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THE HISTORY OF WATER QUALITY IN NORTH CAROLINA
ESTUARINE WATERS AS DOCUMENTED IN THE STRATIGRAPHIC RECORD

by
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ABSTRACT

A paleoecological approach makes it possible to define the naturally occurring state of an ecosystem against which human influences can be measured. For this research, sediment cores were collected from the Neuse and Pamlico River estuaries at 7 different sites. The sediments from these cores were dated using ^{210}Pb , ^{137}Cs , radiocarbon and pollen horizon techniques. Other paleoecological data were collected and analyzed to re-create the history of water quality and diatom assemblages in these estuaries through time. Specific parameters investigated include bulk density, sedimentation rates, nutrient and trace metal flux, bottom water oxygenation, vegetation changes as recorded in the pollen record, and diatom assemblage changes. Results indicate that the greatest increases in sedimentation, nutrient and metal flux, and diatom assemblage changes have occurred in the past 30-50 years in the Pamlico and Neuse estuaries. These results are different from those found in a similar study of the Chesapeake Bay.

(key words: sediment, paleoecology, history, diatoms, pollen, geochemistry, water quality, eutrophication, anoxia, radioisotopes)

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SUMMARY AND CONCLUSIONS

A two year study of sediment cores collected from the Pamlico and Neuse River estuaries has been completed. The purpose of this paleoecological study was to begin to re-create the history of water quality in these estuaries by dating sediment core samples and analyzing indicators of water quality, nutrient and trace metal flux, and diatom assemblages through time. We also analyzed the stratigraphic record of pollen found in the sediments for dating purposes. The results indicate that this type of study is not only feasible in these estuarine systems but also very useful. Sediment chronologies have been developed for the sediment cores collected, and the resolution of each 2-cm increment of each core varies from less than 1 year in recent sediments to 36 years in older sediments. Average sedimentation rate in the past 50 years is 0.65 cm yr⁻¹. Sedimentation rates have generally increased three to 10-fold in the past 50 years over previous sedimentation rates based on the data and the models used.

Results show that nutrient, metal and sulfur flux to the sediments has increased over the past 50 years. Trace element analyses show that surface sediments often contain heavy metal concentrations that exceed "Threshold Effects Levels" (TEL) as reported by the U. S. Environmental Protection Agency. Cadmium shows highest levels in the Pamlico estuary at the core collection site nearest the phosphate mining operations. Most other metals show higher concentrations in the Neuse River estuary.

Diatom valves and pollen grains are well preserved in the sediments of the Neuse and Pamlico. For example, samples analyzed to date from the Pamlico River estuary contain diatom valves in abundances of about 1 to 5 million valves per cubic cm of wet sediment, and pollen grains are present in abundances of about 50,000 to 500,000 per cubic cm of wet sediment. Over 430 diatom species have been identified from subsampled intervals of the Pamlico and Neuse sediment cores to date.

Diatom and pollen assemblages have changed through time. The most dramatic assemblage changes in the diatoms appear to have occurred in the past 30-50 years in the Pamlico and Neuse estuaries, possibly associated with industrial activity, increasing population, and land-use changes. Recent assemblages are composed of higher abundances of small planktonic taxa that are often found in large blooms in higher nutrient waters. These samples exhibit relatively low species richness and diversity compared to older (pre-1950) samples. Older diatom assemblages are composed of more benthic and epiphytic taxa. Changes likely reflect eutrophication, increased turbidity and sedimentation, and increased freshwater flow to the estuaries, as well as an increase in industrial activities. They may also reflect declines in submerged aquatic vegetation in these estuaries. Overall trends are similar to those found in the Chesapeake Bay, although the time frame of major changes is different. Similar changes began to occur much earlier in the Chesapeake. Pollen assemblage changes include an increase in ragweed pollen over the past several hundred years signifying increased land disturbance by humans. Pollen count results also show an increase in nut tree pollen (walnut and pecan) over the last several hundred years and an increase in sweetgum tree pollen in the past 50 years.

The biogenic silica (BSi) results and the determination of diatom valve flux to the sediments both show that more diatom frustules are being deposited to the sediments in recent years. BSi is primarily a measure of diatom frustules, which are composed of biologically

deposited silica. These results indicate higher diatom production, most likely due to increased nutrient inputs to the estuaries. As production increases, dissolved silica in the waters may become limiting, especially if diatoms frustules are preserved in the sediments and not recycled. As silica becomes limiting in the water column, diatoms may be out-competed by other algal species, including dinoflagellates. Diatoms are generally better food sources in the estuarine food web than other algal species, so this change could potentially cause problems in higher trophic levels.

Understanding the historical processes of water quality problems is important for managing the continuing impacts of growing populations in North Carolina. These data are useful for providing information on historical changes in estuarine water quality and realistic goals for management.

RECOMMENDATIONS

- Human impacts on estuarine water quality are evident, especially over the past 30-50 years, and should continue to be addressed.
- Sedimentation rates and nutrient and trace metal flux to both the Pamlico and Neuse estuaries appear to have increased in the past 30-50 years. Trace metal levels in surface sediments exceed “Threshold Effects Levels” as reported by EPA at several sites. Efforts should continue to be made to reduce sediment, nutrient and metal inputs to the estuaries.
- Industrial sources are apparently responsible for some of the increase in nutrient and trace metal accumulations in estuarine sediments. This influence appears to be substantial, and should continue to be monitored.
- Population trends and land clearance also appear to have influenced sedimentation and water quality in the estuaries and appear to be more significant for the Neuse. Careful planning and management of development should be a priority for local and state government.
- Preliminary results indicate that hypoxic and anoxic bottom waters can most likely be reduced in the Pamlico with proper management of nutrients and sedimentation.
- Diatom assemblages have changed significantly in the past 10-50 years. These changes may be related to eutrophication, increased turbidity, loss of submerged aquatic vegetation, and increased freshwater flow to the estuaries. Continued monitoring of water quality and algal species would increase our understanding of linkages and aid in management.
- The time frame of water quality changes seen in the Pamlico and Neuse estuaries occurs more recently than similar changes in the Chesapeake Bay. These differences may be due to several factors, including slower population growth, different land use near the estuaries, and the geomorphology of the estuaries. This may indicate that proper management could reverse trends in water quality changes more quickly for these estuaries than for the Chesapeake Bay.

INTRODUCTION

The Pamlico Sound is the largest sound formed behind barrier beaches along the Atlantic coast of the United States and the second largest estuarine system in the United States. The two largest tributaries along the western shore of the Pamlico Sound are the Pamlico River and the Neuse River. The combined drainage area of these two estuarine systems is over 25,000 square kilometers. Surface area of these systems is large, but the depths are shallow (Table 1). Pamlico Sound is connected with the Atlantic Ocean through several relatively small openings in the Outer Banks. This limited access results in dampened ocean tides (less than 6 cm) except near the inlets. Wind-driven tides are often dominant over lunar tides in both the sound and adjoining tributary systems. Salinities in Pamlico Sound decrease from around 30 ppt near the inlets of the barrier islands to about 15 ppt in the surface waters at the mouths of the Pamlico River and Neuse River estuaries. Seasonal salinity patterns are influenced by variations in freshwater flow, while wind velocity and direction are the dominant short term influence on salinity patterns. Residence time for water in the Pamlico estuary averages about 24 days and varies between 10 days and 2 months depending on freshwater flow (Stanley 1992). The Neuse River residence time is on the order of 2-6 months.

Table 1. Hydrologic data for Pamlico Sound and estuaries (excerpt from Stanley 1992).

Area/location	Drainage area (km ²)	Surface area (km ²)	Volume (km ³)	Average depth (m)
Pamlico Sound	27,092	5,335	26	4.9
Pamlico River estuary	11,137	582	0.82	3.4
Neuse River estuary	14,499	394	1.34	3.6

There are many recent concerns about water quality in these North Carolina estuaries. Eutrophication, low oxygen, algal blooms, toxic algae, shellfish bed closures, decline of submerged aquatic vegetation, and declines in fisheries are just some of the issues. Many of these problems with water quality have not been monitored historically. Therefore causes and consequences of both point source pollutants and land use changes related to water quality are not well understood. Understanding the processes surrounding these problems is important for managing the continuing impacts of growing populations (NRC 1993, Jonge *et al.* 1994).

An alternate source for historical information lies in the stratigraphic record of depositional environments, which is accessible through the use of paleoecological methods. Paleoecology is the study of relationships between past organisms and the environment in which they lived. It is concerned with the reconstruction of past ecosystems by using all available evidence, including biological, chemical, and geological contributions (Birks & Birks 1980).

A paleoecological approach makes it possible to define the naturally occurring state of an ecosystem against which human influences can be measured (e. g., Bradbury & Waddington 1973, Dixit *et al.* 1992, Håkansson & Regnéll 1993, Cooper 1995a, 1999). This has direct bearing on the debate concerning the primary factors contributing to declining water quality in estuaries and for hindcasting of models from which predictions about the effects of future environmental change

on the ecosystem can be made. This approach has played an integral part in providing scientific background for Chesapeake Bay watershed management plans (Brush *et al.* 1979, Brush & Davis 1984, Brush 1986, Cooper & Brush 1991, Harding *et al.* 1992, Mountford 1992, Cooper 1995a).

PURPOSE AND OBJECTIVES

This research was undertaken in order to investigate the feasibility of using paleoecological methods (including dating techniques and analyses of geochemical and biotic indicators of water quality) to study the stratigraphic records of the Neuse and Pamlico estuarine systems of North Carolina. These data are used to begin to re-create the history of water quality and diatom assemblages in these estuaries through time. Specific water quality parameters investigated include eutrophication (nutrient flux), selected trace metal flux, sedimentation rates, bottom water oxygenation, and benthic vs. pelagic habitat quality.

The results of this work help to elucidate mechanisms by which different human activities and land uses are affecting North Carolina estuarine water quality. For example, there are no published data on phytoplankton-related studies in the Pamlico River estuary before 1966 (Mallin 1994), which is after phosphate mining and effluent discharge to the estuary began in 1964 (Copeland & Hobbie 1972). This study documents effects of phosphate mining on the sediment chemistry and diatom assemblages in the Pamlico River estuary, as well as other historical land use and anthropogenic effects on both the Pamlico and Neuse estuarine systems. This research will allow interpretation of land use and anthropogenic input effects, and comparisons between estuarine ecosystem responses. This type of paleoecological study has been done in the Chesapeake Bay, and has provided important data and new perspectives on recent research and ongoing monitoring (Cooper 1995a). Some questions related to temporal scales of water quality issues within the system can be answered only with the use of paleoecological techniques and the study of sediment stratigraphy.

Indicators

There are several important indicators commonly used in paleoecological studies such as plant and animal fossils, sediment characteristics, and sediment composition (sediment chemistry). Fossil indicators used for assessing eutrophication, nutrient availability, light availability, and sedimentation rates include diatoms and pollen (e. g., Dixit *et al.* 1992, Birks & Birks 1980, Brush 1984, 1989). Some geochemical parameters that provide information on nutrient loading, primary productivity and oxidation potential include total organic carbon (TOC), total sulfur (S), the degree of pyritization of iron (DOP), total nitrogen (N), total phosphorus (P) and biogenic silica (BSi). Other indicators such as algal pigments, seeds, phytoliths, charcoal (as an indicator of fire history), chrysophyte and dinoflagellate cysts, foraminifera, ostracodes, and fish otoliths can be analyzed from sediment cores to investigate other aspects of estuarine ecosystem response to change.

Diatoms. Diatoms are unique forms of algae, particularly useful for paleoecological research because they grow a silica shell or exoskeleton (frustules), the morphology of which is species specific. They are preserved, after the cell dies, as fossil evidence in the stratigraphic record. Modern diatom taxonomy is based on frustule characteristics, and therefore a fossil diatom of good preservation can be identified as accurately as a living one. Diatoms are abundant in aquatic environments, generally cosmopolitan in distribution, and have a fairly well studied taxonomy and ecology (Reid *et al.* 1995, Stoermer & Smol 1999). The abundance and

composition of diatom assemblages are determined by the interaction of many environmental factors, including light availability, temperature, salinity, nutrient availability (e. g. P concentration), pH, and pollution (Patrick 1965, 1973, Brush & Davis 1984, Birks *et al.* 1990, Juggins 1992, Nelson & Kashima 1993, Anderson *et al.* 1993, Bennion *et al.* 1996, Cooper *et al.* 1999, Stoermer & Smol 1999). Presence or absence of individual species and diatom assemblages can therefore be interpreted as indicators of eutrophication, climate changes (sea level and precipitation), land clearance (turbidity), pH, and salinity changes (e. g. Cooper 1995a, 1999). Diatom assemblages can also be used to assess changes in benthic vs. pelagic environments, since different species indicate specific habitats. Responses of diatom communities to different land use patterns can show which historical periods or events have shaped changes to the North Carolina estuarine ecosystems.

Geochemistry. TOC in sediments is an indicator of the accumulation of organic matter and is positively related to benthic oxygen demand in estuaries. Preservation of organic matter reflects the balance between initial input with deposition and loss due to bacterially mediated decomposition. Phytoplankton of all types contribute to the organic carbon component of sediments and consume oxygen as they decay. Increased nutrient input contributes to the excess growth of phytoplankton, which causes further depletion of bottom water oxygen. Unless buried with sediments under anoxic conditions, organic carbon is more quickly oxidized and consumed by detritus-feeding organisms and bacteria. Total N and total P provide additional information on nutrient loading of coastal waters and sediments, and BSi measurements indicate diatom and other siliceous organism burial.

Silica may become the limiting nutrient for diatom growth in eutrophic estuaries. As diatom abundance increases, sedimentation and preservation of BSi (diatom frustules) occurs, limiting recycling of the silica (Conley & Malone 1992, Dortch & Whitledge 1992, Conley *et al.* 1993). Silica depletion may cause major changes in species composition and ultimately affect trophic interactions as well as other ecological and biogeochemical changes. Fraser & Wilcox (1981) and Biggs & Cronin (1981) characterize estuarine systems in general as a sink for soluble silica during low discharge and high primary productivity. These two criteria are often met in the Neuse and Pamlico.

The geochemistry of silica is important to understanding preservation of diatom frustules in sediments, as well as its role in the growth of diatoms. Most of the amorphous silica (BSi) found in the sediments of estuaries is in the form of diatom frustules. Other organisms that contribute to BSi found in the sediments include silicoflagellates, radiolarians and sponges, which are rare in estuarine waters. BSi can be a good estimate of diatom silica in sediments (Schelske *et al.* 1986, Conley 1988, Cooper 1993, 1995a), but a linear relationship between BSi and diatom abundance is not necessarily expected because of the large size range and variable silica content of different diatom species within samples.

Total S content of the sediments is an indication of the oxic/anoxic environment at the time of deposition. Under anoxic conditions, sulfate is reduced by anaerobic bacteria to sulfides, which are more likely to be incorporated into the sediments through combination with metals than the highly soluble sulfate. Sulfate-reducing bacteria are widely and abundantly distributed in marine (and estuarine) sediments. At higher sedimentation rates, the S cycle is more insulated

from the water column and sulfide mineral species are more likely to be preserved in the sediments. Under eutrophic conditions, concentrations and reactivity of TOC are increased, oxidants are consumed at a higher rate, and the geochemical environment changes. This change is expressed in the sulfide minerals as part of the authigenic mineral suite.

A chemical method for recognizing the degree of bottom-water oxygenation at the time of deposition in organic bearing sediments has been developed by Raiswell *et al.* (1988). The method uses the parameter "degree of pyritization of iron (Fe)" (DOP), which is the ratio of pyritic iron (Fe associated with pyrite) to acid-soluble Fe plus pyritic Fe. Raiswell *et al.* report that values associated with aerobic samples ($DOP < 0.42$) can be clearly separated from restricted samples ($0.46 < DOP < 0.80$), but that restricted and inhospitable ($0.55 < DOP < 0.93$) categories overlap. This method depends on relatively simple analytical methodology and has been reviewed for its applicability in more recent sediments by Middleburg (1991). This method may not detect changes that occur on a short term or seasonal basis. However, an estimate of DOP was used to show evidence of increasing hypoxia and anoxia in sediments from Chesapeake Bay, where anoxic bottom waters are a seasonal occurrence (Cooper & Brush 1991, 1993, Cooper 1995a). There has been recent debate as to the validity of this measure in estuarine sediments related particularly to Fe availability. These data are included for completeness.

Algal pigments. Algal pigments including fossil carotenoids, chlorophylls and their derivatives can be analyzed by high performance liquid chromatography (HPLC) from sediment sample extracts. In the Neuse and Pamlico River estuaries, the dominant algal groups are represented by diatoms, dinoflagellates, and cryptophytes (Mallin *et al.* 1991). In addition, cyanophyte (blue-green algae) blooms have been a problem in the Neuse River estuary at times (Paerl 1987, Mallin *et al.* 1991). Fossil pigments are promising paleoecological indicators that can discriminate between most major algal groups, including diatoms, dinoflagellates, cryptophytes and cyanobacteria (Leavitt & Findlay 1994, Leavitt *et al.* 1989, Leavitt pers. comm.). Pigment analysis of sediments allows a quantitative measure of algal production as well as a comparison of relative contributions of different algal groups in re-creating the history of changes through time. Among cyanobacterial paleopigments, it is possible to differentiate between N-fixers and filamentous types (Leavitt & Findlay 1994, Leavitt, pers. comm.) This information would be very useful in the North Carolina estuaries for re-creating space and time differences in abundance, productivity and dominance of particular groups.

PROCEDURES

Sediment Core Collection and X-rays

Sediment cores were collected using a modified Livingstone piston-coring device (Wright *et al.* 1965). Selection of sites was based on personal communications (Dr. Stanley Riggs, ECU 1997; Dr. Lawrence Benninger, UNC 1997; Dr. Jesse McNinch, UNC 1997) as well as reports of sedimentation, circulation, and monitoring of bottom water oxygen in the estuaries (Bales & Robbins 1995, Robbins & Bales 1995, Treece 1993, Riggs *et al.* 1992, Garrett 1992, 1994). X-rays of cores before extrusion were done at Seaboard Radiology, Washington, NC, with GE phototiming at 80 kV and 300 mA (at the chest board). All cores were extruded and sectioned every 1-2 cm, and stored in airtight plastic bags in the dark at 4°C.

Bulk Density and LOI

Bulk density of sediments was determined immediately following extrusion and subsampling of the sediment cores. Bulk density was determined by drying one ml of wet sediment (pre-weighed) in a 70°C drying oven for at least 24 hours or until the final mass had stabilized and dividing the dry sample mass by the initial wet volume of sediment. Water content was determined by subtracting the dry mass from the wet mass of each sample. Loss on ignition (LOI) was determined by placing the dried sediment in a muffle furnace at 450°C for at least 24 hours and comparing mass.

Dating of sediments

Dating of sediment cores was accomplished through a combination of methods, the most reliable and accessible including radiocarbon dating of sediments deposited before European settlement (within the range of 500 to 50,000 years), ²¹⁰Pb dating (within the range of 100-150 years), and ¹³⁷Cesium (Cs) for recent sediments (\cong 30 years) (Schelske *et al.* 1994, Binford 1990). Pollen dating techniques were used for determination of the agricultural horizon and sedimentation rates between dated horizons (Brush *et al.* 1982, Brush 1984, 1989).

For ²¹⁰Pb and ¹³⁷Cs, sediments were dried, ground and sieved, and placed in petri dishes to achieve the same grain size and volume for all samples. In this way the errors due to differences in sediment composition and self absorption should be minimized. The samples were not corrected individually although these calculations were done for several samples to check for consistency (Cutshall *et al.* 1983). The samples were taped and left to equilibrate for two weeks before analysis on an EG&G Ortec planar gamma spectrometer. Each sample was analyzed for 24 hours. Peaks were counted as in Schelske *et al.* (1994), and include ²¹⁰Pb (46.5 keV photopeak), Cs¹³⁷ (661.7 keV photopeak), ²¹⁴Bismuth (Bi) (609.3 keV photopeak), and ²¹⁴Pb (295 and 352 keV photopeaks). ²¹⁰Pb data is corrected for radium activity as calculated from the Bi and other Pb isotope activities. ²¹⁰Pb profiles are then modeled according to a "Constant rate of supply" (CRS) model (Binford 1990). The error estimated for each radioisotope analysis was calculated by propagation of errors associated with sample and background counting rates. Radiocarbon

analyses were done by Beta Analytic, Inc., Miami, FL, primarily by Accelerator Mass Spectrometry (AMS) methods on bulk sediment.

The agricultural horizon was determined by analyzing pollen counts from subsamples of the sediment cores. The *Ambrosia* horizon was determined to be the point in each core where the percent *Ambrosia* pollen dropped to 1% or below, and the pine/ragweed ratio showed a marked increase (these two measures coincide). The date assigned to this horizon for eastern North Carolina is determined to be approximately 1720 A. D. This date is based on population records and estimates (e. g., Cooper 1920, Lefler 1954, Merrens 1964, Watson 1975, Reed 1981, Wood et al. 1989) and consultation with archaeologists and historians in the region (Dr. Peter Wood, Duke 1999, Jeffrey Irwin, Fort Bragg 1999 and Susan Yarnell, Duke 1999, personal communication). The uncertainty in this date is not known. Unfortunately, we ran out of time for counting pollen slides, and therefore can not use pollen concentration techniques in as much detail as we had planned. However, general trends in pollen concentrations agree with other data.

Geochemical procedures

TOC was determined by the method described by Krom & Berner (1983), and involved ashing samples overnight at 450°C. Both dried and ashed sediment samples are measured for % C, N and S on a Perkin/Elmer Series II CHNS/O Analyzer 2400 in the Duke Wetland Center (Carter 1993). All analytical runs performed at the Duke Wetland Center are evaluated using external reference standards (obtained from NIST), procedural blanks, and lab replicates. Sediment digestions for P was done using a nitric-perchloric digestion (Carter 1993), and measured colorimetrically on a Bran & Luebbe TRAACS 800 by ascorbic acid reduction (USEPA 1983). Methods for measurement of BSi in sediments are described in Conley (1988) and utilize a weak Na₂CO₃ base to dissolve BSi in a sediment matrix. Silica measurements are made on a Bran/Luebbe TRAACS 800 autoanalyzer (Bran & Luebbe, Inc. no date). For biogenic silica analysis, four intra-lab quality control samples were obtained from D. Conley (Conley 1998) that were routinely run with samples.

The degree of pyritization of Fe (DOP) has been used as an indicator of bottom water hypoxia and anoxia and requires the measurement of acid-soluble Fe and pyritic Fe (Raiswell *et al.* 1988). Acid-soluble Fe was measured on a Perkin/Elmer Model 5100 PC atomic absorption spectrophotometer, after samples were boiled in concentrated HCl for one minute and diluted in known volume (Berner 1970). Estuarine sediments contain more Fe than can be measured by ICP-MS with other trace metals (see below). Total S content of the sediments, as measured on the CNS analyzer, may be used as an estimate of pyritic S for these coastal sediments to calculate pyritic Fe (see Cooper & Brush 1991).

Trace metals were extracted using HCl and HNO₃, and then analyzed using an inductively coupled plasma-mass spectrometer (ICP-MS). The metals studied include: As, Cr, Cd, Co, Cu, Mn, Mo, Ni, Pb, Th, and Zn. NIST estuarine sediment standards, along with internal drift standards, were used for monitoring the accuracy of results. Accumulation or preservation of all parameters were calculated using appropriate sedimentation rates and bulk density determined for each subsample of the sediment cores.

Algal Pigments

Paleopigments were analyzed by Dr. Peter Leavitt at the University of Regina under Duke subcontract 99-SC-NCSU-1009. Frozen sediments were dried under a hard vacuum (0.1 Pa) for 48 hrs using a VirTis Lyophilizer to remove excess water prior to extraction of lipid-soluble carotenoids, chlorophylls (Chls) and their derivatives. Dried sediments were stored at -80°C in the dark under an inert nitrogen gas atmosphere to prevent oxidation prior to quantification of fossil pigment contents. A known quantity of dried sediments (ca. 100 mg dry weight) was combusted for 1 hr at 500°C, cooled and reweighed to determine the organic content of sediments as weight-loss-on-ignition (Leavitt and Findlay 1994).

Pigments and derivatives were extracted (18 h, 4°C, dark, under N₂) from freeze-dried sediments using a standard mixture of acetone:methanol:water (80:15:5, by vol.; Leavitt et al. 1989). Sediment residues were exhaustively extracted with three aliquots of solvent mixture, extracts filtered (0.22 µm Acropore membrane), and solvents evaporated in the dark using N₂ gas. Dried extracts were stored at -20°C under N₂ in the dark until pigment analysis. Just prior to quantification, pigments were brought to room temperature in the dark and dissolved in a precisely known volume of injection solvent (acetone:ion-pairing reagent:methanol; 70:25:5, by volume) containing 3.2 mg litre⁻¹ Sudan II (Sigma Chemical Co.). This chromatographic dye is an internal standard that has carotenoid-like absorption characteristics ($\lambda_{\text{max}} = 485, 442.5 \text{ nm}$ in acetone), runs at a unique position on the chromatogram, and is used to correct for dilution, injection, and chromatographic errors (Leavitt and Findlay 1994). Ion-pairing reagent (IPR) consists of 0.75 g tetrabutyl ammonium acetate and 7.7 g ammonium acetate in 100 ml water.

