PROCEEDINGS OF THE TWENTY-SIXTH ANNUAL KECK RESEARCH SYMPOSIUM IN GEOLOGY

April 2013
Pomona College, Claremont, CA

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RECENT LAND USE AND VEGETATION CHANGES RECORDED BY NITROGEN AND CARBON ISOTOPE VALUES OF LAKE SEDIMENT CORES FROM SOUTHERN WISCONSIN

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Research Advisor: Al Werner

INTRODUCTION

Eutrophication in lakes occurs when nutrients added to the system encourage excess primary productivity that causes detrimental ecological effects such as hypoxia, which can lead to fish kills and loss of biodiversity, as well as increased turbidity and potential health risks to populations utilizing the lake. This project investigated the possibility that Clear Lake has been becoming eutrophic in recent years. To do this, we took sediment cores from several lakes in the area, and documented down core variations in carbon and nitrogen content and isotope values in the sediments. Lake sediments are useful repositories of paleo-environmental conditions because various chemical and physical proxies can be measured, and cores can often be dated to develop a reliable age chronology (Meyers, 1994).

C/N ratios can be used to determine the provenance of organic material in lake sediments (Meyers, 1994; Yu et al., 2010). Land plants have a distinctive C/N ratio of 20:1 or more, whereas aquatic plants have a lower C/N ratio of 5-10:1, due to a lesser quantity of cellulose (Meyers, 1994). Higher C/N ratios in sediments therefore indicate greater influx of terrestrial plant matter.

Carbon isotopes can also be used to infer past environmental conditions. Different types of vegetation have different pathways for carbon fixation, C_3 or C_4, leading to variations in the fractionation of ^{13}C, and noticeable differences of $\delta^{13}C$ values of sediments in surrounding water bodies (Yu et al., 2010). C_4 plants are more capable of dealing with dry climates than C_3 plants (Mampuku et al., 2008). $\delta^{13}C$ values can therefore be used to determine both primary type of surrounding vegetation and changes in climate.

METHODS

Sediment cores were retrieved from four lakes in the area (Clear, Duck, Grass and Mud Lakes) using a Livingstone square-rod piston corer. Two types of coring set-up were used, stainless steel 5cm coring barrel for cores longer than one meter and 7cm polycarbonate coring barrel for capturing the top meter and preserving the sediment-water interface. A detailed description was made of the split/extruded cores. Subsamples of the sediment were taken at 10 cm intervals along the length of the cores and from areas of significant stratigraphic variation. Four cores were chosen for nitrogen and carbon analyses: CL12-11 (Clear Lake, 5m of sediment recovered), GL12-01 (Grass Lake, 41cm of sediment recovered), DL12-01 (Duck Lake, 30cm of sediment recovered) and DL12-02 (Duck Lake, 6m of sediment recovered). Sediment samples from these cores were combusted at 1500°C in an elemental analyzer to produce N_2 and CO_2 gas, which was then inlet in to a Thermo Finnigan Delta Pluas isotope ratio mass spectrometer in continuous flow to determine the %N and %C, from which we could determine C/N ratios, as well as $\delta^{15}N$ and $\delta^{13}C$ values. Samples for ^{14}C dating at the AMS facility at the University of Arizona were taken from near the bottoms of the cores: CL12-11 (4.90m), DL12-02 (6.00m) and GL12-03 (7.5m). These dates were calibrated using the online calibration program OxCal. ArcGIS was used to determine the land use change between pre-settlement times and the present within the Clear Lake groundwater basin.

Regional water table contours by Gaffield et al. (2002) were used to draw and digitize a groundwater basin containing all four lakes in the study. A WISCLAND land cover data set (Wisconsin DNR, 2012) was converted to a polygon feature class and clipped using the groundwater basin. The land use percentages of interest, corn crops and other row crops, were calculated from the resulting polygon layer.

