A Paleolimnological Study of Net Lake and Lac La Belle, Carlton and Pine Counties, Minnesota

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Executive Summary

1) Single sediment cores were recovered from Net Lake and Lac La Belle in Carlton and Pine Counties, Minnesota, on 23 June 2015 and analyzed to reconstruct a historical record of sedimentation and water quality from the early 1800s to present for each lake. Management concerns for both lakes are centered around nutrient levels near state standards, and sustaining high quality recreational and fishing opportunities in the lake.

2) Sediment cores were subjected to multiple analyses including radio-isotopic dating with ^{210}Pb to establish a date-depth relationship for each core, loss-on-ignition to determine major sediment constituents, biogenic silica to estimate historical diatom (a type of algae) productivity, diatom communities to identify ecological changes and estimate historical water column phosphorus, and extraction and determination of sediment phosphorus fractions.

3) Sedimentation rates in the lake increased following Euro-American settlement in both lakes. In Lac La Belle there was a spike in sedimentation in the 1880s and further increases since the 1950s. Sedimentation rates in Net Lake increased after settlement through the 1950s, dropped until the 1970s, but have increased in recent decades.

4) Loss-on-ignition analysis showed that inorganics are the predominant fraction in sediments of both lakes, and that concentration and flux of inorganics increased following settlement.

5) Biogenic silica concentrations, a marker of diatom algae abundance, are lower in Lac La Belle (4-5% by weight) compared to Net Lake (8-12%). Flux or accumulation of biogenic silica has increased in Lac La Belle since the 1950s and since the 1970s in Net Lake.

6) The amount and distribution of phosphorus fractions differ in the two lakes. We note very low levels of Fe-bound P in Lac La Belle sediments, which likely limit internal loading. In contrast, Net Lake sediments have a phosphorus concentration peak at the top of the sediment column and a significant proportion of Fe-bound P, suggesting that internal loading may be problematic in Net Lake. If bottom waters of Net Lake go anoxic during mid-summer followed by the breakdown of stratification in late summer or early fall there may be increased incidence of noxious cyanobacterial blooms.

7) The diatom communities differ between the two lakes; however, neither lake has shown dramatic change in their diatom communities over the last 150 years. Lac La

Belle has a unique diatom community that is not common in Minnesota lakes that can be described by its indicators of low pH and stained waters including species such as *Aulacoseira perglabra* var. *florinae*, *Stauroforma exiguiformis*, *Asterionella ralfsii*, and *Tabellaria flocculosa* strain IV. Net Lake has a well developed planktonic and tychoplanktonic flora that includes indicators of meso- to eutrophy such as *Aulacoseira ambigua*, *A. granulata*, *A. subarctica*, and *A. pusilla* and a low pH benthic *Eunotia* flora. Community change was assessed using multivariate ordination and constrained cluster analysis. The diatom community in Lac La Belle showed the largest change between 1901 and 1918. The greatest turnover in the diatom community in Net Lake occurred during the late 1950s to 1970s when several eutrophic indicator species increased in abundance.

8) Quantitative estimates of historical TP concentration were generated by applying inference models to downcore diatom communities in each lake based on a training set that relates TP levels to modern diatom communities in 89 Minnesota lakes. In Lac La Belle, the unique diatom community had few analogues in the modern diatom training set and showed little change in historical TP levels, perhaps because of this, the model severely underestimated modern TP values (Diatom-Inferred TP = 15 ppb) that have been monitored at 60 ppb TP. The historical TP reconstructions were more robust in Net Lake due to better analog matching in the calibration set and showed that modern TP values in the 40 ppb range have been common in the lake since the 1970s. Higher modern TP in Net Lake contrasted with lower TP values of 26-36 ppb TP that were present from presettlement through the 1950s.

9) Management recommendations based on these paleolimnological results are as follows. For Lac La Belle, paleolimnological evidence suggests that there has been little change in the diatom flora in the last 150 years; there is no evidence of diatom indicators of eutrophy, and what change has occurred in the diatom flora is not strongly related to phosphorus. There is little geochemical evidence to suggest that internal loading of P has increased (no upcore increase in iron-bound P or peak in concentration of TP near the surface). While the diatom model does not perform well in Lac La Belle, evidence suggests that the high levels of TP (monitored values of ca. 60 ppb) are most likely natural and strongly associate with the high DOC of this system. In Net Lake, paleolimnological evidence shows that there has been degradation of water quality since the 1970s that can be associated with increasing nutrient levels. Estimates from TP from pre-settlement through the 1950s suggest that Net Lake has long been a relatively productive system that may not easily be managed to achieve TP levels below 30 ppb. However, the lake does seem sensitive to nutrient additions and continued efforts should be made to control external loading to the lake. Analysis of P fractions in the sediments shows the classic bulge of P at the core top and a significant proportion of Fe-bound P in the sediments, indicating that internal loading may also be a problem in Net Lake with the potential to fuel algal blooms.

10) Other suggestions include additional analysis of fossil pigments in cores to determine whether cyanobacterial blooms are increasing in Net Lake and what types of algae are

contributing to the very high chlorophyll measures in Lac La Belle, an assessment of internal loading potential in each lake, and continued or enhanced monitoring efforts.

Acknowledgements

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Introduction

Within the glaciated regions of the Upper Midwest, lakes feature prominently in the landscape and are a valued resource for lakeshore owners, recreation, fisheries, water management and wildlife. Current and historical land and resource uses around lakes in this region have raised concerns about the state of the lakes and how to best manage them in a future certain to bring change. To effectively develop management plans, knowledge of the natural state of a lake and an understanding of the timing and magnitude of historical ecological changes become critical components. But reliable long-term data sets are generally not available for most regions of the country. Through the use of paleolimnological techniques and quantitative environmental reconstructions, we can estimate past conditions and natural variability, identify timing of ecological changes, and determine rates of change and recovery.

Lac La Belle and Net Lake are located in Carlton and Pine counties. Both lakes are shallow systems with Net Lake reaching approximately 15 feet deep and Lac La Belle at least 16 ft. Net Lake is surrounded by extensive state land holdings and has some development along its north shore. The lake has been dammed at the outlet for at least 50-60 years and is part of the Net River drainage system. Lac La Belle is a shallow, more wetland-like system, with a small area of development on one shoreline. The lake has a long history as a stop with a guesthouse along the route from St. Paul to Duluth that was served by both rail and stagecoach. Concern for the lakes centers on their current condition especially for total phosphorus (TP) levels, because neither lake meets current state standards (30 ppb TP) for shallow lakes in the Northern Lakes and Forest (NLF) ecoregion. Net Lake routinely exceeds 40 ppb TP (long-term average TP 40 ppb, chlorophyll *a* 9 ppb, MPCA 2016a), although there have been no reported algal blooms. Lac La Belle has TP values in excess of 60 ppb and higher long-term average chlorophyll *a* (43 ppb, MPCA 2016b), and similar to Net Lake, has not had any reports of algal blooms. These impairments have led to questions whether the productivity of the lakes have changed over time, what the natural or historical condition of the lakes were, what the current trajectory of each lake is, and how to best set management goals. Knowledge of the natural state of a lake and an understanding of the timing and magnitude of historical ecological changes become critical components for any management and remediation plan.

With any lake management plan it is important to have a basic understanding of natural fluctuations within the system. Long-term water quality data sets, on the order of 30 - 50 years, are typically unavailable for most of the state and country, and Net Lake and Lac La Belle are no exception. The primary aim of this project was to use paleolimnological analysis of dated sediment cores to reconstruct the nutrient and algal history and trends in sedimentation in each lake over the last 150-200 years using multiple lines of evidence including biogeochemistry, sediment accumulation, and diatom remains as biological indicators. Diatoms quite often make up the main types of algae in a lake and therefore changes in diatom community structure are symptomatic of algal changes in response to water quality. Diatoms have been widely used to interpret environmental conditions in lakes (Dixit et al., 1992). Many species are sensitive to specific water conditions and are useful as bioindicators. Over the past 25 years, statistical methods have been developed to estimate quantitative environmental parameters from diatom assemblages (Fritz et al. 1991). These methods are statistically robust and ecologically sound. In the states of Minnesota and Wisconsin, diatom analysis has been used as one line of evidence for developing nutrient criteria (Heiskary and Wilson 2008, Ramstack et al. 2003), lake-specific nutrient standards (Edlund and Ramstack 2007), and prioritizing management actions (Edlund and Ramstack 2006).

In addition, we characterize changes in algal productivity and nutrient availability using geochemical analyses of the cores. Biogenic silica (BSi) is a component of two major algal groups—the diatoms and chrysophytes. The amount of BSi preserved in sediments and its accumulation rate represent a straightforward measure of algal productivity through time that is particularly responsive to nutrient inputs (Edlund et al. 2009). We also characterized the total phosphorus and phosphorus fractions in each core level to understand the historical sources of P to the lake, the distribution of P and P fractions within the cores, and to assess the relative capability (or lack of capability, i.e. internal loading) of the lake to sequester phosphorus in its sediments.

Methods

Lake-Sediment Coring and Analyses

Coring

A single sediment core measuring 1.60 m in length was recovered from the central basin (46.41499° N, 92.45185°W) of Net Lake (Fig. 1). Similarly a single sediment core of 1.80 m in length was recovered from the southern end (46.59975° N, 92.43200°W) of Lac La Belle (Fig. 2). Both cores were collected on 23 June 2015. The Net Lake core was recovered from 4.71 m of water and the Lac La Belle core from 5.01 m of water using a piston corer consisting of a 6.5 cm diameter polycarbonate tube outfitted with a piston and operated with rigid drive rods working from an anchored boat on the lake surface (Wright 1991).

Both cores were transported to shore where the overlying water and sediment interface were stabilized using a gelling agent (Zorbitrol; Tomkins et al. 2008). Cores were next transported back to the laboratory and extruded vertically at 0-2 cm and then in 1-cm increments to 51 cm core depth, and 2-cm increments to 101 cm core depth.

Isotopic Dating and Geochemistry

The sediment cores were analyzed for ^{210}Pb activity to determine age and sediment accumulation rates for the past 150 to 200 years. Pb-210 activity was measured from its daughter product, ^{210}Po, which is considered to be in secular equilibrium with the parent isotope. Aliquots of freeze-dried sediment were spiked with a known quantity of ^{209}Po as an internal yield tracer and the isotopes distilled at 550°C after treatment with concentrated HCl. Polonium isotopes were then directly plated onto silver planchets from a 0.5 N HCl solution. Activity was measured for 1-3 x 10^5 s using an Ortec alpha spectrometry system. Supported ^{210}Pb was estimated by mean activity in the lowest core samples and subtracted from upcore activity to calculate unsupported ^{210}Pb. Core dates and sedimentation rates were calculated using the constant rate of supply (CRS) model (Appleby and Oldfield 1978, Appleby 2001). Dating and sedimentation errors represented first-order propagation of counting uncertainty (Binford 1990).

