

A Paleolimnological Study of Myrtle Lake, St. Louis Co., Minnesota

Mark B. Edlund, Joy M. Ramstack Hobbs, Adam J. Heathcote

St. Croix Watershed Research Station
Science Museum of Minnesota
16910 152nd St N
Marine on St. Croix, MN 55047
medlund@smm.org



Final Report submitted to:

Amy Mustonen
Minnesota Pollution Control Agency
525 S. Lake Ave., Suite 400
Duluth MN 55802
amy.mustonen@state.mn.us, 218-302-6638
July 2019

MPCA SWIFT Nr. 140325, AI# 191410, PRO20180001



Please cite this report as:

Edlund, M.B., Ramstack Hobbs, J.M. and Heathcote, A.J. 2019. A Paleolimnological Study of Myrtle Lake, St. Louis Co., Minnesota. Final Report to the Minnesota Pollution Control Agency. St. Croix Watershed Research Station, Science Museum of Minnesota, Marine on St. Croix, Minnesota, 42 pp.

Executive Summary

1) A long sediment core was recovered from Myrtle Lake in St. Louis County, Minnesota, on 04 June 2018 and analyzed to reconstruct a historical record of sedimentation and water quality from the mid-1800s to present for the lake. Management concerns for Myrtle Lake are centered around nutrient levels, chlorophyll, and water clarity that exceed state standards, and sustaining high quality recreational and fishing opportunities in the lake.

2) The long sediment core was 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) Short sediment cores were also collected from throughout the Myrtle Lake basin for analysis of basin-wide distribution of sediment total phosphorus and phosphorus fractions. At three sites paired cores were subjected to aerobic and anaerobic incubation to estimate the potential for internal loading of soluble reactive phosphorus.

4) A high frequency monitoring buoy measuring water column temperature and dissolved oxygen was deployed in central Myrtle Lake from June to October 2018.

5) Radiometric dating (Pb-210) showed that Myrtle lake has a low sedimentation rate with sediments deposited in the top 25 cm representing the last 150 yrs. Sedimentation rates in the lake increased slightly following Euro-American settlement and have further increased since the 1970s to 2-2.5 times historical rates.

6) Loss-on-ignition analysis showed that inorganics are the predominant fraction in Myrtle Lake sediments, and that concentration and flux of inorganics increased following early settlement. Concentration and flux of organics has also increased since the 1970s.

7) Biogenic silica concentration, a marker of diatom algae abundance, is very high in Myrtle Lake (ca 20% by dry weight). Flux or accumulation of biogenic silica increased in the early 20th century and showed a steady upward trend since the 1970s.

6) Sediment total phosphorus concentrations increased upcore from about 1.0 mg total P/g in pre-1900 to 1.6-1.8 mg P/g at the core surface throughout the basin. The labile organic-P and recalcitrant organic-P fractions made up the largest proportion of P fractions in cores. The Fe-bound P fraction was the next most abundant P fraction, and all cores showed greater concentrations of Fe-bound P near the core tops. Labile organic-P and Fe-bound P are the primary fractions involved in internal loading; this pool of P is important in lakes such as Myrtle that have anoxic bottom waters in mid-summer. These anoxic events allow diffusive P release from the sediments, and can fuel late summer and fall cyanobacteria blooms following mixing events

7) Short cores from three stations were also subjected to incubation under aerobic and anaerobic conditions to determine potential internal loading rates. Aerobic release rates were 0.14 to 0.35 mg P/m² d; the central station and eastern station had higher aerobic release rates than western station. Anaerobic release rates were 1.39 to 8.60 mg P/m² d; the eastern station had markedly higher aerobic release rates. Anaerobic rates were 8.3 to 28.7 times greater than aerobic rate with highest anaerobic release rates in the eastern basin.

8) The sediment diatom assemblage comprises meso-eutrophic species characteristic of shallow lakes and includes the plankter *Aulacoseira ambigua*, one plankter common in stained waters (*Discostella (Cylcotella) stelligera*), planktonic araphid species *F. crotonensis* and *Asterionella formosa*, and a diverse small fragilarioid flora common to polymictic shallow lakes. Ordination, cluster analysis, and stratigraphic plots show little historical change in Myrtle's diatom assemblages. The upper stratigraphic zone (post-1995) has greater *Asterionella formosa* and *Fragilaria crotonensis*; these species can respond to increased nitrogen addition from atmospheric and watershed sources.

9) 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. Historical diatom-inferred TP reconstructions suggest that there has been little change in mean epilimnetic TP concentrations in the last 150 years; diatom-inferred TP has remained around 25-30 ppb with no notable recent increases in inferred TP levels. The most recent reconstructions match some years of monitoring data (2015; mean 19 ppb TP) but do not match all recent mean monitored TP values (e.g., 43 ppb in 2016, 50 ppb in 2018).

10) Cyanobacteria have long been a component of the Myrtle Lake algal flora based on fossil algal pigment analysis. Sediments from before 1940 had high levels of pigments that are interpreted as indicating more abundant colonial cyanobacteria before, perhaps dominated by deeper and/or attached forms. After 1940, there is a shift in the pigment profiles with continued cyanobacteria in the lake but no indication of a major shift in the last few decades. The change by the 1940s may be related to increasing DOC in Myrtle Lake following initial logging of the region. A very slight increase in myxoxanthophyll in the most recent sediments hints at a possible increase in colonial cyanobacteria, including potential toxic planktonic bloom-formers that were noted in June 2018 (*Dolichospermum*, *Microcystis*, *Gloetrichia*).

11) The high frequency water quality monitoring buoy recorded at least six instances in 2018 of short-term summer stratification that rapidly led to bottom water hypoxia/anoxia. This would have generated significant diffusive release of soluble reactive P (SRP) based on our core incubation data. The pulses of SRP following each stratification event appear to have fueled the 2018 summer-long rise in both chlorophyll-a and TP levels, an extreme cyanobacterial bloom year.

12) Management recommendations based on these paleolimnological results are as follows:

Myrtle Lake does not currently meet state standards for nutrient criteria (<30 ppb TP in NLF lakes; Heiskary and Wilson 2008), chlorophyll-a (<9 ppb TP in NLF lakes), or Secchi clarity (>2.0 m in NLF lakes). 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. Paleolimnological evidence suggests Myrtle has long been a meso- to eutrophic system with historical TP in the 25-30 ppb range. Agency monitoring suggests that mean annual TP can range from 19 ppb (2015) to 50 ppb (2018) in Myrtle Lake. These data lend support to considering whether shallow lakes in the northern lakes and forest ecoregion may be better served with modified nutrient standards.

In a watershed that is not undergoing major development, agricultural conversion, or logging, the need to understand what is driving the degraded water quality of Myrtle Lake deserves further study. We used sediment P profiles, aerobic/anaerobic internal loading potential, and high frequency monitoring to clearly link multiple short-term summer stratification events that drive diffusive P loading with the extreme nuisance algae blooms that plagued Myrtle in summer 2018. However, there is also high interannual variability in monitored lake conditions. A cost-effective recommendation would be to continue to run the high frequency buoys in more and different meteorological years to better understand the critical role that links climate/meteorological conditions to summer stratification and internal loading to Myrtle's degraded water quality. This would necessitate some additional monthly monitoring of inflows, in-lake, and outflow, and we would encourage additional analytes also be measured (total and nitrogen species, DOC, phycocyanin). Algae and cyanotoxin monitoring would also be beneficial to understanding Myrtle Lake.

Data presented here support the development of a needed detailed nutrient budget for Myrtle Lake. Internal loading estimates, loss rates of P, and a better understanding of the 2018 worse case internal loading scenario gives the opportunity to consider a P budget that is adaptable to different meteorological year types, i.e. can we predict "good" and "bad" cyanobacteria years? There are several predictive modeling tools available to forecast future lake conditions based on future climate scenarios.

Acknowledgements

We thank the Myrtle Lake Resort for lake access and providing a boat for fieldwork. Amy Mustonen (MPCA) coordinated the project and along with Angus Vaughn of the MPCA and Phil Norvitch of SCWD assisted with fieldwork. We thank Bill James, UW-Stout, for sediment core incubations. Dan Engstrom, Michele Natarajan, Hailey Sauer, Phil Woods, and Erin Mortenson of the St. Croix Watershed Research Station coordinated lab analyses and assisted in the field. Justin Remien and Tyler Jasan of Vermilion Community College and Kevin Stroom of MPCA provided 2018 water quality data, and Jesse Anderson (MPCA) provided background information on the lake.

Introduction

Within the glaciated regions of the Upper Midwest, lakes feature prominently in our 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.

Myrtle Lake is located just west of Orr in St. Louis County, MN. Myrtle Lake runs E-W for a length of about 2.5 miles and has a single basin about 15 ft deep with one central deep spot that reaches approximately 20 ft depth. The lake has a small watershed with 58% forested and about 25% wetland. The has only modest development with the south shore home to a few cabins, homes, and one resort. Concern for the lake centers on its current state of notably poor water quality among northern Minnesota lakes. Recent monitoring shows that the lake experiences frequent nuisance cyanobacterial blooms (20 µg/L chlorophyll a (Chl-a)) and does not meet Minnesota state standards for total phosphorus (TP), Chl-a, and water clarity (Secchi depth). This has led to questions of whether the productivity and condition of the lake have changed over time, what the natural or historical condition of the lake was, what the current trajectory of the 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 plan. This project used paleolimnological techniques to reconstruct the nutrient and algal history and trends in sedimentation of this St. Louis County lake. The results provide a history of ecological changes that have occurred in the lake during the last 150 years and an assessment of background conditions. As phosphorus dynamics are likely key to understanding the current condition of Myrtle Lake, we also conducted a spatial assessment of sediment P and P fractions that drive internal loading, aerobic and anaerobic core incubations to estimate potential internal P loading, and deployed a high frequency temperature-dissolved oxygen (DO) buoy to assess thermal and oxygen conditions that lead to internal loading.

Rationale

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 Myrtle Lake is no exception. The primary aim of this project was to use paleolimnological analysis of a dated sediment core to reconstruct the nutrient and algal history and trends in sedimentation 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 25-30 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 primary core. 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 a single long core and in short cores collected throughout the Myrtle basin to understand the distribution of P and P fractions within the cores and throughout the basin, and assess the relative capability (or lack of capability, i.e. internal loading) of the lake to sequester phosphorus in its sediments. Cores from three sites in the lake basin were also subjected to aerobic (oxic) and anaerobic (anoxic) incubation to determine potential rates of internal P loading under oxygenated and anoxic conditions.

Methods

Lake-Sediment Coring and Analyses

Coring

A single sediment core (core 5) measuring 1.01 m in length was recovered from the central basin (Station 5; 48.08426° N, 92.67472°W) of Myrtle Lake (Fig. 1, Table 1) on 04 June 2018. The Myrtle Lake core was recovered from 4.04 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). The overlying water and sediment interface was stabilized using a gelling agent (Zorbitrol; Tomkins et al. 2008). The long core was next transported back to the laboratory and extruded vertically at 0-2 cm and then in 1-cm increments to 50 cm core depth, and 2-cm increments to 96 cm core depth.

Six short cores (20-30 cm long) were recovered from throughout the basin (stations 1, 2, 3, 4, 6, 7) using an HTH gravity corer (Renberg and Hansson 2008) to determine spatial patterns of P distribution in Myrtle Lake (Fig. 1, Table 1). Short cores were sectioned in the field at 0-2 cm, 2-4 cm, 4-6 cm, 6-8 cm, 8-10 cm, and 18-20 cm. Finally, four

replicate short cores were taken at stations 3, 5, 7 for oxic and anoxic incubation to determine internal P release rates throughout the lake (see below). Incubation cores were placed on ice and brought to the James' lab at UW-Stout within 24 hrs of collection.

Isotopic Dating and Geochemistry

The long sediment core was 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 $1-3 \times 10^5$ 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).

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; $\text{g cm}^{-2} \text{ yr}^{-1}$) for the long 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 long core, 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 Kopáček 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 for Myrtle Lake. Diatoms were analyzed from fifteen core sections in the long core; samples were prepared and analyzed as follows. Diatoms and chrysophyte cysts were prepared by placing approximately 50 mg freeze dried core material in a 50 cm³ 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% H₂O₂ 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. (2019). 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 non-metric multidimensional scaling (NMDS) 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 an NMDS plot is that samples that plot closer to one another have more similar diatom assemblages. Significant breaks in the constrained cluster analysis were evaluated using a broken stick model (Bennett 1996).

Downcore diatom communities were also used to reconstruct historical epilimnetic phosphorus levels. A transfer function for reconstructing historical log₁₀TP (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. 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 in the software package R (R Core Team 2014). Data are presented as both logTP values and as back-transformed values, to TP in $\mu\text{g/l}$ or ppb.

