in conformance with US EPA guidance:

*“All data that are used should be available in typed, dated, and signed hard copy (publication, manuscript, letter, memorandum, etc.) with enough supporting information to indicate that acceptable test procedures were used and that the results are probably reliable. In some cases it may be appropriate to obtain additional written information from the investigator, if possible.*

**Information that is confidential or privileged or otherwise not available for distribution should not be used.**<sup>121</sup> (Emphasis added)

It is also clearly not in conformance with the Minnesota Administrative Rules which provide, in applicable part:

*“The statement must include:*

*A. citations to any economic, scientific, or other manuals or treatises the agency anticipates relying on;”*<sup>122</sup>

MPCA appears to be relying upon the analysis of the DNR data. The SONAR (the TSD is Exhibit 1 to the SONAR) clearly does not supply any required citation.

The other piece of information is the publication by Pillsbury et al.<sup>123</sup> Those authors provide the following insights:

*“Plants closely associated with high and medium wild rice stands included *Potamogeton natans*, *Nymphaea odorata*, *P. foliosis*, *Lemna trisulca*, and *P. richardsonii* (Figure 1a). These *Zizania*-associated macrophytes **may** be tolerant of the shaded conditions produced by emergent *Zizania* stalks and leaves, and might also benefit from increased protection from wind and waves within these stands.”*<sup>124</sup> (Emphasis added)

**“Plants that did not have a close association with wild rice** wetlands included *Elodea canadensis*, ***Nuphar variegata***, filamentous green algae (*Zygnematales*), *Utricularia vulgaris*, *Sparganium eurycarpum*, *Najas flexilis*, and *Potamogeton robbinsii* (Figure 1a). Many of these plants **may not grow well inside dense wild rice stands** due to excessive shading.”<sup>125</sup> (Emphasis added)

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<sup>120</sup> Id

<sup>121</sup> <sup>121</sup> Reference (4)

<sup>122</sup> Minn. R. 1400.2070, Subp.1

<sup>123</sup> Reference (29)

<sup>124</sup> Id.

<sup>125</sup> Id.

**"Nuphar variegata and U. vulgaris are associated with high and medium density rice wetlands in the adjacent site ordination** and low density wetlands with the within-rice ordination (Figures 1a and b). This pattern suggests that without the presence of rice, these plants prefer environmental conditions similar to optimal rice conditions (indicating a possible competitor). This agrees with Vennum (1988) who noted that *Utricularia macrorhiza* was often adjacent to wild rice stands in Minnesota. Meeker (2002) conducted **competition experiments with Nuphar variegata that demonstrated a loss in wild rice survivorship**. Lee (1986) found that **plant competition (based on non-rice plant densities) explained a significant amount of variation in wild rice density** after a large seeding effort in Oval Lake, Ontario.

Resource managers often cite **direct competition** with other aquatic plants, such as cattails (*Typha spp.*), pickerelweed (*Pontederia cordata L.*), or waterlilies (*Nymphaea and Nuphar*) **as a major factor in the disappearance of wild rice stands**. However this hypothesis has rarely been tested."<sup>126</sup> (Emphasis added)

This citation hardly constitutes proof that water lilies indicate that wild rice would "most likely be growing". The authors first cite only an association, not any biological reasons why water lilies and wild rice should cohabit the same area. Second, yellow water lilies do not grow in the same area as wild rice, merely adjacent to it. Third, it may be that in the water tested that the water lilies have outcompeted the wild rice, perhaps due to development, and that the site is no longer conducive to wild rice growth.

It is curious that allow the MPCA feels strongly enough about the presence of water lilies to use data from waters where only water lilies (and not wild rice) grow to develop a "protective" sulfide level, yet the MPCA has not listed those waters as wild rice waters.

MPCA cannot have it both ways. Either the waters which contain water lilies only should be listed as wild rice waters, or they should be excluded from the analysis. Given the fact that the two lines of evidence upon which the MPCA relies are either unpublished (in clear violation of US EPA Guidance and Minnesota rules) or associative at best, MPCA unreasonably included waters in which only water lilies (and not wild rice grew).