RESULTS

Core Description

The cores consisted of mostly organic rich sediment, with some clay/silt interbeds and relatively little clastic material, except in GL12-01. The general sedimentary features are congruous with a depositional environment expected in small seepage-dominated lakes; lack of input to the lakes from stream systems means that there is no source of larger clastic material other than large runoff events. CL12-11 and DL12-02 contain primarily organic sediments, with thin clay lenses near the bottom of the cores. DL12-01 was organic-rich from 0 to 17cm, then a light-colored clay from 17-30cm. GL12-01 contains organic material and a large quantity of sand. GL12-01 had abundant sand between 6 and 15cm, and between 25 and 37cm. As the sand was not deposited by a stream and the core was taken from close to a highway, the sand may be from the highway development, and may have been deposited in a few semi-instantaneous runoff events. No organic material was measured in these sandy deposits, inhibiting the collection of geochemical data. The probability of semi-instantaneous deposition calls into question the accuracy of our consistent sedimentation rate model.

^{14}C Dating

The base of each lake was dated using AMS ^{14}C, which were used to extrapolate sedimentation rates for each of the cores. CL12-11 was used for the Clear Lake age model, with an age of 11,556 +/- 260 years BP (before present, defined as 1950) at 4.9m. Four dates were obtained for DL12-02 the oldest at 6.0m with an age of 7625 +/- 182 years BP. GL12-03 was used for Grass lake, having two dates, the oldest at 7.3 meters with an age of 10565 +/- 154 years BP.

Age estimates down each core assume a consistent sedimentation rate throughout the history of the lake. A linear regression of the age/depth data was done for each core; the top of core was assumed to represent present (0 years). Since all dates are from below four meters, the age estimates for nearer the tops of the cores may not be as accurate, as there is no age control for modern sedimentation rates. For GL12-01 and DL12-01, the sediments used for ^{14}C dating were from cores in different locations in the lake, adding another level of uncertainty, as the sedimentation rate may be different closer or farther from the shore. The sedimentation rates calculated in cm/year for each lake are shown in Table 1.

Carbon and Nitrogen Isotopes and Percentages

A methionine standard with known carbon (40.25%) and nitrogen (9.39%) quantities was used to calibrate the %C and %N the samples, shown in Table 2. Results of the isotopic analysis, reported in delta notation (‰), are given in Table 2 as well. Variations of several per mil exist within each core and between lakes, the potential implications of which are considered in the discussion.

Table 1. Sedimentation rates

Lake	Sedimentation Rate
Clear Lake	0.04 cm/year
Duck Lake	0.07 cm/year
Grass Lake	0.06 cm/year

Table 2. Geochemical data of the first 20 cm of all cores.

Sample	Depth (m)	%N	$\delta^{15}N$ (‰) AIR	%C	$\delta^{13}C$ (‰) VPDB	C/N
CL12-11-01	0.01	4.67	2.54	50.93	-17.04	10.90
CL12-11-10	0.10	4.44	3.30	41.42	-18.01	9.34
CL12-11-20	0.20	4.08	2.70	26.84	-18.37	6.57
DL12-01-03	0.03	1.09	0.90	12.73	-26.04	11.66
DL12-01-04	0.04	0.31	0.33	12.92	-26.35	41.77
DL12-01-05	0.05	1.09	1.58	10.20	-25.49	9.35
DL12-01-06	0.06	0.74	0.37	11.85	-26.55	15.96
DL12-01-07	0.07	0.73	1.52	14.82	-25.78	20.24
DL12-01-08	0.08	0.64	1.98	18.29	-25.64	28.66
DL12-01-10	0.10	0.67	1.98	11.66	-24.83	17.43
DL12-01-11	0.11	0.16	-4.30	5.08	-25.64	30.90
DL12-01-13	0.13	0.11	-4.32	1.17	-27.48	10.68
DL12-01-14	0.14	0.44	2.29	4.50	-28.73	10.30
DL12-01-16	0.16	0.56	1.61	5.76	-28.92	10.21
DL12-01-21	0.21	0.16	0.36	1.76	-28.56	10.80
DL12-02-10	0.10	2.80	2.00	5.92	-23.54	2.11
DL12-02-50	0.50	3.49	2.76	46.95	-26.77	13.45
GL12-01-00	0.00	0.89	-0.31	20.81	-26.24	23.49
GL12-01-01	0.02	1.61	2.02	18.73	-26.09	11.61
GL12-01-03	0.03	0.82	1.68	15.60	-26.27	18.91
GL12-01-05	0.05	0.61	1.62	18.15	-26.19	29.79
GL12-01-16	0.16	0.73	2.89	17.81	-25.34	24.37
GL12-01-17	0.17	0.81	2.52	19.51	-25.66	23.98
GL12-01-18	0.18	0.81	2.56	49.67	-24.99	61.48
GL12-01-19	0.19	0.85	3.33	15.60	-24.67	18.36
GL12-01-20	0.20	0.84	2.90	8.96	-24.21	10.60

