

Historic transitions in primary producer communities in eastern North Carolina lakes

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ABSTRACT

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Historic primary productivity and ecosystem stressors were reconstructed from sediment cores collected from eastern North Carolina lakes. Paleolimnological proxies such as sedimentary photosynthetic pigments, loss on ignition, stable isotopes, lignin oxidation products, and total organic carbon, nitrogen and phosphorus were measured to determine depositional changes in the sediment record. Sediment samples were dated by measuring excess ^{210}Pb using the constant rate of supply model and ^{14}C AMS. Lake Mattamuskeet is the largest lake in North Carolina (surface area=160 km²). Currently, Highway 94 divides the lake into two basins each containing a different primary producer community. The east side is macrophyte dominated and contains less turbid water while the west side is phytoplankton dominated with turbid water. Sediment cores taken from each basin showed that prior to the roadway both sides were phytoplankton dominated. After the building of the roadway, paleolimnological proxies suggest that physical, chemical and biological processes in the lake were altered. Shallow water levels, nutrient deposition differences and hydrological alterations caused the initiation and continuation of the two stable states. In addition, a long core collected from Lake Mattamuskeet showed that primary productivity generally increased from A.D. 1650 until human settlement around 1850. The changes in lignin concentrations and type suggest that the lake's catchment changed in response to cool

and wet conditions of the Little Ice Age (1650-1850). Pungo Lake is a small, shallow dystrophic lake in eastern North Carolina. Paleolimnological proxies from a short sediment core show that the lake was highly productive and algal dominated prior to A.D. 1600. Following the onset of the moist and cool conditions of the Little Ice Age increasing organic carbon and nutrient loading caused an increase in certain algal groups that include cryptophytes, diatoms and cyanobacteria. Following this increase, it is inferred that allochthonous carbon levels reached a critical point where primary productivity became light limited, which is the current state of the ecosystem. General conclusions from this research center on the need to understand algal community responses to increasing organic matter inputs and light attenuation resulting from climatic, environmental and anthropogenic impacts.

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CHAPTER 1: INTRODUCTION

SHALLOW AQUATIC ECOSYSTEMS

Characteristics of shallow lakes include an absence of long-term stratification, a maximum depth of 3 m and frequent resuspension of sediments during wind events, which can cause profound increases in turbidity and internal nutrient loading (Scheffer, 1997). Because of the shallow nature of these lakes, the majority of the lakebed has the potential to support macrophyte and benthic algal growth. Primary producer communities are affected by both external (wind, water level, nutrient loads) and internal (resuspension, grazers, denitrification) forcing features leading to highly complex systems that present obstacles for understanding historic ecosystem alterations as well as forecasting future ecosystem change.

ALTERNATIVE STABLE STATES OF SHALLOW LAKE PRIMARY PRODUCTIVITY

Alternative stable states of primary producers of either submerged macrophytes or phytoplankton have been described for shallow lakes (Scheffer et al., 1993). In most cases, nutrients have been the driving factor of primary producer community structure with low nutrient inputs supporting macrophyte communities and high nutrient inputs supporting phytoplankton communities, but other factors have been shown to cause ecosystem state change such as salinity (Davis et al., 2003), fish populations (McGowan et al, 2005; Meijer et al., 1994), water level (Blindow et al., 1993) and others. Regardless of the factor, researchers

agree that resilience to change slowly decreases prior to an actual primary producer shift (Scheffer et al., 2001; Jeppesen et al., 2003).

A major concern resulting from primary producer shifts is the differential in ecosystem services provided by a macrophyte-dominated system as compared to a phytoplankton-dominated system. Dense phytoplankton communities attenuate light, alter recreational fisheries, decrease the aesthetics of lake property and may include toxin-producing cyanobacteria (Paerl, 1988). Also, phytoplankton dominated systems are difficult to shift with decreased nutrient inputs (Jeppesen et al., 2005). For example, Lake Apopka, Florida has remained phytoplankton dominated following an ecosystem state shift despite nutrient reductions, constructed wetlands and biomass removal (Coveney et al., 2005). This resistance represents hysteresis in the system and supports the need for long term research on shallow ecosystems subjected to known ecological stressors.

ALBEMARLE/PAMLICO PENINSULA LAKES (APPL)

The APPL are a group of shallow lakes located on coastal plain of North Carolina, USA. The four lakes include Lake Mattamuskeet, Lake Phelps, New Lake, and Pungo Lake (Figure 1). These lakes are protected and managed by the Mattamuskeet National Wildlife Refuge (NWR), Pocosin Lakes NWR, and Pettigrew State Park. Very little is known about the limnology of the APPL, which are currently managed to attract and inhabit migratory waterfowl. Ducks, Canada geese, snow geese and tundra swans following the Atlantic Flyway can number over 1,000,000 each year making the APPL one of the nation's most important waterfowl habitats (Sponberg and Lodge, 2005). Aside from manmade canals, the

lakes lack direct surface water inputs causing water levels to be regulated by precipitation, evaporation and runoff from small, agriculturally dominated watersheds surrounding each lake (Figure 1.1).

The primary land use within the catchment of these lakes is agriculture. Due to rich organic soils, fertilizer use was minimal until recent decades (Forrest, *personal communication*). In the spring of 2006 a chicken egg-processing plant was constructed near New Lake. This plant houses over four million hens in fourteen high-rise houses. Manure from each house collects in a central pit where total projected release of ammonia to the atmosphere is over 4.7 million pounds per year (Ward, *personal communication*). These estimates are based on ammonia budgets generated at a similar plant owned and operated by the same company. Solid manure will be processed and distributed to local farms. The effects of atmospheric deposition of nitrogen and agricultural runoff derived from this new type of manure-based fertilizer are unknown at this time.

General geographic and limnological characteristics for the APPL are presented in Table 1. For most lake characteristics, the APPL feature among-lake gradients that facilitate answering comparative limnological questions. Each lake has been extensively canalled, and the canals are used in concert with water control structures to maintain constant water levels. Constructed wetlands and/or littoral aquatic macrophytes are maintained in and around each lake. Water levels and bird counts are the only routine data collected for each lake.

RATIONAL AND SIGNIFICANCE

Humans, migratory waterfowl and other environmental factors have affected the APPL, but the nature and magnitude of these impacts on the lake ecosystems are unknown. Due to a lack of historic limnological data on the APPL, the only effective way to study predisturbance conditions in these lakes is to apply paleolimnological techniques to reconstruct historic patterns and processes. Paleolimnological investigations have successfully reconstructed lake histories from a host of latitudes, longitudes and elevations. Lake-sediment cores provide a continuous record of environmental change and have been used to show changes in climate (Brenner et al., 2002), primary producer communities (Schelske et al., 2005), food web structure (McGowan et al., 2005) and many other environmental alterations in lakes and lake watersheds. The historic record found in the sediment provides a means to reconstruct lake histories, accurately assess current lake characteristics and effectively model future environmental change.

Sedimentary algal pigments can provide important diagnostic information about changes in primary producer community structure. By measuring downcore variations in the array of algal pigments in lake sediments, researchers can gain information of historic lake productivity, occurrence of cyanobacteria, and changes in algal community structure (Leavitt and Hodgson, 2001). Specific photosynthetic pigments have been used to represent the occurrence of different algal and bacterial groups (Paerl et al., 2003; Pinckney et al., 2001) (Table 1.2). In addition to sedimentary algal pigments, several proxies measured on lake sediments can further the understanding of macrophyte primary producer changes in lake ecosystems as well as inputs of allochthonous organic matter. Solid phase elements (organic

C, N, P, S, metals), the ratio of TC to TN (TC/TN), stable isotopes ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$), loss on ignition (LOI) and lignin oxidation products can be measured on sediment samples to characterize inputs into the sediment record. Finally, radiochronometric dating techniques (Accelerator Mass Spectrometry (AMS) ^{14}C , excess ^{210}Pb) can be used to determine ages and sedimentation rates for lake sediments. By applying this suite of paleolimnological techniques and developing an understanding of historic primary producer changes in the APPL, ecosystem factors that regulate primary productivity can be identified and potentially regulated to improve management strategies for migratory waterfowl, recreational fish, and other wildlife.

PURPOSE OF DISSERTATION

The goal of the research included in this dissertation was to reconstruct historic changes in total algal abundance and primary producer community structure within representative lakes of the Albemarle/Peninsula and to link these changes with known environmental and anthropogenic stressors. Further, the conclusions generated from this research were intended to aid in the management, restoration, and sustaining of these ecosystems. The specific objectives of this research were to:

1. Reconstruct historic primary productivity throughout the late Holocene with emphasis on the recent period of European settlement (≈ 200 years) for Lake Mattamuskeet and Pungo Lake
2. Link changes in the inferred primary producer community structure (PPCS) to known environmental and anthropogenic impacts

3. Use historical data to forecast possible future ecosystem state changes as well as the effects of management strategies
4. Infer ecosystem changes driven by natural drivers such as climate change and sea-level rise

The objectives listed above were investigated by measuring sedimentary algal pigments and other paleolimnological proxies on sediment cores retrieved from Lake Mattamuskeet and Pungo Lake. Sediment cores were retrieved from Lake Mattamuskeet and Pungo Lake in March 2006, April 2006 and July 2006.

STRUCTURE OF DISSERTATION

This dissertation includes 5 chapters. This chapter is an introduction, while the subsequent three chapters are focused on specific topics and are freestanding. The concluding chapter (V) is a summary of the major findings of this research. As a result, introductory material, methods, and some results will be repeated.

Chapter II describes the initiation and continuation of alternative stable ecosystem states located on the east and west sides of Lake Mattamuskeet across Highway 94. It reports paleolimnological proxies measured on short cores collected on either side of the highway as well as investigates possible causes for the differences between the two sides. The chapter concludes with suggesting possible mechanisms causing the two stable states as well as direction for future research.

Chapter III describes the general ontogeny and trophic development of Lake Mattamuskeet from the 1500's to the present. It reports paleolimnological proxies measured on a long core (4 m) collected using a vibracoring device. The focus of the chapter is the response of PPCS and total algal abundance to natural and anthropogenic impacts such as land clearance, canal construction, changes in catchment vegetation and the Little Ice Age.

Chapter IV describes changes in the PPCS of Pungo Lake documenting the development of dystrophy in the system. It reports paleolimnological proxies measured on a short core collected from the area of thickest soft sediment. The focus of the chapter is the response of certain algal groups to increasing allochthonous carbon and nutrient levels as well as changes in the organic matter amounts and types entering the lake.

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Figure 1.1. Map of the APPL with numbers identifying each lake: 1. Lake Phelps 2. Pungo Lake 3. New Lake 4. Lake Mattamuskeet.

Table 1.1. General geographic, physical, and limnological characteristics of the APPL. Information from Holman (1978), Lake Mattamuskeet NWR, Pettigrew State Park, Pocosin Lakes NWR, and Benkert (1990). Conductivity, color and pH are from Benkert (1990) and were measured during 1974 except for the Mattamuskeet conductivity, which was measured in 2007. Trophic status is from Division of Environmental Management (DEM) (1985). SA-Surface Area, MAS-Meters above sea level, Cond.-Conductivity.

	SA (km ²)	Elevation (MAS)	1 st Canal	Mean Depth (m)	Cond. µmhos cm ⁻¹	Color Pt-Co units	pH	Trophic State-1986
Lake Mattamuskeet	161	0.15	1840	1.0	335	20	6.7	eutrophic
Lake Phelps	64	3	1787	1.4	75	3	6.0	mesotrophic
New Lake	19. 8	<3	1850's	1.0	70	70	4.6	eutrophic
Pungo Lake	11. 3	3	1850's	0.75	103	500	5.3	dystrophic

Table 1.2. Primary producer groups represented by photosynthetic pigments readily recovered from lake sediments using HPLC. Modified from Leavitt and Hodgson (2001).

<u>Algal/Microbial Group</u>	<u>Pigment(s)</u>
Total Algal Abundance	Chlorophyll- <i>a</i> , Beta Carotene, Pheophytin- <i>a</i>
<i>Chlorophyta</i>	Chlorophyll- <i>b</i> , Pheophytin- <i>b</i> , lutein
<i>Bacillariophyta</i> (Diatoms)	Diatoxanthin, Fucoxanthin
<i>Dinophyta</i> (Dinoflagellates)	Fucoxanthin
<i>Chrysophyta</i>	Fucoxanthin
<i>Cryptophyta</i>	Alloxanthin
<i>Cyanobacteria</i> (general)	Zeaxanthin, Echinenone
<i>Cyanobacteria</i> (attached, colonial)	Canthaxanthin, Myxoxanthophyll
<i>Cyanobacteria</i> (Nitrogen-fixing)	Aphanizophyll

CHAPTER II: THE DEVELOPMENT AND RESILIENCE OF CO-EXISTING ECOSYSTEM STATES IN A LARGE, SHALLOW LAKE

ABSTRACT

Primary producer communities of shallow lakes are often dominated by either macrophytes or phytoplankton, which have significant feedbacks on lake function. In general, water clarity is increased in macrophyte-dominated systems and decreased during phytoplankton-dominance. Lake Mattamuskeet, North Carolina, USA is a large, shallow lake that currently includes algal and macrophyte dominated states in two basins formed by a roadway dividing the lake. Paleolimnological proxy data obtained from sediment cores collected from each side of the lake indicate that initiation of the current states occurred around 1942. K-means cluster analysis identified three sediment types based on sedimentary photosynthetic pigment data: low-productivity sediments, algal-associated sediments and macrophyte-associated sediments. Principal component analysis identified sedimentary photosynthetic pigments that correlated with each sediment type. Macrophyte-associated sediments positively correlated with eigenvectors of chlorophyll *a* and chlorophyll *b* which corresponded to current macrophyte pigment signatures, and algal-associated sediments positively correlated with eigenvectors of alloxanthin and aphanizophyll which are indicative of cryptophytes and nitrogen-fixing cyanobacteria (NFC), respectively. Phosphorus storage in the sediments deposited since 1942 varied with the macrophyte dominated basin averaging 5 $\mu\text{g}/\text{m}^2/\text{yr}$ (SD=0.1) and the algal dominated basin averaging 11 $\mu\text{g}/\text{m}^2/\text{yr}$ (SD=0.2). In

addition, other paleolimnological proxies measured such as loss on ignition, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, TC/TN and sulfur were different in post 1940 sediments within the two basins. These differences suggest that the division of the lake by the roadway changed nutrient dynamics, lake morphology and hydrology between the two basins, which played important roles in regulating primary producer community structure and resilience to ecosystem change.

INTRODUCTION

Within a shallow lake, primary producer communities are often dominated by either macrophytes or phytoplankton, which can occur as alternative ecosystem states (Scheffer et al., 1993). The potential to shift from one of these states to the other has been shown to occur abruptly (Moss et al., 1988; Schelske et al., 2005) and unpredictably (Scheffer, 1998). Changes in environmental factors such as salinity (Davis et al., 2003), fish communities (McGowan et al., 2005; Meijer et al., 1994), water level (Blindow et al., 1993), land-use changes (Schelske et al., 2005), and nutrients (Kenney et al., 2002) can trigger an ecosystem state change. In many cases, nutrient levels drive changes in primary producer structure, with low nutrient supplies supporting macrophyte communities and high nutrient supplies supporting phytoplankton communities. However, with intermediate nutrient supplies either state can exist according to the theory of alternative stable states.

There is concern about primary producer community structure (PPCS) in shallow lakes because of the negative effects phytoplankton dominance can have on the ecosystem. Dense phytoplankton communities attenuate light, alter recreational fisheries, decrease the aesthetics of lake property and may include toxin-producing cyanobacteria (Paerl, 1988). By

contrast, macrophyte communities provide relatively clear water, support recreational fish populations and recruit waterfowl. Macrophyte stands anchor sediments preventing resuspension and internal loading of nutrients thus causing an increase in water clarity (Jeppesen et al., 1990). Macrophytes also provide a refuge for zooplankton that consume phytoplankton and serve as a food source for higher trophic levels (Scheffer, 1997). Finally, a variety of waterfowl species consume macrophytes as a primary food source (Sponberg and Lodge, 2005).

Understanding forcing factors responsible for undesirable shifts in shallow lake primary producer communities is critical for effective forecasting of ecosystem change. Blindow (1992) showed that decreasing water levels can promote macrophyte abundance in shallow lakes. Reducing water depth allows light to reach the bottom sediments over a greater percentage of the lake thus influencing the onset of macrophyte growth. Successful establishment of macrophyte communities stabilizes bottom sediments and reduces sediment resuspension (Jeppesen et al., 1997). Using sediment records from two lakes, McGowan et al. (2005) demonstrated that fish community manipulations accounted for the greatest amount of variance in sedimentary pigment concentrations and other paleolimnological proxies. Carpenter and Leavitt (1991) also showed that changes in food web dynamics could lead to PPCS changes in lake ecosystems. Though it is not a tenable management tool, lake size has been shown to influence PPCS. Vegetation structure surveys of 215 lakes in the Lower Rhine floodplain (Van Geest et al., 2003) and 800 Danish lakes (Søndergaard et al., 2005) showed that the probability of macrophyte dominance was inversely related to lake surface area. Although a variety of factors can affect shallow lake PPCS, nutrient loading

and nutrient dynamics are among the most studied. Phosphorus additions to shallow lakes can cause eutrophication (Kenney et al., 2002) and primary producer community structure changes (Waters et al., 2005). Finally, the importance of nitrogen in determining PPCS has been shown for shallow lakes through co-limitation of primary productivity with phosphorus (Sagario et al. 2005) and nitrogen-fixation (Patione et al., 2006).

In the absence of water quality data, paleolimnological investigations can be used to examine the effects of natural and human impacts on PPCS and to determine whether PPCS has changed historically. One effective tool used to examine historic primary producer communities is sedimentary photosynthetic pigment analysis. By measuring the array of algal pigments in lake sediments, researchers can gain information of historic lake productivity, changes in algal community structure and perturbations of food-web dynamics (Leavitt and Hodgson, 2001). Leavitt and Findlay (1994) showed that photosynthetic pigments in lake sediments represent past algal communities by comparing sedimentary pigments with historic algal data from experimental Lake 227 in Ontario, Canada. Sedimentary photosynthetic pigments have been used successfully to infer historic community structure in many different types of lakes and provide information that cannot be obtained with other proxies such as the occurrence of cyanobacteria and nitrogen-fixing cyanobacteria (Leavitt and Hodgson, 2001).

Here data are presented from Lake Mattamuskeet, North Carolina, USA that detail the historic primary producer community changes in the lake through several periods anthropogenic change. Lake Mattamuskeet currently supports distinct ecosystems in the two

basins formed by a roadway that divides the lake. The west basin is phytoplankton dominated, and the east basin is macrophyte dominated. The primary objective of this research was to determine when the two ecosystem states developed and to link the development with known anthropogenic perturbations. Sediments from the two basins of Lake Mattamuskeet provide a platform for investigating factors affecting PPCS in shallow lakes. Photosynthetic pigments and other paleolimnological proxies (organic matter, nutrients and stable carbon and nitrogen isotopes) were measured in sediment cores collected from each side of the lake. Results suggest that multiple factors influenced the development and duration of each state.

METHODS

Study Site

Lake Mattamuskeet is a large, shallow lake located on the Albemarle/Pamlico peninsula on the coast of North Carolina, USA (Figure 2.1). Lake characteristics are shown in Table 2.1. Lake Mattamuskeet serves as an important ecological habitat for sport fish and migratory waterfowl following the Atlantic Flyway, which can number over 100,000 each winter (Sponberg and Lodge, 2005). A hydrological budget in 1990 showed that precipitation, evaporation and four outflow canals (one on the west side and three on the east side) were the main factors controlling water depth (Figure 2.1; Benkert, 1990). These canals contain water control structures that allow freshwater outflow during wind events and periods of high precipitation while preventing saltwater intrusions from the nearby sounds at other times. In addition to the four outflow canals, numerous smaller canals connect the lake

to adjacent farmlands and wetlands. Water is exchanged between the two basins via five small culverts cut into the 8.5 km (5.3 mile) roadway.

European settlement around Lake Mattamuskeet began in 1850 following the construction of the first canal connecting the lake to the sound. This canal decreased the water level from 3 m to the current depth of one meter and reduced the surface area by half. The most dramatic change to the lake was an attempt to drain the entire lakebed in 1915 using a large pumping system constructed on the lake's shoreline. This effort ultimately failed but did manage to drain about 25% of the southern part of the lake. The project was abandoned in 1932 when the lake was allowed to refill and become the Lake Mattamuskeet National Wildlife Refuge. In 1942, a roadway was built across the lake and divided the lake into two basins. In 1953, catfish and grass carp were removed in an effort to decrease turbidity in the lake. Finally, in 1980 the water control gates were replaced in response to increasing salinity in the lake's canals.

Field methods and laboratory analysis

Water depth and soft sediment surveys were conducted for each side of the lake in order to determine optimal sites for collecting cores (Figure 2.2). Because the southern portion of the lake was drained in 1915 and the labile nature of sedimentary pigments, coring areas were limited to the northern part of the lake to ensure that sediments had not been dry during the past. Two to three short (20 to 60 cm) cores were collected from each side of Lake Mattamuskeet in order to reconstruct the recent primary producer history of each side. Although multiple cores were collected from each side, the results presented here are based

on the core from each side determined to contain the most intact sediment record based on ^{210}Pb profiles and other proxy stratigraphy. Sediment cores were collected using a piston corer designed to retrieve undisturbed surface sediments (Fisher et al., 1992). Short cores were sectioned in the field, stored on ice and immediately returned to the lab. All core sections were frozen, freeze-dried and ground with a mortar and pestle prior to analysis. Bulk density, organic matter as loss on ignition (LOI), total phosphorus (TP), total sulfur (TS), iron (Fe), total nitrogen (TN), total organic carbon (TOC), carbon stable isotopes ($\delta^{13}\text{C}$), nitrogen stable isotopes ($\delta^{15}\text{N}$) and photosynthetic pigments were measured for each core section. Given their labile nature, photosynthetic pigments were measured within the first week following freeze drying.

Bulk density was calculated using the formula from Binford (1990), which expresses sediment density in g dry/cm^3 wet. OM content was assessed by loss on ignition at 550°C and is expressed as a percentage (Håkanson and Jansson, 1983). TP, TS and Fe were measured on dried sediments using an ARL 3560AES ICP analyzer following acid digestion using standard EPA methods. TOC and TN were measured using a Carlo Erba C/N/S analyzer with an attached autosampler. Prior to analysis, samples were acidified for 12 hours in HCl vapors to remove inorganic carbon. $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ were measured by a Finnigan Mat 252 isotope ratio mass spectrometer coupled to a Carlo Erba C/N/S analyzer. Carbon and nitrogen isotopic ratios were measured relative to an internal standard and calibrated to the reference standards of Pee Dee Belemnite and air, respectively. Isotopic ratios were calculated as standard delta notation:

$$\delta \text{ Isotope} = \frac{(\text{Sample}^{\text{heavy}}/\text{Sample}^{\text{light}}) - (\text{Standard}^{\text{heavy}}/\text{Standard}^{\text{light}})}{(\text{Standard}^{\text{heavy}}/\text{Standard}^{\text{light}})} \times 1000$$

and expressed as per mil (‰).

Photosynthetic pigments (chlorophylls and carotenoids) were measured using an HPLC system following the methods of Leavitt and Hodgson (2001) designed particularly for sedimentary pigments. Dried sediment samples were extracted with a solvent mixture of acetone, methanol and water mixed in an 80/15/5 ratio, which contained an internal standard (Sudan II; Sigma Chemical Corp., St. Louis, MO) and allowed to digest 16-24 hours in a -20 °C freezer. Following extraction, samples were centrifuged and filtered through a 0.22 µm syringe filter to remove any particulate matter from the sample. Samples were placed in an autosampler tray where they were mixed with an ion-pairing agent (0.75 g tetrabutyl ammonium acetate and 7.7 g ammonium acetate in 100 ml HPLC-grade water) prior to injection. 200 µL of each sample was injected into a Shimadzu HPLC system following the mobile phase and time sequence of Leavitt and Hodgson (2001). Chlorophylls and carotenoids were separated by passing through a Rainin Model 200 Microsorb C18 column and measured using a photodiode array detector set at 435 nm and 665 nm. Pigments were identified using retention times of known standards and pigment specific spectra recorded by the detector. Pigment concentrations were expressed as µg pigment/g organic matter (org) and calculated by comparing peak areas against standards of known concentration.

Sedimentation rates and core section dates were determined by measuring ^{210}Pb using the constant rate of supply (CRS) model and ^{137}Cs following the methods of Schelske et al. (1994) and Appleby and Oldfield (1983). ^{210}Pb and ^{137}Cs were measured on dried, ground

sediment samples using a low-background germanium well detector. ^{210}Pb data was used to provide sedimentation rates and core section dates for the past 150 years.

Sediment clusters based on primary producer proxies were objectively determined using multivariate statistics. Sedimentary pigment data was incorporated into a database, and principal component analysis was used to determine proxies that account for the largest percent of variance for the entire data set (SAS Jmp, 2006). Photosynthetic pigments were then used in a k-means cluster analysis to group sediments into historic periods of lake trophic status. K-means cluster analysis uses a specified number of cluster seed points and repetitively groups data to minimize standard deviations of means for each group. The number of clusters was determined from inferred changes in the proxy data. This technique has been used successfully in previous paleolimnological investigations to separate macrophyte-associated sediments, transitional sediments and algal-associated sediments in a one-lake study (Waters et al., 2005) and a multiple lake study (Kenney et al., 2002).

