



## Historical water quality and ecological change in Spring Lake, Scott Co., MN

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**SUMMARY**

1. In this project, paleolimnological techniques were used to reconstruct historical (pre-settlement to present day) populations of algae and total phosphorus concentrations in Spring Lake, Scott Co., Minnesota.
2. A sediment core was collected from the lake and analyzed for sediment composition, diatom subfossils and algal pigments. Subfossil diatoms in the sediments were used to reconstruct / model historical total phosphorus (TP in ppb) concentrations and algal pigment concentrations were used to infer production of different algal groups over the last 200 years.
3. Sediment accumulation at the core site increases beginning in the early 1900s, reaching a maximum of around 7 times historical rates at 1980. It appears that sediment accumulation is being driven largely by the precipitation of carbonate minerals in the lake. Furthermore, the abundance of carbonate is related to the algal or primary production of the lake.
4. The diatom assemblages and sediment pigment concentrations indicate that Spring Lake has been a nutrient-rich lake at least for the last 200 years. The presence of cyanobacteria pigments (including pigments from potentially toxic forms) is particularly relevant to this interpretation, as these algae are responsible for large blooms in Spring Lake today.
5. A robust model of water TP concentrations was established using the historical diatom assemblages. Diatom inferred – TP (DI-TP) shows that historical concentrations (pre-settlement ) were in the range of 60 ppb  $\pm$  5 ppb. The trend of DI-TP over time also shows the progressive nutrient enrichment of the lake, overlapping with the range of modern measured TP concentrations for the last 10-15 years.

## INTRODUCTION

Within the glaciated regions of the Upper Midwest, lakes feature prominently in the landscape and are a valued resource for tourism, municipalities, home and cabin owners, recreational enthusiasts, and wildlife. Current and historical land and resource uses around the 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.

With any lake management plan it is important to have a basic understanding of natural fluctuations within the system. Reliable long-term data sets, on the order of 30 - 50 years, are generally not available for most regions of the country. Through the use of paleolimnological techniques and quantitative environmental reconstruction, we can estimate past conditions, natural variability, timing of changes, and determine rates of change and recovery. This type of information allows managers and researchers to put present environmental stresses into perspective with the natural variability of the ecosystem. It can also be used to identify response to and recovery from short-term disturbances. In this project, paleolimnological techniques were used to reconstruct the algal communities and trophic history of Spring Lake, Scott CO., MN. Results provide a management foundation through the determination of the natural or reference condition of this lake and the reconstruction of ecological changes that have occurred in the lake during the last 150-200 years.

Current and historical land and resource uses around Prior Lake, Scott County have led to the eutrophication of Spring and Upper Prior Lakes. Spring Lake is impaired for nutrients, particularly total phosphorus (TP) and was listed in 2002 under Minnesota's 303(d) List of Impaired Waters for recreation use (Wenck, 2011). Current summer TP concentrations are near 100 ppb and chlorophyll *a* are near 60 ppb, classifying the lake as hyper-eutrophic. In the past the lake has also suffered from excessive macrophyte growth, in particular from curly leaf pondweed and Eurasian milfoil. Spring Lake and additional lakes within its watershed have received a number of ecological assessments over the past decade. An assessment of the internal P loading to the lake estimates that between 43% and 78% of the annual P loading to the lake is from the sediments (Wenck, 2011). Previous sediment coring of Spring Lake has also shown that labile P (or loosely-bound P) has increased approximately 8 times from around 1820 to today, however it is unclear whether this is directly proportional to the external P load and what the ecological consequences of this increase has been.

The primary aim of this project is to use paleolimnological analysis of a dated sediment core from Spring Lake to reconstruct ecological histories using biogeochemistry, sediment accumulation, diatom-inferred total phosphorus (DI-TP), and algal pigments as biological indicators. There is currently a total maximum daily load (TMDL) plan in place for the Spring Lake watershed and implementation is underway. In an effort to further understand pre-settlement conditions, and historical lake response to land use and past management, we modeled changes in water column TP concentrations over the last 150 years using diatom assemblages. Diatoms quite often make up the main type of algae in a lake and therefore changes in diatom community structure are symptomatic of algal changes in response to water quality. Multivariate analyses, diatom-based transfer functions, and comparison of diatom assemblages with an 89 Minnesota lake data set were used to establish pre-settlement TP concentrations and changes in trophic conditions. Diatoms have been widely used to interpret environmental conditions in lakes (Smol and Stoermer, 2011). Many species are sensitive to specific water conditions and are useful as bioindicators. Over the past 20 years, statistical methods have been developed to estimate quantitative environmental parameters from diatom assemblages. These methods are statistically robust and environmentally sound. They have been used successfully in reconstructing a wide variety of environmental parameters including pH, total phosphorus (TP), and salinity (e.g. Fritz et al. 1991; Hall and Smol 1992; Ramstack et al. 2003). In the state of Minnesota, diatom analysis has been used as one line of evidence for developing nutrient criteria (Heiskary and Wilson 2008) and lake specific nutrient standards (Edlund and Ramstack 2007).

While diatoms are an important component of the lake algae, other groups of algae can be ecologically

important in eutrophic lakes (e.g. blue-green algae or cyanobacteria). The primary pigments (chlorophylls, carotenoids, and their derivatives) of lake algae are often reliably preserved in lake sediments over time (Leavitt and Hodgson, 2001). The concentration of these pigments is directly proportional to the abundance of each algal group. Whereas the relative percent changes in diatom communities is an effective measure of water quality over time, whole lake algal changes can inform us about the absolute changes in algal production and the historical presence of nuisance algae, such as blue-green algae.