Fossil Pigment Analysis

Algal pigment analyses were performed on 10 subsamples from long core 5. Sediment pigment concentrations were quantified by Dr. Peter Leavitt at the University of Regina, Canada, using reverse-phase high-pressure liquid chromatography (HPLC) (Vinebrooke et al. 2002). Pigments were first extracted from freeze-dried sediments using an acetone:methanol solution. Extracts were then filtered (0.2- μm pore nylon), dried under N_2 , and reconstituted using a precise volume of injection solution. Chromatographic separation were performed with an Agilent 1100 Series HPLC equipped with a Varian Microsorb 100A-C18 column, and pigment detection using in-line diode array and fluorescence detectors. Pigment concentrations were quantified via calibration equations and an electronic spectral library constructed using standards purchased from DHI Water and Environment, Denmark. Jeffrey and Wright (2005) was consulted as a key reference for taxonomically diagnostic pigments. Pigment concentrations are reported relative to sediment core organic carbon.

Sediment core incubations

To determine in-lake and site variability in internal P loading, paired anoxic incubations and paired oxic incubations were run at the Discovery Center, University of Wisconsin – Stout, on 12 short cores collected at stations 3, 5, and 7 using methods outlined in James (2017). In short, overlying water was siphoned off sediment cores; paired cores were used for both anoxic and oxic incubations from each station. The upper 10 cm of sediment was the vertically extruded intact to an acrylic core incubation tube (6.5 cm internal diameter and 20 cm height). Filtered lake water (Gelman A-E, 2 μm nominal pore size) was siphoned (300 mL) onto the sediment to serve as overlying water. The sediment incubation systems were placed in a darkened environmental chamber and incubated at 20 C to simulate typical summer bottom temperatures in Myrtle Lake. The oxidation–reduction environment in the overlying water of each system was controlled by gently bubbling either air (oxic or aerobic) or nitrogen (anoxic or anaerobic) through an air stone placed just above the sediment surface. Bubbling action insured complete mixing of the water column but did not disrupt the sediment. Anoxic conditions were verified using a dissolved oxygen electrode. Water samples (10 mL) were collected from the center of the water column from each sediment incubation system, filtered through a 0.45 μm -pore size membrane syringe filter, and analyzed for soluble reactive phosphorus (SRP). Incubation systems were sampled every 1-3 days for up to 23 days. Rates of diffusive P flux from deposited sediment ($\text{mg/m}^2 \text{ d}$) were calculated as the linear change in concentration in the overlying water ($n = 4$ to 8) divided by time and the area of the incubation core liner. Regression analysis was used to estimate the rate over the linear portion of the data.

High frequency water quality monitoring buoys

A buoyed thermister/dissolved oxygen (DO) string was deployed on 04 June 2018. The buoy consisted of an anchor (35 lbs of cinder blocks), temperature logger (HOBO Temperature Pendants UA-002-64) attached at every meter of depth, a DO logger

(HOBO DO Logger U26-001) placed 0.5 m off the bottom and 2.5 m below the surface. Temperature and DO loggers were set to take readings every 30 minutes to record full water column profiles of temperature and dissolved oxygen conditions to determine patterns of seasonal stratification and hypolimnetic anoxia. The buoy was recovered on 08 October 2018, the data downloaded and processed using R (R Core Team 2014).

Results and Discussion

Pb-210 inventory

Myrtle Lake sediments showed a monotonic decline in ^{210}Pb inventories to supported levels around 25 cm (Fig. 2). Using the CRS model, a date-core depth relationship was established for the core (Table 2). In Myrtle Lake, sediments dated before the 1860s were found below 25 cm, 1900 around 21 cm, 1951 at 13 cm, and 1999 at 6 cm depth. Linear sedimentation rates are very slow in Myrtle Lake compared to many Minnesota lakes; because of its large shallow basin, Myrtle Lake accumulates sediment very slowly.

Sedimentation rates

Sedimentation rates in Myrtle Lake were lowest during pre-Euroamerican settlement times (approximately $0.007 \text{ g/cm}^2 \text{ yr}$) and increased slightly from the late 1800s-1970 to approximately $0.01 \text{ g/cm}^2 \text{ yr}$. From 1970 to present, sedimentation rates have increased in Myrtle Lake with modern rates of about $0.025 \text{ g/cm}^2 \text{ yr}$, approximately 2-2.5 times greater than pre-1970 rates (Fig. 2, Table 2).

Loss-on-ignition

The inorganic or mineral component dominates the sediment in Myrtle Lake at between 60 and 70% by dry weight; there is a notable increase in percent inorganics between 20 and 13 cm (1900 to 1950s), a probable erosion response to initial logging in the region (Fig. 3). Organic matter is the next most common constituent of Myrtle Lake sediments with between 24 and 28% in the top meter of core. There is a slight increase in percent organics since the 1950s (~13 cm). Carbonates remain low and constant in the Myrtle Lake core at 5 to 8% dry weight. Dry mass accumulation of sediment constituents track sedimentation rate changes in Myrtle Lake, with greater accumulation of inorganics and organics from the late 1800s to the 1950s, then rapid increases in accumulation after the 1970s especially of inorganics and organics (Fig. 4).

Biogenic silica (BSi)

Biogenic silica composed 17.1-23.6% of the dry weight of Myrtle Lake sediment, with highest values at 20 cm (1895) and lowest values near the core top (6 cm, 1999) (Fig. 5). When converted to accumulation rates, the flux of BSi increases from pre-settlement to an initial peak in the 1920s, declines slightly to 1970, and then increases rapidly toward the top of the core. Modern accumulation of biogenic silica is approximately two times greater than in pre-Euro-American settlement times suggesting that there has been diatom productivity in Myrtle Lake since the 1970s.

Sediment phosphorus fractions

Sediment total phosphorus and phosphorus fractions were analyzed in short cores taken throughout the Myrtle basin to determine if there were any areas of the lake that may be at greater risk for internal loading. Total phosphorus in Myrtle Lake sediments ranged from 1.0 to 1.8 mg P/g with increasing concentrations in the top 8-10 cm of each core (Fig. 6). The labile organic-P and recalcitrant organic-P fractions made up the largest proportion of P fractions throughout the entire basin. The Fe-bound P fraction was typically the next most abundant P fraction, and all cores showed greater concentrations of Fe-bound P near the core tops (upper 4 cm, Fig. 6). The labile organic and Fe-bound P are the primary fractions involved in internal loading. There is very little variability in cores across the Myrtle basin; station 2 in the far SW basin has slightly lower total P in the near surface sediments (1.5 mg P/g).

The dated sediment core 5 was analyzed in greater detail for total phosphorus and phosphorus fractions (Fig. 7). There is increasing concentration of total P and most fractions above 15 cm (post-1930s) with presettlement concentrations of about 1.0 mg total P/g increasing to 1.6 mg P/g at the core surface. As in the other cores, labile organic-P and recalcitrant organic-P fractions made up the largest proportion of P in core 5, followed by the Fe-bound P fraction. There is greater concentration of both labile organic-P and Fe-bound P above 10 cm core depth (post-1970s). Both of these fractions are important to potential internal loading processes in Myrtle Lake. These pools of P are especially important in lakes that have anoxic bottom waters in mid-summer (as recorded in Myrtle) that release labile P to fuel summer and fall cyanobacteria blooms following mixing events.

Diatom communities and TP reconstructions

Over 140 diatom species were identified in sediment core 5 from Myrtle Lake. The dominant forms in the core were the meso- to eutrophic *Aulacoseira* species, *A. ambigua*, which thrives in regularly mixed lakes, planktonic araphid taxa including fragilarioids (*F. crotonensis* and *Asterionella formosa*), a diverse small fragilarioid flora that can dominate polymictic shallow lakes (e.g., *Staurosira venter*, *S. construens*, *Staurosirella pinnata*), and one plankton common in stained waters (*Discostella (Cylcotella) stelligera*).

Historical changes in the diatom community in the Myrtle Lake sediment core were explored with stratigraphic plots, Non-metric multidimensional scaling (NMDS), and a constrained cluster analysis to identify stratigraphic zones. Samples were also plotted 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. Lastly, the Minnesota diatom calibration set was applied to the diatom communities to estimate historical levels of TP in Myrtle Lake.

The NMDS (Fig. 8) shows how the core samples shifted over time based on similarity of their diatom assemblages. The short gradients in the NMDS indicate that the diatom community in Myrtle Lake has not changed dramatically in the last 150 years. More recent samples are pulled to the left in the ordination by slightly greater abundances of *Asterionella formosa*, *Pseudostaurosira brevistriata* v. *inflata*, and *Staurosira*

(Pseudostaurosira) elliptica. The constrained cluster analysis confirms this and shows a primary break in the diatom assemblages between 1951 and 1959 (Fig. 9), and a secondary break separating the top three core samples (1999-present). It should be noted that testing of clusters using the broken stick model did not identify any clusters of samples in the Myrtle Lake core as significant. The shift in assemblage between 1951 and 1959 is primarily characterized by a decreased upcore abundance of the mesotrophic indicator *Aulacoseira ambigua* simultaneous with a decreased abundance of several small fragilarioid taxa (Fig. 10). The topmost stratigraphic zone represents a shift to greater *Asterionella formosa* and *Fragilaria crotonensis*, and less *Discostella (Cyclotella) stelligera*. In many historical studies, *Asterionella formosa* and *Fragilaria crotonensis* are known to respond to increased nitrogen additions from both atmospheric and watershed sources (Saros et al. 2005).

The diatom communities were also used to reconstruct historical TP levels for Myrtle Lake. Many factors can contribute to changes in diatom communities (nutrients, 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 Myrtle Lake 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 Myrtle Lake core, with no strong directional change (Fig. 11). The lack of correlation with Axis 1 or log TP suggests that TP may not be the primary driver of the changes seen in the diatom community for the majority of the record. Alternative drivers include: habitat alterations, pH, nitrogen, climate drivers, length of growing season or other stressors that were not directly measured in the calibration set. It is also possible that the drivers of ecological shifts change over time, meaning that TP is an important variable during certain time periods.

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 Myrtle Lake, this analysis shows that the fraction of the maximum explainable variation in the diatom data that can be explained by TP is relatively low (46.6%). 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 any changes in the TP reconstruction should be interpreted with caution.

Given those caveats, the TP reconstruction from Myrtle suggests that there has been little change in mean epilimnetic TP concentrations in the last 150 years, and that TP has remained around 25-30 ppb with reconstructions ranging from 23.4 ppb TP (ca 1883) to 33.1 ppb TP (ca 1914; Fig. 12, Table 3). Two observations can be made from these results. First, given the minimal change in the diatom assemblage over time and the lack

of changes among those species that commonly respond to nutrient enrichment, there is reason to believe that TP levels in Myrtle Lake have not changed significantly. For example, there is no change in the percent abundance of planktonic diatoms (Fig. 10); an increased abundance of planktonic forms is universally characteristic of increased nutrient levels. Second, we know that the diatom model has underestimated recent mean annual ice-free TP levels in Myrtle Lake. Modern monitoring data suggest that summer TP levels are well above state nutrient criteria of 30 ppb, and have been measured as high as 60-80 ppb in Myrtle Lake (MPCA 2018 data, see Fig. 15). However, as recently as 2015 (data from Anderson and Mustonen 2017), mean summer TP levels have been measured at 29.7 ppb, nearly identical to the diatom-inferred values at the core top (the top level of the core encompasses sediments deposited from 2013-2018).

Fossil Algal Pigments

While all algae have the pigment chlorophyll-a, the different groups of algae have other accessory pigments that characterize each algal group such as oscilloxanthin in the cyanobacteria, diadinoxanthin in the dinoflagellates, and fucoxanthin in the diatoms. When algae die or are deposited in the sediments, their pigment complements are preserved and can provide a record of the quantity and types of algae historically present in a lake. Some pigments are readily degraded after deposition and do not provide clear record of historical algae, e.g. chlorophyll-a and fucoxanthin. In general the Myrtle Lake core does not have an easily interpreted fossil pigment record. In many lakes that have excessive cyanobacterial blooms, there are very clear pigment signals of historical change that pinpoint when bloom conditions accelerated.

