

HOLOCENE SEDIMENTS IN MISSISQUOI BAY, USA-CANADA:
A PALEOLIMNOLOGICAL STUDY

A Thesis Proposal Presented

by

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Abstract

Lake sediments record the changing conditions of the lake and surrounding watershed. Productivity levels, as well as the amount and type of inputs can be inferred through the analysis of lacustrine sediments, allowing conclusions to be made about past climate and environmental conditions within the watershed. Missisquoi Bay, a shallow section of the Northeast Arm of Lake Champlain, is used for this study because of its well-preserved sediment record and recent environmental issues. Previous paleolimnological studies in Missisquoi Bay have focused on more recent sediment within the bay. Two sediment cores of <3 m in length will be analyzed for %C_{org}, C/N, $\delta^{13}\text{C}$, magnetic susceptibility, biogenic silica, and grain size in order to reconstruct the paleoenvironmental conditions of the lake during the early to mid-Holocene. A better understanding of the past lake environment will aid in our interpretation of the current situation in Missisquoi Bay.

1. Introduction

Sediments deposited on the bottom of a lake act as environmental and climatic archives for the lake and surrounding watershed. Both inorganic and organic matter from within and around the lake are deposited contemporaneously, recording a complex history of the changing environmental conditions over time. The organic fraction of the sediment can indicate changes in lake productivity as well as the amount of terrestrial organic inputs, while the inorganic sediments are influenced by watershed erosion rates, storm events, and lake level.

Lake Champlain, stretching 193 km and covering 1,125 km², is greatly affected by the adjacent lands of Vermont, New York and Quebec (Lake Champlain Basin Program, 2004). Missisquoi Bay, an isolated shallow bay that straddles Vermont and Quebec in the northeast arm of the lake, has received significant attention recently due to high phosphorus levels and algal blooms. Excessive nutrients from agricultural runoff have caused a state of eutrophication in the bay that negatively impacts both the aquatic biota and human recreational activities (LCBP, 2004). The response of the lake to intensive nutrient loading is one reason why it is critical to understand the history of and patterns within the lake sediments.

2. Objectives

Previous paleolimnology studies in Missisquoi Bay focused on the more recent portion of the sedimentary record that spans the last few hundred years (King et al., 1993; Burgess,

2007; Smith, 2009). Burgess (2007) documented an increase in the organic matter content in pre-settlement sediments in both Missisquoi and St. Albans Bay that is comparable to modern lake sediments (Figure 1). This study will investigate a longer record of Holocene sediments, up to 10,000 years old, to gain a better understanding of natural lake variation due to climate, through the analysis of two cores from Missisquoi Bay. The main objectives of this study are as follows:

1. Interpret the environmental conditions and climate of Missisquoi Bay during the early to mid-Holocene by analyzing the lake sediment cores for the following proxies: %C_{org}, C/N, $\delta^{13}\text{C}$, magnetic susceptibility, biogenic silica, and grain size.
2. Compare early and modern sediment records to better understand the past responses of Lake Champlain to changes in climate, advancing the interpretation of the current lake condition.

3. Study Site

Lake Champlain was formed 9–10 thousand years ago (ka), when the Champlain Sea was cut off from the St. Lawrence Seaway as the land isostatically rebounded after the retreat of the Laurentide Ice Sheet (Rayburn et al., 2007). Missisquoi Bay, in the northeastern corner of Lake Champlain, is a large, shallow section of the lake that straddles Vermont and Quebec (Figure 2). The Missisquoi, Rock, and Pike Rivers drain an area of 31,000 km² into the bay. The Missisquoi Bay watershed contains 25% agricultural land, 7% developed areas and 66% forests (Troy et al., 2007). Poorly managed agriculture within the Missisquoi basin has led to an increase in the amount of nutrients in runoff, particularly of phosphorous (P), which now accounts for a quarter of all non-point sources of P in the lake alone (LCBP, 2004). Excess nutrients have led to extreme algal blooms in the summer that severely impact the water quality within the bay.

In general, sediments in Missisquoi Bay consist of mostly clay and silt with low organic matter content (Myer and Gruending, 1979). Studies (e.g. King et al., 1993; Burgess, 2007; Smith, 2009) have found that human induced eutrophication has increased the accumulation rate and organic matter content of the recent sediments within the bay (Figures 3,4).

4. Background

4.1 Lake Sediments

Lake sediments preserve a variety of information that can be used to gain an understanding of the past conditions of a lake, its watershed, and climate (Meyers and Teranes, 2001). Reconstruction of paleoclimates through the use of lake sediments is common (e. g. Meyers and Ishiwatari, 1995; Schelske and Hodell, 1995; Bierman et al., 1997; Brown et al., 2002).

Lakes have a variety of sediment sources and types from within (autochthonous) and outside the lake (allochthonous) (Smol, 2008). The major allochthonous sources are streams, which carry both dissolved chemicals and particulate inorganic and organic matter (OM) into lakes. The watershed geology, climate, and land use directly affect the type and amount of material that enters a lake system (Cohen, 2003). Pollen, dust, aerosols, and other particulates can also fall directly on the lake and accumulate in sediment, albeit at a far lesser rate than stream inputs (Smol, 2008). Autochthonous sources include biological activity and chemical precipitation within the lake. Remains of macrophytes, algae, phytoplankton, zooplankton, bacteria, and aquatic invertebrates have the potential to become incorporated into the sediment.

