**RESEARCH ARTICLE**

**Key Points:**
- Factors controlling pore water sulfide, which can be toxic to wild rice, were identified with structural equation modeling
- Structural equation modeling was used to quantify the relative effects of sulfate, iron, and TOC on pore water sulfide concentrations
- The concentration of pore water sulfide is controlled nearly equally by sulfate in surface water and sediment organic carbon and iron

**Supporting Information:**
- Supporting Information S1
- Data Set S1
- Figure S1
- Figure S2
- Figure S3
- Figure S4
- Figure S5
- Figure S6
- Figure S7
- Figure S8

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# The Evolution of Sulfide in Shallow Aquatic Ecosystem Sediments: An Analysis of the Roles of Sulfate, Organic Carbon, and Iron and Feedback Constraints Using Structural Equation Modeling

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**Abstract** The generation of elevated concentrations of sulfide in sediment pore waters that are toxic to rooted macrophytes is problematic in both marine and freshwaters. In marine waters, biogeochemical conditions that lead to toxic levels of sulfide generally relate to factors that affect oxygen dynamics or the sediment iron concentration. In freshwaters, increases in surface water sulfate have been implicated in decline of *Zizania palustris* (wild rice), which is important in wetlands across the Great Lakes region of North America. We developed a structural equation (SE) model to elucidate key variables that govern the evolution of sulfide in pore waters in shallow aquatic habitats that are potentially capable of supporting wild rice. The conceptual basis for the model is the hypothesis that dissimilatory sulfate reduction is limited by the availability of both sulfate and total organic carbon (TOC) in the sediment. The conceptual model also assumes that pore water sulfide concentrations are constrained by the availability of pore water iron and that sediment iron supports the supply of dissolved iron to the pore water. A key result from the SE model is that variations in three external variables (sulfate, sediment TOC, and sediment iron) contribute nearly equally to the observed variations in pore water sulfide. As a result, management efforts to mitigate against the toxic effects of pore water sulfide on macrophytes such as wild rice should approach defining a protective sulfate threshold as an exercise tailored to the geochemistry of each site that quantitatively considers the effects of ambient concentrations of sediment Fe and TOC.

**Plain Language Summary** Aquatic plants, such as wild rice, white rice, and waterlilies that have roots in the saturated soils of wetlands are vulnerable to the buildup of toxic levels of hydrogen sulfide (also called sulfide). Anaerobic bacteria in the soil make the sulfide from sulfate that penetrates the soil from the overlying water. When sulfate in the waterbody is low, sulfide in the soil is low. But when sulfate is high, sulfide has been hard to predict—sometimes low, sometimes high. The analysis of hundreds of wetland samples finds that sulfide can be predicted if two variables in addition to sulfate are considered: organic carbon in the soil, which is the food for the bacteria, and iron in the soil, which removes sulfide from solution. A model of the chemical reactions finds that the three variables, sulfate, organic carbon, and iron, are equally important in determining sulfide. The sensitivity of individual waterbodies to sulfate pollution effects on wild rice toxicity can thus be predicted from the analysis of the carbon and iron concentrations in the soil of a wetland.

## 1. Introduction

The evolution of sulfide concentrations in sediment pore waters can be toxic to rooted macrophytes in both marine and freshwater environments. Pore water sulfide is the product of anaerobic microbial respiration of sulfate in sediments. Despite the much different sulfate concentrations between the two environments —sulfate concentrations are generally orders of magnitude higher in marine systems than most continental waters—the biogeochemical principles governing the reduction of sulfate to sulfide are the same, and there should be recognition of the commonality of sulfide toxicity concerns and biogeochemical relationships. Here we describe a model of the roles of sulfate, sediment total organic carbon (TOC), and sediment iron (Fe) in determining potentially phytotoxic concentrations of sulfide in relatively sulfate-poor waters. Essentially the same question, the potential toxicity of sulfide to coastal seagrasses as a function of sulfate,

TOC, and Fe has been pursued since at least 2000 (e.g., Eldridge & Morse, 2000). The biggest difference in the approaches between the two environments is that the primary option to reduce sulfide toxicity in freshwater systems has been to control sulfate, whereas other controlling variables (e.g., TOC or water clarity) are not only more practical for control in coastal systems but are more likely to have been altered by human activity.

For example, sulfide has been implicated as the causative agent in a global decline of coastal seagrasses. In this case, the perturbations to sulfur cycling that lead to increased sulfide toxicity relate to anthropogenic activities that reduce light availability. Seagrasses are dependent on high light levels to produce sufficient oxygen to detoxify pore water sulfide and so are particularly vulnerable to any actions that reduce light availability, such as eutrophication or dredging (Orth et al., 2006). In addition, other factors that enhance pore water sulfide concentrations have been implicated in the decline of seagrasses, such as increased temperature (Koch & Erskine, 2001), increased sediment organic matter (Govers et al., 2014), iron-poor sediments (Marbà et al., 2008), and low water column oxygen (Borum et al., 2005).

Similar concerns about sulfide toxicity extend to freshwater systems (Lamers et al., 2013). For example, based on laboratory experiments demonstrating that *Cladium* is less tolerant of sulfide than *Typha*, sulfate enrichment has been implicated in the expansion of *Typha domingensis* (cattail) into areas once dominated by *Cladium jamaicense* (sawgrass) in the Florida Everglades (Li et al., 2009). One plant species of particular concern with respect to sulfide toxicity is *Zizania palustris* (wild rice), which is important in wetland environments across the Great Lakes region of North America, where it can occur in dense monocultures. This importance includes both its role as a food resource for waterfowl and humans and its economic significance to those who harvest and market it. Wild rice is also a very important cultural resource to many Minnesotans, including indigenous peoples such as the Ojibwe peoples who consider wild rice as sacred (Vennum, 1988).

Wild rice is an annual grass that grows best at water depths of 0.3 to 1.0 m in lakes, rivers, and wetlands with soft organic sediment, although it can be found rooting in a wide variety of sediment types, ranging from muck to sand (Aiken et al., 1988). Wild rice seeds are dropped into the water in the fall, lie in the sediment throughout the winter, and germinate in spring. Its occurrence and distribution are influenced by a variety of physical, hydrologic, and biogeochemical factors (Myrbo, Swain, Engstrom, et al., 2017). For example, the rate of seed germination declines greatly if the seeds dry; as a result, wild rice is usually found in permanent waterbodies. Reduced light availability, from turbidity or water color, limits the ability of wild rice to maintain a population in a waterbody (Myrbo, Swain, Engstrom, et al., 2017), because seedlings need photosynthesis to augment the seed's energy reserves in order to successfully reach the water surface (Aiken, 1986).

Sulfate has long been implicated as a variable that influences the occurrence and distribution of wild rice in Minnesota. The first such implication was by Moyle (1944) who, in an analysis of spatial variations in water chemistry in Minnesota surface waters, observed "No large stands of rice occur in waters having a $SO_4$ content greater than 10 ppm, and rice generally is absent from water with more than 50 ppm." This cognition that wild rice occurrence was associated with waters containing lower levels of sulfate, coupled with the importance of wild rice in Minnesota, led to the adoption of a sulfate standard to protect wild rice of 10 mg/L in 1973 by the state of Minnesota. However, the role of sulfate in limiting wild rice habitat has long been confusing, given that wild rice has been observed to grow well in elevated sulfate waters overlying silica sand substrate and in commercial paddies with sulfate concentrations of 170 mg/L (Aiken et al., 1988).

More recently, a series of studies commissioned by the Minnesota Pollution Control Agency (MPCA) indicate that sulfide in sediment pore water is a causative agent for adverse effects to wild rice and that any effect of sulfate is rather more likely indirect through any controls it exerts on the development of sulfide concentrations in pore waters. These studies include a field survey comprising one or more sampling trips to 93 lakes, 32 stream sites, and 7 wild rice paddies, (Myrbo, Swain, Engstrom, et al., 2017), 10 day hydroponic experiments, and multiyear mesocosm studies (Myrbo, Swain, Johnson, et al., 2017; Pastor et al., 2017).