Geospatial Analysis

For the groundwater basin including all lakes in this study, we found that change in row crop coverage between pre-settlement times and the present, a span of about 150 years, was 45% of the total basin area, 89% of which was corn crops alone. Given the heavy application of fertilizer to farm fields, and that corn uses a C_4 carbon fixation pathway, this could be significant for the recent sediment record in all lakes. Clear Lake especially has substantial development directly on the lakeside, whereas the other lakes are more wooded.

DISCUSSION

There are two types of isotopic and C/N ratio variations of interest: 1) variations between the cores, representing differences in situation between lakes, and 2) variations down single cores, representing variations within a single lake over time. Clear Lake is of primary interest with both types of variation. There are noticeable differences between CL12-11 and the other cores, and it also has the most complete long-term record of all cores in this study.

CL12-11 has higher %N and generally higher %C than the other cores. The CL12-11 core top sediments also

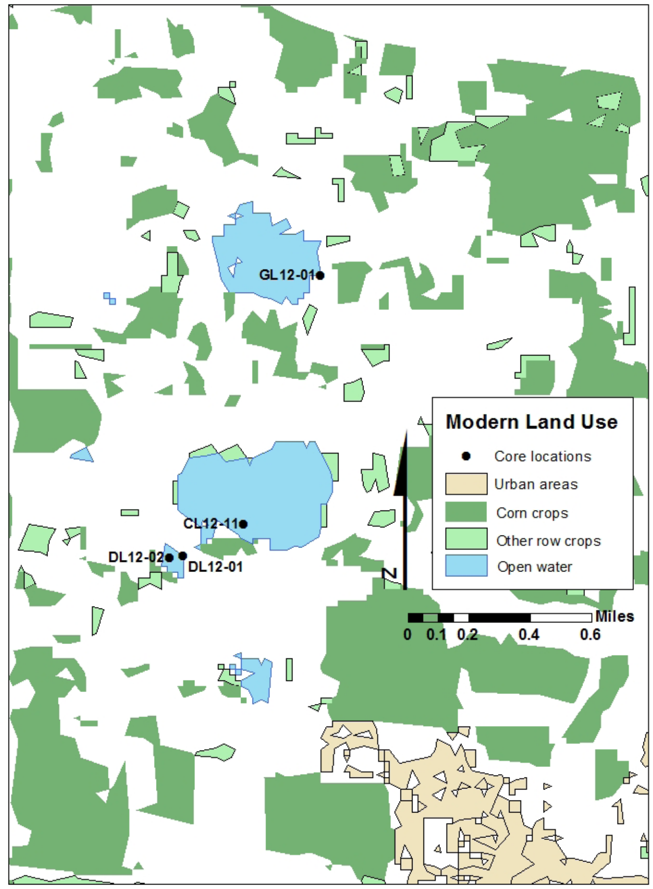

Figure 1. Land use map of the Clear Lake area (Wisconsin DNR, 2012). Core locations are marked with black dots and labeled.

have $\delta^{13}C$ values that are 5-10‰ higher than any of the other cores. As we are assuming that the tops of the cores are related to post-settlement events, these differences between CL12-11 and the other cores are most likely related to land use differences around the lakes.

Clear lake is the most developed area, and should experience the most anthropogenic effects. Higher %N and %C values in theory should reflect greater influx of nutrients due to agricultural runoff and erosion from human activities. The sharp increase in %N after presumed time of settlement, as seen in Figure 2, is very likely to be caused by the use of petrochemical fertilizers.

