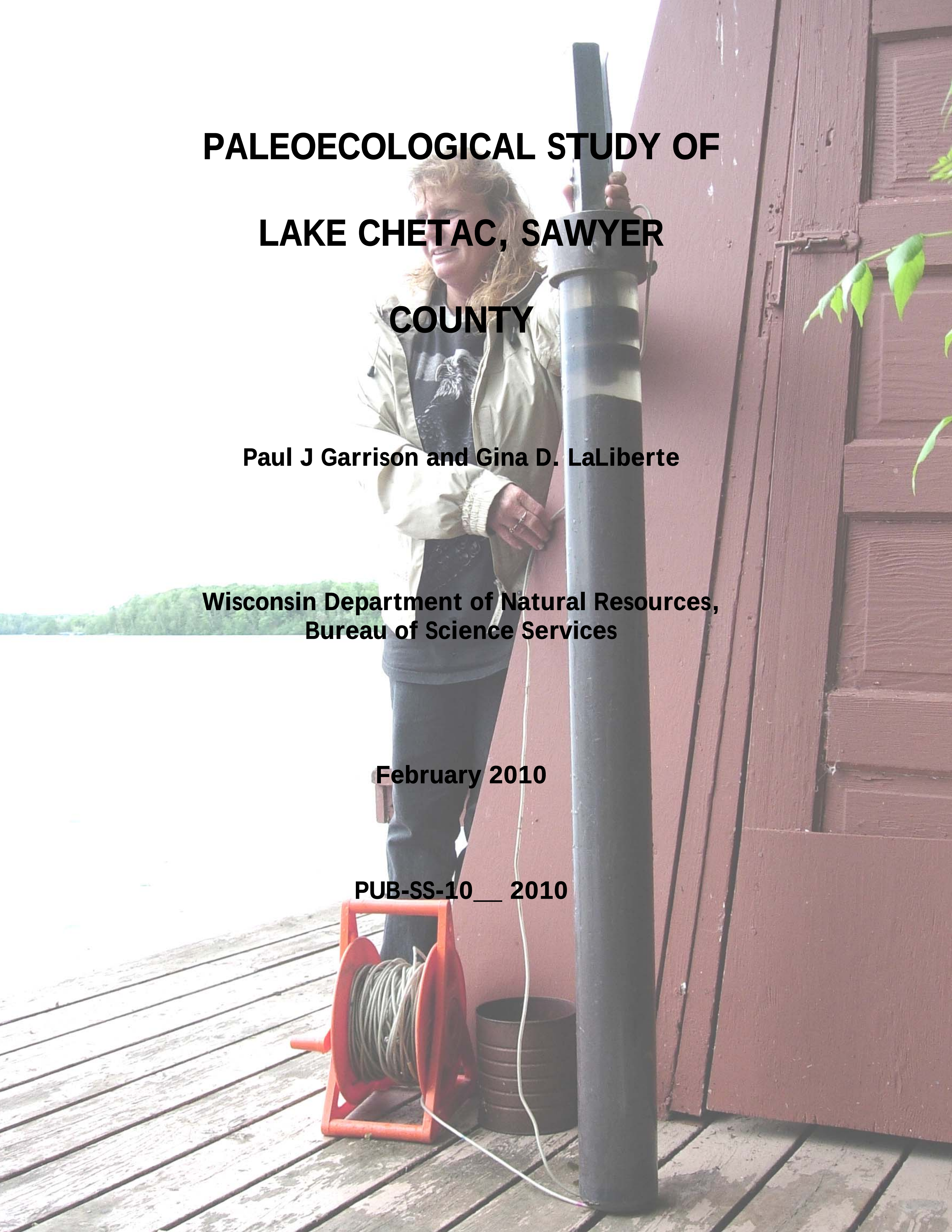

PALEOECOLOGICAL STUDY OF LAKE CHETAC, SAWYER COUNTY

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Introduction

Questions often arise concerning how a lake's water quality has changed through time as a result of watershed disturbances. In most cases there is little or no reliable long-term data. People often wonder about how a lake has changed, when the changes occurred and what the lake was like before the transformations began. Paleoecology offers a way to address these issues. The paleoecological approach depends upon the fact that lakes act as partial sediment traps for particles that are created within the lake or delivered from the watershed. The sediments of the lake entomb a selection of fossil remains that are more or less resistant to bacterial decay or chemical dissolution. These remains include diatom frustules, cell walls of certain algal species, and subfossils from aquatic plants. The chemical composition of the sediments may indicate the composition of particles entering the lake as well as the past chemical environment of the lake itself. Using the fossil remains found in the sediment, one can reconstruct changes in the lake ecosystem over any period of time since the establishment of the lake.

Lake Chetac, Sawyer County, is a 1920 acre lake with a maximum depth of 28 feet and a mean depth of 14 feet. The lake is a drainage lake with a 40 square mile watershed. A sediment core was collected from the deepest area on 13 June 2008. The location of the coring site was 45.72422° north and -91.48368° west in 25 feet of water (Figure 1). The core was collected with a piston corer having an inside diameter of 8.8 cm. The core was sectioned into 1 cm intervals for the top 55 cm and 2 cm intervals from 55 to 93 cm. The core was dated by the ^{210}Pb method and the CRS model used to estimate dates and sedimentation rate. The diatom community was analyzed to assess changes in nutrient levels and geochemical elements were examined to determine the causes of changes in the water quality. Algal fossils, e.g. selected blue green and green algae, were analyzed in the core to assess changes in nutrients.

The area around Lake Chetac was surveyed by the General Land Office during the period 1852-54. A sketch map of the lake is shown in Figure 2. When the township was surveyed there were already lots platted around the lake and an Indian village was located on the southwest part of the lake. The landscape around the lake was hardwood forest dominated by white pines, oak, and aspen.

Results and Discussion

Dating

In order to determine when the various sediment layers were deposited, the samples were analyzed for lead-210 (^{210}Pb). Lead-210 is a naturally occurring radionuclide. It is the result of natural decay of uranium-238 to radium-226 to radon-222. Since radon-222 is a gas (that is why it is sometimes