Fluctuations in the lake level and circulation patterns can affect the amount and location of sediment deposition within a lake (Cohen, 2003), and physical, chemical and biological processes can alter the sediment once deposited. OM is particularly vulnerable to post-burial

diagenesis, and can undergo decomposition, reducing total biomass and releasing N and P back into the water column for use by other organisms (Figure 5). Burrowing organisms, chemical dissolution, and compaction are other types of sediment alteration (Engstrom and Wright, 1983). Despite this, the primary signature of the OM is often preserved, maintaining relative differences throughout the sediment column (Meyers and Ishiwatari, 1993).

4.2 Sediment Chronology

Previous cores from Missisquoi Bay have been dated using lead-210 (^{210}Pb) and radiocarbon (^{14}C) dating techniques (King et al., 1993; Burgess, 2007). Since ^{210}Pb dating is highly accurate on sediments deposited within the last 150 years (Appleby, 2001), we hope to be able to correlate our records to the previously established dates for the most recent sediment. Burgess (2007) used a single ^{14}C date from Missisquoi Bay to estimate the age of the pre-settlement sediments. An important aspect of this study will be to get several accurate ^{14}C dates from plant fragments found in the sediments, in order to better constrain the age and accumulation rates of sediments within the bay.

In general, organic matter from 0.5 to 40 ka can be radiocarbon dated (e.g. Libby, 1955; Walker, 2005). ^{14}C is continually produced in the upper atmosphere as a result of cosmic rays removing a proton from ^{14}N (Bjorck and Wohlfarth, 2001), rapidly reacting with free oxygen producing $^{14}\text{CO}_2$, which is incorporated into plants through photosynthesis. Since $^{14}\text{CO}_2$ is well mixed in the troposphere and organisms continually take up $^{14}\text{CO}_2$ into their tissues, a consistent amount of ^{14}C is found in all living organisms. Once an organism dies, the ^{14}C in their tissues stops being replenished, and it radioactively decays back to ^{14}N with a half-life of 5730 years (Bjorck and Wohlfarth, 2001).

Lake sediments can contain a significant amount of OM, some of which can be used for

radiocarbon dating. In order to avoid sources of error, like hard-water effects and old carbon sources (Cohen, 2003), a piece of a plant that grew in equilibrium with the atmosphere must be found for sampling. For a piece of OM to maintain its original structure it must have been deposited rather quickly, allowing us to apply the age of the OM to the age of the sediment layer.

4.3 Elemental Analysis (%C_{org}, %N, C/N)

The percentage of organic carbon (%C_{org}) of a sediment sample is an important proxy for tracking changes in lake productivity and OM input in the lake system over time. C_{org} is directly proportional to the abundance of OM. Plant tissues are typically composed of 45-50% C_{org} (Schlesinger, 1997), while lake sediment %C_{org} can range from < 1% to 40% (Meyers and Teranes, 2001). An increase in the %C_{org} of sediment can be indicative of an increase in the input of OM and productivity within the watershed. Changes in the %C_{org} are also directly affected by the amount of inorganic matter deposited; for example a decrease in %C_{org} can be attributed to an increased flux of inorganic matter. In general, %C_{org} values are reduced by microbial processing of OM during sedimentation and burial (Meyers, 1997). This process occurs consistently in sediments within a basin, maintaining relative differences in the %C_{org}.

The ratio of %C_{org} to the percent total nitrogen (%N), or C/N, found in sediment indicates the type of OM deposited. Different types of plants have very distinct C/N ratios (Figure 6). In general, vascular land plants have a relatively high C/N ratio of over 20 (Meyers and Teranes, 2001), while algae tend to have distinctly lower C/N ratios, typically below 10. The differences are due to the structure of the plants; vascular plants have more carbon-rich molecules (such as cellulose) and less nitrogen-rich molecules (such as protein) than algae. For example, white spruce wood, which contains mostly cellulose, can have a C/N ratio of over

163, while plankton from a lake can have C/N ratios as low as 6 (Meyers and Teranes, 2001).

By analyzing the C/N ratio of lake sediment it is possible to make conclusions about the OM source. At times of high lake productivity, when the OM is dominated by autochthonous algae and macrophytes, C/N ratios will be much lower than during periods dominated by allochthonous OM. A mix of allochthonous and autochthonous OM is common in lakes, which produces intermediate C/N ratios (~15). C/N ratios of OM can also be altered during deposition and burial. C/N ratios of algae can increase over time due to selective degradation of nitrogen-rich proteins, while the C/N ratio of woody materials tends to decrease over time as carbon rich sugars are more quickly broken down (Meyers and Teranes, 2001). Overall, these alterations are minor and are not significant enough to eliminate the relative differences in sediment samples.