The goal of the MPCA-sponsored research is to determine if it is appropriate to regulate sulfate in order to protect wild rice from sulfide toxicity. The relationship between surface water sulfate and pore water sulfide concentrations, however, is complex, and a standard that seeks to mitigate against the occurrence of sulfide concentrations harmful to the occurrence of wild rice by limiting sulfate concentrations should consider these complexities. These complexities are illustrated by considering the effects of both substrate limitation and geochemical thermodynamics. More specifically, sulfate reduction to sulfide is a microbially mediated process that involves sulfate-reducing bacteria using sulfate as a terminal electron acceptor to metabolize

organic matter in the absence of oxygen. Thus, the availability of both sulfate (Capone & Kiene, 1988; Cook et al., 1986; Perry et al., 1986; Sinke et al., 1992; Myrbo, Swain, Johnson, et al., 2017) and of organic carbon (Al-Raei et al., 2009; Glombitza et al., 2013) can limit sulfate reduction. Conditions favorable to sulfate reduction also can result in iron reduction from insoluble Fe(III) to soluble Fe(II). Fe(II) in turn can react with sulfide to form insoluble FeS and other iron-sulfide minerals (Hansel et al., 2015; Hines & Jones, 1985; van Cappellen & Wang, 1996).

Any model that relates surface water sulfate to pore water sulfide concentrations thus has to consider issues related to model specification—that is, whether the model includes the appropriate variables and whether the intervariable relationships posed in the model are truly representative of the underlying processes and satisfy the inherent assumptions of the model framework. Model specification errors thus can lead to erroneous coefficient estimates for a governing variable, including errors in both magnitude and direction. *Statistical* models that might be developed for the sulfate-sulfide problem also have to accommodate intervariable relationships that include both indirect (mediated) and nonrecursive (i.e., feedback) relationships. Traditional multivariate regression models only control for direct or apparent direct (net) effects and thus are ill suited for quantifying relationships that are either mediated or nonrecursive. As a result, similar to model estimation problems imposed by specificity errors, the misapplication of multivariate regression models can lead to misleading parameter coefficient estimates and a failure to properly quantify the components contributing to the *total* effect of a variable such as sulfate on a response variable such as sulfide, particularly if the model includes mediating variables (Grace et al., 2009; Pollman, 2014).

One approach that allows for and more properly accounts for the effects of mediating variables is structural equation modeling (SEM). Based on the hypothesized relationships that constitute the model, SEM seeks to reproduce the covariance structure of the observed data (Ullman, 2007). SEM can include models comprising measured or observed variables only (path analysis), models that include latent variables representing unmeasured processes (confirmatory factor analysis), or models that link both path and confirmatory analysis together. SEM is often referred to as *causal analysis* (Ullman, 2007) because the approach often is used to test or confirm an a priori, hypothesized model (Austin, 2007). While SEM does not actually prove causality (Bollen & Pearl, 2013; Weston & Gore, 2006), it does provide a framework for selecting or rejecting hypotheses based on the empirical data (Iriondo et al., 2003). Examples include using SEM to model macroinvertebrate distribution in riverine ecosystems (Bizzi et al., 2013) and estuaries (Malaeb et al., 2000), aquatic and estuarine macrophytes (Gustaffson & Boström, 2013; Hung et al., 2007), lacustrine phytoplankton dynamics (Arhonditsis et al., 2006; Korhonen et al., 2011; Liu et al., 2010), and methyl Hg cycling and bioaccumulation in the Florida Everglades, including mediated effects of surface water sulfate (Pollman, 2014). In addition, SEM has been used to construct models with a clear environmental management focus (La Peyre et al., 2001; Reckhow et al., 2005; Stober et al., 2001). For example, La Peyre et al. (2001) used SEM to model national wetland protection efforts as a function of five latent variables (defined as economic capital, social capital, government characteristics, environmental characteristics, and land use pressure). Their model suggested that variations in social capital had the greatest influence on wetland protection efforts and concluded that continued focus on social development was necessary to further wetland protection.

## 2. Objectives and Conceptual Model

The objective of this paper is to use SEM to define the functional role of surface water concentrations of sulfate vis à vis the development of pore water concentrations of sulfide, recognizing that the relationship is complex and likely involves direct, mediated, and feedback pathways. Based on the functional relationships we believe a priori to be important, we can construct a conceptual model that reflects those relationships and use SEM to test both the overall reasonableness of the model and the significance and importance of the individual components or pathways. Conceptually, our model has four components. The first component considers that the magnitude of sulfide production in the sediment pore water expectedly is related to sulfate concentrations in the water column (e.g., Cook & Schindler, 1983; Geurts et al., 2009; Siver et al., 2003; Myrbo, Swain, Johnson, et al., 2017). The second component is that the availability of sedimentary organic carbon can limit sulfate reduction (Al-Raei et al., 2009; Glombitza et al., 2013). The third component is that amorphous FeS or mackinawite formation governs the dynamics of pore water sulfide and Fe(II) concentrations:
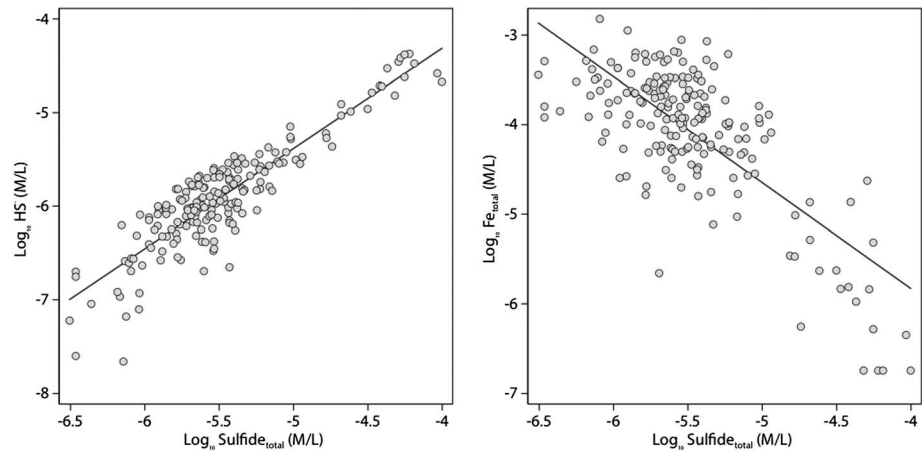
**Figure 1.** Key bivariate relationships for pore water sulfide relevant to assumptions in conceptual sulfide model. Left-hand panel: $HS^-$ concentrations as a function of measured total pore water sulfide. $HS^-$ concentrations based on acidity constants for $H_2S$ and measured pore water pH. Right-hand panel: total dissolved pore water Fe concentrations as a function of measured total pore water sulfide. All variables are $\log_{10}$ molar concentrations. Solid lines denote line of best fit obtained from linear regression. The 70.4% of the variance in the calculated values of the ($\log_{10}$-transformed) concentration of $HS^-$ is due to the variance in ($\log_{10}$-transformed) concentrations of total sulfide; shared variance between total sulfide and the pH-dependent speciation fraction for $HS^-$ accounts for another 5.0%. The coefficient of determination for the pore water Fe and total sulfide relationship (both variables $\log_{10}$ transformed) is 0.547 ($p < 0.0001$).

$$Fe(II) + HS^- \leftrightarrow FeS + H^+ \tag{1}$$

Inherent in our implementation of the model is the notion that pore water concentrations of total sulfide are a reasonable proxy for $HS^-$. Given that assumption, pore water Fe(II) and total sulfide concentrations should be inversely related (cf. Maynard et al., 2011); both assumptions are borne out by bivariate plots of the variables of interest (Figure 1; see also Myrbo, Swain, Engstrom, et al., 2017) constructed from our field data (see section 3.1 below). The last component of the conceptual model is that sediment Fe concentrations influence the pore water Fe concentrations that can develop under reducing conditions. This is an extension of the fact that sediment Fe must be present for dissolved Fe(II) concentrations to develop in the pore water, unless an alternative source of dissolved Fe(II) such as via shallow groundwater discharge is important.

