Statewide Assessment Reveals Spatiotemporal Variability of Iron in Iowa Lakes

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Abstract: The micronutrient iron has been noted to play a crucial role in regulating phytoplankton growth; however, most studies have focused on large lakes with persistent phytoplankton blooms that are known to undergo iron limitation, such as Lake Erie. Iron abundance in boreal lakes is also known to correlate with dissolved organic carbon and increased iron concentrations causing "browning." To assess the spatial distribution of dissolved Fe (DFe) in lakes throughout Iowa, a landscape once dominated by prairies, DFe was measured in surface waters of 124 lakes distributed across the state over the 2018 summer season. Thirty lakes were selected for 15 weeks of weekly DFe monitoring to assess temporal trends over the summer season. Dissolved Fe concentrations in surface waters ranged from 5 to 1000 μ g L⁻¹. Iowan lakes exhibited temporal trends in DFe, with decreasing concentrations from May to mid-July and an increase into August. Unsupervised learning method (k-means) identified three main groups of lakes based on temporal DFe trends. In this study, surface water temperature was associated with DFe trends in some lakes. This study serves as a baseline for DFe in lowa's lakes and can provide insights into iron biogeochemical cycling and its role in phytoplankton blooms, which are important to ecosystem and public health.

Keywords: *dissolved iron, lakes, water quality, trace metal*

The rapid proliferation of phytoplankton biomass in lakes is a nuisance and can be harmful to ecosystem health. Iron (Fe) limitation has been observed to control phytoplankton growth in the Laurentian Great Lakes (McKay et al. 2004; North et al. 2007). The Great Lakes tend to have dissolved Fe (DFe) that exceeds what is found in the oceans (Klein 1975), likely reflecting greater proximity to terrestrial sources of Fe supplied through tributaries or groundwater. Therefore, the quantity of DFe in smaller lakes might be expected to be even greater, given the larger influence of the catchment. However, lacking widespread data on Fe in smaller lakes makes it difficult to evaluate the relationship between Fe and catchment area. It is also difficult to determine how Fe impacts phytoplankton proliferation for other lakes because Fe data are only occasionally collected.

Iron plays an active biogeochemical role in aquatic systems as a vital micronutrient for

Research Implications

- A mid-summer minimum in dissolved iron (DFe) was common and may link to internal iron cycling.
- Iowa lakes have similar amounts of DFe as lakes in other Midwest, U.S.A. states.
- DFe was poorly correlated with dissolved organic carbon (DOC), likely reflecting the dominance of autochthonous DOC.

phytoplankton. It is a cofactor in proteins such as ferrodoxin and cytochrome, which act to transfer electrons during photosynthesis (Campbell et al. 1998). Iron is critical to macronutrient acquisition, as it is required for the synthesis of nitrogenase in diazotrophic organisms (Larson et al. 2018) and in phosphatases that acquire phosphorus (Browning et al. 2017). The amount and form of Fe available can induce changes in phytoplankton physiology. For instance, low Fe availability lowered the efficiency of photosystem II in the chlorophyte, *Dunaliella tertiolecta* (Vassiliev et al. 1995) and cyanobacteria *Microcystis aeruginosa* and *Microcystis wesenbergii* (Xing et al. 2007). If bioavailable forms of Fe are abundant, they may enhance phytoplankton growth (Twiss et al. 2000), while bioavailable Fe scarcity can restrict phytoplankton proliferation (Xu et al. 2013).

