Spofford Lake
Paleolimnology Report

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Prepared For the Spofford Lake Association by

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Purpose

This report summarizes the results of the Spofford Lake Paleolimnology Project (2018-19), a joint effort of Dr. Lisa Doner and M.S. student William Tifft, and Plymouth State University's Sedimentology Lab. In September 2018, the Spofford Lake Association contracted this work in order to develop a scientifically robust sediment history of the last couple hundred years of Spofford Lake. The primary goal was to identify probable causes for deteriorating water quality conditions described in the Spofford Lake Watershed Management Plan, by FB Environmental Associates, Nov 2018: (http://spoffordlakeassoc.org/images/20181101_Spofford_Lake_Watershed_Management_Plan_final_.pdf).

While water quality monitoring is highly effective method for determining current lake conditions and short-term trends, trends that started decades ago are difficult to discern without a long-term history. Using paleolimnology, Plymouth State University researchers created a historical record that reveals long-term trends in organic carbon and mineral accumulations of sediments across the lake basin. This report describes that record and places it in the context of the modern lake concerns.

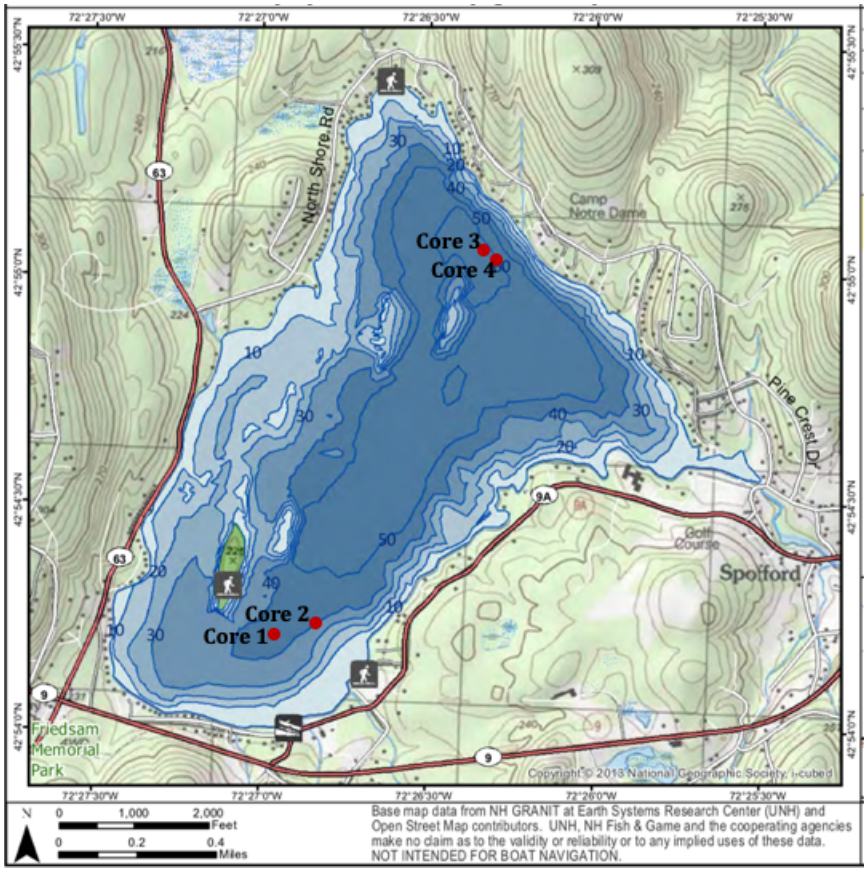
Introduction

Paleolimnology is the study of sediments deposited in sequential layers on the bottom of lakes and wetlands. Sediment is a general term that includes all material transported and deposited. Deep water areas of lakes are calm depositional environments that allow sediment to settle and remain undisturbed. Most natural lakes over 15 feet deep in New England have sediment accumulations in their deeper regions that extend back for 10,000 or more years. The sediments are laid down in chronological order, with older material underlying younger material. The chronological sequence will remain intact unless disturbed by gas or groundwater rising through the sediments, waves, bioturbation (mixing by animals living in the sediments), dredging or landslides. When undisturbed, the sediment layers form an archive of past lake conditions, known as the paleolimnology.

We used a sediment corer to retrieve Spofford Lake's recent sediment sequences. By collecting multiple cores, we are able to trace distinct sediment deposits, and transitions in the character of deposits, across the lake basin. These "marker layers" are sometimes visible as color changes in the sediments, but are more often evident in analyzed data, as changes in organic content, mineralogy, particle-size and magnetism. Sediments move within the lake due to bottom currents, but always downslope towards the deepest parts of a lake. The deepest spot, therefore, collects sediments from all the shallower areas and has the thickest sediment deposit. That is the "sweet spot" for recovering the longest sequence that represents the whole lake condition.

Chemical dating uses the known decay rates of particular radioactive elements, like carbon-14 (radiocarbon) and lead-210, to provide the various ages within a sediment sequence. Radioactive decay "clocks" begin ticking as soon as the radioactive element forms, and the concentration of radiation in a deposit decreases with every tick of that clock. Lead-210 is naturally and continuously created in both the atmosphere, by sunlight, and in the ground, as a byproduct of radon gas. Lead-210 in the atmosphere quickly falls to the ground and becomes part of the sediments deposited at that time. The highest lead-210 concentrations occur at the top of the sediment sequence. Once deposited and buried under fresh sediment, the atmospheric contribution of new Pb210 is blocked off and only background contributions continue. For any sample, we can measure the concentration of radioactivity (the time on the clock) and the decay rate (the time between ticks of the clock) to determine how long ago the sediment was deposited (when the clock started ticking). About 150 years after deposition, all atmosphere-sourced lead-210 in a deposit will be gone, leaving only background amounts. In young deposits with high lead-210 concentrations, the accuracy of the lead-210 age calculation is plus or minus 1 or 2 years. The age accuracy decreases in older (deeper) sediments as levels of unreacted lead-210 drop off. Samples deposited over 100 years ago have a plus or minus15-20 year accuracy.

For this project, we collected four sediment cores from Spofford Lake (Fig. 1). Cores 1 and 2 were collected to study the possible migration of material from the town beach and boat landing into offshore, deeper waters. Cores 3 and 4 are near duplicates, collected from the deepest basin of the lake to provide complete, undisturbed, whole-lake-representative sediment sequences. Core 3, the longest core, was dated using Pb-210.



Base map data from NH GRANIT at Earth Systems Research Center (UNH) and Open Street Map contributors. UNH, NH Fish & Game and the cooperating agencies make no claim as to the validity or reliability or to any implied uses of these data. NOT INTENDED FOR BOAT NAVIGATION.

Figure 1. Locations of the 2018 Spofford Lake sediment cores. Map from NH Fish & Game (https://www.wildlife.state.nh.us/maps/bathymetry.html

Methods Summary – details in Appendix

Coring and Sample Preparation:

All cores were collected off the side of a pontoon boat secured by two anchors limiting drift and swing, using a UWITEC Gravity Corer and polycarbonate tubes of 8.6 cm (3.4 inches) diameter. Two meters (6 ft) above the sediment-water interface, we allowed the corer to free-fall so that bottom sediments were forced up into the plastic core tube. We used a small weight to gently tap the core head and push the core tube deeper into the sediment layers, stopping when the core tube was filled or until repeated taps result in no additional movement on the core cable. During retrieval, the UWITEC design brings a ball up against the bottom of the tube, reducing the risk of sediment loss. Once on the boat, we separate the core tube from the corer, label it with core number and date, and cap the tube's top and bottom. The cores all include some lake water, as well as the sediment-water interface and underlying sediments. We leave this water in place to help stabilize the sediment during transport to the lab but place floral foam in the core top to reduce water slosh. The cores are transported and stored upright until they can be subsampled.

We sampled the cores into slices of known volume by extruding the core upward, in 1 cm or 0.5 cm increments, out the top of the core tube. Each incremental slice became a unique sample, labeled according to its depth below the sediment-water interface. Cores 1 and 2 were sampled at 1 cm (about ½ inch) intervals; cores 3 and 4 at 0.5 cm (about ¼ inch) intervals. We measured the wet weight for each sample, then freeze-dried them (in their sample bags) for at least three days to obtain dry weights. Freeze-drying preserves samples from mold and other alteration and makes them easy to split for additional analyses.

Laboratory Analyses

Wet and dry bulk density – a measure of water versus mineral content in each sample:

We determine wet and dry bulk density (weight per unit volume) as the measured wet and dry weights, respectively, divided by sample volume. Sample volume is based on the inner diameter of the core tube and the thickness of each slice (either 1 cm or 0.5 cm, depending on the core), and the equation: volume = Pi x core radius squared x slice thickness. Bulk density values provide a sense of how much of each sample is low density carbon-rich plant and animal (organic) material versus high density mineral (inorganic) rock products.

Loss-on-Ignition (LOI) – a measure of the amount of organic carbon in each sample:

The organic content in each sample is the non-mineral component created by living matter like plants and animals. Since living things are made largely of water and carbon, we can measure the amount of this material by drying the sample and then burning off (igniting) the carbon into carbon dioxide gas. The difference between the dry weight and the weight after burning is the amount lost on ignition (LOI). We measured 0.5 g of each dry sample into porcelain crucibles, burned them for two hours at 550°C (1022°F), cooled them in a vacuum desiccator to prevent reabsorption of moisture and measured the ash weights. The results are traditionally given as percentages using dry sample weight and ash weight:

LOI (%) = $100 * (\frac{dry\ weight - ash\ weight}{dry\ weight})$. Higher values indicate higher organic content.