The resultant conceptual model is shown schematically in Figure 2 and includes pore water sulfide, pore water Fe, and sediment total sulfur (S) as dependent or endogenous variables and sulfate, sediment Fe, and sediment total organic carbon (TOC) as independent or exogenous variables. The model also includes a mediated pathway for the effect of sulfate on pore water sulfide through links between sulfate and sediment total S and between sediment total S and pore water sulfide. This mediated pathway considers that a second route for sediment sulfur accretion is by biogenic uptake of sulfate in the water column (Pérez-Castiñeira et al., 1998) followed by deposition to and incorporation within the bottom sediments. An important feature of the conceptual model is that, consistent with the thermodynamic or equilibrium chemistry defined by equation (1), the link between pore water sulfide and Fe is nonrecursive rather than recursive. Recursive models allow for causation to flow in a single direction only, while nonrecursive models allow for feedback relationships such as the thermodynamic relationship between pore water Fe(II) and $HS^-$. While the use of nonrecursive models to model aquatic ecosystems has precedent—for example, evaluating the reciprocal relationships between sediment substrate
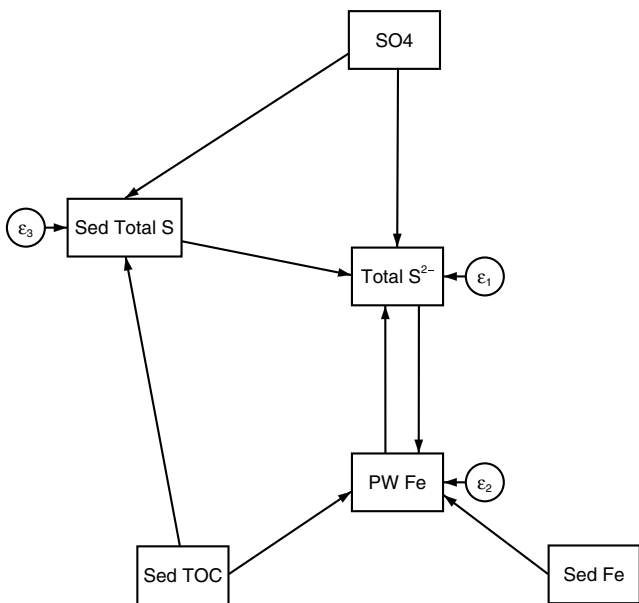


**Figure 2.** Conceptual model for biogeochemical controls on pore water sulfide in wetland sediments. Sed refers to sediment solid phase concentrations (mass parameter per dry mass sediment). PW Fe is pore water Fe; total $S_2^-$ is total pore water sulfide, and $SO_4$ is surface water $SO_4$.

characteristics and seagrass density (Folmer et al., 2012; van der Heide et al., 2011)—we believe that our use of a nonrecursive SEM to model pore water chemistry is the first such application.

## 3. Materials and Methods

### 3.1. Data

The data used to construct and evaluate the structural equation (SE) model were collected by the MPCA as part of a field survey designed to investigate the relationship between physical and chemical conditions in shallow waterbodies and the presence and absence of wild rice (Myrbo, Swain, Engstrom, et al., 2017). The field survey included pilot sampling conducted in 2011 comprising 58 samples collected from 48 different lake and stream sites, followed in 2012 and 2013 by a field survey that was broadened to include more sites with elevated sulfate concentrations and 7 different cultivated wild rice paddies. The broader survey included 121 different waterbodies, of which 40 were sampled on multiple occasions across time (2 to 6 times, except for one site sampled 10 times). The broader survey also included some sites that were also sampled during the pilot survey; thus, the total number of unique sites sampled during the entirety of the 3 year field survey included 131 different sites, with a total of 260 site visits. Field sampling included surface water, sediment, and pore water samples for a variety of physical, chemical, and habitat related variables, although some site visits were not able to collect the full suite of samples. Sampling protocols and methods for more than 65 parameters potentially measured at each site are detailed in Myrbo, Swain, Engstrom, et al., (2017).

Several considerations guided the selection of observations from the field survey data set for developing the SE model. SEM is generally regarded as data intensive, although perhaps not more so than multivariate regression (McCune & Grace, 2002). Estimates of minimum sample sizes to adequately conduct SEM vary but generally are related to the complexity of the model. Simulation studies by Jackson (2003), for example, suggest that improved model performance is achieved as the ratio of the number of observations to fitted model parameters increases. Model performance, however, appears to be more sensitive to the absolute number of samples (Jackson, 2003), with a typical sample size for SE models published in the literature approximating 200 (Kline, 2011). As a result, our overarching principle in data selection was to maximize the number of samples available to fit the model without compromising the integrity of the analysis. For example, we excluded paddy sites from the wild rice model data set because modeling natural systems is our ultimate goal, and paddies are manipulated in ways that likely cause the biogeochemistry to differ from natural sites. For instance, N and P fertilizers are used and, in a fundamental departure from natural sites, paddies are dewatered each summer, which may alter the oxidation state of the sediment. After eliminating paddies, we further screened the data set to exclude those sites that did not have a complete set of measurements for surface water sulfate, pore water sulfide, pore water Fe, sediment Fe, sediment TOC, and sediment total S. This latter set of criteria also resulted in the exclusion of a relatively small number of samples. In an effort to assess potentially redox-active Fe, sediment Fe in this data set was quantified using a 0.5 N HCl extraction (Myrbo, Swain, Engstrom, et al., 2017), rather than a stronger acid digestion, which would have included relatively inert Fe.

We conducted preliminary multiple linear regression (MLR) analyses, using pore water sulfide as the dependent variable and surface water sulfate, sediment TOC, and sediment Fe as the independent variables, to identify possible outliers and influential observations. Based on the MLR analyses, we identified two clear outliers (Hoffs Slough and one sample from Sandy Lake) based on both inspecting model residuals and plotting values for hat leverage versus Cook's D distance (Hamilton, 2013). Hoffs Slough is a ditch in an agricultural area, while the Sandy Lake observation is one of a total of 10 samples collected from Sandy Lake; as a result, both outliers were excluded from further analysis. In addition, we excluded two observations with unusually high pore water sulfide (Bean and Lady Slipper; pore water sulfide 16.0 and 14.8 mg/L, respectively; the next highest sulfide concentration was 3.19 mg/L).

The resultant screened data set, which was named for internal purposes "Class D," includes a total of 194 observations from 111 different waterbodies. This number of observations was considered sufficient to engage in SEM given the relatively simple nature of the conceptual model and is consistent with the number of observations used by many published studies (Kline, 2011). The data include 20 observations collected in 2011, 107 in 2012, and 67 in 2013. Because 43 of the Class D sites were sampled more than once, we created a subset called "Class B" with which to compare results. Class B consists of one sample from each site and excludes samples collected in 2011, which were analyzed with slightly different lab methods (see Myrbo,
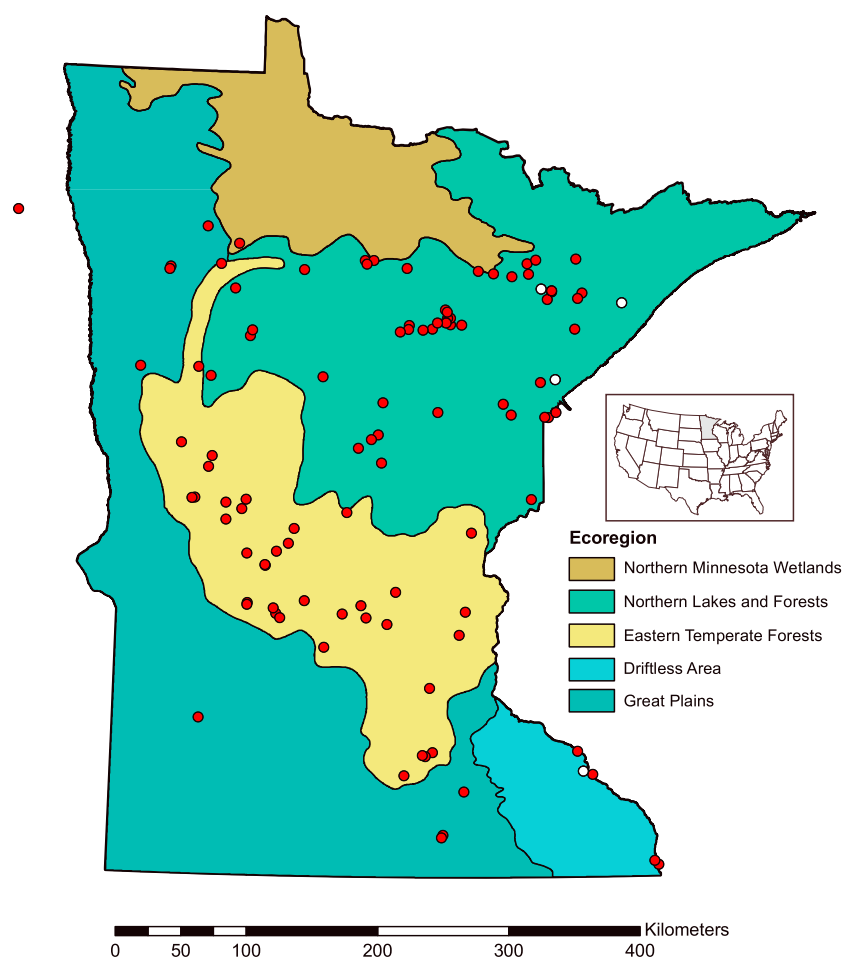
**Figure 3.** Locations for lakes and stream sites (Class D and Class B) sampled by Myrbo, Swain, Engstrom, et al. (2017) used to construct the SE model. Red-filled circles show sites that belong to both Class D and Class B data sets, while the open circles show sites that belong solely to Class D. The single site in North Dakota (westernmost site) lies in the Great Plains ecoregion.