Fossil pigments were isolated using a Hewlett Packard (HP) model 1040 HPLC system with HP model 1040 photo-diode array detector and model 1046A fluorescence detector following the reversed-phase liquid chromatography procedure of Leavitt et al. (1989). Briefly, analytical separation was achieved by isocratic delivery (1.5 ml min⁻¹; 21,000 kPa) of a mobile phase A (10% IPR in methanol) for 1.5 min, a linear succession to 100% solution B (27% acetone in methanol) over 7 min, and isocratic hold for 12.5 min. Rainin C-18 columns (10 cm, 5 µm particles) were re-equilibrated by continued isocratic delivery for 3 min, a linear return to 100% A over 3 min, and isocratic supply for a final 4 min.

Pigments isolated from sediments were compared to those from uni-algal cultures of known pigment composition (Leavitt et al. 1989; Leavitt and Findlay 1994) and authentic standards provided by the US Environmental Protection agency. Spectral characteristics and chromatographic mobility were used to tentatively identify pigments from sediments (Leavitt et al. 1989). Normally, analysis of fossil pigments would be restricted to carotenoids characteristic of cryptophytes (alloxanthin), mainly diatoms (diatoxanthin), diatoms with chrysophytes and some dinoflagellates (fucoxanthin), chlorophytes and cyanobacteria (lutein-zeaxanthin), cyanobacteria (echinenone), filamentous cyanobacteria (myxoxanthophyll), and N₂-fixing cyanobacteria (aphanizophyll), as well as the major *a*, *b*, and *c*-phorbins. However, because pigment preservation was exceptionally poor and few undegraded compounds were identified, ecological interpretations were not possible and fossil abundance could not be determined.

Microfossil extractions

Diatoms were extracted using a modification of the method published by Funkhauser & Evitt (1959). This method involves several steps, including use of H₂O₂, HCl, HNO₃ and size fractionation. A measured volume of the diatom residue for each sample was mounted on a glass slide with Naphrax® and at least 300 diatom valves identified (usually more than 400). For statistical purposes, a minimum of 300 diatom valves (two valves constitute a diatom frustule) identified per sample is recommended (van Dam 1982, Sullivan & Moncreiff 1988, Shaffer & Sullivan 1988). Identifications were done using light microscopy (Leitz DM RB with Nomarski optics at 100X), according to available taxonomic references (e. g., Hustedt 1927-1930, 1955, Hendey 1964, Patrick and Reimer 1966, Krammer & Lange-Bertalot 1986-1991, Snoeijs 1993, Cooper 1995*b*, Tomas 1997).

The diatom counts were converted to relative abundances of each species present. The average error associated with the relative abundance of each species when counting 250 diatom valves per sample has been calculated to be about 7.5% (Parsons 1996), and the error will be much less with > 400 valves counted. The average counting error is small relative to the overall diatom analysis, which focuses on dominant taxa and comparisons between samples. Digital images of representative diatoms were collected and archived using a video camera attached to the microscope and image capture hardware and software at the Duke University Wetland Center.

Diatom assemblage diversity was calculated for each sample using Shannon's H' (Shannon &

Weaver 1949):
$$H' = - \sum_{i=1}^s \frac{n_i}{n} \ln \frac{n_i}{n}$$
, where H' is the assemblage diversity, n is the total number of diatom valves counted per sample, n_i is the number of valves of the i -th taxon and s is the total number of taxa in the sample. Diversity, under this definition, is an index of assemblage structure in which it is possible for diversity to increase while species number decreases, if evenness increases. This is the most widely used diversity index in aquatic systems (Washington 1984), and has been used to study the effects of stresses on algal communities in coastal systems (Patten 1962, Hendey 1976).

Centric diatoms (a classification term) are generally planktonic forms in estuarine waters, and pennate diatoms (another classification) are generally benthic, littoral, or epiphytic forms. Centric diatoms are more prevalent in eutrophic waters than pennate diatoms in certain areas (Cooper, 1995*a*, 1999). The centric to pennate ratio (c:p) may therefore be useful in determining changes from predominantly benthic to predominantly planktonic communities (and vice versa), as well as being a possible indicator of eutrophication (Cooper 1993, 1999).

Multivariate cluster analyses using Euclidean distance were performed on the diatom data to identify time periods of major changes in the assemblages. An average-linkage cluster analysis method was used for this study, using all diatom taxa identified. The average-linkage method views the dissimilarity between clusters as the average of the dissimilarities between members of those clusters (Venables & Ripley 1994). This method produced a dendrogram with greater distances between samples when compared to the single-linkage or connected clustering method (Clarke 1993).

Pollen was extracted from sediments following the methods of Faegri & Iverson (1989) and Moore *et al.* (1991). Processing includes KOH to remove organic material, HF to remove silicates and HCl to remove carbonates, followed by acetolysis to stain the pollen. One tablet of *Lycopodium* spike was added to each sample prior to extraction and acetolysis for calculation of absolute pollen concentration (Stockmarr 1971). The extract was suspended in silicone oil and stored. Slides of pollen were prepared using silicone oil. Pollen grains were identified using light microscopy (Leitz Wetzlar at 40X). Counts were made of at least 300 pollen grains per sample, and approximately 500 were counted for many samples. Dinoflagellate cysts and foraminifera were also enumerated from the same slides.

Historical data collection

Historical data was collected from U. S. census records and North Carolina recent and colonial records (e. g., Saunders 1887, Andriot 1993). Additional references were researched for useful historical data related to eastern North Carolina population and land use activities. Research and data collection were focused on the counties immediately adjacent to the estuaries. These include Beaufort and Hyde counties for the Pamlico estuary, and Carteret, Craven and Pamlico counties for the Neuse estuary.

RESULTS

Field collection of sediment cores

On Tuesday, June 3, 1997, we collected sediment cores from the Pamlico River estuary. The coring crew consisted of S. Cooper, G. Dwyer, S. Kim, and M. Madritch. At 7:45 a.m. we left Whitchard's Beach, NC, aboard "Mar-Be-Jon" with Laird Harrington as captain. The weather was overcast, foggy, and cool (about 69°F). Our first stop was at the mouth of Bath Creek, between Markers 1 & 2. Locations of coring sites, water depth at sampling sites, length of cores, and label for each core collected from the Pamlico estuary are shown in Table 2 and Figure 1. Core diameters were 2 or 3 inches, designated as the final number in the core labels.

On Sunday and Monday, July 27-28, 1997, we collected sediment cores on the Neuse River estuary. The coring crew consisted of S. Cooper, D. Jones, S. Kim, and M. Madritch. On Sunday at 1:30 p.m., we left Dawson Creek on the north shore of the Neuse River estuary aboard "Cape Tel" with Jesse McNinch as captain. We got an earlier start on Monday morning. The weather both Sunday and Monday was sunny, humid, and hot (about 93°F). Our first stop was off Oriental, not far from Channel Marker 7. The water was fairly calm at the start, but the breeze picked up with seas becoming 3-4 feet by the time we left the station. Locations of coring sites, water depth at sampling sites, length of cores, and labels assigned to each core collected from the Neuse are shown in Table 2 and Figure 2.

Table 2. Location, water depth and labels given to sediment cores collected from the Neuse and Pamlico estuaries.

Location	Water depth (m)	Core label	Core length (cm)	Latitude	Longitude
Pamlico River:					
Bath Creek	3.35	BC2-3	82	35 27 .01 N	76 49 .19 W
		BC3-2	117		
Channel Marker 4	5.4	M41-3	97	35 24 .44 N	76 45 .51 W
Gum Point		M42-2	135		
Channel Marker 7	4.2	M71-2	138	35 27 .07 N	76 55 .03 W
Maules Point		M72-3	93		
Blounts Bay	3.4	BB1-3	83	35 26 .51 N	76 56 .28 W
		BB2-3	88		
Neuse River:					
off Oriental	6.6	OR1-3	87	35 00 .383 N	76 40 .191 W
near Marker 7		OR3-2	147.5		
off Whitakers Creek	7.01	WP1-2	135	34 57 .413 N	76 47 .905 W
near Marker 9		WP2-3	81.5		
L. Benninger's site	4.04	UNC2-3	82	34 58 .213 N	76 51 .491 W
South of Beard's Creek		UNC3-2	129		

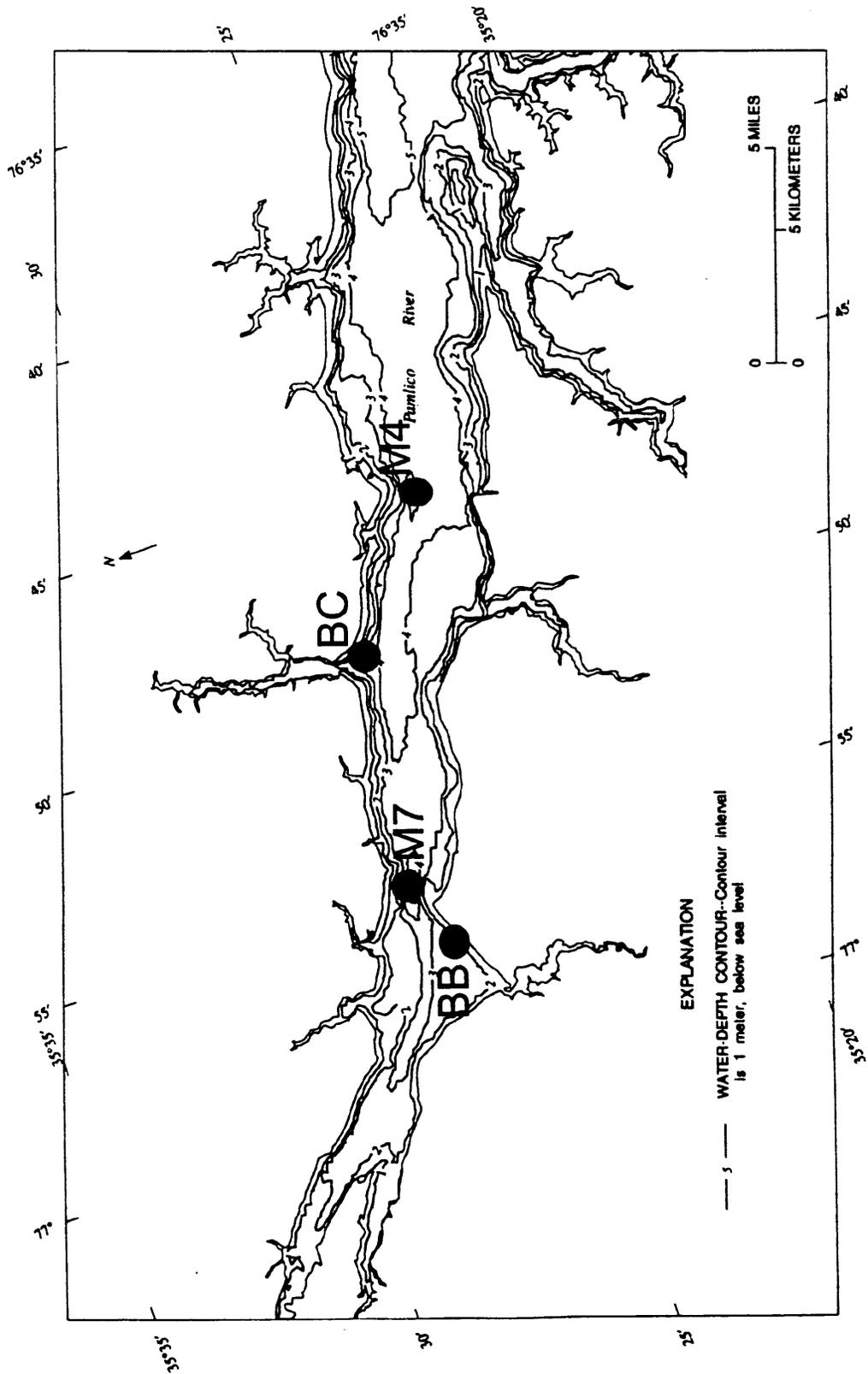


Figure 1. Location of sampling sites in the Pamlico River estuary. Map modified from Bales and Robbins (1995).

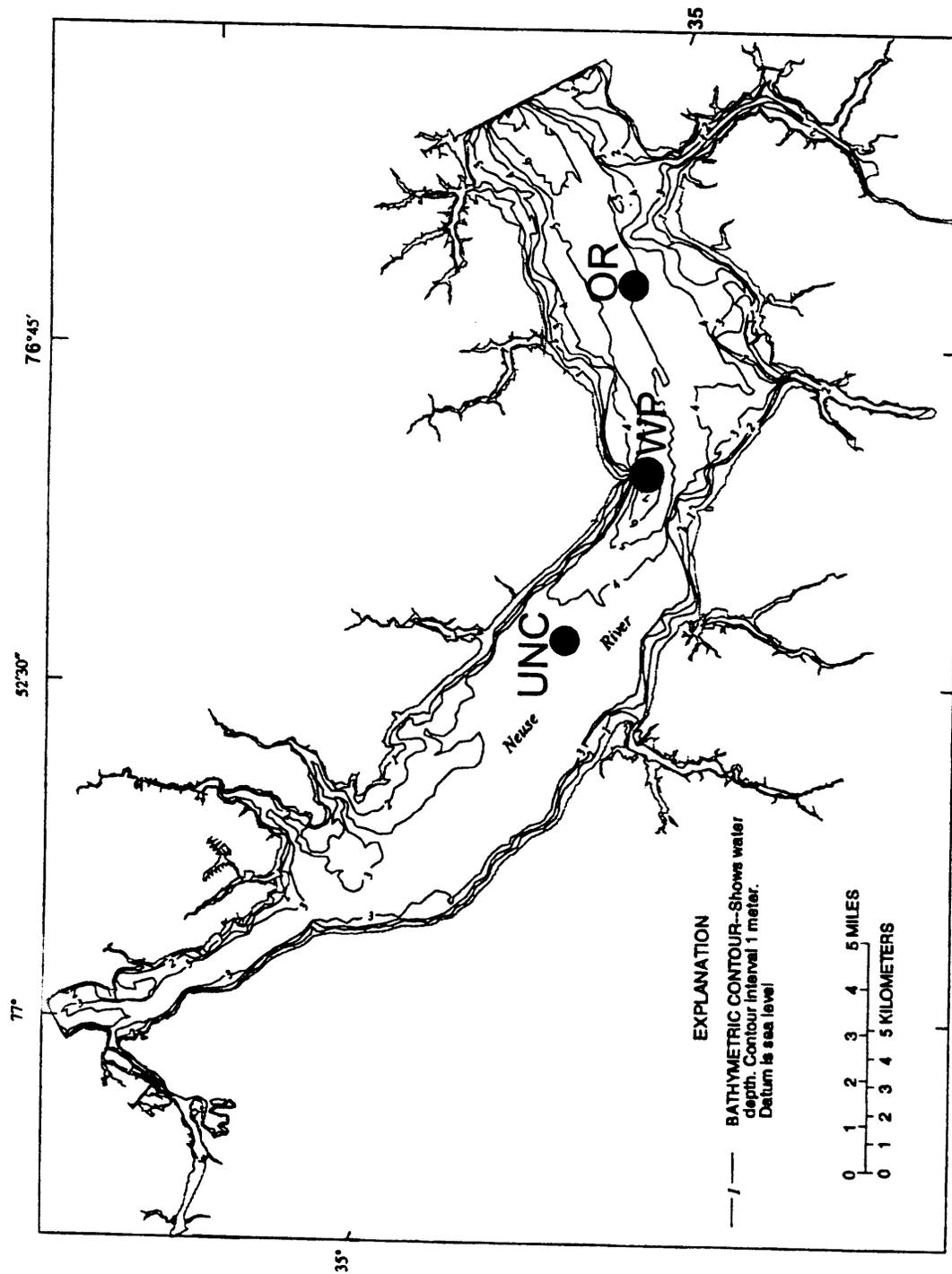


Figure 2. Location of sampling sites in the Neuse River estuary. Map modified from Robbins and Bales (1995).

X-rays of the cores showed uniform stratigraphy for all the cores. The X-rays did not show any significant sand layers, areas of severe mixing, or evidence of deep bioturbation. Extrusion of the sediment cores did not result in any significant compaction. All sediment cores consisted primarily of clay, silt and small sand particles.

The bulk density and LOI of the sediment subsamples were only slightly more variable from the sites in the Pamlico than in the Neuse. Bulk density varied from 0.13-1.73 g cm⁻³ in the Pamlico samples, and from 0.2-1.12 g cm⁻³ in the Neuse samples. LOI (% mass lost on burning) varied from 4.1-26.2 in the Pamlico samples, and from 5.8-24.2 in the Neuse samples. Bulk density and loss on ignition for subsamples from the cores collected at the seven sites are shown in Figure 3. Two core sites in the Pamlico (BC and M7) show a pattern of bulk density at the top of the cores that indicates more mixing of surface sediments or possible periods of excessive sedimentation (possibly due to storm activity), or even scouring. Constant sedimentation in a basin generally results in lower bulk density in the surface sediments, becoming higher as compaction occurs down-core. In the Neuse, core sites WP and UNC show similar bulk density and LOI, whereas core site OR results indicate sedimentation of a higher percentage of inorganic material at this site.

Dating of sediment cores

The results of the ²¹⁰Pb and ¹³⁷Cs dating show clear ¹³⁷Cs peaks and reasonable declines in unsupported ²¹⁰Pb (see Fig. 4 and Appendix A). Total and excess ²¹⁰Pb activity decreased somewhat irregularly with depth (expected with variable sedimentation). The ¹³⁷Cs peak represents a date of approximately 1963 A. D. (Olsson 1986, Sugai *et al.* 1994). The dates derived from the ²¹⁰Pb data according to the CRS model (Binford 1990) agree fairly well with the ¹³⁷Cs data (Table 3). It appears that Cesium may be slightly mobile within the estuarine sediments, as the peak for ¹³⁷Cs was consistently deeper by one to a few cm than the associated ²¹⁰Pb level determined to represent approximately 1963 A. D. by the CRS model.

The CRS model allows for temporal variability in sedimentation rates, but assumes that sediments are not significantly mixed by bioturbation. This assumption is more appropriate at deeper water coring sites than shallow water coring sites. If this assumption is not met, the model may tend to overestimate sedimentation rates in the uppermost sediments that experience surface mixing. Ideally, several models for the ²¹⁰Pb should be used and compared. However, the CRS model was chosen because it allows for temporal variability in sedimentation rates.

Average sedimentation rates for the past 35 years, and range of sedimentation over the past 50 years based on these data are shown in Table 3.

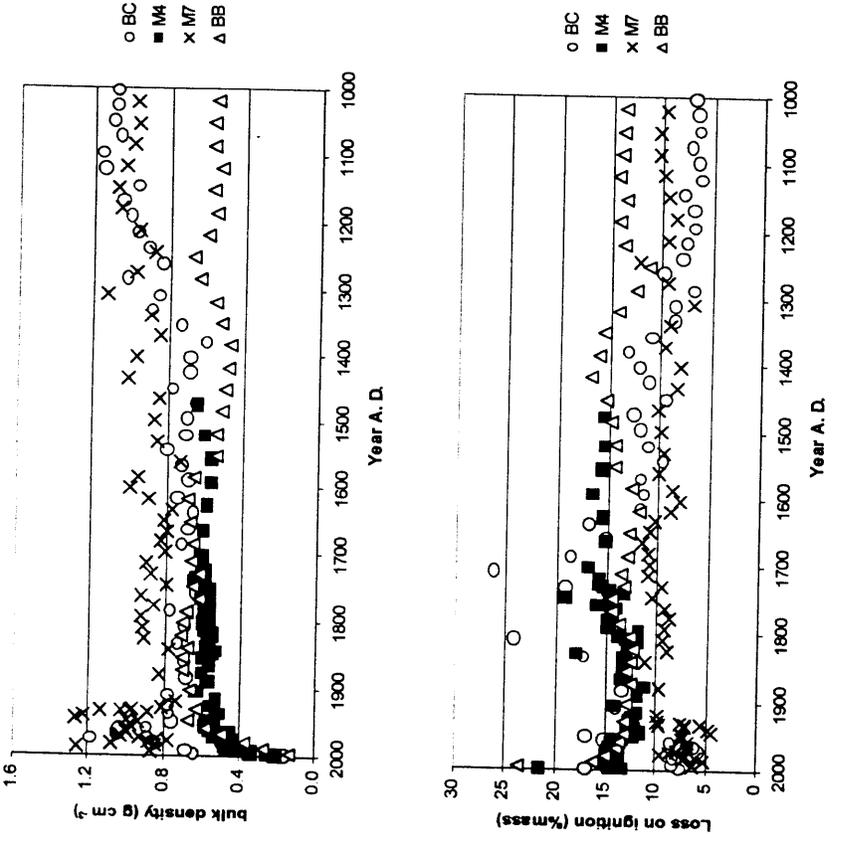
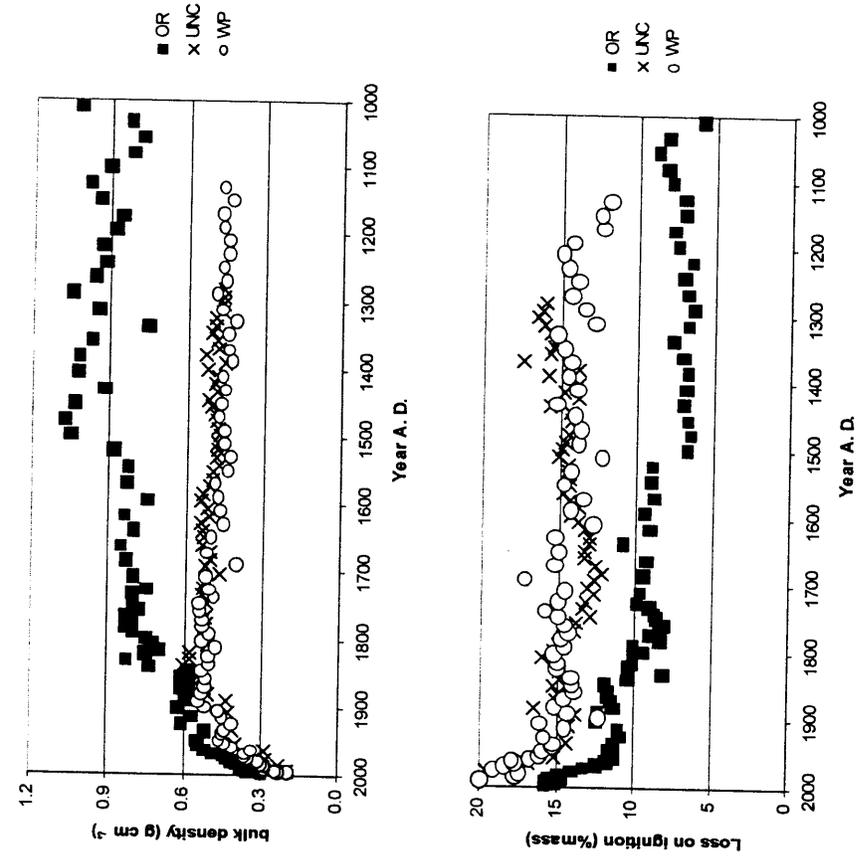


Figure 3. Bulk density and loss on ignition for the Pamlico core sites shown in the left graphs, and the Neuse core sites shown in the right graphs.

Table 3. Depth of ^{137}Cs peak and ^{210}Pb ~1963 A. D. level determined by the CRS model (Binford 1990) for each core site in the Pamlico and Neuse. The average resolution of 2 cm sections or subsamples from each core over the past 35 years and the range in resolution for the past 50 years are also shown.

core location	^{137}Cs peak (~1963 A. D.) depth (cm)	^{210}Pb determined ~1963 A. D. depth (cm)	Average resolution (years per sample) last 35 years	Absolute resolution (years per sample) CRS model last 50 yrs.
Pamlico-BC	16	14	4.7	0.4-16
Pamlico-M4	40	38	1.8	0.5-5
Pamlico-M7	16	13	4.9	0.6-4
Pamlico-BB	10	8	7.9	3-13
Neuse-OR	26	22	2.9	2-9
Neuse-WP	24	20	3.3	2-9
Neuse-UNC	8	7	9.4	6-11

Radiocarbon dates were obtained for a subset of samples including bottom sediments of cores from each site (Table 4). The *Ambrosia* (ragweed) horizon was determined from pollen counts for 6 of 7 sites, and average sedimentation rates calculated from all these dating methods for different depths in the cores from the 7 sites (Table 5). The radiocarbon dates obtained indicate that there is a component of old carbon present in the sediments. The date associated with the depth of the *Ambrosia* horizon (analyzed in three cores) is significantly older than the date assigned to this horizon based on historical data. Benninger and Martens (1983) measured ^{14}C ages of ~1000 years for the organic matter in Neuse River sediments that contained finite ^{210}Pb (half-life = 22 years). These results confirm the expectation that the organic matter flux to the sediments includes both recently produced and aged organic matter. For this reason the radiocarbon dates of the bottom sediments from the cores were not used directly, but the difference between the radiocarbon dates for different depths in the same cores were used to calculate average sedimentation rates between these sample depths for the older sediments. For cores with only one radiocarbon date available, estimates based on other cores in the same estuary were used to determine older average sedimentation rates. In this way, a chronology was developed for each core so that every sample was assigned a sedimentation rate and an average date (Figure 5). These chronologies were used along with bulk density measurements of sediments for calculating and presenting accumulation of all geochemical and biotic indicators extracted from the sediments.