RESULTS

Sedimentary chronology

Excess ^{210}Pb activity in Lake Mattamuskeet sediments decreased with increasing depth (Figure 2.3) in cores collected from the east and west sides. Changes in activity at 2.5 cm in the eastern core and 6 cm in the western core indicate variations in sedimentation rates thus supporting the use of the CRS model in determining age (Appleby and Oldfield, 1983). Age vs. depth profiles (Figure 2.3) demonstrated fairly constant sedimentation rates in the top 8 and 13 cm of the east and west basin sediment cores, respectively. CRS age models

indicate this top section of increased sedimentation contains sediments deposited since 1924 \pm 5 years, which corresponds to the period where the lake was being drained. Sediment accumulation rates for each core during this period were 128 mg/cm²/yr (SD=23) for the east basin core and 74 mg/cm²/yr (SD=24) for the west basin core. Prior to lake drainage, sediment accumulation rates were lower as shown in the slope decrease of the age verses depth figure (Figure 2.3). In order to incorporate pre-human disturbance periods into figure plots, age verses depth profiles were used to extrapolate core sample dates to the late 1700's. Although these dates were used in figure plots of other paleolimnological proxies, k-means cluster breaks did not occur at any of the extrapolated dates.

The cores reported here did not show a ¹³⁷Cs “bomb” peak around 1963 as has been shown in less mixed sediments. Brenner et al. (1999a) observed similar ¹³⁷Cs patterns in sediment cores from Orange Lake, FL citing post depositional downward mobility of the soluble radioisotope. It was assumed that similar processes occurred in Lake Mattamuskeet.

Sediment zonation

K-means cluster analysis of all photosynthetic pigments separated sediments into three clusters: low productivity (LP), algal-associated (AA) and macrophyte-associated (MA). In addition, principal component analysis identified sedimentary photosynthetic pigments whose eigenvectors correlated with MA (chlorophyll *a* and *b*) and AA (alloxanthin and aphanizophyll) sediments (Figure 2.4). Eigenvectors for alloxanthin and aphanizophyll positively correlated with principal component 2 (PC2) yielding r^2 values of 0.37 and 0.63, respectively, while eigenvectors for chlorophyll *a* and *b* negatively correlated with PC2

yielding r^2 values of 0.30 and 0.46, respectively. LP sediments did not correlate with any specific pigments since the cluster is defined by low pigment deposition. In addition, both cores were divided into three zones based on paleolimnological proxy changes, cluster breaks, and known human impacts on the lake. Zone I (ZI) corresponds to the pre-European settlement period prior to 1850. Zone II (ZII) sediments represent the period of human impacts (1940-1850) incorporating the building of the first canal that decreased the depth of the lake and the drainage project. Zone III (ZIII) corresponds to the recent period of two stable states in the lake that formed following the roadway construction around 1940.

Sedimentary photosynthetic pigments

Sedimentary pigment deposition was low in ZI for all pigments measured (Figure 2.5). Although concentrations were lowest in this zone, all pigments measured were detected by the HPLC method. Zone II contains AA sediments, which were deposited from 1850 until the early 1940's for both cores. Photosynthetic pigment concentrations begin to increase during Zone II when compared to Zone I. In the east core all pigments increased upcore with the exception of aphanizophyll, which maintained consistent values around 0.01 $\mu\text{g/g}$ org. throughout the core. The increase in the west core for Zone II sediments was gradual but did occur for all pigments measured. Post 1940 sediments comprise Zone III and represent the period of increased pigment deposition for both cores and changes in pigment composition between cores. With the exception of aphanizophyll in the east core, pigment concentrations increased during Zone III. Likewise, when comparing Zone III pigment concentrations between the two cores, the most pronounced differences occurred with the pigments identified by the principal component analysis. Aphanizophyll and alloxanthin

were higher in concentration in the west core Zone III sediments and chlorophyll *a* and *b* were higher in the east core. Photosynthetic pigments measured on fresh macrophyte material from eastern Lake Mattamuskeet showed that the current macrophyte-pigment signature consists of high concentrations of chlorophyll *a*, chlorophyll *b* and lutein, which are the pigments identified by the PCA given that the applied method fails to separate lutein and zeaxanthin. The only other pigments negatively correlating with PC2 were lutein+zeaxanthin, pheophytin *b*, and beta-carotene.

Bulk sediment paleolimnological proxies

Paleolimnological proxies measured on Zone I sediments support differences in the lithology of both cores. Zone I in the east core was primarily sandy sediments mixed with organic particles, while the west core sediments contained peat mixed with sand. Bulk density was highest in Zone I for both cores with maximum values between 1.7 and 1.8 g dry/cc wet (Figure 2.6). LOI was the opposite with the lowest percentages occurring in Zone I sediments with the eastern core below 1% and the western core slightly increasing from 2% to around 6%. Likewise, total phosphorus was low for Zone I sediments in both cores with concentrations below 100 ppm. TC/TN in Zone I was constant for the east core with values around 17 but decreased in the western core from 48 down to 26. Stable isotopes were variable for both cores in Zone I sediments ranging from -2.0 to 0.9‰ and from -28 to -25‰ for $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$, respectively. Bulk density decreased throughout Zone II and Zone III from 1.7 to 0.09 and from 1.8 to 0.1 g dry/cc wet in the east and west cores, respectively. The eastern core experienced LOI increases from below 1% to a maximum of 30% in the top sample while phosphorus concentrations increased from below 100 to 291 ppm in the top

sample. Likewise, LOI in the western core increased from below 1% to values ranging from 17 to 36% in the top samples, and phosphorus increased from below 100 ppm to a range of 360 to 513 ppm in Zone III. Aside from the top sample, TC/TN values in Zones II and III in the eastern core averaged 19 (SD=1.1), while TC/TN values for the same region in the western core decreased from 26 to 11 in the top sample. Stable isotopes were variable for both cores in Zones II and III with $\delta^{15}\text{N}$ values ranging from -0.34 to 2.6 ‰ for the east core and from 0.92 to 1.7 in the western core and $\delta^{13}\text{C}$ values between -27 and -26 ‰ for the eastern core and increasing from -28 to -27 ‰ in the west core.

Zone III sediment proxies

Sediment proxy means measured on post-1940 sediments from the eastern and western sides of Lake Mattamuskeet show distinct differences (Table 2.2) corresponding to different PPCS. West side, algal-associated sediments in core samples were flocculent (low bulk density) and contained more than two times the phosphorus content than eastern side sediments (Figure 2.3 and 2.4). Despite the low bulk density for western core sediments, phosphorus accumulation was also higher with the western algal-dominated side averaging $11 \mu\text{g}/\text{m}^2/\text{yr}$ and the eastern macrophyte-dominated side averaging $5 \mu\text{g}/\text{m}^2/\text{yr}$. Total sulfur concentrations were also higher in western sediments than in eastern sediments by more than 200%. Eastern TC/TN ratios were higher than the western side sediments indicating a greater amount of structural carbon in the organic matter. $\delta^{15}\text{N}$ signatures for upper sediments in the east core were around 1‰ higher than west core sediments, while $\delta^{13}\text{C}$ signatures were close to 3‰ heavier in the east core than the west core.

DISCUSSION

Shallow lake primary producer communities have been the focus of extensive research over the past 20 years (Moss et al., 1988; Scheffer et al., 1993; Meijer et al., 1994; Sayer et al., 1999; Kenney et al., 2002; Schelske et al., 2005; and Zhu et al., 2007). Significant strides have been made in the theoretical (Scheffer, 1997; Scheffer et al., 1997) and applied (Schelske et al., 2005; Jeppesen et al., 2005) understanding of the interactions between primary producers and shallow lake function. This study took advantage of a lake with distinct primary producer communities in its two basins. These communities developed as a response to multiple perturbations (both human and natural).

Soft sediment distribution in Lake Mattamuskeet is heterogenous as has been shown in other shallow lakes (Whitmore et al., 1993) and Lake Apopka, Florida (Schelske et al., 2006). Soft sediment thickness was surprisingly low for both sides of Lake Mattamuskeet given the high level of primary productivity occurring in the lake. Nevertheless, sediment cores contain a historic record predating the building of the first canal in 1850 and the onset of European settlement (Chapter III). The effects of wind and microbial degradation are possible factors that determine soft sediment distribution and depth. During wind events, resuspension occurs depositing sediment in a small portion of the lakebed and in the extensive canal system surrounding the lake. These canals require frequent dredging due to deposition of highly organic sediments (Benkert, 1990). In addition, the shallow lake depth and high summer temperatures produce optimal conditions for rapid heterotrophic degradation of suspended and recently deposited organic sediments. Regardless of the mechanism, the paucity of sediment recovered at some sites and the heterogeneous

distribution of soft sediment underscored the need for soft sediment surveys and multiple cores in paleolimnological studies.

Many of the cores collected from Lake Mattamuskeet contained less than 15 cm of soft sediment which is insufficient for resolving and identifying recent changes in the PPCS and the temporal pattern of the current stable states. The two cores reported here met three requirements needed to answer the research questions. They were collected in the northern areas of the lake in order to avoid the formerly drained areas in the southern portion of the lake. Sedimentary algal pigments would rapidly degrade in the oxygen rich environment of the drained areas, and agricultural practices may have disturbed the sediment record.

Second, coring efforts targeted areas of the lake less likely to experience frequent resuspension from wind events. The middle of both basins of the lake contained less soft sediment than the outer edges, presumably the result of scouring during wind events. Third, coring was focused in the deeper portions of the lake in an attempt to collect less disturbed sediment.

Zone I (pre-European settlement)

Sedimentary pigment concentrations and paleolimnological proxy data suggest low algal abundance and very little organic matter deposition prior to 1850. This inference is supported by results from a longer core collected from Lake Mattamuskeet that included sediments dating to the 1500's (Chapter III). The lack of organic material (LOI<6%) and the high bulk density for both cores reflect the high sand content in the sediments prior to 1850. It is likely that at this time the delivery of organic material into the lake from the surrounding

watershed would have been small. As a result, the primary producers in the lake would be limited by the availability of nutrients typically delivered with organic inputs (Schippers et al., 2006). As seen in the TC/TN ratios in the west core (>30), the lake did contain peat deposits that could mix with the sandy sediments. These peat deposits are in the northern most section of the lake (Ingram, 1987) but have not been dated to determine the historic period of origin. The clustering of these sediments by the k-means cluster analysis and the lack of relationship between the pigment data and the principal components suggest that the lake was oligotrophic prior to 1850.

Zone II (European settlement-drainage)

The beginning of European settlement around the catchment of Lake Mattamuskeet increased organic matter, phosphorus and algal pigment deposition into the sediments. Sediments from both cores clustered together and were identified as algal-associated sediments using principal component analysis. Increased nutrient inputs and turbidity resulting from the draining and farming of the lake may have increased algal abundance by giving a competitive advantage to phytoplankton capable of photosynthesizing in shallow photic zones. PCA identified alloxanthin and aphanizophyll as the dominant pigments for ZII sediments indicating cryptophytes and nitrogen-fixing cyanobacteria were important components of the algal community. Cryptophytes and cyanobacteria use various mechanisms such as flagella and lipid storage for regulating buoyancy in a shallow photic zone (Reynolds, 2006). This algal dominated state persisted throughout the drainage period and continued through the refilling of the entire lakebed in 1932. It is likely that the large lake surface area promoted resuspension of sediments establishing unfavorable conditions for

macrophyte colonization. The extensive canal system constructed during this period would have increased the delivery of nutrients into the lake (Schippers et al., 2006). These conditions stabilized the primary producer community until the construction of the roadway in 1942. Therefore, from 1850 to 1942 Lake Mattamuskeet experienced increased nutrient inputs and increased turbidity from sediment resuspension, which supported an algal community dominated by nitrogen-fixing cyanobacteria and cryptophytes.

Zone III (roadway-present)

Paleolimnological proxies (phosphorus, TC/TN) and multivariate statistics (cluster analysis and PCA) showed that Zone III sediments were different in the two cores. It is inferred from these data as well as the current PPCS for each side that the development of the two ecosystem states began around 1940 corresponding to the building of the roadway. The eastern side shifted from phytoplankton dominance experienced in Zone II to macrophyte dominance consisting of species such as: *Vallisneria americana*, *Potamogeton perfectolis*, *Najas guadalupensis*, and *Chara* sp. Sedimentary photosynthetic pigments, macrophyte surveys (Piehler and Waters, *In preparation*), and historic reports (Benkert, 1990) show that the macrophyte coverage on the eastern side of the lake has persisted until today. This persistence of the macrophyte community is surprising given the intense herbivory experienced each year from the migratory bird population (Sponberg and Lodge, 2005) and the land-use changes that have occurred since 1940 (Benkert, 1990). Herbivory by waterfowl can be a negative factor in submerged aquatic macrophyte success (Jeppensen et al., 2005), but Lake Mattamuskeet does not appear to follow the same pattern. Sponberg and Lodge (2005) demonstrated that although herbivory from migratory birds was intense during

the winter months, macrophyte biomass during the growing season was unaffected.

Although many of the sedimentary photosynthetic pigments measured on each core were similar suggesting that both sides of the lake contain viable algal communities, pigments indicative of macrophytes (chlorophyll *a* and *b*) and phytoplankton (aphanizophyll and alloxanthin) support inferences of different ecosystem states in the two basins of Lake Mattamuskeet.

Other paleolimnological proxies support the existence and persistence of two ecosystem states in Lake Mattamuskeet. First, TC/TN values were higher on the eastern, macrophyte-dominated side. Although these ratios appear elevated from what is expected from sediments containing a majority of autochthonous material (8-15, Meyers and Teranes, 2001), they demonstrate the relative differences expected between algal and macrophyte derived sediments (Schelske et al., 2005). Aquatic macrophytes contain higher amounts of structural carbon than phytoplankton, which cause higher TC/TN ratios. The elevated numbers reflect significant amounts of terrestrial material entering the system, as well as the possibility of high rates of denitrification (Scheffer, 1997), which would also increase ratios. Finally, the higher concentrations of sulfur in the western sediments were surprising since the eastern side of the lake contains three canals connecting it to the saline waters of Pamlico Sound versus only one canal for the western side. Although these structures can leak from deterioration and debris blockage (Benkert, 1990), they are monitored collectively and therefore would most likely be similarly maintained.

Mechanisms supporting dual ecosystem states

The shift from phytoplankton dominance to macrophyte dominance in the eastern basin of Lake Mattamuskeet is unexpected in the context of shallow lakes experiencing anthropogenic ecosystem stressors. Generally, shallow lake ecosystems receiving increased nutrient loads and other anthropogenic stressors promote phytoplankton-dominated, turbid environments (Scheffer et al., 1993). Although management practices and human impacts on the lake have included canal construction, land-use change from forest to agriculture, biomanipulation and salinity increases, the macrophyte dominance of the eastern side has remained extremely stable since the construction of the roadway. This information supports the idea that the shift from phytoplankton dominance to macrophyte dominance in the eastern basin of Lake Mattamuskeet reflected variations in multiple physical and chemical factors of Lake Mattamuskeet including basin morphometry, hydrology and nutrient dynamics. Given the lack of historic data concerning primary producer community structure, these four factors are considered here in light of the sediment record and other studies on similar shallow lake systems.

The roadway modified the lake's morphology by decreasing lake surface area and fetch on each side of the lake. As a result, internal loading of phosphorus and turbidity increases from sediment resuspension would require stronger wind speeds and occur less frequently due to the decreased fetch for each side of the lake (Scheffer, 1997). Vegetation structure surveys of 215 lakes in the Lower Rhine floodplain (Van Geest, 2003) and 800 Danish lakes (Søndergaard, 2005) showed that the probability of macrophyte dominance was inversely related to lake surface area. Although the decrease in sediment resuspension

possibly influenced macrophyte recruitment in the east basin, other factors must have also contributed since the surface area of the west is less than the east. If lake surface area was the sole cause of the shift, the west should contain macrophyte abundance as well as the east. Another shallow lake characteristic linked to morphology and known to positively influence macrophyte growth is low water levels. The average depth for the east and west sides of Lake Mattamuskeet is 0.97 m (SD=0.2) and 1.1 m (SD=0.3), respectively, showing the homogeneity of the lakebed morphology. The lower water levels maintained in Lake Mattamuskeet by water control structures could promote macrophyte dominance on the eastern side by increasing the amount of light reaching the canopy of the macrophytes (Moss, 1988) as well as the inability of a shallow water column to attenuate enough light to prevent macrophyte recruitment (Hodgson, 1966).

The roadway potentially altered the hydrology of each side of Lake Mattamuskeet as related to the export of water and connectivity between the two sides. The east side contains three outflow canals on the eastern and southeastern sides of the lake, while the west basin is connected to one outflow canal. The one hydrological study conducted on Lake Mattamuskeet failed to consider differing hydrologies for the two sides and the varying number of canals (Benkert, 1990). The primary wind direction is from the southwest, which would push water to the eastern side and out the canals to Pamlico Sound. The western outflow canal is oriented due west and located behind several tree island barriers. During a wind event, the western side of the lake would more likely export water through the five small culverts cut through the roadway rather than the canal cut to the sound. This suggests that the eastern side of the lake would promote a removal of nutrients greater than the west

through canal export. Therefore, the west side of the lake would act as a depositional area for nutrients coming into the lake while the eastern side possesses the ability to export nutrients via the three outflow canals. Additionally, a natural flow for the lake could be from the west to the east. The Albemarle/Pamlico peninsula is a coastal plain containing a very shallow gradient toward Pamlico Sound. During periods of high rainfall and flooding, water could be moving as sheet flow from the west to the east causing differences in the hydrological inputs between the two basins. Phosphorus flux to the sediments further supports these differences in hydrological dynamics between the two sides with Zone III sediments averaging $5 \mu\text{g}/\text{m}^2/\text{yr}$ for the east basin and $12 \mu\text{g}/\text{m}^2/\text{yr}$ for the west basin.

Nutrient inputs and nutrient dynamics are among the most common determinants of PPCS in shallow lakes (Scheffer, 1999; Moss et al., 2005; Jeppensen et al., 2005). Nitrogen (Sagario et al., 2005) and phosphorus (Kenney et al., 2002) have been shown to promote phytoplankton dominance in mesocosm experiments and paleolimnological studies, respectively. The empirical evidence recovered in this study shows that phosphorus flux to the west basin sediments is greater than two times that of the east basin (see above). In addition, the high concentration of aphanizophyll in west basin sediments supports the inference that high phosphorus levels occurred in the water column and were capable of driving primary producer growth to be nitrogen limited. Given that the two basins of the lake exist within the same catchment and receive nutrients from areas with the same land use (Benkert, 1990), it is assumed that nutrient inputs are similar for the two sides. Since the validity of this assumption is questionable, several possible mechanisms will be discussed in order to account for different variations in nutrient inputs/exports and nutrient dynamics for

the two basins. First, the hydrology of each side of the lake could have been altered with the building of the roadway causing phosphorus flux to the sediments to be greater on the western side. As mentioned above, the canal structure, wind directions and minimal exchange between the two basins would promote a depositional basin in the west and a greater flushing of nutrients in the east.

Second, biogeochemical processes could be different based on redox characteristics and lability of the sediments. The phytoplankton-dominated west basin would favor internal nutrient loading through resuspension relative to the eastern side by containing sediments that are more flocculent (lower bulk density), contain more phosphorus and less structural material (TC/TN). Also, given the close proximity of Lake Mattamuskeet to the Pamlico Sound, the sediments contain a significant amount of sulfur (>2 ppt). During periods of organic sediment degradation, reduced sulfur compounds could bind to iron forming pyrite and rendering phosphorus into a soluble and reactive form. Algal-derived sediments are considered more labile than macrophyte-derived sediments suggesting that pyrite formation would be more common in the western basin. Higher concentrations of sulfur (west-6.2 ppt, east-2.5 ppt) and iron (west-8.3 ppt, east-3.6 ppt) in the western sediments support this inference. Martens et al. (1978) showed that this mechanism in sediments from Cape Lookout Bight, North Carolina can account for significant phosphorus release from the sediments. Likewise, Klump and Martens (1989) demonstrated that the release of phosphorus as a consequence of pyrite formation was seasonal.

Third, trophic interactions could be altering nutrient deposition and inputs between the two basins. The large numbers of migratory waterfowl favor the eastern side of the lake (Waters and Pielher, *unpublished*) and feed on the macrophyte tubers in the sediments. Although yearly macrophyte biomass is preserved following waterfowl herbivory in Lake Mattamuskeet, Sponberg and Lodge (2005) did show that waterfowl consumed over 50% of winter macrophyte biomass. This form of nutrient removal would support the lower phosphorus storage in the eastern sediments. In addition, the nutrient additions to the sediments from waterfowl manure have not been calculated. Whether this form of nutrients is rapidly sequestered by macrophyte regrowth or removed by flushing is unknown. Regardless, the nutrient inputs from waterfowl do not appear to equal processes controlling nutrient flux to the west basin sediments.

Fourth, nutrient inputs between the basins could be different. Although the two basins share similar land use, climate, and geology, other mechanisms could be delivering greater amounts of nutrients to the west. The Mattamuskeet National Wildlife refuge currently manages wetland areas around the lake as additional food sources for the waterfowl. These areas are periodically flooded and drained to maintain conditions suitable for wetland plant growth. The water from these areas is likely high in nutrients. It is possible that the west receives a greater amount of wetland drainage than the east. Also, greater amounts of nutrients could be entering into the west as a sheet flow across the peninsula. The entire Albemarle/Pamlico peninsula is a wetland type environment. It is possible that during periods of intense precipitation such as floods, sheet flow could deliver nutrient rich flood water to the west basin as it flows toward the sound. Regardless of the

mechanism, total phosphorus flux to the sediments and periods of nitrogen limitation suggest that nutrient dynamics and/or nutrient inputs are different between the two basins.

Conclusion

The PPCS of Lake Mattamuskeet, North Carolina exists as two alternative states with the western basin supporting a phytoplankton community and the eastern basin supporting a macrophyte community. Paleolimnological proxy data show that the current primary producer communities established around 1940 when the roadway was built and have remained stable despite repeated human management practices (fish removal, salinity changes, macrophyte transplants, etc.). Prior to 1940 the entire lake was phytoplankton dominant in response to decreasing water levels, canal construction and a partial drainage of the lake. Sediments predating European settlement contained lower concentrations of photosynthetic pigments and organic material indicating a lower trophic status. The initiation and continuance of the current stable states is proposed as resulting from changes in lake morphology and nutrient characteristics in the lake. Decreasing water levels, hydrological patterns and alterations to surface area support the dominance of phytoplankton in the western basin and macrophytes in the east. Likewise, differences in phosphorus flux to east and west basin sediments suggest that lake morphology and PPCS feedback mechanisms promote dissimilar nutrient dynamics in each side. Specifically, nitrogen-fixing cyanobacteria constitute a significant component of the primary producer community on the west side but are a minor component of the east side. These findings provide new insights into shallow lake PPCS dynamics as well as uncover the importance of physical and chemical processes in addition to nutrient inputs in governing ecosystem state.

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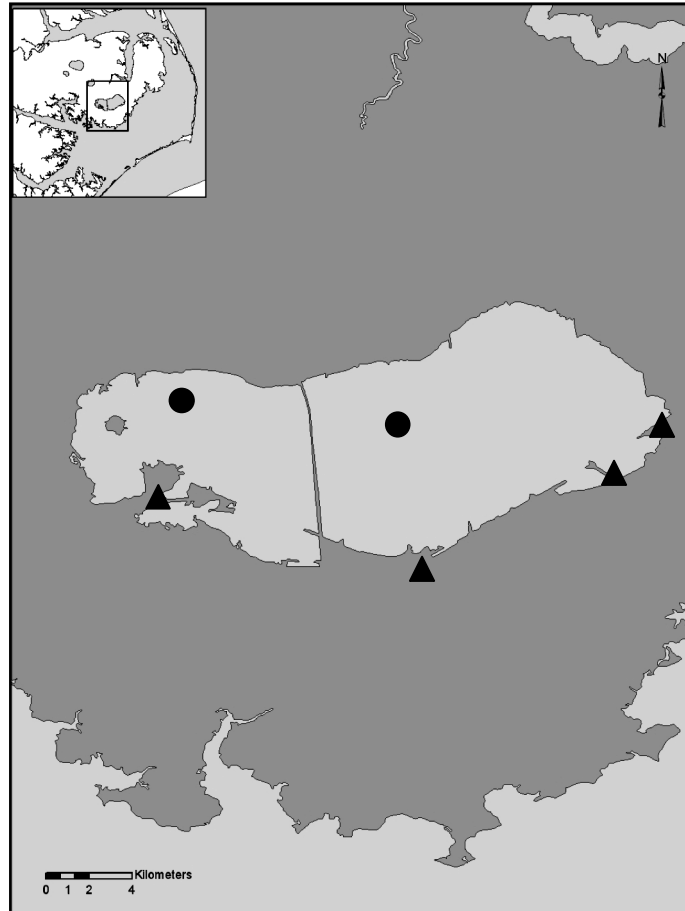


Figure 2.1. Map of Lake Mattamuskeet with points (●) representing core stations and triangles (▲) representing the location of the canals connecting the lake to the sound.