Swain, Engstrom, et al., 2017). The Class B data thus include a set of 105 unique observations with a full complement of measured model parameters, including 78 lake and 27 stream sites (Figure 3).

### 3.2. Statistical Analysis and Modeling
### 3.2.1. Model Estimation
We conducted all statistical analyses, including SEM, using Stata 14 (StataCorp, 2015). Two key underlying assumptions with SEM are multivariate normality of the endogenous variables and linear relationships between the endogenous and exogenous variables (Kline, 2011; Ullman, 2007). We $\log_{10}$-transformed all variables both to improve linearity and to yield variable distributions that more closely approximated normality, although multivariate normality was not achieved.

When multivariate normality is uncertain, estimation methods that assume multivariate normality can produce misleading or incorrect estimates of the standard error of the individual model coefficients. Several approaches are potentially useful when estimating SEM models with nonnormal multivariate data distributions. These methods include *asymptotic distribution-free* (*adf*) estimation (Acock, 2013; Kline, 2011), bootstrapping (Acock, 2013; McIntosh, 2007; Tomarken & Waller, 2005), and estimation using the Satorra-Bentler scaled $\chi^2$ test (StataCorp, 2015; Tomarken & Waller, 2005). The *adf* method makes no assumptions regarding data normality but may require in excess of 200 to 500 observations for even relatively simple models (Kline, 2011). Bootstrapping, which uses resampling with replacement of the individual observations to produce estimates of the standard errors and resulting significance of the model coefficients, also makes

no assumptions regarding underlying multivariate normality and thus produces more robust estimates of coefficient confidence. The Satorra-Bentler test seeks to correct the $\chi^2$ statistic by scaling the estimate based on the kurtosis of the data (Kline, 2011). Initial analyses implemented all three methods. Bootstrapping was conducted using 1,000 replications. We used comparative evaluations of the fitted model coefficients (the *adf* method can yield model coefficients that differ compared to the maximum likelihood estimation used by the bootstrapping and Satorra-Bentler methods) and their significance, which indicated that estimation of the final model was relatively insensitive to the choice of estimation method coefficients. However, because *adf* methods can be misleading with sample sizes of fewer than 200, final model estimation was conducted using the Satorra-Bentler test and bootstrapping.

### 3.2.2. Model Robustness

A critical assumption that SEM shares with linear regression is that the underlying relationships between a given endogenous variable and the variables that influence it are indeed linear. Unlike SEM, MLR has a rich set of tools available for a variety of post hoc analyses to evaluate adherence to underlying model assumptions. Given the similarities between path analysis (of which our modeling herein is a form) and MLR (Li, 1975), we verified linearity by initially conducting MLR on pore water sulfide concentrations using the same variables used to directly model pore water sulfide in the SE model. We then evaluated the presence of nonlinearities and apparent outliers by constructing augmented component plus residual (ACPR) plots for each direct independent variable (Hamilton, 2013; Mallows, 1986; see supporting information Figure S1).

### 3.2.3. Assessment of Goodness of Fit

We assessed model goodness of fit using several different metrics. Because SEM seeks to reproduce the observed covariance matrix for the variables in the model, a primary metric for model performance is a chi-square ($\chi^2$) test that assesses the magnitude and significance of the discrepancy between the fitted covariance matrix for the model in question and the observed covariance matrix. Restated, the $\chi^2$ statistic compares the covariance matrix for the model we seek to evaluate with that of a model that has no degrees of freedom and thus fits the observed data perfectly. The null hypothesis is that the two models are not different. $\chi^2$ $p$ values <0.05 appear to be a commonly used threshold for rejecting the null hypothesis and thus rejecting the model (e.g., Bizzi et al., 2013; Hayduk & Glaser, 2000; Hu & Bentler, 1999), although this threshold is controversial (cf. Barrett, 2007; Lance et al., 2006; McIntosh, 2007).

The $\chi^2$ test is the approach most used to evaluate the fit of SEM models (Grace, 2008) and was used in this study as the initial criterion for retaining a given model. Other fit indices used as alternatives or adjuncts to the $\chi^2$ test include both absolute and incremental or approximate fit indices (Hu & Bentler, 1999; Kline, 2011). Stata provides several alternative fit indices of both types, including the root-mean-square error of approximation (RMSEA), the standardized root-mean-square residual (SRMR), the comparative fit index (CFI), and the Tucker-Lewis index (TLI). Recommended target values for the RMSEA and SRMR are 0.05 and 0.08, respectively, while values greater than 0.95 are recommended targets for both the CFI and TLI (Acock, 2013; Hu & Bentler, 1999).

### 3.2.4. Model Validation

We validated the SE model by conducting a "leave one out cross validation" or jackknife analysis where we refit the SEM model by withholding a single observation from model estimation and then used the refit model to predict the $\log_{10}$-transformed value for pore water sulfide of the withheld observation. This process was repeated for each of the observations comprising the Class D and Class B data sets. A major advantage of this process is that it uses all of the available observations to both fit and validate the model.

### 3.2.5. Alternative Model Specifications

As mentioned previously, the issue of model specification is an important consideration. As a result, we also expanded our conceptual model to consider several other model specifications. These models included

1. expanding the model to include sediment acid volatile sulfide (AVS). AVS is an operationally defined, reactive sulfide fraction that is believed to comprise dissolved hydrogen sulfides and mackinawite (Morse & Rickard, 2004) and thus arguably better represents the pool of reduced sedimentary sulfur actively exchanging with pore water sulfide. A primary feature of this model thus was to include a second reciprocal relationship involving pore water sulfide—viz., a path between pore water sulfide and sediment AVS;

2. identifying pore water dissolved organic carbon (DOC) as an exogenous variable. The rationale behind evaluating pore water DOC was twofold. First, DOC forms strong complexes with dissolved $Fe^{2+}$ (Jansen et al., 2002) that can then reduce the concentration of free $Fe^{2+}$ available to bind with sulfide and form amorphous FeS or mackinawite. The SE model does not consider dissolved Fe or sulfide speciation, and
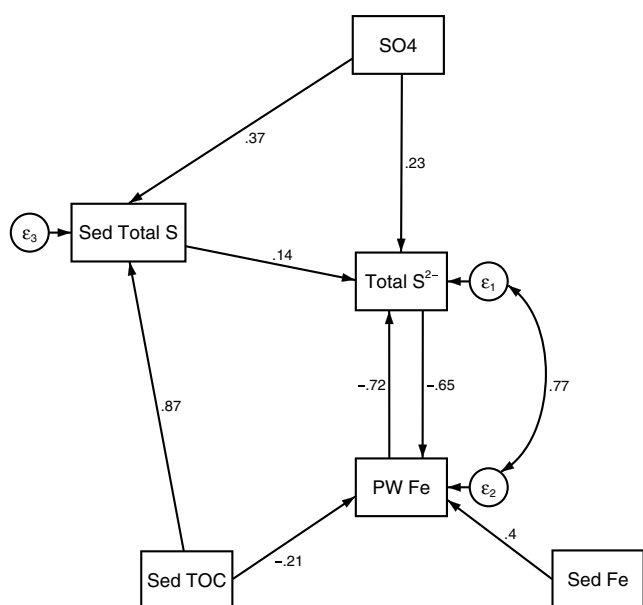
**Figure 4.** Final SE model for biogeochemical controls on pore water sulfide in wetland sediments. Final model extends conceptual model (Figure 1) by allowing for the correlation of errors between pore water Fe and sulfide. The diagram also shows the standardized path coefficient for each interaction pathway.

thus, inclusion of pore water DOC was considered as a first-order approximation for evaluating the potential efficacy of modeling with speciated values; and

3. including surface water total phosphorus (TP) as an exogenous variable in the model. Increasing eutrophication is expected to increase sulfide production and sedimentary AVS through both the stimulatory effects of additional phosphorus on bacterial activity and rates of organic matter decomposition and through the increased delivery of autochthonous organic matter to the sediments, which in turn serves as a substrate to drive the development of anaerobic conditions and promote dissimilatory sulfate reduction. Anaerobic conditions are a necessary prerequisite for the solubilization of solid phase Fe(III) through its reduction to Fe(II). This alternative model thus considered direct pathways between TP and both pore water Fe and sediment AVS.

