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EDITED BY
Zimin Li,
Chinese Academy of Sciences (CAS), China

REVIEWED BY
Xiaodong Zhang,
Tianjin University, China
Natalia Borrelli,
Universidad Nacional de Mar del Plata,
Argentina

*CORRESPONDENCE
Lienne R. Sethna,
lsethna@smm.org

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Dynamics of dissolved silicon in a large mesotrophic reservoir in south-central Indiana, U.S.A

Lienne R. Sethna [1,2]*, Lindsey M. Rasnake [1], Sarah R. Powers[1], Zoe I. Plechaty[2], Ariel H. Pouchak[2], William O. Hobbs [3] and Todd V. Royer [1]

[1]Indiana University, O'Neill School of Public and Environmental Affairs, Bloomington, IN, United States, [2]St. Croix Watershed Research Station, Marine on St. Croix, MN, United States, [3]Washington State Department of Ecology, Lacey, WA, United States

River damming disturbs the transport and fate of nutrients, which alters biogeochemical cycling within reservoirs and alters the flux of nutrients downstream. In reservoirs, silicon (Si) is retained in larger proportions relative to nitrogen (N) and phosphorus (P) which can reduce dissolved Si (DSi) availability and push phytoplankton communities to be dominated by non-siliceous, potentially harmful taxa, such as cyanobacteria. Lake Monroe is the largest reservoir in Indiana and provides drinking water for more than 140,000 people, making it a critical water resource and exemplar for potential Si retention within the Mississippi River basin. To quantify the retention of DSi in Lake Monroe, we calculated an annual DSi budget using measured DSi inputs and outputs between April 2020 and March 2021. We also measured in-lake DSi and phytoplankton community composition between May and October 2020 as well as long-term biogenic Si fluxes to the sediment to better quantify the mechanisms controlling DSi retention. We found that Lake Monroe retained over half of its annual DSi inputs over the monitoring period and that retention was driven by diatom growth and sedimentation. As the construction of large dams continues globally, it is important to quantify how the biogeochemical cycling and transport of DSi is changing and the role of reservoirs in potentially shifting diatoms from N- or P- limited to Si-limited.

KEYWORDS

silicon, river damming, reservoirs, silicon retention, silicon flux, silicon budget

Introduction

The importance of silicon (Si) to inland and coastal ecosystems is well described, particularly in the context of eutrophication and harmful algal blooms (Officer and Ryther, 1980; Conley et al., 1993; Billen and Garnier, 2007). The Si depletion hypothesis posits that nutrient loading, particularly of phosphorus (P), can increase diatom production in lakes and the sequestration of biogenic Si in lake sediments (Schelske and Stoermer, 1971; Schelske et al., 1986). Over periods of years to decades, increased sequestration of biogenic Si in lake sediments disrupts the steady-state processes of dissolved Si (DSi) uptake and biogenic Si dissolution, thereby reducing DSi availability in the epilimnion of stratified lakes (Crowe, 2006; Carey and Fulweiler, 2013; Chen et al., 2014). Often, this results in nutrient conditions that limit diatom production and favor blooms of non-siliceous taxa, such as cyanobacteria. The process of long-term depletion of Si is distinct from the annual utilization of DSi by diatoms that temporarily reduces DSi concentrations (Conway et al., 1977; Schelske et al., 1986), though both phenomena result from the coupled cycling of nitrogen (N), P, and Si by phytoplankton (Hobbs et al., 2010; Scibona et al., 2022; Sethna and Royer, 2024).

Damming of rivers alters the quantity, timing, and stoichiometry of nutrient delivery to downstream water bodies which affects phytoplankton productivity and, subsequently, food web dynamics, carbon sequestration, and water quality (Smith, 2003; Paerl et al., 2006; Conley et al., 2009; Poff and Schmidt, 2016). Previous work has quantified global Si retention by river damming, which significantly alters the export of Si to downstream ecosystems and the stoichiometry of available nutrients (Beusen et al., 2009; Laruelle et al., 2009; Maavara et al., 2014). Additionally, reservoirs can alter the limiting nutrient in freshwater and marine systems, including potentially shifting diatoms from N- or P- limited to Si-limited (Paerl et al., 2006; Howarth and Marino, 2006), yet few studies have examined reservoir Si budgets and the role of Si stoichiometry in phytoplankton community succession.

The load of DSi transported by the Mississippi River to the northern Gulf of Mexico declined by approximately 50% during the middle of the 20th century (Turner et al., 1998; Turner and Rabalais, 2004). One proposed mechanism for the decline in DSi loads in the Mississippi River is sequestration of biogenic Si in nutrient-rich reservoirs on streams and rivers within the Mississippi River basin. Indeed, mass balance studies have shown reservoirs to be retention structures for Si (Maavara et al., 2014; Maavara et al., 2015a); however, there are very few published Si mass balance studies for lakes or reservoirs within the Mississippi River basin. Triplett et al. (2008) reported annual Si retention for two natural riverine lakes in Minnesota, Lakes Pepin and St. Croix, with higher retention occurring in eutrophic Lake Pepin. At present, the role of constructed reservoirs on DSi fate and transport in the Mississippi basin is largely unquantified.

Here we detail a 1-year DSi budget for Lake Monroe, a reservoir in southern Indiana and within the Mississippi River basin, using inputs from major tributaries and precipitation, outflow from the dam, drinking water withdrawal, in-lake changes in DSi concentrations and diatom abundance, and biogenic Si sequestration in reservoir sediments. Our study had three main objectives: (1) use a mass-balance approach to determine whether, and to what degree, Lake Monroe retained DSi, (2) explore the role of diatoms in driving DSi retention, and (3) calculate the relative retention of DSi and compare it with published values across a gradient of reservoir trophic status. We hypothesized Lake Monroe would show net retention of DSi during the sampling period; the main driver of this retention was expected to be uptake by diatoms, which can effectively sequester DSi through sedimentation (Turner et al., 1998; Frings et al., 2014; Wang et al., 2016; Liu et al., 2019). Diatoms are the most significant user of DSi in freshwater systems (Wetzel, 2001; Thamatrakoln and Kustka, 2009); therefore, the concentration of DSi in the epilimnion should correspond to the relative proportion of diatoms versus non-siliceous phytoplankton. If DSi concentrations decreased with increasing diatom abundance, this would indicate the growth of diatoms affected the availability of DSi for downstream transport. Finally, calculating the relative retention of DSi (R_{DSi}, Maavara et al., 2014) in Lake Monroe quantified the proportion of DSi inputs retained in the reservoir and allowed for a comparison with other reservoirs and natural impoundments. As the rate of dam construction continues to increase globally (Zarfl et al., 2015), it is critical to quantify DSi retention in reservoirs, and this study provides estimates of retention within the Mississippi River basin where the load of DSi can strongly influence coastal food webs and ecological processes (Turner and Rabalais, 2004; Turner et al., 2007). For example, the timing of DSi delivery to the Gulf of Mexico can influence the growth of diatoms whose productivity provides the majority of the organic matter which drives the respiration that contributes to the formation of the hypoxic zone (Turner and Rabalais, 1994; Royer, 2020).

