

1 A MULTI-PROXY PALEOLIMNOLOGY STUDY OF HOLOCENE SEDIMENTS IN
2 MISSISQUOI BAY, USA-CANADA
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5 A Thesis Progress Report Presented
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13 The Faculty of the Geology Department
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17 The University of Vermont
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24 in partial fulfillment of the requirements for the degree of Masters of Science specializing
25 in Geology.
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28 The following members of the Thesis Committee
29 have read and approved this document
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I. Introduction

This project aim is to use a multi-proxy analysis of sediment cores from Missisquoi Bay (MB) to make interpretations about environmental changes within the bay and surrounding watershed during the last 9,000 years. Located at the end of the Northeast arm of Lake Champlain (Figure 1), MB is a shallow and unstratified embayment that has recently been experiencing an increase in non point-source pollution, leading to eutrophication (LCBP, 2004). Excessive nutrient runoff from agricultural fields in particular, has greatly contributed to high phosphorus concentrations found in surface waters and sediments within the bay (VTDEC, 2009; Smith, 2009). Algal blooms are common in the summer and greatly impact water quality, wildlife habitat, and recreational opportunities. Measures have been taken and continue to be implemented to limit nutrient runoff (e.g. Vermont Clean and Clear Action Plan) in order to return the bay to its natural or baseline condition as an oligotrophic body of water (Burgess, 2007; Levine et al., 2010, in review). This study's goal is to gain a better understanding of the pre-settlement state of the bay, as it may be less static than it is assumed to be. A similar study by Johanna Palmer is also being completed in St. Albans Bay, which has recently experienced similar issues to MB. A better understanding of the past lake environment may aid in our interpretation of the current situation in MB and in making predictions of future responses to climate change.

As a consequence of eutrophication, recent sediments deposited in the bay have elevated amounts of organic matter when compared with pre-settlement values (King et al., 1993; Burgess, 2007; Figure 2). Prior to this period, the sedimentary record in MB appears to be relatively monotonous for an extended period (King et al., 1993; Burgess,

1 2007). The only exception is represented by a much older period, around 8,000 calendar
2 years ago (Cya) at a depth of 180-190 cm in core MSB2006 (Figure 2b), where there is
3 elevated organic matter accumulation in the sediment, as identified by Burgess (2007).
4 An intention of this study is to further investigate this period in order to shed light on the
5 environmental and climatic conditions at the time. While other variations in the sediment
6 record exist and will be investigated, this period appears to be a significant departure
7 from the proceeding period and might be able to help us understand how this particular
8 lake system, and lake systems in general, respond to climatic, environmental and/or
9 human-induced perturbations.

10 **Hypotheses**

- 11 • Pre-settlement temporal variations in the MB sediment cores can be explained by
12 shifting lake level, variable lake productivity, altered environmental conditions within
13 the watershed, and/or climate variability.
- 14 • Spatial variations in the MB sediment cores are minor and can be attributed to the
15 proximity of core locations to allochthonous sediment sources and shorelines.

16 **II. Completed Work**

17 **2.1 Core Collection and Processing**

18 In February and March, 2010, two sediment cores were retrieved from MB
19 (Figure 1, Table 1). Core 1MSB is 275 cm in length and was retrieved from the central
20 bay near the US-Canada border. Core 2MSB is 235 cm in length and was retrieved at
21 more southerly site near Goose Bay. Cores were retrieved using a modified Reasoner
22 piston coring device, using the >1 ft of ice as a stable platform.

1 Before the cores were split, the magnetic susceptibility was measured at 1 cm
2 intervals. Magnetic susceptibility is a measure of the amount of magnetic minerals
3 present in the sediment and is indicative of the relative amount of terrestrial inorganic
4 material in a given portion of the sediment column (Nowaczyk, 2001; Smol, 2008).
5 Thus, variations in the magnetic susceptibility aid the interpretation of changing
6 environmental conditions within the bay.

7 Once the cores were opened, digital photos and visual descriptions were recorded
8 along the entire length of the core (Figure 3). One half was wrapped and sealed as an
9 archive, and the other half was sampled at 1 cm intervals, with a total 505 samples
10 between both cores. Macrofossils, when found, were sub-sampled for radiocarbon
11 dating (Figure 4).

12 Each sample was then freeze-dried and divided into two sample aliquots (stored in
13 plastic vials), one of which was milled to a fine powder using a modified hotdog roller.
14 The powdered samples are used for elemental, stable carbon, and biogenic silica
15 analyses, whereas the unmilled samples will be used for grain size analysis.

16 **2.2 Laboratory Analyses**

17 All sample vials were weighed three times: before and after sediment was added,
18 and after the sediment was freeze-dried. With these weights, the water content of each
19 sampled interval was calculated as a ratio of the weight of the water in the sample to the
20 total weight of the original sediment. This is a proxy that is related to compaction,
21 amount of organic matter, and grain size distribution within the sediment (Cohen, 2003).