## **METHODS - SEDIMENT CORING AND SEDIMENT COMPOSITION**

A sediment core was collected in February, 2012 by SCWRS and the Department of Geology, University of St. Thomas using a modified piston corer with a clear polycarbonate tube (Figure 1; Wright, 1991). The core was covered in tin foil following recovery to prevent the photo-oxidation of algal pigments and transported to SCWRS with sufficient overlying lake water to preserve the sediment-water interface. The entire length of the core was subsampled at 0.5 cm resolution. Subsamples were taken from regular intervals throughout the core for loss-on-ignition (LOI) analysis to determine bulk and dry density and dry weight percent of organic, carbonate, and mineral material. Sediment subsamples were heated at 105°C to determine dry density, then sequentially heated at 550°C and 1000°C to determine organic and carbonate content from post-ignition weight loss, respectively. Material fluxes were also calculated for the different components of the sediment by multiplying the percent composition by the sediment accumulation rate (g/cm<sup>2</sup>/yr), which is described in the subsequent section.

## **METHODS – SEDIMENT DATING**

A previously collected and dated sediment core (2009; Czeck, 2010) from Spring Lake was used to establish an age-depth model or sediment dates for the core used in this investigation. The dating approach relies on the analysis of 16-20 sediment intervals for lead-210 activity. The activity is then modeled using the known radioactive decay rate of lead-210 to determine age and sediment accumulation rate for the past 150-200 years. Lead-210 was measured by lead-210 distillation and alpha spectrometry methods, and dates and sedimentation rates were determined according to the c.r.s. (constant rate of supply) model (Appleby and Oldfield 1978). Dating and sedimentation errors were determined by first-order propagation of counting uncertainty (Binford 1990). In order to confirm that consistent sedimentation occurred between the 2009 and 2012 sediment cores, the dry bulk density of the sediment was compared downcore (Figure 2a). Specific depths were used to anchor the existing 2009 age-depth model to the new core and establish a complete chronology for the 2012 core. Sediment accumulation rate at the core site was established using the previous age-depth model (Figure 2b)

## **METHODS - DIATOM AND NUMERICAL ANALYSES**

Fifteen samples were analyzed for subfossil diatoms. Diatoms samples were prepared by placing approximately 0.25 cm<sup>3</sup> of homogenized sediment in a 50 cm<sup>3</sup> 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% hydrogen peroxide and heating for 3 hours in an 85°C water bath. After cooling, the samples were rinsed with distilled deionized water to remove oxidation byproducts. Aliquots of the remaining material, which contains the diatoms, were dried onto 22x22 mm #1 coverglasses, which were then permanently attached to microscope slides using Zrax mounting medium. Diatoms were identified along random transects to the lowest taxonomic level under 1250X magnification (full immersion optics of NA 1.4). A minimum of 400 valves was counted in each sample. Abundances are reported as percentage abundance relative to total diatom counts. Identification of diatoms used regional floras (e.g. Patrick and Reimer 1966, 1975) and primary literature to achieve consistent taxonomy.

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. The sediment record of diatom assemblages through time was analyzed for significant shifts or changes based on the dissimilarity between samples,

otherwise called cluster analysis. This was carried out in a manner to constrain the analysis to time or depth in order to maintain the stratigraphic integrity of the sediment record. The approach is similar to that used by Grimm (1987). When results are compared with a random model, significant changes in the diatom community can be identified from those that may occur by chance.

Downcore diatom communities were also used to reconstruct historical epilimnetic phosphorus levels. A transfer function for reconstructing historical 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 deshrinking 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=0.208) because the same data are used to both generate and test the WA model. 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 backtransformed values, to TP in  $\mu\text{g/l}$ .

## **METHODS – ALGAL PIGMENT ANALYSES**

Sediment pigment concentrations were quantified by Dr. Rolf Vinebrooke at the University of Alberta, Canada, using reverse-phase high-pressure liquid chromatography (HPLC) (Vinebrooke et al. 2002). Subsamples from Spring Lake were freeze-dried and stored in a freezer under nitrogen to prevent degradation of the pigments until shipping to the lab. Pigments were first extracted from freeze-dried sediments using an acetone:methanol solution. Extracts were then filtered (0.2- $\mu\text{m}$  pore nylon), dried under  $\text{N}_2$ , 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<sup>®</sup> 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 et al. (2005) was consulted as a key reference for taxonomically diagnostic pigments.

## **RESULTS AND DISCUSSION - DATING AND SEDIMENTATION**

There is excellent agreement in the sediment dry bulk density trends between the 2009 and 2012 (Figure 2). Based on this, the adjustment of the existing age-depth model to the 2012 core was straightforward and reliable. The trend of sediment accumulation at the core site is fairly low and stable from the mid to the late-1880s, ranging from 0.02 to 0.03  $\text{g/cm}^2/\text{yr}$  (Figure 2b). The rate rises steadily in the 1900s, and reaches a peak of 0.14  $\text{g/cm}^2/\text{yr}$  at around 1980, before declining slightly to 0.11  $\text{g/cm}^2/\text{yr}$  at 1990 and then increasing again through the 2000s. The post-1980 period represents a sediment accumulation rate approximately seven times higher than it was in the 1800s.