Methods

Site description

Lake Monroe is the largest lake in Indiana, with a surface area of approximately 44 km^2 at normal pool and a maximum depth of 17 m (Jones et al., 1997). Globally, reservoirs ranging between 10 and 100 km^2 are estimated to make up between 9%–12% of the total volume of impounded water (Downing et al., 2006; Lehner et al., 2011). The average volume and residence time calculated during the study period were 0.25 km^3 and 186 days, respectively, based on the daily volume and outflow from the dam measured by the U.S. Army Corps of Engineers (ACOE). The lake is an impoundment on Salt Creek and was constructed in 1965 for the primary purpose of flood control and flow regulation during dry periods. The main tributaries to the lake are the North, Middle, and South Forks of the Salt Creek (Figure 1). The Lake Monroe watershed is approximately 1,095 km^2 consisting of more than 86% forested land and about 12% agricultural land. Soils in the watershed are poorly to well drained and are all classified as "highly erodible lands" given the steep slopes within the watershed (Jones et al., 1997). The watershed is underlain primarily by limestone and siltstone of the Mississippian Borden Group (Jones et al., 1997). Today, Lake Monroe provides drinking water for more than 140,000 people, with withdrawals totaling 0.02 km^3 between April 2020 and March 2021 (City of Bloomington Utilities). Lake Monroe is meso-eutrophic according to the Trophic State Index (Carlson, 1977), which was calculated using chlorophyll-*a* concentrations measured during our sampling period.

Sampling regime

We monitored four tributaries and the dam outflow monthly for one calendar year between April 2020 and March 2021, collecting samples for DSi analysis and measuring instantaneous discharge. Each of the four tributaries drained sub-watersheds that, combined, account for about 55% of the Lake Monroe watershed area (Table 1; Figure 1). Stream water samples were filtered in the field using 0.45 μm cellulose filters (Fisherbrand), transported on ice, and frozen until analysis. Instantaneous discharge (Q) was measured using an electromagnetic water velocity probe (March-McBirney Model 2000 FloMate) as described in Hauer and Lamberti (2006). We also used instantaneous discharge measurements recorded by the U.S. Geological Survey at the North and South Forks of the Salt Creek (gage numbers 03371650 and 03371600, respectively). We sampled after one

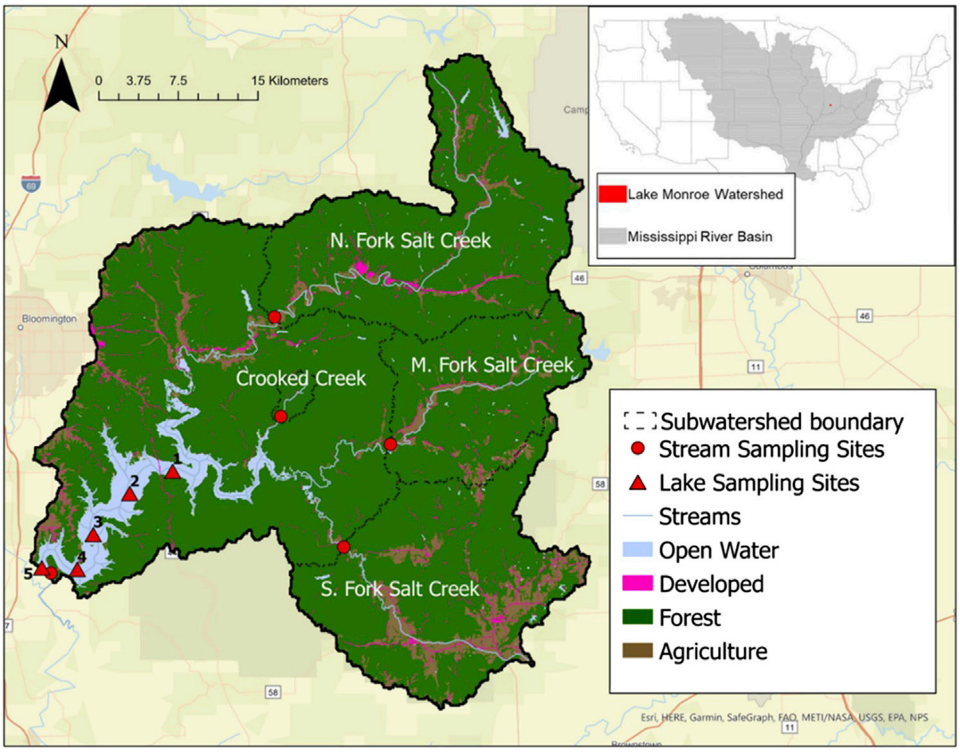

FIGURE 1
Map of the Lake Monroe Watershed. Lake sampling sites are numbered 1–5. Land cover data is a subset of the 2011 National Land Cover Database. Inset map shows the location of the Lake Monroe Watershed within the Mississippi River Basin.

storm event in March 2021 in order to capture nutrient conditions and tributary discharge during high flows.