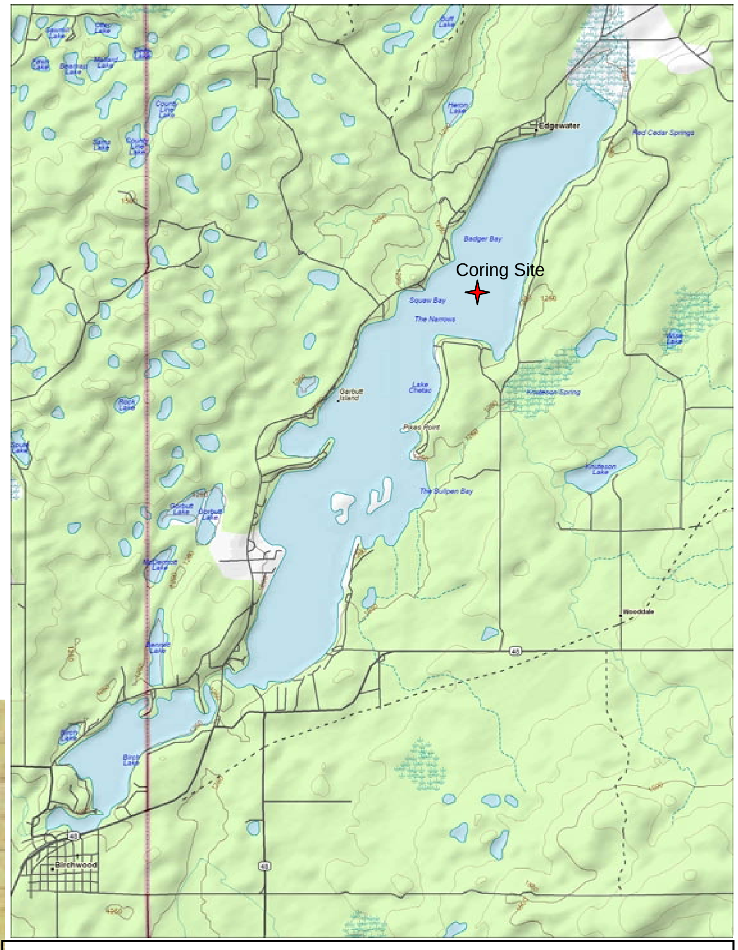

Figure 1. Map of Lake Chetac showing the coring site. The water depth at the site was 25 feet.

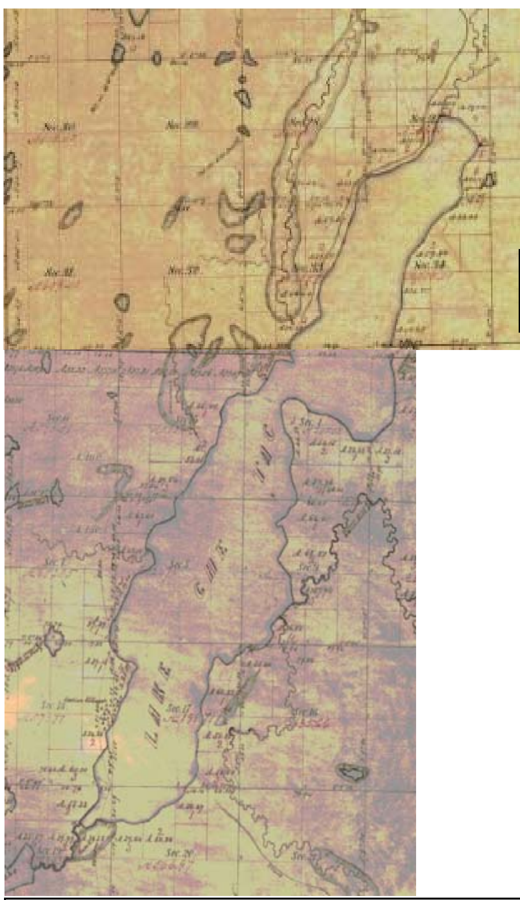

Figure 2. Map of the area around Lake Chetac drawn from survey notes taken from 1852-54. At this time there are a number of lots platted around Lake Chetac.

found in high levels in basements) it moves into the atmosphere where it decays to lead-210. The ^{210}Pb is deposited on the lake during precipitation and with dust particles. After it enters the lake and is in the lake sediments, it slowly decays. The half-life of ^{210}Pb is 22.26 years (time it takes to lose one half of the concentration of ^{210}Pb) which means that it can be detected for about 130-150 years. This makes ^{210}Pb a good choice to determine the age of the sediment since European settlement began in the mid-1800s. Sediment age for the various depths of sediment were determined by constant rate of supply (CRS) model (Appleby and Oldfield, 1978). Bulk sediment accumulation rates (g cm^{-2} yr^{-1}) were calculated from output of the CRS model.

Sedimentation Rate

The mean mass sedimentation rate for the last 200 years was 0.025 cm-^{2} yr^{-1}. This is near the median for the rate measured in 52 Wisconsin lakes. The rate is lower than many other lakes around the state. The partial reason for this lower rate is that the lake is a moderately hardwater lake so there is not a significant amount of precipitation of calcium carbonate. Shallower lakes tend to have a lower rate than deep lakes since fine grained sediment tends to move to the deepest area in deep lakes while it is more evenly distributed in shallow lakes like Lake Chetac. The average linear rate for the same time period is 3 cm yr^{-1}, which equates to 1.2 inches per year.

To account for sediment compaction and to interpret past patterns of sediment accumulation, the dry

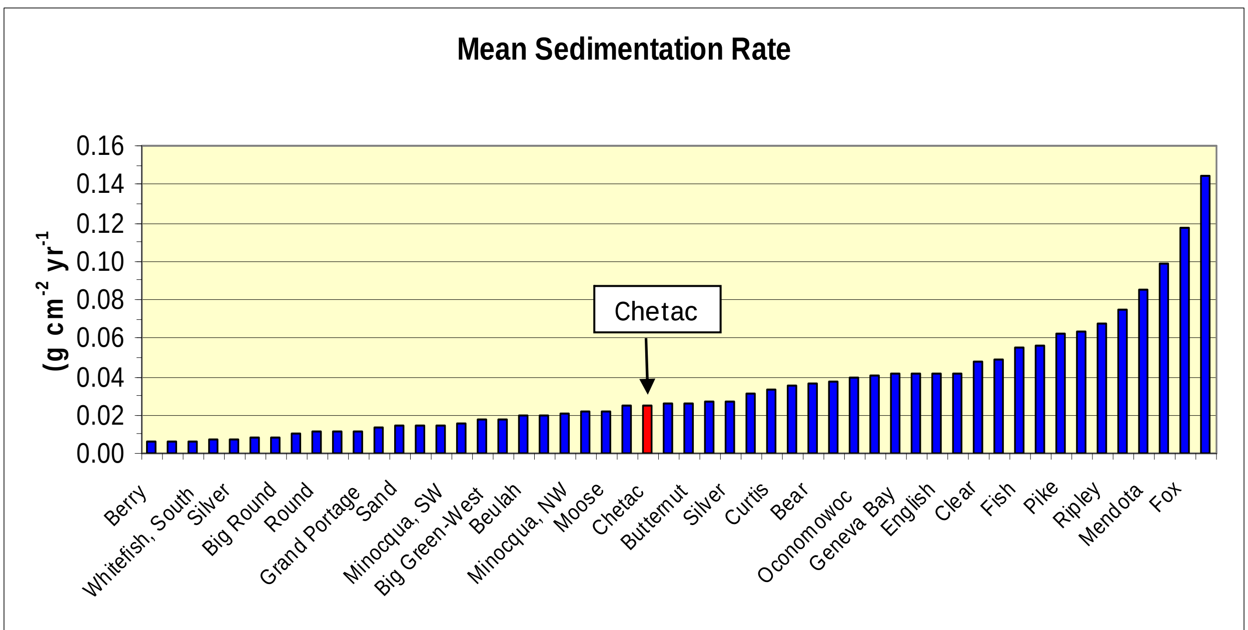

Figure 3. Mean sedimentation rate for the last 150 years for 52 Wisconsin lakes. The arrow indicates Lake Chetac. The rate in this lake is lower than many of the lakes. This is partially because the lake is a moderately hardwater lake.

