6-2012

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Documenting the Anthropogenic Impact on Ballston Lake, New York from a short core using stable isotopes of carbon and nitrogen, and trace metals

By

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Submitted in partial fulfillment

of the requirements for the degree of

Bachelor of Science

Department of Geology

Union College

June, 2012

ACKNOWLEDGEMENTS

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ABSTRACT

        Ballston Lake occupies a portion of an avulsed channel of the Mohawk River
between Schenectady and Saratoga Springs, New York. The lake is about 5 km long,
generally less than 200m wide, ~8-15m deep, dimictic, with a catchment basin area of
~22km^2. Long cores (>8 m) indicate that the lake formed ~13,000 cal yr BP. This study
was undertaken to document recent environmental change recorded in the upper portion
of sediment in Ballston Lake. Three sediment cores ~40 cm long were acquired from ~8
m water depth at the north end of Ballston Lake (42°57.101'N, 73°51.066'W), and were
analyzed for exchangeable metals, magnetic susceptibility, total organic carbon (TOC),
total inorganic carbon (TIC), organic carbon to nitrogen ratios (C/N), and stable isotopes
of carbon and nitrogen. An age model of the cores was established by correlating a
prominent increase in Pb (1882 AD) and the Pb maximum (1970) based on ^{210}Pb dating
of cores from nearby lakes (Round Pond and Long Pond). Cu and Zn reflect similar
increasing trends at this time, and these increases are likely attributed to industrialization
and the burning of fossil fuels throughout the 20th century. δ^{13}C values become more
negative through time, declining from -29 to -30.5‰, suggesting the organic carbon is
more aquatically derived. Percent TOC increases towards the surface of the core
demonstrating increased productivity that is unrelated to nitrogen input, as %N and δ^{15}N
values are relatively constant. Though the data suggests that development around
Ballston Lake has had only a minor impact on productivity and pollution, there are
apparent changes that occurred in the lake between *AD* ~1970 and 1981. The increase in
TIC and decrease in TOC, δ^{13}C values, and grey scale values suggest there was an
increase in clastic sediment input into the lake and reduction in terrestrial organic matter
input. This event could be caused by the severe drought in New England that occurred in
the 1960s, killing vegetation and weakening the erodible surfaces. Ballston Lake should
be monitored for anthropogenic pollution in the future, though there has been little
anthropogenic impact at this point in time

INTRODUCTION

Lakes are enclosed bodies of standing water surrounded by land that persistently accumulate sediment from the surrounding watershed (Cohen, 2003). Lake sediments can record changes in air temperature or regional land use within months to decades, though sedimentation rates vary between lakes (Cohen, 2003). Lakes possess a favorable environment for highly resolved records because most lakes are surrounded by watersheds that are large relative to the lake's area, resulting in rapid sediment accumulation rates in comparison to other settings, such as the ocean. Lake sediments provide records of past climates in many ways; these records vary with preservation, which is influenced by sedimentation rate, and composition, which is dependent on the surrounding environment. Examples of paleolimnological archives include sediment cores, outcrops, and geomorphic and geophysical studies. The composition of sediment in a lake can vary depending on the morphology of the lake, and on drainage basin parameters, regional climate, surrounding vegetation, and the amount of decomposition after deposition (Cohen, 2003) The lake environment is affected by climate, watershed geology, watershed and regional vegetation, regional aquatic biota, and human activities (Cohen, 2003). On short time scales, paleolimnological data can be used to monitor and maintain lake health, to assess human impacts, and on long time scales the data can be used to create records of climate, tectonics and biotic evolution (Cohen, 2003). The contents of the sediment record include terrigenous sediment, chemical/biogenic sediment, cosmogenic/volcanogenic sediment, exogenic/endogenic fossils, and aerosols and waterborne pollutants.

Carbon and nitrogen isotopes in lake sediments record relative amounts of terrestrial to lacustrine organic matter. The cycling of carbon and nitrogen is a response to rates of photosynthesis, respiration, and secondary consumption (Cohen, 2003). Nitrogen and carbon are both derived in lakes from terrestrial and lake-derived organic matter. The dominant sources of organic matter (OM) in lake sediments are aquatic plants and algae, (phytoplankton and macrophyte), terrestrial plants, and soil humus. The greatest input can be altered by changes in lake productivity, climate, and human intervention (Cohen, 2003). A small portion of nitrogen can also occur in sediment absorbed on clay minerals and in frustules of diatoms.

Though nitrogen is derived from both aquatic and terrestrial sources, nitrogen ratios are dominantly controlled by lacustrine, autochthonous organic matter because aquatic organic matter from phytoplankton is much richer in N and has much lower C/N ratios than terrestrial organic matter (Talbot, 2001). There are various factors that could influence the $\delta^{15}N$ of lake water including: aquatic productivity, nitrogen sources, algal flora, and diagenesis (Talbot, 2001). The typical $\delta^{15}N$ is ~+1 for C3 photosynthetic pathways of terrestrial plants, ~0 for cyanobacterial phytoplankton and ~2-14 for non-N_2 fixing phytoplankton (Cohen, 2003). Lakes have responded to excess nitrogen from agricultural and industrial sources since ~1950, reflecting an increasing depletion of $\delta^{15}N$ values in lake as a result of this pollution (Wolfe et al., 2001). Nitrogen oxide emissions from sources such as automobiles generally include NO and $\delta^{15}N$ values ranging from -7 to +12‰ (Heaton, 1990). Fertilizer incorporates NH_3 and NO typically with δ15N values of ~ -3 to +3‰ (Macko & Ostom, 1994). Sewage waste causes enriched nitrogen values

(Elliot & Brush, 2006; Lake et al., 2001), which effect the overall health of the ecosystem including plant species and fish (Schlacher et al., 2007).

While nitrogen isotope ratios are controlled by lacustrine organic matter, temporal changes in carbon isotopes in organic matter can vary from internal and external processes. Each of the sources of terrestrial organic carbon maintains a distinct isotopic signature that contributes to the overall $\delta^{13}C$ value of the organic carbon within the sediment of the lake that can be identified via isotopic analysis of organic matter. Variations in the dominant input of organic carbon dictate the $\delta^{13}C$ values of the lake. Isotopes of carbon are enriched or depleted with fluctuations in primary productivity within the lake and has been used as a proxy for lake productivity (Hodell & Schelske, 1995). Aquatic-produced organic carbon has a lower $\delta^{13}C$ value than terrestrial organic carbon because of the differences in carbon sources. Terrestrial plants derive carbon from the atmosphere, which has a $\delta^{13}C$ value between 6-8 in the past ~200 years, while the $\delta^{13}C$ values in lakes is ~10 (Schlesinger, 1997). The source of carbon for aquatic organisms is water, which is generally more negative than the source of carbon for terrestrial plants (atmosphere). There are three types photosynthetic pathways of terrestrial plants (C3, C4 and crassulacean acid metabolism) that yield distinct values of $\delta^{13}C$, -25 to -32, -14 to -10, and -10 to -20, respectively (Cerling & Quade, 1993). Photosynthesis by phytoplankton within lakes has a $\delta^{13}C$ typically ~-25 to -30.

In addition to depleted $\delta^{13}C$ values as a result of increased productivity within the lake, increased productivity is also reflected in higher TOC. Total organic carbon (TOC) is an indicator of aquatic productivity, which quantitatively reflects the amount of biomass that sinks to the lakebed (Cohen, 2003). The total mass and isotopic signature of

TOC is composed of carbon from aquatic and terrestrial sources. TOC reflects the dominant vegetation within and around the lake.

Studies show that the C/N ratio is a useful tool for distinguishing long-term transitions between terrestrial to algal-input in lake sediment OM (Meyers & Ishiwatari, 1995). Organic matter is composed of decomposing organisms derived from terrestrial or aquatic sources. C/N ratios vary by the source of organic matter: mean C/N of phytoplankton, terrestrial plants, and soils are 6-7, ~160, and 15, respectively (Schlesinger, 1997; Talbot, 2001). The vast difference between phytoplankton and terrestrial plants is attributed to the high protein and lipid content of phytoplankton compared to the cellulose and lignin enrichment in terrestrial plants, a major component of the rigid cell wall (Cohen, 2003).