## 4. Results and Discussion

### 4.1. Model Fit and Evaluation With Class D data

The initial fit of the conceptual model was conducted using maximum likelihood estimation. This resulted in a model that performed reasonably well with respect to predicting the variations in the three endogenous variables (corrected $r^2$ values ranging from 0.582 to 0.650) but also resulted in a $\chi^2$ value reflecting overall model fit that was unacceptably large ($\chi^2 = 35.54$, degrees of freedom [$df$] = 4, and $p < 0.0001$). Evaluation of the effect of different structural changes to the model that would result in statistically significant reductions in the $\chi^2$ value (modification indices) indicated several choices: (1) linking sediment Fe (negatively) to pore water sulfide, (2) linking either or both sulfate and sediment total sulfur directly (and negatively) to pore water Fe, and (3) allowing the error terms for pore water Fe and sulfide to be correlated. Correlating the error terms recognizes the possibility of either other variables missing from the model or sampling error (or both) affecting both pore water Fe and sulfide. For example, both dissolved Fe and sulfide are highly sensitive to oxidizing shifts in the redox environment of the pore water that potentially can occur during sampling or sample handling and transportation. The effect of such shifts in redox on both constituents is a reduction in concentration. Given its current framework, the other possible choices for improving the overall fit of the model are more reasonably considered only as indirect pathways and do not necessarily add to the conceptual understanding of the model or otherwise lead to an improvement in the utility of the model. For example, the conceptual model includes an indirect pathway defining the effect of sediment Fe on pore water sulfide. Allowing sediment Fe to directly interact with pore water sulfide negates the statistical significance of this pathway; removing the pathway in turn considerably weakens our ability to predict pore water sulfide.

As a result, we modified the conceptual model to allow error correlation between pore water Fe and sulfide (Figure 4). The resultant $\chi^2$ value for the modified model was reduced to an acceptable level ($\chi^2 = 1.110$, $df = 3$, and $p = 0.775$). In addition, the values for the incremental fit indices reported by Stata were all below recommended target levels (Table 1). We further evaluated model fit by examining the matrix of fitted covariance residuals (Table 2). Kline (2011) suggests that values >0.10 indicate that the model does not fit the covariance matrix particularly well, and large residuals can provide guidance regarding possible modifications to improve model fit (StataCorp, 2015). The maximum absolute value for the covariance residuals was 0.007, which is well below this suggested threshold and provides further confidence that the fitted model is well supported by the data.

Model estimation of the modified conceptual model conducted by bootstrapping and the Satorra-Bentler method both verify that the model overall fit is good ($\chi^2 = 0.998$, $p = 0.874$, and Table 1) and that the estimates of the model coefficients are highly significant when accounting for multivariate nonnormality. With the exception of the path coefficient for the effect of sediment total sulfur on pore water sulfide ($p = 0.011$), all path coefficients had $p < 0.001$. We estimated the fit between each observed and predicted

**Table 1**
*Comparison of Goodness of Fit Statistics Resulting From Fitting the Pore Water Sulfide SEM Model to the Class D and Class B Data Sets*

| Metric | Threshold or target value | Class D | Class B | Class B (no sediment TS) |
|---|---|---|---|---|
| $\chi^2$—degrees of freedom | | 3 | 3 | 1 |
| $\chi^2$ (maximum likelihood) | | 1.110 | 3.019 | 2.268 |
| $p > \chi^2$ (maximum likelihood) | >0.05 | 0.775 | 0.389 | 0.132 |
| $\chi^2$ (Satorra-Bentler) | | 0.998 | 3.000 | 2.098 |
| $p > \chi^2$ (Satorra-Bentler) | >0.05 | 0.802 | 0.392 | 0.148 |
| RMSEA[a] (maximum likelihood) | 0.05 | <0.001 | 0.008 | 0.110 |
| RMSEA (Satorra-Bentler) | 0.05 | <0.001 | <0.001 | 0.102 |
| 90% CI[b], lower bound | 0 | <0.001 | <0.001 | <0.001 |
| 90% CI, upper bound | 0.1 | 0.080 | 0.165 | 0.308 |
| $p$ RMSEA ≤ 0.05 | | 0.874 | 0.501 | 0.182 |
| Comparative fit index (maximum likelihood) | 0.95 | 1.000 | 1.000 | 0.993 |
| Tucker-Lewis index (maximum likelihood) | 0.95 | 1.014 | 1.001 | 0.954 |
| Comparative fit index (Satorra-Bentler) | 0.95 | 1.000 | 1.000 | 0.994 |
| Tucker-Lewis index (Satorra-Bentler) | 0.95 | 1.016 | 1.001 | 0.959 |
| SRMR[c] | 0.08 | 0.007 | 0.017 | 0.020 |
| Residuals coefficient of determination | | 0.959 | 0.974 | 0.947 |
| Stability index | | 0.687 | 0.733 | 0.786 |
| Pore water total sulfide ($log_{10}$-transformed) coefficient of determination[d] | | 0.622 | 0.633 | 0.623 |
| Pore water Fe ($log_{10}$-transformed) coefficient of determination | | 0.685 | 0.687 | 0.676 |
| Sediment total S ($log_{10}$-transformed) coefficient of determination | | 0.650 | 0.697 | |
| $N$ | | 194 | 105 | 105 |

*Note.* Pore water sulfide coefficient of determination is the Bentler-Raykov squared multiple correlation coefficient.
[a]RMSEA—root-mean-square error of approximation.   [b]CI—confidence interval.   [c]SRMR—standardized root-mean-square residual.   [d]Bentler-Raykov squared multiple correlation coefficient.

endogenous variable using the Bentler-Raykov squared multiple correlation coefficient (StataCorp, 2015). This coefficient is a corrected version of the coefficient of determination ($r^2$) that should be implemented when evaluating the explained variance of variables in nonrecursive models that have reciprocal causations such as pore water Fe and sulfide. Corrected $r^2$ values ranged from 0.622 to 0.685 for pore water sulfide and Fe, respectively (Table 1). Figure 5 plots the actual fit between observed and predicted values for $log_{10}$-transformed pore water sulfide. Included in the plot is a locally weighted scatterplot smoothing (LOWESS) curve that is useful for elucidating any undesired curvilinearity in the predicted relationship. The LOWESS curve shows no such evidence.

One concern with nonrecursive models relates to possible inherent instabilities owing to the fact that variables involved in feedback relationships are dependent upon themselves. The potential for such instability is evaluated through a *stability index* that estimates whether direct effects influencing variables in the model can become infinitely larger (Kline, 2011). Stata uses the method of Bentler and Freeman (1983) to calculate this index. Stability requires that the index value be less than 1; the stability index for the modified model was 0.687 (Table 1).

Results from jackknife cross-validation simulations showing the agreement between the full model predictions and the out-of-sample predictions are shown in Figure 6. Those results illustrate that the out-of-sample predictions closely match the predictions obtained from the fully calibrated model. As a result, the root-mean-square error (RMSE) for the out-of-sample predictions (0.300) agrees well with, and is only slightly

**Table 2**
*Matrix of Fitted Covariance Residuals for the Final SE Model Fitted With Class D Data (See Figure 4 for Model Structure)*

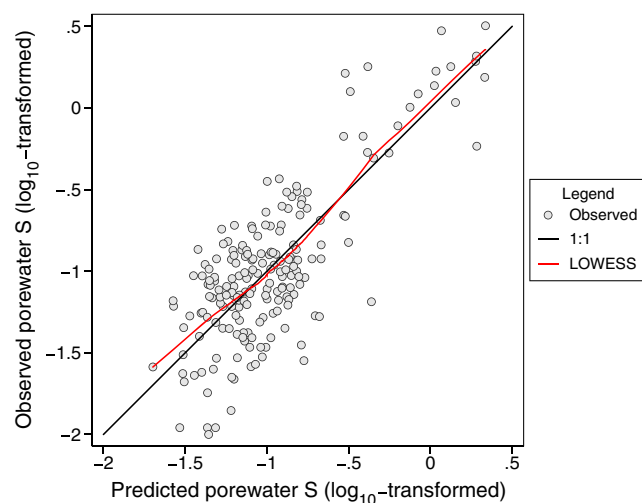| Variable | Pore water sulfide | Pore water Fe | Sediment total S | Sulfate | Sediment Fe | Sediment TOC |
|---|---|---|---|---|---|---|
| Pore water sulfide | 0.001 | | | | | |
| Pore water Fe | −0.001 | 0.002 | | | | |
| Sediment Total S | 0.003 | 0.004 | 0.000 | | | |
| Sulfate | −0.001 | −0.007 | 0.000 | 0.000 | | |
| Sediment Fe | 0.002 | 0.001 | −0.003 | 0.000 | 0.000 | |
| Sediment TOC | 0.007 | 0.001 | 0.000 | 0.000 | 0.000 | 0.000 |

**Figure 5.** Comparison of observed with predicted pore water sulfide (both $\log_{10}$ transformed) for the SE model fit with Class D data. Plot includes lines showing expected 1:1 fit and the fit obtained from LOWESS smoothing (bandwidth = 0.8).

larger than, the calibration RMSE 0.294. The jackknife analysis also demonstrates no problems with unusually influential observations in the Class D data set.