Iron is the fourth most abundant element in the Earth's crust; however, only a small fraction of total Fe may be bioavailable to phytoplankton in aquatic systems (Wells et al. 1995). Iron availability in lakes is controlled by many factors, such as regional geology, soil composition, watershed characteristics, mixing regime, and periodic anoxia (Gorham et al. 1983; Davison 1993; Nürnberg 1995; Dillon and Molot 2005). Aside from physicochemical processes in waters (e.g., redox reactions, mineral precipitation, adsorption-desorption, complexation-dissociation), Fe availability is also regulated by the presence of phosphates, sulfides, and organic matter in lakes (Azzoni et al. 2005; Hoffman et al. 2013). Iron exists in two oxidation states: reduced (ferrous) Fe²⁺ and oxidized (ferric) Fe³⁺. Ferrous Fe predominates in acidic and/or anoxic waters while Fe³⁺ predominates in oxygenated waters. However, the dissolved form of Fe accessible to phytoplankton [Fe³⁺ (aq)] is often in low abundance in aquatic systems. Oxidized Fe³⁺ is poorly soluble in oxygenated waters due to the formation of highly insoluble oxides and hydroxides. Furthermore, it can also be complexed with organic ligands and not directly available for phytoplankton uptake (Nagai et al. 2007; Hassler et al. 2009). This leaves inorganic, unchelated Fe³⁺ as the preferred form of Fe for phytoplankton uptake (Kranzler et al. 2011; Du et al. 2019); however, this form comprises only a small fraction of DFe in well-oxygenated environments with a pH > 7 (Wells et al. 1995; Liu and Millero 2002; Morel et al. 2008).

Lakes provide environmental and economic benefits, serving as a source for food, recreation, and habitat for aquatic animals. Lakes in the Midwest, U.S.A. are impaired from eutrophication, primarily due to their location in watersheds dominated by row crop agriculture. For instance, Iowa's lakes are susceptible to phytoplankton proliferation, which are often linked with toxin production (Iowa Department of Natural Resources 2018). It is unclear whether Fe is associated with phytoplankton growth in Iowa's lakes because there is a lack of data on the presence and abundance of Fe. In this study, we establish a spatial and temporal dataset of DFe in surface waters of both natural and artificial (borrow pits or impoundments) lakes throughout Iowa. A subset of these lakes were monitored for DFe trends in surface waters over the summer season. Data collected may be used to understand whether this micronutrient may influence phytoplankton biomass in these lakes. Herein, the term DFe refers to concentrations measured in lakes within this study, whereas Fe refers to concentrations reported in other studies. Lake surface water was analyzed for DFe and evaluated against Fe in regional lakes that were also susceptible to phytoplankton bloom events. Results were compared with other variables: chlorophyll a (chl-a), dissolved organic carbon (DOC), pH, and temperature. Data collected from this survey will aid researchers in understanding the biogeochemistry of Fe in freshwater systems, its relationship to phytoplankton bloom events, and can be used in lake modeling studies.

Methods

Study Sites and Sample Collection

Lakes in this study were participants of Iowa Department of Natural Resources' (IDNR) Ambient Lakes Monitoring (ALM) program. To assess spatial distribution of DFe in Iowa, 124 lakes were surveyed for one summer in 2018 (Figure 1). Of the ALM lakes, 24 lakes are natural and 100 lakes are artificial, designated as borrow pits or impoundments. Most lakes in this study are considered eutrophic, and the remainder are mesotrophic lakes. From May through August, composite water samples were collected from the epilimnion (up to 2 m depth, depending on thermocline) at the deepest part of the lake and transported (maintained at 4°C) back to Iowa State University for analysis.

To better observe temporal trends in DFe, an additional subset of lakes (n = 30; Figure 2) were monitored weekly from May through August 2018 (15 weeks). Of the 30 lakes, four are mesotrophic and the remaining lakes are eutrophic. These lakes



Figure 1. Mean DFe varied among ALM lakes, with no strong association with geological landforms. Measurements comprised of three sampling events in summer season 2018 (beginning, middle, and end of summer).