4.4 Stable Carbon Isotopes

Stable carbon isotopes are another useful proxy to differentiate the type of OM deposited within a layer of sediment (e.g., Schelske and Hodell, 1991; Meyers and Teranes, 2001). The amount of ^{13}C incorporated into a plant structure during photosynthesis, reported as $\delta^{13}\text{C}$ values (see methods), is determined by the concentration of ^{13}C in the environment, photosynthetic pathway (e.g. C_3 , C_4 , or CAM), and the stomatal conductance of the plant (O'Leary, 1988). In general, algae in lakes and C_3 vascular land plants tend to have similar $\delta^{13}\text{C}$ values (-25 to -30 ‰), compared to C_4 plants (mostly grasses), which have values up to -10 ‰ (Figure 6). However, Lini et al. (1998, 2000) found that algae can exhibit a broad range of isotopic signatures from -36 to -16 ‰ due to varying environmental conditions. The $\delta^{13}\text{C}$ values of algae can increase during periods of high lake productivity, which can cause disequilibrium conditions within the lake with respect to CO_2 (Hollander and McKenzie,

1991). When CO₂ ($\delta^{13}\text{C}$ value = -7‰) is limited, algae can use bicarbonate ($\delta^{13}\text{C}$ value = 1‰) as a carbon source, causing the OM to become enriched in ¹³C (Meyers and Teranes, 2001). Thus, $\delta^{13}\text{C}$ values of sediment can be useful in identifying types of OM as well as productivity levels.

Diagenetic alterations of $\delta^{13}\text{C}$ values of sediments tend to be minor (Schelske and Hodell, 1995), although microbial activity can select for light C isotopes, increasing the $\delta^{13}\text{C}$ value of the remaining OM (Nadelhoffer and Fry, 1988). However, relative differences in $\delta^{13}\text{C}$ values are maintained throughout the burial process.

4.5 Magnetic Susceptibility

Magnetic susceptibility is a measure of the magnetic retention of a sample after exposure to a magnetic field (Smol, 2008). It is a relatively fast, inexpensive measure of the relative concentration of magnetic minerals within the sediment throughout the entire core (Nowaczyk, 2001). This information can be indicative of historical erosion rates and also aid in the correlation between cores (Smol, 2008). Since King (1993) analyzed his Missisquoi Bay cores for magnetic susceptibility (Figure 7), it might be possible to match his data to ours, allowing for the calculation of the sedimentation rate for the last 17 years. King (1993) found a decrease in the magnetic susceptibility of the recent sediments, due to increased amounts of organic matter that lacks magnetic minerals (Figure 7).

4.6 Grain Size and Biogenic Silica

Grain size and biogenic silica are additional analyses that will aid in the interpretation of past climate and autochthonous productivity levels. Grain size analysis of the core is a proxy for the overall energy level of the surrounding environment and can indicate changes in lake level and record large storm events (e.g. Noren, 2002; Noren, et al., 2002; Parris, 2003; Paris et al.,

2009). Biogenic (amorphous) silica is a proxy for the abundance of diatoms, a common phytoplankton that produce silica frustules, and is easier and faster than counting the organisms directly (Conley & Schelske, 2001).

5.0 Methods

5.1 Field Methods

Previous sediment cores in Missisquoi Bay were taken at a site in the middle of the bay due west of Phillipsburg, Quebec (Table 1). This study will focus on the southeastern portion of the bay in US waters (Figure 2), where two long cores (2.4 and 2.7 m in length) were taken this winter. Additional short cores (~50 cm) will be taken in the summer in order to get a better record of the uppermost layers of sediment, as the piston corer tends to disrupt the sediment-water interface.

The cores were collected using a modified Reasoner coring device (Figure 8) that consists of a 10 ft PVC pipe fitted with a piston that retains the sediments in the core during retrieval. A weighted cap, or hammer, is used to drive the PVC tube into the sediment. Once the core has been retrieved, it is then cut and capped into 1.5 m intervals. In the summer, a modified Glew gravity corer (Glew, 1988, 1989) can be lowered from a boat to the lake bottom to retrieve shorter cores of approximately 50 cm in length.

In the lab, the PVC tube is carefully cut down the length of the core on opposite sides and a steel blade is inserted, cutting the core in half length-wise. One half is sealed and refrigerated for archival purposes and the other half used for sampling. A visual log of the cores will be recorded and samples will be taken out of the core at 1 cm intervals and stored in 20 ml bottles for use in analyses.

5.2 Laboratory Methods

Macrofossils found within the core may be radiocarbon (^{14}C) dated using accelerator mass spectrometry (AMS) at Arizona State University. ^{14}C dates will be converted to years before present using the CALIB 6 calibration program (Stuiver and Reimer, 1993; Stuiver et al., 2010). Sediment accumulation rates will be calculated based on the radiocarbon dates from throughout the core. The cores in this study may also be dated through correlation to previous cores by “wigglematching” of magnetic susceptibility profiles and $\%C_{\text{org}}$ records, a common approach to correlating layers and, thus, dates between two nearby cores (Cohen, 2003).