## **RESULTS AND DISCUSSION – SEDIMENT COMPOSITION OVER TIME**

Changes in sediment composition in Spring Lake over time shows a progressive increase in carbonates and decrease in organic matter beginning in the early 1800s (Figure 3). Mineral inputs to the sediment change very little over the last 150-200 years. The concentration of carbonates in the sediment begins to exceed pre-settlement or background values in the early 1900s. It is unclear whether the carbonates are being formed within the lake or being washed in from watershed. However given that mineral material, which would be largely from the watershed, has remained fairly constant it would seem that the carbonates are formed within the lake. The mechanism by which this occurs can be related to algal productivity and lake temperature. Spring Lake can be considered alkaline with an average pH of 7.7 (ranging from 6.6 to 9.3 over the last 7 years). In alkaline lake systems as the  $\text{CO}_{2[\text{aq}]}$  is consumed during

photosynthesis, the inorganic carbon can become predominately bicarbonate ( $\text{HCO}_3^-$ ) or carbonate ( $\text{CO}_3^{2-}$ ). Under these conditions carbonates can readily combine with  $\text{Ca}^{2+}$  to form  $\text{CaCO}_3$ , or calcite; in warm summer lake water the solubility of calcite decreases leading to a solid calcite crystal in the water which is then deposited on the lake bottom. Calcite is more than likely the type of carbonate deposit found in Spring Lake. During significant peaks in productivity  $\text{CaCO}_3$  can be visible in the water column, giving these events the name “whiting events”. To further assess whether primary production is leading to carbonate precipitation in Spring Lake we can look at the linear relationship between %  $\text{CO}_3$  in sediment and the pigment concentration for total algal production and %  $\text{CO}_3$  in sediment and the historical TP concentrations (results and discussion in subsequent sections). In both cases we find a significant positive linear relationship with % $\text{CO}_3$  and algal production ( $r = 0.51$ ;  $p = 0.05$ ) and historical TP concentrations ( $r = 0.70$ ;  $p = 0.004$ ), suggesting that carbonate deposition is driven by primary production.

When we look at the material fluxes of the sediment to the core site (black lines on Figure 3) it appears that carbonate deposition is the main driver of sediment accumulation. This is also confirmed through a multiple linear regression between sediment accumulation rate and sediment composition, where carbonates are strongly significantly positively correlated ( $p < 0.001$ ), organics are negatively correlated ( $p = 0.003$ ) and mineral inputs are not related at all.

## RESULTS AND DISCUSSION - DIATOM COMMUNITIES

The stratigraphic diagram shows the predominant diatoms whose abundances are driving the shifts in the community assemblage (Figure 4). Many of the predominant diatom species found in the Spring Lake core are indicators of eutrophic nutrient concentrations (e.g. *Stephanodiscus* spp., *Fragilaria crotenensis* and *Aulacoseira granulata*), while *Aulacoseira ambigua* and *Fragilaria capucina* var. *mesolepta* are indicators of mesotrophic conditions. The assemblages are dominated by a planktonic flora with the presence of some tychoplanktonic or benthic species (*Staurosirella pinnata*, *Staurosira construens*, and *Pseudostaurosira brevistriata*). In general, the diatom communities change very little over the last ~200 years, with indicators of elevated nutrient conditions prior to European settlement of the area (~1850 - 1880). The production of chrysophyte algae (*Chrysophyceae*) was significantly greater historically as detailed by the abundance of heterocysts in the sediments. Chrysophytes are planktonic and the decrease in the concentration of them since settlement may represent competition from other planktonic algae (including diatoms and cyanobacteria) under more nutrient rich conditions. There is only one significant shift in the diatom communities, which occurs around 1985. The few benthic species decrease in abundance, while *Stephanodiscus niagarae* and *Aulacoseira ambigua* increase. This transition suggests a further increase in nutrient concentrations in Spring Lake and / or a loss of benthic habitat due to turbidity. At the time of this transition diatom production (concentration) increases dramatically.

## RESULTS AND DISCUSSION - PHOSPHORUS RECONSTRUCTION

In order for a diatom-inferred total phosphorus (TP) reconstruction to be meaningful, changes in the diatom community assemblage over time must be primarily driven by changes in TP concentrations, as opposed to other factors that could drive community change such as pH, light penetration, and habitat availability. One way to evaluate TP as a driver of change in Spring Lake is to project the core sections on the MN calibration set (the model 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 demonstrates that most of the change in the Spring Lake core follows the TP gradient (Figure 5), which is closely correlated with Axis 1. Another way to evaluate the 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 (Juggins et al. 2013). In Spring Lake, this analysis shows that the fraction of the maximum explainable variation in the diatom data that can be explained by TP is 0.83. An additional means to test



the validity of a TP reconstruction is to see if the DI-TP values are correlated with the first or second axis of an unconstrained ordination. In Spring Lake we find a strong negative correlation between the first axis and DI-TP ( $r=-0.87$ ;  $p < 0.001$ ), adding further validation to the TP reconstruction.

The total phosphorus (TP) reconstruction shows small fluctuations in TP since the early-1800s; the reconstruction is presented as back-transformed values to  $\mu\text{g/l}$  or ppb (Figure 6). The TP reconstruction suggests that Spring Lake was historically quite nutrient rich, probably existing in a eutrophic state prior to human settlement in the area. The reconstruction also tracks increases of TP in Spring Lake into the present monitored range of concentrations measured during the summer over the last ~ 10 -15 years. Currently the total maximum daily load TP standard set for Spring Lake is 40 ppb (Wenck, 2011), however the sediment TP-reconstruction suggests that a more realistic standard may be 60 ppb ( $\pm 5$  ppb for the historical range of the data).