Table 2.1. Limnological characteristics for Lake Mattamuskeet, North Carolina. Units for elevation are meters above sea level.

<u>Characteristic/Year</u>	<u>Units</u>	<u>Value/Description</u>
Latitude		35° 29'N
Longitude		76° 12'W
Depth-average	m	1.01
East	m	0.97
West	m	1.09
Depth-maximum	m	1.75
Surface Area	km ²	162
Elevation	mas	0.15

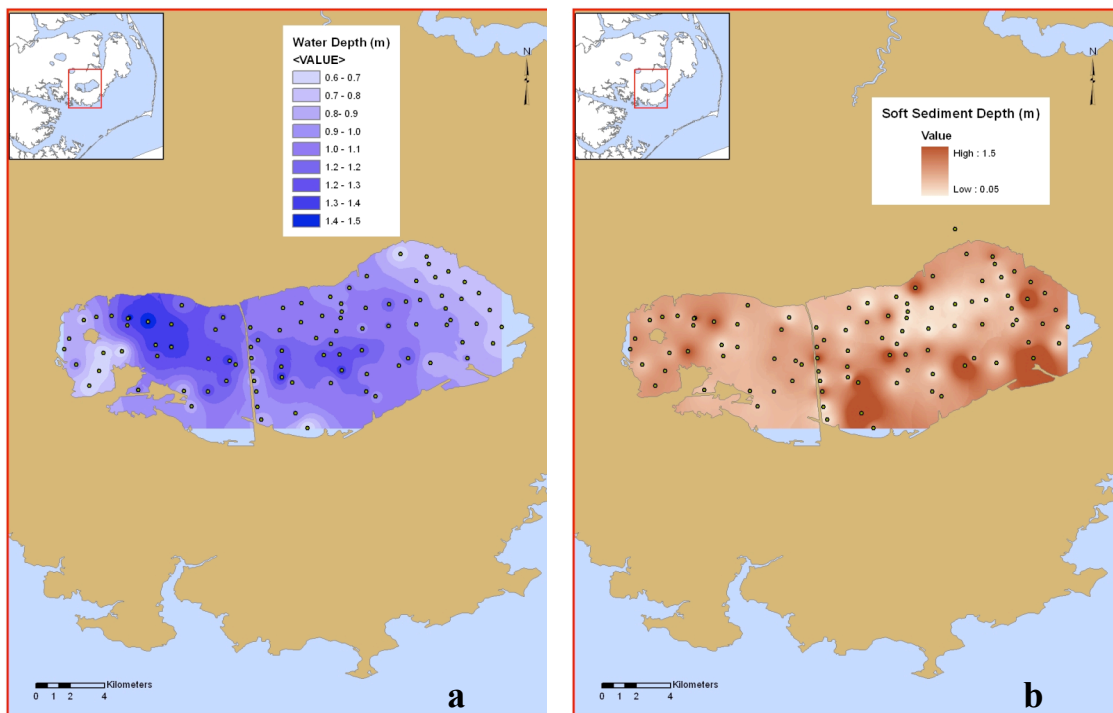


Figure 2.2. Water depth (a) and soft sediment depth (b) maps for Lake Mattamuskeet, North Carolina.

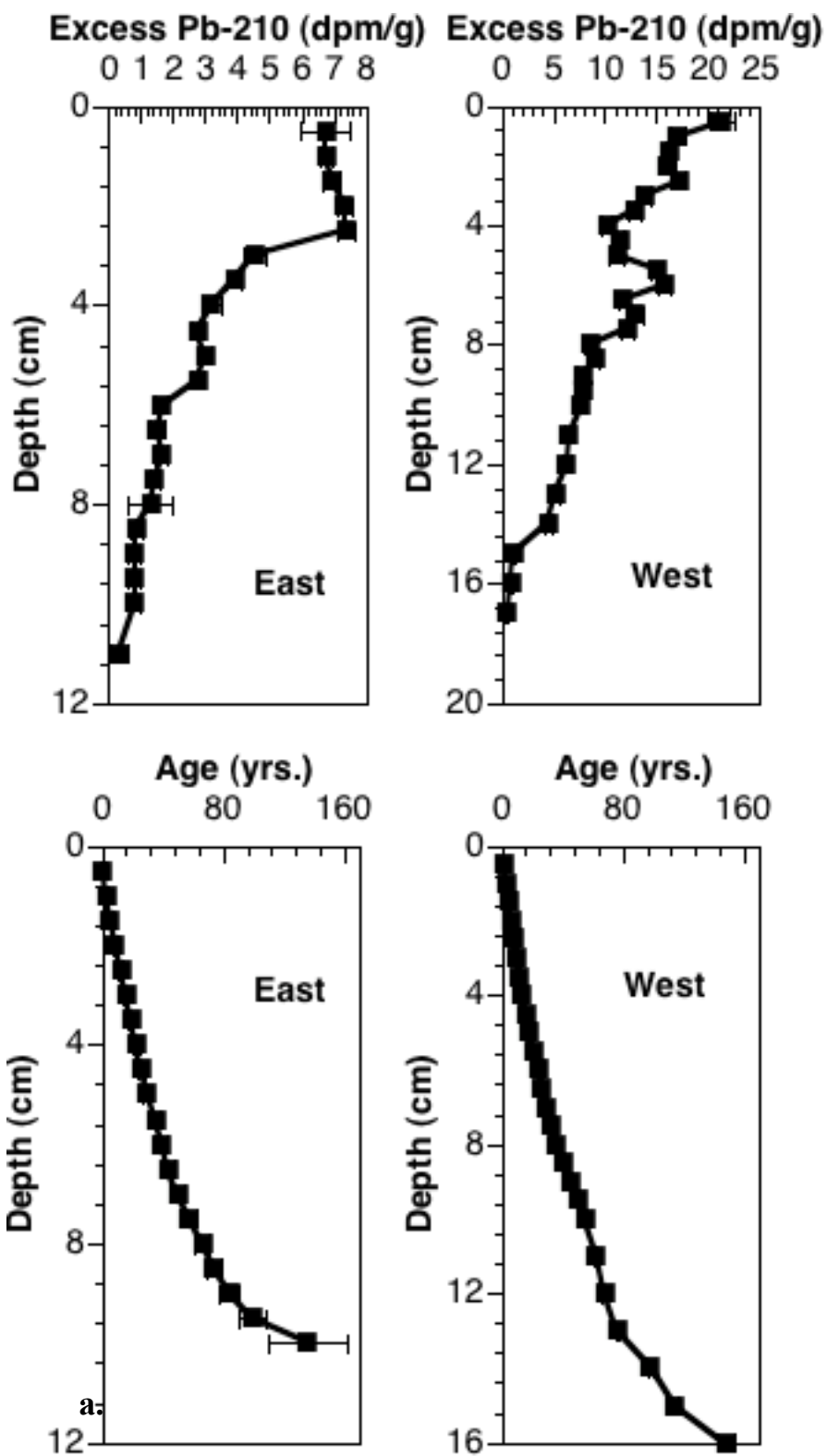


Figure 2.3. Excess ^{210}Pb activity and Age versus Depth in sediment cores from the east and west sides of Lake Mattamuskeet. Error bars show one standard deviation.

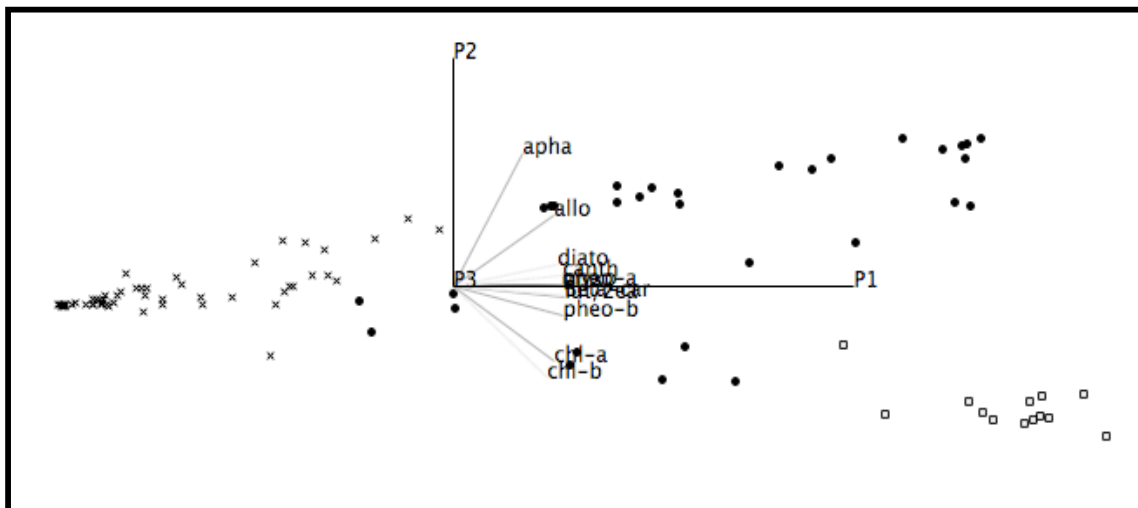


Figure 2.4. Scatterplot of principal components 1 (P1) and 2 (P2) showing correlations with sedimentary photosynthetic pigments. Percent of variance represented by P1 and P2 is 88% and 10%, respectively. Zones determined by k-means cluster analysis are low productivity sediments (x), algal-associated sediments (●) and plant-associated sediments (□).

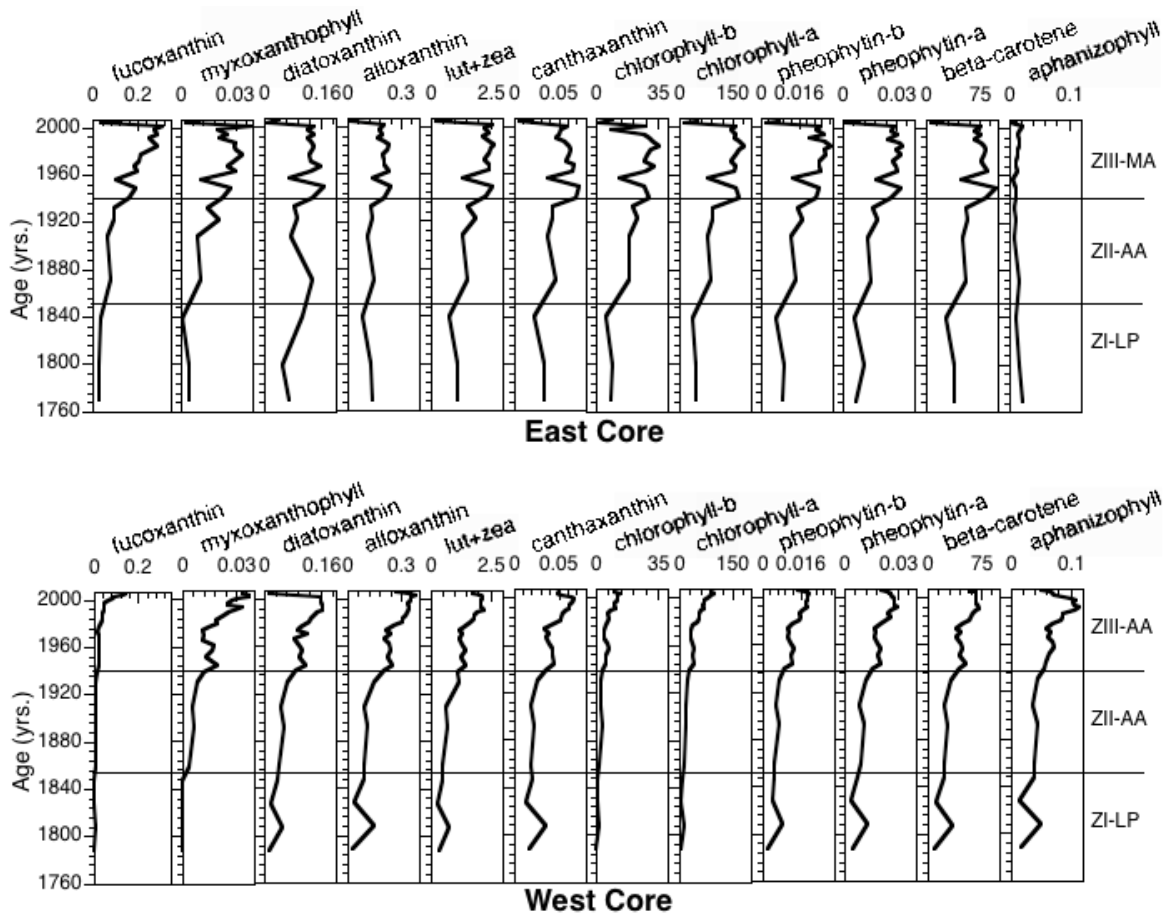


Figure 2.5. Sedimentary photosynthetic pigments measured on sediment cores collected from the east and west sides of Lake Mattamuskeet. Pigment concentrations are reported as $\mu\text{g pigment/g org.}$ Zones I (ZI), II (ZII) and III (ZIII) were determined using paleolimnological proxies, clusters and known human impacts. Sediment clusters determined by k-means cluster analysis using sedimentary photosynthetic pigments represent algal-associated (AA), macrophyte-associated (MA) and low productivity (LP) sediments. Lut+zea is the sum of lutein and zeaxanthin concentrations.

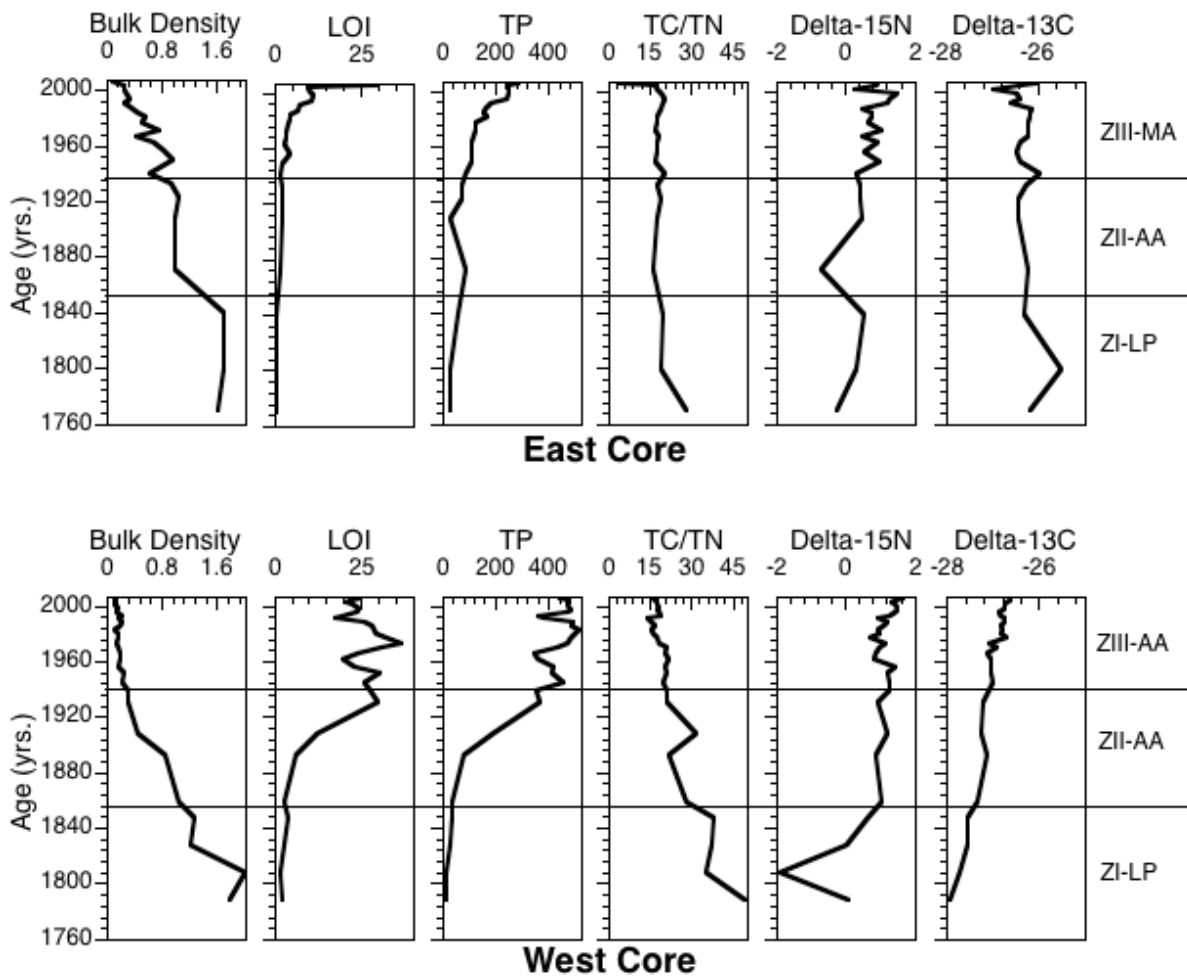


Figure 2.6. Paleolimnological proxies measured on sediment cores collected from the east and west sides of Lake Mattamuskeet. Units for the proxies are as follows: Bulk Density (g dry/cc wet), LOI (%), TP (ppm), TC/TN, $\delta^{15}\text{N}$ (‰) and $\delta^{13}\text{C}$ (‰). Zones I (ZI), II (ZII) and III (ZIII) were determined using paleolimnological proxies, clusters and known human impacts. Sediment clusters determined by k-means cluster analysis using sedimentary photosynthetic pigments represent algal-associated (AA), macrophyte-associated (MA) and low productivity (LP) sediments.

Table 2.2. Paleolimnological proxy means for Zone III sediments collected from the east and west sides of Lake Mattamuskeet. Standard deviations are in parentheses.

	<u>EAST</u>	<u>WEST</u>
Inferred Primary Producer State	Macrophytes	Phytoplankton
Total Phosphorus (ppm)	173.4 (64.11)	449.01 (49.89)
Total Sulfur (ppt)	2.50 (1.44)	6.17 (0.81)
Total Iron (ppt)	3.57 (1.81)	8.31 (1.22)
Fe/S	1.49 (0.18)	1.35 (0.08)
TOC/TN	17.8 (3.18)	11.35 (0.97)
$\delta^{15}\text{N}$ (‰)	2.04 (0.34)	1.07 (0.26)
$\delta^{13}\text{C}$ (‰)	-24.74 (0.18)	-27.59 (0.15)

CHAPTER 3. RELATING SHALLOW LAKE TROPHIC STATUS TO HUMAN AND CLIMATE IMPACTS THROUGH ANALYSIS OF LATE-HOLOCENE SEDIMENTS

ABSTRACT

Paleolimnological proxies were measured on a 4 m sediment core collected from Lake Mattamuskeet, North Carolina, USA to examine climatic and human impacts on the lake during the late Holocene to present. Lake Mattamuskeet is a large (162 km²) and shallow (mean depth=1 m) coastal lake, which has experienced dramatic human impacts since European settlement in 1850. Stratigraphic changes in organic matter content, nutrients, metals, lignin oxidation products and sedimentary photosynthetic pigments were used to divide the sediments into three intervals. Interval I includes sediments deposited between A.D. 7-1640 and indicates a clear-water, sand-bottom state with low algal abundance. In addition, the lake catchment area experienced two significant fires during this interval that were recorded as charcoal layers in the sediments around A.D. 307 and A.D. 1535 (¹⁴C AMS dates). Trophic structure changed with the onset of Interval II (A.D. 1640-1850) when total algal abundance increased, and the primary producer community was comprised primarily of diatoms, chrysophytes, cryptophytes and cyanobacteria. During this interval there was also an increase in terrestrial organic material input into the lake as well as a shift in plant type from woody gymnosperms to non-woody angiosperms as determined from lignin data. Recent sediments deposited in Lake Mattamuskeet (Interval III, A.D. 1850-present) suggest a dramatic increase in organic matter deposition, metals, primary producer

abundance and the onset of cyanobacterial dominance. The inferred characteristics from each interval coincide with known climatic events (Little Ice Age), human impacts and oral histories from the area.

INTRODUCTION

The coastal plain of eastern North Carolina, USA contains over 20 natural lakes and many more paleolake beds. Most of these depressions are Carolina Bays that range from less than one acre to over 40,000 acres (162 km²) in surface area (Firestone et al., 2006). Lake orientation is in a similar direction and each contains a sand rim on the eastern side. The systems that currently hold water have experienced extensive human impacts including land-use changes, hydrological alterations and biomanipulations (Benkert, 1990; Allen et al., 1979; and Casterlin et al., 1984). Unfortunately, lack of historic data precludes the understanding of predisturbance conditions during the Holocene, but late Pleistocene climatic impacts on these systems have been studied (Frey, 1953; Whitehead, 1981; Goman and Leigh, 2004; Firestone et al., 2007). Climatic events such as the Little Ice Age and the Medieval Warm Period coincide with the original European settlements of the United States and Native American settlements in this area (Stahle et al., 1998; Willard et al., 2003). Researchers investigating the origin of these systems have proposed aeolian transport (Thom, 1970), desilicification of sand (May and Warne, 1999) and extraterrestrial impacts (Prouty, 1952; Firestone et al., 2007) as possible mechanisms.

The largest lake located on the coastal plain of North Carolina is Lake Mattamuskeet (Figure 3.1 and Table 3.1). Lake Mattamuskeet has been proposed to originate from either a

peat fire or wind events (Benkert, 1990), but recently the idea of an extraterrestrial event around 12,900 BP has been considered as a mechanism in either starting the peat fires or creating a depression from falling debris (Firestone et al., 2007). European settlers first visited Lake Mattamuskeet from the Roanoke Colony in 1585 (Forrest, 2000), where they noted a substantial indigenous settlement and recorded the general shape of the lake in a painting by colonist John White (Forrest, 2000). Soon after this visit, the Roanoke Colony disappeared and the fate of the colonists has remained a mystery. Using tree ring chronologies collected in southern Virginia, Stahle et al. (1998) proposed that a series of droughts occurring at this time played a role in the disappearance of the Roanoke Colony. Although Lake Mattamuskeet is in close proximity to the site of the Roanoke Colony (50 km), its sediment record has not been incorporated into investigations focusing on the area's history.

Discernable human impacts on Lake Mattamuskeet began around 1850 when European settlers constructed the first canal from the lake to nearby Pamlico Sound. This connection decreased the water depth from 3 m to 1 m and the size of the lake from over 300 km² to the current 162 km². The remaining three canals were constructed in the early 1900's to drain the area around the lake for agricultural use. In 1915 a large pumping station was constructed in an effort to drain the entire lakebed for agriculture. The maximum exposure of the lakebed by the end of this project was the southern 49 km² (12,000 acres) of the lake. In 1932 the drainage project was abandoned and the lake was allowed to refill. The lake became part of the Mattamuskeet National Wildlife Refuge and is currently managed for recreational fish, wildlife and migratory waterfowl, which follow the Atlantic Flyway and

can number over 100,000 in the winter months (Sponberg and Lodge, 2006). Management practices affecting the lake have included biomanipulation, macrophyte transplants, water level maintenance, and the prevention of salinity rise through water control structures built in the canals. Finally, a roadway was constructed in 1942 and divided the lake into two basins. Following construction, the two basins of the lake developed distinct primary producer community structures with phytoplankton dominance on the west side and macrophyte dominance on the east (Piehler and Waters, *In preparation*). These two distinct ecosystem states remain today.

The coastal areas of North Carolina and Virginia are sensitive to changing climate due to changes in the prevailing atmospheric circulation and meridional flow (Willard et al., 2003). Studies using pollen, tree ring chronologies, diatoms and other proxies have confirmed that climatic changes have occurred in this area throughout the Pleistocene and Holocene. Frey (1953) and Whitehead (1981) used pollen analysis from North Carolina lake sediment cores to show shifts in the terrestrial vegetation community during the early and middle Holocene that resulted from wetter conditions developing around 5000 YBP. Gaiser et al. (2004) used diatom frustules and sponge spicules from a South Carolina Bay sediment core to infer that hydrological and limnological characteristics have remained constant for the past 3500 years. Tree-ring chronologies (Stahle and Cleaveland, 1994) and pollen analysis (Willard et al., 2003) confirmed fluctuating moisture regimes throughout the Holocene and linked some of the changes to historic megadroughts in the western parts of North America (Stahle et al., 2007). Given the documented wet/dry periods during the Holocene in this region, reconstructed responses of coastal lakes to these climate changes could aid in

forecasting potential alterations to freshwater ecosystems resulting from future climate change such as warming or sea level rise.