Samples taken from throughout the cores will be analyzed for percent organic carbon ($\%C_{\text{org}}$) and percent total nitrogen ($\%N$). Powdered and weighed samples are sealed in tin capsules and processed using a CE Instruments NC 2500 Elemental Analyzer. C/N ratios, by mass, will be calculated using the $\%C_{\text{org}}$ and $\%N$ results. Standards and blank samples are used throughout sample runs to calibrate values and minimize drift. Sample precision is greater than 1% of the quantity measured.

Stable carbon isotopes will be analyzed using a VG SIRA II stable isotope ratio mass spectrometer with a precision of $\pm 0.05\text{‰}$ based on replicate standards (USGS-22 and internal-lab standards). The isotopic composition of the sample will be reported using the $\delta^{13}\text{C}$ notation:

$$\delta^{13}\text{C}(\text{‰}) = \left(\frac{{}^{13}\text{C}/{}^{12}\text{C}_{\text{sample}}}{{}^{13}\text{C}/{}^{12}\text{C}_{\text{V-PDB}}} - 1 \right) \times 1000$$

Where $\delta^{13}\text{C}$ is the isotopic composition of the sample in units of per mil (‰), ${}^{13}\text{C}/{}^{12}\text{C}_{\text{sample}}$ is the absolute isotope ratio of the sample and ${}^{13}\text{C}/{}^{12}\text{C}_{\text{V-PDB}}$ is the corresponding ratio in the laboratory standard Vienna Pee Dee Belemnite (V-PDB), introduced by the IAEA in Vienna in 1985 (Hut, 1987).

Magnetic susceptibility (k) will be analyzed for the entire length of the core and is a proportion of magnetization (M) of a sample when introduced to a known magnetic field (H), such that $k = M/H$. Magnetic susceptibility is unit-less, and indicates relative concentrations of magnetic minerals in a sample. A Bartington magnetic susceptibility meter (model MS2) with an automated core-logging system is used to measure this proxy at 1 cm intervals.

Grain size samples will be treated with H_2O_2 and NaOH to dissolve any organic matter before analysis in a Horiba LA-950 laser scattering particle size analyzer. Biogenic silica analysis will follow a method from DeMaster (1981) that involves hourly extractions of sample aliquots in a 0.1 M NaOH solution in order to distinguish the mineral and biogenic silica. Reagents are then added to develop a blue color that is measured in a spectrophotometer. Both proxies will be measured at up to 1 cm intervals.

6. Summary

This study aims to gain a better understanding of the climate and environmental conditions surrounding Lake Champlain throughout the Holocene. To my knowledge, previous work has never sampled and analyzed early to mid-Holocene sediments from Missisquoi Bay. Many studies have analyzed the upper, recent sediments to study human impacts on Missisquoi Bay and Lake Champlain. This thesis hopes to improve our understanding of the “baseline” condition of Missisquoi Bay, as it may not be as static as it was assumed to be. Burgess (2007) found variations in the OM content of Missisquoi around 8 ka and other variations may exist in the two long cores that we have retrieved. This study’s goal is to link these variations in the sediment of Missisquoi Bay to changes in the regional climate, watershed and lake. Variation in the older lake sediments may help us better understand and interpret the changes in the recent sediments of Missisquoi Bay.

7. Thesis Timeline

Spring 2010	<ul style="list-style-type: none">• Collect cores• Log core and run magnetic susceptibility• Sample sediment core at 1 cm intervals• Sample plant fragments for radiocarbon dating
Summer 2010	<ul style="list-style-type: none">• Collect short cores• Sample analysis (elemental analysis and stable carbon isotopes)
Fall 2010	<ul style="list-style-type: none">• Sample analysis (grain size and BSi)• Progress Report
Spring 2011	<ul style="list-style-type: none">• Write and defend thesis