All stable isotopic studies must consider the potential that original isotope ratios have been altered by diagenetic processes (Talbot, 2001). Stemming from the possible alterations of carbon and nitrogen isotope ratio due to diagenetic processes, C/N ratios can also reflect diagenetic loss. Loss of nitrogen would result in enhanced C/N ratios, suggesting terrestrial-derived OM, when it is actually aquatic. In considering the effect diagenesis would have on isotopes, it's likely that fractionation would result in $\delta^{15}N$ to become more positive (Talbot, 2001). Through N-rich compounds tend to be more labile studies have found that diagenetic impact on nitrogen isotopes in lake core organic matter is minor (reviewed in Talbot, 2001). The loss can sometimes be inferred from a lack of correlation between C/N ratio and the other indicators of terrestrial organic matter (Cohen, 2003). Recent limnological studies regarding diagenetic reworking of nitrogen isotopes in lake cores have been inconclusive, yielding minimal alterations (Meyers &

Eadie, 1993; Hodell & Schelske, 1998; Ostrom et al., 1998; Teranes & Bernasconi, 2000).

Trace element concentrations such as Pb, Cu, Zn, Cd, Fe, Mn, and Mg can reflect pollution inputs from airfall or point-source inputs (Cohen, 2003). Bedrock erosion, overland or groundwater discharges from mine tailings, industrial waste, sewage, and atmospheric emission are among the many pathways that metals could potentially enter lacustrine environments (Cohen, 2003). Eroded soils often have naturally elevated concentrations of heavy metals, causing increasing metal flux to be correlated with accelerated erosion.

Pb in particular has become a good indicator of regional anthropogenic pollution because it is produced in smelting, coal burning, and combustion of leaded fuels (Cohen, 2003). Bertine & Mendeck (1978) acquired lake sediments in Connecticut producing a record of changes in metal concentrations as a result of the industrialization. This study concluded that increased levels of Pb were a result of two anthropogenic processes: coal burning during the late 1800's and early 1900's, and leaded gasoline after the 1920's.

Various studies have used Pb in lake-sediment cores to reconstruct local histories of Pb pollution (Cooke et al., 2008), and many have documented a widespread rise of lead levels as a result of an increase in leaded gasoline combustion (Bertine & Mendeck, 1978; McMeekin, 2004). These widespread rises in lead concentrations have been dated using ^{210}Pb dating methods (Bertine & Mendeck, 1978) for various locations. Results suggest that many lakes, particularly in the northeastern United States, reflect an increase in lead and peak lead around the same time, indicating that Anthropogenic-derived Pb can also be used to correlate ^{210}Pb-dated cores. This homogenous increase in deposition

of lead occurs because lead inputs are typically aerosolic and effect areas regionally

(Cooke et al., 2008). Correlation between lead peaks of sediment cores acquired from

lakes in close proximity to each other increases the accuracy of date estimation.

This study analyzes various parameters including trace metals, magnetic

susceptibility, total organic carbon (TOC), total inorganic carbon (TIC), greyscale, C/N,

dry bulk density, water content, and stable isotopes of carbon and nitrogen from an ~40

cm sediment core from Ballston Lake (Saratoga County, New York State) (Figure 1) to

determine changes within the lacustrine environment over the past ~200 years.

STUDY SITE AND HISTORY

Ballston Lake is located in upstate, NY, between Schenectady and Saratoga

Springs (Figure 1). The lake is about 5 km long and occupies an avulsed channel of the

Mohawk River. Radiocarbon ages from the bottom of long cores (>8 meters) indicate that

the channel avulsed ~13,200 ybp and the lake has been accumulating sediment since

(Toney et al., 2003). Ballston Lake is long and narrow, generally dimictic (turning over in

the spring and fall) with depth ranging from 8-15 meters in the North Basin (Rodbell,

personal communications). The catchment basin area of Ballston Lake is 22km^2.
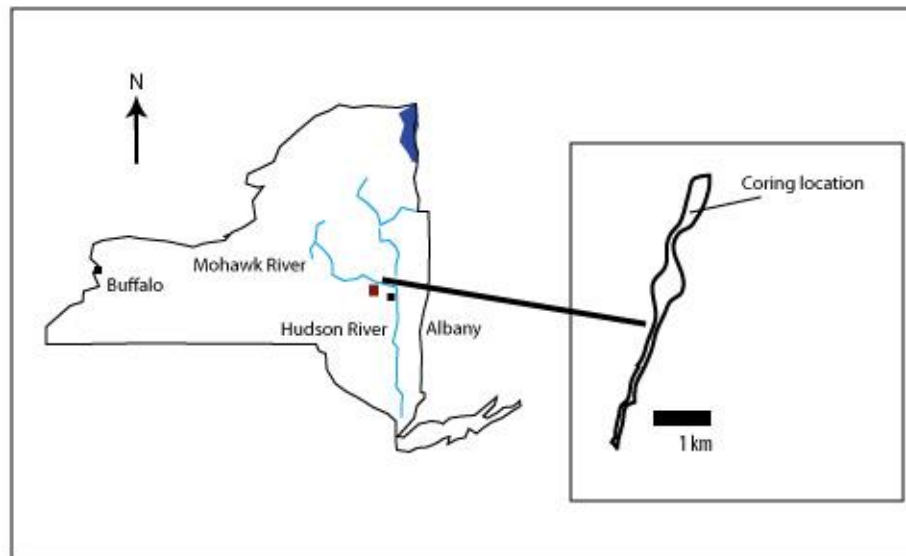
Figure 1: Location map with study site (Ballston Lake) north of Schenectady, NY and coring location in the north end of lake at (42°57.101'N, 73°51.066'W).

The development around Ballston Lake began in the 19th century. Shortly before the year 1800, hotels were constructed in Ballston Springs beginning the transformation from a "swamp" to a popular settlement (Dunn et al., 1974). By 1811 the two forms of transportation between Schenectady and Ballston Spa were a stagecoach line and a horse-drawn railroad, and then later a steam-powered railroad travelling from Schenectady to Saratoga. The increased market availability and water power made it possible for the Ballston Spa area to become industrialized (Dunn et al., 1974). The factories produced axes, scythes, knives etc. Other portions of the Ballston Township developed into farming areas exporting produce to other locations within New York State. With the emergence of electrical power and internal combustion engine, it was not necessary for industries to be as close to the energy source (water) industries were moved farther from this location. (Dunn et al., 1974).

Just south of Ballston and Saratoga, Schenectady was a giant of rail transportation, which was the premier form of transportation throughout the first half of the 20th century (Buell, 2009). Within the next two decades after 1832, Schenectady was also one of the nation's top manufacturers of steam locomotives. The General Electric Company (GE) and the American Locomotive Company (ALCO) contributed to Schenectady's success in the technological community throughout the end of the 19th and first half of the 20th century. ALCO developed into the largest producer of locomotives in the world, producing 75,000 diesel locomotives. GE has downsized and ALCO closed around 1970 (Buell, 2009).

METHODS

Three ~40 cm long sediment cores were obtained from ~8 m water depth at the north end of Ballston Lake (42°57.101'N, 73°51.066'W) using a short Glew Corer. All three cores were acquired on May 14th, 2011 from a semi-stationary soft-bottomed inflatable boat. The three cores were taken from the same coordinate points, (42°57.101'N, 73°51.066'W). Core 1 was extruded and sectioned in the field in 1 cm intervals while the same methods were executed in the lab on core 2 in ½ cm intervals. The samples from core 1 and 2 were freeze-dried while core 3 was split with one half used as an archive. The samples were weighed before and after freeze-drying to calculate water content. The stable isotopes of carbon and nitrogen of the organic matter were measured via isotope ratio mass spectrometer (IRMS) in core 1 and then in core 2 at higher resolution. The nitrogen samples consisted of 0.05 mg of sediment packed in tin

cups while the carbon samples contained 0.1 mg of sediment placed in silver cups with 3 drops of HCl to remove any inorganic carbon. The carbon samples were put in an oven at 50°C for 24 hours to evaporate the acid and were folded in silver cups. Samples were measured via a Finnigan MAT Delta Plus XL IRMS in continuous flow mode connected to a Costech Elemental Analyzer at Iowa State University (Department of Geological and Atmospheric Sciences). Reference standards (Caffeine [IAEA-600], IAEA-N1, and Acetanilide [laboratory standard]) were used for isotopic corrections, and to assign the data to the appropriate isotopic scale. Corrections were done using a regression method. The combined uncertainty (analytical uncertainty and average correction factor) for $\delta^{13}C$ values is $\pm 0.03‰$ (VPDB) and $\delta^{15}N$ is $\pm 0.13‰$ (Air). Percentage C and N were calculated from peak area using the acetanilide as a known sample. TOC is equivalent to the % C values, and total inorganic carbon (TIC) was calculated as the difference between acidified carbon values and non-acidified values. Acid removes all inorganic carbon from the sample, leaving only organic carbon.

Trace metals (Co, Cu, Zn, Sr, Ba, Pb, Fe, and Mn) were measured in samples from core 2 by inductively coupled plasma mass spectrometry (ICP-MS) after extraction and nitric acid dilution (Appendix 1). Leach time of the sediment with 9.5 ml of DI water and 1.0 ml nitric acid in the container was tested by leaving three samples (from 1.25 cm, 16.25 cm, and 31.25 cm core depths) for three different periods of time (24, 48, 144 hours) followed by the same nitric acid dilution procedure to ensure accuracy of the values.