Magnetic Susceptibility – a measure of soil formation and erosion:
Changes that affect watersheds can alter the magnetic characteristics of the sediments. For example, watersheds that go from fully forested to clear-cut often erode minerals that have strong susceptibility to low frequency magnetic fields, such as magnetite and other iron-oxides. Soil formation and weathering, on the other hand, transform iron oxides into smaller grains of limonite and hematite, which respond most strongly to high frequency magnetic fields. To analyze sediment magnetism, we packed dry sediment from each sample into pre-weighed polystyrene cubes and weighed the packed cubes to obtain magnetic sample weight. We applied a magnetic field to each sample cube at two frequencies, low (600 Hz) and high (6000Hz), using a Bartington MS2B Dual-Frequency Sensor and a MS3 Bartington Magnetic Susceptibility Meter to measure sample susceptibility (χ). Since one cube might contain more or less mineral sediment than another cube, we corrected for this effect by dividing average susceptibility by magnetic sample weight. These corrected values are known as mass susceptibility (MS). Changes in MS indicate a change in sediment source, with high MS values indicative of more rock-rich material, and low MS values indicative of stable, well-formed soils. Very low MS can also result from the transformation of magnetite to pyrite in anoxic (no oxygen) environments, like deep lake basins. Magnetic susceptibility was measured on all cores.

Particle Size – a measure of the energy transporting sediment to the core site:
Natural sediment deposits include a diversity of grain sizes, with the frequency of certain sizes related to the energy of deposition. In lake sediments, an abundance of larger-sized grains suggests transport under high energy conditions such as storm-generated waves or strong currents and floods. Smaller grain sizes point to prevailing low energy conditions, such as calm water or weak currents. Exceptions to this occur when sediment is artificially transported to a lake, for beach replenishment or nearshore construction. The farther away from shore a core is collected, the less likely it is to contain sand-sized particles, and the more likely that the core will contain primarily clay and fine-silts. Particle sizes of the mineral fraction in each sample were analyzed for Spofford Core 3 using a Horiba LA-920 Laser Particle Size Analyzer.

Lead 210 Dating - St. Croix Watershed Research Laboratory, Minnesota:
The radioactive isotope ^{210}Pb is used to date sediments deposited within the last 150 to 200 years. The rate of ^{210}Pb input and the concentration measured in each sample establishes the age of each sediment sample and rates of sedimentation accumulation. Dr. Daniel Engstrom at the St. Croix Watershed Research Laboratory in Minnesota supervised analysis of the lead-210 activity in samples from SPO 2018-4 with an EG&G Nuclear alpha spectrometry system, polonium distillation equipment, and polonium-209 and lead-210 standards. From the results, he developed an age model of sediment depth versus age and sediment accumulation rates. We applied the age model to the core data, using linear interpolation of ages between measured samples and extrapolating age beyond the last dated sample using the sedimentation rate of the two oldest measured ages. All the results from core 4 are presented using the lead-210-predicted ages for each sample.

Sediment Geochemistry by XRF – Hamilton Analytical Lab (HAL), New York:
X-Ray Florescence (XRF) involves use of x-rays to measure element concentrations in rocks, sediments and other materials. In an XRF spectrometer, high-energy x-rays excite atoms within a sample and causes those atoms to fluoresce. Hamilton College's XRF laboratory uses a Thermo

ARL Perform'X XRF spectrometer and crystal-collimator. The instrument's detectors count the fluorescence at particular wavelengths per unit of time (intensity) and convert the data to element concentrations. Measurements include elements ranging from carbon to uranium at concentrations from the low parts per million (ppm) range to parts per hundred (%). PSU graduate student William Tifft prepared dried samples from Spofford core 3 at Hamilton College, using a mill to grind each sample into a very fine powder and then adding a stabilizer. Each sample was fused, reground and fused again at 1000°C in graphite crucibles. The resulting beads were run in the Hamilton XRF spectrophotometer for approximately 2 hours and measured. The results include a suite of 44 elements.

Results

Details about the cores are provided in Table 1. While all the cores have been analyzed, the majority of effort was put into Core 3 which has the longest record and has been directly dated with lead-210. Archival material is available from all the cores from additional work, as desired, although the uppermost 1 cm in Core 3 has no material left.

Core Name	Lat	Lon	Collection Date & Time	Core Length (cm)
SPO 2018-1	42.904127	-72.449071	2018-10-20 14:44:56Z	41
SPO 2018-2	42.904259	-72.44874	2018-10-20 15:45:34Z	25
SPO 2018-3	42.904505	-72.444602	2018-10-20 16:06:02Z	53.5
SPO 2018-4	42.917204	-72.438494	2018-10-20 18:05:02Z	37

Chronology

In Core SPO 2018-4, atmospheric lead-210 activity was measurable in the top 24 cm of the core. The top of the core had an activity of 58.32 pCi/g. Seven samples below 24 cm indicate background levels are 0.67 ± 0.01 pCi/g. The oldest sample with measurable activity was at A.D. 1836 ± 13 years. Based on a near exponential decay curve and constant but low rate of sediment accumulation, the overall dating reliability is deemed excellent. After A.D. 1900, sediment accumulation averaged 0.14 cm/year, or 14 cm (5.5 inches) in 100 years (Fig 2).

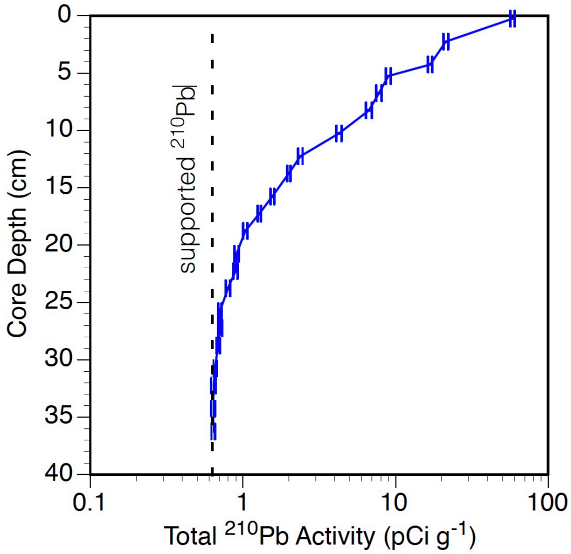
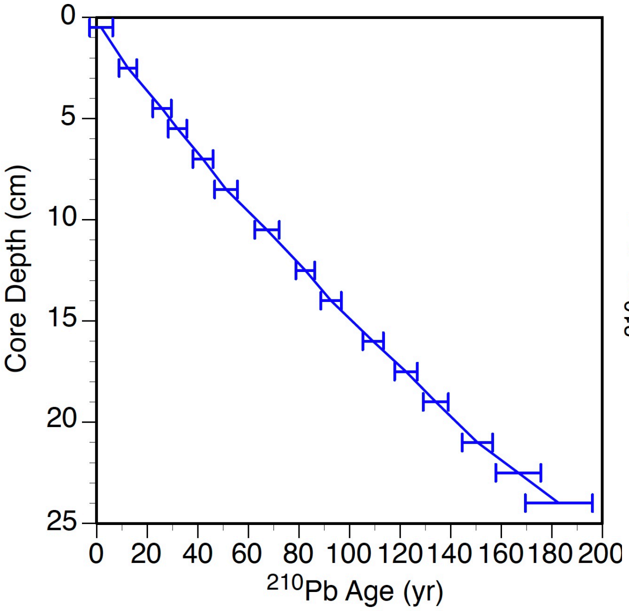
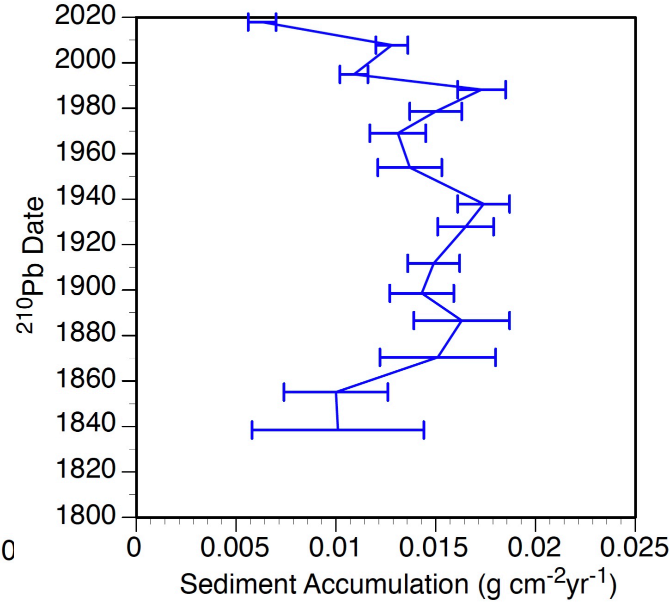


Figure 2. The lead-210 activity in SPO 2018-4 steadily and predictably decreases, providing an excellent date-depth relationship (left). For any sample in this core, we can use this relationship to determine the time the sediments were deposited and the rate of accumulation (below). In these figures, the margin of uncertainty for each sample is indicated by a bar. The longer the bar, the more uncertainty there is in the value. For the deep hole, the sediment accumulation rate is about 14 cm per 100 years, with a distinct decrease in rate after 1980 (below left).





Loss on Ignition

Loss on Ignition (LOI) is an indicator of sediment organic content. High values of LOI generally indicate abundant organic material reaching the sediment and high rates of decomposition and dissolved oxygen depletion below the thermocline and within the sediment layers. All four cores show increases in organic content near the top of the core (Fig 3). These are commonly seen patterns in lakes because European settlement and land use practices increasingly disrupted the soils, releasing nutrients into the lake. This continues today with shorefront property development, leaking septic systems, landscape fertilizers, and manure accumulations from cows, sheep, chickens and pets. Organic carbon in lake sediments can come from lake productivity (algal and macrophyte growth), from upland sources (grasses, shrubs and trees), or both.