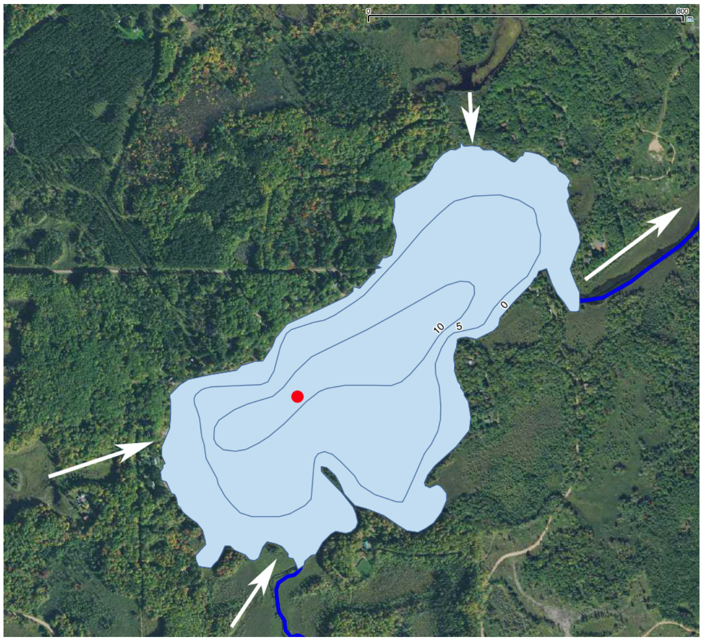


Figure 1. Net Lake, Pine and Carlton Counties, Minnesota. Coring site (red circle) and lake inflows and outflows (arrows) indicated, bathymetry in feet.

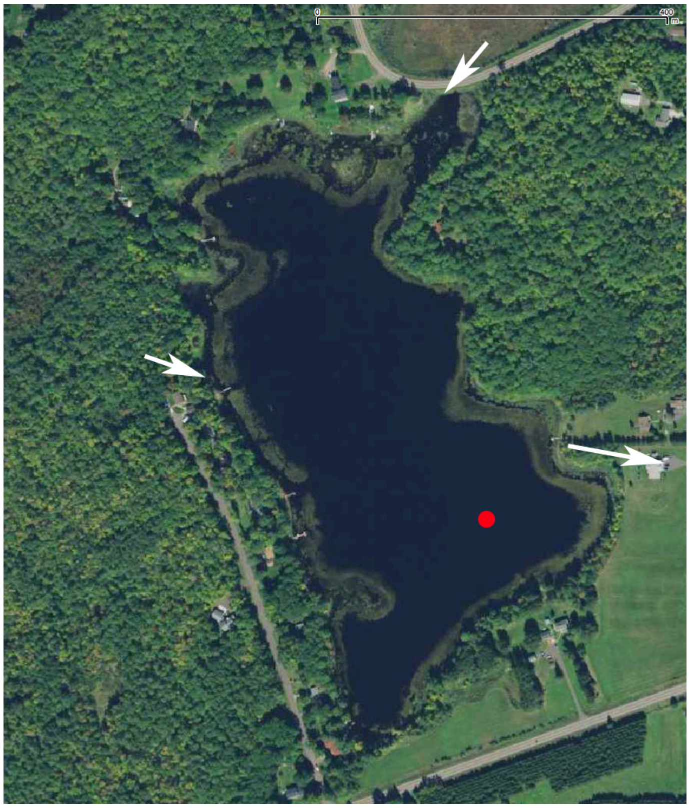


Figure 2. Lac La Belle, Carlton County, Minnesota. Coring site (red circle) and lake inflows and outflows (arrows) indicated.

Bulk-density (dry mass per volume of fresh sediment), water content, organic content, and carbonate content of sediments were determined by standard loss-on-ignition techniques (Dean 1974). Weighed sediment subsamples were dried at 105°C for 24 hr to determine water content and dry bulk density, then heated at 550°C and 1000°C to calculate organic and carbonate content from post-ignition weight loss, respectively. These data were used in combination with ^{210}Pb dating to calculate sedimentation rates as dry mass accumulation rates (DMAR; g cm^{-2} yr^{-1}) for each core and its sediment constituents.

Biogenic silica (BSi), a proxy for historical diatom and chrysophyte algal productivity, was measured using weighed subsamples (30 mg) from the cores, which were digested for BSi analysis using 40 ml of 1% (w/v) Na_2CO_3 solution heated at 85°C in a reciprocating water bath for five hours (DeMaster 1979, Conley and Schelske 2001). A 0.5 g aliquot of supernatant was removed from each sample at 3, 4, and 5 hr. After cooling and neutralization with 4.5 g of 0.021N HCl solution, dissolved silica was measured colorimetrically on a Unity Scientific SmartChem 170 discrete analyzer as molybdate reactive silica (SmartChem 2012a).

Sediment phosphorus fractions were analyzed following the sequential extraction procedures in Engstrom (2005), Engstrom and Wright (1984), Psenner and Puckso (2008, and Kopácek et al. (2005). Extracts were analyzed colorimetrically on a Unity Scientific SmartChem 170 discrete analyzer using methods described by SmartChem (2012b). Measured sediment P concentrations were also converted to flux using bulk sedimentation rates in each core. In addition to total phosphorus in cores, sediment fractions include the refractory forms *Mineral-bound P*, *Recalcitrant Organic-P*, *Al-bound P* and the labile or readily exchangeable forms of *Fe-bound*, *labile Organic-P*, and *loosely-bound P*.

Diatom Analysis

Diatoms were used in this study to provide a timeline of changes in the algal communities and estimates of historical water column total phosphorus concentrations from each lake. In short the analytical steps are as follows. Diatoms and chrysophyte cysts were prepared by placing approximately 50 mg freeze dried core material in a 50 cm^3 polycarbonate centrifuge tube and adding 2-5 drops of 10% v/v HCl solution to dissolve carbonates. Organic material was subsequently oxidized by adding 10 ml of 30% H_2O_2 and heating for 3 hr in an 85°C water bath. After cooling, the samples were centrifuged and rinsed 4-6 times with deionized water to remove oxidation byproducts. Material was then transferred to 22×22 mm #1 coverglasses. Coverglasses were permanently attached to microscope slides using Zrax mounting medium (Ramstack et al. 2008). Diatoms were identified along measured random transects to the lowest taxonomic level under 1000-1250× magnification (full immersion optics of NA > 1.3). A minimum of 400 valves was counted in each sample. Identification of diatoms relied on available floras and monographs including Hustedt (1927-1966, 1930), Patrick and Reimer (1966, 1975), Krammer and Lange-Bertalot (1986-1991), Reavie and Smol (1998), Camburn and Charles (2000), Fallu et al. (2000), and Spaulding et al. (2010). All diatom counts were converted to percentage abundances by species or taxon; abundances are reported relative to total diatom counts in each sample.

A stratigraphy of predominant diatoms (species with greater than or equal to 5% relative abundance in one or more core depths) was plotted against core date. Relationships among diatom communities within the sediment core were explored using constrained cluster analysis (CONISS) and the unconstrained ordination method of Detrended Correspondence Analysis (DCA), in the software package R (R Core Team 2014). Core depths/dates were plotted in ordinate space and their relationships and variability used to identify periods of change, sample groups, and ecological variability among core samples. A general rule for interpreting a DCA is that samples that plot closer to one another have more similar diatom assemblages.

Downcore diatom communities were also used to reconstruct historical epilimnetic phosphorus levels. A transfer function for reconstructing historical $\log_{10}$TP (hereafter logTP) was developed earlier based on the relationship between modern diatom communities and modern environmental variables in 89 Minnesota lakes (Ramstack et al. 2003, Edlund and Ramstack 2006) using weighted averaging (WA) regression with inverse de-shrinking and bootstrap error estimation (C2 software; Juggins 2003). The strength of the transfer function was evaluated by calculating the squared correlation coefficient (r^2=0.83) and the root mean square error (RMSE=0.181) between the observed logTP with the model estimates of logTP for all samples. Bootstrapping was used in model validation to provide a more realistic error estimate (RMSEP, the root mean square error of prediction=0.209 logTP units) because the same data are used to both generate and test the WA model (Fritz et al. 1991). Reconstructed estimates of logTP (diatom-inferred TP, or DI-TP) for each downcore sample were determined by taking the logTP optimum of each species, weighting it by its abundance in that sample, and determining the average of the combined weighted species optima. Data are presented as both logTP values and as back-transformed values, to TP in µg/l or ppb.

Results and Discussion

Pb-210 inventory

Lac La Belle—Lac La Belle sediments showed a decline in ^{210}Pb inventories to an initial minimum at 44 cm and supported levels around 72 cm (Fig. 3); the initial minimum in ^{210}Pb is uncommon in cores and indicates significant changes in sediment source to the lake. Using the CRS model, a date-core depth relationship was established for the core. In Lac La Belle, sediments dated before the 1860s were found below 57 cm, 1900 around 38 cm, 1950 at 31 cm, and 2000 at 9 cm depth. We note that the odd decline in ^{210}Pb inventory corresponds to the 1880s when farming began in the area (Sheetz and Wisuri 2007).

Net Lake—The Net Lake core showed a more typical monotonic exponential decline in ^{210}Pb inventories to supported depths (Fig. 3); the core reached supported levels of ^{210}Pb at 24 cm depth. Using the CRS model, a date-core depth relationship was established for the core. In Net Lake, sediments dated before the 1860s were found below 23 cm, 1900 around 18 cm, 1950 at 12 cm, and 2000 at 3 cm depth.