The Pb values produced from the nitric acid dilution method were used to establish an age model by correlating peaks to previously-dated ^{210}Pb records from nearby lakes: Long Pond and Round Pond (Figure 2) to assign dates to intervals within the short core acquired in this study. Peaks in lead concentrations occur due to regional inputs such as coal smelting and the burning of leaded gasoline, which are regional events that occur simultaneously over a broad area. The three identifiable features of the curves from the ^{210}Pb dated cores of Round Pond and Long Pond (Figure 2), the initial rise in Pb at ~*AD* 1882, peak Pb at ~ *AD* 1970, and the top of the core at 2011, were all correlated to core 1 from Ballston Lake. Ages were assigned to the points between the three dated intervals (*AD* 1882, *AD* 1970 and 2011) assuming a linear sedimentation rate.
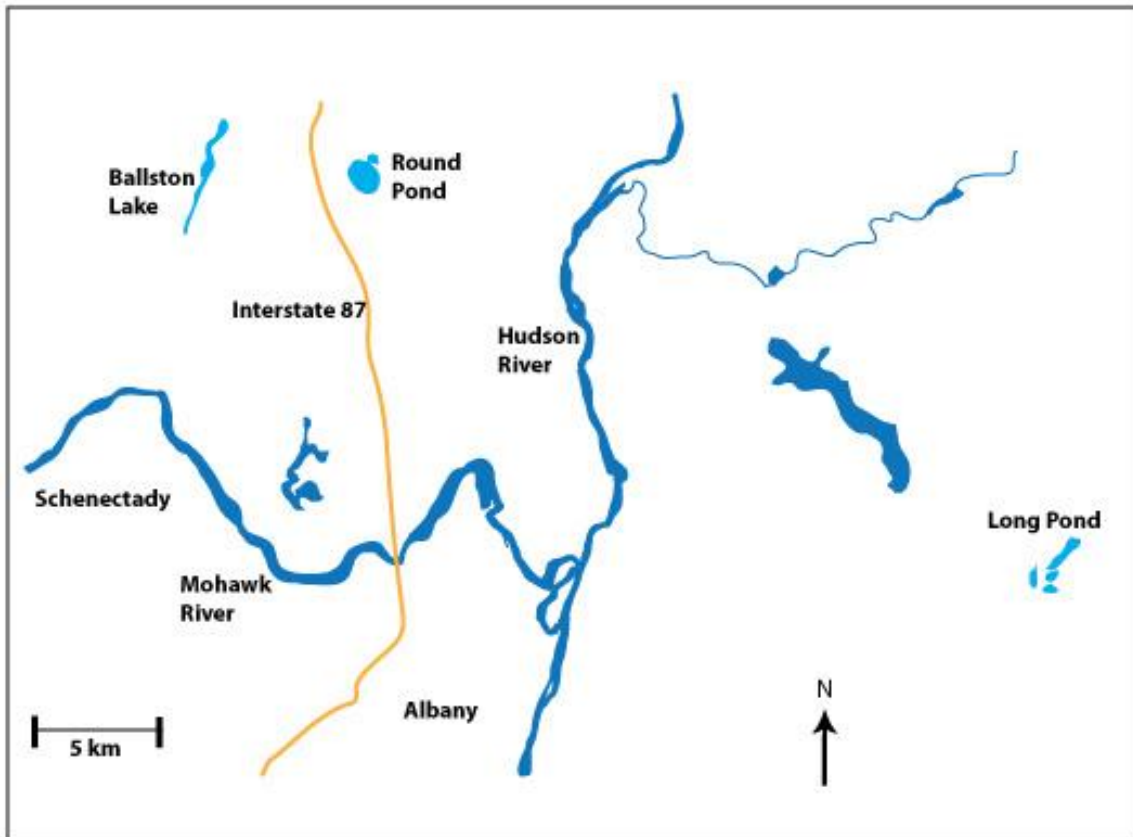

Figure 2: Map of study site (Ballston Lake) and other local lakes including Long Pond and Round Pond in upstate New York.

Core 3 was split in half using a knife and magnetic susceptibility (MS) was measured twice (Surface T1 and Surface T2) using a Bartington MS2C core-logging sensor at 2-cm intervals. Magnetic susceptibility (MS) is the ratio of induced magnetization to the strength of the magnetic field causing the magnetization (Bates & Jackson, 1983). Water content (%) was measured on samples taken in 5-cm increments from core 3 by measuring the mass of 1 cm^3 before and after freeze-drying the sediment. Bulk density is reported as the mass of dry sediment in 1 cm^3. Grey scale values were obtained using the computer program ImageJ on digital color photographs of Core 3. Grey scale values quantitatively record the darkness and lightness of laminae at ~0.025 cm resolution.

RESULTS

The photograph and grey scale of Core 3 show darker sediment between 29-20 cm and 11-3 cm (Figure 3A). The MS values of the core in both Surface T1 and Surface T2 are generally constant throughout the core but increase towards the surface of the core between 0 and 5 cm (Figure 3B). MS and grey scale increase simultaneously in the top 5 cm of the core. There is little variation between MS trials T1 and T2.
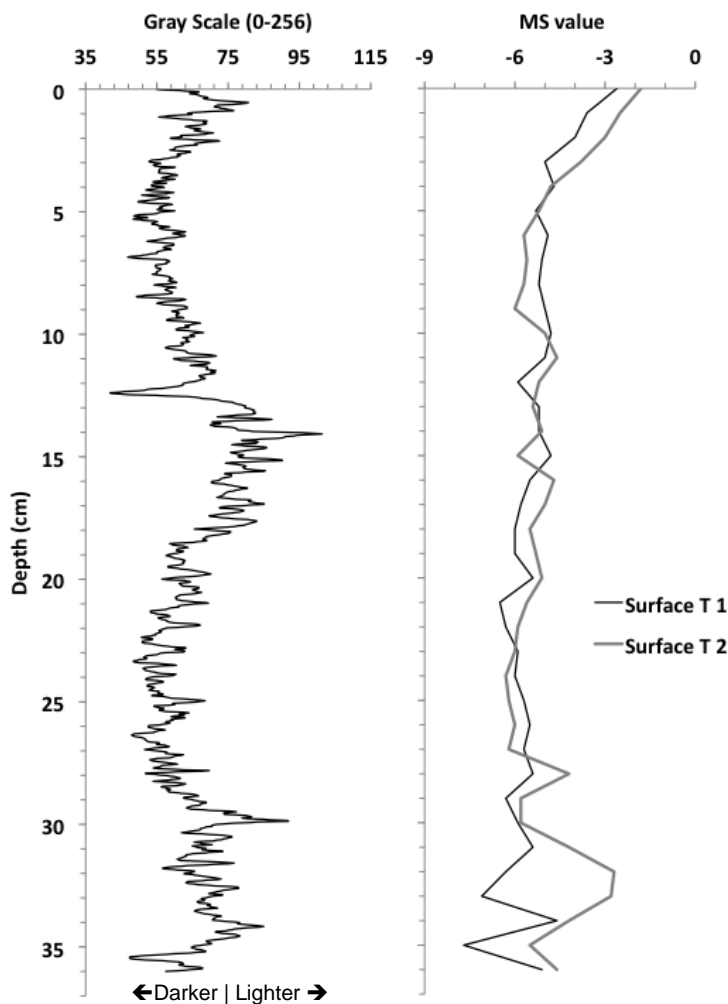
Figure 3: Gray Scale (A) and Magnetic Susceptibility (B) of sediment of core 3 display increasing gray value with increasing MS in the top 5 cm.