At Spofford Lake, the cores each show a distinct increase in LOI values in the upper 6 cm (~2.5 in) (Fig 3 top). For the deep basin, the longer-term background values of LOI are 20-22%, with a recent increase to 28-30%. In the shallower, southern region of the lake, long-term background levels of 3% in Core 1, and 17% in Core 2, increased recently to 22% in both cores. The lead-210 data show that increases in LOI began about 1930, but all cores show a sharp up-tic in the rate of increase in organic content after 1970 (Fig 3 bottom). The coherency of the LOI increase at all core sites indicates that this is a lake-wide change in organic loading to the lake. Comparison with other lakes in the region show that Spofford's recent increase in organic-rich sediments is not unusual (Fig 4). These other lakes are also experiencing recent increases in bottom water (hypolimnion) anoxia.

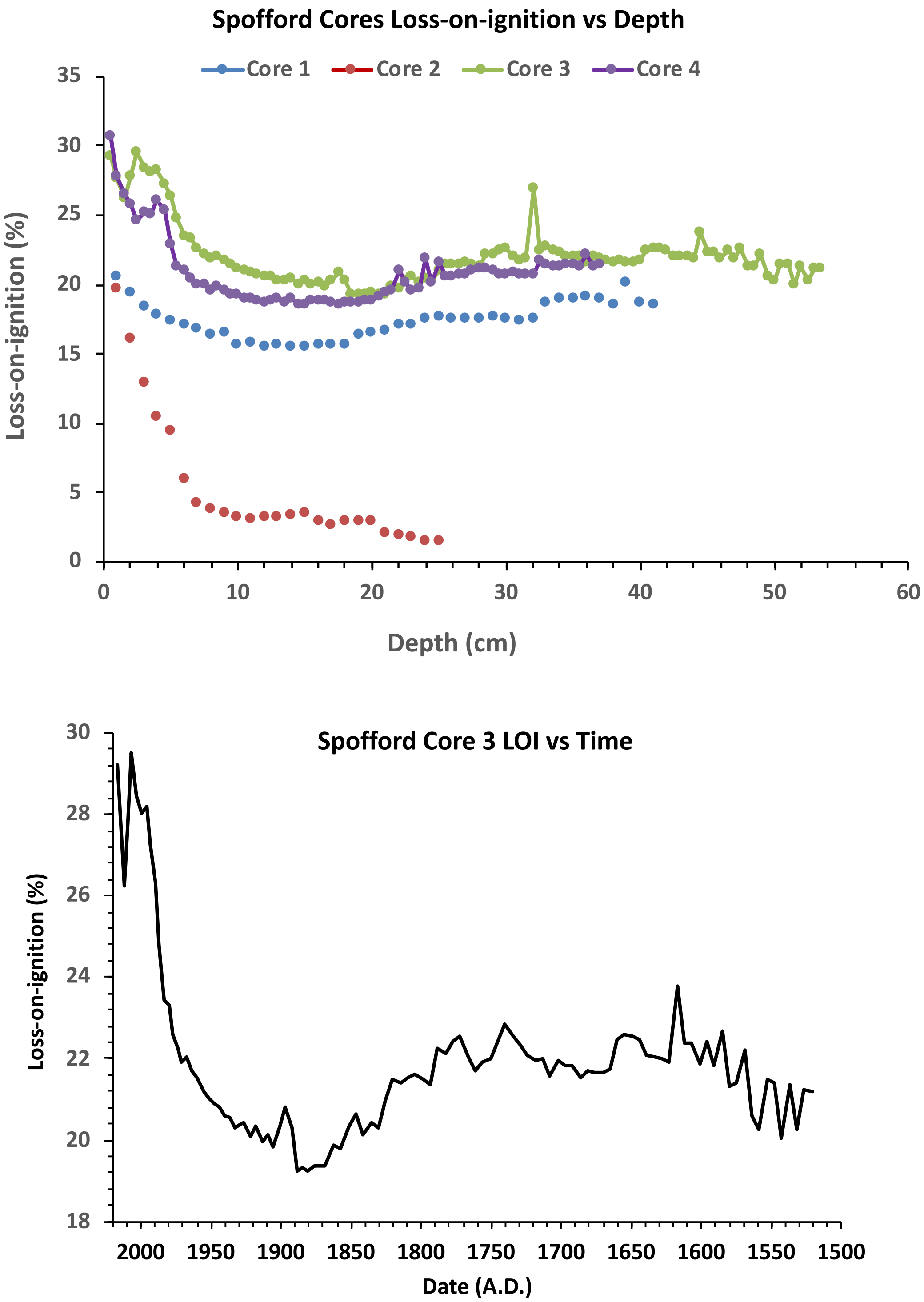


Figure 3. Loss-on-ignition results for all four Spofford cores plotted against depth (top). Core 3 LOI results plotted on an exaggerated y-axis, with lead-210 age on the x-axis (bottom).

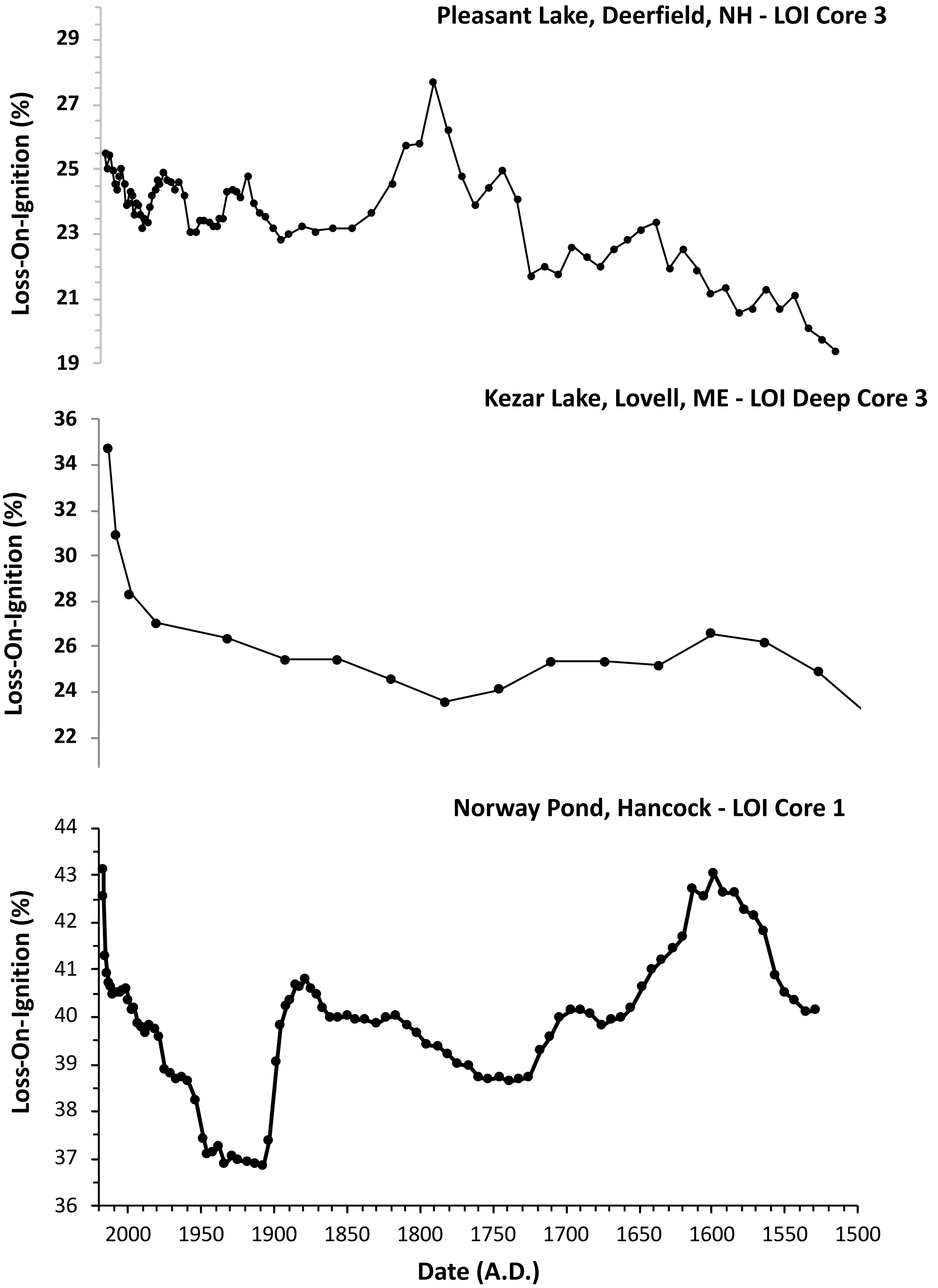


Figure 4. Loss-on-ignition values from this century to 1500 for other lakes in New Hampshire and Maine, with age determined by lead-210 dating and linear extrapolation of sedimentation rates.

Magnetic Susceptibility

Overall magnetic susceptibility is affected by magnetic grain size, the concentration of magnetic minerals in a sample and oxygen levels at the site of deposition. MS changes can indicate a change in the sediment source or a change in dissolved oxygen levels. All of the cores have magnetic values that increase sharply near the top of each core, pointing to a recent increase in mineral inputs, or an increase in the size of the magnetic grains (Fig. 5). Because each sample is a constant volume, as the mineral content increases, we normally expect organic content to decrease. These cores are somewhat unusual because we see both MS and LOI trending together in the uppermost part of the cores. This suggests that the material in the uppermost samples, after circa 1980, has a different composition and probably derives from a different source than what was deposited prior to 1980. This determination is also supported by the particle size results (below).