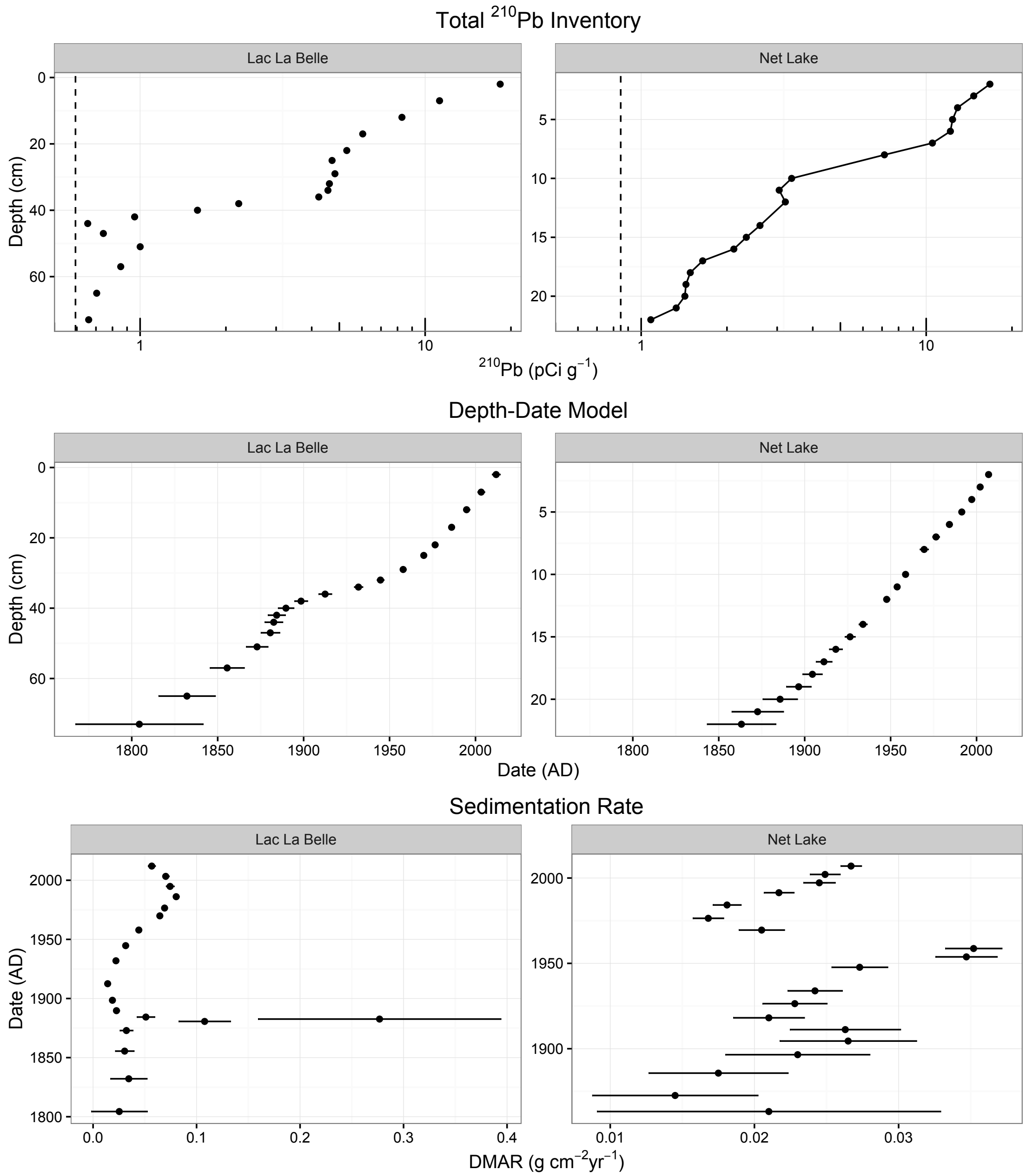


Figure 3. Inventory of 210-Pb by depth (cm), date-depth (cm) model, and bulk sedimentation rates (dry mass accumulation rates, DMAR, g/cm^2 yr) by date (AD) for Net Lake and Lac La Belle. Dashed line in 210-Pb inventory is supported level of 210-Pb. Horizontal bars represent standard error estimates.

Sedimentation rates

Lac La Belle—Sedimentation rates in Lac La Belle were relatively constant from pre-settlement through the 1940s except for a dramatic spike in sedimentation in the 1880s (Fig 3). Historical increases in sedimentation are common in midwestern lakes following logging and land clearance for agriculture, which may have been the primary factor that caused the sedimentation spike as land use changed around Lac La Belle in the 1880s (Sheetz and Wisuri 2007). Sedimentation rates increased again after the 1940s in Lac La Belle from 0.03 g/cm^2 yr to recent rates of 0.06-0.08 g/cm^2 yr from the 1980s to present, suggesting that modern sedimentation rate in Lac La Belle are at least 2-fold greater than pre-1950 rates.

Net Lake—Net Lake has one of the lowest linear sedimentation rates we have encountered in Minnesota lakes with only 23 cm (about 9 inches of sediment!) accumulated since 1850 (Fig 3). The Net Lake core showed a general trend toward increasing sedimentation rates from European settlement until the 1950s, a decline to the 1980s, and then increased sedimentation in recent decades (Fig. 2). Modern rates are approximately 1.6-fold greater than pre-1890 rates (Fig. 2). Pre-settlement sedimentation rates in Net Lake were approximately 0.016 g/cm^2 yr compared to sedimentation rates since the 1980s of 0.025 g/cm^2 yr.

Loss-on-ignition

Lac La Belle—Sediment in Lac La Belle is dominated by the inorganic or mineral fraction, which generally composed between 50 and 70% of the dry sediment weight (Fig. 4), with increased abundance of inorganics after the 1880s, and near constant levels above 36 cm (ca. 1912). Organic matter comprised the next predominant sediment constituent with the Lac La Belle core having 25 to 48% organics by dry weight with the lower measures above 35 cm depth (ca. 1912) as organics were diluted by mineral erosion. Carbonates made up approximately 3.5% dry weight of the Lac La Belle core, with little fluctuation in the top meter of core material. Sediment constituents were also converted to accumulation (DMAR) or flux rates. All constituents showed the most dramatic increase in accumulation rates after in the 1880s, but have secondarily increased in accumulation since the 1950s with slight decreases in DMAR since the 1980s.

Net Lake—Similar to Lac La Belle, the inorganic or mineral component dominates the sediment in Net Lake with between 60 and 69% by dry weight with highest amounts in the 1950s (Fig. 4). Organic matter is the next most common constituent of Net Lake sediments with between 29 and 35% in the top meter of core. There is a slight increase in organic percent since the 1950s (~10 cm). Carbonates remain low and constant in the Net Lake core. Dry mass accumulation of sediment constituents track sedimentation rate changes in Net Lake, with peaks in accumulation of inorganics and organics from settlement to the 1950s, a decrease through the 1970s, and then recent increases since the 1980s.

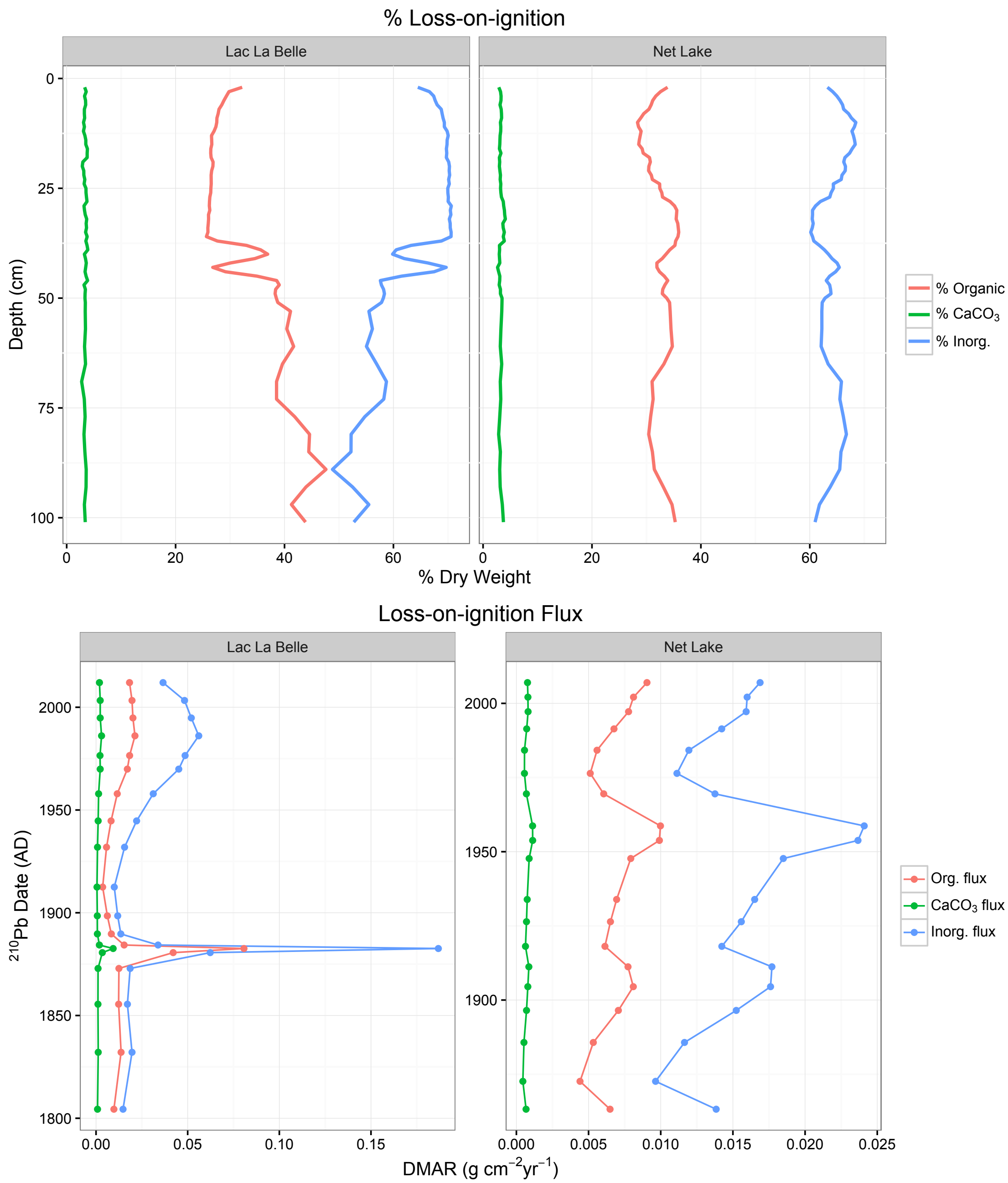


Figure 4. Sediment constituents in Net Lake and Lac La Belle cores based on loss-on-ignition analysis. Top panels show fractions of inorganics, organics, and carbonates ($CaCO_3$) by dry weight percent; lower panels show flux or dry mass accumulation rates (DMAR; g/cm^2 yr) of the same constituents.