## RESULTS AND DISCUSSION – HISTORICAL ALGAL COMMUNITIES AND PRODUCTION

Algal pigments deposited in the sediments of Spring Lake were successfully quantified to give an idea of the historical concentrations or production of different algal groups (Figure 7). Only those pigments which were predominant in the sediments are shown. Interestingly, diatom carotenoids were not recorded in measurable amounts, suggesting that they are not one of the main groups of algae in the lake. By far the most dominant type of algae is the blue-greens or cyanobacteria. In fact cyanobacteria have been present in Spring Lake prior to settlement, as shown by concentrations of zeaxanthin (Figure 7). This finding is complementary to the result that Spring Lake was historically quite nutrient-rich because cyanobacteria tend to flourish in eutrophic waters. Pigments from the cyanobacteria could also be further attributed to different types, where there is evidence that potentially toxic forms (myxoxanthophyll) were also present at around 1900 and that bloom forming pico-cyanobacteria (canthaxanthin) were present in the late-1800s. The most reliable measure of total algal production we found was  $\beta$ -carotene, which details increasing algal production starting in the late-1800s, with two peaks occurring during the 1930s and post-2000. The peak during the drier climatic period of the 1930s is interesting, as it appears driven by hydrologic changes (less groundwater and surface water inputs) and possibly warmer temperatures typical of the ‘Dust Bowl’ era (Schubert et al., 2004). The DI-TP concentrations do not suggest that there was further nutrient enrichment of Spring Lake during the 1930s. The modern peak in algal production seems driven by increasing nutrient concentrations as the DI-TP and measured TP during this period classify the lake as hyper-eutrophic. Lastly, there are significant concentrations of the pigment astaxanthin, which is attributable to zooplankton and suggests that populations of zooplankton have increased and decreased over time with fluctuations in algae.

## CONCLUSIONS

This study of the paleoecology and historical phosphorus concentrations of Spring Lake over the last 200 years reveals that the long-term condition of the lake is nutrient-rich, probably meso – to eutrophic with blooms of cyanobacteria. Over the last ~200 years the lake diatom communities have actually changed very little, being dominated by planktonic eutrophic species. There is a single significant shift in the diatom communities occurring around 1985, a time when the lake was increasingly eutrophic and perhaps light availability became an issue, shading the benthic flora. When we compare the production of diatoms with other algal groups over time, diatoms are not the most predominant group. Historically, cyanobacteria are the most common type of algae found in Spring Lake. The reliable reconstruction of TP concentrations suggests that background is around  $60 \pm 5$  ppb.

The sediment accumulation rate at the location we cored in Spring Lake has experienced some significant changes over the last 200 years. Beginning in the early 1900s the rate of sediment accumulation increases monotonically to a peak at around 1980, which is seven times greater than historical rates. Based on the composition of the sediment this increase seems due to an increase in carbonate precipitation within the lake. This conclusion is supported by strong relationships between the carbonate concentrations and algal production and historical TP concentrations. Overall, the paleoecological record



presented here shows the steady progression of a historically nutrient-rich lake to a nutrient impaired lake. This slow steady change in the lake began in the early 1900s and seems to have peaked or reached the current threshold in the early 1980s.

## ACKNOWLEDGEMENTS

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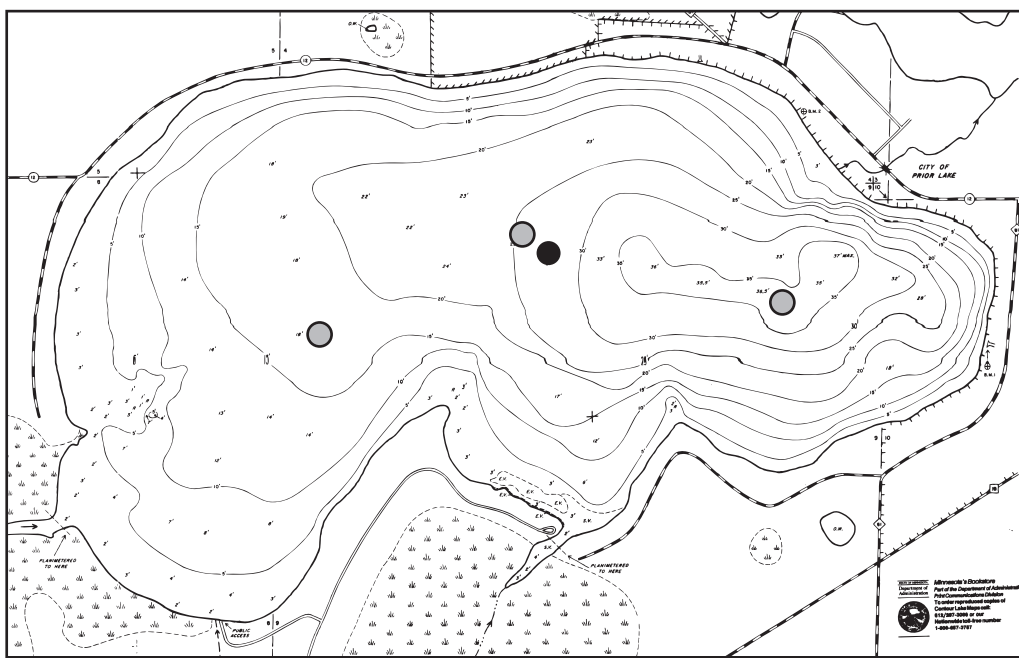


Figure 1: Spring Lake bathymetry map showing sediment core location from this study (black circle) and previous sediment cores (Czeck, 2010; grey circles). The age-depth model from the 2009 sediment core nearest to the 2012 one was used to infer sediment dates.