22 Samples were processed on the elemental analyzer for %C and %N, which are
23 indicative of the amount and type of organic material found in the sediment. This

1 analysis allows for the calculation of the C/N ratio of the sediment samples, a proxy
2 related to the type of plant material contained in the sediment (Meyers and Teranes,
3 2001).

4 The analysis of samples for biogenic silica (BSi) is almost complete. This
5 lengthy lab procedure involves hourly extraction of dissolved silica, followed by color
6 development and analysis on a spectrophotometer (Demaster, 1981). Units are reported
7 in mg SiO₂ per gram of sediment. BSi is incorporated into lake sediments predominately
8 in the form of diatom remains (Conley & Schelske, 2001). Similar to C/N ratios, this
9 proxy will help determine the types of organic material that has been deposited in the
10 sediment, with greater amounts of BSi being indicative of elevated diatom populations.

11 The %C record has allowed for a very good correlation of sediment layers
12 between our northern core (1MSB) and core MSB2006 (Burgess, 2007) located 3.65 km
13 to the NNE in the center of the bay (Figure 1). Using the age model of Burgess (2007),
14 we were able to approximate the age and sedimentation rates of both the 1MSB and
15 2MSB core (figure 5).

16 Five plant fragments from throughout our cores were cleaned and sent to be
17 radiocarbon dated at the Wood Hole Oceanographic Institute's mass spectrometer (Figure
18 4). Samples ranged from a twig to leaf and wood fragments. Four samples were taken
19 from 1MSB and one from 2MSB (Figure 4). The goal in dating these samples is to
20 improve accuracy of the ages found through correlation in order to better constrain the
21 timing of sediment deposition.

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III. Initial results and interpretations

3.1 Sediment description

Both sediment cores are composed of predominately homogenous grey silt and clay (90-97%) with black streaks and plant fragments that decrease in frequency with depth. Varves, or seasonal layers, are not present due to the shallow and unstratified nature of MB. Despite the presence of an entire mussel in the top of core 2MSB, bioturbation appears minimal, as the horizontal layering of plant fragments is common. A greater amount of large plant fragments were found within core 2MSB compared to core 1MSB. Many of these samples, in both cores, have been identified as pieces of macrophytes or rooted aquatic vegetation due to the visible striae on the leafy material (figure 6). The location of core 2MSB receives more of this type of plant remains because it is shallower and closer to the wetlands that are located south of the bay. Due to this and the proximity of site 2MSB to the Missisquoi and Rock Rivers, the sedimentation rate at this location was expected to be higher than at the 1MSB site; a finding which was verified through the correlation of these cores.

3.2 Correlation of cores

There is a very clear connection between the %C values for core MSB2006 and 1MSB that have allowed for a correlation of sediment layers between cores. Despite the closer proximity of 1MSB to 2MSB than to MSB2006 (1.67 km and 3.65 km, respectively), the sediments of 1MSB appear to be more similar to MSB2006 than 2MSB. An initial age approximation of layers within 1MSB was determined from the already established ages of MSB2006, which was both radiocarbon and ^{210}Pb dated (Figure 6; Burgess, 2007). A plant fragment at 174 cm was dated to $6,160 \pm 20$ ^{14}C yrs

1 (7,220-7,050 Cya) and the top 26 cm of MSB2006 were dated from the calendar years
2 2006 to 1874 (Burgess, 2007). The first cm of 1MSB was matched to cm 11 of
3 MSB2006, which was dated to the year 1980. MSB2006, which was a combination of a
4 piston core and a gravity core, contained sediment from water-sediment interface that
5 was clearly not present in 1MSB. Core 1MSB may thus be missing the top 11-13 cm of
6 sediment. Other points used to correlate the cores (Figure 7) were chosen where obvious
7 similarities were present. The sediments at the bottom of core MSB2006 are estimated
8 to be ~8,000 Cya (Burgess, 2007), where as the bottom 1MSB sediments may be ~9,200
9 Cya using the same age model. Core 1MSB captures an older record than previous cores
10 by Burgess (2007) and King et al. (1993) and core 2MSB.

11 Core 2MSB was correlated to 1MSB and MSB2006 using the %C record. This
12 correlation was not as clear as the one between 1MSB and MSB2006 due to likely
13 differences in the sedimentation patterns in this part of MB. The top 10 cm of 2MSB
14 correlate well with the upper portion of MSB2006 since the recent sediments were better
15 captured in this core. Age extrapolation indicates that bottom sediments of 2MSB are
16 only ~6,300 Cya, since it is 40 cm shorter than 1MSB and has a higher sedimentation rate
17 due to its closer proximity to the Missisquoi delta and lake shore.

18 **3.3 Core 1MSB**

19 There is a clear relationship amongst many of the proxies analyzed in 1MSB that
20 begins to reveal a story of the sedimentation pattern within the basin (Figure 8). Before
21 the settlement period in MB with elevated levels of productivity, there was a long period
22 of rather stable conditions between 60 and 240 cm, where productivity within the lake
23 was lower and %C values ranged from ~1-1.5%. It is likely that the trophic state of MB

1 was either oligotrophic or mesotrophic (Levine et al., 2010, in review). Small variations
2 in the parameters measured during that period exist, although they are minor compared to
3 the main period of interest for this study—between 240 and 270 cm, where there is a two-
4 fold change in the %C values.