Figure 2. A subset of lakes (BM) which were monitored for temporal trends in DFe.

are part of IDNRs' statewide swimming beach monitoring program (BM), which monitors water quality conditions in shallow swimming areas (surface waters of littoral zone). Therefore, the DFe measurements for BM lakes are representative of near-shore surface water less than 1 m deep, and not representative of the whole lake. Homogenized surface water grab samples were collected between 7 am and 3 pm from the surface of the littoral zone. Three transects (maximum 6 m distance from lake shoreline) were established at the littoral zone. Next, three points were sampled per transect (250 mL volume at each sample point) and then mixed into a 2.25 L composite sample. This sampling protocol was adapted to monitor water quality conditions within littoral zones and inform lake swimmers in a timely and cost-effective manner. It needs to be noted that DFe measurements in this study are not representative of an entire lake or open waters. Physical parameters (surface water temperature, dissolved oxygen pH, and turbidity) were also measured during weekly sampling at the littoral zone. Surface water temperature and dissolved oxygen were measured by a YSI 55 (temperature resolution 0.1°C, accuracy \pm 0.2°C; air saturation resolution 0.01 mg L⁻¹, accuracy \pm 0.3 mg L⁻¹), pH was measured using an Oakton pH meter (mV resolution 0.01 to 1, with an accuracy of \pm 2%), and a Hach P2100 measured turbidity (resolution at 0.01 FNU, with accuracy of \pm 2%). All meters were calibrated on a weekly basis, one day prior to sample collection. Physical characteristics are available from the IDNR at https://programs.iowadnr.gov/aquia.

Dissolved Fe Analysis

Prior to sample collection, 15 mL polypropylene tubes were acid washed in 10% HCl (trace metal grade) overnight and rinsed three times with deionized water (> 18.0 M Ω ·cm⁻¹). However, single-use nylon syringe filters (0.22 µm) did not undergo this cleaning procedure. To address the possibility of contamination from syringe filters, field blanks were also passed through nylon syringe filters. Furthermore, field duplicates (10%) were used to assess for variability and contamination.

Water samples were filtered (0.22 μ m, nylon membrane) into 15 mL conical tubes and acidified with 2% trace metal grade nitric acid to pH < 2.

Total DFe was analyzed by ICP-OES at the Iowa State University Environmental Engineering Research Laboratory (Shimadzu ICP-ES9800, detection limit of $0.2 \ \mu g \ L^{-1}$, and quantification limit of $0.5 \ \mu g \ L^{-1}$). For quality control and assurance, lake water samples were analyzed in duplicate to ensure readings were below 3% relative standard deviation. Blanks, calibration standard checks, and lab duplicates were measured every tenth sample. Dissolved Fe data collected in this study are accessible from Environmental Data Initiative (https://doi.org/10.6073/pasta/642c014e2af89958 e42860c6712912fd).

Phytoplankton Data

A multi-wavelength Pulse Amplitude Modulated (PAM) II fluorometer (Phyto-PAM II; Heinz Walz GmbH, Effeltrich, Germany) measured in situ chl-a fluorescence to monitor biomass and identify the phytoplankton community structure in seven of BM lakes, weekly. The Phyto-PAM II uses five light-emitting diodes (440, 480, 540, 590, and 625 nm) to distinguish chl-a and auxiliary pigments. Community composition is characterized based on different accessory pigment assemblages, which are identified based on their absorption and fluorescence at specific regions of the visible spectrum. For instance, the pigment phycocyanin (PC) in cyanobacteria is excited by red light and not by blue light, whereas fucoxanthin and carotenoids in brown algae are excited by blue and green light. In order to classify phytoplankton taxa, measured spectrum of a water sample is deconvoluted into several components (via linear-unmixing) based on the reference fluorescence spectra of each group, or "fingerprints" (MacIntyre et. al 2010). This study utilized the references provided by the manufacturer, Heinz Walz GmbH, Germany. To obtain biomass and community composition data, chlorophyll fluorescence was measured immediately upon obtaining the composite subsample. Samples were measured in triplicate to ensure reproducibility. Approximately 4 mL of grab sample was loaded into the glass cuvette. The gain was adjusted to the fluorescence given off by the sample. A zero offset was performed on 0.22 um-filtered lake water to eliminate fluorescence signal from natural organic matter. Biomass (indicated by chl-a) are reported as averages of the triplicate measurements. Chl-*a* data collected in this study are accessible from Environmental Data Initiative (<u>https://doi.org/10.6073/pasta/</u> e17b351933e981f369a058076f14c328).

