Analysis of the Wild Rice Sulfate Standard Study: Draft for Scientific Peer Review

Minnesota Pollution Control Agency

June 9, 2014

Minnesota Pollution Control Agency
651-296-6300 | 800-657-3864 | TTY 651-282-5332 or 800-657-3864

June 2014 | wq-s6-42z
Available in alternative formats

Contents

Introduction 3
Background 4
  Wild Rice and Sulfate in Minnesota 4
  Water Quality Standards 4
  Minnesota's Wild Rice Sulfate Standard 4
  Wild Rice Sulfate Standard Study 5
Analysis of theWild Rice Sulfate Standard Study: Draft for Scientific Peer Review 7
  Evaluating and Integrating Multiple Lines of Evidence 7
  Organization of this Analysis 8
Environmental Setting for Wild Rice Growth in Minnesota 9
The Wild Rice Sulfate Standard Study: Methods and Results 13
  Laboratory Hydroponic Experiments 13
  Field Survey 17
  Utility of the Wild Rice Field Survey Data 21
  Mesocosm Experiment 26
  Rooting Zone Depth Profiles 33
  Sediment Incubation Laboratory Experiment 34
Discussion 35
  Wild Rice in Relation to Sulfate, Sulfide, and Iron 35
  Conversion of Sulfate to Sulfide 40
  Role of Iron in Controlling Sulfide in Porewater 41
  Sulfide Consumption of Available Iron 42
  Control of Porewater Sulfide by the Availability of Sulfate and Iron 45
  Application of Quantile Regression to the Wild Rice Field Survey Data 46
  Prediction of Sulfate and Iron at Wild Rice Sites 48
  Synthesis: How Sulfate, Sulfide, and Iron Interact to Affect Wild Rice 51
Contributors 53
Literature Cited 54
Appendix A. Sulfide Hydroponic Tests: Analysis of Variance 56
Appendix B. Sulfide Hydroponic Tests: Logistic Models 60
Appendix C. Explanation of Quantile Regression 64
Appendix D. Summary Statistics for Survey Data Sets 65
Appendix E. Spearman Correlation Coefficients for Survey Data Sets 75
Appendix F. Statistical Analysis for Figures 20 and 21 86
Appendix G. Multiple Quantile Regression Statistical Analysis 89

Introduction

In 2011, the Minnesota Legislature directed the Minnesota Pollution Control Agency (MPCA) to conduct research on the effects of sulfate and other substances on the growth of wild rice. This research was intended to inform an evaluation of the existing wild rice sulfate standard. In 1973 MPCA adopted, and the U.S. Environmental Protection Agency (USEPA) approved, that standard to protect the beneficial use of “water used for production of wild rice” during periods when the rice “may be susceptible to damage by high sulfate levels.” (Minn. R. 7050.0224, subp. 2).

Following the development of a detailed research protocol in 2011 (MPCA 2011), in 2012 MPCA contracted with groups of scientists at the University of Minnesota Duluth and Twin Cities to collect data for a Wild Rice Sulfate Standard Study (Study). The Study’s main hypothesis was that wild rice is impacted by sulfate via the conversion of sulfate to sulfide in the sediment porewater. Each of the Study components has a specific purpose and associated strengths and limitations. Data collection was completed in December 2013 and is documented in individual reports from the researchers.

During the first few months of 2014, MPCA staff integrated the Study results; analyzed the data as a whole; gained input from the Wild Rice Standards Study Advisory Committee; and reviewed existing monitoring data, other relevant scientific studies/information, and the original basis for the wild rice sulfate standard to develop a Preliminary Analysis (MPCA 2014). Following the release of this Preliminary Analysis, MPCA sought feedback from the Wild Rice Standards Study Advisory Committee and continued to converse with the Study researchers. The Preliminary Analysis was refined and expanded based on this feedback and additional data analysis by MPCA, to form this Analysis of the Wild Rice Sulfate Standard Study: Draft for Scientific Peer Review (Analysis).

Peer review is a step in the larger process in which MPCA will consider scientific information to determine if changes to the wild rice sulfate standard are needed. The peer review will inform MPCA’s efforts to further enhance and refine the analysis of the effects of sulfate on wild rice. MPCA will consider the scientific peer review responses as the agency further refines its technical analysis and develops a Technical Support Document, if warranted, to describe the scientific basis for any proposed changes to Minnesota’s water quality standards.

MPCA has not yet developed recommendations or a proposal regarding any changes to the wild rice sulfate standard. If a rulemaking proposal for such changes is needed, MPCA will also seek informal and formal public comment on any recommendations and rulemaking proposal that are developed. Any proposed change to the wild rice sulfate standard would be adopted into Minnesota’s water quality standard rule (Minnesota Rules Chapter 7050) in accordance with the procedural requirements of the Minnesota Administrative Procedures Act and would require the approval of USEPA.

Background

Wild Rice and Sulfate in Minnesota

Wild rice is an important plant species in aquatic environments in parts of Minnesota, particularly northern Minnesota. It provides food for waterfowl, is economically important to those who harvest and market wild rice for human consumption, and is also a very important cultural resource to many Minnesotans.

Sulfate is a natural chemical found in surface and groundwater. It can be found at varying concentrations in discharges from permitted facilities such as mining operations, municipal wastewater treatment plants, and industrial facilities. In some areas, permitted facility discharges are elevated because groundwater high in sulfate is used for drinking water or industrial needs. The primary factor controlling natural concentrations of sulfate in surface water is the surface geology of Minnesota. For example, glaciation left relatively high-sulfur soils across southwestern Minnesota, which contribute sulfate to lakes and streams. Past studies have shown that wild rice is primarily found in waters with relatively low sulfate concentrations.

This recognition of the importance of wild rice in Minnesota, and the observed relationship between the presence of wild rice in waters with lower sulfate levels (and its absence in waters with elevated sulfate), led to the adoption of the wild rice sulfate standard in 1973.

Water Quality Standards

Water quality standards are fundamental tools under the federal Clean Water Act (CWA) and Minnesota Statutes, designed to help protect and improve the quality of the state's waters. Minnesota water quality standards consist of three components:

1. The beneficial use(s) for which a water body is to be protected,
2. The narrative and/or numeric criteria that specify what conditions in the water are protective of the beneficial uses, and
3. Antidegradation provisions (also known in Minnesota as nondegradation) to minimize the lowering of water quality that is better than the minimum level needed to protect beneficial uses.

Under the CWA, states and federally authorized Indian Tribes are required to identify the beneficial uses for which their waters are to be protected, then to adopt criteria and antidegradation provisions to protect those beneficial uses. Explicit in the CWA is the presumption that a water body should attain healthy aquatic life and recreation uses unless a rigorous analysis finds that such uses are not attainable. Minnesota's water quality standards rules provide a framework that includes these broad uses, and also the following additional uses: domestic consumption, industrial, agriculture and wildlife, navigation and aesthetic enjoyment.

Minnesota's Wild Rice Sulfate Standard

Minnesota's Class 4 Agriculture and Wildlife use classification covers agricultural uses as well as wildlife uses. Under the Class 4A use classification, Minnesota currently has a water quality standard of "*10 mg/L sulfate applicable to water used for production of wild rice during periods when the rice may be susceptible to damage by high sulfate levels*" (Minn. R. 7050.0224, subp. 2). MPCA is unaware of any other state with a wild rice sulfate standard though three tribal authorities in the region have such standards in their rules.

This 10 mg/L wild rice sulfate standard was adopted into Minnesota's water quality standards in 1973. Based on testimony presented at public hearings leading to the adoption of the sulfate standard, it was intended to apply both to waters with naturally occurring wild rice and to waters used for paddy rice production.

The standard was based on field observations and water chemistry correlations made by Dr. John Moyle primarily in the late 1930s and early 1940s (Moyle 1944). Dr. Moyle was a highly respected biologist with the then Minnesota Department of Conservation, and later the Minnesota Department of Natural Resources (DNR), who concluded that "No large stands of rice occur in water having sulfate content greater than 10 ppm [parts per million, or mg/L], and rice generally is absent from water with more than 50 ppm" (Moyle 1944).

The wild rice sulfate standard is intended to protect a single species from the negative effects of sulfate. This is different from a more typical toxicity standard that is based on protecting a community of organisms (such as a warm-water fishery, or a rooted plant community). Community-based standards are calculated from data about the toxic effects of the pollutant of concern on the most sensitive species in the community, and standards development guidance developed by USEPA provides that a certain percentage of the most sensitive species can be affected by the pollutant and still result in a standard that protects the community as a whole. Similar USEPA guidance does not exist for species-specific standards other than the development of human health-based standards; therefore, MPCA needs to consider the question of "what is protective" in its analysis and any future rulemaking.

The wild rice sulfate standard was developed based on study-derived correlations of Dr. Moyle's observations and water chemistry data. However, the specific mechanism by which sulfate appears to be impacting wild rice was not the subject of Dr. Moyle's study. This, along with questions that have arisen regarding the implementation of the current standard, led to MPCA's interest in further understanding the effects of sulfate on wild rice to inform a review of the wild rice sulfate standard.

Wild Rice Sulfate Standard Study

The goal of the Wild Rice Sulfate Standard Study was to enhance scientific understanding of the effects of sulfate on wild rice and to inform a decision by MPCA as to whether a revision of the wild rice sulfate standard is warranted. The data-collection phase of the Study was conducted by scientists at the University of Minnesota Duluth and Twin Cities under contract with MPCA, with input from a diverse group of interested parties and technical experts, referred to as the Wild Rice Standards Study Advisory Committee.

The data collection consisted of parallel research efforts (Study components) that each have a specific purpose and associated strengths and limitations (Table 1). The Study was designed so that the individual components together provide a better understanding of the effects of sulfate on wild rice. The Study components are:

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

Each of the reports for the study components may be accessed via the MPCA's wild rice sulfate standard web page at http://www.pca.state.mn.us/ktqh1083 (a link to an FTP site with all the reports and data is available on this page). A brief summary of the Study is also available on this web page.

Table 1. Purpose, strengths, and limitations of Study components.

	Field Survey	Laboratory Hydroponic Experiments		Outdoor Container Experiments	Collection and Analysis of Rooting Zone Depth Profiles	Sediment Incubation Laboratory Experiments
		Sulfate (SO_4)	Sulfide (H_2S)			
Main Purpose	Expand understanding of environmental conditions correlated with presence/ absence of wild rice.	Evaluate effects of sulfate on wild rice seed germination and growth of sprouts.	Evaluate effects of sulfide on wild rice seed germination and growth of sprouts.	Evaluate effects of sulfate on wild rice plants over full life cycle, and multiple years.	Characterize sulfate, sulfide, and iron in the rooting zone of wild rice container experiments and field sites.	Evaluate effect of temperature on movement of sulfate into and out of underlying sediment.
Endpoints	Concentrations of chemicals in surface water & rooting zone (e.g. SO_4 & H_2S vs. wild rice occurrence).	Growth of wild rice sprouts (biomass, root & shoot elongation). Germination rate of seeds.	Growth of wild rice sprouts (biomass, root & shoot elongation). Germination rate of seeds.	Growth of wild rice (biomass, plus number & weight of seeds). Sulfide concentrations in rooting zone.	Concentrations of sulfate, sulfide and iron in porewater.	Sulfate concentrations in overlying water over time; SO_4, iron, H_2S, & anion tracers in sediment porewater. Simple model.
Key Strengths	Most reflective of actual environmental conditions. Multiple wild rice stands and breadth of characteristics sampled.	Controlled dose-response experiment. Controlled exposure to known concentrations of SO_4.	Controlled dose-response experiment. Controlled exposure to known concentrations of H_2S.	Controlled dose-response experiment. Includes natural sediment matrix as rooting environment. Involves entire growth cycle, multiple years.	Provides additional data to understand and interpret container experiments and field sites.	Controlled experiment with natural sediment and water.
Key Limitations	Least controlled. Annual visit for most sites, 3x/year for a subset. Not definitive on cause and effect.	Only evaluates early growth stages. Leading hypothesis is that sulfate is converted to sulfide, which is directly toxic.	Only evaluates early growth stages. Unable to simultaneously keep roots anaerobic & shoots aerobic.	Full effect of sulfate may take longer than several years to realize. No groundwater movement.	Utility lies in the integration of this data with the other Study components, not in this data set alone.	Provides preliminary assessment of sediment from two sites that may inform but is not fully transferrable to other sites. No groundwater movement. No wild rice plants grown.

Analysis of the Wild Rice Sulfate Standard Study: Draft for Scientific Peer Review

During the first few months of 2014, MPCA staff integrated the Study results; analyzed the data as a whole; gained input from the Wild Rice Standards Study Advisory Committee; and reviewed existing monitoring data, other relevant scientific studies/information, and the original basis for the wild rice sulfate standard to develop a Preliminary Analysis (MPCA 2014). Following the release of the Preliminary Analysis, MPCA sought feedback from the Wild Rice Standards Study Advisory Committee and continued to converse with the Study researchers. The Preliminary Analysis was refined and expanded based on this feedback and additional data analysis by MPCA to form this Analysis of the Wild Rice Sulfate Standard Study: Draft for Scientific Peer Review (Analysis).

This Analysis presents an interpretation of data collected in the Study, as one part of the larger task of determining whether a revision of the wild rice sulfate standard is warranted. This interpretation focuses almost exclusively on the interactions of sulfate, sulfide, and iron and how those interactions affect wild rice. There is additional analysis to be conducted on the data in the future, especially for other constituents.

Evaluating and Integrating Multiple Lines of Evidence

In developing this Analysis, MPCA staff focused on additional data analysis of the effects of sulfate and sulfide on wild rice, and particularly, interactions of sulfate, sulfide, and iron in the environment. The design of the overall Study relied on an approach that views each of the individual study components as providing complementary lines of evidence. These key lines of evidence, along with relevant scientific literature, provide a more complete understanding of the complex biogeochemical interactions of sulfate in the environment, and the effects of sulfate or its derivatives on wild rice.

The benefit of conducting a laboratory toxicity test is that many external factors can be controlled, which allows for a better interpretation of the effects of sulfate or sulfide on wild rice. Statistical analyses of controlled hydroponic growth tests were used to evaluate the extent to which elevated sulfate and sulfide concentrations are toxic to wild rice seed and seedlings.

Hydroponic experiments are by their nature removed from the natural environment, and provide a basic understanding of chemical exposure and effects. In contrast, the Field Survey provides observational evidence of the environmental conditions that are supportive (or unsupportive) of wild rice. The Field Survey is not controlled in the sense of isolating individual variables that may be affecting wild rice, but by monitoring for the likely variables and analyzing that data, an understanding of the strength of the relationships between specific variables and wild rice presence or absence can be gained. Overlap or agreement between the hydroponics data and the Field Survey data were strong evidence to consider in developing this Analysis, particularly where there is also scientific literature that further reinforces the agreement.

MPCA also reviewed and analyzed the data from the Mesocosm (outdoor container) Experiment. That experiment showed significant effects on the growth and development of wild rice at relatively high sulfate treatment concentrations. However, it appears that the containers may not have reached equilibrium for the sulfide, sulfate and iron reactions (meaning there may be excess iron available to "buffer" the elevated sulfate, but once the iron is used up a toxic effect may be seen at lower sulfate concentrations). Additional analysis of the sediment chemistry from the Mesocosm Experiment provided helpful insight in comparison to sediment chemistry from the field sites. Finally, the results from the rooting zone depth profiles and Sediment Incubation Experiment are briefly summarized, though further analysis and possibly additional study is needed before general findings can be drawn from these two Study components.

Organization of this Analysis

The Analysis begins with a presentation of the environmental setting in which wild rice grows in Minnesota, with an emphasis on sulfate in surface water. Among Midwestern states, Minnesota is unusually heterogeneous in its geology, climate, and native vegetation, which originally ranged from prairie in the west and south (now largely corn and soybeans), to what is still boreal forest in the northeast.

The components of the Study are then presented, outlining the methods employed and the data produced. More detail about the five different components can be obtained from the reports associated with each. Integration of the components is the focus of the Discussion.

The Discussion addresses the major hypotheses that were presented and discussed in the Study Protocol (MPCA 2011). Specifically, the Discussion evaluates the hypothesis that sulfate is not directly toxic to wild rice in Minnesota, but can affect the health of wild rice when it is converted into sulfide in the substrate in which wild rice grows. Because there is not a simple relationship between sulfate and sulfide, due to mediation by iron, the Discussion proceeds methodically through the data that document the role of iron.

Environmental Setting for Wild Rice Growth in Minnesota

Dr. John Moyle published his observations on the correlation between wild rice occurrence and the chemistry of surface waters. Moyle stated that wild rice is a species that requires hard water, but low sulfate concentrations: "…no large stands are known from waters where the sulphate ions exceed 10 ppm. Plantings of wild rice in the high-sulphate waters area have generally failed. The cause-and-effect relationship between sulphates and the distribution of plants is not known, but may be related to sulfur demands in plant nutrition, osmotic pressure of the water solution, or the toxicity of magnesium usually associated with sulphates" (Moyle 1956).

The correlation observed by Moyle between wild rice occurrence and the broad trends in the chemistry of surface water has held up over time. The general trend is that wild rice tends to be present in low-sulfate waters of the state (Figure 1).

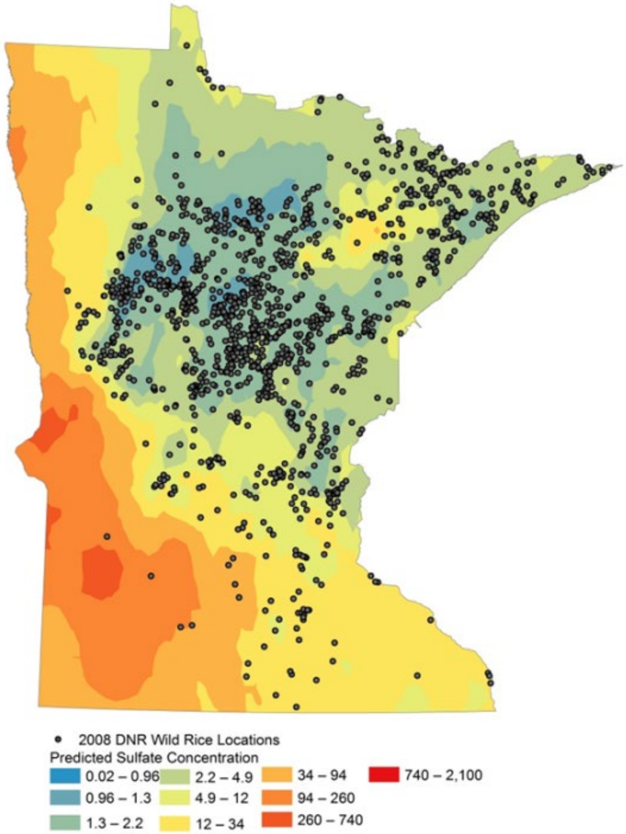
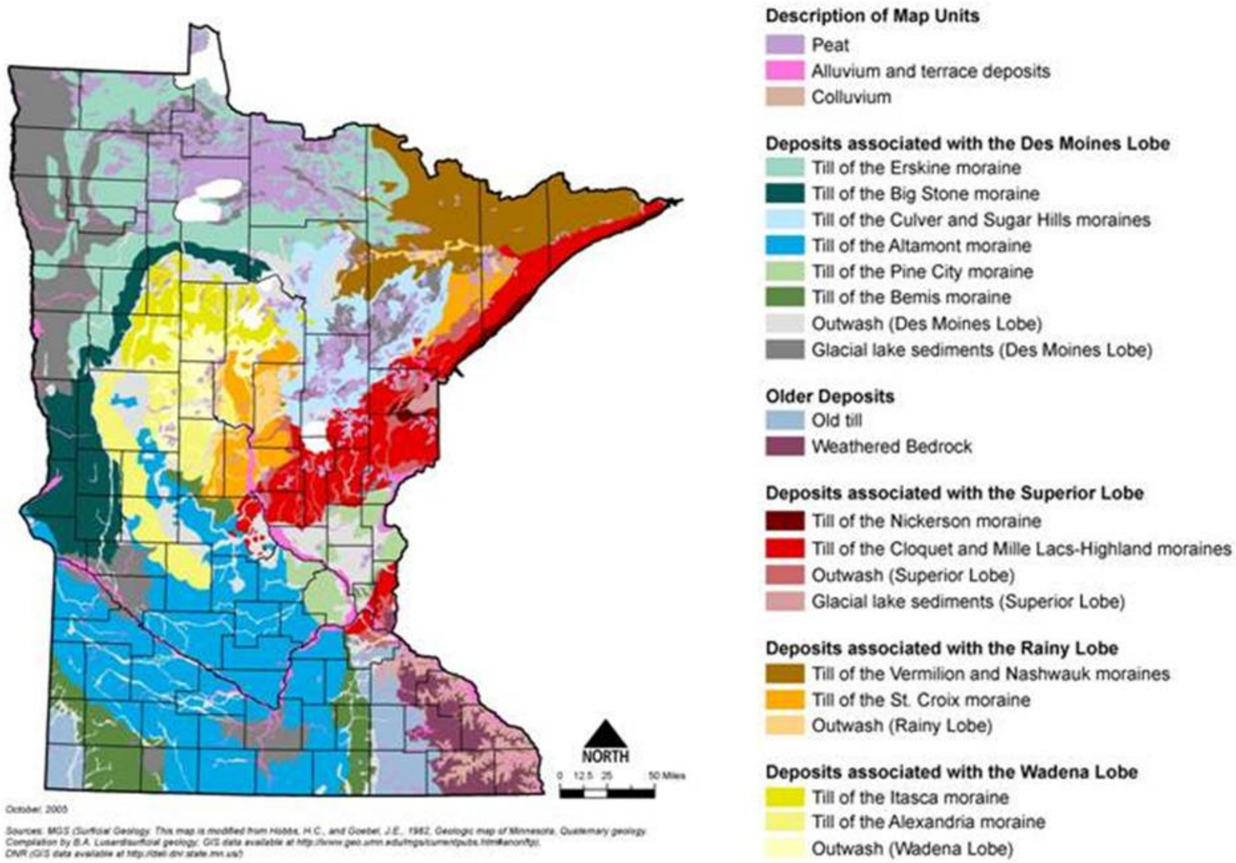


Figure 1. Locations of reported lakes with wild rice (black symbols; from DNR 2008) as compared to surface water sulfate concentrations (in mg/L). The sulfate contours were generated from 3,230 surface water sulfate values in DNR and MPCA databases (see Table 6 for summary statistics of these data).

Natural sources of sulfur in surface waters are influenced by the surficial geology of the watershed. Except for the southeastern corner of the state, Minnesota's surficial geology is dominated by its history of glaciation. Glacial lobes advanced from the northeast (Superior and Rainy lobes), north (Wadena Lobe) and northwest (Des Moines Lobe) (Figure 2). The different glacial lobes left soil parent material of varying sulfur and iron contents, which provide broad differences in sulfur concentrations in soil (Figure 3) and groundwater chemistry. The sulfur content of Minnesota's surficial soils and soil parent material do not always align with each other (Figure 3), but are both low in sulfur in north-central Minnesota, where wild rice sites are common (Figure 1).



Sources: MGS (Surficial Geology. This map is modified from Hobbs, H.C., and Goebel, J.E., 1982, Geologic map of Minnesota, Quaternary geology. Compilation by B.A. Lusardi/surficial geology; GIS data available at http://www.geo.umn.edu/mgs/current/pubs.html#anonftp). DNR (GIS data available at http://deli.dnr.state.mn.us/)

Figure 2. Glacial deposits in Minnesota. (Modified from Hobbs and Goebel 1982.)

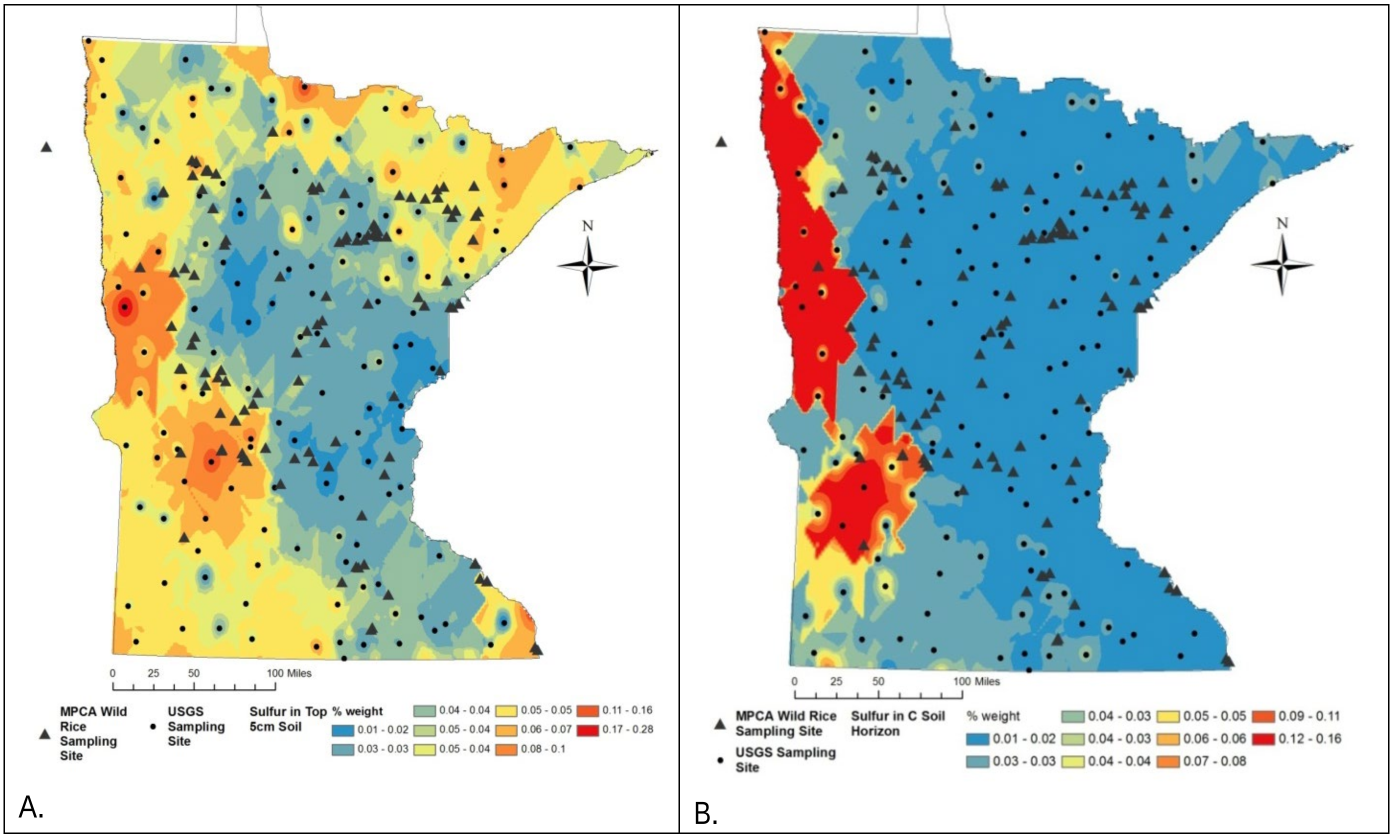


Figure 3. A. Sulfur in the top 5 centimeters of soil. **B.** Sulfur in the soil parent material (C horizon). Data from USGS 2013. Black dots = USGS sampling sites; black triangles = Wild Rice Sulfate Standard Study sampling sites.

Minnesota's climate also greatly influences the chemistry of the state's surface waters. The net effect of the precipitation gradient (Figure 4A) and north-to-south temperature gradient produces a strong east-to-west moisture gradient across Minnesota (Figure 4B). This climatic phenomenon, combined with the generally higher sulfur content of soils (Figure 3) and groundwater in western Minnesota, produces a strong gradient in sulfate concentrations in surface water across the state (Figure 1). This gradient can be seen in the frequency distribution of sulfate concentrations in lakes within each of Minnesota's three major ecoregions (Figure 5).

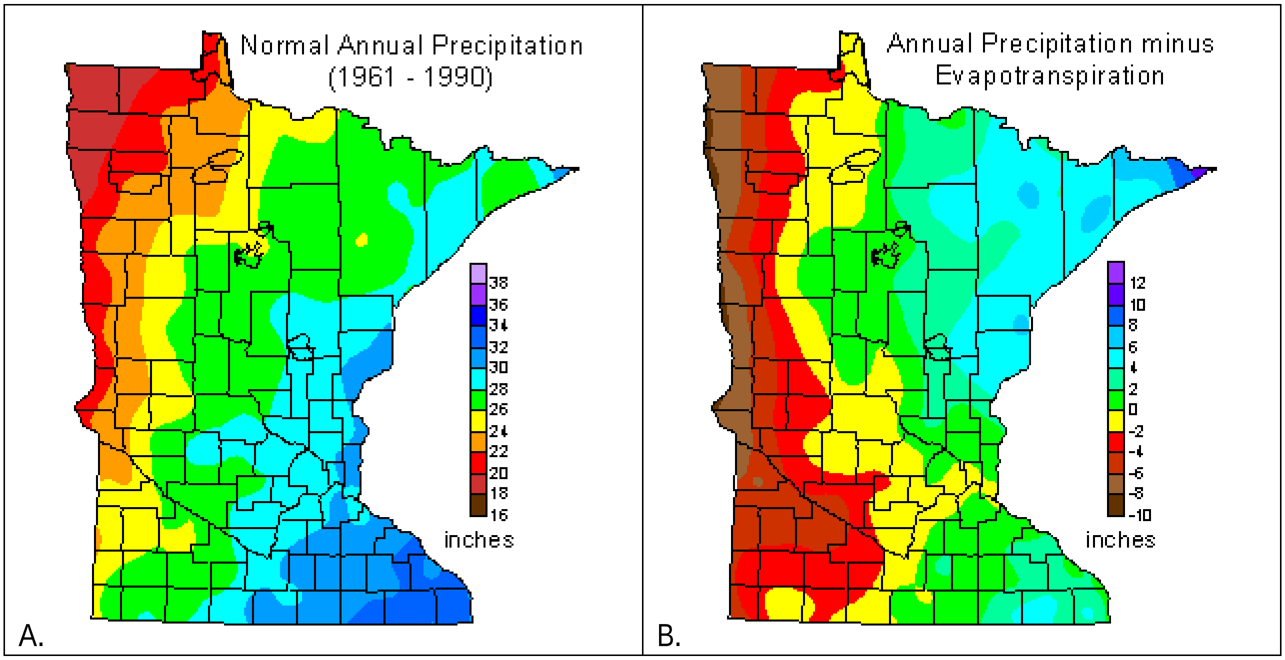


Figure 4. A. Average annual precipitation across Minnesota. **B.** Average difference between precipitation and evapotranspiration across Minnesota. From: http://www.dnr.state.mn.us/climate/water_availability.html

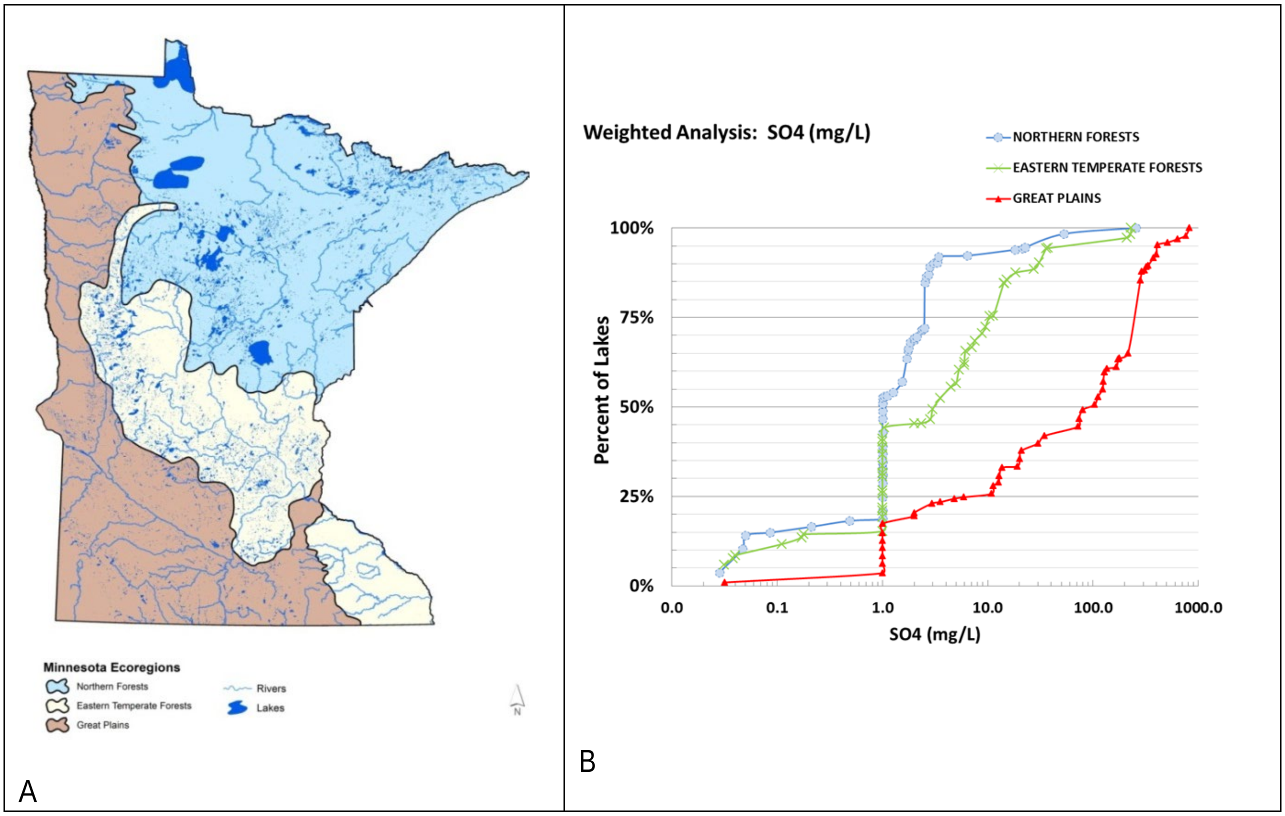


Figure. 5. A. Major ecoregions in Minnesota: Great Plains (tan), Eastern Temperate Forests (white), and Northern Forests (blue). **B.** Frequency distributions of sulfate concentrations in lakes in each of the three major ecoregions (developed from data collected as part of the 2012 USEPA National Lake Assessment, a probabilistic sampling of Minnesota lakes, USEPA 2012). The vertical distribution of points at 1.0 mg/L occurs because two analytical laboratories were used, and one of them had a reporting limit of 1.0 mg/L.

The Wild Rice Sulfate Standard Study: Methods and Results

As stated earlier, a primary intent of the Wild Rice Sulfate Standard Study was to enhance scientific understanding of the effects of sulfate on wild rice and to inform a decision by MPCA as to whether a revision of the wild rice sulfate standard is warranted. The Study was designed so that individual components together provide a better understanding of the effects of sulfate on wild rice.

This section summarizes the methods and key results of the Study components. Additional details can be found in individual reports for each of the Study components, which are referenced in this section and available on MPCA's wild rice sulfate standard web page at http://www.pca.state.mn.us/ktqh1083 (a link to an FTP site with all the reports and data is available on this page). The Study results highlighted in this section are analyzed and integrated as a whole in the Discussion section.

Laboratory Hydroponic Experiments

Methods

The Hydroponic Experiments involved a series of aquatic toxicity tests designed to evaluate the relationship between a controlled exposure of wild rice plants to a dilution series of sulfate or sulfide concentrations (Table 2), and the biological responses observed in the plant's growth and development. Selected biological endpoints (detailed below) were measured and then tested statistically to determine if significant difference between treatments occurred. These measures provided a means of quantifying an environmentally relevant exposure concentration or range of concentrations associated with an effect on wild rice growth and development. This approach is often used for developing water quality standards, where a dose-response relationship that is empirically derived in a controlled setting informs the development or evaluation of a standard. This approach also enabled the estimation of effect concentrations of sulfate and sulfide that may be used to describe effects on populations of wild rice in the environment. Furthermore, laboratory-controlled experiments provided an important line of information to complement other components of the Study. Details of the Hydroponic Experiment methods are found on pages 5-10 of Pastor (2013a), a summary of which is presented here.

Table 2. Exposure levels and associated nominal (target) test concentrations of sulfate and sulfide used in Hydroponic Experiments.

Exposure Level	0	#1	#2	#3	#4	#5
Sulfate Concentration (mg/L)	Control	10	50	100	400	1,600
Sulfide Concentration (µg/L)	Control	96	320	960	2,880	--

The Hydroponic Experiments were conducted from August to November, 2013, following an extensive investigation of methods development. All tests were performed using *Zizania palustris* (northern wild rice) at one of two stages of development: seeds or juvenile seedlings. For tests of germination response to sulfate or sulfide exposure, conditioned seeds were selected and randomly assigned to treatment groups. For tests of juvenile seedling response, the seeds selected were allowed to germinate until a 1 millimeter (mm) to 2 mm long mesocotyl shoot appeared. Seedlings were selected and randomly assigned to treatment groups in a similar manner to the germination tests. Preliminary range-finding tests were conducted prior to all definitive tests to determine the appropriate range of concentrations and responses necessary to calculate a useful dose-response curve.

For the 11-day duration of each test performed, wild rice seeds or juvenile seedlings were entirely submerged in a hydroponic growth media containing dissolved sulfate or sulfide at concentrations that were assigned to the treatment group. Sulfate treatments were made by dissolving sodium sulfate in stock hydroponic growth media in amounts that corresponded to a desired nominal concentration. Sulfide treatments were made by dissolving sodium sulfide hydrate in anoxic hydroponic growth media. Sulfate and sulfide test solutions were renewed every 2 to 3 days. Responses of the wild rice seed germination experiments were measured as germination success and mesocotyl length. The responses of the juvenile seedling experiments were measured as plant length and dry weight change.

The pH of the hydroponic growth media for both sulfate and sulfide tests was monitored and the values were recorded during test solution renewals. Sulfide exists predominantly as either hydrogen sulfide or bisulfide in water that has a pH at or near 7. Knowledge of the pH of the solution was needed to accurately calculate the concentration of each of these sulfide chemical species at equilibrium.

Although there were many similarities in methodology and design between the tests using sulfate or sulfide, necessary test method variations arose due to differences in the reactivity and stability of the two compounds. These method variations involved both the way the sulfate and sulfide tests were initially set up and how they were maintained during each test run. In particular, because sulfide oxidizes to sulfate it was necessary to minimize the introduction of atmospheric oxygen to the sulfide solutions that would oxidize sulfide to sulfate. Conversely, sulfate is stable under oxygenated conditions and sulfate exposure tests were conducted in an oxic environment.

The sulfide seedling experiment involved immersing photosynthesizing seedlings in an anoxic sulfide solution. Over time sulfide was oxidized by the oxygen the seedlings produced. This led to a decrease in the sulfide exposure concentration between each renewal of the test solution. The average reduction from the initial sulfide concentrations in each renewal (hydroponic solutions were renewed on day 2, 4, 7 and 9) ranged from about a 30% loss at the two highest sulfide concentrations (exposure levels #3 and #4) to a 90% loss at exposure level #2, and a 96% loss at exposure level #1. There was little loss of sulfide in the chemistry control containers that did not contain wild rice seedlings (John Pastor, personal communication with Edward Swain), indicating that the loss of sulfide was primarily due to the oxygen released by the seedlings. It is unclear to what degree the young stem and leaf of the seedlings would be exposed to sulfide in nature. This question is addressed further in the Discussion section.

Results

A complete report of the hydroponic test results is found in Pastor (2013a). The following paragraphs summarize MPCA's analysis to date of these results.

Sulfate tests

The experiments exposing wild rice to elevated sulfate did not reveal significant effects on wild rice seed germination and seedling growth at concentrations that would be encountered in Minnesota surface waters. Elevated sulfate concentrations of up to 1,600 mg/L, under aerobic conditions, did not affect germination rates of wild rice or the growth of the germinated plants over eleven days. This finding is corroborated by an independent Hydroponic Experiment carried out by Fort et al. (2013).

It must be noted that the Study Hydroponic Experiments were designed to evaluate only the direct effect of sulfate on wild rice seed germination and seedling growth, and not to evaluate any indirect effect of sulfate conversion to sulfide in the organic-rich saturated soils in which wild rice grows.

Sulfide tests

A rangefinder test (R in Table 3) is often conducted to determine the appropriate concentration range for subsequent definitive tests of a toxicant. In the MPCA Study, the sulfide concentrations chosen for the rangefinder test were similar to the definitive tests (D1 and D2 in Table 3). Since the methods used in the rangefinder test were the same as the methods for the two definitive tests, the data from all three tests were relied upon for assessing the effect of sulfide on wild rice growth. It is unknown whether the plants were most affected by the initial concentration (the measured concentrations of the test solutions that were prepared at the start of the test and each renewal of solution), or the declining concentrations that the plants were exposed to between solution renewals. MPCA staff relied on the initial sulfide concentration, rather than the lower sulfide concentrations that developed between renewals, as the operative exposure concentration in this analysis, as this was the highest, and presumably most toxic, concentration to which the plants were exposed. Particularly for sulfide exposure levels #1 and #2, the initial concentrations were much greater than the concentrations measured two to three days later and therefore had the most potential to negatively affect the growth of the seedlings.

Table 3. Hydroponic sulfide juvenile growth test concentrations (average of the initial concentrations of the test solution and renewal solutions). R = Rangefinder test, D1= Definitive test #1, D2 = Definitive test #2.

Sulfide Exposure Level (See Table 2)	Average measured initial sulfide concentration, by test (average of three replicates for each test; µg/L)	Average measured initial sulfide concentration, by exposure level (average of R, D1 and D2 tests; µg/L)
#1	R: 109	134
	D1: 140	
	D2: 153	
#2	R: 333	309
	D1: 291	
	D2: 302	

Sulfide did not show an effect on seed germination. However, an effect was observed on seedling growth, which was defined as final seedling weight minus initial seedling weight. To evaluate differences between the effects of sulfide exposure levels on seedling growth, an analysis of variance (ANOVA) test followed by a Dunnett's Contrast multiple comparisons test was used. This statistical analysis included both test (R, D1, D2) and sulfide exposure level (control, #1, #2) as categorical explanatory variables. Results show that seedling growth differed significantly between the sulfide exposure levels ($p = 0.04$). Seedling growth was significantly lower in exposure level #2 compared to the control ($p = 0.03$), whereas in exposure level #1 seedling growth was not significantly different than the control ($p = 0.32$). In other words, the average initial sulfide concentration of exposure level #2, 309 µg/L, was toxic, while the average of exposure level #1, 134 µg/L, was not. These results suggest that the concentration of sulfide below which growth is not likely to be adversely affected is between 134 and 309 µg/L, or in rounded numbers, 150 and 300 µg/L.

It is important to note that the average initial sulfide concentration at each sulfide exposure level varied among the three tests (R, D1, D2) and among the replicates (n = 3) in the same test. Recognizing this variability, an analysis of covariance (ANCOVA) test was employed to evaluate the effect of average initial sulfide concentration on seedling growth. This statistical analysis included average initial sulfide concentration as a continuous explanatory variable, and test (R, D1, D2) as a categorical explanatory variable. Results showed that increased sulfide concentrations significantly reduced seedling growth by 0.004 mg per 1 µg/L sulfide ($p = 0.009$). These results were consistent across all three tests. The ANOVA, ANCOVA and Dunnett's Contrast calculations and associated parameter values are provided in Appendix A. The consistent results from the ANOVA and ANCOVA tests emphasize the overall conclusion that sulfide has a negative effect on wild rice seedling growth.

The hydroponic data from the sulfide tests were also analyzed through nonlinear regression analysis. This allowed for estimation of particular reductions in seedling growth due to sulfide toxicity, such as a 50% reduction in growth relative to the control (EC50) or a 20% reduction in growth relative to the control (EC20). In aquatic toxicology, an EC50 is generally interpreted to characterize a concentration that has an unquestioned deleterious effect, whereas an EC20 is sometimes used to characterize a no-effect concentration. Specifically, a four-parameter logistic equation was fit to the data, which is a standard approach to developing dose-response curves in toxicology studies.

Regression analysis was completed for each of the three sulfide seedling exposure tests, and the resulting EC20 and EC50 estimates were averaged (see Figure 6 and Table 4). The average EC20 estimate (257 µg/L; Table 4) is between the concentrations associated with exposure levels #1 and #2, and the average EC50 estimate (383 µg/L; Table 4) is higher than the concentrations associated with exposure level #2 (309 µg/L). Therefore, both the average EC20 and EC50 estimates are compatible with the conclusion that a sulfide concentration greater than 300 µg/L is likely to be harmful to wild rice.

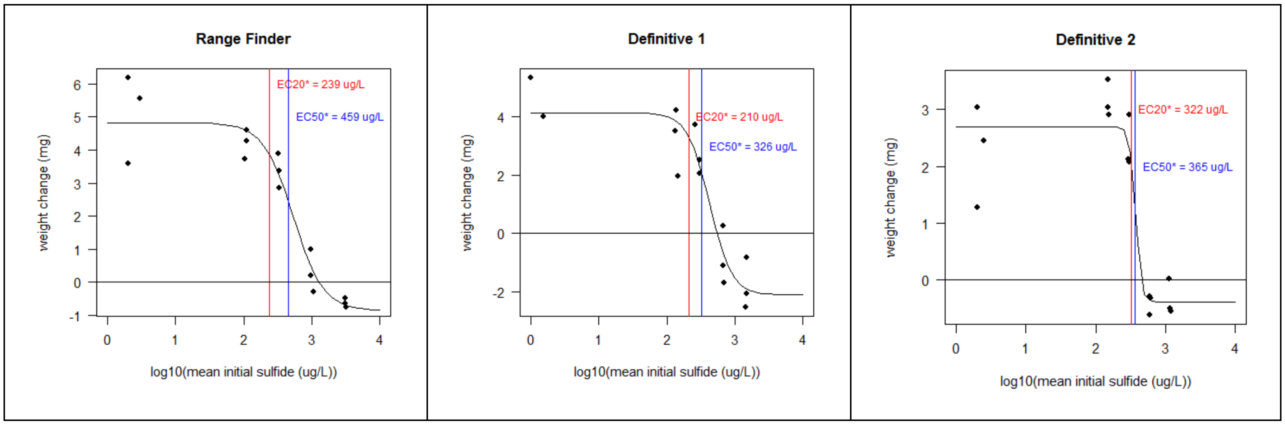


Figure 6. Estimates of EC20 and EC50 from regression curve calculations using test results for all three hydroponic tests. Full details of the regression statistics and parameters are found in Appendix B.

Table 4. EC20 and EC50 sulfide concentrations estimated by regression analysis of the hydroponic sulfide seedling test data. The estimates are based on the measured initial concentrations of sulfide in the exposure tests. Growth is measured as net change (final weight minus initial weight) of dry weight.

Effect Concentration Percentile	Effect Concentration for Each Test (µg/L)	Mean Effect Concentration (µg/L)
EC20	R: 239 D1: 210 D2: 322	257
EC50	R: 459 D1: 326 D2: 365	383

Field Survey

Methods

The Field Survey was designed to investigate physical and chemical conditions correlated with the presence of wild rice in Minnesota water bodies. Efforts also were made to identify and sample sites with characteristics that seemed favorable to wild rice growth, but where wild rice was not present. The data were used to investigate correlations between the biological, chemical, and physical conditions recorded for each site. Additionally, the Survey design allowed for the investigation of biogeochemical relationships between sulfate in the overlying water, sulfide in the sediment porewater, iron in the dissolved and solid phases of the sediment, and other environmental parameters. Finally, results of the Field Survey provide additional context and support of results from other components of the overall Wild Rice Sulfate Standard Study. This section briefly summarizes the field survey methods, and then presents key analyses of the collected data.

Details of the field and analytical methods employed throughout the survey can be found in the Field Survey report (Myrbo 2013). Habitats sampled included lakes, shallow lakes, large rivers, small streams, wetlands, and cultivated wild rice paddies. Surface water, sediment porewater, and sediment core samples were collected and wild rice abundance was measured at each sampling site. If wild rice was not found at a site, field protocol called for the crew to identify and sample potential wild rice habitat, which was primarily determined by the presence of rooted aquatic macrophytes, such as lily pads, that can co-occur with wild rice. The presence of these macrophytes indicated that the water depth, wave exposure, water transparency, and sediment matrix did not exclude rooted aquatic macrophytes even if wild rice was not present.

Field work occurred during 2011, 2012 and 2013, first with a Pilot Survey in 2011 and then the Study Field Survey during 2012-2013. Although the field work was conducted in a relatively uniform manner over the three field seasons, some important differences should be noted. The 2011 Pilot Survey was focused on developing and testing the methods for the larger Field Survey in 2012 and 2013. After the 2011 season, MPCA identified a need to identify and sample sites with elevated sulfate concentrations (above 10 mg/L) that conceivably could host wild rice based on suitable wild rice habitat. The 2011 and 2012 field efforts consisted of one-time visits to sites, mostly between early July and the middle of September. In 2013, 19 sites were selected as “multiple visit” sites and were sampled 3 to 5 times between May and the middle of September; an additional 17 sites were sampled once that year. In 2013, field crews also visited the Mesocosm Experiment to sample the same environmental parameters as in the field. In addition, stratigraphic porewater chemistry sampling was conducted at two of the field sites using porewater equilibrators known as “peepers” (Johnson 2013).

Over the course of the Field Survey (2012-2013), 119 individual field sites were sampled during 193 total site visits (some sites were sampled more than once), and more than 75 chemical and physical parameters were quantified at each site. The Pilot Survey involved sampling 39 individual sites, some of which were also sampled during the Field Survey.

Results

An overview of the Field Survey data is found in Myrbo (2013). The following paragraphs summarize MPCA’s analysis to date of the data.

In this Analysis, the data collected in the 2011 Pilot Survey of 39 different sites (also called Data Set 1) are usually analyzed separately from the 2012-2013 Field Survey of 119 different sites. The reasons for this separation are multiple: the laboratories analyzing surface water, porewater, and acid-volatile sulfide changed between the two surveys and some field and laboratory parameters also changed. Furthermore, as noted above there was some overlap in the sites sampled between the two surveys, so combining the data sets would not have increased the number of sites, and therefore the statistical power, substantially. A benefit of keeping the data sets separate is that significant correlations between parameters that are common to both surveys are less likely to be due to chance.

The Field Survey documented a large range in surface-water sulfate concentrations (Figure 7). The measured sulfate concentrations at the field sites follow the general pattern of sulfate concentrations across the state (Figure 1).

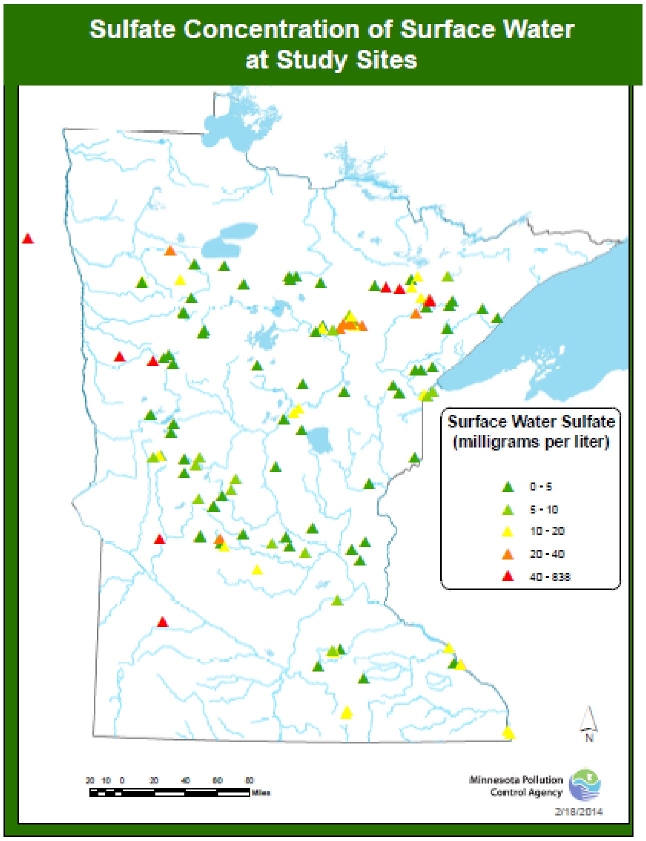


Figure 7. Sulfate concentration of surface water from Field Survey sites.