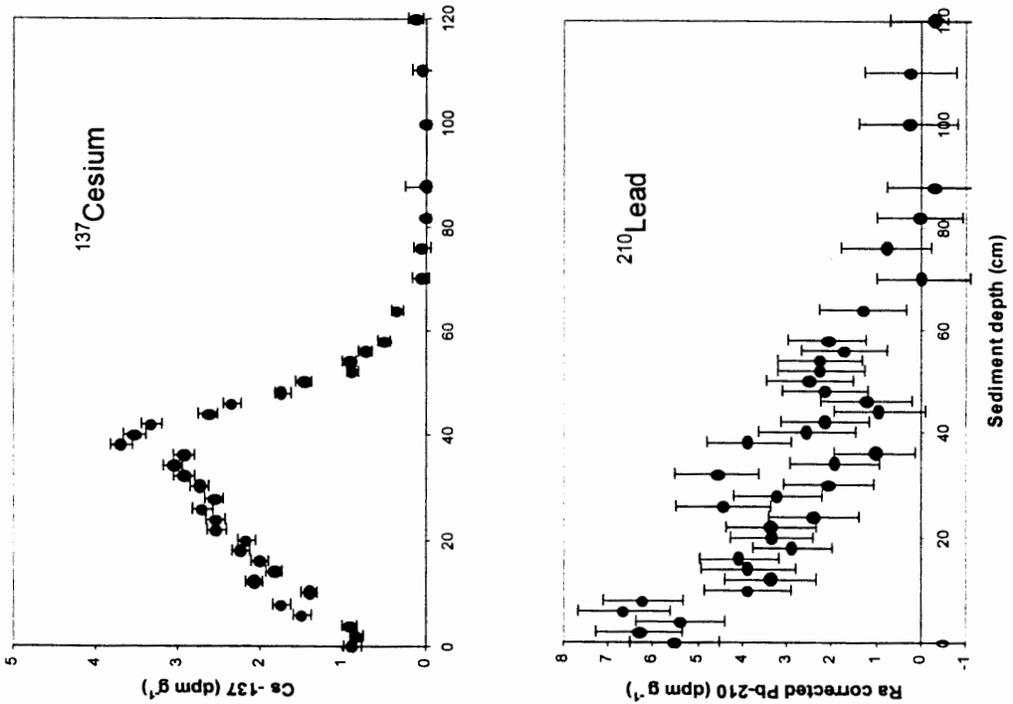
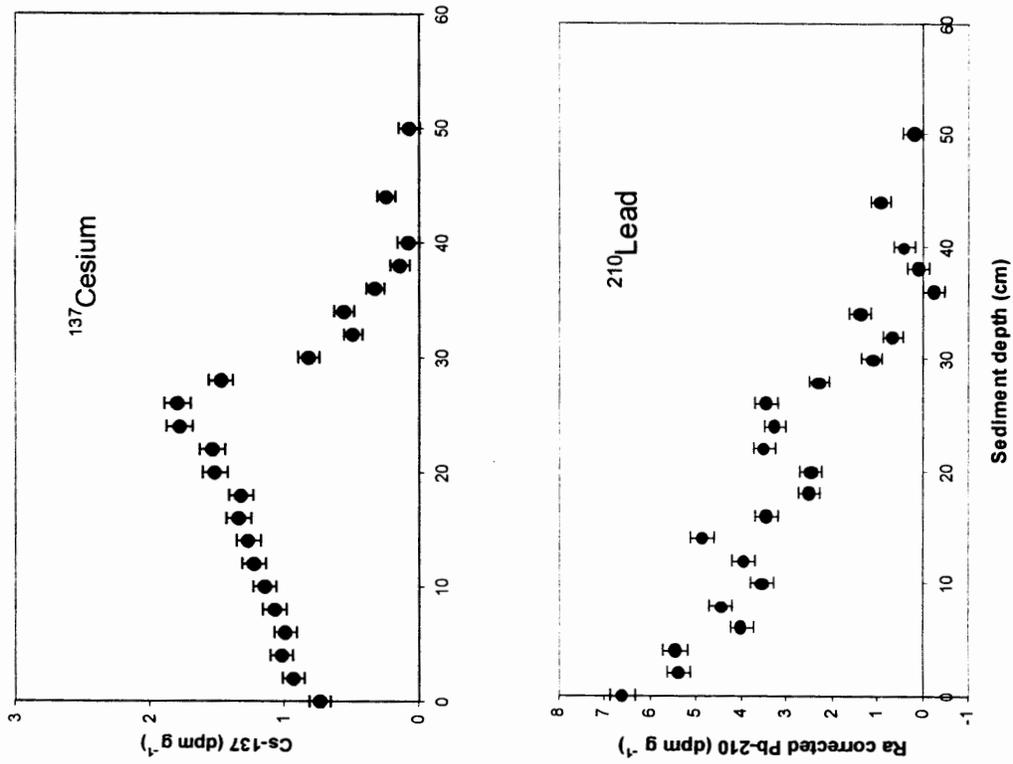


Figure 4. ^{210}Pb and ^{137}Cs results for core sites M4 in the Pamlico estuary on the left and OR in the Neuse estuary on the right. ^{137}Cs results are presented as dpm g^{-1} (disintegrations per minute per gram), and ^{210}Pb are presented as dpm g^{-1} after correction for radium levels (background ^{210}Pb) in each sample.

Table 4. Radiocarbon dates assigned to sediments as provided by Beta Analytic Inc., Miami, FL.

Sediment core	Depth in core analyzed	Type of Analysis	Intercept data	Calibrated results (95% probability)	Beta Analytic lab number
BC3	116-121 cm	AMS	AD 885	AD 775 to 995	Beta-112739
M42	114-118 cm	AMS	AD 1265	AD 1205 to 1290	Beta-125232
M42	130-137 cm	radiometric	AD 1290	AD 1175 to 1420	Beta-112740
M71	137-139 cm	AMS	AD 1175	AD 1025 to 1260	Beta-120395
BB2	84-87 cm	AMS	AD 370	AD 220 to 450	Beta-120394
OR1	74-76 cm	AMS	AD 995	AD 895 to 1030	Beta-125233
OR3	140-148 cm	AMS	AD 350	AD 225 to 430	Beta-112741
WP1	132-136 cm	AMS	AD 665	AD 600 to 780	Beta-120396
UNC2	50-56 cm	AMS	AD 70	BC 50 to AD 220	Beta-125234
UNC3	124-130 cm	AMS	BC 40	BC 180 to AD 70	Beta-112742

Table 5. Depth of the *Ambrosia* horizon for each core site, and average sedimentation rates calculated using all dating methods for different time periods.

core location	<i>Ambrosia</i> horizon (~1720 A. D.)	Average sedimentation rates (cm yr ⁻¹)			
		~1947-1997	~1850-1997	~1720-1850	pre-1720
Pamlico-BC	40 cm	1.2	0.312	0.080	0.085
Pamlico-M4	121 cm	1.2	0.473	0.394	0.056
Pamlico-M7	no pollen (43 cm)	0.438	0.236	0.063	0.063
Pamlico-BB	34 cm	0.269	0.135	0.109	0.060
Neuse-OR	76 cm	0.595	0.319	0.245	0.086
Neuse-WP	72 cm	0.613	0.375	0.181	0.100
Neuse-UNC	48 cm	0.222	0.157	0.192	0.185

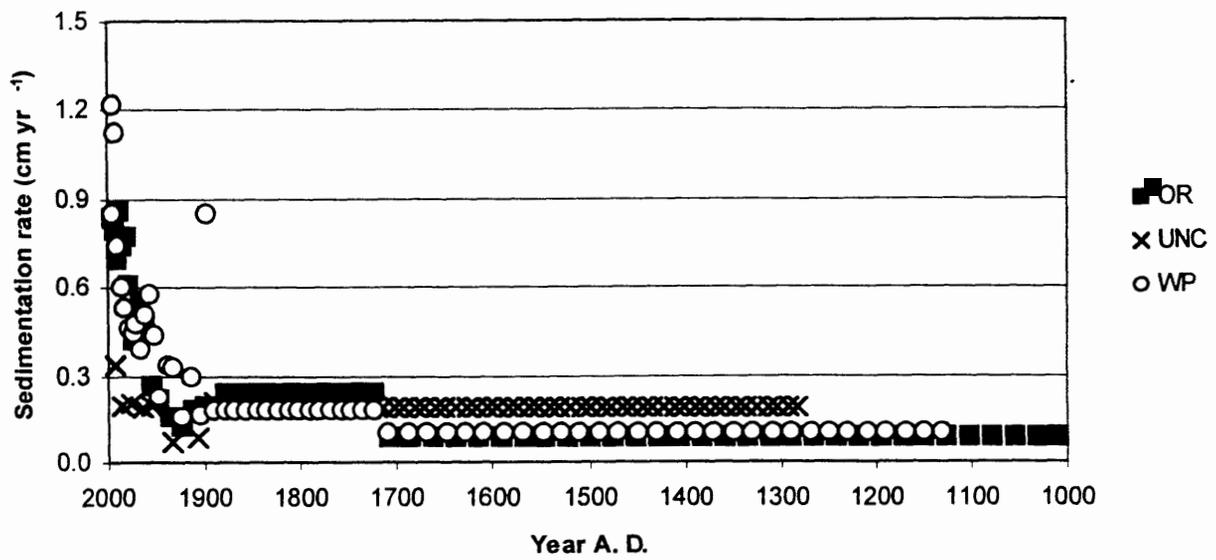
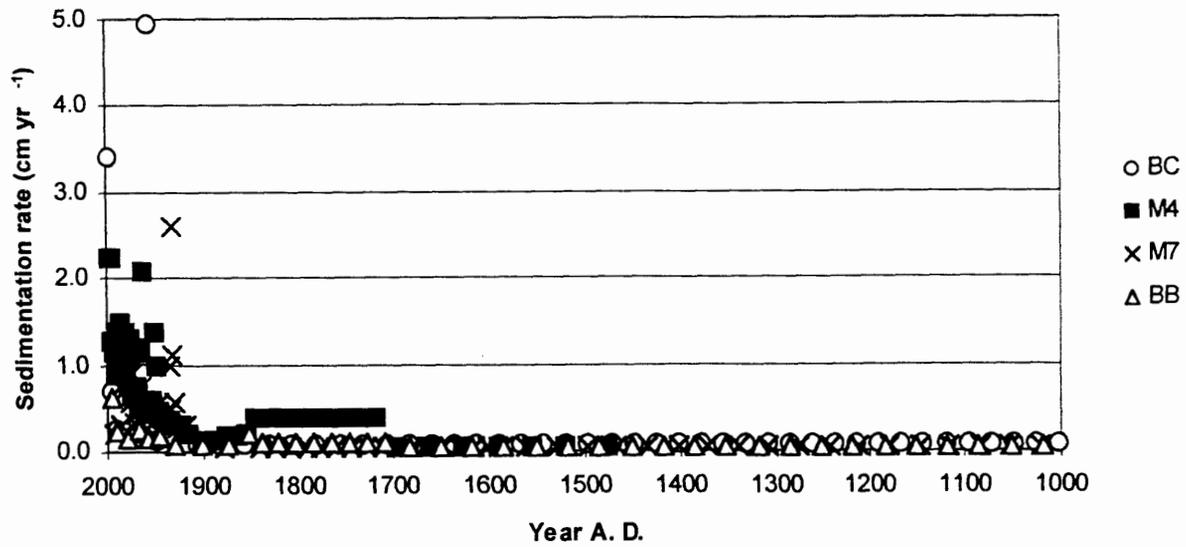


Figure 5. Sedimentation rates by date as calculated for the seven core sites. Four in the Pamlico (top graph) and three in the Neuse (bottom graph).

Geochemical Analyses

P, TOC, N, BSi, and S. Graphs of [P] ($\mu\text{g g}^{-1}$) and calculated P flux ($\mu\text{g cm}^{-2} \text{ yr}^{-1}$) are shown in Figure 6. Calculated fluxes of TOC, N, BSi, and S for the seven core sites are shown in Figures 7 & 8. [P] varied from 149-1852 $\mu\text{g g}^{-1}$ (12.7-1699 $\mu\text{g cm}^{-2} \text{ yr}^{-1}$), and was generally highest in core M4 especially since 1950. P flux to the sediments in the Neuse estuary sites averages about half that of the Pamlico sites. Results from all the cores show TOC content of 1.3-7.5% of sediment dry mass (0.1-10.5 $\text{mg cm}^{-2} \text{ yr}^{-1}$), and N levels of < 0.1%-3.5% (<0.01-0.75 $\text{mg cm}^{-2} \text{ yr}^{-1}$). BSi measurements varied from 1.9-17.7% of sediment dry mass (0.2-4.0 $\text{mg cm}^{-2} \text{ yr}^{-1}$). S varied from 0.2-4.6% of dry mass (0.03-8.0 $\text{mg cm}^{-2} \text{ yr}^{-1}$). Variability in all geochemical parameters was higher in the Pamlico samples than in the Neuse samples. Original data in concentration by depth is available from the author of this report.

Fe and estimated DOP. Acid-soluble Fe in sediments ranged from 2.6 – 21.2 mg g^{-1} , varying by depth and core. The average for all samples analyzed in the Pamlico was 9.4 mg g^{-1} Fe. For the Neuse samples, the average was 10.0 mg g^{-1} Fe. Values for estimated DOP range from 0.21 to 0.87. These values include levels associated with aerobic bottom water conditions (DOP <0.42) to inhospitable conditions (0.55 < DOP < 0.93). Estimated DOP results are presented in Figure 9. Estimated DOP in the Pamlico averages 0.64 for all samples analyzed, and is more variable down core. Values of estimated DOP in the Pamlico show an increase over the past 200 years to the present in three of the four cores. If estimated DOP values from core BC are left out of the average DOP calculation (the one core that did not show the same trend as the other three), the average is 0.61. Estimated DOP values for the Neuse average 0.68 for all samples analyzed and remain fairly high down-core at all three sites.

Trace metal analyses. The extractions and measurement of trace metals from surface samples and from cores M4, OR and UNC were done by S. Kim as part of her Master's project for the Nicholas School of the Environment (Kim 1998). Extractions and analyses from cores BC, M7, BB and WP were completed in the past year (1998-99). Analysis of rare earth elements (REE) were done on all samples and several standards to check uniformity (normalization) of sediment origin through time and space (Taylor & McLennan 1995). The bulk of the REE reside in the fine-grained fraction (clay and silt). The results show that downcore sediments are from the same crustal material and are of recent origin

Levels of most trace metals found in surface samples of the cores collected from the Neuse and Pamlico exceed U. S. EPA published "Threshold Effects Levels" (TEL) for sediments (USEPA 1997) at several sites (Figures 10-12). Levels of Cadmium (Cd) are highest (and more than double the TEL) in the M4 core collected in the Pamlico River nearest the phosphate mining operations. Levels of most trace metals, including Zn, Cu, Cr, As and Ni are generally higher in the Neuse River sediments. Results are presented for core M4 in Figure 13. The samples from this core had the best resolution over the recent past and therefore show changes in more detail. Other selected trace metal results for all cores are presented in Table 6.

Patterns in Pb flux in Core M4 (Fig. 13) most likely reflect leaded gasoline use. The decline in Pb in the 1980's follows the government ban on leaded gasoline in the late 1970's. Cd and Ag accumulation may reflect discharges from the phosphate mining facility, as these metals are known to be discharged from the plant. The phosphate mining operations were forced to reduce water emissions in recent years. More research is needed on possible sources and fates of other trace metals measured. S. Kim's Master's report (Kim 1998) contains some additional information.

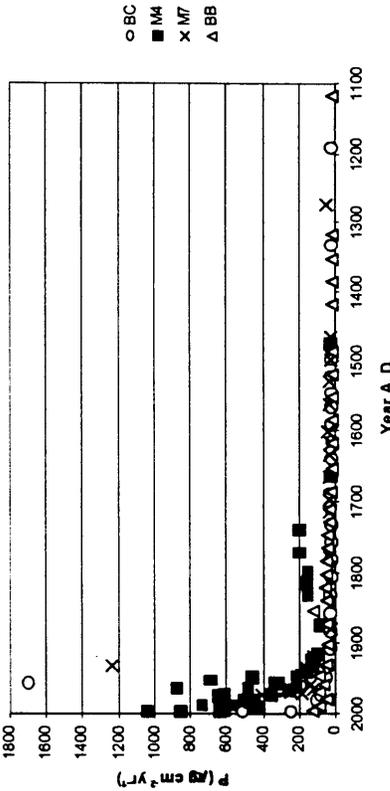
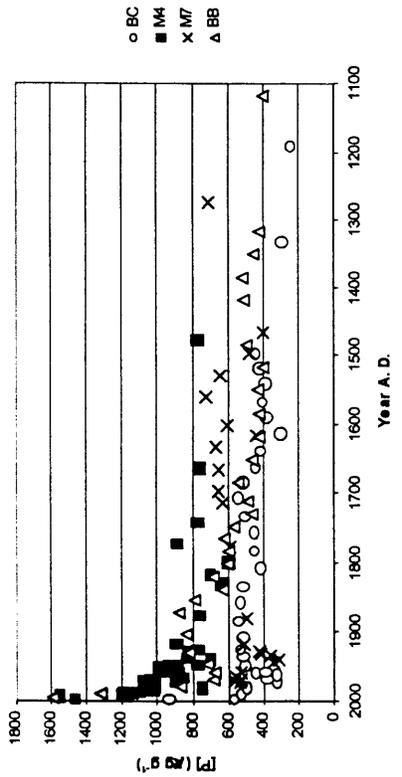
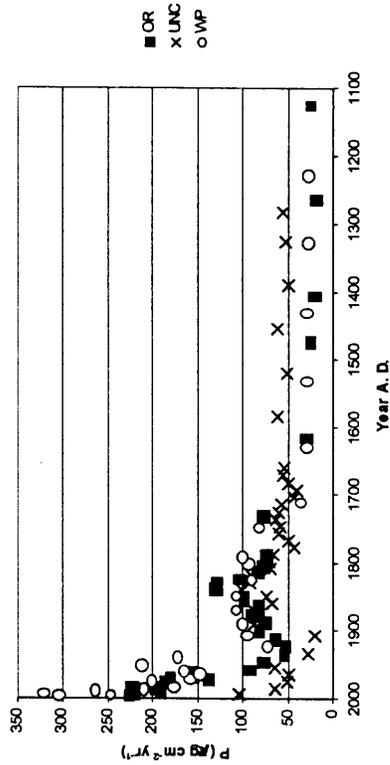
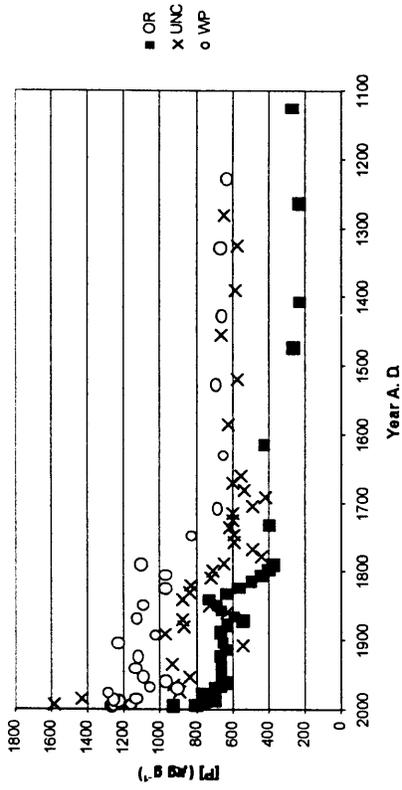


Figure 6. Phosphorus levels measured (above), and calculated flux of P to the sediments (below) by date for the core sites in the Pamlico (on the left) and Neuse (on the right). Note that y-axis values vary.

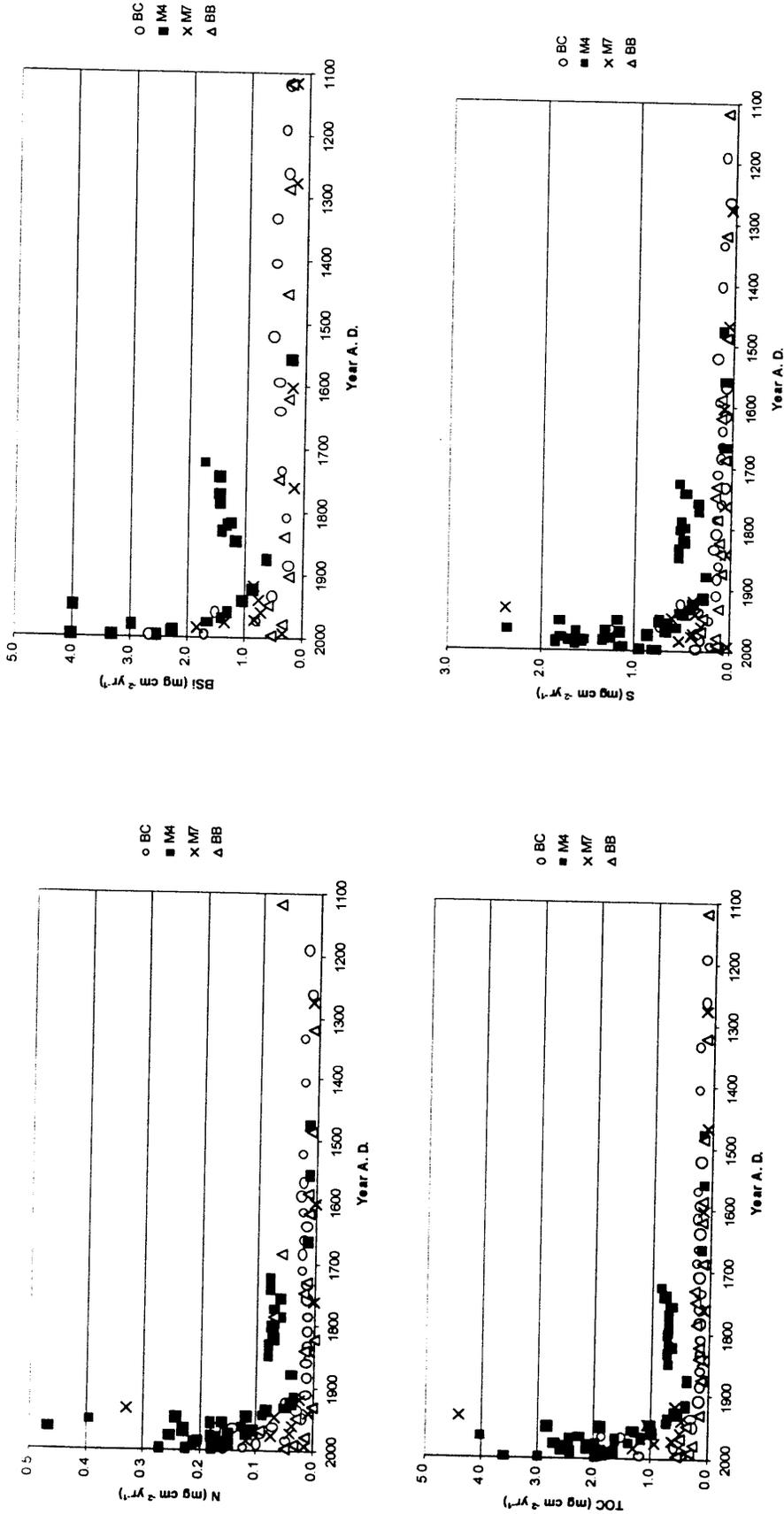


Figure 7. Calculated flux of TOC and N (on the left) and BSi and S (on the right) to the sediments as measured for the four core sites from the Pamlico estuary. Note that y-axis values vary.