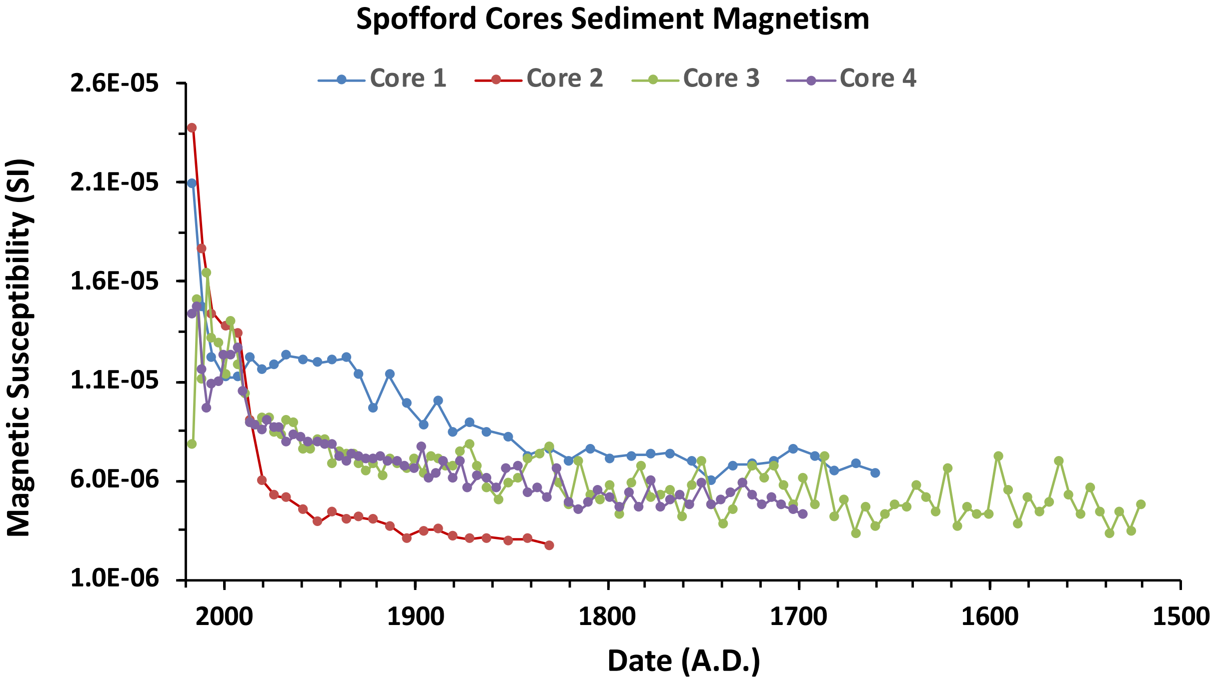


Figure 5. Magnetic signature of the Spofford Lake sediment cores plotted against core depth.

Particle Size

Particle (grain) size was analyzed on Spofford Core 3, the deepest and longest core. The results reveal three intervals when larger particle sizes were more prevalent: 2019 to 1920 (0-15 cm); 1840 to 1810 (23.5-26.5 cm); and, to a lesser amount, 1720 to 1640 (34-42 cm) (Fig. 6). Sand-sized grains (greater than 63 microns diameter) are difficult to transport long distances unless flow rates are rapid or the grains are carried down a steep slope. These conditions can develop during floods, especially during spring melt when the incoming flood water is colder than the lake water. In that situation, sediment-rich turbidity flows can develop where stream flood waters enter the lake. These cold, dense currents can travel as a nearly frictionless bottom currents the entire length of the lake, coming to rest in the deepest basin. When flooding occurs when the lake is ice-covered, then large-grained stream sediments may spill out onto the ice surface and eventually fall into the lake when the ice melts.

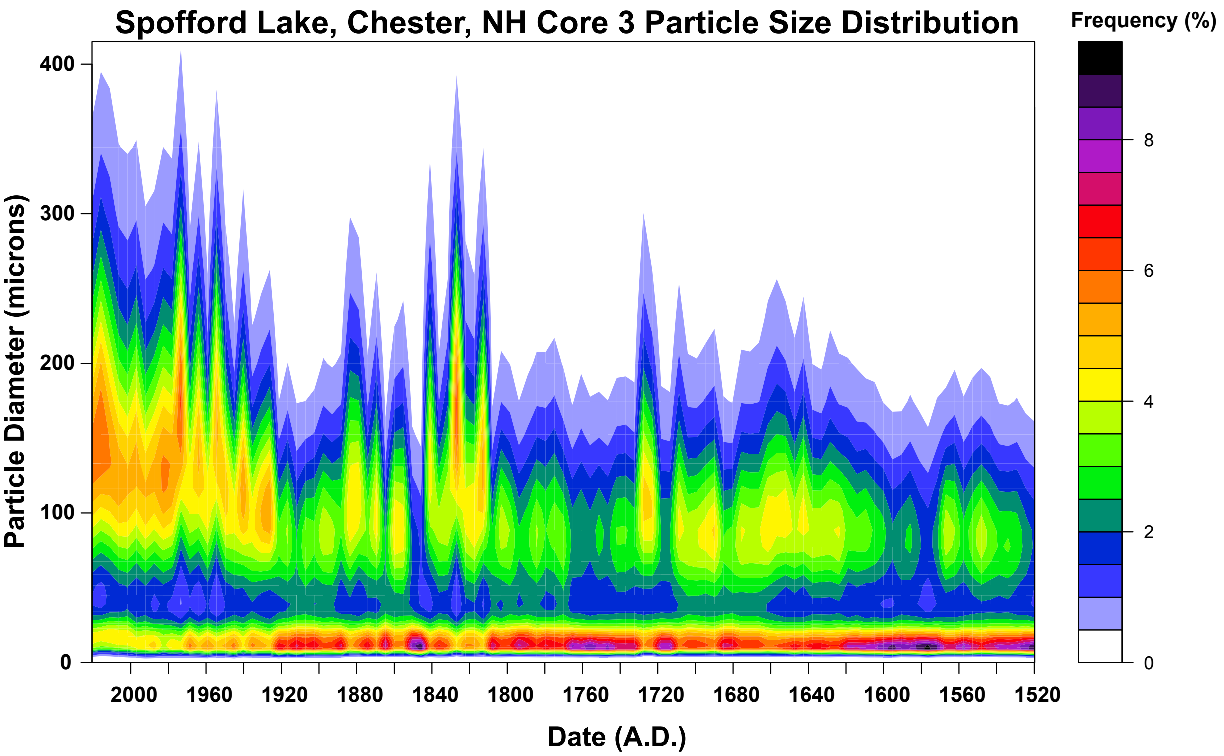


Figure 6. Frequency of particles of different diameters in SPO Core 3, measured using laser scattering. In this plot, the particle (grain) sizes are on the left vertical axis, in microns (or micrometers). By international convention, sand-sized particles are 63 microns and larger, silts are 4-63 microns, and clays are less than 4 microns (Wentworth Scale). The colors, and color scale on the right, indicate how often a particular size of particle is measured in each sample, with black and deep red the most frequent (above 8%), and blues to white rarely encountered (0-2%). The horizontal axis is the calendar date associated with each sample. For most of the past 600 years, the dominant particle size in the deep hole has been fine silts and clays. From A.D. 1920-1975, the dominant particle size changed, to about equal amounts of fine silts and clays versus sand. After A.D. 1975, the dominant size has been fine- to medium-sized sands.

Floods, however, are episodic and short-lived. In order to create long intervals of coarser sediment deposition, flooding must be very frequent, or else the land surface needs to be disturbed and easily eroded in small-scale runoff events. Climate change can create a set-up for more frequent flooding and also land erosion. For instance, from about 1350-1890, climates in many regions of the world, including New England, were cooler than today, with deeper snow accumulations and more months with frozen ground and ice cover on the lakes and rivers. This interval is nicknamed the “Little Ice Age” in climate records all over the globe. Within the Little Ice Age, the interval from 1645 to 1715 (the Maunder Minimum) is one of the coldest periods because of unusually low solar energy output. Spofford Lake’s record appears to show a response to the Maunder minimum, with a slight dip in the organic accumulation and increase in sand-sized particles reaching the deep hole.

After A.D. 1800, increasing intensity of European Settlement, land clearance, soil tilling, lumbering activities and watershed development periodically disturbed the slopes around the lake so that, even as climate conditions ameliorated at the end of the Little Ice Age (by A.D. 1900), it appears that some forms of erosion intensified. This is particularly evident after A.D. 1920, and even more so after A.D. 1975. The cause of this late-20th Century intensification should be investigated further. The most recent samples (i.e. from A.D. 2018), contain more sand in the deep spot than at any time since massive deforestation occurred nearly 200 years ago. Given the evidence of high energy transport with more sand, it is surprising that this mineral influx apparently hasn't diluted the organic content of these deposits. Although the mineral grains in each layer are larger after A.D. 1975, each sample contains less mineral material, and more organic material overall (Fig. 7). This opposite trend, of larger mineral sizes but fewer mineral grains, is unique to the last several decades.