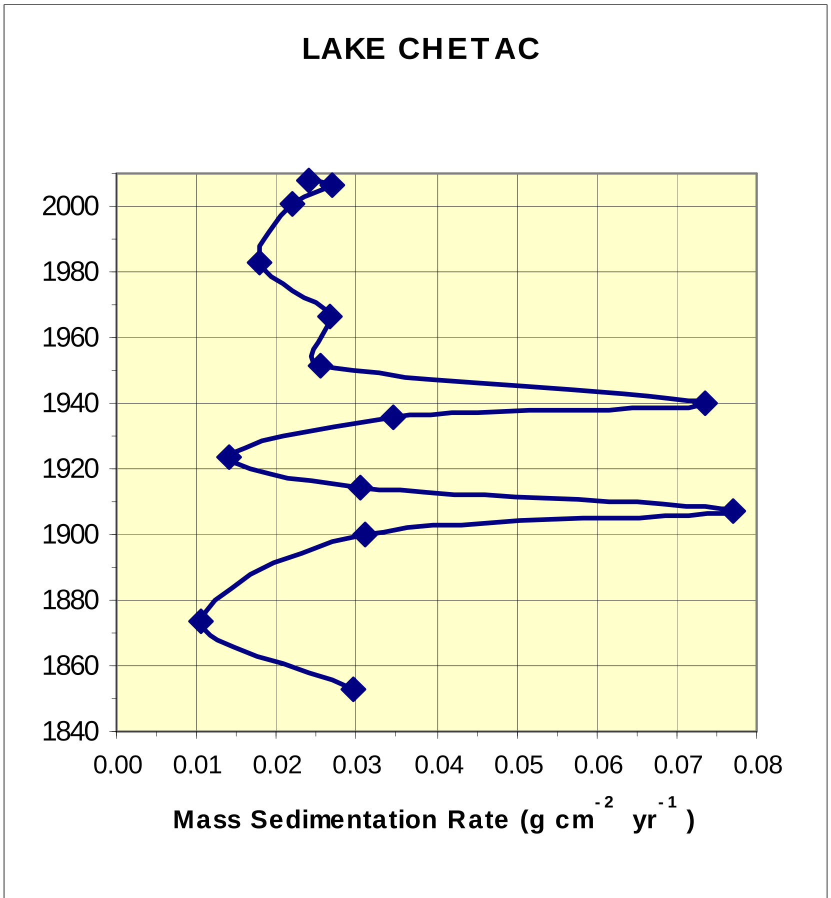

Figure 4. Sediment accumulation rate in Lake Chetac. The historical rate was relatively low. The peak around 1910 was the result of land that was flooded when the dam was installed. The peak around 1940 was largely the result of soil erosion, probably from agricultural activities.

sediment accumulation rate was calculated. The sedimentation rate peaked around 1910 and again around 1940. It is likely that the first peak is the result of the installation of the dam in 1911 which raised the water level of the lake. The higher water level would have flooded land that previously was dry. This flooding apparently resulted in a short lived input of sediment.

A second peak occurred around 1940 (Figure 4). It is unclear what caused this peak but it likely was related to a large disturbance in the lake's watershed.

The sedimentation rate for the last few decades is similar to historical rates (Figure 4). In fact, with the exception of the two peaks around 1910 and 1940, the sedimentation rate is fairly constant for the last 150 years.

Sediment Geochemistry

Geochemical variables are analyzed to estimate which watershed activities are having the greatest impact on the lake (Table 1). The chemicals aluminum and titanium are surrogates of detrital aluminosilicate materials and thus changes in their profiles are an indication of changes in soil erosion. Potassium is found in both soils and synthetic fertilizers. Therefore its profile will reflect changes both from soil erosion and the addition of commercial fertilizers in the watershed. Nutrients like phosphorus and nitrogen are important for plant growth, especially algae and aquatic plants. General lake productivity is reflected in the profiles of organic matter. The organic matter determination includes a number of elements, especially carbon.

Table 1. Selected chemical indicators of watershed or in lake processes.

Process	Chemical Variable
Soil erosion	aluminum, potassium, titanium
Synthetic fertilizer	potassium
Nutrients	phosphorus, nitrogen
Lake productivity	Organic matter

The accumulation rate of selected geochemical elements was calculated by combining the elemental concentrations with the sedimentation rate. The accumulation rate gives an indication of how the deposition of the elements change through time. This provides an indication of what watershed and inlake processes have occurred that consequently affected the lake ecosystem.

The accumulation of titanium, which indicates soil erosion, was fairly constant since the arrival of Europeans in the mid nineteenth century except for around 1910 and 1940 (Figure 5). These peaks correspond with elevated rates of bulk sediment (Figure 4). The peak around 1910 corresponds with the installation of the dam in 1911. It is not clear what the source of the sediment is around 1940 but it undoubtedly is associated with a large disturbance in the watershed. In fact all of the geochemical elements shown in Figure 5 have similar profiles during the last 150 years, with the exception of phosphorus. These elements have similar accumulation rates through time except for 1910 and 1940.

Unlike the other elements, phosphorus accumulation rates are highest at the top of the core. The phosphorus profile does show deposition peaks at 1910 and 1940 but these rates are less than the subsurface peak (Figure 5). The deposition rate at the top of the core is three times as high as most of the time prior to 1980. Several authors have noted that phosphorus and nitrogen profiles may not reflect the lake's eutrophication history because of diagenesis (Schelske et al. 1988, Anderson and Rippey 1994, Fitzpatrick et al. 2003). Over the course of a few years some organic fractions of P and N breakdown into the inorganic components. Some of this material then may be recycled into the water column and out of the sediments. Since nitrogen and organic matter accumulation rates do not increase in the surface sediments, at least much less than phosphorus, the increased phosphorus deposition rate reflects increased phosphorus delivery from the watershed. The sources could be from shoreline development or landuse in the watershed further away from the lake.