### 5.3.2 Ignoring other stressors of wild rice

MPCA admits that a number of factors, other than sulfide or sulfate, can stress wild rice and inhibit its growth. Table 1-3 "Correlations of field variables with wild rice and porewater sulfide"<sup>127</sup> lists the following additional parameters (beyond porewater sulfide), that are significantly correlated with wild rice growth:

- Porewater potassium (PW K)

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<sup>126</sup> Id.

<sup>127</sup> Reference (2)

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- Water depth (m)
  - Water Transparency (cm)
  - Surface water nitrogen (SW N)
  - Sediment Selenium (% dry) (Sed Se)
  - Surface water temperature (SW Temp)
  - Porewater Iron (PW Fe)
  - Surface water pH (SW pH)
  - Surface water phosphorus (SW P)
  - Latitude
  - Sediment Total Sulfur (Sed TS)

States and tribal governments who restore wild rice list additional significant stressors of wild rice:

- Water level fluctuations
  - Natural seasonal fluctuations
  - Influences of beaver dams
- Invasive species
  - cattail, purple loosestrife, and Eurasian watermilfoil
  - carp
- Competitive plants (see above discussion)
- Motorized boat limitations and/or no wake zones during floating leaf stage<sup>128</sup>

Yet the MPCA unreasonably and single-mindedly focuses on sulfide as the one causative factor for the health and growth of wild rice. The correlations developed by the MPCA are unreasonable, as they do not take into consideration statistically significant and long known factors other than sulfide which affects the growth and health of wild rice.

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<sup>128</sup> References (28), (29), (30), (47)

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## 5.4 MPCA does not resolve the inconsistencies between the multiple lines of evidence

The hydroponic studies (properly interpreting the Pastor et al work to look at effects on only those parts of the wild rice plant in the sediment), show that sulfide is not toxic to wild rice at levels below 2,880 to 3,200 µg/L. The statistical analysis of the field survey data purport to show a “protective” sulfide level of 120 µg/L – more than a factor of 10 lower. The hydroponic studies, conducted in accordance with US EPA guidance, with sufficient controls in place and sufficient elimination of other confounding stressors, clearly demonstrated that sulfate and sulfide, in and of themselves, are not toxic to wild rice at concentrations not typically seen in Minnesota wild rice waters.

In stark contrast, the analyses of the field surveys, which are advised against in US EPA guidance, and which have no controls in place and which include the influence of myriad, statistically significant confounding stressors, shows a “protective” sulfide level of only 120 µg/L.

MPCA needs to reconcile the 10-fold difference between the “protective” sulfide levels determined in its analysis of the field surveys and the hydroponic studies which controlled all of the other myriad statistically significant confounding stressors.

It is likely that if MPCA used **only those waters which actually are listed wild rice waters**, and used the “protective” sulfide levels from the hydroponic studies, that the calculated “protective” sulfate level would be in line with the measured hydroponic sulfate levels.

MPCA needs to explain the large differences between the proposed “protective” sulfide level and “protective” sulfate level derived from that sulfide level, and the actual toxicity of sulfate to the wild rice plants or sulfide to those portions of the wild rice plants in the root zone (e.g. the sediment in contact with the porewater). Considering that the hydroponic studies were conducted in accordance with US EPA guidance and employed state-of-the-art toxicity testing procedures, and that the field surveys are fraught with the very issues with which the US EPA cautions against their use, MPCA needs to give a much higher weight to the hydroponic studies, and weight them at least as highly, if not higher, than the field surveys.

## 6.0 MPCA did not adequately consider the costs to comply with the proposed rule

### 6.1 The cost to comply with this standard is “prohibitively expensive”

The MPCA in the SONAR admits that the costs to reduce sulfate in discharges from municipalities and industry are “prohibitively expensive”.