5 This period of increased %C is only partially captured at the bottom of core
6 MSB2006 (which was part of the motivation for this study), and is not captured in 2MSB
7 due to its shorter length and higher sedimentation rates. Using the correlation of dates
8 from MSB2006, the period of greater productivity between 240-270 cm is roughly 8,000-
9 9,000 Cya. The drastic change in the %C occurs 60 cm deeper than in MSB2006, despite
10 the loss of around 11 cm at the top of 1MSB, due to an increased average sedimentation
11 rate within the bay at the 1MSB location.

12 The proxies studied suggest a period of increased productivity at this time that
13 was the result of variations in environmental and climatic conditions rather than
14 anthropogenic disturbances. Elevated %C, %N, C/N, BSi and water content, coupled
15 with a decrease in the magnetic susceptibility of the sediment are all indicative of a more
16 productive lake system. It is also possible that allochthonous sources of organic matter
17 and/or reduced mineral matter sedimentation were a contributing factor to the change in
18 the sediment composition. Studies of Holocene climate in the region (e.g. Jackson and
19 Whitehall, 1991; Webb et al., 1993; Shuman et al., 2004) will be used to help explain this
20 interval once better age constraints are established.

21 This older period of productivity appears to be distinctly different to the current
22 period of eutrophication in MB (in the top 10 cm of 1MSB). Although both periods have
23 elevated %C and %N values, lower BSi and higher magnetic susceptibility values

1 indicate a that the older period may have had relatively lower phytoplankton populations
2 and more allochthonous sediment inputs compared to the modern input. Diagenesis and
3 compaction of the sediments over time may slightly alter the signal of the current period
4 of productivity, although differences are expected to be maintained. Analysis of the
5 sediment for stable carbon isotopes and grain size during these periods should help with
6 the comparison of these two periods. Although we don't know if, how or when the
7 current period of productivity in MB will end, the sudden end to older period at a depth
8 of 240 cm is indicative of major changes within the bay and surrounding watershed.

9 **3.4 Core 2MSB**

10 Although core 2MSB did not capture as long of a record as 1MSB, it will help
11 shed light on the processes that are occurring at the margin of the lake. Due to its
12 shallower location close to shore, the 2MSB site is more sensitive to pulses of sediment
13 from the surrounding watershed and changes to lake level. The more “spiky” nature of
14 the water content and %C values is indicative of more variable conditions present closer
15 to the lake margin. Grain size analysis may highlight event horizons where coarser
16 sediments were deposited. Several studies in this region (e.g. Brown et al. ,2002; Noren
17 et al., 2002; Parris et al, 2009) have found these event horizons and dated their age in
18 smaller lakes, and a similar signal may be present in 2MSB.

19 **3.5 %C versus water content**

20 The water content data from both cores is surprisingly informative since it appears
21 to be very sensitive to changes in sediment composition. The water content appears to be
22 very dependent on the relative amount of organic matter, and has a strong linear
23 correlation ($r^2 = 0.834$ and 0.853 in 1MSB and 2MSB respectively) when plotted against

1 %C (Figure 9). This surprising relationship gives added significance to some of the
2 more small-scale variations in %C values and adds robustness to the dataset as a whole.
3 This study highlights the importance of this easy and cheap proxy that integrates changes
4 in the organic matter, compaction and composition of sediments.

5 **IV. Work remaining**

6 After finishing the biogenic silica analysis, I will begin the grain size analysis.
7 This analysis will help me better delineate the effects of river inputs versus internal lake
8 productivity. I will analyze the stable carbon isotopes of parts of the cores to aid in the
9 interpretation of the variation of organic matter type. I will do a multivariate statistical
10 analysis of the sediment cores this spring using JMP software. I am enrolled in Ruth
11 Mickey's multivariate statistics course this spring that will help with the completion of
12 this task.

13 I will continue to spend time reading relevant literature to help explain and relate
14 my findings into a more general and regional context. This will help prepare me for the
15 writing of my thesis and the NE GSA conference presentation we are planning.