Ten dated levels of Myrtle core 5 were analyzed for fossil algal pigments. Samples deposited before the 1940s had markedly higher levels of echinenone (cyanobacteria), canthaxanthin (colonial cyanobacteria/Nostocales), lutein/zeaxanthin (green and cyanobacteria), diatoxanthin (diatoms), alloxanthin (cryptophytes), and beta-carotene (total algae). We interpret this pattern to suggest that there was a shift in especially cyanobacteria in the history of Myrtle Lake from having more colonial cyanobacteria before the 1940s, perhaps earlier dominated by deeper and/or attached forms. After 1940, there is a shift in the pigment profiles with continued cyanobacteria in the lake but no indication of a major shift in the last few decades. The change by the 1940s may be related to increasing DOC in Myrtle Lake following initial logging of the region (Schelker et al. 2012) that shifted the cyanobacteria from more deepwater forms to more surface blooms. A very slight uptick in myxoxanthophyll in the most recent sediments hints at a possible increase in colonial cyanobacteria, including potential toxic planktonic forms that were noted in June 2018 (*Dolichospermum*, *Microcystis*, *Gloeotrichia*). Although there is also a pre-1940s peak in the diatom pigment diatoxanthin, the fossil diatom assemblage oddly does not track a similar pattern with a shift in historical diatoms. Rather the diatom community in Myrtle Lake, based on siliceous microfossils, records no significant shifts in community composition over this time period, although biogenic silica flux records slightly greater diatom productivity since the 1970s. The diatom community has long been dominated by species that are generalists in shallow polymictic meso- to eutrophic lakes.

High frequency water quality monitoring buoys

Data from the high frequency buoy deployed in 2018 generated continuous temperature data which are plotted as water column isopleths, while dissolved oxygen data are plotted as percent saturation in near surface and bottom loggers (Fig. 14). These data show three key behaviors of the Myrtle water column: multiple periods with rapid stratification during calm periods, hypolimnetic oxygen levels during stratification that rapidly reach hypoxic levels, and a strong linkage to seasonal water quality.

The buoy site showed at least six periods of thermal stratification during June-October 2018. These periods primarily occurred from mid-June to early September in 2018 with four instances in June-July 2018, and two stratifications in early and late August 2018 (Fig. 14).

Although we did not compare these data to wind records, the multiple periods of stratification appeared to have each occurred very rapidly in Myrtle when calm conditions set up over the lake. As stratification occurs in Myrtle, hypolimnetic oxygen levels begin to fall rapidly regardless of timing within the open water season. The rate of oxygen loss in bottom waters occurred at ~10% per day (Fig. 14), with anoxic conditions reached in less than a week. Hypoxic/anoxic conditions, once set up, lasted for between a week and 10 days at least four times during summer 2018. This, of course, would lead to multiple episodes of rapid diffusive internal loading. A comparison of the buoy data with monitored water quality (TP and Chl-a) data collected from the lake in 2018 bears out the connection between multiple short-term stratification events, diffusive internal loading, and rising TP and Chl-a levels in June and July 2018 (Fig. 15). Following each short-term stratification event, in-lake TP and Chl-a levels incrementally increased during the growing season in Myrtle Lake as readily usable soluble reactive phosphorus was distributed to the entire water column each time a stratification event ended (Fig. 15).

Sediment core incubations

To determine variability in potential internal loading of soluble reactive phosphorus across the Myrtle basin, we subjected paired short cores from stations 3, 5, and 7 to aerobic (oxic) and anaerobic (anoxic) incubations (Fig 16, 17). Mean aerobic release rates varied from 0.14 to 0.35 mg P/m² d with central station 5 and eastern station 7 having higher aerobic release rates than western station 3 (Table 4). Mean anaerobic release rates varied from 1.39 to 8.60 mg P/m² d with eastern station 7 having markedly higher aerobic release rates than western station 3 or central station 5 (Table 5). Comparison of anaerobic and aerobic rates showed that anaerobic rates were 9.9 times larger than aerobic rates at station 3, 8.3 times greater at station 5, and 28.7 times greater at station 7!

The variability in release rates among stations was not predicted given the lack of variability in distribution of total P and P fractions among cores (Figs 6, 7). Anecdotal evidence of greater bloom intensity in the eastern half of the lake may be a direct consequence of the higher aerobic and anaerobic release rates especially in the lake's eastern basin.

Summary and Recommendations

The dated sediment core from Myrtle's central basin provided a 150-year record of sedimentation, geochemistry, and diatom and algae communities in Myrtle Lake. Myrtle Lake has a very slow linear sedimentation rate; the Pb-210 dated core indicates that the last 150 years of sedimentation are preserved in the top 25 cm of sediments. Myrtle is characterized by sediments that are low in carbonates and dominated by inorganics. Sedimentation rates increased slightly with initial settlement and logging in the late 1800s but have increased more dramatically since the 1970s to levels that are about 2-2.5 times greater in recent decades. Other geochemical indicators measured included biogenic silica, a measure of productivity by the algal groups diatoms and chrysophytes. Biogenic silica levels are high in Myrtle Lake sediments; their accumulation rate tracks bulk sedimentation rates and suggests that there was slightly greater diatom productivity in the early 20th century and since the 1970s.

Total phosphorus and phosphorus fractions were analyzed in short cores collected from throughout the basin and in greater detail from long core 5 in the central basin. Total phosphorus concentrations increased upcore from about 1.0 mg total P/g increasing to 1.6-1.8 mg P/g at the core surface throughout the basin. The labile organic-P and recalcitrant organic-P fractions made up the largest proportion of P fractions in cores. The Fe-bound P fraction was typically the next most abundant P fraction, and all cores showed greater concentrations of Fe-bound P near the core tops. Labile organic-P and Fe-bound P are the primary fractions involved in internal loading.

Short cores from three stations were also subjected to incubation under aerobic and anaerobic conditions to determine potential internal loading rates. Aerobic release rates were 0.14 to 0.35 mg P/m² d; the central station and eastern station had higher aerobic release rates than western station. Anaerobic release rates were 1.39 to 8.60 mg P/m² d; the eastern station had markedly higher aerobic release rates. Anaerobic rates were 8.3 to 28.7 times greater than aerobic rate with highest anaerobic release rates in the eastern basin.

The diatom assemblage preserved in Myrtle sediment comprises meso-eutrophic species characteristic of shallow lakes and includes the plankter *Aulacoseira ambigua*, one plankter common in stained waters (*Discostella (Cylcotella) stelligera*), planktonic araphid taxa *F. crotonensis* and *Asterionella formosa*, and a diverse small fragilarioid flora common to polymictic shallow lakes (e.g., *Staurosira venter*, *S. construens*, *Staurosirella pinnata*). Ordination, cluster analysis, and stratigraphic plots show little historical change in Myrtle's diatom assemblages. A shift between 1951 and 1959 is primarily characterized by a decreased upcore abundance of the mesotrophic indicator *Aulacoseira ambigua*. The upper stratigraphic zone (post-1995) has greater *Asterionella formosa* and *Fragilaria crotonensis*, and less *Discostella (Cyclotella) stelligera*. *Asterionella formosa* and *Fragilaria crotonensis* can respond to increased nitrogen addition from atmospheric and watershed sources.

Quantitative estimates of historical total phosphorus (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 Myrtle Lake, historical diatom-inferred TP reconstructions suggest that there has been little change in mean epilimnetic TP concentrations in the last 150 years; diatom-inferred TP has remained around 25-30 ppb with no notable recent increases in inferred TP levels. The most recent reconstructions do not match with recent mean monitored TP values of 43 ppb (2016) to 50 ppb (2018) but do align with other recent monitored years such as 2015 (19 ppb TP).

Fossil algal pigments indicate that cyanobacteria have long been a component of the Myrtle Lake algal flora. Sediments deposited before 1940 had the highest levels of pigments that are interpreted as indicating more abundant colonial cyanobacteria before the 1940s, perhaps earlier dominated by deeper and/or attached forms. After 1940, there is a shift in the pigment profiles with continued cyanobacteria in the lake but no indication of a major shift in the last few decades. A slight uptick in myxoxanthophyll in the most recent sediments hints at a possible increase in colonial cyanobacteria, including potential toxic planktonic bloom-formers that were noted in June 2018 (*Dolichospermum*, *Microcystis*, *Gloeotrichia*).

A high frequency water quality monitoring buoy was deployed in the central basin of Myrtle Lake from June-October 2018 to measure water column temperature and dissolved oxygen conditions. There were at least six instances in 2018 of short-term summer stratification that rapidly led to bottom water hypoxia/anoxia that would have generated significant diffusive release of soluble reactive P (SRP). The pulse of SRP following each destratification event appears to have fueled the 2018 summer-long rise in both chlorophyll-a and TP levels associated with the extreme cyanobacterial bloom conditions noted that year.

Management recommendations based on this paleolimnological analysis include:

1. Myrtle Lake does not currently meet state standards for nutrient criteria (<30 ppb TP in NLF lakes; Heiskary and Wilson 2008), chlorophyll-a (<9 ppb TP in NLF lakes), or Secchi clarity (>2.0 m in NLF lakes). 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. Diatom inferred total phosphorus shows that Myrtle has long been a meso- to eutrophic system with historical TP in the 25-30 ppb. Interannual monitoring suggests that mean annual TP can range from 19 ppb (2015) to 50 ppb (2018) in Myrtle Lake. These data lend support to considering whether shallow lakes in the northern lakes and forest (NLF) ecoregion may be better served with their own TP standard. A table comparing pre-Euroamerican diatom inferred TP against modern monitored TP is presented for 19 shallow lakes in the NLF ecoregion (Table 6).
2. In a watershed that is not undergoing major development, agricultural conversion, or logging, the need to understand what is driving the degraded water quality of Myrtle

Lake deserves further study. Our analyses of sediment P profiles, aerobic/anaerobic interal loading potential, and high frequency monitoring clearly link multiple short-term summer stratification events that drive diffusive P loading in a series of internal loading events that incrementally bolstered the extreme nuisance algae blooms that plagued Myrtle Lake in summer 2018. But there also appears to be high interannual variability in monitored lake conditions. A cost-effective recommendation would be to run the high frequency buoys in more and different meteorological years to better understand the critical role that links summer stratification and internal loading to Myrtle's degraded water quality. This would necessitate some additional monthly monitoring of inflows, in-lake, and outflow, and we would encourage additional analytes also be measured (total and nitrogen species, DOC, phycocyanin). Algae and cyanotoxin monitoring would also be beneficial to understanding Myrtle Lake.

3. Coupled with several years of monitoring data, the data presented in this report offer the potential to develop a needed detailed nutrient budget for Myrtle Lake. Internal loading estimates, loss rates of P, and a better understanding of the 2018 worse case internal loading scenario gives the opportunity to consider a P budget that is adaptable to different meteorological year types. Furthermore, predictive modeling tools are available to forecast future lake conditions based on future climate scenarios.