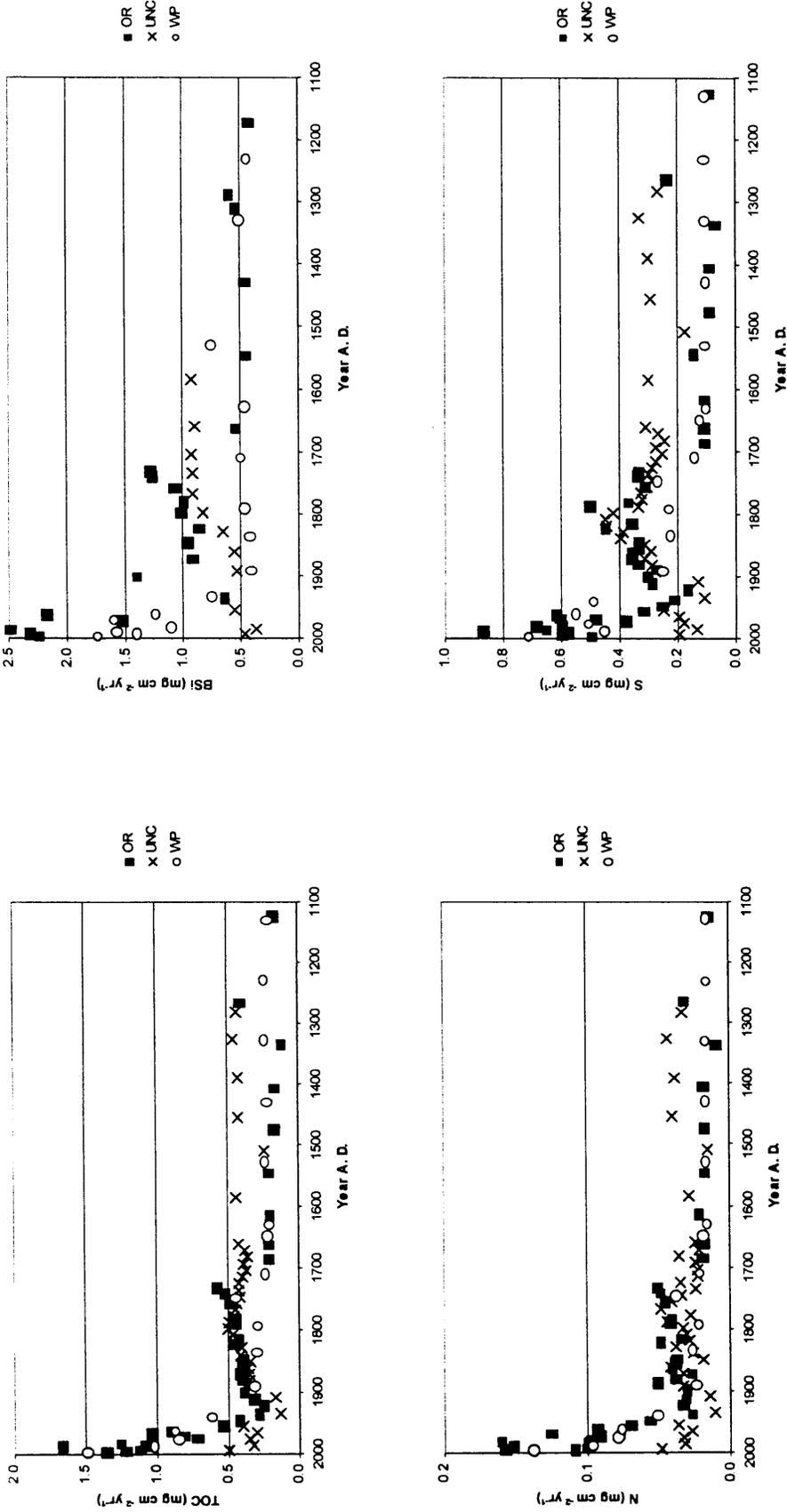


Figure 8. Calculated flux of TOC and N (on the left) and BSi and S (on the right) to the sediments as measured for the four core sites from the Neuse estuary. Note that y-axis values vary.

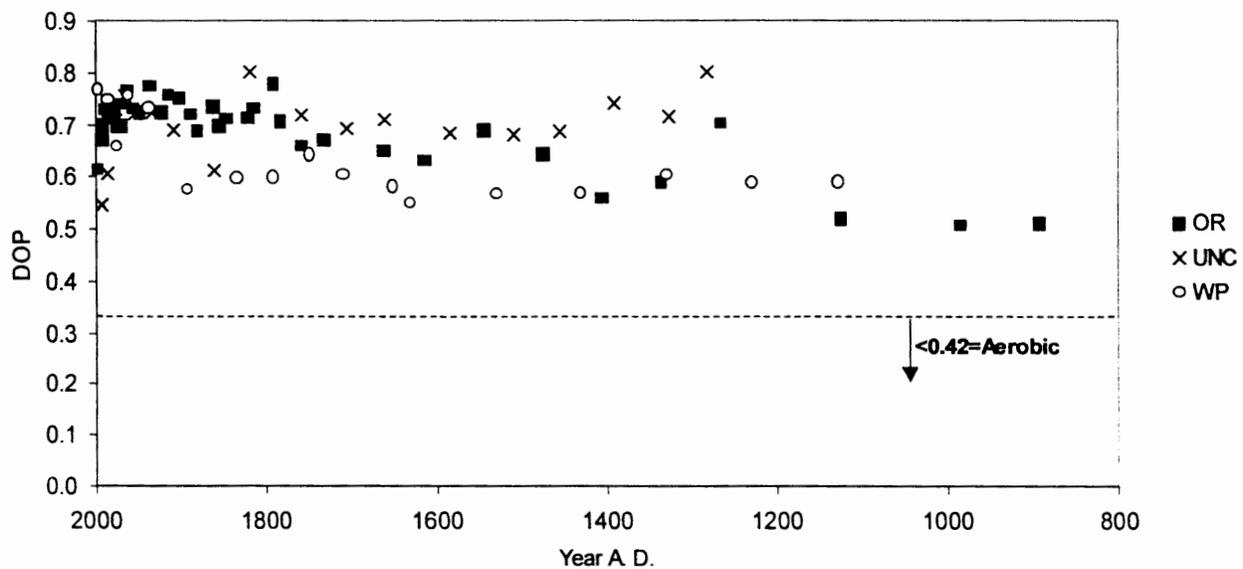
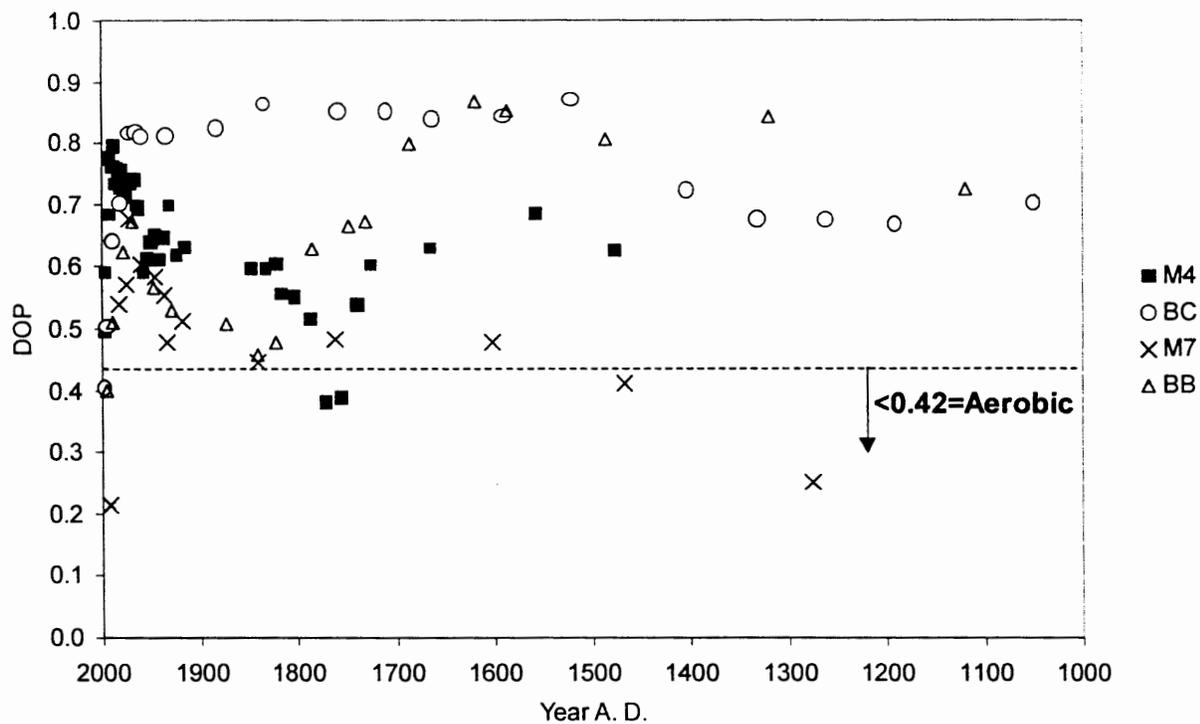


Figure 9. Calculated DOP values for Pamlico (top graph) and Neuse (bottom graph) core samples. The horizontal line through each graph is the level of DOP (0.42) below which indicates aerobic bottom water conditions (Raiswell *et al.* 1988). Values above this line indicate restricted bottom water oxygen conditions.

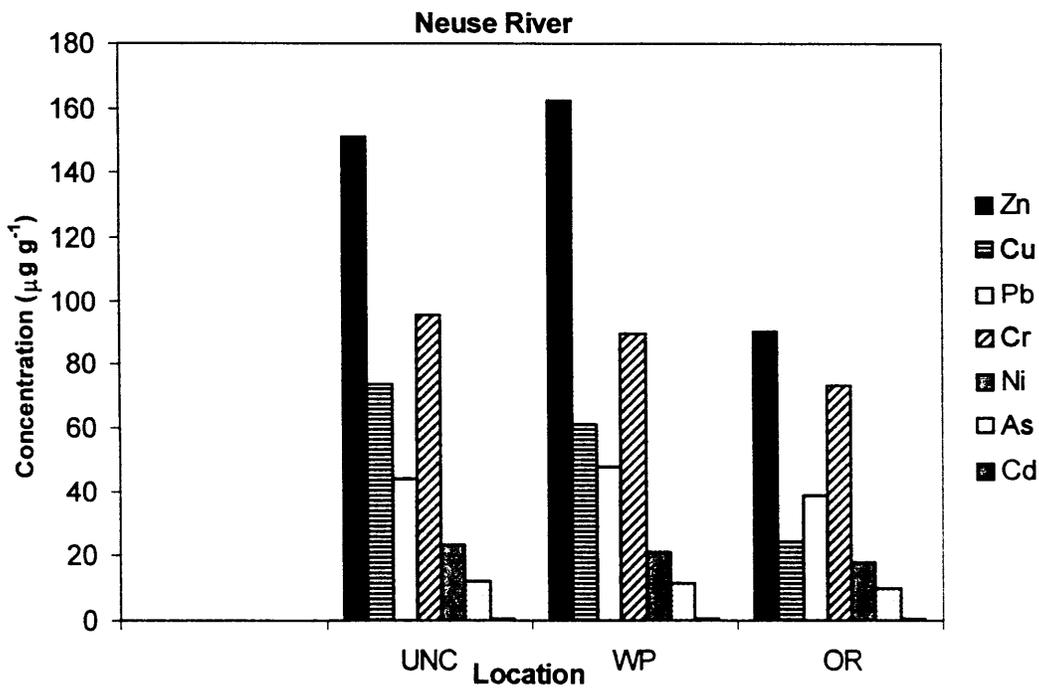
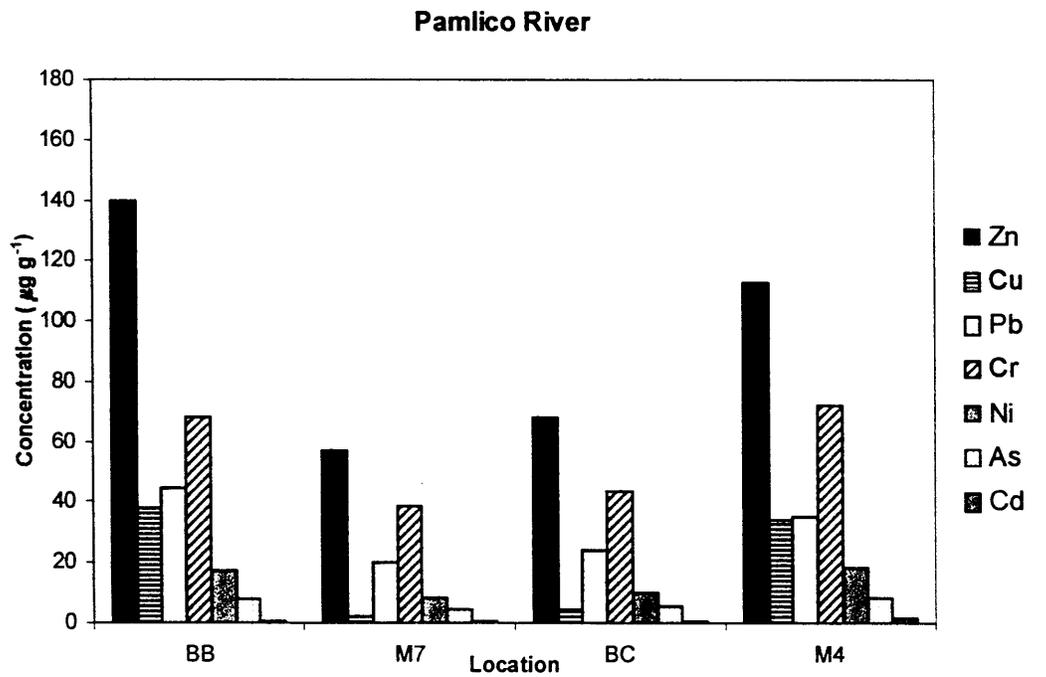


Figure 10. Concentration of EPA priority metals in the Pamlico and Neuse River estuarine surface sediments at coring sites.

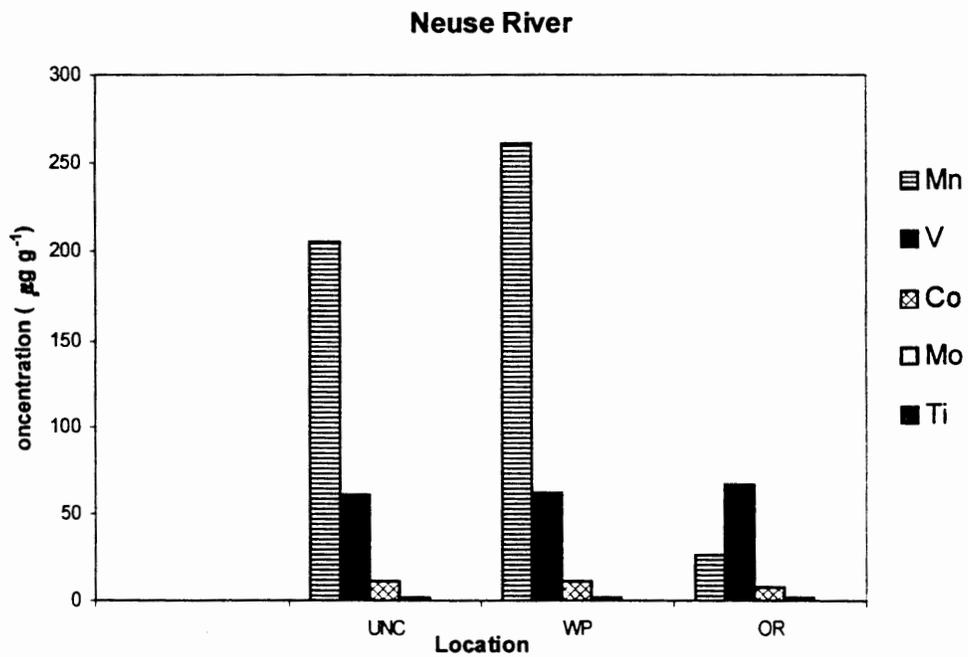
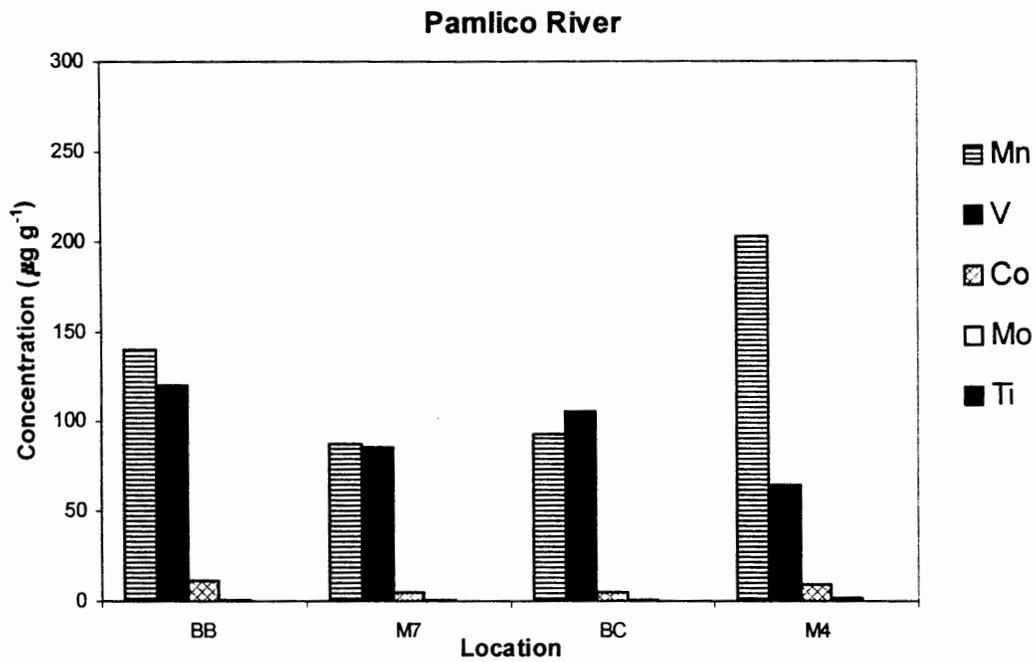


Figure 11. Other trace metal concentrations in the Pamlico and Neuse River estuarine surface sediments collected at all coring sites. Sites are from upstream to downstream along the x-axis.

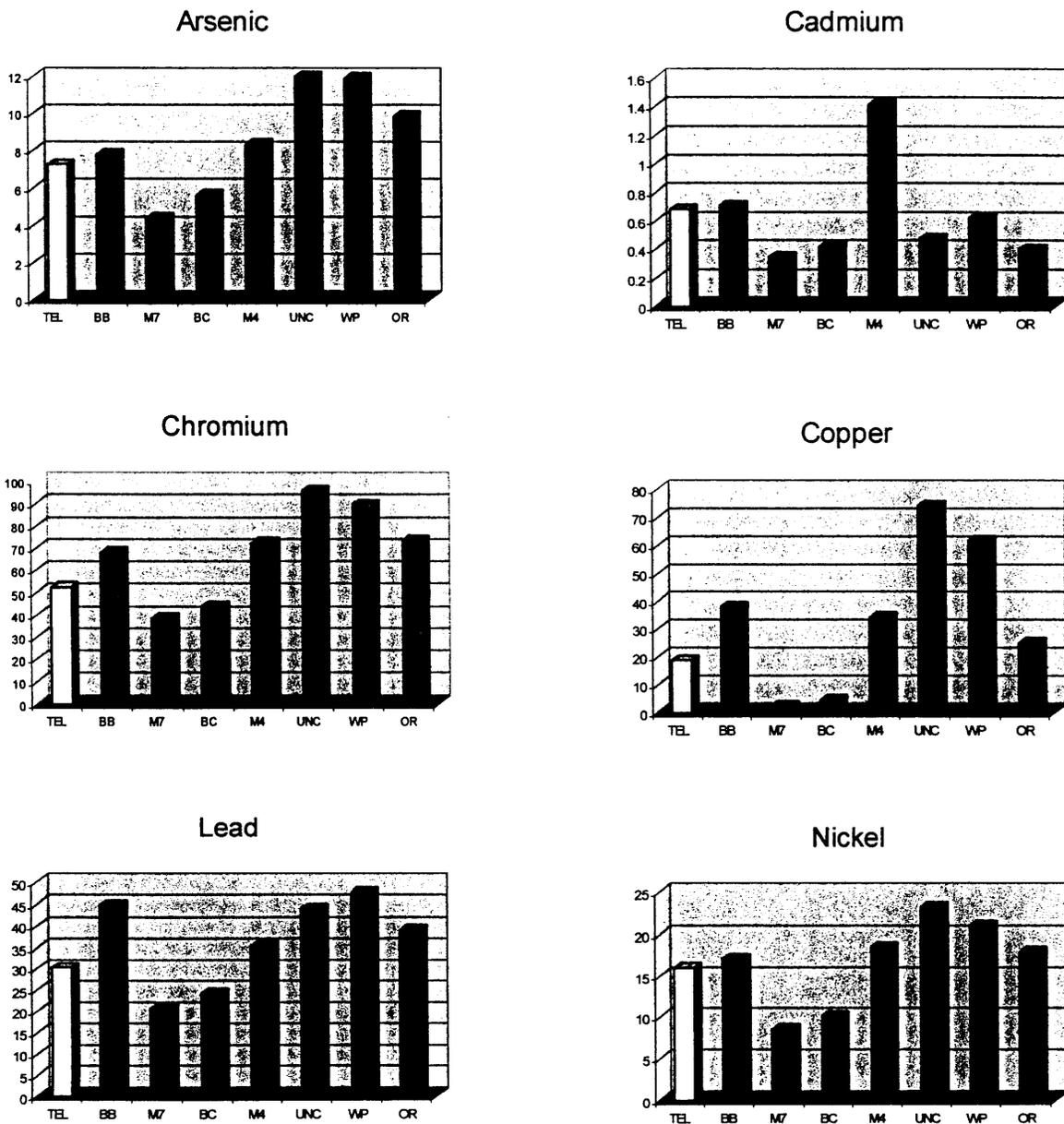


Figure 12. Comparisons of selected metal concentrations with “Threshold effects levels” (TEL) described in USEPA (1997). TEL levels are shown as the white bar on the left in each graph. The Pamlico and Neuse surface samples (in order) are from upstream to downstream along the x-axis. Y-axis values are in $\mu\text{g g}^{-1}$ for each graph.

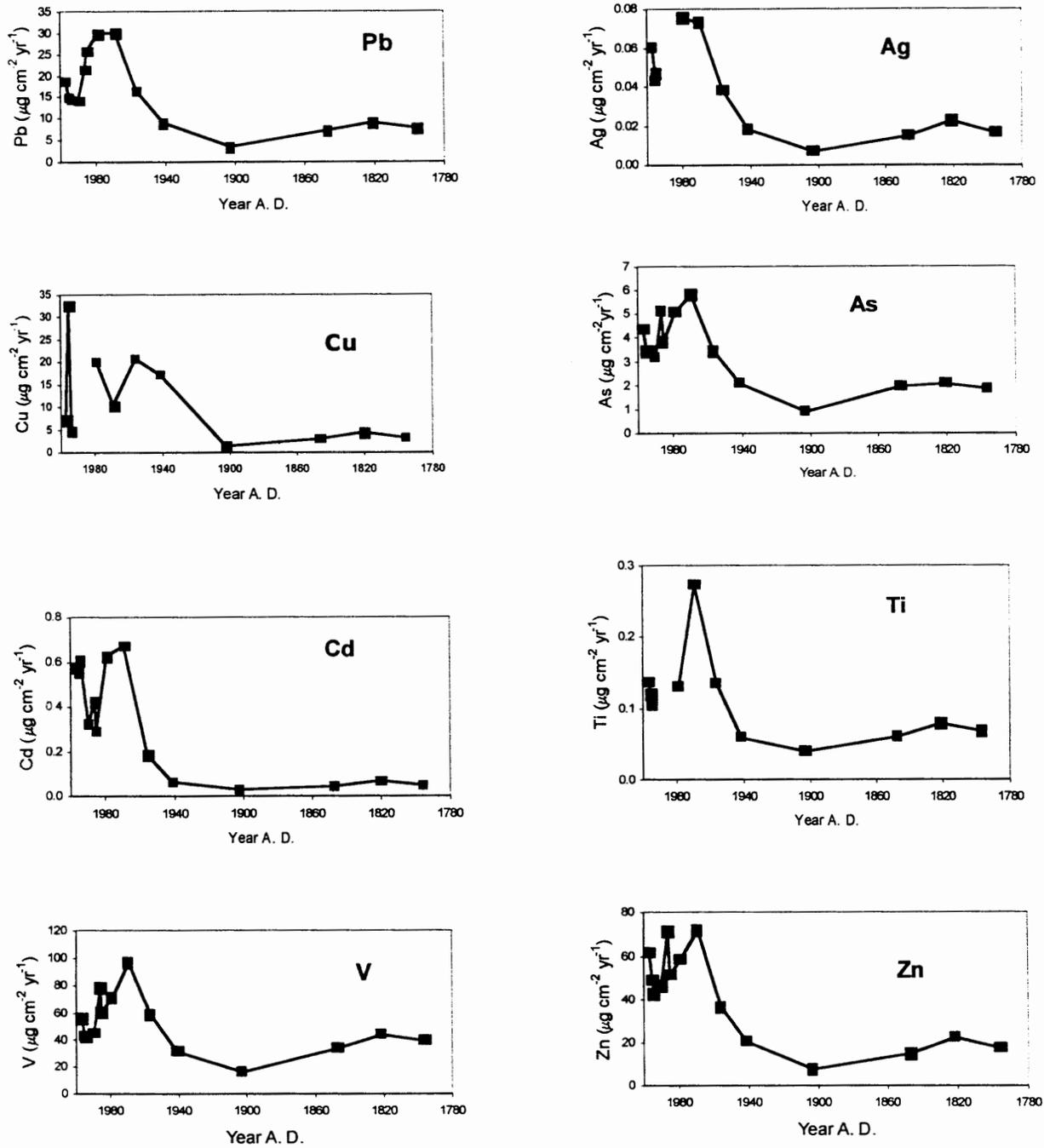


Figure 13. Estimated flux of selected metals from Pamlico core M4 from the late 1700's to the present. Note that y-axis values vary.