least 20% of chl-a At fluorescence measurements were validated by chl-a extraction and spectrophotometric quantification. After chl-a fluorescence was measured, between 20 to 200 mL (depending on algal density) of the composite samples were collected onto 0.3 µm glass fiber filters (ADVANTEC, Japan) and frozen at -20°C until extraction. Three freeze-thaw cycles were applied to filters prior to being steeped in 15 mL of 90% acetone at -20°C overnight. Samples were then centrifuged at 8,000 rpm for 20 minutes. Next, 2 mL of supernatant was transferred into a quartz cuvette and absorbance was measured at 750 nm to ensure that the optical density was <0.005. Supernatant with an optical density > 0.005was passed through a 0.45 µm glass fiber filter (not often needed in this study). In order to determine chl-a concentrations, absorbance was measured at 664 nm (Genesys 30, ThermoScientific) and chl-a was quantified using an extinction coefficient with correction for phaeophytin at 665 nm after adding 60 µL of 0.1 N hydrochloric acid to the sample (Lorenzen 1967).

Dissolved Organic Carbon Analysis

Prior to sample collection for DOC analysis (defined as any carbon passing through a 0.45 μ m filter) from BM lakes, amber glass vials and caps were acid-washed with 10% HCl overnight and rinsed with deionized water threefold (> 18.0 M $\Omega \cdot \text{cm}^{-1}$). Next, vials, caps, and glass fiber filters (Whatman, 0.45 μ m) were wrapped in aluminum foil and pre-combusted at 400°C for at least 1 hour.

Water samples were collected from a subset of 30 lakes and filtered (0.22 μ m, glass fiber membrane) into 25 mL acid-washed vials and acidified with phosphoric acid until pH < 2. Dissolved organic carbon was analyzed by persulfate digestion at the Iowa State University Environmental Engineering Research Laboratory (Shimadzu TOC).

Statistical Analysis

All statistical analyses were conducted in R (version 4.0.2; R Development Core Team). The Shapiro-Wilk test was used to assess for normality

prior to analysis, which produced a p-value < 0.05. Therefore, normal distributions were achieved after applying a log transformation.

To determine whether DFe was different between artificial versus natural lakes, the Kruskal-Wallis test was applied to the ALM dataset. K-means hierarchical clustering was applied to the BM dataset to identify and group lakes with similar DFe patterns over the 15-week period. The optimal number of groups was determined by the elbow method. To further investigate variability in DFe, the effects of other variables (pH, temperature, turbidity, dissolved oxygen, and DOC) on DFe were determined by linear mixed modeling (R package "lme4"; Bates et al. 2015). Linear regression was used to determine whether chl-*a* also influenced DFe availability.

Results

Physical Parameters

Surface waters exhibited a temporal variability over the summer season. Surface water temperature and pH in BM lakes increased from May into June, with peak values in July (27°C and pH 8.49, respectively; Table 1). Surface water temperature dropped in August while pH increased slightly (Figure 3). Brushy Creek held the lowest temperature at 17°C in May and warmest surface water temperature was observed at Lake of Three Fires in July (33°C). Both minimum and maximum pH were observed in July, with the lowest pH in Lake Macbride in July (7.05) and peak pH at Lake Keomah (10.1).

Similarly, dissolved oxygen and turbidity in surface waters also varied spatially and from May through September (Table 1). Dissolved oxygen levels ranged between 0.7 to 19.9 mg L⁻¹ and decreased from May to August (Supplemental Material Figure 1). Turbidity ranged from 0.8 to 84.0 FNU and increased from May to August, with higher levels observed at Green Valley Lake, Lake Keomah, and Union Grove Lake.

Dissolved Fe Variability

Dissolved Fe in lakes varied throughout Iowa, both spatially and temporally. Of the 124 ALM lakes, DFe concentrations in artificial lakes ranged from 5 to 1015 μ g L⁻¹, with a mean at 41.3 μ g L⁻¹.