Percent TOC in core 2 has an increasing trend toward the surface and ranges from ~13% at 32 cm depth to ~17% at the surface (Figure 4A). The fluctuation in TOC increases between ~22 and 16 cm. $\delta^{13}C$ values increase from ~32 to 27 cm, after which it remains constant at ~-29.5‰, and then becomes more negative from 27 to 18cm, after which, it remains constant (Figure 4C). The range of $\delta^{13}C$ values is between -29 and -31 ‰. Percent TIC in core 2 fluctuates between 0 and 4 with an increasing variability between

~32 and 18 cm depth, where levels decrease abruptly and continue to fluctuate around 0-1% (Figure 4B). Percent TOC is much higher throughout core 2 than TIC.
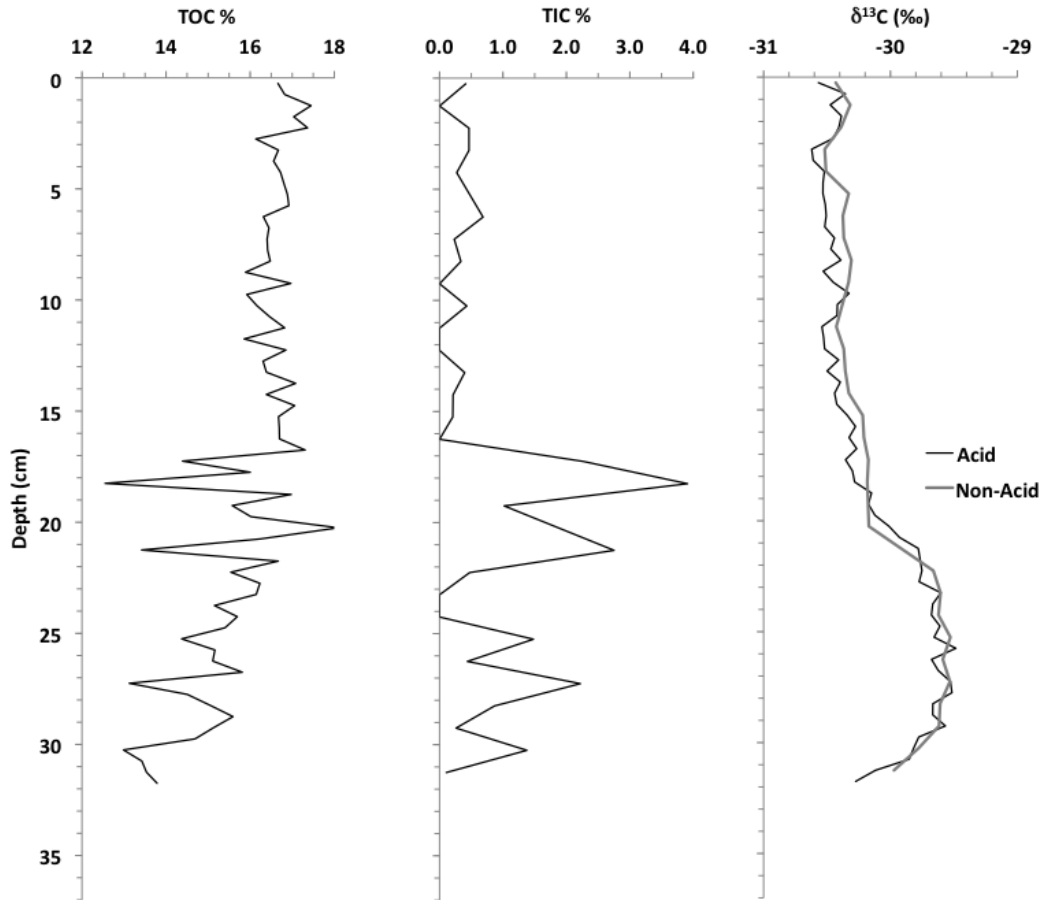
Figure 4: TOC% (A), TIC% (B), and $\delta^{13}C$ values (C) co-vary with depth in core 2 of Ballston Lake.

Percentage N in core 1 ranges from 1.3% to 1.7% with a small increasing trend from bottom to top (Figure 5). There are no obvious trends in $\delta^{15}N$ values but they do fluctuate between 3.2 and 4 ‰ throughout the core (Figure 5). The C/N ratio fluctuates between 7.5 and 11.5 with the lowest values between ~17 and 22 cm depth (Figure 5). The samples from core 2, prepared for the $\delta^{13}C$ values with the addition of acid, have

slightly more positive $\delta^{15}N$ values than the same samples from core 1 without acid

(Figure 5).
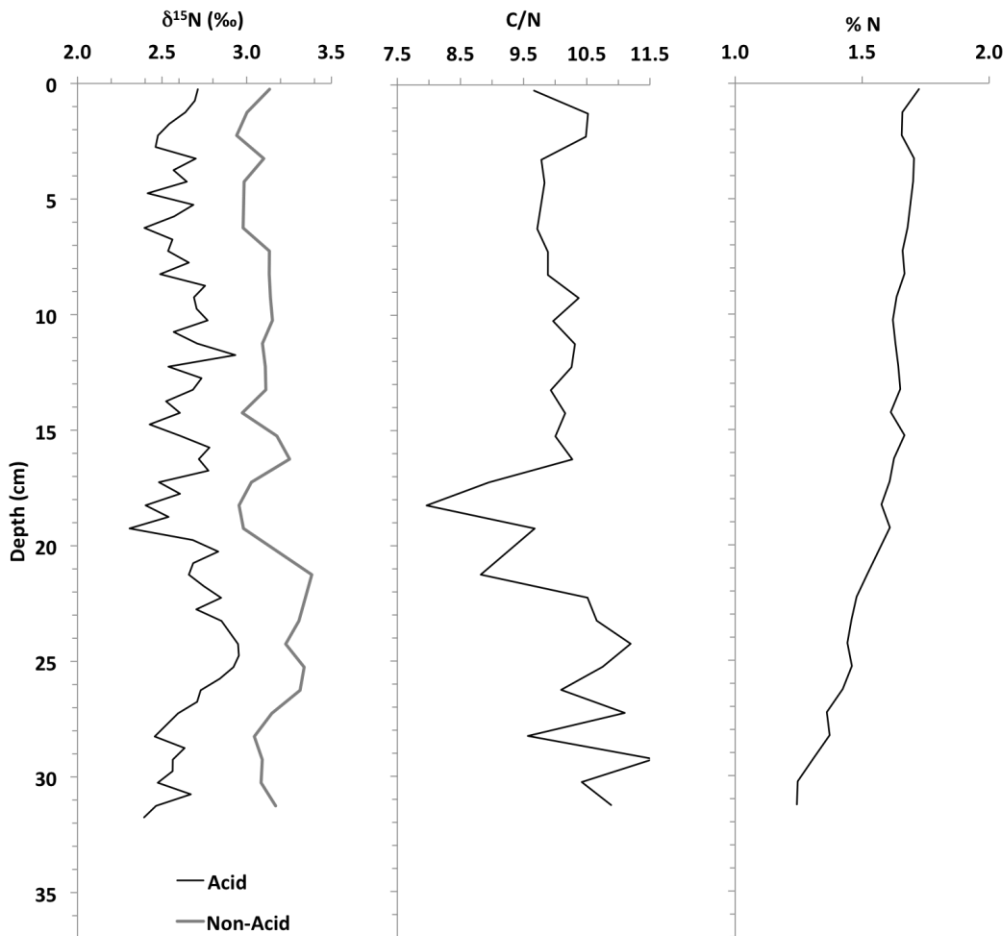
Figure 5: $\delta^{15}N$ values (A), C/N (B), %N (C) remain relatively constant throughout the length of cores 1 and 2. Core 1 is represented by the non-acid values and core 2 is the acid values. Non-acid values of nitrogen are more accurate, acid is simply used to remove inorganic carbon to determine accurate %TOC.

Of the trace metals analyzed, Co, Ba, Sr, and Fe show little down-core variation

in concentrations (Figure 6). Mn increases in concentration from ~360 to 870 ppm around

5 cm depth, followed by a more rapid increase to 1580 ppm over 2 cm, after which

concentrations return to ~700 ppm (Figure 6). Pb increases rapidly from 29 to 196 ppm

between 32 and 22 cm with a peak at 22.5 cm (Figure 6). The greatest peak is only

represented by a single point. Following this peak, Pb concentrations return to ~100 ppm.

Cu increases between 32 and 20 cm where concentrations remain at 200 ppm for the

remainder of the core (Figure 6). Zn concentrations increase from ~90 to ~155 ppm

between 32 cm and 25 cm, followed by constant values at ~150 ppm until present day.