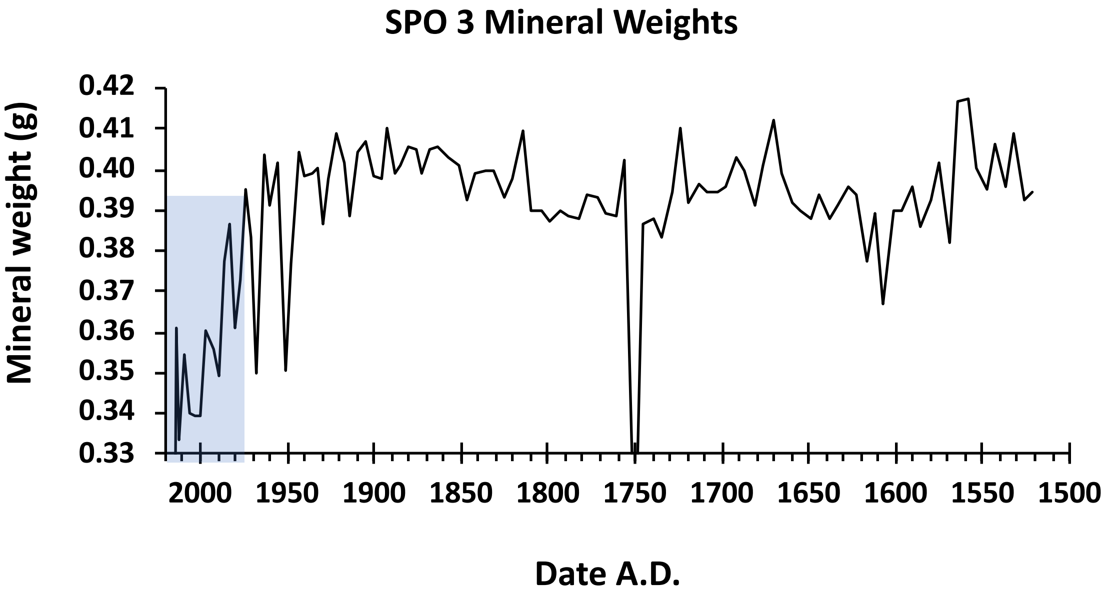


Figure 7. Mineral weights for Core 3 samples, determined after burning off the organic material at 550°C. Ages are based on lead-210 analyses. The shaded portion coincides with a period of lower mineral influx but larger mineral particles. The only other sample with low mineral input, in A.D. 1750, involved much smaller sized mineral grains.

XRF-Geochemistry

Core 3 was analyzed for mineral chemistry at Hamilton Analytical Lab in New York using X-Ray Fluorescence (XRF). For this report, the results have been simplified, with elements grouped into categories depending on what they typically indicate: soil erosion (Fig. 8), bottom water oxygen levels (Fig. 9), and anthropogenic influences (Fig. 10). Detailed results can be found in Appendix A, or by emailing Dr. Lisa Doner (ladoner@plymouth.edu).

Elements associated with soil erosion are barium (Ba), sodium (Na), magnesium (Mg), calcium (Ca), and titanium (Ti), (Fig. 8). These elements tend to track each other, with highest values between A.D. 1825-1985 (25-5 cm) indicating higher rates of watershed erosion. The concentrations drop after A.D. 1990, reaching pre- A.D. 1825 levels, suggesting improved soil retention either by better runoff management, lower development rates, and/or re-forestation.

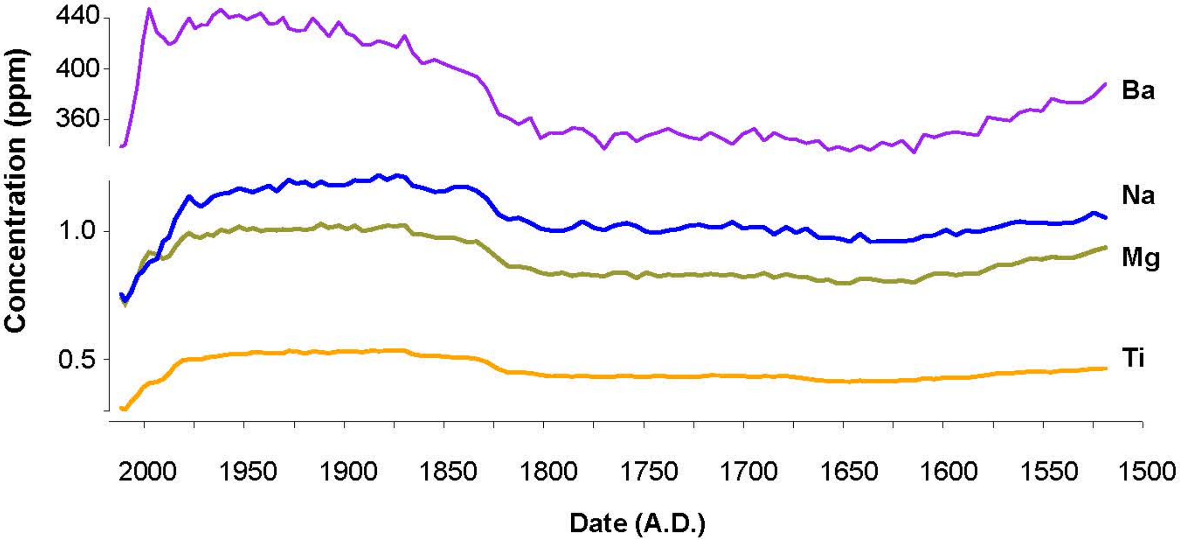


Figure 8. Common elements in SPO 3 that indicate soil erosion: titanium (Ti), magnesium (Mg), sodium (Na) and barium (Ba). The decrease in all of these indicators in the last 30 years suggests that overland erosion of soils is not the source of larger particles noted in Fig 6.

The most common elements used as low oxygen (anoxia) indicators in lake sediments are molybdenum, iron, and manganese (Fig. 9). Higher concentrations of these elements occur when mineral deposits rich in these elements are repeatedly exposed to anoxic water conditions such as often occurs at the sediment-water interface in deep lake basins. In anoxic conditions, these metals leach out of the near-surface sediments and, over the year, accumulate as dissolved elements in the bottom water. During fall and spring overturn circulation, sudden oxygenation of the bottom water causes these elements to mineralize again, often forming an orange-colored floc on the lake bottom. Every time anoxia occurs, these same minerals will re-dissolve into the water. The concentrations increase with each anoxia event because new material is constantly coming in from the watershed and the bottom water cannot escape the lake. Eventually a sediment layer becomes buried deep enough that it is isolated from the lake water and so no longer dissolves. This usually occurs at 5-10 cm below the sediment-water interface. Elements like molybdenum are particularly sensitive to changes at low levels of dissolved oxygen and will not precipitate if any oxygen is present. Iron and manganese, by comparison, will form iron-rich precipitate in the presence of low levels of oxygen. This is often seen as orange floc on anchors, cables, and bottom sediments.

In the deep basin of Spofford Lake, concentrations of redox sensitive elements progressively increase above background levels starting shortly after Settlement in A.D. 1660 (Mn data), after A.D. 1775 and 1830 (Mn and Fe data), after A.D. 1925 and more sharply after A.D. 1955 (Mn and Mo data), with the highest rate of increase after A.D. 1985 (all indicators). At each of these inflection points, Spofford Lake's bottom waters would have become less oxygenated over longer intervals. Many of these transitions are coincident with significant climate and land use changes and watershed development.

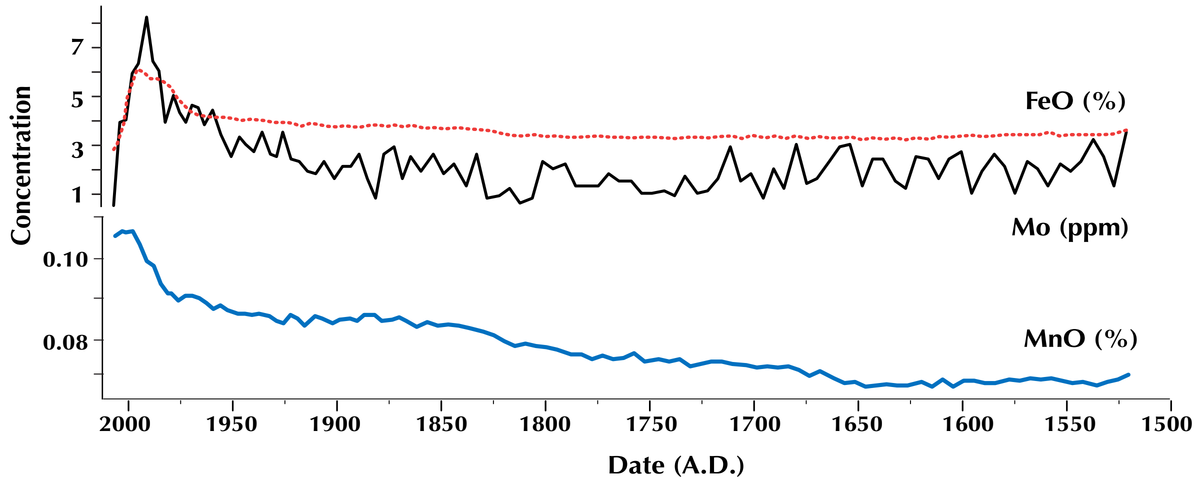


Figure 9. Sediment concentrations of reduction-oxidation (redox) sensitive elements: iron (FeO, red), manganese (MnO, blue), and molybdenum (Mo, black). Reducing environments develop when oxygen is absent or nearly absent. Molybdenum, in particular, forms deposits of insoluble MoO_2 and MoS_2 in highly reducing (no oxygen) conditions.

Lead (Pb) and zinc (Zn) occur in higher-than-background concentrations in sediments containing petroleum-based fuels and oils. Globally, levels of these elements show up in lake sediment after A.D. 1910, some from direct spillage from motors but also as deposits from atmospheric pollution. Most lake sediment records show a distinct decline in lead concentrations after 1975, when the A.D. 1974 Clean Air Act promoted catalytic convertors and unleaded gasoline. Spofford Lake's sediment chemistry reflects these global trends, with increases in fuel indicators after A.D. 1900 and a lead peak in A.D. 1974 (Fig. 10). But Spofford Lake's lead and zinc levels increase again after A.D. 1980, attain a new peak in A.D. 1996, and it isn't until A.D. 2009 that lead concentrations drop below A.D. 1974 levels. Despite this 35-year delay in lead response, Spofford Lake's deep basin sediments are now similar to those in other lakes (Fig. 10).