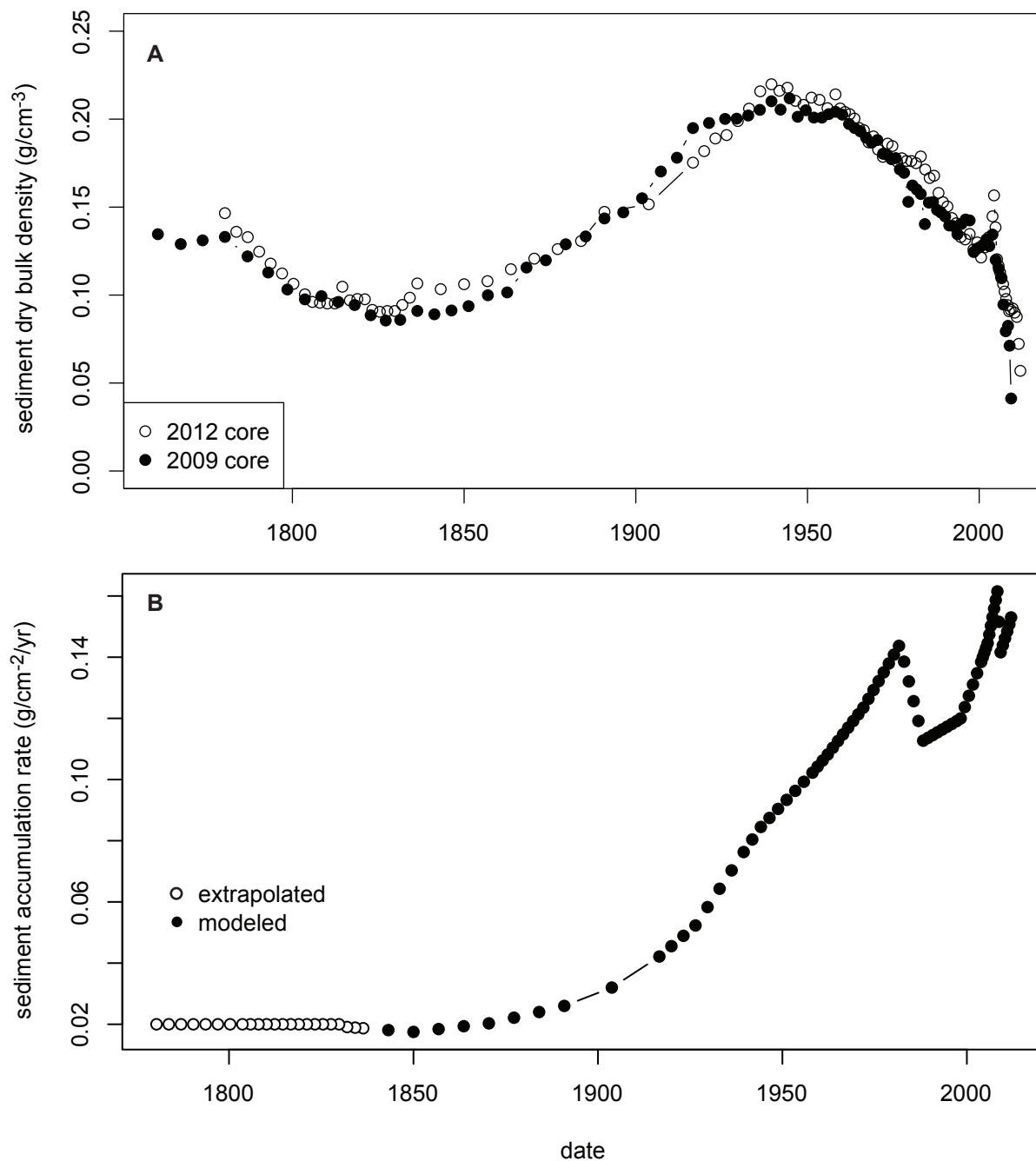


Figure 2: Upper panel shows the sediment dry bulk density measurements from the 2009 and 2012 cores. This strong relationship was used to infer sediment dates from the lead-210 dated 2009 core to the 2012 core. The lower panel shows the sediment accumulation rate over time at the core site in Spring Lake.