To characterize nutrient concentrations and phytoplankton community composition, we sampled five sites along a longitudinal transect through the lake monthly between late May and late October 2020 (Figure 1). From the three main sampling locations (Sites 1, 3, and 5), we collected epilimnetic samples using a 2-m integrated sampler and, during periods of stratification, hypolimnetic samples about 1 m above the lake bed using a Van Dorn sampler. Lake DSi samples were filtered and stored in the same way as tributary nutrient samples and additional, unfiltered samples were collected for total nitrogen (TN) and total phosphorus (TP) analysis. We used TN and TP to calculate stoichiometric ratios since bioavailable N and P in the water column are made up of particulate and organic forms which can rapidly remineralize (Dodds, 2003; Bergström, 2010; Carey et al., 2019). We also measured photosynthetically active radiation (Li-Cor Model LI-189 Quantum Radiometer-Photometer; Lincoln, NE) just below the water surface and collected temperature profiles (In-Situ Aquatroll 500 Multiparameter Sonde; Fort Collins, CO) at 1-m intervals to determine thermal stratification and metalimnion depth. At two midpoint sites between the main sites (Sites 2 and 4), we collected epilimnetic temperature and DSi samples. Lastly, we collected depth profiles of DSi concentration at 2-m intervals at Site 5, the deepest site located approximately 500 m upstream of the dam.

Phytoplankton samples were collected from the epilimnion of the three main sites, stored in dark plastic, and preserved with glutaraldehyde. Samples were imaged and identified to the genus level by PhycoTech, Inc. (St. Joseph, MI, United States) using the Imaging FlowCytobot (IFCB; McLane Research Laboratories, Inc., East Falmouth, MA, United States). The IFCB produced at least 2000 images per sample which were normalized to the volume of sample analyzed and identified to the genus level at 80% accuracy; however, classification at the functional group level is more accurate and provides an ecological assessment of the phytoplankton community. Biovolume of the phytoplankton was estimated for each individually imaged cell (Moberg and Sosik, 2012). In this analysis, we focus on the biovolume of diatoms (Bacillariophyta), which were dominated by the taxa *Aulacoseira*, *Fragilaria*, *Nitzschia*, and other less abundant centric and pennate diatoms.

All tributary and lake DSi samples were analyzed using the heteropoly blue method (Sultan, 2014) on a Lachat QuikChem flow injection analyzer (Model 8500; Hach Company; Loveland, CO). Samples were analyzed for TN and TP colorimetrically following an alkaline persulfate digestion (APHA, 2017) using an Alpkem FLOW Solution Autoanalyzer (Model 3570; OI Analytical; College Station, TX). For all nutrient analyses, we ensured the standard curves had coefficients of determination of at least 0.9, ran certified, external standards, and routinely calculated the method detection limits. Detection limits for DSi, TN, and TP were 0.06, 0.1, and 0.002 mg L^{-1}, respectively. Samples below the detection limit included four TN samples from Crooked Creek and one TP sample from the epilimnion of Site 5. No DSi samples were below detection. Samples below detection were set to one half of the measured detection limit for purposes of statistical analysis.

TABLE 1 Summary statistics for Lake Monroe tributary and outlet sampling sites, including mean DSi concentrations, instantaneous discharge (Q) descriptors, and instantaneous DSi loads during the sampling period (April 2020–March 2021). Each site was sampled monthly to construct a DSi budget for the watershed.

River	Flow	USGS gage number	Drainage area (km^2)	Fraction of watershed (%)	% Forest	% Cultivated	Mean DSi (mg SiO_2 L^{-1})	Mean Q (m^3 s^{-1})	Min. Q (m^3 s^{-1})	Max. Q (m^3 s^{-1})	Annual DSi Load (Mg SiO_2)	n
Crooked Creek	Inlet	not gaged	7	0.6	97	0	9.6	0.1	0	0.3	27	10
N. Fork Salt Creek	Inlet	3371650	276	25	80	5	7.4	4.1	0.01	36.1	1,049	12
M. Fork Salt Creek	Inlet	not gaged	99	9	84	8	9.1	0.7	0	5.5	376	12
S. Fork Salt Creek	Inlet	3371600	230	21	76	17	8.9	1	0.01	5.9	876	12
Salt Creek	Outlet	3372500	1,095	100	86	12	7	11.8	1.5	55.8	2,181	12

We collected a sediment core from the deepest point in the reservoir, close to Site 5, in an area of the basin that was away from steep slopes that might be subject to slumping that was identified using sonar and bathymetric maps. The sediment core was collected using a piston corer with a 6.5-cm diameter polycarbonate core barrel and operated from the lake surface by metal drive rods (Wright, 1991). We recovered 23 cm of sediment which was transported vertically to the laboratory where the core was sectioned at 1-cm intervals and stored in polypropylene jars for the subsequent quantification of dry-density, water, organic, and mineral content, radiometric dating, and Si content.

The dry-density (dry mass per volume of fresh sediment), water content, and organic and mineral composition of each interval were determined using standard loss-on-ignition techniques (Dean, 1974). Lake diatoms were identified throughout the core, indicating the core represented sediment deposited after the reservoir was constructed. In order to accurately estimate the age of the sediment intervals, we used Gamma spectrometry to quantify the activity of lead (Pb) radioisotopes (^{214}Pb and ^{210}Pb) and construct a dating model for the core (Appleby, 2002). Briefly, we fit an exponential regression to the measured ^{210}Pb activity to estimate the total inventory of unsupported ^{210}Pb (Binford, 1990; Appleby, 2002). We used the activity of ^{214}Pb as a measure of supported ^{210}Pb; ^{214}Pb is the daughter isotope of ^{226}Ra which is in secular equilibrium with supported ^{210}Pb (Appleby, 2002). We then used a constant rate of supply model to estimate the age and dry mass accumulation rates of each of the sediment core intervals (Krishnaswamy et al., 1971; Appleby, 2002; Supplementary Figure S1). Finally, we calculated a sediment focusing factor to correct for the spatial heterogeneity in sedimentation rates and to allow for a whole-basin estimate of Si burial (Hobbs et al., 2013; Engstrom and Rose, 2013).