8. References

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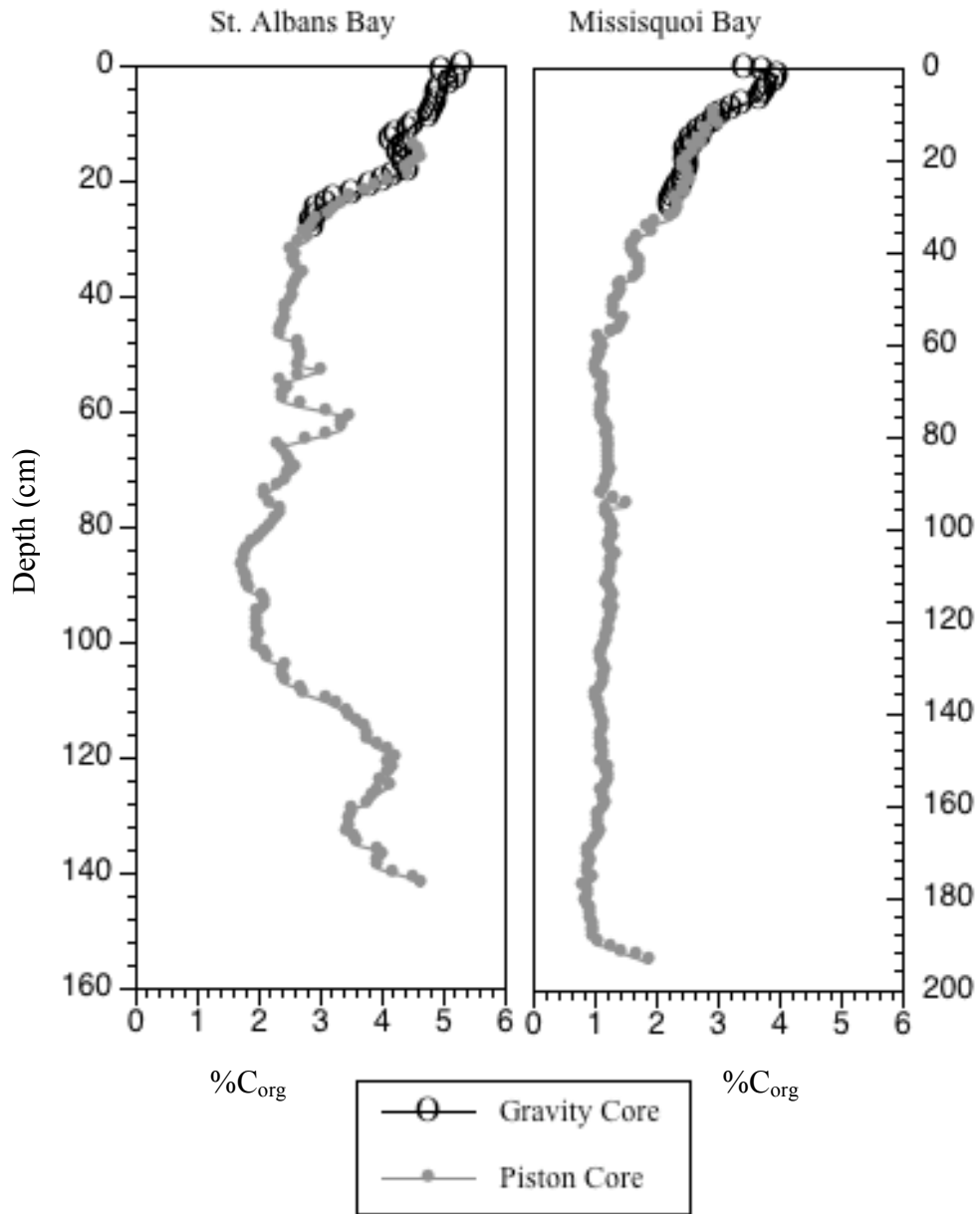
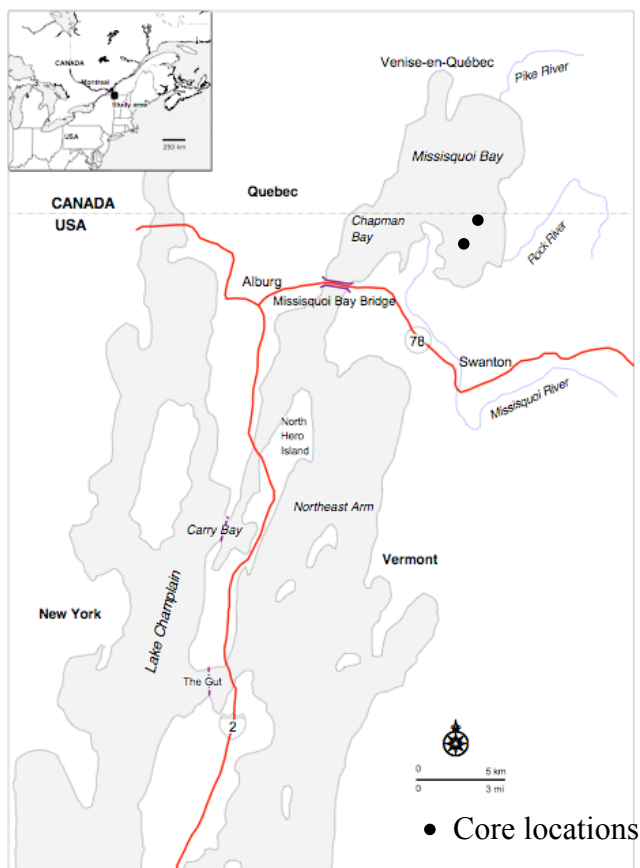


Figure 1. %C_{org} data for the combined piston and gravity cores from St. Albans Bay and Missisquoi Bay. From Burgess (2007).



Map of northern Lake Champlain

Figure 2. Map of Northern Lake Champlain showing two core locations in Missisquoi Bay.