Table 6. Flux of selected trace metals for subsamples of the Pamlico and Neuse core sites. These data are calculated from absolute concentration of trace metals multiplied by the bulk density and sedimentation rates determined for each subsample. Different isotopes of various metals were measured on ICPMS. Values for Ti, Cu and Mn are not included, as they were measured only for surface samples and are shown in Figures 10 and 11.

Sample depth (cm)	Date Year A. D.	As	Cd	Cr	Co	Ni	Pb	Zn	
$\mu\text{g cm}^{-2} \text{ yr}^{-1}$									
BC	0-2	1997	3.3	0.22	-	2.8	5.1	13.3	36.4
	2-4	1995	2.1	0.17	-	2.3	4.4	10.2	29.4
	4-6	1990	1.1	0.08	-	1.1	2.2	4.7	12.7
	6-8	1982	1.4	0.05	-	1.2	2.1	3.9	12.2
	12-14	1963	5.7	0.13	-	4.2	7.6	19.1	38.8
	20-22	1934	0.8	0.01	-	0.8	1.6	3.9	5.9
	30-32	1833	0.3	0.00	-	0.5	0.8	1.1	2.9
	40-42	1708	0.3	0.00	-	0.5	0.8	0.9	2.7
	50-52	1591	0.3	0.00	-	0.4	0.7	0.7	2.2
	66-68	1403	0.4	0.01	-	0.4	0.7	0.7	2.4
M4	0-2	1996	4.4	0.58	42.0	5.0	10.1	18.6	59.9
	2-4	1995	3.4	0.56	28.3	4.0	7.4	14.9	48.5
	4-6	1994	3.4	0.61	27.7	3.9	7.5	14.3	45.9
	8-10	1990	3.2	0.32	31.6	3.9	7.3	14.1	45.2
	12-14	1986	5.1	0.42	55.2	6.3	12.9	21.3	71.2
	16-18	1983	3.8	0.29	40.5	4.5	9.1	25.6	53.2
	20-22	1979	5.0	0.63	44.2	5.5	10.6	30.0	58.4
	30-32	1969	5.8	0.67	62.0	7.2	16.0	30.3	72.1
	40-42	1956	3.4	0.19	32.3	3.9	8.2	16.5	36.7
	50-52	1941	2.1	0.06	16.7	2.2	4.2	9.0	20.5
	60-62	1903	0.9	0.03	7.8	1.1	2.2	3.4	7.6
	70-72	1863	1.9	0.04	16.4	2.2	4.1	7.4	18.8
	80-82	1841	2.1	0.07	21.1	3.1	5.9	9.0	28.2
90-92	1821	1.9	0.05	18.9	2.6	4.8	7.9	21.6	
M7	0-2	1992	0.6	0.03	6.7	0.6	0.9	2.3	7.4
	2-3	1986	1.9	0.15	15.4	2.3	3.7	8.1	25.8
	3-5	1983	3.0	0.19	25.7	3.3	5.1	12.1	67.9
	5-6	1981	4.5	0.36	42.0	5.6	9.2	22.4	62.2
	8-10	1974	3.5	0.14	30.0	3.8	6.8	14.9	40.2
	13-15	1959	1.3	0.08	10.4	1.6	2.5	7.4	19.8
	18-19	1944	2.1	0.08	20.5	2.3	3.7	10.7	26.3
	20-22	1935	2.2	0.08	18.1	2.7	4.6	11.5	42.7
	24-25	1932	6.0	0.17	48.4	6.8	12.2	28.9	69.6
	27-32	1918	1.6	0.03	11.0	1.8	3.6	7.7	18.0

37-38	1809	0.3	0.01	2.5	0.4	0.7	1.4	3.4
39-40	1777	0.3	0.01	2.1	0.4	0.8	1.4	3.6
43-44	1713	0.3	0.01	2.1	0.5	1.0	1.6	4.1
48-49	1634	0.3	0.01	1.1	0.4	0.8	1.3	3.3
58-60	1467	0.3	0.01	2.6	0.5	0.9	1.3	3.8
70-72	1276	0.3	0.00	2.6	0.6	1.0	1.6	4.1
80-82	1116	0.3	0.00	2.4	0.6	1.1	1.4	3.5
90-92	957	0.2	0.00	2.2	0.6	1.1	1.2	3.4
100-102	798	0.2	0.00	2.5	0.6	0.9	1.0	3.3

BB	0-2	1995	0.7	0.03	5.3	1.0	1.8	3.1	10.1
	2-4	1990	0.5	0.05	4.4	0.7	1.1	3.1	10.1
	4-6	1979	0.5	0.04	4.3	0.7	1.1	2.8	8.4
	8-10	1958	1.0	0.04	7.5	1.2	2.1	4.7	11.2
	12-14	1929	0.4	0.01	3.7	0.6	1.2	2.0	4.6
	16-18	1873	0.4	0.01	3.1	0.6	1.0	1.6	4.2
	20-22	1840	0.4	0.01	4.9	0.9	1.6	2.4	5.5
	24-26	1803	0.4	0.01	4.4	1.1	1.7	2.0	5.1
	28-30	1766	0.4	0.01	3.7	0.8	1.4	1.5	3.8
	32-34	1730	0.3	0.01	2.4	0.8	1.3	1.1	3.8
	36-38	1685	0.2	0.00	1.9	0.5	0.7	0.6	2.0
	40-42	1619	0.2	0.00	1.4	0.4	0.6	0.5	1.8
	50-52	1452	0.2	0.00	1.9	0.3	0.6	0.5	1.6
	60-62	1285	0.2	0.00	2.2	0.3	0.6	0.5	1.8
	70-72	1119	0.2	0.00	1.6	0.3	0.6	0.4	1.7
	80-82	952	0.2	0.00	2.2	0.3	0.6	0.5	1.7

OR	0-2	1996	2.5	0.10	16.8	2.0	4.2	8.9	21.2
	2-4	1993	2.8	0.12	21.6	2.4	5.4	11.2	26.1
	4-6	1991	2.3	0.09	18.2	2.0	4.3	10.0	22.4
	8-10	1985	1.9	0.05	20.2	1.9	4.9	6.8	21.4
	12-14	1978	1.8	0.05	18.5	1.8	4.0	6.2	18.8
	16-18	1970	2.2	0.05	18.7	1.9	4.2	6.4	19.1
	20-22	1963	2.4	0.06	20.7	2.2	4.9	7.1	22.4
	30-32	1913	1.2	0.02	8.6	1.0	2.0	3.2	9.5
	40-42	1863	1.3	0.02	11.3	1.3	2.8	2.7	10.3
	50-52	1822	1.7	0.02	13.9	1.7	3.6	2.9	10.7
	60-62	1782	1.5	0.01	11.4	1.5	2.8	2.1	7.8
	70-72	1741	2.9	0.02	6.3	2.3	5.9	2.0	7.5
	90-92	1545	0.5	0.01	3.5	0.5	0.8	0.9	2.4

UNC	0-2	1994	0.7	0.05	6.0	0.8	1.4	3.2	11.4
	2-4	1986	0.6	0.01	4.6	0.5	1.1	1.9	7.4
	4-6	1976	0.7	0.04	4.6	0.6	1.0	3.0	8.5
	8-10	1955	1.0	0.03	7.1	0.8	1.7	3.0	10.9
	12-14	1908	0.3	0.00	3.0	0.4	0.8	0.8	2.5
	14-16	1892	1.1	0.02	7.7	1.0	1.9	2.4	8.6
	18-20	1871	1.1	0.01	8.1	1.1	2.1	2.6	8.4
	22-24	1850	0.9	0.01	8.4	1.2	2.2	2.0	8.0
	30-32	1809	1.0	0.01	6.9	1.1	1.9	1.5	6.3
WP	0-2	1996	2.3	0.06	16.5	1.8	4.2	9.9	19.9
	6-8	1990	1.8	0.09	15.2	2.0	3.6	9.1	21.6
	10-12	1983	1.6	0.09	15.6	1.6	3.4	6.8	17.8
	14-16	1975	1.7	0.06	12.6	1.5	3.3	7.6	17.2
	18-20	1966	1.2	0.04	7.6	1.0	1.9	6.0	12.7
	22-24	1957	2.4	0.08	17.6	2.0	4.5	10.9	24.3
	26-28	1947	1.0	0.03	5.9	0.9	1.5	4.4	8.5
	30-32	1933	2.4	0.04	15.4	1.7	3.5	5.9	15.0
	34-36	1914	1.4	0.03	10.5	1.6	3.2	4.3	11.9
	44-46	1869	0.7	0.01	3.4	0.9	1.6	2.3	5.0
	50-52	1836	0.6	0.01	3.8	0.9	1.5	2.2	5.2
	58-60	1791	0.5	0.01	2.9	0.9	1.4	2.1	4.9
	70-72	1725	0.8	0.01	6.1	0.9	1.4	1.5	5.0
	80-82	1630	0.4	0.00	2.2	0.4	0.7	0.6	2.5
	90-92	1530	0.5	0.00	3.0	0.5	0.9	0.6	2.8
	100-102	1430	0.6	0.00	5.0	0.6	1.1	0.8	3.3
	110-112	1330	0.4	0.01	2.6	0.5	0.7	0.6	2.6
	120-122	1220	0.4	0.00	1.9	0.5	0.7	0.8	2.5
	130-132	1130	0.4	0.01	2.5	0.5	0.9	0.7	2.8

Paleopigment Analyses

In general, the organic matter contents of all sediment samples were similar to those seen in productive lakes, and were substantially greater than values recorded from profundal marine systems. In all cases, LOI values were >10% of dry mass, suggesting that both estuaries were moderately productive and that the biological and chemical oxygen demand of estuary sediments should have produced anoxia within the upper cm of sedimentary deposits. However, despite this observation, pigment preservation was poor in all cores.

Algal and bacterial pigments. Undegraded carotenoids and native chlorophylls were notably absent from all estuary sediment samples. While analysis by HPLC detected many colored compounds in each core, the spectral characteristics of these pigments suggested that they were derived mainly from Chl degradation products. In all cases, the spectral characteristics of sedimentary isolates were distinctly different from those recorded for undegraded carotenoids and Chls. Although the precise parent compound producing stable derivatives is unknown, it seems likely that many of these compounds arose from post-depositional degradation of Chl *a*, a pigment ubiquitous in algal and plants (Leavitt 1993). As mentioned above, the absence of identifiable carotenoids is particularly surprising given the comparatively high organic content of the estuarine sediments and the relative stability of these biomarkers (Leavitt and Findlay 1994). Chromatograms are available upon request from the author.

Photoprotective pigments characteristic of UV-transparent environments were recorded from multiple samples from all cores. These UV-absorbing compounds are produced by benthic algae (often cyanobacteria) in response to prolonged exposure to UV radiation (UVR; Leavitt et al 1997). Consequently, elevated abundance of photoprotective pigments suggested that integral attenuation of UV radiation (UVR) was low, either because of low concentrations of UVR-absorbing dissolved organic carbon (DOC) compounds (<2 mg/l) or because the estuary was shallow (<5 m average depth) at the coring site. Unfortunately, because few undegraded carotenoids were recovered from the sediments, we could not calculate an index of historical changes in the penetration of UVR (cf. Leavitt et al. 1997; UV compound : carotenoids, as %).

Overall, pigment chromatograms were most similar to those seen in the early Holocene era of lakes in glaciated regions (e.g. Leavitt et al. 1997), despite a large difference in the organic matter content of the sediments from two environments (<0.5% vs >10%). In both cases, sedimentary profiles were dominated by pigment derivatives rather than native compounds, and ecological interpretation cannot be easily made.

Microfossil Analyses

Diatoms. Diatoms are well preserved in the sediments of the Neuse and Pamlico, with approximately 1 million to 5 million valves preserved in each cubic cm of wet sediment. Over 430 taxa have been identified from the 49 subsamples in 6 cores analyzed (see Appendix B for a complete listing). The ten most abundant species identified followed by their highest percent abundance include: *Thalassiosira proschkiniae* Makarova (44.1%), *Cyclotella meneghiniana* Kützing (30.6%), *Stephanocostis* af. *chantaicus* Genkal & Kuzmin (19%), *Cyclotella*

choctawhatcheeana Prasad (17.6%), *Aulacoseira* af. *granulata* (Ehrenberg) Simonsen (10%) *Skeletonema* spp. (8.1%), *Cocconeis peltoides* Hustedt (7.6%), *Cymatosira belgica* Grunow (7.6%), *Diploneis* sp. A (6.3%) and *Nitzschia palea* (Kützing) W. Smith (5.8%). The genera with the most species represented include *Navicula* (94 species), *Nitzschia* (49 species), *Achnanthes* (26 species) and *Fragilaria* (25 species). Results of diatom counts are shown in Tables 7 & 8. Changes in diatom species richness and diversity show the same declining trend in all cores analyzed. While small planktonic forms such as *Thalassiosira proschkiniae* have been increasing in abundance in recent years, epiphytic diatom taxa including species in the genus *Cocconeis* have declined significantly over time in both estuaries.

Table 7. Diatom data from subsamples analyzed in the Pamlico estuary cores. Centric to pennate ratios designated as c:p.

Core	Sample depth	Date Year A.D.	Diatoms counted	Diversity H'	# Taxa	diatom flux # cm ⁻² yr ⁻¹	c:p	<i>T. proschkiniae</i> . % abundance	<i>Cocconeis</i> % abundance
BC	0-2	1997	451	2.6	51	1840804	5.4	40.4	2.2
BC	2-4	1995	478	3.0	62	1060599	3.6	30.1	2.9
BC	8-10	1972	449	3.6	72	477068	1.8	13.1	5.4
BC	20-22	1934	454	4.2	100	229543	0.9	4.4	10.8
BC	32-34	1808	427	4.1	93	67991	0.8	4.5	11.0
BC	80-82	1238	440	4.1	101	186504	0.4	8.4	11.1
M4	0-2	1997	490	2.5	51	1575098	6.2	44.1	0.4
M4	8-10	1990	459	2.9	56	1890079	3.3	25.9	0.9
M4	20-22	1979	442	3.1	62	1810596	4.3	14.9	1.4
M4	32-34	1967	468	3.3	80	606249	2.3	15.6	3.8
M4	38-40	1961	496	3.8	98	357415	1.4	8.1	6.7
M4	50-52	1941	485	3.9	111	477249	1.1	12.6	6.4
M4	62-64	1888	478	3.8	97	163478	1.2	6.5	9.0
M4	74-76	1836	484	4.0	110	693800	1.0	9.9	7.2
M4	86-88	1806	510	3.9	96	323827	0.7	7.3	9.2
M4	92-94	1791	497	3.8	101	564272	0.9	10.9	7.6
M4	110-112	1745	426	3.9	90	408424	0.9	4.7	8.9
M4	130-132	1556	502	4.0	101	33504	0.8	6.2	12.9
BB	0-2	1995	497	2.4	48	191492	9.8	28.4	1.0
BB	10-12	1947	490	3.4	79	107086	2.5	8.4	2.0
BB	20-22	1840	457	3.7	80	99543	1.1	3.9	4.8
BB	30-32	1748	458	3.6	78	93737	1.1	9.6	3.9
BB	40-42	1619	425	4.1	92	53775	0.6	2.8	7.8
BB	50-52	1452	425	3.9	92	30560	1.1	12.7	8.5

Table 8. Diatom data from subsamples analyzed in the Neuse estuary cores. Centric to pennate ratios designated as c:p.

Core	Sample depth	Date Year A.D.	Diatoms counted	Diversity H'	# Taxa	diatom flux # cm ⁻² yr ⁻¹	c:p	<i>T. proschkiniae</i> % abundance	<i>Cocconeis</i> % abundance
OR	0-2	1996	485	2.9	67	521297	3.6	35.1	2.7
OR	2-4	1993	428	2.3	42	972658	4.7	48.8	1.2
OR	8-10	1985	339	2.9	57	1358126	4.7	32.5	1.5
OR	14-16	1974	413	2.9	67	372515	3.4	38.5	1.7
OR	20-22	1963	416	3.3	67	803820	1.9	26.0	4.1
OR	32-34	1901	423	3.6	82	521787	1.2	17.5	6.9
OR	44-46	1847	427	3.7	86	232124	1.1	16.9	5.2
OR	56-58	1798	425	3.6	90	388074	1.0	15.5	9.4
OR	74-76	1724	453	3.9	109	353693	0.8	9.7	9.7
OR	90-92	1545	478	3.8	96	131835	1.0	16.1	11.1
OR	120-122	1195	447	3.8	96	237250	1.2	14.5	9.6
OR	130-132	1079	487	4.0	103	141729	0.7	10.3	7.4
UNC	0-2	1994	410	2.5	42	115760	11.0	28.0	0.2
UNC	4-6	1976	458	2.6	52	282607	7.2	37.1	1.8
UNC	8-10	1955	435	3.0	65	168590	4.1	25.3	2.0
UNC	14-16	1892	447	3.4	71	156823	2.3	20.4	7.3
UNC	20-22	1861	420	3.7	85	129506	0.8	11.4	10.0
UNC	38-40	1767	408	3.8	97	137106	1.0	17.9	8.4
UNC	70-72	1596	442	3.6	84	123209	1.9	16.7	6.1
WP	0-2	1996	429	2.7	54	564189	6.3	38.0	0.7
WP	10-12	1983	430	2.6	47	542130	6.3	37.4	0.7
WP	20-22	1961	437	3.0	58	741643	4.7	30.2	0.9
WP	30-32	1933	474	3.5	70	262406	1.9	19.6	5.1
WP	40-42	1891	464	3.8	89	126402	1.0	8.8	8.0
WP	50-52	1836	436	3.8	82	80337	1.1	11.5	8.3

Pamlico core M4 and Neuse core OR were analyzed in the most detail for diatoms and selected data is shown graphically (Figures 14 & 15). Significant changes in diversity, taxonomic composition of assemblages and centric:pennate ratios have occurred in the recent past in both estuaries.

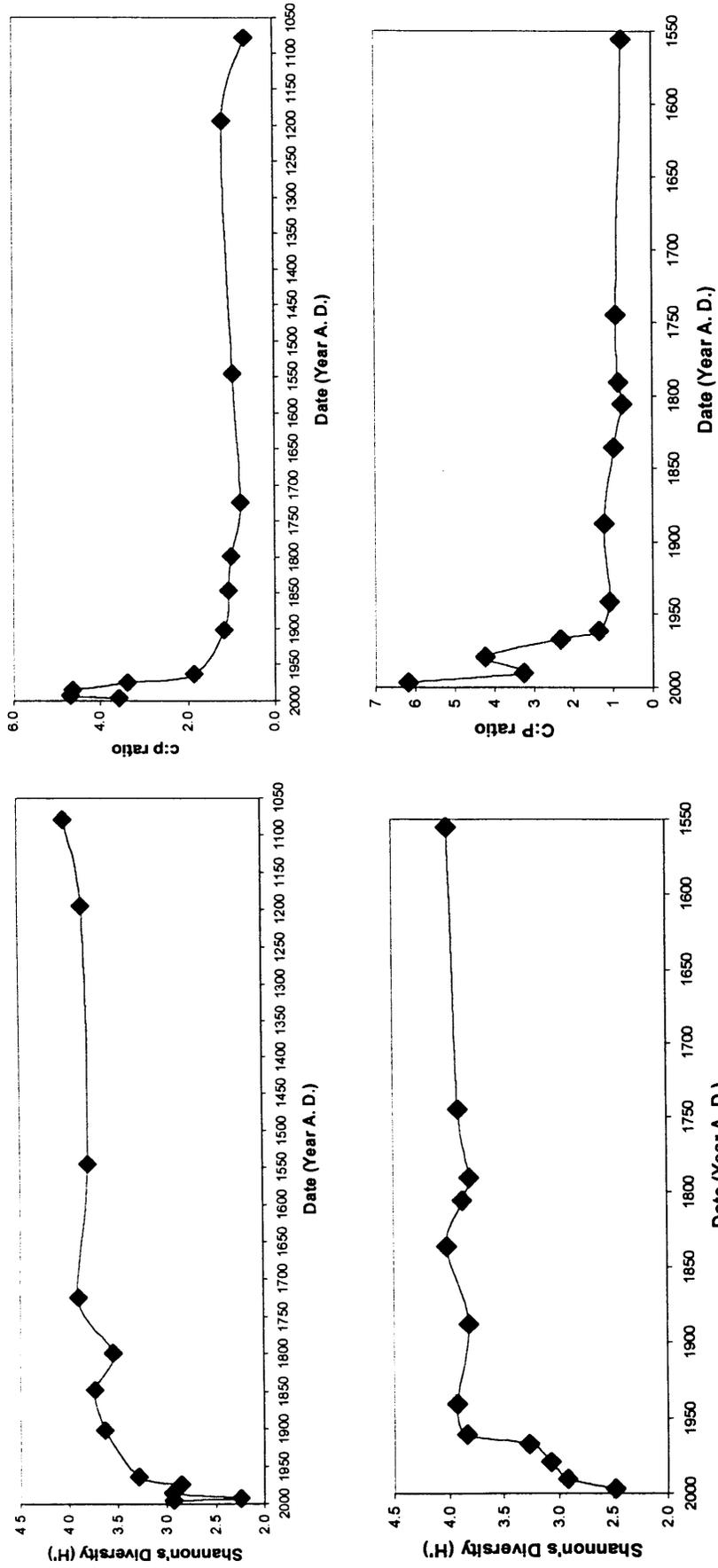


Figure 14. Diatom results from Pamlico core M4 (on the left) and Neuse core OR (on the right). Shown are graphs of diatom assemblage diversity (above) and centric to pennate diatom ratio changes (below) over time. Note that x-axis range of dates is different for M4 and OR cores.

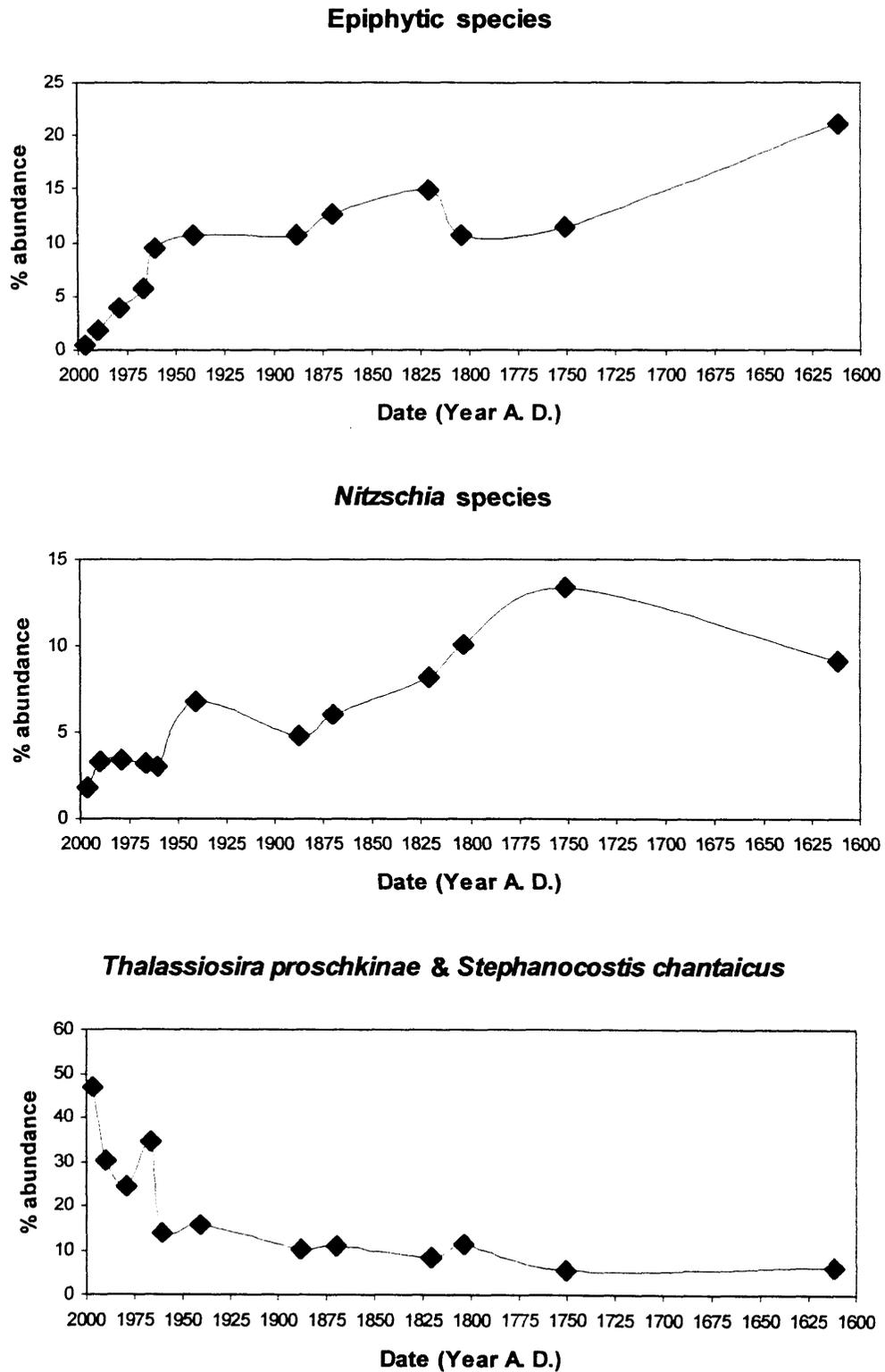


Figure 15. Percent abundance of selected species from Pamlico core M4. *Cocconeis* and *Mastogloia* species are primarily epiphytic species (top graph). *Nitzschia* species are benthic, and *Thalassiosira proschkiniae* and *Stephanocostis chantaicus* are planktonic species.