DSi budget calculations

We quantified DSi inputs and outputs for Lake Monroe to construct an annual DSi mass balance from April 2020 through March 2021. Tributary DSi loads and atmospheric wet deposition were considered watershed inputs while the dam outflow and drinking water withdrawal were considered outputs. Total DSi retained in Lake Monroe during the sampling period was therefore calculated as the difference between total watershed inputs and outputs. The relative retention of DSi (R_{DSi}) was calculated as:

$$R_{DSi} = \frac{DSi_{in} - DSi_{out}}{DSi_{in}}$$

where DSi_{in} and DSi_{out} are the total fluxes of DSi in and out of Lake Monroe, respectively (Maavara et al., 2014). We then compared the R_{DSi} of Lake Monroe to the global dataset of reservoirs compiled by Maavara et al. (2014).

Daily loads in the tributaries and outflows were modeled using *Loadflex*, a package in R that allows for the simple, linear interpolation of solute loads between sampling events (Appling et al., 2015). Loads were interpolated between sampling events since DSi concentrations exhibited a chemostatic relationship with discharge at all sampling sites (Supplementary Figure S2).

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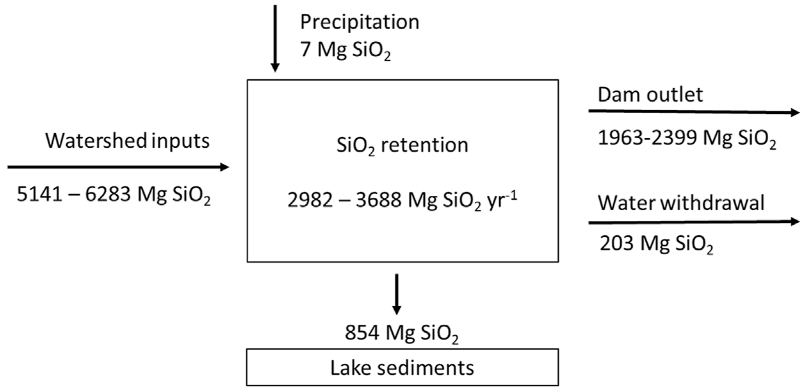

FIGURE 2
DSi budget for Lake Monroe for the period April 2020 through March 2021. Inputs include DSi loads from monitored and unmonitored tributaries as well as precipitation over the lake. The outputs from the watershed include the dam outflow and drinking water withdrawals. The ranges in tributary inputs and dam outflow represent the uncertainty applied to discharge measurements. The difference between the inputs and outputs, between 2,982 and 3,688 Mg SiO_2, represents the net retention of DSi in the reservoir during the study period, of which 854 Mg are estimated to be buried annually in the sediments as biogenic Si.

We used U.S. Geological Survey (USGS) continuous, daily discharge data, monthly DSi concentrations, and a simple linear interpolation model to estimate total daily DSi loads from the North and South Forks of the Salt Creek (Table 1). We used these daily loads to calculate daily DSi yields which were scaled to the outlet of the North and South Fork tributaries. We used the average of the North and South Fork yields to scale total loads from other sampled watersheds and the unmonitored portion of the Lake Monroe watershed. Similarities in watershed land use and DSi concentrations between sub-watersheds and sampled tributaries allowed us to reasonably assume proportional contributions of DSi from unmonitored portions of the watershed (David et al., 2006). Due to the inherent uncertainty associated with stream discharge measurements, we applied 10% error to each value measured at the U.S. Geologic Survey gaging stations (Harmel et al., 2006) and calculated the DSi loads using ±10% of the reported discharge values. Atmospheric deposition of DSi was calculated by multiplying the annual volume of precipitation over the lake by the average DSi concentration in precipitation (both rain and snow) collected during three distinct events during the monitoring period. Outflow DSi loads were modeled using the same *Loadflex* methods, but discharge data were provided by the U.S. ACOE. The City of Bloomington drinking water plant is located near Site 2 and monitors daily withdrawals. We estimated the total mass of DSi removed with drinking water using the average DSi concentration at Site 2 measured between April and October of 2020 multiplied by the total volume of water withdrawn.

We estimated the mass of DSi retained in the hypolimnion by multiplying the measured hypolimnetic DSi concentration by the volume of the hypolimnion before lake turnover, estimated based on the depth of the metalimnion and area of the lake. To quantify the mass of Si sequestration in reservoir sediments, we analyzed biogenic silica (BSi) concentrations using 30 mg subsamples of freeze-dried sediment representing the last 10 years. Samples were digested in 40 mL of 1% Na_2CO_3 solution heated at 85 °C in a reciprocating water bath for 5 hours (Conley and Schelske, 2002). After cooling and neutralization with 4.5 g of 0.021 N HCl solution, DSi was measured colorimetrically on a Unity Scientific SmartChem 170 discrete analyzer (SmartChem 2012a). The concentration of DSi in each sediment interval was converted to the flux of BSi over time using the dry mass accumulation rates.

Statistical analysis

All analyses and statistical tests were carried out in R (The R Foundation for Statistical Computer, Version 4.0.5, 2021) and data were visualized using the *ggplot2* package (version 3.5.1; Wickham, 2016). We hypothesized that uptake by diatoms was the main driver of DSi retention in the lake; therefore, we expected a declining trend in DSi concentrations along the downstream gradient of the reservoir, higher DSi concentrations in the hypolimnion relative to the epilimnion, and a relationship between DSi concentrations and the relative abundance of diatoms that reflected uptake and sedimentation. We used simple linear regression to model the spatial trend in DSi concentrations as well as a one-way analysis of variance (ANOVA) to test for differences in DSi concentrations between lake sampling sites for each sampling date. We also used t-tests to detect significant differences in DSi concentrations between the epilimnion and hypolimnion. The relationship between DSi concentrations and the abundance of diatoms relative to the total phytoplankton community was modeled using simple linear regression. Prior to running each statistical analysis, we tested all data to ensure the assumptions for each test were met, including normality using the Shapiro-Wilk test and homoskedasticity by plotting model residuals against fitted results.