On page 107:

“In the case of wild rice and sulfate, the MPCA recognizes that **sulfate treatment is currently prohibitively expensive** for many dischargers, and therefore when the proposed rule revisions are adopted, dischargers (industrial and municipal) may apply for variances from the standard until economically feasible treatment systems can be designed and constructed.”<sup>129</sup> (Emphasis added)

At page 182:

“Treatment for sulfate removal can be **extremely expensive**. As discussed above, there are few options for sulfate removal, with RO/membrane filtration being the most reliable method for effectively removing sulfate from wastewater discharges.”<sup>130</sup> (Emphasis added)

And at page 184:

“Membrane treatment with evaporation and crystallization also has **significant secondary costs** such as high-energy requirements leading to high carbon emissions, advanced operator training requirements and an increased need for operator labor hours. The combination of these secondary considerations could prove **prohibitively burdensome for affected communities**.”<sup>131</sup> (Emphasis added)

Although MPCA notes that it intends to grant variances “until economically feasible treatment systems can be designed and constructed”,<sup>132</sup> the only technology that can effectively remove sulfate to the levels required under the proposed rule is membrane filtration – nanofiltration or reverse osmosis. MPCA explains the operation and costs of reverse osmosis in the SONAR at pages 178 to 181.

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<sup>129</sup> Reference (3), page 107.

<sup>130</sup> Reference (3), page 182

<sup>131</sup> Reference (3), page 184

<sup>132</sup> Reference (3), page 107



## 6.2 For cities, annual costs can exceed \$1 million/year

For cities, capital costs can range from \$10 million to over \$50 million (depending upon flows and concentrations)

MPCA's Draft Cost Analysis<sup>133</sup> determined that the annual operation and maintenance costs ranged from \$500,000/year to nearly \$1 million/year, depending upon flow rates, initial sulfate concentrations and the "protective" sulfate concentration. The majority of the operation and maintenance cost is energy cost to evaporate and crystallize the salts removed.

Combining the annualized capital costs with the annual operation and maintenance costs yield an annualized cost of over \$1 million/ year for a 1 million gallon/day city.<sup>134</sup> Assuming 100gallons/person/day<sup>135</sup>, a 1 million gallon/day city would have a population of 10,000, about the size of the cities of Fairmont or Grand Rapids.<sup>136</sup> For the City of Fairmont, the number of households is 4,793.<sup>137</sup> A cost of \$1 million amounts to \$209/year per household. For the city of Grand Rapids, the number of households is 4,996<sup>138</sup>. A cost of \$1 million amounts to \$200/year per household.

The median household income for Martin County, in which the city of Fairmont is located, is \$8,831.<sup>139</sup> The median household income for Itasca County, in which the city of Grand Rapids is located is \$18,965.<sup>140</sup> MPCA, quoting the Minnesota Public Facilities Authority (PFA), lists a 1.4% "benchmark for combined capital and operation & maintenance costs of an "affordable" wastewater infrastructure".<sup>141</sup> For the city of Fairmont, an affordable annual cost would be 1.4% x \$8,831 = \$123/year, about ½ of what a membrane treatment system would cost. For the city of Grand Rapids, an affordable annual cost would be 1.4% x \$18,965 = \$265, about what a membrane system would cost.

However, these costs are over and above the current treatment costs which those cities face, so these costs, on top of the current wastewater charges, would be clearly not "affordable". And, at the December 2016 MPCA Wild Rice Advisory Committee meeting, the MPCA admitted that the cost estimates presented in MPCA's Draft Cost Analysis Components of Regulatory Analysis Proposed Sulfate Standard for Protection of Wild Rice December 2016<sup>142</sup> may be low by a factor of two. Thus, these costs are more than twice what these cities could reasonably afford.

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<sup>133</sup> Reference (34)Table 9 of Reference (34), page 25

<sup>134</sup> Table 10 of Reference (34), page 26

<sup>135</sup> Reference (35)

<sup>136</sup> Minnesota Cities by Population, Minnesota Demographer at [https://www.minnesota-demographics.com/cities\\_by\\_population](https://www.minnesota-demographics.com/cities_by_population)

<sup>137</sup> Minnesota State Demographic Center, Population Finder for Cities and Townships at <https://mn.gov/admin/demography/data-by-topic/population-data/our-estimates/pop-finder2.jsp>

<sup>138</sup> Id.