Although most of the geochemical elements show little change in deposition rates during the last 150 years, by examining the ratios of key elements we can get a better understanding of causes of

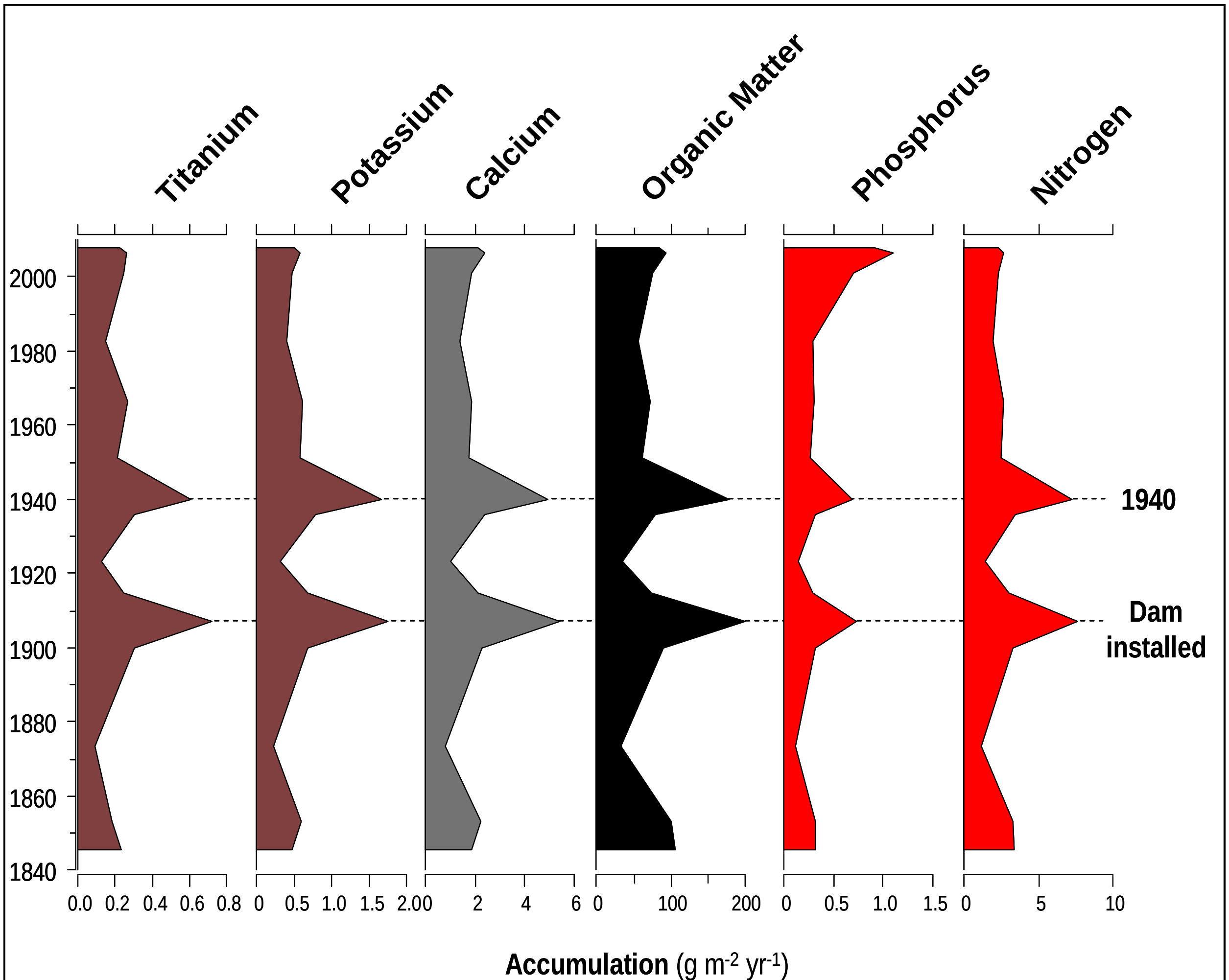

Figure 5. Profiles of the accumulation rate of selected geochemical elements. Titanium profiles are indicative of soil erosional rates in the watershed. Potassium profiles are indicative of both soil erosion and use of synthetic fertilizers. Calcium is often used as a soil additive.Organic matter reflects the productivity of the lake. Nitrogen and phosphorus profiles reflect changes in nutrient deposition rates.

changes in the lake's nutrient levels. One of the common sources of phosphorus to a lake is soil erosion. Using titanium as an indicator of soil erosion, we can determine the importance of soil erosion as a phosphorus source. The ratio declines after 1970 indicating the much of the phosphorus the entered the lake during the last 4 decades is not from soil erosion since a decline in the ratio indicates that phosphorus levels are increasing at a faster rate than soil erosion (Figure 6).

Another common source of phosphorus is from synthetic fertilizers. Their use greatly accelerated after the end of World War II with the conversion of plants that made ammunition to fertilizer production. Although potassium (K) is a common component of synthetic fertilizer, it is also found in soils associated with clays. A decline in the ratio of titanium to potassium indicates that there is a source of potassium other than soil particles. The Ti:K ratio declines after 1960 (Figure 6), confirming that synthetic fertilizers have been used in the lake's watershed. Although it is likely that fertilizers contribute some of the phosphorus, the decline in the ratio of potassium to phosphorus after 1950 indicates that fertilizers are not a large source of the phosphorus.

Both nitrogen and phosphorus are essential nutrients for aquatic plant growth. The ratio of nitrogen to phosphorus declines after 1940 (Figure 6) indicating that phosphorus is being enriched to a greater extent than nitrogen. Whatever the source of phosphorus it may not be contributing significant nitrogen to the lake.