Cluster analysis of all diatom data was performed and compared to cluster analysis of a subset of dominant diatom taxa (only those species with at least 1% abundance in three samples or 5% abundance in one sample per estuary). The results were almost identical. Dendrograms of cluster analyses performed using all the diatom data for the Neuse and Pamlico estuaries separately are shown in Figures 16 & 17.

Two main clusters are evident for the Neuse estuary diatom samples. Cluster A includes all samples from all three cores dated before 1940 A. D. and cluster group B includes all samples dated after 1950 A. D. These two clusters are clearly separated by Euclidean distance. The Pamlico diatom data is also clearly separated into two main clusters by Euclidean distance. They include all samples dated before 1980 A. D. (clusters A-C) and all those dated after 1980 A. D. from the three cores analyzed (cluster D). I have designated three clusters based on Euclidean distance and sample date in the large group of samples dated before 1980 A. D. from the Pamlico estuary (clusters A-C). Cluster group A includes all samples from the cores BC and BB dated before 1940 A. D. and the two oldest samples from core M4. Cluster groups B and C include 80% samples from core M4 and are separated into groups of samples from core M4 dated before 1963 A. D. and those dated after 1963 A. D. (but before the past decade). When all diatom data from both estuaries are combined there are two main clusters and two outliers from Pamlico core BB (the two most recent samples from core BB). These two main clusters are separated by Euclidean distance into most recent (post 1950 A. D.), and older samples (pre-1950 A. D.), indicating that both estuaries are showing similar changes in diatom assemblages over the past 50 years.

Examples of images of diatom valves captured via video camera attached to the microscope are shown in Figure 18. A complete listing of all diatom species identified is contained in Appendix B.

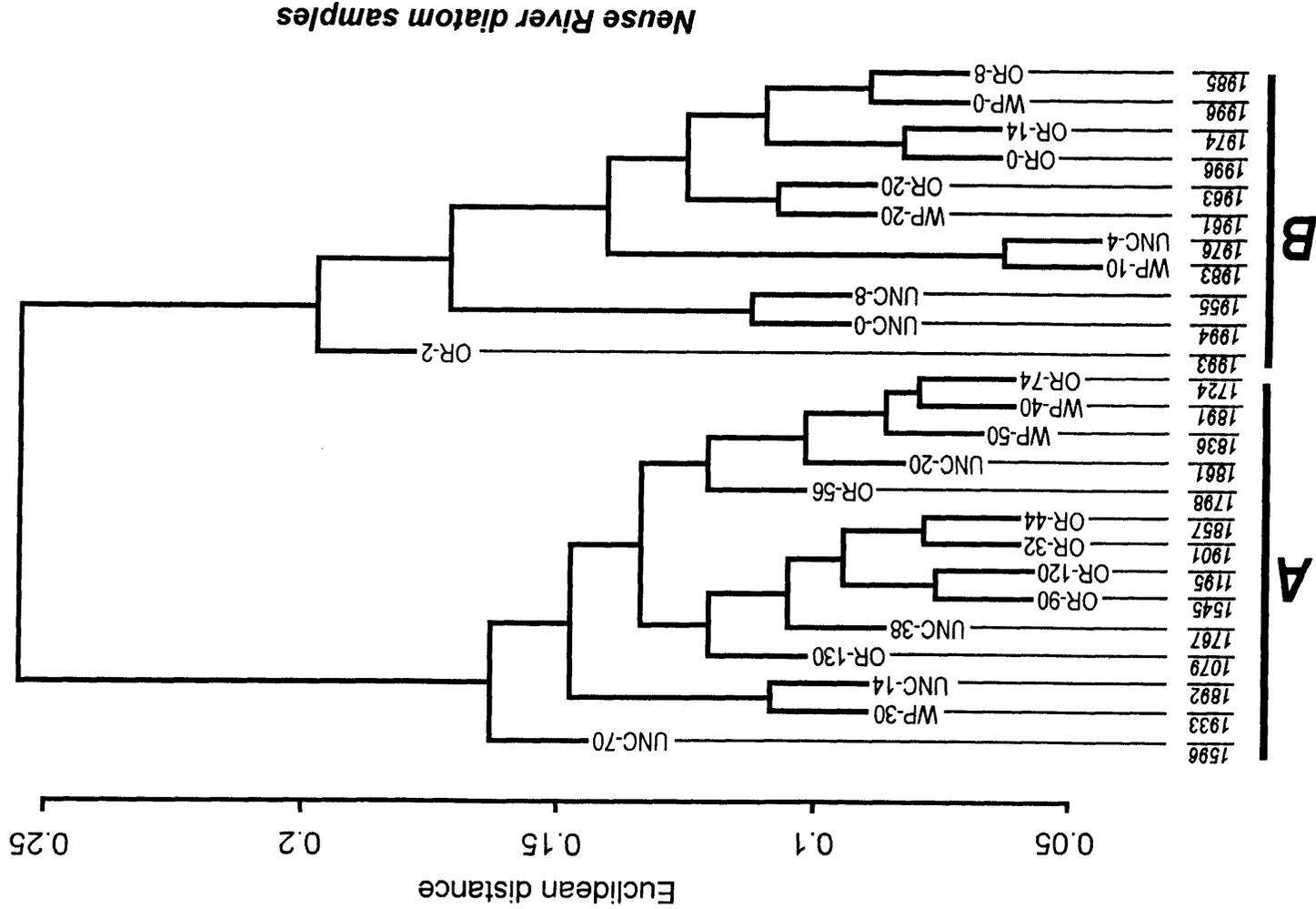


Figure 16. Cluster analysis of diatom assemblages found in subsamples of Neuse estuary cores.

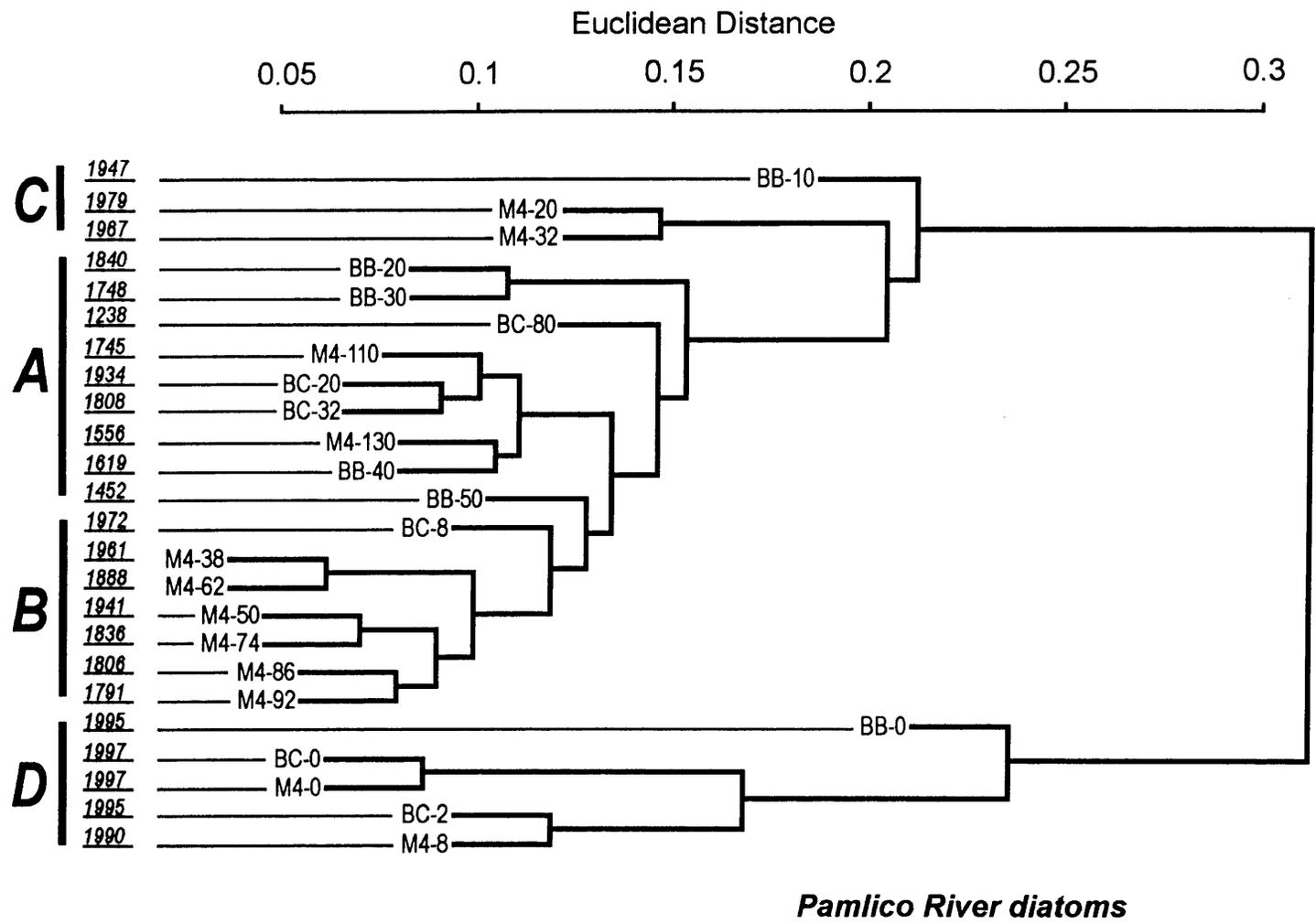
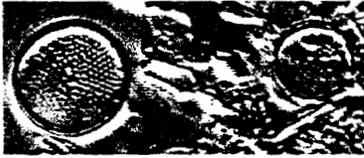
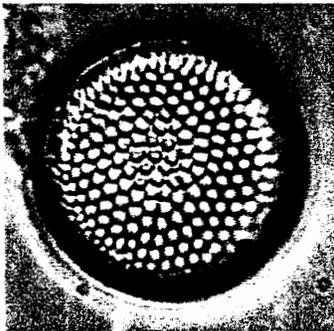


Figure 17. Cluster analysis of diatom assemblages found in subsamples of Pamlico estuary cores.



Neuse Core UNC 0-2 cm
1994 A.D.

10 μ m



Neuse Core UNC 38-40 cm
~1767 A.D.

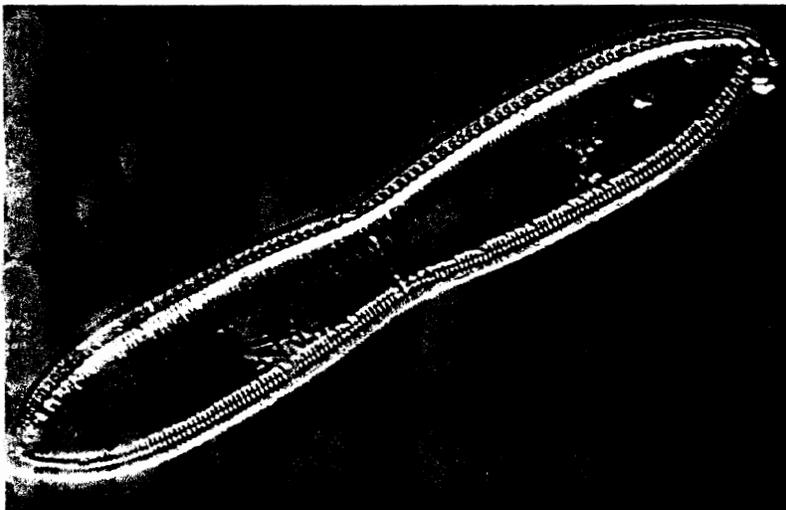
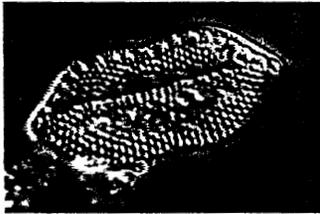
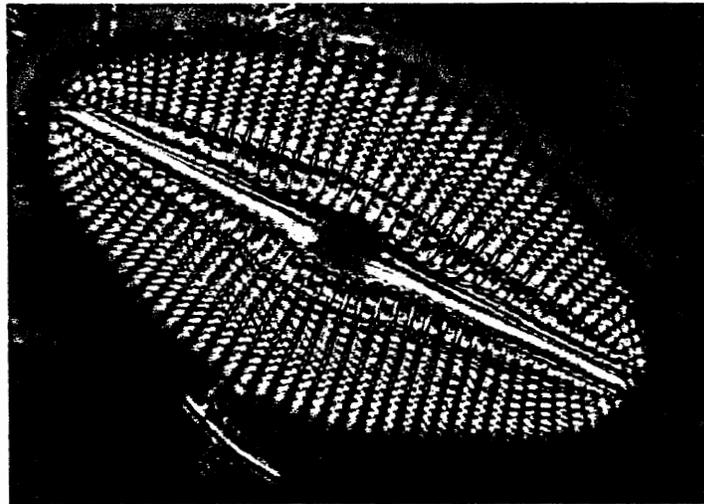


Figure 18. Diatom images from Neuse core UNC: Three from recent sediments (mostly planktonic), and five from sediments dated ~1767 A. D. (primarily benthic). All images are the same scale.

The results of calculated flux of diatom valves (from slide counts) to the sediments and the flux of measured sediment BSi show very similar trends for all cores. This evidence supports the assumption that BSi represents primarily diatom valve preservation in the sediments. Diatom abundance as determined by counts is shown compared to the pattern of BSi concentration downcore for one core in Figure 19.

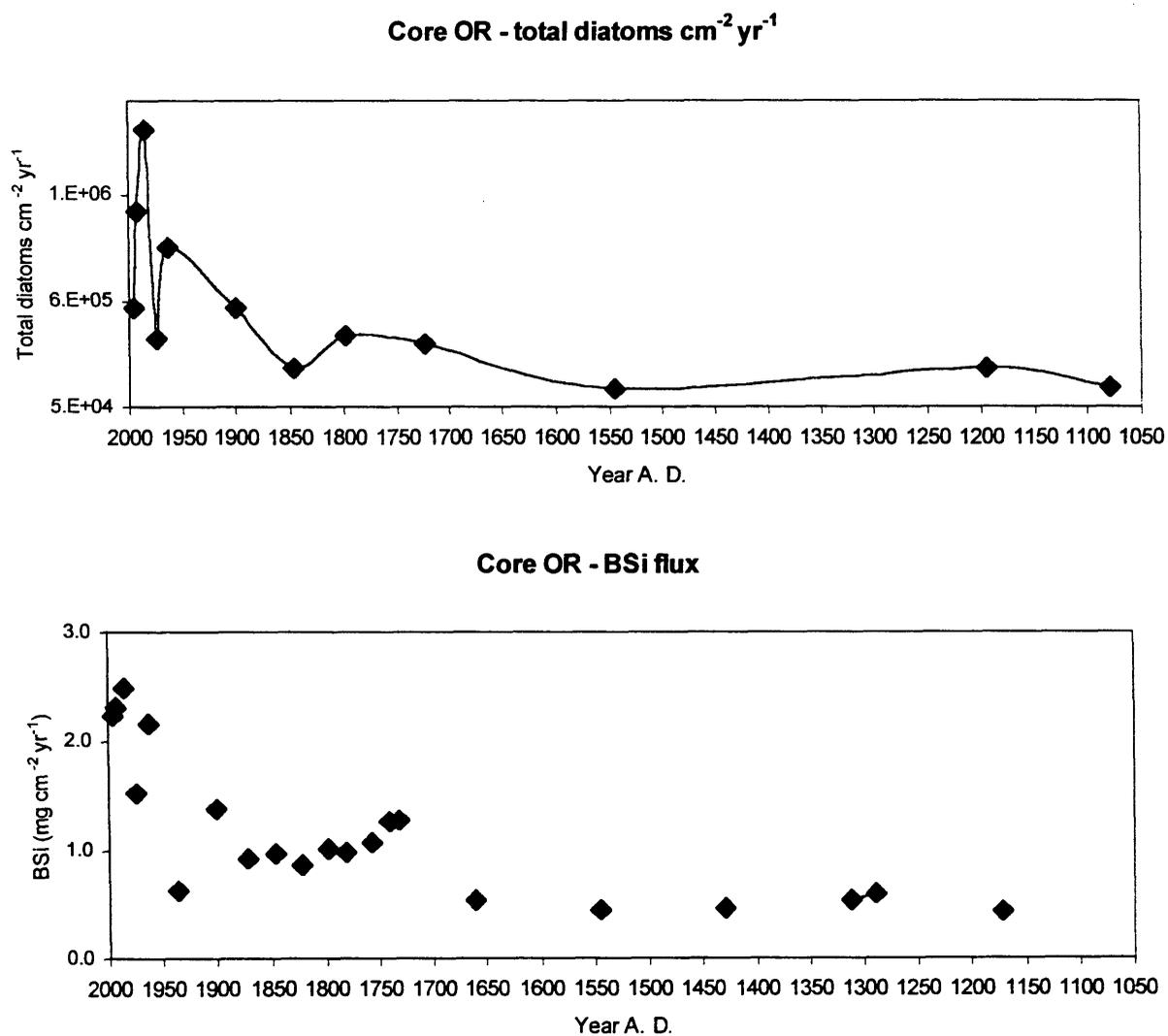


Figure 19. Calculated diatom valve flux and BSi flux for Neuse core OR from diatom valve counts and BSi measurements.

Pollen. Pollen was counted for subsamples of the same six of seven core sites analyzed for diatoms in the Neuse and Pamlico estuaries. Representative results of pollen counts for these cores are shown in Tables 9 & 10, including flux of pollen, dinoflagellate cysts and foraminifera as seen on the pollen slides. The dinocysts and forams that survive the pollen extraction process are only certain forms and do not represent the entire suite of available fossil indicators in these groups. Graphs of pine to ragweed (*Pinus* to *Ambrosia*) ratios for two of the cores are shown in Figure 20. These data along with % abundance of *Ambrosia* pollen were used to determine the agricultural horizon (1720 A. D.) in the sediment cores (Table 5).

Table 9. Selected pollen data from Neuse core samples.

core	Depth(cm)	Year A. D.	pollen counted	pine/ragweed	Pollen % abundance				Flux (# cm ⁻² yr ⁻¹)		
					<i>Ambrosia</i>	<i>Pinus</i>	Nut tree	Sweet gum	pollen	dinocysts	forams
OR	0-2	1996	300	10	5.3	53.0	4.7	3.0	11944	40	-
OR	10-12	1982	301	4	5.3	23.6	2.0	5.6	8843	118	59
OR	12-14	1978	501	18	3.4	61.1	0.8	1.8	29454	412	59
OR	14-16	1974	500	19	2.8	52.4	2.0	2.0	13309	186	-
OR	20-22	1963	300	12	3.7	43.3	3.7	3.7	20138	269	67
OR	24-26	1947	509	31	1.8	54.8	1.0	2.0	7306	72	-
OR	30-32	1913	311	23	2.9	65.3	1.3	0.3	11151	287	466
OR	40-42	1863	309	20	3.2	65.7	2.3	1.3	8723	480	254
OR	50-52	1822	300	15	4.0	60.0	1.0	1.3	11627	581	620
OR	60-62	1782	306	28	2.6	73.2	1.0	0.7	23580	925	1926
OR	70-72	1741	303	27	2.6	70.0	1.0	0.3	24222	1199	2558
OR	74-76	1724	301	74	1.0	73.4	0.3	0.7	28763	669	860
OR	80-82	1662	320	130	0.6	81.3	0.0	0.3	12407	543	388
OR	82-83.5	1639	305	228	0.3	74.8	0.7	1.0	27586	271	1990
OR	90-92	1545	500	320	0.2	64.0	2.0	1.0	17161	137	103
OR	100-102	1429	501	180	0.4	71.7	0.8	0.2	11361	567	45
OR	110-112	1312	504	159	0.4	63.1	1.6	0.8	24083	717	96
OR	120-122	1195	511	367	0.2	71.8	0.2	0.4	22918	583	90
OR	130-132	1079	509	169	0.4	66.2	0.2	0.2	15928	250	219
OR	140-142	962	501	172	0.4	68.5	0.6	0.2	15163	303	242
UNC	0-2	1994	301	13	4.3	56.8	1.0	6.6	5667	56	151
UNC	2-4	1986	502	27	2.2	59.4	1.2	1.6	4274	34	-
UNC	6-8	1965	500	21	2.8	59.4	1.8	1.8	4621	9	18
UNC	10-12	1935	302	16	3.3	53.0	3.3	2.0	3533	117	187
UNC	14-16	1892	502	27	2.4	65.1	1.0	0.0	8756	105	122
UNC	20-22	1861	305	20	3.3	65.6	2.6	0.7	14561	286	573
UNC	24-26	1840	303	50	1.3	66.0	2.6	0.7	13543	134	447
UNC	30-32	1809	307	32	2.0	61.9	0.7	0.0	16380	587	1227
UNC	36-38	1777	303	41	1.7	67.3	1.0	0.7	19040	628	754
UNC	40-42	1757	304	54	1.3	71.4	1.0	0.7	25485	1174	922

UNC	42-44	1746	316	46	1.6	72.2	0.3	0.0	20275	513	257
UNC	44-46	1736	305	70	1.0	68.9	0.3	0.3	19747	583	259
UNC	46-48	1725	505	125	0.6	74.3	0.4	0.2	27458	489	163
UNC	50-52	1704	502	74	1.0	73.9	0.6	0.6	21641	560	776
UNC	52-54	1693	313	215	0.3	68.7	0.3	0.3	38107	1583	1339
UNC	54-56	1682	503	209	0.4	82.9	0.2	0.0	25043	498	199
UNC	60-62	1650	307	258	0.3	84.0	0.3	0.3	33252	866	542
UNC	70-72	1596	309	240	0.3	77.7	0.0	0.0	41152	799	799
UNC	80-82	1542	508	55	1.4	75.4	0.4	0.0	36477	287	287
UNC	90-92	1488	510	120	0.6	70.4	0.2	0.2	28071	936	385
UNC	100-102	1434	507	92	0.8	72.8	0.2	0.2	21430	423	42
UNC	110-112	1380	500	377	0.2	75.4	0.0	0.2	34761	1043	487
UNC	120-122	1326	502	384	0.2	76.5	0.2	0.2	29637	531	413
WP	0-2	1996	500	25	2.6	64.0	1.2	2.4	19007	190	76
WP	4-6	1992	508	30	2.2	65.9	0.0	2.8	27831	219	55
WP	10-12	1983	503	29	2.2	62.6	0.4	2.0	17054	305	34
WP	14-16	1975	502	22	2.4	52.2	3.2	1.6	14865	59	-
WP	20-22	1961	508	11	4.7	51.8	1.6	3.3	24461	433	241
WP	24-26	1953	504	12	4.0	49.2	2.6	1.8	17018	169	236
WP	26-28	1947	502	11	4.6	50.6	2.4	1.2	12824	383	77
WP	30-32	1933	500	12	4.0	47.6	2.0	0.2	11816	378	142
WP	36-38	1905	500	14	4.2	60.2	1.8	1.6	7028	183	112
WP	40-42	1891	500	33	1.8	59.2	0.8	0.6	9906	436	198
WP	50-52	1836	500	27	2.2	59.6	1.2	0.6	9994	400	200
WP	60-62	1780	500	25	2.6	66.2	0.0	0.4	7743	418	139
WP	64-66	1758	505	36	1.8	63.4	1.2	0.4	15889	346	189
WP	70-72	1725	500	393	0.2	78.6	1.0	0.2	24815	596	248
WP	80-82	1630	507	170	0.4	66.9	0.8	0.4	9352	424	92
WP	90-92	1530	501	86	0.8	68.3	0.2	0.4	11944	310	119
WP	100-102	1430	501	92	0.8	73.1	0.0	0.4	11160	156	22
WP	110-112	1330	527	182	0.4	69.1	0.8	0.6	8316	221	95
WP	120-122	1230	501	193	0.4	76.8	0.2	0.2	6575	262	39

Table 10. Selected pollen data from Pamlico core samples.