In addition to sulfate, many other parameters were quantified for each field site. The data include extensive chemical analyses of surface water, sediment porewater, and the solids in the sediment at each site.

One way to examine the field data for significant relationships between field parameters is through correlation analysis. A Spearman Correlation analysis of a number of parameters measured in the Field Survey (Table 5) shows that no one parameter is strongly correlated with the cover of wild rice at the sampling sites. Wild rice percent cover at the sample sites (measured as percent cover within 1-meter rings) had no significant correlation with surface-water sulfate, but was negatively correlated with porewater sulfide (*rho*=-0.25; p <0.01). Other pertinent correlations include: surface-water sulfate is positively correlated with sulfide in porewater (Spearman's correlation coefficient (*rho*) = 0.37; p<0.001); and porewater sulfide is negatively correlated with porewater iron (*rho* = -0.56; p <0.001). The negative correlation between iron and sulfide in the sediment porewater is graphically represented in Figure 8, which shows that at most of the field sites, high porewater sulfide concentrations occur where porewater iron concentrations are low, and vice versa.

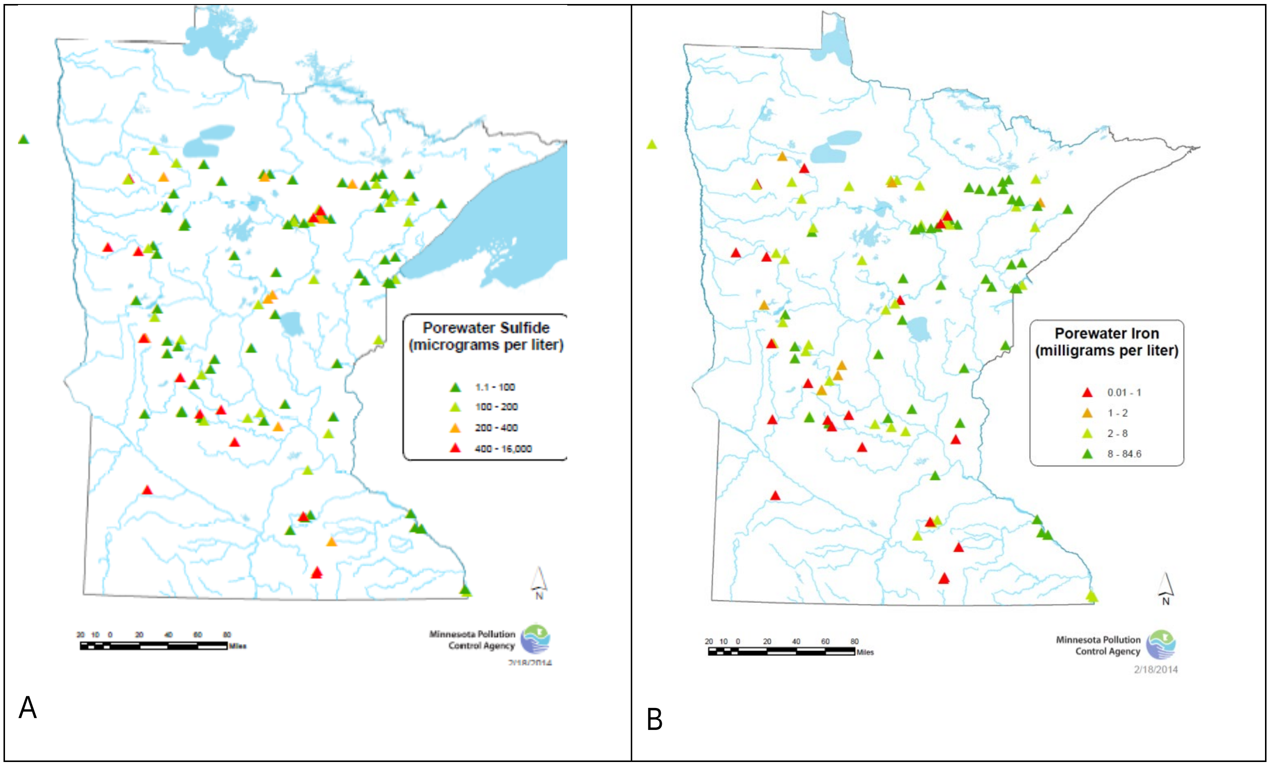


Figure 8. A. Sulfide concentrations in the sediment porewater at the sample sites. **B.** Iron concentrations in the sediment porewater at the sample sites.

Table 5. Correlation coefficients for selected parameters analyzed in the 2012-2013 Field Survey. Pairs of parameters are more closely correlated as the correlation coefficient approaches one (1) or negative one (-1) for positive (red) or negative (green) correlations, respectively. (Data Set 4; consists of one site visit to each of 119 different sites, including 82 lakes, 30 streams, and 7 cultivated paddies; correlation matrix from Appendix E).

All sites in the 2012-2013 Survey (N=119) **Spearman Correlation Coefficients (rho)** **P<0.05 for |rho| > 0.187**	Latitude	Longitude	Wild rice % cover in ring	Wild rice ave # stems/m2	Floating leaf % cover in ring	Water depth	T tube transparency	Surface water Ca	Surface water Mg	Surface water K	Surface water Fe	Surface water SO4	Surface water alkalinity	Surface water color (Pt Co units)	Porewater pH	Porewater sulfide	Porewater free H2S	Porewater DOC	Porewater Ca	Porewater Mg	Porewater K	Porewater Fe	Porewater silica	Sediment % water	Sediment % organic (LOI)	Sediment TS/TOC	Sediment AVS/TOC	Sediment Fe	Sediment Fe/AVS	Sediment Fe-AVS	Sediment TP/TOC	Sediment TN/TOC	Sediment TOC
Latitude		-0.09	0.22	0.22	-0.33	-0.45	0.05	0.01	-0.06	-0.19	0.25	0.05	-0.05	0.16	-0.03	0.03	-0.03	0.15	-0.15	-0.12	-0.07	0.06	-0.17	0.06	0.23	-0.08	-0.22	0.11	0.17	0.15	-0.28	-0.44	0.24
Longitude	-0.09		-0.08	-0.19	0.39	0.06	-0.15	-0.20	-0.60	-0.43	0.47	0.13	-0.62	0.43	-0.04	-0.25	-0.20	0.03	-0.47	-0.51	-0.39	0.44	-0.26	0.01	-0.01	0.12	0.20	0.46	0.12	0.47	0.12	-0.12	-0.03
Wild rice % cover in ring	0.22	-0.08		0.96	-0.20	-0.29	0.14	0.30	0.19	0.05	0.10	-0.07	0.25	-0.05	0.02	-0.25	-0.26	0.01	0.16	0.13	-0.27	0.09	-0.10	-0.13	-0.04	-0.13	-0.06	-0.03	0.15	0.04	-0.05	0.03	-0.04
Wild rice ave # stems/m2	0.22	-0.19	0.96		-0.24	-0.28	0.19	0.29	0.24	0.08	0.02	-0.12	0.30	-0.13	0.01	-0.23	-0.24	-0.02	0.22	0.17	-0.24	0.04	-0.06	-0.08	-0.01	-0.18	-0.11	-0.07	0.13	-0.01	-0.09	0.04	0.00
Floating leaf % cover in ring	-0.33	0.39	-0.20	-0.24		0.32	-0.02	0.11	-0.26	-0.19	-0.14	0.08	-0.19	0.03	-0.16	-0.02	0.08	-0.15	-0.01	-0.22	-0.13	0.14	0.04	0.10	0.00	0.16	0.11	0.17	-0.07	0.12	0.02	0.04	0.01
Water depth	-0.45	0.06	-0.29	-0.28	0.32		0.25	-0.13	-0.14	-0.13	-0.28	-0.05	-0.16	-0.24	-0.03	0.03	0.10	-0.11	0.00	-0.12	-0.03	0.06	0.09	0.08	-0.02	0.08	0.08	0.09	-0.03	0.04	0.05	0.26	-0.03
T tube transparency	0.05	-0.15	0.14	0.19	-0.02	0.25		0.07	0.02	-0.18	-0.34	-0.01	0.09	-0.71	-0.04	-0.13	-0.08	-0.24	0.22	-0.02	-0.14	0.09	0.03	0.09	0.03	0.05	0.00	0.01	-0.03	-0.01	-0.12	0.07	0.03
Surface water Ca	0.01	-0.20	0.30	0.29	0.11	-0.13	0.07		0.42	0.25	-0.25	0.17	0.67	-0.17	0.07	-0.01	-0.07	-0.25	0.50	0.26	0.02	-0.06	0.10	-0.20	-0.18	0.06	0.12	-0.03	-0.02	-0.07	0.13	0.13	-0.15
Surface water Mg	-0.06	-0.60	0.19	0.24	-0.26	-0.14	0.02	0.42		0.69	-0.48	0.42	0.86	-0.34	0.27	0.37	0.25	-0.20	0.47	0.73	0.40	-0.36	0.36	-0.31	-0.33	0.27	0.28	-0.42	-0.44	-0.48	0.27	0.21	-0.33
Surface water K	-0.19	-0.43	0.05	0.08	-0.19	-0.13	-0.18	0.25	0.69		-0.31	0.34	0.56	-0.15	0.14	0.30	0.22	-0.04	0.30	0.51	0.51	-0.38	0.12	-0.30	-0.28	0.12	0.20	-0.45	-0.37	-0.49	0.21	0.16	-0.27
Surface water Fe	0.25	0.47	0.10	0.02	-0.14	-0.28	-0.34	-0.25	-0.48	-0.31		-0.15	-0.51	0.69	-0.08	-0.29	-0.27	0.48	-0.42	-0.36	-0.27	0.38	-0.31	-0.01	0.17	-0.23	-0.11	0.49	0.41	0.57	-0.06	-0.35	0.16
Surface water SO4	0.05	0.13	-0.07	-0.12	0.08	-0.05	-0.01	0.17	0.42	0.34	-0.15		0.21	-0.08	0.24	0.37	0.31	-0.21	-0.03	0.25	0.21	-0.22	0.04	-0.36	-0.40	0.55	0.56	-0.08	-0.47	-0.20	0.44	-0.08	-0.40
Surface water alkalinity	-0.05	-0.62	0.25	0.30	-0.19	-0.16	0.09	0.67	0.86	0.56	-0.51	0.21		-0.41	0.21	0.24	0.14	-0.25	0.59	0.64	0.28	-0.31	0.35	-0.23	-0.25	0.15	0.15	-0.35	-0.28	-0.39	0.17	0.24	-0.24
Surface water color (Pt Co units)	0.16	0.43	-0.05	-0.13	0.03	-0.24	-0.71	-0.17	-0.34	-0.15	0.69	-0.08	-0.41		-0.13	-0.05	-0.02	0.40	-0.41	-0.24	-0.09	0.15	-0.16	0.04	0.18	-0.11	-0.10	0.31	0.25	0.36	-0.03	-0.17	0.17
Porewater pH	-0.03	-0.04	0.02	0.01	-0.16	-0.03	-0.04	0.07	0.27	0.14	-0.08	0.24	0.21	-0.13		-0.02	-0.36	-0.32	-0.16	0.08	-0.12	-0.01	-0.07	-0.35	-0.46	0.41	0.49	-0.15	-0.31	-0.20	0.46	0.13	-0.47
Porewater sulfide	0.03	-0.25	-0.25	-0.23	-0.02	0.03	-0.13	-0.01	0.37	0.30	-0.29	0.37	0.24	-0.05	-0.02		0.90	0.00	0.05	0.33	0.40	-0.56	0.38	0.20	0.17	0.35	0.02	-0.34	-0.50	-0.46	-0.12	0.19	0.17
Porewater free H2S	-0.03	-0.20	-0.26	-0.24	0.08	0.10	-0.08	-0.07	0.25	0.22	-0.27	0.31	0.14	-0.02	-0.36	0.90		0.05	0.07	0.29	0.39	-0.54	0.37	0.28	0.26	0.23	-0.09	-0.24	-0.40	-0.36	-0.20	0.15	0.27
Porewater DOC	0.15	0.03	0.01	-0.02	-0.15	-0.11	-0.24	-0.25	-0.20	-0.04	0.48	-0.21	-0.25	0.40	-0.32	0.00	0.05		-0.01	0.01	0.15	0.26	-0.01	0.01	0.22	-0.28	-0.28	0.24	0.36	0.35	-0.21	-0.29	0.24
Porewater Ca	-0.15	-0.47	0.16	0.22	-0.01	0.00	0.22	0.50	0.47	0.30	-0.42	-0.03	0.59	-0.41	-0.16	0.05	0.07	-0.01		0.73	0.34	-0.12	0.42	-0.11	-0.05	-0.09	-0.09	-0.21	-0.07	-0.21	-0.08	0.12	-0.02
Porewater Mg	-0.12	-0.51	0.13	0.17	-0.22	-0.12	-0.02	0.26	0.73	0.51	-0.36	0.25	0.64	-0.24	0.08	0.33	0.29	0.01	0.73		0.51	-0.34	0.42	-0.24	-0.17	0.15	0.11	-0.33	-0.30	-0.35	0.09	0.11	-0.15
Porewater K	-0.07	-0.39	-0.27	-0.24	-0.13	-0.03	-0.14	0.02	0.40	0.51	-0.27	0.21	0.28	-0.09	-0.12	0.40	0.39	0.15	0.34	0.51		-0.35	0.27	-0.13	-0.06	0.09	0.01	-0.31	-0.21	-0.32	0.01	0.06	-0.04
Porewater Fe	0.06	0.44	0.09	0.04	0.14	0.06	0.09	-0.06	-0.36	-0.38	0.38	-0.22	-0.31	0.15	-0.01	-0.56	-0.54	0.26	-0.12	-0.34	-0.35		-0.20	-0.12	-0.11	-0.11	0.21	0.64	0.32	0.67	0.15	-0.19	-0.11
Porewater silica	-0.17	-0.26	-0.10	-0.06	0.04	0.09	0.03	0.10	0.36	0.12	-0.31	0.04	0.35	-0.16	-0.07	0.38	0.37	-0.01	0.42	0.42	0.27	-0.20		0.15	0.05	0.14	0.01	-0.15	-0.25	-0.17	-0.01	0.33	0.04
Sediment % water	0.06	0.01	-0.13	-0.08	0.10	0.08	0.09	-0.20	-0.31	-0.30	-0.01	-0.36	-0.23	0.04	-0.35	0.20	0.28	0.01	-0.11	-0.24	-0.13	-0.12	0.15		0.90	-0.09	-0.55	0.27	0.02	0.21	-0.73	0.07	0.89
Sediment % organic (LOI)	0.23	-0.01	-0.04	-0.01	0.00	-0.02	0.03	-0.18	-0.33	-0.28	0.17	-0.40	-0.25	0.18	-0.46	0.17	0.26	0.22	-0.05	-0.17	-0.06	-0.11	0.05	0.90		-0.25	-0.70	0.31	0.20	0.30	-0.88	-0.13	0.99
Sediment TS/TOC	-0.08	0.12	-0.13	-0.18	0.16	0.08	0.05	0.06	0.27	0.12	-0.23	0.55	0.15	-0.11	0.41	0.35	0.23	-0.28	-0.09	0.15	0.09	-0.11	0.14	-0.09	-0.25		0.60	-0.09	-0.66	-0.26	0.36	0.30	-0.29
Sediment AVS/TOC	-0.22	0.20	-0.06	-0.11	0.11	0.08	0.00	0.12	0.28	0.20	-0.11	0.56	0.15	-0.10	0.49	0.02	-0.09	-0.28	-0.09	0.11	0.01	0.21	0.01	-0.55	-0.70	0.60		0.08	-0.64	-0.08	0.77	0.15	-0.72
Sediment Fe	0.11	0.46	-0.03	-0.07	0.17	0.09	0.01	-0.03	-0.42	-0.45	0.49	-0.08	-0.35	0.31	-0.15	-0.34	-0.24	0.24	-0.21	-0.33	-0.31	0.64	-0.15	0.27	0.31	-0.09	0.08		0.25	0.94	-0.09	-0.31	0.30
Sediment Fe/AVS	0.17	0.12	0.15	0.13	-0.07	-0.03	-0.03	-0.02	-0.44	-0.37	0.41	-0.47	-0.28	0.25	-0.31	-0.50	-0.40	0.36	-0.07	-0.30	-0.21	0.32	-0.25	0.02	0.20	-0.66	-0.64	0.25		0.49	-0.23	-0.27	0.21
Sediment Fe-AVS	0.15	0.47	0.04	-0.01	0.12	0.04	-0.01	-0.07	-0.48	-0.49	0.57	-0.20	-0.39	0.36	-0.20	-0.46	-0.36	0.35	-0.21	-0.35	-0.32	0.67	-0.17	0.21	0.30	-0.26	-0.08	0.94	0.49		-0.13	-0.37	0.29
Sediment TP/TOC	-0.28	0.12	-0.05	-0.09	0.02	0.05	-0.12	0.13	0.27	0.21	-0.06	0.44	0.17	-0.03	0.46	-0.12	-0.20	-0.21	-0.08	0.09	0.01	0.15	-0.01	-0.73	-0.88	0.36	0.77	-0.09	-0.23	-0.13		0.18	-0.90
Sediment TN/TOC	-0.44	-0.12	0.03	0.04	0.04	0.26	0.07	0.13	0.21	0.16	-0.35	-0.08	0.24	-0.17	0.13	0.19	0.15	-0.29	0.12	0.11	0.06	-0.19	0.33	0.07	-0.13	0.30	0.15	-0.31	-0.27	-0.37	0.18		-0.17
Sediment TOC	0.24	-0.03	-0.04	0.00	0.01	-0.03	0.03	-0.15	-0.33	-0.27	0.16	-0.40	-0.24	0.17	-0.47	0.17	0.27	0.24	-0.02	-0.15	-0.04	-0.11	0.04	0.89	0.99	-0.29	-0.72	0.30	0.21	0.29	-0.90	-0.17	

Utility of the Wild Rice Field Survey Data

The Field Survey data are used for two purposes in this Analysis:

1. To examine the chemical relationships between sulfate in surface water and the major chemical actors in the sediment, solid-phase iron, AVS, and porewater concentrations of sulfide and iron, and
2. To statistically characterize (via quantile regression) the relationships between sulfate and the other major chemical actors measured at the sites (see Discussion section).

The first purpose does not rely on a probabilistic sampling of sites, but rather requires that the range of sulfate, sulfide, and iron data be large enough to reveal the important chemical reactions that are fundamental to understanding sulfate-sulfide dynamics in Minnesota lakes, streams and paddies. The second purpose that the data are used for, the quantile regression, does require a certain level of representativeness of the data if the results are to be applied to other wild-rice-producing sites that were not part of the Field Survey data collection.

Statisticians recommend that surveys be probability-based when the point of the survey is to characterize the population being sampled. Probability-based surveys allow survey results to be extrapolated back to a larger population. The 2012-2013 Field Survey was purposefully not probability based, in that the point was not to characterize the population of wild rice production waters, but rather to explore the effect of elevated sulfate on the chemistry of the porewater of actual and potential wild rice habitat. If wild rice habitats had been sampled probabilistically, most of the sites would have had very low sulfate concentrations and little would have been learned about the effect of elevated sulfate. To ensure that the Study included samples from waters with elevated sulfate concentrations, the survey sites were intentionally not chosen in a random manner.

The “representativeness” of the wild rice Field Survey data

A direct way to explore the “representativeness” of the wild rice Field Survey data for sulfate is to compare the survey data to the distribution of data sets from other Minnesota field sampling. In 2008, the Minnesota DNR reviewed available data and surveyed wild rice harvesters to compile a natural wild rice site inventory as part of a legislatively directed report (DNR 2008). Of the 1,290 wild rice sites identified in the 2008 inventory, sulfate data are available from state databases for 513 sites, all of which are lake sites. For these 513 sites, the interquartile range (the middle 50%) of the sulfate concentration in the surface water is 1.0 to 3.6 mg/L. These data can be compared to the sulfate monitoring results from a 2012 probability-based sampling of lakes across the entire state of Minnesota (USEPA 2012). In that study, the interquartile range was 0.3 to 13.1 mg/L sulfate (Figure 9, Table 6). The large difference in the 75th percentile from the wild rice sites compared to Minnesota lakes as a whole—3.6 vs. 13.1 mg/L—further illustrates the association of wild rice with lower-sulfate-concentration lakes in Minnesota.

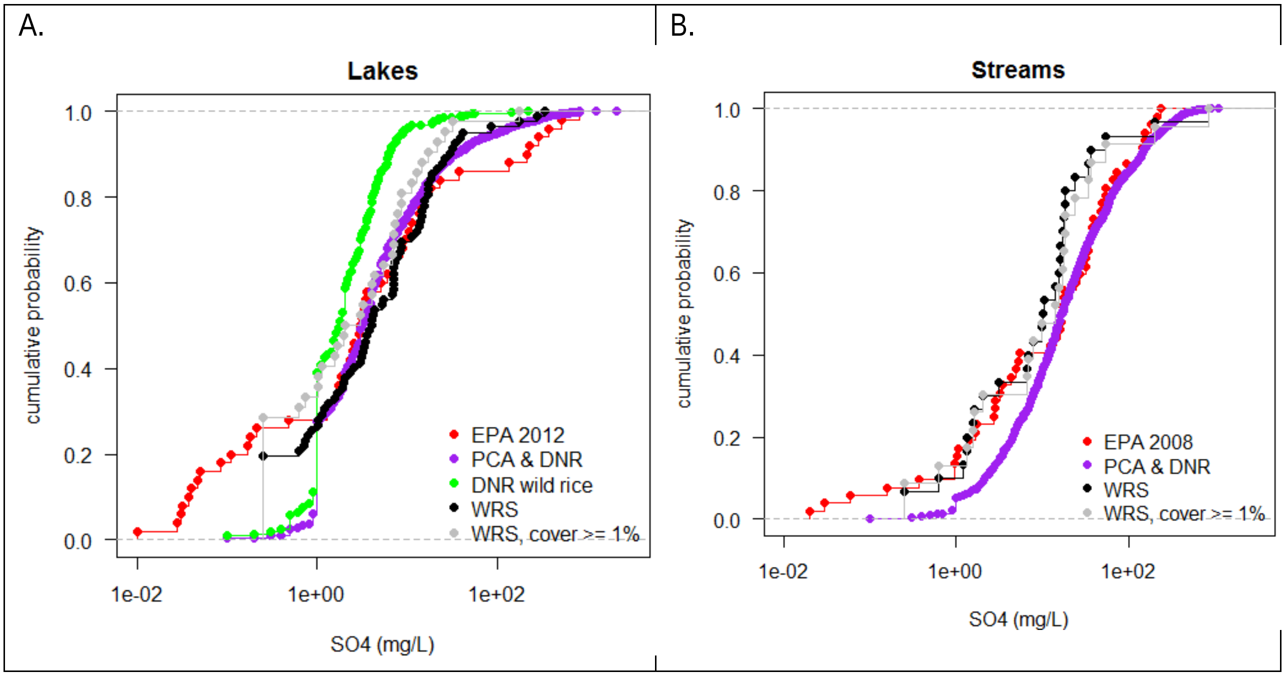


Figure 9. Sulfate frequency distributions of selected data sets defined in Table 6. **A.** Sulfate in Minnesota lakes. **B.** Sulfate in Minnesota streams and rivers. “WRS” are the data from the 2012-2013 Field Survey. PCA & DNR = data from state databases for lakes identified in a DNR wild rice site inventory (DNR 2008). EPA 2012 and EPA 2008 are probability-based surveys (USEPA 2008, 2012).

The interquartile range of sulfate concentrations in the 2012-2013 Field Survey data from the lake sites is 2.5 to 14.5 mg/L, which is more similar to the statewide probability-based distribution than to that of the DNR wild rice site inventory. If the 2012-2013 Field Survey data are limited to only those lake sites with more than 1% wild rice coverage observed at the sampling site (measured as percent cover within a 1-meter ring), the Field Survey interquartile distribution (0.3 to 7.7 mg/L) is intermediate between the DNR wild rice site inventory and the probability-based sampling of all Minnesota lakes (Figure 9A).

It is less clear how the 2012-2013 Field Survey data from stream sites relates to the larger population of Minnesota streams that support wild rice and to Minnesota streams as a whole. Streams are significantly more difficult to characterize than lakes, in that a stream is more variable in time and space than is a lake. It is also more difficult to inspect a stream for the occurrence of wild rice than a lake, since access and navigation are more difficult, and flow can be too high or too low for navigation. The DNR did not compile a list of stream sites with wild rice as a part of their 2008 inventory, so there is no data currently available from that effort that can be used to help characterize sulfate concentrations associated with wild rice in streams. A probability-based assessment of Minnesota streams (USEPA 2008) found that the interquartile range of sulfate is higher than for lakes (2.8 to 47.3 mg/L, compared to 0.3 to 13.1 mg/L). The interquartile range for the 2012-2013 Field Survey stream sites was 2.5 to 17.9 mg/L, and the subset of sites with wild rice (23 of 30 sites with wild rice cover greater than 1 percent) had a similar interquartile range: 1.8 to 21.0 mg/L. The lowest 25th percentile of the Field Survey sulfate frequency distribution is similar to the probability-based USEPA (2008) survey, but notably lower above the 50th percentile (Figure 9B). This pattern reaffirms the finding that wild rice tends to occur in lower-sulfate waters in Minnesota. However, based on the Field Survey data one might conclude that wild rice is more likely to occur in streams with elevated sulfate than lakes with elevated sulfate: the sulfate interquartile range of stream sites with wild rice (1.8 to 21.0 mg/L) was clearly greater than that for the Field Survey lakes with wild rice (0.3 to 7.7 mg/L).

Minnesota streams in general have higher concentrations of sulfate than lakes (e.g., median sulfate concentrations of 17.0 mg/L in streams vs. 3.0 in lakes, in the 2008 and 2012 USEPA probability-based samplings). The median sulfate concentrations at sites in which wild rice occurs may be generally higher in streams than in lakes (14.2 mg/L from the Field Survey stream data, 2.5 mg/L for the Field Survey lake data, and 1.8 mg/L for the DNR wild rice sites; Table 6). However, the median value for the eight stream sites with wild rice sampled during the 2011 Pilot Survey was only 2.4 mg/L, compared to the median of 14.2 mg/L for the 23 streams in the Field Survey (Table 6), which calls into question the assumption that the data from the streams sites sampled during the 2012-2013 Field Survey truly represents the population of stream sites where wild rice grows in Minnesota.

In summary, the 2012-2013 Field Survey of lakes has a sulfate frequency distribution that is intermediate between the probability-based USEPA survey and the 513 sulfate values that were available for the 1,290 wild rice lakes identified by the DNR (2008). The intermediate position means that the Field Survey sampled more high-sulfate lakes than would be expected if only known wild rice lakes were sampled, but fewer than would be expected if all lakes in the state were sampled probabilistically. Given that wild rice does not occur naturally in all lakes of the state, and that a major goal of the Field Survey was to assess the effect of elevated sulfate on wild rice, the site selection approach used for the Field Survey could be just right. The intent of the sampling was to find variation in sulfate while maintaining all other parameters suitable for wild rice growth (water transparency, water depth, pH, alkalinity, hardness, etc.). If this was accomplished, then the Field Survey could be interpreted as functioning as a sampling of a natural experiment that can be used to evaluate the effect of sulfate on wild rice.

It appears that streams that have wild rice may have a different, higher, sulfate frequency distribution than lakes, although the data may be inadequate to draw that conclusion. If wild rice can generally grow in streams at higher sulfate concentrations than in lakes, there are likely differences in the biogeochemistry of the two types of aquatic systems. Further evidence of a hypothesized difference is presented at several points in the Discussion.

Table 6. Sulfate concentration summary statistics from data sets cited in this report*.

Data Set		Data Source	Sampling Design	Quantile Sulfate Concentration (mg/L)			n	Percent with wild rice > 0 cover
				25%	50%	75%		
			Lakes					
1	Lakes	2011 Pilot Survey for the WRS	Reported wild rice sites.	0.4	0.8	3.0	30	90.0
1	Lakes with WR ring cover ≥ 1%	"	"	0.3	0.8	2.0	27	100.0
4	Lakes	2012-2013 WRS Field Survey	Reported wild rice (WR) sites plus potential WR sites with elevated sulfate	2.5	4.0	14.5	82	54.8
4	Lakes with WR ring cover ≥ 1%	"	"	0.3	2.5	7.7	42	100.0
4	Lakes with WR ring cover ≥ 2%	"	"	0.3	2.0	7.4	37	100.0
4	Lakes with WR ring cover ≥ 5%	"	"	0.3	3.6	7.4	30	100.0
4	Lakes with wild rice cover 1 to 5%	"	"	1.9	2.5	7.9	12	100.0
A	Lakes in the Northern Forests ecoregion of Minnesota	USEPA National Lakes Assessment (2012)	Probability-based for that ecoregion in Minnesota	< 1.0	1.0	2.5	50	Unknown
B	Lakes in the Eastern Temperate Forests ecoregion of Minnesota	"	Probability-based for that ecoregion in Minnesota	< 1.0	3.0	10.0	50	Unknown
C	Lakes in the Great Plains ecoregion of Minnesota	"	Probability-based for that ecoregion in Minnesota	6.0	80.0	248.0	50	Unknown
D	All Minnesota Lakes	"	Probability-based for the entire state of Minnesota	0.3	3.0	13.1	50	Unknown
E	Lakes	PCA and DNR databases for entire state of Minnesota.	Existing data, obtained for multiple reasons	1.0	3.2	9.8	3,230	Unknown
F	Lakes with reported WR	DNR wild rice site inventory database (DNR 2008)	Overlap between databases E and F.	1.0	1.8	3.6	520	~100.0

(Continued)

Table 6, cont.

Data Set		Data Source	Sampling Design	Quantile Sulfate Concentration (mg/L)			n	Percent with wild rice > 0 cover
				25%	50%	75%		
Streams and Rivers								
1	Streams	2011 Pilot Survey for the WRS	Reported wild rice sites	1.1	3.7	8.3	9	88.9
1	Streams with WR ring cover ≥ 1%	"	"	1.1	2.4	7.8	8	
4	Streams (including rivers)	2012-2013 WRS Field Survey	Reported WR sites plus potential WR sites with elevated sulfate	2.5	10.1	17.9	30	80.0
4	Streams with WR ring cover ≥ 1%	"	"	1.8	14.2	21.0	23	100.0
4	Streams with WR ring cover ≥ 2%	"	"	1.6	9.6	18.0	21	100.0
4	Streams with WR ring cover ≥ 5%	"	"	1.6	9.6	18.0	21	100.0
G	All Minnesota Streams and Rivers	USEPA National Rivers & Streams Assessment (2008)	Probability-based for the entire state of Minnesota	2.8	17.0	47.3	52	Unknown
H	Streams and Rivers	PCA and DNR databases for entire state of Minnesota	Existing data, obtained for multiple reasons	6.0	16.7	54.0	1,752	Unknown

*WR= wild rice. WRS is this wild rice study, which includes the 2012-2013 Field Survey. In 2011 a Pilot Survey of sites was carried out before the WRS was conducted. “WR ring cover” refers to the density of wild rice at the sample site, as the average in four 1-m diameter rings placed around the boat at the sampling site.

Mesocosm Experiment

Methods

The Mesocosm (outdoor container) Experiment was part of a multi-year study designed to understand the cumulative effects of elevated sulfate concentrations on wild rice growth. This experiment was initiated by Dr. Pastor in 2011 and conducted over the 2011-2012 field seasons under funding that was independent of the Wild Rice Sulfate Standard Study. After the independent funding ended, Dr. Pastor conducted the 2013 field season as part of the Study. Full details of the mesocosm experimental methods are described in Pastor (2013b). An overview follows.

Wild rice was grown from seed in large polyethylene containers containing sediments from natural wild rice beds. Concentrations of sulfate in the overlying water were maintained at desired experimental treatment levels, and wild rice was allowed to grow and self-propagate for three seasons (2011-2013). The mesocosms contained 12 cm of lake sediment over 10 cm of clean sand; the containers were then filled with well water. Each container was designated one of four sulfate treatment concentrations or as a control. Each of these treatments, nominally 50, 100, 150, and 300 mg/L sulfate, was replicated six times. The control, which only received sulfate from the well water, had a sulfate concentration of about 7 mg/L. Sulfate in the overlying water was monitored throughout the growing seasons and sulfate amendments were made as necessary to maintain sulfate concentrations at the designated treatment levels. Wild rice was allowed to grow and reseed each year. During the growing season, wild rice was thinned from the containers to achieve a plant density of 40 plants per square meter. In 2011 and 2012, five plants in each container were randomly chosen for measurement of multiple parameters throughout the growing season. At the end of the growing season, these five plants were extracted from the containers with roots intact for additional measurements. In addition, all plant material above the sediment from all containers was clipped and collected at the end of each growing season for biomass measurements. The collected plant material was returned to its respective container as plant litter.

Containers were sampled and analyzed for various parameters in the overlying water, sediment porewater, and sediment solid phases using methods described in *Field Study of Wild Rice Habitats* (Myrbo 2013). The biological endpoints of plant weight, plant length, seed weight, number of seeds, and number of viable seeds were measured at various times throughout the growing season, with most being measured at the end of the growing season. These endpoints were then compared between successive seasons within the same sulfate treatment group and also between treatments groups in the same growing season. Wild rice responses were also analyzed with the results from other biogeochemical parameters taken from the same container to determine any associations or covariances.

An unusual rate of wild rice mortality occurred in all the containers at the beginning of the 2013 growing season. The mortality may be related to an unusually cold spring and subsequent late start to the growing season. This experiment is proceeding in 2014 under separate funding, which will allow researchers to see if this mortality occurs again.

Because of the low numbers of plants in each mesocosm, experimental methods were adapted in 2013 to account for this change (see pages 8-10, Pastor 2013b). In addition, in 2013, field crews collected surface water, porewater, and sediment samples from the mesocosms using methods that were, to the extent possible, identical to those employed in the 2012-2013 Field Survey. The largest difference in methods was in the collection of porewater. In the Field Survey, porewater was extracted by inserting a Rhizon® into the surface of a 66-mm diameter (I.D.) core extracted from the bottom substrate at the site. Taking such large cores from the mesocosms during the growing season would have unduly disrupted the sediment. Instead of coring, porewater was obtained by inserting the Rhizon® directly into the undisturbed sediment within the mesocosms.

In 2013, stratigraphic porewater sampling was conducted in the mesocosms, parallel to the same sampling done in the Field Survey. This effort examined, in part, the potential influence wild rice roots have on sediment and porewater chemistry. Results of this effort included sediment and porewater chemistry characterized from the mesocosm containers. Additional information on this effort is reported in the section titled "Rooting zone depth profiles" and in Johnson (2013).

Results

A complete report of the Mesocosm Experiment results are found in Pastor (2013b). The following paragraphs summarize MPCA's analysis to date of these results.

Response of Wild Rice

Analysis of the mesocosm treatments between years showed a declining trend in some wild rice growth parameters. Seed weights in the control tanks remained relatively constant during the three years, but seed weights in the 300 mg SO_4 /L tanks decreased significantly compared to seeds from plants in the control tanks, by 12% in 2011, 21% in 2012, and 50% in 2013 (Figure 10, Table 7). The declines in seed weights were significant ($p < 0.055$) for 2011 and 2012, but less so for 2013 ($p = 0.122$). All ANOVA statistics and tables for the Mesocosm Experiment can be found in Pastor (2013b).

Although the total number of seeds produced did not change significantly across all sulfate concentrations, the proportion of viable seeds (those determined to be able to germinate and grow) from each plant remained relatively constant during all three years in the controls (55 – 60%) but decreased to 48% in 2011, 40% in 2012, and 31% in 2013 at the 300 mg SO_4/L treatment level. These decreases were statistically significant for all three years (Figure 10).

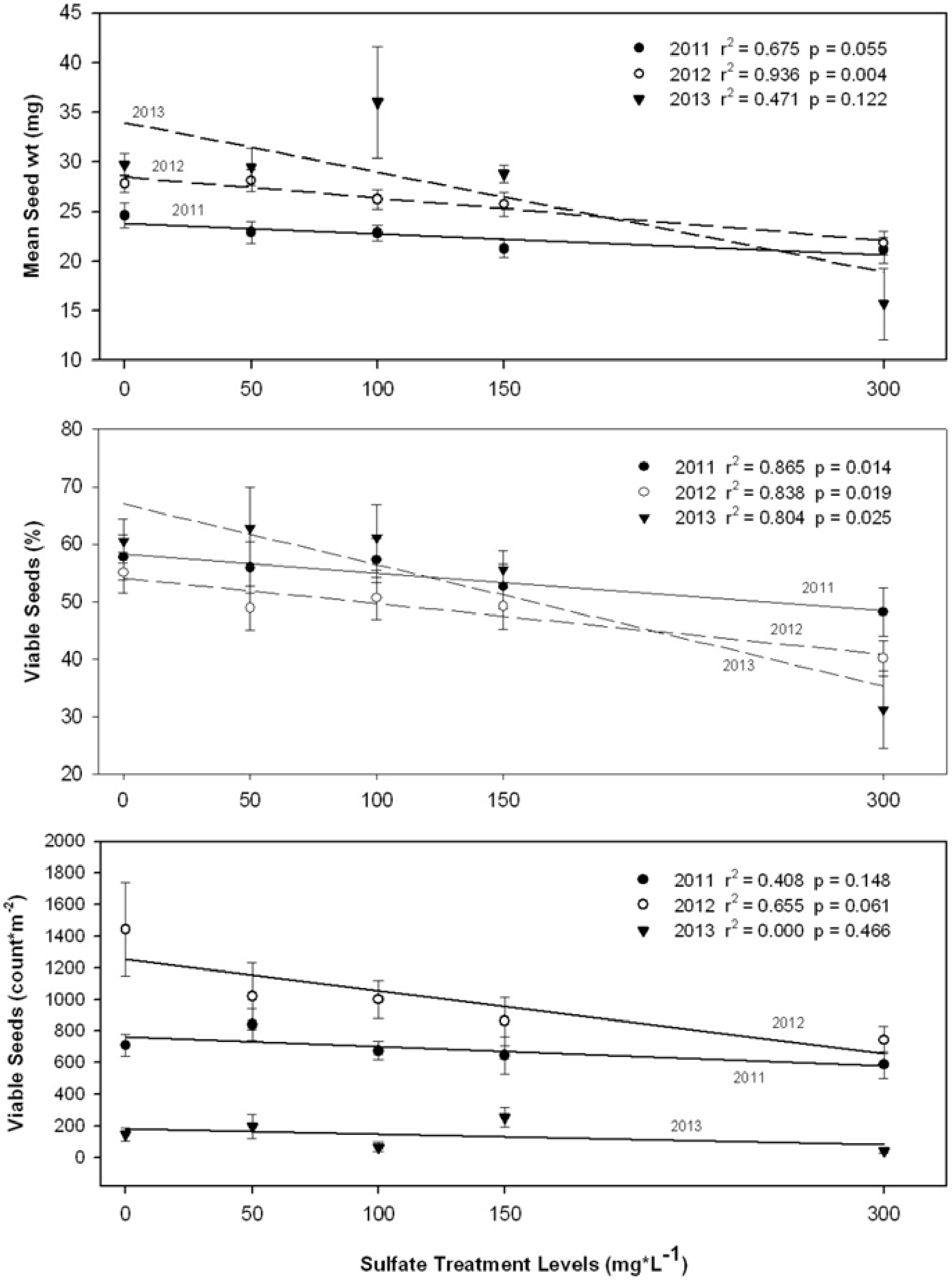


Figure 10. Decline in seed production associated with increased sulfate treatment levels. Treatment levels represent nominal concentrations targeted for the exposure tanks. Control tanks (labeled "0" on the x-axis) had an average sulfate concentration of 7 mg/L. From Pastor 2013b.

Table 7. Association of sulfate concentrations (in mg SO_4 /L) with wild rice properties. Values are means of samples from 6 tanks with standard errors in parentheses. From Pastor 2013b.

Measure	**Year**	**Sulfate Treatment Concentrations**				
		0 mg/L (Control)	50 mg/L	100 mg/L	150 mg/L	300 mg/L
Seed wt (mg)	2011	24.6 (1.24)	22.9 (1.1)	22.8 (0.8)	21.2 (0.9)	21.1 (1.26)
	2012	27.8 (0.9)	28.1 (1.1)	26.2 (1.0)	25.7 (1.2)	21.8 (1.2)
	2013	29.7 (1.1)	29.5 (1.9)	36.0(5.6)	28.8 (0.9)	15.7 (3.6)
Viable seeds (%)	2011	57.7 (3.9)	55.9 (4.5)	57.23.9)	52.6 (3.9)	48.2 (4.2)
	2012	55.1 (3.5)	48.9 (3.8)	50.6 (3.7)	49.2 (4.0)	40.1 (3.0)
	2013	60.6 (3.8)	62.8 (7.0)	61.2 (5.7)	55.6 (3.3)	31.2 (6.8)
Viable seeds (count * m^{-2})	2011	710.1 (69.2)	841.8 (101.6)	674.6 (58.3)	646.2 (116.0)	586.2 (84.1)
	2012	1442.5 (296.1)	1021.2 (210.6)	1001.0 (120.3)	863.0 (152.7)	744.1 (84.7)
	2013	147.1 (41.0)	196.6 (73.9)	67.0 (31.1)	255.5 (63.3)	40.5 (12.4)
Plant Biomass (g * m^{-2})	2011	47.38 (3.54)	55.32 (10.55)	49.99 (2.97)	50.65 (4.69)	34.89 (1.24)
	2012	117.25 (7.48)	138.24 (15.84)	127.49 (8.62)	102.42 (3.54)	95.64 (10.35)
	2013	15.21 (4.18)	16.12 (5.26)	7.10 (2.90)	36.09 (16.37)	5.61 (1.52)
Number of Seedlings	2012	183.0 (17.0)	163.0 (16.9)	148.7 (12.0)	144.3 (12.6)	120.8 (18.4)
	2013	162.8 (10.8)	177.8 (33.8)	140.5 (18.3)	142.5 (20.3)	60.3 (8.3)
Seedling Survival (#)	2012	28.2 (4.7)	27.5 (2.1)	26.0 (3.4)	24.8 (3.8)	18.2 (1.2)
	2013	16.5 (1.6)	12.0 (3.1)	5.2 (2.1)	11.8 (3.2)	3.0 (0.9)

In the springs of 2012 and 2013, the number of seedlings that emerged from the sediment decreased significantly (*p* < 0.01) with increased sulfate levels (Figure 11, Table 7). Though seedling survival in the 2013 season was poor in all treatments, the trend of less survival with increasing sulfate test concentration remained. In addition, the survival of those seedlings that remained after thinning declined with increased sulfate concentrations (Figure 11, Table 7).

Mortality of seedlings was especially high in late June and early July just prior to the floating leaf stage. A couple of reasons for this loss of seedlings could be disruption from the activity of thinning and the amount of thatch on the sediment surface. However, the number of surviving seedlings was not correlated with the number of seedlings removed by thinning (*p* > 0.10), which suggests that the magnitude of thinning itself had no effect on seedling survival. The number of surviving seedlings was also not correlated with the production of straw litter from 2012 (*p* > 0.10), so the decline in seedling survival does not appear to be an artifact of inhibition by thatch accumulation.

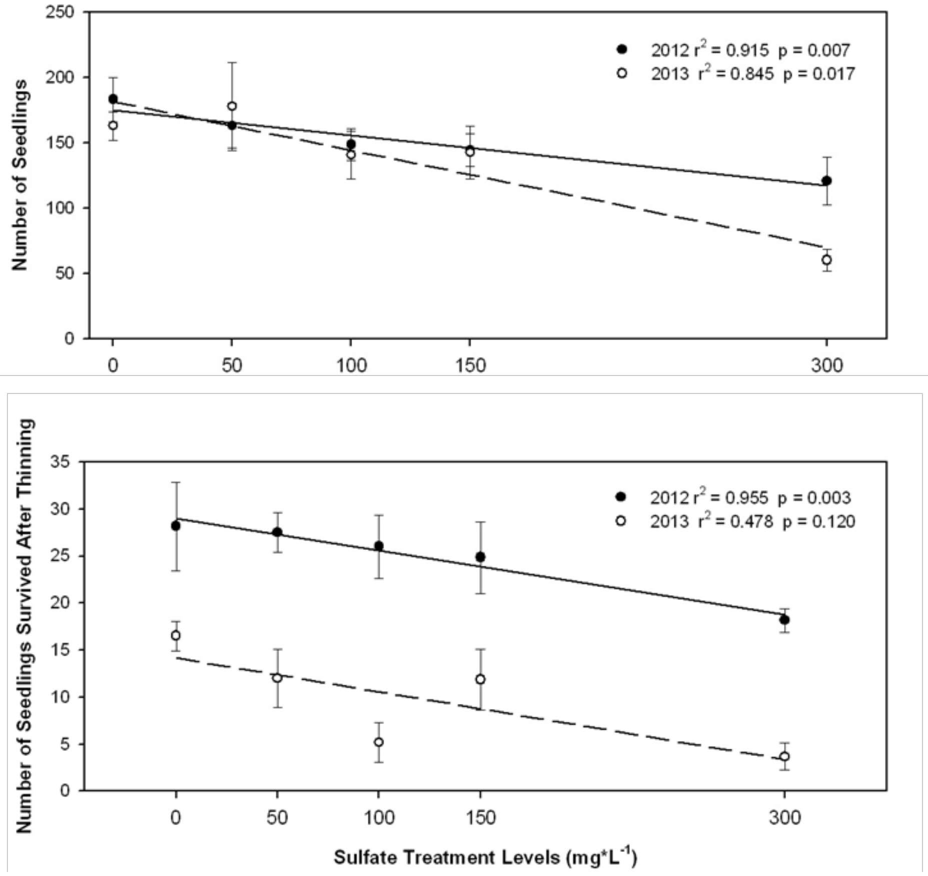


Figure 11. Declines in seedling survival with increased sulfate treatment level. Treatment levels represent nominal concentrations targeted for the exposure tanks. Control tanks (labeled "0" on the x-axis) had an average sulfate concentration of 7 mg/L. From Pastor 2013b.

Patterns in mesocosm surface water, porewater, and sediment chemistry

Figure 12 shows the response of porewater sulfide, porewater iron, and surface water alkalinity to a range of sulfate concentrations. Porewater sulfide was positively correlated with increasing sulfate concentrations (Spearman's correlation coefficient (*rho*)=0.60; *p*<0.005). Porewater iron was negatively correlated with increasing sulfate concentrations (*rho*=-0.48; *p*<0.02). Also, alkalinity increased in a similar fashion as a product of the conversion of sulfate to sulfide (Figure 12). Figure 13 depicts the similar dose-related increase in acid volatile sulfide (AVS) (*rho*=0.68; *p*<0.001). Apparently sufficient iron was available to precipitate much of the sulfide (as AVS) as it was produced, yielding an increase in AVS with increasing sulfate treatments concentrations. Table 8 shows the correlation coefficients of selected chemistry parameters analyzed from the mesocosms.

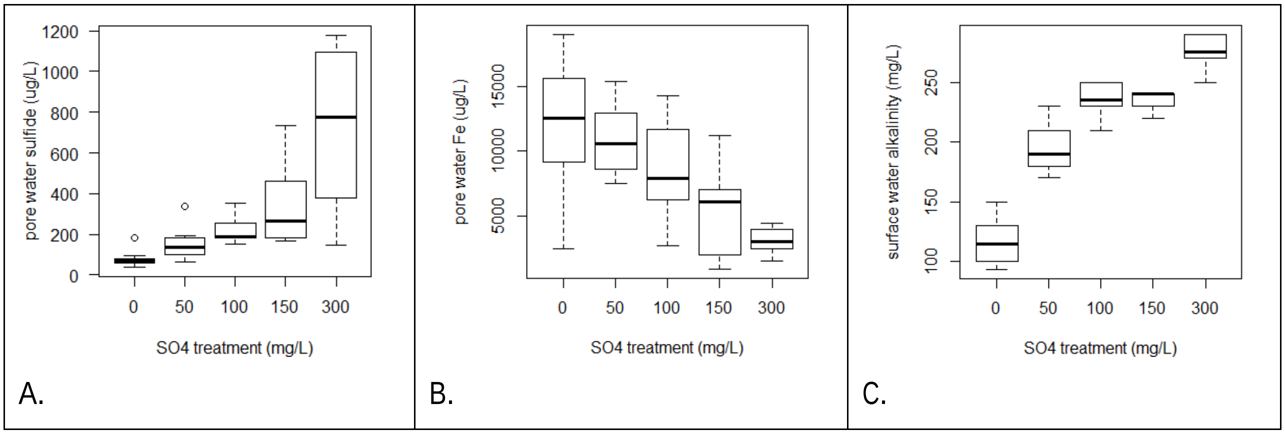


Figure 12. Response of (**A**) porewater sulfide, (**B**) porewater iron, and (**C**) surface water alkalinity to sulfate treatments in the Mesocosm Experiment, as assessed in the synoptic sampling carried out August 28, 2013, when all 30 mesocosms were sampled.

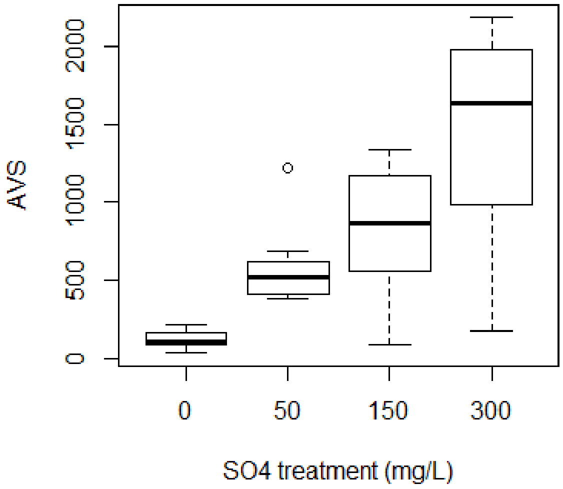


Figure 13. Effect of mesocosm sulfate treatments on acid volatile sulfide (AVS) concentrations (mg/kg). Mesocosms were sampled monthly May-October 2013 (n=24). Monthly data were pooled because the sample period was not significant (a mixed effects model was used to test seasonality; sample period was included as a categorical variable, and treatment was included as a random effect; *p*=0.21.

Table 8. Spearman correlation coefficients for selected parameters from the mesocosm sulfate treatment experiment (n=24). Pairs of parameters are more closely correlated as the correlation coefficient approaches one (1) or negative one (-1) for positive (red) or negative (green) correlations, respectively.

Mesocosm Sulfate-Addition Experiment (N=24) Spearman Correlation Coefficients (rho) P<0.05 (1-tailed) for |rho|>0.344	Nominal Sulfate Concentration	Porewater Calcium	Porewater Iron	Porewater Magnesium	Porewater Sulfide	Acid volatile sulfide (AVS)	Surface water potassium	Porewater zinc	Surface water sulfate	Surface water total phosphorus
Nominal Sulfate Concentration		-0.19	-0.50	-0.16	0.60	0.68	-0.32	0.41	0.87	0.41
Porewater Calcium	-0.19		0.28	0.99	-0.24	-0.11	-0.25	-0.29	-0.18	0.12
Porewater Iron	-0.50	0.28		0.28	-0.30	-0.35	-0.35	-0.10	-0.48	-0.28
Porewater Magnesium	-0.16	0.99	0.28		-0.24	-0.07	-0.30	-0.29	-0.14	0.13
Porewater Sulfide	0.60	-0.24	-0.30	-0.24		0.68	0.19	0.05	0.61	0.27
Acid volatile sulfide (AVS)	0.68	-0.11	-0.35	-0.07	0.68		0.08	0.28	0.68	0.25
Surface water potassium	-0.32	-0.25	-0.35	-0.30	0.19	0.08		-0.34	-0.04	-0.07
Porewater zinc	0.41	-0.29	-0.10	-0.29	0.05	0.28	-0.34		0.20	-0.14
Surface water sulfate	0.87	-0.18	-0.48	-0.14	0.61	0.68	-0.04	0.20		0.42
Surface water total phosphorus	0.41	0.12	-0.28	0.13	0.27	0.25	-0.07	-0.14	0.42	

Rooting Zone Depth Profiles

Integrated with both the Mesocosm Experiment and Field Survey were the collection and analysis of stratigraphic porewater samples using porewater equilibrators commonly referred to as “peepers.” This porewater sampling and analysis involved the collection of stratigraphic samples (1.5 cm intervals in the sediment) as follows:

1. Monthly sampling of the wild rice Mesocosm Experiment monthly throughout the summer of 2013; samples were analyzed for sulfate, sulfide, iron, pH and two trace metals (copper and zinc).
2. Sampling of two field sites (Second Creek and Sandy Lake) during 2013, in an attempt to characterize seasonal variability of porewater geochemistry in a field setting.