Given that the vast majority of agriculture in the area is corn, agricultural runoff effects could explain the $\delta^{13}C$ values as well. Corn is a C_4 plant, so it discriminates against ^{13}C relative to C_3 plants. As a result, $\delta^{13}C$ values of corn organic material are those of a C_4 plant, between -15 and -10‰ (Meyers, 1994). Most other plants in the area are C_3 plants, which give δ13C values between -30 and -25‰ (Meyers, 1994). As the values for CL12-11 top of core sediments are closer to those expected of organic material with C_4 plant origins, Clear Lake is most likely more influenced by nearby agriculture than the other lakes.

C/N ratios vary near the tops of the cores, but generally DL12-01 and GL12-01 have somewhat higher values than CL12-11 and DL12-02. DL12-02 has an unusual spike in the C/N ratios at the top of the core due to an extremely low %C value at 10 cm. This may be an error, as DL12-02 is visually organic-rich in this area, and the only other times %C is so low in any Duck Lake core is in the clay layer of DL12-01. Generally, Clear Lake is the outlier again. Greater influx of aquatic organic material than the other lakes could be due to increased productivity within the lake due to greater nutrient availability, less influx of terrestrial plant material due deforestation in the area, or both. Since agricultural runoff is likely affecting the Clear Lake system, it is probable that the low C/N ratio comes from higher productivity within the lake.

For the downcore variation analysis we focused on CL12-11, as it has the best length and sampling frequency combination and likely represents the greatest degree of anthropogenic modification of the lakeshore. The top of the core shows variations consistent with anthropogenic modifications to the landscape such as high %N and %C, and low C/N ratios indicative of high production.