Table 1: Missisquoi Bay Coring Sites

core name	date	latitude (°N)	longitude (°W)	core length (cm)	water depth (m)
King	1992	45.0367	73.1300	90	4
Burgess	3/07	45.0367	73.1300	185	4
Koff 1	3/6/10	45.0131	73.1088	270	4.75
Koff 2	2/17/10	44.9918	73.1133	240	3.66

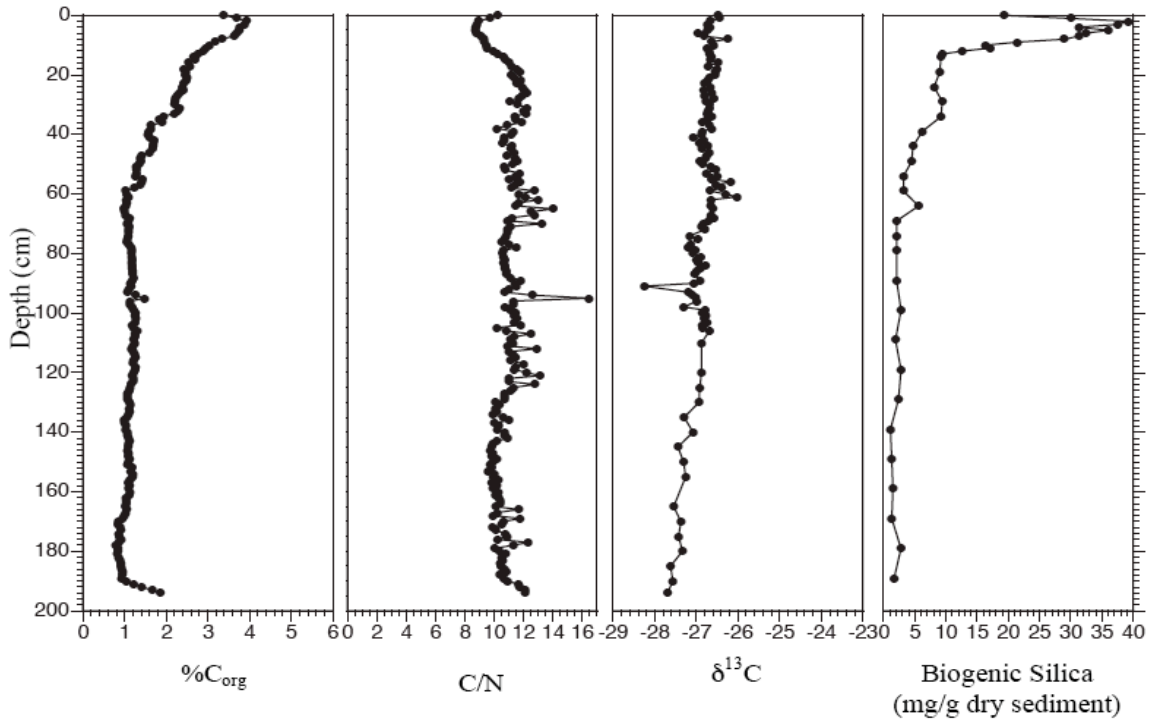


Figure 3. Data from Missisquoi Bay from Burgess (2007).

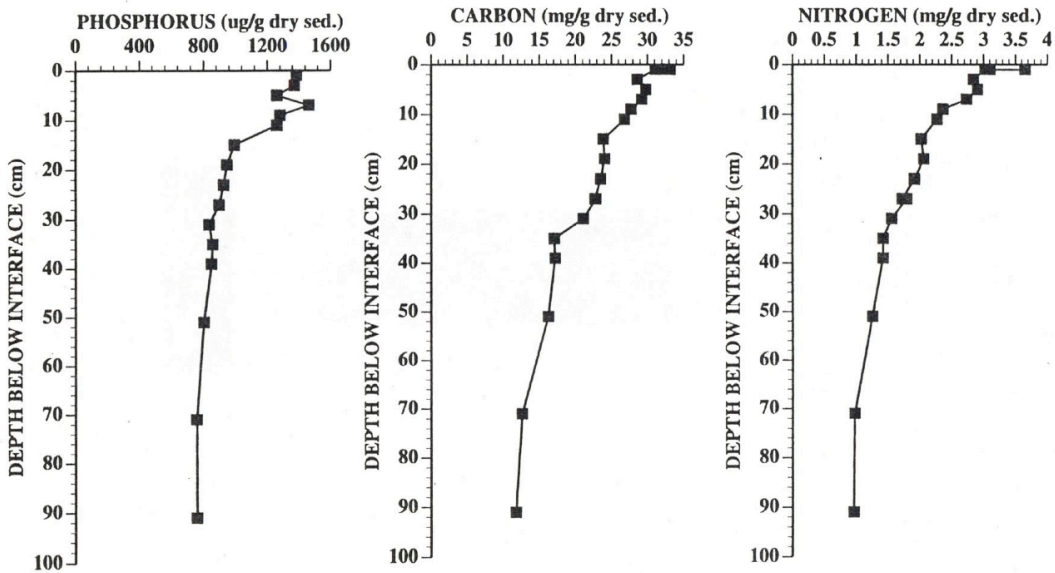


Figure 4. Nutrient data from Missisquoi Bay showing elevated values of surface sediments. From King (1993).