Details of these sampling efforts and the associated data can be found in Johnson (2013).

The depth profiles yielded detailed characterizations of porewater chemistry, both in time and stratigraphically. For instance, in the mesocosms, porewater sulfide increased as sulfate treatment concentrations increased, and over the summer. Porewater iron decreased as sulfate treatment concentrations increased (Figure 14).

Results can be used to characterize the effect of elevated sulfate concentrations on rooting zone geochemistry and to define seasonal differences in the rooting zone geochemistry from both mesocosm and field sites. The detailed information produced by this study component has not been explored in this Analysis.

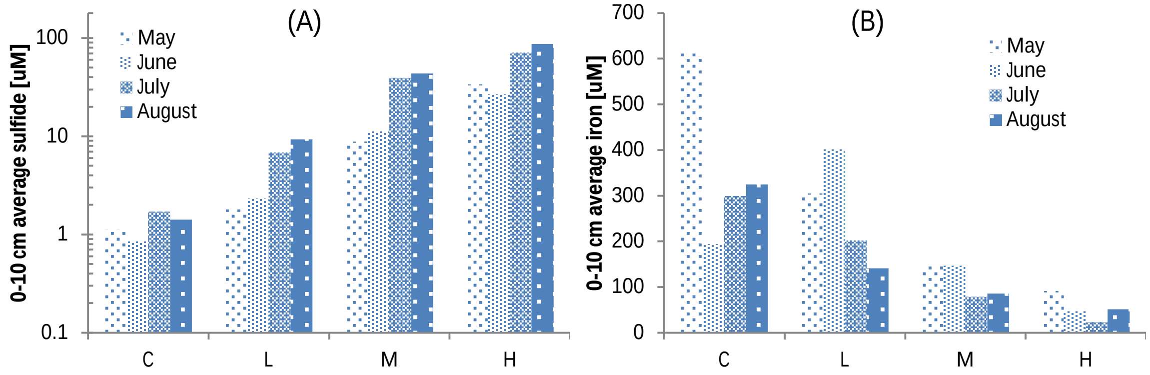


Figure 14. Seasonal average porewater concentrations sampled monthly using “peeper” porewater equilibrators in control (C) and mesocosm treatments (L=50 mg/L; M=150 mg/L; H=300 mg/L). **A.** 0-10 cm average porewater sulfide. **B.** 0-10 cm average porewater iron.

Sediment Incubation Laboratory Experiment

Methods

Sediment from two rivers with contrasting organic carbon content, Partridge River (high organic carbon) and the lower St. Louis River (low organic carbon) were incubated in the laboratory under warm and cold conditions to observe the temperature dependence of ion transport between overlying water and sediment porewater. Two identical sets of laboratory microcosms, incubated under warm and cold conditions, were subjected to a sulfate "loading" phase in which the overlying water was spiked with sodium sulfate to induce a concentration gradient between the overlying water and the sediment.

At the end of the sulfate loading phase, the sulfate gradient was reversed by replacing the overlying water with low-sulfate water, causing a flux of sulfate out of the sediment back into the overlying water. During this sulfate "recovery" phase, sodium bromide was spiked into the overlying water. Bromide, acting as an inert chemical tracer, provided a diffusional baseline with which to compare sulfate. Sulfate loading and recovery phase concentration changes were determined by closely monitoring the anion concentrations in the overlying waters. Non-destructive porewater samples were collected using Rhizon® soil moisture samplers to measure concentrations of sulfate, bromide, ferrous iron, pH and sulfide at discrete depths in the sediment during key times after changes in surface conditions. A complete report of this effort is found in DeRocher and Johnson (2013).

Results

Sulfate movement occurred 49% faster from the overlying waters into the sediments at 23°C when compared to 4.5°C; estimated rates of sulfate reduction at 4.5°C were an average of 40% of what was observed at 23° C. After seven weeks of recovery from the sulfate loading, porewater sulfate concentrations in the warm microcosms had dropped back to ambient levels, while slightly elevated sulfate levels were still noticed in the cold microcosms. More sulfate diffused into the warm sediments; sulfate diffusion into the cold sediments occurred much more slowly. Under experimental conditions, porewater ferrous iron concentrations were significantly elevated (78-606%) above *in situ* observations. The high iron concentrations in sediment porewater observed throughout this study inhibited a quantifiable increase in porewater sulfide content (Figures 9, 10, 13, and 14 in DeRocher and Johnson (2013).

This experiment was carried out as a preliminary investigation into how ambient temperature can affect the fate of elevated sulfate loading into Minnesota streams and rivers. A great deal was learned about how to conduct such an experiment, partly because of the problems encountered in conducting the experiment. For instance, it was planned to conduct the experiment with undisturbed 8-inch diameter sediment cores, but it was not possible to obtain such large cores through the ice cover when the project began in January 2013. Smaller-diameter cores would have been easier to obtain without disturbing the established stratigraphy, but would not have yielded a suitable volume of sediment to allow for stratigraphic porewater sampling during the incubation. Instead, sediment was dredged from the sites, homogenized, and dispensed into the microcosms. The microcosms were allowed to equilibrate for nine weeks prior to conducting the experiment, but it later became clear that steady state was not reestablished. Sediment from the Partridge River, which had a history of elevated sulfate discharge, released elevated sulfate into the overlying water during the nine weeks, which made it difficult to conduct and interpret the sulfate loading experiment.

The data that was obtained do illuminate important temperature-dependent processes that occur in the diffusion of sulfate into and out of the sediment, including conversion to sulfide and precipitation with iron. However, while it may be tempting to transfer some of the findings to untested sites, more investigation is likely needed prior to developing general findings or conclusions about the behavior of elevated sulfate in streams.

Discussion

This section presents the MPCA's integrative analysis of the Study results. The Discussion addresses the major hypotheses laid out in the wild rice study protocol (MPCA 2011).

As noted previously, the Study was designed to evaluate the primary hypothesis that sulfate—at concentrations encountered in Minnesota—is not directly toxic to wild rice, but that sulfate can affect the health of wild rice when it is converted into sulfide in the sediment in which wild rice germinates and roots. It has long been recognized that plants growing in saturated soils are potentially vulnerable to the elevated sulfide that anaerobic bacteria can produce (Koch et al. 1990, Jacq et al. 1991, Lamers 2013). The extent to which the multiple lines of evidence provided by the Study support this hypothesis is examined in this Discussion.

The Discussion also explores the notion that there is not a simple relationship between sulfate and sulfide. The rapid reaction of iron with sulfide is thought to greatly reduce the potential toxicity of sulfide to aquatic plants that are rooted in sediment (Van Der Welle et al. 2006). Sulfide can be precipitated—and detoxified—by metals other than iron, but such metals (silver, copper, lead, cadmium, zinc, nickel) are unlikely to be in sufficient abundance to precipitate appreciable amounts of sulfide in Minnesota waters in which most wild rice grows. None of the Field Survey sites had elevated concentrations of these metals. The Discussion proceeds methodically through the data that document the role of iron as a "mediator" in the sulfate-sulfide relationship.

Wild Rice in Relation to Sulfate, Sulfide, and Iron

The hydroponic exposure of wild rice to sulfate showed that sulfate is not directly toxic to wild rice at the concentrations likely encountered in waterbodies across Minnesota. A plot of wild rice cover against sulfate (Figure 1) shows that wild rice can be found at relatively high sulfate concentrations at some sites in Minnesota. When wild rice cover is shown as a function of both sulfate and porewater iron, it is evident that wild rice cover is generally diminished in high sulfate waters if porewater iron is low (Figure 15). Porewater iron is low at sites where the elevated sulfate has allowed the bacteria to produce enough sulfide to consume the available iron (see sections above). Wild rice is not abundant at sites where porewaters are high in sulfide and low in iron (Figure 16).

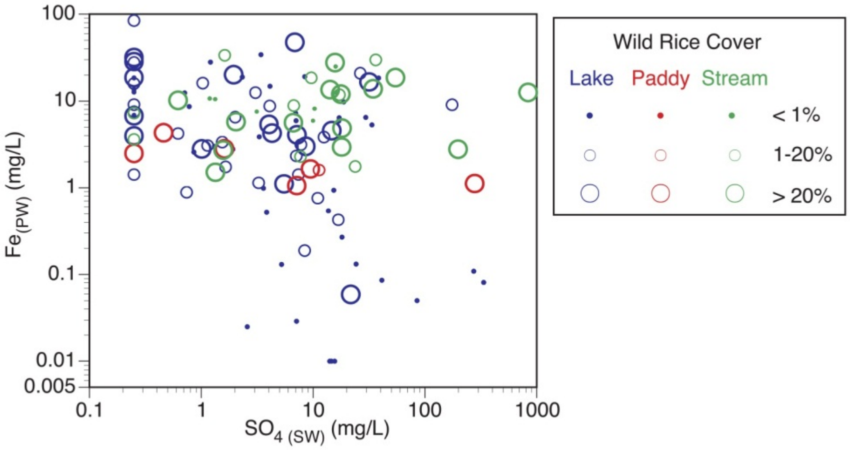


Figure 15. Wild rice percent cover in relation to sulfate in surface water and iron in porewater at the 119 Field Survey sites sampled 2012-2013. (Wild rice percent cover is the average value from four 1-meter rings at the sampling site.)

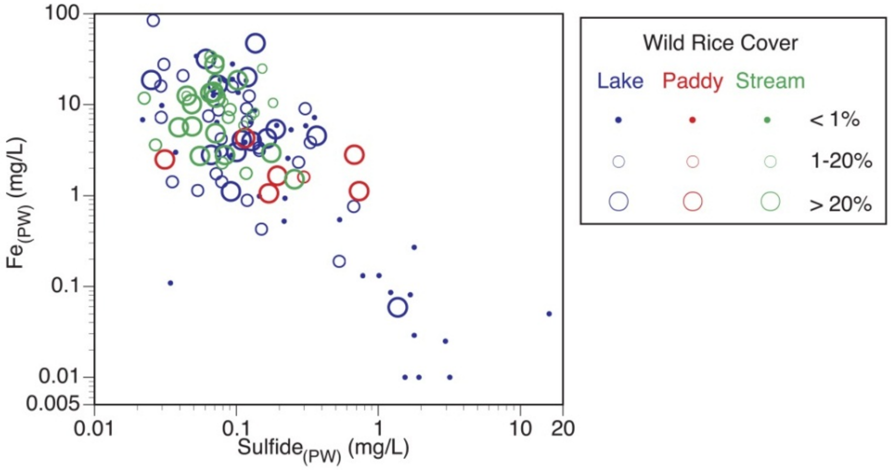


Figure 16. Wild rice percent cover in relation to sulfide and iron in porewater at the 119 Field Survey sites sampled 2012-2013. (Wild rice percent cover is the average value from four 1-meter rings at the sampling site.)

Hydroponic results compared to data from the Field Survey and Mesocosm Experiment

The three hydroponic sulfide tests demonstrated that sulfide concentrations ranging from 210 to 322 µg/L reduced the growth of wild rice seedlings by 20%, and concentrations ranging from 326 to 459 µg/L reduced the growth of seedlings by 50% (Figure 6, Table 4). These EC20 and EC50 estimates can be compared to results from the Field Survey and the Mesocosm Experiment.

Comparing the hydroponic results to the field data is complicated by the fact that sulfide is not the only environmental factor that affects the density and distribution of wild rice at sites across Minnesota. For instance, an abrupt water level fluctuation early in the growing season can virtually eliminate wild rice from a lake or stream for that growing season, when dense growth has been observed other years. To the greatest extent possible, field sites were chosen that could potentially support wild rice growth, while having a range of sulfate concentrations, but wild rice presence may also be affected by unknown and unmeasured variables aside from sulfate, sulfide, and iron.

One way to compare the hydroponic results to the distribution of wild rice in the field—while acknowledging that uncontrolled variables may also be affecting the distribution—is to arrange the sites by their porewater sulfide concentration and to examine whether the proportion of sites with wild rice changes in relation to the concentration of sulfide. Because multiple factors in addition to sulfide may affect the density of rice at a particular site (e.g., sediment disturbance by carp, grazing by geese, and nitrogen availability), it is desirable to use a minimum threshold to identify wild rice as being present at the sample site. After choosing a threshold for determining that wild rice is present at a site, the field data can be examined to determine if sulfide in porewater affects the proportion of sites, in a given sulfide range, that have wild rice present.

The presence of wild rice at a given sampling site can be defined a number of ways; however, there is little difference in the sulfide concentrations of the sites if the threshold is defined as exceeding 1%, 2%, or 5% (Table 6). During the 2012-2013 Field Survey, wild rice abundance was quantified with two methods, a visual assessment of percent cover in four 1-meter rings, and counting the stems in the same rings. The two metrics are highly correlated (Spearman's *rho* = 0.97), with a slope of 2.3 stems/% cover, and an intercept of 0.0. Therefore, estimates of 1%, 2%, and 5% cover correspond to about 2.3, 4.6, and 11.5 stems per square meter, respectively.

If the Field Survey data are consistent with the hydroponic results, it would be expected that at or above the hydroponics-derived EC20 in the sediment porewater there would be a decline in the proportion of sites where wild rice exceeded the minimum threshold for presence. A histogram (Figure 17) of the proportion of sites with at least 5 percent wild rice cover, shows a) that 69 to 80% of the sites had wild rice present above the presence threshold when porewater sulfide was less than 75 µg/L, and b) a more-or-less continuous decline in the percent of sites with wild rice present occurred above 75 µg/L.

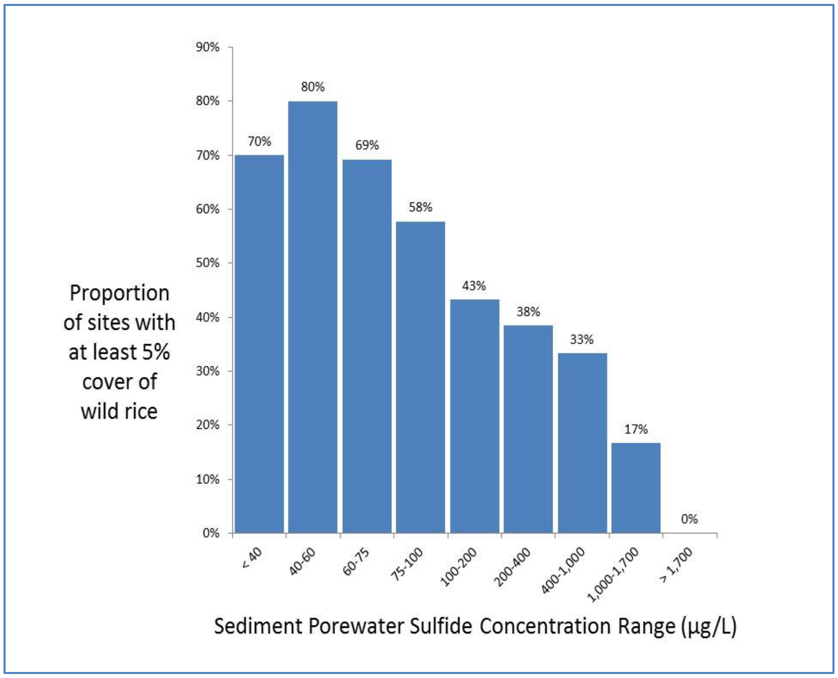


Figure 17. As sediment porewater sulfide concentrations increase at the Field Survey and Pilot Survey sites, there is a decreased proportion of sites where the wild rice exceeded 5 percent cover. (Based on 171 lake and stream samplings, where no site was sampled more than once a year, 2011-2013).

The Mesocosm Experiment results further support that sediment porewater sulfide concentrations above the sulfide EC20 (range of 210 to 322 µg/L) negatively affect the growth of wild rice. The declines in seed production were linearly related to the sulfate treatment concentrations (Figure 10), and it is also clear that the porewater sulfide is linearly related to the sulfate concentration in the overlying water (Figure 18). Although the regression is significant, it is interesting that the variance in the sulfide concentration increases with the sulfate concentration. This variance cannot be attributed to variability in the available iron in the sediment, since in this experiment the sediment is all from the same source. Therefore, there must be other, uncontrolled variables that are affecting the net concentration of sulfide in the porewater. Two likely uncontrolled variables are 1) the location of roots of wild rice that release oxygen, and 2) the abundance and species of benthic invertebrates that mix the sediment and introduce oxygen.

The median porewater sulfide concentrations in the control, 50, and 100 mg/L sulfate treatments were all below 200 µg/L (68, 138, and 190 µg/L, respectively). The 150 and 300 mg/L sulfate treatments yielded sulfide concentrations (median values of 265 and 778 µg/L, respectively) that would be predicted to impair wild rice growth based on the EC20 from the Hydroponic Experiments.

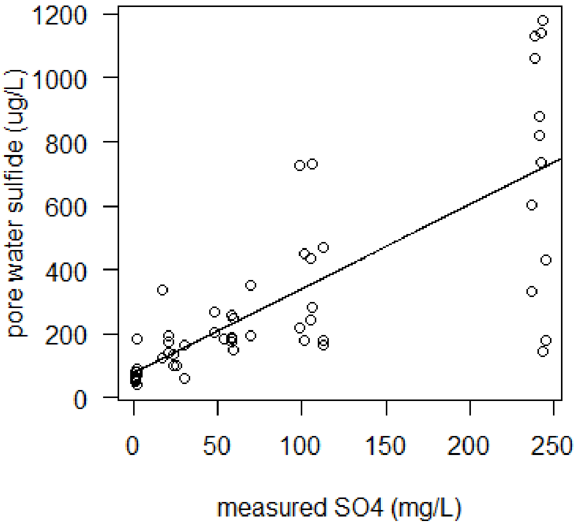


Figure 18. Porewater sulfide concentrations as a function of sulfate treatment concentrations sampled in the Mesocosm Experiment August 28, 2013. Two sulfide samples were taken from each of the six mesocosms at each of the five treatment levels (nominally 0, 50, 100, 150, and 300 mg sulfate/L). Sulfate samples were also taken from the overlying water at the same time. (r^2=0.57; p<0.0001).

Potential for wild rice seedling leaves to be exposed to sulfide

Recall that the hydroponic sulfide test method immersed photosynthesizing seedlings, with at least one leaf, in an anoxic solution containing variable amounts of sulfide. Although the effects of hydroponic exposure of the juvenile (3-day old) seedlings to elevated sulfide appear to be compatible with results from the Field Survey and the outdoor Mesocosm Experiment, it is uncertain if the leaves of seedlings would ever be exposed to sulfide in a natural setting. If, in natural settings, wild rice seeds germinate in sediment prior to sending a leaf upward out of a well-defined sediment-water interface into oxygenated water, then it might be argued that the hydroponic method mimicked an exposure that never occurs.

There is very little information in the scientific literature on the nature of the sediment-water interface in wild rice beds: is the interface always well-defined? Or is there sometimes a litter layer of decaying plants, with low oxygen and perhaps some sulfide, that the seedling must send its leaves through as it reaches towards sunlight? The only pertinent data from the Study that can be used to address this question was collected during the 2013 Field Survey, when oxygen was measured at the surface of each site and 2 cm above the sediment (the oxygen was measured by a sonde, which was allowed to rest vertically on the sediment, thereby positioning the oxygen sensor 2 cm above the sediment upon which the sonde was resting). Oxygen concentrations in the surface waters of the lake and stream sites were broadly similar (Table 9; interquartile range of sites sampled in 2013 was 6.5 to 9.6 mg/L in lake samples, and 6.8 to 8.9 mg/L in the stream samples). However, oxygen levels measured 2 cm above the sediment were significantly lower at the lake sites than at the stream sites; the median oxygen concentration just above the sediment in the lakes was only 1.9 mg/L, compared to 6.9 mg/L for the streams. The first quartile concentrations show an even bigger difference: oxygen in 25% of the lake sites was below 0.35 mg/L, compared to 5.3 mg/L for the stream sites.

It is not clear why oxygen levels just above the sediment are much greater at the stream sites than at the lake sites. Water flow rates were not measured as part of this study, but conceivably could be responsible for transporting waters with more oxygen either vertically or laterally to the stream sample site. Surficial groundwater could deliver more oxygen to stream sites than lake sites, but sulfide in sediment porewater was measurable at all sites except two lakes, which weakens that hypothesis since any oxygen delivered by groundwater would inhibit the reduction of sulfate to sulfide.

A more likely explanation is that the high flows that streams occasionally experience carry away plant litter, reducing the amount of organic matter available to support the bacterial activity that consumes oxygen. Evidence from the Study in support of this hypothesized link between organic matter and oxygen concentrations just above the sediment is that the concentration of total organic carbon in sediment at the sampling sites is higher in lakes (median = 13.9%) than in streams (median = 3.8%; Survey Set 4 data, Appendix D9). The smaller 2011 Pilot Survey also found that the sampled lake sites had more organic carbon than the stream sites (lake median = 12.2%; stream median = 6.8%; Survey Set 1 data, Appendix D10).

Given that oxygen just above the sediment was below 0.35 mg/L at 25% of the lake sites sampled in 2013, it is conceivable that the leaves of wild rice seedlings could be exposed to sulfide diffusing out of the sediment. Furthermore, the sediment-water interface may be poorly defined, potentially resulting in additional exposure of seedling leaves to sulfide (and which further complicates this question). Together this evidence suggests that it cannot be asserted with confidence that the experimental method used for the hydroponic sulfide seedling test mimicked an exposure that never occurs.

Table 9. Range and frequency distribution of oxygen and depth parameters measured 77 times at 38 different sites sampled during the 2013 Field Survey. During the 2013 Field Survey, oxygen was measured at each site both at the surface and at the bottom, about 2 cm above the water-sediment interface, which was sometimes indistinct due to residual plant litter. Of the 38 different sites that were sampled, 14 were sampled monthly. In all, 27 different lakes were sampled in 45 visits to lakes, and 11 different streams were sampled in 32 visits to streams.

	Lakes				**Streams**		
	Surface Oxygen (mg/L)	Bottom oxygen (mg/L)	Bottom Oxygen as % of Surface		Surface Oxygen (mg/L)	Bottom oxygen (mg/L)	Bottom Oxygen as % of Surface
Min=	1.59	0.11	1%		4.85	0.21	3%
10%=	3.60	0.17	2%		6.06	4.22	54%
25%=	6.53	0.35	7%		6.80	5.31	79%
50%=	8.30	1.85	23%		7.97	6.86	92%
75%=	9.57	6.89	83%		8.91	8.37	98%
90%=	10.53	8.39	95%		10.02	9.74	100%
Max=	16.13	9.47	111%		16.63	12.46	134%

Conversion of Sulfate to Sulfide

The scientific literature generally predicts that the bacterial community in an organic-rich saturated soil will proceed in a more-or-less orderly fashion through a sequence of electron acceptors, in the order predicted by energetics of: oxygen, nitrate, oxidized manganese, oxidized iron, sulfate, and carbon dioxide. Investigators have found that the different bacterial functional groups overlap with each other, but the general order holds fairly well. To help understand how bacterial activity may affect the substances dissolved in the sediment porewater, the Field Survey included measuring a wide range of chemical constituents in the porewater at the field sites. It is important to understand the porewater chemistry, as that is the medium by which it was hypothesized that sulfide is affecting wild rice.

The most energetically favorable pathway for bacteria is to respire oxygen, releasing water. When oxygen is depleted, nitrate is respired, producing nitrite or ammonia. In reviewing the Field Survey data nitrate was not elevated at any site in the Field Survey (Myrbo 2013; Appendix D). The next-most energetic electron acceptor available to bacteria, manganese, is not as abundant as iron in the Field Survey data set, having a median concentration of 434 µg/g, about a tenth of the median concentration of iron (4,917 µg/g). When oxidized manganese and oxidized iron are respired by bacteria, they are converted to forms that are water soluble. The porewater at the field sites had considerable concentrations of both (median concentrations of 1,620 and 5,510 µg/L, for manganese and iron, respectively, Appendix D1), which suggests that both manganese and iron were being respired by bacteria in the sediment.

Next in the progression of potential electron receptors for bacterial respiration is sulfate. Sulfate in the surface water can move into the organic sediment via diffusion, advection, or bioturbation. There bacteria can remove the sulfate from solution by converting the sulfate into sulfide, as occurred in the Mesocosm Experiment (Figure 12A). One potential limiting factor in this process is a lack of sufficient labile organic matter to supply the bacteria with the energy needed to convert sulfate to sulfide. However, there is no evidence from the field data that the bacterial community is generally limited by the availability of labile organic matter. Among the 119 sites sampled, there is no significant correlation between the organic content of the sediment and either porewater sulfide concentrations or porewater iron concentrations (Table 5). Dissolved organic carbon (DOC), which may be the most bioavailable form of organic matter, had a Spearman correlation coefficient of 0.00 with porewater sulfide, but a statistically significant correlation with porewater iron ($p<0.01$). However, it is not obvious that this correlation is the result of iron reduction being limited by bacterial consumption of organic matter. Rather, the correlation may be caused by the well-known chelation of iron by DOC. For instance, surface water iron and DOC were significantly correlated in the Pilot Survey ($p<0.02$, Appendix E5); DOC was not measured in the surface water in the 2012-2013 Field Survey.

Sulfide was detected at measurable levels in porewater at all but two of the 119 sites in the 2012-2013 Field Survey, indicating that the bacterial community normally respires all of the available electron acceptors that are energetically favored more than sulfate (oxygen, nitrate, manganese, and iron), so that sulfate is needed for bacterial respiration.

This assertion is further supported by evidence that in much of Minnesota, the concentration of sulfate in surface waters is lower than the concentrations supplied to surface water from precipitation and the watershed (note: plants also take up sulfate for nutritional purposes). For instance, the sulfate concentration of precipitation in north-central Minnesota averages a little over 0.7 mg/L (1998-2012 concentrations at the Camp Ripley and Marcell Forest National Atmospheric Deposition Program sites; http://nadp.sws.uiuc.edu/), yet 25% of lakes in Minnesota have sulfate concentrations less than 0.3 mg/L (USEPA 2012). The implication is that movement of sulfate from surface water into the sediment porewater and subsequent bacterial conversion to sulfide drives sulfate concentrations lower in these waters. In this way, the Study results support the hypothesis that sulfate in overlying water moves into the sediment porewater and is converted by bacteria into sulfide. Similarly, sulfate had to be added periodically to the treatment mesocosms to maintain target sulfate concentrations, indicating that sulfate was being converted to sulfide.

Role of Iron in Controlling Sulfide in Porewater

Because of the sequential order in which bacteria utilize electron acceptors, when bacteria start to respire sulfate, producing sulfide, there is iron already in solution (since the oxidized forms of iron have already been reduced by bacteria) that immediately produces an iron-sulfide precipitate, removing the sulfide from the dissolved phase of the porewater. However, if the production of sulfide ultimately exceeds the rate that available iron is supplied to bacteria, then sulfide concentrations can accumulate in the porewater.

The 2012-2013 Field Survey data can be examined to see if elevated sulfide was observed at any of the sites, and how sulfide and iron concentrations compare in the sediment porewater at the sites. In a portion of the sites sampled, iron was depleted, and sulfide was elevated (Figure 19). In the data set, porewater sulfide concentrations are only high when iron concentrations are low.

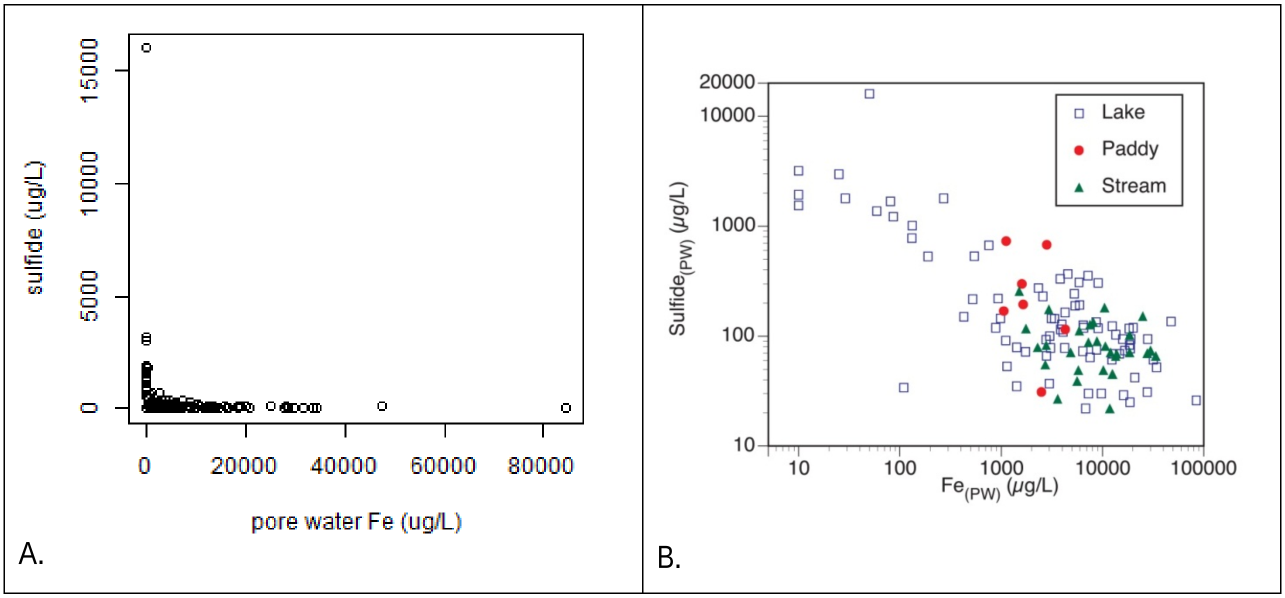


Figure 19. The relationship between porewater sulfide and porewater iron at the 119 sites sampled in the 2012-2013 Field Survey. **A.** Linear plot. **B.** Log-log plot, with lakes, streams, and cultivated paddies identified by symbol. (Spearman's *rho*=-0.56, p<0.001)

While this general pattern can be observed in the field data, it is not possible to use this relationship to predict the effects of an increase in the sulfate concentration of surface water at any given site because porewater iron is not a variable that is independent of the sulfate concentration. If sulfate concentrations increased, more sulfide might be produced, which would precipitate porewater iron to an unknown degree, changing the relationship.

Sulfide Consumption of Available Iron

Not all of the iron in the sediment is available to solubilize and interact with sulfide. Some iron is a constituent of minerals, and is essentially inert until the mineral breaks down through weathering, which is a long-term biogeochemical process.

The iron that is available to participate in redox reactions, including bacterial respiration, can be quantified through an acid extraction. The extraction techniques vary, but many researchers use a 0.5 or 1.0 N HCl extraction. The addition of HCl solubilizes many forms of iron, including oxy-hydroxides and iron-sulfide precipitates. The 2012-2013 Field Survey quantified the sulfide in the iron-sulfide precipitate through the addition of 1.0 N HCl, the standard method for quantifying acid volatile sulfide (AVS). The metals that are released in such a procedure are sometimes called simultaneously extracted metals (SEM), which in the Field Survey was mostly iron, since the other metals that are likely to precipitate sulfide (silver, copper, lead, cadmium, zinc, nickel) were not elevated at the field sites. In the Field Survey, to be consistent with the 2011 Pilot Survey, the iron and other metals were extracted with a 0.5 N HCl addition, a procedure that likely produces a similar extraction of iron as compared to the 1.0 N HCl method. The lower concentration of HCl was consciously chosen to ensure that iron was only extracted from the solid phase that would be available to participate in redox reactions (i.e. a stronger HCl concentration was avoided so as not to extract iron from minerals). The extracted iron can be termed “redox-available iron” or simply “available iron.”

The reservoir of available iron resides mainly in the solid phase of the sediment at the Field Survey sites, rather than in the porewater. The percent of the available iron in the solid phase can be calculated from the Field Survey data set. The median, or typical, site has 99.7% of the available iron in the top 10 cm of the sediment in a solid form, and only 0.3% is dissolved in the porewater (Appendix D1; porewater Fe/Sediment Fe) where it could immediately react with any newly produced sulfide. However, not all of the iron in the acid-extractable solid phase is potentially available to react with sulfide, since some of that iron was already bound with sulfide: ferric oxy-hydroxides are potentially available for bacteria to convert into soluble ferrous iron, but iron-sulfide compounds are essentially unavailable to remove more sulfide from solution.

The total potential reservoir of iron is estimated as the concentration of acid-extractable iron (Fe) in the sediment, whereas the portion that has been precipitated as an iron-sulfide can be estimated from the concentration of acid-volatile sulfide, AVS (since sulfide almost exclusively precipitates as an iron compound in Minnesota systems). Therefore, the progressive depletion of available iron by elevated sulfate in Minnesota waters is documented by a positive correlation between sulfate and AVS in the Field Survey (e.g. Figure 20). Because AVS, and other constituents of interest in sediment, are variably diluted by essentially inert mineral matter from the various watersheds, it is common in a field survey to normalize sediment variables to the concentration of organic carbon, removing the effect of the variable dilution. Thus, for the Field Survey data, AVS per unit total organic carbon (TOC) is plotted against sulfate, rather than simply AVS (Figure 20).

When the relationship between AVS and sulfate is explored based on the waterbody type of the field site (i.e. lake, stream or paddy), the paddy AVS-sulfate line is significantly below the lines for streams and lakes (Figure 20). This indicates that paddies have significantly less AVS for a given amount of sulfate in surface water, even though the reservoir of available iron is similar. It is not known if less sulfide is produced, or less sulfide is preserved at paddy sites. The rate of sulfide production may not have been lower at the paddy sites than the other field sites; it could be that the sulfide is not preserved as well at paddy sites compared to sites that are not actively managed as with paddies. The management of the cultivated paddies may be responsible for the difference, in that the paddies are dried every summer for harvest of the wild rice, and every few years alternative crops, such as potatoes or soybeans, are cultivated through rotation. These management practices may at least annually oxidize much of the sulfide, iron, and manganese, thereby decreasing the AVS and increasing the time before the bacterial community begins to produce sulfide after re-saturating the soil by flooding the paddy.

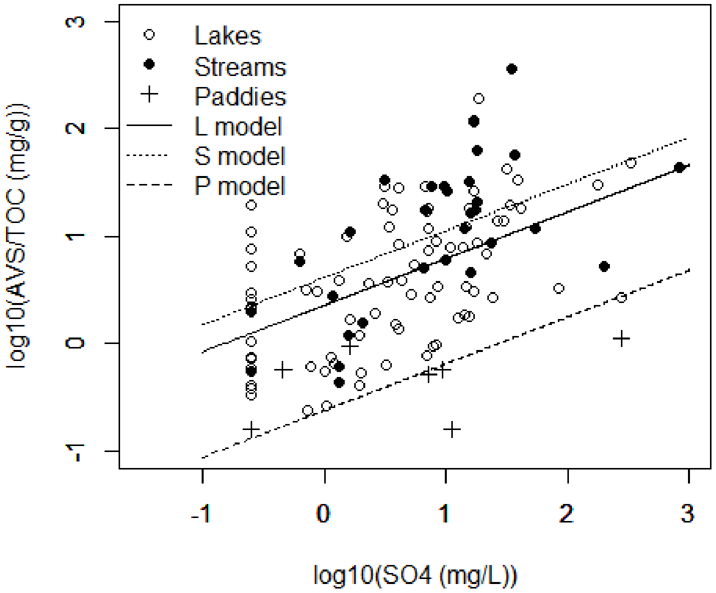


Figure 20. The relationship between AVS/TOC and sulfate in surface water in the 119 sites sampled 2012-2013. The linear fits to lake, stream, and paddy data have significantly different intercepts, but similar slopes. Equation: log10(AVS/TOC) = 0.35*(lake=TRUE) + 0.61*(stream=TRUE) -0.62*(paddy=TRUE) + 0.44*log10(SO4) (r^2=0.40; $p<0.001$). “L model” = linear fit of the lake site data, “S model” = linear fit of the stream site data, and “P model” = linear fit of the paddy site data. See Appendix F for a more complete presentation of the statistical analysis.

The positive correlations between sulfate and AVS in both the Mesocosm Experiment and the Field Survey (Figures 13 and 20, respectively) are evidence that iron is being consumed by sulfide that is produced from the sulfate. Another way of examining this phenomenon is to calculate the ratio between the total amount of iron and the portion of the iron that has been precipitated by sulfide—the Fe/AVS ratio. There is a progressive decrease in the Fe/AVS ratio as sulfate concentrations increase (Figure 21). The parallel nature of the regression lines through paddy, lake, and stream sites indicates that the biological and chemical reactions are fundamentally similar, but that there are differences in oxidation of AVS, or in the supply of iron to the systems. Lower values of Fe/AVS are indicative of a smaller reservoir of available iron to precipitate sulfide. In general, based on the Field Survey data it appears that for a given concentration of sulfate in the surface water, lakes are more likely to exhibit available iron depletion than streams, and cultivated paddies are less likely to exhibit available iron depletion than either of the natural systems.

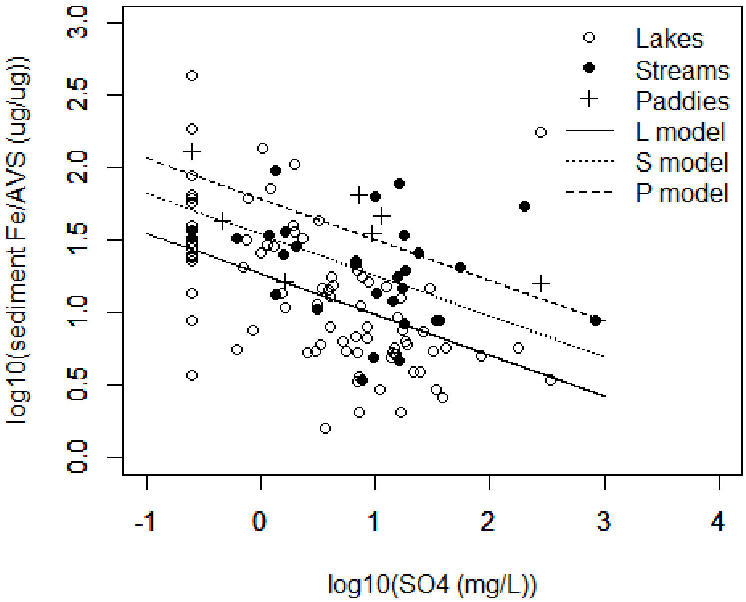


Figure 21. The relationship between the Fe/AVS ratio and sulfate in surface water in the 119 sites sampled 2012-2013. The linear fits to lake, stream, and paddy data have significantly different intercepts, but similar slopes. Equation: log10(sed Fe/AVS) = 1.27*(lake=TRUE) + 1.53*(stream=TRUE) + 1.78*(paddy=TRUE) - 0.28*log10(SO4). (r^2=0.28; p< 0.001). "L model" = linear fit of the lake site data, "S model" = linear fit of the stream site data, and "P model" = linear fit of the paddy site data. See Appendix F for a more complete presentation of the statistical analysis.

As sulfide is produced, and iron-sulfide precipitates are formed, the reservoir of iron that is potentially available to react with sulfide is diminished. The reservoir can potentially be replenished if the sediment dries and is exposed to oxygen, or if there is a source of iron, such as groundwater might supply.

In summary, as sulfide is produced by bacteria, it reacts immediately with any ferrous iron in the porewater and iron-sulfide precipitates form. The iron in the porewater is a small proportion of the reservoir of iron that can potentially react with sulfide, because about 99% of the available iron is in the solid phase. If sulfate becomes elevated and enough sulfide is produced to deplete iron faster than it is supplied, it likely takes multiple years for the available iron to become depleted to the point that little addition iron is available to go into solution. Therefore, the most useful measure of the reservoir of iron that can remove sulfide from solution is the available iron concentration in the sediment, rather than the iron concentration in the porewater.

Control of Porewater Sulfide by the Availability of Sulfate and Iron

As was noted above, sulfide is produced from sulfate by bacteria; however, the Field Survey data exhibit a significant ($p<0.001$) but weak correlation (Spearman's *rho*=0.37) between sulfate in surface water and sulfide in porewater (Figure 22). In the data set, when sulfate concentrations are low, sulfide concentrations are also low, consistent with the hypothesis that the bacterial community is limited by sulfate availability. But when sulfate concentrations are high, sulfide concentrations are variable and only sometimes also high.

The Field Survey data set indicates that sulfide concentrations are only high if available iron has been consumed and porewater iron is less than 1.0 mg/L (Figure 22). In a minority of systems, the pool of available iron is very low and can be consumed with relatively low production of sulfide. Note that low sulfide concentrations associated with high sulfate concentrations do not mean that sulfide has not been produced; in those cases, the sulfide is sequestered in the AVS (Figure 21). If iron availability were universally low, the sulfide-sulfate relationship would most likely follow the red dashed line in Figure 22, which is empirically fit.

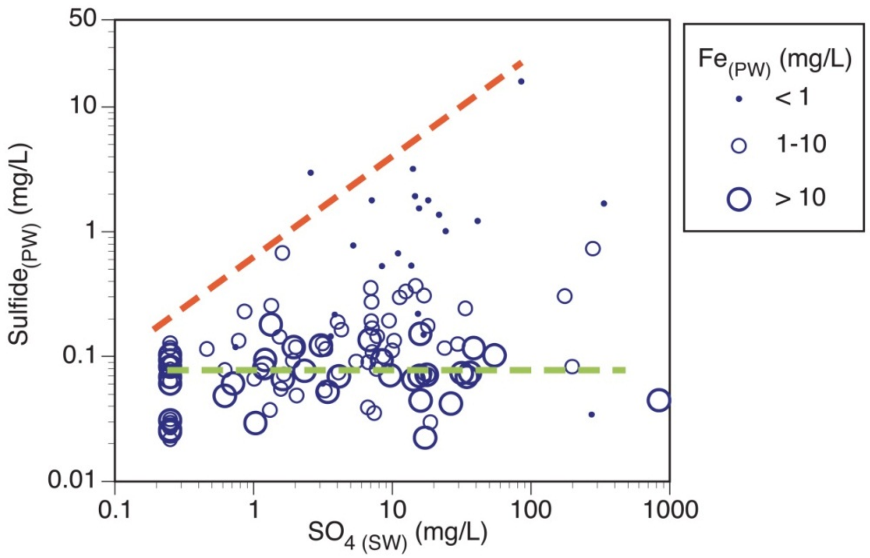


Figure 22. Relationship between sulfide in porewater and sulfate in surface water in the 119 sites sampled in the 2012-2013 Field Survey. The red dashed line indicates an empirically-fit maximum potential concentration of sulfide for a given concentration of sulfate.

There is a need to investigate the relationship between sulfate in surface water and sulfide in porewater, and, if possible, to account for the role of iron. Ultimately, the MPCA needs to translate the results of this Study to the protection of wild rice from elevated sulfide. One statistical tool that can be used to relate sulfate to sulfide is quantile regression.

Application of Quantile Regression to the Wild Rice Field Survey Data

If the understanding of the chemistry derived from the analysis of the Field Survey data is to be applied to other wild-rice-producing sites that were not part of the Field Survey data collection, a method must be developed. For those untested wild-rice-producing sites, if wild rice has been healthy for many years at a given sulfate concentration, then this is evidence that excessively high sulfide is not being produced. At those sites the sulfate and sulfide could be measured, but an important question cannot be addressed even if the sulfate and sulfide are known: “What will the porewater sulfide concentration be, and what will the effect on the wild rice be, if the sulfate concentration is increased by a given amount?” Quantile regression that incorporates information about the available iron may address that important question.

An objective way to develop a quantitative description of the red line in Figure 22 is the statistical technique of quantile regression (see Appendix C for an introduction to quantile regression). The Field Survey data include measurements of surface water sulfate and sediment porewater sulfide concentrations at each site. Quantile regression of the field data was used to analyze the wedge-shaped relationship between sulfate and sulfide (Figure 23). By fitting the outer limits of the wedge using upper quantiles (i.e., 75th, 80th, 85th, 90th, and 95th percentiles), the maximum potential relationship between sulfate and sulfide can be estimated. These quantile regressions further document the relationship between sulfate and sulfide (Figure 23).

It is more statistically robust to work with the 75th percentile, compared to higher percentiles, because as the number of data points progressively declines the uncertainty of the regressions increases significantly. However, because the role of iron is not controlled for in this quantile regression, there is a great deal of noise in the relationship. If the 75th percentile line was used to translate sulfate in the surface water to sulfide in the sediment porewater, sulfide concentrations at sites with high iron would be over-estimated, and sites with low iron would be under-estimated.

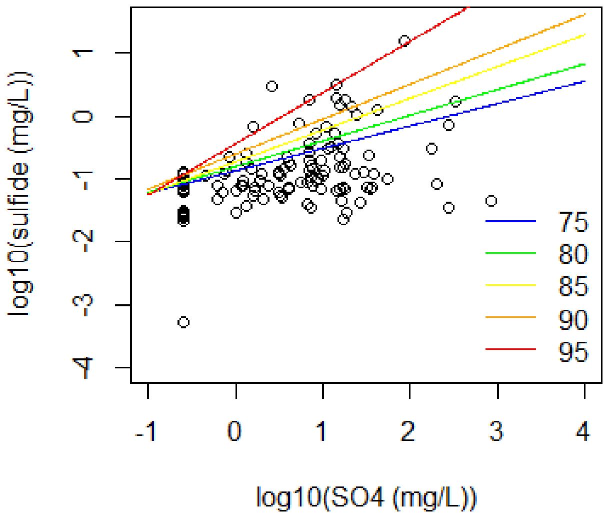


Figure 23. Quantile regression for surface water sulfate versus porewater sulfide for lakes and streams (2012-2013 survey data; n=119). Regression fits are semi-parametric quantile regressions.

It is possible to incorporate iron into the quantile regression by performing a multiple quantile regression (Figure 24). By incorporating information on the available iron in the solid phase of the sediment, 75th percentile lines can be drawn that relate sulfate to sulfide at a given concentration of iron. The iron concentrations in Figure 24 are derived from the Field Survey data; the concentrations correspond to the 5th percentile (1,609 µg/g dry sediment), 25th percentile (2,923 µg/g), 50th percentile (4,917 µg/g), 75th percentile (9,361 µg/g), and 95th percentile (20,646 µg/g) of iron at the sites. Note that the position of the 50th percentile line (the median concentration of iron) corresponds to the 75th percentile line in Figure 23, which makes sense because Figure 23 did not account for the iron content of the sediment, and therefore simply plotted the median value.

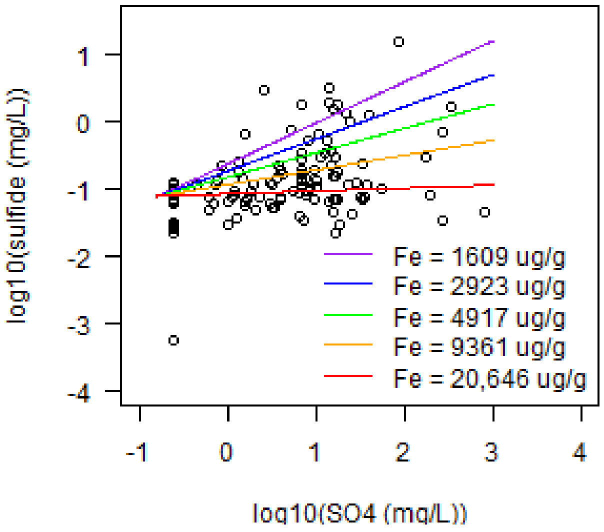


Figure 24. Multiple quantile regression, incorporating the concentration of available iron in the sediment (2012-2013 survey data; n=119). Each line corresponds to the 75th percentile of the data for that concentration of iron. See Appendix G for a more complete presentation of the statistical analysis.

In summary, multiple quantile regression, by relating both sulfate and iron to sulfide in porewater, offers a method to predict the potential production of sulfide at a site without over-estimating sulfide concentrations at high iron sites, or under-estimating sulfide concentrations at sites low in iron.

Prediction of Sulfate and Iron at Wild Rice Sites

It would be useful if surface water sulfate and available iron in sediment could be predicted from geographic patterns of sulfur and iron in soils (Figures 3 and 25A, respectively). Surface water sulfate is not difficult to measure, but the important measure of iron, the acid-extractable "available" iron in the sediment, requires a sediment core and a multi-step analytical procedure. The potential for prediction was assessed by contouring available soil and groundwater data and predicting concentrations at the 119 Field Survey sites. The predicted values were then compared to the measured values using the non-parametric Spearman Ranked Correlation to evaluate the degree of agreement between the two numbers (predicted sulfur or iron concentrations based on contour data, compared to measured surface water sulfate and iron concentrations in porewater and sediment).

Surface water sulfate at the 119 field survey sites is not significantly correlated with the sulfur content of soil, measured either in the surface soil horizon or the soil parent material (Table 10). The lack of predictability of surface water sulfate from soil sulfur concentrations alone suggests that other factors, such as Minnesota's climate gradient (Figure 4) are involved.

The United States Geological Survey (USGS) measure of iron in soil and sediment (Figure 25A), which is of total iron rather than available iron, is not predictive of the iron metrics used in this study—the Spearman correlations were not significant (Table 10). The significant correlation between Field Survey iron and the well water is puzzling, since it is negative (Table 10, Figure 25B). One would not expect a very good correlation with well water, since the wells are often deeply cased into bedrock. If groundwater is the source of iron in sediment, it would be shallow groundwater. An effort to correlate sediment iron with iron in wells that draw from surficial quaternary deposits, which are much less numerous than other wells, produced non-significant correlations (Table 10). If groundwater is an important source of iron to sediment in lakes or streams, it probably is a local phenomenon that is not captured very well by the iron content of soil or drinking water wells.

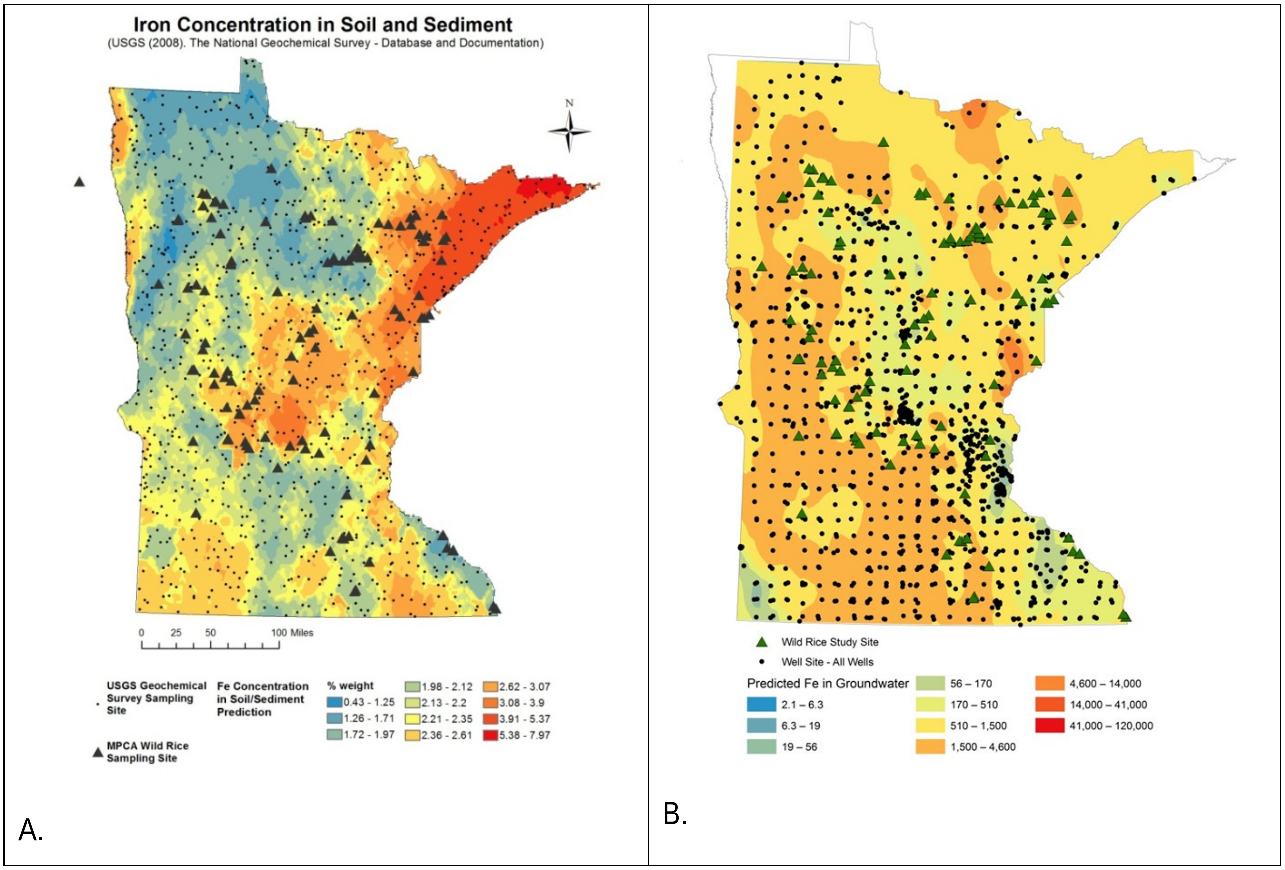


Figure 25. A. Iron concentration in soil and stream sediment (USGS 2008). B. Iron concentration in well water (from MPCA EQuIS database).