The leach time test on the trace metals reveals that there is little variation between the

different durations that the sediment remains exposed to HNO_3 (Figure 7).
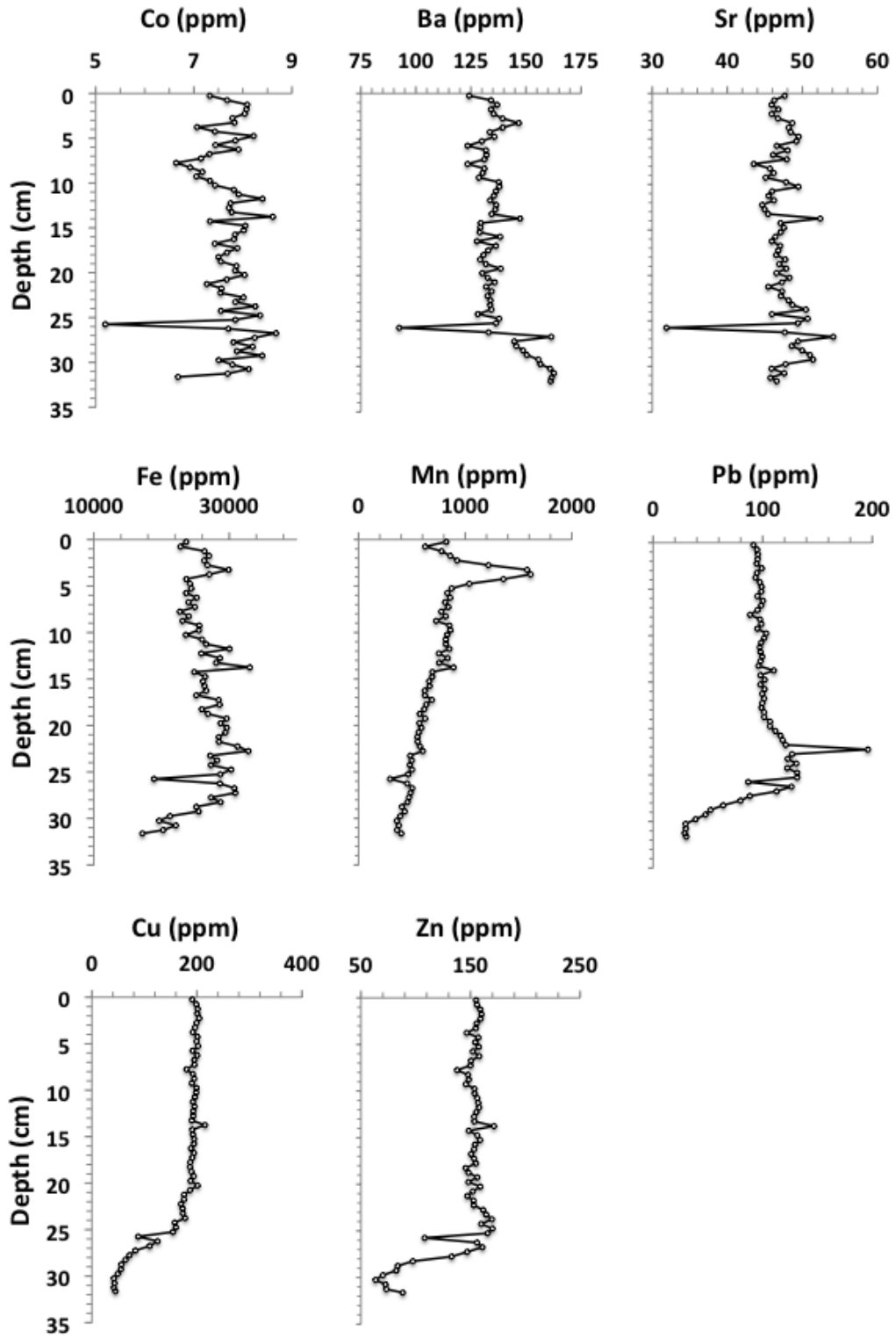
Figure 6: Trace metal values in core 2 show that Co, Ba, Sr, and Fe show no obvious patterns with time, while Mn, Pb, Cu and Zn have increasing trends.
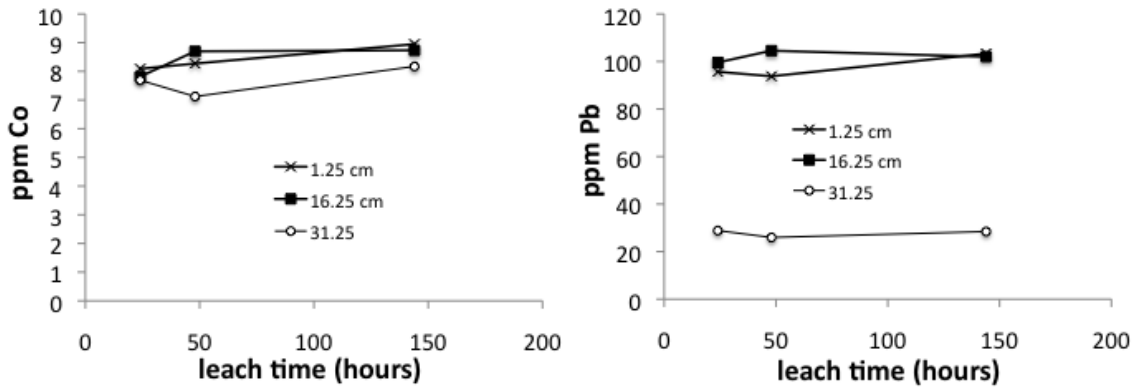
Figure 7: Leach times of Co and Pb in samples from three locations within the core (1.25 cm, 16.25 cm, 21.25 cm) for different amounts of time. Little change occurred between the varying times.

The age model from nearby previously ^{210}Pb-dated cores (Godfrey, 2002) reveal that the 3 ponds (Long Pond, Ballston Lake, and Round Pond) all have similar Pb patterns, with an increase in concentrations starting at ~1882, 15 cm depth at Long Pond, ~31 cm depth at Ballston Lake, and ~75 cm depth at Round Pond (Figure 8). Two different sedimentation rates were calculated throughout the length of the core using the designated age values and depth, one between the initial rise (*AD* 1882) and peak Pb (*AD* 1970) and the other between the peak Pb and present day (*AD* 2011). The sedimentation rates calculated from the age model are 0.107 cm/yr from 31.5 to 23.5 cm and 0.543 cm/yr from 22.5 to 0.5 cm.

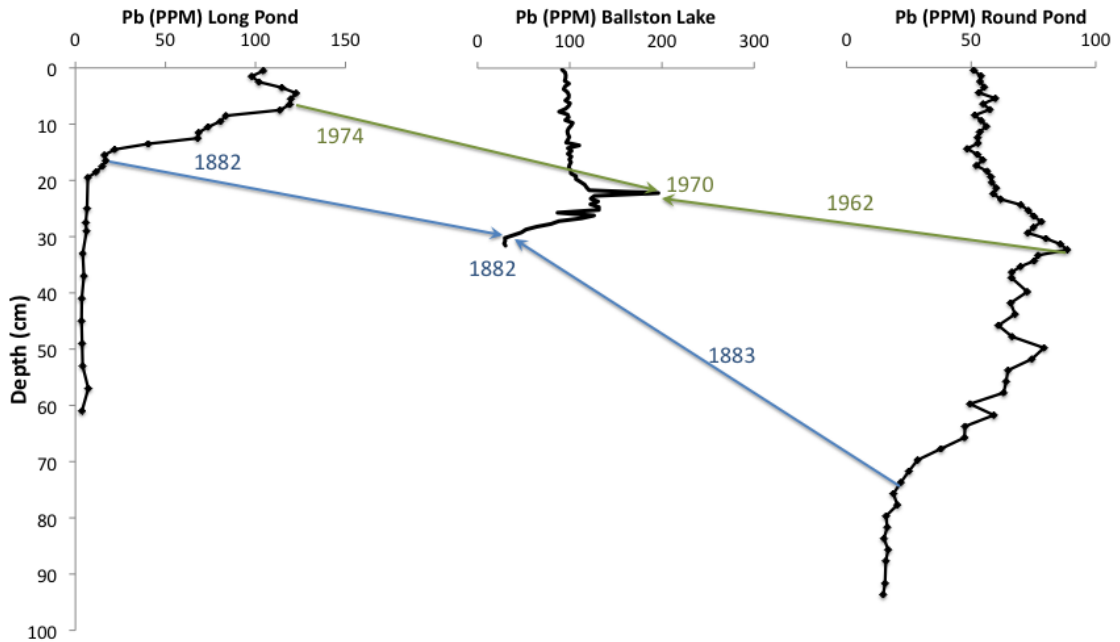Figure 8: Correlation between Pb values of two previously dated lakes (Round Pond and Long Pond; Godfrey, 2002) to Ballston Lake with assigned values in Ballston Lake at 1882, 1970 and 2011.
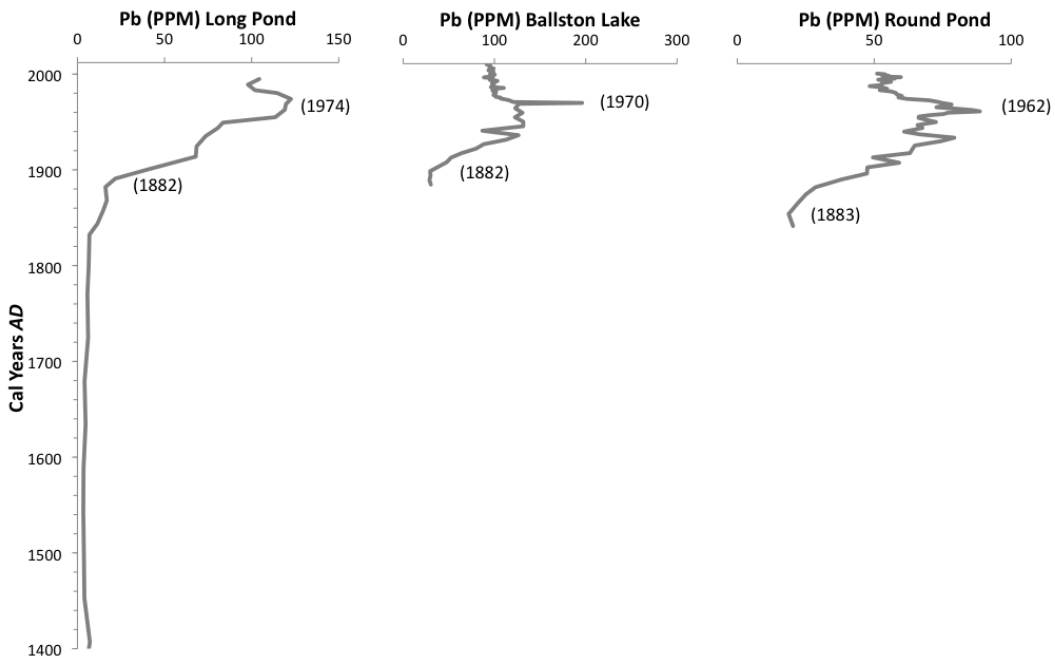