	May	June	July	August
T	22	25	27	25
Temperature (°C)	(17-27)	(18-31)	(23-33)	(18-31)
	8.36	8.3	8.49	8.53
рп	(8-8.7)	(7.27-9.13)	(7.05-10.1)	(7.4-9.9)
\mathbf{DO} (mg L-1)	9.9	8.0	8.9	7.5
DO (ling L ⁻)	(5.9-15.5)	(1.3-17.5)	(3.8-34.0)	(0.7-15.4)
DOC (mg L l)	5.9	5.8	6.7	7.5
DOC (ling L ⁻)	(2.8-8.3)	(1.5-25.4)	(1.5-39.1)	(1.5-38.1)
Turbidity (FNU)	8.5	10.5	15.2	16.7
furbluity (FNU)	(1.0-20.0)	(0.8-70.0)	(0.8-84.0)	(0.8-82.3)

Table 1. Temperature, pH, dissolved oxygen (DO), dissolved organic carbon (DOC), and turbidity measured in BM lakes (n = 30). The minimum and maximum values are in parenthesis. Surface water temperature, pH, DOC, and turbidity increased while DO declined throughout the summer season.



Figure 3. Linear regression of chlorophyll (measured by Phyto-PAM II) and DFe. The decline in DFe coincided with increased chl-*a* in some lakes. Measurements are representative of surface waters in the littoral zone, collected from seven BM lakes. Three lakes have multiple monitoring sites: Clear Lake-McIntosh Woods, North Twin Lake East-West, and Black Hawk-Denison.

Approximately 75% were below 40 μ g L⁻¹, with 50% below 24 μ g L⁻¹ (Figure 1). Dissolved Fe in natural lakes ranged from 5 to 900 μ g L⁻¹, with a mean at 46 μ g L⁻¹ (median DFe at 22 μ g L⁻¹). Minimum DFe was observed at Greenfield Lake during August (5 μ g L⁻¹) and the maximum DFe was at Bob White Lake during July (1015 μ g L⁻¹), with both lakes located in southern Iowa. In fact, several lakes exhibiting DFe > 100 μ g L⁻¹ were in southern Iowa (Figure 1).

Weekly monitoring of the BM lakes revealed temporal variations in DFe, with elevated DFe in May (mean at 18.5 μ g L⁻¹), declining DFe into June (13.2 μ g L⁻¹) and July (9.3 μ g L⁻¹), then rebounding DFe in August (11.2 μ g L⁻¹; Figure 3). Each lake exhibited a similar concave trend even though the steepness of decline in June and July varied from lake to lake.

Phytoplankton Biomass

Total chl-*a* derived from PhytoPAM II varied across lakes in this study and ranged from 0 to > 200 µg L⁻¹. In general, chl-*a* was initially low in May, with total chl-*a* values as low as 3 µg L⁻¹ at Black Hawk Lake. Chl-*a* continued to increase throughout the summer, with peak levels in August and September. Chl-*a* values were notably high in late summer, especially at North Twin Lake where values exceeded 200 μ g L⁻¹ (Figure 3).

Dissolved Organic Carbon Variability

Temporal trends in DOC were assessed for BM lakes. Both maximum and minimum values were observed in July, but at different sites. Maximum DOC was observed at Clear Lake (39 mg L⁻¹) and minimum DOC at Backbone (2 mg L⁻¹). Temporal DOC trends also showed a concave trend, with lower DOC in May (mean of 5.9 mg L⁻¹) and increased DOC into August (Supplemental Material Figure 2).

Statistical Analysis

The BM lakes were categorized into four groups based on their DFe trends over the summer season and k-means hierarchical clustering (Figure 4). The first group of BM lakes (Pink group) had only a slight variation of DFe with time compared to the other three groups (Figure 5). The second and third groups (Green and Orange groups) displayed a gradual decline in DFe during June and July, while the fourth group (Blue group) showed a sharp decline in DFe during June and July.



Figure 4. BM lakes were classified into four main groups based on DFe patterns over the summer (via k-means hierarchical clustering); Group 1 (pink), Group 2 (green), Group 3 (orange), and Group 4 (blue).