As mentioned previously, the Class D data set includes a number of sites with multiple observations over time. The inclusion of sites with multiple observations raises the possibility that the resultant model errors are not truly independent from a spatial perspective, unless each observation can be regarded as an independent characterization of the biogeochemical quasi steady state existing among pore water, sediment, and surface water parameters. We tested the possibility of such spatial autocorrelation of errors post hoc using analysis of variance (ANOVA). The analysis focused on Class D sites with four or more observations (10 sites with 48 observations). Figure 7 is a box plot that shows the distribution of model residuals for each of the sites with four or more observations; the plot also includes the residuals distribution for the remaining sites with only a single observation. The ANOVA indicates no overall significant clustering of residual values related to inclusion within a given site group ($p = 0.541$) and thus supports the use of multiple observations from the same site.

## 4.2. Model Results With Class B Data

The conceptual model with linked covariance between the pore water Fe and sulfide error terms was fit with the Class B data to further evaluate whether excluding sites with multiple observations would result in a substantively different set of results. Initial results indicated that the path between sediment total S and pore water sulfide was no longer significant, although the overall fit was acceptable with the exception of the upper limit for the RMSEA (Table 1). Thus, we refit the model without this pathway. In addition, eliminating this pathway also rendered modeling sediment total S irrelevant; as a result, and in order to avoid biasing the overall significance of the fit statistics, we dropped sediment total S from the model.

While the overall fit of the subsequent reduced form model is still significant ($\chi^2 = 2.268$ and $p = 0.132$), the RMSEA values were further degraded, such that the RMSEA value itself, and not just the upper limit, was unac-



**Figure 6.** Comparison of predictions of pore water sulfide ($\log_{10}$ transformed) obtained for the SE model fit with Class D data and "out-of-sample" predictions obtained from jackknife cross validation.

ceptably high. This degradation in model performance for both forms of the model is likely more a reflection of using an inadequate number of observations to fit the model, rather than a fundamental weakness in the model structure. This evidenced by (1) the significance of all the model path coefficients (all values of $p \leq 0.002$, with exception of the sediment total S—pore water sulfide path coefficient) and (2) a comparison of the fitted model coefficients that express the total effect (direct plus indirect) of all three exogenous variables influencing pore water sulfide for the two Class B models and the Class D model (Figure 8). This comparison shows that the differences in the coefficient estimates are small and lie well within the coefficient standard errors. Model integrity was further demonstrated by MLR conducted with the Class B data using pore water sulfide as the dependent variable and each of the SE model variables with direct paths to pore water sulfide. We constructed ACPR plots post hoc to evaluate linearity for each connection. Those results, which are included in the supporting information (Figures S2 and S3) confirm the underlying linearity of these pathways.
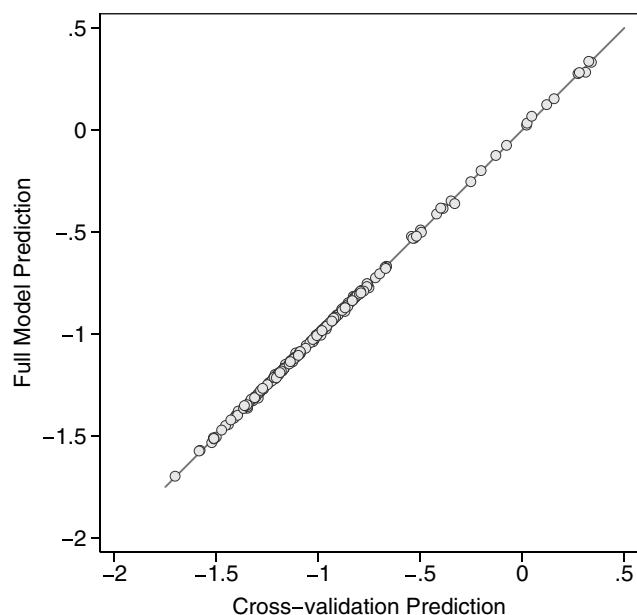
## 4.3. Alternative Models

We compared the set of postulated alternative models with the original model by evaluating both the suite of exact and approximate fit statistics described previously as well as the Akaike and Bayesian
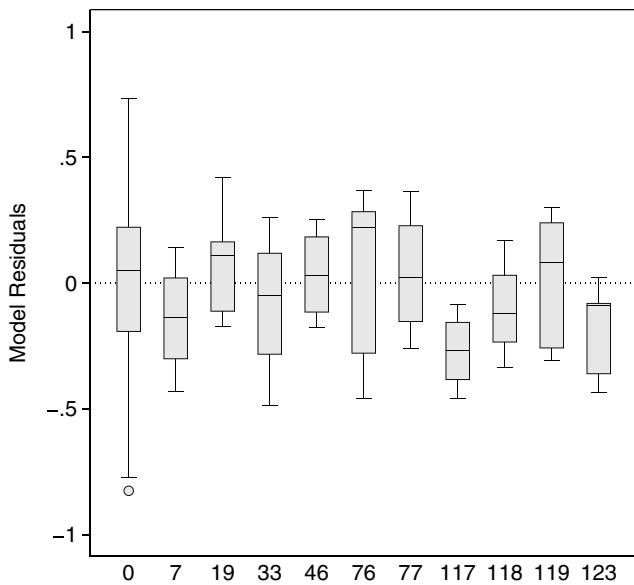
**Figure 7.** Box and whisker plot of the distribution of model residuals for individual sites with four or more observations. Each number on the abscissa denotes a unique site except for "0," which includes values for all sites ($N = 68$) without multiple observations.

information criteria (AIC and BIC) values for each model. Comparing AIC/BIC values are meaningful only if the same number of observations is used to fit each model. Because several of the alternative models included variables with a missing observation, all the models thus were fit with the same set of reduced observations ($N = 193$).

The path diagrams for the original conceptual model along with each of the alternative models are included in the supporting information (Figures S4–S7). The diagrams depict the models in "final form" with the fitted standardized coefficients; final form is intended to convey that no further changes in the model structure are suggested by either modification indices that are conceptually supportable or by eliminating nonsignificant ($p > 0.05$) pathways.

Based on $\chi^2$ values, the strongest models are the original model and the conceptual model modified to include sediment AVS (AVS model, Figure S6). This latter model includes a reciprocal relationship between pore water sulfide and AVS, as well as direct pathways between sulfate and sediment AVS and pore water Fe and AVS. This structure is consistent with the hypothesis that increased sulfate leads to increased dissimilatory sulfate reduction, and thus increases in AVS (Ramamoorthy et al., 2009). While this model is conceptually more satisfying, it is not necessarily superior to the original model for several reasons. First, the value for the SRMR was somewhat higher for the AVS model (0.013 versus 0.007). Second, AIC and BIC values indicate the original, more parsimonious model is superior. Moreover, the ability to predict pore water sulfide, pore water Fe, or sediment total sulfur is not markedly improved by inclusion of sediment AVS (Table S1). Lastly, including sediment AVS as an endogenous variable does not change the overall relationship between the exogenous variables and the endogenous variables of interest. This is illustrated in Table S2, which compares the total effects of a given variable on a specific endogenous variable. Using pore water sulfide as an example, the coefficient for the total effect of sulfate for the original and AVS models is 0.539 and 0.529, respectively; for sediment Fe and TOC, the coefficients are $-0.551$ versus $-0.557$ and 0.515 versus 0.532, respectively.