16 **V. Timeline**

Dec, 2010	Finish biogenic silica analysis, begin grain size analysis
Jan-Feb, 2011	Grain size, stable carbon isotopes, and statistical analysis. Begin writing thesis.
March, 2011	Present research at the NE GSA meeting
April, 2011	Continued thesis writing
May, 2011	Finish and defend thesis

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VI. References

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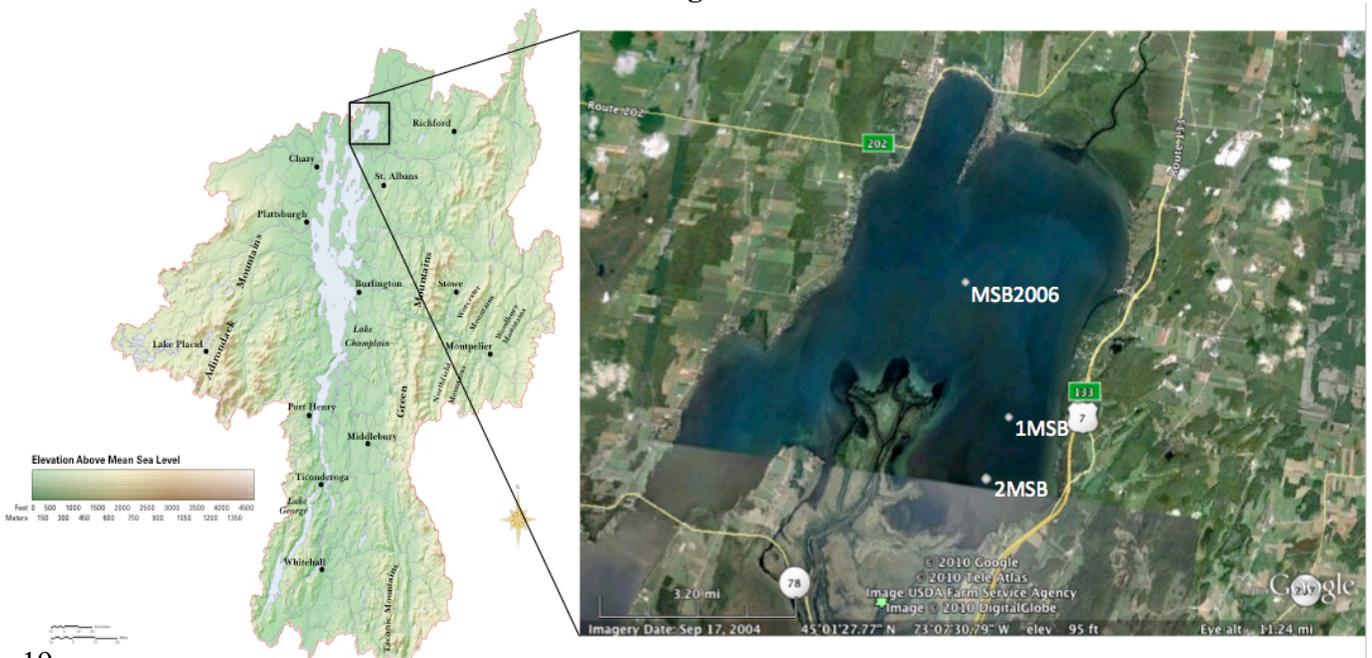
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 18 **VII. Figures**



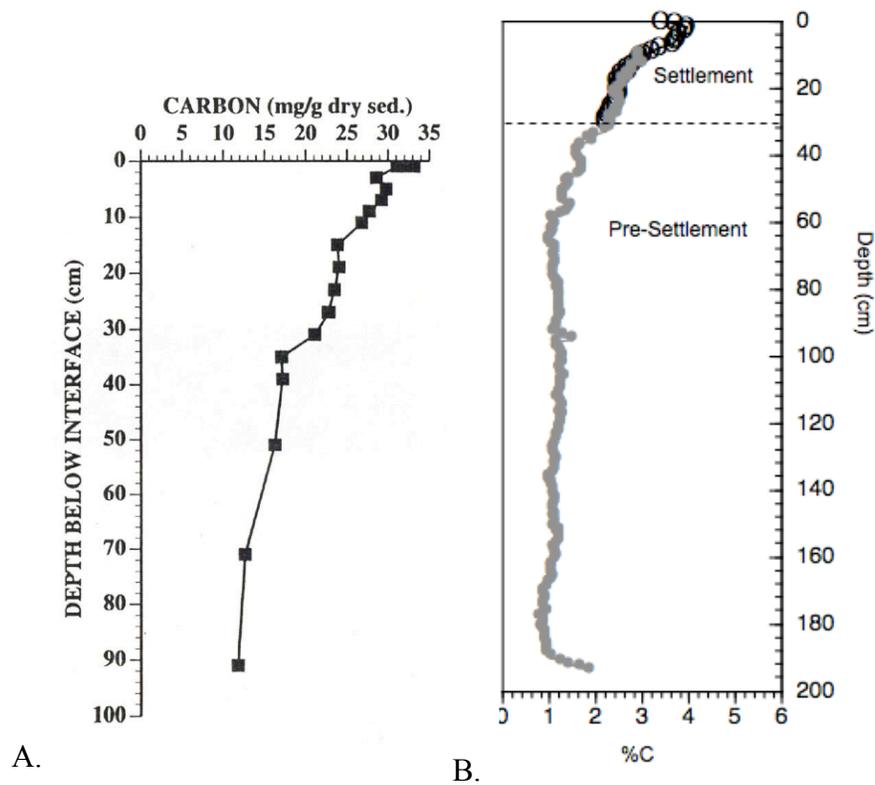
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 20 Figure 1. Watershed map of Lake Champlain with an inset of an aerial photo of Missisquoi Bay. Although
 21 political boundaries are not shown, the northern half of the bay is located in Quebec, Canada and the
 22 southern half is located in VT, USA. Cores 1MSB and 2MSB are the focus of this study and were taken in
 23 March 2010. MSB2006 is the site where Burgess (2007) and King et al. (1993) retrieved sediment cores.