<sup>139</sup> US Census Bureau, MEDIAN INCOME IN THE PAST 12 MONTHS (IN 2015 INFLATION-ADJUSTED DOLLARS) more information 2011-2015 American Community Survey 5-Year Estimates at

<https://factfinder.census.gov/faces/tableservices/jsf/pages/productview.xhtml?src=bkmk> Note that median household income is only available at the county level, not at the city level.

<sup>140</sup> Id

<sup>141</sup> Chart 13 of reference (33), page 17.

<sup>142</sup> MPCA presentation at the December 2016 Wild Rice Advisory Committee Meeting, Duluth, MN

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### 6.3 For Industry, costs are even higher, especially taconite processors

For industry, because flows are generally higher and sulfate concentrations are higher than municipal wastewater, costs are even more “prohibitive”. For taconite mines and processing plants, there are multiple discharge points and multiple sources of sulfate, including scrubbers, mines and waste rock piles, tailings basin, as well as rainfall over the vast areas which encompass a taconite mine and plant.

MPCA estimates a net present value of \$62.5 million to treat a single discharge from a taconite plant.<sup>143</sup> This includes capital costs of \$21 million and annual O&M costs of \$2.8 million/year. Note that this is for a single discharge at a facility which have multiple discharges (e.g. from mines, tailings basins, processing plants). Such costs are in addition to additional costs taconite plants are facing to meet the MPCA's mercury TMDL<sup>144</sup>, which are additional millions in capital costs and millions/year in operation and maintenance costs.

Again, as noted above MPCA admits that its cost estimates may be low by a factor of 2<sup>145</sup>.

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<sup>143</sup> Table 11 of Reference (34), page 25

<sup>144</sup> Chapter 4 of reference (36), page 9

<sup>145</sup> MPCA statements at the December 2015 Wild Rice Advisory Committee Meeting.

## 7.0 Summary

While MPCA's use of multiple lines of evidence, and the use of US EPA's "weight of evidence" guidance may be reasonable, there are fundamental problems with both the underlying evidence and with MPCA's policy decisions on weighting the relative value of each line of evidence.

### 7.1 MPCA's model and Key Hypothesis are incorrect and not supported by the evidence

First, MPCA's model is unreasonable in that it paints all wild rice waters as essentially bathtubs, with no interaction between the surface water, sediment and groundwater, when multiple lines of research show that the groundwater may be the source of the very compounds which may influence the formation of sulfide, and its effect upon wild rice. Sulfate, iron and organic carbon are brought into the sediment and water column with groundwater discharging into the surface water. At least one researcher has noted that wild rice prefers locations of groundwater inflow.<sup>146</sup>

Second MPCA's model is unreasonable in that it assumes that all sulfate migrates to the sediment from the water column, and that all dissolved iron and organic carbon in the porewater (root zone) comes from the sediment. Dissolved iron and organic carbon could just as easily migrate from the water column to the sediment and porewater, and from the groundwater to the sediment and porewater. Research has shown that, in fact, groundwater is the more likely source of all of these compounds. MPCA unreasonably ignores the potential contribution of these migrations, and unreasonably relies upon an overly-simplified model to determine the "protective" level of sulfide and sulfate.

### 7.2 Multiple Lines of Evidence were incorrectly and unreasonably relied upon

#### 7.2.1 Hydroponic data

Using the standard, hydroponic toxicity tests per US EPA guidance, sulfate is not toxic to wild rice at concentrations well above the concentrations seen in MN wild rice waters. Therefore, the current standard of 10 mg/L sulfate has no scientific validity. The mode of action of sulfate is also now well understood – it, like other salts, exerts osmotic pressure on the plant, and is no more toxic than any other salt. Therefore, there is no need for a "protective" sulfate standard.

Similarly, based on the effects of sulfide on the rooting zone (and those portions of the plant in the sediment and exposed to the porewater), sulfide is not toxic to wild rice at concentrations seen in most Minnesota wild rice waters. While the mode of action is not well understood at this point, it is clear from these experiments, un-confounded by other wild rice stressors, that sulfide is not toxic to wild rice at concentrations seen in Minnesota wild rice waters. Therefore there is no need for a "protective" sulfide standard.