Figure 5. BM lakes are grouped into four categories (via k-means hierarchical clustering) based on DFe trends over time. In reference to Figure 4, Group 1 is the pink group, Group 2 is the green group, Group 3 is the orange group, and Group 4 is the blue group as defined in Figure 4.

To determine the effects of other variables on DFe, linear mixed modeling was applied to each group identified by k-means hierarchical clustering. Temperature was the main variable associated with DFe in all groups, while DOC was only negatively associated with lakes in Group 3 (Orange group; Table 2).

Discussion

DOC

Turbidity

This study conducted a statewide assessment of DFe in Iowa's lakes. Although there is limited literature regarding Fe in Iowa lakes, current DFe at West Okoboji Lake falls within the lower range of those previously measured (10 to 300 μ g L⁻¹; Bachmann and Jones 1974). The wide range in DFe measured in this survey is similar to other lakes in the region. For example, lakes in Wisconsin also demonstrate a wide range, with mean Fe values from 10 to 400 μ g L⁻¹ (Magnuson et al. 2019).

Factors such as regional geology, watershed characteristics, and biological productivity, as well as mixing regime, influence the amount of DFe in freshwater systems (Gorham et al. 1983; Davison 1993; Nürnberg 1995; Dillon and Molot 2005; Leung et al. 2021). Dissolved Fe from ALM lakes was used to probe for spatial variability across lakes. Dissolved Fe was not significantly different between artificial and natural lakes (p > 0.05). In this study, lake max depth in artificial lakes (ranged from 3 to 33 m) was similar to those of natural lakes (5 to 40 m). Several lakes with DFe exceeding 100 µg L⁻¹ are in southern Iowa, where regional bedrock is primarily Pennsylvanian aged (Figure 1). However, other lakes within the same

region have DFe concentrations below 50 μ g L⁻¹, indicating variables other than regional geology likely also contribute to DFe variability.

Dissolved Fe from BM lakes was used to assess for temporal variability, and DFe concentrations varied from May to August, with declining DFe in June and July and rebounding DFe in August (Figure 5). BM lakes were categorized into four groups based on the concave trend. It is unlikely that residence time affected the temporal variability in these lakes. In a prior study, there was a slight difference in the magnitude of DFe between individual monitoring sites on West Okoboji, although all sites displayed a similar temporal pattern (Leung et al.2021). The spatial variability in DFe within a lake is also seen in BM lakes with multiple monitoring sites (Black Hawk/Denison, Clear Lake/McIntosh Woods, and North Twin Lake East/West; Figure 5). The magnitude of DFe in Black Hawk Lake ranged from 1 to $3 \mu g L^{-1}$, while the magnitude ranged up to 10 µg L-1 in West Okoboji (monitoring sites include Gull Point, Triboji Beach, and Emmerson Bay). Therefore, DFe variation within lakes suggests an alternative mechanism for DFe temporal trends.

Alternative mechanisms for temporal patterns in DFe could be Fe cycling within the lake due to biological uptake, decomposition, and complexation. Additionally, precipitation of Fe oxides and hydroxides, their deposition to the sediment, and reductive dissolution under anoxic conditions can also influence temporal DFe trends.

To explore whether temporal changes in DFe were due to biological uptake, a subset of BM lakes (n = 7) were monitored for chl-*a* (a proxy

$\leq 0.001.$	lotes significal	ice, with	indicating p-va	ilue < 0.05,	mulcating	-value < 0	.01, indicat	ing p-value
	Group 1		Group 2		Group 3		Group 4	
	Coefficient	SE	Coefficient	SE	Coefficient	SE	Coefficient	SE
Intercept	13.92	16.88	37.54	5.06	15.82	4.51	12.84	9.12
рН	0.94	2.04	-1.36	0.61*	1.37	0.53	0.61	0.93
Temperature	-0.33	0.31	-0.56	0.10***	-0.55	0.09**	-0.33	0.16*
DO	0.19	0.25	-0.14	0.09	0.04	0.09	-0.24	0.13

0.07

0.02*

-0.20

-0.05

0.05**

0.01

0.04

0.02

Table 2. Based on the linear mixed model, temperature is potentially associated with DFe trends in Iowa's lakes. The table shows coefficient and standard error (SE) for each grouping identified by k-means hierarchical clustering. *Note: asterisk (*) denotes significance, with * indicating p-value < 0.05; ** indicating p-value < 0.01; *** indicating p-value < 0.001.