Biogenic silica (BSi)

Lac La Belle—Biogenic silica composed 4-5.5% of the dry weight of Lac La Belle sediment, with lowest values in the core bottom during the sedimentation spike in the 1880s and several periods between 1960-2000. Highest values of BSi were in the late

1800s (Fig. 5). When converted to accumulation rates, the flux of BSi increases toward the top of the Lac La Belle core (post-1950s) and remained constant since the 1970s. Modern accumulation of biogenic silica is approximately two times greater than in pre-Euro-American settlement times.

Net Lake—Biogenic silica content of Net Lake core material varies from 8 to 12% by dry weight. The lowest BSi concentrations are found in the 1950s (10 cm) with two peaks in BSi concentrations in the early 1900s and at the core top. Accumulation rates decreased in the early 1900s through the 1950s before rising from the 1970s to present (Fig. 5).

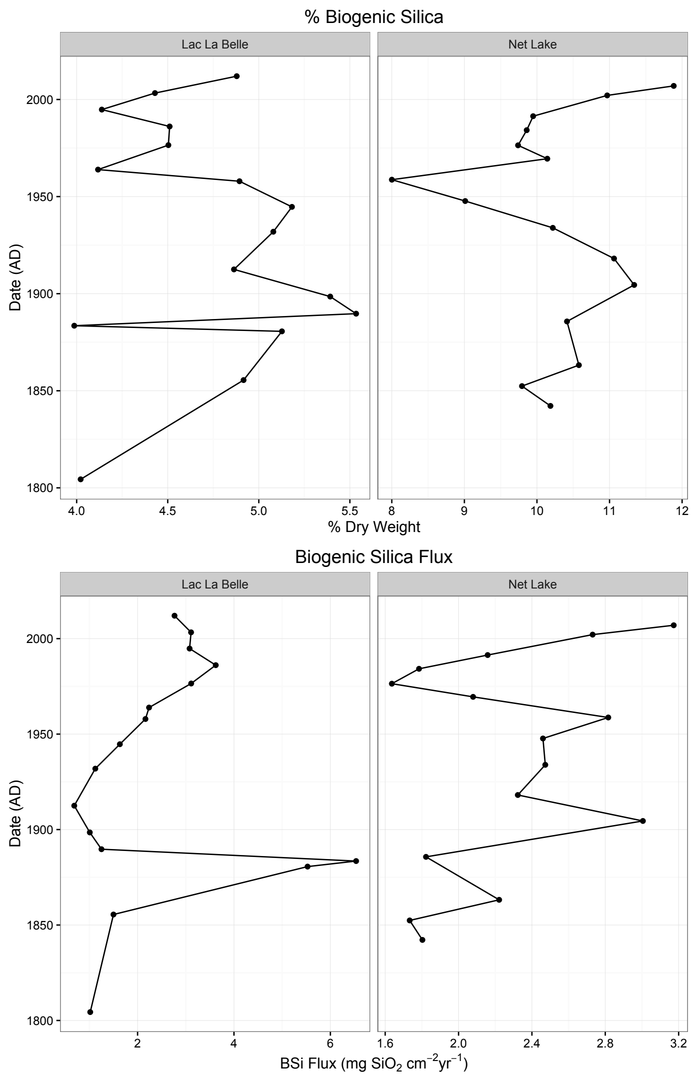


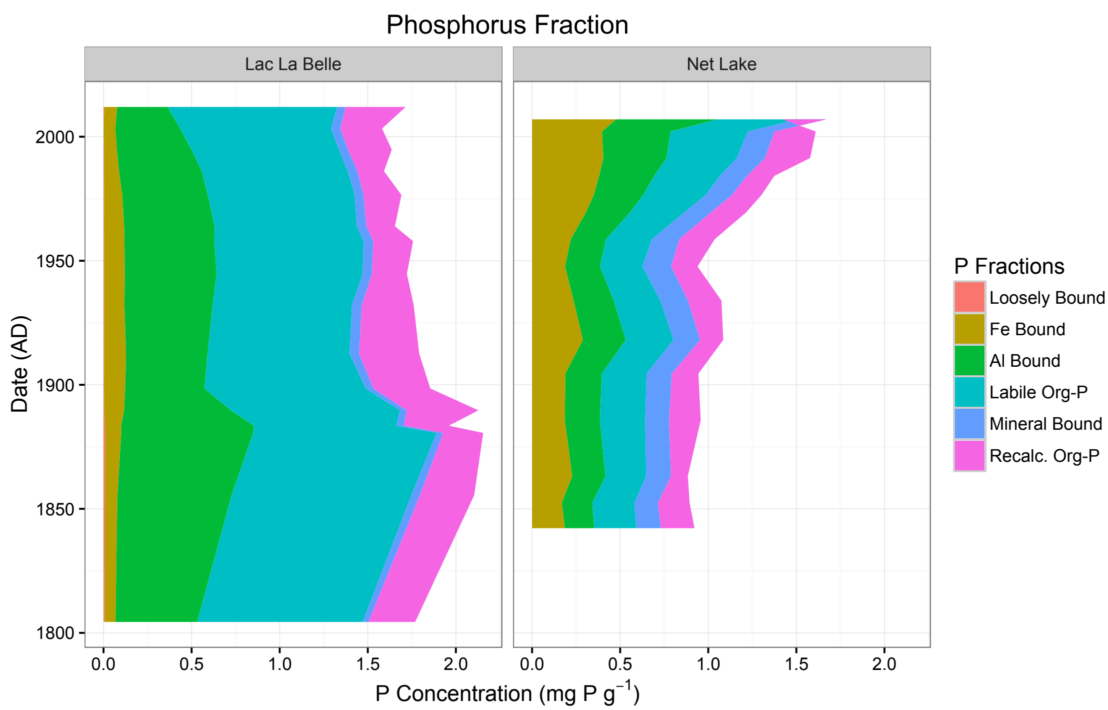
Figure 5. Biogenic silica content (top panels, percent dry weight) and accumulation rate (bottom panels, mg/cm² yr) for Lac La Belle and Net Lake.

Sediment phosphorus fractions

Lac La Belle—Total phosphorus in Lac La Belle sediment ranged from 1.6 to nearly 2.2 mg P/g with decreasing concentrations upcore (Fig. 6a). The labile organic-P and Al-bound fractions made up the largest proportion of P fractions throughout the entire core length that was analyzed. Notable in the Lac La Belle record is the very low levels of Fe-bound P, which is the fraction that is primarily responsible for internal P loading.

Accumulation rates of P fraction show two major patterns (Fig. 6a). First, the 1880s spike in sedimentation represents a singular event in the lake's history as sedimentation rates and P fraction fluxes return to presettlement rates after this large erosional event. Second, there is a slight increase in P accumulation especially since the 1950s that is mostly attributable to Al-bound P and labile Organic-P, signaling increased erosion of mineral matter to the lake and some additional organic accumulation. The Al-bound P fraction is not active in internal loading processes in lakes, which bodes well for Lac La Belle.

Net Lake—Concentrations of P fractions in Net Lake sediments are relatively constant from the 1850s to the 1950s (total P is about 1.0 mg P/g), but then three constituents increase dramatically upcore—the Fe-bound, the Al-bound, and the labile Organic P fractions (Fig. 6b). In contrast to Lac La Belle, the Fe-bound fraction is much greater in Net Lake and the upcore increase in concentration suggests that internal loading of P is a larger concern in Net Lake.



Phosphorus Fraction Flux

Figure 6a. Sediment phosphorus fractions in Lac La Belle and Net Lake cores including Loosely Bound P, Fe-Bound P, Al-Bound P, Labile Organic P, Mineral-Bound P, and Recalcitrant Organic P. The sum of these fraction equals sediment total phosphorus. P fraction data shown as concentration (mg P/g sediment) by core date.

Accumulation of P in Net Lake shows two periods of change. First, there is an increase in P accumulation from pre-settlement to a peak in the 1950s (Fig. 6b). Flux of P fractions falls after the 1950s through the 1970s, before increasing to the highest levels in the surface sediments. The upcore peak contains a significant amount of Fe-bound P that may serve to facilitate internal loading of P to Net Lake. This pool of P is important in lakes that have anoxic bottom waters in mid-summer which release labile P to fuel late summer and fall cyanobacteria blooms following mixing events.

Figure 6b. Flux or accumulation of sediment phosphorus fractions in Lac La Belle and Net Lake cores including Loosely Bound P, Fe-Bound P, Al-Bound P, Labile Organic P, Mineral-Bound P, and Recalcitrant Organic P. The sum of these fractional fluxes equals sediment total phosphorus flux. P fraction flux data shown as accumulation rate (mg P/cm^2 yr) of each P fraction by core date.

Diatom communities and TP reconstructions

Lac La Belle—Over 140 diatom species were present in the samples analyzed from the Lac La Belle core. The diatom flora is best described as an acidophilic flora that would characterize Lac La Belle as a low pH and DOC stained system. The most common species were species that are not common in Minnesota lakes including the planktonic and tychoplanktonic forms *Aulacoseira perglabra* var. *florinae*, *Stauroforma exiguiformis*, *Asterionella ralfsii*, and *Tabellaria flocculosa* strain IV. Benthic forms included the widespread species *Staurosira venter* and *Sellaphora pupula*, but also many uncommon species only found in low pH lakes such as *Navicula modica*, *Pinnularia* *biceps* var. *pusilla*, and *Chamaepinnularia mediocris*. All levels of the core except the lowest level analyzed had less than 50% of the diatoms representing planktonic forms, which is attributable to the shallow nature of Lac La Belle.

To determine how the diatom communities in each level of the core were related to one another, several analyses were run to develop stratigraphic groupings within the core. We first show an ordination bi-plot from detrended correspondence analysis (DCA) that shows how the core samples cluster based on similarity of diatom assemblage (Fig. 7). We note that the amount of change in the diatom community in Lac La Belle from the 1800s to modern times is relatively small. We also ran a constrained cluster analysis (Fig. 8) that confirmed the DCA results; significance of the clusters was assessed against a random broken stick model (Bennett 1996), which suggests that the only significant break among diatom assemblages occurs between the 1901 and 1918 samples. The diatom community shows most of its change from the 1901 and 1918 along Axis 1 of the DCA plot; change over the last two decades is largely along Axis 2, suggesting that the lake may be experiencing multiple stressors over the past few decades.