The frequency distribution of iron in sediment

The representativeness of the Field Survey data for the other variable that appears to be controlling porewater sulfide, namely iron in the sediment, is much more difficult to evaluate. The Study has compiled the only survey of iron in the sediment of Minnesota lakes and streams of which MPCA is aware. The USGS has compiled iron data for soil and stream sediments across the United States, including Minnesota (USGS 2013). Unfortunately, the USGS measured total iron, which MPCA's analysis has found is not predictive of the iron available to precipitate sulfide (based on the available iron metric used in the MPCA Study).

If there is a bias in the Field Survey sites in the frequency distribution of iron data, it might be toward sites with relatively higher iron concentrations, especially stream sites. The reasoning behind this thought is that the field crews were sent to some stream sites with elevated sulfate where wild rice had been reported. The analysis reported here suggests that there was sufficient available iron at these sites to keep sulfide low enough for wild rice growth. Any bias in iron would be less for lakes, in that field crews were sent to suspected high-sulfate lakes without regard for the presence of wild rice; the only criterion was that the water body must support rooted macrophytes of some kind, indicating that turbidity or water level was not excluding rooted macrophytes.

Table 10. Spearman rank correlations (negative or positive) and associate *p* levels (2-tailed, except for the a priori hypotheses, indicated by #, that wild rice is negatively correlated to sulfate and sulfide is correlated to sulfate (from correlation coefficients in Appendix E).

		2012-2013 Survey					**2011 Pilot Survey**		
Parameter	**Parameter**	**All Sites (n=119)**	**Lakes (n=82)**	**Streams (n=30)**	**Paddies (n=7)**		**All Sites (n-39)***	**Lakes (n=30)***	**Streams (n=9)***
Wild rice % cover in ring	Porewater Sulfide	- 0.005#	- 0.025#	- 0.025#	N.S.		N.S.	- 0.05#	N.S.
Wild rice % cover in ring	Porewater K	- 0.001	- 0.001	N.S.	N.S.			N.S.	
Wild rice % cover in ring	Porewater NH4	- 0.002	N.S.	- 0.001	N.S.			N.S.	
Wild rice % cover in ring	Surface water SO4	N.S.	- 0.01	N.S.	N.S.		- 0.025#	- 0.025#	- 0.0025
Porewater Sulfide	Porewater Fe	- 0.001	- 0.001	N.S.				- 0.005	
Porewater Sulfide	Porewater K	+ 0.001	+ 0.005	N.S.	+ 0.01			+ 0.005	
Porewater Sulfide	Porewater NH4	+ 0.001	+ 0.001	N.S.	N.S.				
Porewater Sulfide	Porewater Silica	+ 0.001	+ 0.001	N.S.	N.S.				
Porewater Sulfide	Surface water SO4	+ 0.001	+ 0.001	N.S.	+ 0.05#		+ 0.05#	+ 0.01	N.S.
Porewater Sulfide	Porewater DOC	N.S.	N.S.	N.S.	N.S.			N.S.	
Surface sulfate	Predicted S: top 5 cm soil	N.S.	N.S.	N.S.	N.S.				
Surface sulfate	Predicted S: A horizon soil	N.S.	N.S.	N.S.	N.S.				
Surface sulfate	Predicted S: C horizon soil	N.S.	N.S.	N.S.	N.S.				
Porewater Fe	Porewater Sulfide	- 0.001	- 0.001	N.S.	N.S.			- 0.001	
Porewater Fe	Sediment Fe	+ 0.001	+ 0.001	+ 0.01	N.S.			+ 0.001	
Porewater Fe	Surface water Fe	+ 0.001	+ 0.005	+ 0.01	N.S.			+ 0.005	
Porewater Fe	Porewater NH4	- 0.01	- 0.05	N.S.	N.S.				
Porewater Fe	Predicted Fe in soil	N.S.	N.S.	N.S.	N.S.				
Porewater Fe	Predicted Fe in aquifer	N.S.	N.S.	N.S.	N.S.				
Sediment Fe	Predicted Fe in soil	N.S.	N.S.	N.S.	N.S.				
Sediment Fe	Predicted Fe in well water	-0.001	-0.005	N.S.	N.S.				
Porewater Fe	Porewater DOC	+ 0.02	+ 0.02	+ 0.02	N.S.			N.S.	
Porewater Fe	Surface water SO4	- 0.02	- 0.002	N.S.	N.S.			N.S.	

*The 2011 Pilot Survey analyses of porewater initially only included pH and sulfide. Additional porewater parameters were added to the analytical suite part way through the survey, so that the complete suite is available for only 18 sites, all of them lakes. The *p* levels are adjusted appropriately.

Synthesis: How Sulfate, Sulfide, and Iron Interact to Affect Wild Rice

The Hydroponic Experiments revealed that elevated sulfide has a negative effect on the growth of wild rice above EC20 concentration estimates in the range of 210-322 µg/L (Table 4), or about 10 micromoles per liter. The response of wild rice estimated from the Field Survey data and Mesocosm Experiment are consistent with the hydroponic results. In their review of the toxicity of sulfide to plants that grow in saturated soils, Lamers et al. (2013) found that in general, freshwater plants are more sensitive than marine plants, and that some species of freshwater plants, such as white rice, experience sulfide toxicity at sulfide concentrations as low as 10 micromoles per liter. In other words, it is not surprising or inconsistent with the scientific literature that sulfide was found to be toxic to wild rice at or above 10 micromoles per liter (320 µg/L).

The conversion of sulfate to sulfide is well documented in the scientific literature as a potential hazard for plants rooted in saturated soils (Jacq et al. 1991; Koch et al. 1990; Lamers et al. 2013). The basic scientific questions to be addressed here concern wild rice in general, and specifically sites where wild rice grows in Minnesota:

a) what concentrations of sulfide are deleterious to wild rice growth;
b) to what degree is sulfate converted into sulfide;
c) what controls the accumulation of sulfide in the porewater; and
d) under what conditions does sulfide accumulate to concentrations that are deleterious to wild rice growth?

The Study results reported here are sufficient to postulate a conceptual model that describes how and under what circumstances sulfate negatively affects wild rice growth in Minnesota.

Sulfate in surface water penetrates into the anoxic, saturated, soils where wild rice grows and bacteria convert sulfate to sulfide. Sulfide was detected at measurable levels in the sediment porewater at all but two sites in the 2012-2013 Field Survey of 119 sites, indicating that the bacterial community normally respires all of the available electron acceptors that are energetically favored more than sulfate (oxygen, nitrate, manganese, and iron), so that sulfate is utilized for bacterial respiration. Respiration of sulfate converts it into sulfide, removing sulfate from solution. The sulfide that is produced in the water-saturated soils and sediments can have a variety of fates, but the particular fate largely depends on whether there is a pool of dissolved iron in the porewater where sulfide is produced. At many sites, prior to producing sulfide, the bacterial community has already utilized iron for respiration (because iron is energetically favored over sulfate), which converts ferric iron to ferrous iron—the water-soluble form that can react with sulfide. So, unless the reservoir of available iron in the sediment was low, or the rate that sulfide is produced has outpaced the rate that new iron is supplied (from groundwater or surface water), newly produced sulfide immediately reacts with iron and precipitates, removing the sulfide from solution and from potential harm to wild rice.

However, if dissolved ferrous iron is not available in the porewater, as bacteria produce sulfide the concentration of sulfide can build up in the porewater in which the wild rice is rooted. Some of that sulfide can diffuse into the overlying water, where it may encounter oxygen and oxidize back to sulfate. In addition, the chemical form of the sulfide is controlled by the pH of the porewater. At the median pH of the Study sites, 6.8, more than half of the sulfide in the porewater is in the form of hydrogen sulfide, which is a dissolved gas. Some of this gaseous sulfide may be carried along with other gases (such as carbon dioxide and methane), to the overlying water or atmosphere.

Plants that normally root in saturated soils, such as wild rice, have adaptations to deal with the anoxic environment and associated chemistry of the porewater. These plants have special channels called aerenchyma that are a pathway for the exchange of gases between the roots and the atmosphere (so long as wild rice has leaves floating or emerging from the water surface). Aerenchyma allows oxygen to diffuse into the roots of wild rice, which is thought to serve two purposes: 1) the oxygen allows the plant tissue living in the anoxic sediment to respire oxygen, thereby avoiding the disadvantages of anaerobic respiration (which is less efficient and produces potentially toxic metabolites such as ethanol), and 2) some of the oxygen leaks out of the roots into the surrounding porewater, which may oxidize potentially toxic chemicals that accumulated because of the anoxic conditions, such as sulfide, iron, or manganese.

Plant roots may develop a coating of a brown crust, which is the insoluble ferric hydroxide precipitate that forms when ferrous iron reacts with oxygen. The scientific literature is equivocal as to whether this crust, or plaque, is a) a by-product of an adaptation to oxidize sulfide, b) an adaptation to precipitate iron, to avoid excess iron uptake by the roots or, c) as Ernst (1990) proposed, an adaptation to build up an iron barrier during the iron respiration phase of the bacterial community that later intercepts and precipitates sulfide, decreasing the exposure of the plant to sulfide. The iron plaque later intercepts sulfide that begins to accumulate to potentially toxic levels after the bacteria community starts producing sulfide after having depleted available iron. The data set collected in this Study tend to favor Ernst's hypothesis, given that wild rice abundance is not diminished when iron concentrations are high in the porewater, but is diminished when sulfide concentrations are high and iron is low.

As sulfide is produced, and iron-sulfide precipitates are formed, the reservoir of iron that is potentially available to react with sulfide is diminished. The reservoir mainly resides in the solid phase of the sediment, given that in the median case of the Field Survey, 99.7% of the iron in the top 10 cm of the sediment is in a solid form, and only 0.3% is dissolved in the porewater, where it can immediately react with any newly produced sulfide. But not all of the iron in the acid-extractable solid phase is potentially available to react with sulfide: the ferric oxy-hydroxides are potentially available for bacteria to convert into soluble ferrous iron, but the iron-sulfide compounds are essentially unavailable to remove more sulfide from solution.

The total potential reservoir of iron is estimated as the concentration of acid-extractable iron (Fe) in the sediment, whereas the portion that has been precipitated as an iron-sulfide can be estimated by the concentration of acid-volatile sulfide, AVS (since sulfide almost exclusively precipitates as an iron compound in Minnesota systems). Therefore, the progressive depletion of iron reserves by elevated sulfate in Minnesota waters is documented by a positive correlation between sulfate and AVS (e.g. Figure 20), and a progressive decline in the Fe/AVS ratio as sulfate increases (Figure 21). High values of Fe/AVS are indicative of systems that have a large reservoir of iron to keep sulfide from accumulating in porewater, and low values of Fe/AVS are indicative of systems where the production of sulfide is outpacing the rate that iron is supplied.

The concentration of iron in the solid phase is an indicator of the potential accumulation of sulfide in porewater, for a given amount of sulfate in the surface water. The existing sulfide, and any potential increase in sulfide, can be estimated based on the relationship illustrated in Figure 24, so long as surface water sulfate concentration and the iron concentration of the sediment solid phase are known. The concentration of iron in the porewater is much less useful as a predictive variable, in that it represents such a small fraction of the reservoir of iron and because porewater iron concentrations are not predictive of sulfide porewater levels, but rather are functions of how much sulfide has been produced.

In summary, the equation that produced the lines in Figure 24 can be employed to predict the potential maximum sulfide concentration that would be produced from a given concentration of sulfate in surface water, if the iron content of the sediment is known. That prediction, which could be accompanied by a measure of uncertainty, can be compared to sulfide levels of concern derived from the Hydroponic Experiments and observations from the Field Survey and Mesocosm Experiment. If there is concern that the available iron at the site has already been consumed, or titrated, by past production of sulfide, the Fe/AVS ratio can be examined. A high value of Fe/AVS would indicate that the site has the capacity to consume more sulfide, and that perhaps the supply of iron is keeping pace with the production of sulfide. A relatively low value of Fe/AVS would indicate that the iron supply is not keeping pace with the production of sulfide, and that increasing the sulfate concentration should be viewed with caution.

Contributors

Minnesota Pollution Control Agency

Eric Alms
Gerald Blaha
Will Bouchard
Patricia Engelking
Nancy Flandrick
Katrina Kessler
Shannon Lotthammer
Phil Monson
Shawn Nelson
Emily Peters
Bill Scruton
Summer Streets
Edward Swain
Mark Tomasek

University of Minnesota, Duluth

John Pastor
Brad Dewey

Nathan Johnson
Will DeRocher
Alexandra Dickhaus
Joseph Sternberg
Ryan Armstrong

University of Minnesota, Twin Cities

Amy Myrbo
Field work, coordination, sample analysis, and database management:
Cynthia Frickle, Jessica Heck, Aaron Lingwall, Jimmy Marty, Ailsa McCulloch, June Sayers, Sean Rogers, Chris Schodt, Val Stanley, and Amanda Yourd

St. Croix Watershed Research Station, Science Museum of Minnesota

Daniel R. Engstrom
Jill Coleman Wasik
Erin Mittag
Erin Mortenson
Joy Ramstack Hobbs

Literature Cited

Cade, B. S. and B. R. Noon. 2003. A gentle introduction to quantile regression for ecologists. Frontiers in Ecology 1(8):412-420

DeRocher, Will and Nathan W. Johnson. 2013. “Temperature Dependent Diffusion Rates of Sulfate in Aquatic Sediments” [submitted to] Minnesota Pollution Control Agency. Electronic file: Temperature_Dependent_Diffusion_Rates_of_Sulfate_in_Aquatic_Sediments_final.pdf found at: ftp://files.pca.state.mn.us/pub/tmp/wildRice/Sediment_Incubation_Experiments/

DNR. 2008. Natural Wild Rice in Minnesota. Minnesota Department of Natural Resources. http://files.dnr.state.mn.us/fish_wildlife/wildlife/shallowlakes/natural-wild-rice-in-minnesota.pdf

Ernst, W. H. O. 1990. Ecophysiology of plants in waterlogged and flooded environments. Aquatic botany 38:73-90.

Fort, Douglas J. 2013. Definitive Hydroponics-Based Wild Rice (Zizania palustris) Sulfate Toxicity Testing. Fort Environmental Laboratories, Inc. sponsored by Minnesota Chamber of Commerce.

Hobbs, H.C. and J. E. Goebel. 1982. Geologic Map of Minnesota, Quaternary Geology. Minnesota Geological Survey, Minneapolis.

Jacq, V. A., K. Prade, and J. C. G. Ottow. 1991. Iron sulphide accumulation in the rhizosphere of wetland rice (Oryza sativa L.) as the result of microbial activities. In: Developments in Geochemistry. Vol 6. Diversity of Environmental Biogeochemistry (Berthelin, J., Ed). Elsevier. pp. 453–468.

Johnson, Nathan W. 2013. “Response of Rooting Zone Geochemistry to Experimental Manipulation of Sulfate Levels in Wild Rice Mesocosms” [submitted to] Minnesota Pollution Control Agency. Electronic file: Sulfate_Manipulation_Rooting_Zone_Geochemistry_final.pdf, found at: ftp://files.pca.state.mn.us/pub/tmp/wildRice/Collection_and_Analysis_of_Rooting%20Zone_Depth_Profiles/

Koch, M. S., I. A. Mendelssohn, and K. L. McKee. 1990. Mechanism for the hydrogen sulfide-induced growth limitation in wetland macrophytes. Limnology and Oceanography. 35(2):399-408.

Lamers, L. P. M. G., et al. 2013. Sulfide as a soil phytotoxin - a review. Frontiers in Plant Science 4:1-14.

Moyle, John B. 1944. Wild rice in Minnesota. Journal of Wildlife Management. 8(3):177-184.

Moyle, John B. 1956. Relationships between the chemistry of Minnesota surface waters and wildlife management. Journal of Wildlife Management. 20(3):303-320.

MPCA. 2011. The Sulfate Standard to Protect Wild Rice. Study Protocol. Minnesota Pollution Control Agency. November 8, 2011. wq-s6-42b 33 pp. available at: http://www.pca.state.mn.us/u3uw4ya

MPCA. 2014. Wild Rice Sulfate Standard Study Preliminary Analysis. Minnesota Pollution Control Agency. March 2014. 22 pp. wq-s6-42w available at: http://www.pca.state.mn.us/ktqh1083

Myrbo, Amy. 2013. “Wild Rice Sulfate Standard Field Surveys 2011, 2012, 2013: Final Report” Electronic file: Myrbo_Final_Report_ on_2011_2012_2013_Field_Surveys_20131231.pdf, found at: ftp://files.pca.state.mn.us/pub/tmp/wildRice/2011_2012_2013_Field_Survey/

Pastor, John. 2013a. “Effects of Enhanced Sulfate And Sulfide Concentrations on Wild Rice Germination and Growth: Results from a Hydroponics Experiment” [presented to] Minnesota Pollution Control Agency. Electronic file: Pastor_Hydroponics_Experiment_Report.pdf, found at: ftp://files.pca.state.mn.us/pub/tmp/wildRice/Laboratory_Hydroponics_Experiments/

Pastor, John. 2013b. “Effects of Enhanced Sulfate Concentrations on Wild Rice Populations: Results from a Mesocosm Experiment” [presented to] Minnesota Pollution Control Agency. Electronic file: Pastor_Mesocosm_report.pdf, found at: ftp://files.pca.state.mn.us/pub/tmp/wildRice/Outdoor_Container_Experiments/

USEPA. 2008. National Rivers and Streams Assessment. United States Environmental Protection Agency. http://water.epa.gov/type/rsl/monitoring/riverssurvey/

USEPA. 2012. National Lakes Assessment. United States Environmental Protection Agency. http://water.epa.gov/type/lakes/lakessurvey_index.cfm

USGS. 2013. National Geochemical Survey database. http://tin.er.usgs.gov/geochem/

Van der Welle, M. E. W., M. Cuppens, L. P. M. Lamers, and J. G. M. Roelofs. 2006. Detoxifying toxicants: interactions between sulfide and iron toxicity in freshwater wetlands. Environmental Toxicology and Chemistry 25:1592-1597.

Appendix A. Sulfide Hydroponic Tests: Analysis of Variance

Results and model statistics for ANOVA, Dunnett's multiple comparison, and ANCOVA procedures performed using results of hydroponic sulfide toxicity tests.

Objective

To test whether the effects of sulfide Treatment 2 were significantly different from the Control on wild rice growth.

Data set

3 hydroponic tests (Range Finder, Definitive 1, Definitive 2)

- 3 sulfide treatments were used (Control, Treatment 1, Treatment 2)
- 2 sulfide treatments were excluded (Treatment 3, Treatment 4) because A) they were irrelevant to the question at hand and B) sulfide concentrations for these treatment levels differed greatly among the three tests.

Response variable

- Weight change (final-initial) in units of mg

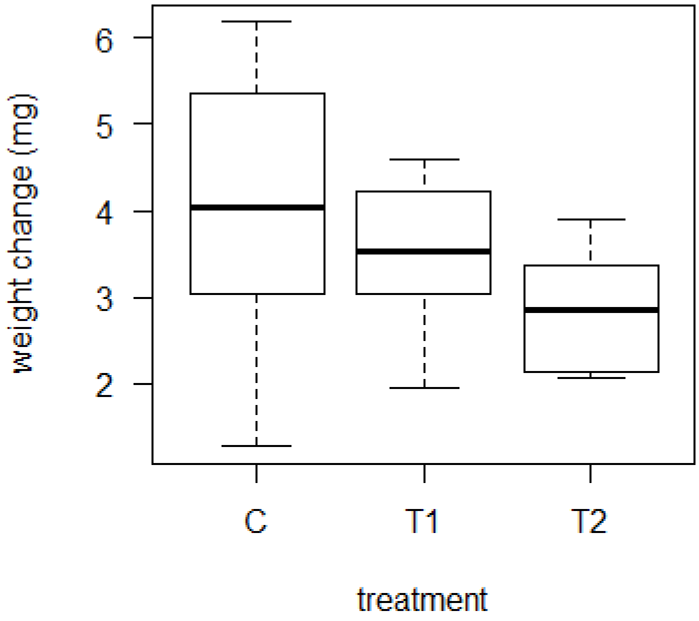
Analysis

Analysis of variance (ANOVA) was used to test the effect of sulfide treatment on wild rice weight change. Test (Range Finder, Definitive 1, Definitive 2) and treatment (Control, Treatment 1, Treatment 2) were both included as categorical explanatory variables. Dunnett's contrasts test was used to evaluate whether Treatment 2 was significantly different from the Control. It's important to note that sulfide concentrations at each treatment level were not exactly the same across tests or between replicates. Recognizing this, Analysis of covariance (ANCOVA) was used to test the overall effect of sulfide concentration on wild rice weight change. Mean initial sulfide concentration was included as a continuous explanatory variable and test (Range Finder, Definitive 1, Definitive 2) was included as a categorical explanatory variable.

Summary

The ANOVA and Dunnett's Contrast test show that wild rice weight gain was significantly lower in Treatment 2 compared to the Control. The ANCOVAs show that wild rice weight gain declined significantly as mean and mean initial sulfide concentrations increased.

Analysis of variance (ANOVA)
Y = weight change
X1 = treatment (3 factors: C, T1, T2)
X2 = test (3 factors: Range Finder, Definitive 1, Definitive 2)



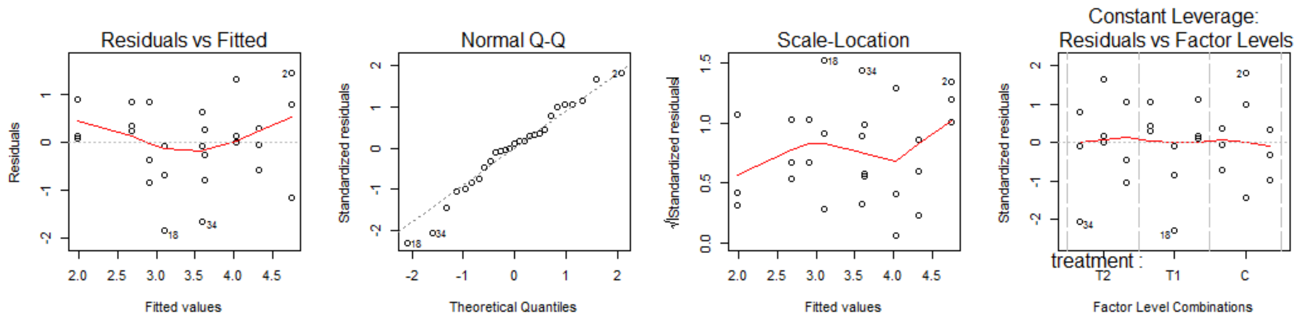
Minimal adequate model
lm(formula = weight_change_mg ~ treatment + test, data = dataC12)

Residuals:

Min	1Q	Median	3Q	Max
-1.83789	-0.47406	0.08178	0.49489	1.44656

Coefficients:				
	Estimate	Std. Error	t value	Pr(>|t|)
(Intercept)	4.0233	0.3810	10.560	4.44e-10 ***
treatmentT1	-0.4260	0.4174	-1.021	0.3185
treatmentT2	**-1.1197**	**0.4174**	**-2.683**	**0.0136 ***
testdefinitive2	-0.9144	0.4174	-2.191	0.0393 *
testrangefinder	0.7191	0.4174	1.723	0.0989

Residual standard error: 0.8854 on 22 degrees of freedom
Multiple r-squared: 0.5081,   Adjusted r-squared: 0.4187
F-statistic: 5.682 on 4 and 22 DF, *p*-value: 0.002687

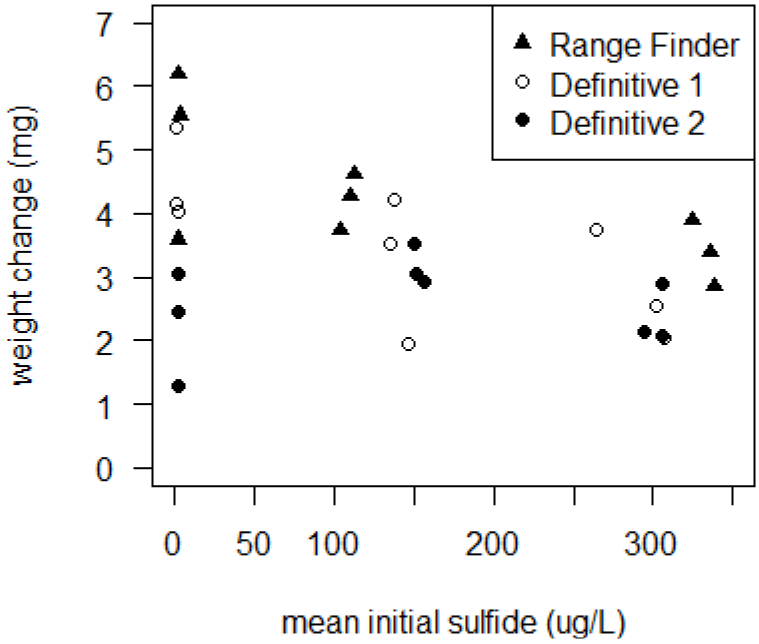


Dunnett Contrasts Test

== 0
== 0

Linear Hypotheses:	Estimate	Std. Error	t value	Pr(>|t|)
T1 - C	-0.4260	0.4174	-1.021	0.4997
T2 - C	**-1.1197**	**0.4174**	**-2.683**	**0.0252 ***

Analysis of covariance (ANCOVA)
Y = weight change
X1 = mean sulfide concentration
X2 = test (3 factors: Range Finder, Definitive 1, Definitive 2)



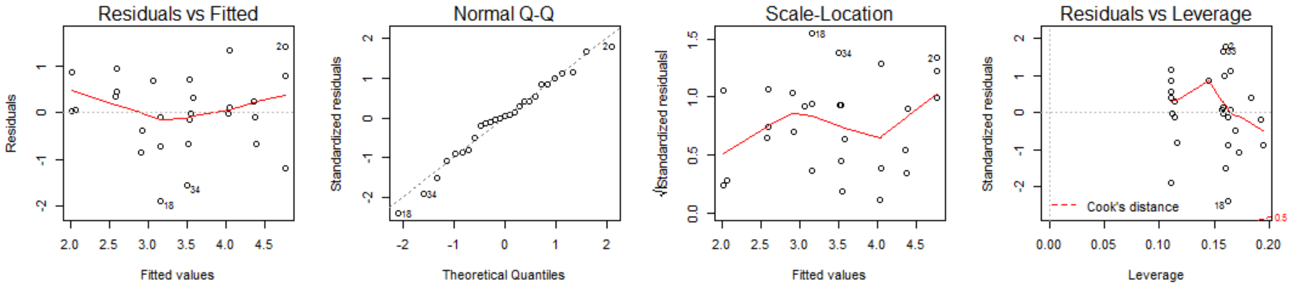
lm(formula = weight_change_mg ~ meaninitialsulfide_ugL + test, data = dataC12)

Min	1Q	Median	3Q	Max
-1.88002	-0.52064	0.04537	0.56428	1.41972

Coefficients:				
	Estimate	Std. Error	t value	Pr(>|t|)
(Intercept)	4.042632	0.343042	11.785	3.17e-11 ***
meansulfide	**-0.003711**	**0.001307**	**-2.840**	**0.00928 ****
testdefinitive2	-0.884074	0.405717	-2.179	0.03983 *
testrangefinder	0.734192	0.405611	1.810	0.08337

Signif. codes: 0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1

Residual standard error: 0.8604 on 23 degrees of freedom
Multiple r-squared: 0.5144,   Adjusted r-squared: 0.4511
F-statistic: 8.121 on 3 and 23 DF, *p*-value: 0.0007245



Appendix B. Sulfide Hydroponic Tests: Logistic Models

Statistical models and associated parameters

Objective: To model the wild rice growth response to increasing concentrations of total sulfide and use the dose response curves to estimate EC20 and EC50 values.

Data

3 Hydroponic Tests (Range Finder, Definitive 1, Definitive 2)

Independent variables

- Log10(mean initial total sulfide)
- Log10(mean initial H2S)

Response variable

- Weight change = final – initial in units of mg

Analysis

A dose response curve was fit using a 4–parameter logistic model using R software. These analyses use weight change as the response variable, which provides a better indication of whole-plant growth change (compared to length change) and does not assume exponential growth was occurring (growth rate constant makes this assumption).

General 4-Parameter Logistic Model

- y = A+(B-A)/(1+e^((C-x)/D))
- A = left-side horizontal asymptote (max response)
- B = right-side horizontal asymptote (min response)
- C = x value at the inflection point of the curve.
- D = slope parameter, indicating the speed with which the curve rises between min and max responses.

EC50 and EC20

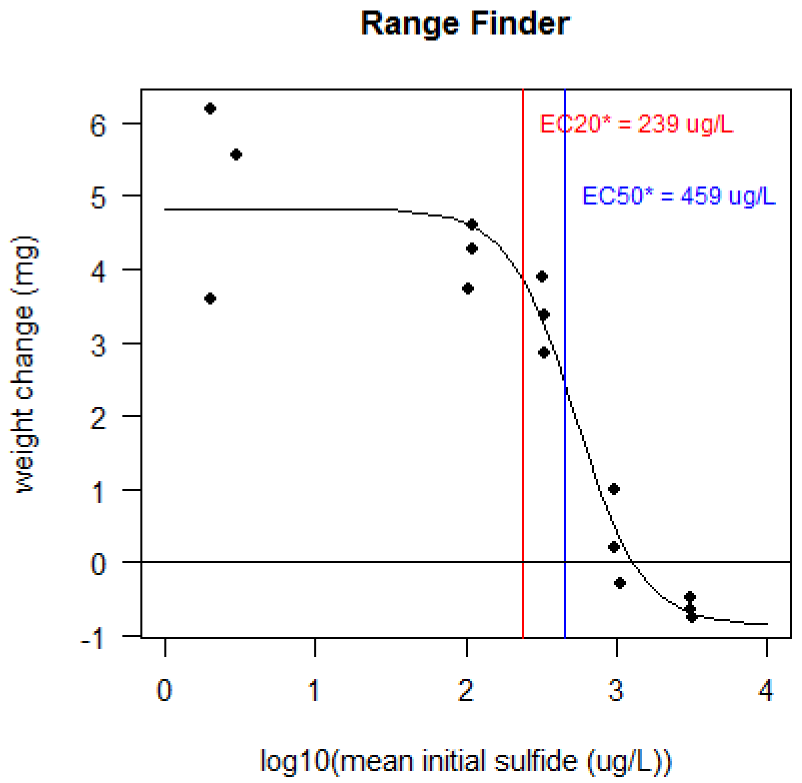
- EC20 and EC50 are calculated for positive values of y. EC20 = f(0.8A). EC50 = f(0.5A).
- EC50 is a more statistically robust estimate than EC20.
- Additional work is required to calculate the error around these estimates.

Model 1
Data set = Range Finder
Y = weight change
X = log10(mean initial total sulfide)

Formula: weight_change_mg ~ SSfpl(log_meaninitialsulfide_ugL, A, B, C, D)

Parameters:	Estimate	Std. Error	t value	Pr(>|t|)
A	4.82655	0.36116	13.364	3.82e-08 ***
B	-0.85718	0.59441	-1.442	0.1771
C	2.72890	0.09719	28.079	1.37e-11 ***
D	0.22054	0.07586	2.907	0.0143 *

\-\-\-
Signif. codes: 0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1
Residual standard error: 0.7411 on 11 degrees of freedom



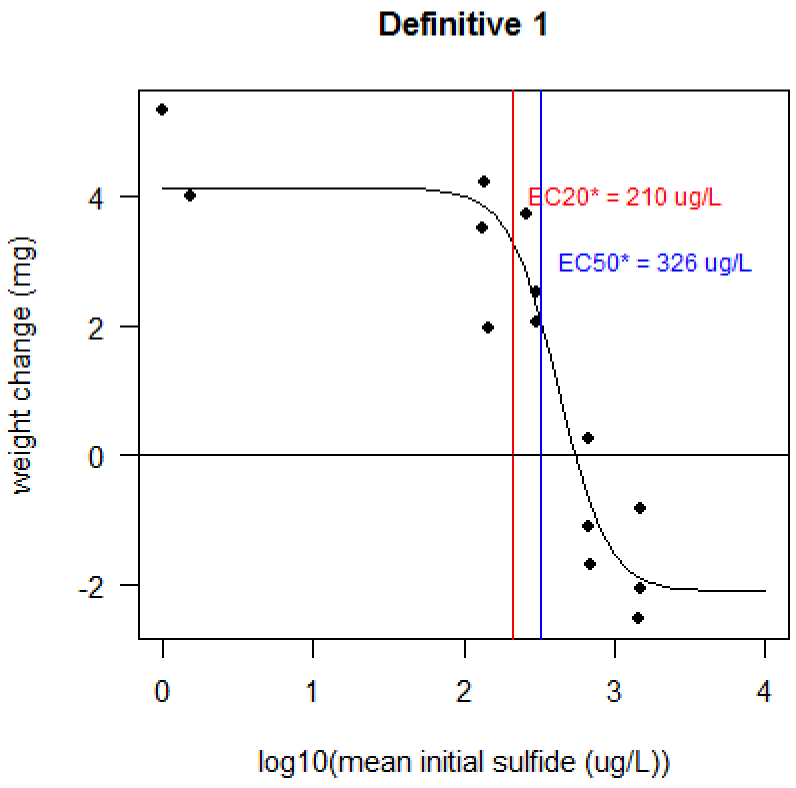
Model 2
Data set = Definitive 1
Y = weight change
X = log10(mean initial total sulfide)

Formula: weight_change_mg ~ SSfpl(log_meaninitialsulfide_ugL, A, B, C, D)

Parameters:	Estimate	Std. Error	t value	Pr(>|t|)
A	4.15236	0.47167	8.804	2.60e-06 ***
B	-2.11048	0.80162	-2.633	0.0233 *
C	2.62819	0.08731	30.102	6.43e-12 ***
D	0.16320	0.06513	2.506	0.0292 *

Signif. codes: 0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1

Residual standard error: 0.9422 on 11 degrees of freedom



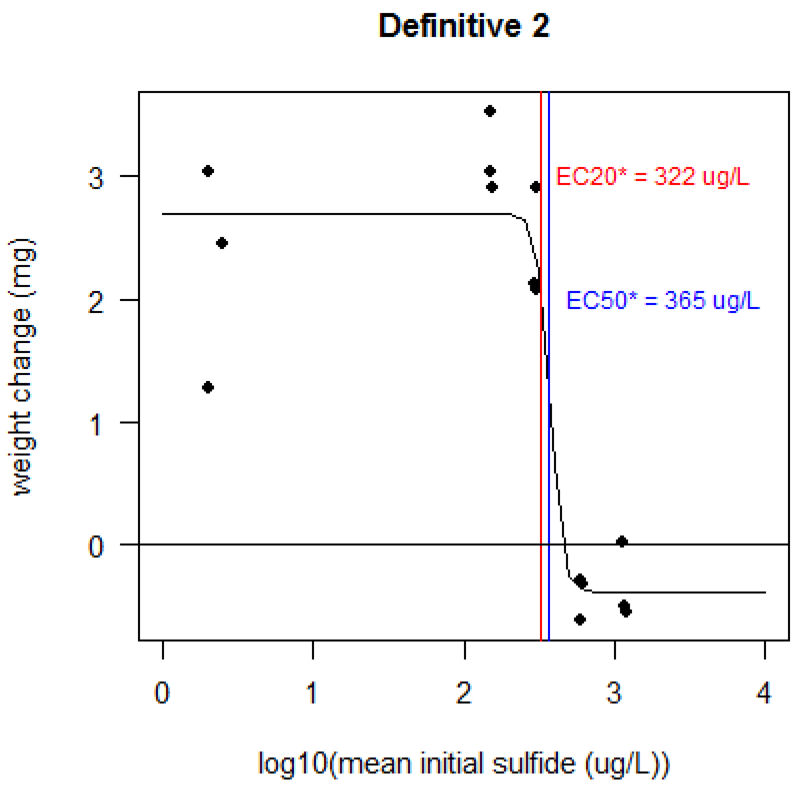
Model 3
Data set = Definitive 2
Y = weight change
X = log10(mean initial total sulfide)

Formula: weight_change_mg ~ SSfpl(log_meaninitialsulfide_ugL, A, B, C, D)

Parameters:	Estimate	Std. Error	t value	Pr(>|t|)
A	2.69365	0.24067	11.192	2.37e-07 ***
B	-0.38667	0.32920	-1.175	0.265
C	2.57251	0.26466	9.720	9.81e-07 ***
D	0.04166	0.11854	0.351	0.732

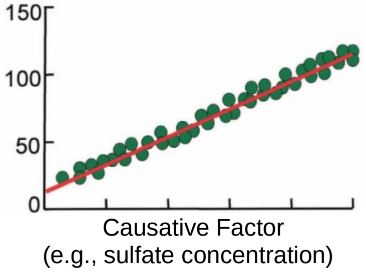
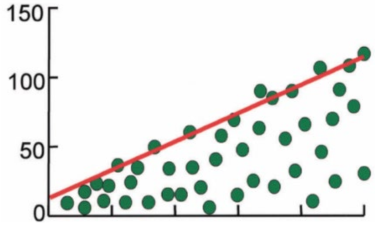
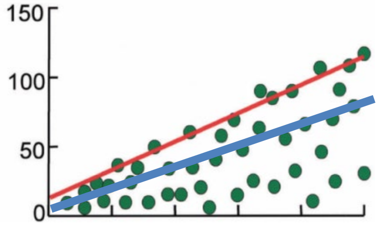
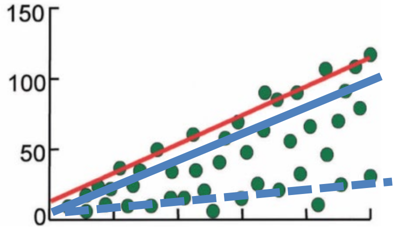
\-\-\-
Signif. codes: 0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1

Residual standard error: 0.5907 on 11 degrees of freedom



Appendix C. Explanation of Quantile Regression

Explanation of the utility of quantile regression for relationships where the causative factor (e.g., sulfate) and the response (e.g., sulfide) is affected by other variables. These graphics are adapted from Cade & Noon (2003), Frontiers in Ecology 1(8):412-420.

Application of quantile regression to the relationship between sulfate and sulfide	Theory of quantile regression
The top graph (A) represents the ideal statistical situation where a response (e.g., sulfide in porewater) is driven primarily by one factor (sulfate in surface water).	 A. When the relationship between a causative factor and the response is simple, the response is proportional to the causative factor.
In (B) other factors limit the response to the causative factor. In the case of sulfate, the potential maximum response (sulfide concentration in the porewater) is limited when iron is available to precipitate the sulfide.	 B. When other, perhaps unknown, factors aside from the causative factor affect the response, the shape of the graph becomes a wedge, because low causative values have a low response, but higher causative values do not necessarily have a proportional response.
In (C), a quantile regression line (blue) has been fit to the 75th percentile, estimating the potential maximum response for 75% of the sampled population. There is a great deal of uncertainty in the predicted response because the relationship between the causative factor (sulfate) and the response (sulfide) is poorly understood; the other factors (e.g., iron availability) affecting the response have not been quantified and included in the analysis.	 C. When the data form a wedge, traditional regression analysis is not informative. Instead, a line can be fitted to a particular percentile, or quantile, of the data (quantile regression). Here the blue line is fit to the 75th percentile of the data.
In (D), a *multiple quantile regression* analysis has been conducted because the response is being modified by a factor (iron) that is quantified and can be included in predicting the response. In the case of sulfate, the dashed line corresponds to a wild rice site rich in iron (so that the sulfide response is relatively flat) and the solid blue line corresponds to a site poor in iron (so that the sulfide response is steeper). Each of the blue lines corresponds to the maximum response for 75% of the population with a particular level of iron.	 D. Sometimes a factor affecting the response to the causative factor can be quantified and included in a *multiple quantile regression*, significantly reducing the uncertainty in the estimate of the potential maximum response.

Appendix D. Summary Statistics for Survey Data Sets.

Appendix D1. Summary statistics for all sites sampled in the Field Survey conducted 2012-2013 (Data Set 4; 119 sites). In the plant rings at the 119 sample sites, 80 had wild rice present.

Parameter	min	10%	25%	50%	75%	90%	max	N
Date	6/25/2012	7/24/2012	8/7/2012	8/27/2012	9/11/2012	9/20/2012	9/12/2013	119
Latitude	43.5758	44.3583	45.3752	46.6712	47.4855	47.7257	48.2161	119
Longitude	-97.6276	-95.6767	-95.2110	-93.8915	-93.0311	-92.1836	-91.2334	119
Wild rice cover in rings (%)	0.00	0.00	0.00	4.30	23.80	46.54	80.00	119
Wild rice stems in rings (stems/m2)	0.0	0.0	0.0	11.5	56.9	100.4	148.3	118
Floating leaf % cover	0.0	0.0	0.8	21.3	52.2	78.6	100.0	119
Water depth (m)	0.05	0.20	0.40	0.50	0.70	0.90	1.20	119
T-tube Transparency (cm)	3.00	29.80	58.50	101.00	101.00	101.00	101.00	119
surface water pH	5.90	7.05	7.35	7.87	8.65	9.25	9.76	118
surface water Temp (C)	11.3	16.2	20.3	23.3	26.1	28.2	32.9	119
surface water Conductance (µS/cm)	50	142	228	300	368	491	1789	119
surface water Ca (mg/L)	6.6	17.0	23.3	30.0	39.0	49.0	150.0	118
surface water Mg (mg/L)	2.8	7.7	11.5	17.8	27.4	34.7	266.0	118
surface water K (mg/L)	0.5	0.9	1.6	2.3	3.4	5.3	18.3	112
surface water Na (mg/L)	1.2	2.8	3.7	5.9	8.7	14.1	76.3	118
surface water Fe (µg/L)	3	3	3	6	78	1020	4120	119
surface water SO4 (mg SO4/L)	0.3	1.2	2.5	6.7	15.8	33.8	838.0	119
surface water Cl (mg/L)	0.3	1.3	3.7	7.3	15.4	21.5	77.1	119
surface water Alk (meq/L)	0.3	1.3	2.0	2.8	3.4	4.6	9.2	119
surface water TP (mg P/L)	0.01	0.01	0.01	0.02	0.06	0.13	1.58	119
surface water TN (mg N/L)	0.24	0.49	0.64	0.82	1.25	1.99	5.05	119
Surface Water NH4 (mg N/L)	0.02	0.02	0.02	0.02	0.02	0.12	0.78	118
Surface Water Color (Pt-Co units)	4	15	30	60	100	304	520	119
pore water pH	5.4	6.3	6.5	6.8	7.2	7.5	8.1	117
pore water Total Sulfide (TS, mg S/L)	0.001	0.034	0.066	0.102	0.193	0.741	16.000	119
pore water H2S (% of TS)	0.08	0.27	0.39	0.62	0.75	0.85	0.98	117
Free H2S (µg/L)	0.55	15.69	26.96	57.82	135.75	463.22	5120.00	117
pore water HS- (% of TS)	0.02	0.15	0.25	0.38	0.61	0.73	0.92	117
pore water Cl (mg/L)	0.0	0.6	2.9	7.7	15.6	22.4	99.2	118
pore water DOC (mg C/L)	6.0	12.3	16.2	22.8	31.6	46.1	129.0	119
pore water Ca (mg/L)	11.3	39.6	55.7	86.4	114.5	148.1	397.0	118
pore water Mg (mg/L)	4.6	13.3	18.0	27.4	40.6	60.1	116.0	118
pore water K (mg/L)	0.3	0.5	1.4	3.6	6.5	12.3	29.5	118
pore water Na (mg/L)	0.3	2.4	4.3	6.7	10.7	13.7	97.5	118
pore water Fe (µg/L)	5	172	1,673	5,510	12,500	20,340	84,600	118
pore water Mn (µg/L)	146	466	857	1,620	2,550	4,380	17,400	119
pore water TP (mg/L)	0.01	0.02	0.14	0.52	1.38	2.65	5.62	119
pore water TN (mg/L)	0.39	1.23	1.95	3.65	7.75	11.45	30.05	119
pore water NH4 (mg N/L)	0.05	0.13	0.25	2.00	6.25	11.00	26.00	119
pore water Si (mg/L)	16.80	31.24	38.25	50.20	62.05	72.74	97.80	119
Pore Water As (µg/L)	0.50	0.50	0.50	1.80	4.41	13.78	66.50	118
Pore Water Co (µg/L)	0.25	0.50	0.50	0.50	0.99	2.48	4.70	118
Pore Water Cu (µg/L)	0.25	5.00	5.00	5.00	5.00	5.00	48.70	118
Pore Water Se (µg/L)	0.50	0.50	0.50	0.50	0.50	0.50	3.39	118
Pore Water Zn (µg/L)	3.75	5.00	5.00	5.00	12.18	18.74	46.60	118
Sediment Water content (%)	12.50	34.56	60.35	79.40	88.95	92.42	95.40	119
Sediment organic (% LOI)	1.10	3.00	8.50	19.60	41.85	54.34	81.10	119
Sediment carbonate (% LOI)	0.70	2.18	4.30	6.60	13.05	31.36	70.00	119
Sediment inorganic (% LOI)	14.67	31.67	40.13	63.89	85.15	91.71	98.24	119
Sediment Fine organics (%)	30.00	66.00	74.25	85.00	91.00	95.00	98.00	118
Sediment Coarse organics (%)	2.00	5.00	9.00	15.00	25.75	34.00	70.00	118
Sediment Fine inorganics (%)	2.00	15.70	34.50	70.00	84.00	94.30	98.00	118
Sediment Coarse inorganics (%)	2.00	5.70	16.00	30.00	63.75	84.30	99.00	118
Sediment Total S (mg/g)	0.13	0.36	1.17	3.02	6.59	10.30	45.38	119
TS/TOC mg/g	3.7	12.1	19.0	30.7	52.6	99.1	589.4	119
Sediment AVS (µg/g)	20	80	155	280	745	1726	9170	119
AVS/TOC mg/g	0.2	0.6	1.1	3.9	17.2	30.8	366.4	119
AVS/ Total S (%)	1.1%	2.1%	4.4%	14.3%	39.7%	74.9%	145.5%	119
Sediment Ca (µg/g)	961	4,567	8,673	20,322	54,831	135,044	276,847	119
Sediment Mg (µg/g)	306	988	1,772	3,250	5,933	9,008	25,745	119
Sediment Fe (µg/g)	895	1,855	2,923	4,917	9,361	14,776	83,421	119
Porewater Fe / Sediment Fe (%)	0.001%	0.023%	0.102%	0.252%	0.657%	1.240%	2.951%	118
Fe/AVS (µg/µg)	1.6	3.8	6.0	14.7	32.8	63.9	439.1	119
Fe-AVS (µMol/g)	-4.38	21.91	39.08	65.30	148.94	236.21	1487.87	119
(Fe-AVS) / TOC (µMol) / mMol)	-0.66	2.49	4.17	9.91	29.79	74.34	563.13	119
Sediment Al (µg/g)	418	689	1,065	1,880	2,948	4,557	9,042	119
Sediment Mn (µg/g)	39	146	215	434	712	1,250	11,941	119
Sediment Zn (µg/g)	3.54	10.11	17.09	30.34	51.71	85.47	256.16	119
Sediment Ni (µg/g)	1.15	1.98	2.81	4.61	8.39	12.00	29.00	119
Sediment Cr (µg/g)	0.41	1.28	1.60	2.50	4.68	6.52	16.66	119
Sediment As (µg/g)	0.27	0.81	1.32	2.02	2.90	4.95	18.94	119
Sediment Cu (µg/g)	0.82	2.20	3.91	6.18	10.53	16.65	33.48	119
Sediment Total-P (mg P/g)	0.13	0.29	0.46	0.75	0.91	1.13	2.18	119
TP/TOC mg/g	0.77	2.92	4.17	6.58	14.02	28.72	254.55	119
Sediment Exchangeable-P (mg P/g)	0.03	0.03	0.04	0.04	0.05	0.07	0.15	119
Sediment NAI-P (mg P/g)	0.02	0.04	0.06	0.11	0.17	0.24	1.39	119
Sediment Apatite-P (mg P/g)	0.00	0.04	0.09	0.15	0.22	0.28	0.77	119
Sediment Org-P (mg P/g)	0.01	0.02	0.14	0.30	0.59	0.75	1.27	119
Sediment Total-N (mg/g)	0.36	0.99	2.73	9.15	16.63	21.93	32.10	118
TN/TOC mg/g	7.61	54.11	72.64	84.71	93.37	106.87	445.45	118
Sediment TIC (%)	0.00	0.00	0.01	0.43	1.57	3.91	8.72	118
Sediment TOC (%)	0.11	1.31	3.38	10.07	21.56	28.94	44.21	119
Sediment Se (µg/g)	0.30	0.53	0.80	1.03	1.34	1.83	2.71	109

Appendix D2. Summary statistics for the lake sites included in the 2012-13 Field Survey (82 of the 119 sites in Data Set 4). In the plant rings at the 82 sample sites, 48 had wild rice present.