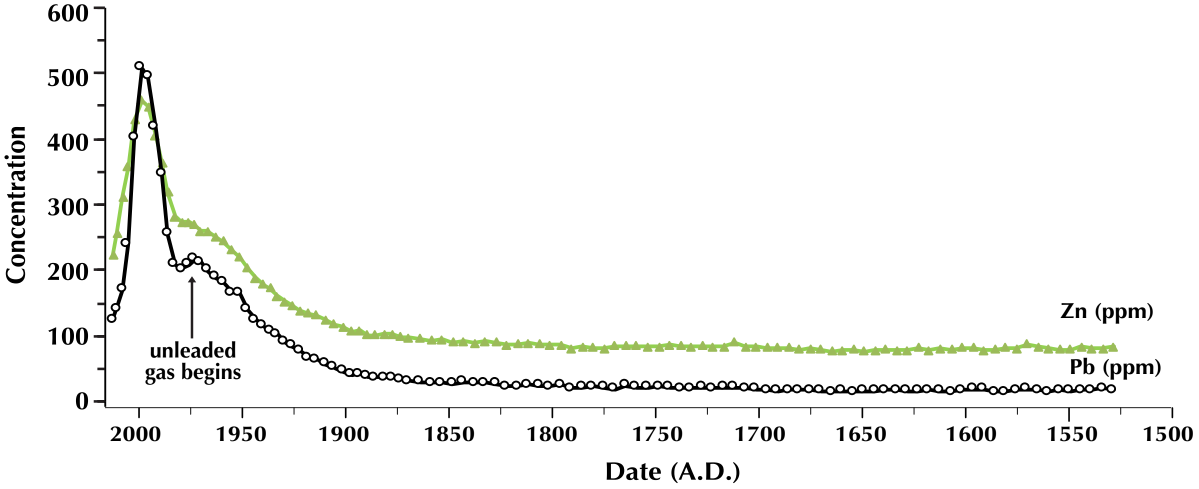


Figure 9. Elemental indicators of anthropogenic influence: lead and zinc. These elements are found in gasoline and fuel oils. Leaded gasoline was phased out after 1975 (arrow). The recent increase in lead after 1975 suggests a fuel leak into the lake.

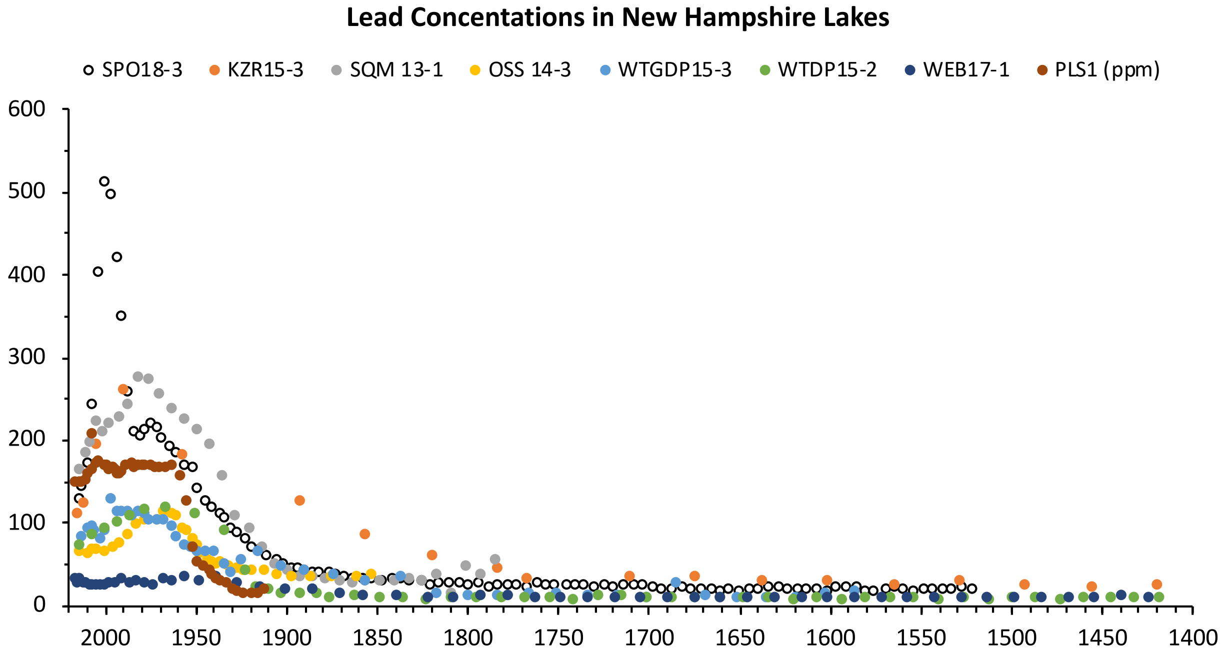


Figure 10. Comparison of lead concentrations (from ICP-OES analyses) in lake sediments of northern and central New Hampshire: Spofford Lake (SPO), Squam Lake (SQM), Ossipee Lake (OSS), Lake Wentworth (WTGP and WTDP), Webster Lake (WEB), and Pleasant Lake (PLS) and western Maine: Kezar Lake, ME (KZR). Note the early 20th Century increase in lead concentrations, with a peak or plateau in all lakes around 1970-1980. The high lead excursion in Spofford Lake after 1980 (hollow circles) is very different than in any of these other lakes.

Conclusions

Several key findings have come out of this investigation of Spofford Lake's sedimentary record:

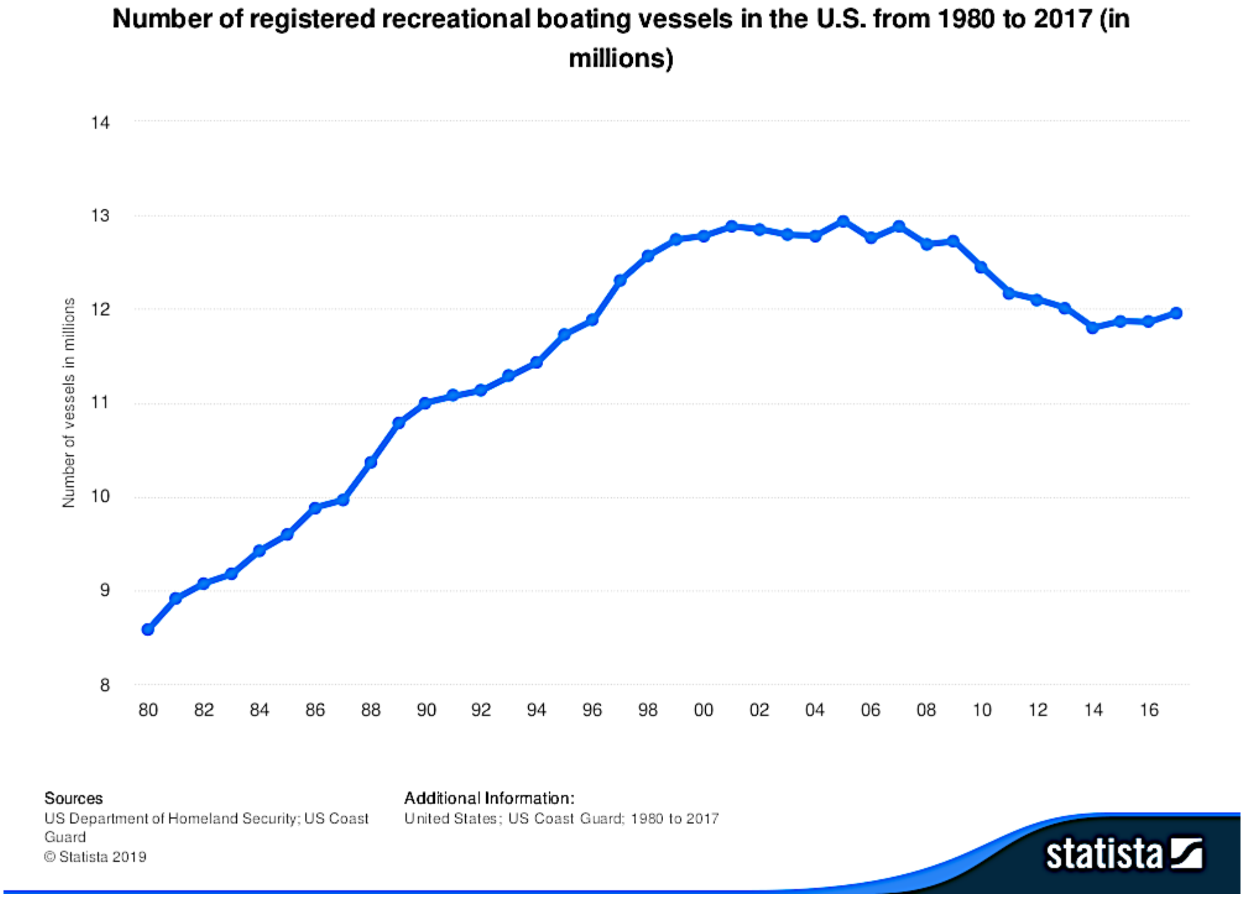
1. the time period captured by these sediment cores covers the last 300 years and includes material up to 2018, the year the cores were collected, and lead-210 dating provides a closely constrained and reliable chronology of events for SPO 2018-4, with less than ± 5-year uncertainty back to A.D. 1885;
2. in the most recent deposits (post-1980), the sediment characteristics have changed more than at any other time in the past several hundred years;
3. there has been a distinct and prolonged trend towards more organic material in the accumulating sediments after A.D. 1910, and after A.D. 1980 the amount of organic material reaching the lake bottom exceeds that of any prior time period;
4. the increase in organic deposition is associated with increases in anoxia and reducing conditions in the deep basin; and
5. sand-sized particles increase after 1980, but this cannot be attributed to runoff of chemically weathered soil to the lake.