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<sup>146</sup> Reference (22)

## 7.2.2 Outdoor Container studies

There were serious issues with the outdoor container studies conducted by Pastor et al. The outdoor containers were, in fact, “bathtubs” which had no interaction with the groundwater. The solutions were not replenished, per US EPA guidelines, and so critical nutrients, not least iron, were depleted. Other nutrients or critical elements may also have been depleted, as 85% of the plants, including controls, died in year three of the five year study. Results from years 4 and 5 were also characterized by poor wild rice growth. As a result, the outdoor container study did not meet Good Laboratory Practices, nor did it conform to US EPA guidance. MPCA was unreasonable when it relied upon the outdoor container study results in determining the “protective” level of sulfide.

## 7.2.3 Field Surveys

The field surveys suffered from very shortcomings for which US EPA guidance cautions against its use: many confounding factors make it difficult, if not impossible, to isolate the impact of a single stressor (e.g. sulfide) on the growth and health of wild rice. MPCA admits that there are multiple statistically significant other stressors which impact the presence and density of wild rice, and MPCA made no effort to sort out the impacts from these other stressors. Rather, MPCA blithely ignored their impacts, and ascribed all deleterious wild rice impacts to sulfide and sulfide alone. This is unreasonable and MPCA should not have relied on the field surveys in developing a “protective” sulfide level.

The field surveys were also confounded by the fact that MPCA unreasonably included waters which are not wild rice in determining a “protective” level of sulfide to protect wild rice. Again, MPCA cannot have it both ways – those waters which are not listed as wild rice waters should have been excluded from the analysis. As the purpose of the standard is to protect the “the harvest and use of grains from this plant serve as a food source for wildlife and humans”<sup>147</sup>, MPCA unreasonably included waters which do not produce wild rice for “harvest and use” and which are not protected for such uses.

Because of these significant shortcomings, because MPCA cannot reasonably ascribe all deleterious effects on wild rice to sulfide, MPCA unreasonably relied upon the field surveys in developing a “protective” sulfide level.

Thus, only the hydroponic studies are able to show the impacts of sulfate and sulfide on wild rice, without either other confounding stressors (e.g. the field surveys) or depletion of iron and other critical growth factors (e.g. the outdoor container studies). MPCA unreasonably relied upon the field surveys and outdoor container studies, and unreasonably denigrated the hydroponic studies in determining “protective” levels of sulfide and sulfate.

The hydroponic studies clearly show that neither sulfate nor sulfide are toxic to wild rice at concentrations seen in Minnesota wild rice waters. Therefore, MPCA has not demonstrated that there is a need for

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<sup>147</sup> Chapter 1.D. of reference (3), page 13

“protective” levels of either sulfide or sulfate to protect the use of “the harvest and use of grains from this plant serve as a food source for wildlife and humans”.

### 7.3 MPCA is lacking critical evidence “connecting the dots”

While MPCA has spent over \$1.5 million on research, and other entities (e.g. the MN Chamber of Commerce) have spent additional monies, the results are, at best, inconsistent. The state-of-the-art controlled tests clearly show that neither sulfate nor sulfide are toxic to wild rice at concentrations observed in Minnesota wild rice waters. While MPCA conducts a series of statistical analyses to allegedly show that a “protective” sulfide in porewater standard is needed, both the underlying data and the statistical analysis are fraught with errors, and contradicted by the literature. The result is an inconsistent body of evidence, some of which shows that a sulfide in porewater and sulfate in the water column water quality standard may be necessary, and other showing that such standards are neither needed nor reasonable.

Even if we accept for the moment, MPCA’s conclusions that a porewater sulfide and water column sulfate “protective” water quality standard is needed, MPCA has failed to present evidence to show that making the changes which such water quality standards will actually result in protection of the beneficial use – “the use of the wild rice grain as a food source for wildlife and humans”.<sup>148</sup>

For example, the MPCA has not and cannot provide any studies, literature or other evidence that reducing sulfate in discharges to surface waters will effectively reduce sulfide in the porewater in wild rice waters. Indeed, Berndt et al<sup>149</sup> reach an entirely opposite conclusion.