Parameter	min	10%	25%	50%	75%	90%	max	N
Date	6/27/2012	7/26/2012	8/2/2012	8/22/2012	9/9/2012	9/19/2012	9/12/2013	82
Latitude	43.7709	44.5923	45.3377	46.3148	47.2867	47.6162	47.8258	82
Longitude	-96.3171	-95.7259	-95.2140	-94.0114	-93.2475	-92.4539	-91.8857	82
Wild rice cover in rings (%)	0.00	0.00	0.00	1.15	15.98	34.75	70.00	82
Wild rice stems in rings (stems/m2)	0.0	0.0	0.0	3.8	40.1	102.2	144.8	81
Floating leaf % cover	0.0	0.0	0.9	21.3	51.4	78.1	100.0	82
Water depth (m)	0.10	0.20	0.46	0.60	0.70	0.90	1.10	82
T-tube Transparency (cm)	3.00	26.40	60.25	101.00	101.00	101.00	101.00	82
surface water pH	5.90	7.05	7.41	8.29	8.72	9.35	9.76	81
surface water Temp (C)	11.3	16.0	20.2	23.8	27.1	29.5	32.9	82
surface water Conductance (µS/cm)	50	133	230	306	359	440	1136	82
surface water Ca (mg/L)	6.6	16.0	22.0	29.0	37.0	42.0	150.0	81
surface water Mg (mg/L)	2.8	6.7	11.3	19.9	27.0	34.2	107.0	81
surface water K (mg/L)	0.5	0.7	1.6	2.4	3.4	5.0	18.3	76
surface water Na (mg/L)	1.2	2.5	3.6	5.4	8.3	10.8	76.3	81
surface water Fe (µg/L)	3	3	3	3	17	724	4120	82
surface water SO4 (mg SO4/L)	0.6	1.2	2.5	4.1	14.5	29.3	335.0	82
surface water Cl (mg/L)	0.3	1.5	4.0	8.0	15.2	22.0	77.1	82
surface water Alk (meq/L)	0.3	1.3	2.2	2.8	3.4	4.0	6.2	82
surface water TP (mg P/L)	0.01	0.01	0.01	0.02	0.04	0.10	0.43	82
surface water TN (mg N/L)	0.24	0.48	0.62	0.83	1.25	1.84	3.15	82
Surface Water NH4 (mg N/L)	0.02	0.02	0.02	0.02	0.02	0.11	0.78	81
Surface Water Color (Pt-Co units)	4	15	25	52	82	200	450	82
pore water pH	5.8	6.3	6.5	6.7	7.1	7.5	8.1	81
pore water Total Sulfide (TS, mg S/L)	0.001	0.031	0.069	0.118	0.266	1.355	16.000	82
pore water H2S (% of TS)	8%	27%	47%	66%	76%	84%	94%	81
Free H2S (µg/L)	0.55	16.42	27.30	71.94	144.76	483.30	5120.00	81
pore water HS- (% of TS)	6%	16%	24%	34%	53%	73%	92%	81
pore water Cl (mg/L)	0.0	0.5	2.8	6.9	15.2	23.9	99.2	82
pore water DOC (mg C/L)	6.5	13.2	16.0	22.4	29.0	37.2	99.8	82
pore water Ca (mg/L)	11.3	44.0	59.2	87.2	115.0	138.0	231.0	81
pore water Mg (mg/L)	4.6	13.4	18.9	28.6	40.6	59.3	116.0	81
pore water K (mg/L)	0.3	0.3	1.4	4.0	6.6	10.6	25.1	81
pore water Na (mg/L)	0.3	2.1	4.2	6.5	9.9	13.9	97.5	81
pore water Fe (µg/L)	5	86	986	4,270	12,500	20,100	84,600	81
pore water Mn (µg/L)	146	441	788	1,360	2,243	4,109	14,100	82
pore water TP (mg/L)	0.01	0.02	0.07	0.37	1.10	2.47	4.79	82
pore water TN (mg/L)	0.49	1.16	2.08	5.05	8.23	14.05	30.05	82
pore water NH4 (mg N/L)	0.06	0.13	0.25	3.05	8.25	12.00	26.00	82
pore water Si (mg/L)	19.00	33.06	40.25	52.55	65.65	74.44	97.80	82
Pore Water As (µg/L)	0.50	0.50	0.50	1.37	2.36	5.44	24.20	81
Pore Water Co (µg/L)	0.25	0.50	0.50	0.50	0.89	1.82	4.30	81
Pore Water Cu (µg/L)	0.25	5.00	5.00	5.00	5.00	5.00	48.70	81
Pore Water Se (µg/L)	0.50	0.50	0.50	0.50	0.50	0.50	2.50	81
Pore Water Zn (µg/L)	3.75	5.00	5.00	5.00	10.60	16.90	29.50	81
Sediment Water content (%)	14.70	48.19	69.05	85.05	90.75	92.69	95.40	82
Sediment organic (% LOI)	1.10	4.36	12.40	26.20	45.03	54.48	63.00	82
Sediment carbonate (% LOI)	0.70	3.21	5.33	8.40	21.35	35.04	70.00	82
Sediment inorganic (% LOI)	16.74	31.86	37.84	53.00	75.50	86.39	98.24	82
Sediment Fine organics (%)	35.00	66.00	74.00	83.00	91.00	94.90	98.00	82
Sediment Coarse organics (%)	2.00	6.00	9.00	17.00	26.00	34.00	65.00	82
Sediment Fine inorganics (%)	2.00	15.50	39.25	72.00	85.75	91.90	98.00	82
Sediment Coarse inorganics (%)	2.00	8.10	14.25	28.00	61.50	84.60	99.00	82
Sediment Total S (mg/g)	0.13	0.77	1.74	4.31	7.78	11.34	45.38	82
TS/TOC mg/g	5.7	12.3	19.2	31.0	55.1	99.6	589.4	82
Sediment AVS (µg/g)	20	92	175	306	843	2084	9170	82
AVS/TOC mg/g	0.2	0.6	1.2	3.4	12.1	27.6	192.1	82
AVS/ Total S (%)	1.1%	2.2%	4.2%	13.3%	22.8%	57.4%	145.5%	82
Sediment Ca (µg/g)	1,158	7,002	10,145	22,659	73,532	153,233	276,847	82
Sediment Mg (µg/g)	306	1,174	1,860	3,663	6,241	9,075	25,745	82
Sediment Fe (µg/g)	895	1,740	2,321	4,300	9,517	14,916	83,421	82
Porewater Fe / Sediment Fe (%)	0.001%	0.013%	0.118%	0.417%	0.784%	1.400%	2.951%	81
Fe/AVS (µg/µg)	1.6	3.6	5.4	11.3	27.4	62.6	439.1	82
Fe-AVS (µMol/g)	-4.38	19.90	30.20	58.16	143.50	237.67	1487.87	82
(Fe-AVS) / TOC (µMol) / mMol)	-0.66	2.26	3.36	7.91	16.71	33.18	176.67	82
Sediment Al (µg/g)	418	657	955	1,771	2,745	4,500	6,367	82
Sediment Mn (µg/g)	39	141	217	477	747	1,252	11,941	82
Sediment Zn (µg/g)	3.54	9.88	17.97	28.65	55.63	88.52	256.16	82
Sediment Ni (µg/g)	1.15	1.83	2.56	4.22	7.66	10.70	19.48	82
Sediment Cr (µg/g)	0.71	1.26	1.50	2.39	3.99	5.57	12.16	82
Sediment As (µg/g)	0.27	0.82	1.32	2.06	3.24	5.41	18.94	82
Sediment Cu (µg/g)	0.82	2.71	4.00	6.38	10.72	16.33	25.69	82
Sediment Total-P (mg P/g)	0.13	0.33	0.49	0.79	0.95	1.22	2.18	82
TP/TOC mg/g	1.76	2.90	4.17	5.96	10.35	18.76	44.00	82
Sediment Exchangeable-P (mg P/g)	0.03	0.03	0.04	0.04	0.05	0.07	0.15	82
Sediment NAI-P (mg P/g)	0.02	0.04	0.07	0.12	0.18	0.25	1.39	82
Sediment Apatite-P (mg P/g)	0.00	0.03	0.08	0.14	0.20	0.27	0.59	82
Sediment Org-P (mg P/g)	0.01	0.04	0.21	0.40	0.66	0.78	1.27	82
Sediment Total-N (mg/g)	0.40	1.60	5.10	11.10	18.00	23.15	32.10	81
TN/TOC mg/g	9.02	66.00	78.00	89.23	95.13	106.52	156.63	81
Sediment TIC (%)	0.00	0.00	0.03	0.88	2.35	4.51	8.72	82
Sediment TOC (%)	0.43	1.78	5.83	13.87	22.03	29.38	33.30	82
Sediment Se (µg/g)	0.30	0.53	0.85	1.05	1.34	1.93	2.71	78

Appendix D3. Summary statistics for the stream sites included in the 2012-13 Field Survey (30 of the 119 sites in Data Set 4). In the plant rings at the 30 sample sites, 25 had wild rice present.

Parameter	min	10%	25%	50%	75%	90%	max	N
Date	8/6/2012	8/9/2012	8/16/2012	9/5/2012	9/11/2012	7/26/2013	9/10/2013	30
Latitude	43.5758	44.2014	45.9815	47.2535	47.6508	47.7277	47.9952	30
Longitude	-97.6276	-95.2761	-94.0437	-92.6775	-92.1678	-91.8459	-91.2334	30
Wild rice cover in rings (%)	0.00	0.00	1.58	18.15	40.10	52.32	61.30	30
Wild rice stems in rings (stems/m2)	0.0	0.0	3.7	37.1	64.7	80.4	148.3	30
Floating leaf % cover	0.0	0.0	1.5	37.6	58.5	92.0	100.0	30
Water depth (m)	0.12	0.20	0.30	0.50	0.60	0.90	1.20	30
T-tube Transparency (cm)	26.00	42.80	60.00	101.00	101.00	101.00	101.00	30
surface water pH	6.91	7.09	7.34	7.60	7.87	8.16	9.16	30
surface water Temp (C)	15.0	16.5	19.5	21.9	24.3	25.7	27.6	30
surface water Conductance (µS/cm)	75	191	226	271	344	493	1789	30
surface water Ca (mg/L)	8.8	18.8	25.3	34.0	39.0	49.2	100.0	30
surface water Mg (mg/L)	4.7	8.7	11.5	16.0	22.0	28.5	266.0	30
surface water K (mg/L)	0.5	1.0	1.4	1.7	2.6	4.0	11.1	30
surface water Na (mg/L)	1.7	3.5	4.5	6.7	12.0	18.3	39.5	30
surface water Fe (µg/L)	3	3	6	29	652	1259	3400	30
surface water SO4 (mg SO4/L)	0.6	1.3	2.5	10.1	17.9	38.1	838.0	30
surface water Cl (mg/L)	0.4	2.3	3.4	6.6	16.2	21.3	33.0	30
surface water Alk (meq/L)	0.6	1.5	1.8	2.6	2.8	4.6	8.2	30
surface water TP (mg P/L)	0.01	0.01	0.02	0.03	0.08	0.14	0.39	30
surface water TN (mg N/L)	0.38	0.53	0.65	0.76	0.98	1.40	1.98	30
Surface Water NH4 (mg N/L)	0.02	0.02	0.02	0.02	0.02	0.06	0.12	30
Surface Water Color (Pt-Co units)	10	20	42	68	150	321	520	30
pore water pH	6.4	6.7	6.8	7.0	7.3	7.4	7.9	29
pore water Total Sulfide (TS, mg S/L)	0.022	0.044	0.058	0.073	0.110	0.154	0.256	30
pore water H2S (% of TS)	11%	28%	34%	52%	62%	70%	79%	29
Free H2S (µg/L)	2.46	14.05	20.75	37.74	56.01	75.82	168.96	29
pore water HS- (% of TS)	21%	30%	38%	48%	66%	72%	89%	29
pore water Cl (mg/L)	0.1	1.8	2.7	7.3	14.9	20.4	64.7	30
pore water DOC (mg C/L)	6.0	11.2	15.5	20.7	30.4	43.4	52.4	30
pore water Ca (mg/L)	13.0	31.9	47.4	66.0	95.3	110.5	175.0	30
pore water Mg (mg/L)	6.8	14.1	16.7	23.0	34.8	41.1	53.9	30
pore water K (mg/L)	0.3	0.6	1.2	2.0	3.0	4.2	6.8	30
pore water Na (mg/L)	1.7	3.1	4.8	6.2	10.9	12.5	51.2	30
pore water Fe (µg/L)	1,510	2,686	5,063	9,530	13,275	25,280	33,700	30
pore water Mn (µg/L)	420	953	1,173	2,375	3,938	9,387	17,400	30
pore water TP (mg/L)	0.01	0.20	0.37	0.70	1.50	2.18	4.11	30
pore water TN (mg/L)	0.39	1.23	1.35	2.25	2.95	4.11	6.85	30
pore water NH4 (mg N/L)	0.05	0.13	0.27	1.05	2.55	3.60	6.60	30
pore water Si (mg/L)	21.90	30.91	36.85	41.65	55.05	59.44	69.80	30
Pore Water As (µg/L)	0.50	1.09	2.40	3.89	7.72	16.64	24.60	30
Pore Water Co (µg/L)	0.25	0.25	0.50	0.50	0.50	1.19	2.99	30
Pore Water Cu (µg/L)	0.25	0.93	5.00	5.00	5.00	5.00	5.00	30
Pore Water Se (µg/L)	0.50	0.50	0.50	0.50	0.50	0.50	1.04	30
Pore Water Zn (µg/L)	4.84	5.00	5.00	10.50	16.30	21.17	46.60	30
Sediment Water content (%)	12.50	27.38	35.25	57.30	71.15	83.53	89.60	30
Sediment organic (% LOI)	1.10	2.04	3.40	8.50	16.45	28.20	50.20	30
Sediment carbonate (% LOI)	0.80	1.78	2.23	3.20	5.95	9.11	30.00	30
Sediment inorganic (% LOI)	31.01	68.64	78.07	87.20	93.19	96.90	97.12	30
Sediment Fine organics (%)	30.00	67.60	82.00	86.00	90.00	94.20	97.00	29
Sediment Coarse organics (%)	3.00	5.80	11.00	14.00	18.00	32.20	70.00	29
Sediment Fine inorganics (%)	5.00	15.00	25.00	41.00	79.00	97.00	98.00	29
Sediment Coarse inorganics (%)	2.00	2.00	20.00	59.00	75.00	85.20	96.00	29
Sediment Total S (mg/g)	0.18	0.26	0.38	1.06	2.35	4.00	7.93	30
TS/TOC mg/g	3.7	13.0	20.6	32.9	55.0	92.1	363.6	30
Sediment AVS (µg/g)	70	80	135	270	530	1309	3370	30
AVS/TOC mg/g	0.4	1.1	4.7	11.8	29.4	58.0	366.4	30
AVS/ Total S (%)	1.9%	5.8%	21.4%	39.7%	66.8%	96.5%	100.8%	30
Sediment Ca (µg/g)	961	2,786	3,610	8,025	13,596	26,952	144,193	30
Sediment Mg (µg/g)	434	895	1,298	2,220	4,824	9,119	13,130	30
Sediment Fe (µg/g)	1,974	2,821	3,350	6,310	9,257	14,121	29,463	30
Porewater Fe / Sediment Fe (%)	0.009%	0.074%	0.107%	0.157%	0.362%	0.602%	0.792%	30
Fe/AVS (µg/µg)	3.4	8.0	10.9	21.1	34.0	54.8	95.2	30
Fe-AVS (µMol/g)	25.68	41.50	52.32	98.07	157.26	205.26	422.49	30
(Fe-AVS) / TOC (µMol) / mMol)	1.51	8.60	14.84	53.40	78.79	109.08	563.13	30
Sediment Al (µg/g)	556	780	1,152	1,991	3,394	4,788	9,042	30
Sediment Mn (µg/g)	109	166	204	385	574	998	4,748	30
Sediment Zn (µg/g)	7.24	10.67	16.40	32.75	51.76	77.42	109.53	30
Sediment Ni (µg/g)	2.03	2.67	3.50	5.87	9.19	16.48	29.00	30
Sediment Cr (µg/g)	0.78	1.82	1.98	4.28	6.06	7.51	16.66	30
Sediment As (µg/g)	0.44	0.64	1.18	1.77	2.47	4.72	6.54	30
Sediment Cu (µg/g)	1.36	1.85	3.15	5.31	10.53	18.33	33.48	30
Sediment Total-P (mg P/g)	0.24	0.29	0.38	0.51	0.74	0.86	0.94	30
TP/TOC mg/g	2.42	4.12	7.62	18.22	30.83	57.02	254.55	30
Sediment Exchangeable-P (mg P/g)	0.03	0.03	0.04	0.04	0.04	0.04	0.05	30
Sediment NAI-P (mg P/g)	0.03	0.05	0.05	0.10	0.15	0.19	0.36	30
Sediment Apatite-P (mg P/g)	0.05	0.09	0.12	0.23	0.28	0.38	0.77	30
Sediment Org-P (mg P/g)	0.01	0.02	0.06	0.13	0.24	0.40	0.69	30
Sediment Total-N (mg/g)	0.36	0.50	0.92	2.50	4.64	11.62	20.90	30
TN/TOC mg/g	7.61	51.55	59.83	72.78	86.12	109.12	445.45	30
Sediment TIC (%)	0.00	0.00	0.00	0.19	0.40	0.95	3.34	29
Sediment TOC (%)	0.11	0.63	1.53	3.77	8.90	15.20	27.16	30
Sediment Se (µg/g)	0.36	0.69	0.75	0.97	1.35	1.58	2.34	25

Appendix D4. Summary statistics for the cultivated paddy sites sampled in the 2012-13 Field Survey (7 of the 119 sites in Data Set 4). In the plant rings at the 7 sample sites, 7 had wild rice present.

Parameter	min	25%	50%	75%	max	N
Date	6/25/2012	6/26/2012	6/28/2012	6/28/2012	7/16/2013	7
Latitude	46.2460	47.8267	47.8521	47.8894	48.2161	7
Longitude	-95.6732	-95.5633	-95.4865	-95.0460	-94.2548	7
Wild rice cover in rings (%)	4.30	24.40	33.80	45.30	80.00	7
Wild rice stems in rings (stems/m2)	8.3	52.7	58.9	86.6	134.3	7
Floating leaf % cover	0.0	0.0	0.0	0.9	1.3	7
Water depth (m)	0.05	0.20	0.30	0.35	0.50	7
T-tube Transparency (cm)	23.00	36.00	68.00	84.00	101.00	7
surface water pH	6.44	7.23	7.34	8.01	8.55	7
surface water Temp (C)	21.4	22.6	23.7	24.2	27.9	7
surface water Conductance (µS/cm)	132	332	467	693	927	7
surface water Ca (mg/L)	21.0	40.5	51.0	83.0	130.0	7
surface water Mg (mg/L)	5.0	18.7	30.3	37.4	74.8	7
surface water K (mg/L)	1.9	3.5	5.4	10.0	13.3	6
surface water Na (mg/L)	1.9	3.3	5.5	7.1	23.9	7
surface water Fe (µg/L)	32	66	147	387	428	7
surface water SO4 (mg SO4/L)	0.3	1.0	7.1	10.4	279.0	7
surface water Cl (mg/L)	0.3	3.4	6.8	12.0	39.8	7
surface water Alk (meq/L)	1.3	2.5	4.2	5.3	9.2	7
surface water TP (mg P/L)	0.02	0.07	0.09	0.94	1.58	7
surface water TN (mg N/L)	0.69	2.05	3.25	3.65	5.05	7
Surface Water NH4 (mg N/L)	0.02	0.06	0.11	0.19	0.32	7
Surface Water Color (Pt-Co units)	67	158	230	292	383	7
pore water pH	5.4	5.9	6.2	6.3	7.7	7
pore water Total Sulfide (TS, mg S/L)	0.031	0.142	0.194	0.488	0.732	7
pore water H2S (% of TS)	18%	85%	87%	93%	98%	7
Free H2S (µg/L)	20.70	92.29	168.78	440.52	607.56	7
pore water HS- (% of TS)	2%	8%	13%	15%	82%	7
pore water Cl (mg/L)	7.7	15.0	18.5	20.8	30.8	6
pore water DOC (mg C/L)	67.1	71.1	90.4	117.5	129.0	7
pore water Ca (mg/L)	40.3	231.5	267.0	366.5	397.0	7
pore water Mg (mg/L)	11.8	66.1	89.3	102.6	115.0	7
pore water K (mg/L)	7.7	11.8	16.1	18.8	29.5	7
pore water Na (mg/L)	3.1	9.0	11.5	12.4	19.3	7
pore water Fe (µg/L)	1,060	1,360	1,650	2,660	4,300	7
pore water Mn (µg/L)	194	970	1,840	2,210	3,840	7
pore water TP (mg/L)	0.48	0.96	2.68	4.65	5.62	7
pore water TN (mg/L)	4.05	5.55	8.15	10.00	13.05	7
pore water NH4 (mg N/L)	0.19	1.03	2.80	4.65	6.50	7
pore water Si (mg/L)	16.80	37.55	44.30	64.25	75.00	7
Pore Water As (µg/L)	5.85	17.28	35.10	58.60	66.50	7
Pore Water Co (µg/L)	1.23	2.55	3.09	3.51	4.70	7
Pore Water Cu (µg/L)	1.94	5.00	5.00	5.00	10.70	7
Pore Water Se (µg/L)	0.50	1.84	2.08	2.42	3.39	7
Pore Water Zn (µg/L)	5.00	5.00	11.70	17.45	37.10	7
Sediment Water content (%)	46.90	68.35	77.50	81.05	83.90	7
Sediment organic (% LOI)	16.10	38.60	52.20	65.50	81.10	7
Sediment carbonate (% LOI)	4.30	5.55	7.70	8.30	35.40	7
Sediment inorganic (% LOI)	14.67	25.91	33.01	44.67	78.60	7
Sediment Fine organics (%)	72.00	80.50	92.00	95.50	97.00	7
Sediment Coarse organics (%)	3.00	4.50	7.00	19.50	28.00	7
Sediment Fine inorganics (%)	21.00	64.50	74.00	81.00	91.00	7
Sediment Coarse inorganics (%)	10.00	19.00	27.00	35.50	79.00	7
Sediment Total S (mg/g)	1.99	3.35	3.77	6.07	8.17	7
TS/TOC mg/g	8.0	13.4	16.7	23.0	36.7	7
Sediment AVS (µg/g)	50	65	109	185	300	7
AVS/TOC mg/g	0.2	0.3	0.6	0.8	1.1	7
AVS/ Total S (%)	1.2%	1.8%	2.5%	4.0%	6.6%	7
Sediment Ca (µg/g)	14,441	28,861	34,512	38,685	149,585	7
Sediment Mg (µg/g)	2,757	3,005	5,578	5,930	8,132	7
Sediment Fe (µg/g)	3,242	3,326	4,673	5,290	7,874	7
Porewater Fe / Sediment Fe (%)	0.029%	0.086%	0.152%	0.211%	0.254%	7
Fe/AVS (µg/µg)	16.0	25.9	42.9	55.9	131.2	7
Fe-AVS (µMol/g)	53.74	56.56	78.96	88.20	139.13	7
(Fe-AVS) / TOC (µMol) / mMol)	1.54	3.19	4.11	4.71	6.96	7
Sediment Al (µg/g)	1,568	1,873	2,059	2,437	2,561	7
Sediment Mn (µg/g)	106	257	381	387	1,106	7
Sediment Zn (µg/g)	10.79	15.69	24.28	33.44	43.02	7
Sediment Ni (µg/g)	2.48	6.15	8.26	10.08	11.93	7
Sediment Cr (µg/g)	0.41	1.46	2.13	2.51	5.72	7
Sediment As (µg/g)	0.67	2.53	2.80	3.47	4.36	7
Sediment Cu (µg/g)	2.45	5.62	6.15	8.21	11.79	7
Sediment Total-P (mg P/g)	0.34	0.55	0.75	0.80	1.11	7
TP/TOC mg/g	0.77	2.66	2.99	3.65	4.62	7
Sediment Exchangeable-P (mg P/g)	0.03	0.04	0.05	0.07	0.10	7
Sediment NAI-P (mg P/g)	0.04	0.08	0.10	0.16	0.26	7
Sediment Apatite-P (mg P/g)	0.01	0.07	0.11	0.14	0.18	7
Sediment Org-P (mg P/g)	0.24	0.29	0.31	0.50	0.83	7
Sediment Total-N (mg/g)	7.60	16.25	18.50	20.15	23.60	7
TN/TOC mg/g	41.85	62.72	74.17	80.96	85.74	7
Sediment TIC (%)	0.00	0.17	0.34	0.62	4.04	7
Sediment TOC (%)	9.75	19.15	28.09	34.85	44.21	7
Sediment Se (µg/g)	0.43	0.60	0.83	0.86	1.07	6

Appendix D5. Summary statistics for all sites sampled in the 2011 Pilot Survey (Data set 1; 39 sites). In the plant rings at the 39 sample sites, 35 had wild rice present.

Parameter	min	10%	25%	50%	75%	90%	max	N
Date	8/19/2011	8/24/2011	8/30/2011	9/8/2011	9/20/2011	9/22/2011	9/29/2011	39
Latitude	44.1940	45.2272	45.9258	47.1946	47.3916	47.6712	47.8255	39
Longitude	-95.7404	-95.6347	-95.2160	-94.4339	-92.4004	-91.9413	93.3380	39
Wild rice cover in rings (%)	0.0	1.0	8.2	18.8	31.3	53.3	71.3	39
Floating leaf % cover	0.0	0.0	0.0	1.5	9.1	20.6	51.3	39
T-tube Transparency (cm)	8.0	53.9	85.3	101.0	101.0	101.0	101.0	32
surface water pH	6.4	6.6	7.0	7.3	7.7	8.2	8.7	36
surface water Temp (C)	11.7	13.0	16.3	19.4	21.8	22.9	24.1	36
surface water Conduc-tance (µS/cm)	11.0	101.5	190.0	253.5	344.3	390.0	1082.0	36
surface water Ca (mg/L)	4.9	10.1	22.5	28.0	35.5	42.6	87.7	39
surface water Mg (mg/L)	3.2	5.1	11.4	17.2	25.9	32.2	95.4	39
surface water K (mg/L)	0.4	0.6	1.2	1.8	3.1	4.9	16.5	39
surface water Na (mg/L)	1.0	2.4	3.2	5.7	7.0	9.6	69.4	39
surface water Fe (µg/L)	6.3	10.2	21.3	81.1	361.6	1164.8	4739.9	39
surface water SO4 (mg SO4/L)	0.2	0.3	0.6	1.1	5.0	10.3	107.7	39
surface water Cl (mg/L)	0.5	0.8	1.1	6.1	12.3	18.9	29.7	39
surface water Alk (meq/L)	0.2	0.6	1.3	2.6	3.2	3.9	5.1	38
surface water TP (mg P/L)	0.0	0.0	0.0	0.0	0.0	0.1	0.3	39
surface water TN (mg N/L)	0.5	0.6	0.6	0.8	1.2	1.5	2.0	39
Surface Water NO3 (mg N/L)	0.0	0.0	0.0	0.0	0.0	0.0	0.8	39
Surface Water NH4 (mg N/L)	0.0	0.0	0.0	0.0	0.0	0.1	0.1	39
Surface Water DOC (mg C/L)	6.6	7.5	8.9	16.1	21.3	27.8	43.6	39
Surface Water SUVA Fe correct	1.0	1.2	1.5	2.1	2.6	3.3	3.8	39
Surface Water UV ABS 254 nm	0.1	0.1	0.2	0.2	0.6	1.1	2.0	39
Surface Water DO surface (mg/L)	2.1	5.3	6.1	7.3	8.7	9.6	10.5	36
pore water pH	5.5	6.0	6.4	6.5	6.7	7.0	7.5	38
pore water Total Sulfide (TS, mg S/L)	0.0	0.0	0.0	0.1	0.1	0.2	14.8	39
pore water H2S (% of TS)	0.3	0.5	0.7	0.8	0.8	0.9	1.0	38
Free H2S (µg/L)	8.2	16.3	24.5	36.1	59.1	118.8	3710.0	38
pore water HS- (% of TS)	0.0	0.1	0.2	0.2	0.3	0.5	0.8	38
pore water Cl (mg/L)	4.9	8.6	15.0	23.9	27.5	32.8	36.4	18
pore water DOC (mg C/L)	14.1	16.9	18.7	22.1	28.3	29.9	33.3	18
pore water Ca (mg/L)	24.5	29.7	38.6	50.7	65.9	77.1	80.8	18
pore water Mg (mg/L)	7.8	10.3	13.7	25.8	32.9	40.7	134.4	18
pore water K (mg/L)	0.3	0.4	0.9	2.4	4.7	6.9	26.7	18
pore water Na (mg/L)	0.6	2.2	3.7	4.8	7.2	10.3	92.0	18
pore water Fe (µg/L)	193	533	2718	8862	17520	24864	35586	18
pore water Mn (µg/L)	253	423	719	1094	1689	5019	16725	18
pore water TP (mg/L)	0.0	0.1	0.2	0.6	1.7	2.7	3.2	18
pore water TN (mg/L)	1.0	1.3	3.5	6.7	11.1	15.1	17.9	18
pore water NH4 (mg N/L)	0.1	0.1	2.3	6.3	11.5	17.1	19.4	18
Pore Water NO3 (mg N/L)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	18
Pore Water Al (µg/L)	20.0	29.7	33.2	44.0	52.7	66.9	89.4	18
Pore Water Ba (µg/L)	21.3	25.2	31.8	38.2	60.0	143.5	197.4	18
Pore Water Sr (µg/L)	66.7	100.5	117.9	134.2	202.7	244.3	511.3	18
Pore Water Ag (µg/L)	0.0	0.0	0.0	0.0	0.1	0.1	0.2	18
Pore Water As (µg/L)	0.6	0.6	0.8	1.4	2.2	4.1	6.6	18
Pore Water Cd (µg/L)	0.0	0.0	0.0	0.0	0.0	0.1	0.2	18
Pore Water Co (µg/L)	0.2	0.3	0.3	0.5	0.7	1.0	1.6	18
Pore Water Cr (µg/L)	0.5	0.5	0.6	1.1	5.6	9.9	14.2	18
Pore Water Ga (µg/L)	4.0	5.5	6.5	7.6	12.7	28.3	39.2	18
Pore Water Ni (µg/L)	0.7	0.7	0.9	1.7	5.0	7.3	129.0	18
Pore Water Pb (µg/L)	0.0	0.0	0.0	0.1	0.1	0.2	0.3	18
Pore Water Rb (µg/L)	0.2	0.6	1.1	1.7	2.9	3.1	4.5	18
Pore Water Zn (µg/L)	11.4	17.3	25.7	41.1	76.7	108.6	137.5	18
Sediment Water content (%)	20.1	58.1	66.7	82.1	88.6	92.4	96.0	38
Sediment organic (% LOI)	0.4	7.6	12.2	21.2	40.6	58.7	66.3	38
Sediment carbonate (% LOI)	0.6	3.1	4.8	7.4	14.0	40.0	77.1	38
Sediment inorganic (% LOI)	8.7	26.6	38.7	58.0	80.0	85.1	99.0	38
Sediment Fine organics (%)	49.0	69.6	75.0	87.0	91.0	96.4	138.0	37
Sediment Coarse organics (%)	0.0	4.6	9.0	15.0	25.0	30.4	52.0	37
Sediment Fine inorganics (%)	9.0	22.0	28.0	45.0	54.0	75.8	92.0	37
Sediment Coarse inorganics (%)	8.0	24.2	44.0	54.0	71.0	77.4	91.0	37
Sediment Total S (mg/g)	0.1	0.5	1.5	2.5	4.3	7.3	12.5	39
TS/TOC mg/g	1.8	7.4	15.0	23.1	42.5	61.0	165.1	39
Sediment AVS (µg/g)	1.2	24.2	40.0	93.7	248.3	839.0	4017.5	39
AVS/TOC mg/g	0.1	0.2	0.3	1.2	4.2	17.1	52.2	39
AVS/ Total S (%)	0.3%	0.9%	1.5%	4.6%	14.0%	40.9%	225.2%	39
Sediment Ca (µg/g)	777	4,495	8,374	19,343	58,980	149,316	297,257	39
Sediment Mg (µg/g)	162	1,215	1,901	3,608	5,550	8,564	16,232	39
Sediment Fe (µg/g)	1,298	1,584	2,324	5,555	9,977	17,447	50,389	39
Fe/AVS (µg/µg)	4.0	8.6	17.8	57.4	117.6	286.9	1240.0	39
Fe-AVS (µMol/g)	22.5	26.7	35.9	97.9	166.5	283.6	899.4	39
(Fe-AVS) / TOC (µMol) / mMol)	1.3	2.9	5.7	12.2	27.3	47.7	319.6	39
Sediment Al (µg/g)	203	517	831	1,908	2,710	4,345	5,163	39
Sediment Mn (µg/g)	46	113	216	431	725	1,187	3,815	39
Sediment Zn (µg/g)	4.9	17.6	26.7	36.7	50.8	73.0	104.0	39
Sediment Ni (µg/g)	0.8	1.4	2.5	4.9	8.9	11.1	16.1	39
Sediment Cr (µg/g)	0.6	1.1	1.6	2.4	3.7	5.3	11.3	39
Sediment As (µg/g)	0.4	1.0	1.5	2.2	2.9	3.4	11.9	39
Sediment Cu (µg/g)	0.7	2.4	4.4	6.5	9.7	13.3	22.7	39
Sediment Total-P (mg P/g)	0.2	0.4	0.5	0.7	0.8	1.1	1.5	39
TP/TOC mg/g	1.4	3.1	4.2	6.5	10.8	17.5	280.0	39
Sediment Exchangeable-P (mg P/g)	0.0	0.0	0.0	0.0	0.0	0.0	0.1	39
Sediment NAI-P (mg P/g)	0.0	0.0	0.0	0.1	0.1	0.2	1.2	39
Sediment Apatite-P (mg P/g)	0.0	0.1	0.1	0.2	0.2	0.3	0.4	39
Sediment Org-P (mg P/g)	0.1	0.1	0.2	0.3	0.5	0.7	1.0	38
Sediment Total-N (mg/g)	0.1	1.8	4.4	8.5	16.3	22.9	34.2	39
TN/TOC mg/g	43.0	57.3	75.4	88.8	100.5	108.2	125.7	39
Sediment TIC (%)	0.0	0.0	0.0	0.4	1.6	4.8	9.1	38
Sediment TOC (%)	0.1	2.7	5.5	10.2	20.1	26.9	35.6	39

Appendix D6. Summary statistics for the lake sites sampled in 2011 Pilot Survey (30 of the 39 sites in Data Set 1). In the plant rings at the 30 sample sites, 27 had wild rice present.

Parameter	min	10%	25%	50%	75%	90%	max	N
Date	8/19/2011	8/24/2011	8/30/2011	9/14/2011	9/21/2011	9/23/2011	9/29/2011	30
Latitude	44.1940	45.0163	45.6224	46.8275	47.2535	47.6639	47.8255	30
Longitude	-95.7404	-95.6706	-95.2207	-94.8323	-93.0695	-91.9418	93.3380	30
Wild rice cover in rings (%)	0.0	1.2	7.8	17.8	29.4	38.3	70.0	30
Floating leaf % cover	0.0	0.0	0.0	1.8	9.8	30.6	51.3	30
T-tube Transparency (cm)	8.0	44.6	77.0	101.0	101.0	101.0	101.0	25
surface water pH	6.5	6.9	7.2	7.5	7.9	8.4	8.7	27
surface water Temp (C)	11.7	12.8	14.6	18.6	22.0	23.0	24.1	27
surface water Conductance (µS/cm)	18.0	103.4	191.5	266.0	366.0	482.0	1082.0	27
surface water Ca (mg/L)	6.5	10.3	25.3	28.7	35.5	39.0	87.7	30
surface water Mg (mg/L)	3.2	5.2	11.4	17.3	26.5	34.1	95.4	30
surface water K (mg/L)	0.4	0.9	1.2	2.1	3.5	5.3	16.5	30
surface water Na (mg/L)	1.0	2.5	3.3	5.8	7.0	9.8	69.4	30
surface water Fe (µg/L)	6.3	9.1	14.2	57.7	199.7	1033.9	4739.9	30
surface water SO4 (mg SO4/L)	0.2	0.3	0.4	0.8	3.0	10.2	107.7	30
surface water Cl (mg/L)	0.5	0.8	1.2	6.7	14.6	20.6	29.7	30
surface water Alk (meq/L)	0.2	0.7	2.0	2.8	3.4	4.2	5.1	29
surface water TP (mg P/L)	0.0	0.0	0.0	0.0	0.0	0.1	0.3	30
surface water TN (mg N/L)	0.5	0.6	0.6	0.8	1.3	1.5	2.0	30
Surface Water NO3 (mg N/L)	0.000	0.002	0.003	0.004	0.006	0.009	0.780	30
Surface Water NH4 (mg N/L)	0.000	0.002	0.007	0.013	0.019	0.076	0.106	30
Surface Water DOC (mg C/L)	6.6	6.9	8.5	12.0	18.2	26.3	43.6	30
Surface Water SUVA Fe correct	1.0	1.1	1.4	1.9	2.5	3.0	3.8	30
Surface Water UV ABS 254 nm	0.1	0.1	0.1	0.2	0.5	0.7	2.0	30
Surface Water DO surface (mg/L)	2.1	5.7	6.3	7.9	9.0	9.7	10.5	27
pore water pH	5.5	5.9	6.4	6.5	6.7	6.9	7.5	29
pore water Total Sulfide (TS, mg S/L)	0.0	0.0	0.0	0.1	0.1	0.3	14.8	30
pore water H2S (% of TS)	25%	56%	67%	76%	82%	93%	97%	29
Free H2S (µg/L)	8.2	16.0	22.3	32.8	73.6	139.4	3710.0	29
pore water HS- (% of TS)	3%	7%	18%	24%	33%	44%	75%	29
pore water Cl (mg/L)	4.9	8.6	15.0	23.9	27.5	32.8	36.4	18
pore water DOC (mg C/L)	14.1	16.9	18.7	22.1	28.3	29.9	33.3	18
pore water Ca (mg/L)	24.5	29.7	38.6	50.7	65.9	77.1	80.8	18
pore water Mg (mg/L)	7.8	10.3	13.7	25.8	32.9	40.7	134.4	18
pore water K (mg/L)	0.3	0.4	0.9	2.4	4.7	6.9	26.7	18
pore water Na (mg/L)	0.6	2.2	3.7	4.8	7.2	10.3	92.0	18
pore water Fe (µg/L)	193	533	2,718	8,862	17,520	24,864	35,586	18
pore water Mn (µg/L)	253	423	719	1,094	1,689	5,019	16,725	18
pore water TP (mg/L)	0.02	0.08	0.24	0.55	1.67	2.70	3.19	18
pore water TN (mg/L)	0.96	1.29	3.50	6.73	11.06	15.15	17.89	18
pore water NH4 (mg N/L)	0.08	0.11	2.32	6.29	11.52	17.07	19.42	18
Pore Water NO3 (mg N/L)	0.00	0.02	0.02	0.03	0.03	0.04	0.04	18
Pore Water Al (µg/L)	20.0	29.7	33.2	44.0	52.7	66.9	89.4	18
Pore Water Ba (µg/L)	21.3	25.2	31.8	38.2	60.0	143.5	197.4	18
Pore Water Sr (µg/L)	66.7	100.5	117.9	134.2	202.7	244.3	511.3	18
Pore Water Ag (µg/L)	0.0	0.0	0.0	0.0	0.1	0.1	0.2	18
Pore Water As (µg/L)	0.6	0.6	0.8	1.4	2.2	4.1	6.6	18
Pore Water Cd (µg/L)	0.0	0.0	0.0	0.0	0.0	0.1	0.2	18
Pore Water Co (µg/L)	0.2	0.3	0.3	0.5	0.7	1.0	1.6	18
Pore Water Cr (µg/L)	0.5	0.5	0.6	1.1	5.6	9.9	14.2	18
Pore Water Ga (µg/L)	4.0	5.5	6.5	7.6	12.7	28.3	39.2	18
Pore Water Ni (µg/L)	0.7	0.7	0.9	1.7	5.0	7.3	129.0	18
Pore Water Pb (µg/L)	0.0	0.0	0.0	0.1	0.1	0.2	0.3	18
Pore Water Rb (µg/L)	0.2	0.6	1.1	1.7	2.9	3.1	4.5	18
Pore Water Zn (µg/L)	11.4	17.3	25.7	41.1	76.7	108.6	137.5	18
Sediment Water content (%)	36.8	63.0	72.7	85.8	89.6	93.1	96.0	29
Sediment organic (% LOI)	3.2	9.4	12.3	29.9	41.5	63.6	66.3	29
Sediment carbonate (% LOI)	2.8	3.4	4.8	8.8	14.5	40.1	77.1	29
Sediment inorganic (% LOI)	8.7	26.9	35.8	50.7	75.6	84.4	86.2	29
Sediment Fine organics (%)	49.0	69.7	75.8	84.0	91.0	92.6	98.0	28
Sediment Coarse organics (%)	2.0	7.0	9.8	16.0	24.3	30.3	52.0	28
Sediment Fine inorganics (%)	17.0	26.5	33.5	46.0	51.8	79.1	92.0	28
Sediment Coarse inorganics (%)	8.0	20.9	49.3	53.5	65.8	73.5	84.0	28
Sediment Total S (mg/g)	0.1	0.9	1.7	2.7	4.3	7.6	12.5	30
TS/TOC mg/g	1.8	9.5	15.8	22.2	38.5	66.6	165.1	30
Sediment AVS (µg/g)	11.3	24.4	50.2	95.4	249.1	744.3	4017.5	30
AVS/TOC mg/g	0.1	0.2	0.3	0.9	3.4	22.3	52.2	30
AVS/ Total S (%)	0.3%	0.8%	1.2%	4.7%	12.3%	51.0%	225.2%	30
Sediment Ca (µg/g)	2,899	7,747	9,477	23,497	62,538	148,390	297,257	30
Sediment Mg (µg/g)	747	1,407	1,922	3,954	5,714	7,834	16,232	30
Sediment Fe (µg/g)	1,298	1,596	2,205	4,715	9,384	18,322	50,389	30
Porewater Fe / Sediment Fe (%)	0.013	0.160	0.299	0.502	0.653	1.215	1.670	17
Fe/AVS (µg/µg)	4.0	8.7	16.2	45.1	114.7	241.2	537.8	30
Fe-AVS (µMol/g)	22.5	26.6	34.1	76.8	159.7	266.0	899.4	30
(Fe-AVS) / TOC (µMol) / mMol)	1.3	2.8	5.0	9.6	20.6	46.5	57.7	30
Sediment Al (µg/g)	203	579	847	1,811	2,685	4,332	5,163	30
Sediment Mn (µg/g)	81	116	201	415	765	1,371	3,815	30
Sediment Zn (µg/g)	5.4	22.8	26.6	36.6	50.3	67.7	104.0	30
Sediment Ni (µg/g)	0.8	2.1	2.6	4.3	8.3	11.0	16.1	30
Sediment Cr (µg/g)	0.6	1.1	1.8	2.3	3.5	4.1	11.0	30
Sediment As (µg/g)	0.5	1.0	1.4	2.2	3.0	4.4	11.9	30
Sediment Cu (µg/g)	0.7	2.4	4.5	6.3	9.7	13.1	18.7	30
Sediment Total-P (mg P/g)	0.2	0.4	0.5	0.7	0.9	1.1	1.5	30
TP/TOC mg/g	1.4	3.1	4.2	6.4	9.9	13.7	22.9	30
Sediment Exchangeable-P (mg P/g)	0.0	0.0	0.0	0.0	0.0	0.1	0.1	30
Sediment NAI-P (mg P/g)	0.0	0.0	0.0	0.1	0.1	0.3	1.2	30
Sediment Apatite-P (mg P/g)	0.0	0.1	0.1	0.1	0.2	0.3	0.4	30
Sediment Org-P (mg P/g)	0.1	0.1	0.2	0.3	0.6	0.7	1.0	30
Sediment Total-N (mg/g)	1.3	2.9	4.2	10.5	17.1	24.9	34.2	30
TN/TOC mg/g	43.0	61.8	80.0	90.5	100.6	108.1	114.5	30
Sediment TIC (%)	0.0	0.0	0.0	0.5	1.8	5.2	9.1	29
Sediment TOC (%)	1.8	3.7	5.3	12.2	20.7	26.9	35.6	30

Appendix D7. Summary statistics for the stream sites sampled in the 2011 Pilot Survey (9 of the 39 sites in Data Set 1). In the plant rings at the 9 sample sites, 8 had wild rice present.

Parameter	min	25%	50%	75%	max	N
Date	8/30/2011	8/31/2011	9/1/2011	9/1/2011	9/8/2011	9
Latitude	47.2379	47.3793	47.4015	47.5212	47.7325	9
Longitude	-95.4926	-93.7196	-92.4235	-92.3468	-91.9355	9
Wild rice cover in rings (%)	0	18.8	30	50	71.3	9
Floating leaf % cover	0	0	1.5	7.5	11.3	9
T-tube Transparency (cm)	62	98	101	101	101	7
surface water pH	6.4	6.5	6.8	7.2	7.8	9
surface water Temp (C)	18.1	19	19.6	21.3	22.2	9
surface water Conductance (µS/cm)	11	191	251	323	343	9
surface water Ca (mg/L)	4.9	17.5	22.4	28.1	44.7	9
surface water Mg (mg/L)	4.4	11.8	14.7	18.6	28.3	9
surface water K (mg/L)	0.4	0.6	1.8	1.9	2.3	9
surface water Na (mg/L)	1.6	2.8	5.2	7.3	9.9	9
surface water Fe (µg/L)	75.3	94.8	358.1	1132.3	1344.2	9
surface water SO4 (mg SO4/L)	0.6	1.1	3.7	8.3	24.5	9
surface water Cl (mg/L)	0.5	1.2	3.9	8	15.6	9
surface water Alk (meq/L)	0.2	0.9	1.3	2.7	3.1	9
surface water TP (mg P/L)	0.016	0.027	0.029	0.038	0.050	9
surface water TN (mg N/L)	0.5	0.8	0.9	1.1	1.4	9
Surface Water NO3 (mg N/L)	0.000	0.010	0.010	0.020	0.040	9
Surface Water NH4 (mg N/L)	0.010	0.010	0.010	0.020	0.070	9
Surface Water DOC (mg C/L)	9.8	16.1	23.5	27.7	36.2	9
Surface Water SUVA Fe correct	1.9	2	2.2	3.1	3.5	9
Surface Water UV ABS 254 nm	0.2	0.5	0.5	0.8	1.1	9
Surface Water DO surface (mg/L)	3.9	5.1	6.8	7.1	7.9	9
pore water pH	6.0	6.6	6.6	6.8	7.2	9
pore water Total Sulfide (TS, mg S/L)	0.025	0.04	0.053	0.07	0.097	9
pore water H2S (% of TS)	42%	65%	72%	73%	91%	9
Free H2S (µg/L)	14.25	35.88	38.16	45.5	54	9
pore water HS- (% of TS)	9%	27%	28%	35%	58%	9
Sediment Water content (%)	20.1	64.7	71.3	82.3	85.9	9
Sediment organic (% LOI)	0.4	12.2	17.7	33.1	53.9	9
Sediment carbonate (% LOI)	0.6	4.8	6.4	8.3	41.4	9
Sediment inorganic (% LOI)	22	60.6	75	81.4	99	9
Sediment Fine organics (%)	66	72	91	97	138	9
Sediment Coarse organics (%)	0	4	13	28	33	9
Sediment Fine inorganics (%)	9	22	27	56	75	9
Sediment Coarse inorganics (%)	26	42	58	74	91	9
Sediment Total S (mg/g)	0.06	0.87	2.19	3.77	7.28	9
TS/TOC mg/g	5.18	12.4	41.62	43.12	60.42	9
Sediment AVS (µg/g)	1.2	39.2	82.6	205.3	2797	9
AVS/TOC mg/g	0.11	0.58	1.2	6.18	15.99	9
AVS/ Total S (%)	1%	3%	4%	15%	38%	9
Sediment Ca (µg/g)	777	4,847	6,493	22,682	160,172	9
Sediment Mg (µg/g)	162	1,645	2,263	4,943	11,016	9
Sediment Fe (µg/g)	1,488	2,364	8,667	11,026	22,677	9
Fe/AVS (µg/µg)	8.1	53.7	60.3	120.9	1240	9
Fe-AVS (µMol/g)	26.6	41.1	143.5	191	318.8	9
(Fe-AVS) / TOC (µMol) / mMol)	2.7	7.3	26.2	30.3	319.6	9
Sediment Al (µg/g)	427	554	2,005	3,721	4,470	9
Sediment Mn (µg/g)	46	322	561	720	838	9
Sediment Zn (µg/g)	4.9	27.2	37.3	65.9	79.7	9
Sediment Ni (µg/g)	1.11	2.49	7.65	9.07	12.87	9
Sediment Cr (µg/g)	0.63	1.17	2.75	4.71	11.26	9
Sediment As (µg/g)	0.44	1.71	2.04	2.46	3.15	9
Sediment Cu (µg/g)	0.69	2.96	7.97	9.37	22.65	9
Sediment Total-P (mg P/g)	0.28	0.48	0.66	0.67	0.78	9
TP/TOC mg/g	2.2	4.5	7	11.3	280	9
Sediment Exchangeable-P (mg P/g)	0.01	0.01	0.01	0.02	0.03	9
Sediment NAI-P (mg P/g)	0.02	0.04	0.08	0.09	0.22	9
Sediment Apatite-P (mg P/g)	0.08	0.18	0.22	0.31	0.4	9
Sediment Org-P (mg P/g)	0.09	0.2	0.24	0.41	0.49	8
Sediment Total-N (mg/g)	0.1	4.9	7	9.4	18.1	9
TN/TOC mg/g	52	64.2	80.7	100	125.7	9
Sediment TIC (%)	0	0	0.01	1.01	4.64	9
Sediment TOC (%)	0.1	6.07	6.76	17.49	30.4	9

Appendix D8. Summary statistics for surface waters selected parameters analyzed during both the 2011 Pilot Survey (Class 1 samples) and the 2012-2013 survey (Class 4 samples).