When investigating both climatic and limnological changes using lake sediments, a multi-proxy approach utilizing both aquatic and terrestrial proxies is paramount. Multiple proxy studies incorporate inferences from geological, chemical and biological components of the ecosystem and help discern limnological and terrestrial ecosystem change from post-depositional changes to the sediment record. Stable isotopes (Brenner et al., 1999), TC/TN ratios (Schelske et al., 2005), nutrients (Kenney et al., 2002) and metals (Davies et al., 2004) have been used successfully to track human impacts, primary productivity changes and other environmental changes in studies incorporating lacustrine sediments. The primary proxy used in this study for historic lake water quality is sedimentary photosynthetic pigments. By measuring temporal changes in the array of algal pigments in lake sediments, researchers can gain information of historic lake productivity, occurrence of cyanobacteria, and changes in algal community structure (Leavitt and Hodgson, 2001). Leavitt and Findlay (1994) showed that photosynthetic pigments in lake sediments can be used to quantify past algal communities by comparing sedimentary pigments with historic algal data from experimental Lake 227 in Ontario, Canada. Pigments are labile and degrade during increases in light, oxygen and temperature, but Leavitt (1993) stated that pigments are preserved at a constant rate provided that the lake conditions, such as temperature and depth, remain stable over time. Nevertheless, changes in pigment concentrations should be compared to their degradation products (pheophytins) as well as other sedimentary proxies to insure that they represent historic algal standing crops.

Lignin oxidation products have frequently been used to infer the sources of terrestrial organic material entering aquatic ecosystems. Hedges et al. (1986) used lignin analysis to show the origin of particulate material in the Amazon River to be primarily soil-derived and not from C-4 grasses that line the riverbanks. Gordon and Goni (2004) used lignin oxidation products measured on core sediments to show that carbon inputs into the Mississippi River derived from grass species rather than higher terrestrial plants. Likewise, the ratios of certain lignin phenols such as cinnamyl and syringyl phenols to vanillyl phenols can be used to infer angiosperm/gymnosperm and woody/nonwoody inputs into aquatic ecosystems (Goni et al. 2003). For example, Bianchi et al. (1997) reported that carbon compounds deposited in Baltic Sea sediments were associated with freshwater inflow and consisted of primarily woody-gymnosperms. Finally, the ratio of acid to aldehyde lignin phenols can be used as a proxy for changes resulting from bacterial degradation or inputs from terrestrial soils (Onstad et al., 2000). Lignin oxidation products have been used extensively as a proxy for terrestrial inputs into aquatic ecosystems and should provide valued information concerning terrestrial changes around Lake Mattamuskeet.

Reported here are results from a multiproxy study on a 4 m sediment core collected from Lake Mattamuskeet. A multiproxy approach was taken by measuring organic matter, nutrients, metals, stable isotopes, photosynthetic pigments and lignin oxidation products to investigate historic water quality conditions as well as climatic change impacts on the lake's catchment throughout the late Holocene. Results indicate significant changes in the lake

ecosystem in response to both climatic and human impacts and are supported by other paleostudies in the area.

METHODS

Water depth and soft sediment surveys were conducted for Lake Mattamuskeet to identify optimal coring sites (Chapter II). Shallow lakes contain variable sedimentation patterns due to wind resuspension and lack deep areas that promote deposition (Whitmore et al., 1996). Given the draining of the southern portion of the lake in 1915 and the labile nature of sedimentary pigments, coring areas were limited to the northern part of the lake to ensure that sediments had not been dry during the drainage period. A 4 m sediment core was collected from the deepest area of the lake using a vibracoring device (Figure 3.1 and 3.2). The core was opened, photographed and sectioned within 2 weeks of collection. All core sections were frozen, freeze-dried and ground with a mortar and pestle prior to analysis. Organic matter (OM), metals (Fe, Mn, Zn, Cd, Cr, Mo, Al, and Cu), elements (P, N, S and C), total organic carbon (TOC), stable isotopes ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$) and photosynthetic pigments were measured on all sediment samples. Given their labile nature, photosynthetic pigments were measured within the first week following freeze-drying. Samples for lignin oxidation product analysis were chosen to represent the periods of change in the lacustrine sediments.

Organic matter (OM) content was assessed by loss on ignition (LOI) at 550 °C and expressed as a percentage (Håkanson and Jansson, 1983). Total phosphorus (TP), total sulfur (TS) and all metals were measured on dried sediments using an ARL 3560AES ICP analyzer following acid digestion using standard EPA methods. TOC and TN were measured using a

Carlo Erba C/N/S analyzer with an attached autosampler. Prior to analysis, TOC and TN samples were acidified for 12 hours in HCl vapors to remove inorganic carbon. $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ were measured by a Finnigan Mat 252 isotope ratio mass spectrometer coupled to a Carlo Erba C/N/S analyzer. Carbon and nitrogen isotopic ratios were determined relative to an internal standard and calibrated to the reference standards of Pee Dee Belemnite and air, respectively. Isotopic ratios were calculated as standard delta notation following the equation:

$$\delta \text{ Isotope} = \frac{(\text{Sample}^{\text{heavy}}/\text{Sample}^{\text{light}}) - (\text{Standard}^{\text{heavy}}/\text{Standard}^{\text{light}})}{(\text{Standard}^{\text{heavy}}/\text{Standard}^{\text{light}})} \times 1000$$

and expressed as per mil (‰).

Lignin oxidation products were measured on dried, bulk sediment samples following the cupric oxide method described in Hedges and Ertel (1982), Goñi and Hedges (1992) and Duan et al. (2007). Sediment samples containing 3 to 5 mg of organic carbon were transferred to stainless steel reaction vessels. Samples were digested with CuO in 2 N NaOH in the absence of O_2 at 150 °C for 3 h. Diethyl ether was used to extract reaction products, which were then dried and derivatized using bis-(trimethylsilyl)-trifluoroacetamide (BSTFA). Lignin oxidation products were measured using a Varian model CP 3800/2000 gas chromatograph/mass spectrometric detector (GC-MS). Lignin identification and quantification were determined against a mixed standard and internal standards of ethyl vanillin as an internal recovery standard and methyl 3,4 dimethoxy benzoate as an absolute recovery standard. Eight lignin oxidation products (vanillin, acetovanillone, syringaldehyde, vanillic acid, acetosyringone, syringic acid, p-coumaric acid and ferulic acid) were quantified and used as molecular indicators for source and diagenetic state of vascular plant tissue.

Lambda 6 is defined as the sum of vanillyl (vanillin, acetovanillone, vanillic acid) and syringyl (syringaldehyde, acetosyringone, syringic acid) phenols, while Lambda-8 also includes the cinnamyl (p-coumaric and ferulic acid) phenols. The ratios of total amount of cinnamyl (C) and syringyl (S) phenols to vanillyl (V) phenols are represented as C/V and S/V, and ratios of vanillic acid to vanillin and syringic acid to syringaldehyde were abbreviated as Ad/Al_v and Ad/Al_s, respectively.

Photosynthetic pigments (chlorophylls and carotenoids) were measured using an HPLC system following the methods of Leavitt and Hodgson (2001) designed particularly for sedimentary pigments. Dried sediment samples were extracted with a solvent mixture of acetone, methanol and water mixed in an 80/15/5 ratio, which contained an internal standard (Sudan II; Sigma Chemical Corp., St. Louis, MO) and allowed to digest 16-24 hours in a -20 °C freezer. Following extraction, samples were centrifuged and filtered through a 0.22 µm syringe filter to remove any particulate matter from the sample. Samples were placed in an autosampler tray where they were mixed with an ion-pairing agent (0.75 g tetrabutyl ammonium acetate and 7.7 g ammonium acetate in 100 ml HPLC-grade water) prior to injection. 200 µL of each sample was injected into a Shimadzu HPLC system following the mobile phase and time sequence of Leavitt and Hodgson (2001). Chlorophylls and carotenoids were separated by passing through a Rainin Model 200 Microsorb C18 column and measured using a photodiode array detector set at 435 nm and 665 nm. Pigment identification was made using retention times of known standards and pigment specific spectra recorded by the detector. Pigment concentrations are expressed as µg pigment/g OM and calculated by comparing peak areas against standards of known concentration.

Core section dates were determined for sediments spanning European settlement (1850-present) by measuring ^{210}Pb using the constant rate of supply (CRS) model following the methods of Schelske et al. (1994) and Appleby and Oldfield (1983). ^{210}Pb was measured on dried, ground sediment samples using a low-background germanium well detector and was used to provide core section dates for the past 150 years. In addition, the two charcoal layers (80 cm and 120 cm) were radiocarbon dated by the ^{14}C accelerated mass spectrometry (AMS) facility at Woods Hole Oceanographic Institute (sample #57953 and 57954). The organic combustion method was used following acid pretreatment of each sample.

RESULTS

Lithology and Chronology

Sediment types for the 400 cm core are shown in Figure 3.2. The top 20 cm of the core contained organic-rich sediments followed by organic-rich sands down to 60 cm. From 60 cm to 150 cm the core contained primarily sand with two highly organic-rich charcoal layers at 80 cm and 120 cm. Below 150 cm the core contained shell fragments as well as whole bivalve species characteristic of marine sediments. The most abundant shell fragments at 324, 380 and 400 cm were identified as *Mulina lateralis*, a bivalve that lives in estuarine and shallow marine environments. Due to the dramatic change in appearance and the location of shell fragments, the upper 150 cm of the core were classified as lacustrine sediments and will be the focus of the results reported here.

Excess ^{210}Pb decreased downcore and reached 0 dpm/g at 20-22 cm (Figure 3.3). Excess water and possibly flocculent sediments were removed from the top of the core upon collection, which could have violated assumptions made when using the CRS model. Nevertheless, excess ^{210}Pb values in the top samples of the vibracore correspond to sediments in the top 5 cm of a piston core collected near the core site (Chapter II) indicating that the vibracore retrieved the majority of the upper sediment column. Excess ^{210}Pb in the upper 22 cm suggests that these sediments were deposited within the past 150 years corresponding to the period of European settlement and land-use change (Forrest, 2000). AMS radiocarbon dates for the two charcoal layers at 80 and 120 cm were 470 ± 25 YBP (A.D. 1535) and 1700 ± 25 YBP (A.D. 307), respectively.

Organic Proxy Measurements

Organic proxy measurements are reported in Figure 3.4. LOI and TOC followed similar patterns throughout the core with low concentrations below the top 22 cm. LOI and TOC percentages were below 0.4% and 0.2%, respectively, from 150 cm up to 50 cm. From 50 cm to 22 cm LOI percentages increased to around 5%, and TOC percentages increased to 4%. In the top 22 cm, LOI and TOC increased to maximum values of 24% and 14%, respectively. TN demonstrated a similar trend with percentages staying below 0.05% from 150 cm up to 44 cm. A general increase occurred in the top 44 cm reaching a maximum of 0.15% in the top of the core. TC/TN values were variable throughout the core with peaks of 27, 17, and 32 at 120 cm, 80 cm and 12 cm, respectively. A general increase occurred up core from 60 cm to 12 cm with TC/TN values increasing from 10 to 32. $\delta^{13}\text{C}$ values were similar in the upper 74 cm of the core with values averaging -27 ‰ (SD = 0.3). Below 74 cm

$\delta^{13}\text{C}$ values were variable ranging from -28 to -23 ‰. $\delta^{15}\text{N}$ values were similar in the upper 90 cm with maximum values reaching 2 ‰ at 10 cm. Below 90 cm $\delta^{15}\text{N}$ values were variable ranging from 0.7 to -5 ‰ and are somewhat suspect due to the low concentrations of TN in the sediments. Lamda 8 and 6 followed similar patterns with low concentrations from 0 to 20 cm and 50 to 150 cm and high lignin deposition from 20 to 50 cm.

Sedimentary photosynthetic pigments

Sedimentary pigments were divided into three zones based on total pigment deposition, differences in primary productivity community structure and known historic events such as European settlement. Interval dates were based on an extrapolation using the bottom of the ^{210}Pb profile and the two ^{14}C AMS dates obtained for the two charcoal layers. Interval I represents sediments deposited from around 7 A.D. until the mid 1600's (150-60 cm). Pigment deposition was below detectable limits with the exception of the two charcoal layers and surrounding samples (Figure 3.5). These layers contained a higher amount of organic material as seen in the LOI and TOC profiles (Figure 3.4). Replicates were run on several sediment samples in this zone using a large amount of material, which failed to yield detectable levels.

Interval II represents sediments deposited from approximately 1650 to 1850 (60-22 cm). Sedimentary pigment deposition greatly increased during this period for all pigments measured except for aphanizophyll, myxoxanthophyll and chlorophyll *b* (Figure 3.5). Dominant pigments deposited during this time were beta-carotene, fucoxanthin, alloxanthin,

and pheophytin *a*. Beta-carotene is a proxy for total algal abundance while fucoxanthin and alloxanthin represent siliceous algae and cryptophytes, respectively.

Interval III represents sediments deposited from 1850 until the present (top 22 cm) and coincides with the period of European settlement around Lake Mattamuskeet. Sediments containing the highest concentration of most pigments were deposited during this period (Figure 3.5). A similar increase in pigment concentrations was measured in short cores taken from Lake Mattamuskeet (Chapter II). Most pigments doubled in concentration during this time when compared to Interval II. Fucoxanthin and alloxanthin showed decreases during this period while myxoxanthophyll, aphanizophyll and chlorophyll *b* experienced increases in concentration.

Nutrients and Metals

All nutrients and metals measured demonstrated a very similar pattern. Low concentrations were deposited below 22 cm in the core aside from small peaks at 120 cm (Figure 3.6). P, Zn, Cr, and Al showed slight increases from low levels beginning around 56 cm up to the dramatic increase at 22 cm. The high concentrations deposited in the upper 22 cm of the core coincide with Interval III.

Lignin Oxidation Products

Lignin concentration means and standard deviations are shown in Table 3.2. Acid to aldehyde ratios for syringic (Ad/Al_s) and vanillic (Ad/Al_v) lignin oxidation products are low in the top 60 cm of the core. Below 60 cm, Ad/Al_v concentrations are higher at 96 cm and

140 cm while the two charcoal layers and the 116 cm sample contained low Ad/Al_v ratios. Ad/Al_s ratios were similar throughout the core with the exception of the sample at 96 cm, which contained values greater than two times any other sample in the core. Using known relationships between the ratios of C/V and S/V (Figure 3.7), lignin deposited in Interval III and I are derived from woody gymnosperms while Interval II sediments contain C/V and S/V ratios suggesting a greater proportion of non-woody angiosperm material in the organic sediments.

DISCUSSION

Paleolimnological proxies measured on vibracore sediments collected from Lake Mattamuskeet characterized three intervals of differing deposition in the lake. The goal of this research was not to attach proxy changes to specific dates, but rather to investigate change over broad intervals (i.e. European settlement, Little Ice Age, Late Holocene). As a result, the interval dates should be seen as estimates for the periods represented, but the small error obtained from the ^{14}C dates and the excess ^{210}Pb profile appear to match well with the periods discussed in the text. Interval I corresponds to roughly A.D. 7 to 1640. This era for Lake Mattamuskeet was a period of low algal abundance and low organic matter deposition. Interval II represents the period from A.D. 1640 to 1850 and corresponds to the Little Ice Age. Total algal abundance, organic matter deposition, and lignin deposition all increased during this period suggesting changes in lake development and catchment vegetation. Interval III spans 1850 until the present and is believed to represent the period of European settlement. All proxies were highest during this period aside from lignin oxidation products. Specifically, metals and nutrients showed dramatic increases in concentrations believed to

result from canal construction and land clearance for agriculture. In addition, the primary producer community indicated a shift to poorer water quality as suggested by increases in cyanobacterial pigments.

Interval I (A.D. 7-1640)

Interval I documents a period of low algal abundance, low organic matter input and high water clarity based on low concentrations of all organic proxies. Total algal abundance was relatively low during this time, however benthic algal communities could have been present. Due to the shallow water depth and the lack of organic deposition during this period, pigment preservation would be compromised due to the presence of light, oxygen and high temperatures at the sediment surface. Lake Phelps, a lake 20 km from Lake Mattamuskeet, currently has clear water and light penetration to the lakebed. During summer months, a significant community of benthic algae cover the bottom of the lake but fail to be preserved in the sediment record (Waters and Piehler, *unpublished*). Lake Mattamuskeet may have had similar conditions during this period. Lignin oxidation products were present in low concentrations during this interval indicating that poor preservation alone cannot account for the lack of organic material in the sediments. Lignin is a form of structural material in terrestrial plants and macrophytes and is recalcitrant when compared to photosynthetic pigments. The low concentrations of total lignin summaries (Lamda 6 and 8) indicate that low amounts of organic material were deposited into Lake Mattamuskeet at this time thus supporting the inference that the lake was a clear, sand-bottom system. One deviation from this trend was the high aldehyde to acid ratios (Ad/Al_v and Ad/Al_s) at 96 cm. These ratios are indicative of predeposition degradation of lignin by microbes as would be

found in soils instead of particulate terrestrial vegetation (Hedges et al., 1986). This increase suggests an influx of terrestrial soils into the lake at this time. The cause of this input is unknown, but possible sources include transport of material by a hurricane, wind or Native American activity.

The two charcoal layers at 80 cm and 120 cm are believed to represent two periods of drought and forest fires in the area. The deep peat deposits around Lake Mattamuskeet are known to burn following lightning strikes during dry periods (Ingram, 1987). The AMS ^{14}C dates for the 80 and 120 cm layers correspond with known drought periods in the region derived from tree rings (Stahle et al., 1988) and pollen (Willard et al., 2003). The bottom charcoal layer at 120 cm precedes the climate reconstruction from tree rings but does correspond to the period P1/D1 developed from Chesapeake Bay pollen records (Willard et al., 2003). This period was inferred as the onset of dry conditions in the mid-Atlantic and southeastern USA. These conditions would promote the accumulation of dry vegetation and peat, which would support the occurrence of a fire during this period. The top charcoal layer at 80 cm corresponds to the P4 interval from the Chesapeake Bay pollen record (Willard et al., 2003) and a drought period from the tree-ring analysis (Stahle et al., 1988). Both Willard et al. (2003) and Stahle et al. (1988) inferred that this period experienced several decadal-scale dry intervals, which affected both the Roanoke (1587-89) and Jamestown (1606-1612) colonies. The lack of charcoal layers in other areas of the core is surprising given the continuation of dry conditions throughout various periods of the Holocene in this region of the United States (Stahle et al., 1988).

Interval II (A.D. 1640-1850)

Interval II was a period where organic matter inputs increased into the lake suggesting greater exchange between the lake and its catchment. In light of previous paleolimnological studies and known historic events, climate change and Native American activity are possible causes for the increase in organic material. Changes in climate are well documented in this region (Vega et al., 1998; Vega et al., 1999) and could promote vegetation changes in and around the lake altering the delivery and concentration of organic material. Willard et al. (2003) measured pollen deposition in Chesapeake Bay sediments and showed that the vegetative community in the surrounding land fluctuated several times during this interval in response to changing precipitation. In addition, members of the Roanoke Colony visited Mattamuskeet in 1585 prior to their disappearance (Forrest, 2000). This documentation noted a substantial Native American community living around the lake at the time. Given that agricultural lands in this region have been ditched throughout recorded history, the Native American tribes could have been using this method to direct water either to or from Lake Mattamuskeet. As a result, hydrological connections between the lake and the surrounding areas could have increased particulate inputs into the lake.

Increased lignin deposition further suggests increasing terrestrial inputs into the lake or increasing development of macrophyte vegetation on the shoreline of the lake. Currently, Lake Mattamuskeet is a closed basin in which the water depth is determined primarily through precipitation (Benkert, 1990). Historic accounts fail to mention riverine or stream inputs into the lake, but the extensive wetland system in the surrounding areas could provide overland flow during wet periods. One mechanism that would increase interactions between

Lake Mattamuskeet and the surrounding wetland systems would be an increase in precipitation. Based on the AMS ^{14}C dates, Interval II sediments were deposited during the climate period known as The Little Ice Age, which was believed to be cool and moist in this area based on pollen and tree ring studies (Willard et al., 2003; Stahle and Cleaveland, 1994). This precipitation regime would have lead to changes in terrestrial and emergent species in and around the lake, potentially resulting in changes in nutrient inputs and organic matter deposition as seen in the upper portions of Interval II. Furthermore, as seen in the S/V to C/V ratio comparison the sources of lignin entering the lake changed during this time from woody-gymnosperms characteristic of pine and cypress species to nonwoody-angiosperms, which include emergent macrophytes and marsh grasses.

Primary producers appeared to increase during Interval II as indicated by sedimentary photosynthetic pigment profiles. All pigments measured except for chlorophyll *b* and aphanizophyll experienced dramatic increases in concentration. Beta-carotene and chlorophyll *a* concentrations, proxies for total algal abundance, suggest a change in the trophic state of the lake. These profiles indicate that total algal abundance increased from low levels in response to climatic and environmental changes. Given the lack of organic matter in the sediments during this interval and the shallow water depth of Lake Mattamuskeet, preservation was probably low implying that these concentrations could have been higher than inferred from the sediment record (Leavitt et al., 1993). Low preservation is further supported by the low chlorophyll *a*/pheophytin *a* index showing that pheophytin *a*, which is a degradation product of chlorophyll *a*, maintained higher concentrations in relationship to chlorophyll *a* throughout the majority of the interval. In addition, the lack of

deposition of chlorophyll *b* and the presence of pheophytin *b* further support increased degradation of pigments during this interval. The low LOI concentrations in the sediments would preclude preservation by limiting anoxic conditions caused by microbial respiration (Leavitt and Hodgson, 2001).

The primary producer community structure in Lake Mattamuskeet during Interval II was diverse with most algal groups represented in the sedimentary pigment record. These algal groups included species that could be both benthic and pelagic and suggest that Lake Mattamuskeet was algal dominated during this period. Pigment data indicate that cyanobacteria and chlorophytes were decreasing in abundance at the end of the interval and were replaced by other algal groups. Cryptophytes increased in abundance suggesting a possible shift from a benthic to a pelagic community since cryptophytes have flagella that permit them to remain in the water column (Reynolds, 2006). Increasing organic material in the lake would have included nutrients that promote algal growth as well as particulate material that attenuates light. As a result, the change in the algal community appears to be a response to increase organic matter inputs into the lake. The relationship between lignin inputs and the algal community structure in the lake is not known, but the occurrence of both changes during the Little Ice Age illustrates the sensitivity of terrestrial and aquatic ecosystems of eastern North Carolina to changes in climate.

Interval III (A.D. 1850-present)

Lake Mattamuskeet was visited by European settlers in the 1500's and 1600's, but substantial settlement of the lake's catchment area did not begin until 1850 with the

construction of the first canal connecting the lake to the Pamlico Sound. This change in hydrology decreased the lake level from 3 m to 1 m exposing the rim of the lake for agricultural use as well as promoting intrusion of saltwater into the lake (Forrest, 2000). The exposed areas of the lakebed were canalled and cleared for agricultural use, which would have caused the tremendous increases in most organic parameters measured during this interval. The peak in λ_{860} values at 20 cm is believed to result from the original influx of terrestrial material flowing into the lake from the canal construction. This influx of allochthonous carbon is also recorded in the increase in TC/TN at the same depth interval. Terrestrial material contains a substantial amount of structural carbon that is absent in aquatic primary producers and would produce higher TC/TN ratios. Likewise, canal construction would increase delivery of nutrients and metals leached from the newly exposed soils. Sedimentary metal concentrations have been used to accurately track periods of human impacts in aquatic environments (Cooper et al., 2004; Davies et al., 2004) and to separate urban and landscape erosion (Wyn et al., 2007). Although research has been conducted in Lake Mattamuskeet on the effects of high metal concentrations on wildlife (Benkert, 1990), the origin of the metals was not identified. Finally, land clearance around the lake likely promoted runoff and erosion from newly exposed soils as has been shown in multiple paleolimnological studies (Smol, 2002).

High concentrations for most photosynthetic pigments suggest that the hypereutrophic state in the lake today has resulted from human impacts. Most pigments have remained high in concentration up to the present. In addition, chlorophyll *b* and aphanizophyll were only deposited during this period. Chlorophyll *b* deposition could

suggest an increase in pigment preservation but could also represent an increasing deposition of aquatic macrophyte material. The eastern side of the lake is currently macrophyte dominated (Chapter II), and pigment analysis of fresh macrophyte material contains a pigment signature comprised of chlorophyll *a*, chlorophyll *b* and lutein (Chapter II). The increasing concentrations of chlorophyll *b* could be a result of increasing chlorophyll *b* production from macrophytes as well as preservation of recalcitrant particulate detritus over labile algal detritus. A lack of dramatic change in pheophytin *a* concentration supports the addition of macrophyte material over preservation changes to explain the chlorophyll *b* occurrence.

Paleopigment profiles indicate that the primary producer community shifted from the diverse community present in Interval II to a cyanobacterial-dominated community in Interval III. Likewise, pigments from other algal groups such as fucoxanthin (siliceous algae) show slight decreases during this period when compared to Interval II. These changes suggest that the influx of organic material from canal construction and land clearance promoted an environment that favored cyanobacteria. Increased terrestrial inputs would contain both nutrients and particulate material, which would select for fast growing cyanobacteria capable of reproduction in a low light, high nutrient environment. The high concentrations of aphanizophyll suggest that the phytoplankton community experienced periods of nitrogen limitation during this interval. Patience et al. (2006) used aphanizophyll concentrations in boreal lake sediments to track the occurrence of nitrogen limitation in lake waters. The influx of material from the surrounding catchment area increased TP flux to the sediments suggesting increased phosphorus in the water column, thus promoting nitrogen

limitation. Further promotion of N-limitation could have occurred from high rates of denitrification and internal phosphorus loading from resuspension events (Scheffer, 1998). Finally, Lake Mattamuskeet currently experiences periods of nitrogen limitation to phytoplankton growth, which has been confirmed with bioassays (Piehler and Waters, *In preparation*) and aphanizophyll presence in surface sediments (Chapter II).