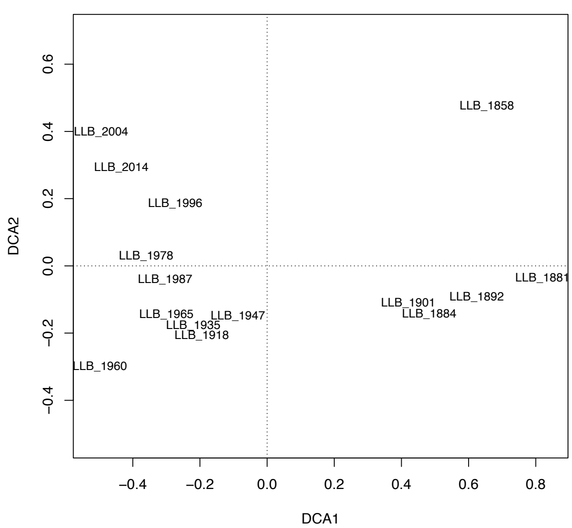


Figure 7. Detrended Correspondence Analysis (DCA) of diatom communities (by dated core level) from Lac La Belle sediment core. In general, core levels that plot closer to each other are more similar.

A stratigraphic diagram shows the changes in abundance of predominant diatoms (greater than 5% relative abundance) throughout the core (Fig. 9). The major shift in diatoms between 1901 and 1918 involves a decrease in abundance of the tychoplanktonic form *Aulacoseira perglabra* var. *florinae* and the benthic taxa *Navicula modica* and *Pinnularia biceps* var. *pusilla*, coupled with an increase in the abundance of the planktonic *Stauroforma exiguiformis* and the ubiquitous benthic *Staurosira venter*. There is a final increase near the core top in the last two samples of the low pH indicator and planktonic form *Asterionella ralfsii*.

The diatom communities were also used to reconstruct historical TP levels for Lac La Belle. Many factors can contribute to changes in diatom communities (pH, light penetration, and habitat availability), and in order for a diatom-inferred total phosphorus

(TP) reconstruction to be meaningful, changes in the diatom community assemblage over time should be primarily driven by changes in TP concentrations. One way to evaluate TP as a driver of change in Lac La Belle is to project the core sections on the MN calibration set that we used to reconstruct TP to determine if changes in the diatom assemblage in the core correlate with the TP gradient in the model (Juggins et al. 2013). This analysis results in a cloud of data points for the Lac La Belle core, with no strong directional change (Fig. 10). The lack of correlation with Axis 1 or log TP suggests that nutrients are not the primary driver of the changes seen in the diatom community for the majority of the record. Alternative drivers include: habitat alterations, changes in turbidity due to sediment load, pH, nitrogen, climate drivers, or other stressors that were not directly measured in the calibration set. It is possible that the drivers of ecological shifts change over time, meaning that TP is an important variable during certain time periods.

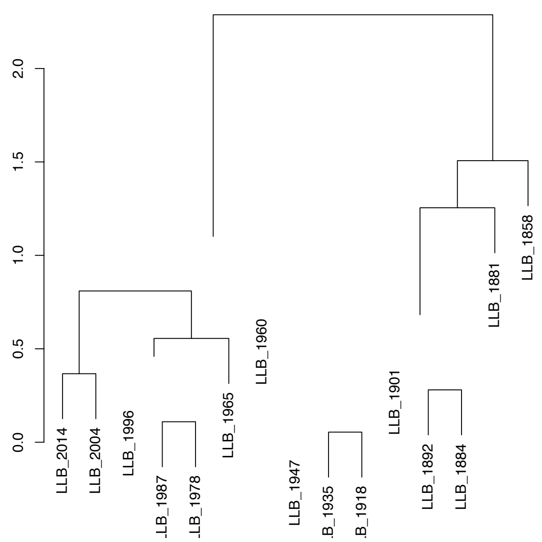


Figure 8. Constrained Cluster Analysis of diatom communities (by dated core level) from Lac La Belle sediment core based on Euclidean distance. Only the two primary core groups are significant.

Another way to evaluate the strength of a TP reconstruction is to determine the amount of variance in the diatom data that can be accounted for by the TP reconstruction. This can be calculated by the variance explained by the first axis of an ordination of the sediment assemblages constrained to diatom-inferred TP, divided by the variation explained by an unconstrained ordination of the sediment assemblages (known as the λ_r/λ_p score; Juggins et al. 2013). In Lac La Belle, this analysis shows that the fraction of the maximum explainable variation in the diatom data that can be explained by TP is relatively low (39%). The low score from this analysis, coupled with the lack of correlation with the logTP axis in the passive plot, suggests that TP has not always been the significant driver of diatom community change in this lake and therefore the TP reconstruction should be interpreted with caution. Last we considered that the diatom flora of Lac La Belle is not commonly seen in Minnesota lakes and note that only 3-8 species of diatom are informing the TP reconstruction for Lac La Belle depending on core depth, i.e. this unique flora is not represented in the phosphorus model that has been used to develop nutrient criteria for Minnesota lakes (Ramstack et al. 2003, Heiskary and Wilson 2008).

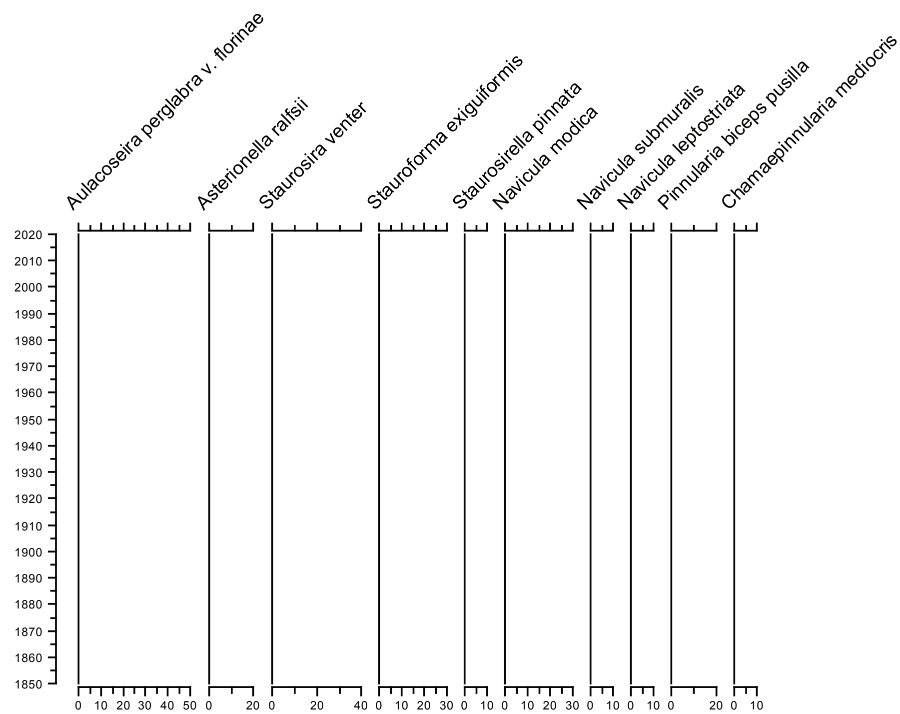


Figure 9. Downcore distribution of predominant diatoms in the Lac La Belle sediment core. Species shown were present in one or more core levels at greater than 5% abundance.

Given those caveats, the TP reconstruction from Lac La Belle suggests that there has been little change in TP concentrations in the last 150 years, and that TP has remained around 15 ppb. Two observations can be made from these results. First, given the minimal change in the diatom community over time and the lack of species that commonly respond to nutrient enrichment, there is reason to believe that TP levels in Lac La Belle have not changed significantly. Second, we know that the diatom model has severely underestimated TP levels in Lac La Belle. Modern monitoring data suggest that TP levels are above state nutrient criteria of 30 ppb, and are commonly measured as high as 60 ppb in Lac La Belle (MPCA 2016b). Because the diatom community of Lac La Belle does not have an analog in the calibration set, we have to be very cautious in over-interpreting the diatom-TP reconstruction for Lac La Belle.

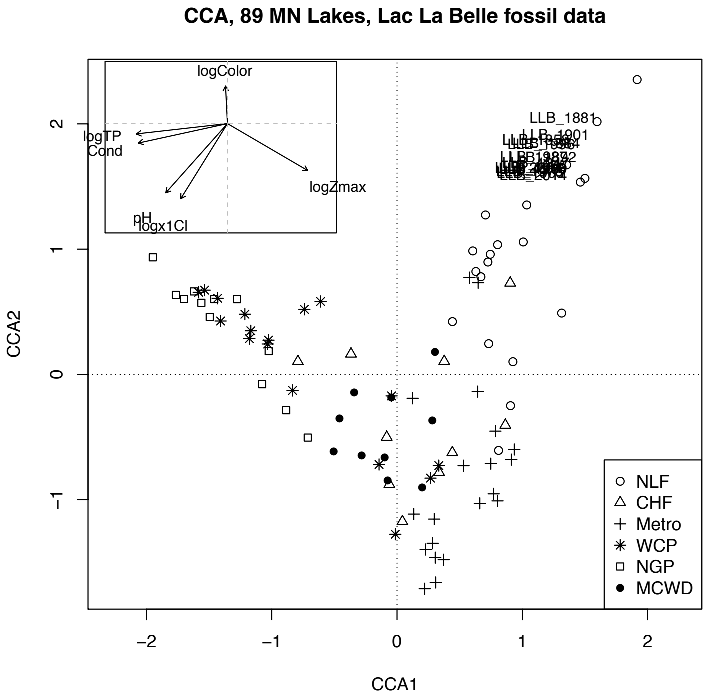


Figure 10. Diatom communities in dated Lac La Belle core sections passively plotted onto the calibration set of 89 Minnesota lakes. The inset shows the strength and direction of environmental gradients that significantly explain diatom abundance in the calibration set lakes. If the historical diatom communities in Lac La Belle were responding solely to changes in TP, we would expect them to be aligned with the logTP axis (see text).