Figure 9: Lead concentrations (PPM) in Long Pond, Ballston Lake and Round Pond over time, with correlated peaks at ~1970. Long and Round Pond data from Godfrey, 2002.

DISCUSSION

Age Model

The age model from previously dated cores from Round Pond and Long Pond (dated by Godfrey, 2002) suggest that that the initial rise in Pb concentrations in Ballston Lake occurred ~1882 (Figure 9), likely caused by an increase in burning fossil fuels and coal at this time. Over the next 100 years, Pb values increased ~4x base levels. Peak Pb in Ballston Lake, was set between dates assigned to Long Pond and Round Pond, 1974 and 1962, respectively. The Clean Air Act of 1970 that resulted in the removal of lead from gasoline was also taken into consideration for this date. The sedimentation rate from 1882 to 1970 is ~2x lower than that from 1970 to present. The increase in sedimentation rate after 1970 appears to be abrupt, however the true increase in sedimentation was probably more gradual. The abrupt increase in sedimentation rate is directly related to the choice of a linear age model between dated intervals. This increase in sedimentation rate reflects either an increase in productivity or an increase in erosion of clastic sediments and deposition into the lake, or both.

Core Stratigraphy

The photographed core and grey scale from core 3 in Ballston Lake show alternating light and dark sediments throughout the core. Sediments are lightest from 35-30 cm, 18-13 cm, and 3-0 cm, suggesting decreased organic matter at these locations (cf.

Cohen, 2003). Bulk density increases with the lighter sediment that represents decreased organic matter (Figure 10). MS values are correlated with clastic sediment (Cohen, 2003). The similar trends in MS and bulk density suggests that the clastic sediment has a high density (Figure 10). MS and bulk density increase, and grey scale grows lighter, from 18-13 cm and within the top ~5cm of the core, suggesting an increase clastic sediment input into the lake.
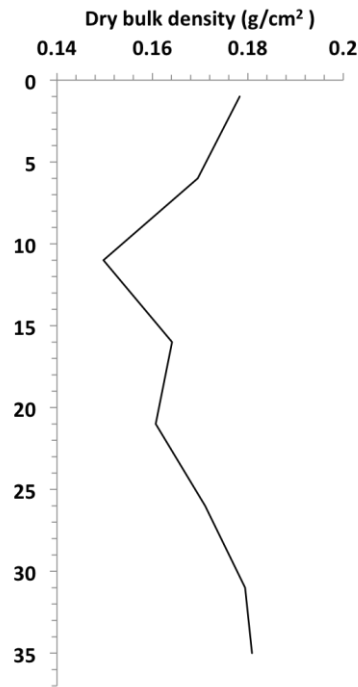
Figure 10: Bulk density varies with depth between 0.14 and 0.2. Increasing density is correlated with increase magnetic susceptibility and clastic sediment.

Percent TIC in Ballston Lake are generally very low, indicating minimal source of inorganic carbon to the lake. The drop in TIC values at ~18 cm suggest the lake or lake sediment may be slightly acidic resulting in rapid dissolution of inorganic carbon or there was a rapid input of inorganic sediment. Between 32 and ~19 cm depth, inorganic carbon values continually increase until this abrupt decrease in concentrations at ~18 cm, after

which they remain constant to the top of the core. If this were an acidification event, it could have been caused by a natural eutrophication event within the lake. Water acidification in lakes is generally the result of enhanced carbon dioxide production from increased respiration caused by enhanced productivity (eutrophication). Acidification due to eutrophication would be a possibility, however, N% and $\delta^{15}N$ values remain constant, and there is not a drastic increase in OM at this time. Nitrogen is a limiting nutrient to many lacustrine organisms and in lakes and increased atmospheric deposition from human sources has caused changes in $\delta^{15}N$ values in lakes (Holtgrieve et al., 2011). This increase has resulted in increased productivity causing acidification of lakes in other studies, however the OM and nitrogen data suggest this did not occur in Ballston Lake in the past ~200 years. The consistent nitrogen concentrations and $\delta^{15}N$ values recorded in the sediments from Ballston Lake suggest that the lake has experienced little impact from the human development surround the lake. Additionally, $\delta^{15}N$ values in Ballston Lake, of ~3, are much more positive than $\delta^{15}N$ values in other Northern Hemisphere lakes in North America, which increase from ~-2 in 1850 to ~-14 at present (Holtgrieve et al., 2001). These more positive $\delta^{15}N$ values in Ballston Lake suggest it was less impacted by agricultural and industrial pollution than other lakes in North America. The nitrogen is likely naturally produced by non-nitrogen fixing phytoplankton because $\delta^{15}N$ values above +1 are typical of non-N_2 assimilating phytoplankton (Cohen, 2003). It is more likely that there was a rapid input of clastic sediment from 31-19 cm depth that increased the concentrations of inorganic carbon at this time. This is supported by the lighter color in the grey scale values after ~19 cm depth.

Ballston Lake maintains much higher concentrations of organic carbon than inorganic carbon. Percentage TOC increases from 32-18 cm depth, followed by a relatively constant value of 16-18 %. Increased organic carbon is generally indicative of increased productivity (Cohen, 2003). This increased productivity displayed in TOC % is correlated with the increased erosion of clastic sediment into the lake, seen by the decrease in TIC % at ~17 cm. The decreasing trend in C/N until ~18 cm depth also suggests that more organic matter is being produced in situ, as the lake becomes more productive. C/N remains low until ~18 cm, around the time when TIC decreases, suggesting these changes are correlated.

Carbon flux, defined as the rate of accumulation of carbon over time ($g/cm^2/yr$), $\delta^{13}C$ values, MS, and TOC % all suggest that terrestrial inputs of clastic sediment from erosion increased towards the surface of the core (Figure 11). The correlation between C flux and MS values (Figure 11), along with the consistent water content (Figure 12), suggest that the changes are not due to dilution of sediment. The progressive enrichment in ^{13}C values may be caused by increased productivity within the lake. The transition of $\delta^{13}C$ values from -29.5 to -30.5 ‰ towards the surface of the core indicates that the organic matter is growing more aquatically derived. The $\delta^{13}C$ values in Ballston Lake are typical of a lake that derives much of its organic carbon from aquatic sources, between ~ -25 and -30. (Cohen, 2003; Schelske & Hodell, 1995). Between ~1970 and 1981, TOC %, TIC %, and $\delta^{13}C$ values suggest an increase in clastic sediment input into the lake, enhanced productivity, and reduced input of terrestrial organic matter. One potential cause of increased clastic sediment and aquatic productivity and reduced terrestrial input of OM could be local deforestation at *AD* ~1970 as population around the lake grew. The