core	Depth(cm)	Year	pollen A. D.	pine/ counted	ragweed	Pollen % abundance				Flux (# cm ⁻² yr ⁻¹)		
						<i>Ambrosia</i>	<i>Pinus</i>	Nut tree	Sweet gum	pollen	dinocysts	forams
BC	0-2	1997	300	17	3.7	63.7	2.0	4.3	29311	-	293	
BC	2-4	1995	307	28	2.3	63.8	0.7	4.9	37943	247	618	
BC	8-10	1972	300	40	1.7	66.0	1.7	1.7	30018	-	400	
BC	14-16	1959	301	36	2.0	72.4	0.3	1.3	69406	461	1153	
BC	20-22	1934	300	31	2.0	61.3	0.7	0.7	11585	39	425	
BC	30-32	1833	304	33	2.3	75.0	1.0	0.0	6534	-	172	
BC	34-36	1783	500	58	1.4	81.0	0.2	0.0	10628	-	170	
BC	36-38	1758	305	76	1.0	74.4	0.3	0.0	10641	70	-	
BC	40-42	1708	300	262	0.3	87.3	0.0	1.3	12499	-	83	

BC	50-52	1591	305	123	0.7	80.7	1.3	0.3	16528	217	542
BC	60-62	1473	304	239	0.0	78.6	0.7	0.3	15430	-	761
BC	80-82	1238	305	75	1.0	73.4	1.0	0.3	11353	149	744
BC	100-102	1003	314	236	0.0	75.2	1.3	0.3	15204	339	629
BC	118-121	791	305	227	0.0	74.4	1.0	0.3	24469	160	1364
<hr/>											
M4	0-1	1997	300	15	3.7	55.3	0.7	3.3	29713	99	297
M4	4-6	1994	302	18	3.3	59.6	1.7	1.7	50604	503	1005
M4	10-12	1988	300	25	2.3	58.7	1.3	1.7	75054	500	1001
M4	14-16	1985	310	24	2.6	62.6	1.6	1.6	59610	385	192
M4	20-22	1979	312	6	7.4	43.9	4.8	0.6	59501	-	572
M4	30-32	1969	304	14	4.3	58.6	2.3	1.6	73224	723	1204
M4	38-40	1961	301	9	6.3	58.1	3.3	2.3	23915	79	636
M4	42-44	1953	301	13	4.7	58.8	2.3	1.0	40058	-	1065
M4	52-54	1936	300	19	3.3	64.7	0.7	1.3	19882	199	199
M4	60-62	1903	303	19	3.0	56.4	1.0	2.6	9056	90	90
M4	70-72	1847	300	14	4.7	67.3	0.7	0.7	34187	1367	570
M4	80-82	1821	306	17	3.9	66.3	0.3	2.0	20121	197	329
M4	90-92	1796	303	14	5.0	67.3	0.7	1.0	18453	244	365
M4	92-94	1791	312	7	6.7	50.3	1.9	0.3	32581	209	1671
M4	98-100	1775	307	10	7.2	69.1	0.7	1.0	19696	192	321
M4	102-104	1765	311	13	4.8	63.0	1.6	0.6	20609	-	530
M4	106-108	1755	300	24	3.0	71.0	0.0	0.3	24693	494	741
M4	112-114	1740	308	24	2.6	63.0	2.6	0.3	37144	241	1930
M4	114-116	1735	304	19	3.9	75.7	0.0	0.0	30841	304	1015
M4	116-118	1730	308	17	4.2	71.4	0.3	0.3	45413	442	1769
M4	122-124	1699	461	49	1.3	64.2	2.0	0.2	6589	86	186
M4	126-128	1628	505	40	1.8	71.7	0.0	0.6	6420	102	-
M4	132-134	1521	304	28	2.3	64.5	0.0	0.3	3387	22	78
<hr/>											
BB	0-2	1995	502	36	1.6	57.6	2.6	3.8	11837	-	-
BB	4-6	1979	503	52	1.0	52.1	1.0	4.0	9724	-	-
BB	10-12	1947	500	7	7.8	51.6	3.4	2.8	12543	50	25
BB	20-22	1840	501	9	5.6	51.7	2.8	0.6	7242	29	145
BB	26-28	1785	502	15	3.8	58.4	2.2	0.0	7435	15	118
BB	30-32	1748	503	23	2.8	64.6	0.8	0.2	10262	61	102
BB	32-34	1730	502	50	1.4	69.1	1.2	0.4	20015	80	159
BB	34-36	1711	500	116	0.6	69.4	1.2	0.2	16243	130	32
BB	38-40	1652	514	69	1.0	67.3	0.8	0.2	11334	132	243
BB	40-42	1619	547	194	0.4	70.9	1.3	0.4	17878	261	654
BB	50-52	1452	500	103	0.6	61.6	1.0	0.0	10873	87	109
BB	60-62	1285	507	173	0.4	68.0	0.4	0.4	11304	111	111
BB	70-72	1119	527	106	0.6	60.5	1.7	0.6	11660	243	66
BB	80-82	952	502	105	0.6	62.9	0.8	0.4	14402	287	287

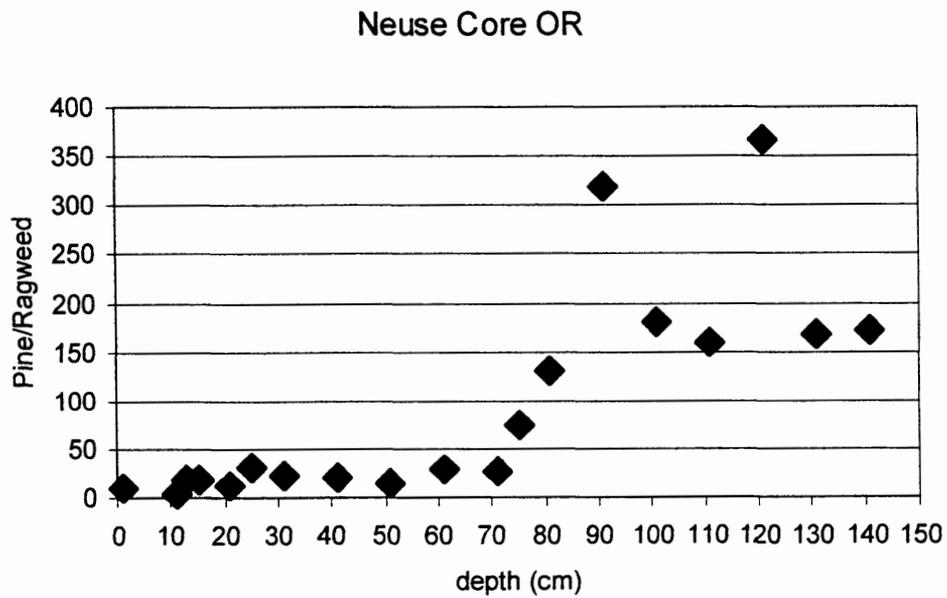
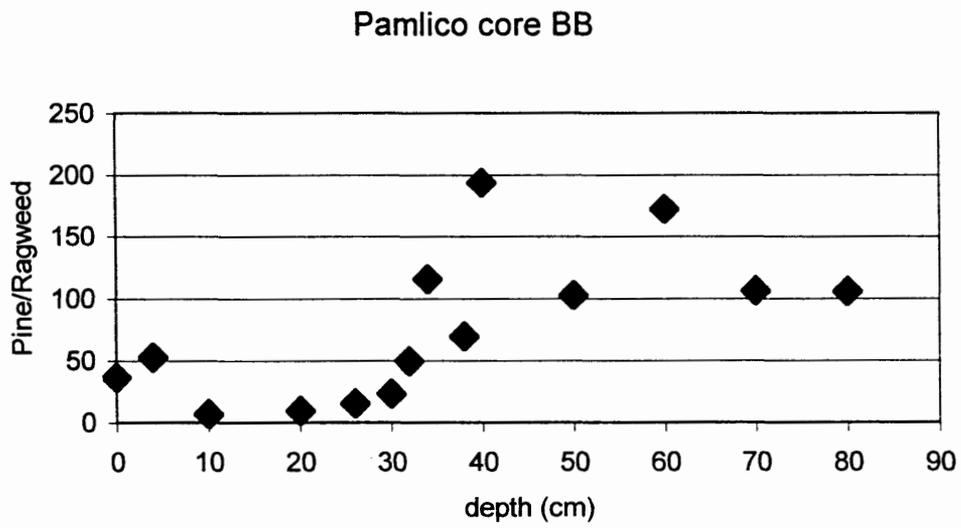
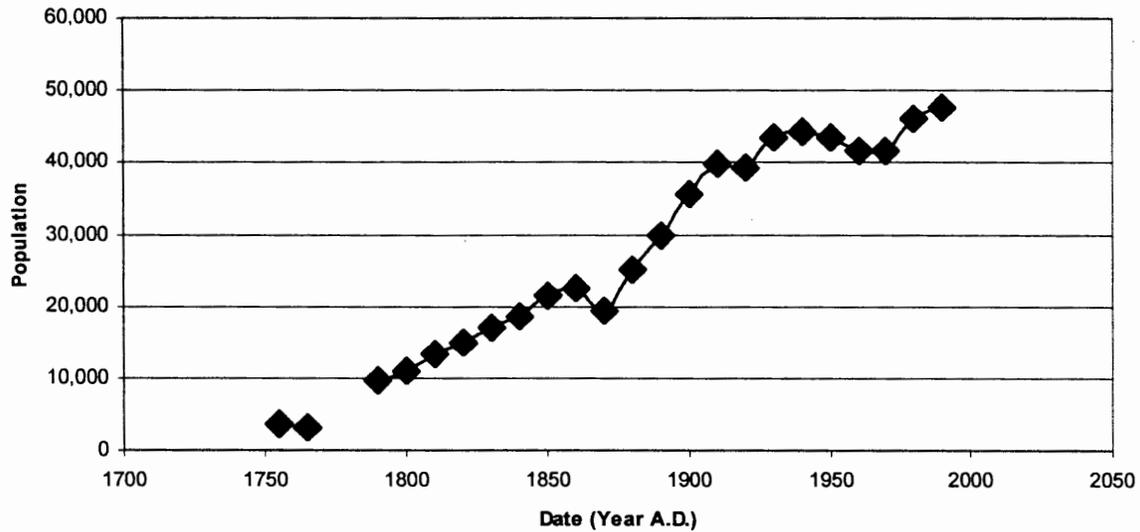


Figure 20. Graphs of pine to ragweed ratios for Pamlico core BB and Neuse core OR.

Historical data

Selected results of our historical data search are presented here in Figures 21 & 22 (population graphs) and Tables 11-14 .

Population Pamlico



Population Neuse

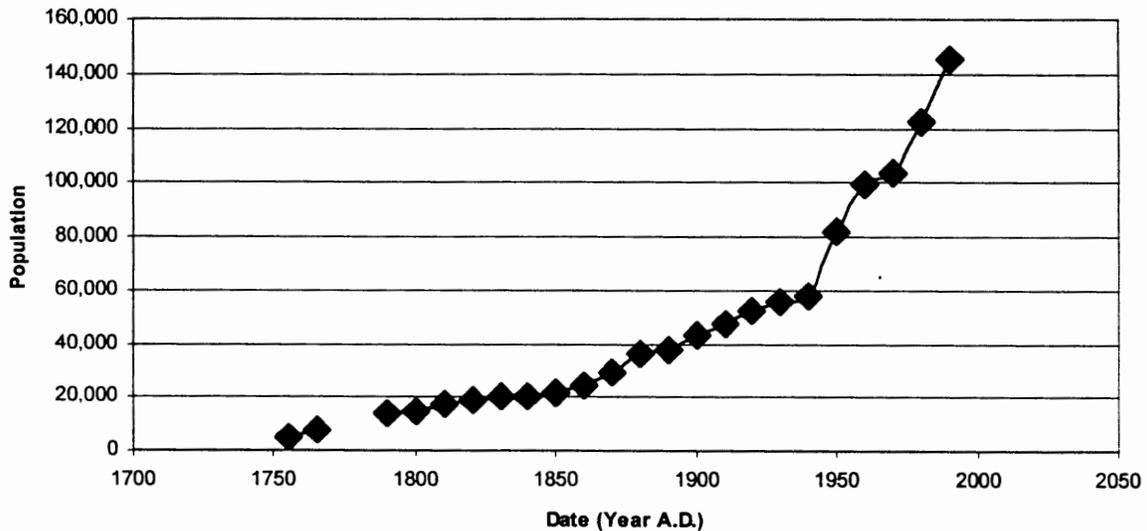


Figure 21. Population data for counties, 1755-1990. Pamlico data includes Beaufort and Hyde county data only. Neuse data includes Craven, Carteret and Pamlico county data. Data for 1790-1990 collected from Population Abstracts of the United States. (Andriot 1993). Data for 1755 and 1765 includes "White Taxables" and "Blacks" only. No white women or white men under 18 counted (Saunders 1887).

Population - eastern NC

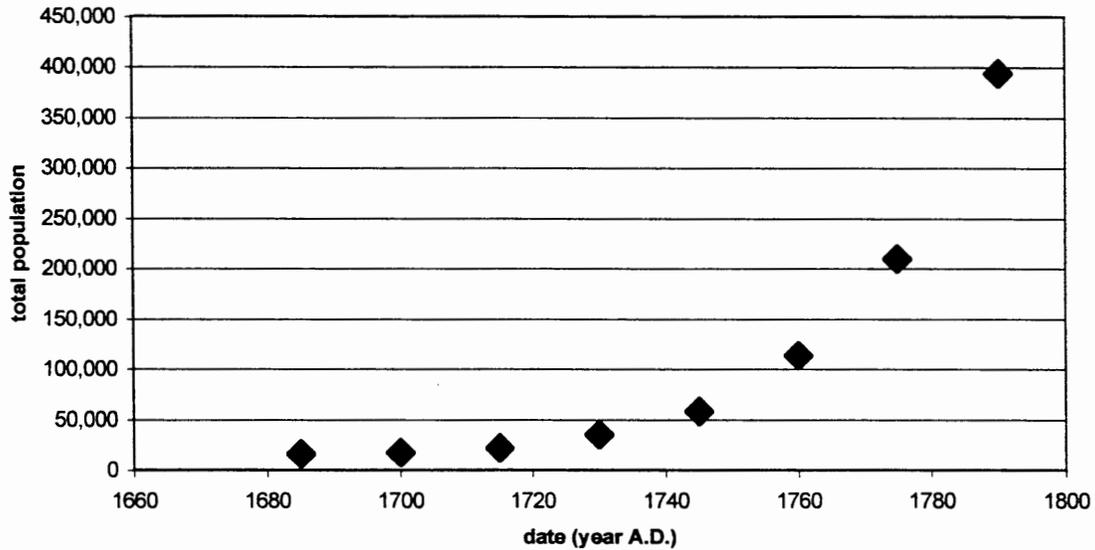


Figure 22. Estimated population of eastern North Carolina (east of the Appalachian mountains, including all modern counties EXCEPT for the western tier of 18 “Mountain counties” of Cherokee, Graham, Clay, Macon, Swan, Jackson, Haywood, Transylvania, Henderson, Buncombe, Madison, Yancey, Mitchell, Avery, Watauga, Ashe, Allegheny and Wilkes) from 1680 through 1790 (when census data began to be collected). Data is taken from Wood (1989).

Data was collected on manufacturing companies and various other types of industry in the counties immediately around the Pamlico and Neuse estuaries. However, the data were difficult to interpret as size and income of these companies were not listed. Therefore, number of workers was also researched and selected data are presented here (Table 11).

Table 11. Combined data on number of machines/electronics workers, metal and fabricated metal workers, chemical workers, and transportation workers. Data were compiled by adding mean numbers for each number bracket from North Carolina Manufacturers Directories, 1944-1995. Manufacturers Directories attempt to be comprehensive in collecting data.

Dates	Beaufort	Carteret	Craven	Hyde	Pamlico	Total
1944	122	483	585	0	0	1190
1952	50	1350	480	0	0	1880
1956	50	350	250	0	0	650
1960	125	475	350	0	0	950
1964	136	62	536	0	0	734
1968	624	325	885	0	0	1834
1972-3	1568	173	1043	0	0	2784
1974-5	2493	639	1477	0	0	4609

Table 11 cont.

Dates	Beaufort	Carteret	Craven	Hyde	Pamlico	Total
1979-80	2564	297	1384	0	0	4245
1985-86	4819	214	2133	0	0	7166
1989-90	5050	342	3248	0	0	8640
1994	2956	225	2001	0	0	5182
1995	3175	221	5790	0	17	9203

Information on cropland, farmland, livestock, fertilizer use, and many other types of data for each county can be found in the U.S. Census. Data on commercial fertilizer use and number of swine, and number of cars and trucks registered in the counties immediately adjacent to the Neuse and Pamlico estuaries are presented in Tables 12-13. Additional data were obtained from North Carolina records, such as number of cars and trucks registered in these counties (Table 14).

Table 12. Acres of land fertilized (with commercial materials) in various counties. Data collected from U.S. Census, 1954-1992. * indicates data not reported.

Dates	Beaufort	Carteret	Craven	Hyde	Pamlico	Total
1954	88,419	14,480	42,751	23,032	24,721	193,403
1959	73,840	10,795	43,281	27,670	19,593	175,179
1964	81,095	9,965	36,513	32,499	21,082	181,154
1969	70,599	7,249	27,971	39,132	15,890	160,841
1978	100,427	21,508	51,430	51,203	25,252	249,820
1982	90,678	*	40,650	58,554	25,088	214,970
1987	85,174	25,428	42,014	55,518	25,632	233,766
1992	102,977	40,437	46,508	61,871	31,468	283,261

Table 13. Number of pigs and hogs for counties, 1840-1992. Data collected from U.S. Census. NA indicates "data not available".

Dates	Beaufort	Carteret	Craven	Hyde	Pamlico	Total
1840	24,717	7,034	19,222	1,629	NA	52,602
1850	18,279	5,107	17,330	10,232	NA	50,948
1860	22,146	4,694	24,556	11,496	NA	62,892
1870	16,730	3,765	15,431	15,731	NA	51,657
1880	18,826	4,960	13,599	8,642	6,959	52,986
1890	17,988	7,097	11,000	8,535	7,315	51,935
1900	19,595	5,942	13,081	6,557	6,476	51,651
1910	24,707	8,922	16,469	10,723	8,979	69,800
1920	25,967	6,096	14,695	13,953	9,079	69,790
1930	19,226	5,794	11,313	6,390	5,820	48,543
1935	18,913	4,039	13,394	6,393	6,465	49,204
1940	10,780	2,785	7,439	4,583	3,086	28,673

Table 13 cont.

Dates	Beaufort	Carteret	Craven	Hyde	Pamlico	Total
1945	20,864	5,754	14,265	6,342	3,590	50,815
1950	20,773	4,256	14,099	6,562	4,417	50,107
1954	26,887	6,897	16,112	5,728	5,964	61,588
1959	29,728	5,669	16,059	6,543	6,243	64,242
1964	23,236	2,580	8,349	6,257	2,791	43,213
1969	24,153	1,918	14,052	7,744	1,377	49,244
1974	25,238	1,351	13,367	8,598	837	49,391
1978	44,793	1,381	19,328	11,578	2,777	79,857
1982	64,028	1,049	27,854	14,429	1,832	109,192
1987	75,748	882	58,686	15,817	4,744	155,877
1992	72,180	2,408	59,046	16,497	6,529	156,660

Table 14. Data on total number of registered cars and trucks in counties immediately adjacent to the Neuse and Pamlico. Sources: Statistical abstract of NC counties -- vols ca.1982 and 1990. 1991 - 1995 data from LINC (Look into North Carolina) -- <scc.sips.state.nc.us>.

Dates	Beaufort	Carteret	Craven	Hyde	Pamlico
1960	12,222	9,715	19,162	1,590	2,652
1965	15,021	11,937	23,798	1,906	3,118
1970	17,421	15,023	26,870	2,236	4,059
1975	23,014	21,102	35,846	3,058	5,540
1980	26,862	26,502	42,807	3,645	6,931
1982	27,101	27,862	42,597	3,316	6,969
1986	32,052	36,649	50,945	3,938	8,462
1987	30,151	34,853	49,676	3,818	8,004
1988	30,882	35,425	51,033	3,941	8,165
1989	31,243	36,532	53,420	3,950	8,299
1990	31,404	37,347	53,414	3,990	8,364
1991	31,546	38,419	55,210	3,966	8,437
1992	32,316	40,365	57,037	4,010	8,672
1993	33,235	42,233	58,500	4,073	8,981
1994	34,088	43,732	60,224	4,214	9,346
1995	34,148	44,202	61,035	4,212	9,394

DISCUSSION

Results show that sediment cores collected from the Neuse and Pamlico estuaries contain valuable information about past and present water quality. The sediments show good stratigraphy with minimal mixing or bioturbation, especially at deeper sites. Cores of approximately one meter in depth record the history of the estuaries back 700 years to over a thousand years. These sediments can be dated, and although sedimentation rates vary from site to site, good resolution of recent sediments (since 1950 A. D.) can be obtained (e.g. average resolution of 1.8-9.4 years per sample over the past 35 years). The BC and M7 sites in the Pamlico estuary show higher sedimentation at a few sample depths based on ^{210}Pb results, possibly related to storm activity or increased mixing of sediments during certain periods at these sites. Other data such as bulk density of sediments would appear to corroborate some recent mixing of sediments in these cores.

Most changes in indicators of water quality in both the Neuse and the Pamlico analyzed for this study occur in the past 50 years (according to the dates calculated and assigned in this study). Sedimentation rates and nutrient and trace metal fluxes to the sediments appear to have increased significantly in this time frame (by as much as an order of magnitude). The organic content of the sediments (including TOC) has increased over this time frame as well, reflecting increased primary production within the estuaries relative to degradation. The highest overall nutrient content (concentration) is found in the Pamlico core M4, which was collected at a location closest to the PCS phosphate mining operations on the Pamlico estuary. Highest trace metal concentrations were found in the Neuse River, and are most likely associated with industrial and military operations. These results confirm previous research (Riggs *et al.* 1989, Riggs *et al.* 1991) and provide a temporal framework for these changes.

Previous research on these estuaries has shown that P loadings in the Pamlico estuary are unusually high in comparison with other U. S. river basins, due to large inputs from the phosphate mining facility, which accounts for about half of the total point source P loadings to this estuary (Stanley 1992). Phosphate mining and effluent discharge to the Pamlico estuary began in 1964 (Copeland & Hobbie 1972). Total annual P loadings into the Neuse River are estimated to have increased 60% in the last century, mostly in the past 40 years, due to increased sewage discharge (Steel 1991). Other nutrient loadings to the estuaries and the Pamlico Sound are considered high (Quinn *et al.* 1989, Christian *et al.* 1991, Robert Christian, ECU pers. comm. 1997). Point source nitrogen (N) loadings are highest in the Neuse, and account for about 20% of the total N load (Stanley 1992), although it is estimated that point source N inputs can account for as much as 60-70% of total N during summer months when non-point source N is at its lowest levels (Steel 1991).

Most reports of hypoxic and anoxic waters in the Neuse and Pamlico appear to be events of short duration. Lack of long-term monitoring data makes it impossible to determine how much anthropogenic influences have affected dissolved oxygen conditions (Stanley 1992). For the Pamlico River estuary, hypoxia has become one of the most important environmental issues. Hypoxia was first documented in the late 1960s (Hobbie *et al.* 1975). Many fish kills in the estuary in recent years have been attributed to hypoxia or anoxia in the bottom waters. As in other estuarine systems such as the Chesapeake Bay, anthropogenic nutrient input and phytoplankton

blooms are thought to be a factor in the establishment of hypoxic bottom waters, but stratification of the water column and climatic events are more clearly correlated with year-to-year variability of oxygen conditions (Stanley 1992).

From initial S, Fe, and estimated DOP results, it appears that the Neuse and Pamlico estuaries have more periods of hypoxic and anoxic bottom waters than are generally found in the Chesapeake Bay. Sulfur levels are consistently above 1% of sediment dry mass, indicating anoxic sediments below the water interface. The sulfur measurements indicate an increase in deposition of sulfur to the sediments over time which would support increasing hypoxia and/or anoxia in these estuaries. Availability of Fe can affect the geochemistry and pyritization of Fe, but both estuaries appear to be very similar in this regard. Based on the estimated DOP results, the Neuse estuary may have experienced anoxic or hypoxic bottom waters for the last several thousand years at the sites studied. Results from the Pamlico indicate that hypoxic and anoxic bottom waters have increased over time in the last 200 years at three out of four of the sites studied. The most recent sediments will most likely show higher DOP values as they are buried deeper in the sediments. Recent increases in this parameter may be significant.

Nutrient enrichment of the Pamlico and Neuse estuarine waters and blooms of noxious phytoplankton have been documented (e. g. Paerl 1983, 1987, 1988, Steel 1991, Christian *et al.* 1991, Boyer *et al.* 1994). Some of the most notable blooms have occurred in the Neuse River in the last two decades. Other tributaries experience periodic blooms, depending on nutrient loading and climatic conditions. Stanley (1993) reports that trends within the Pamlico River estuary in terms of nutrient loading and hypoxic conditions have remained fairly stable over the past two decades. He claims that watershed nutrient production is estimated to have increased several fold between 1880 and 1970 but stabilized in recent decades due to decreased application of fertilizer on croplands.