Results

Annual DSi budget

The primary source of DSi to Lake Monroe was tributary inputs, which varied through time and between sites. Between all sites and

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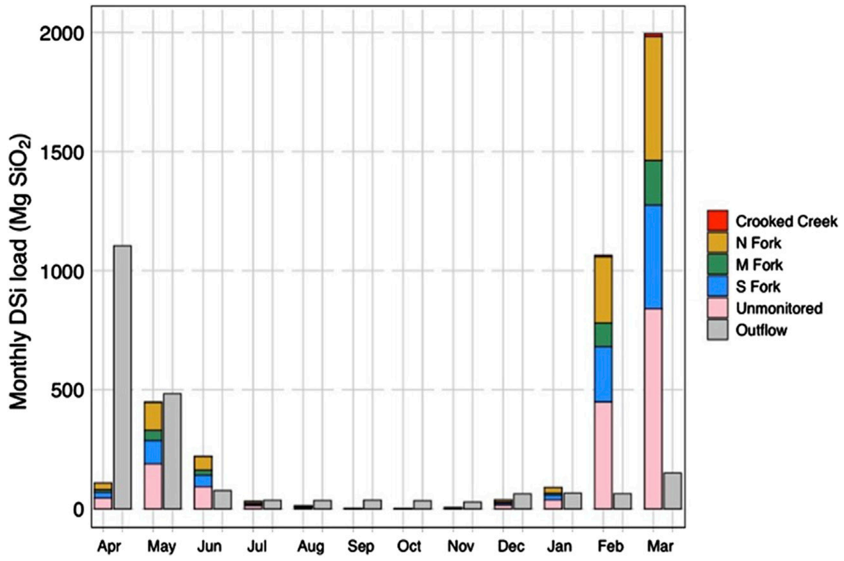

FIGURE 3
Total monthly DSi loads (as megagrams [Mg] SiO_2) from each sub-watershed (stacked bars) and the dam outflow (gray bars).

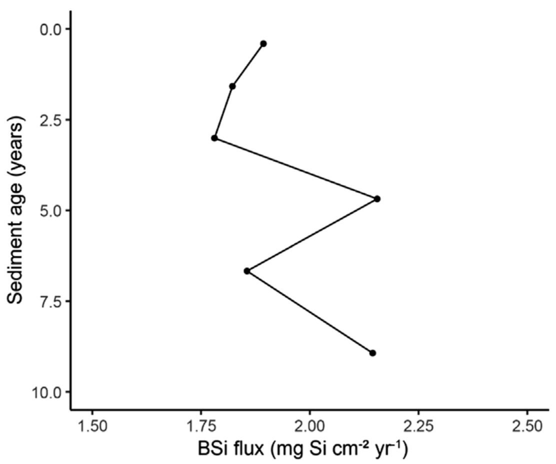

FIGURE 4
The annual, focus-corrected, areal flux of BSi measured over the last decade in Lake Monroe.

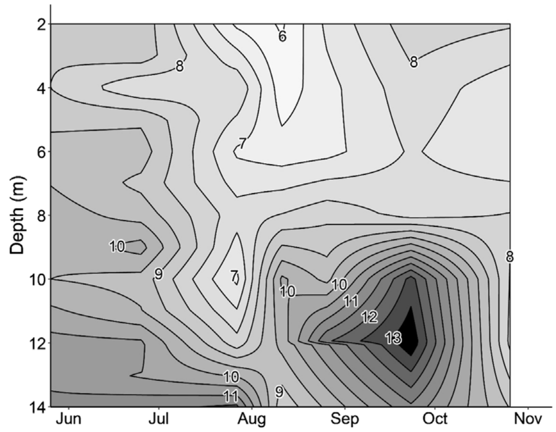

FIGURE 5
Isopleth diagram of DSi concentrations (mg SiO_2 L^{-1}) from Site 5 during the monitoring period. Samples were collected at 2-m intervals through the water column. Isopleths are spaced at 0.5 mg L^{-1} intervals.

sampling dates, DSi concentrations in the tributaries ranged between 3.6 and 13.3 mg L^{-1} while discharge ranged over multiple orders of magnitude (Table 1). Due to the inherent uncertainty associated with stream discharge measurements, we applied 10% error to each value measured at the U.S. Geologic Survey gaging stations (Harmel et al., 2006). Annual input from the watershed was estimated to be 5,712 (±571) Mg SiO_2. The total annual DSi input from precipitation onto the lake was approximately 7 Mg SiO_2, which represents ~0.1% of the total DSi inputs to the lake during the study period (Figure 2).

Outflows from Lake Monroe include the dam outlet and drinking water withdrawals. DSi concentrations from the outlet fluctuated between 8 and 10 mg L^{-1} between April and October 2020 before declining to 3–5 mg L^{-1} through the winter and early spring of 2021. The total output of DSi from the dam was 2,181 (±218) Mg SiO_2 over the period of record. The drinking water withdrawals totaled 0.02 km^3 from April 2020 to May 2021 and we calculated the total mass of DSi removed with drinking water to be 203 Mg SiO_2. There was intra-annual variation in DSi retention within the lake; loads in the outflow exceeded the total incoming load for most months in 2020 but were much less than the total input during the winter and early spring of 2021 (Figure 3). Based on total average input and output estimates, the annual retention of DSi was 3,335 (±335) Mg SiO_2 and the annual R_{DSi} was 0.58 (±0.08), meaning that during the study period, DSi outflow was equivalent to less than half of the DSi inputs. Even with the most conservative estimates of DSi retention (minimum inputs,

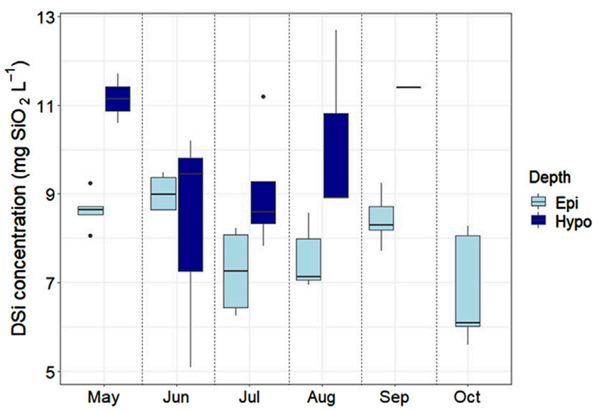

FIGURE 6
Epilimnetic (light blue) and hypolimnetic (dark blue) DSi concentrations during the sampling period across all sampled sites. Epilimnetic concentrations were measured using a 2 m integrated sampling tube at the surface of the lake, and hypolimnetic samples were collected 1 m from the lake bed using a Van Dorn sampler. Data are grouped by depth and sampling month. Each box represents the 25th to 75th percentiles, the horizontal line indicates the median value, whiskers extend to ±1.5 Interquartile Range, and points indicate outliers in each group.

maximum outputs), R_{DSi} was 0.49, showing meaningful DSi retention in Lake Monroe.