Sites	Parameter	min	10%	25%	50%	75%	90%	max	N
Lakes Class 1	surface water SO4 (mg SO4/L)	0.2	0.3	0.4	0.8	3.0	10.2	107.7	30
Lakes Class 4	surface water SO4 (mg SO4/L)	0.6	1.2	2.5	4.1	14.5	29.3	335.0	82
Streams Class 1	surface water SO4 (mg SO4/L)	0.6		1.1	3.7	8.3		24.5	9
Streams Class 4	surface water SO4 (mg SO4/L)	0.6	1.3	2.5	10.1	17.9	38.1	838.0	30
Paddies Class 4	surface water SO4 (mg SO4/L)	0.3		1.0	7.1	10.4		279.0	7
Lakes Class 1	surface water Alk (meq/L)	0.2	0.7	2.0	2.8	3.4	4.2	5.1	29
Lakes Class 4	surface water Alk (meq/L)	0.3	1.3	2.2	2.8	3.4	4.0	6.2	82
Streams Class 1	surface water Alk (meq/L)	0.2		0.9	1.3	2.7		3.1	9
Streams Class 4	surface water Alk (meq/L)	0.6	1.5	1.8	2.6	2.8	4.6	8.2	30
Paddies Class 4	surface water Alk (meq/L)	1.3		2.5	4.2	5.3		9.2	7
Lakes Class 1	surface water Ca (mg/L)	6.5	10.3	25.3	28.7	35.5	39.0	87.7	30
Lakes Class 4	surface water Ca (mg/L)	6.6	16.0	22.0	29.0	37.0	42.0	150.0	81
Streams Class 1	surface water Ca (mg/L)	4.9		17.5	22.4	28.1		44.7	9
Streams Class 4	surface water Ca (mg/L)	8.8	18.8	25.3	34.0	39.0	49.2	100.0	30
Paddies Class 4	surface water Ca (mg/L)	21.0		40.5	51.0	83.0		130.0	7
Lakes Class 1	surface water Cl (mg/L)	0.5	0.8	1.2	6.7	14.6	20.6	29.7	30
Lakes Class 4	surface water Cl (mg/L)	0.3	1.5	4.0	8.0	15.2	22.0	77.1	82
Streams Class 1	surface water Cl (mg/L)	0.5		1.2	3.9	8		15.6	9
Streams Class 4	surface water Cl (mg/L)	0.4	2.3	3.4	6.6	16.2	21.3	33.0	30
Paddies Class 4	surface water Cl (mg/L)	0.3		3.4	6.8	12.0		39.8	7
Lakes Class 4	Surface Water Color (Pt-Co units)	4	15	25	52	82	200	450	82
Streams Class 4	Surface Water Color (Pt-Co units)	10	20	42	68	150	321	520	30
Paddies Class 4	Surface Water Color (Pt-Co units)	67		158	230	292		383	7
Lakes Class 1	surface water Conductance (µS/cm)	18	103	192	266	366	482	1082	27
Lakes Class 4	surface water Conductance (µS/cm)	50	133	230	306	359	440	1136	82
Streams Class 1	surface water Conductance (µS/cm)	11		191	251	323		343	9
Streams Class 4	surface water Conductance (µS/cm)	75	191	226	271	344	493	1789	30
Paddies Class 4	surface water Conductance (µS/cm)	132		332	467	693		927	7
Lakes Class 1	Surface Water DOC (mg C/L)	6.6	6.9	8.5	12.0	18.2	26.3	43.6	30
Streams Class 1	Surface Water DOC (mg C/L)	9.8		16.1	23.5	27.7		36.2	9
Lakes Class 1	surface water Fe (µg/L)	6	9	14	58	200	1,034	4,740	30
Lakes Class 4	surface water Fe (µg/L)	<5	<5	<5	<5	17	724	4,120	82
Streams Class 1	surface water Fe (µg/L)	75		95	358	1,132		1,344	9
Streams Class 4	surface water Fe (µg/L)	<5	<5	6	29	652	1,259	3,400	30
Paddies Class 4	surface water Fe (µg/L)	32		66	147	387		428	7
Lakes Class 1	surface water K (mg/L)	0.4	0.9	1.2	2.1	3.5	5.3	16.5	30
Lakes Class 4	surface water K (mg/L)	0.5	0.7	1.6	2.4	3.4	5.0	18.3	76
Streams Class 1	surface water K (mg/L)	0.4		0.6	1.8	1.9		2.3	9
Streams Class 4	surface water K (mg/L)	0.5	1.0	1.4	1.7	2.6	4.0	11.1	30
Paddies Class 4	surface water K (mg/L)	1.9		3.5	5.4	10.0		13.3	6
Lakes Class 1	surface water Mg (mg/L)	3.2	5.2	11.4	17.3	26.5	34.1	95.4	30
Lakes Class 4	surface water Mg (mg/L)	2.8	6.7	11.3	19.9	27.0	34.2	107.0	81
Streams Class 1	surface water Mg (mg/L)	4.4		11.8	14.7	18.6		28.3	9
Streams Class 4	surface water Mg (mg/L)	4.7	8.7	11.5	16.0	22.0	28.5	266.0	30
Paddies Class 4	surface water Mg (mg/L)	5.0		18.7	30.3	37.4		74.8	7
Lakes Class 1	surface water Na (mg/L)	1.0	2.5	3.3	5.8	7.0	9.8	69.4	30
Lakes Class 4	surface water Na (mg/L)	1.2	2.5	3.6	5.4	8.3	10.8	76.3	81
Streams Class 1	surface water Na (mg/L)	1.6		2.8	5.2	7.3		9.9	9
Streams Class 4	surface water Na (mg/L)	1.7	3.5	4.5	6.7	12.0	18.3	39.5	30
Paddies Class 4	surface water Na (mg/L)	1.9		3.3	5.5	7.1		23.9	7
Lakes Class 1	Surface Water NO3 (mg N/L)	<0.001	0.002	0.003	0.004	0.006	0.009	0.780	30
Streams Class 1	Surface Water NO3 (mg N/L)	<0.001		0.010	0.010	0.020		0.040	9
Lakes Class 1	surface water pH	6.5	6.9	7.2	7.5	7.9	8.4	8.7	27
Lakes Class 4	surface water pH	5.9	7.1	7.4	8.3	8.7	9.4	9.8	81
Streams Class 1	surface water pH	6.4		6.5	6.8	7.2		7.8	9
Streams Class 4	surface water pH	6.9	7.1	7.3	7.6	7.9	8.2	9.2	30
Paddies Class 4	surface water pH	6.4		7.2	7.3	8.0		8.6	7
Lakes Class 1	surface water Temp (C)	11.7	12.8	14.6	18.6	22.0	23.0	24.1	27
Lakes Class 4	surface water Temp (C)	11.3	16.0	20.2	23.8	27.1	29.5	32.9	82
Streams Class 1	surface water Temp (C)	18.1		19	19.6	21.3		22.2	9
Streams Class 4	surface water Temp (C)	15.0	16.5	19.5	21.9	24.3	25.7	27.6	30
Paddies Class 4	surface water Temp (C)	21.4		22.6	23.7	24.2		27.9	7
Lakes Class 1	surface water TN (mg N/L)	0.52	0.56	0.64	0.78	1.27	1.53	1.97	30
Lakes Class 4	surface water TN (mg N/L)	0.24	0.48	0.62	0.83	1.25	1.84	3.15	82
Streams Class 1	surface water TN (mg N/L)	0.50		0.80	0.90	1.10		1.40	9
Streams Class 4	surface water TN (mg N/L)	0.38	0.53	0.65	0.76	0.98	1.40	1.98	30
Paddies Class 4	surface water TN (mg N/L)	0.69		2.05	3.25	3.65		5.05	7
Lakes Class 1	surface water TP (mg P/L)	0.013	0.017	0.023	0.031	0.042	0.124	0.279	30
Lakes Class 4	surface water TP (mg P/L)	<0.01	0.005	0.011	0.021	0.042	0.105	0.431	82
Streams Class 1	surface water TP (mg P/L)	0.016		0.027	0.029	0.038		0.050	9
Streams Class 4	surface water TP (mg P/L)	0.005	0.012	0.018	0.032	0.079	0.136	0.391	30
Paddies Class 4	surface water TP (mg P/L)	0.021		0.068	0.093	0.937		1.580	7
Lakes Class 1	T-tube Transparency (cm)	8	45	77	101	101	101	101	25
Lakes Class 4	T-tube Transparency (cm)	3	26	60	101	101	101	101	82
Streams Class 1	T-tube Transparency (cm)	62		98	101	101		101	7
Streams Class 4	T-tube Transparency (cm)	26	43	60	101	101	101	101	30
Paddies Class 4	T-tube Transparency (cm)	23		36	68	84		101	7
Lakes Class 1	Wild rice cover in rings (%)	0.0	1.2	7.8	17.8	29.4	38.3	70.0	30
Lakes Class 4	Wild rice cover in rings (%)	0.0	0.0	0.0	1.2	16.0	34.8	70.0	82
Streams Class 1	Wild rice cover in rings (%)	0.0		18.8	30.0	50.0		71.3	9
Streams Class 4	Wild rice cover in rings (%)	0.0	0.0	1.6	18.2	40.1	52.3	61.3	30
Paddies Class 4	Wild rice cover in rings (%)	4.3		24.4	33.8	45.3		80.0	7
Lakes Class 4	Wild rice stems in rings (stems/m2)	0.0	0.0	0.0	3.8	40.1	102.2	144.8	81
Streams Class 4	Wild rice stems in rings (stems/m2)	0.0	0.0	3.7	37.1	64.7	80.4	148.3	30
Paddies Class 4	Wild rice stems in rings (stems/m2)	8.3		52.7	58.9	86.6		134.3	7

Appendix D9. Summary statistics for selected porewater parameters analyzed during both the 2011 Pilot Survey (Class 1 samples) and the 2012-2013 survey (Class 4 samples).

Sites	Parameter	min	10%	25%	50%	75%	90%	max	N
Lakes Class 1	Porewater DOC (mg C/L)	14.1	16.9	18.7	22.1	28.3	29.9	33.3	18
Lakes Class 4	Porewater DOC (mg C/L)	6.5	13.2	16.0	22.4	29.0	37.2	99.8	82
Streams Class 4	Porewater DOC (mg C/L)	6.0	11.2	15.5	20.7	30.4	43.4	52.4	30
Paddies Class 4	Porewater DOC (mg C/L)	67.1		71.1	90.4	117.5		129.0	7
Lakes Class 1	Porewater Fe (µg/L)	193	533	2,718	8,862	17,520	24,864	35,586	18
Lakes Class 4	Porewater Fe (µg/L)	<10	86	986	4,270	12,500	20,100	84,600	81
Streams Class 4	Porewater Fe (µg/L)	1,510	2,686	5,063	9,530	13,275	25,280	33,700	30
Paddies Class 4	Porewater Fe (µg/L)	1,060		1,360	1,650	2,660		4,300	7
Lakes Class 1	Porewater Fe / Sediment Fe (%)	0.013%	0.160%	0.299%	0.502%	0.653%	1.215%	1.670%	17
Lakes Class 4	Porewater Fe / Sediment Fe (%)	0.001%	0.013%	0.118%	0.417%	0.784%	1.400%	2.951%	81
Streams Class 4	Porewater Fe / Sediment Fe (%)	0.009%	0.074%	0.107%	0.157%	0.362%	0.602%	0.792%	30
Paddies Class 4	Porewater Fe / Sediment Fe (%)	0.029%		0.086%	0.152%	0.211%		0.254%	7
Lakes Class 1	Porewater Free H2S (µg/L)	8.2	16.0	22.3	32.8	73.6	139.4	3710.0	29
Lakes Class 4	Porewater Free H2S (µg/L)	0.6	16.4	27.3	71.9	144.8	483.3	5120.0	81
Streams Class 1	Porewater Free H2S (µg/L)	14.3		35.9	38.2	45.5		54.0	9
Streams Class 4	Porewater Free H2S (µg/L)	2.5	14.1	20.7	37.7	56.0	75.8	169.0	29
Paddies Class 4	Porewater Free H2S (µg/L)	20.7		92.3	168.8	440.5		607.6	7
Lakes Class 1	Porewater H2S (% of TS)	25%	56%	67%	76%	82%	93%	97%	29
Lakes Class 4	Porewater H2S (% of TS)	8%	27%	47%	66%	76%	84%	94%	81
Streams Class 1	Porewater H2S (% of TS)	42%		65%	72%	73%		91%	9
Streams Class 4	Porewater H2S (% of TS)	11%	28%	34%	52%	62%	70%	79%	29
Paddies Class 4	Porewater H2S (% of TS)	18%		85%	87%	93%		98%	7
Lakes Class 1	Porewater HS- (% of TS)	3%	7%	18%	24%	33%	44%	75%	29
Lakes Class 4	Porewater HS- (% of TS)	6%	16%	24%	34%	53%	73%	92%	81
Streams Class 1	Porewater HS- (% of TS)	9%		27%	28%	35%		58%	9
Streams Class 4	Porewater HS- (% of TS)	21%	30%	38%	48%	66%	72%	89%	29
Paddies Class 4	Porewater HS- (% of TS)	2%		8%	13%	15%		82%	7
Lakes Class 1	Porewater K (mg/L)	0.3	0.4	0.9	2.4	4.7	6.9	26.7	18
Lakes Class 4	Porewater K (mg/L)	0.3	0.3	1.4	4.0	6.6	10.6	25.1	81
Streams Class 4	Porewater K (mg/L)	0.3	0.6	1.2	2.0	3.0	4.2	6.8	30
Paddies Class 4	Porewater K (mg/L)	7.7		11.8	16.1	18.8		29.5	7
Lakes Class 1	Porewater NH4 (mg N/L)	0.08	0.11	2.32	6.29	11.52	17.07	19.42	18
Lakes Class 4	Porewater NH4 (mg N/L)	0.06	0.13	0.25	3.05	8.25	12.00	26.00	82
Streams Class 4	Porewater NH4 (mg N/L)	0.05	0.13	0.27	1.05	2.55	3.60	6.60	30
Paddies Class 4	Porewater NH4 (mg N/L)	0.19		1.03	2.80	4.65		6.50	7
Lakes Class 1	Porewater pH	5.5	5.9	6.4	6.5	6.7	6.9	7.5	29
Lakes Class 4	Porewater pH	5.8	6.3	6.5	6.7	7.1	7.5	8.1	81
Streams Class 1	Porewater pH	6.0		6.6	6.6	6.8		7.2	9
Streams Class 4	Porewater pH	6.4	6.7	6.8	7.0	7.3	7.4	7.9	29
Paddies Class 4	Porewater pH	5.4		5.9	6.2	6.3		7.7	7
Lakes Class 4	Porewater Si (mg/L)	19.00	33.06	40.25	52.55	65.65	74.44	97.80	82
Streams Class 4	Porewater Si (mg/L)	21.90	30.91	36.85	41.65	55.05	59.44	69.80	30
Paddies Class 4	Porewater Si (mg/L)	16.80		37.55	44.30	64.25		75.00	7
Lakes Class 1	Porewater TN (mg/L)	0.96	1.29	3.50	6.73	11.06	15.15	17.89	18
Lakes Class 4	Porewater TN (mg/L)	0.49	1.16	2.08	5.05	8.23	14.05	30.05	82
Streams Class 4	Porewater TN (mg/L)	0.39	1.23	1.35	2.25	2.95	4.11	6.85	30
Paddies Class 4	Porewater TN (mg/L)	4.05		5.55	8.15	10.00		13.05	7
Lakes Class 1	Porewater Total Sulfide (TS, mg S/L)	0.010	0.020	0.030	0.055	0.104	0.307	14.840	30
Lakes Class 4	Porewater Total Sulfide (TS, mg S/L)	<.0011	0.031	0.069	0.118	0.266	1.355	16.000	82
Streams Class 1	Porewater Total Sulfide (TS, mg S/L)	0.025		0.04	0.053	0.07		0.097	9
Streams Class 4	Porewater Total Sulfide (TS, mg S/L)	0.022	0.044	0.058	0.073	0.110	0.154	0.256	30
Paddies Class 4	Porewater Total Sulfide (TS, mg S/L)	0.031		0.142	0.194	0.488		0.732	7
Lakes Class 1	Porewater TP (mg/L)	0.02	0.08	0.24	0.55	1.67	2.70	3.19	18.00
Lakes Class 4	Porewater TP (mg/L)	<.01	0.02	0.07	0.37	1.10	2.47	4.79	82.00
Streams Class 4	Porewater TP (mg/L)	<.01	0.20	0.37	0.70	1.50	2.18	4.11	30.00
Paddies Class 4	Porewater TP (mg/L)	0.48		0.96	2.68	4.65		5.62	7.00
Lakes Class 1	Porewater Zn (µg/L)	11.4	17.3	25.7	41.1	76.7	108.6	137.5	18
Lakes Class 4	Porewater Zn (µg/L)	3.8	<10	<10	<10	10.6	16.9	29.5	81
Streams Class 4	Porewater Zn (µg/L)	4.8	<10	<10	10.5	16.3	21.2	46.6	30
Paddies Class 4	Porewater Zn (µg/L)	<10		<10	11.7	17.5		37.1	7

Appendix D10. Summary statistics for selected sediment parameters analyzed during both the 2011 Pilot Survey (Class 1 samples) and the 2012-2013 survey (Class 4 samples).

Sites	Parameter	min	10%	25%	50%	75%	90%	max	N
Lakes Class 1	Sediment AVS (µg/g)	11	24	50	95	249	744	4018	30
Lakes Class 4	Sediment AVS (µg/g)	20	92	175	306	843	2084	9170	82
Streams Class 1	Sediment AVS (µg/g)	1		39	83	205		2797	9
Streams Class 4	Sediment AVS (µg/g)	70	80	135	270	530	1309	3370	30
Paddies Class 4	Sediment AVS (µg/g)	50		65	109	185		300	7
Lakes Class 1	Sediment AVS/ Total S (%)	0.3%	0.8%	1.2%	4.7%	12.3%	51.0%	225.2%	30
Lakes Class 4	Sediment AVS/ Total S (%)	1.1%	2.2%	4.2%	13.3%	22.8%	57.4%	145.5%	82
Streams Class 1	Sediment AVS/ Total S (%)	1.0%		3.0%	4.0%	15.0%		38.0%	9
Streams Class 4	Sediment AVS/ Total S (%)	1.9%	5.8%	21.4%	39.7%	66.8%	96.5%	100.8%	30
Paddies Class 4	Sediment AVS/ Total S (%)	1.2%		1.8%	2.5%	4.0%		6.6%	7
Lakes Class 1	Sediment AVS/TOC mg/g	0.1	0.2	0.3	0.9	3.4	22.3	52.2	30
Lakes Class 4	Sediment AVS/TOC mg/g	0.2	0.6	1.2	3.4	12.1	27.6	192.1	82
Streams Class 1	Sediment AVS/TOC mg/g	0.1		0.6	1.2	6.2		16.0	9
Streams Class 4	Sediment AVS/TOC mg/g	0.4	1.1	4.7	11.8	29.4	58.0	366.4	30
Paddies Class 4	Sediment AVS/TOC mg/g	0.2		0.3	0.6	0.8		1.1	7
Lakes Class 1	Sediment Cu (µg/g)	0.68	2.39	4.50	6.31	9.68	13.09	18.74	30
Lakes Class 4	Sediment Cu (µg/g)	0.82	2.71	4.00	6.38	10.72	16.33	25.69	82
Streams Class 1	Sediment Cu (µg/g)	0.69		2.96	7.97	9.37		22.65	9
Streams Class 4	Sediment Cu (µg/g)	1.36	1.85	3.15	5.31	10.53	18.33	33.48	30
Paddies Class 4	Sediment Cu (µg/g)	2.45		5.62	6.15	8.21		11.79	7
Lakes Class 1	Sediment Fe (µg/g)	1,298	1,596	2,205	4,715	9,384	18,322	50,389	30
Lakes Class 4	Sediment Fe (µg/g)	895	1,740	2,321	4,300	9,517	14,916	83,421	82
Streams Class 1	Sediment Fe (µg/g)	1,488		2,364	8,667	11,026		22,677	9
Streams Class 4	Sediment Fe (µg/g)	1,974	2,821	3,350	6,310	9,257	14,121	29,463	30
Paddies Class 4	Sediment Fe (µg/g)	3,242		3,326	4,673	5,290		7,874	7
Lakes Class 1	Sediment Fe/AVS (µg/µg)	4.0	8.7	16.2	45.1	114.7	241.2	537.8	30
Lakes Class 4	Sediment Fe/AVS (µg/µg)	1.6	3.6	5.4	11.3	27.4	62.6	439.1	82
Streams Class 1	Sediment Fe/AVS (µg/µg)	8.1		53.7	60.3	120.9		1240	9
Streams Class 4	Sediment Fe/AVS (µg/µg)	3.4	8.0	10.9	21.1	34.0	54.8	95.2	30
Paddies Class 4	Sediment Fe/AVS (µg/µg)	16.0		25.9	42.9	55.9		131.2	7
Lakes Class 1	Sediment organic (% LOI)	3.2	9.4	12.3	29.9	41.5	63.6	66.3	29
Lakes Class 4	Sediment organic (% LOI)	1.1	4.4	12.4	26.2	45.0	54.5	63.0	82
Streams Class 1	Sediment organic (% LOI)	0.4		12.2	17.7	33.1		53.9	9
Streams Class 4	Sediment organic (% LOI)	1.1	2.0	3.4	8.5	16.5	28.2	50.2	30
Paddies Class 4	Sediment organic (% LOI)	16.1		38.6	52.2	65.5		81.1	7
Lakes Class 1	Sediment TN/TOC mg/g	43.0	61.8	80.0	90.5	100.6	108.1	114.5	30
Lakes Class 4	Sediment TN/TOC mg/g	9.0	66.0	78.0	89.2	95.1	106.5	156.6	81
Streams Class 1	Sediment TN/TOC mg/g	52.0		64.2	80.7	100.0		125.7	9
Streams Class 4	Sediment TN/TOC mg/g	7.6	51.5	59.8	72.8	86.1	109.1	445.5	30
Paddies Class 4	Sediment TN/TOC mg/g	41.8		62.7	74.2	81.0		85.7	7
Lakes Class 1	Sediment TOC (%)	1.76	3.66	5.31	12.15	20.72	26.86	35.55	30
Lakes Class 4	Sediment TOC (%)	0.43	1.78	5.83	13.87	22.03	29.38	33.30	82
Streams Class 1	Sediment TOC (%)	0.10		6.07	6.76	17.49		30.40	9
Streams Class 4	Sediment TOC (%)	0.11	0.63	1.53	3.77	8.90	15.20	27.16	30
Paddies Class 4	Sediment TOC (%)	9.75		19.15	28.09	34.85		44.21	7
Lakes Class 1	Sediment Total S (mg/g)	0.11	0.92	1.69	2.65	4.33	7.57	12.52	30
Lakes Class 4	Sediment Total S (mg/g)	0.13	0.77	1.74	4.31	7.78	11.34	45.38	82
Streams Class 1	Sediment Total S (mg/g)	0.06		0.87	2.19	3.77		7.28	9
Streams Class 4	Sediment Total S (mg/g)	0.18	0.26	0.38	1.06	2.35	4.00	7.93	30
Paddies Class 4	Sediment Total S (mg/g)	1.99		3.35	3.77	6.07		8.17	7
Lakes Class 1	Sediment Total-N (mg/g)	1.30	2.89	4.18	10.45	17.08	24.90	34.20	30
Lakes Class 4	Sediment Total-N (mg/g)	0.40	1.60	5.10	11.10	18.00	23.15	32.10	81
Streams Class 1	Sediment Total-N (mg/g)	0.10		4.90	7.00	9.40		18.10	9
Streams Class 4	Sediment Total-N (mg/g)	0.36	0.50	0.92	2.50	4.64	11.62	20.90	30
Paddies Class 4	Sediment Total-N (mg/g)	7.60		16.25	18.50	20.15		23.60	7
Lakes Class 1	Sediment Total-P (mg P/g)	0.20	0.40	0.48	0.70	0.86	1.10	1.49	30
Lakes Class 4	Sediment Total-P (mg P/g)	0.13	0.33	0.49	0.79	0.95	1.22	2.18	82
Streams Class 1	Sediment Total-P (mg P/g)	0.28		0.48	0.66	0.67		0.78	9
Streams Class 4	Sediment Total-P (mg P/g)	0.24	0.29	0.38	0.51	0.74	0.86	0.94	30
Paddies Class 4	Sediment Total-P (mg P/g)	0.34		0.55	0.75	0.80		1.11	7
Lakes Class 1	Sediment TP/TOC mg/g	1.4	3.1	4.2	6.4	9.9	13.7	22.9	30
Lakes Class 4	Sediment TP/TOC mg/g	1.8	2.9	4.2	6.0	10.3	18.8	44.0	82
Streams Class 1	Sediment TP/TOC mg/g	2.2		4.5	7.0	11.3		280.0	9
Streams Class 4	Sediment TP/TOC mg/g	2.4	4.1	7.6	18.2	30.8	57.0	254.5	30
Paddies Class 4	Sediment TP/TOC mg/g	0.8		2.7	3.0	3.7		4.6	7
Lakes Class 1	Sediment TS/TOC mg/g	1.8	9.5	15.8	22.2	38.5	66.6	165.1	30
Lakes Class 4	Sediment TS/TOC mg/g	5.7	12.3	19.2	31.0	55.1	99.6	589.4	82
Streams Class 1	Sediment TS/TOC mg/g	5.2		12.4	41.6	43.1		60.4	9
Streams Class 4	Sediment TS/TOC mg/g	3.7	13.0	20.6	32.9	55.0	92.1	363.6	30
Paddies Class 4	Sediment TS/TOC mg/g	8.0		13.4	16.7	23.0		36.7	7
Lakes Class 1	Sediment Water content (%)	36.80	63.00	72.70	85.80	89.60	93.08	96.00	29
Lakes Class 4	Sediment Water content (%)	14.70	48.19	69.05	85.05	90.75	92.69	95.40	82
Streams Class 1	Sediment Water content (%)	20.10		64.70	71.30	82.30		85.90	9
Streams Class 4	Sediment Water content (%)	12.50	27.38	35.25	57.30	71.15	83.53	89.60	30
Paddies Class 4	Sediment Water content (%)	46.90		68.35	77.50	81.05		83.90	7
Lakes Class 1	Sediment Zn (µg/g)	5.4	22.8	26.6	36.6	50.3	67.7	104.0	30
Lakes Class 4	Sediment Zn (µg/g)	3.5	9.9	18.0	28.7	55.6	88.5	256.2	82
Streams Class 1	Sediment Zn (µg/g)	4.9		27.2	37.3	65.9		79.7	9
Streams Class 4	Sediment Zn (µg/g)	7.2	10.7	16.4	32.7	51.8	77.4	109.5	30
Paddies Class 4	Sediment Zn (µg/g)	10.8		15.7	24.3	33.4		43.0	7

Appendix E. Spearman Correlation Coefficients for Survey Data Sets

Appendix E1. Correlation coefficients for selected parameters analyzed in the 2012-2013 field survey (Data Set 4; consists of one site visit to each of 119 different sites, including 82 lakes, 30 streams, and 7 cultivated paddies).

All sites in the 2012-2013 Survey (N=119) Spearman Correlation Coefficients (rho) P<0.05 for |rho| > 0.187	Latitude	Longitude	Wild rice % cover in ring	Wild rice ave # stems/m2	Floating leaf % cover in ring	Water depth	T tube transparency	Surface water Ca	Surface water Mg	Surface water K	Surface water Fe	Surface water SO4	Surface water alkalinity	Surface water color (Pt Co units)	Porewater pH	Porewater sulfide	Porewater free H2S	Porewater DOC	Porewater Ca	Porewater Mg	Porewater K	Porewater Fe	Porewater silica	Sediment % water	Sediment % organic (LOI)	Sediment TS/TOC	Sediment AVS/TOC	Sediment Fe	Sediment Fe/AVS	Sediment Fe-AVS	Sediment TP/TOC	Sediment TN/TOC	Sediment TOC
Latitude		-0.09	0.22	0.22	-0.33	-0.45	0.05	0.01	-0.06	-0.19	0.25	0.05	-0.05	0.16	-0.03	0.03	-0.03	0.15	-0.15	-0.12	-0.07	0.06	-0.17	0.06	0.23	-0.08	-0.22	0.11	0.17	0.15	-0.28	-0.44	0.24
Longitude	-0.09		-0.08	-0.19	0.39	0.06	-0.15	-0.20	-0.60	-0.43	0.47	0.13	-0.62	0.43	-0.04	-0.25	-0.20	0.03	-0.47	-0.51	-0.39	0.44	-0.26	0.01	-0.01	0.12	0.20	0.46	0.12	0.47	0.12	-0.12	-0.03
Wild rice % cover in ring	0.22	-0.08		0.96	-0.20	-0.29	0.14	0.30	0.19	0.05	0.10	-0.07	0.25	-0.05	0.02	-0.25	-0.26	0.01	0.16	0.13	-0.27	0.09	-0.10	-0.13	-0.04	-0.13	-0.06	-0.03	0.15	0.04	-0.05	0.03	-0.04
Wild rice ave # stems/m2	0.22	-0.19	0.96		-0.24	-0.28	0.19	0.29	0.24	0.08	0.02	-0.12	0.30	-0.13	0.01	-0.23	-0.24	-0.02	0.22	0.17	-0.24	0.04	-0.06	-0.08	-0.01	-0.18	-0.11	-0.07	0.13	-0.01	-0.09	0.04	0.00
Floating leaf % cover in ring	-0.33	0.39	-0.20	-0.24		0.32	-0.02	0.11	-0.26	-0.19	-0.14	0.08	-0.19	0.03	-0.16	-0.02	0.08	-0.15	-0.01	-0.22	-0.13	0.14	0.04	0.10	0.00	0.16	0.11	0.17	-0.07	0.12	0.02	0.04	0.01
Water depth	-0.45	0.06	-0.29	-0.28	0.32		0.25	-0.13	-0.14	-0.13	-0.28	-0.05	-0.16	-0.24	-0.03	0.03	0.10	-0.11	0.00	-0.12	-0.03	0.06	0.09	0.08	-0.02	0.08	0.08	0.09	-0.03	0.04	0.05	0.26	-0.03
T tube transparency	0.05	-0.15	0.14	0.19	-0.02	0.25		0.07	0.02	-0.18	-0.34	-0.01	0.09	-0.71	-0.04	-0.13	-0.08	-0.24	0.22	-0.02	-0.14	0.09	0.03	0.09	0.03	0.05	0.00	0.01	-0.03	-0.01	-0.12	0.07	0.03
Surface water Ca	0.01	-0.20	0.30	0.29	0.11	-0.13	0.07		0.42	0.25	-0.25	0.17	0.67	-0.17	0.07	-0.01	-0.07	-0.25	0.50	0.26	0.02	-0.06	0.10	-0.20	-0.18	0.06	0.12	-0.03	-0.02	-0.07	0.13	0.13	-0.15
Surface water Mg	-0.06	-0.60	0.19	0.24	-0.26	-0.14	0.02	0.42		0.69	-0.48	0.42	0.86	-0.34	0.27	0.37	0.25	-0.20	0.47	0.73	0.40	-0.36	0.36	-0.31	-0.33	0.27	0.28	-0.42	-0.44	-0.48	0.27	0.21	-0.33
Surface water K	-0.19	-0.43	0.05	0.08	-0.19	-0.13	-0.18	0.25	0.69		-0.31	0.34	0.56	-0.15	0.14	0.30	0.22	-0.04	0.30	0.51	0.51	-0.38	0.12	-0.30	-0.28	0.12	0.20	-0.45	-0.37	-0.49	0.21	0.16	-0.27
Surface water Fe	0.25	0.47	0.10	0.02	-0.14	-0.28	-0.34	-0.25	-0.48	-0.31		-0.15	-0.51	0.69	-0.08	-0.29	-0.27	0.48	-0.42	-0.36	-0.27	0.38	-0.31	-0.01	0.17	-0.23	-0.11	0.49	0.41	0.57	-0.06	-0.35	0.16
Surface water SO4	0.05	0.13	-0.07	-0.12	0.08	-0.05	-0.01	0.17	0.42	0.34	-0.15		0.21	-0.08	0.24	0.37	0.31	-0.21	-0.03	0.25	0.21	-0.22	0.04	-0.36	-0.40	0.55	0.56	-0.08	-0.47	-0.20	0.44	-0.08	-0.40
Surface water alkalinity	-0.05	-0.62	0.25	0.30	-0.19	-0.16	0.09	0.67	0.86	0.56	-0.51	0.21		-0.41	0.21	0.24	0.14	-0.25	0.59	0.64	0.28	-0.31	0.35	-0.23	-0.25	0.15	0.15	-0.35	-0.28	-0.39	0.17	0.24	-0.24
Surface water color (Pt Co units)	0.16	0.43	-0.05	-0.13	0.03	-0.24	-0.71	-0.17	-0.34	-0.15	0.69	-0.08	-0.41		-0.13	-0.05	-0.02	0.40	-0.41	-0.24	-0.09	0.15	-0.16	0.04	0.18	-0.11	-0.10	0.31	0.25	0.36	-0.03	-0.17	0.17
Porewater pH	-0.03	-0.04	0.02	0.01	-0.16	-0.03	-0.04	0.07	0.27	0.14	-0.08	0.24	0.21	-0.13		-0.02	-0.36	-0.32	-0.16	0.08	-0.12	-0.01	-0.07	-0.35	-0.46	0.41	0.49	-0.15	-0.31	-0.20	0.46	0.13	-0.47
Porewater sulfide	0.03	-0.25	-0.25	-0.23	-0.02	0.03	-0.13	-0.01	0.37	0.30	-0.29	0.37	0.24	-0.05	-0.02		0.90	0.00	0.05	0.33	0.40	-0.56	0.38	0.20	0.17	0.35	0.02	-0.34	-0.50	-0.46	-0.12	0.19	0.17
Porewater free H2S	-0.03	-0.20	-0.26	-0.24	0.08	0.10	-0.08	-0.07	0.25	0.22	-0.27	0.31	0.14	-0.02	-0.36	0.90		0.05	0.07	0.29	0.39	-0.54	0.37	0.28	0.26	0.23	-0.09	-0.24	-0.40	-0.36	-0.20	0.15	0.27
Porewater DOC	0.15	0.03	0.01	-0.02	-0.15	-0.11	-0.24	-0.25	-0.20	-0.04	0.48	-0.21	-0.25	0.40	-0.32	0.00	0.05		-0.01	0.01	0.15	0.26	-0.01	0.01	0.22	-0.28	-0.28	0.24	0.36	0.35	-0.21	-0.29	0.24
Porewater Ca	-0.15	-0.47	0.16	0.22	-0.01	0.00	0.22	0.50	0.47	0.30	-0.42	-0.03	0.59	-0.41	-0.16	0.05	0.07	-0.01		0.73	0.34	-0.12	0.42	-0.11	-0.05	-0.09	-0.09	-0.21	-0.07	-0.21	-0.08	0.12	-0.02
Porewater Mg	-0.12	-0.51	0.13	0.17	-0.22	-0.12	-0.02	0.26	0.73	0.51	-0.36	0.25	0.64	-0.24	0.08	0.33	0.29	0.01	0.73		0.51	-0.34	0.42	-0.24	-0.17	0.15	0.11	-0.33	-0.30	-0.35	0.09	0.11	-0.15
Porewater K	-0.07	-0.39	-0.27	-0.24	-0.13	-0.03	-0.14	0.02	0.40	0.51	-0.27	0.21	0.28	-0.09	-0.12	0.40	0.39	0.15	0.34	0.51		-0.35	0.27	-0.13	-0.06	0.09	0.01	-0.31	-0.21	-0.32	0.01	0.06	-0.04
Porewater Fe	0.06	0.44	0.09	0.04	0.14	0.06	0.09	-0.06	-0.36	-0.38	0.38	-0.22	-0.31	0.15	-0.01	-0.56	-0.54	0.26	-0.12	-0.34	-0.35		-0.20	-0.12	-0.11	-0.11	0.21	0.64	0.32	0.67	0.15	-0.19	-0.11
Porewater silica	-0.17	-0.26	-0.10	-0.06	0.04	0.09	0.03	0.10	0.36	0.12	-0.31	0.04	0.35	-0.16	-0.07	0.38	0.37	-0.01	0.42	0.42	0.27	-0.20		0.15	0.05	0.14	0.01	-0.15	-0.25	-0.17	-0.01	0.33	0.04
Sediment % water	0.06	0.01	-0.13	-0.08	0.10	0.08	0.09	-0.20	-0.31	-0.30	-0.01	-0.36	-0.23	0.04	-0.35	0.20	0.28	0.01	-0.11	-0.24	-0.13	-0.12	0.15		0.90	-0.09	-0.55	0.27	0.02	0.21	-0.73	0.07	0.89
Sediment % organic (LOI)	0.23	-0.01	-0.04	-0.01	0.00	-0.02	0.03	-0.18	-0.33	-0.28	0.17	-0.40	-0.25	0.18	-0.46	0.17	0.26	0.22	-0.05	-0.17	-0.06	-0.11	0.05	0.90		-0.25	-0.70	0.31	0.20	0.30	-0.88	-0.13	0.99
Sediment TS/TOC	-0.08	0.12	-0.13	-0.18	0.16	0.08	0.05	0.06	0.27	0.12	-0.23	0.55	0.15	-0.11	0.41	0.35	0.23	-0.28	-0.09	0.15	0.09	-0.11	0.14	-0.09	-0.25		0.60	-0.09	-0.66	-0.26	0.36	0.30	-0.29
Sediment AVS/TOC	-0.22	0.20	-0.06	-0.11	0.11	0.08	0.00	0.12	0.28	0.20	-0.11	0.56	0.15	-0.10	0.49	0.02	-0.09	-0.28	-0.09	0.11	0.01	0.21	0.01	-0.55	-0.70	0.60		0.08	-0.64	-0.08	0.77	0.15	-0.72
Sediment Fe	0.11	0.46	-0.03	-0.07	0.17	0.09	0.01	-0.03	-0.42	-0.45	0.49	-0.08	-0.35	0.31	-0.15	-0.34	-0.24	0.24	-0.21	-0.33	-0.31	0.64	-0.15	0.27	0.31	-0.09	0.08		0.25	0.94	-0.09	-0.31	0.30
Sediment Fe/AVS	0.17	0.12	0.15	0.13	-0.07	-0.03	-0.03	-0.02	-0.44	-0.37	0.41	-0.47	-0.28	0.25	-0.31	-0.50	-0.40	0.36	-0.07	-0.30	-0.21	0.32	-0.25	0.02	0.20	-0.66	-0.64	0.25		0.49	-0.23	-0.27	0.21
Sediment Fe-AVS	0.15	0.47	0.04	-0.01	0.12	0.04	-0.01	-0.07	-0.48	-0.49	0.57	-0.20	-0.39	0.36	-0.20	-0.46	-0.36	0.35	-0.21	-0.35	-0.32	0.67	-0.17	0.21	0.30	-0.26	-0.08	0.94	0.49		-0.13	-0.37	0.29
Sediment TP/TOC	-0.28	0.12	-0.05	-0.09	0.02	0.05	-0.12	0.13	0.27	0.21	-0.06	0.44	0.17	-0.03	0.46	-0.12	-0.20	-0.21	-0.08	0.09	0.01	0.15	-0.01	-0.73	-0.88	0.36	0.77	-0.09	-0.23	-0.13		0.18	-0.90
Sediment TN/TOC	-0.44	-0.12	0.03	0.04	0.04	0.26	0.07	0.13	0.21	0.16	-0.35	-0.08	0.24	-0.17	0.13	0.19	0.15	-0.29	0.12	0.11	0.06	-0.19	0.33	0.07	-0.13	0.30	0.15	-0.31	-0.27	-0.37	0.18		-0.17
Sediment TOC	0.24	-0.03	-0.04	0.00	0.01	-0.03	0.03	-0.15	-0.33	-0.27	0.16	-0.40	-0.24	0.17	-0.47	0.17	0.27	0.24	-0.02	-0.15	-0.04	-0.11	0.04	0.89	0.99	-0.29	-0.72	0.30	0.21	0.29	-0.90	-0.17	

Appendix E2. Correlation coefficients for selected parameters analyzed from lakes sampled in the 2012-2013 survey (one site visit to each of 82 different lakes included in Data Set 4).

Lakes in the 2012-2013 Survey (N=82) Spearman Correlation Coefficients (rho) P<0.05 for |rho| > 0.217	Latitude	Longitude	Wild rice % cover in ring	Wild rice ave # stems/m2	Floating leaf % cover in ring	Water depth	T tube transparency	Surface water Ca	Surface water Mg	Surface water K	Surface water Fe	Surface water SO4	Surface water alkalinity	Surface water color (Pt Co units)	Porewater pH	Porewater sulfide	Porewater free H2S	Porewater DOC	Porewater Ca	Porewater Mg	Porewater K	Porewater Fe	Porewater silica	Sediment % water	Sediment % organic (LOI)	Sediment TS/TOC	Sediment AVS/TOC	Sediment Fe	Sediment Fe/AVS	Sediment Fe-AVS	Sediment TP/TOC	Sediment TN/TOC	Sediment TOC
Latitude		0.12	0.24	0.22	-0.27	-0.21	0.23	-0.15	-0.22	-0.40	0.15	0.11	-0.18	0.06	0.01	-0.07	-0.10	0.03	-0.24	-0.28	-0.33	0.18	-0.08	0.16	0.23	0.12	-0.03	0.20	0.04	0.19	-0.22	-0.28	0.22
Longitude	0.12		-0.17	-0.22	0.35	-0.11	-0.17	-0.10	-0.65	-0.38	0.55	0.01	-0.62	0.45	-0.26	-0.19	-0.15	0.07	-0.37	-0.51	-0.32	0.31	-0.32	0.24	0.32	-0.02	-0.07	0.50	0.18	0.51	-0.20	-0.29	0.31
Wild rice % cover in ring	0.24	-0.17		0.98	-0.32	-0.31	0.16	0.11	0.15	-0.05	0.04	-0.23	0.21	-0.16	0.02	-0.23	-0.27	0.08	0.08	-0.02	-0.36	0.16	-0.01	0.07	0.03	-0.19	-0.11	-0.06	0.10	0.00	-0.11	0.10	0.02
Wild rice ave # stems/m2	0.22	-0.22	0.98		-0.33	-0.28	0.20	0.10	0.18	-0.03	0.01	-0.24	0.23	-0.21	0.04	-0.24	-0.27	0.06	0.11	0.01	-0.35	0.14	0.01	0.06	0.01	-0.20	-0.12	-0.08	0.08	-0.03	-0.12	0.12	0.01
Floating leaf % cover in ring	-0.27	0.35	-0.32	-0.33		0.23	-0.02	0.27	-0.24	-0.13	-0.04	0.12	-0.16	0.04	-0.28	0.03	0.13	-0.02	0.18	-0.11	0.06	0.06	-0.01	0.08	0.09	0.06	-0.04	0.18	-0.01	0.14	-0.13	-0.11	0.11
Water depth	-0.21	-0.11	-0.31	-0.28	0.23		0.31	-0.07	-0.05	-0.05	-0.24	-0.01	-0.13	-0.31	-0.04	0.03	0.07	-0.06	0.10	-0.01	0.10	0.08	0.00	0.00	0.02	-0.02	-0.03	0.13	0.06	0.09	-0.06	0.03	0.03
T tube transparency	0.23	-0.17	0.16	0.20	-0.02	0.31		0.01	-0.01	-0.32	-0.33	0.04	-0.02	-0.72	-0.14	-0.13	-0.06	-0.12	0.27	0.01	-0.05	0.14	0.05	0.11	0.13	0.01	-0.09	0.10	0.05	0.10	-0.29	-0.04	0.13
Surface water Ca	-0.15	-0.10	0.11	0.10	0.27	-0.07	0.01		0.29	0.07	-0.30	0.13	0.56	-0.16	0.06	0.00	-0.05	-0.30	0.50	0.16	-0.02	0.08	0.10	-0.06	-0.18	0.12	0.21	0.04	-0.14	-0.04	0.19	0.19	-0.16
Surface water Mg	-0.22	-0.65	0.15	0.18	-0.24	-0.05	-0.01	0.29		0.62	-0.61	0.46	0.86	-0.39	0.35	0.42	0.35	-0.22	0.48	0.80	0.44	-0.39	0.46	-0.43	-0.55	0.37	0.45	-0.50	-0.52	-0.57	0.50	0.31	-0.55
Surface water K	-0.40	-0.38	-0.05	-0.03	-0.13	-0.05	-0.32	0.07	0.62		-0.37	0.29	0.47	-0.10	0.30	0.29	0.19	0.02	0.22	0.52	0.54	-0.33	0.19	-0.43	-0.53	0.16	0.36	-0.51	-0.40	-0.53	0.49	0.24	-0.51
Surface water Fe	0.15	0.55	0.04	0.01	-0.04	-0.24	-0.33	-0.30	-0.61	-0.37		-0.38	-0.59	0.68	-0.16	-0.39	-0.35	0.38	-0.51	-0.52	-0.44	0.40	-0.31	0.22	0.36	-0.32	-0.25	0.48	0.41	0.54	-0.20	-0.28	0.36
Surface water SO4	0.11	0.01	-0.23	-0.24	0.12	-0.01	0.04	0.13	0.46	0.29	-0.38		0.29	-0.19	0.23	0.55	0.51	-0.31	0.06	0.38	0.32	-0.43	0.18	-0.27	-0.34	0.64	0.54	-0.19	-0.61	-0.33	0.38	-0.08	-0.35
Surface water alkalinity	-0.18	-0.62	0.21	0.23	-0.16	-0.13	-0.02	0.56	0.86	0.47	-0.59	0.29		-0.38	0.28	0.29	0.22	-0.24	0.59	0.70	0.29	-0.24	0.41	-0.31	-0.43	0.26	0.35	-0.35	-0.38	-0.41	0.37	0.32	-0.43
Surface water color (Pt Co units)	0.06	0.45	-0.16	-0.21	0.04	-0.31	-0.72	-0.16	-0.39	-0.10	0.68	-0.19	-0.38		-0.11	-0.11	-0.08	0.23	-0.51	-0.34	-0.24	0.09	-0.17	0.20	0.23	-0.12	-0.10	0.28	0.16	0.30	-0.01	-0.10	0.23
Porewater pH	0.01	-0.26	0.02	0.04	-0.28	-0.04	-0.14	0.06	0.35	0.30	-0.16	0.23	0.28	-0.11		0.16	-0.16	-0.31	-0.11	0.21	0.03	-0.18	-0.10	-0.29	-0.37	0.39	0.49	-0.24	-0.38	-0.31	0.40	0.18	-0.38
Porewater sulfide	-0.07	-0.19	-0.23	-0.24	0.03	0.03	-0.13	0.00	0.42	0.29	-0.39	0.55	0.29	-0.11	0.16		0.92	-0.17	0.04	0.44	0.37	-0.63	0.42	0.08	0.01	0.53	0.18	-0.38	-0.61	-0.52	0.07	0.25	0.01
Porewater free H2S	-0.10	-0.15	-0.27	-0.27	0.13	0.07	-0.06	-0.05	0.35	0.19	-0.35	0.51	0.22	-0.08	-0.16	0.92		-0.10	0.05	0.39	0.37	-0.60	0.44	0.16	0.11	0.42	0.06	-0.27	-0.52	-0.40	-0.03	0.17	0.11
Porewater DOC	0.03	0.07	0.08	0.06	-0.02	-0.06	-0.12	-0.30	-0.22	0.02	0.38	-0.31	-0.24	0.23	-0.31	-0.17	-0.10		-0.06	-0.06	-0.04	0.34	-0.03	0.03	0.18	-0.29	-0.25	0.22	0.35	0.34	-0.18	-0.32	0.20
Porewater Ca	-0.24	-0.37	0.08	0.11	0.18	0.10	0.27	0.50	0.48	0.22	-0.51	0.06	0.59	-0.51	-0.11	0.04	0.05	-0.06		0.63	0.31	0.07	0.44	-0.22	-0.27	0.04	0.15	-0.17	-0.20	-0.19	0.10	0.11	-0.25
Porewater Mg	-0.28	-0.51	-0.02	0.01	-0.11	-0.01	0.01	0.16	0.80	0.52	-0.52	0.38	0.70	-0.34	0.21	0.44	0.39	-0.06	0.63		0.54	-0.34	0.49	-0.34	-0.40	0.36	0.39	-0.40	-0.50	-0.44	0.33	0.23	-0.40
Porewater K	-0.33	-0.32	-0.36	-0.35	0.06	0.10	-0.05	-0.02	0.44	0.54	-0.44	0.32	0.29	-0.24	0.03	0.37	0.37	-0.04	0.31	0.54		-0.27	0.38	-0.29	-0.35	0.27	0.30	-0.32	-0.33	-0.34	0.30	0.16	-0.34
Porewater Fe	0.18	0.31	0.16	0.14	0.06	0.08	0.14	0.08	-0.39	-0.33	0.40	-0.43	-0.24	0.09	-0.18	-0.63	-0.60	0.34	0.07	-0.34	-0.27		-0.21	-0.03	0.06	-0.29	0.02	0.64	0.45	0.69	-0.04	-0.28	0.07
Porewater silica	-0.08	-0.32	-0.01	0.01	-0.01	0.00	0.05	0.10	0.46	0.19	-0.31	0.18	0.41	-0.17	-0.10	0.42	0.44	-0.03	0.44	0.49	0.38	-0.21		0.07	-0.02	0.16	0.08	-0.14	-0.31	-0.18	0.03	0.22	-0.02
Sediment % water	0.16	0.24	0.07	0.06	0.08	0.00	0.11	-0.06	-0.43	-0.43	0.22	-0.27	-0.31	0.20	-0.29	0.08	0.16	0.03	-0.22	-0.34	-0.29	-0.03	0.07		0.92	-0.10	-0.58	0.35	0.18	0.33	-0.71	0.02	0.91
Sediment % organic (LOI)	0.23	0.32	0.03	0.01	0.09	0.02	0.13	-0.18	-0.55	-0.53	0.36	-0.34	-0.43	0.23	-0.37	0.01	0.11	0.18	-0.27	-0.40	-0.35	0.06	-0.02	0.92		-0.23	-0.67	0.43	0.31	0.45	-0.85	-0.18	0.99
Sediment TS/TOC	0.12	-0.02	-0.19	-0.20	0.06	-0.02	0.01	0.12	0.37	0.16	-0.32	0.64	0.26	-0.12	0.39	0.53	0.42	-0.29	0.04	0.36	0.27	-0.29	0.16	-0.10	-0.23		0.55	-0.15	-0.68	-0.35	0.34	0.24	-0.25
Sediment AVS/TOC	-0.03	-0.07	-0.11	-0.12	-0.04	-0.03	-0.09	0.21	0.45	0.36	-0.25	0.54	0.35	-0.10	0.49	0.18	0.06	-0.25	0.15	0.39	0.30	0.02	0.08	-0.58	-0.67	0.55		-0.01	-0.72	-0.21	0.72	0.11	-0.68
Sediment Fe	0.20	0.50	-0.06	-0.08	0.18	0.13	0.10	0.04	-0.50	-0.51	0.48	-0.19	-0.35	0.28	-0.24	-0.38	-0.27	0.22	-0.17	-0.40	-0.32	0.64	-0.14	0.35	0.43	-0.15	-0.01		0.26	0.92	-0.22	-0.31	0.43
Sediment Fe/AVS	0.04	0.18	0.10	0.08	-0.01	0.06	0.05	-0.14	-0.52	-0.40	0.41	-0.61	-0.38	0.16	-0.38	-0.61	-0.52	0.35	-0.20	-0.50	-0.33	0.45	-0.31	0.18	0.31	-0.68	-0.72	0.26		0.53	-0.35	-0.24	0.31
Sediment Fe-AVS	0.19	0.51	0.00	-0.03	0.14	0.09	0.10	-0.04	-0.57	-0.53	0.54	-0.33	-0.41	0.30	-0.31	-0.52	-0.40	0.34	-0.19	-0.44	-0.34	0.69	-0.18	0.33	0.45	-0.35	-0.21	0.92	0.53		-0.29	-0.37	0.45
Sediment TP/TOC	-0.22	-0.20	-0.11	-0.12	-0.13	-0.06	-0.29	0.19	0.50	0.49	-0.20	0.38	0.37	-0.01	0.40	0.07	-0.03	-0.18	0.10	0.33	0.30	-0.04	0.03	-0.71	-0.85	0.34	0.72	-0.22	-0.35	-0.29		0.25	-0.86
Sediment TN/TOC	-0.28	-0.29	0.10	0.12	-0.11	0.03	-0.04	0.19	0.31	0.24	-0.28	-0.08	0.32	-0.10	0.18	0.25	0.17	-0.32	0.11	0.23	0.16	-0.28	0.22	0.02	-0.18	0.24	0.11	-0.31	-0.24	-0.37	0.25		-0.21
Sediment TOC	0.22	0.31	0.02	0.01	0.11	0.03	0.13	-0.16	-0.55	-0.51	0.36	-0.35	-0.43	0.23	-0.38	0.01	0.11	0.20	-0.25	-0.40	-0.34	0.07	-0.02	0.91	0.99	-0.25	-0.68	0.43	0.31	0.45	-0.86	-0.21	

Appendix E3. Correlation coefficients for selected parameters analyzed from streams sampled in the 2012-2013 survey (one site visit to each of 30 different stream sites included in Data Set 4).