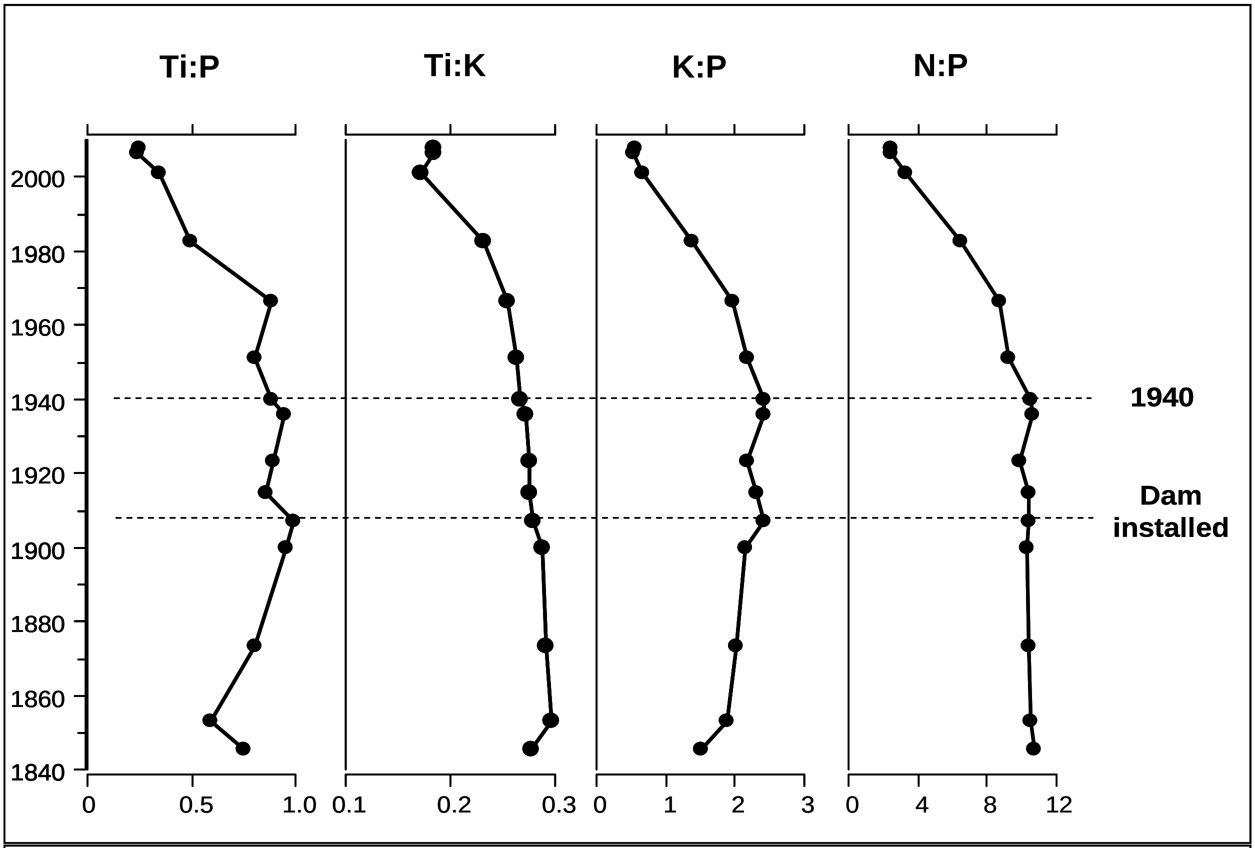

Figure 6. Profiles of the ratio of selected geochemical elements. Titanium (Ti) reflects past soil erosion. Potassium (K) is found in soil particles and fertilizers. Phosphorus (P) and nitrogen (N) are essential nutrients for algal growth. The decline in Ti:P near the top of the core reflects that soil erosion is not an important source of phosphorus. Since Ti:K is declining near the top of the core, fertilizers are the source of some of the potassium. However K:P is declining at the same time indicating that there are important phosphorus sources other than fertilizers and soil erosion. The decline in N:P indicates that phosphosphorus is being enriched in relation to nitrogen.

While it is not clear what is the source of the elevated phosphorus deposition rate after 1980, one possibility is internal loading of phosphorus. As lakes become more eutrophic, phosphorus levels in their sediments become high enough that it is recycled within the lake. This means that phosphorus in the lake sediments migrates into the water column either by algal transport, sediment resuspension during wind events, or during algal blooms as a result of elevated pH levels. Since the smallest sediment particles tend to accumulate in the deepest part of the lake, phosphorus is transported to the shallower parts of the lake to the deepest area, which is where the sediment core was taken.

Diatom Community

Aquatic organisms are good indicators of water chemistry because they are in direct contact with the water and are strongly affected by the chemical composition of their surroundings. Most indicator groups grow rapidly and are short lived so the community composition responds rapidly to changing environmental conditions. One of the most useful organisms for paleolimnological analysis is diatoms. They are a type of alga which possess siliceous cell walls and are usually abundant, diverse, and well preserved in sediments. They are especially useful as they are ecologically diverse and their ecological optima and tolerances can be quantified. Certain taxa are usually found under nutrient poor conditions while others are more common under elevated nutrient levels. They also live under a variety of habitats, which enables us to reconstruct changes in nutrient levels in the open water as well as changes in benthic environments such as aquatic plant communities. Figure 7 shows photographs of four diatom species that were found in the sediment core.

The diatom community throughout the core was indicative of an eutrophic lake. The dominant species were *Aulacoseira granulata* (pictured in Figure 7D) and several species in the group *Fragilaria* (Figure 8). *A. granulata* is as filamentous, planktonic diatom that grows in the open water of the lake. It is

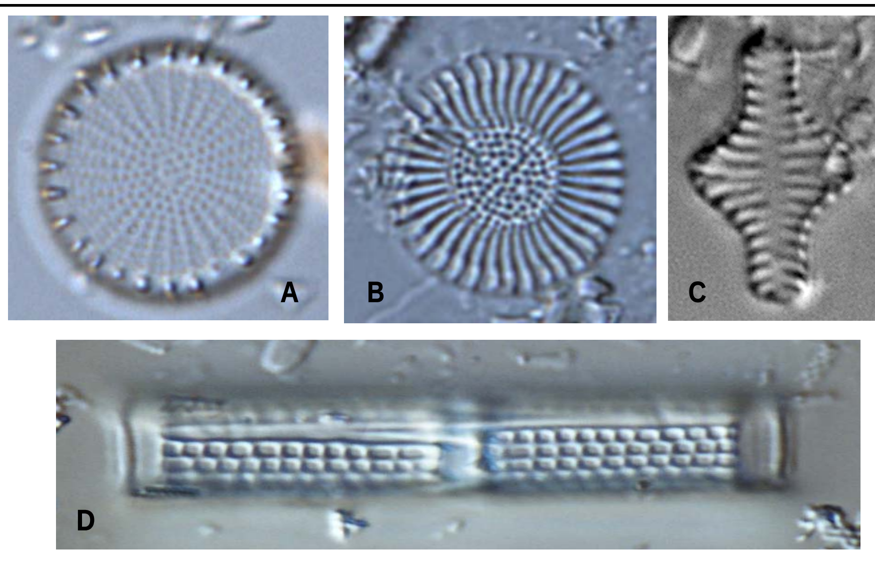

Figure 7. Photomicrographs of diatoms found in the sediment core. These diatoms are typically found in open water environments or attached to substrates, such as aquatic plants. The diatom at the top left (A) *Stephanodiscus hantzschii,* the diatom at the top center (B), *Cyclostephanos dubius*, and the diatom at the bottom, (D) *Aulacoseira granulata*, indicate elevated nutrient levels. The diatom at the top right (C) *Staurosira construens*, grows attached to substrates such as aquatic plants and is part of the benthic *Fragilaria* shown in Figure 8.

common in larger, windswept lakes that have elevated nutrient levels (Reavie et al. 1995). Its dominance during the mid-nineteenth century indicates that Lake Chetac naturally has elevated phosphorus. Other important plantonic diatoms, *Stephanodiscus hantzschii* and *S. parvus* and *Cyclostephanos* spp. also are indicative of elevated phosphorus levels. *S. parvus* especially is found under high nutrient levels (Bennion et al. 1996).

The diatom group benthic *Fragilaria* grow attached to substrates in the lake such as aquatic plants or even on the lake sediment. They were a common part of the diatom community prior to the installation of the dam in 1911. With the increased water depth there was less light reaching the lake bottom and the abundance of this diatom diminished. With the increased water level the percentage of planktonic diatoms (diatom that grow in the open water) increased as there was more water volume for these diatoms to grow.