A 2018 report by FB Environmental Associates found that both total phosphorus and chlorophyll-a in Spofford Lake are well below the NHDES Aquatic Life Use criteria for oligotrophic lakes, reflecting excellent water quality. Despite this, there is extremely low dissolved oxygen (anoxia, <1 ppm) in the hypolimnion, triggering a release of phosphorus from lake sediments. Our lake sediment data agree with these earlier findings and show that anoxia indicators are especially prevalent after A.D. 1980.

FB Environmental Associates also suggest that small tributaries feeding into Spofford Lake contribute fine particles that elevate turbidity during storm events and that wetter summers, in general, may bring more materials off the land and into the lake. While this is a reasonable conjecture, the core data show that, after A.D. 1980, there was a shift in the characteristics of material coming to the lake and that the change is from nonpoint source areas. The core results suggest that, for the past 30 years, more and more sediments are coming from deep soils that are both sandy and rich in undegraded organic material, of a nonpoint origin that supplies all areas of the lake basin. The most probable source for this combination of characteristics is the soil surrounding the lake and exposed along the shoreline. These deep soils include sands transported downhill and deposited during post-glacial landscape adjustments, mixed with thousands of years of accumulation of forest detritus like needles, leaves and twigs. These ancient soils are normally buried and protected from erosion. Along the lake shore, however, deep soil layers are continuously exposed and eroded by waves and can supply material to the lake along the entire length of shoreline.

Most lake shores have developed armored shorelines on the downwind side, where millennia of wind-driven waves and currents have battered the lake edge and pulled off all the easily transported material, leaving behind bedrock or else a surface layer of boulders and cobbles that protect underlying sediments. Human activities, however, have altered the natural distribution of wave energy along lakes all over the world. At Spofford Lake, a NHDOT Report (Benier, 2013) indicates that the natural low water level of the lake is at 711.6 feet elevation, but lake levels have been artificially high by damming for over 100 years. Further, in 2013, the minimum water level was at least one foot higher than natural levels and there were no naturally occurring shores. In nearly all undeveloped locations around the lake the water level was at the tree line. With these high-water conditions, the entire perimeter of the lake is susceptible to erosion of old, deep soils. It is probable, therefore, that a large fraction of the organic matter accumulating and decomposing in the deep basin, and contributing to the intensification of anoxia, comes from erosion of organic rich soils along the lake shores.

In addition to the impact of natural waves during high lake level conditions, after A.D. 1980, rapid growth in availability of low-cost watercraft led to record numbers of motorboat sales across the US (Fig 10). In particular, small personal watercraft like Jet Skis grew in popularity. Wave energy is exponentially proportional to wave height, and wave height is a function of the speed the generating force. Sustained wind speeds of 20 mph can create wave heights on a lake of 3 feet, about the size of a motorboat boat wake travelling at full speed. But wind waves only impact the armored, downwind shores of the lake while boat wakes can impact every shore, most of which are highly vulnerable to wave action. Personal watercraft, in particular, can travel in shallow water at relatively high speeds, causing wakes that travel up onto the fragile shores, directly hitting soils, and exposing roots of tree and shoreline shrubs. The signature of sediment characteristics found in the core data strongly indicates that Spofford's shoreline soils are eroding and, furthermore, comprise a major source of sediment to Spofford Lake, and that this trend started about A.D. 1980.


Number of registered recreational boating vessels in the U.S. from 1980 to 2017 (in millions)

Sources
US Department of Homeland Security; US Coast Guard
© Statista 2019

Additional Information:
United States; US Coast Guard; 1980 to 2017

Figure 10. Data on boats registered in the U.S. since 1980. These statistics include kayaks and canoes, but also motorboats and Jet Skis. While many of these boats are used in marine waters, use on inland lakes accounts for the greatest growth in registrations. Note that the numbers of boats are in millions, and that number grew by over 50% within 15 years.

This study also revealed a concerning anomaly in lead concentrations (figures 9 & 10). We expected, and detected, an increase in lead from circa 1900 to 1975. This follows the advent of gasoline powered engines, with leaded gasoline, in the early 1900's and subsequent introduction of unleaded fuels in 1975. But we also detected a large increase in lead between A.D. 1980-2000, to 500 ppm, well above 400 ppm, the EPA guidelines for safe playground levels in soil. The rapid increase, and levels well above background amounts in Spofford and other lakes, points to a fuel spill into the lake that is now part of the sediments. Since 2000, lead levels have fallen to below 150 ppm, which indicates cessation of the spill. The oil enriched sediments are still in place across the lake bed, however. Dredging operations, and boating activities that disturb bottom sediments below 5 cm (2 inches) should be carefully considered in light of the potential they have to remobilize harmful elements buried in the lake sediments.

References:

Beaudoin, A., 2003. A Comparison of Two Methods for Estimating the Organic Content of Sediments. Journal of Paleolimnology 29: 387–390.

Boyle J.F., 2001. Inorganic geochemical methods in paleolimnology. In: Last W.M. and Smol J.P. (eds), Tracking Environmental Change Using Lake Sediments: Volume 2: Physical and Geochemical Methods. Developments in Paleoenvironmental Research. Kluwer Academic Publishers, Dordrecht, The Netherlands, pp 83-141.

Bernier, T. F. 2013. Report of the natural mean high water elevation of Spofford Lake, Chesterfield, New Hampshire, New Hampshire Department of Transportation Reference Project #13597. T.F. Bernier Inc., 39 Warren Street, Concord, NH 03301.

Dean, W.E. Jr., 1974. Determination of Carbonate and Organic Matter in Calcareous Sediments and Sedimentary Rocks by Loss on Ignition: Comparison With Other Methods. SEPM Journal of Sedimentary Research 44.

Engstrom D.R. & Wright H.E. Jr., 1984. Chemical stratigraphy of lake sediments as a record of environmental change. In Haworth E.Y. & Lund J.W.G. (eds.) Lake Sediments and Environmental History. Leicester University Press, Leicester: 11-68.

F.B. Environmental Associates, 2018. Water quality analysis, Spofford Lake Watershed. Report for the Southwest Region Planning Commission, 37 Ashuelot Street, Keene, NH 03431. www.swrpc.org

Ferro V., and Mirabile S., 2009. Comparing Particle Size Distribution Analysis By Sedimentation And Laser Diffraction Method. Journal of Agricultural Engineering 40: 35.

McKeague J.A. (ed.) 1976. Manual on Soil Sampling and Methods of Analysis. Prepared by Subcommittee on Methods of Analysis of Canadian Soil Survey Committee. Ottawa, Ontario.

Parris A.S., Bierman P.R., Noren A.J., Prins M.A., Lini A., 2009. Holocene paleostorms identified by particle size signatures in lake sediments from the northeastern United States. Journal of Paleolimnology.

Santisteban, J.I., Dabrio, C.J., Gil-Garcia, M.J., Castano, S.C., 2004. Loss on Ignition: a Qualitative or Quantitative Method for Organic Matter and Carbonate Mineral Content in Sediments. Journal of Paleolimnology 32: 287–299.

Schaller, T., Christoph Moor, H. & Wehrli, B. Sedimentary profiles of Fe, Mn, V, Cr, As and Mo as indicators of benthic redox conditions in Baldeggersee. *Aquatic Science* **59,** 345–361 (1997). https://doi.org/10.1007/BF02522363

Thompson, R., Battarbee R.W., O'Sullivan P.E., Oldfield F., 1975. Magnetic Susceptibility of Lake Sediments Limnology and Oceanography 20: 687–698.

Thompson, R., Bloemendal J., Dearing A., Oldfield F., Rummery A., Stober J.C. and Turner G.M., 1980. Environmental applications of Magnetic Measurments. Science: American Association for the Advancement of Science 207: 481-486.

Turetsky M.R., Manning S.W., and Wieder R.K., 2004. Dating Recent Peat Deposits. Wetlands, 24: 324-356.

Websites:

Hamilton Analytical Lab (HAL). Methods & Instruments. https://www.hamilton.edu/academics/analytical-lab/instrumentation

Appendix - Laboratory Analysis Details

Loss on Ignition:

Loss on Ignition (LOI) is a differential thermal analysis for organic carbon (OC). This method of OC analysis has been proven to be a simple, cost- and time-effective, in-house way of analyzing sediment OC content (Dean 1974). Still, there is ongoing debate over variations in this method. In Beaudoin's 2003 paper the samples were burned at 375°C for 16 hours (following McKeague 1976). Santiseban et al. (2004) used three different heats and times: 105°C for 12-24 hours, 550°C for four hours, and 950°C for 2 hours to compare the differences. Still others agree with Dean's original method 500-550°C for two to four hours (Heiri et al. 2001). Ignition of some samples above 400°C may cause " loss of interstitial water from clays as well as the breakdown of carbonates", while burning at the higher temperature for too short a time interval may not induce complete combustion of the samples (Beaudoin, 2003). Santistebien et al. (2004) notes that the loss of some volatile non-carbon aspects of the sediments can increase the overall LOI values while the water within clay lattices can account for up to 5% of LOI due to dehydration, leading to overestimation of OC. Most researchers conclude that 550°C produces the most accurate LOI values with the least added error, and this temperature is used for this study.

In this study a 0.5 g of sample is placed into pre-weighed ceramic crucibles. The crucibles sit in non-combustible firebrick blocks that hold either 9 larger or 25 smaller crucibles. The blocks are placed into a furnace pre-heated to 550C (Dean, 1974). After two hours the samples are removed from the furnace and placed in a vacuum desiccator, to prevent condensation of ambient moister during the cool-down period. Once the samples were cooled, they were weighed, and the post-combustion weight recorded. To determine the percent LOI, I calculate: $100 * \left(\frac{dry\ weight - burned\ weight}{dry\ weight}\right)$.