References

- Anderson, J. and Mustonen, A. 2017. Myrtle Lake Assessment Summary. Minnesota Pollution Control Agency, 23 pp.
- 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.
- Christensen, V.G., Jones, P.M., Edlund, M.B., and Ramstack, J.M. 2010. Water quality (2000–08) and historical phosphorus concentrations from paleolimnological studies of Swamp and Speckled Trout Lakes, Grand Portage Reservation, northeastern Minnesota: U.S. Geological Survey Scientific Investigations Report 2010–5192, 53 p. < <http://pubs.usgs.gov/sir/2010/5192/> >
- 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. 2005. Using Diatom-based Analysis of Sediment Records from Central Minnesota Lakes for TMDL and Nutrient Criteria Development. Final Report to Minnesota Pollution Control Agency, CFMS Contract no. A45276, Amendment 1, 25 pp.
- 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.
- Edlund, M.B., Ramstack Hobbs, J.M., Burge, D.R.L. and Heathcote, A.J. 2016. A Paleolimnological Study of Net Lake and Lac La Belle, Carlton and Pine Counties, Minnesota. Final Report to Minnesota Pollution Control Agency. St. Croix Watershed Research Station, Science Museum of Minnesota, Marine on St. Croix, Minnesota.
- Edlund, M.B., Ramstack Hobbs, J.M., Burge, D.R.L. and Heathcote, A.J. 2019. A Paleolimnological Study of Myrtle Lake, St. Louis Co., Minnesota. Final Report to the Minnesota Pollution Control Agency. St. Croix Watershed Research Station, Science Museum of Minnesota, Marine on St. Croix, Minnesota.
- Edlund, M.B., Ramstack, J.M., Engstrom, D.R., Elias, J.E. and Moraska Lafrancois, B. 2011. Biomonitoring using diatoms and paleolimnology in the western Great Lakes national parks. Natural Resource Technical Report NPS/GLKN/NRTR—2011/447. National Park Service, Fort Collins, Colorado. 196 pp.
<http://science.nature.nps.gov/im/units/glkn/publications.cfm>
- 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 Meeresgebiete. In Dr. L. Rabenhorst's Kryptogrammen-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.
- James, W.F. (2017) Internal phosphorus loading contributions from deposited and resuspended sediment to the Lake of the Woods, *Lake and Reservoir Management*, 33:4, 347-359, DOI: 10.1080/10402381.2017.1312647
- Jeffrey, S.W. and Wright, S.W. 2005. Photosynthetic pigments in marine microalgae: insights from cultures and the sea. In: Subba Rao, D. V. (Ed.). *Algal cultures, analogues of blooms and applications*. Enfield, USA: Science Publishers, pp 33-90.
- Juggins, S., Anderson, N.J., Ramstack Hobbs, J.M. and Heathcote, A.J. 2013. Reconstructing epilimnetic total phosphorus using diatoms: statistical and ecological constraints. *Journal of Paleolimnology*. DOI 10.1007/s10933-013-9678-x.
- Kopáček, 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.
- Patrick, R. and Reimer, C.W. 1966. The diatoms of the United States, exclusive of Alaska and Hawaii, Volume 1-Fragilariaceae, Eunotiaceae, Achnantheaceae, 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 Hobbs, J.M., and M.B. Edlund. 2018. A paleolimnological study of Deer Yard and Poplar Lakes in Cook County, MN. Final report submitted to the Minnesota Pollution Control Agency. St. Croix Watershed Research Station, Science Museum of Minnesota, Marine on St. Croix, Minnesota, 55047.
- Ramstack Hobbs, J.M., M.B. Edlund, A.J. Heathcote and D.R. Engstrom. 2017. A paleolimnological study of Bartlett Lake, Koochiching County, Minnesota. Final report submitted to the Minnesota Pollution Control Agency. St. Croix Watershed Research Station, Science Museum of Minnesota, Marine on St. Croix, Minnesota, 55047.
- 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.
- Renberg, I. and Hansson, H. (2008). The HTH sediment corer. *Journal of Paleolimnology*, 40(2): 655-659.
- Saros, J.E., Michel, T.J., Interlandi, S.J. and Wolfe, A.P. 2005. Resource requirements of *Asterionella formosa* and *Fragilaria crotonensis* in oligotrophic alpine lakes: implications for recent phytoplankton community reorganizations. *Canadian Journal of Fisheries and Aquatic Sciences* 62(7): 1681-1689.
- Schelker, J., K. Eklöf, K. Bishop, and H. Laudon. 2012. Effects of forestry operations on dissolved organic carbon concentrations and export in boreal first-order streams, *J. Geophys. Res.* 117, G01011, doi:10.1029/2011JG001827.
- 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 SiO₂/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. et al. 2019. Diatoms of North America. (diatoms.org). Accessed on 01 July 2019.
- Tomkins, J.D., Antoniadis, 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.

- VanderMeulen, D.D., Lafrancois, B.M., Edlund, M.B., Ramstack Hobbs, J.M. and Damstra, R. 2016. Pairing modern and paleolimnological approaches to evaluate the nutrient status of lakes in Upper Midwest National Parks. *Journal of the American Water Resources Association (JAWRA)*: 1-19. doi: 10.1111/1752-1688.12458
- Vinebrooke, R.D., Dixit, S.S., Graham, M.D., Gunn, J.M., Chen, Y.W. and Belzile, N., 2002. Whole-lake algal responses to a century of acidic industrial deposition on the Canadian Shield. *Canadian Journal of Fisheries and Aquatic Sciences*, 59(3): 483-493.
- Wright, H.E. 1991. Coring tips. *Journal of Paleolimnology* 6: 37-49.

Tables

Table 1. Location (latitude °N, longitude °W) and water depth (m) at seven coring stations and at the buoy deployment sites in Myrtle Lake, St. Louis Co., Minnesota.

Station	Latitude (°N)	Longitude (°W)	Depth (m)
Myrtle_1	48.08182	92.67499	6.2
Myrtle_2	48.07293	92.69687	2.2
Myrtle_3	48.07707	92.68961	2.88
Myrtle_4	48.08084	92.68298	2.95
Myrtle_5P	48.08426	92.67472	4.04
Myrtle_6	48.08557	92.66722	4.05
Myrtle_7	48.08003	92.66282	3.68
Buoy	48.08349	92.67286	4.37

Table 2. Pb-210 date (A.D.), core depth (cm) and sediment accumulation rates (dry mass accumulation rate, DMAR, g/cm² yr) for Myrtle Lake core 5.

Base of Interval (cm)	Date: Base A.D.	Error of Age (±s.d.)	Sediment DMAR (g/cm ² yr)	Error of DMAR (±s.d.)
2	2013.0	1.76	0.0274	0.0014
4	2006.4	1.99	0.0234	0.0013
6	1998.8	2.33	0.0217	0.0014
8	1989.4	2.94	0.0176	0.0014
10	1976.2	4.23	0.0127	0.0015
13	1951.0	2.95	0.0109	0.0009
15	1935.6	2.56	0.0130	0.0010
17	1922.1	2.83	0.0138	0.0012
19	1906.7	4.15	0.0108	0.0013
21	1892.8	5.13	0.0136	0.0022
23	1873.3	9.17	0.0078	0.0019
25	1854.2	14.40	0.0098	0.0048

Table 3. Historical diatom-inferred epilimnetic total phosphorus (DI-TP) for Myrtle Lake core 5. Model error as logTP units reported as root mean square error of prediction (RMSEP).

Sample	log TP	Date (AD)	TP ($\mu\text{g/l}$)	RMSEP
Myrtle_2013	1.45	2013	28.1	0.2064
Myrtle_2006	1.39	2006	24.7	
Myrtle_1999	1.37	1999	23.5	
Myrtle_1989	1.44	1989	27.8	
Myrtle_1976	1.43	1976	26.8	
Myrtle_1968	1.48	1968	30.1	
Myrtle_1959	1.43	1959	27.2	
Myrtle_1951	1.49	1951	30.7	
Myrtle_1943	1.43	1943	27.1	
Myrtle_1936	1.46	1936	28.6	
Myrtle_1922	1.45	1922	28.2	
Myrtle_1914	1.52	1914	33.1	
Myrtle_1900	1.42	1900	26.4	
Myrtle_1883	1.37	1883	23.4	
Myrtle_1864	1.48	1864	30.5	

Table 4. Aerobic or oxic soluble reactive phosphorus (SRP) release rates ($\text{mg/m}^2 \text{ day}$) for paired cores from three stations (3, 5, 7) in Myrtle Lake; Time period represents days (d) used to model SRP release rate.

	Oxic P Releases Rates					
	Station 3		Station 5		Station 7	
	Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2
Time period (d)	0-10	0-10	0-10	0-10	0-15	0-15
SRP release rate, $\text{mg/m}^2 \text{ d}$	0.11	0.18	0.19	0.51	0.23	0.37
SRP release rate, $\text{mg/m}^2 \text{ d}$	mean	0.14		0.35		0.30
	se	0.04		0.16		0.07

Table 5. Anaerobic or anoxic soluble reactive phosphorus (SRP) release rates ($\text{mg/m}^2 \text{ day}$) for paired cores from three stations (3, 5, 7) in Myrtle Lake; Time period represents days (d) used to model SRP release rate.

	Anoxic P Release Rates					
	Station 3		Station 5		Station 7	
	Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2
Time period (d)	2-11	2-11	2-11	2-11	2-11	2-11
SRP release rate, $\text{mg/m}^2 \text{ d}$	1.11	1.67	2.15	3.69	6.38	10.81
SRP release rate, $\text{mg/m}^2 \text{ d}$	mean	1.39		2.92		8.60
	se	0.28		0.77		2.21

Table 6. Shallow Lakes in Northern Lakes and Forests (NLF) Ecoregion, Minnesota, with observed maximum depth (D), percent littoral zone, observed modern total phosphorus, TP ($\mu\text{g/L}$ or ppb) and historical diatom-inferred TP values ($\mu\text{g/L}$ or ppb).

Lake Name	ID	D max (ft)	% littoral	Obs. TP (1990 or current assessment mean)	DI Inferred TP (~ 1800-1900)	Study Name
Dyers	16-0634	23	85	27	21	Ramstack et al. 2003
Forsythe	31-0560	17		23	14	Ramstack et al. 2003
Nine Mile	38-0033	40	97	9	12	Ramstack et al. 2003
Tetagouche	38-0231	20	99	17	14	Ramstack et al. 2003
August	38-0691	19	96	15	17	Ramstack et al. 2003
Shoepack	69-0870	24	82	23	18	Ramstack et al. 2003
Platte	18-0088	23	97	37	23	Edlund 2005
Red Sand	18-0386	23	96	22	64	Edlund 2005
1 st Crow Wing	29-0086	15	100	56	~ 100	Edlund 2005
*Swamp	16-0009	14	100	23	19-25	Christensen et al. 2010
*Speckled Trout	16-0005	11	100	12	11-14	Christensen et al. 2010
*Ek	69-084300	19.7	82	17.1	12.1	VOYA NPS I&M, Edlund et al. 2011
*Peary	69-083300	16.4	100	17.0	13.6	VOYA NPS I&M, Edlund et al. 2011
*Ryan	69-083500	13.1	100	10.0	15.9	Van der Meulen et al. 2016
*Net	58-0038	15	100	40	31.5	Edlund et al., 2016; lake TMDL
*Lac La Belle	09-001100	16.4	?	(2017, 23-32), 60?	14	Edlund et al. 2016
*Bartlett	36-001800	16	96	38	19-20	Ramstack Hobbs et al. 2017
*Deer Yard	16-025300	20	58	10-22	17-21	Ramstack Hobbs et al. 2018
*Myrtle	69074900	20	98	19-50	23-31	Edlund et al. 2019

*DI-TP inferred values represent range or mean DI-TP of all pre-1900 sediment core samples analyzed.

Figures

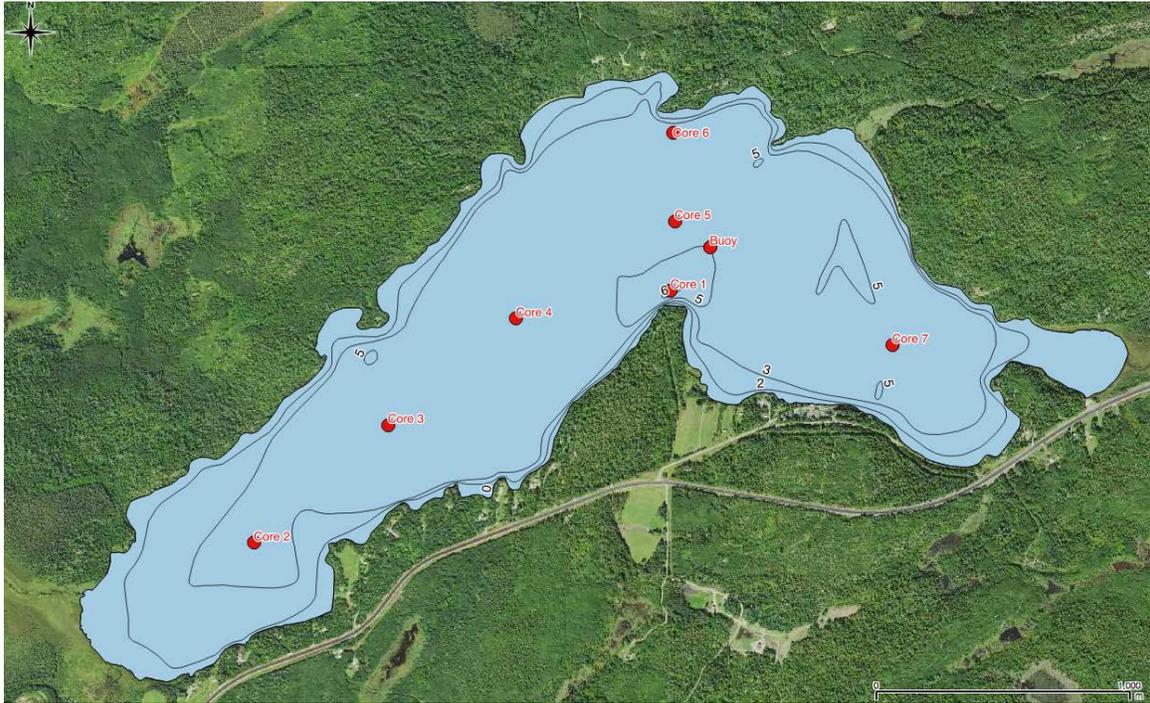


Figure 1. Myrtle Lake, St. Louis County, Minnesota. Coring sites (red circles) and buoy site indicated, bathymetry in meters.