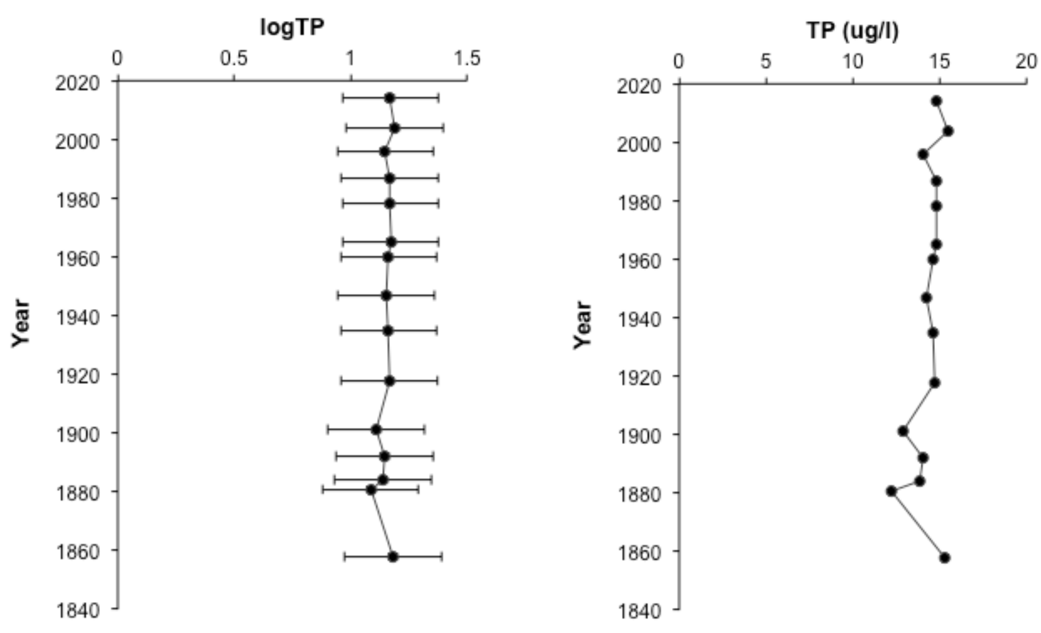


Figure 11. Historical diatom-inferred TP levels for Lac La Belle. Model reconstructions (left panel) are in log TP units and error bars represent the root mean square error of prediction or the model error estimates of 0.209 logTP units (RMSEP). The back transformed diatom-inferred TP levels are given in the right panel in the more commonly reported units of µg/l or ppb. See text for discussion of validity of this reconstruction.

Net Lake—Over 175 diatom species were identified in the sediment core from Net Lake. The dominant forms in the core were the meso- to eutrophic *Aulacoseira* species including *A. ambigua*, *A. granulata*, *A. subarctica*, and *A. pusilla* that thrive in regularly mixed lakes, planktonic araphid taxa including fragilarioids (*Pseudostaurosira brevistriata*, *Fragilaria vaucheriae*, *F. crotonensis*), a diverse *Tabellaria* flora (*T. flocculosa* III, IV, and *T. fenestrata*), the low pH *Fragilariforma virescens*, and other plankters such as *Asterionella formosa* and *Discostella stelligera*. Among the common benthic or attached diatom species were species often associated with low pH and stained lakes such as *Eunotia* species.

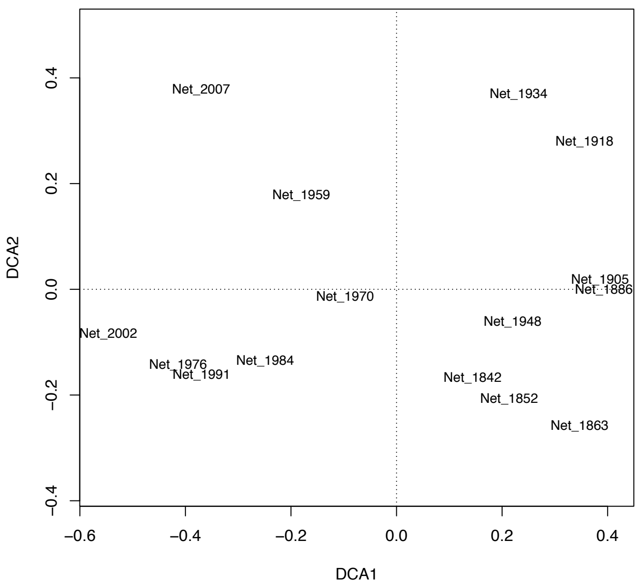


Figure 12. Detrended Correspondence Analysis (DCA) of diatom communities (by dated core level) from the Net Lake sediment core. In general, core levels that plot closer to each other are more similar.

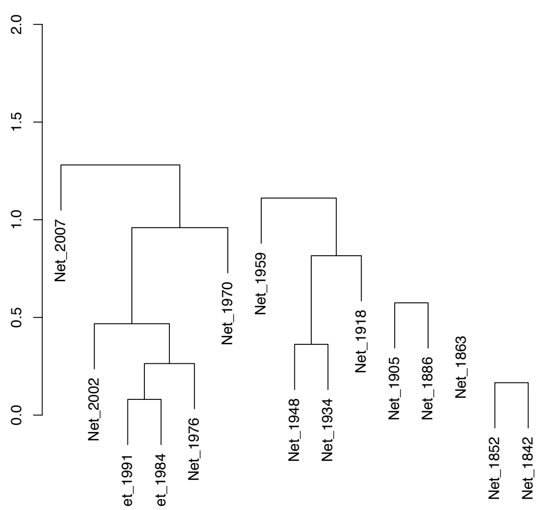


Figure 13. Constrained Cluster Analysis of diatom communities (by dated core level) from the Net Lake sediment core based on Euclidean distance. No sample groups are significant based on the broken stick model.

Similar to Lac La Belle, the diatom communities in the Net Lake sediment core were explored with Detrended Correspondence Analysis (DCA) and a constrained cluster analysis to identify stratigraphic zones, plotted stratigraphically and passively on the Minnesota diatom calibration set to identify community changes and the likelihood that those changes were attributable to changes in the lake's phosphorus dynamics, and lastly the Minnesota diatom calibration set was applied to the diatom communities to estimate historical levels of TP in Net Lake.

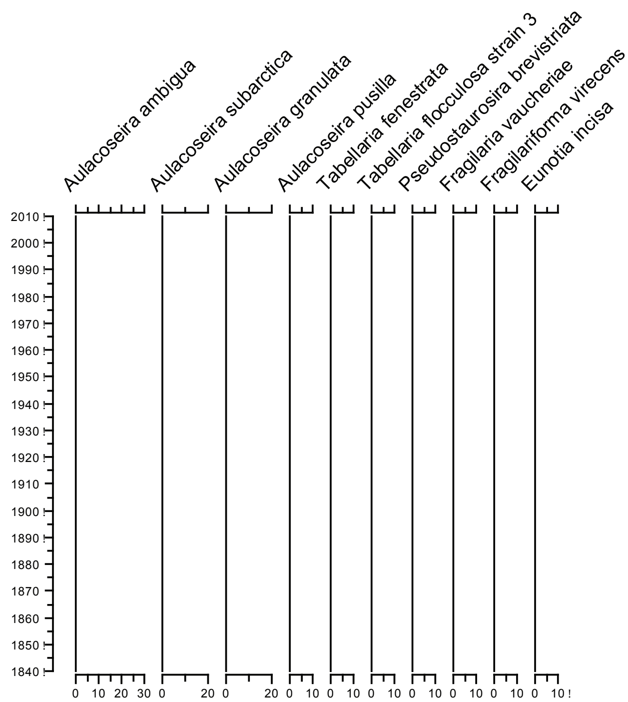


Figure 14. Downcore distribution of predominant diatom in the Net Lake sediment core. Species shown were present in one or more core levels at greater than 5% abundance.

The DCA (Fig. 12) shows how the core samples cluster based on similarity of diatom assemblage. Similar to Lac La Belle, the short gradients in the DCA indicate that the diatom community in Net Lake has not changed dramatically in the last 150 years. The constrained cluster analysis shows a primary break in the diatom assemblages between 1959 and 1970 (Fig. 13), although tests using the broken stick model do not identify any clusters of samples in the Net Lake core as significant. The shift in assemblage between 1959 and 1970 is primarily characterized by an increased upcore abundance of the mesotrophic indicator *Aulacoseira ambigua* and the eutrophic indicator *A. granulata*, simultaneous with a decreased abundance of the mesotrophic form *A. subarctica* (Fig. 14).

The passive plot of Net Lake samples on the 89 MN lakes calibration set shows that the chronological sequence of samples moves negative on both the CCA axes 1 and 2 (Fig. 15). Importantly this direction of change in the core is aligned in part with the TP axis of variation among Minnesota lakes. Along with a high λ_r/λ_p score of 0.8257 for Net Lake, this evidence strongly indicates that changes in the diatom community of Net Lake are related to changes in TP.

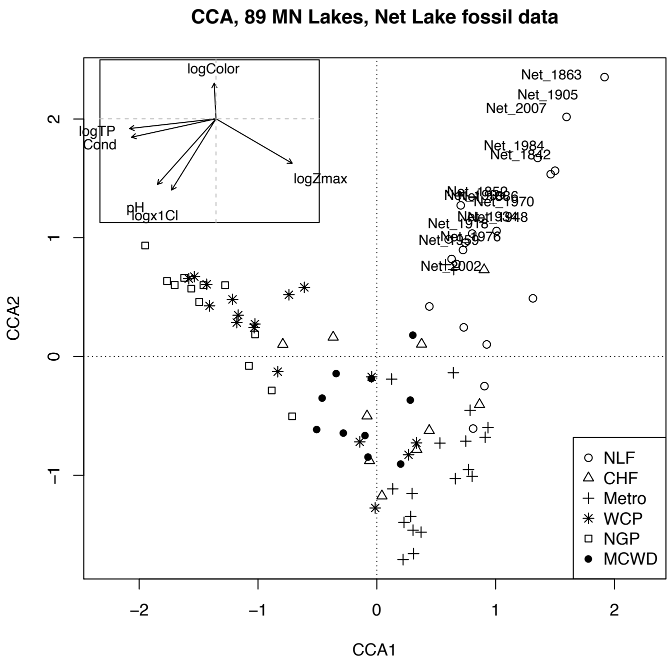


Figure 15. Diatom communities in dated Net Lake core sections passively plotted onto the calibration set of 89 Minnesota lakes. The inset shows the strength and direction of environmental gradients that significantly explain diatom abundance in the calibration set lakes. The historical diatom communities in Net Lake are aligned with the logTP axis, which suggests they have responded strongly to historical changes in TP, (see text).