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core location	Extraction date	Latitude (°N)	Longitude (°W)	core length (cm)	water depth (m)
MSB2006	March 2006	45.0367	73.13	185	4
1MSB	March 2010	45.0131	73.1088	275	3.66
2MSB	March 2010	44.9918	73.1133	230	2.75

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Table 1. Missisquoi Bay core information



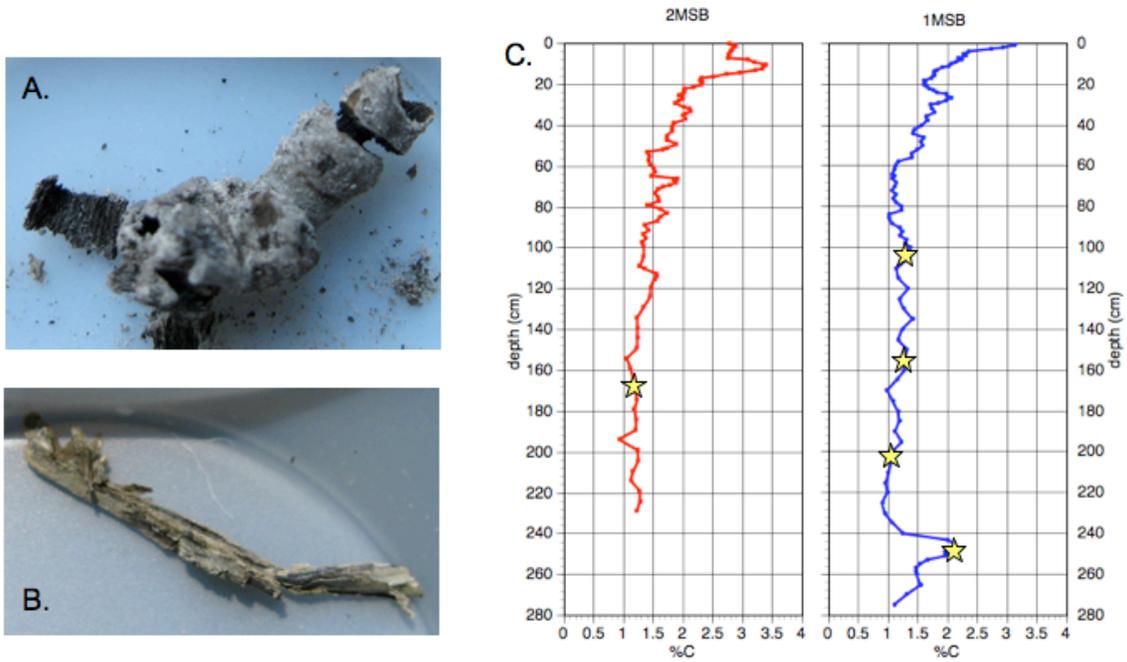
4 Figure 2. %C values from previous cores retrieved from Missisquoi Bay from (A.) King et al. (1993) and
5 (B.) Burgess (2007). Dashed line indicates approximate interval when the area was settled by Europeans as
6 reported by Burgess (2007).

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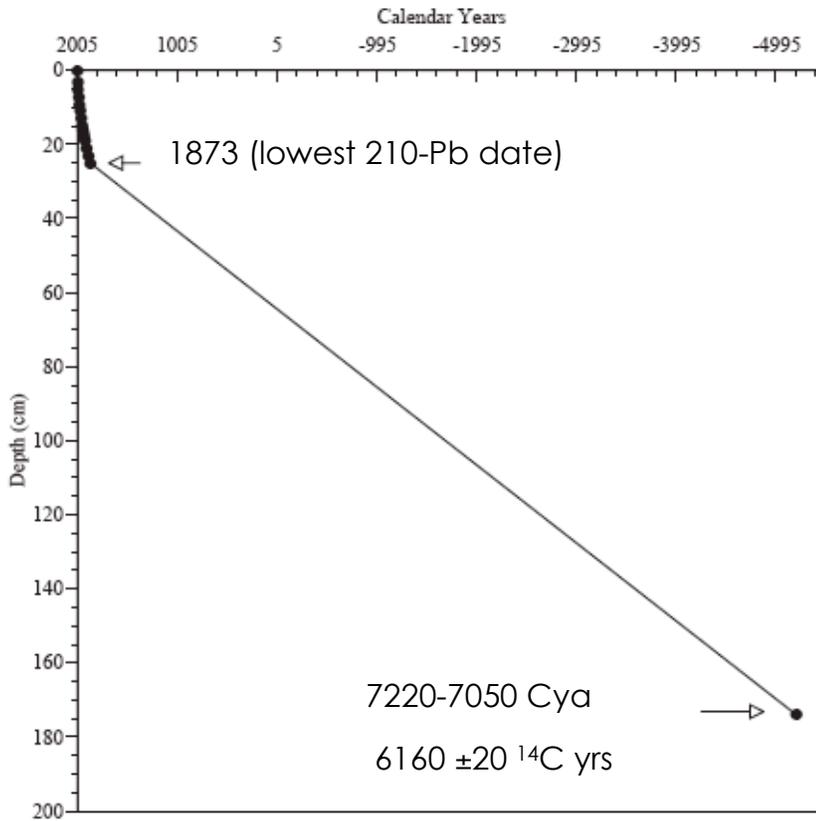
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Figure 3. Photograph of 1MSB, from 240-264cm.