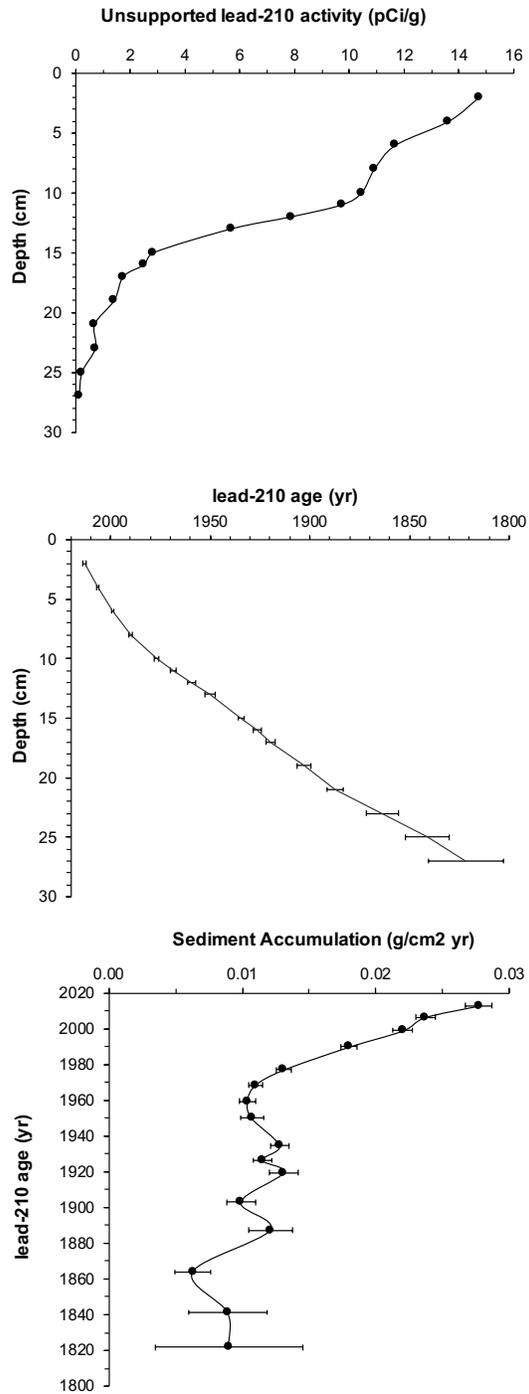


Figure 2. Inventory of ²¹⁰Pb by depth (cm), date-depth (cm) model, and bulk sedimentation rates (dry mass accumulation rates, DMAR, g/cm² yr) by date (AD) for Myrtle Lake. Horizontal bars represent standard error estimates.

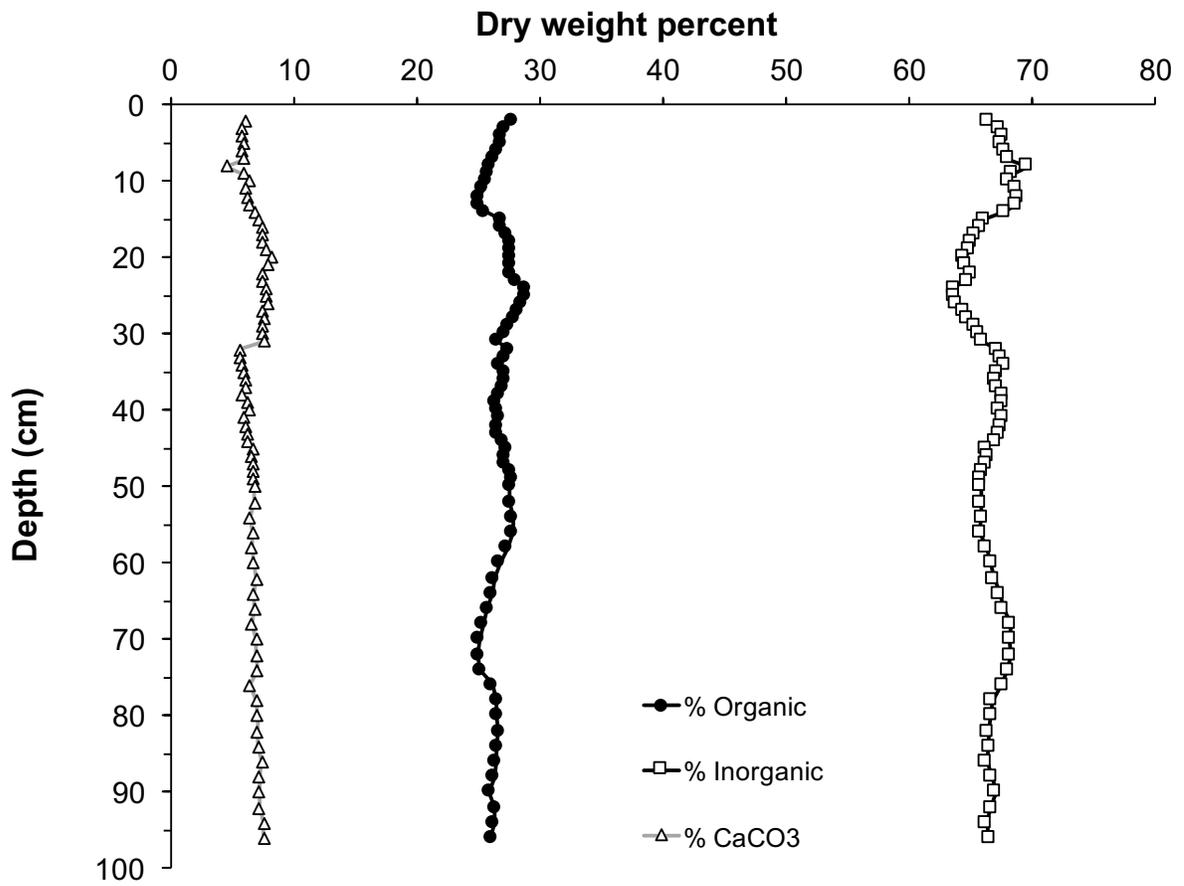


Figure 3. Sediment constituents in Myrtle Lake core 5 based on loss-on-ignition analysis. Inorganics, organics, and carbonates (CaCO_3) by dry weight percent.

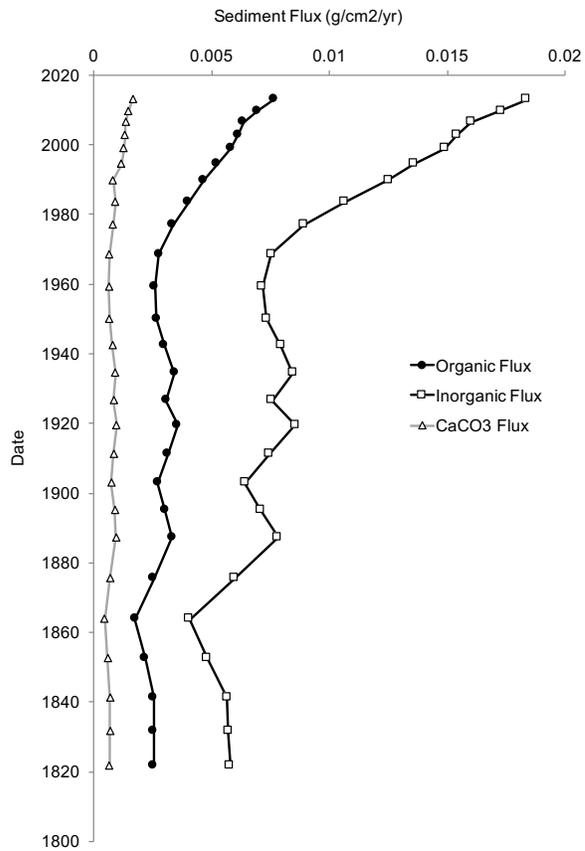


Figure 4. Sediment constituents in Myrtle Lake core 5 based on loss-on-ignition analysis. Inorganics, organics, and carbonates (CaCO₃); flux or dry mass accumulation rates (DMAR; g/cm² yr) of the same constituents.

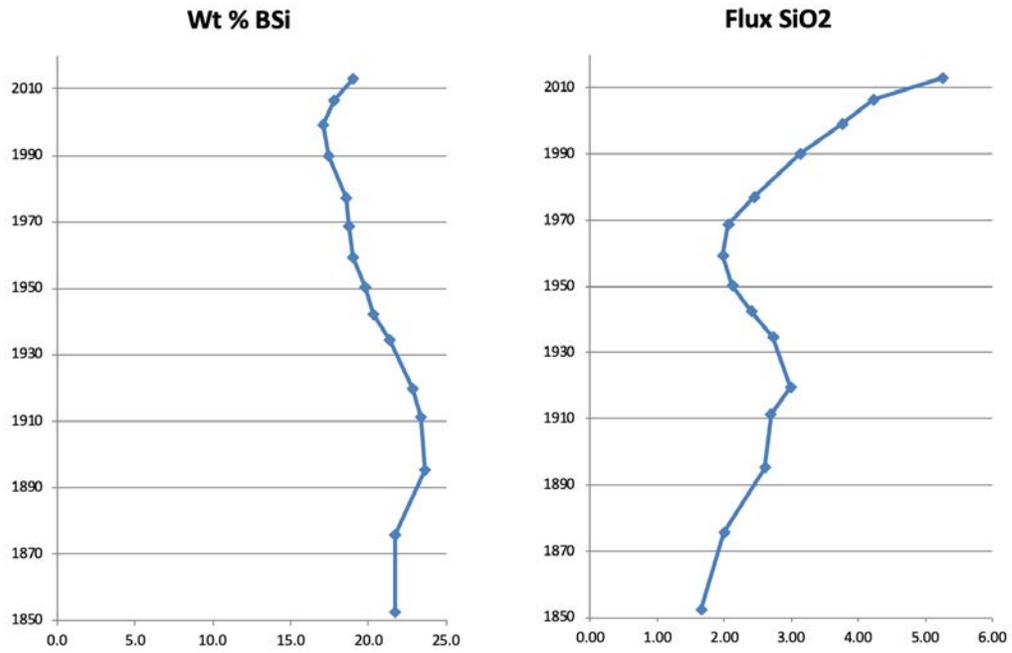


Figure 5. Biogenic silica content (left panel, percent dry weight) and flux or accumulation rate (right panel, mg/cm² yr) by core date for Myrtle Lake.

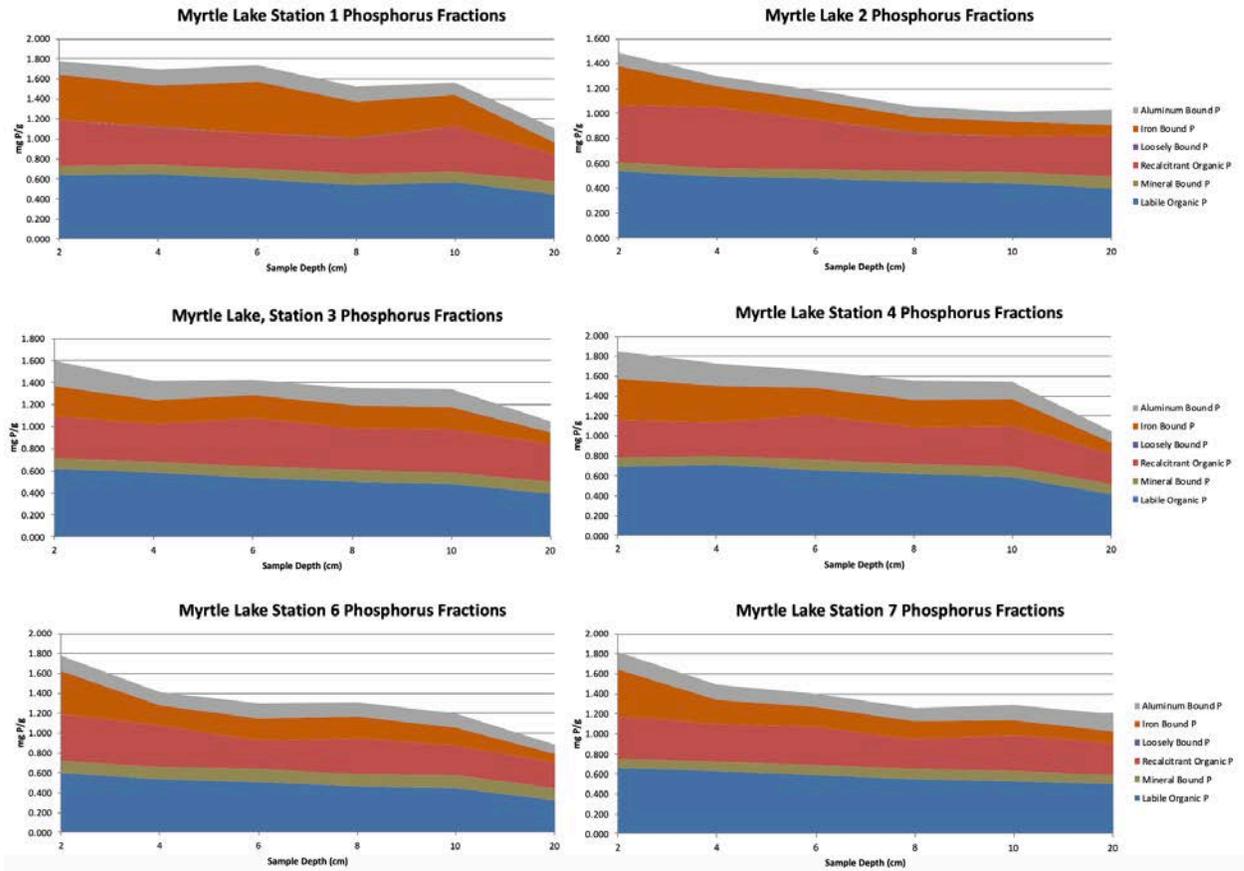
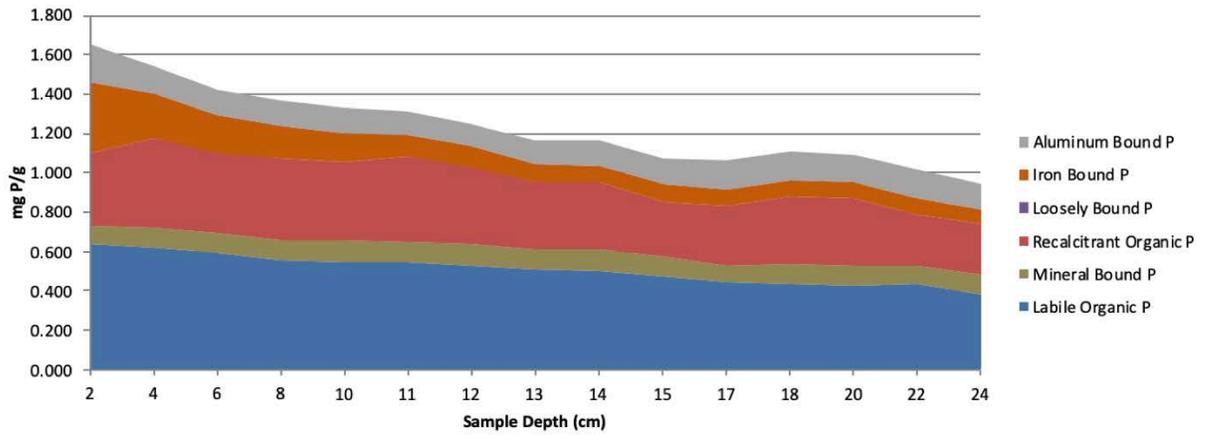