The dating model for the sediment core produced a continuous age-depth relationship for the full length of the sediment core. The base of the core was dated to approximately 2007 and the top 14 cm of core were found to represent the last decade of sedimentation in Lake Monroe. Focus-corrected, areal sediment BSi fluxes averaged 1.9 (±0.1) mg Si cm^{-2} $year^{-1}$ and the consistent flux values within the last decade indicate Si sequestration has remained consistent over this time period (Figure 4). We calculated the annual flux of Si to the sediments within the entire Monroe basin by multiplying the average areal flux by the surface area of the lake (44 km^2), yielding a whole basin burial of 854 Mg of Si annually and indicating that nearly 30% of the DSi retained in the reservoir is permanently buried as BSi in the lake sediments.

Variation in DSi concentrations in Lake Monroe

Contrary to our predictions, epilimnetic DSi concentrations did not significantly decline along the longitudinal gradient of the lake. In fact, epilimnetic DSi concentrations were not significantly different among any of the epilimnion sampling sites during the monitoring period. However, there were differences between epilimnion and hypolimnion concentrations that indicated changes in DSi storage through time within the lake (Figure 5). Specifically, in May, July, August, and September, DSi concentrations in the hypolimnion were significantly greater than epilimnion DSi (t-test, $p < 0.01$; Figure 6). Lake Monroe was stratified between May and September, limiting mixing between the epilimnion and hypolimnion; therefore, changes in DSi concentrations were likely a result of diatom uptake in the epilimnion and dissolution of biogenic Si in the hypolimnion. Based on the hypolimnetic DSi concentration measured at the Lower site (13.4 mg L^{-1}) and the depth of the metalimnion (10.5 m) in late September, we estimated 2,653 Mg of DSi were recycled from the hypolimnion to the epilimnion during fall turnover, representing the other 70% of the DSi retained in the reservoir.

As we expected, DSi concentrations had a significant, negative relationship (simple linear regression, $p < 0.001$ for all sites) with diatom biovolume at sites 1 and 3 throughout the monitoring period (Supplementary Figure S3). We modeled the relationship between each sampling site individually to account for the differences between site behavior along the downstream gradient of the reservoir. DSi concentrations at sites 1 and 3 explained 84% and 66% of the variance in relative diatom biovolume, respectively, while there was no significant relationship between diatom biovolume and DSi concentrations at site 5. This suggests diatoms, as the most significant user of DSi, reduced epilimnetic DSi concentrations differently along the downstream gradient within the reservoir. The relationship between diatom biovolume and DSi concentrations is especially pronounced when comparing changes in diatom biovolume simultaneously with DSi concentrations through time (Figure 7). When diatoms peaked in July and October, there was a corresponding decline in DSi concentrations. While there was a significant relationship between diatom biovolume and DSi concentrations, there was no effect on diatom biovolume with changes in molar Si:TN, Si:TP, or TN:TP (Supplementary Figure S4).

Discussion

Understanding DSi cycling in inland waters is critical to resolving how modified landscapes influence nutrient delivery along the land-ocean continuum. Reservoirs represent a major gap in our knowledge of Si retention and transformation, despite their growing prevalence and known impacts on biogeochemical cycles (Maavara et al., 2020a; Maavara et al., 2020b). To our knowledge, our DSi budget in Lake Monroe is the first to quantify DSi retention within the Mississippi River basin, which contributes increasingly imbalanced loads of N, P, and Si to the Gulf of Mexico that can favor non-siliceous and potentially harmful algal taxa (Turner and Rabalais, 2004; Royer, 2020). We found that Lake Monroe retained approximately 58% of its annual DSi inputs, providing clear evidence that reservoirs with relatively short residence times can act as substantial Si sinks. Diatom uptake and sedimentation were key drivers of DSi retention, indicated by a strong, inverse relationship between DSi concentrations and diatom biovolume as well as the permanent burial of BSi in lake sediments. When compared to published estimates from reservoirs with similar water residence times, the DSi retention in Lake Monroe was higher than expected, underscoring the largely unquantified role of reservoirs in global Si retention. Taken together, our results highlight the important role of reservoirs in modulating Si transport to downstream ecosystems and coastal waters.

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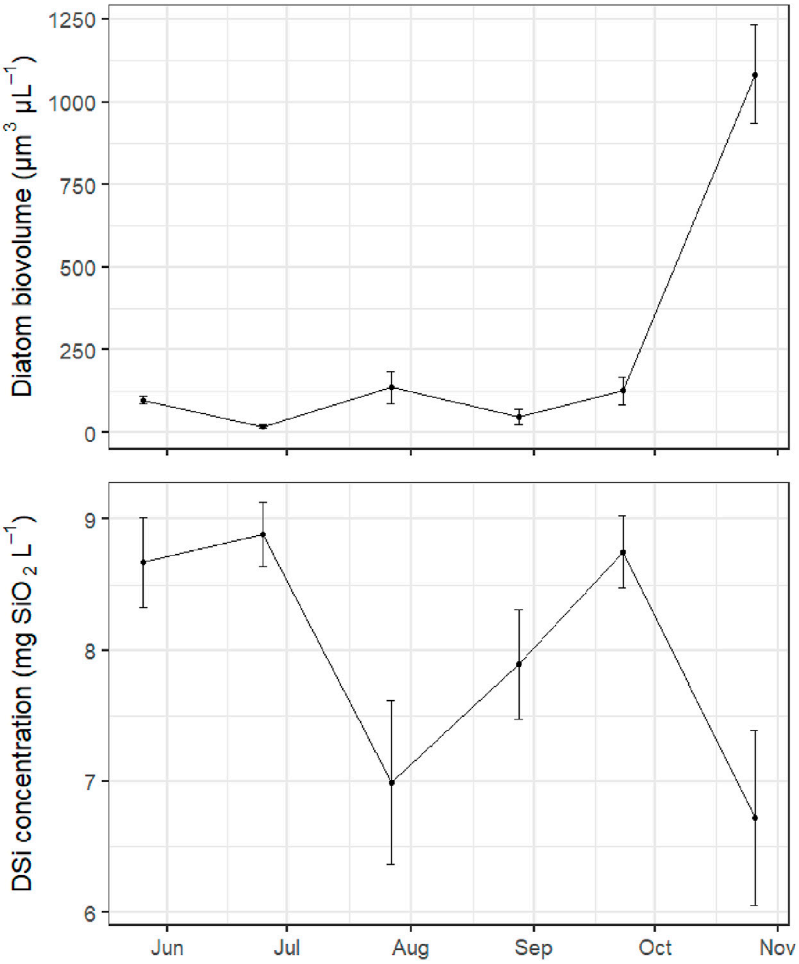