Magnetic Susceptibility:

Magnetic Susceptibility is a non-destructive sample analysis used to identify past changes that may have affected the watershed's sediment. Changes in land use around a lake such as forested to clear-cut are reflected by increased values for magnetic susceptibility (Thompson et al. 1975). Magnetic susceptibility also varies with mineral concentrations, which can reflect weathering, pedogenic, and denudational patterns throughout the region (Thompson et al. 1980). Dried sediment material is packed into pre-weighed labeled polystyrene cubes and weighed to obtain the magnetic sample weight. The cubes are analyzed in a Bartington MS2B Dual-Frequency Sensor at 600 and 6000 Hz, using a MS3 Bartington Magnetic Susceptibility Meter. Sample runs at each frequency included two or more duplicate measurements. Averages derived from absolute values, excluding outliers; yield magnetic susceptibility (X), which is then normalized by weight to generate mass susceptibility (MS).

Lead 210 Dating – St. Croix Watershed Research Laboratory, Minnesota:

The radioactive isotope ^{210}Pb is used to date sediment deposited within the last 150 to 200 years (Turetsky et al. 2004). Different of ^{210}Pb supply are used to determine the sediment age and to predict the sedimentation rate. The most commonly used model for lake sediments is the constant initial concentration (CIC) as noted by Turetsky et al. (2004). This project uses the St. Croix Watershed Research Station ^{210}Pb dating service, which assesses results using constant rate of supply (crs) and constant flux, constant sedimentation (cf:cs) models and offers guidance about model fit to other core analyses and known lake histories.

Table 2. Results of the lead-210 analyses of the SPO2018-4 core. Interval is the sample interval. We sampled at 0.5 cm intervals. Not all samples were analyzed for lead-210, but the entire core is represented by the 22 samples that were analyzed. Cum is cumulative. Unsup is the unsupported lead that derived from the atmosphere. DMAR is dry mass accumulation rate. The radioactivity is measured in pico-curies per gram (pCi/g).

Spofford Lake Core 2018-4

Top of Interval (cm)	Base of Interval (cm)	Mid of Interval (cm)	Total 210Pb (pCi/g)	Error of Total Pb (±s.d.)	Cum. Dry Mass (g/cm2)	Unsup. 210Pb (pCi/g)	Error of Unsup Pb (±s.d.)	Age: Base of Int. (yr)	Error of Age (±s.d.)	Date: Base A.D.	Date: Mid A.D.	Sediment DMAR (g/cm2 yr)	Error of DMAR (±s.d.)
0	0.5	0.25	58.323	1.909	0.011	57.658	1.909	1.79	4.55	2017.0	2017.9	0.0063	0.0007
2	2.5	2.25	21.331	0.758	0.117	20.665	0.758	12.34	3.51	2006.4	2007.8	0.0128	0.0008
4	4.5	4.25	16.847	0.550	0.274	16.181	0.551	25.84	3.64	1992.9	1994.9	0.0109	0.0007
5	5.5	5.25	8.963	0.336	0.368	8.297	0.336	31.99	3.66	1986.8	1988.2	0.0173	0.0012
6.5	7	6.75	7.775	0.305	0.526	7.109	0.305	42.00	4.00	1976.8	1978.6	0.0150	0.0013
8	8.5	8.25	6.688	0.284	0.651	6.023	0.285	51.18	4.51	1967.6	1969.0	0.0131	0.0014
10	10.5	10.25	4.257	0.161	0.872	3.591	0.161	67.34	4.84	1951.4	1953.9	0.0137	0.0016
12	12.5	12.25	2.377	0.082	1.108	1.712	0.083	82.52	3.72	1936.3	1937.9	0.0174	0.0013
13.5	14	13.75	1.996	0.049	1.279	1.330	0.051	92.69	4.04	1926.1	1927.9	0.0165	0.0014
15.5	16	15.75	1.557	0.044	1.537	0.891	0.046	109.29	4.07	1909.5	1911.8	0.0149	0.0013
17	17.5	17.25	1.280	0.032	1.725	0.614	0.035	122.32	4.51	1896.5	1898.6	0.0143	0.0016
18.5	19	18.75	1.037	0.032	1.907	0.371	0.035	134.12	4.97	1884.7	1886.6	0.0163	0.0024
20.5	21	20.75	0.908	0.029	2.161	0.242	0.032	150.57	6.02	1868.2	1870.4	0.0151	0.0029
22	22.5	22.25	0.894	0.026	2.348	0.228	0.029	166.74	8.91	1852.0	1855.1	0.0100	0.0026
23.5	24	23.75	0.798	0.027	2.506	0.132	0.030	182.81	13.27	1836.0	1838.4	0.0101	0.0043
25.5	26	25.75	0.707	0.018									
27	27.5	27.25	0.710	0.022									
28.5	29	28.75	0.688	0.017									
30.5	31	30.75	0.655	0.017									
32	32.5	32.25	0.643	0.021									
34	34.5	34.25	0.638	0.016									
36	36.5	36.25	0.639	0.016									

Supported Pb-210: 0.6658 ± 0.0135 pCi/g

Number of Supported Samples: 7

Cum. Unsup. Pb-210: 11.9276 pCi/cm2

Unsup. Pb-210 Flux: 0.3849 pCi/cm2 yr

Particle Size:

Laser diffraction is an efficient, cost effective method for determining particle-size (Ferro & Mirabile, 2009). Within depositional environments such as lakes, particle size can be used to identify high-magnitude storm events (Parris et al. 2009). During these storms, precipitation can increase water velocity in streams and rivers and their capacity to transport more coarse-grained sediment to deep-water depositional basins (Parris et al. 2009). These coarser-grained intervals within a sedimentary sequence can be used with a stratigraphic age model to determine the frequency of large precipitation or flood events, and the general storminess of a region (Parris et al. 2009). Relative changes in the size of particles transported into a depositional environment, along with any intermittent coarse-grained layers, can give us an insight into land use changes throughout the watershed (Thompson et al. 1975) and their impacts on erosion. To digest and remove organic materials in the sample, 0.1 g of sample is placed into 150 ml beakers mixed with 25 ml of 30% hydrogen peroxide (H_2O_2) and heated on a hot plate at 70-90°C for 90 minutes. Distilled water is added periodically to ensure the samples do not dry out. After 90 minutes, additional 5 ml of H_2O_2 are added to the sample, up to 25 ml total as needed to ensure complete reaction. The samples are heated for an additional 90 minutes, or until the digestion process is done and all evidence of reaction has ceased. After this digestion process the samples are dried for 24 hours at 100°C to remove the remaining H_2O_2. To rehydrate the samples, disperse the grains and prepare them for laser diffraction analysis, 5 ml of sodium pyrophosphate (Na_4P_2O) is added to the sample and the samples are sonicated for three minutes at 60Hz. Once the sediment is suspended in solution, the sample is added drop by drop to the Horiba LA-920 Laser Scattering Particle Size Distribution Analyzer. At the start of the day distilled water was circulated for 30 minutes, at the end of this time it was debubbled by sonicating it, making sure that when it was aligned the water was clear. The lasers were then aligned, and the chamber blanked. This was repeated if the transparency percentage was not between 97 and 100%. The display conditions were then set with the distribution form being standard deviation, the refractive index set as 120a0001, and the distribution base as volume. The standard was used for the density distribution graph, and logX-linY was used for the axis selection. Cumulative distribution was turned on, with the axis set to bar, and the laser scans set to 10. When running the samples, the circulation seed was set to three. After each run the chamber was drained and rinsed three times. Water was fed back in and circulated before being sonicated and blanked. Each sample measurement is repeated three times to ensure a statistically rigorous distribution curve. The distributions are compared during the analysis and rerun if needed.

Sediment Geochemistry by XRF – Hamilton Analytical Lab (HAL), New York:
At Hamilton University, XRF samples are prepared using a low-dilution fused bead method and graphite crucibles. One gram of sample is added to a Li-tetraborate flux (Merck Spectromelt A-10) in a ratio of 1part sediment to 2 parts flux. The sediment and flux are blended using a vortex mixer and fused at 1000 °C in graphite crucibles (Mersen grade UF-4S). This cleans the pellets of residual carbon. The pellets are then reground to a fine powder in a Rocklabs tungsten carbide (WC) or alumina ring mill, and fused again at 1000 °C. The doubly fused pellets are flattened in four stages using progressively finer diamond laps to a surface finish of 15 microns, then ultrasonically cleaned in ethanol.

The pellets are analyzed on a Thermo ARL Perform'X sequential x-ray fluorescence spectrometer with 45 kV accelerating voltage at 45 mA, measuring a suite of 44 elements in two hours. The instrument is recalibrated in 10 month intervals using ~70 certified reference standards to build a normal calibration. Drift is monitored with in-house standards run several times per week. One or more international standards are run with each sample batch. At least one duplicate is prepared and analyzed for every batch of 10 samples to check for sample homogeneity and reproducibility of data. The Perform'X goniometer has a very short time between successive measurements. Crystal temperatures are maintained by heaters at 43.00±0.02 °C. Spectrometer vacuum is maintained at a near constant 2.0 Pa. Thermo-ARL XRF spectrometers have very low backgrounds due to their unique optical alignment design. The low background improves signal to noise ratio for all elements and allows determination of several elements not normally measured with XRF in geologic samples. Our instrument is equipped with a He flush for the analysis of liquid and powdered samples. The spectrometer is equipped with LiF200, LiF220, Ge111, PET, and two synthetic long wavelength analyzing crystals for elements with atomic number down to $Z = 5$ (B).