Figure 6. Sediment phosphorus fractions in Myrtle Lake cores including Loosely Bound P, Fe-Bound P, Al-Bound P, Labile Organic P, Mineral-Bound P, and Recalcitrant Organic P. The sum of these fraction equals sediment total phosphorus. P fraction data shown as concentration (mg P/g sediment) by core depth from Stations 1-4, 6-7.

Myrtle Lake, Station 5 Phosphorus Fractions



Myrtle Lake, Station 5 Phosphorus Fractions

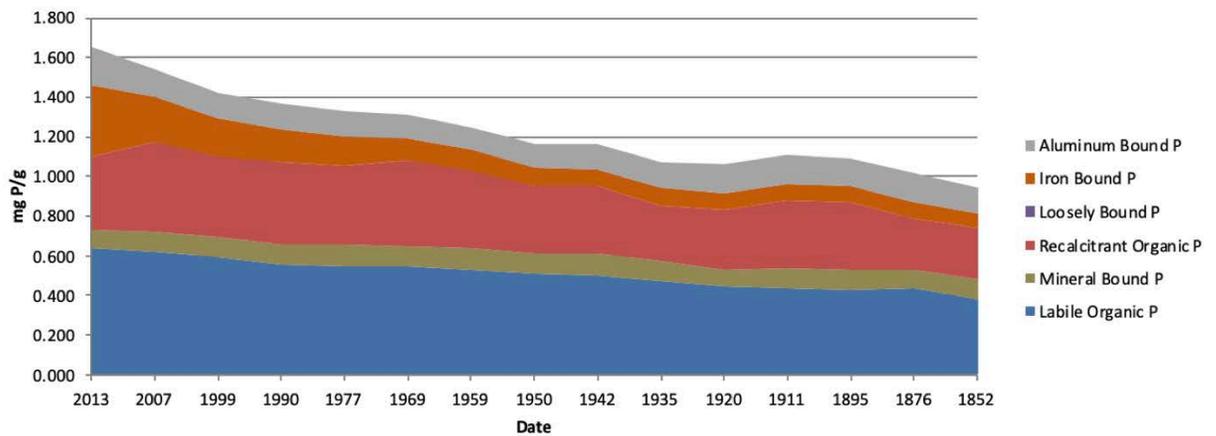


Figure 7. Sediment phosphorus fractions in Myrtle Lake core 5 including Loosely Bound P, Fe-Bound P, Al-Bound P, Labile Organic P, Mineral-Bound P, and Recalcitrant Organic P. The sum of these fraction equals sediment total phosphorus. P fraction data shown as concentration (mg P/g sediment) by core depth (top panel) and core date (bottom panel) from Station 5.

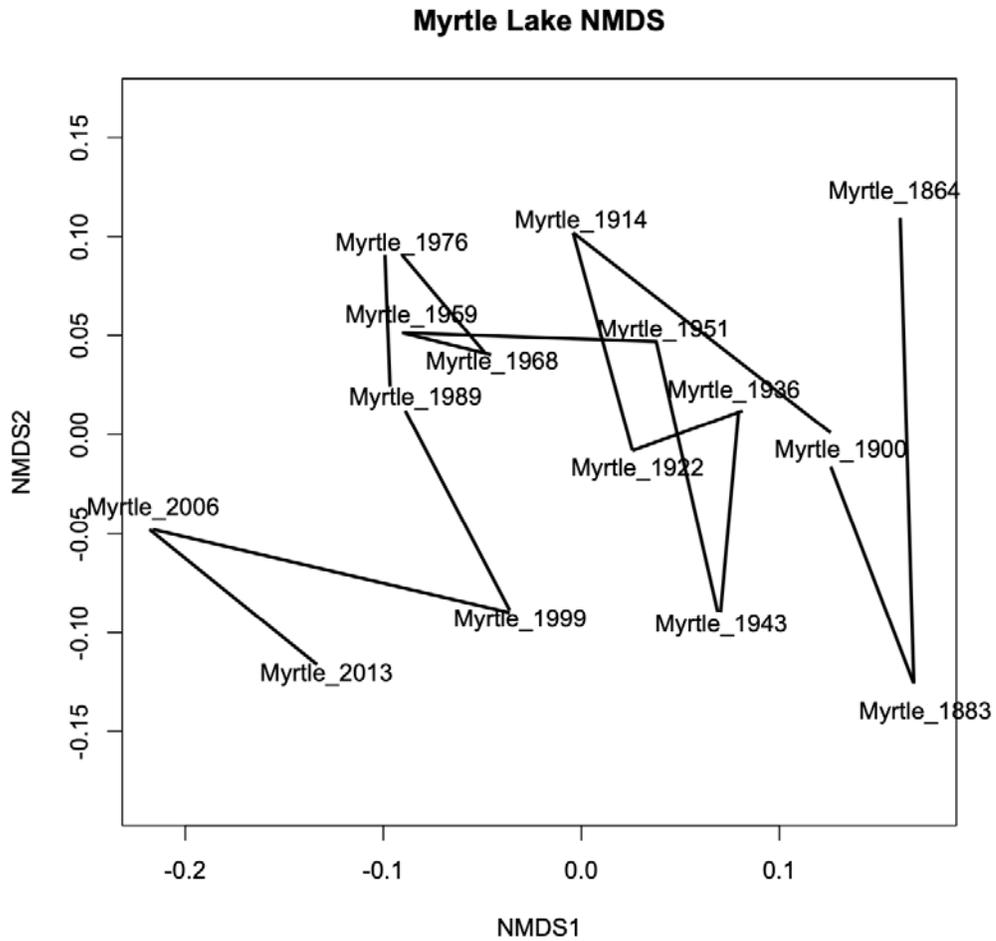


Figure 8. Non-metric Multi-dimensional Scaling (NMDS) ordination of diatom communities (by dated core level) from Myrtle Lake sediment core 5. In general, core levels that plot closer to each other are more similar. For the NMDS, $k=3$ and $stress=0.07369$.

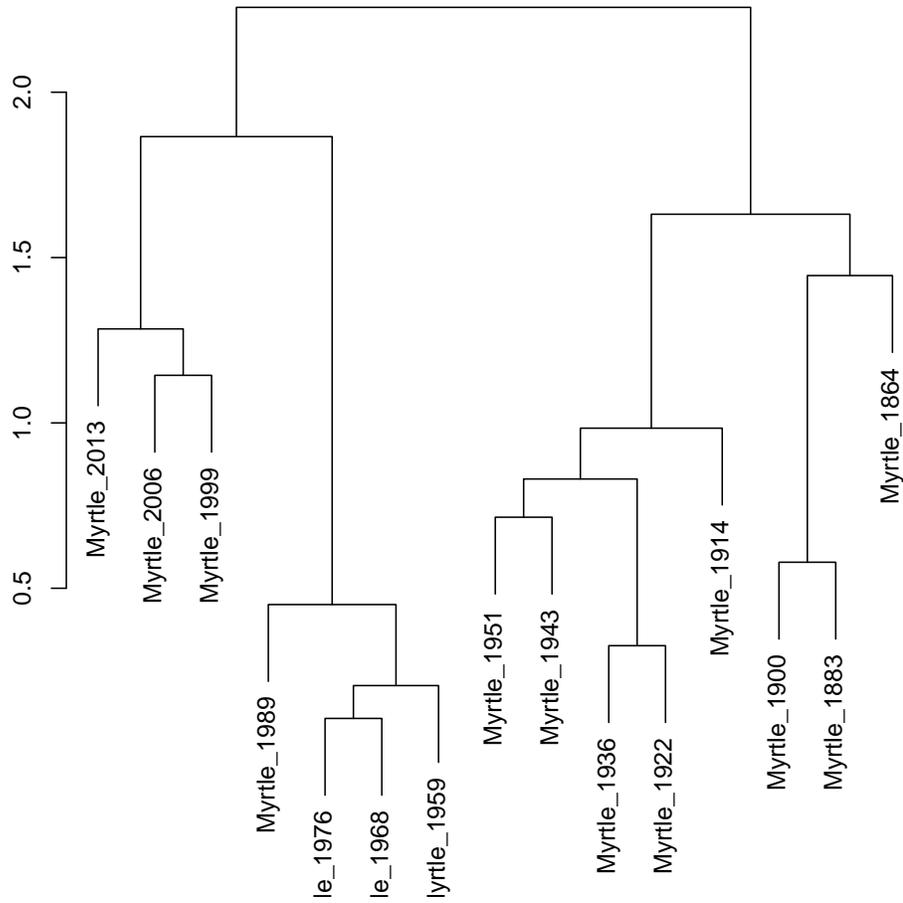


Figure 9. Constrained Cluster Analysis (CONISS) of diatom communities (by dated core level) from Myrtle Lake sediment core 5 based on Euclidean distance. No core clusters are significant when compared with a broken stick model (see text).