FIGURE 7
The biovolume of diatoms, averaged across Sites 1, 3, and 5 (top) and the mean epilimnetic DSi concentration (bottom) during the sampling period in 2020. Error bars extend to the standard error of the mean and in some cases are too small to be visible.

Lake Monroe was a net sink of DSi

Based on our measurements over the course of 1 year, Lake Monroe retained about 58% of the total DSi inputs. Compared with other reservoirs around the world, the R_{DSi} of Lake Monroe is in the top 25th percentile but is similar to the median value of reservoirs with similar residence times (Harrison et al., 2012; Maavara et al., 2014). Globally, the average R_{DSi} is 0.13, with values above 0.3 generally associated with water residence times greater than 5 years (Maavara et al., 2014; Maavara et al., 2015a). The average water residence time of Lake Monroe during the sampling period was about 0.5 years, indicating the DSi retention observed in Lake Monroe during our monitoring period was higher than expected based on the relationship between water residence times and DSi retention described by Maavara et al. (2014); however, this is not unexpected since the relationship in Maavara et al. (2014) was established using budgets for just 20 reservoirs from a global population of more than 75,000 reservoirs with a surface area >0.1 km^2 (Lehner et al., 2011). The water retention time in Lake Monroe during the sample period was similar to the median value of historic water volume and dam outflow, indicating the DSi retention we measured is likely representative of annual Si retention during the last decade (Supplementary Table S1). Furthermore, sediment Si fluxes indicated relatively constant Si depositional rates, suggesting Si retention rates have not changed in the last 10 years and providing no evidence for Si depletion in Lake Monroe. The significant DSi retention observed in Lake Monroe provides further evidence of the impact of reservoirs on nutrient delivery to downstream waters and, ultimately, coastal ecosystems. In the midwestern U.S., occurrences of heavy precipitation are predicted to increase with climate change (Hamlet et al., 2020), which could increase inputs of DSi to the Mississippi River. However, high flow events will likely disproportionately increase N loads, reducing the availability of DSi relative to N in receiving waters (Leong et al., 2014; Sinha et al., 2017; Royer, 2020; Sethna et al., 2022).

Retention of DSi in reservoirs, as observed in Lake Monroe, has significant implications for the transport of DSi to the Mississippi River and, ultimately, the Gulf of Mexico. Two natural impoundments in the Mississippi River basin in Minnesota, Lakes Saint Croix and Pepin, had R_{DSi} values of 0.04 and −0.11, respectively, with the lower of the two corresponding to Lake Pepin, which had an order of magnitude greater Si inputs and was also more eutrophic relative to Lake Saint Croix

(Triplett et al., 2008; Maavara et al., 2014). Lake Monroe and the lakes studied by Triplett et al. (2008) all are in the upper portions of the Mississippi River basin and DSi released from these lakes is subject to retention and sedimentation before reaching the Gulf of Mexico. Interestingly, Downing et al. (2016) concluded that impoundments within several agricultural watersheds of the Mississippi River basin did not increase Si retention, rather, this was attributed to the low abundance of diatoms relative to cyanobacteria in those reservoirs. Together, Lakes Monroe, Saint Croix, and Pepin represent <0.001% of the Mississippi River basin area and <5% of the total Si load to the Gulf of Mexico, highlighting the significant uncertainty that exists in scaling up our measurements of Si retention in small reservoirs to Si retention at a continental scale.

Continued study of Si transport and availability in rivers and reservoirs throughout the basin are necessary to identify nutrient management practices that alleviate cultural eutrophication and hypoxia in the Gulf of Mexico. These types of studies are also critical in other large rivers such as the Yangtze River in China and the Amazon River in Brazil, where many large dams are currently under construction, or planned for in the near future (Yang et al., 2011; Zarfl et al., 2015; Anderson et al., 2018; Flecker et al., 2022). Increasing Si retention in these basins, coupled with increased anthropogenic loads of N and P, will likely contribute to more frequent and intense Si limitation in coastal systems, with implications for phytoplankton productivity, water quality, and carbon cycling (Garnier et al., 2010; Maavara et al., 2020a). These issues are compounded by dam-driven changes to the timing of nutrient loading, which could increase the potential for Si limitation during the growing season and contribute to increased blooms of harmful or nuisance algal taxa.

Contrary to our predictions, epilimnetic DSi concentrations did not decrease along the lake continuum suggesting watershed inputs maintained relatively constant Si concentrations. There were, however, significant differences in DSi concentrations between the epilimnion and hypolimnion, indicating that the probable mechanism facilitating retention is the growth and sedimentation of diatoms. Diatom growth reduces DSi concentrations during blooms and frustules sink after death or consumption, effectively sequestering the biogenic Si in lake sediments. As biogenic Si is more soluble than crystalline Si (Cornelis et al., 2011), some diatom frustules are recycled to DSi, thereby increasing the DSi concentration in the hypolimnion (Scibona et al., 2022). The storage and dissolution of diatom frustules in the hypolimnion explains why hypolimnetic DSi concentrations were higher than epilimnetic DSi.