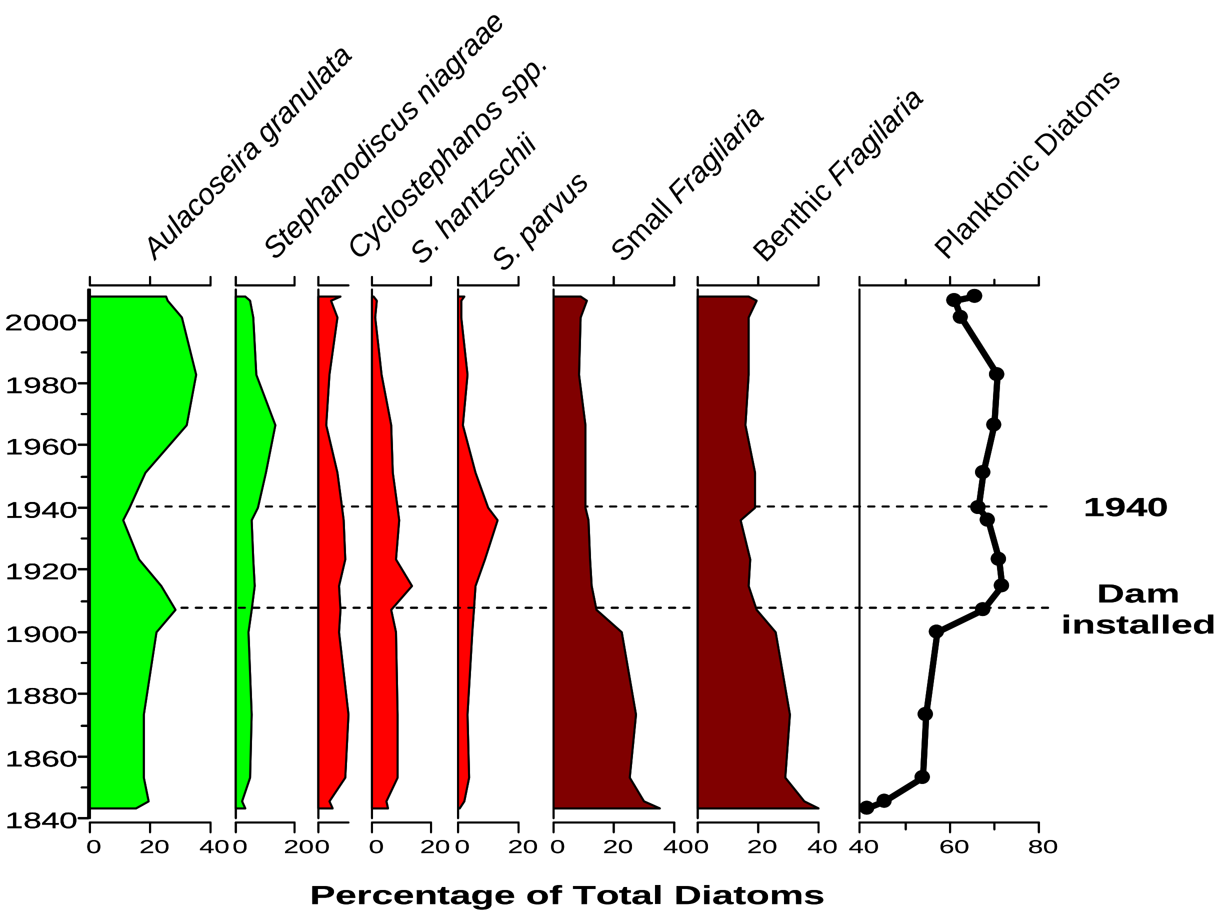

Figure 8. Profiles of common diatoms found in the core. The diatoms in green are indicative of moderate nutrient levels and the red-higher nutrient levels. The brown colored diatoms are the only ones shown which grow attached to plants. The other diatoms float in the open water.

Following the installation of the dam, the abundance of *A. granulata* declined and was largely replaced with diatoms that prefer even higher nutrient levels, e.g. *S. parvus* (Figure 8). The group of diatoms that grow in the open water, planktonic diatoms, increased in the years following the installation of the dam (Figure 8). This is further indication of an increase in nutrients since other studies have found that the production of planktonic diatoms increase as nutrient levels rise (Bradbury and Winter 1976; Batterbee 1978; Garrison and Wakeman 2000).

Diatom assemblages historically have been used as indicators of trophic changes in a qualitative way (Bradbury, 1975; Anderson et al., 1990; Carney, 1982). In recent years, ecologically relevant statistical methods have been developed to infer environmental conditions from diatom assemblages. These methods are based on multivariate ordination and weighted averaging regression and calibration (Birks et al., 1990). Ecological preferences of diatom species are determined by relating modern limnological variables to surface sediment diatom assemblages. The species-environment relationships are then used to infer environmental conditions from fossil diatom assemblages found in the sediment core.

The diatom community was used to estimate changes in water clarity and phosphorus levels during the last 2 centuries. Prior to the arrival of Europeans in the mid-1800s the mean summer Secchi depth was about 3.5 feet (Figure 9). This is similar to the present day water clarity. Water clarity was worse during the period 1900 to 1940 when mean Secchi values were about 2 feet.

The mean summer phosphorus values prior to the mid-1800s were about 55-60 $\mu g\ L^{-1}$ which is not much lower than concentrations observed in 2007-08. The diatom community indicates that during the last half 1800s, phosphorus levels were similar to present day values. This means that Lake Chetac is naturally eutrophic and we should not expect that we could reduce phosphorus levels significantly lower than they are now. The diatom community does show that phosphorus levels were highest immediately following the dam installation in 1911 until the 1960s, During this time, mean summer phosphorus concentrations exceeded 100 $\mu g\ L^{-1}$.

While at the present time, phosphorus levels can increase during the summer as a result of internal loading to values that exceed 150 $\mu g\ L^{-1}$, we can not be sure that occurred historically. It is likely that this has been a long term occurrence in Lake Chetac but the model only gives the summer average.

Non-Diatom Algal Fossils

Other algae besides diatoms are sometimes preserved in the sediments. These groups include blue-green algae, green algae, and Chrysophytes. While nearly all diatom taxa are preserved, in the other