Conclusions

The sediment record from Lake Mattamuskeet, North Carolina showed similar trends for most paleolimnological proxies measured. In general, the bottom most sediments believed to be lacustrine (Interval I) were deposited during a clear water, sand bottom phase of the lake from A.D. 7-1640. Most paleolimnological proxies were near the lower limits of detection, which is primarily shown in the lack of organic material deposited at this time. Interval II included sediments deposited from the beginning of the Little Ice Age (1640) until the beginning of intense European settlement around the lake (1850). Paleolimnological proxies measured on the organic fraction of the sediment show that this period marked the beginning of substantial productivity as well as a change in the lignin material entering the lake. Although both Native American activity and European colonists were documented around the lake, data suggest a response to climate change as being the driver for biological change in and around the lake. The uppermost sediments in the Lake Mattamuskeet vibracore represent the period of intense human impacts (Interval III, 1850-present). Canal construction, land clearance and nutrient inputs caused rapid increases in algal abundance as well as a shift to cyanobacterial dominance in the algal community.

The southeastern region of the United States has been identified as an area of significant climatic change during both the Medieval Warm Period and the Little Ice Age (Soon and Baliunas, 2003). Stahle et al. (1988) and Stahle and Cleaveland (1992) documented periods of wet and dry conditions from tree-ring chronologies taken from the coastal plain of North Carolina. Although the data presented here do not reflect periods of decadal and subdecadal time scales, Lake Mattamuskeet sediments did preserve forest fire occurrence and changes in vegetation over broader time intervals. The charcoal deposits occurring at 80 cm and 120 cm reflect periods of intense forest fires that correspond to periods where the lake catchment was very dry (Stahle and Cleaveland, 1992; Willard et al., 2003). Habersettl et al. (2006) showed that charcoal layers represented periods of dryness in cores collected from lakes in the Yucatan peninsula. Also, the high concentration of peat in the area would provide substantial fuel for a forest fire to burn for an extended period of time (Ingram, 1987). Regional oral history makes reference to the lake originating from a fire that burned for “thirteen moons” (Barefoot, 1995). Interval II (A.D. 1640-1850) marked a period of increased algal abundance as well as increased lignin deposition and change in lignin type. These changes in lignin suggest a colonization of terrestrial and wetland species around the lake. Likewise, lignin oxidation products changed from woody gymnosperms to non-woody angiosperms during this time. This variation most likely marks a vegetation change from trees to marsh grasses and emergent macrophytes in response to the cool and wet climate. The alterations in organic material deposition in the sediments show that the area was experiencing climatic change that altered both the terrestrial community and the aquatic community concomitant with the disappearance of the Roanoke Colony. Although direct

evidence is not presented here, this research does support the previous inference that climate change could have played a role in the colony's disappearance (Stahle et al., 1989).

Total algal abundance and primary producer community structure in Lake Mattamuskeet has also gone through significant change throughout the late Holocene. Sedimentary photosynthetic pigments recorded periods of extremely low algal abundance and preservation (Interval I), increasing algal abundance (Interval II), and hypereutrophication with dominance of cyanobacteria (Interval III). The clear water, low algal abundance phase has been shown in other North Carolina lakes in this region (Chapters IV and V). Lake Phelps, which is located just 20 km northwest of Lake Mattamuskeet is currently clear with a sand bottom and is believed to represent the trophic state experienced by all the lakes in the area at one time. Pungo Lake, a dystrophic lake located less than 20 km northwest of Lake Mattamuskeet, also contained low organic, sandy sediments in the bottom of sediment cores (Chapter IV). With the onset of the Little Ice Age and apparent change in both climate and terrestrial vegetation in the area, Lake Mattamuskeet's primary producer community included cryptophytes, diatoms, chrysophytes and cyanobacteria. This primary producer community structure persisted until the beginning of intense human impacts. Sedimentary pigments have been used in previous studies to infer climate change (Pienitz et al., 2000; Leavitt et al., 2003; and Hodgson et al., 2006), where the pigment record is compared to other more recalcitrant proxies in an effort to infer primary productivity changes in response to climatic changes. Here, paleolimnological proxy data suggest that the onset of the wet and cool conditions of the Little Ice Age altered the higher plant structure in the catchment area of Lake Mattamuskeet, thus increasing organic input into the lake and

increasing total algal abundance. The onset of European settlement changed the primary producer community structure to cyanobacterial dominance including nitrogen fixing cyanobacteria. Land clearance (Benkert, 1990) and canal construction (Schippers et al., 2006) would increase nutrient and organic matter inputs into the lake subsequently causing a change in the algal community.

Long-term, whole-ecosystem studies are needed for coastal areas that target human and climatic impacts, but coastal lakes generally have shallow water levels, large surface areas, and intense winds that suggest the sediment record would be compromised. This study on Lake Mattamuskeet sediments shows that decadal fluctuations in climate are not preserved in shallow lake sediments, but large changes resulting from climate and human impacts can be preserved. Coastal lakes in Brazil and Argentina have been studied using paleolimnological techniques on Holocene sediments to successfully document trophic state change (Inda et al., 2006), sea-level variations (Bracco et al., 2005), human impacts (Garcia-Rodriguez et al., 2002), and salt water intrusions (Garcia-Rodriguez et al., 2004). Likewise, Lake Mattamuskeet sediments recorded periods of forest fires, climatic induced changes in vegetation, and human induced changes to organic matter inputs and primary producer community structure. These findings support the need for paleolimnological research on shallow coastal lakes as records of climatic and human impacts.

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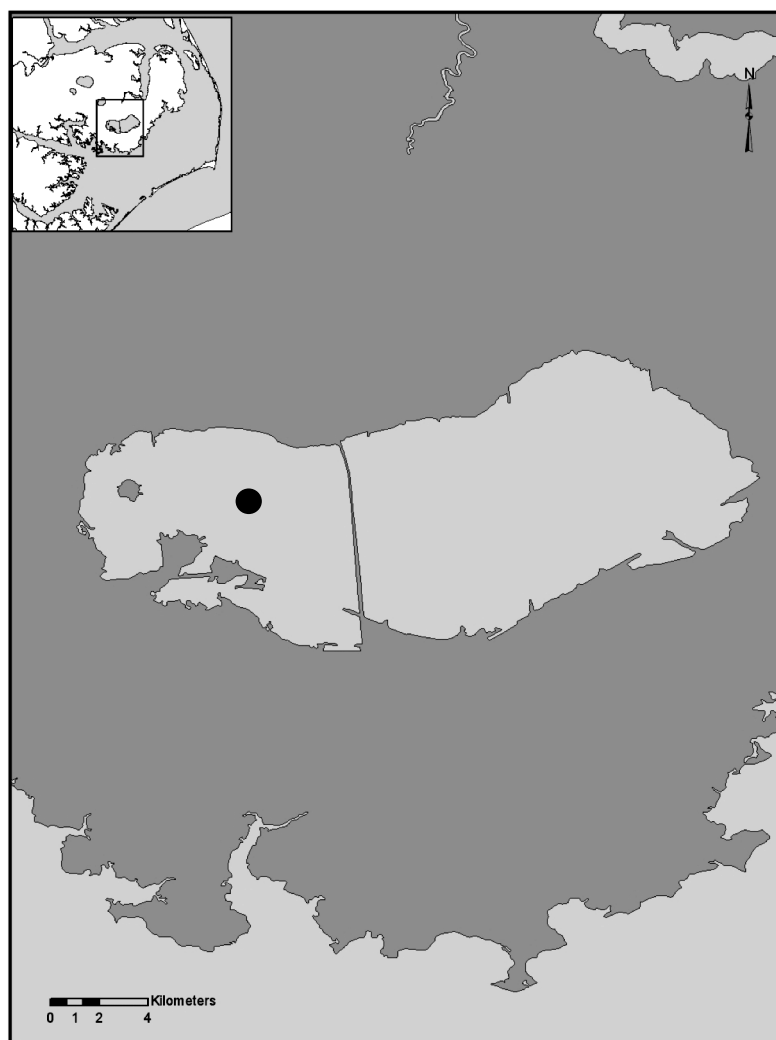


Figure 3.1. Map of Lake Mattamuskeet showing the vibracore site.

Table 3.1. Limnological characteristics for Lake Mattamuskeet. All depth measurements are in m, surface area is in km² and elevation is meters above sea level.

<u>Characteristic</u>	<u>Value</u>
Latitude	35° 29'N
Longitude	76° 12'W
Depth-average	1.01
Depth-maximum	1.75
Surface Area	162
Elevation	0.15

Lake Mattamuskeet Long Core

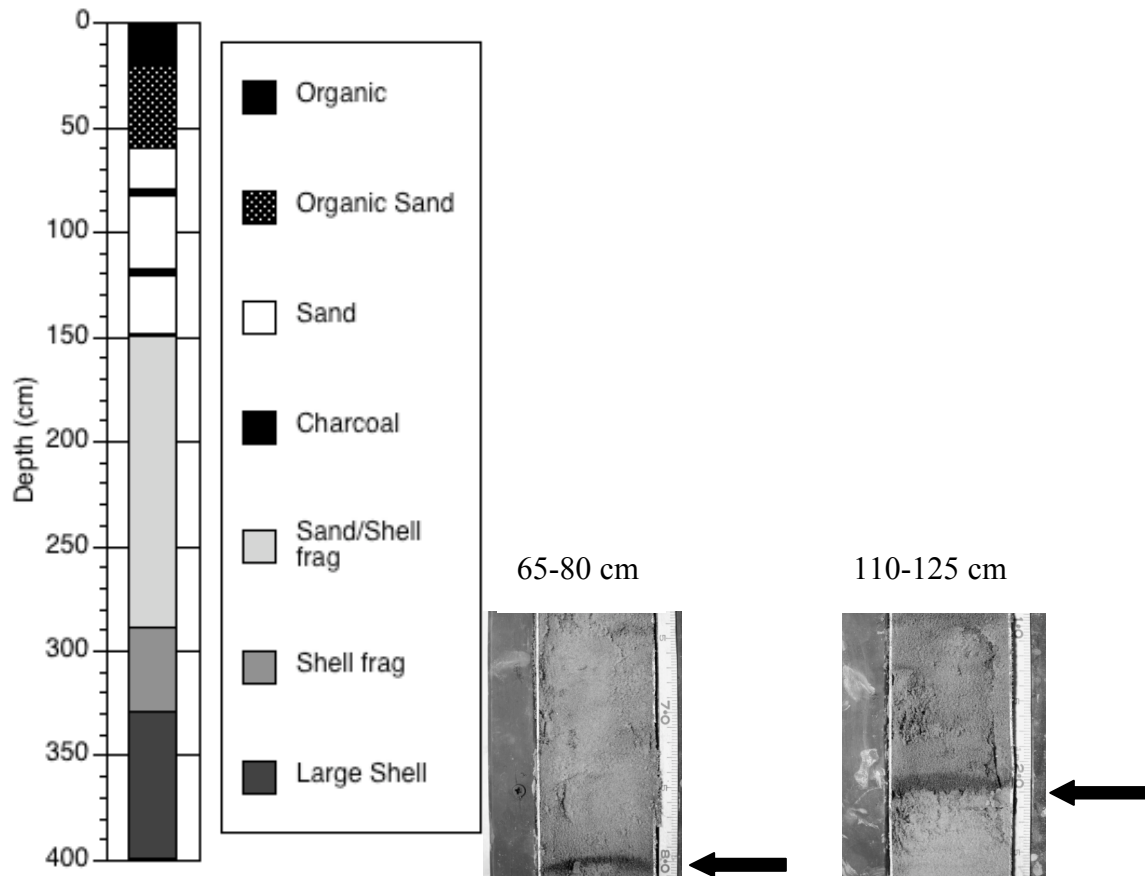


Figure 3.2. Lithological description of the Lake Mattamuskeet vibracore. Images are of core sections containing charcoal layers (arrows) located at 80 cm and 120 cm.

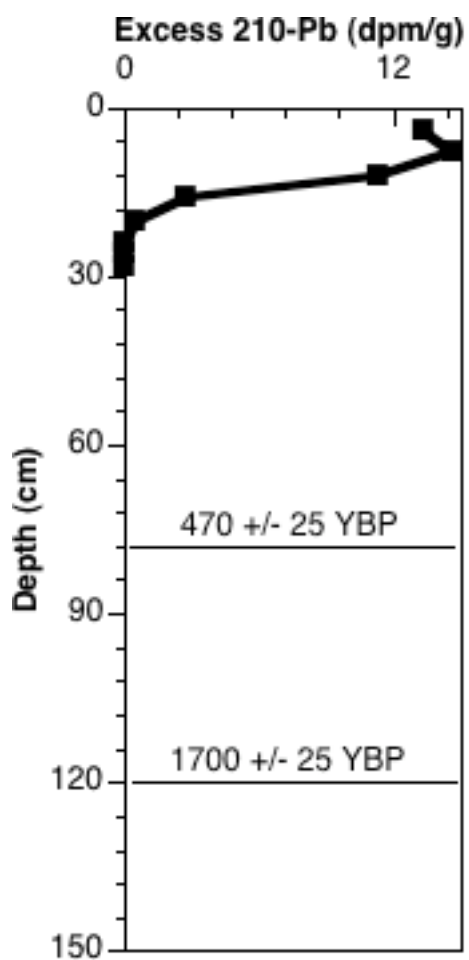


Figure 3.3. Excess ^{210}Pb activity verses depth in a vibracore collected from Lake Mattamuskeet. Solid lines show the depths AMS ^{14}C results from the charcoal layers.

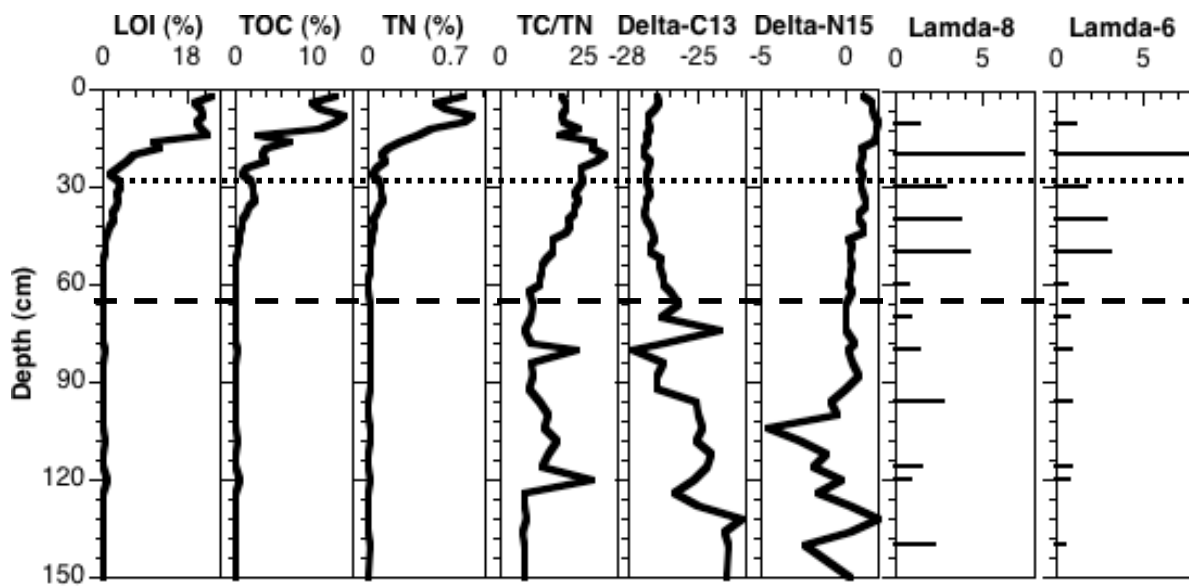


Figure 3.4. Paleolimnological proxies measured on the organic fraction of sediments from Lake Mattamuskeet vibracore. Units for Lamda 8 and 6 are mg/100 mg OC. Lines separate the intervals established from the pigment record.

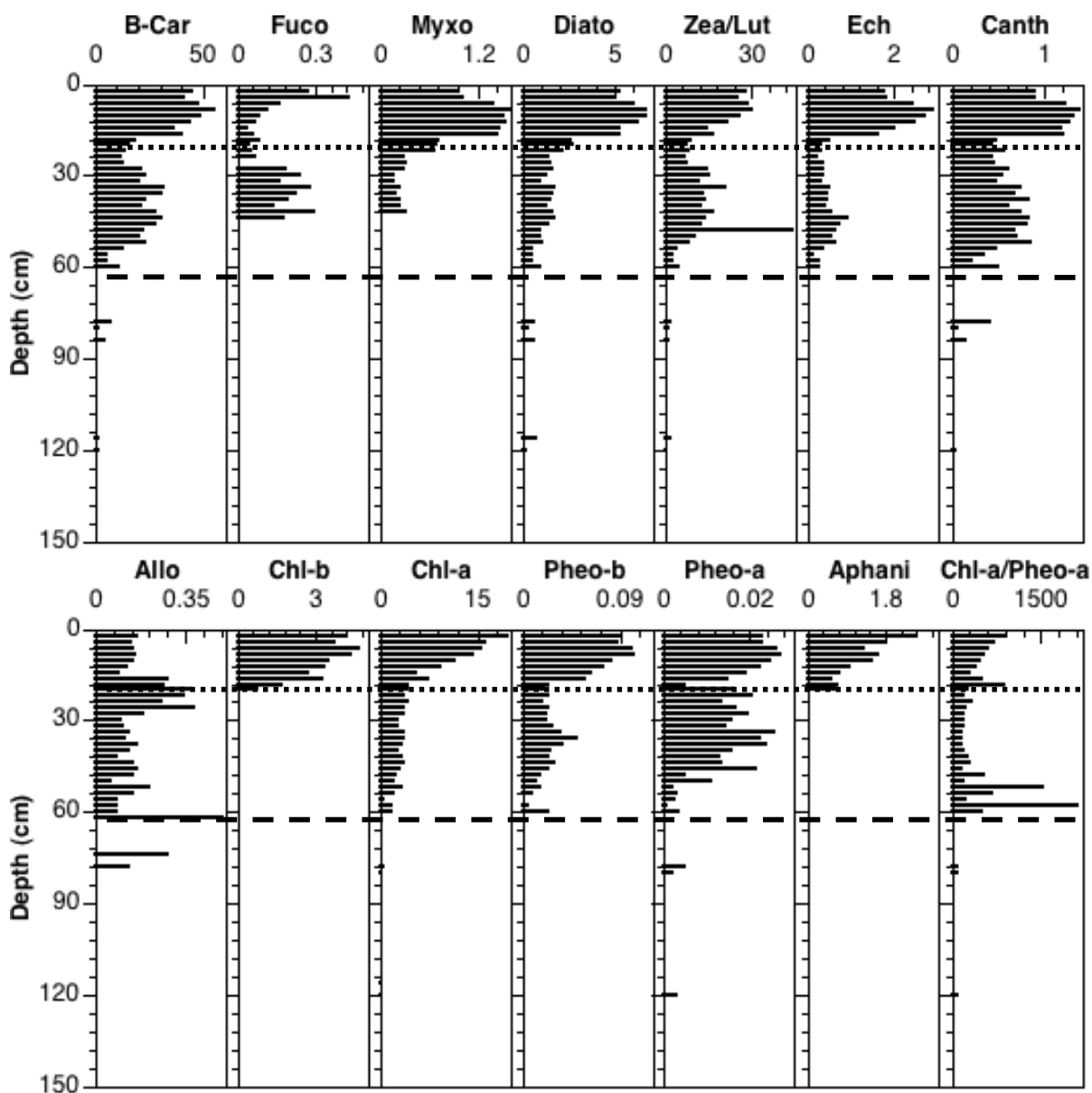


Figure 3.5. Sedimentary photosynthetic pigments measured on Lake Mattamuskeet vibracore. Units are μg pigment/ g. organic material. Pigments presented are beta-carotene (B-Car: total abundance), fucoxanthin (Fuco-siliceous algae), myxoxanthophyll (Myxo-colonial cyanobacteria), diatoxanthin (Diato-diatoms), Zeaxanthin-Lutein (Zea/Lut: cyanobacteria-chlorophytes), echinenone (Ech-cyanobacteria), Canthaxanthin (Canth-colonial cyanobacteria), alloxanthin (Allo-cryptophytes), chlorophyll-b (Chl-b, chlorophytes), chlorophyll-a (Chl-a, total abundance), pheophytin-b (Pheo-b, chlorophytes), pheophytin-a (Pheo-a, total abundance) and aphanizophyll (Aphani- nitrogen-fixing cyanobacteria). Lines separate the intervals established from the pigment record.

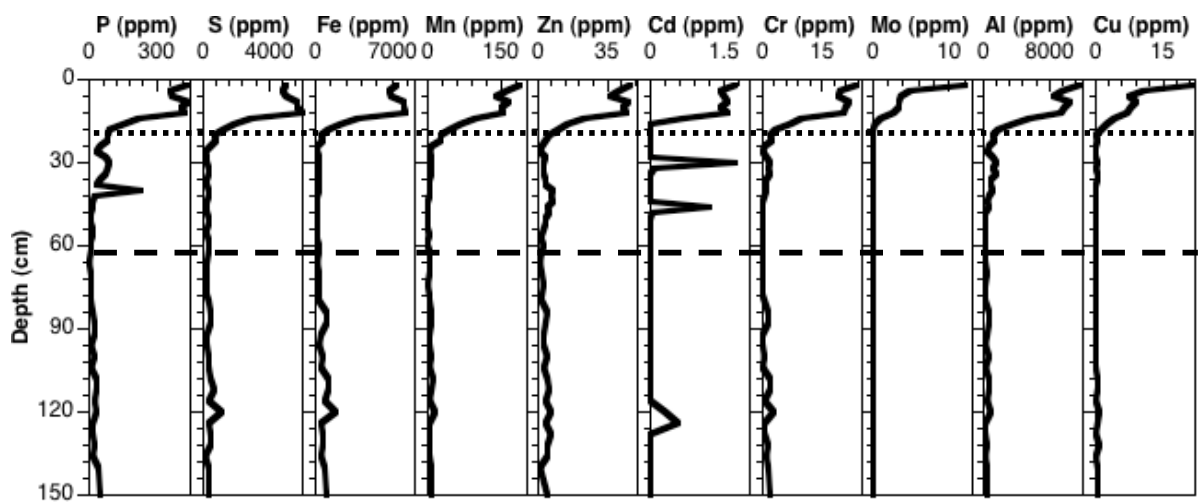


Figure 3.6. Nutrients and metals measured on bulk sediment from Lake Mattamuskeet vibracore. Lines separate the intervals established from the pigment record.

Table 3.2. Lignin oxidation product ratio and Lamda concentrations (mg/100 mg organic carbon) measured on Lake Mattamuskeet sediments following CuO oxidation. Standard deviations for replicate samples are shown in parenthesis.

<u>Depth (cm)</u>	<u>Lamda-8</u>	<u>Lamda-6</u>	<u>Ad/Al_v</u>	<u>Ad/Al_s</u>	<u>C/V</u>	<u>S/V</u>
10	1.5 (0.15)	1.3 (0.19)	0.51 (0.29)	0.62 (0.44)	0.20 (0.08)	0.27 (0.04)
20	7.4	6.8	0.34	0.28	0.14	0.28
30	2.9	2.3	0.54	0.43	0.46	0.58
40	3.8 (0.24)	3.1 (0.35)	0.36 (0.17)	0.36 (0.21)	0.34 (0.10)	0.55 (0.03)
50	4.3 (0.79)	3.7 (0.84)	0.33 (0.12)	0.23 (0.13)	0.25 (0.08)	0.56 (0.02)
60	0.77	0.63	0.35	0.39	0.38	0.68
70	0.92 (0.03)	0.83 (0.07)	0.64 (0.51)	0.29 (0.19)	0.16 (0.08)	0.46 (0.08)
80	1.4 (0.61)	1.3 (0.58)	1.3 (0.50)	0.83 (0.09)	0.08 (0.01)	0.30 (0.06)
96	2.9	2.0	4.4	2.4	0.33	0.29
116	1.5 (0.8)	1.5 (0.76)	1.4 (0.82)	0.63 (0.11)	0.03 (0.01)	0.24 (0.08)
120	0.93 (0.10)	0.91 (0.09)	0.72 (0.32)	0.41 (0.19)	0.03 (0.01)	0.29 (0.01)
140	2.3 (2)	2.1 (2)	2.4 (3)	0.47 (0.17)	0.08 (0.03)	0.33 (0.01)

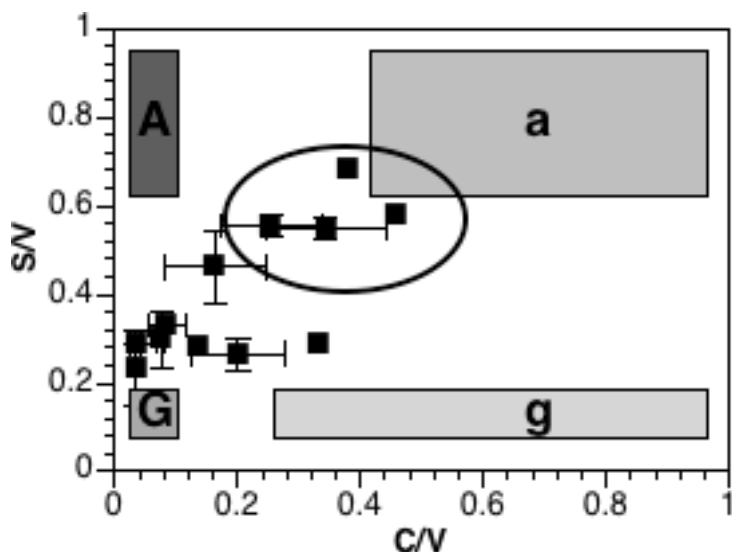


Figure 3.7. Ratios of lignin derived oxidation products from the Lake Mattamuskeet vibracore. Labels are for lignin ratios of cinnamyl/vanillyl (C/V) and syringyl/vanillyl (S/V). Also plotted are compositional ranges for different vascular plant endmembers (data from Goni and Hedges, 1992; Goni and Thomas, 2000) with a's representing angiosperms, g's representing gymnosperms, uppercase representing woody material and lowercase representing non-woody material. Error bars represent one standard deviation from replicated samples. The circle encompasses the sediments from the depths of 30, 40, 50 and 60 cm, which correspond to sediments deposited during the Little Ice Age (1650-1850).