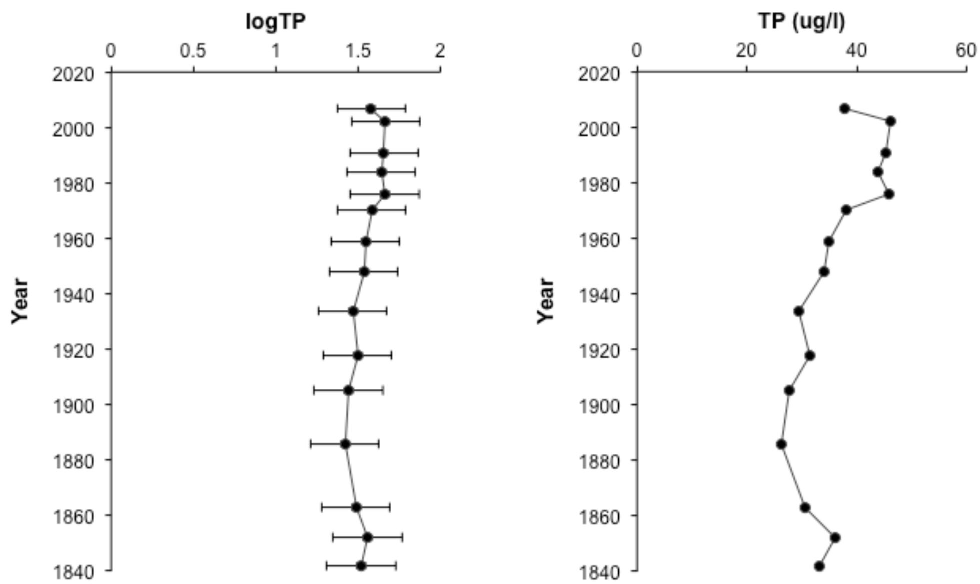


Figure 16. Historical diatom-inferred TP levels for Net Lake. Model reconstructions (left panel) are in log TP units and error bars represent the root mean square error of prediction or the model error estimates of 0.209 logTP units (RMSEP). The back transformed diatom-inferred TP levels are given in the right panel in the more commonly reported units of µg/l or ppb.

Diatom-inferred estimates of historical TP in Net Lake show that from pre-settlement through the 1950s, TP levels in the lake varied from 26-36 ppb TP (Fig. 16). Since the

1970s, TP levels have been higher and reconstruct at levels around 45 ppb TP. The top-most sample in the core (0-2 cm, ca. 2015-2007) reconstructed slightly lower at 38 ppb TP. Reconstructed values since the 1970s are very close to monitored values for Net Lake where the long-term average TP is about 40 ppb (MPCA 2016a).

Summary and Recommendations

The dated sections of the Lac La Belle and Net Lake sediment cores provided a nearly 200-year record of sedimentation, geochemistry, and diatom algae communities in each lake. Both lakes are characterized by sediments that are low in carbonates and dominated by inorganics. The lakes have their first evidence of change at the time of Euro-American settlement in the late 1800s. Inorganic constituents show the most dramatic increase in accumulation likely reflecting changes in sediment loading following logging, land clearance, and development of the shoreline. Sedimentation rates in Net Lake begin to increase at settlement and peak in the 1950s. Sedimentation rates dropped from the 1950s through the 1970s in Net Lake, but have increased in more recent times. In Lac La Belle, a large erosional event is recorded in the 1880s that may be associated with initial land clearance and conversion to agriculture. Sedimentation returned to presettlement rates but has increased somewhat since the 1950s.

Additional geochemical indicators that were measured in the two lakes included biogenic silica, a measure of productivity by the algal groups diatoms and chrysophytes, and phosphorus fractions. Net Lake has approximately two times more biogenic silica in its sediments (4-5% by weight in Lac La Belle vs 8-12% by weight in Net Lake). Flux or accumulation of biogenic silica has increased in Lac La Belle since the 1950s and since the 1970s in Net Lake. Phosphorus fractions in the two lakes are very different. We note very low levels of Fe-bound P in Lac La Belle sediments, which likely limit internal loading. In contrast, Net Lake sediments have a phosphorus peak at the top of the sediment column and a significant proportion of Fe-bound P, suggesting that internal loading may be problematic in Net Lake.

The diatom communities are very different between the two lakes; however, neither lake has shown dramatic change in their diatom communities over the last 150 years. In Lac La Belle, the unique diatom community can be described by its indicators of low pH and stained waters including species such as *Aulacoseira perglabra* var. *florinae*, *Stauroforma exiguiformis*, *Asterionella ralfsii*, and *Tabellaria flocculosa* IV. Net Lake has a much more typical planktonic and tychoplanktonic flora that includes indicators of meso- to eutrophy such as *Aulacoseira ambigua*, *A. granulata*, *A. subarctica*, and *A. pusilla* and a low pH benthic *Eunotia* flora. Lac La Belle's diatom community has its greatest change between 1901 and 1918. Net Lake's shift in diatom communities is centered during the late 1950s to 1970s as several eutrophic indicator species increase in abundance.

Quantitative estimates of historical TP concentration were generated by applying inference models to downcore diatom communities in each lake based on a training set that relates TP levels to modern diatom communities in 89 Minnesota lakes. In Lac La Belle, the unique diatom community had few analogues in the modern diatom training set and showed little change in historical TP levels, but also severely underestimated modern TP values. In Net Lake, the strenght of the historical TP reconstructions was much greater and showed that modern TP values in the 40 ppb range have been common in the lake since the 1970s, and contrast with lower TP values of 26-36 ppb TP that were present from presettlement through the 1950s.

Management recommendations based on this paleolimnological analysis include:

1. Both lakes do not currently meet state standards for nutrient criteria (30 ppb in NLF lakes; Heiskary and Wilson 2008). For Lac La Belle, paleolimnological evidence suggests that there has been little change in the diatom flora in the last 150 years, there is no evidence of diatom indicators of eutrophy, what change has occurred in the diatom flora is not strongly related to phosphorus, and there is little geochemical evidence to suggest that internal loading of P has increased (no upcore increase in iron-bound P or peak in concentration of P upcore). While the diatom model does not perform well in Lac La Belle, evidence suggests that the high levels of TP (monitored values of ca. 60 ppb) are most likely natural and strongly associate with the high DOC of this system. The high chlorophyll values measured in Lac La Belle have not yet been attributed to nuisance algal blooms; plankton collections made at the time of coring showed that the late June algal community in Lac La Belle was heavily dominated by cryptophytes, a group of algae capable of both autotrophic and heterotrophic metabolism.

2. In Net Lake, paleolimnological evidence shows that there has been degradation of water quality since the 1970s that can be associated with increasing nutrient levels. Diatom-based estimates of TP from pre-settlement through the 1950s suggest that Net Lake has long been a relatively productive system that may not easily be managed to achieve TP levels below 30 ppb. However, the lake does seem sensitive to nutrient additions and efforts should be made to control external loading to the lake. Analysis of P fractions in the sediments shows the classic bulge of P at the core top and a significant proportion of Fe-bound P in the sediments, indicating that internal loading may also be a problem in Net Lake with the potential to fuel algal blooms. Although there have not been widespread reports of cyanobacterial blooms in Net Lake, we noted at the time of coring that there were surface scums of cyanobacteria including *Aphanizomenon*, *Dolichospermum*, and *Anabaena*.

3. There are additional analyses that can be run on sediments. Perhaps the most important question remaining is whether occurrences of cyanobacterial blooms that were visible when we cored have been increasing in Net Lake. All algal groups contain pigments that are preserved in sediment cores in approximate ratios and quantities that reflect their historical abundance in a lake. It would be informative to do an analysis of a sediment core for fossil algal pigments to determine if cyanobacterial blooms are a recent or long-term characteristic of Net Lake's seasonal cycle. A similar approach would be informative in Lac La Belle to ascertain what algal groups are associated with the high water column measures of chlorophyll. For example, with the high levels of DOC in

both of these lakes, understanding the extent of heterotrophic production would be valuable for understanding how these two lakes that seem superficially similar are behaving differently in both their modern and historical records. An assessment of the potential for internal loading from Net Lake sediments may be informative. Last, continued monitoring of these systems through traditional strategies (citizen monitoring, monthly open-water profiles and chemistry by agency personnel) might be coupled with high frequency data collection using buoys to better link in-lake nutrient dynamics with meteorological/climate forcing.

References

Appleby, P.G. 2001. Chronostratigraphic techniques in recent sediments. In: Last, W.M. and Smol, J.P. (Eds) Tracking Environmental Change Using Lake Sediments. Volume 1: Basin analysis, Coring, and Chronological Techniques. Kluwer Academic Publishers, Dordrecht, pp 171-203.

Appleby, P.G. and Oldfield, F. 1978. The calculation of lead-210 dates assuming a constant rate of supply of the unsupported lead-210 to the sediment. Catena 5:1-8.

Bennett, K.D. 1996. Determination of the number of zones in a biostratigraphical sequence. New Phytologist 132: 155-170.

Binford, M.W. 1990. Calculation and uncertainty analysis of 210-Pb dates for PIRLA project lake sediment cores. Journal of Paleolimnology 3: 253-267.

Camburn, K.E., and D.F. Charles. 2000. Diatoms of low-Alkalinity Lakes in the Northeastern United States. Academy of Natural Sciences of Philadelphia Special Publication 18: 152 pp.

Conley, D.J. and Schelske, C.L. 2001. 14. Biogenic silica. In: Smol, J.P., Birks, H.J.B., Last, W.M. [eds], Tracking Environmental Change Using Lake Sediments. Volume 3: Terrestrial, Algal, Siliceous Indicators. Kluwer Academic Publishers, Dordrecht, The Netherlands, pp 281-293.

Dean, W.E. 1974. Determination of carbonate and organic matter in calcareous sediments and sedimentary rocks by loss on ignition: comparison with other methods. Journal of Sedimentary Research 44: 242-248.

DeMaster D.J. 1979. The marine budgets of silica and ^{32}Si. Ph.D. Dissertation, Yale University.

Dixit, S. S. and J.P. Smol. 1994. Diatoms as indicators in the Environmental Monitoring and Assessment Program-Surface Waters (EMAP-SW). Environmental Monitoring and Assessment 31:275-306.

Edlund, M.B. and J.M. Ramstack. 2006. Diatom-Inferred TP in MCWD Lakes. Final Report to Minnehaha Creek Watershed District, Work Order #116-04, 33 pp.