Stream sites in the 2012-2013 Survey (N=30) **Spearman Correlation Coefficients (rho)** **P<0.05 for |rho| > 0.362**	Latitude	Longitude	Wild rice % cover in ring	Wild rice ave # stems/m2	Floating leaf % cover in ring	Water depth	T tube transparency	Surface water Ca	Surface water Mg	Surface water K	Surface water Fe	Surface water SO4	Surface water alkalinity	Surface water color (Pt Co units)	Porewater pH	Porewater sulfide	Porewater free H2S	Porewater DOC	Porewater Ca	Porewater Mg	Porewater K	Porewater Fe	Porewater silica	Sediment % water	Sediment % organic (LOI)	Sediment TS/TOC	Sediment AVS/TOC	Sediment Fe	Sediment Fe/AVS	Sediment Fe-AVS	Sediment TP/TOC	Sediment TN/TOC	Sediment TOC
Latitude		-0.57	-0.12	0.05	-0.34	-0.68	-0.08	-0.05	0.05	-0.06	-0.09	-0.15	0.02	-0.05	0.08	0.13	-0.08	-0.10	-0.16	-0.03	0.22	-0.12	-0.46	0.23	0.35	-0.30	-0.54	-0.16	0.20	-0.18	-0.44	-0.56	0.42
Longitude	-0.57		0.10	-0.13	0.41	0.48	-0.22	-0.26	-0.20	-0.12	0.28	0.40	-0.43	0.52	-0.14	0.01	0.24	0.24	-0.35	-0.26	-0.05	0.49	0.13	-0.21	-0.25	0.39	0.48	0.24	-0.13	0.26	0.37	0.38	-0.33
Wild rice % cover in ring	-0.12	0.10		0.90	0.09	0.11	0.29	0.45	0.34	0.36	-0.34	0.20	0.33	-0.27	0.00	-0.37	-0.24	-0.53	0.25	0.38	-0.29	-0.08	-0.13	-0.07	0.01	0.10	0.04	-0.04	-0.13	-0.04	-0.06	0.21	0.01
Wild rice ave # stems/m2	0.05	-0.13	0.90		0.00	0.04	0.38	0.49	0.30	0.26	-0.44	0.08	0.39	-0.41	-0.05	-0.31	-0.22	-0.65	0.35	0.39	-0.24	-0.23	-0.17	0.00	0.07	-0.13	-0.13	-0.10	0.00	-0.11	-0.11	0.07	0.11
Floating leaf % cover in ring	-0.34	0.41	0.09	0.00		0.41	-0.18	0.00	-0.27	-0.18	-0.19	-0.01	-0.23	0.25	-0.51	0.10	0.37	-0.09	-0.02	-0.23	-0.31	0.07	0.29	0.20	0.12	0.17	0.16	0.16	-0.05	0.19	-0.02	0.29	0.03
Water depth	-0.68	0.48	0.11	0.04	0.41		-0.03	0.00	-0.42	-0.33	-0.05	-0.21	-0.17	0.12	-0.34	0.02	0.32	0.10	0.08	-0.18	-0.12	-0.12	0.38	0.02	-0.13	0.12	0.16	0.07	0.10	0.13	0.24	0.59	-0.18
T tube transparency	-0.08	-0.22	0.29	0.38	-0.18	-0.03		0.47	0.21	0.31	-0.51	-0.06	0.52	-0.75	0.28	-0.11	-0.22	-0.42	0.40	0.13	-0.24	-0.21	0.03	-0.23	-0.27	0.01	0.05	-0.45	-0.09	-0.46	0.19	0.27	-0.23
Surface water Ca	-0.05	-0.26	0.45	0.49	0.00	0.00	0.47		0.65	0.72	-0.75	0.25	0.91	-0.68	0.32	-0.26	-0.38	-0.68	0.58	0.42	-0.15	-0.41	0.07	-0.33	-0.31	0.01	0.08	-0.25	-0.02	-0.24	0.19	0.22	-0.27
Surface water Mg	0.05	-0.20	0.34	0.30	-0.27	-0.42	0.21	0.65		0.89	-0.30	0.54	0.74	-0.41	0.54	-0.06	-0.36	-0.43	0.27	0.47	0.07	-0.13	-0.11	-0.33	-0.25	0.17	0.20	-0.08	-0.23	-0.14	0.12	-0.05	-0.23
Surface water K	-0.06	-0.12	0.36	0.26	-0.18	-0.33	0.31	0.72	0.89		-0.36	0.57	0.75	-0.49	0.47	-0.10	-0.31	-0.46	0.29	0.42	0.09	-0.13	-0.17	-0.43	-0.37	0.25	0.34	-0.19	-0.36	-0.25	0.22	0.10	-0.35
Surface water Fe	-0.09	0.28	-0.34	-0.44	-0.19	-0.05	-0.51	-0.75	-0.30	-0.36		0.03	-0.65	0.68	0.01	0.10	0.10	0.67	-0.58	-0.21	0.17	0.47	-0.12	0.16	0.17	0.05	0.07	0.52	0.03	0.50	-0.08	-0.25	0.15
Surface water SO4	-0.15	0.40	0.20	0.08	-0.01	-0.21	-0.06	0.25	0.54	0.57	0.03		0.13	0.08	0.44	0.03	-0.14	-0.14	-0.05	0.17	0.26	0.25	-0.21	-0.51	-0.49	0.51	0.64	0.15	-0.35	0.13	0.56	-0.04	-0.53
Surface water alkalinity	0.02	-0.43	0.33	0.39	-0.23	-0.17	0.52	0.91	0.74	0.75	-0.65	0.13		-0.78	0.43	-0.20	-0.42	-0.64	0.49	0.38	-0.09	-0.49	0.04	-0.24	-0.21	-0.06	0.00	-0.31	-0.08	-0.33	0.08	0.12	-0.16
Surface water color (Pt Co units)	-0.05	0.52	-0.27	-0.41	0.25	0.12	-0.75	-0.68	-0.41	-0.49	0.68	0.08	-0.78		-0.27	0.13	0.29	0.61	-0.59	-0.31	0.12	0.57	-0.05	0.08	0.12	0.12	0.11	0.50	0.13	0.52	-0.02	-0.17	0.06
Porewater pH	0.08	-0.14	0.00	-0.05	-0.51	-0.34	0.28	0.32	0.54	0.47	0.01	0.44	0.43	-0.27		-0.17	-0.66	-0.10	0.08	0.22	0.12	-0.02	-0.10	-0.32	-0.33	0.28	0.21	-0.12	-0.12	-0.11	0.25	-0.02	-0.28
Porewater sulfide	0.13	0.01	-0.37	-0.31	0.10	0.02	-0.11	-0.26	-0.06	-0.10	0.10	0.03	-0.20	0.13	-0.17		0.80	0.29	-0.26	-0.22	0.33	-0.20	0.06	0.17	0.10	0.03	0.00	0.01	-0.15	-0.01	-0.08	-0.13	0.08
Porewater free H2S	-0.08	0.24	-0.24	-0.22	0.37	0.32	-0.22	-0.38	-0.36	-0.31	0.10	-0.14	-0.42	0.29	-0.66	0.80		0.36	-0.23	-0.31	0.19	-0.03	0.16	0.19	0.13	0.00	0.03	0.09	-0.15	0.08	-0.06	0.05	0.08
Porewater DOC	-0.10	0.24	-0.53	-0.65	-0.09	0.10	-0.42	-0.68	-0.43	-0.46	0.67	-0.14	-0.64	0.61	-0.10	0.29	0.36		-0.37	-0.25	0.23	0.42	0.11	0.13	0.08	-0.10	-0.06	0.44	0.17	0.46	-0.03	-0.15	0.09
Porewater Ca	-0.16	-0.35	0.25	0.35	-0.02	0.08	0.40	0.58	0.27	0.29	-0.58	-0.05	0.49	-0.59	0.08	-0.26	-0.23	-0.37		0.77	-0.13	-0.36	0.34	-0.31	-0.27	-0.26	-0.18	-0.33	0.18	-0.27	0.13	0.11	-0.20
Porewater Mg	-0.03	-0.26	0.38	0.39	-0.23	-0.18	0.13	0.42	0.47	0.42	-0.21	0.17	0.38	-0.31	0.22	-0.22	-0.31	-0.25	0.77		0.02	-0.16	0.13	-0.34	-0.19	-0.27	-0.21	-0.14	0.18	-0.12	0.03	-0.14	-0.12
Porewater K	0.22	-0.05	-0.29	-0.24	-0.31	-0.12	-0.24	-0.15	0.07	0.09	0.17	0.26	-0.09	0.12	0.12	0.33	0.19	0.23	-0.13	0.02		-0.19	-0.31	-0.27	-0.30	-0.18	-0.03	-0.25	0.05	-0.24	0.28	-0.30	-0.23
Porewater Fe	-0.12	0.49	-0.08	-0.23	0.07	-0.12	-0.21	-0.41	-0.13	-0.13	0.47	0.25	-0.49	0.57	-0.02	-0.20	-0.03	0.42	-0.36	-0.16	-0.19		-0.10	-0.12	-0.04	0.36	0.39	0.47	-0.15	0.43	0.13	-0.01	-0.12
Porewater silica	-0.46	0.13	-0.13	-0.17	0.29	0.38	0.03	0.07	-0.11	-0.17	-0.12	-0.21	0.04	-0.05	-0.10	0.06	0.16	0.11	0.34	0.13	-0.31	-0.10		-0.03	-0.12	0.02	-0.02	0.00	0.24	0.09	0.16	0.49	-0.16
Sediment % water	0.23	-0.21	-0.07	0.00	0.20	0.02	-0.23	-0.33	-0.33	-0.43	0.16	-0.51	-0.24	0.08	-0.32	0.17	0.19	0.13	-0.31	-0.34	-0.27	-0.12	-0.03		0.95	-0.16	-0.45	0.42	0.00	0.38	-0.84	-0.29	0.92
Sediment % organic (LOI)	0.35	-0.25	0.01	0.07	0.12	-0.13	-0.27	-0.31	-0.25	-0.37	0.17	-0.49	-0.21	0.12	-0.33	0.10	0.13	0.08	-0.27	-0.19	-0.30	-0.04	-0.12	0.95		-0.24	-0.53	0.44	0.04	0.40	-0.91	-0.43	0.97
Sediment TS/TOC	-0.30	0.39	0.10	-0.13	0.17	0.12	0.01	0.01	0.17	0.25	0.05	0.51	-0.06	0.12	0.28	0.03	0.00	-0.10	-0.26	-0.27	-0.18	0.36	0.02	-0.16	-0.24		0.80	0.10	-0.67	0.04	0.35	0.36	-0.37
Sediment AVS/TOC	-0.54	0.48	0.04	-0.13	0.16	0.16	0.05	0.08	0.20	0.34	0.07	0.64	0.00	0.11	0.21	0.00	0.03	-0.06	-0.18	-0.21	-0.03	0.39	-0.02	-0.45	-0.53	0.80		0.10	-0.71	0.04	0.63	0.37	-0.64
Sediment Fe	-0.16	0.24	-0.04	-0.10	0.16	0.07	-0.45	-0.25	-0.08	-0.19	0.52	0.15	-0.31	0.50	-0.12	0.01	0.09	0.44	-0.33	-0.14	-0.25	0.47	0.00	0.42	0.44	0.10	0.10		0.04	0.98	-0.23	-0.34	0.37
Sediment Fe/AVS	0.20	-0.13	-0.13	0.00	-0.05	0.10	-0.09	-0.02	-0.23	-0.36	0.03	-0.35	-0.08	0.13	-0.12	-0.15	-0.15	0.17	0.18	0.18	0.05	-0.15	0.24	0.00	0.04	-0.67	-0.71	0.04		0.16	-0.06	-0.13	0.10
Sediment Fe-AVS	-0.18	0.26	-0.04	-0.11	0.19	0.13	-0.46	-0.24	-0.14	-0.25	0.50	0.13	-0.33	0.52	-0.11	-0.01	0.08	0.46	-0.27	-0.12	-0.24	0.43	0.09	0.38	0.40	0.04	0.04	0.98	0.16		-0.19	-0.30	0.33
Sediment TP/TOC	-0.44	0.37	-0.06	-0.11	-0.02	0.24	0.19	0.19	0.12	0.22	-0.08	0.56	0.08	-0.02	0.25	-0.08	-0.06	-0.03	0.13	0.03	0.28	0.13	0.16	-0.84	-0.91	0.35	0.63	-0.23	-0.06	-0.19		0.38	-0.94
Sediment TN/TOC	-0.56	0.38	0.21	0.07	0.29	0.59	0.27	0.22	-0.05	0.10	-0.25	-0.04	0.12	-0.17	-0.02	-0.13	0.05	-0.15	0.11	-0.14	-0.30	-0.01	0.49	-0.29	-0.43	0.36	0.37	-0.34	-0.13	-0.30	0.38		-0.48
Sediment TOC	0.42	-0.33	0.01	0.11	0.03	-0.18	-0.23	-0.27	-0.23	-0.35	0.15	-0.53	-0.16	0.06	-0.28	0.08	0.08	0.09	-0.20	-0.12	-0.23	-0.12	-0.16	0.92	0.97	-0.37	-0.64	0.37	0.10	0.33	-0.94	-0.48	

Appendix E4. Correlation coefficients for selected parameters analyzed from cultivated paddies sampled in the 2012-2013 survey (one site visit to each of 7 different paddies included in Data Set 4).

Paddy sites in the 2012-2013 Survey (N=7) Spearman Correlation Coefficients (rho) P<0.05 for |rho| > 0.786	Latitude	Longitude	Wild rice % cover in ring	Wild rice ave # stems/m2	Floating leaf % cover in ring	Water depth	T tube transparency	Surface water Ca	Surface water Mg	Surface water K	Surface water Fe	Surface water SO4	Surface water alkalinity	Surface water color (Pt Co units)	Porewater pH	Porewater sulfide	Porewater free H2S	Porewater DOC	Porewater Ca	Porewater Mg	Porewater K	Porewater Fe	Porewater silica	Sediment % water	Sediment % organic (LOI)	Sediment TS/TOC	Sediment AVS/TOC	Sediment Fe	Sediment Fe/AVS	Sediment Fe-AVS	Sediment TP/TOC	Sediment TN/TOC	Sediment TOC
Latitude		0.00	-0.21	-0.18	0.43	0.55	0.23	0.11	0.00	-0.14	0.61	0.32	0.32	0.29	-0.32	0.39	0.32	0.46	-0.07	-0.04	-0.07	-0.14	-0.29	0.25	0.25	-0.04	-0.21	-0.50	-0.07	-0.32	-0.39	-0.36	0.25
Longitude	0.00		-0.21	-0.64	0.08	0.07	0.14	-0.93	-1.00	-0.77	-0.14	-0.46	-0.61	-0.18	-0.75	-0.75	-0.64	0.00	-0.29	-0.71	-0.40	0.00	-0.68	0.46	0.46	-0.50	-0.96	0.04	0.96	0.43	-0.18	-0.68	0.46
Wild rice % cover in ring	-0.21	-0.21		0.86	0.04	-0.11	0.45	0.29	0.21	-0.20	0.00	-0.50	0.64	-0.25	0.46	-0.36	-0.43	-0.43	0.96	0.82	-0.16	0.64	0.32	-0.11	-0.11	0.46	0.32	0.64	-0.14	0.68	0.21	0.11	-0.11
Wild rice ave # stems/m2	-0.18	-0.64	0.86		-0.04	0.04	0.36	0.64	0.64	0.26	0.14	-0.14	0.71	-0.07	0.64	0.14	0.07	-0.29	0.82	0.96	0.02	0.54	0.46	-0.14	-0.14	0.46	0.71	0.61	-0.61	0.39	0.07	0.29	-0.14
Floating leaf % cover in ring	0.43	0.08	0.04	-0.04		0.04	-0.20	0.20	-0.08	-0.52	0.79	-0.18	0.37	0.77	0.22	-0.02	-0.20	0.79	0.04	-0.04	0.64	0.59	0.22	0.33	0.33	0.32	-0.22	-0.18	-0.06	0.04	-0.26	-0.06	0.33
Water depth	0.55	0.07	-0.11	0.04	0.04		0.70	-0.04	-0.07	0.49	0.51	0.05	-0.02	0.05	-0.53	0.35	0.47	0.36	-0.18	-0.04	-0.33	0.11	-0.60	0.75	0.75	-0.44	-0.13	0.27	-0.05	0.18	-0.89	-0.71	0.75
T tube transparency	0.23	0.14	0.45	0.36	-0.20	0.70		-0.05	-0.14	0.09	0.04	-0.47	0.25	-0.52	-0.32	-0.16	-0.04	-0.18	0.40	0.31	-0.57	0.31	-0.38	0.40	0.40	-0.05	-0.05	0.56	0.18	0.56	-0.41	-0.52	0.40
Surface water Ca	0.11	-0.93	0.29	0.64	0.20	-0.04	-0.05		0.93	0.54	0.29	0.21	0.79	0.25	0.82	0.64	0.50	0.21	0.36	0.71	0.58	0.25	0.79	-0.39	-0.39	0.71	0.89	-0.04	-0.89	-0.36	0.14	0.68	-0.39
Surface water Mg	0.00	-1.00	0.21	0.64	-0.08	-0.07	-0.14	0.93		0.77	0.14	0.46	0.61	0.18	0.75	0.75	0.64	0.00	0.29	0.71	0.40	0.00	0.68	-0.46	-0.46	0.50	0.96	-0.04	-0.96	-0.43	0.18	0.68	-0.46
Surface water K	-0.14	-0.77	-0.20	0.26	-0.52	0.49	0.09	0.54	0.77		-0.03	0.60	-0.09	-0.09	0.09	0.94	0.94	-0.03	-0.20	0.26	-0.03	-0.20	-0.03	0.14	0.14	-0.31	0.77	0.31	-0.83	-0.31	-0.43	0.09	0.14
Surface water Fe	0.61	-0.14	0.00	0.14	0.79	0.51	0.04	0.29	0.14	-0.03		0.18	0.32	0.82	0.04	0.39	0.29	0.79	-0.04	0.11	0.38	0.46	-0.07	0.61	0.61	-0.04	-0.04	0.00	-0.36	0.04	-0.68	-0.32	0.61
Surface water SO4	0.32	-0.46	-0.50	-0.14	-0.18	0.05	-0.47	0.21	0.46	0.60	0.18		-0.14	0.36	-0.04	0.79	0.75	0.07	-0.39	-0.04	0.02	-0.68	-0.07	-0.18	-0.18	-0.32	0.29	-0.54	-0.54	-0.71	-0.07	0.14	-0.18
Surface water alkalinity	0.32	-0.61	0.64	0.71	0.37	-0.02	0.25	0.79	0.61	-0.09	0.32	-0.14		0.07	0.68	0.21	0.04	0.07	0.75	0.82	0.31	0.46	0.64	-0.32	-0.32	0.82	0.57	0.04	-0.54	0.00	0.21	0.43	-0.32
Surface water color (Pt Co units)	0.29	-0.18	-0.25	-0.07	0.77	0.05	-0.52	0.25	0.18	-0.09	0.82	0.36	0.07		0.21	0.39	0.25	0.79	-0.29	-0.11	0.67	0.29	0.14	0.36	0.36	-0.04	0.00	-0.21	-0.39	-0.21	-0.39	0.00	0.36
Porewater pH	-0.32	-0.75	0.46	0.64	0.22	-0.53	-0.32	0.82	0.75	0.09	0.04	-0.04	0.68	0.21		0.21	0.04	0.00	0.50	0.68	0.67	0.39	0.96	-0.57	-0.57	0.82	0.79	0.07	-0.68	-0.14	0.50	0.86	-0.57
Porewater sulfide	0.39	-0.75	-0.36	0.14	-0.02	0.35	-0.16	0.64	0.75	0.94	0.39	0.79	0.21	0.39	0.21		0.96	0.36	-0.29	0.21	0.29	-0.32	0.18	-0.07	-0.07	0.00	0.61	-0.32	-0.82	-0.68	-0.29	0.25	-0.07
Porewater free H2S	0.32	-0.64	-0.43	0.07	-0.20	0.47	-0.04	0.50	0.64	0.94	0.29	0.75	0.04	0.25	0.04	0.96		0.29	-0.39	0.11	0.13	-0.39	0.00	0.04	0.04	-0.18	0.54	-0.21	-0.71	-0.61	-0.39	0.11	0.04
Porewater DOC	0.46	0.00	-0.43	-0.29	0.79	0.36	-0.18	0.21	0.00	-0.03	0.79	0.07	0.07	0.79	0.00	0.36	0.29		-0.46	-0.32	0.67	0.32	0.04	0.50	0.50	0.04	-0.14	-0.25	-0.18	-0.25	-0.57	-0.14	0.50
Porewater Ca	-0.07	-0.29	0.96	0.82	0.04	-0.18	0.40	0.36	0.29	-0.20	-0.04	-0.39	0.75	-0.29	0.50	-0.29	-0.39	-0.46		0.86	-0.16	0.50	0.39	-0.29	-0.29	0.57	0.36	0.43	-0.18	0.50	0.36	0.21	-0.29
Porewater Mg	-0.04	-0.71	0.82	0.96	-0.04	-0.04	0.31	0.71	0.71	0.26	0.11	-0.04	0.82	-0.11	0.68	0.21	0.11	-0.32	0.86		0.02	0.39	0.54	-0.32	-0.32	0.57	0.75	0.39	-0.64	0.21	0.21	0.39	-0.32
Porewater K	-0.07	-0.40	-0.16	0.02	0.64	-0.33	-0.57	0.58	0.40	-0.03	0.38	0.02	0.31	0.67	0.67	0.29	0.13	0.67	-0.16	0.02		0.36	0.72	-0.16	-0.16	0.56	0.34	-0.25	-0.45	-0.38	0.11	0.59	-0.16
Porewater Fe	-0.14	0.00	0.64	0.54	0.59	0.11	0.31	0.25	0.00	-0.20	0.46	-0.68	0.46	0.29	0.39	-0.32	-0.39	0.32	0.50	0.39	0.36		0.29	0.39	0.39	0.39	0.07	0.64	-0.07	0.68	-0.25	-0.07	0.39
Porewater silica	-0.29	-0.68	0.32	0.46	0.22	-0.60	-0.38	0.79	0.68	-0.03	-0.07	-0.07	0.64	0.14	0.96	0.18	0.00	0.04	0.39	0.54	0.72	0.29		-0.68	-0.68	0.89	0.71	-0.11	-0.57	-0.29	0.61	0.93	-0.68
Sediment % water	0.25	0.46	-0.11	-0.14	0.33	0.75	0.40	-0.39	-0.46	0.14	0.61	-0.18	-0.32	0.36	-0.57	-0.07	0.04	0.50	-0.29	-0.32	-0.16	0.39	-0.68		1.00	-0.61	-0.50	0.43	0.25	0.50	-0.93	-0.86	1.00
Sediment % organic (LOI)	0.25	0.46	-0.11	-0.14	0.33	0.75	0.40	-0.39	-0.46	0.14	0.61	-0.18	-0.32	0.36	-0.57	-0.07	0.04	0.50	-0.29	-0.32	-0.16	0.39	-0.68	1.00		-0.61	-0.50	0.43	0.25	0.50	-0.93	-0.86	1.00
Sediment TS/TOC	-0.04	-0.50	0.46	0.46	0.32	-0.44	-0.05	0.71	0.50	-0.31	-0.04	-0.32	0.82	-0.04	0.82	0.00	-0.18	0.04	0.57	0.57	0.56	0.39	0.89	-0.61	-0.61		0.54	-0.11	-0.36	-0.14	0.57	0.75	-0.61
Sediment AVS/TOC	-0.21	-0.96	0.32	0.71	-0.22	-0.13	-0.05	0.89	0.96	0.77	-0.04	0.29	0.57	0.00	0.79	0.61	0.54	-0.14	0.36	0.75	0.34	0.07	0.71	-0.50	-0.50	0.54		0.14	-0.89	-0.29	0.25	0.71	-0.50
Sediment Fe	-0.50	0.04	0.64	0.61	-0.18	0.27	0.56	-0.04	-0.04	0.31	0.00	-0.54	0.04	-0.21	0.07	-0.32	-0.21	-0.25	0.43	0.39	-0.25	0.64	-0.11	0.43	0.43	-0.11	0.14		0.00	0.86	-0.32	-0.29	0.43
Sediment Fe/AVS	-0.07	0.96	-0.14	-0.61	-0.06	-0.05	0.18	-0.89	-0.96	-0.83	-0.36	-0.54	-0.54	-0.39	-0.68	-0.82	-0.71	-0.18	-0.18	-0.64	-0.45	-0.07	-0.57	0.25	0.25	-0.36	-0.89	0.00		0.39	0.04	-0.54	0.25
Sediment Fe-AVS	-0.32	0.43	0.68	0.39	0.04	0.18	0.56	-0.36	-0.43	-0.31	0.04	-0.71	0.00	-0.21	-0.14	-0.68	-0.61	-0.25	0.50	0.21	-0.38	0.68	-0.29	0.50	0.50	-0.14	-0.29	0.86	0.39		-0.25	-0.50	0.50
Sediment TP/TOC	-0.39	-0.18	0.21	0.07	-0.26	-0.89	-0.41	0.14	0.18	-0.43	-0.68	-0.07	0.21	-0.39	0.50	-0.29	-0.39	-0.57	0.36	0.21	0.11	-0.25	0.61	-0.93	-0.93	0.57	0.25	-0.32	0.04	-0.25		0.75	-0.93
Sediment TN/TOC	-0.36	-0.68	0.11	0.29	-0.06	-0.71	-0.52	0.68	0.68	0.09	-0.32	0.14	0.43	0.00	0.86	0.25	0.11	-0.14	0.21	0.39	0.59	-0.07	0.93	-0.86	-0.86	0.75	0.71	-0.29	-0.54	-0.50	0.75		-0.86
Sediment TOC	0.25	0.46	-0.11	-0.14	0.33	0.75	0.40	-0.39	-0.46	0.14	0.61	-0.18	-0.32	0.36	-0.57	-0.07	0.04	0.50	-0.29	-0.32	-0.16	0.39	-0.68	1.00	1.00	-0.61	-0.50	0.43	0.25	0.50	-0.93	-0.86	

Appendix E5. Correlation coefficients for selected parameters analyzed in the 2011 Pilot Survey (Data Set 1; consists of one site visit to each of 39 different sites, including 30 lakes, and 9 streams). Additional porewater analyses were added partway through the survey, so that the complete suite of porewater analyses is available for only 18 sites, all of them lakes.

All sites in the 2011 Pilot Survey (N=39; N=18 for Porewater parameters other than sulfide & pH) Spearman Correlation Coefficients (rho) **N=39: P<0.05 for rho > 0.317** **N=18: P<0.05 for rho > 0.472**	Latitude	Longitude	Wild rice % cover in ring	Floating leaf % cover in ring	T tube transparency	Surface water Ca	Surface water Mg	Surface water K	Surface water Fe	Surface water SO4	Surface water alkalinity	Surface water DOC	Porewater pH	Porewater sulfide	Porewater free H2S	Porewater DOC	Porewater Ca	Porewater Mg	Porewater K	Porewater Fe	Sediment % water	Sediment % organic (LOI)	Sediment TS/TOC	Sediment AVS/TOC	Sediment Fe	Sediment Fe/AVS	Sediment Fe-AVS	Sediment TP/TOC	Sediment TN/TOC	Sediment TOC
Latitude		0.21	0.05	-0.09	0.21	-0.39	-0.48	-0.55	0.38	0.08	-0.52	0.43	0.08	0.02	0.09	0.39	-0.60	-0.41	-0.49	0.49	-0.02	0.09	0.01	-0.33	0.05	0.33	0.10	-0.27	-0.17	0.17
Longitude	0.21		0.22	0.11	0.07	-0.46	-0.56	-0.30	0.68	0.29	-0.63	0.31	-0.55	-0.38	-0.22	-0.03	-0.26	-0.51	-0.74	0.76	-0.34	-0.11	0.15	0.09	0.56	0.35	0.57	0.12	-0.51	-0.10
Wild rice % cover in ring	0.05	0.22		0.10	0.10	0.00	-0.35	-0.38	0.26	-0.33	-0.19	0.17	-0.12	-0.18	-0.18	-0.28	-0.05	-0.29	-0.41	0.11	0.01	0.18	-0.46	-0.41	0.05	0.40	0.08	-0.24	0.08	0.20
Floating leaf % cover in ring	-0.09	0.11	0.10		0.18	0.10	-0.18	-0.04	0.19	-0.14	0.04	-0.22	-0.19	-0.19	-0.05	-0.17	-0.01	-0.31	-0.35	0.35	0.09	0.05	-0.29	0.00	0.39	0.15	0.41	-0.11	-0.03	0.17
T tube transparency	0.21	0.07	0.10	0.18		0.11	-0.14	-0.27	-0.01	0.05	-0.14	-0.13	-0.14	-0.27	-0.18	-0.44	-0.02	-0.25	-0.18	0.20	0.02	0.07	-0.30	-0.22	-0.05	0.20	0.00	-0.01	0.02	0.04
Surface water Ca	-0.39	-0.46	0.00	0.10	0.11		0.57	0.34	-0.32	-0.09	0.75	-0.47	0.29	-0.08	-0.16	-0.35	0.57	0.23	-0.05	0.26	0.18	0.04	-0.14	0.22	0.02	-0.38	-0.03	0.11	0.49	0.00
Surface water Mg	-0.48	-0.56	-0.35	-0.18	-0.14	0.57		0.79	-0.53	0.32	0.86	-0.58	0.50	0.22	0.07	-0.24	0.59	0.76	0.40	-0.48	-0.04	-0.25	0.29	0.42	-0.31	-0.64	-0.37	0.33	0.33	-0.28
Surface water K	-0.55	-0.30	-0.38	-0.04	-0.27	0.34	0.79		-0.49	0.38	0.66	-0.54	0.28	0.21	0.11	-0.01	0.55	0.68	0.69	-0.58	-0.12	-0.26	0.49	0.49	-0.12	-0.62	-0.19	0.33	0.04	-0.28
Surface water Fe	0.38	0.68	0.26	0.19	-0.01	-0.32	-0.53	-0.49		0.02	-0.58	0.57	-0.42	-0.43	-0.31	0.30	-0.58	-0.64	-0.80	0.69	0.02	0.27	-0.09	-0.16	0.69	0.50	0.72	-0.23	-0.25	0.34
Surface water SO4	0.08	0.29	-0.33	-0.14	0.05	-0.09	0.32	0.38	0.02		0.05	0.00	0.17	0.28	0.30	-0.28	0.57	0.64	0.36	-0.22	-0.39	-0.35	0.67	0.56	0.22	-0.40	0.19	0.39	-0.48	-0.37
Surface water alkalinity	-0.52	-0.63	-0.19	0.04	-0.14	0.75	0.86	0.66	-0.58	0.05		-0.71	0.48	0.11	-0.02	-0.26	0.68	0.71	0.27	-0.18	0.07	-0.21	0.09	0.35	-0.22	-0.63	-0.30	0.27	0.44	-0.20
Surface water DOC	0.43	0.31	0.17	-0.22	-0.13	-0.47	-0.58	-0.54	0.57	0.00	-0.71		-0.09	0.17	0.20	0.67	-0.69	-0.39	-0.14	0.01	0.01	0.28	-0.02	-0.33	0.18	0.38	0.25	-0.37	-0.26	0.30
Porewater pH	0.08	-0.55	-0.12	-0.19	-0.14	0.29	0.50	0.28	-0.42	0.17	0.48	-0.09		0.34	0.13	0.12	0.36	0.66	0.38	-0.45	-0.29	-0.36	0.22	0.14	-0.46	-0.30	-0.49	0.20	0.37	-0.28
Porewater sulfide	0.02	-0.38	-0.18	-0.19	-0.27	-0.08	0.22	0.21	-0.43	0.28	0.11	0.17	0.34		0.94	0.17	0.27	0.63	0.69	-0.75	0.08	0.00	0.24	0.08	-0.34	-0.40	-0.32	-0.11	-0.02	-0.03
Porewater free H2S	0.09	-0.22	-0.18	-0.05	-0.18	-0.16	0.07	0.11	-0.31	0.30	-0.02	0.20	0.13	0.94		0.06	0.34	0.53	0.65	-0.67	0.04	-0.02	0.20	0.09	-0.22	-0.36	-0.18	-0.10	-0.20	-0.04
Porewater DOC	0.39	-0.03	-0.28	-0.17	-0.44	-0.35	-0.24	-0.01	0.30	-0.28	-0.26	0.67	0.12	0.17	0.06		-0.24	0.08	0.18	0.10	-0.02	0.03	0.26	-0.06	0.10	0.03	0.16	-0.13	0.06	0.16
Porewater Ca	-0.60	-0.26	-0.05	-0.01	-0.02	0.57	0.59	0.55	-0.58	0.57	0.68	-0.69	0.36	0.27	0.34	-0.24		0.80	0.47	-0.11	-0.49	-0.53	0.28	0.63	-0.17	-0.63	-0.24	0.59	-0.13	-0.58
Porewater Mg	-0.41	-0.51	-0.29	-0.31	-0.25	0.23	0.76	0.68	-0.64	0.64	0.71	-0.39	0.66	0.63	0.53	0.08	0.80		0.66	-0.43	-0.40	-0.44	0.63	0.51	-0.44	-0.70	-0.48	0.45	-0.18	-0.44
Porewater K	-0.49	-0.74	-0.41	-0.35	-0.18	-0.05	0.40	0.69	-0.80	0.36	0.27	-0.14	0.38	0.69	0.65	0.18	0.47	0.66		-0.66	-0.08	-0.12	0.49	0.19	-0.60	-0.41	-0.63	0.15	-0.14	-0.21
Porewater Fe	0.49	0.76	0.11	0.35	0.20	0.26	-0.48	-0.58	0.69	-0.22	-0.18	0.01	-0.45	-0.75	-0.67	0.10	-0.11	-0.43	-0.66		-0.25	-0.27	-0.20	0.15	0.78	0.27	0.79	0.23	-0.11	-0.13
Sediment % water	-0.02	-0.34	0.01	0.09	0.02	0.18	-0.04	-0.12	0.02	-0.39	0.07	0.01	-0.29	0.08	0.04	-0.02	-0.49	-0.40	-0.08	-0.25		0.88	-0.42	-0.51	0.03	0.09	0.04	-0.81	0.27	0.86
Sediment % organic (LOI)	0.09	-0.11	0.18	0.05	0.07	0.04	-0.25	-0.26	0.27	-0.35	-0.21	0.28	-0.36	0.00	-0.02	0.03	-0.53	-0.44	-0.12	-0.27	0.88		-0.43	-0.65	0.19	0.32	0.23	-0.91	0.04	0.98
Sediment TS/TOC	0.01	0.15	-0.46	-0.29	-0.30	-0.14	0.29	0.49	-0.09	0.67	0.09	-0.02	0.22	0.24	0.20	0.26	0.28	0.63	0.49	-0.20	-0.42	-0.43		0.49	0.06	-0.34	0.02	0.47	-0.37	-0.47
Sediment AVS/TOC	-0.33	0.09	-0.41	0.00	-0.22	0.22	0.42	0.49	-0.16	0.56	0.35	-0.33	0.14	0.08	0.09	-0.06	0.63	0.51	0.19	0.15	-0.51	-0.65	0.49		0.27	-0.72	0.19	0.76	-0.12	-0.65
Sediment Fe	0.05	0.56	0.05	0.39	-0.05	0.02	-0.31	-0.12	0.69	0.22	-0.22	0.18	-0.46	-0.34	-0.22	0.10	-0.17	-0.44	-0.60	0.78	0.03	0.19	0.06	0.27		0.10	0.99	-0.05	-0.41	0.26
Sediment Fe/AVS	0.33	0.35	0.40	0.15	0.20	-0.38	-0.64	-0.62	0.50	-0.40	-0.63	0.38	-0.30	-0.40	-0.36	0.03	-0.63	-0.70	-0.41	0.27	0.09	0.32	-0.34	-0.72	0.10		0.18	-0.36	-0.09	0.35
Sediment Fe-AVS	0.10	0.57	0.08	0.41	0.00	-0.03	-0.37	-0.19	0.72	0.19	-0.30	0.25	-0.49	-0.32	-0.18	0.16	-0.24	-0.48	-0.63	0.79	0.04	0.23	0.02	0.19	0.99	0.18		-0.10	-0.44	0.29
Sediment TP/TOC	-0.27	0.12	-0.24	-0.11	-0.01	0.11	0.33	0.33	-0.23	0.39	0.27	-0.37	0.20	-0.11	-0.10	-0.13	0.59	0.45	0.15	0.23	-0.81	-0.91	0.47	0.76	-0.05	-0.36	-0.10		-0.03	-0.93
Sediment TN/TOC	-0.17	-0.51	0.08	-0.03	0.02	0.49	0.33	0.04	-0.25	-0.48	0.44	-0.26	0.37	-0.02	-0.20	0.06	-0.13	-0.18	-0.14	-0.11	0.27	0.04	-0.37	-0.12	-0.41	-0.09	-0.44	-0.03		0.03
Sediment TOC	0.17	-0.10	0.20	0.17	0.04	0.00	-0.28	-0.28	0.34	-0.37	-0.20	0.30	-0.28	-0.03	-0.04	0.16	-0.58	-0.44	-0.21	-0.13	0.86	0.98	-0.47	-0.65	0.26	0.35	0.29	-0.93	0.03	

Appendix E6. Correlation coefficients for selected parameters analyzed from lakes in the 2011 Pilot Survey (one site visit to each of 30 different lakes included in Data Set 1). Additional porewater analyses were added partway through the survey, so that the complete suite of porewater analyses is available for only 18 sites.

Lake sites in the 2011 Pilot Survey (N=30; N=18 for porewater parameters other than sulfide & pH) **Spearman Correlation Coefficients (rho)** **N=30: P<0.05 for rho > 0.362** **N=18: P<0.05 for rho > 0.472**	Latitude	Longitude	Wild rice % cover in ring	Floating leaf % cover in ring	T tube transparency	Surface water Ca	Surface water Mg	Surface water K	Surface water Fe	Surface water SO4	Surface water alkalinity	Surface water DOC	Porewater pH	Porewater sulfide	Porewater free H2S	Porewater DOC	Porewater Ca	Porewater Mg	Porewater K	Porewater Fe	Sediment % water	Sediment % organic (LOI)	Sediment TS/TOC	Sediment AVS/TOC	Sediment Fe	Sediment Fe/AVS	Sediment Fe-AVS	Sediment TP/TOC	Sediment TN/TOC	Sediment TOC
Latitude	■	0.03	-0.02	-0.07	0.25	-0.34	-0.49	-0.59	0.26	-0.19	-0.39	0.23	-0.02	-0.02	0.01	0.39	-0.60	-0.41	-0.49	0.49	0.21	0.19	-0.09	-0.44	-0.08	0.33	-0.04	-0.37	-0.03	0.29
Longitude	0.03	■	0.31	0.06	0.11	-0.19	-0.52	-0.39	0.61	0.16	-0.50	0.27	-0.59	-0.38	-0.27	-0.03	-0.26	-0.51	-0.74	0.76	-0.34	-0.08	0.00	0.05	0.57	0.30	0.59	0.13	-0.41	-0.09
Wild rice % cover in ring	-0.02	0.31	■	0.12	0.01	-0.10	-0.32	-0.32	0.34	-0.39	-0.30	0.13	-0.24	-0.33	-0.34	-0.28	-0.05	-0.29	-0.41	0.11	0.11	0.27	-0.48	-0.48	0.04	0.54	0.04	-0.35	0.12	0.27
Floating leaf % cover in ring	-0.07	0.06	0.12	■	0.29	0.31	-0.08	-0.10	0.16	-0.24	0.11	-0.28	-0.02	-0.21	-0.10	-0.17	-0.01	-0.31	-0.35	0.35	0.09	0.00	-0.46	0.00	0.32	0.17	0.32	-0.08	0.16	0.15
T tube transparency	0.25	0.11	0.01	0.29	■	0.13	-0.20	-0.23	0.02	0.09	-0.14	-0.26	-0.22	-0.31	-0.18	-0.44	-0.02	-0.25	-0.18	0.20	0.12	0.18	-0.30	-0.18	0.09	0.15	0.11	-0.08	-0.12	0.14
Surface water Ca	-0.34	-0.19	-0.10	0.31	0.13	■	0.55	0.45	-0.10	0.15	0.69	-0.51	0.23	-0.24	-0.24	-0.35	0.57	0.23	-0.05	0.26	0.17	0.05	0.06	0.36	0.27	-0.37	0.23	0.18	0.28	0.01
Surface water Mg	-0.49	-0.52	-0.32	-0.08	-0.20	0.55	■	0.87	-0.51	0.45	0.93	-0.59	0.52	0.28	0.19	-0.24	0.59	0.76	0.40	-0.48	-0.05	-0.25	0.36	0.49	-0.17	-0.75	-0.22	0.35	0.18	-0.27
Surface water K	-0.59	-0.39	-0.32	-0.10	-0.23	0.45	0.87	■	-0.52	0.43	0.75	-0.44	0.41	0.29	0.22	-0.01	0.55	0.68	0.69	-0.58	-0.13	-0.24	0.42	0.46	-0.15	-0.70	-0.19	0.29	0.10	-0.26
Surface water Fe	0.26	0.61	0.34	0.16	0.02	-0.10	-0.51	-0.52	■	-0.24	-0.45	0.46	-0.52	-0.49	-0.46	0.30	-0.58	-0.64	-0.80	0.69	0.21	0.42	-0.27	-0.28	0.73	0.53	0.76	-0.32	-0.08	0.50
Surface water SO4	-0.19	0.16	-0.39	-0.24	0.09	0.15	0.45	0.43	-0.24	■	0.31	-0.12	0.13	0.43	0.43	-0.28	0.57	0.64	0.36	-0.22	-0.27	-0.24	0.61	0.52	0.12	-0.59	0.10	0.36	-0.45	-0.32
Surface water alkalinity	-0.39	-0.50	-0.30	0.11	-0.14	0.69	0.93	0.75	-0.45	0.31	■	-0.71	0.53	0.07	0.00	-0.26	0.68	0.71	0.27	-0.18	-0.04	-0.31	0.25	0.49	-0.07	-0.69	-0.13	0.40	0.26	-0.29
Surface water DOC	0.23	0.27	0.13	-0.28	-0.26	-0.51	-0.59	-0.44	0.46	-0.12	-0.71	■	-0.17	0.17	0.13	0.67	-0.69	-0.39	-0.14	0.01	0.09	0.34	0.05	-0.43	0.10	0.48	0.16	-0.41	-0.23	0.35
Porewater pH	-0.02	-0.59	-0.24	-0.02	-0.22	0.23	0.52	0.41	-0.52	0.13	0.53	-0.17	■	0.35	0.19	0.12	0.36	0.66	0.38	-0.45	-0.20	-0.30	0.24	0.18	-0.46	-0.42	-0.48	0.13	0.31	-0.19
Porewater sulfide	-0.02	-0.38	-0.33	-0.21	-0.31	-0.24	0.28	0.29	-0.49	0.43	0.07	0.17	0.35	■	0.96	0.17	0.27	0.63	0.69	-0.75	0.06	-0.04	0.39	0.12	-0.43	-0.40	-0.41	-0.09	-0.04	-0.06
Porewater free H2S	0.01	-0.27	-0.34	-0.10	-0.18	-0.24	0.19	0.22	-0.46	0.43	0.00	0.13	0.19	0.96	■	0.06	0.34	0.53	0.65	-0.67	0.01	-0.09	0.32	0.14	-0.37	-0.38	-0.34	-0.07	-0.17	-0.10
Porewater DOC	0.39	-0.03	-0.28	-0.17	-0.44	-0.35	-0.24	-0.01	0.30	-0.28	-0.26	0.67	0.12	0.17	0.06	■	-0.24	0.08	0.18	0.10	-0.02	0.03	0.26	-0.06	0.10	0.03	0.16	-0.13	0.06	0.16
Porewater Ca	-0.60	-0.26	-0.05	-0.01	-0.02	0.57	0.59	0.55	-0.58	0.57	0.68	-0.69	0.36	0.27	0.34	-0.24	■	0.80	0.47	-0.11	-0.49	-0.53	0.28	0.63	-0.17	-0.63	-0.24	0.59	-0.13	-0.58
Porewater Mg	-0.41	-0.51	-0.29	-0.31	-0.25	0.23	0.76	0.68	-0.64	0.64	0.71	-0.39	0.66	0.63	0.53	0.08	0.80	■	0.66	-0.43	-0.40	-0.44	0.63	0.51	-0.44	-0.70	-0.48	0.45	-0.18	-0.44
Porewater K	-0.49	-0.74	-0.41	-0.35	-0.18	-0.05	0.40	0.69	-0.80	0.36	0.27	-0.14	0.38	0.69	0.65	0.18	0.47	0.66	■	-0.66	-0.08	-0.12	0.49	0.19	-0.60	-0.41	-0.63	0.15	-0.14	-0.21
Porewater Fe	0.49	0.76	0.11	0.35	0.20	0.26	-0.48	-0.58	0.69	-0.22	-0.18	0.01	-0.45	-0.75	-0.67	0.10	-0.11	-0.43	-0.66	■	-0.25	-0.27	-0.20	0.15	0.78	0.27	0.79	0.23	-0.11	-0.13
Sediment % water	0.21	-0.34	0.11	0.09	0.12	0.17	-0.05	-0.13	0.21	-0.27	-0.04	0.09	-0.20	0.06	0.01	-0.02	-0.49	-0.40	-0.08	-0.25	■	0.86	-0.33	-0.53	0.05	0.24	0.06	-0.80	0.35	0.86
Sediment % organic (LOI)	0.19	-0.08	0.27	0.00	0.18	0.05	-0.25	-0.24	0.42	-0.24	-0.31	0.34	-0.30	-0.04	-0.09	0.03	-0.53	-0.44	-0.12	-0.27	0.86	■	-0.35	-0.66	0.22	0.47	0.25	-0.89	0.09	0.98
Sediment TS/TOC	-0.09	0.00	-0.48	-0.46	-0.30	0.06	0.36	0.42	-0.27	0.61	0.25	0.05	0.24	0.39	0.32	0.26	0.28	0.63	0.49	-0.20	-0.33	-0.35	■	0.37	-0.09	-0.43	-0.10	0.37	-0.28	-0.41
Sediment AVS/TOC	-0.44	0.05	-0.48	0.00	-0.18	0.36	0.49	0.46	-0.28	0.52	0.49	-0.43	0.18	0.12	0.14	-0.06	0.63	0.51	0.19	0.15	-0.53	-0.66	0.37	■	0.18	-0.80	0.12	0.81	-0.04	-0.68
Sediment Fe	-0.08	0.57	0.04	0.32	0.09	0.27	-0.17	-0.15	0.73	0.12	-0.07	0.10	-0.46	-0.43	-0.37	0.10	-0.17	-0.44	-0.60	0.78	0.05	0.22	-0.09	0.18	■	0.20	0.99	0.00	-0.27	0.29
Sediment Fe/AVS	0.33	0.30	0.54	0.17	0.15	-0.37	-0.75	-0.70	0.53	-0.59	-0.69	0.48	-0.42	-0.40	-0.38	0.03	-0.63	-0.70	-0.41	0.27	0.24	0.47	-0.43	-0.80	0.20	■	0.25	-0.54	-0.12	0.52
Sediment Fe-AVS	-0.04	0.59	0.04	0.32	0.11	0.23	-0.22	-0.19	0.76	0.10	-0.13	0.16	-0.48	-0.41	-0.34	0.16	-0.24	-0.48	-0.63	0.79	0.06	0.25	-0.10	0.12	0.99	0.25	■	-0.04	-0.29	0.32
Sediment TP/TOC	-0.37	0.13	-0.35	-0.08	-0.08	0.18	0.35	0.29	-0.32	0.36	0.40	-0.41	0.13	-0.09	-0.07	-0.13	0.59	0.45	0.15	0.23	-0.80	-0.89	0.37	0.81	0.00	-0.54	-0.04	■	-0.12	-0.91
Sediment TN/TOC	-0.03	-0.41	0.12	0.16	-0.12	0.28	0.18	0.10	-0.08	-0.45	0.26	-0.23	0.31	-0.04	-0.17	0.06	-0.13	-0.18	-0.14	-0.11	0.35	0.09	-0.28	-0.04	-0.27	-0.12	-0.29	-0.12	■	0.12
Sediment TOC	0.29	-0.09	0.27	0.15	0.14	0.01	-0.27	-0.26	0.50	-0.32	-0.29	0.35	-0.19	-0.06	-0.10	0.16	-0.58	-0.44	-0.21	-0.13	0.86	0.98	-0.41	-0.68	0.29	0.52	0.32	-0.91	0.12	■

Appendix E7. Correlation coefficients for selected parameters analyzed from streams in the 2011 Pilot Survey (one site visit to each of 9 different streams included in Data Set 1). Additional porewater analyses were added to the survey after all the streams had been sampled, so that the complete suite of porewater analyses is not available for this set.

Stream sites in the 2011 Pilot Survey **Spearman Correlation Coefficients (rho)** **N=9** **P<0.05 for |rho| > 0.700**	Latitude	Longitude	Wild rice % cover in ring	Floating leaf % cover in ring	T tube transparency	Surface water Ca	Surface water Mg	Surface water K	Surface water Fe	Surface water SO4	Surface water alkalinity	Surface water DOC	Porewater pH	Porewater sulfide	Porewater free H2S	Porewater DOC	Porewater Ca	Porewater Mg	Porewater K	Porewater Fe	Sediment % water	Sediment % organic (LOI)	Sediment TS/TOC	Sediment AVS/TOC	Sediment Fe	Sediment Fe/AVS	Sediment Fe-AVS	Sediment TP/TOC	Sediment TN/TOC	Sediment TOC
Latitude		0.65	-0.75	0.27	-0.80	-0.73	-0.30	-0.22	0.77	0.57	-0.70	0.63	-0.58	0.07	0.30	NA	NA	NA	NA	NA	0.13	0.20	0.42	0.13	0.68	0.03	0.68	-0.22	-0.62	0.20
Longitude	0.65		-0.63	0.66	-0.04	-0.90	-0.68	-0.07	0.90	0.70	-0.93	0.37	-0.67	-0.30	0.03	NA	NA	NA	NA	NA	-0.08	0.00	0.62	0.07	0.52	0.30	0.52	-0.02	-0.80	0.00
Wild rice % cover in ring	-0.75	-0.63		0.02	0.45	0.62	-0.05	-0.33	-0.65	-0.87	0.62	-0.27	0.32	0.42	0.28	NA	NA	NA	NA	NA	0.22	0.18	-0.68	-0.32	-0.33	-0.12	-0.33	-0.13	0.47	0.18
Floating leaf % cover in ring	0.27	0.66	0.02		-0.37	-0.73	-0.93	-0.19	0.70	0.15	-0.63	0.05	-0.76	-0.12	0.24	NA	NA	NA	NA	NA	0.12	0.25	0.20	-0.05	0.61	0.22	0.61	-0.22	-0.76	0.25
T tube transparency	-0.80	-0.04	0.45	-0.37		0.49	0.18	-0.45	-0.49	-0.18	0.13	0.09	0.45	0.13	-0.09	NA	NA	NA	NA	NA	0.04	-0.13	-0.18	-0.40	-0.76	0.22	-0.76	0.13	0.45	-0.13
Surface water Ca	-0.73	-0.90	0.62	-0.73	0.49		0.67	0.08	-0.97	-0.57	0.90	-0.37	0.81	0.30	0.00	NA	NA	NA	NA	NA	-0.13	-0.27	-0.43	-0.07	-0.68	-0.27	-0.68	0.25	0.92	-0.27
Surface water Mg	-0.30	-0.68	-0.05	-0.93	0.18	0.67		0.35	-0.63	-0.13	0.67	-0.28	0.73	-0.10	-0.40	NA	NA	NA	NA	NA	-0.17	-0.27	-0.22	0.00	-0.65	-0.02	-0.65	0.25	0.75	-0.27
Surface water K	-0.22	-0.07	-0.33	-0.19	-0.45	0.08	0.35		-0.08	0.53	0.12	-0.63	0.20	-0.58	-0.58	NA	NA	NA	NA	NA	-0.72	-0.68	0.58	0.62	-0.13	-0.05	-0.13	0.67	0.10	-0.68
Surface water Fe	0.77	0.90	-0.65	0.70	-0.49	-0.97	-0.63	-0.08		0.58	-0.93	0.37	-0.87	-0.38	-0.03	NA	NA	NA	NA	NA	0.12	0.20	0.45	0.10	0.72	0.22	0.72	-0.22	-0.92	0.20
Surface water SO4	0.57	0.70	-0.87	0.15	-0.18	-0.57	-0.13	0.53	0.58		-0.62	0.08	-0.24	-0.40	-0.17	NA	NA	NA	NA	NA	-0.60	-0.53	0.95	0.50	0.30	0.13	0.30	0.50	-0.42	-0.53
Surface water alkalinity	-0.70	-0.93	0.62	-0.63	0.13	0.90	0.67	0.12	-0.93	-0.62		-0.53	0.82	0.32	0.00	NA	NA	NA	NA	NA	-0.02	-0.07	-0.52	-0.23	-0.68	-0.08	-0.68	0.08	0.88	-0.07
Surface water DOC	0.63	0.37	-0.27	0.05	0.09	-0.37	-0.28	-0.63	0.37	0.08	-0.53		-0.37	0.43	0.45	NA	NA	NA	NA	NA	0.35	0.33	-0.02	0.07	0.47	-0.25	0.47	-0.32	-0.37	0.33
Porewater pH	-0.58	-0.67	0.32	-0.76	0.45	0.81	0.73	0.20	-0.87	-0.24	0.82	-0.37		0.28	-0.01	NA	NA	NA	NA	NA	-0.33	-0.38	-0.18	-0.19	-0.87	0.13	-0.87	0.40	0.95	-0.38
Porewater sulfide	0.07	-0.30	0.42	-0.12	0.13	0.30	-0.10	-0.58	-0.38	-0.40	0.32	0.43	0.28		0.87	NA	NA	NA	NA	NA	0.23	0.27	-0.28	-0.17	0.05	-0.28	0.05	-0.22	0.30	0.27
Porewater free H2S	0.30	0.03	0.28	0.24	-0.09	0.00	-0.40	-0.58	-0.03	-0.17	0.00	0.45	-0.01	0.87		NA	NA	NA	NA	NA	0.07	0.13	-0.03	-0.13	0.28	-0.08	0.28	-0.08	0.05	0.13
Porewater DOC	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Porewater Ca	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Porewater Mg	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Porewater K	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Porewater Fe	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Sediment % water	0.13	-0.08	0.22	0.12	0.04	-0.13	-0.17	-0.72	0.12	-0.60	-0.02	0.35	-0.33	0.23	0.07	NA	NA	NA	NA	NA		0.97	-0.73	-0.53	0.22	-0.13	0.22	-0.98	-0.27	0.97
Sediment % organic (LOI)	0.20	0.00	0.18	0.25	-0.13	-0.27	-0.27	-0.68	0.20	-0.53	-0.07	0.33	-0.38	0.27	0.13	NA	NA	NA	NA	NA	0.97		-0.67	-0.53	0.28	-0.03	0.28	-0.98	-0.35	1.00
Sediment TS/TOC	0.42	0.62	-0.68	0.20	-0.18	-0.43	-0.22	0.58	0.45	0.95	-0.52	-0.02	-0.18	-0.28	-0.03	NA	NA	NA	NA	NA	-0.73	-0.67		0.60	0.30	0.02	0.30	0.63	-0.33	-0.67
Sediment AVS/TOC	0.13	0.07	-0.32	-0.05	-0.40	-0.07	0.00	0.62	0.10	0.50	-0.23	0.07	-0.19	-0.17	-0.13	NA	NA	NA	NA	NA	-0.53	-0.53	0.60		0.45	-0.63	0.45	0.52	-0.22	-0.53
Sediment Fe	0.68	0.52	-0.33	0.61	-0.76	-0.68	-0.65	-0.13	0.72	0.30	-0.68	0.47	-0.87	0.05	0.28	NA	NA	NA	NA	NA	0.22	0.28	0.30	0.45		-0.42	1.00	-0.30	-0.83	0.28
Sediment Fe/AVS	0.03	0.30	-0.12	0.22	0.22	-0.27	-0.02	-0.05	0.22	0.13	-0.08	-0.25	0.13	-0.28	-0.08	NA	NA	NA	NA	NA	-0.13	-0.03	0.02	-0.63	-0.42		-0.42	0.10	0.07	-0.03
Sediment Fe-AVS	0.68	0.52	-0.33	0.61	-0.76	-0.68	-0.65	-0.13	0.72	0.30	-0.68	0.47	-0.87	0.05	0.28	NA	NA	NA	NA	NA	0.22	0.28	0.30	0.45	1.00	-0.42		-0.30	-0.83	0.28
Sediment TP/TOC	-0.22	-0.02	-0.13	-0.22	0.13	0.25	0.25	0.67	-0.22	0.50	0.08	-0.32	0.40	-0.22	-0.08	NA	NA	NA	NA	NA	-0.98	-0.98	0.63	0.52	-0.30	0.10	-0.30		0.37	-0.98
Sediment TN/TOC	-0.62	-0.80	0.47	-0.76	0.45	0.92	0.75	0.10	-0.92	-0.42	0.88	-0.37	0.95	0.30	0.05	NA	NA	NA	NA	NA	-0.27	-0.35	-0.33	-0.22	-0.83	0.07	-0.83	0.37		-0.35
Sediment TOC	0.20	0.00	0.18	0.25	-0.13	-0.27	-0.27	-0.68	0.20	-0.53	-0.07	0.33	-0.38	0.27	0.13	NA	NA	NA	NA	NA	0.97	1.00	-0.67	-0.53	0.28	-0.03	0.28	-0.98	-0.35	

Appendix E8. Correlation coefficients between predicted soil and groundwater concentrations of iron, sulfur, sulfate and potassium (from Kriging of statewide data, as described in the text) and selected parameters analyzed in the 2012-2013 survey (one site visit to each of 119 different sites, including 82 lakes, 30 streams, and 7 cultivated paddies).