removal of trees and shrubs surrounding the lake could have promoted erosion of clastic sediment. The sediment eroded likely contained limiting nutrients (carbon, nitrogen, phosphorous), thus promoting aquatic productivity. In addition, there would have been be less terrestrial organic matter available to the lake, such as leaf litter, thus reducing terrestrial input and causing ^{13}C to become more enriched. Another potential cause of increased clastic sediment around 1970 is severe drought leading to the death of terrestrial organic matter. In New York, there were prolonged droughts throughout the 1960's (Seager et al., 2011) that contributed to the decline in many plant species throughout the Northeast (Cook et al., 1977). The correlation between TOC, TIC, grey scale, C/N, and $\delta^{13}C$ values in Ballston Lake between ~1970 and 1981 all suggest increased erosion with a lack of terrestrial organic matter due to drought or deforestation.
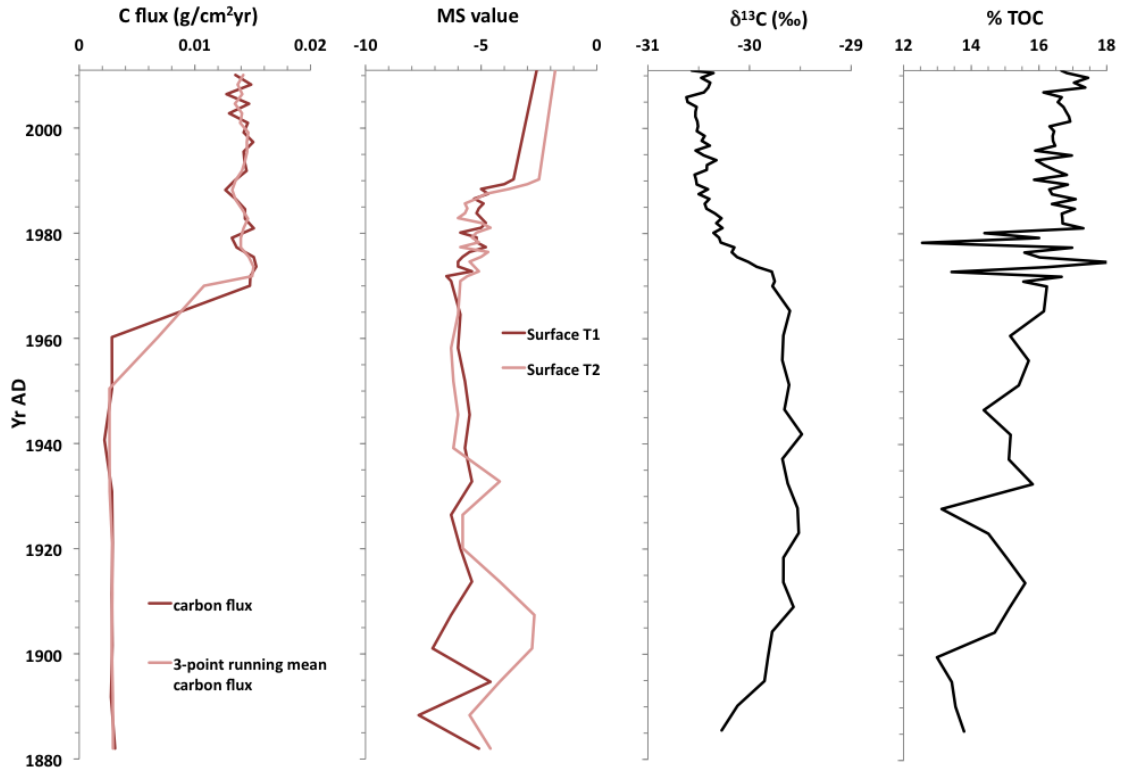
Figure 11: Carbon flux, Magnetic Susceptibility, $\delta^{13}C$ values, and %TOC of Ballston Lake co-vary over time.
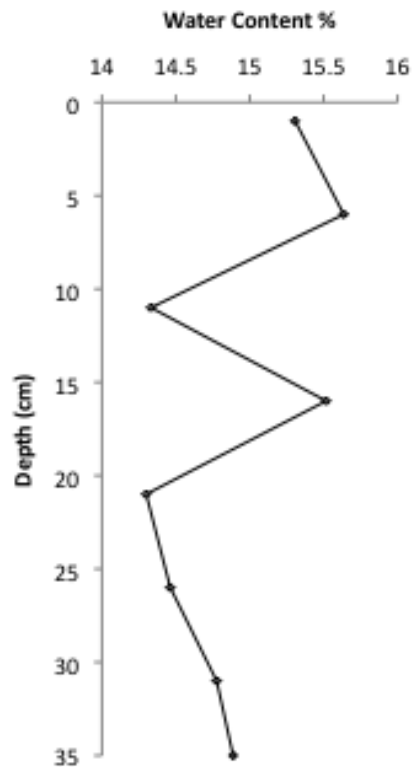
Figure 12: Water content fluctuates little (between 14.5-15.5%) with depth of core 3.

Trace Metals

Lead, Manganese, Zinc, and Copper all show influence of human development

around Ballston Lake between ~ *AD* 1890-2010 (Figure 13). Eroded soils often have

naturally elevated concentrations of heavy metals, causing increasing metal flux to be

correlated with accelerated erosion. Zinc, lead, and copper are three of the many bi-

products produced in industrial emissions during the industrial revolution. All three have

been deposited via airfall from these sources. Studies of Greenland snow reveal

increasing concentrations of zinc, lead, and copper in the past ~200 years, followed by a

decline as improvements were made to industrial emission processes (Boutron, 1995).

Throughout the late 20th century, there were major industrial companies located in Schenectady, NY, such as General Electric and American Locomotive Company (Buell, 2009), that were likely contaminated the local watersheds.
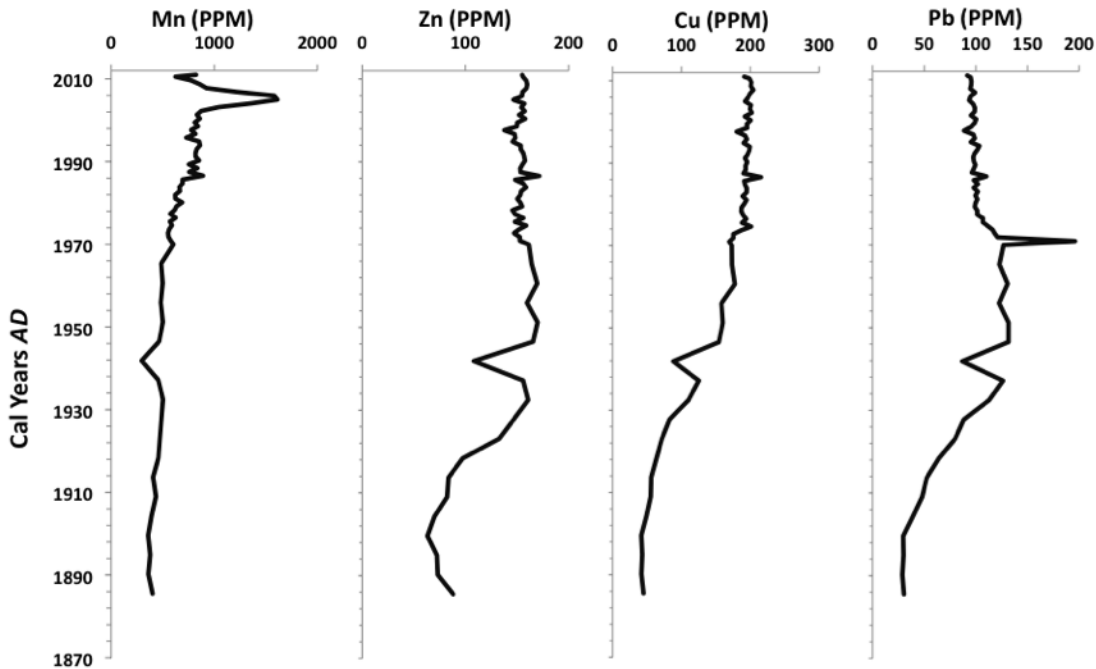
Figure 13: Trace metals (Mn, Zn, Cu, Pb) that reflect varying concentrations throughout the depth of the core with dates assigned using the age model.

It is common knowledge that leaded gasoline increased airborne lead concentrations globally (Bertine, 1978; Cohen, 2003). The lead concentrations are correlated with ^{210}Pb dated cores from Long Pond and Round Pond suggesting the initial rise at ~1882 was caused by an increase in burning of coal, followed by leaded gasoline. The peak in 1970 occurs at the same time as the Clean Air Act that removed lead from gasoline and is followed by decreasing concentrations until present day. Lead, copper, and zinc all have similar curves that increase from ~1882 to 1970 (Figure 13), suggesting all three are emitted in the burning of leaded gasoline.

These industrial companies likely released manganese into the local environment as well, as it is used in iron and steel production (Buell, 2009). The Mn curve is different from the curve of Pb, Cu and Zn (Figure 13), suggesting it is not emitted at such high concentrations from the burning of fossil fuels and industrial companies. Manganese and iron are both redox sensitive elements and if oxygenated, they could precipitate and be deposited in the sediment (Cohen, 2003). The increased concentrations of manganese during ~2002 suggests an oxidation event occurred. There is a similar, but smaller peak at this time in iron as well.