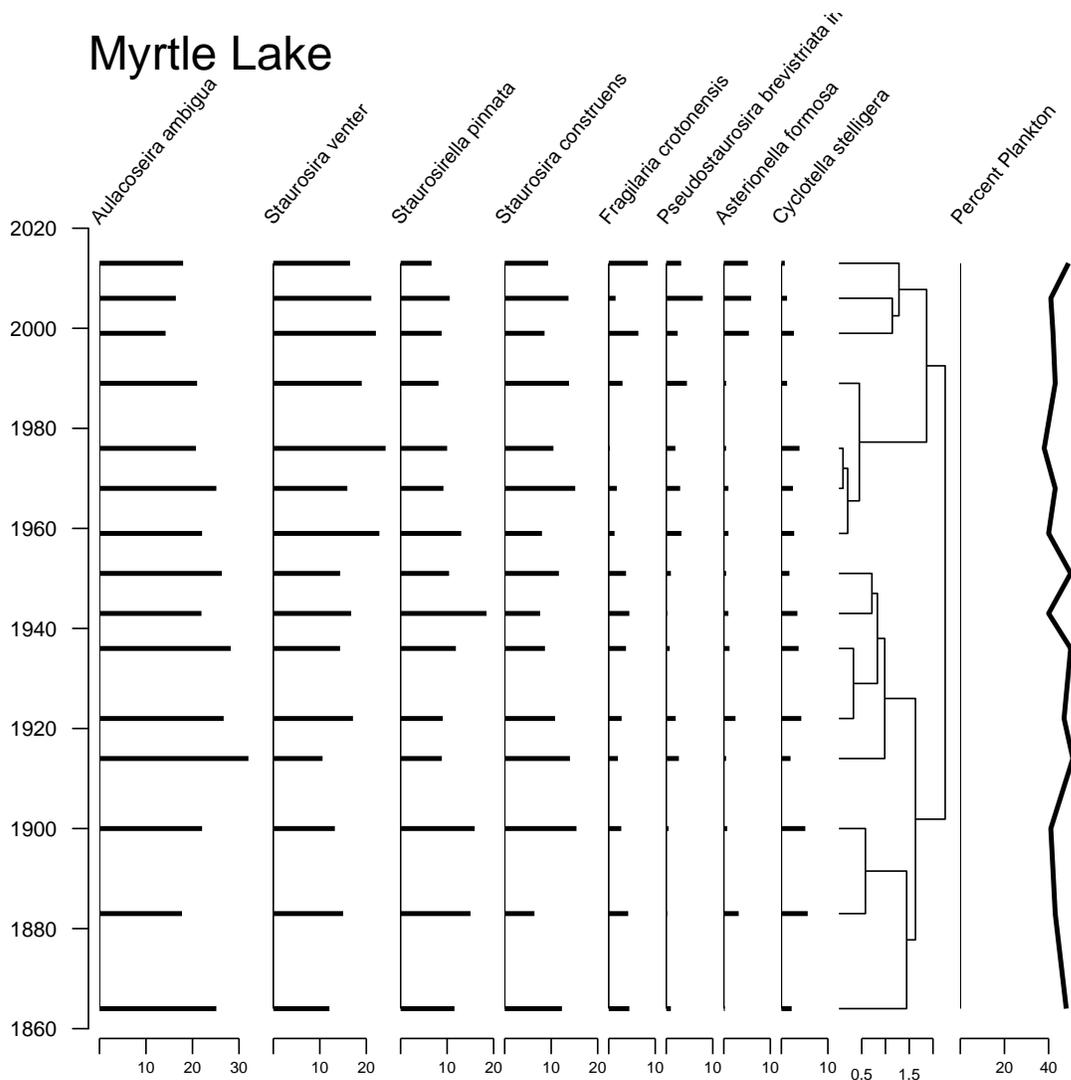


Figure 10. Downcore distribution (by percent abundance) of predominant diatoms in Myrtle Lake sediment core 5. Species shown were present in one or more core levels at greater than 5% abundance. Rightmost panel is percent planktonic diatom species.

CCA, 89 MN Lakes, Myrtle Lake fossil data

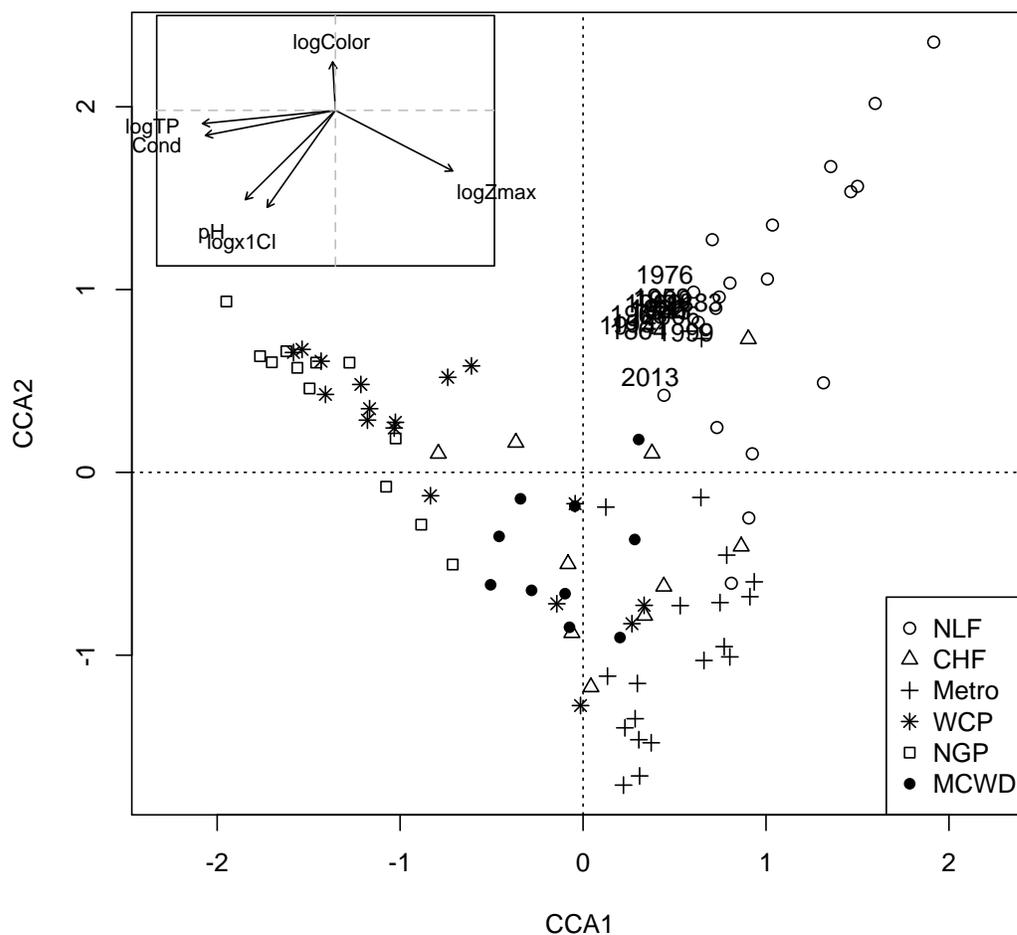


Figure 11. Diatom communities in dated Myrtle Lake core sections passively plotted onto the calibration set of 89 Minnesota lakes. The inset shows the strength and direction of environmental gradients that significantly explain diatom abundance in the calibration set lakes. If the historical diatom communities in Myrtle Lake were responding solely to changes in TP, we would expect them to be aligned with the logTP axis (see text).

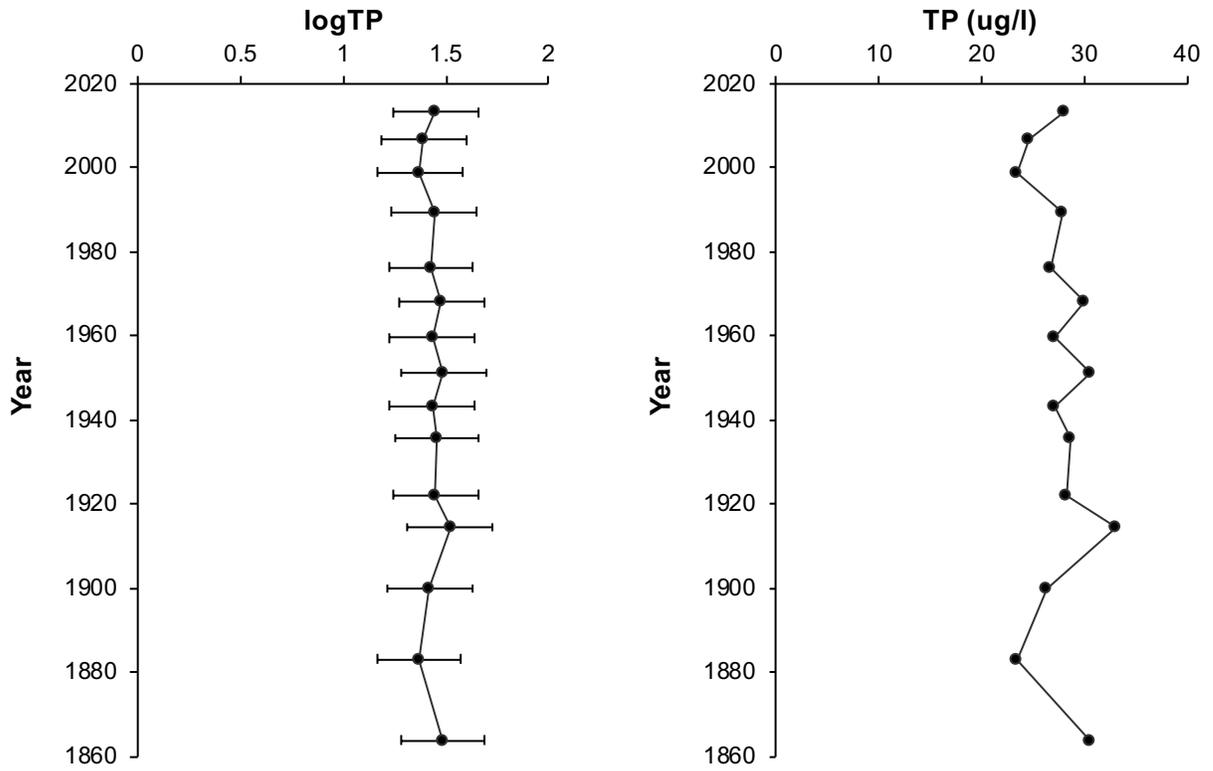


Figure 12. Historical diatom-inferred TP levels for Myrtle Lake. Model reconstructions (left panel) are in log TP units and error bars represent the root mean square error of prediction or the model error estimates of 0.209 logTP units (RMSEP). The back transformed diatom-inferred TP levels are given in the right panel in the more commonly reported units of $\mu\text{g/l}$ or ppb. See text for discussion of validity of this reconstruction.

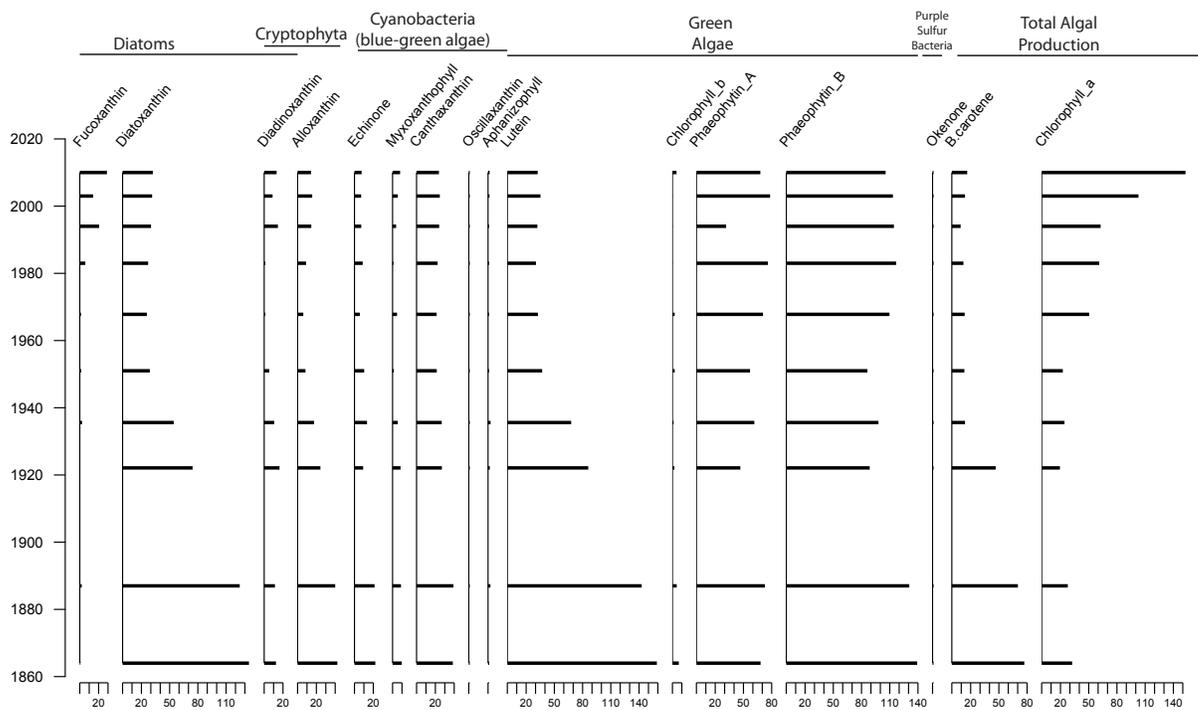


Figure 13. Sediment algal pigments quantified in ten dated core sections from Myrtle Lake (nmol pigment / g total C). The group of algae associated with each pigment is shown along the upper x-axis.