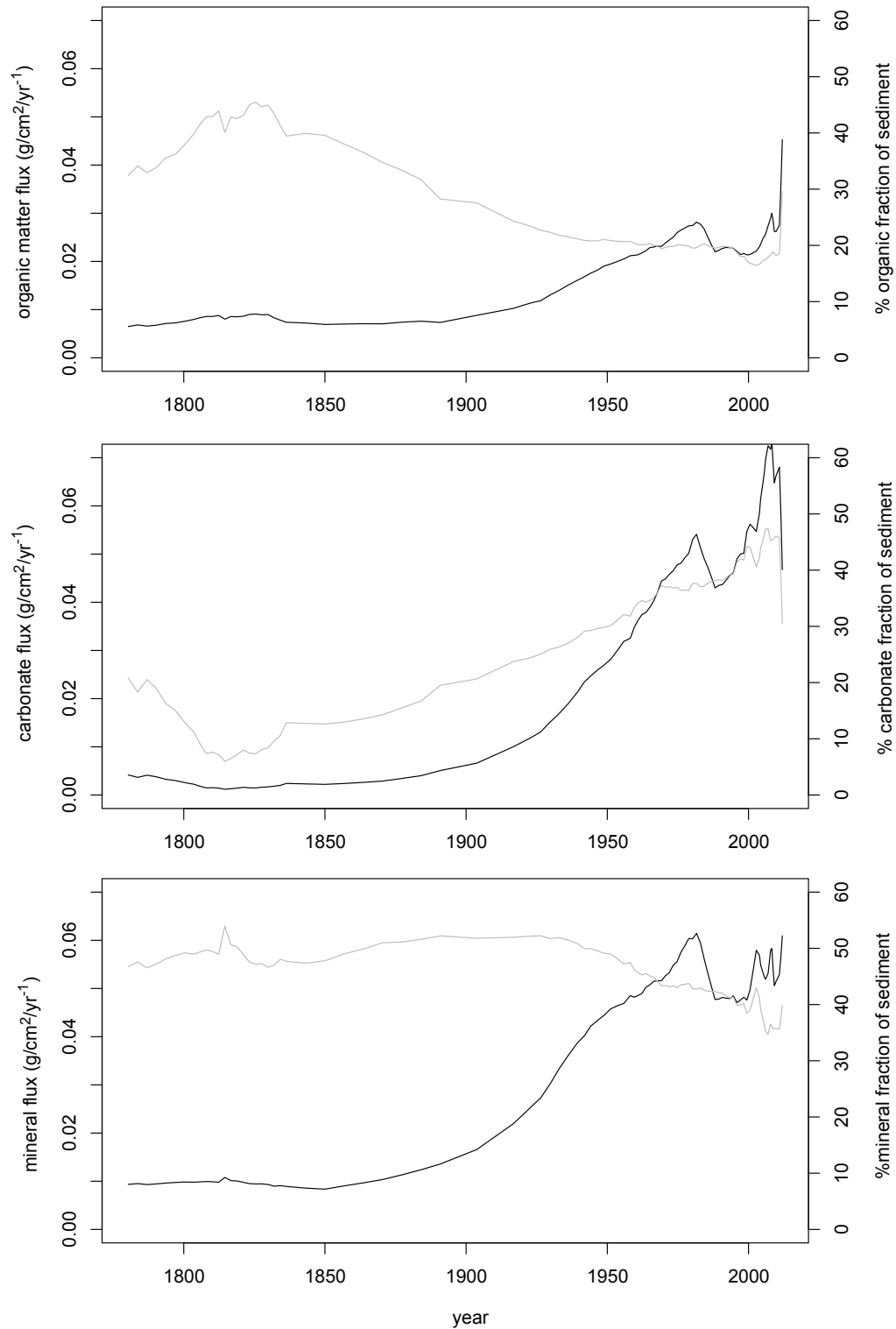


Figure 3: Sediment composition of the core from Spring Lake. Organic matter, carbonates and mineral material are shown as both concentration (grey line) and flux (black line; concentration multiplied by sediment accumulation rate).

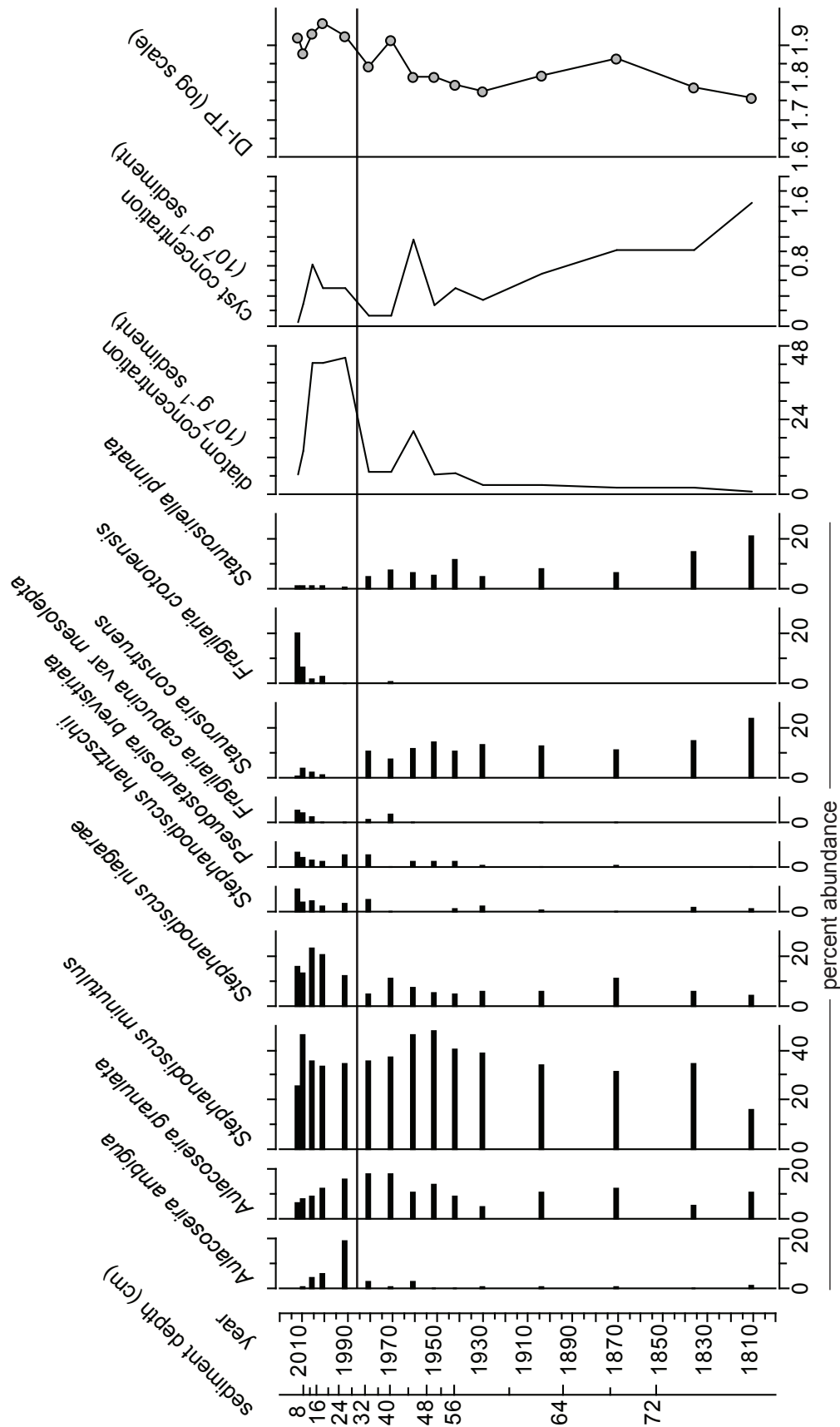


Figure 4: Sediment diatom assemblages showing the percent abundance of the dominant species. The concentrations of diatoms and chrysophyte cysts are shown as line graphs, with the diatom-inferred TP of Spring Lake water.