CHAPTER IV. HISTORIC PHYTOPLANKTON COMMUNITY RESPONSES TO INCREASING ORGANIC MATTER INPUTS INTO A SHALLOW DYSTROPHIC LAKE.

ABSTRACT

Dystrophic aquatic ecosystems contain high amounts of allochthonous carbon that limit productivity, attenuate light and decrease pH, but little is known concerning dystrophic development and its effects on phytoplankton communities. Here, results are presented from a paleolimnological investigation of Pungo Lake, a shallow dystrophic system near the coast of North Carolina, USA. Multiple chemical and biological proxies were measured on a sediment core, including sedimentary photosynthetic pigments, lignin oxidation products, nutrients, metals and stable isotopes. Data analysis identified three zones of differing phytoplankton community structure corresponding to three periods of organic matter inputs. Zone I sediments were deposited prior to the mid 1600's and represented a period of high algal abundance and low organic input. Zone II sediments roughly correspond to the Little Ice Age and showed a decrease in algal abundance, an increase in algal groups that favor low light environments, an increase in lignin and a change in lignin type. Lignin oxidation products and $\delta^{13}\text{C}$ signatures of organic matter showed that terrestrial organic matter inputs increased during this period, possibly as a result of wetland expansion in response to the cool and wet conditions during the Little Ice Age. Zone III sediments incorporated the period of human impacts on the lake and were a period of high organic matter input from terrestrial sources and low algal abundance. This research details long term changes in a shallow lake

system and documents changes in the primary producer community with the development of dystrophy within the system.

INTRODUCTION

Aquatic ecosystems are subject to multiple environmental and human impacts. Land-use changes, nutrient inputs, hydrological modifications, biomanipulation, and climate change can all induce alterations to a lake ecosystem's trophic status and community structure. In shallow lakes, the strong relationship between nutrient inputs and trophic status has been the focus of considerable research on primary producer communities (e.g. Scheffer et al, 1993; Carpenter and Pace, 1997). Less is known concerning the development, response and change of primary producers in dystrophic shallow lakes. Lake dystrophication can occur when large amounts of allochthonous carbon enter a lake ecosystem from terrestrial/marsh environments (Wetzel, 2001; Williamson et al, 1999). Ecological drivers such as moisture changes, terrestrial community structure and land-use change can all result in alterations to organic matter (OM) inputs into lakes. Therefore, whole-lake research on dystrophic development that allows for quantitative linking of community changes and human and environmental impacts is needed for developing ecosystem response models capable of forecasting future alterations.

Allochthonous carbon in lake ecosystems is generally comprised of recalcitrant humic and fulvic acids as well as particulate organic material (Wetzel, 2001). These colored compounds attenuate light, decrease pH and bind nutrients in the water column causing changes to primary productivity, bacterial mineralization, and UV-radiation (Christersen et

al., 1996; Leavitt et al., 2003; Vinebrooke and Leavitt, 1998; Schalles and Shure, 1989).

Given the acidic and light-limited environment, autotrophic productivity decreases as allochthonous carbon increases in the system, but little is known about long-term, temporal changes of dystrophic lakes. Allochthonous carbon has been shown to have both a positive and negative relationship with nutrient availability in fresh waters (Klug, 2002). High phosphorus concentrations can occur in ecosystems containing significant OM concentrations (Nurnberg and Shaw, 1998) and photolysis of OM can release nitrogen into the ecosystem (Carlsson and Graneli, 1993), but the causes of an overall effect on nutrient availability in dystrophic systems is unknown. Conversely, OM-iron-phosphorus complexes can form and render phosphorus unavailable for primary producer growth (Jones et al., 1988). Allochthonous carbon and nutrient additions to phytoplankton communities induced significant increases in total primary productivity in short term, mesocosm experiments (Klug, 2002) and multiyear, whole lake experiments (Klug and Cottingham, 2001). These studies identified initial increases in certain algal groups prior to light limitation when OM and nutrients were added together. Given the experimental nature of these studies, research is needed that allows dystrophic development of aquatic ecosystems to be related to changes in primary producer community structure. Long-term data sets are extremely rare for most ecosystems, so paleolimnological investigations using the sediment record can be used to reconstruct long-term changes in dystrophic lakes.

By measuring the array of algal pigments in lake sediments, researchers can gain information on historic lake productivity, occurrence of cyanobacteria, and changes in algal community structure as well as food web dynamics (Leavitt and Hodgson, 2001). Leavitt

and Findlay (1994) showed that photosynthetic pigments in lake sediments represent past algal communities by comparing sedimentary pigments with historic algal data from experimental Lake 227 in Ontario, Canada. Pigments are labile and degrade with increases in light, oxygen and temperature. However, Leavitt (1993) stated that pigments are preserved at a constant rate provided that the lake conditions, such as temperature and depth, remain stable over time. Lignin oxidation product analysis is an analytical technique that has been used to infer the origin of terrestrial material entering aquatic ecosystems. Hedges et al. (1986) used lignin phenol analysis to show that the majority of particulate material in the Amazon River was primarily soil-derived and not from grasses that line the banks of the river. The ratios of certain lignin oxidation products such as cinnamyl (C) and syringyl (S) phenols to vanillyl (V) phenols can be used to infer the relative importance of angiosperm and gymnosperm inputs and woody and nonwoody inputs into aquatic ecosystems (Goni et al., 2003). For example, Bianchi et al. (1997) used lignin phenol ratios to report that carbon compounds deposited in Baltic Sea sediments consisted of primarily woody-gymnosperms. Finally, the ratio of acid to aldehyde phenols can be used as a proxy to determine the extent of lignin degradation resulting from bacteria (Onstad et al., 2000). These two proxies along with other proxies measured in bulk sediment samples can serve as powerful tools to investigate historic variations of primary productivity and vegetation changes within and around a lake ecosystem.

This study investigated the responses of the primary producer community to changes in the amount and type of organic material deposited in Pungo Lake, a small, dystrophic shallow lake located in eastern North Carolina. Paleolimnological proxies were measured

verses depth in sediment cores to determine changes in the primary producer community structure and terrestrial inputs throughout the development of dystrophy in the lake. Sedimentary photosynthetic pigments were measured to trace changes in total algal abundance and primary producer community structure. Likewise, lignin oxidation products were measured to trace temporal changes in the type of terrestrial organic material entering the aquatic ecosystem. Other paleolimnological proxies were used to track ecosystem changes in response to climatic, environmental and human stressors. It was hypothesized that a positive response in phytoplankton growth would be inferred from OM increases subsequently followed by a severe decrease in phytoplankton due to light limitation.

Study Site

Pungo Lake is a small, shallow dystrophic lake located on the Albemarle/Pamlico Peninsula, North Carolina, USA (Figure 4.1, Table 4.1). In 1986, color was greater than 500 Pt-Co units (Benkert, 1990). The lake is part of the Pocosin Lakes National Wildlife Refuge and is managed primarily for wintering waterfowl and wildlife. Dense populations of ducks, geese and swans following the Atlantic Flyway occupy the lake during winter months. Water levels are maintained through a series of gates built within an extensive canal system linking the lake to adjacent wetlands and agricultural fields. Very few macrophytes are in the lake, but significant macrophyte stands can occur in the canals themselves. Recreational boating is prevented on the lake and fish are scarce given the low productivity of the system (*North Carolina Wildlife Resource Commission*). Human settlement and modifications of the area occurred in the 1800's and consisted of the building of canals and the clearing of surrounding land for agriculture.

METHODS

Water depth and soft sediment surveys were conducted in Pungo Lake to determine optimal sites for collecting cores (Figure 4.1; Table 4.2). Coring areas were focused where soft sediments were thickest. Two short (60 to 80 cm) cores were collected from Pungo Lake in order to obtain proxy data that could be used to reconstruct changes in primary producer communities, climatic impacts and human impacts. Although two cores were collected, the results presented here are based on the core that was ^{210}Pb dated and contained the longer temporal sediment record. The other core was used to establish reproducibility of results but was not included in statistical analysis. Sediment cores were collected using a piston corer designed to retrieve undisturbed surface sediments (Fisher et al., 1992). Sediment cores were sectioned in the field, stored on ice and returned to the lab. Core section intervals were frozen, freeze-dried and ground with a mortar and pestle prior to analysis. Bulk density, organic matter as loss on ignition (LOI), nutrients (TN, TP, TS), metals (Fe, Mn, Al, Ca, Cd, Cr, Mo and Pb), total organic carbon (TOC) and photosynthetic pigments were measured for each core section. Lignin oxidation products and stable isotopes ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$) were measured on selected samples spanning the entire length of the core. Given their labile nature, photosynthetic pigments were measured within the first week following freeze-drying.

Bulk density was calculated following the formula from Binford (1990), which expresses sediment density in $\text{g dry}/\text{cm}^3$ wet. LOI content was assessed by loss on ignition at 550°C in a muffle furnace and expressed as a percentage (Håkanson and Jansson, 1983). TP, TS and metals were measured on dried sediments using an ARL 3560AES ICP analyzer

following acid digestion using standard EPA methods. TOC and TN were measured using a Carlo Erba C/N/S analyzer with an attached autosampler. Prior to analysis, TOC and TN samples were acidified for 12 hours in HCl vapors to remove inorganic carbon. $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ were measured by a Finnigan Mat 252 isotope ratio mass spectrometer coupled to a Carlo Erba C/N/S analyzer. Carbon and nitrogen isotopic ratios were measured relative to an internal standard and calibrated to the reference standards of Pee Dee Belemnite and air, respectively. Isotopic ratios were calculated as standard delta notation following the equation:

$$\delta \text{ Isotope} = \frac{(\text{Sample}^{\text{heavy}}/\text{Sample}^{\text{light}}) - (\text{Standard}^{\text{heavy}}/\text{Standard}^{\text{light}})}{(\text{Standard}^{\text{heavy}}/\text{Standard}^{\text{light}})} \times 1000$$

and expressed as per mil (‰).

Photosynthetic pigments (chlorophylls and carotenoids) were measured using an HPLC system following the methods of Leavitt and Hodgson (2001) designed particularly for sedimentary pigments. Dried sediment samples were extracted with a solvent mixture of acetone, methanol and water mixed in an 80/15/5 ratio, which contained an internal standard (Sudan II; Sigma Chemical Corp., St. Louis, MO) and allowed to digest 16-24 hours in a -20 °C freezer. Following extraction, samples were centrifuged and filtered through a 0.22 μm syringe filter to remove any particulate matter from the sample. Samples were placed in an autosampler tray where they were mixed with an ion-pairing agent (0.75 g tetrabutyl ammonium acetate and 7.7 g ammonium acetate in 100 ml HPLC-grade water) prior to injection. 200 μL of each sample was injected into a Shimadzu HPLC system following the mobile phase and time sequence of Leavitt and Hodgson (2001). Chlorophylls and carotenoids were separated by passing through a Rainin Model 200 Microsorb C18 column

and measured using a photodiode array detector. Pigment identification was made using retention times of known standards and pigment specific spectra recorded by the detector. Pigment concentrations are expressed as $\mu\text{g pigment/g OM}$ and calculated by comparing peak areas against standards of known concentration.

Lignin oxidation products were measured on dried, bulk sediment samples following the cupric oxide method described in Hedges and Ertel (1982), Goñi and Hedges (1992) and Duan et al. (2007). Sediment samples containing 3 to 5 mg of organic carbon were transferred to stainless steel reaction vessels. Samples were digested with CuO in 2 N NaOH in the absence of O_2 at 150 °C for 3 h. Diethyl ether was used to extract reaction products, which were then dried and derivatized using bis-(trimethylsilyl)-trifluoroacetamide (BSTFA). Lignin oxidation products were measured using a Varian model CP 3800/2000 gas chromatograph/mass spectrometric detector (GC-MS). Lignin identification and quantification was determined against a mixed standard and internal standards of ethyl vanillin as an internal recovery standard and methyl 3,4 dimethoxy benzoate as an absolute recovery standard. Eight lignin oxidation products (vanillin, acetovanillone, syringaldehyde, vanillic acid, acetosyringone, syringic acid, p-coumaric acid and ferulic acid) were quantified and used as molecular indicators for source and diagenetic state of vascular plant tissue. Lambda-6 is defined as the sum of vanillyl (vanillin, acetovanillone, vanillic acid) and syringyl (syringaldehyde, acetosyringone, syringic acid) oxidation products, while Lambda-8 also includes the cinnamyl (p-coumaric and ferulic acid) oxidation products. The ratios of total cinnamyl and syringyl oxidation products to vanillyl oxidation products are represented

as C/V and S/V, and ratios of vanillic acid to vanillin and syringic acid to syringaldehyde were abbreviated as Ad/Al_v and Ad/Al_s, respectively.

Sedimentation rates and core section dates were determined by measuring ²¹⁰Pb using the constant rate of supply (CRS) model following the methods of Schelske et al. (1994) and Appleby and Oldfield (1983). ²¹⁰Pb was measured on dried, ground sediment samples using a low-background germanium well detector. ²¹⁰Pb data was used to provide sedimentation rates and core section dates for the past 100-150 years.

Sediment zones based on algal pigment signatures were objectively determined using multivariate statistics. Sedimentary pigment data were incorporated into a database, and principal component analysis was used to determine proxies that account for the largest percent of variance for the entire data set (SAS Imp, 2006). Photosynthetic pigments were then used in a k-means cluster analysis to group sediments into historic periods of lake trophic status and primary producer community structure. K-means cluster analysis uses a specified number of cluster seed points and repetitively groups data to minimize standard deviations of means for each group. The number of clusters was determined from assumed changes in the proxy data. This technique has been used successfully in previous paleolimnological investigations to separate macrophyte detrital sediments, transitional sediments and phytoplankton detrital sediments within a lake (Waters et al., 2005) and in a multiple lake study (Kenney et al., 2002).

RESULTS

Water depth in Pungo Lake varied little among stations while soft sediment thickness was focused toward the northwestern portion of the lake (Table 4.2). Water depth averaged 1.4 m (SD=0.05) for nine stations, while soft sediment thickness ranged from 0.1 to 0.95 m. Two sediment cores were collected from the stations containing the thickest soft sediments (PuL-01 and PuL-08), and both contained similar lithology. The results reported here are for the core collected at PuL-01, which contained the thickest soft sediments. The top 40 cm of the core contained dark organic sediments. An abrupt change to organic sand with macrofossils of plant material from a variety of unidentified species occurred from 40-60 cm. Below 60 cm the core was primarily sand.

Excess ^{210}Pb decreased down core with the exception of the sediment interval at 8 cm (Figure 4.2-A). This change in excess ^{210}Pb deposition indicates a change in sedimentation rate and requires the use of the CRS model. Excess ^{210}Pb was not measurable at 22 cm and was confirmed by subsequent immeasurable activity in samples just below 22 cm. The CRS model was used to determine accumulation rates as well as estimated ages from 2-18 cm (Figure 4.2-B) with the 18 cm sample being deposited around 1918. The depth verses age plot demonstrates the consistent sedimentation experienced in the lake from about 1918 to 1974 (samples 8-18), which averaged 12 years per sediment section (SD=3). Mass sedimentation rates for the entire dated section of the core ranged from 12 to 28 $\text{mg}/\text{cm}^2/\text{yr}$. Although the sedimentation rates were variable, the majority of the samples were between 15 and 20 $\text{mg}/\text{cm}^2/\text{yr}$ further supporting the constant sedimentation throughout most of the ^{210}Pb datable portion of the core.

Loss on ignition demonstrated a general increase from 60 cm to the top of the core (Figure 4.3). Below 60 cm LOI percentages were consistently around 3 % with very little variation. From 60 cm to 42 cm LOI steadily increased from 3 % to 35 %. In the top 42 cm of the core, LOI increased from 35 % to around 60 % in the top of the core. Phosphorus concentrations also reached minimum concentrations in the bottom of the core with a steady increase from 23 to 113 ppm from 78 to 60 cm, respectively. From 60 cm to 44 cm, concentrations dramatically increased reaching 790 ppm at 44 cm. Above 44 cm, levels increased until maximum concentrations of 900 ppm were attained in the top 8 cm of the core. Bulk density followed the general description of the sediment types of the core. Highest bulk density values were measured in the bottom of the core indicating the high sand content. From 60 cm to 40 cm bulk density steadily decreased indicating the transition from sandy sediments to high organic sediments. The top 40 cm of the core contained consistently low bulk densities. S, Fe, Mn, Al, Ca, Cd and Cr all showed similar patterns as the phosphorus data (Figure 4.3). In general, from 78 cm to 60 cm, most elements were low in concentration aside from a small peak in S, Fe, Al, and Cr at 72 cm. From 60 cm to 42 cm all elements increased to high concentrations followed by a decrease at 36 cm. The top 36 cm contained high concentrations for each element with little variation. Mo followed the same pattern except for a major peak at 62 cm. Pb concentrations were extremely variable throughout the core with a slight increase from the bottom of the core to the top.

Although photosynthetic pigments were detected in each sediment sample, pigment concentrations were low throughout the cores when compared to sediment samples from

other lakes in the area (Chapter II). Beta-carotene, lutein+zeaxanthin and echinenone steadily decreased upcore experiencing maximum values in the bottom sediments and minimum values in the top 42 cm of the core. Chlorophyll *a* and *b* were below detection throughout most of the core with the exception of the upper sediments. Although the majority of the core contained little chlorophyll, chromatograms of most sediments contained multiple unidentifiable peaks resulting from spectra similar to chlorophyll *a* and *b*. Profiles of pheophytin *a* and *b* contained the most constant concentrations throughout the entire core. Pheophytin *a* concentrations were low in the bottom sediments of the core but increased to constant concentrations in the top 60 cm of the core. Pheophytin *b* was variable throughout the entire core with maximum concentrations from 60 cm up to 42 cm. Alloxanthin, canthaxanthin, myxoxanthophyll and diatoxanthin contained similar profiles throughout the core. Lower concentrations were measured in the bottom sediments and in the upper 40 cm of the core while the core section from 42 cm to 60 cm for each pigment contained the maximum concentrations for the core. Likewise, myxoxanthophyll contained concentrations below detection in the upper 12 cm and the interval from 60 cm to 78 cm. Both fucoxanthin and myxoxanthophyll contained maximum concentrations between 42 and 60 cm.

K-means cluster analysis of all photosynthetic pigment data divided the sediment core samples into three clusters. The core samples from 60 cm to the bottom of the core clustered together and were labeled Zone I, 60 cm to 42 cm as Zone II, and 42 cm to the top of the core as Zone III. Clustering did not show stratigraphic overlap between clustered sediments. Principal component analysis using photosynthetic pigment data identified pigments that correlated with each cluster (Figure 4.5). A plot of principal components 1 (PC1) and 2

(PC2) show a separation of the clusters and the orientation of pigment eigenvectors. PC1 represented 45.8% of the variance of the data set, and PC2 represented 25.3% (Figure 4.5). The bottom sediments (Zone I) were most strongly represented by the photosynthetic pigments, beta-carotene, zeaxanthin+lutein, echinenone and fucoxanthin. These pigments positively correlated with PC1 and negatively correlated with PC2. The strongest relationship was -0.41 between PC2 and the eigenvector for beta-carotene. Zone II sediments were most strongly represented by photosynthetic pigments myxoxanthophyll, alloxanthin, canthaxanthin, pheophytin-*b* and diatoxanthin. These pigments positively correlated with both PC1 and PC2. The strongest relationship was between myxoxanthophyll and PC2 (0.40), and the second strongest relationship was between alloxanthin and PC2 (0.29). The top 42 cm of the core (Zone III) were most strongly represented by the photosynthetic pigments chlorophyll *a* and *b* and pheophytin *a*. These pigments negatively correlated with PC1 and positively correlated with PC2. Chlorophyll *a* and *b* eigenvectors correlated with PC1 with values of -0.29 and -0.23, respectively. The eigenvector for pheophytin *a* most strongly correlated with PC2 with a value of 0.54.

TN and TOC concentrations were low in Zone I sediments with TN being below 0.14% and TOC being below 3% for all samples. For both proxies Zone II represents a period of increasing deposition with TN values increasing from 0.08% to 1.64%, and TOC values increasing from 2.9 to 39 %. Zone III values for TN and TOC remained high throughout the zone with TN averaging 1.6 % (SD=0.25) and TOC averaging 41 % (SD=4.1). TC/TN ratios were greater than 25 for the entire core with a maximum value of 43 obtained at 62 cm. $\delta^{15}\text{N}$ values were variable throughout the core with a maximum value of

6.2‰ at 14 cm and a minimum value of 1.4‰ at 70 cm. $\delta^{13}\text{C}$ values were lowest in Zone I with values averaging -33 ‰ (SD=0.3). $\delta^{13}\text{C}$ values shifted to a heavier and constant isotopic signature throughout Zones II and III with an average of -27 ‰ (SD=0.3). Lamda 6 and 8 values followed the same trend with low concentrations in Zones I and III and maximum values in Zone II for the sediments at 50 and 54 cm. Maximum values for Lamda 6 and 8 in Zone II were 7.3 and 10.7 mg lignin/100 mg organic carbon, respectively.

Ad/Al_v ratios were lowest in Zone I sediments ranging from 0.24-0.36 and highest in Zone II with a maximum ratio of 0.88 at 50 cm (Table 4.3). Ad/Al_s ratios generally increased upcore with the exception of high values at 50 and 54 cm. Core sections at 54 and 4 cm experienced the highest ratios although the 4 cm sample contained a much higher standard deviation than the other samples. C/V ratios followed the same pattern as the Ad/Al_v ratios with lowest values in Zone I and highest values in Zone II. S/V ratios generally decreased upcore. The relationship between C/V and S/V showed that most samples grouped together with the exception of Zone II sediments, which contained higher C/V ratios (Figure 4.7).

DISCUSSION

The complexity of multiple human and environmental impacts on lake ecosystems limits the number of studies that have focused on the consequences of long term changes in biological, chemical and physical processes. These complexities support the need for whole ecosystem, long-term studies (Schindler et al., 1998; Carpenter et al., 1995; Christensen et al., 1996). Due to budget limitations and the lack of ecosystems available for manipulative

research, whole-lake studies are not practical in many contexts. In addition, long-term data sets are rare and the establishment of baseline/predisturbance conditions can be problematic. This application of paleolimnological techniques to Pungo Lake sediments provides a unique opportunity to determine the impacts of developing dystrophy in a shallow, coastal lake system.

The challenge of using paleolimnological research in determining long-term ecological change centers on the interpretation of proxy data to reconstruct predisturbance conditions. The pre-dystrophic conditions inferred from the sections of the sediment core deposited before 1650 (60 cm) consisted of sand and very little organic material. Proxy data promoted the assumption that during this period the lake's water column contained very little allochthonous carbon. Likewise, OM concentrations in sediment samples increased during the period represented by the top 60 cm of the core. This assumption is based on the increasing organic matter deposition (LOI), elevated lignin oxidation product concentrations and lighter $\delta^{13}\text{C}$ values suggesting an increase in terrestrial inputs along with the current dystrophic state of the lake. In addition, the assumption that Pungo Lake was historically a low OM and sand-bottom system matches the current state of nearby Lake Phelps and Lake Mattamuskeet, which featured observed and inferred clear water conditions, respectively (Chapter III).

Sediment zonation

K-means cluster analysis and principal component analysis identified three historic periods of variable algal abundance as well as changes in algal community structure.