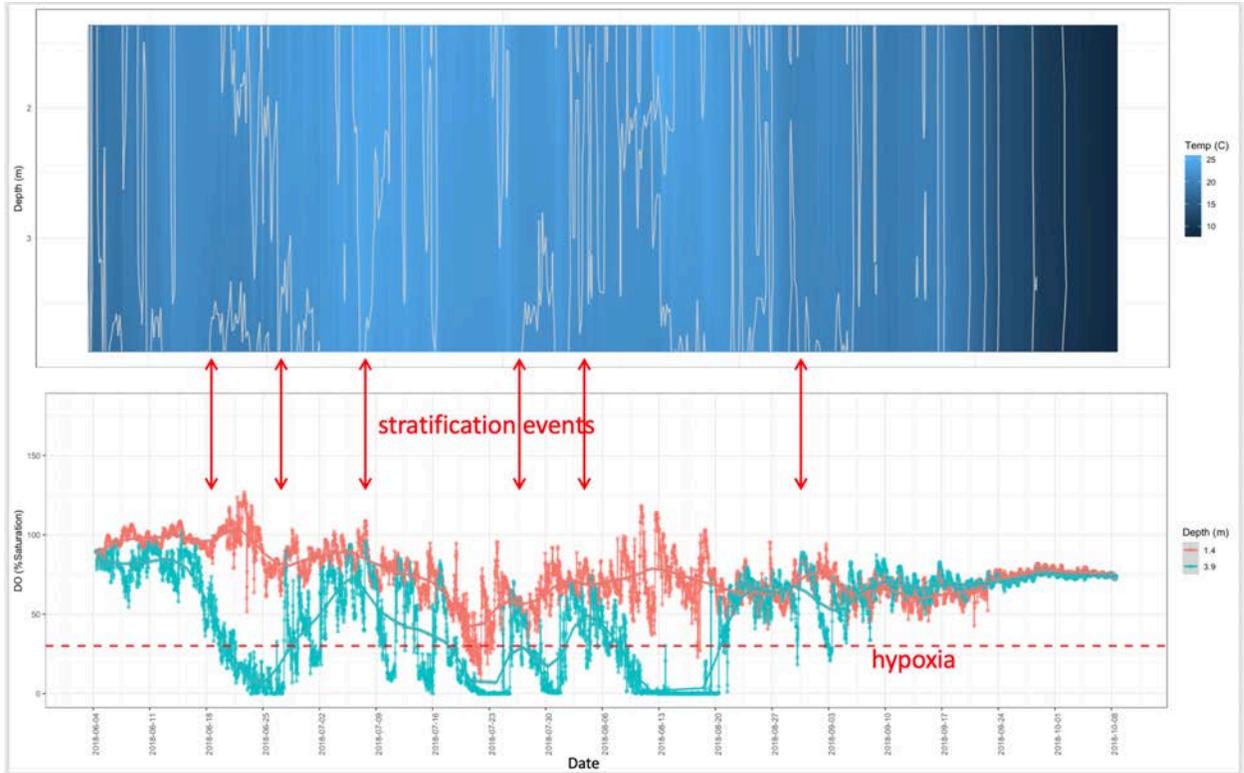


Figure 14. High frequency data from the monitoring buoy deployed near station 5 in Myrtle Lake June-Oct 2018. Buoy data are expressed as temperature isopleths ($^{\circ}\text{C}$, top panel), dissolved oxygen (% saturation) from top (1.4 m deep) and bottom (3.9 m deep) depths. Red dashed line represents hypoxia or $<30\%$ oxygen saturation. Red double-ended arrows indicate multiple summer stratification events that led to rapid bottom hypoxia-anoxia in Myrtle Lake.

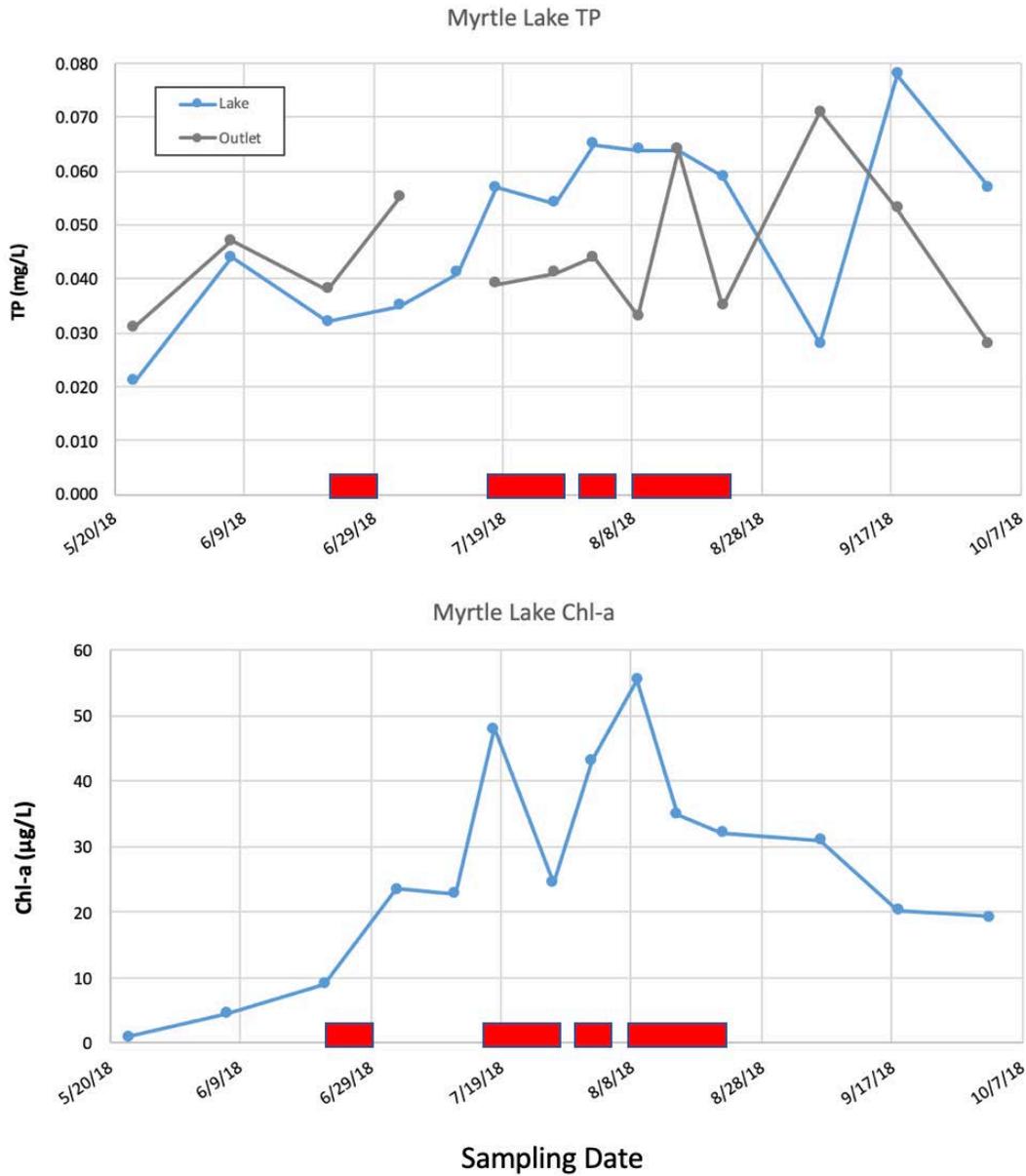


Figure 15. Water quality measured in 2018 from Myrtle Lake (MPCA data). Top panel is total phosphorus (TP) in mg/L, and bottom panel is chlorophyll-a (Chl-a) in µg/L. Red shaded blocks represent periods during summer 2018 when short term stratification events greater than a week long led to hypoxic/anoxic bottom waters conducive to diffusive internal loading. Current Northern Lakes & Forest ecoregion water quality standards are <0.030 mg/L TP and <9 µg/L.

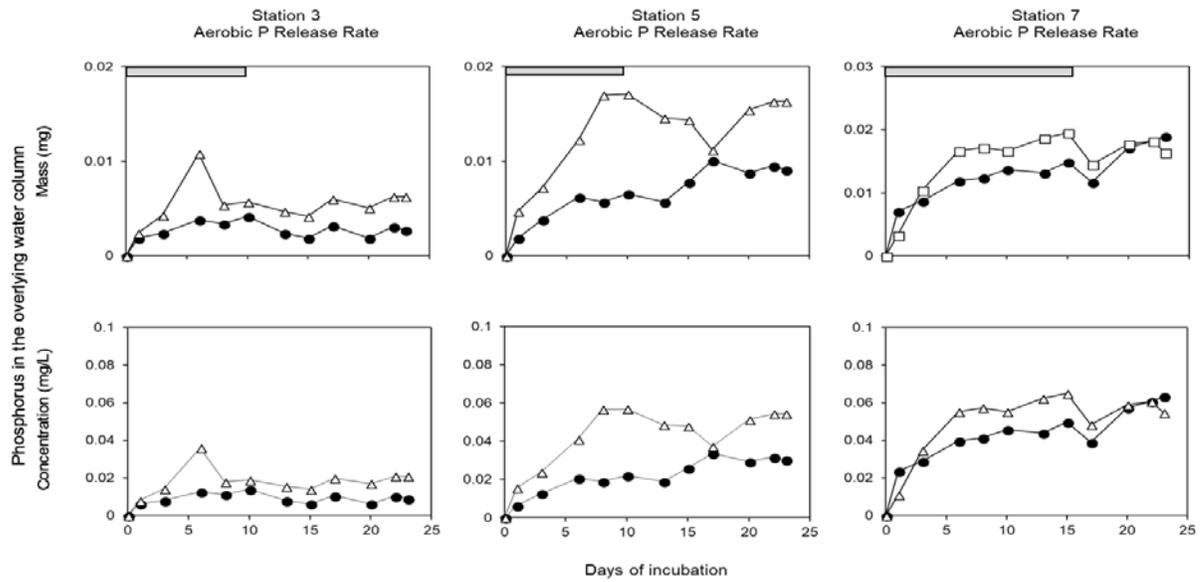


Figure 16. Release of soluble reactive phosphorus by mass (mg; top panels) and concentration (mg/L; bottom panels) during 23 days of paired cores incubated under aerobic or oxic conditions from three stations in Myrtle Lake. The gray bars (top panels) indicate time periods used for calculation of release rates (see Table 3).

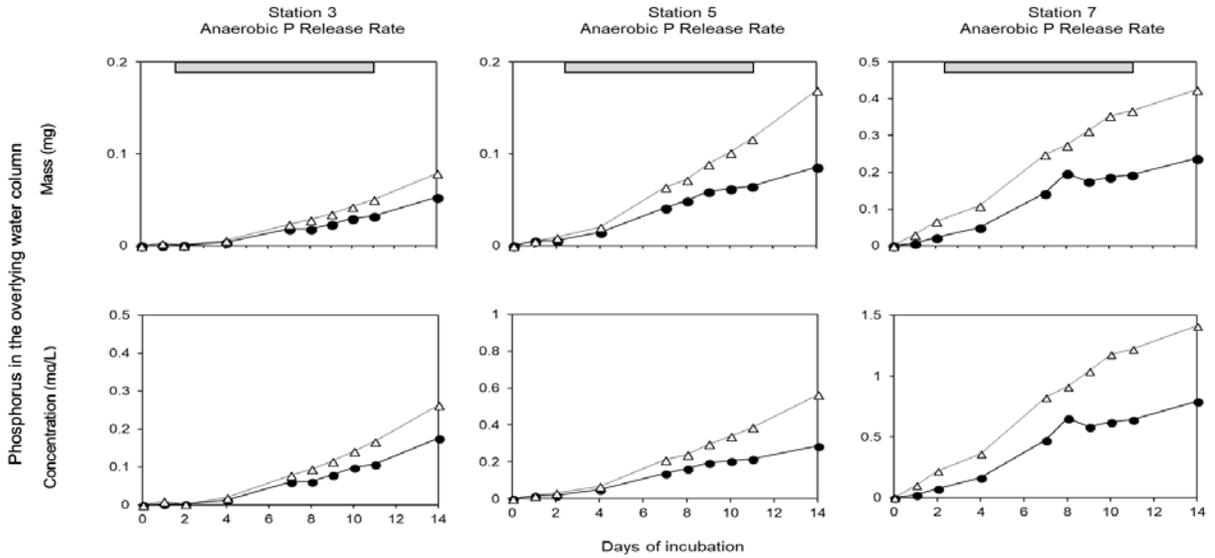


Figure 17. Release of soluble reactive phosphorus by mass (mg; top panels) and concentration (mg/L; bottom panels) during 14 days of paired cores incubated under anaerobic or anoxic conditions from three stations in Myrtle Lake. The gray bars (top panels) indicate time periods used for calculation of release rates (see Table 4).