## CCA, 89 MN Lakes, SLPL Lake fossil data

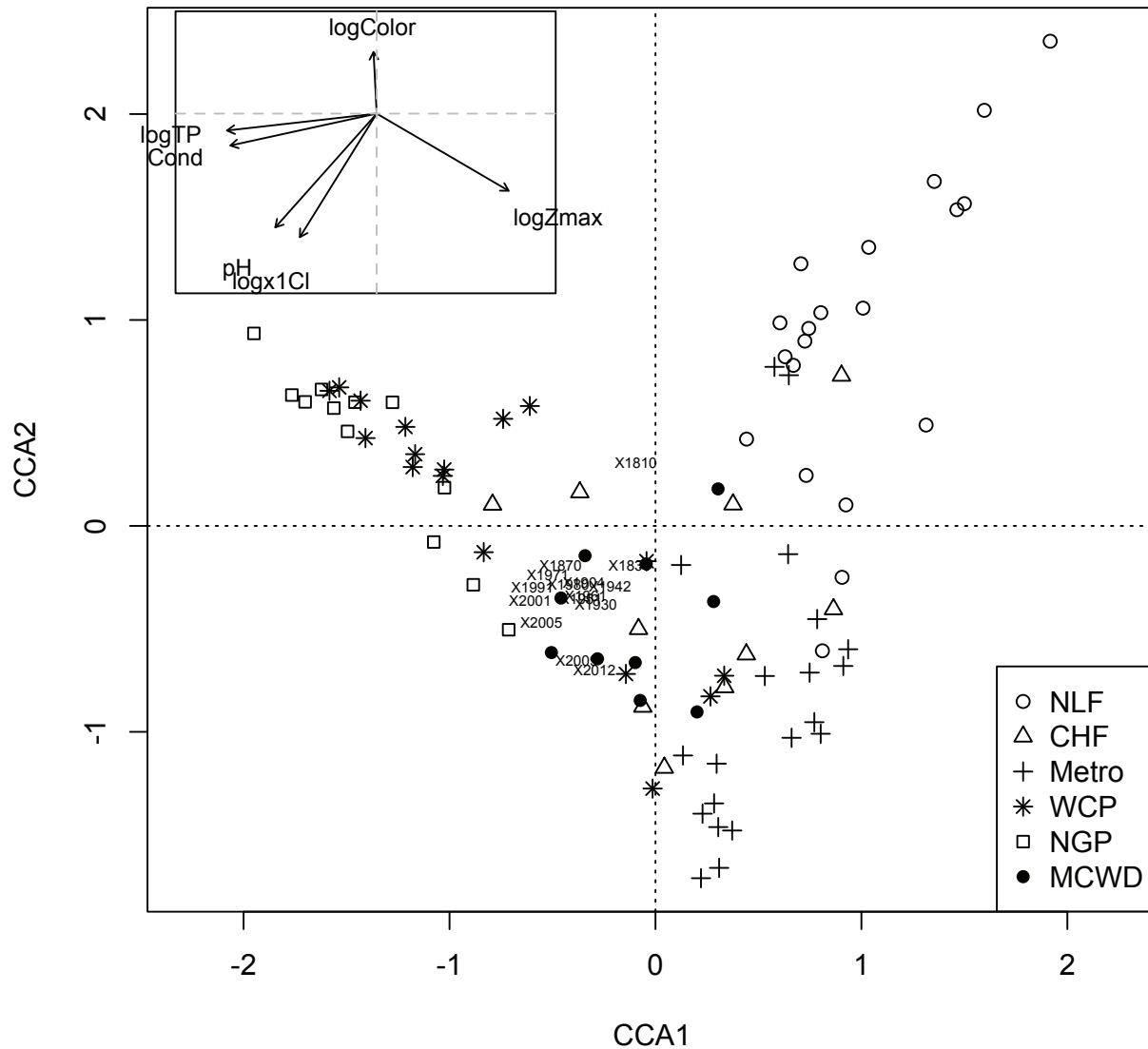


Figure 5: Ordination biplot of a canonical correspondence analysis of the diatom training set or modern samples used to reconstruct Spring Lake TP concentrations. Significant environmental gradients are shown in the upper left and the sites are identified according to ecoregion (Ramstack et al., 2003). The sediment samples from Spring Lake are shown as 'X' with the corresponding date. Note how the Spring Lake samples progress through time in a similar direction to the logTP gradient.