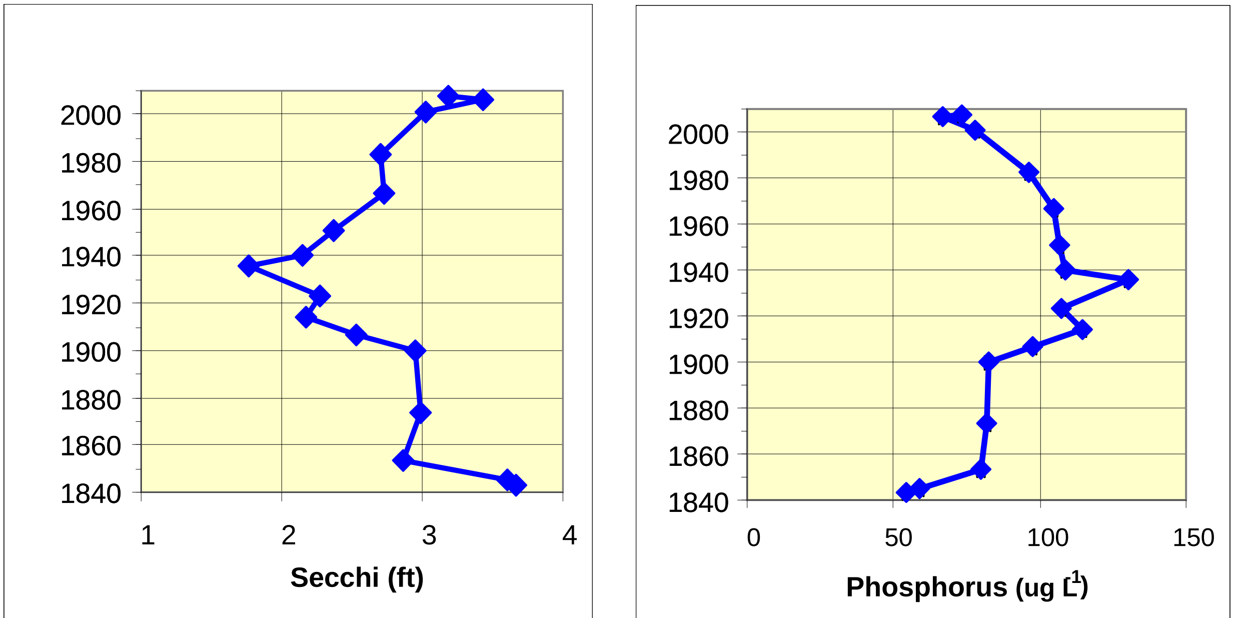

Figure 8. Estimated mean summer Secchi depth and summer phosphorus concentrations in the core. These values were inferred from the diatom community using weighted averaging modeling.

groups only certain taxa are fossilized. In blue-green algae only the genera *Aphanizomenon, Anabaena,* and *Gloeotrichia* fossils are found in sediments. Green algae that produce coenobia are also found in the sediments. Since only some taxa are preserved in each of these algal groups, interpretation of the results is more limited than with the diatom community. However, since blue-green algae are numerous at the present time in Lake Chetac, remains of other algal groups, especially blue-green algae, were examined in the core.

The blue-green algae that most frequently dominate algal blooms are *Aphanizomenon, Anabaena,* and *Microcystis*. The first two genera produce fossils while *Microcystis* does not. Although interpreting past nutrient levels is more speculative with blue-green algae than with diatoms since not all blue-green algae are preserved in the sediments, it is clear that blue-green algae have been common in Lake Chetac for at least the last 150 years. Since *Aphanizomenon* is reported to be more competitive under lower phosphorus levels than *Anabaena* (van Geel et al. 1994), the decrease in the former taxa after 1860 likely indicates an increase in phosphorus in the lake. While *Anabaena* begins to decline around 1860, its abundance does not reach a minimum until around 1920 (Figure 10). After the dam was installed in 1911,both *Aphanizomenon* and *Anabaena* numbers became low. It is very likely that the blue-green alga *Microcystis,* which can form large blooms but does not leave fossils in the sediments, became more important after this time.

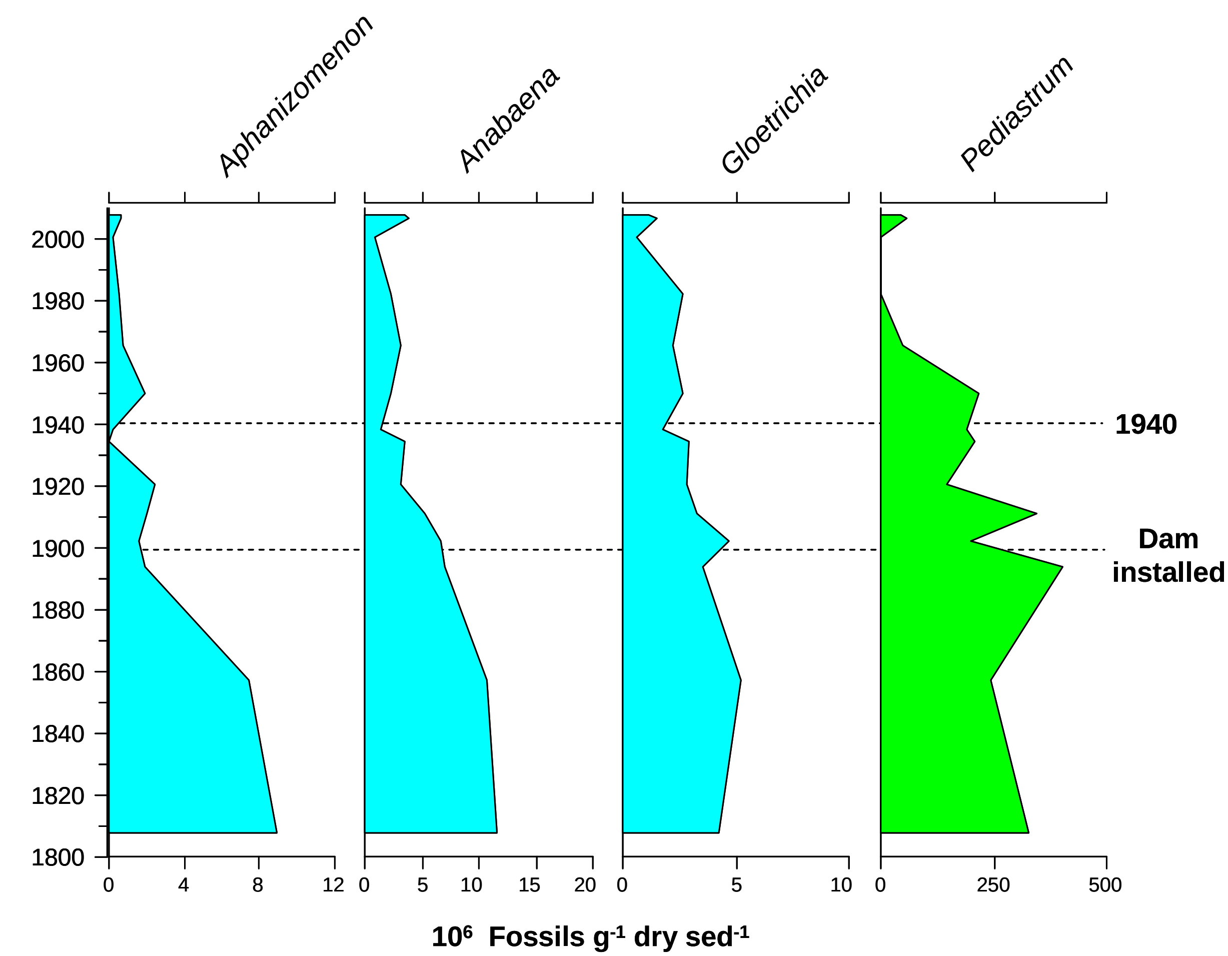

Figure 10. Profiles of non-diatom algal fossils found in the Lake Chetac sediment core. The three alga on the left side are blue-green algae. *Aphanizomenon* and *Anabaena* often form surface scums. These algae are present throughout the core indicating blue-green blooms have been common during at least the last 150 years. The decline of these algae since 1910, likely reflects a shift to blue-green algae which do not leave fossils, e.g. *Microcystis*. The blue green alga *Gloetrichia* has been present during the last 150 years. The green alga, *Pediastrum*, declined during the 1950s.