The other two alternative models—inclusion of pore water DOC effects on pore water sulfide and pore water Fe (Figure S5) and inclusion of sediment AVS, pore water DOC, and surface water TP effects (Figure S7)—were somewhat inferior models, although both models were well supported based on $\chi^2$ significance. In particular, weaker model fits were suggested based on an unacceptably high RMSEA value for the DOC model (0.058 compared to a guideline threshold of 0.05) and elevated RMSEA value for the AVS-DOC-TP model (0.028); this accordingly resulted in lower probabilities that the RMSEA $\leq 0.05$. CFI and TLI values were somewhat lower as well. While increasing TP concentrations can directly promote higher rates of microbial activity, the lack of importance of TP in the models may indicate that the effects of TP on pore water sulfide are predominantly indirect and exerted through its effect on the accretion of sediment organic matter (which in turn stimulates sulfate reduction). Because sediment organic matter content is only weakly related to trophic state variables such as TP (cf. Brenner & Binford, 1988) and more strongly reflects the physical depositional environment, the statistical relationship between TP and sulfide dynamics expectedly would be weak as well. Nonetheless, in freshwater wetlands such as portions of the Florida Everglades where high sulfate loadings are coupled with high phosphorus loadings, extremely high sulfide concentrations can occur, although the primary
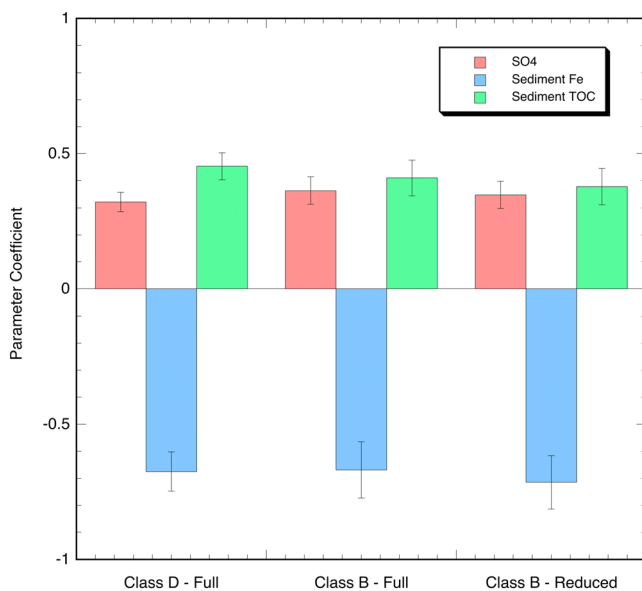


**Figure 8.** Comparison of the estimated coefficients depicting variable total effect on pore water sulfide for the three exogenous variables included in the SE model. The comparison includes fitting the SE model to the Class D and Class B data to the full conceptual model and fitting the Class B data to the conceptual model without including sediment total sulfur as a variable. Error bars are standard errors for the individual coefficient estimates.
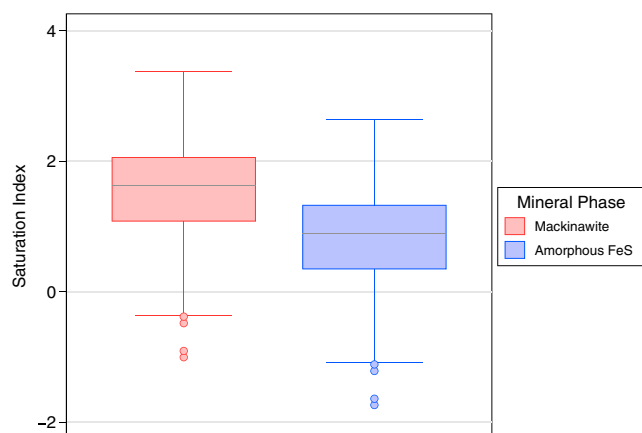
**Figure 9.** Distribution of amorphous FeS and mackinawite saturation index (SI) values calculated for the Class D data set. Values greater than 0 indicate supersaturation, while values less than 0 indicated undersaturation.

determinant appears to be high concentrations of sulfate more than phosphorus (Figure S8 and data from Scheidt & Kalla, 2007).

### 4.4. Geochemical Implications

The core of the conceptual model is the reciprocal relationship between pore water concentrations of Fe and sulfide, and which is embodied in the equilibrium dynamics of amorphous FeS or mackinawite precipitation and dissolution (equation (1)). We can test this hypothesis by calculating the ratio of the ion activity products (IAP) for equation (1) to the equilibrium solubility product constant ($K_{sp}$) for both solid phases ($10^{-3.915}$ and $10^{-4.648}$ for amorphous FeS and mackinawite, respectively) (Parkhurst & Appelo, 2013). Log ratios or saturation index (SI) values in excess of 0 suggest supersaturation, while values less than 0 are indicative of under or subsaturation (Appelo & Postma, 2010). Free concentrations of $Fe^{2+}$ and $HS^-$ were calculated based on measured pore water pH, and the hydrolysis constant for $Fe^{2+}$ and dissociation constants for $H_2S$ (Parkhurst & Appelo, 2013). Because they do not include corrections for ionic strength nor the possible effects of other ions such as DOC effects on $Fe^{2+}$ speciation, the resultant IAP values are biased somewhat high. Thus, these SI calculations can provide evidence only of conditions not sufficiently adequate for amorphous FeS or mackinawite precipitation to occur, rather than confirm that either phase is controlling.

The distribution of SI values calculated for both mineral phases are shown in the box plot contained within Figure 9. Only a small fraction of Class D sites had $SI_{mackinawite} < 0$ (6.7%), with over 75% of the sites suggesting supersaturation by an order of magnitude. $SI_{FeS}$ values were, by definition, lower but still largely supportive of supersaturation (84% of the sites with values $SI \geq 0$). Holdren and Armstrong (1986) conducted similar IAP calculations for Lake Mendota sediments and, based on those calculations, concluded that FeS precipitation may control Fe solubility in sediment pore waters as well.

Our SE modeling coupled with the SI calculations thus suggest a solid aqueous phase dynamic between Fe supply and sulfide sequestration that buffers the evolution of pore water sulfide concentrations resulting from dissimilatory sulfate reduction. This buffering system is well recognized—for example, Heijs et al. (1999) developed a quantitative measure for the ability of sediments to buffer free $S^{2-}$ concentrations dependent on the availability of both Fe(II) and Fe(III). In part, this buffer system includes the reduction of Fe(III) minerals such as ferrihydrite by $H_2S$, leading to the formation of metastable FeS (Poulton et al., 2002).

It should be noted that sediment organic matter also can react with sulfides to form organic sulfur, including thiols, organic monosulfides, and organic disulfides (Zeng et al., 2013), and that this pathway can be an important removal mechanism for pore water sulfide in many lakes (e.g., Holmer & Storkholm, 2001; Rudd et al., 1986; Urban et al., 1999). Moreover, this mechanism may be particularly important as a constraint on pore water sulfide concentrations in aquatic ecosystems where low iron availability is coupled with high sediment organic content. Because the SE model does not include a sediment organic S-sulfide relationship, modifying the SE model to account for organic sulfur formation likely will be important if it is extended to such ecosystems.

A key advantage of the SE model is that it provides a framework for quantifying the relative effects of different variables on pore water sulfide concentrations. Such an analysis can include direct effects, indirect effects, and total effects. Placing the effects of different variables in context with each other is perhaps most easily understood through the use of standardized coefficients. Standardized coefficients give the corresponding response relative to a single standard deviation for a dependent variable when a given independent variable has been increased by a single standard deviation. As such, standardized coefficients provide a convenient means for directly comparing the relative importance or strength of association of different independent variables, while the unstandardized coefficients reflect the form of the relationship (Acock, 2013).