Edlund, M.B., and J.M. Ramstack. 2007. Historical water quality and biological change in Peltier Lake, Anoka Co., MN. Final report submitted to Emmons and Olivier Resources, Inc. and the Rice Creek Watershed District, 19 pp.

Edlund, M.B., Engstrom, D.R., Triplett, L., Lafrancois, B.M. and Leavitt, P.R. 2009. Twentieth-century eutrophication of the St. Croix River (Minnesota-Wisconsin, USA) reconstructed from the sediments of its natural impoundment. Journal of Paleolimnology 41: 641-657.

Engstrom, D.R. 2005. Long-term changes in iron and phosphorus sedimentation in Vadnais Lake, Minnesota, resulting from ferric chloride addition and hypolimnetic aeration. Lake and Reservoir Management 21: 95-105.

Engstrom, D.R. and Wright, H.E. Jr. 1984. Chemical stratigraphy of lake sediments as a record of environmental change. Lake sediments and environmental history. E.Y. Haworth (Ed.), Leicester University Press: 11-67.

Fallu, M.-A., Allaire, N. and Pienitz, R. 2000. Freshwater diatoms from northern Québec and Labrador (Canada). Species-environment relationships in lakes of boreal forest, forest-tundra and tundra regions. Bibliotheca Diatomologica 45: 1-200.

Fritz, S.C., S. Juggins, R.W. Battarbee, and D.R. Engstrom. 1991. Reconstruction of past changes in salinity and climate using a diatom-based transfer function. Nature 352:706-708.

Heiskary, S.A., and Wilson, C.B. 2008. Minnesota's approach to lake nutrient criteria development. Lake and Reservoir Management 24:282-297.

Hustedt, F. 1927-1966. Die Kieselalgen Deutschlands, Österreichs und der Schweiz mit Berücksichtigung der übrigen Länder Europas sowie der angrenzenden Meeresgebeite. In Dr. L. Rabenhorst's Kryptogramen-Flora von Deutschland, Österreich und der Schweiz. Band VII. Teil 1: Lieferung 1, seite 1-272, 1927: Lieferung 2, seite 273-464, 1928: Lieferung 3, seite 465-608, 1929: Lieferung 4, seite 609-784, 1930: Lieferung 5, seite 785-920, 1930: Teil 2: Lieferung 1, seite 1-176, 1931: Lieferung 2, seite 177-320, 1932: Lieferung 3, seite 321-432, 1933: Lieferung 4, seite 433-576, 1933: Lieferung 5, seite 577-736, 1937: Lieferung 6, seite 737-845, 1959: Teil 3: Lieferung 1, seite 1-160, 1961: Lieferung 2, seite 161-348, 1962: Lieferung 3, seite 349-556, 1964: Lieferung 4, seite 557-816, 1966. Leipzig, Akademische Verlagsgesellschaft Geest und Portig K.-G.

Hustedt, F. 1930. Die Süsswasserflora Mitteleuropas. Heft 10. 2nd Edition. Bacillariophyta (Diatomeae). A. Pascher (ed.) Verlag von Gustav Fischer, Germany. 466 p.

Kopácek, J., Borovec, J., Hejzlar, J., Ulrich, K.U., Norton, S.A. and Amirbahman, A. 2005. Aluminum control of phosphorus sorption by lake sediments. Environmental Science & Technology 39(22): 8784-8789.

Krammer, K. and Lange-Bertalot, H. 1986-1991. Bacillariophyceae. in Ettl, H., Gerloff, J., Heynig, H. and Mollenhauer, D. (eds) Süsswasser flora von Mitteleuropa, Band 2/1-4. Gustav Fischer Verlag: Stuttgart, New York.

MPCA, Minnesota Pollution Control Agency. 2016a. Environmental Data Application, web site accessed April 2016, Net Lake, http://cf.pca.state.mn.us/water/watershedweb/wdip/waterunit.cfm?wid=58-0038-00

MPCA, Minnesota Pollution Control Agency. 2016b. Environmental Data Application, web site accessed April 2016, Lac La Belle, http://cf.pca.state.mn.us/water/watershedweb/wdip/waterunit.cfm?wid=09-0011-00

Patrick, R. and Reimer, C.W. 1966. The diatoms of the United States, exclusive of Alaska and Hawaii, Volume 1-Fragilariaceae, Eunotiaceae, Achnanthaceae,

Naviculaceae. Academy of Natural Sciences of Philadelphia Monograph No. 13, 699 pp.
Patrick, R. and Reimer, C.W. 1975. The diatoms of the United States, exclusive of Alaska and Hawaii, Volume 2, Part 1-Entomoneidaceae, Cymbellaceae, Gomphonemaceae, Epithemaceae. Academy of Natural Sciences of Philadelphia Monograph No. 13, 213 pp.
Psenner, R., and R. Puckso. 1988. Phosphorus fractionation: Advantages and limits of the method for the study of sediment P origins and interactions. Archiv für Hydrobiologie 30: 43-59.
R Core Team. 2014. R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria. www.R-project.org
Ramstack, J., Edlund, M., Engstrom, D., Moraska Lafrancois, B. and Elias, J. 2008. Diatom Monitoring Protocol, Version 1.0. National Park Service, Great Lakes Inventory and Monitoring Network, Natural Resource Report NPS/GLKN/NRR—2008/068. U.S. Department of the Interior, Fort Collins, CO. < http://science.nature.nps.gov/im/units/GLKN/protocolreportpubs.cfm >
Ramstack, J.M., S.C. Fritz, D.R. Engstrom, and S.A. Heiskary. 2003. The application of a diatom-based transfer function to evaluate regional water-quality trends in Minnesota since 1970. Journal of Paleolimnology 29:79-94.
Reavie, E.D. and Smol, J.P. 1998. Freshwater diatoms from the St. Lawrence River. Bibliotheca Diatomologica 41: 1-137.
Sheetz, J. and Wisuri, M. 2007. Scott House Souvenirs. Dovetailed Press LLC, Duluth, Minnesota.
SmartChem. 2012a. SmartChem 170 Method SIL-001-A (Rev: May 2012). Silica in Water, Waste Water and Soil Extracts and Other Aqueous Samples, 0.1-20 mg SiO_2/L. Unity Scientific 1117 Old State Road, Brookfield, CT 06804.
SmartChem. 2012b. SmartChem 170 Method PHO-001-A (Rev: may 2012). Phosphorus, All Forms, Orthophosphate, Hydrolyzable, and Total in Water, Waste Water and Soil Extracts and Other Aqueous Samples. Unity Scientific 1117 Old State Road, Brookfield, CT 06804.
Spaulding, S.A., Lubinski, D.J. and Potapova, M. 2010. Diatoms of the United States. http://westerndiatoms.colorado.edu Accessed on 13 April, 2016.
Tomkins, J.D., Antoniades, D., Lamoureux, S.F. and Vincent, W.F. 2008. A simple and effective method for preserving the sediment–water interface of sediment cores during transport. Journal of Paleolimnology 40: 577-582.
Wright, H.E. 1991. Coring tips. Journal of Paleolimnology 6: 37-49

Appendices

Appendix Table 1. Inventory of 210-Pb, modeled calendar date, and sediment accumulation rate (g/cm2 yr) of each Lac La Belle core section.

Lac La Belle Base of Interval	Total 210Pb	Base Date:	Sediment DMAR
(cm)	(pCi/g)	A.D.	(g/cm2 yr)
2	18.338	2012.0	0.0567
7	11.235	2003.3	0.0702
12	8.291	1994.8	0.0744
17	6.040	1986.1	0.0803
22	5.310	1976.5	0.0691
25	4.715	1969.9	0.0645
29	4.826	1957.9	0.0442
32	4.615	1944.7	0.0315
34	4.560	1931.9	0.0221
36	4.235	1912.5	0.0141
38	2.218	1898.5	0.0187
40	1.590	1889.7	0.0226
42	0.957	1884.3	0.0510
44	0.655	1882.6	0.2768
47	0.743	1880.6	0.1078
51	1.001	1872.9	0.0322
57	0.855	1855.5	0.0305
65	0.704	1832.1	0.0345
73	0.660	1804.4	0.0253

Appendix Table 2. Inventory of 210-Pb, modeled calendar date, and sediment accumulation rate (g/cm2 yr) of each Net Lake core section.

Net Lake Base of Interval	Total 210Pb	Base Date:	Sediment DMAR
(cm)	(pCi/g)	A.D.	(g/cm2 yr)
2	16.730	2007.0	0.0267
3	14.680	2002.1	0.0249
4	12.884	1997.2	0.0245
5	12.375	1991.4	0.0217
6	12.161	1984.2	0.0181
7	10.513	1976.4	0.0168
8	7.137	1969.5	0.0205
10	3.372	1958.7	0.0352
11	3.050	1953.8	0.0347
12	3.205	1947.7	0.0273
14	2.612	1933.9	0.0242
15	2.338	1926.4	0.0228
16	2.114	1918.1	0.0210
17	1.644	1911.2	0.0263
18	1.487	1904.5	0.0265
19	1.436	1896.5	0.0230
20	1.424	1885.7	0.0175
21	1.327	1872.6	0.0145
22	1.081	1863.2	0.0210

Appendix Tables 3, 4. Diatom-inferred total phosphorus (TP) reconstructions for Lac La Belle and Net Lake. Model reconstructions are in logTP units and have been back transformed to µg/l). Please consult the text and note that the diatom-inferred reconstruction of TP for Lac La Belle is highly suspect due to poor model analogues, and should be very cautiously considered in any management decisions.

Lac La Belle

Date (A.D.)	log TP	TP (ug/l)
2014	1.17	14.8
2004	1.19	15.5
1996	1.15	14.1
1987	1.17	14.8
1978	1.17	14.8
1965	1.17	14.8
1960	1.16	14.6
1947	1.15	14.2
1935	1.16	14.6
1918	1.17	14.7
1901	1.11	12.9
1892	1.15	14.0
1884	1.14	13.8
1881	1.09	12.2
1858	1.18	15.3

Net Lake

Date (A.D.)	log TP	TP (ug/l)
2007	1.58	37.9
2002	1.66	46.2
1991	1.66	45.3
1984	1.64	43.7
1976	1.66	45.9
1970	1.58	38.1
1959	1.54	34.9
1948	1.53	34.1
1934	1.47	29.4
1918	1.50	31.4
1905	1.44	27.6
1886	1.42	26.2
1863	1.48	30.5
1852	1.56	36.2
1842	1.52	33.1