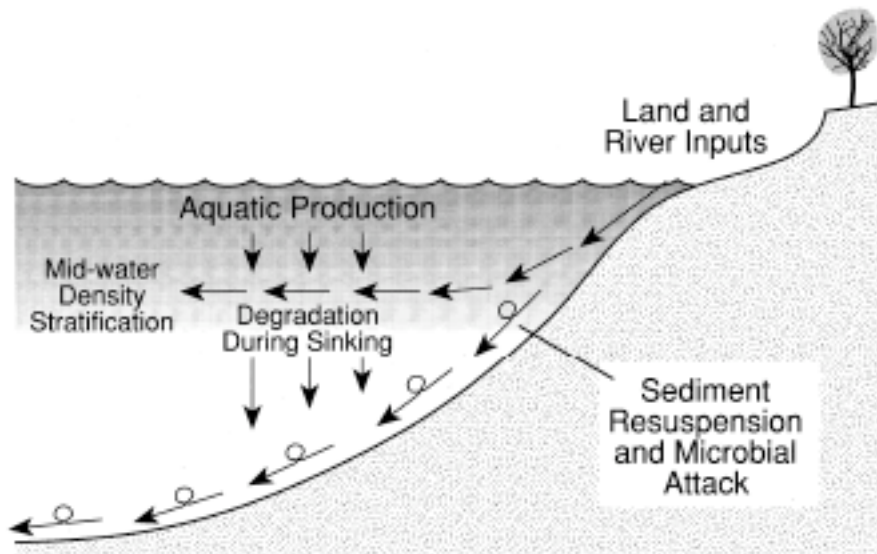


Figure 5. Summary of the principal sources and alterations of organic matter in lake sediment. Microbial reprocessing can alter the amount, type and location of organic matter that is deposited on the lake bottom. From Meyers (1999).

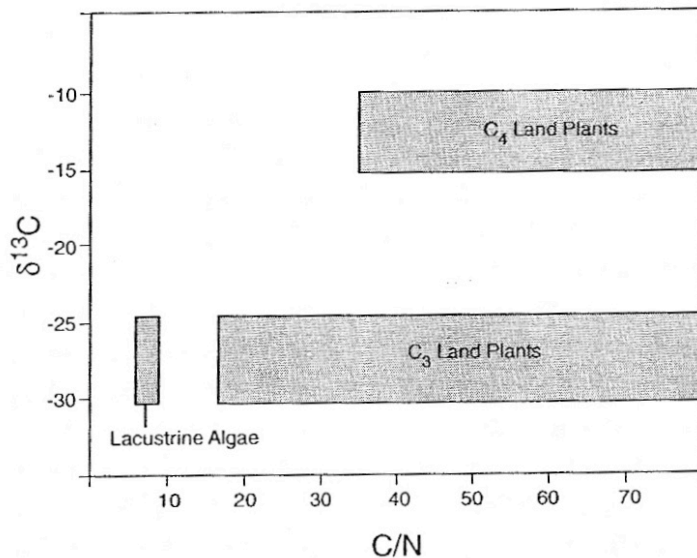


Figure 6. Common C/N and stable carbon isotopes values for photosynthetic plants. Together, these proxies can identify the type of organic matter found in lake sediment. From Meyers and Teranes (2001).