Although the depth of the ^{210}Pb profile limits accurate dating of cluster breaks within the core, it is inferred that the bottom two core-clusters containing the majority of photosynthetic pigments were deposited prior to human impacts in the area. Age intervals were calculated for the cluster breaks by extrapolating best fit lines on the entire age vs. depth profile and the bottom three points of the age vs. depth profile. These two best-fit lines were used to provide a rough interval of ages for the cluster breaks. The estimated age for the cluster break at 42 cm was A.D. 1785 ± 25 years, and the age for the 60 cm cluster break was A.D. 1657 ± 47 years. The lack of dated intervals in the lower portions of the Lake Pungo core preclude strict adherence to these dates. Nevertheless, these intervals provide a rough framework with which to compare paleoecological changes to known periods of climatic and human impacts such as European settlement and the Little Ice Age.

Zone I (60-78 cm, A.D. pre-1650)

Paleolimnological proxies measured on Zone I sediments indicate that this period included low organic matter inputs into the lake but with greater algal abundance than the other two zones. Most photosynthetic pigments were deposited and preserved despite the lack of organic material indicating that total algal abundance and pigment concentrations might have been higher than measured. Furthermore, nutrients (TN and TP) were low during this period, which is surprising given the pigment concentrations. The inferences for total algal abundance are primarily based on beta-carotene measurements in the sediments, which have been used as a total algal abundance proxy in many different lake locations and types (Leavitt and Findlay, 1994; Leavitt and Carpenter, 1990; McGowan et al., 2005; Patience et al., 2006). Chlorophyll *a*, the most ubiquitous pigment in primary producers, is extremely

labile when compared to other sedimented pigments and thus has limited preservation in deeper sediments. It is also important to note that pheophytin *a* can degrade into colorless compounds under low preservation conditions. The lack of organic material in the sediments and wind resuspension would limit anoxic conditions needed for optimal pigment preservation. Conversely, the labile pigment, fucoxanthin, was deposited and preserved in high concentrations in Zone I sediments relative to the top of the core. One possible explanation is that Pungo Lake contained a substantial population of siliceous algae during this period causing high fucoxanthin concentrations even though degradation was occurring. An alternative explanation would be that the lack of chlorophyll *a* in Zone I sediments is a reflection of the many pathways of degradation for chlorophyll. Several peaks containing similar spectra as chlorophyll were noted in the analysis, but these peaks were not reported as chlorophyll *a* due to the lack of an exact match of spectrum as well as different retention times in HPLC chromatograms. This example further supports the use of beta-carotene as a proxy for historic algal abundance. The concentrations of beta-carotene measured in Zone I sediments are comparable with sediments from nearby Lake Mattamuskeet (Interval II; Chapter III) that also contained low organic matter yet significant pigment deposition. Therefore, based on photosynthetic pigment deposition of beta carotene and other more diagnostic pigments, it is inferred that Zone I represents a period of substantial algal abundance.

The lack of nutrient and metal deposition as well as the low lignin concentrations suggests that Pungo Lake had little connection with the surrounding terrestrial environments during this period. All four lakes of the Albemarle/Pamlico Peninsula lack groundwater or

riverine connections (Benkert, 1990). As a result, their water budgets depend on rainfall and overland flow. The low organic matter deposition coupled with low nutrient and metal deposition indicates that Pungo Lake acted as a hydrologically closed system depending primarily on precipitation as its water source. This would suggest that the organic matter deposited during this period consisted primarily of autochthonous material from the primary producers, but the TC/TN ratios indicate that the organic inputs contained material from higher plant species (Meyers and Teranes, 2001). Macro-particles in Zone I sediments and current observations suggest the elevated TC/TN numbers could be the result of tree species growing into the littoral zones of the lake. Zone I sediments contain large pieces of woody material homogenized with the sand, and cypress stumps have been noted along the shoreline of Pungo Lake showing a historic period of tree growth in the littoral areas of the lake (Benkert, 1990). Nearby Lake Phelps currently contains dense cypress tree populations in littoral areas around most of the lake. Also, the low elevation of the peninsula would suggest that aeolian inputs could contribute to sedimented organic material. As a result, Pungo Lake lacked direct inputs from the terrestrial environment, but aeolian inputs and vascular plants growing in littoral areas supplied a measurable amount of organic matter to the lake.

Zone II (42-60 cm; A.D. 1650-1810)

Zone II sediments contained higher concentrations of organic matter, nutrients and metals than Zone I sediments, indicating a period of increased loading into the lake. PCA identified cyanobacteria (myxoxanthophyll, canthaxanthin), cryptophytes (alloxanthin) and diatoms (diatoxanthin) as the primary algal groups responding to the increasing organic matter and nutrients. Cyanobacteria and cryptophytes are algal groups capable of

maintaining an existence in a shallow photic zone and have been shown in other studies to positively respond in nutrient rich and low light situations. Klug (2002) showed that phytoplankton growth experienced both positive and negative responses to allochthonous carbon and inorganic nutrient additions in short term experiments. Although the positive effects outweighed the negative effects, Klug (2002) concluded that the response was determined by nutrient availability and OM interactions as well as the physiological status of the algal community. Likewise, Klug and Cottingham (2001) obtained similar results from a whole lake, multi-year experiment in Long Lake, Michigan. They noted that the primary response group to OM and nutrient additions was an increase in cryptophyte abundance. In Pungo Lake, cryptophytes exhibit the second most positive relationship for the Zone II algal community behind colonial cyanobacteria (myxoxanthophyll).

The initial input of organic material to Pungo Lake contained significant concentrations of nutrients as recorded in sedimentary TP and TN concentrations. Although OM within the lake is believed to have increased during this time, it is inferred from algal community shifts that certain algal groups positively responded to the environmental impacts on the lake. The inputs of OM and nutrients provided an environment favorable to phytoplankton groups capable of utilizing the available nutrients and low light conditions. The sharp peak recorded in the sediments for the myxoxanthophyll, alloxanthin, canthaxanthin and diatoxanthin pigments show that the phytoplankton groups of cyanobacteria, cryptophytes and diatoms experienced a threshold where growth became limited either by nutrient availability or light limitation. The complex mixture of compounds comprising allochthonous OM in lake waters can bind or surround nutrients rendering them

unavailable for phytoplankton growth (Williamson et al., 1999). Likewise, OM compounds are often chromophoric and can attenuate light to levels where photosynthesis is limited (Vinebrooke and Leavitt, 1998).

Based on increasing LOI percentages and other OM proxies, Zone II is believed to represent a period where OM inputs into the lake from the terrestrial areas increased. OM quantity is affected by inundation of catchment areas (Rasmussen et al., 1989), vegetation type (Cronin and Aiken, 1985), climate (Angstrom, 1987), forest fires (Schindler et al., 1992) and autotrophic production (Williamson et al., 1999). In Pungo Lake, the increase in lignin concentrations and organic matter deposition in Zone II sediments suggests that the connectivity between the lake and catchment increased during this period. This material is believed to be primarily terrestrial and a result of the expansion and inundation of vegetation areas around the lake. Currently, Pungo Lake is surrounded by an extensive area of wetlands (Benkert, 1990). The paleolimnological proxies measured on Zone II sediments suggest that the wetland communities most likely increased during this period. For example, the $\delta^{13}\text{C}$ shifting to heavier values could indicate a greater input from C-3 grass species. S/V and C/V ratios demonstrate a change in the type of lignin entering the lake from woody to non-woody species. These proxies provide evidence that the wetland area surrounding Pungo Lake changed either through expansion, development or connectivity to the lake during the period when Zone II sediments were deposited. These inputs included large concentrations of organic material, nutrients and metals, which would have increased OM in the lake as well as provided an initial influx of nutrients to the phytoplankton community.

As seen in other lakes in this region (Chapter III), changes in Zone II sediments could be the result of climatic impacts. Using extrapolated dates from the ^{210}Pb profiles, Zone II sediments roughly correspond to the period known as the Little Ice Age. Tree ring chronologies (Stahle and Cleaveland, 1994) as well as pollen records (Willard et al., 2003) from areas near Pungo Lake have concluded that the southeastern USA was cool and wet during this period. These conditions would promote wetland expansion and increase the period of inundation for these systems. It is probable that these responses would increase OM inputs and support the findings of this study (Kortelainen, 1993). This wet and cool period would increase the inundation of the entire peninsula and would also cause the leaching of the peat soils in this area. Increasing nutrient and metal concentrations deposited during this time further suggest a change in the type of material entering the lake. Finally, a similar paleolimnological study in nearby Lake Mattamuskeet identified a similar shift in lignin type during sediments deposited during the Little Ice Age (Chapter III).

Most biologically linked proxies began to decrease in concentration in the upper sediments of Zone II suggesting the beginning of light or nutrient limitation resulting from increasing OM concentrations in the lake. By comparing Zone II sediments to sedimentation rates in the top of the core, Zone II sediments represent roughly 100 years in the lake's history. These estimates suggest that the positive effects of dystrophic development on primary productivity in the lake changed to negative effects within a span of 50 to 100 years. Although these estimates are based on extrapolated ^{210}Pb profiles they do suggest that following increases in OM inputs into the lake dystrophy developed rapidly within the system.

Zone III (0-42 cm; A.D. 1810-present)

The top 42 cm of the Pungo Lake core represent a period of high organic matter input and decreasing algal abundance. All fossil algal carotenoids decreased to lower concentrations than in Zones I and II. Given the high OM and light-limited conditions currently existing in the lake, the change in pigment concentrations indicate that the current state of the lake developed in the 1800's and could have been influenced by human interactions with the lake. Like all of the lakes located on the Albemarle/Pamlico Peninsula, Pungo Lake is connected to an extensive canal system in order to regulate lake depth and drain and irrigate adjacent farmlands (Benkert, 1990). These connections have been shown in other paleolimnological studies to increase inputs of organic matter, nutrients and metals (Chapter III). In Lake Mattamuskeet, canals caused tremendous changes in the phytoplankton community, which included a shift to cyanobacterial dominance (Chapter III). Although Zone II sediments indicate increasing allochthonous material in the lake, the construction of the canals during the deposition of Zone III sediments would have increased OM inputs to concentrations much higher than previously experienced in the lake from natural and climatic effects.

The high concentrations of chlorophyll pigments in the upper sediments of Zone III are inferred as either a lack of degradation or an artifact of organic material entering the lake rather than an increase in algal abundance. The pheophytin *a* profile supports the idea that the labile chlorophyll *a* has been deposited throughout Zones II and III and preserved as pheophytin *a*. Chlorophyll *a* is extremely labile and is generally not reported in sediment studies, or it is inferred from degradation products (Leavitt and Hodgson, 2001; Hodgson et

al., 1998; Bunting et al., 2007). The high chlorophyll concentrations in the upper sediments could also be explained by the dense communities of aquatic macrophytes existing in the canal system around Pungo Lake. Macrophyte samples collected from nearby Lake Mattamuskeet contained high concentrations of chlorophyll *a* and *b* (Chapter II). Macrophytes grow extensively in the canals connected to Pungo Lake and are a possible source of the chlorophylls to the upper sediments. Regardless of the mechanism of input and preservation, proxy data suggest that the increase in chlorophylls does not indicate increases in algal abundance given the lack of carotenoids in upper sediments and the current dystrophic conditions in the lake.

Other paleolimnological proxies measured on Zone III sediments indicate a period of high organic matter, nutrient and metal inputs into the lake. Although nutrient inputs were highest in Zone III sediments, primary productivity appears to have been limited by light rather than nutrients as has been shown in other dystrophic lakes containing high concentrations of phosphorus (Carpenter and Pace, 1997). In addition, the increase in metal concentrations can be linked to the canals. By digging and trenching the canals, peat soils are exposed to stagnant water, which can leach metals and other materials (Wyn et al., 2007). The decrease in total lignin deposited in Zone III sediments relative to Zone II sediments is puzzling given the dystrophic conditions in Pungo Lake today. Ad/Al ratios suggest a significant amount of soil-derived lignin instead of fresh plant material in Zone III sediments, but the ratios are still below Zone II ratios. Possible explanations for these differences are that the soils were originally leached during the wet periods of the Little Ice Age or a natural change in landscape following the warming after the Little Ice Age. Regardless of the

mechanism, Zone III sediments represent a continuance of the dystrophic conditions that began in Zone II.

Conclusions

The sediment record collected from shallow, dystrophic Pungo Lake contains three periods of phytoplankton community structure corresponding to three periods of organic matter inputs. Prior to the 1600's Pungo Lake received little organic matter input but contained the highest algal abundance recorded in the sediment core. Sedimentary algal pigments show that most algal groups were abundant during this period even though nutrient deposition to the sediments was minimal. Multiple proxies indicate that OM was dramatically less than the dystrophic conditions experienced in the lake today allowing for a deeper photic zone in the water column. Zone II sediments roughly corresponded to the Little Ice Age and recorded a decrease in total algal abundance. Conversely, fossil pigments, myxoxanthophyll, alloxanthin, canthaxanthin and diatoxanthin experienced increases in deposition to the sediments during this period showing a change in the primary producer community from cyanobacteria, cyanobacteria+chlorophytes and diatoms to colonial cyanobacteria, cryptophytes and diatoms. These shifts are inferred as representing a response of the algal community to increased allochthonous OM and nutrients within the lake. Similar responses were observed in mesocosm (Klug, 2002) and whole lake (Klug and Cottingham, 2001) experiments investigating the effects of OM and nutrients on phytoplankton communities. Zone II sediments also experienced an increase in lignin deposition, organic material, and nutrient deposition as well as shifts in $\delta^{13}\text{C}$ and lignin type. Finally, Zone III sediments were deposited during the past 150 years and represent the dystrophic conditions

experienced in the lake today. All measured carotenoids decreased to minimum levels in this zone showing decreased algal abundance for all groups. Furthermore, increases in chlorophyll deposition are believed to be either a preservation issue demonstrating recent chlorophyll deposition or an artifact of macrophyte material entering the lakes through the extensive canal system surrounding the lake. Regardless, the current dystrophic nature of the system limits primary productivity and appears to have been established prior to European settlement of the area. Dystrophic development is rarely studied, but this research demonstrates changes in the primary producer community structure in response to climatic, environmental and human impacts.

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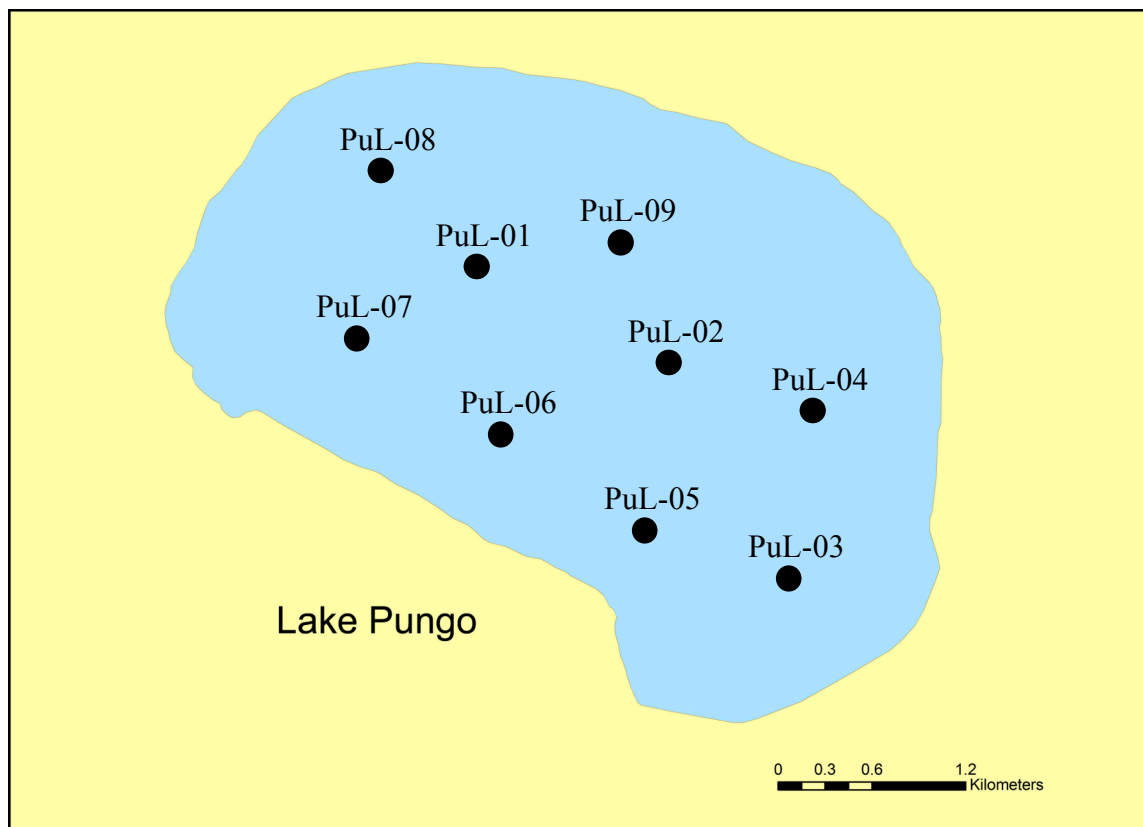


Figure 4.1. Map of Pungo Lake showing sampling stations. Inset map shows Pungo Lake among the other lakes of the Albemarle/Pamlico peninsula. Sediment cores were collected at stations PuL-01 and PuL-08.

Table 4.1. Limnological characteristics for Pungo Lake. All depth measurements are in m, surface area is in km² and elevation is meters above sea level.

<u>Characteristic</u>	<u>Value</u>
Latitude	35° 42'N
Longitude	76° 32'W
Depth-average	1.42
Depth-maximum	1.50
Surface Area	11.3
Elevation	2.75

Table 4.2. Water depth and soft sediment thickness for Pungo Lake stations.

Station	Water Depth (m)	Soft Sediment Thickness (m)
PuL-01	1.35	0.95
PuL-02	1.4	0.5
PuL-03	1.5	0.3
PuL-04	1.4	0.25
PuL-05	1.4	0.2
PuL-06	1.5	0.4
PuL-07	1.45	0.8
PuL-08	1.4	0.8
PuL-09	1.4	0.1

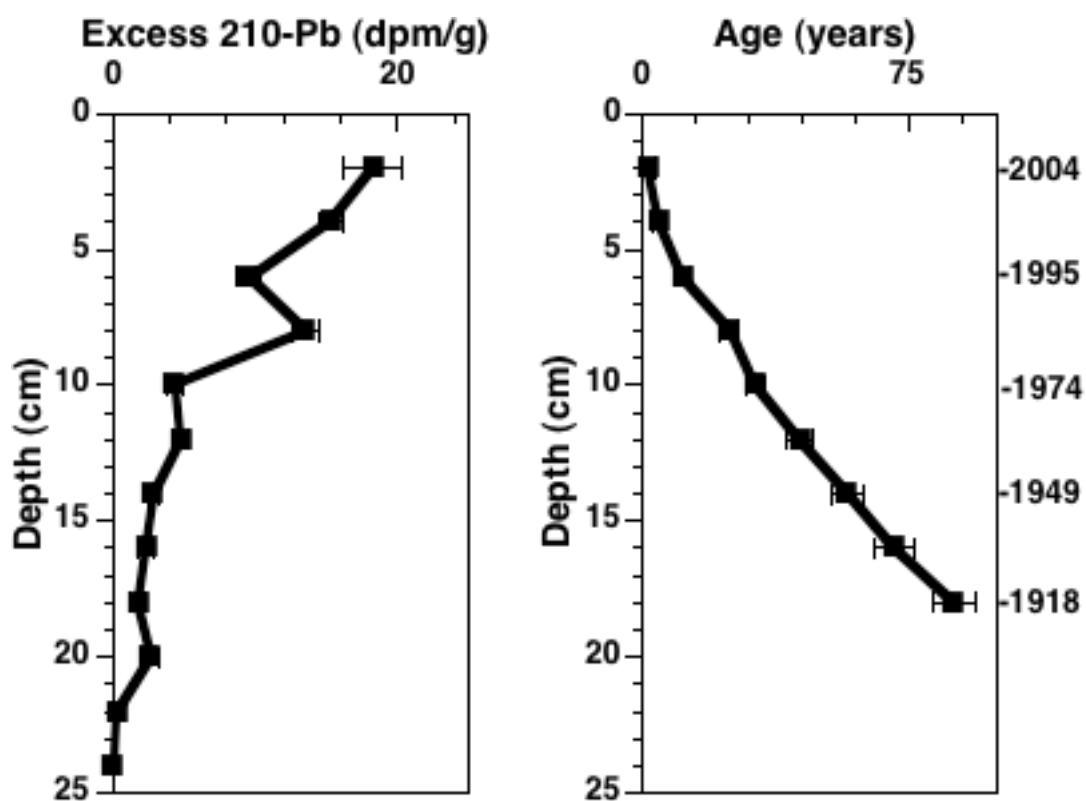


Figure 4.2. Excess ^{210}Pb and ^{210}Pb -Age versus depth for the Pungo Lake core. Error bars show one standard deviation for each core section measured.

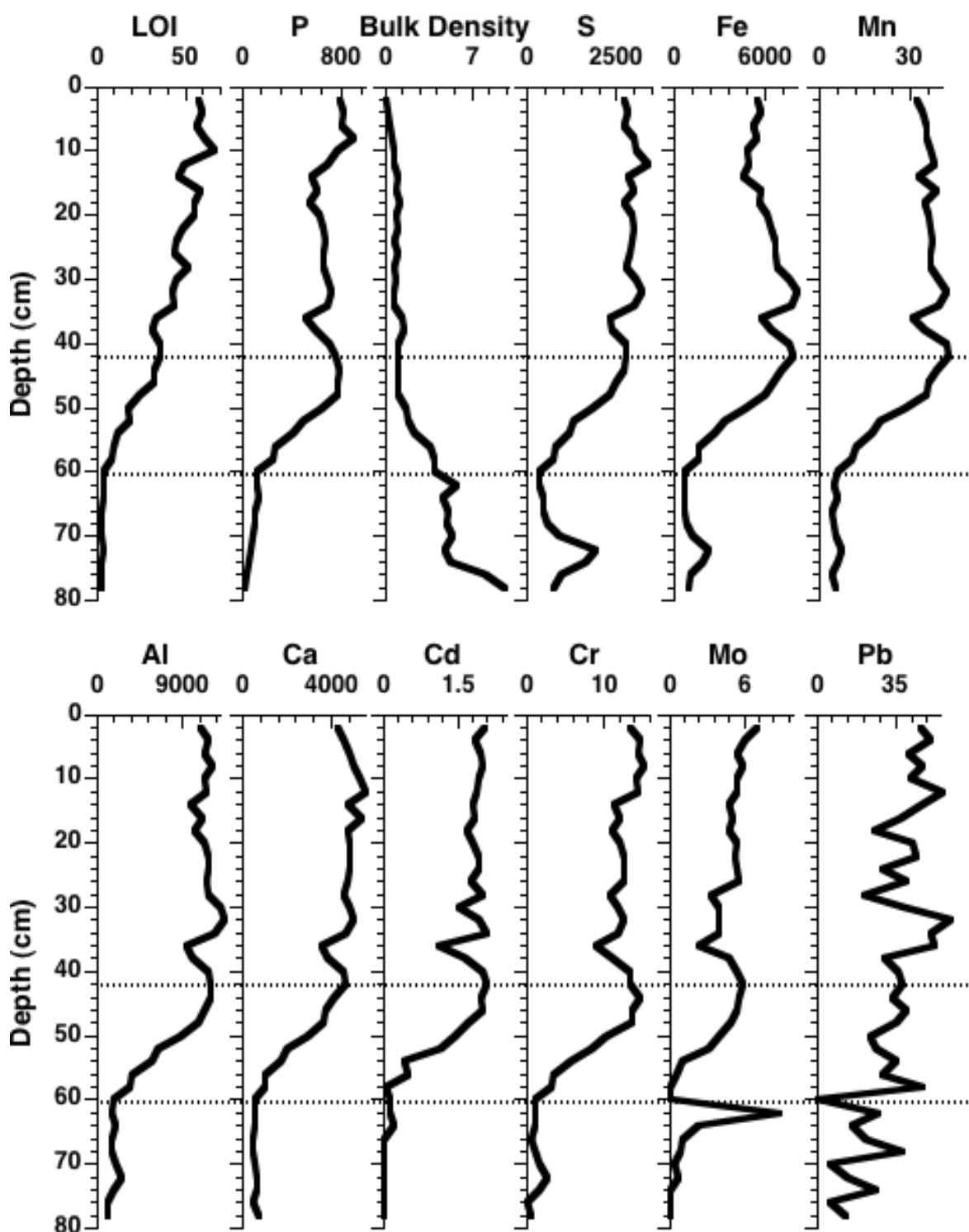


Figure 4.3. Loss on ignition, bulk density, nutrients and metals measured on bulk sediments from Pungo Lake sediment core. Units are ppm except for LOI (%) and Bulk Density (g dry/cc wet). Lines separate the zones established from k-means cluster analysis of the pigment record.