Gloetrichia is another blue-green alga that can reach bloom proportions. This alga grows in spherical balls and appears in the water as furry particles. This alga usually starts growing on the lake sediments early in the year when water clarity is better. While growing on the bottom, it extracts nutrients from the sediments which it then carries into the water column later in the summer. *Gloetrichia* was found throughout the core in relatively high numbers.

Pediastrum is a green alga that is common in lakes under a wide variety of nutrient levels. The nutrient requirements of this alga are not well understood but it is known to do well under elevated nutrient levels. The numbers were high from the mid-1800s until about 1950 (Figure 10). The low numbers for the last 60 years may indicate poor water clarity since this large alga grows on the lake bottom or among algal mats.

Summary

The results of the sediment core study indicate that Lake Chetac is naturally eutrophic with elevated phosphorus levels. At the bottom of the core, mid-1800s, the diatom community is composed of taxa that are found in wind swept lakes with high phosphorus levels. The blue-green algal fossils indicate these algae, which often form surface algal scums were common in the lake prior to the arrival of Europeans in the nineteenth century. The finding that Lake Chetac is naturally eutrophic has been documented in Big Round Lake, Polk County, WI, another relatively large shallow lake (Garrison and LaLiberte, 2007). This lake also historically had blue-green algal blooms although nutrient levels appear to have increased in the last two decades in this lake. In Big Round Lake, soil erosion was not a large source of phosphorus but commercial fertilizer was. Both the diatom and blue-green algal communities do indicate that there have been some changes in nutrient levels during the last 150 years. They indicate that phosphorus levels and water clarity at the present are similar to values in the lake in the mid-1800s. Water clarity was worse and phosphorus levels higher during the mid part of the twentieth century but they are lower at the present time.

The geochemical analysis indicates there were two periods of high sediment input, immediately following the raising of the water level in 1911 when the dam was installed and again around 1940. It is not clear what event around 1940 resulted in the episodic imput of sediment, but it was short lived. The present day input of sediment is similar to levels prior to the arrival Europeans in the mid-1800s.

The geochemical analysis indicates that phosphorus is the most significant element that has an increased deposition rate in recent times. Soil erosion and commercial fertilizers do not appear to be a significant source of this increased phosphorus. The increased phosphorus may be from internal loading from the sediments.

The increased phosphorus deposition is not reflected in the diatom or the blue-green algal fossils. This may be due to the fact that most of the diatoms found in the core grow during the spring, early summer, and fall. The worse blue-green algal blooms occur in late summer. Since the dominant blue-green alga at this time is *Microcystis*, which does not leave fossils, its increase was not detected in the core.

- The mean sedimentation rate for the last 150 years in Lake Chetac was near the median measured in 52 Wisconsin lakes. This was partially because it is a moderately hardwater lake and relatively shallow.

- Their were two episodic peaks in the sedimentation rate, around 1910 and 1940. The first peak was likely the result the increased water level from the dam flooding land along the lake shore. It is unclear what watershed disturbance contributed to the 1940 peak.

- Other than the short lived peaks around 1910 and 1940, the sedimentation rate for the last 150 years has largely been unchanged.

- Phosphorus was the only element that exhibited significant changes in the last 150 years. Phosphorus deposition rates have increased in the last 2 decades probably as a result of internal loading of phosphorus from the sediments. Soil erosion and commercial fertilzers do not appear to be a significant source of the elevated phosphorus deposition.

- The diatom and blue-green algal communities indicate that phosphorus levels are naturally high in Lake Chetac. Before the arrival of Europeans in the mid-1800s, algal blooms were common. Historical phosphorus concentrations were 55-60 µg L^{-1}.

- Phosphorus levels were at their highest levels in the period 1910 to 1980 although it is likely that internal loading has resulted in higher summer phosphorus concentrations in recent years that is not reflected in either the diatom or blue-green algal fossils.

References

Anderson. N.J. and B. Rippey. 1994. Monitoring lake recovery from point-source eutrophication—the use of diatom-inferred epilimnetic total phosphorus and sediment chemistry. Freshwater Biol. 32:625-639.

Anderson, N.J., B. Rippey, and A.C. Stevenson. 1990. Diatom assemblage changes in a eutrophic lake following point source nutrient re-direction: a palaeolimnological approach. Freshwat. Biol. 23:205-217.

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

Batterbee, R.W., 1978. Observations on the recent history of Lough Neagh and its drainage basin. Phil. Trans. R. Soc. B. 281:303-345.

Bennion, H., S. Juggins, and N.J. Anderson. 1996. Predicting epilimnetic phosphorus concentrations using an improved diatom-based transfer function and its application to lake management. Environ. Sci. Tech. 30:2004-2007.

Bradbury, J.P. 1975. Diatom stratigraphy and human settlement in Minnesota. Geol. Soc. America Spec. Paper 171:1-74.

Birks, H.J.B., J.M. Line, S. Juggins, A.C. Stevenson, and C.J.F. ter Braak. 1990. Diatoms and pH reconstruction. Phil. Trans. R. Soc., Lond., series B 327:263-278.

Bradbury, J.P. and T.C. Winter. 1976. Areal distribution and stratigraphy of diatoms in the sediments of Lake Sallie, Minnesota. ecology 57:1005-1014.

Carney, H.J. 1982. Algal dynamics and trophic interactions in the recent history of Frains Lake, Michigan. Ecology. 63:1814-1826.

Fitzpatrick F.A., P.J. Garrison, S.A. Fitzgerald, and J.F. Elder. 2003. Nutrient, trace-element, and ecological history of Musky Bay, Lac Courte Oreilles, Wisconsin, as inferred from sediment cores. U.S. Geological Survey Water-Resources Investigation Report 02-4225. 141 pp.

Garrison P.J. and R.S. Wakeman. 2000. Use of paleolimnology to document the effect of lake shoreland development on water quality. J. Paleolim. 24:369-393.

Reavie, E.D., R.I. Hall, and J.P. Smol. 1995. An expanded weighted-averaging model for inferring past total phosphorus concentrations from diatom assemblages in eutrophic British Columbia (Canada) lakes. J. Paleolim. 14:49-67.

Fitzpatrick F.A., P.J. Garrison, S.A. Fitzgerald, and J.F. Elder. 2003. Nutrient, trace-element, and ecological history of Musky Bay, Lac Courte Oreilles, Wisconsin, as inferred from sediment cores. U.S. Geological Survey Water-Resources Investigation Report 02-4225. 141 pp.

van Geel, B. L.R. Mur, M. Ralska-Jasiewiczowa, and T. Goslar. 1994. Fossil akinetes of Aphanizomenon and Anabaena as indicators for medieval phosphate-eutrophication of Lake Gosciaz. Rev. Palaeobot. Paly. 83:97-105.

Wilson, S.E., J.P. Smol, and D.J. Sauchyn. 1997. A holocene paleosalinity diatom record from south-western Saskatchewan, Canada: Harris Lake revisited. J. Paleolim. 17:23-31.

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