Figure 10 compares the standardized coefficients for model variable effects on pore water sulfide. These results indicate that internal dynamics between pore water Fe and sulfide exert the greatest degree of control on pore water sulfide (standardized coefficients for total effects equal to −1.37 and 0.90, respectively).
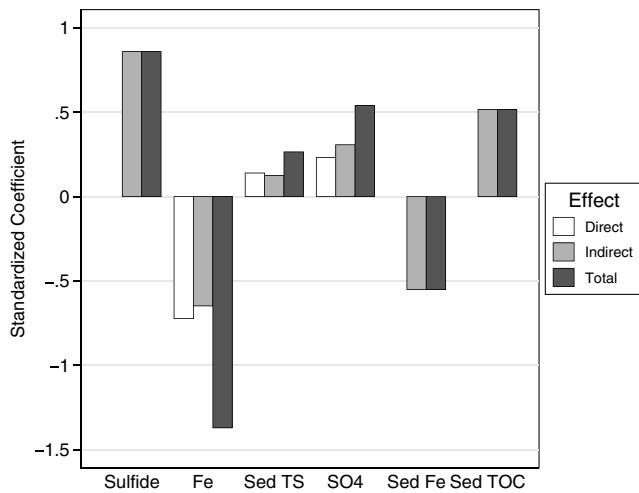
**Figure 10.** Standardized coefficients for direct, indirect, and total effects of each of the variables influencing pore water sulfide in the SE model. The use of standardized coefficients allows direct comparison of the relative importance of each variable relationship on variations in pore water sulfide, while the estimated coefficients (cf. Figure 8) allow one to estimate the marginal or instantaneous effects of changing a given exogenous variable on pore water sulfide while holding all other exogenous variables constant. Note that categories labeled as "sulfide" and "Fe" refer to pore water.

The effect of pore water sulfide on itself is of course indirect and exerted through its direct relationship with pore water Fe. The effect of pore water Fe in turn is largely direct, although it also exerts a substantial indirect effect through the pore water Fe-pore water sulfide feedback loop.

From a management perspective, the effects of the exogenous variables are of particular interest. Our comparison indicates the magnitudes of relative total effects for the exogenous variables are nearly identical: sulfate (0.54), sediment Fe (−0.55), and sediment TOC (0.52). These results thus suggest that given their distributional characteristics in our model data set, the ambient variations in each of the exogenous variables contribute in nearly an equivalent manner to the observed variations in pore water sulfide. In other words, while the importance of the role of sulfate as a controlling variable for pore water sulfide concentrations is validated both conceptually and statistically with respect to significance, the SE model also underscores the importance of the sediment Fe buffering system and the effect of the availability of sediment organic matter. The practical consequence of this buffering system is that the sensitivity of macrophytes such as wild rice that are adversely impacted by the occurrence of sulfide is likely exacerbated in sediments relatively low in iron. In such sediments, increases in organic carbon and sulfate will, *ceteris paribus,* result in higher concentrations of sulfide (cf. Calleja et al. 2007).

## 5. Practical Application of the SE Model

The ultimate goal of the MPCA-sponsored field survey upon which this modeling effort is based (Myrbo, Swain, Engstrom, et al., 2017) is to determine if it is appropriate to regulate sulfate and, if so, how to structure the regulation in order to protect wild rice from exposure to pore water sulfide concentrations above a protective threshold—the identification of which is a separate task from the modeling exercise described here. This modeling effort demonstrates that pore water sulfide concentrations can be successfully modeled with three exogenous variables—sulfate, sediment TOC, and sediment Fe. The latter two measurements are the average concentrations in the top 10 cm of sediment in a wild rice waterbody and likely reflect the natural ambient condition of the wild rice habitat. Although our modeling shows that both sediment TOC and sediment Fe are important contributors to the toxic impacts of sulfide, regulating sulfate is the only viable mechanism to protect wild rice against sulfide toxicity.

However, because each wild rice waterbody has different sediment TOC and Fe concentrations, any given fixed sulfate standard applied to multiple wild rice waters would produce a wide range of sulfide concentrations, some of which would likely be above the protective threshold. Because of the varying efficiency in converting sulfate to sulfide, if the goal is to keep wild rice waters below a particular sulfide threshold, then sulfate limits should be different for each waterbody.

To identify a protective sulfate concentration for a particular waterbody, it would be logical to employ the relationships revealed by the SE model and to work backward from an identified protective sulfide threshold to calculate a surface water sulfate standard tailored to the geochemistry of that particular waterbody. A direct way to accomplish this task would be to first arrange the SE model into a single equation that expresses pore water sulfide as a function of the exogenous variables in the model (sulfate, sediment Fe, and sediment TOC). By substituting the protective sulfide concentration in for that variable and rearranging the equation, a revised equation for the protective sulfate concentration as a function of Fe and TOC concentrations can be derived. Such an equation could be applied to any wild rice waterbody for which sediment Fe and TOC are known.

An important concern with the above approach, however, relates to both confidence intervals associated with predicted sulfide concentrations and biases in predicted values resulting from back-transforming a predicted log-transformed concentration to its original arithmetic form (Duan, 1983). Stata does not

provide confidence intervals for predicted endogenous variables obtained from SEM. With respect to the latter problem, solutions have been proposed (Duan, 1983; Manning & Mullahy, 2001), but they are complicated.

There are at least two approaches toward resolving the difficulty of practically using the SEM results to predict sulfate concentrations that reflect a target or threshold pore water sulfide concentration. Both approaches rely on the SE model to define the driving variables of interest—viz., sediment Fe and TOC and surface water sulfate. The first approach uses generalized linear modeling with an appropriate link function (in this case a log link for the dependent variable) and specification of the residual error distribution. This approach capitalizes on the fact that path analysis and MLR are very similar (Li, 1975) and yield very similar estimated model coefficients for predicting pore water sulfide; with proper error distribution specification, it also avoids the issue of back-transformation bias. The second approach is multiple binary logistic regression (MBLR). MBLR simulates the likelihood that the response variable of interest exceeds a defined threshold given a set of independent variables. This type of binary response modeling is particularly well suited for the management question of whether, *ceteris paribus*, a given sulfate concentration is likely to result in pore water sulfide concentrations above or below a specified toxicity threshold. This approach also avoids the problem of back-transformation bias.

A MBLR model can be developed using the same field data that were used to construct, calibrate, and validate the SE model. MBLR would directly predict the probability of exceeding the protective sulfide concentration threshold as a function of sulfate, Fe, and TOC. An acceptable probability threshold can then be defined (for example, 0.5 or some other value; the choice would be a policy decision), and the model used to "inverse" predict the sulfate concentration that will produce the threshold as a function of Fe and TOC. Operationally, this equation to determine the protective sulfate threshold for any particular waterbody could then be applied in the same manner as the equation derived from the SEM, as described above.

In summary, it is desirable to use SEM to better understand and characterize the relationships between the important parameters in the system that relates sulfate and sulfide but then to use MBLR to translate the understanding gleaned from SEM into a water quality standard for sulfate. A standard that is an equation, rather than a uniform concentration that is applied to all waterbodies, would be a reflection of the biogeochemical diversity of the environment. New approaches are needed as environmental regulation progresses from protecting organisms from pollutants that are directly toxic, to pollutants whose negative effects are indirect and a function of environmental conditions that vary from site to site.

## 6. Conclusions

We used SEM to help elucidate and quantify the underlying structure of water quality and sediment chemistry variables governing the evolution of pore water sulfide concentrations in lakes and streams in the Upper Midwest/Great Lakes region. Three key "external" variables were initially hypothesized to be important—surface water sulfate, sediment Fe, and sediment TOC. Intermediate, mediating variables included pore water Fe and sediment total sulfur. Inherent in the model structure is a reciprocal relationship between pore water Fe and sulfide. This structure defines a sediment iron-based buffering system that is supported both empirically by other observational studies in wetlands and conceptually by the thermodynamics of amorphous FeS or mackinawite dissolution. The conceptual structure of the SE model is well supported both by model fit statistics and a suite of model diagnostic and post hoc analyses and by SI analyses that suggest that amorphous FeS or mackinawite precipitation-dissolution dynamics help control or impose constraints on the reciprocal relationship between pore water Fe and sulfide. Our use of SEM to model pore water chemistry dynamics, including the nonrecursive nature of those dynamics in particular, is believed to be the first such application in the open literature.

An important consequence of the sediment buffering system is that it serves to help limit the effects of increases in either surface water sulfate or sediment organic carbon on pore water sulfide. Based on total effects estimated from the SE model, all three external variables all essentially equivalent in importance with respect to influencing pore water sulfide. When considering the policy implications of trying to protect wild rice against the toxic effects of sulfide by limiting sulfate inputs to the ecosystem, our results thus demonstrate that the problem is multidimensional and that any such standard must consider the effects of

ambient concentrations of sediment Fe and sediment TOC to ensure the imposed sulfate standard is neither unduly or insufficiently protective. Multiple binary logistic regression would be a practical way to tailor sulfate standards to the specific geochemistry of sites so that a uniform level of protection for organisms sensitive to sulfide would be achieved.

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