MPCA has not and cannot provide any studies, literature or other evidence that reducing sulfate in the water column will better protect wild rice. None of the controlled hydroponic studies show any evidence for this, nor do the outdoor container studies nor do the field surveys. Again, Berndt et al <sup>150</sup>shows that sulfate in the surface water has little to do with sulfate reduction in the sediment, while groundwater flow provides the bulk of flow as well as sulfate, organic carbon and iron in the sediment.

MPCA has not and cannot provide any studies, literature or other evidence that reducing sulfate in the water column will reduce sulfide in the porewater. This was simply not tested in any of the studies, nor in any of the literature cited by the MPCA. Yet the proposed rule explicitly says that this is what needs to happen to comply with the rule. In wild rice waters where the porewater sulfide exceeds the protective level, dischargers of sulfate will need to reduce their discharges of sulfate. Yet there is no evidence that reducing sulfate in discharges will result in significant reductions in water column sulfate, or that reducing sulfate in the water column will reduce sulfide in the porewater. Considering that cities and industries may be required to expend billions of dollars to reduce sulfate in their discharges, through the use of membrane filtration treatment, MPCA should be able to solidly demonstrate, in at least one wild rice

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<sup>148</sup> Reference (3) page 14

<sup>149</sup> Reference (17)

<sup>150</sup> Id.

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water, that reduction in sulfate results in reduction in porewater sulfide. MPCA has not done so, and thus the proposed rules are unreasonable.

MPCA has not and cannot provide any studies, literature or other evidence that reducing sulfide in the porewater will better protect wild rice. While MPCA has presented a statistical analysis of field survey data to show that sulfide may be toxic to wild rice at levels above 120 µg/L, MPCA can point to no test, no literature nor any other piece of evidence that shows that a wild rice water with high porewater sulfide had wild rice presence or density restored by reducing sulfide in the porewater. Again, given the “prohibitively expensive” (MPCA’s own words) costs to reduce sulfate in discharges will result in reduced porewater sulfide, or that reduced porewater sulfide will result in the presence or increased density or health of wild rice.

Therefore, the “prohibitively expensive” costs to comply with the proposed rule may provide no additional protection for wild rice. MPCA has not and cannot provide any studies, literature or other evidence that these “prohibitively expensive” costs will have any positive impacts on wild rice.

#### **7.4 The Cost to comply with the proposed rule is “prohibitively expensive”**

MPCA admits that the costs to comply with the proposed rule is “prohibitively expensive”. The only technology that can achieve the low levels required by the proposed rule is membrane treatment – nanofiltration or reverse osmosis. There are no other technologies on the horizon that can remove +2 anions at a reduced cost. Coupled with the lack of evidence, as noted above, that reducing sulfate in discharges from municipal and industrial sources will affect the water column sulfate concentration, the porewater sulfide concentration, or have any effect on wild rice, such “prohibitive” costs are unreasonable.

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## 8.0 Recommendations

We respectfully request that the current sulfate standard of 10 mg/L<sup>151</sup> be eliminated, as the weight of evidence clearly shows that sulfate is not toxic to wild rice at that concentration or at any other concentration observed in Minnesota wild rice waters.

We respectfully request that the rule be remanded to the MPCA, to address the errors, uncertainties and inconsistencies noted above, particularly the inconsistency that multiple studies show that concentrations of sulfate and sulfide are not toxic to wild rice at concentrations observed in Minnesota wild rice waters, while other studies show that a “protective” concentration of 120 µg/L, and a “protective” concentration of sulfate, which are orders of magnitude smaller than the controlled, state-of-the-art hydroponic test results.

We respectfully request that the rule be remanded to the MPCA until it does a more complete cost analysis, and can demonstrate that the expenditure of billions of dollars will result in better protection of the use of wild rice for harvest by humans and wild life.

We respectfully suggest that MPCA has not met its obligations under the Administrative Procedures Act to demonstrate the need for and reasonableness of the proposed rule, specifically Proposed MN Rules 7050.0224 Subp. 5. A. (Line 7.17 – 7.12), and Proposed MN Rules 7050.0224 Subp. 5. B.1. (Line 7.25 – 8.17)

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<sup>151</sup> Reference (15), per Minnesota Reviser RD4324A, Proposed Minn. R. 7050.0224, Subp.2

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