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Figure 4. Information and pictures of Macrofossils sampled for radiocarbon dating. (A.) 2cm x 0.5cm twig sample from 1MSB104 (104 cm depth in 1MSB). (B.) 2.5cm stem of macrophyte sample from 2MSB168. (C.) Stars indicate locations of sampled sent to be radiocarbon dated from both cores. Due to the longer record in 1MSB, more samples were taken from this core.

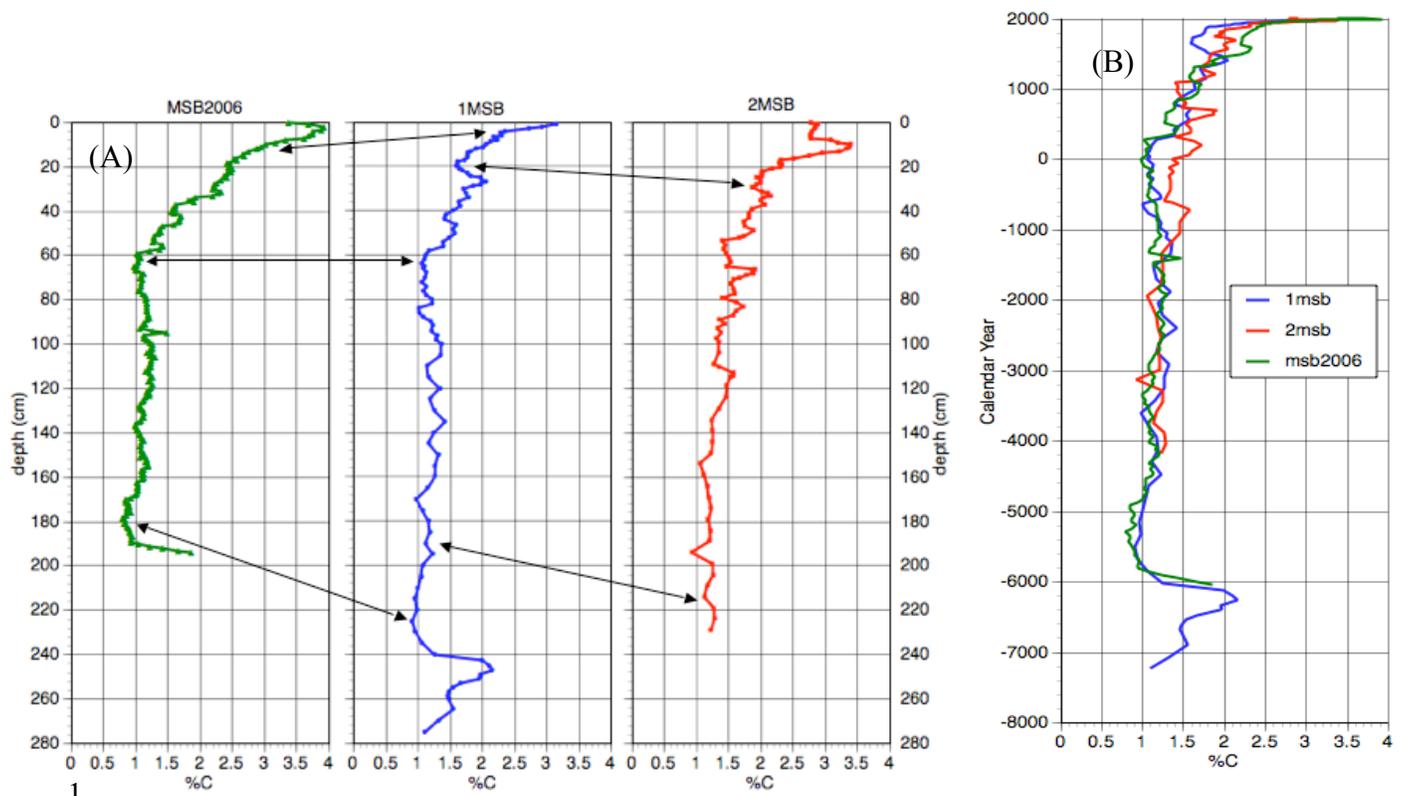


19 Figure 5. MSB2006 age model used to approximate age of 1MSB and 2MSB. Additional radiocarbon
 20 dates of plant fragments in 1MSB and 2MSB hope to address the undated interval between 30 cm and 170
 21 cm (Burgess, 2007).