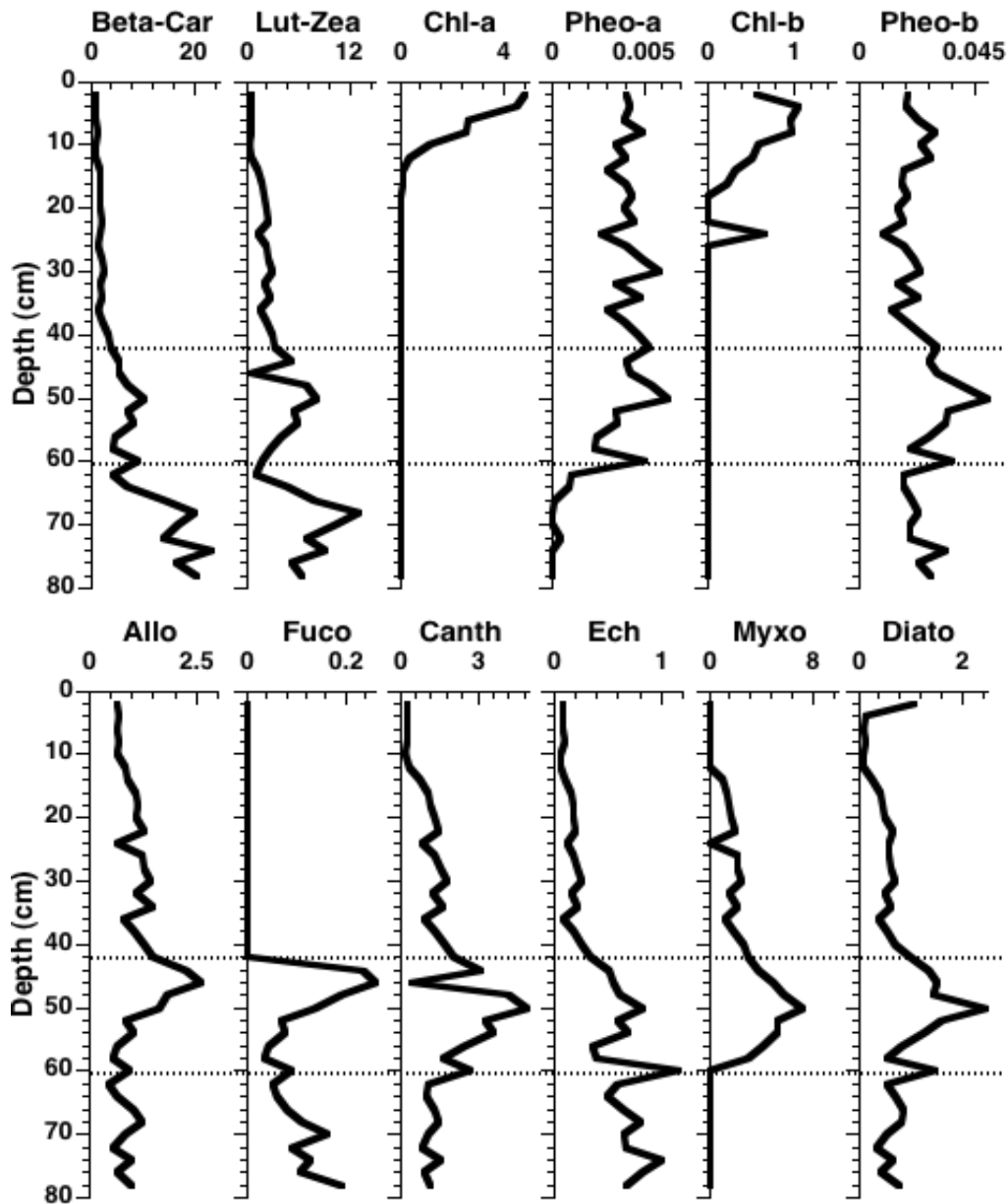


Figure 4.4. Sedimentary photosynthetic pigments measured on Pungo Lake sediments. Units are $\mu\text{g pigment/g. organic material}$. Pigments presented are beta-carotene (Beta-Car: total abundance), Zeaxanthin-Lutein (Zea-Lut: cyanobacteria-chlorophytes), Chlorophyll-a (Chl-a, total abundance), Pheophytin-a (Pheo-a, total abundance), Chlorophyll-b (Chl-b, chlorophytes), Pheophytin-b (Pheo-b, chlorophytes), Alloxanthin (Allo-cryptophytes), Fucoxanthin (Fuco-siliceous algae), Canthaxanthin (Canth-colonial cyanobacteria), Echineone (Ech-cyanobacteria), Myxoxanthophyll (Myxo-colonial cyanobacteria) and Diatoxanthin (Diato-diatoms). Lines separate the zones established from k-means cluster analysis of pigments.

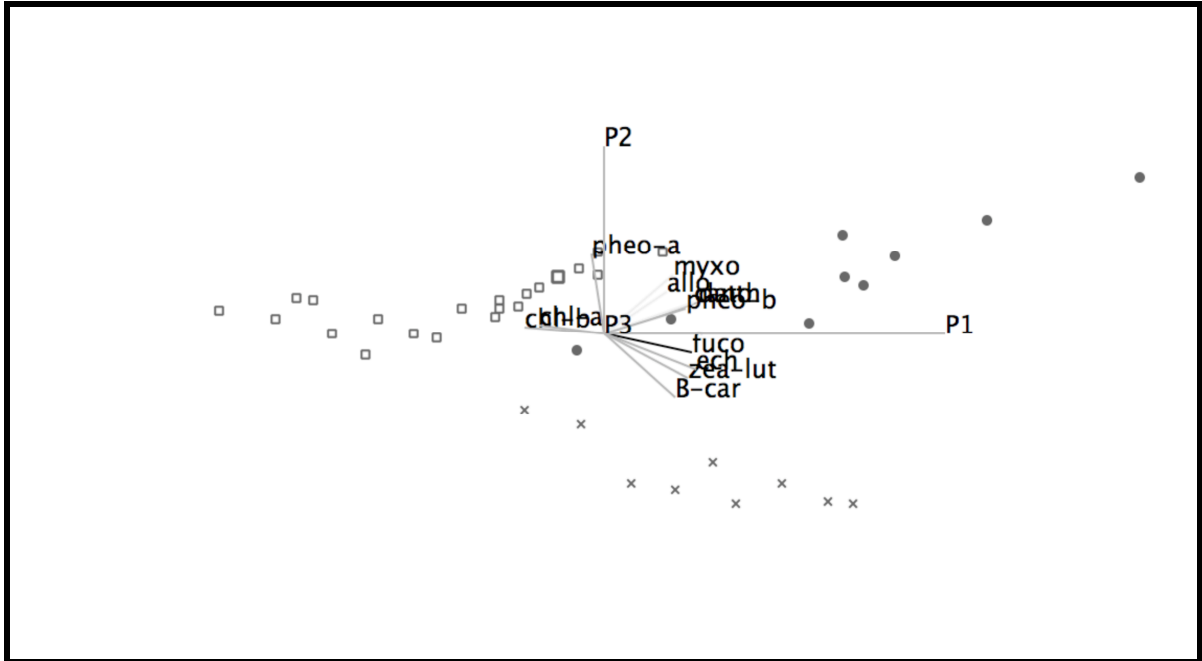


Figure 4.5. Scatterplot of principal components 1 (PC1) and 2 (PC2) showing correlations with sedimentary photosynthetic pigments. Percent of variance represented by PC1 and PC2 is 45.8% and 25.3%, respectively. Zones determined by k-means cluster analysis are I (x), II (●) and III (□).

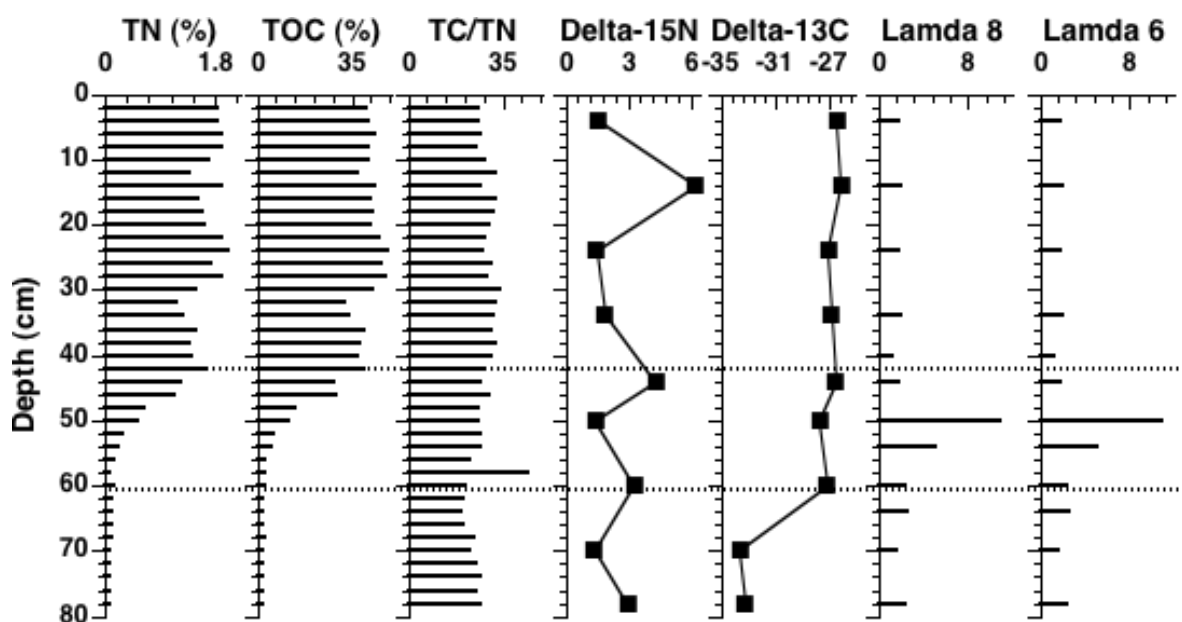


Figure 4.6. Paleolimnological proxies measured on the organic fraction of Pungo Lake sediments. Stable isotope units are per mil (‰), and lignin oxidation product concentrations (Lamda 8 and 6) are reported as mg lignin/100 mg organic carbon. Dotted lines indicate sediment zones separated by K-means cluster analysis using sedimentary photosynthetic pigments.

Table 4.3. Lamda concentrations and lignin oxidation product ratios (mg/100 mg organic carbon) measured on Pungo Lake sediments following CuO oxidation. Standard deviations for replicate samples are shown in parenthesis.

<u>Depth (cm)</u>	<u>Lamda-8</u>	<u>Lamda-6</u>	<u>Ad/Al_v</u>	<u>Ad/Al_s</u>	<u>C/V</u>	<u>S/V</u>
4	1.8 (0.06)	1.4 (0.05)	0.52 (0.01)	0.64 (0.2)	0.44 (0.01)	0.35 (0.03)
14	1.9 (0.02)	1.5 (0.04)	0.54 (0.02)	0.44 (0.05)	0.31 (0.02)	0.34 (0.01)
24	1.9 (0.01)	1.4 (0.02)	0.59 (0.03)	0.46 (0.03)	0.41 (0.02)	0.37 (0.04)
34	1.9 (0.05)	1.4 (0.03)	0.58 (0.01)	0.46 (0.01)	0.42 (0.01)	0.36 (0.01)
40	1.3 (1.5)	1.0 (1.2)	0.56 (0.03)	0.44 (0.01)	0.34 (0.02)	0.34 (0.01)
44	1.9 (0.1)	1.4 (0.07)	0.59 (0.04)	0.44 (0.04)	0.42 (0.06)	0.41 (0.02)
50	11 (2.0)	7.3 (1.3)	0.88 (0.08)	0.64 (0.05)	0.67 (0.02)	0.41 (0.01)
54	5.1 (1.8)	3.4 (1.2)	0.73 (0.08)	0.57 (0.04)	0.70 (0.02)	0.43 (0.01)
60	2.3 (1.5)	1.6 (1.1)	0.57 (0.05)	0.44 (0.09)	0.69 (0.06)	0.48 (0.06)
64	2.6 (1.3)	2.1 (1.0)	0.36 (0.02)	0.32 (0.07)	0.37 (0.02)	0.50 (0.02)
70	1.6 (0.42)	1.4 (0.4)	0.26 (0.02)	0.24 (0.02)	0.23 (0.01)	0.52 (0.06)
78	2.4 (1.0)	2.1 (0.9)	0.24 (0.01)	0.21 (0.02)	0.22 (0.02)	0.53 (0.02)

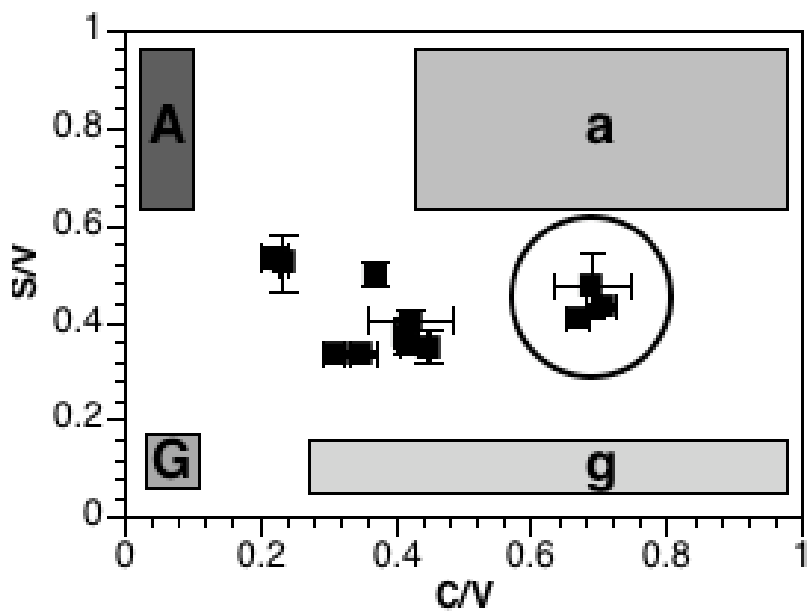


Figure 4.7. Ratios of lignin derived oxidation products from the Pungo Lake piston core. Axes are for lignin ratios of cinnamyl/vanillyl (C/V) and syringyl/vanillyl (S/V). Also plotted are compositional ranges for different vascular plant endmembers (data from Goni and Hedges, 1992; Goni and Thomas, 2000) with a's representing angiosperms, g's representing gymnosperms, uppercase representing woody material and lowercase representing non-woody material. Error bars represent one standard deviation from replicated samples. The circle encompasses the sediments from Zone II.

CHAPTER V. SUMMARY

Shallow lake ecosystems are unique environments that can dramatically respond to human and environmental perturbations. Unfortunately, paleolimnological investigations of shallow lakes are uncommon due to the difficulty in identifying premier coring areas. Variable soft sediment patterns (Whitmore et al., 1996) and lack of depositional areas create difficulties in collecting sediment cores that preserve an intact historic record. In addition, wind resuspension of sediments as well as light reaching surface sediments create conditions where proxy preservation can be compromised. The cores collected for this research utilized extensive soft sediment surveys and water depth surveys to determine optimal coring conditions. Although seasonal and short term changes in the lakes were not resolved, these cores were useful in recording historic shifts in lake trophic state and primary producer community structure changes. This research reconstructed historic primary producer communities in response to environmental and human impacts in Lake Mattamuskeet and Pungo Lake, North Carolina. Also, results and inferences were compared to nearby Lake Phelps, a lake currently experiencing clear water, oligotrophic conditions with sandy sediments.

CURRENT STATES OF THE LAKES

Lake Mattamuskeet, Pungo Lake and Lake Phelps currently exist as hypereutrophic, dystrophic and oligotrophic systems, respectively. Lake Mattamuskeet supports distinct

primary producer communities in each basin of the lake with macrophytes dominating the east side and phytoplankton dominating the west. These two communities have existed since 1942. Pungo Lake is a dystrophic system possessing extensive amounts of allochthonous carbon throughout the water column. This particulate and dissolved organic carbon attenuates light and limits primary productivity. Lake Phelps is a clear water system with minimal light attenuation from either primary producers or allochthonous carbon. Lake Phelps contains sandy sediments throughout the lakebed and can experience periods of benthic algal growth. The three different lake types are quite surprising given their similarities in climate, geography and land use. All three lakes exist within the same geological area as well as experience similar wind and precipitation patterns. Aside from the attempted drainage of Lake Mattamuskeet, similar human impacts have affected each lake including canal construction, decreased forested catchment area, water level maintenance and agriculture. As a result, the primary objective of this research was to identify historic perturbations that caused change in primary producer community structure and organic matter inputs into the lakes. The cores presented here represent late Holocene sediments and recorded human, climatic and other environmental alterations to these lakes. Paleolimnological proxies were used to track lake and catchment change with the primary response variable being total algal abundance and primary producer community structure as inferred from sedimentary photosynthetic pigments.

CORE LITHOLOGY

The Lake Mattamuskeet and Pungo Lake cores both contained organic sediments in the top of the cores. For both lakes these sediments corresponded to the period of intense

human impacts on the lakes. Below these areas both cores gradually decreased in organic material until sediments consisted of primarily sand. This transition period for both cores represented the Little Ice Age and contained a different type of lignin than sediments above and below the transition zone. The sandy sediments for both cores contained low concentrations for most proxies measured. Likewise, these sandy sediments also occurred throughout the entire Lake Phelps core. Below these sandy sediments, long vibracores contained elements of marine environments such as shell material. Even though marine sediments were obtained from each lake, this research was unable to resolve information on the origin of these systems from the proxies measured and the cores collected.

CLEAR-WATER PHASES

The sandy sediments occurring in the historic record of each lake suggest that these lakes experienced synonymous periods of high water clarity and low organic matter deposition. This is further supported by LOI (<1%) and low concentrations of nutrients and metals. Lignin deposition was low in these sediments and indicates a lack of input from the terrestrial environment. Pigment concentrations were low for the Lake Mattamuskeet and Lake Phelps cores indicating low algal abundance during this period. Currently Lake Phelps experiences periods of benthic algal growth, which is also believed to have occurred in Lake Mattamuskeet when the sandy sediments were deposited. Bottom sediments in the Pungo Lake core contained moderate pigment concentrations, which resembled pigment concentrations found in Lake Mattamuskeet sediments deposited prior to European Settlement.

The occurrence of a clear water phase for each of these lakes is surprising and unexpected for this research. The lack of organic inputs during these periods demonstrates the importance of understanding shallow lake connectivity with its catchment. Deeper lakes can act as sinks for material entering from the surrounding areas, but shallow lakes tend to reprocess inputs through resuspension and lack of depositional areas. As a result, an understanding of a lake's inputs and catchment constituents can lead to more effective management practices. The lack of nutrient and organic matter inputs influenced the low algal abundance experienced in these lakes.

CLIMATIC EFFECTS

Paleolimnological proxies measured on sediments from Lake Mattamuskeet and Pungo Lake suggest climatic effects on the limnology and catchment of the lakes. In Lake Mattamuskeet, two periods of intense forest fires were recorded in the sediments as distinct charcoal layers (7 and 1535 A.D.). Although these fires had little effect on the limnology of the lake, they did coincide with the periods of Native American and European settlement around the lake. Dry periods have been proposed as contributing to the demise of the Roanoke Colony in previous research using tree-ring chronologies (Stahle et al., 1998), and this research provides independent evidence that periods of dryness were occurring at that time. Furthermore, cores collected from Lake Mattamuskeet and Pungo Lake contain changes in organic matter amount and type corresponding to the climatic period known as the Little Ice Age (1650-1850 A.D.). Specifically, LOI and lignin inputs increased during this period for both cores suggesting increasing hydrological connectivity between the lake and its catchment or increasing vegetation development in the littoral and wetland areas

connected to the lake. Lignin type also changed during this period from those found in woody species to more non-woody lignin oxidation products. This shift could represent a period of increased development of wetland grasses in the lowland areas around the lakes. The Little Ice Age for this area has been described as being wet and cool (Stahle and Cleaveland, 1994). The increase in precipitation would maintain a longer inundated state in the low areas of the peninsula thus supporting wetland plant growth.

Primary producer community structure and total algal abundance also changed during the Little Ice Age. Sedimentary pigment concentrations increased in Lake Mattamuskeet during this period from low levels indicating an increase in algal abundance. Primary producer community structure consisted of algal groups such as diatoms, cryptophytes and cyanobacteria. During the Little Ice Age, Pungo Lake experienced a decrease in total algal abundance but a tremendous increase in algal groups favoring low light environments such as cryptophytes and cyanobacteria. Given the dystrophic nature of Pungo Lake, the increases in these algal groups are believed to reflect increased turbidity and light attenuation in the system during this time. In addition to organic matter, nutrient concentrations also increased in Lake Pungo sediments deposited during the Little Ice Age. These increases in nutrient, organic matter and other elemental inputs are proposed as being the main factors influencing algal abundance and changes in the primary producer community structure.

HUMAN IMPACTS

Paleolimnological proxy data for Lake Mattamuskeet and Pungo Lake confirmed that management and development practices impacted lake trophic structure. Increases in organic

matter and nutrient inputs caused changes in the primary producer community structure with Lake Mattamuskeet developing a eutrophic ecosystem and Pungo Lake becoming dystrophic. For Lake Phelps, surface sediment profiles and a short sediment core suggests that the lake's primary producers have been unaffected by human impacts. Given that the human, environmental and climatic impacts have been similar for these lakes, the different responses are surprising. Although the above-mentioned human impacts have been identified as ecosystem drivers for primary producer community structure, the development of the three different lake types implies other factors are influencing shallow lake trophic status. Possible mechanisms for future investigation are lake size, basin orientation, elevation and atmospheric inputs of nutrients and particulate material.

Most forecasting of shallow lake responses to ecosystem drivers use models incorporating one to two variables (Scheffer, 1997). This research proposes that multiple drivers working in concert instigated ecosystem changes. In Lake Mattamuskeet and Pungo Lake, the canals and land clearance combined to increase organic matter inputs into the lakes as well as change the type of material entering the lake to include nutrients and elements leached from the exposed soils. These drivers caused increased nutrients, turbidity and organic carbon to exist in the water column selecting for algal groups accustomed to low light environments. Sedimentary photosynthetic pigments showed that cryptophytes and cyanobacteria responded in both lakes to increasing organic matter inputs. Pungo Lake decreased in algal abundance over the past decades due to increases in allochthonous carbon in the ecosystem, which attenuated light to the point where algal growth was limited. In addition, Lake Mattamuskeet developed two distinct ecosystems (macrophyte-dominance

and algal-dominance) within the two basins. Differences in nutrient dynamics, hydrology, and lake morphometry are believed to be possible mechanisms for the development and resilience of Lake Mattamuskeet's two states. Furthermore, the phytoplankton-dominated side contained high concentrations of the pigment, aphanizophyll, a proxy for nitrogen-fixing cyanobacteria. These inferences introduce a need for further research investigating the complexities of ecosystem drivers working together to affect resilience and ecosystem state change.

MANAGEMENT

Another objective of this research was to understand historic changes in these shallow lakes so that future management practices would be more effective. Currently, the three lakes studied here are managed for recreational fish and waterfowl by regulating water levels, monitoring waterfowl populations and documenting dominant fish species. Water quality, ecosystem state and primary producer community structure are not monitored nor included in management decisions. The three lakes studied in this research possessed similar historic states, but currently exist as three different lake types. Given this information, several management applications have emerged for these and other shallow lakes.

Photosynthetic pigment analysis proved to be a tenable proxy for lake response to human and environmental stressors in Lake Mattamuskeet and Pungo Lake. Results from sediment core analysis prescribe light attenuation as one of the primary factors of concern in these lakes. The low light availability of Pungo Lake and Lake Mattamuskeet west basin is dramatically different from the clear water conditions of Lake Mattamuskeet east basin and

Lake Phelps. Traditionally, light attenuation has been measured using Secchi disc depth and light meters. Although these methods have proven useful in deep lakes, the effects of wind, water depth and sediment resuspension complicate these measurements with characteristics that change on a daily basis. As a result, this research proposes that long-term light attenuation state be inferred from algal pigments of species known to exist in low light environments. Specifically, alloxanthin, a proxy for cryptophytes, and myxoxanthophyll, a proxy for cyanobacteria, need to be measured six times a year for each lake. These measurements would provide critical assessment of the ecological state of the lake in regards to light attenuation rather than daily responses to current weather conditions.

Like light attenuation, the construction of the extensive canal systems and water control structures correspond to historic increases in nutrients and organic material into these lakes. As a result, a detailed hydrological budget for each lake needs to be established. Factors shown to affect primary producer community structure in shallow lakes are usually related to the hydrology of the system. Wind resuspension, water depth, nutrient inputs, nutrient exports, disturbance of sediments by fish and flushing rate are linked to the hydrological processes within the system (Scheffer, 1998). Benkert (1990) constructed a hydrological budget for Lake Mattamuskeet and Pungo Lake stating that ground water inputs were minimal, but follow up research on the two basins of Lake Mattamuskeet and Lake Phelps has not been conducted. With the existence of the four different ecosystem states currently in the lakes and the importance of flushing rate on shallow lake primary producer community structure, separate hydrological budgets need to be established for the four basins in order to determine the relationship between hydrology and biogeochemical processes.

Hydrological differences could explain the differences among these three lakes given that they share climatic, land-use and geographical conditions.

The Albemarle/Pamlico peninsula lakes are unique and shallow lake environments. They are valuable ecosystems both to wildlife and migratory waterfowl. This research uncovered historic changes in these lakes in response to climatic and human impacts. Future change is occurring in the area including increasing land clearance, industry and proposed military bases. It is uncertain what effects these alterations will have on the lakes, but an increased monitoring program and focus on understanding their ecology will benefit the successful management of these valuable ecosystems.

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