2012-2013 Survey **All Sites (N=119)** **Spearman Non-Parametric Correlation Coefficients (rho)** **P < 0.05 for |rho| > 0.187**	Wild rice % cover in ring	Surface water K	Surface water Fe	Surface water SO4	Surface water Color	Porewater Sulfide	Porewater DOC	Porewater K	Porewater Fe	Porewater NH4	Porewater Silica	Sediment Total S	Sediment AVS	Sediment Fe	Predicted K in soil	Predicted Fe in soil	Predicted S in top 5 cm of soil	Predicted S in soil A horizon	Predicted S in soil C horizon	Predicted SO4 in surficial gravel & sand aquifers (A)	Predicted Fe in surficial gravel & sand aquifers (A)	Predicted Fe from all wells	Predicted SO4 from all wells	Predicted SO4 in surficial gravel & sand aquifers (B)	Predicted Fe in surficial gravel & sand aquifers (B)
Wild rice % cover in ring		0.04	0.11	-0.07	-0.01	-0.25	-0.01	-0.32	0.10	-0.29	-0.10	-0.15	-0.10	-0.02	-0.12	-0.04	-0.08	-0.02	-0.10	0.08	0.08	-0.09	0.08	-0.09	0.15
Surface water K	0.04		-0.33	0.34	-0.14	0.29	-0.05	0.51	-0.38	0.02	0.13	-0.14	0.08	-0.44	-0.14	0.13	0.06	-0.11	-0.03	0.13	-0.08	0.16	0.57	0.13	0.09
Surface water Fe	0.11	-0.33		-0.08	0.68	-0.24	0.42	-0.23	0.34	-0.06	-0.24	-0.10	-0.03	0.46	0.16	-0.12	0.07	0.13	0.01	-0.19	0.05	-0.35	-0.27	-0.29	-0.05
Surface water SO4	-0.07	0.34	-0.08		-0.02	0.30	-0.15	0.17	-0.17	-0.01	-0.03	0.01	0.37	0.00	0.05	0.05	0.04	0.00	0.12	0.03	-0.02	0.01	0.11	0.01	-0.03
Surface water Color	-0.01	-0.14	0.68	-0.02		-0.01	0.37	-0.05	0.15	0.00	-0.11	0.01	0.01	0.29	-0.01	-0.08	0.18	0.03	-0.11	-0.15	0.02	-0.19	-0.20	-0.20	0.05
Porewater Sulfide	-0.25	0.29	-0.24	0.30	-0.01		0.07	0.40	-0.55	0.37	0.35	0.44	0.22	-0.26	0.00	0.06	0.00	-0.07	-0.13	-0.02	-0.04	0.30	0.14	0.18	-0.09
Porewater DOC	-0.01	-0.05	0.42	-0.15	0.37	0.07		0.20	0.22	0.03	0.09	-0.04	-0.15	0.21	0.03	0.04	0.20	0.13	-0.09	-0.07	-0.03	-0.20	-0.04	-0.16	-0.09
Porewater K	-0.32	0.51	-0.23	0.17	-0.05	0.40	0.20		-0.30	0.35	0.26	0.07	-0.03	-0.27	0.01	-0.04	0.03	-0.14	-0.11	0.07	-0.12	0.21	0.39	0.11	-0.11
Porewater Fe	0.10	-0.38	0.34	-0.17	0.15	-0.55	0.22	-0.30		-0.24	-0.16	-0.22	0.14	0.61	0.02	-0.05	0.03	0.03	0.02	0.04	0.04	-0.31	-0.35	-0.04	0.01
Porewater NH4	-0.29	0.02	-0.06	-0.01	0.00	0.37	0.03	0.35	-0.24		0.37	0.26	0.11	-0.12	-0.02	0.07	0.04	0.07	-0.02	0.05	-0.12	0.06	0.07	-0.02	-0.21
Porewater Silica	-0.10	0.13	-0.24	-0.03	-0.11	0.35	0.09	0.26	-0.16	0.37		0.18	0.15	-0.09	0.08	-0.06	-0.01	0.17	-0.04	-0.09	0.12	-0.03	0.19	-0.08	-0.01
Sediment Total S	-0.15	-0.14	-0.10	0.01	0.01	0.44	-0.04	0.07	-0.22	0.26	0.18		0.41	0.23	0.00	0.08	0.15	0.04	-0.02	0.02	-0.12	0.22	-0.33	0.36	-0.07
Sediment AVS	-0.10	0.08	-0.03	0.37	0.01	0.22	-0.15	-0.03	0.14	0.11	0.15	0.41		0.44	0.06	0.16	0.07	0.09	0.05	0.00	-0.03	-0.11	-0.10	0.19	-0.02
Sediment Fe	-0.02	-0.44	0.46	0.00	0.29	-0.26	0.21	-0.27	0.61	-0.12	-0.09	0.23	0.44		0.10	-0.01	0.10	0.16	0.02	-0.15	0.04	-0.38	-0.42	-0.12	-0.09
Predicted K in soil	-0.12	-0.14	0.16	0.05	-0.01	0.00	0.03	0.01	0.02	-0.02	0.08	0.00	0.06	0.10		0.03	-0.28	0.33	0.26	-0.59	-0.04	-0.07	-0.08	-0.08	0.02
Predicted Fe in soil	-0.04	0.13	-0.12	0.05	-0.08	0.06	0.04	-0.04	-0.05	0.07	-0.06	0.08	0.16	-0.01	0.03		0.10	0.25	0.18	-0.25	-0.08	0.00	0.00	0.02	-0.09
Predicted S in top 5 cm of soil	-0.08	0.06	0.07	0.04	0.18	0.00	0.20	0.03	0.03	0.04	-0.01	0.15	0.07	0.10	-0.28	0.10		0.14	0.07	0.17	-0.15	-0.04	-0.11	0.04	0.04
Predicted S in soil A horizon	-0.02	-0.11	0.13	0.00	0.03	-0.07	0.13	-0.14	0.03	0.07	0.17	0.04	0.09	0.16	0.33	0.25	0.14		0.33	-0.34	-0.03	-0.07	-0.08	-0.21	-0.13
Predicted S in soil C horizon	-0.10	-0.03	0.01	0.12	-0.11	-0.13	-0.09	-0.11	0.02	-0.02	-0.04	-0.02	0.05	0.02	0.26	0.18	0.07	0.33		-0.06	0.09	0.05	0.02	0.00	0.05
Predicted SO4 in surficial gravel & sand aquifers (A)	0.08	0.13	-0.19	0.03	-0.15	-0.02	-0.07	0.07	0.04	0.05	-0.09	0.02	0.00	-0.15	-0.59	-0.25	0.17	-0.34	-0.06		-0.23	0.13	0.07	0.25	-0.03
Predicted Fe in surficial gravel & sand aquifers (A)	0.08	-0.08	0.05	-0.02	0.02	-0.04	-0.03	-0.12	0.04	-0.12	0.12	-0.12	-0.03	0.04	-0.04	-0.08	-0.15	-0.03	0.09	-0.23		-0.12	0.05	-0.17	0.17
Predicted Fe from all wells	-0.09	0.16	-0.35	0.01	-0.19	0.30	-0.20	0.21	-0.31	0.06	-0.03	0.22	-0.11	-0.38	-0.07	0.00	-0.04	-0.07	0.05	0.13	-0.12		0.05	0.44	-0.13
Predicted SO4 from all wells	0.08	0.57	-0.27	0.11	-0.20	0.14	-0.04	0.39	-0.35	0.07	0.19	-0.33	-0.10	-0.42	-0.08	0.00	-0.11	-0.08	0.02	0.07	0.05	0.05		-0.33	0.22
Predicted SO4 in surficial gravel & sand aquifers (B)	-0.09	0.13	-0.29	0.01	-0.20	0.18	-0.16	0.11	-0.04	-0.02	-0.08	0.36	0.19	-0.12	-0.08	0.02	0.04	-0.21	0.00	0.25	-0.17	0.44	-0.33		-0.03
Predicted Fe in surficial gravel & sand aquifers (B)	0.15	0.09	-0.05	-0.03	0.05	-0.09	-0.09	-0.11	0.01	-0.21	-0.01	-0.07	-0.02	-0.09	0.02	-0.09	0.04	-0.13	0.05	-0.03	0.17	-0.13	0.22	-0.03	

Appendix E9. Correlation coefficients between predicted soil and groundwater concentrations of iron, sulfur, sulfate and potassium (from Kriging of statewide data, as described in the text) and selected parameters analyzed in lake samples in the 2012-2013 survey (one site visit to each of 82 different lakes).

2012-2013 Survey Lakes (N=82) Spearman Non-Parametric Correlation Coefficients (rho) P < 0.05 for |rho| > 0.217	Wild rice % cover in ring	Surface water K	Surface water Fe	Surface water SO4	Surface water Color	Porewater Sulfide	Porewater DOC	Porewater K	Porewater Fe	Porewater NH4	Porewater Silica	Sediment Total S	Sediment AVS	Sediment Fe	Predicted K in soil	Predicted Fe in soil	Predicted S in top 5 cm of soil	Predicted S in soil A horizon	Predicted S in soil C horizon	Predicted SO4 in surficial gravel & sand aquifers (A)	Predicted Fe in surficial gravel & sand aquifers (A)	Predicted Fe from all wells	Predicted SO4 from all wells	Predicted SO4 in surficial gravel & sand aquifers (B)	Predicted Fe in surficial gravel & sand aquifers (B)
Wild rice % cover in ring		-0.07	0.04	-0.24	-0.12	-0.23	0.07	-0.40	0.15	-0.16	-0.01	-0.14	-0.11	-0.06	-0.13	-0.03	-0.10	-0.06	-0.08	0.11	0.04	0.06	0.01	-0.07	0.06
Surface water K	-0.07		-0.38	0.29	-0.09	0.27	0.00	0.55	-0.33	0.06	0.20	-0.31	0.07	-0.50	-0.17	0.18	0.06	0.04	0.07	0.14	0.05	0.18	0.62	0.04	0.08
Surface water Fe	0.04	-0.38		-0.30	0.67	-0.32	0.28	-0.35	0.31	0.00	-0.20	0.02	-0.01	0.42	0.07	-0.02	0.08	0.04	-0.14	-0.18	-0.13	-0.36	-0.27	-0.29	0.04
Surface water SO4	-0.24	0.29	-0.30		-0.14	0.50	-0.25	0.25	-0.35	0.10	0.11	0.21	0.43	-0.10	0.02	0.11	0.01	0.06	0.11	0.08	-0.05	0.23	0.05	0.22	-0.12
Surface water Color	-0.12	-0.09	0.67	-0.14		-0.05	0.18	-0.15	0.04	0.05	-0.10	0.08	0.09	0.24	-0.05	-0.02	0.22	0.03	-0.08	-0.11	-0.16	-0.15	-0.22	-0.09	-0.02
Porewater Sulfide	-0.23	0.27	-0.32	0.50	-0.05		-0.11	0.31	-0.59	0.38	0.37	0.41	0.31	-0.28	0.14	0.10	-0.08	0.08	0.02	-0.06	0.03	0.29	0.17	0.17	-0.02
Porewater DOC	0.07	0.00	0.28	-0.25	0.18	-0.11		0.07	0.26	-0.07	0.10	-0.10	-0.16	0.16	0.06	0.10	0.14	0.23	-0.03	-0.03	-0.07	-0.24	0.03	-0.24	-0.06
Porewater K	-0.40	0.55	-0.35	0.25	-0.15	0.31	0.07		-0.19	0.30	0.32	-0.08	0.08	-0.25	0.05	-0.08	0.03	0.02	0.00	0.05	0.01	0.16	0.46	-0.01	-0.07
Porewater Fe	0.15	-0.33	0.31	-0.35	0.04	-0.59	0.26	-0.19		-0.23	-0.13	-0.19	0.05	0.58	-0.08	-0.16	0.01	-0.14	-0.16	0.10	-0.04	-0.29	-0.35	0.09	-0.08
Porewater NH4	-0.16	0.06	0.00	0.10	0.05	0.38	-0.07	0.30	-0.23		0.40	0.17	0.13	-0.09	0.00	0.05	0.05	0.15	0.03	0.05	-0.10	-0.01	0.17	-0.17	-0.06
Porewater Silica	-0.01	0.20	-0.20	0.11	-0.10	0.37	0.10	0.32	-0.13	0.40		0.11	0.23	-0.06	0.19	-0.13	-0.04	0.19	0.04	-0.10	0.09	0.00	0.20	-0.16	-0.05
Sediment Total S	-0.14	-0.31	0.02	0.21	0.08	0.41	-0.10	-0.08	-0.19	0.17	0.11		0.45	0.34	0.12	0.08	0.19	0.14	0.13	-0.05	-0.18	0.08	-0.35	0.26	-0.06
Sediment AVS	-0.11	0.07	-0.01	0.43	0.09	0.31	-0.16	0.08	0.05	0.13	0.23	0.45		0.46	0.10	0.06	0.01	0.10	0.02	-0.06	-0.03	-0.12	-0.09	0.19	-0.06
Sediment Fe	-0.06	-0.50	0.42	-0.10	0.24	-0.28	0.16	-0.25	0.58	-0.09	-0.06	0.34	0.46		0.04	-0.03	0.15	0.11	-0.03	-0.09	-0.14	-0.33	-0.44	-0.08	-0.23
Predicted K in soil	-0.13	-0.17	0.07	0.02	-0.05	0.14	0.06	0.05	-0.08	0.00	0.19	0.12	0.10	0.04		-0.05	-0.25	0.22	0.23	-0.63	0.07	-0.03	-0.03	-0.13	0.13
Predicted Fe in soil	-0.03	0.18	-0.02	0.11	-0.02	0.10	0.10	-0.08	-0.16	0.05	-0.13	0.08	0.06	-0.03	-0.05		0.15	0.41	0.34	-0.25	0.08	0.07	0.02	-0.05	-0.04
Predicted S in top 5 cm of soil	-0.10	0.06	0.08	0.01	0.22	-0.08	0.14	0.03	0.01	0.05	-0.04	0.19	0.01	0.15	-0.25	0.15		0.24	0.14	0.21	-0.24	-0.04	-0.17	0.07	0.09
Predicted S in soil A horizon	-0.06	0.04	0.04	0.06	0.03	0.08	0.23	0.02	-0.14	0.15	0.19	0.14	0.10	0.11	0.22	0.41	0.24		0.33	-0.30	-0.09	0.07	0.02	-0.23	-0.20
Predicted S in soil C horizon	-0.08	0.07	-0.14	0.11	-0.08	0.02	-0.03	0.00	-0.16	0.03	0.04	0.13	0.02	-0.03	0.23	0.34	0.14	0.33		-0.13	0.12	0.08	0.03	0.00	0.19
Predicted SO4 in surficial gravel & sand aquifers (A)	0.11	0.14	-0.18	0.08	-0.11	-0.06	-0.03	0.05	0.10	0.05	-0.10	-0.05	-0.06	-0.09	-0.63	-0.25	0.21	-0.30	-0.13		-0.26	0.00	0.07	0.20	-0.04
Predicted Fe in surficial gravel & sand aquifers (A)	0.04	0.05	-0.13	-0.05	-0.16	0.03	-0.07	0.01	-0.04	-0.10	0.09	-0.18	-0.03	-0.14	0.07	0.08	-0.24	-0.09	0.12	-0.26		0.02	0.05	-0.02	0.14
Predicted Fe from all wells	0.06	0.18	-0.36	0.23	-0.15	0.29	-0.24	0.16	-0.29	-0.01	0.00	0.08	-0.12	-0.33	-0.03	0.07	-0.04	0.07	0.08	0.00	0.02		0.16	0.28	-0.12
Predicted SO4 from all wells	0.01	0.62	-0.27	0.05	-0.22	0.17	0.03	0.46	-0.35	0.17	0.20	-0.35	-0.09	-0.44	-0.03	0.02	-0.17	0.02	0.03	0.07	0.05	0.16		-0.39	0.18
Predicted SO4 in surficial gravel & sand aquifers (B)	-0.07	0.04	-0.29	0.22	-0.09	0.17	-0.24	-0.01	0.09	-0.17	-0.16	0.26	0.19	-0.08	-0.13	-0.05	0.07	-0.23	0.00	0.20	-0.02	0.28	-0.39		0.08
Predicted Fe in surficial gravel & sand aquifers (B)	0.06	0.08	0.04	-0.12	-0.02	-0.02	-0.06	-0.07	-0.08	-0.06	-0.05	-0.06	-0.06	-0.23	0.13	-0.04	0.09	-0.20	0.19	-0.04	0.14	-0.12	0.18	0.08	

Appendix E10. Correlation coefficients between predicted soil and groundwater concentrations of iron, sulfur, sulfate and potassium (from Kriging of statewide data, as described in the text) and selected parameters analyzed in stream samples in the 2012-2013 survey (one site visit to each of 30 different streams).

2012-2013 Survey Streams (N=30) **Spearman Non-Parametric Correlation Coefficients (rho)** **P < 0.05 for |rho| > 0.36**	Wild rice % cover in ring	Surface water K	Surface water Fe	Surface water SO4	Surface water Color	Porewater Sulfide	Porewater DOC	Porewater K	Porewater Fe	Porewater NH4	Porewater Silica	Sediment Total S	Sediment AVS	Sediment Fe	Predicted K in soil	Predicted Fe in soil	Predicted S in top 5 cm of soil	Predicted S in soil A horizon	Predicted S in soil C horizon	Predicted SO4 in surficial gravel & sand aquifers (A)	Predicted Fe in surficial gravel & sand aquifers (A)	Predicted Fe from all wells	Predicted SO4 from all wells	Predicted SO4 in surficial gravel & sand aquifers (B)	Predicted Fe in surficial gravel & sand aquifers (B)
Wild rice % cover in ring		0.36	-0.34	0.20	-0.27	-0.37	-0.53	-0.29	-0.08	-0.65	-0.13	0.10	0.13	-0.04	-0.12	0.04	-0.28	-0.05	-0.22	0.10	-0.13	0.02	0.23	0.08	0.29
Surface water K	0.36		-0.36	0.57	-0.49	-0.10	-0.46	0.09	-0.13	-0.38	-0.17	-0.14	0.22	-0.19	0.03	0.13	-0.15	-0.21	0.19	0.15	-0.28	-0.15	0.54	0.04	0.21
Surface water Fe	-0.34	-0.36		0.03	0.68	0.10	0.67	0.17	0.47	0.15	-0.12	0.15	0.28	0.52	0.29	-0.18	0.07	0.28	0.45	-0.11	0.10	-0.03	-0.49	0.19	-0.21
Surface water SO4	0.20	0.57	0.03		0.08	0.03	-0.14	0.26	0.25	-0.22	-0.21	-0.15	0.35	0.15	0.06	0.08	0.02	-0.12	0.22	0.07	0.01	-0.42	0.26	-0.21	0.10
Surface water Color	-0.27	-0.49	0.68	0.08		0.13	0.61	0.12	0.57	0.01	-0.05	0.09	0.18	0.50	0.11	-0.03	0.09	0.08	0.01	-0.16	0.20	-0.15	-0.34	-0.13	0.13
Porewater Sulfide	-0.37	-0.10	0.10	0.03	0.13		0.29	0.33	-0.20	0.20	0.06	0.10	0.09	0.01	-0.14	0.10	0.04	-0.01	-0.16	-0.12	0.03	0.08	-0.02	-0.16	-0.18
Porewater DOC	-0.53	-0.46	0.67	-0.14	0.61	0.29		0.23	0.42	0.35	0.11	0.00	0.09	0.44	0.11	0.10	0.28	0.19	0.18	-0.18	-0.05	-0.20	-0.42	-0.02	-0.17
Porewater K	-0.29	0.09	0.17	0.26	0.12	0.33	0.23		-0.19	0.38	-0.31	-0.32	-0.18	-0.25	0.26	0.19	-0.24	-0.23	0.20	-0.01	-0.36	0.05	0.13	0.08	-0.28
Porewater Fe	-0.08	-0.13	0.47	0.25	0.57	-0.20	0.42	-0.19		-0.12	-0.10	0.09	0.41	0.47	0.18	0.16	0.34	0.18	0.15	-0.05	0.06	-0.23	-0.47	0.01	0.23
Porewater NH4	-0.65	-0.38	0.15	-0.22	0.01	0.20	0.35	0.38	-0.12		0.01	0.20	0.01	-0.05	0.04	0.06	0.19	0.21	0.05	-0.04	0.01	0.02	-0.37	0.08	-0.52
Porewater Silica	-0.13	-0.17	-0.12	-0.21	-0.05	0.06	0.11	-0.31	-0.10	0.01		-0.14	-0.16	0.00	-0.06	-0.23	0.02	0.23	-0.34	-0.24	0.23	-0.44	0.13	-0.59	0.11
Sediment Total S	0.10	-0.14	0.15	-0.15	0.09	0.10	0.00	-0.32	0.09	0.20	-0.14		0.55	0.47	-0.11	-0.02	-0.01	0.25	-0.18	-0.07	0.29	0.11	-0.45	0.26	-0.04
Sediment AVS	0.13	0.22	0.28	0.35	0.18	0.09	0.09	-0.18	0.41	0.01	-0.16	0.55		0.55	-0.14	0.26	0.24	0.12	-0.05	0.04	0.04	-0.30	-0.23	0.08	0.03
Sediment Fe	-0.04	-0.19	0.52	0.15	0.50	0.01	0.44	-0.25	0.47	-0.05	0.00	0.47	0.55		0.10	0.07	0.06	0.11	0.02	-0.23	0.38	-0.34	-0.42	0.10	0.15
Predicted K in soil	-0.12	0.03	0.29	0.06	0.11	-0.14	0.11	0.26	0.18	0.04	-0.06	-0.11	-0.14	0.10		0.22	-0.35	0.36	0.19	-0.46	-0.37	-0.13	-0.24	0.22	-0.18
Predicted Fe in soil	0.04	0.13	-0.18	0.08	-0.03	0.10	0.10	0.19	0.16	0.06	-0.23	-0.02	0.26	0.07	0.22		0.12	0.00	-0.26	-0.41	-0.42	-0.27	-0.05	-0.05	-0.10
Predicted S in top 5 cm of soil	-0.28	-0.15	0.07	0.02	0.09	0.04	0.28	-0.24	0.34	0.19	0.02	-0.01	0.24	0.06	-0.35	0.12		0.23	0.24	0.12	0.11	-0.26	-0.10	-0.24	-0.01
Predicted S in soil A horizon	-0.05	-0.21	0.28	-0.12	0.08	-0.01	0.19	-0.23	0.18	0.21	0.23	0.25	0.12	0.11	0.36	0.00	0.23		0.14	-0.41	-0.05	-0.19	-0.36	0.03	-0.17
Predicted S in soil C horizon	-0.22	0.19	0.45	0.22	0.01	-0.16	0.18	0.20	0.15	0.05	-0.34	-0.18	-0.05	0.02	0.19	-0.26	0.24	0.14		0.13	-0.09	0.10	-0.01	0.25	-0.19
Predicted SO4 in surficial gravel & sand aquifers (A)	0.10	0.15	-0.11	0.07	-0.16	-0.12	-0.18	-0.01	-0.05	-0.04	-0.24	-0.07	0.04	-0.23	-0.46	-0.41	0.12	-0.41	0.13		-0.02	0.37	0.07	0.23	0.04
Predicted Fe in surficial gravel & sand aquifers (A)	-0.13	-0.28	0.10	0.01	0.20	0.03	-0.05	-0.36	0.06	0.01	0.23	0.29	0.04	0.38	-0.37	-0.42	0.11	-0.05	-0.09	-0.02		-0.07	-0.07	-0.21	0.14
Predicted Fe from all wells	0.02	-0.15	-0.03	-0.42	-0.15	0.08	-0.20	0.05	-0.23	0.02	-0.44	0.11	-0.30	-0.34	-0.13	-0.27	-0.26	-0.19	0.10	0.37	-0.07		-0.20	0.60	-0.20
Predicted SO4 from all wells	0.23	0.54	-0.49	0.26	-0.34	-0.02	-0.42	0.13	-0.47	-0.37	0.13	-0.45	-0.23	-0.42	-0.24	-0.05	-0.10	-0.36	-0.01	0.07	-0.07	-0.20		-0.47	0.37
Predicted SO4 in surficial gravel & sand aquifers (B)	0.08	0.04	0.19	-0.21	-0.13	-0.16	-0.02	0.08	0.01	0.08	-0.59	0.26	0.08	0.10	0.22	-0.05	-0.24	0.03	0.25	0.23	-0.21	0.60	-0.47		-0.28
Predicted Fe in surficial gravel & sand aquifers (B)	0.29	0.21	-0.21	0.10	0.13	-0.18	-0.17	-0.28	0.23	-0.52	0.11	-0.04	0.03	0.15	-0.18	-0.10	-0.01	-0.17	-0.19	0.04	0.14	-0.20	0.37	-0.28	

Appendix E11. Correlation coefficients between predicted soil and groundwater concentrations of iron, sulfur, sulfate and potassium (from Kriging of statewide data, as described in the text) and selected parameters analyzed in paddy samples in the 2012-2013 survey (one site visit to each of 7 different paddies).

2012-2013 Survey Paddies (N=7) Spearman Non-Parametric Correlation Coefficients (rho) P < 0.05 for |rho| > 0.79	Wild rice % cover in ring	Surface water K	Surface water Fe	Surface water SO4	Surface water Color	Porewater Sulfide	Porewater DOC	Porewater K	Porewater Fe	Porewater NH4	Porewater Silica	Sediment Total S	Sediment AVS	Sediment Fe	Predicted K in soil	Predicted Fe in soil	Predicted S in top 5 cm of soil	Predicted S in soil A horizon	Predicted S in soil C horizon	Predicted SO4 in surficial gravel & sand aquifers (A)	Predicted Fe in surficial gravel & sand aquifers (A)	Predicted Fe from all wells	Predicted SO4 from all wells	Predicted SO4 in surficial gravel & sand aquifers (B)	Predicted Fe in surficial gravel & sand aquifers (B)
Wild rice % cover in ring		-0.20	-0.14	-0.60	-0.43	-0.49	-0.54	-0.14	0.60	-0.71	0.26	0.54	0.26	0.77	0.20	0.37	0.09	0.43	0.43	0.60	0.49	-0.94	0.43	0.37	NA
Surface water K	-0.20		-0.03	0.60	-0.09	0.94	-0.03	-0.03	-0.20	0.26	-0.03	0.03	0.77	0.31	-0.20	-0.09	0.70	-0.71	-0.71	-0.60	-0.14	0.37	0.49	0.31	NA
Surface water Fe	-0.14	-0.03		-0.14	0.71	0.14	0.83	0.20	0.60	0.26	-0.26	0.66	0.20	0.26	-0.89	-0.09	-0.21	-0.54	-0.54	0.14	-0.49	0.37	-0.43	-0.66	NA
Surface water SO4	-0.60	0.60	-0.14		0.14	0.66	-0.09	-0.26	-0.66	0.43	-0.43	-0.60	0.03	-0.26	0.20	-0.66	0.09	-0.37	-0.37	-1.00	-0.20	0.54	0.20	0.26	NA
Surface water Color	-0.43	-0.09	0.71	0.14		0.14	0.77	0.60	0.37	0.77	0.09	0.26	0.03	-0.09	-0.66	0.03	-0.64	-0.20	-0.20	-0.14	-0.03	0.54	-0.14	-0.26	NA
Porewater Sulfide	-0.49	0.94	0.14	0.66	0.14		0.26	0.09	-0.26	0.49	-0.09	-0.03	0.66	0.09	-0.37	-0.14	0.58	-0.83	-0.83	-0.66	-0.31	0.66	0.26	0.09	NA
Porewater DOC	-0.54	-0.03	0.83	-0.09	0.77	0.26		0.49	0.31	0.60	-0.03	0.37	0.09	-0.20	-0.89	0.09	-0.21	-0.54	-0.54	0.09	-0.49	0.71	-0.54	-0.71	NA
Porewater K	-0.14	-0.03	0.20	-0.26	0.60	0.09	0.49		0.43	0.71	0.83	0.31	0.31	-0.03	-0.49	0.77	-0.33	0.09	0.09	0.26	0.49	0.26	0.26	0.14	NA
Porewater Fe	0.60	-0.20	0.60	-0.66	0.37	-0.26	0.31	0.43		-0.09	0.37	0.94	0.43	0.71	-0.60	0.54	-0.21	0.03	0.03	0.66	0.26	-0.37	0.14	-0.09	NA
Porewater NH4	-0.71	0.26	0.26	0.43	0.77	0.49	0.60	0.71	-0.09		0.31	-0.14	0.14	-0.37	-0.43	0.14	-0.33	-0.26	-0.26	-0.43	0.09	0.77	0.09	0.03	NA
Porewater Silica	0.26	-0.03	-0.26	-0.43	0.09	-0.09	-0.03	0.83	0.37	0.31		0.26	0.37	0.14	-0.09	0.94	-0.09	0.37	0.37	0.43	0.77	-0.20	0.54	0.49	NA
Sediment Total S	0.54	0.03	0.66	-0.60	0.26	-0.03	0.37	0.31	0.94	-0.14	0.26		0.60	0.77	-0.71	0.49	0.09	-0.26	-0.26	0.60	0.03	-0.26	0.09	-0.20	NA
Sediment AVS	0.26	0.77	0.20	0.03	0.03	0.66	0.09	0.31	0.43	0.14	0.37	0.60		0.71	-0.49	0.43	0.58	-0.54	-0.54	-0.03	0.14	0.03	0.60	0.31	NA
Sediment Fe	0.77	0.31	0.26	-0.26	-0.09	0.09	-0.20	-0.03	0.71	-0.37	0.14	0.77	0.71		-0.26	0.26	0.27	-0.14	-0.14	0.26	0.26	-0.54	0.54	0.31	NA
Predicted K in soil	0.20	-0.20	-0.89	0.20	-0.66	-0.37	-0.89	-0.49	-0.60	-0.43	-0.09	-0.71	-0.49	-0.26		-0.26	-0.03	0.66	0.66	-0.20	0.37	-0.49	0.26	0.54	NA
Predicted Fe in soil	0.37	-0.09	-0.09	-0.66	0.03	-0.14	0.09	0.77	0.54	0.14	0.94	0.49	0.43	0.26	-0.26		0.03	0.26	0.26	0.66	0.60	-0.26	0.37	0.26	NA
Predicted S in top 5 cm of soil	0.09	0.70	-0.21	0.09	-0.64	0.58	-0.21	-0.33	-0.21	-0.33	-0.09	0.09	0.58	0.27	-0.03	0.03		-0.58	-0.58	-0.09	-0.33	0.03	0.15	0.03	NA
Predicted S in soil A horizon	0.43	-0.71	-0.54	-0.37	-0.20	-0.83	-0.54	0.09	0.03	-0.26	0.37	-0.26	-0.54	-0.14	0.66	0.26	-0.58		1.00	0.37	0.71	-0.66	0.20	0.43	NA
Predicted S in soil C horizon	0.43	-0.71	-0.54	-0.37	-0.20	-0.83	-0.54	0.09	0.03	-0.26	0.37	-0.26	-0.54	-0.14	0.66	0.26	-0.58	1.00		0.37	0.71	-0.66	0.20	0.43	NA
Predicted SO4 in surficial gravel & sand aquifers (A)	0.60	-0.60	0.14	-1.00	-0.14	-0.66	0.09	0.26	0.66	-0.43	0.43	0.60	-0.03	0.26	-0.20	0.66	-0.09	0.37	0.37		0.20	-0.54	-0.20	-0.26	NA
Predicted Fe in surficial gravel & sand aquifers (A)	0.49	-0.14	-0.49	-0.20	-0.03	-0.31	-0.49	0.49	0.26	0.09	0.77	0.03	0.14	0.26	0.37	0.60	-0.33	0.71	0.71	0.20		-0.54	0.77	0.83	NA
Predicted Fe from all wells	-0.94	0.37	0.37	0.54	0.54	0.66	0.71	0.26	-0.37	0.77	-0.20	-0.26	0.03	-0.54	-0.49	-0.26	0.03	-0.66	-0.66	-0.54	-0.54		-0.37	-0.43	NA
Predicted SO4 from all wells	0.43	0.49	-0.43	0.20	-0.14	0.26	-0.54	0.26	0.14	0.09	0.54	0.09	0.60	0.54	0.26	0.37	0.15	0.20	0.20	-0.20	0.77	-0.37		0.94	NA
Predicted SO4 in surficial gravel & sand aquifers (B)	0.37	0.31	-0.66	0.26	-0.26	0.09	-0.71	0.14	-0.09	0.03	0.49	-0.20	0.31	0.31	0.54	0.26	0.03	0.43	0.43	-0.26	0.83	-0.43	0.94		NA
Predicted Fe in surficial gravel & sand aquifers (B)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	

Appendix F. Statistical Analysis for Figures 20 and 21

Objective

To assess the relationship between surface water SO4 and the sediment variables AVS, AVS/TOC, and Fe/AVS, and to assess whether these relationships differ among lakes, streams, and paddies.

Data sets

Field Survey (data set = 4)
Lakes: n=82
Streams: n=30
Paddies: n=7
Censored data were replaced by half the detection value.

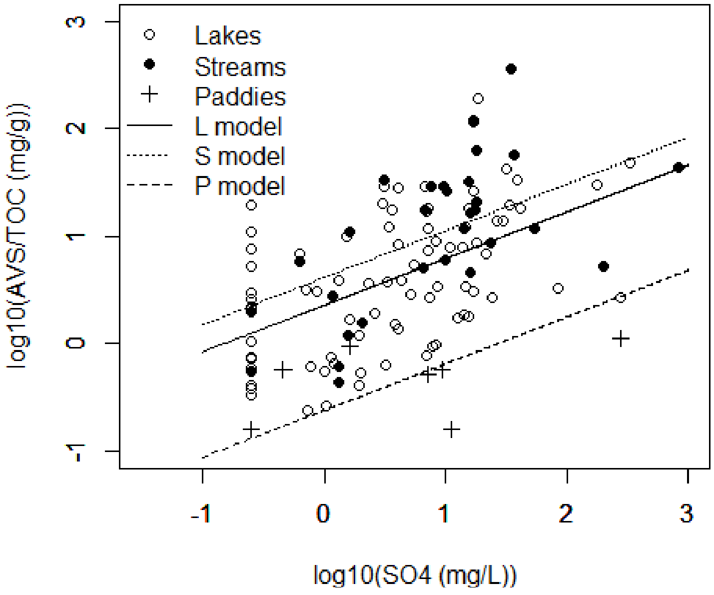
Sediment variables assessed:
sediment AVS/TOC
sediment Fe/AVS

Analyses

Spearman rank correlation tests were used to evaluate the significance of a monotonic correlation between SO4 and the sediment variables. Parametric multiple regression models were used to test the significance of a linear fit. Model simplification was used to determine whether the linear fit differed significantly among lakes, streams, and paddies. To better meet parametric assumptions of normal residuals with constant variance, water chemistry variables were transformed using log base 10.

AVS/TOC vs. SO4

Data set = Field Survey

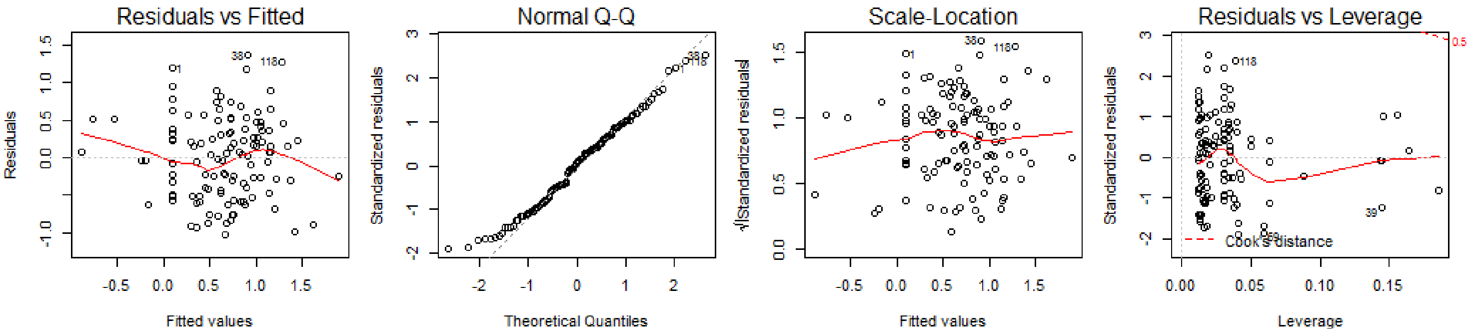


Correlation test & linear fits

	Spearman rho	Linear fit using transformed variables: intercept (SE)	Linear fit using transformed variables: slope (SE)
All	0.56	0.35(0.07)	0.46(0.07)
Lakes	0.54	0.36(0.08)	0.43(0.08)
Streams	0.64	0.50(0.15)	0.56(0.13)
Paddies	0.29	-0.43(0.15)	0.14(0.13)

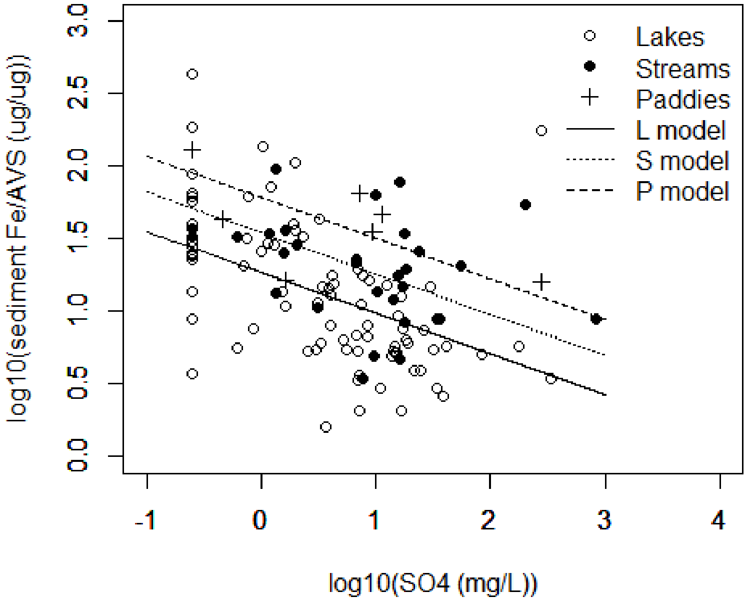
Minimal adequate regression model

- Significantly different intercepts, but not significantly different slopes between lakes, streams, and paddies.
  - **Equation: log10(AVS/TOC) = 0.35*(lake=TRUE) + 0.61*(stream=TRUE) -0.62*(paddy=TRUE) + 0.44*log10(SO4)**
- $r^2 = 0.4025$, $p < 0.001$



Sediment Fe/AVS vs. SO4

Data set = Field Survey

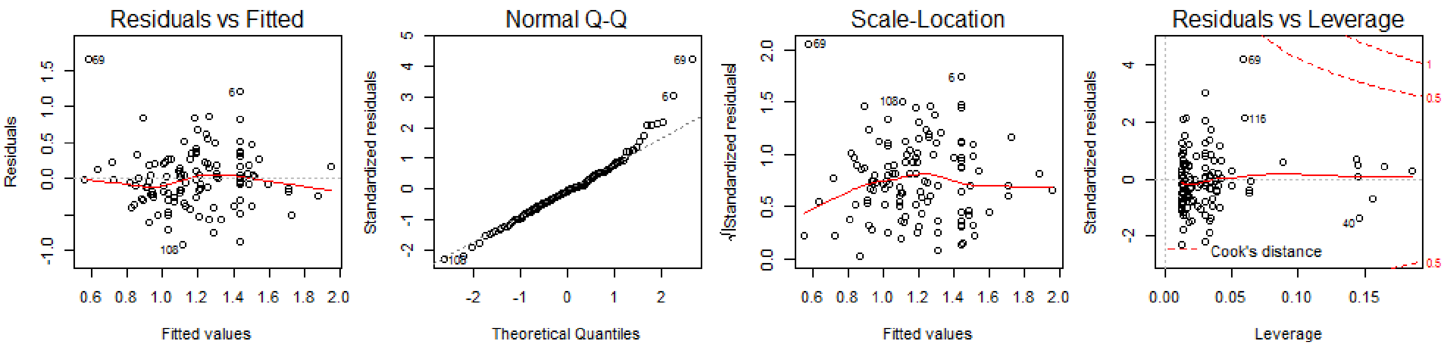


Correlation test & linear fits

	Spearman rho	Linear fit using transformed variables: intercept (SE)	Linear fit using transformed variables: slope (SE)
All	-0.47	1.35(0.05)	-0.26(0.05)
Lakes	-0.62	1.30(0.06)	-0.34(0.06)
Streams	-0.35	1.41(0.10)	-0.14(0.08)
Paddies	-0.54	1.72(0.13)	-0.19(0.11)

Minimal adequate regression model

- Significantly different intercepts, but not significantly different slopes between lakes, streams, and paddies.
- **Equation: log10(sed Fe/AVS) = 1.27*(lake=TRUE) + 1.53*(stream=TRUE) + 1.78*(paddy=TRUE) - 0.28*log10(SO4)**
- $r^2 = 0.2779$, $p < 0.001$



Appendix G. Multiple Quantile Regression Statistical Analysis

Objective

Build quantile regression model to predict pore water sulfide from surface water SO4 and sediment Fe.

Dataset

Field survey data, data set = 4 (n=119)

Data below reporting limit were substituted with half the reporting limit.

Analysis

A semi-parametric linear quantile regression model was used to define the relationship between pore water sulfide, surface water SO4, and acid-extractable sediment Fe. All variables were transformed using log base 10. To illustrate the model results, 5 specified sediment Fe concentrations were used (1609, 2923, 4917, 9361, 20,646 ug/g) that correspond to the 5, 25, 50, 75, and 95th percentiles.

Summary

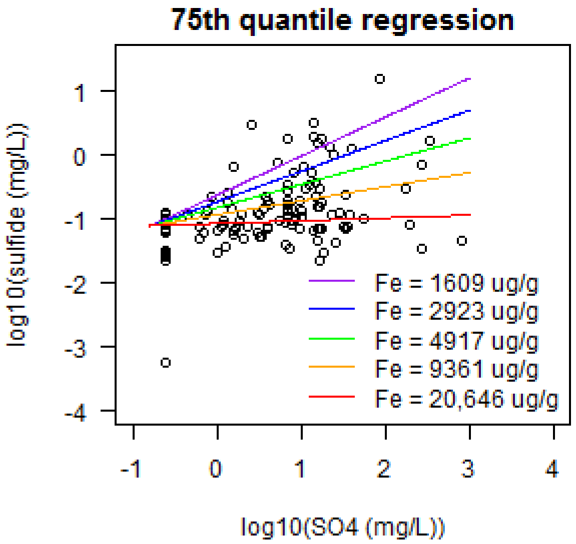
Results show that the slope of the relationship between sulfide and SO4 decreases with increasing sediment Fe. Uncertainty associated with model coefficients increases at the higher quantile regressions.

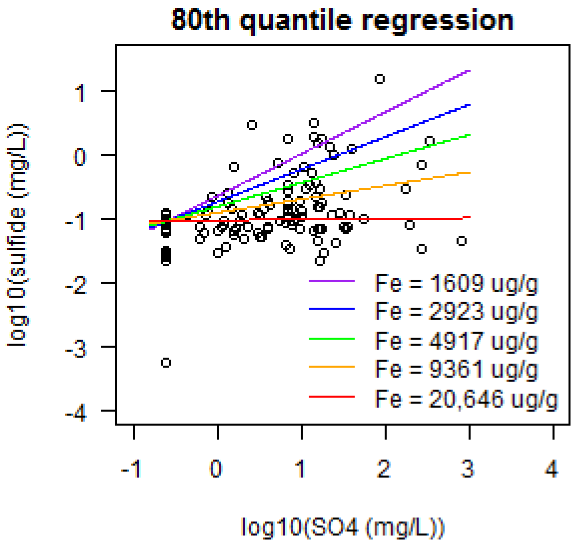
Model

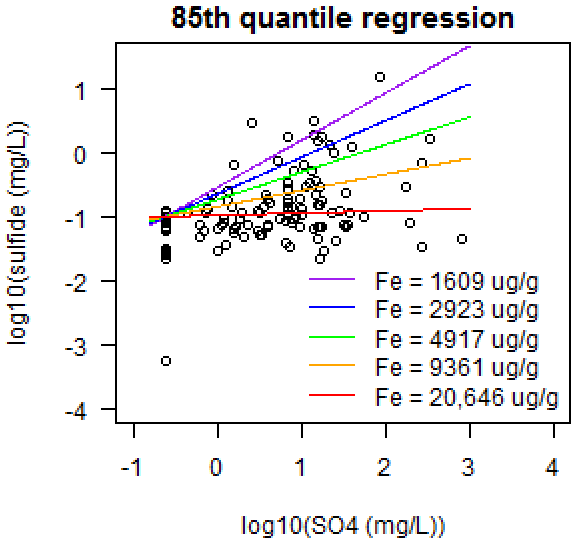
Y =log10(pore water sulfide)

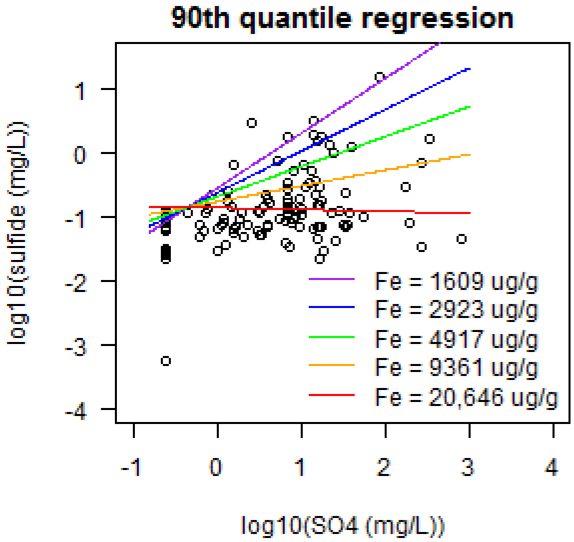
X1 =log10(surface water SO4)

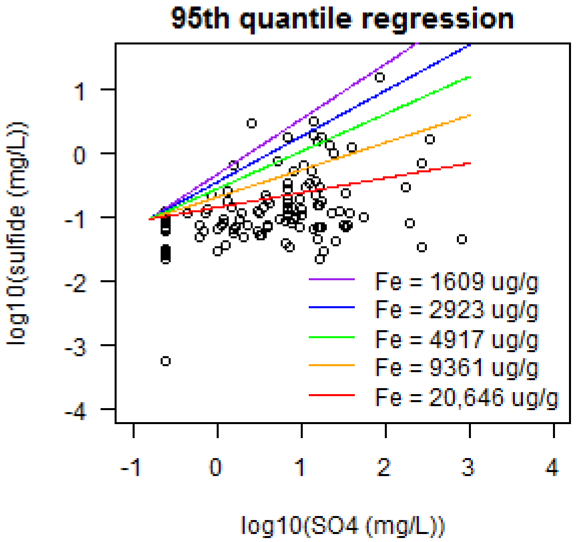
X2 =log10(sediment Fe)


75th quantile regression


80th quantile regression

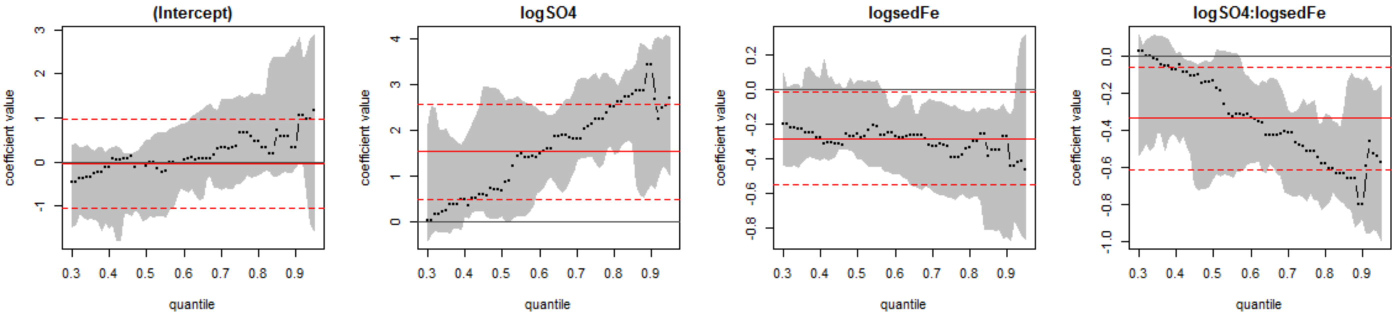

85th quantile regression


90th quantile regression


95th quantile regression

Evaluation of model coefficients

black dotted line = quantile regression coefficient estimate, grey line = 95% confidence interval around quantile regression coefficient estimates, red line = regular ordinary least squares model coefficient estimate, red dotted lines = 95% confidence interval around ordinary least squares coefficient estimate.



75th quantile model: AIC = 175 coefficients lower bd upper bd (Intercept) 0.65259 -0.48603 1.51118 logSO4 2.25455 1.30719 3.26089 logsedFe -0.39944 -0.62640 -0.10042 logSO4:logsedFe -0.51238 -0.78264 -0.26261	90th quantile model: AIC = 212 coefficients lower bd upper bd (Intercept) 0.32528 -0.12316 2.60593 logSO4 3.42986 0.81403 3.73791 logsedFe -0.27241 -0.85609 -0.12987 logSO4:logsedFe -0.80157 -0.87395 -0.13314
80th quantile model: AIC = 182 coefficients lower bd upper bd (Intercept) 0.45532 -0.29283 1.54397 logSO4 2.52426 1.48797 3.10325 logsedFe -0.34111 -0.63140 -0.13170 logSO4:logsedFe -0.58218 -0.80628 -0.31330	95th quantile model: AIC = 235 coefficients lower bd upper bd (Intercept) 1.16002 -1.55909 2.89590 logSO4 2.70274 1.03760 4.02075 logsedFe -0.46432 -0.86490 0.31458 logSO4:logsedFe -0.57296 -0.99508 -0.15538
85th quantile model: AIC = 194 coefficients lower bd upper bd (Intercept) 0.71730 -0.30902 2.36999 logSO4 2.77921 1.71415 3.35134 logsedFe -0.39093 -0.81083 -0.10970 logSO4:logsedFe -0.63623 -0.79433 -0.29289	