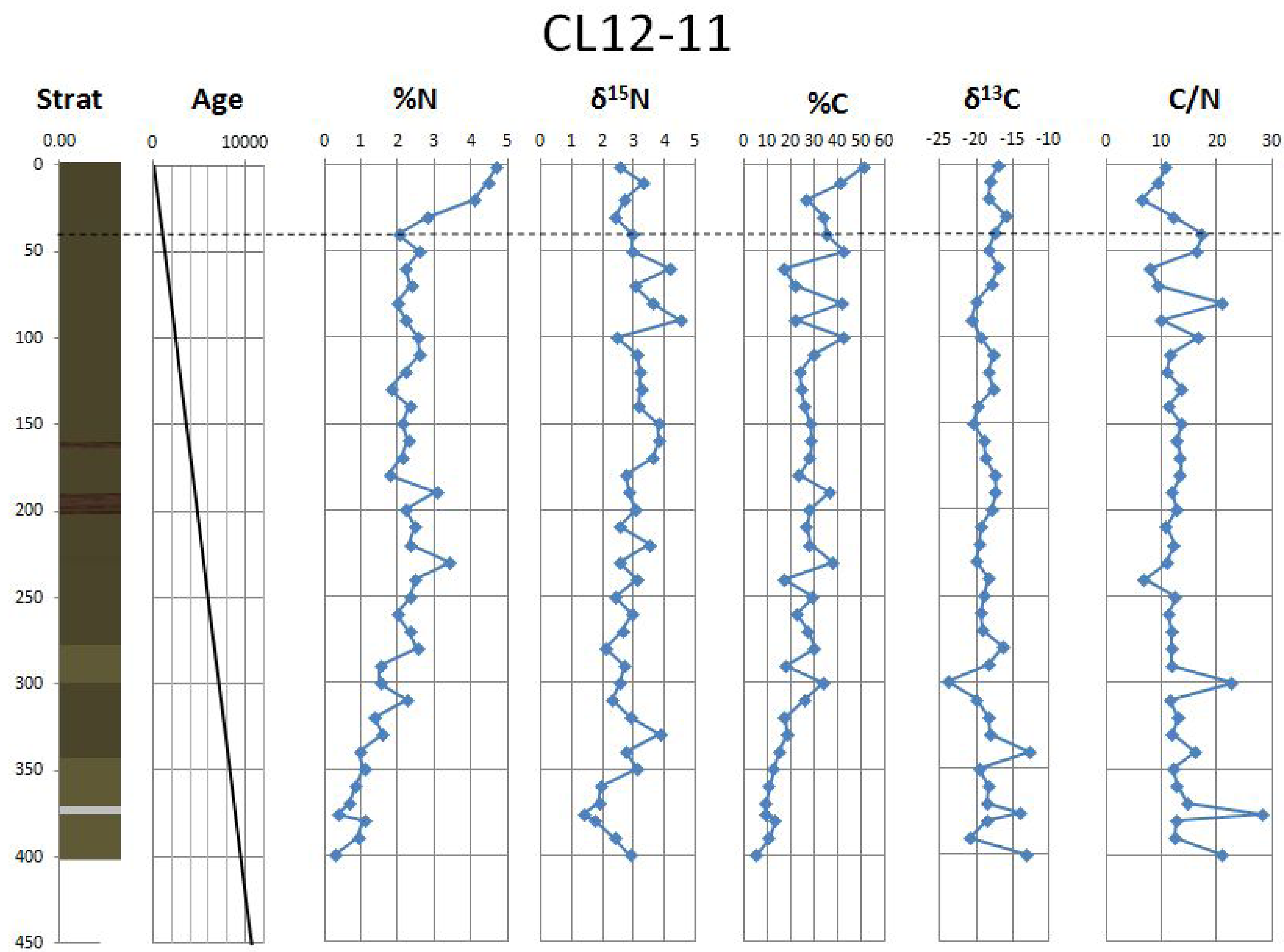

Figure 2. Plots of carbon and nitrogen data from CL12-11. Depth (cm) is given on the left. In the stratigraphy column, browns represent small variations in organic matter; the gray layer at 372-376cm is clay. The dashed black line across the graphs is an estimate of the time of European settlement.

The C/N values down the core are fairly steady at around 11-12:1 below 1m. This means that while the primary input of organic matter to the sediment is lake productivity, and there has historically been a consistent input of terrestrial plant material as well. Closer to the present, the C/N ratios become more erratic, indicating a perturbation of that system that is potentially the result of increased eutrophication of the lake. Towards the bottom of the core, the C/N ratios are also more erratic. The deposition of the sediments near the bottom of the core, a little less than 10,000 years ago, was around the time of the end of the last major glaciations in the area. The C/N values of this time period may reflect post-glaciation equilibration of the climate vegetation system.

Between the top of the core and 3m there is an apparent oscillation of $\delta^{13}C$ values between -15 and -20‰, with a periodicity of approximately 2500 years. Here the $\delta^{13}C$ values could indicate the abundance of C_4 vs. C_3 plants in the area. If that is the case, it would seem that the ratio of those populations oscillates over the span of a few thousand years. Most varieties of terrestrial plant are C_3 plants, but most grasses (of which corn is one) are C_4 plants (Mampuku et al., 2008; McInerney et al., 2011). C_4 plants are generally more able to withstand drier climates, so this could indicate cycles of wetter and drier weather (Clark et al., 2001; Mampuku et al., 2008). Prairies and savannas were historically ecosystems native to Wisconsin (Clark et al., 2001). It is possible that there has been oscillation between savannas in drier time periods and forests in wetter time periods in this region since the end of deglaciation. If this were the case, it would be a large-scale phenomenon, which would be seen in the Duck Lake core as well, but due to low sampling frequency it is hard to discern similar oscillations in DL12-02.

CONCLUSIONS

There is evidence that human activity has affected the vegetation history and aquatic productivity of the Clear Lake region. There is also evidence of oscillating wet and dry cycles in the area throughout the past 7500 years. The uncertainty of our age models and the limited amount of correlation between the cores makes it difficult to say much with confidence.

Further studies in this area would do well to collect more sediment cores, including several from each lake to be able to determine changes within the lake area as well as between lakes. They would also acquire more ^{14}C dates from along the length of the cores to gain more accurate sedimentation rates.

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