The sequestration and dissolution of diatoms in lake sediments is the most likely fate of the retained DSi in Lake Monroe. Increased hypolimnetic DSi concentrations support the hypothesis that some of the diatom frustules dissolve in the hypolimnion and are recycled to the epilimnion at turnover (Figure 4); however, the flux of BSi to the sediments indicates that nearly a third of the DSi retained in the reservoir is buried in lake sediments (Triplett et al., 2008; Humborg et al., 2008; Maavara et al., 2015a). The other 70% of the Si was recycled back into the water column during fall turnover in late September (Figure 5). The recycling of DSi from the hypolimnion elevated epilimnetic DSi concentrations and likely facilitated the observed diatom bloom in late October (Figure 7). Further examination of the biogeochemical cycling of DSi between the water column and lake sediments could help us better describe the processes that facilitate BSi sequestration and recycling at lake turnover.

Silica utilization in Lake Monroe

The inverse relationship between the biovolume of diatoms and DSi concentrations indicated that DSi availability was influenced by diatom productivity. Our data suggest the elevated DSi concentrations created conditions suitable for diatom growth and their growth depleted the available DSi in the lake, thus creating conditions more favorable for the growth of non-siliceous phytoplankton groups (Beusen et al., 2009; Carey et al., 2019). The relationship between DSi concentrations and diatom biovolume likely differed between sites because Site 1, as the most upstream site, was most strongly influenced by riverine inputs, while conditions at Sites 3 and 5 were influenced by in-lake processes. Interestingly, the minimum DSi concentration in Lake Monroe was 5.09 mg SiO_2 L^{-1}, well above the limiting concentration of 0.1 mg SiO_2 L^{-1} reported by Schelske and Stoermer (1971). In fact, Si:TN and Si:TP molar ratios indicated abundant DSi availability relative to both N and P even though non-siliceous phytoplankton taxa dominated the community throughout most of the monitoring period. Our monthly sampling frequency was likely not of fine enough resolution to capture the minimum DSi concentration at the peak of the diatom bloom; however, there was a clear decline in diatom biovolume after DSi concentrations decreased, and a large increase in diatom productivity once DSi concentrations rose above 8 mg SiO_2 L^{-1} (Figure 7). This study is a clear example of annual Si utilization by diatoms, but quantitative studies of nutrient limitation are necessary to determine how N and P availability affect Si uptake and patterns in phytoplankton succession. As we only collected DSi data over the course of one calendar year, we do not have sufficient evidence to determine whether the occasional reduction in DSi concentrations due to diatom growth will cause long-term DSi depletion in Lake Monroe.

Concentrations of DSi explained much of the variation in diatom biovolume; however, nutrient stoichiometry (Supplementary Figure S4), temperature, or photosynthetically active radiation had little explanatory power (Supplementary Figure S5). This suggests DSi concentrations had the strongest control on diatom growth, despite previous work connecting decreasing Si:N and Si:P ratios with increasing occurrences of eutrophication and harmful algal blooms (Officer and Ryther, 1980; Justić et al., 1995; Turner et al., 1998; Teubner and Dokulil, 2002). Reservoirs have been shown to preferentially retain TN and TP over Si thereby increasing the relative Si availability to downstream waters (Maavara et al., 2020b; Maavara et al., 2020a). In other words, while reservoirs can induce DSi depletion and subsequent reductions in riverine DSi flux, in some cases they reduce TN and TP to an even greater extent, thus increasing Si:N and Si:P ratios to those favoring siliceous algal taxa in downstream waters (Humborg et al., 2000; Humborg et al., 2008). Increased DSi loads to the Gulf of Mexico could exacerbate hypoxia as diatom productivity provides much of the organic matter fueling hypoxic zone formation (Turner and Rabalais, 1994; Dortch et al., 2001). However, in human-dominated regions, reservoirs cannot buffer riverine stoichiometry against the ever increasing anthropogenic inputs of N and P relative to Si, which results in a declining trend of Si:N and Si:P in coastal receiving waters (Beusen et al., 2009; Laruelle et al., 2009; Maavara et al., 2014).

Implications and direction for future work

Reservoirs play a vital role in human civilization through flood protection, maintenance of water supplies, support for transportation and navigation, and as a source of renewable power generation (Lehner et al., 2011). At the same time, reservoirs have negative environmental impacts including declines in biodiversity, contributing significant quantities of greenhouse gas emissions to the atmosphere, and altering biogeochemical processing along the river continuum (Deemer et al., 2016; Grill et al., 2019; Maavara et al., 2020b). Empirical studies of N, P, and Si retention in reservoirs are lacking in published literature, limiting our ability to accurately model changes in nutrient delivery to coastal systems (Maavara et al., 2014; 2015b; Akbarzadeh et al., 2019). As dam construction continues to impede free-flowing rivers, an improved understanding of biogeochemical nutrient cycling is necessary for accurate environmental assessments and water quality projections (Friedl and Wüest, 2002; Maranger et al., 2018).

Our study is the first report of DSi dynamics in Lake Monroe and provides further evidence of DSi retention in reservoirs. Recent reviews of the global retention of DSi through reservoirs highlight the significant fraction of DSi sequestered in lentic systems which represents an important component of the global biogeochemical cycle of Si (Harrison et al., 2012; Frings et al., 2014; Maavara et al., 2014). Our results align with previous research that shows reservoirs can be significant sinks of DSi, with diatom-mediated uptake and sediment burial acting as dominant retention mechanisms, underscoring the importance of including reservoirs, across a wide range in water residence time, in regional and global Si budgets. Longer term analyses of DSi retention within Lake Monroe and other similar reservoirs would allow for better characterization of DSi dynamics under a range of hydrologic conditions and an examination of trends in retention through time, including explicit testing of the silica depletion hypothesis.

Data availability statement

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

Author contributions

LS: Conceptualization, Methodology, Writing – original draft, Investigation, Visualization, Supervision, Writing – review and editing, Formal Analysis. LR: Investigation, Writing – review and editing. SP: Investigation, Writing – review and editing. ZP: Formal Analysis, Writing – review and editing. AP: Writing – review and editing, Formal Analysis. WH: Supervision, Writing – review and editing, Conceptualization. TR: Resources, Writing – original draft, Supervision, Writing – review and editing, Conceptualization.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

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