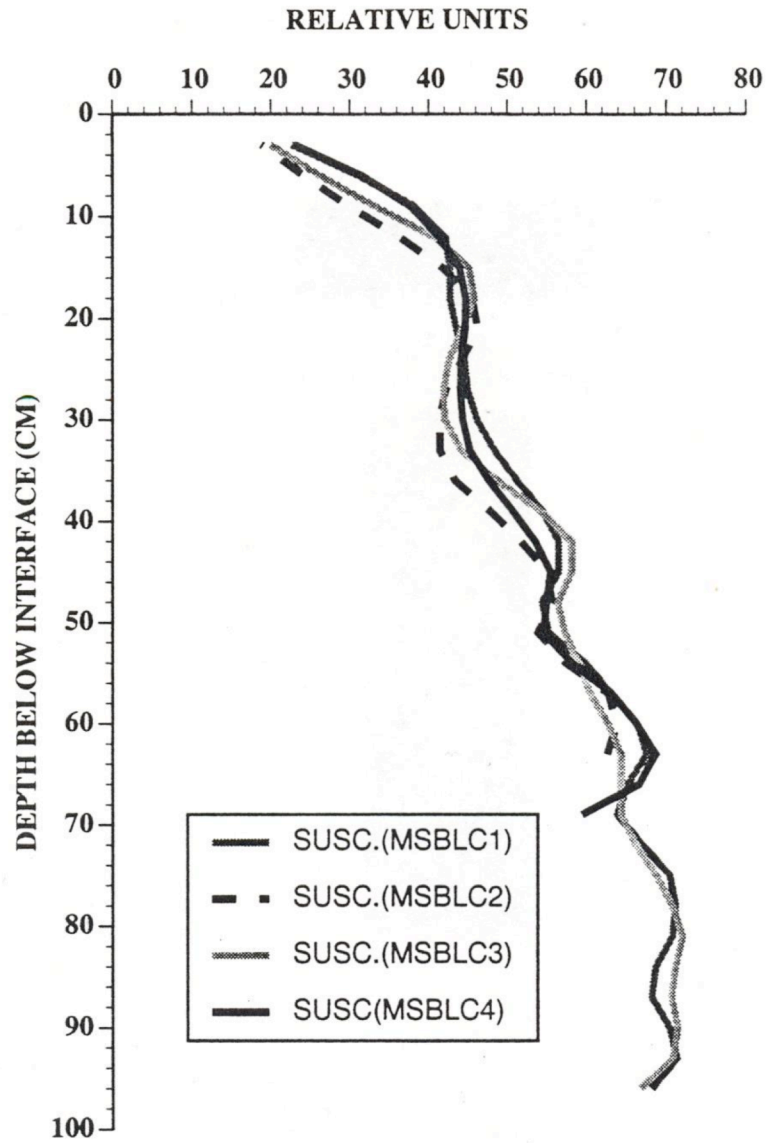


Figure 7. Magnetic susceptibility data from Missisquoi Bay from King (1993). The decrease in the top portion of sediment can be attributed to an increase in organic matter content of the sediment.

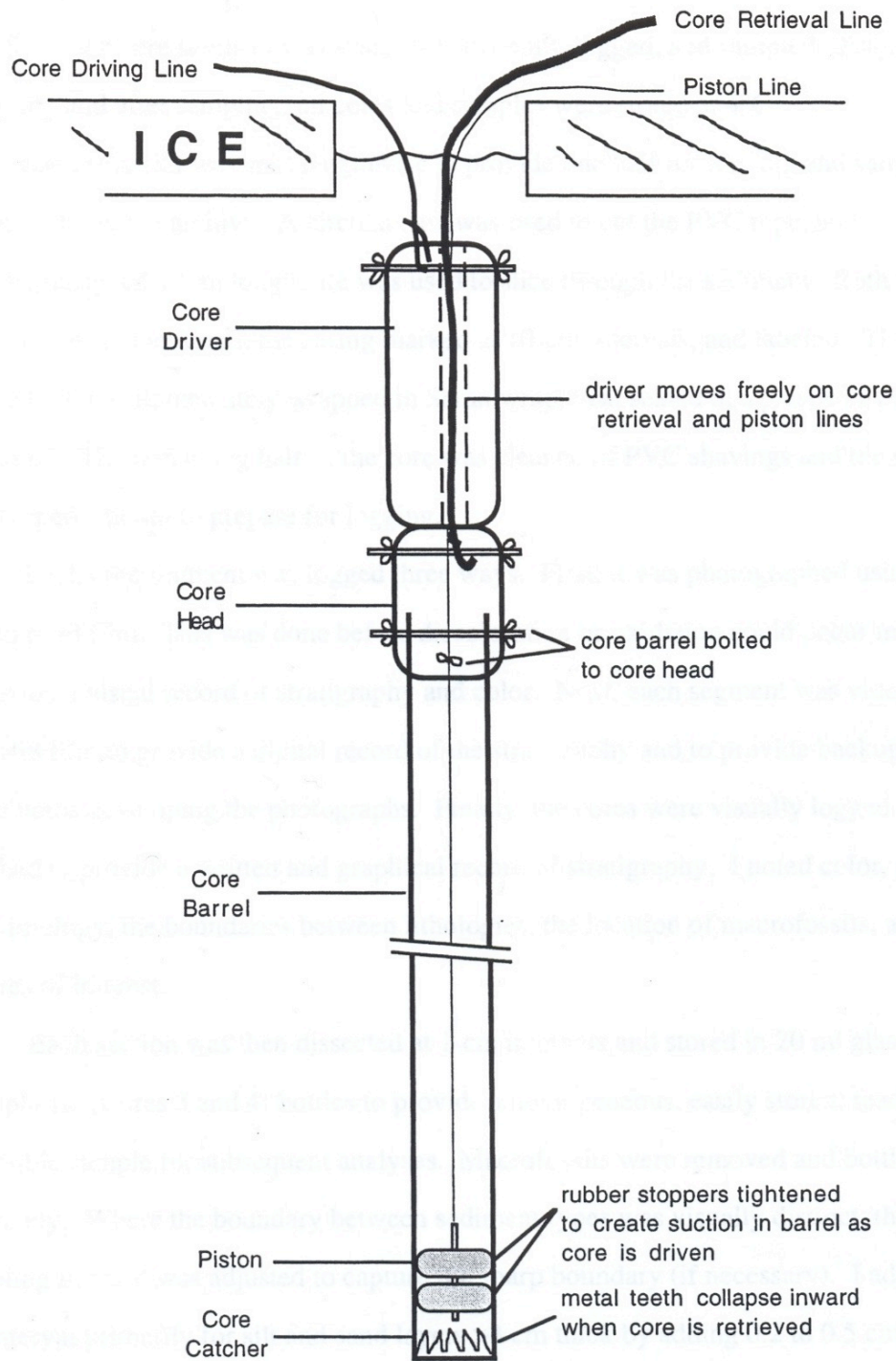


Figure 8. Modified Reasoner coring device, similar to the one used to sample Missisquoi Bay. From Brown (1999).