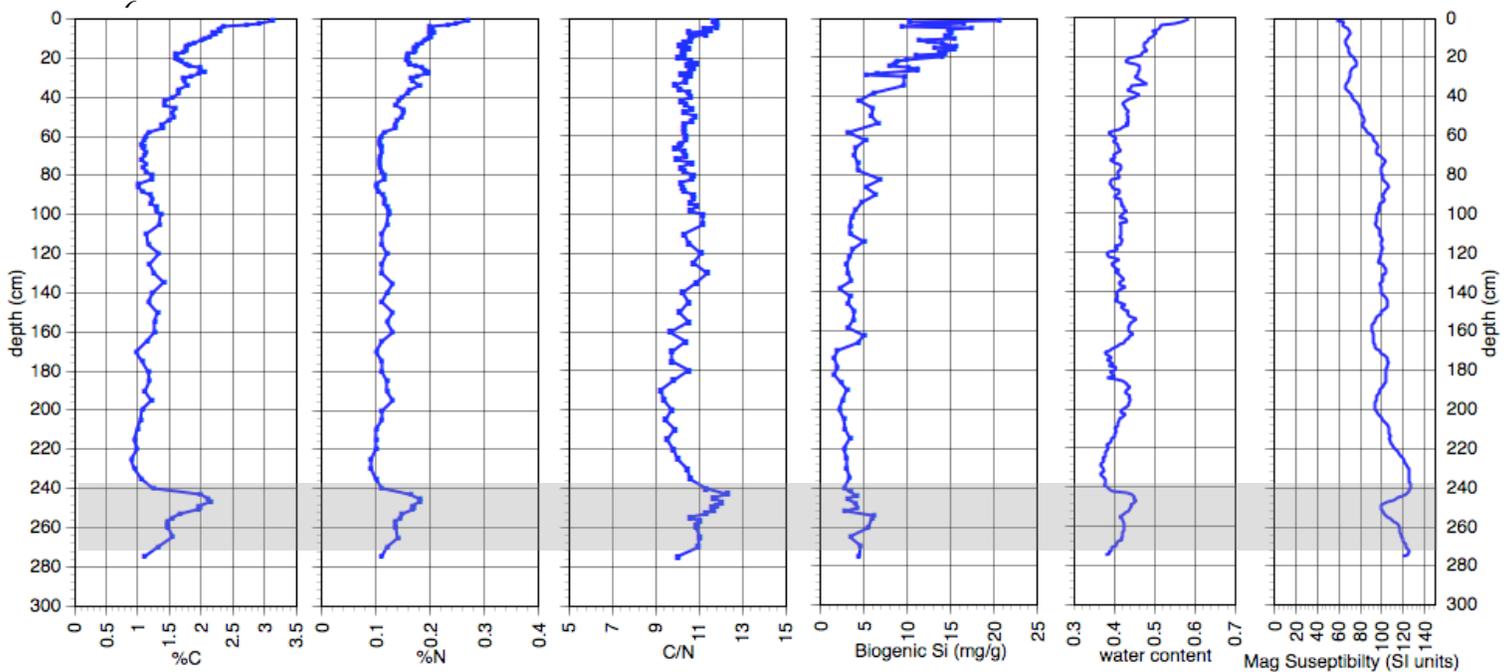


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 23 Figure 6. Marcophyte fragment (1x2 cm in size) found in sample 2MSB152 (152 cm depth in core 2MSB).
 24 Other samples similar to this were found throughout core 2MSB.