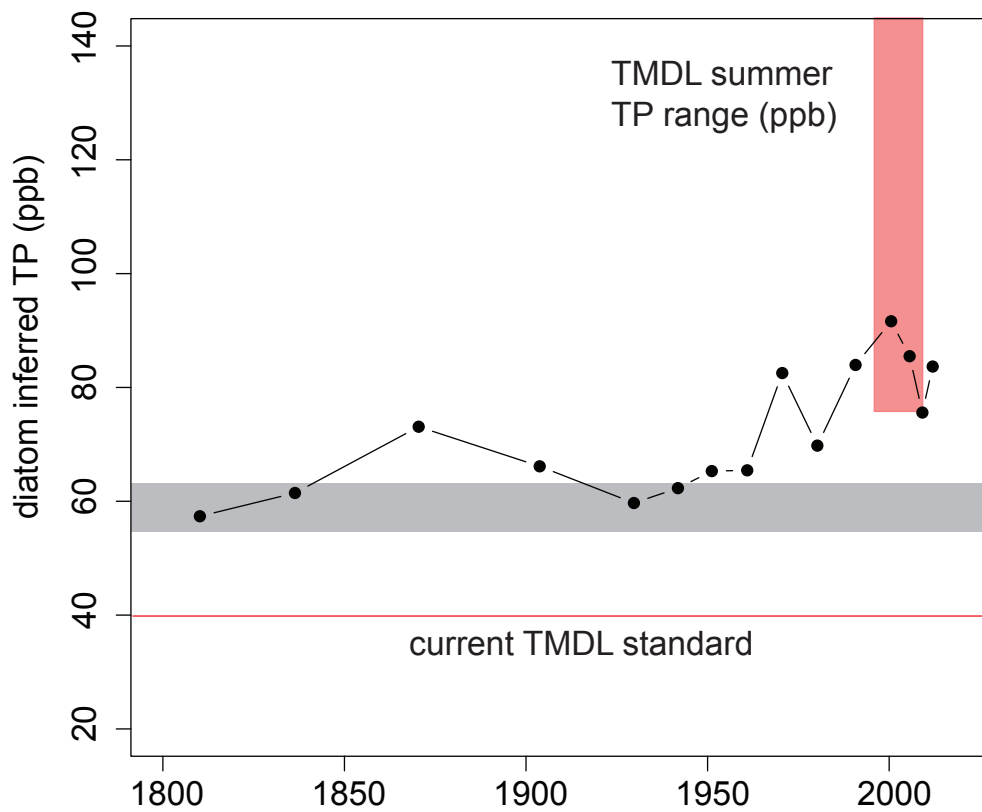


Figure 6: The diatom-inferred total phosphorus reconstruction. The grey bar is the approximate historical background for Spring Lake prior to settlement. The red line is the current background or TMDL standard set for Spring Lake and the red shaded are represents the measured summer TP range over the last 10-15 years (Wenck, 2011).

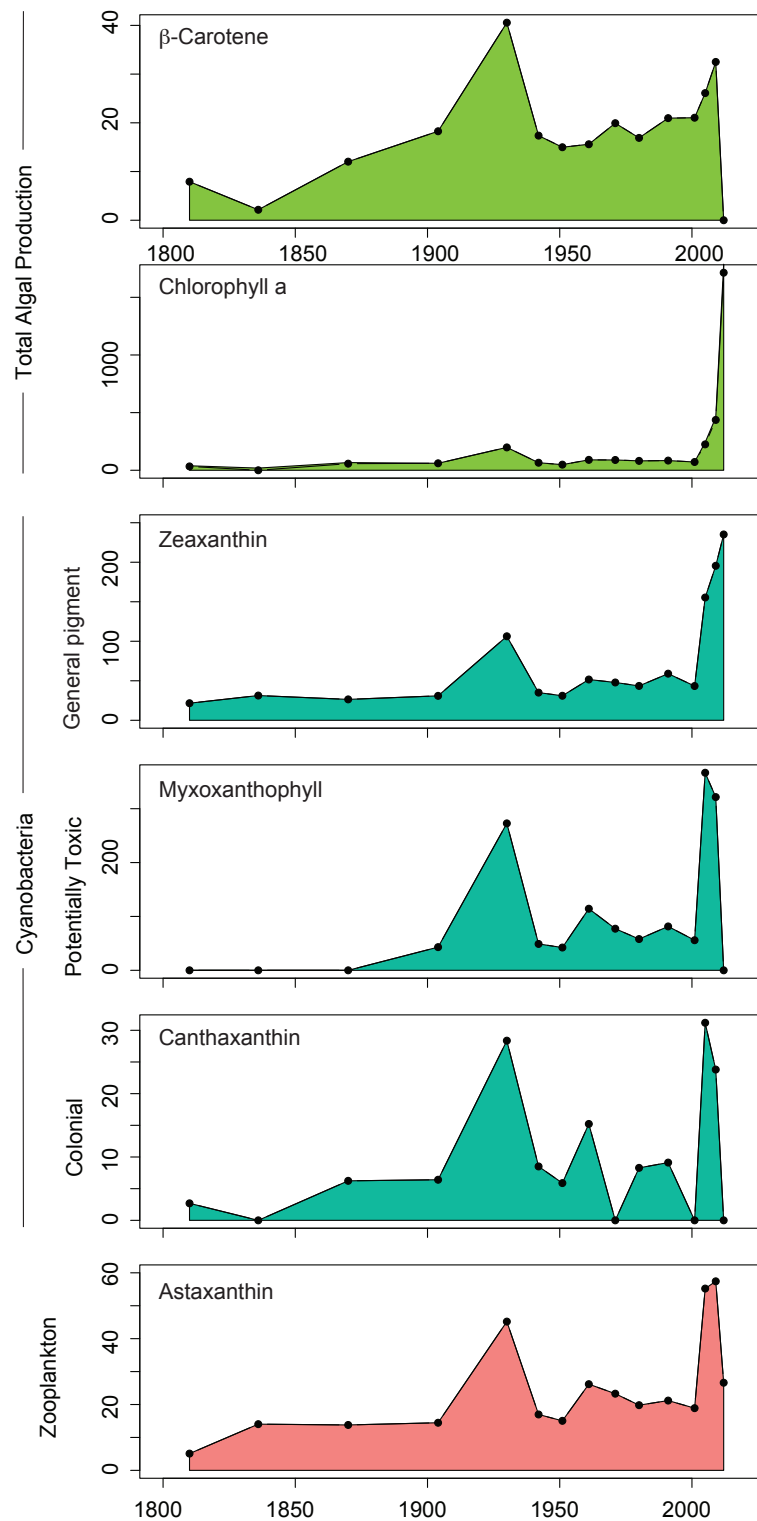


Figure 7: The sediment algal pigments present in Spring Lake. The group of algae associated with each pigment is shown along the y-axis. In addition to algal pigments, zoo-plankton pigment is present in large abundance.