Copper concentrations in Ballston Lake increased rapidly between 1910 and 1990, after which levels remained constant. This rapid increase may be caused by the use of copper as a local treatment for eutrophication (Bertine & Mendeck 1978).

The metal concentrations in Ballston Lake are similar to levels in the local lakes, Round Pond and Long Pond, though concentrations of Co, Cu, and Zn in Ballston Lake are much greater than Round Pond and Long Pond (Table 1). In comparison to other lakes, Mn, Fe, Cu, Zn, and Pb concentrations are all high (Solecki & Chibowski, 2000).

	Co (ppm)	Cu (ppm)	Zn (ppm)	Sr (ppm)	Ba (ppm)	Pb (ppm)	Fe (ppm)	Mn (ppm)
Ballston Lake	7.78	187.95	153.07	47.10	134.35	99.53	26513.64	603.53
Round Pond	5.53	37.38	105.31	45.53	141.11	59.41	20571.13	570.47
Long Pond	3.89	17.01	89.22	9.42	56.81	90.71	6675426.12	436.09

Table 1: Median metal concentrations in Ballston lake, Round Pond, and Long Pond from ~1882 to present. Concentrations in Ballston Lake are more similar to Round Pond than Long Pond.

CONCLUSION

The change that occurred in the various parameters (trace metals, stable isotopes
of carbon and nitrogen, TIC, TOC, magnetic susceptibility, and grey scale) can all be
attribute to increased erosion and clastic input due to a prolonged drought in the 1960s
and late 20th century development. The simultaneous enrichment in ^{13}C and increase in
TOC and clastic sediment (recorded in MS, grey-scale values, and TIC), between *AD*
1970-1981, suggests increased erosion of inorganic matter.

Other impacts on the lake include enhanced metal concentrations due to pollution
from local industrial companies such as General Electric and the American Locomotive
Company during the early 1900's, along with anthropogenic burning of leaded gasoline
in transportation. Increased lead concentrations have been documented in many lakes in
close proximity to Ballston Lake, including Round Pond and Long Pond (Godfrey, 2002).
The records from both Round Pond and Long Pond reflect a peak in lead concentrations
at ~1970, around the time of the Clean Air Act starting the prohibition of use of leaded
gasoline. The lead record from Ballston Lake correlates nicely with the other records
from the area, indicating it had been subject to many of the same influences as the other
lakes.

Sediment cores hold excellent records of changes within lakes over time,
particularly in light of anthropogenic impact. These records will be beneficial in
monitoring the health of lakes and in the event of environmental regulations and policies
against industrial companies. Though there have been some changes in metal
concentrations and the stables isotopes of carbon and nitrogen, these data from Ballston

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Lake suggest that the lake has not been seriously impacted by human development and the local industries.

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APPENDIX 1: ICPS-MS procedure for trace metal analysis in sediments

Materials

*   13 ml plastic test tubes (ICP-MS tube; 1 per sample, with tops).
*   Centrifuge tubes.
*   High-purity HNO3.
*   Kimwipes.
*   DI water.
*   Teflon spatula.
*   Various pipettes.

Dissolution and preliminary work

1.   Collect your samples and dry them.
2.   Label tube with sample name and depth.
3.   On a semi-micro balance, tare one ICP-MS tube (cap on) and add between ~50 and 100 mg of sample using a Teflon spatula. Record the actual sample weight to five decimals.
4.   Calibrate a 10 ml pipette to 9.5 ml by taring a beaker on the semi-micro balance and adding 9.5 ml of D.I. Record the weight to four decimals and repeat this roughly ten times. Sum the weight values and average them. This number = the weight of D.I. added to the samples in their ICP-MS tubes. Do the same to the .500 ml pipette. Multiply this number by 2 and this product = the weight of high purity HNO_3 that will be added to the tube.
5.   Add 9.5 ml of DI water, and 1.0 ml of high-purity HNO3.
6.   Shake horizontally for 12 hours.
7.   Store in refrigerator for 24 hours.
8.   After 24 hours of refrigeration, take the samples out of the refrigerator and let them sit at room temperature for 1 hour.
9.   Take 1 ml from the particle-free top of the sample solution with the 0.5 ml pipette and put it in a new, labeled ICP-MS tube.
10.   Sum the weights of the tube, sample and solution. A) Total weight - tube weight = solution weight. B) Solution weight / sample weight = **dilution factor #1**.
11.   Put these new tubes into the refrigerator until later

Blank Preparation
   1. Add 47.5 ml (5 x 9.5 ml from above) of DI water and 5 ml (5 x 1.0 ml from above) of high purity HNO3 to a 50 ml falcon tube and shake-this is **blank solution 1**
   2. Take 5 ml from the solution in step 1 and add this to a 50 ml falcon tube.
   3. Add 45 ml of diluting solution to this falcon tube—this is **blank solution 2; this will be used in the analyses.**

Internal standard solution

1. Fill a clean 100 ml volumetric flask half full with DI water.
2. Add 7 ml of high-purity HNO3.
3. Add to the flask 0.1 ml each of the 1000g/g (ppm) stock solutions of Rh, In, and Bi.
4. Fill the flask to volume and transfer to a clean storage bottle. Internal standard concentrations are ~1 ppm.

Basic Trace Element Standard, concentrated solution

Element	Stock Bottle Concentration (ppm)	ml of stock solutions used, diluted to 100 ml	Solution 1 concentration (ppm)	ml of solution 1 used, diluted to 50 ml to make solution 2	Solution 2 concentration (**ppb**)
Al	1000	1	10.00	0.5	**98.04**
Mn	1009	1	10.09		**98.92**
Fe	1001				**9813.73**
Co	996	0.1	1.00		**9.76**
Zn	1002	2	20.04		**196.47**
Cu	1005	0.1	1.01		**9.85**
Sr	997	0.5	4.99		**48.87**
Ba	1000	1	10.00		**98.04**
Pb	1003	1	10.03		**98.33**

standard solution 1 is made in a 100 ml volumetric flask, solution 2 is made in a 50 ml autosampler tube; note that concentration of Fe in Standard Solution 2 is result of Fe standard addition directly to standard solution 2 after dilution.

1. Fill a clean 100 ml volumetric flask half full with DI water.
2. Add 7 ml of high-purity HNO3.
3. Add to the flask the volumes of 1000 g/ml (~ppm) stock solutions indicated in the green region of the table above.
4. Fill the flask to volume and transfer it to a clean storage bottle. **This is standard solution 1**.

Diluting solution
* roughly calculate the amount of diluting solution you'll need and make sure to prepare enough for all of the samples for the entire ICP-MS run.

The empirical recipe is as follows…

Half fill a clean one-liter liter bottle with DI water. Add 14 ml of high purity HNO3, and 10 ml of the internal standard solution, and mix. This is the diluting solution. Note that it does not have to be mixed in a volumetric flask. The important thing is that all samples are the same, not that the concentrations are exactly known.

Calibrate the pipettes

Set the 10 ml pipette to 9 ml. Use ~10 samples and determine the weight of the average sample. This will not be exactly 9 g, do not worry. Use this pipette exclusively in doing the dilutions below. Repeat for 0.5 ml pipette

Dilute the samples

1.   Add 9 ml of the diluting solution to the ICP-MS tubes with the 1 ml of the particle free solution, and mix. **Dilution Factor #2**=(volume (weight) of diluting solution+volume (weight) of particle free solution)/ volume (weight) of particle free solution

Dilute the standards

1.   Transfer 0.5 ml of the standard solution 1 to a 50 ml autosampler tube.
2.   Add 50 ml of the diluting solution.
3.   Add 0.5 ml of the 1000 mg/l (~ppm) stock Fe solution, and mix.

Diluting solution weight + standard solution 1 weight + Fe solution weight / standard solution 1 weight = **dilution factor #3**.

Sample calculations

1.   For each sample, calculate: **Total dilution factor** = **dilution factor #1 * dilution factor #2**.
2.   These dilution factors should be put into the ICP-MS analysis program prior to analysis.

Standard concentrations

The nominal standard concentrations in the table above are not quite correct.

A = the actual standard concentration labeled on the stock standard bottle (e.g., 1002 ug/ml; ~ppm).

B = volume of stock standard diluted to 100 ml in standard solution 1.

Actual concentration for all elements except Fe = A * B/100 / dilution factor #3.

Actual Fe concentration = (A * volume of Fe stock solution used (~0.5 ml)) / (Diluting solution weight + standard solution 1 weight + Fe solution weight)

These calculated standard concentrations should be entered into the ICP-MS analysis program after the samples are run.