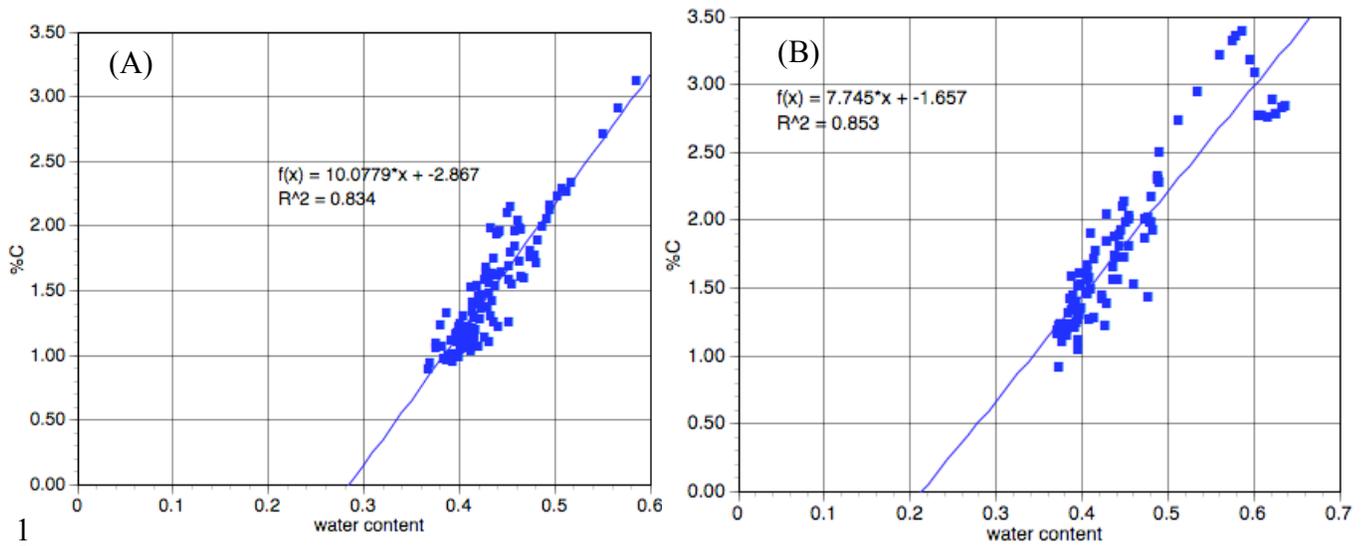
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 2 Figure 7. (A) Correlation of layers in MSB2006, 1MSB and 2MSB using %C data. Arrows point to
 3 depths that were used to calculate approximate ages of each core. (B) Calendar Years vs. %C plot of
 4 combined cores after correlation to established age model of MSB2006.

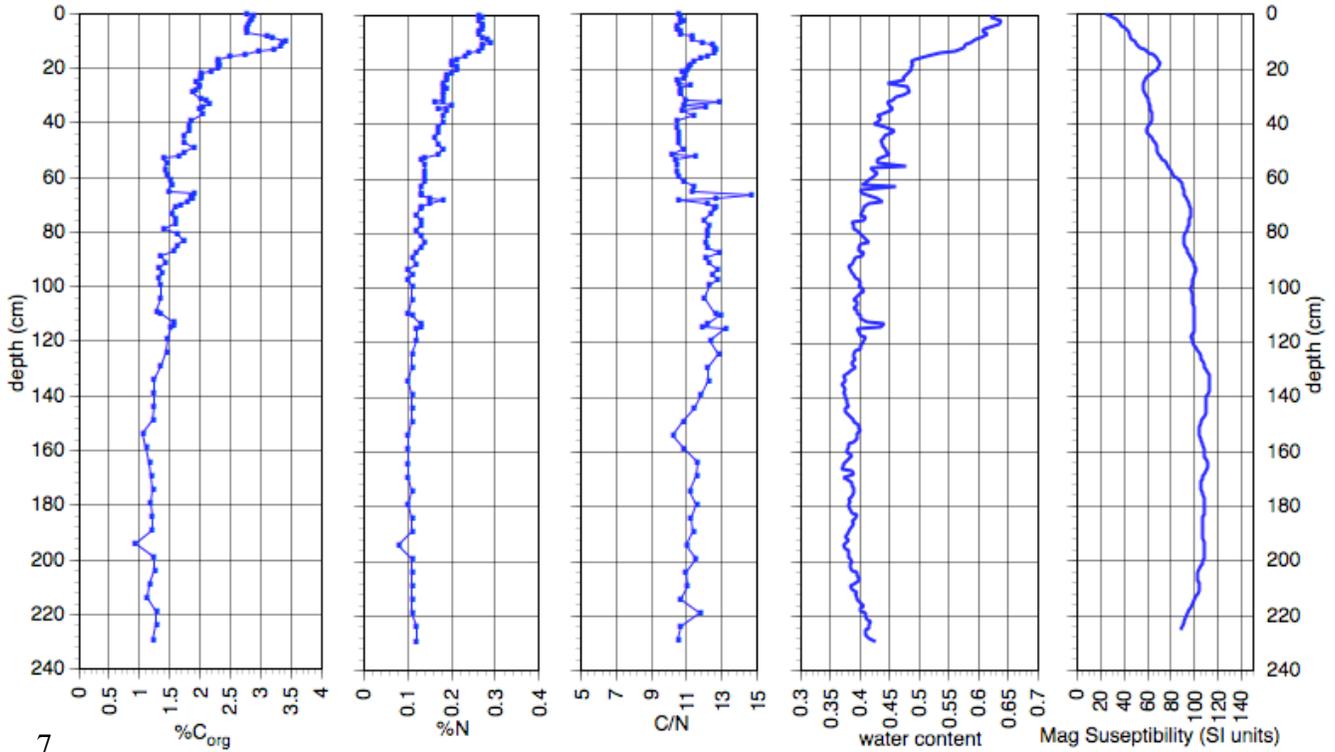


25 Figure 8. 1MSB data plotted versus depth (cm). The grey interval from 240 to 270 cm is the period of
 26 greatest interest in this study.
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Figure 9. Scatter plot of %C versus water content with a linear regression line in (A) 1MSB and (B) 2MSB.



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Figure 10. 2MSB data plotted versus depth (cm).