0.13

0.06

-0.02

-0.04

-0.05

0.05

0.07

0.03

for phytoplankton biomass). At Black Hawk and Brushy Creek, chl-*a* exhibited negative correlation with DFe (r < 0.7; Figure 3), suggesting that DFe availability may have enhanced growth in those lakes. The rebounding DFe in some lakes (e.g., Black Hawk, Brushy Creek) in August coincided with a decrease in chl-*a*. This potentially hints at an internal cycling of Fe from decomposition of phytoplankton biomass as a mechanism driving the rebounding in these lakes. However, this was not always the case for the other five lakes. The inverse correlation between DFe and phytoplankton is similar to lakes in Alberta, Canada, where Du et al. (2019) found that phytoplankton utilize Fe-binding ligands to acquire Fe.

Based on the linear mixed model, there is a negative correlation between temperature and DFe in the majority of lakes belonging to Groups 2 and 4 (Table 2). This relationship was more obvious in Brushy Creek, Blue Lake, and North Twin; the change in DFe coincided with warmer surface water temperatures. Although dissolved oxygen was not profiled in this study, it is also plausible that the increase in DFe during warmer temperatures may have led to Fe remobilization from anoxic sediments under a stronger stratification (Davison 1993; Saeed et al. 2018). Iron could be transported into the hypolimnion more efficiently at strongly thermally stratified lakes (Loh et al. 2013). As no data on stratification or mixing were collected in this study, we cannot further evaluate this hypothesis.

The presence of DOC in BM lakes potentially increases the solubility of DFe for biological uptake. In freshwater systems, DFe can bind with DOC to form complex ligands (Kikuchi et al. 2017; Qiu et al. 2020) and siderophores (Wilhelm and Trick 1994). A positive correlation between Fe and DOC has been noted in lakes from Minnesota, Wisconsin, and Michigan (Björnerås et al. 2017; Lebret et al. 2018; Brezonik et al. 2019). This is generally attributable to allochthonous organic carbon. However, DOC was poorly correlated with DFe in this study, which may hint at the dominance of autochthonous DOC rather than allochthonous organic carbon. Dissolved organic carbon was a secondary factor for lakes categorized to Group 3 but it was not an important variable in Groups 1, 2, and 4. For group 3, the correlations of both

temperature and DOC with DFe may suggest DFe assimilation by phytoplankton.

Conclusion

Biogeochemical cycling of Fe in aquatic systems regulates the global carbon cycle through its role as an important micronutrient for phytoplankton primary productivity (Smetacek et al. 2012). Furthermore, Fe bioavailability in aquatic systems may have far-reaching implications for ecosystem and public health. The survey of lake DFe conducted in this study serves as baseline for DFe concentrations in Iowa. Weekly monitoring revealed a concave DFe trend throughout the summer. While some lakes exhibit a correlation between DFe and chl-a, it is necessary to tease apart other factors that affect DFe in order to understand the mechanisms driving Fe variability in Iowa's lakes. Future work may distinguish the effects of regional bedrock from catchment-specific sources of Fe (e.g., wetlands and farmland soils) on Fe mobilization to lakes. A long-term survey of Fe in lakes would aid in developing an Fe budget for lakes, and provide insight into the biogeochemical cycle of Fe in lakes.

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Supplemental Figures

Supplemental Material Figure 1. Dissolved oxygen in surface lake waters varied over the summer season.



Supplemental Material Figure 2. Dissolved organic carbon in surface lake waters varied over the summer season.