Measurements of C, P, N and BSi for this study indicate higher accumulation of these elements in the sediments in the past 50 years, especially at deeper sites. The increase is more than double that of older sediments and sometimes several fold, primarily since the late 1800's. Some increase in recent sediments would be expected due to the diagenesis patterns of these elements in buried sediments. However, bioturbation should decrease the surface levels by allowing more oxidation of organic material in the recent sediments. The highest concentrations over the past 50 years are in Pamlico core M4, although accumulations are occasionally higher at other locations (possibly due to agricultural inputs). U. S. Census data do not support the report by Stanley (1993) of lower fertilizer use in the past decades, at least for commercially available fertilizer in the counties immediately adjacent to the Neuse and Pamlico estuaries (see Table 12).

Because the poor preservation of paleopigments seems to be incongruous with the elevated organic content of the sediments and probable anoxic condition of the sediments, it is possible that poor pigment preservation reflects exposure of samples to harsh conditions following their collection (e.g., dry, oxic, lighted), rather than intrinsically poor preservation within the estuary environment. Although the sediments were kept in the dark and refrigerated as much as possible, they had been stored for a year before samples were analyzed. This possibility can be most easily tested by collecting surface sediments using a grab sampler, freezing the mud

immediately, and submitting samples for further pigment analyses. Alternately, further identification and sampling of sites in which deep-water anoxia is more prevalent may be useful.

An overview of phytoplankton studies for the Pamlico and Neuse River estuaries can be found in Mallin (1994), and include work by Boyer, Christian, Copeland, Hobbie, Mallin, Paerl, Rudek, Stanley and others. According to Mallin (1994), all phytoplankton related studies on the Pamlico were established since 1966, after the phosphate mining and effluent discharge to the Pamlico was initiated in 1964. Therefore there are no baseline data available on species abundance and community structure prior to this major change in the watershed of the Pamlico estuary. In the Pamlico River, dinoflagellates are currently the dominant phytoplankton species (Hobbie 1971, Stanley 1992), with diatoms becoming dominant in higher salinity waters (Mallin 1994). In the Neuse River, noxious blooms of blue-green algae have become problematic in the oligohaline reaches of the estuary (Paerl 1987). Phytoplankton in the mesohaline lower Neuse estuary are dominated by diatoms in summer and early spring (Mallin 1994).

Diatom assemblage changes found in this study are significant through time. Recent assemblages are composed primarily of small planktonic forms, species that are often found in large blooms in higher nutrient waters. Recent diatom assemblages show relatively low species richness and diversity compared to older (pre-1950) samples, with higher number of valves being deposited to the sediments. Older assemblages are composed of more benthic and epiphytic species. The decline in epiphytic species may be related to declines in submerged aquatic vegetation. Changes likely reflect eutrophication, increased turbidity and sedimentation, and freshwater flow to the estuaries, as well as an increase in industrial activities. Overall trends are similar to those found in the Chesapeake Bay (Cooper 1995a), although the time frame of major changes is different. Dominant small planktonic species are not the same. Differences in paleoecological indicators between these mid-Atlantic estuaries may be due to geomorphology and land use history.

The BSi results from this study also show that more diatom frustules are being deposited to the sediments in recent years. This indicates higher production, most likely due to increased nutrient inputs. As production increases, dissolved silica in the waters may become limiting, especially if diatom frustules are not recycled, but preserved in the sediments. As silica becomes limiting in the water column, diatoms may be out-competed by other algal species, including dinoflagellates. Diatoms are generally better food sources in the estuarine food web than other algal species, so this change could potentially cause problems in higher trophic levels.

Pollen grains appear to be well preserved in the sediments of the Neuse and Pamlico as well. Pollen assemblage changes include an increase in *Ambrosia* (ragweed) pollen over the past several hundred years, signifying increased land disturbance by humans. Counts also show an increase in nut tree pollen (walnut and pecan) over the last several hundred years, and an increase in Sweetgum tree pollen in the past 50 years. The ragweed horizon was not difficult to identify in any of the cores sampled. A significant increase in % *Ambrosia* along with a large drop in the pine:ragweed ratio were clearly discernable in each core. The date assigned to this "agricultural" horizon is subject to debate, but historical records researched corroborate a date near 1720 A. D. for this change.

Understanding the historical processes of water quality problems is important for managing the continuing impacts of growing populations in North Carolina. This research is useful for providing historical data on changes in estuarine water quality related to changing land use through time. These data can be used to hindcast water quality models, and to provide realistic goals for management.

Historically, land-use in the Albemarle-Pamlico region includes agriculture but mostly forest. According to Stanley (1992), forests comprise 60% of the total basin area, with about 20% of the land in agricultural crops. The urbanized percentage of the basin is low (estimated 2%), but large numbers of people are being drawn to this area due to the diverse resource base, healthy economy and pleasant climate. During the mid 1980's, animal agriculture surged past crop production in North Carolina (primarily in eastern North Carolina) to reverse the historic relationship of these two sectors. Hog production in particular has expanded rapidly between 1991 and 1995 with an average annual growth rate of nearly 30% (Legislative Research Commission 1996).

Three references that address land use and water quality in North Carolina estuaries, and attempt to address issues of management, include Hoban *et al.* (1992), Leffler *et al.* (1995) and the Legislative Research Commission (1996). These reports recognize the need for documentation of land use effects on water quality, development of quantitative models to link land use patterns to their water quality effects, and setting realistic management goals.

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MEDIA PARTICIPATION RELATED TO WRII FUNDED PROJECT

Washington Post newspaper. In "Environment section" article by Joe Warrick. Monday, September 14, 1998. Research funded by WRII of UNC.

Coastwatch magazine, North Carolina Sea Grant, Raleigh, NC. Feature article titled "*Nature Remembers*", by David Cecelski. This article is about the research conducted by Sherri Cooper and funded by WRII 1997-99. September issue, 1998. Research funded by WRII of UNC.

Durham Herald newspaper. September 3, 1998. AP release. Titled "*Coastal estuaries rapidly changing: big jump in metals, sediments found in past 50 years*". Research funded by WRII of UNC.

Winston-Salem Journal. September 3, 1998. AP Release. Titled "*Population rise hurts estuaries, study says: large increases of sediments, nutrients, metals found in waters*". Research funded by WRII of UNC.

Duke Dialogue, Volume 13, No. 2, page 5. (September 4, 1998). *Changes in N. C. estuaries happened in last 50 years*. Article by Monte Basgall, Duke University. Research funded by WRII of UNC.

National Public Radio of UNC, announcement related to AP release and Duke Dialogue article. September 2, 1998.

Happenings newsletter, No. 3.08, September 22, 1998. Nicholas School of the Environment, Duke University. Front page article titled "Most changes in NC estuary water quality happened in past 50 years", about current research funded by WRII of UNC.

Wetland Wire 1(2): 4. Cooper, S. Fall 1998. "The history of water quality in North Carolina estuarine waters as documented in the stratigraphic record". A short description of the current research funded by WRII of UNC.

PUBLICATIONS RELATED TO WRII FUNDED PROJECT

Kim, S. 1998. *Heavy metal assessment in the Pamlico and Neuse River estuaries of North Carolina*. Masters Project. Nicholas School of the Environment, Duke University.

Cooper, S. R. 1999. A journey through time: Paleoecology of estuaries. *Geotimes* 44, 14-18.

GLOSSARY

Abbreviations:

%	percent
$\mu\text{g g}^{-1}$	micrograms per gram
$^{\circ}\text{C}$	degrees centigrade
$^{\circ}\text{F}$	degrees Fahrenheit
μg	microgram
$\mu\text{g cm}^{-2} \text{ yr}^{-1}$	micrograms per square centimeter per year
A. D.	(anno Domini), in the year of our Lord
As	arsenic
cm	centimeters
Co	cobalt
Cr	chromium
Cu	copper
e. g.	(<i>exempli gratia</i>), for example
EPA	United States Environmental Protection Agency
et al.	(<i>et alii</i>), and others
g	gram
H'	Shannon's diversity (Shannon & Weaver 1949)
H_2O_2	hydrogen peroxide
HCl	hydrochloric acid
HF	hydroflouric acid
HNO_3	nitric acid
keV	kiloelectron-volts
km^2	square kilometer
km^3	cubic kilometer
KOH	Potassium hydroxide
kV	kilovolts
m	meter
mA	milliamperes
mg	milligram
$\text{mg cm}^{-2} \text{ yr}^{-1}$	milligrams per square centimeter per year
ml	milliliter
Mn	manganese
Mo	molybdenum
N	north
Na_2CO_3	Sodium carbonate
Ni	nickel
ppt	parts per thousand
Th	thorium
Ti	titanium
USGS	United States Geological Survey
V	Vanadium
W	West
Zn	Zinc

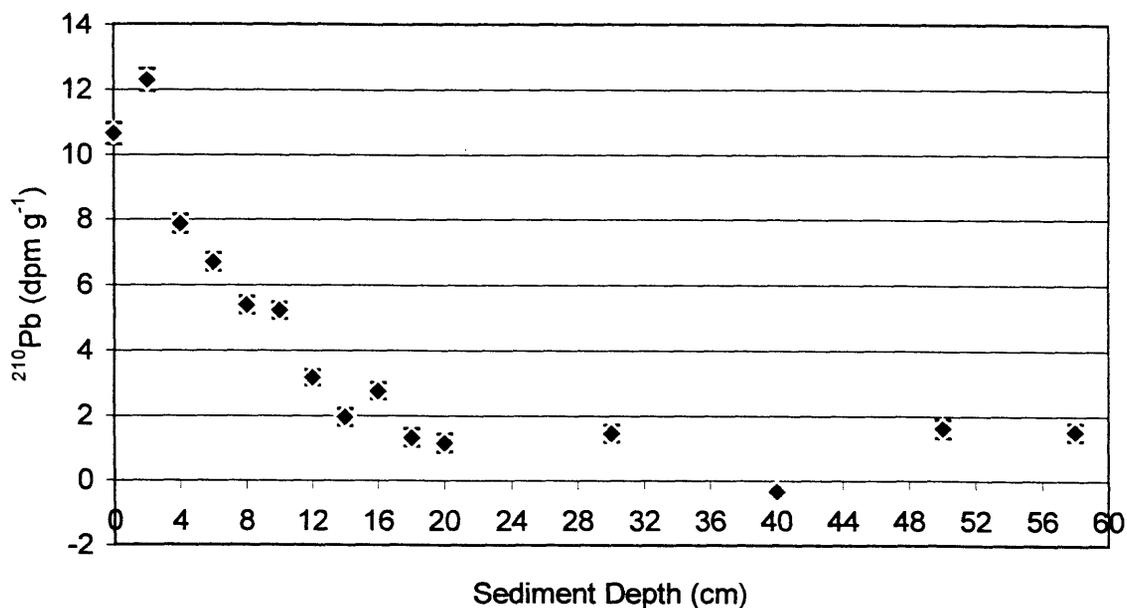
Terms:

Anoxia	Anoxia is the condition of zero oxygen. Anoxic waters contain no dissolved oxygen.
Anthropogenic	Of or related to human activity
Benthic	Of or pertaining to the bottom of a water body, often attached to substrate
Biogeochemistry	Biogeochemistry is the science that deals with the relation of earth chemicals to plant and animal life in an area.
Blooms	Blooms are large increases in numbers of planktonic organisms, some times associated with eutrophication and seasonal temperature changes.
Epiphytic	Plants or algae that grow attached to other plants; in this case, primarily diatoms on submerged macrophytes
Estuary	“An estuary is a semi-enclosed coastal body of water which has a free connection with the open sea and within which sea water is measurably diluted with fresh water derived from land drainage.” Pritchard (1967)
Eutrophication	Eutrophication is the process of becoming more eutrophic. Eutrophic waters are rich in dissolved nutrients, often by anthropogenic fertilization (for example, sewage outfalls or agricultural runoff). Eutrophic waters often experience seasonal oxygen deficiency.
Geomorphology	Geomorphology is the study of the classification, description, nature, origin, and development of landforms and their relationships to underlying structures, and the history of geologic changes as recorded by these surface features.
Hypoxia	Hypoxic waters are deficient in dissolved oxygen ($<2 \text{ mg O}_2 \text{ L}^{-1}$).
Paleoecology	Paleoecology is the study of relationships between past organisms and the environment in which they lived. It is concerned with the reconstruction of past ecosystems by using all available evidence, including biological, chemical, and geological contributions
Planktonic	Floating or drifting in a water body, primarily refers to microorganisms
Sound	A Sound is a long and/or broad inlet of the ocean, generally with its larger part extending roughly parallel to the shore.
Stratigraphy	Stratigraphy is the science or description of relative position of strata in sediments or rock.

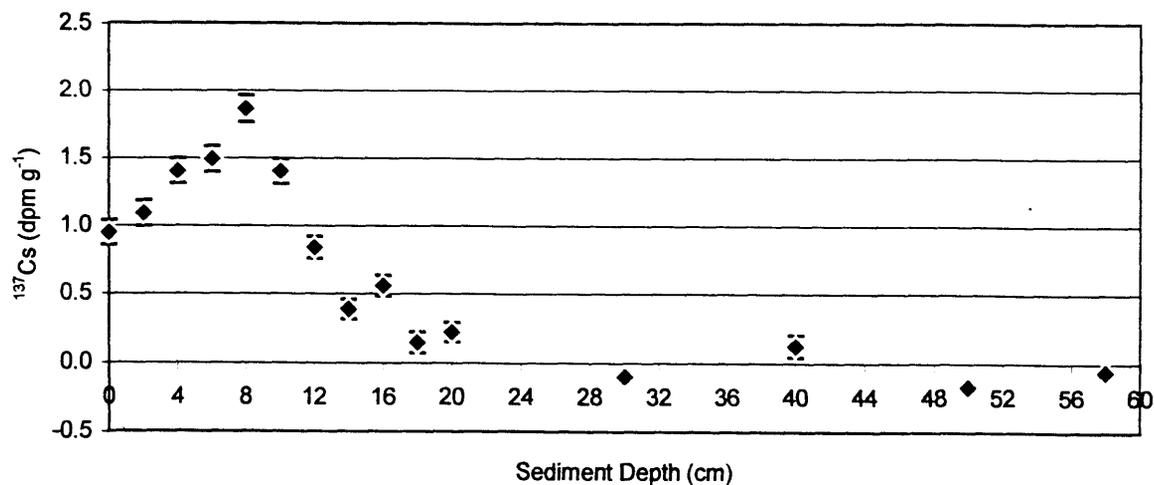
APPENDICES

Appendix A. Graphs of ^{210}Pb and ^{137}Cs measurements for all sediment cores collected for this study from the Neuse and Pamlico Rivers except for M4 and OR (contained within the text of the report).

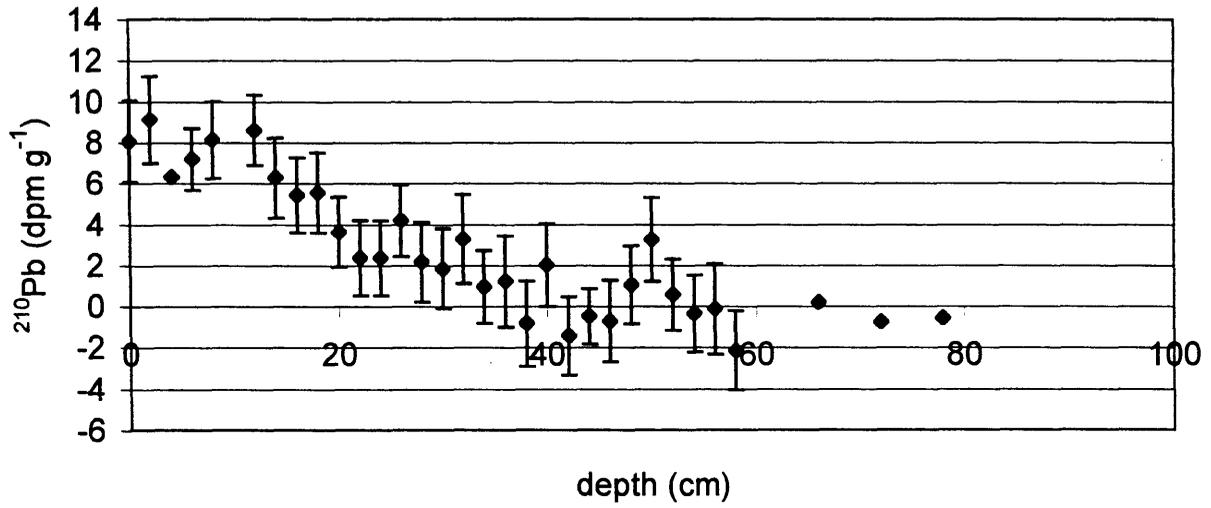
Neuse Core UNC2-3 ^{210}Pb activity vs. depth



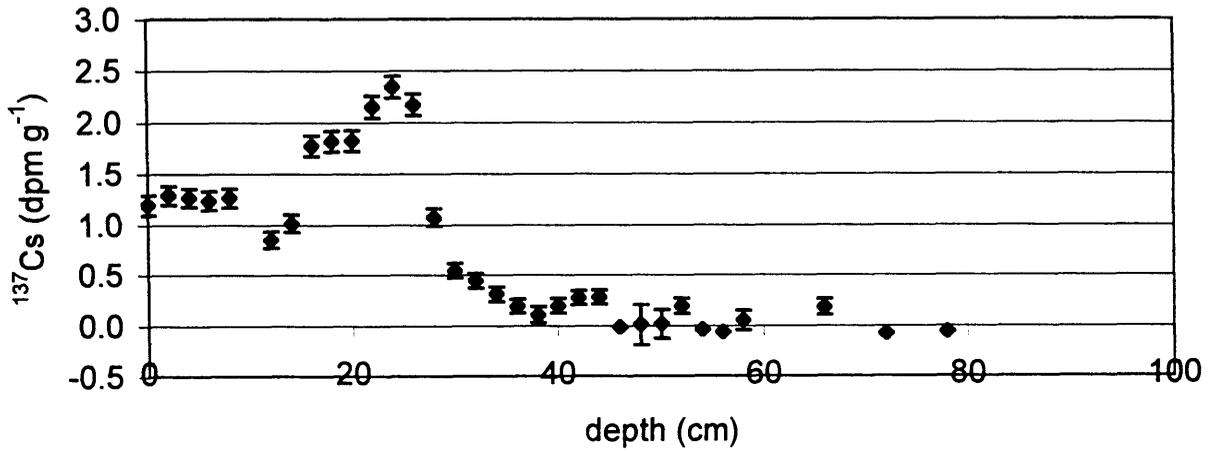
Neuse Core UNC2-3 ^{137}Cs activity vs. depth



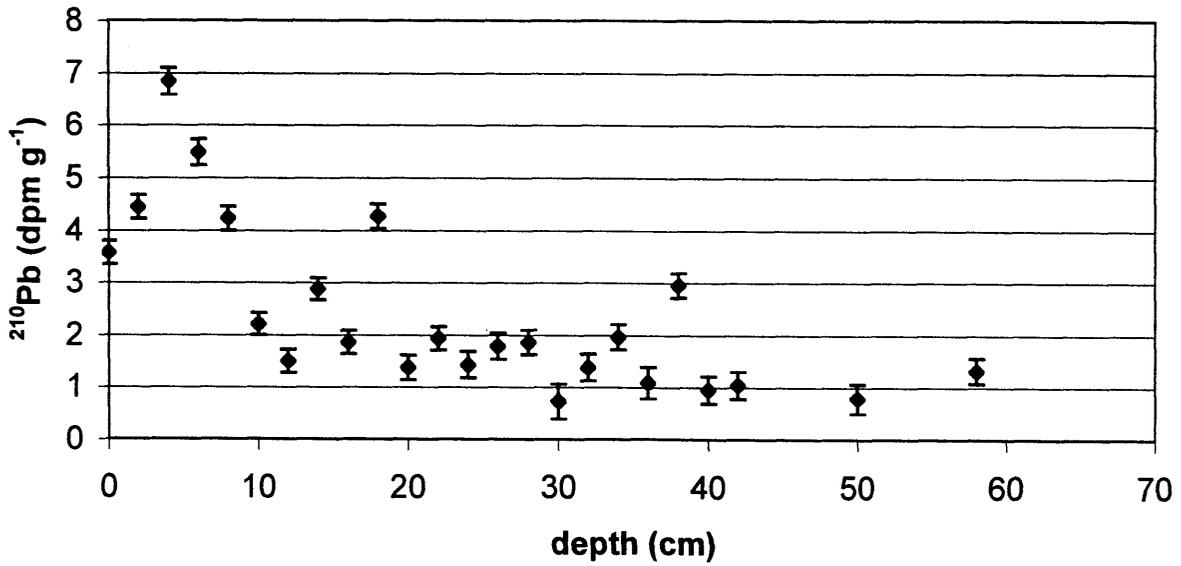
Neuse Core WP ^{210}Pb activity vs. depth



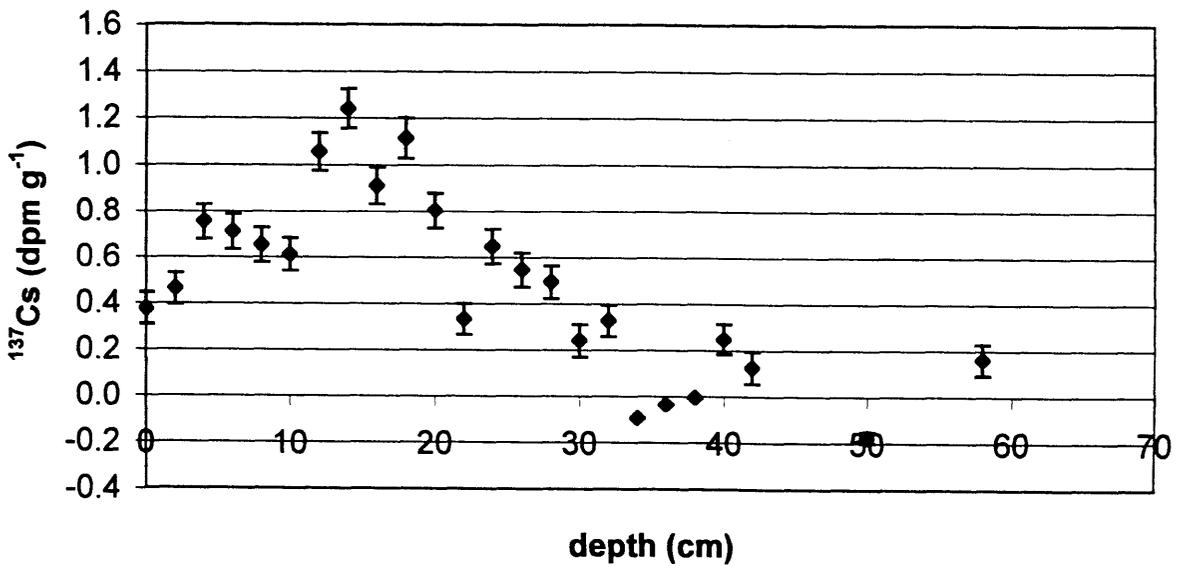
Neuse Core WP ^{137}Cs activity vs. depth



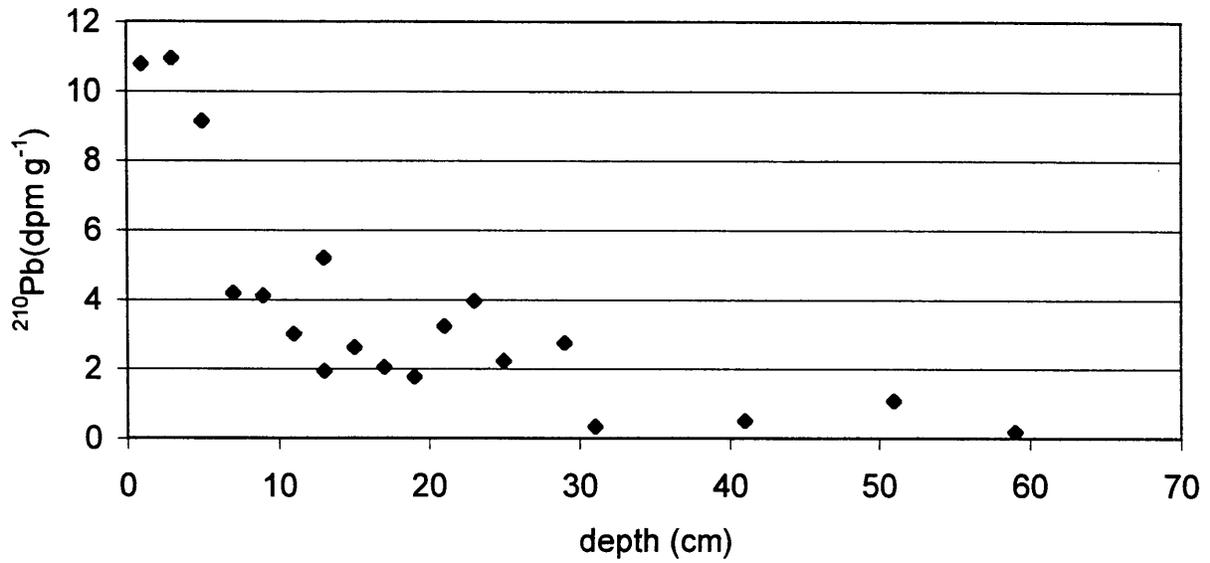
Pamlico Core BC ^{210}Pb activity vs. depth



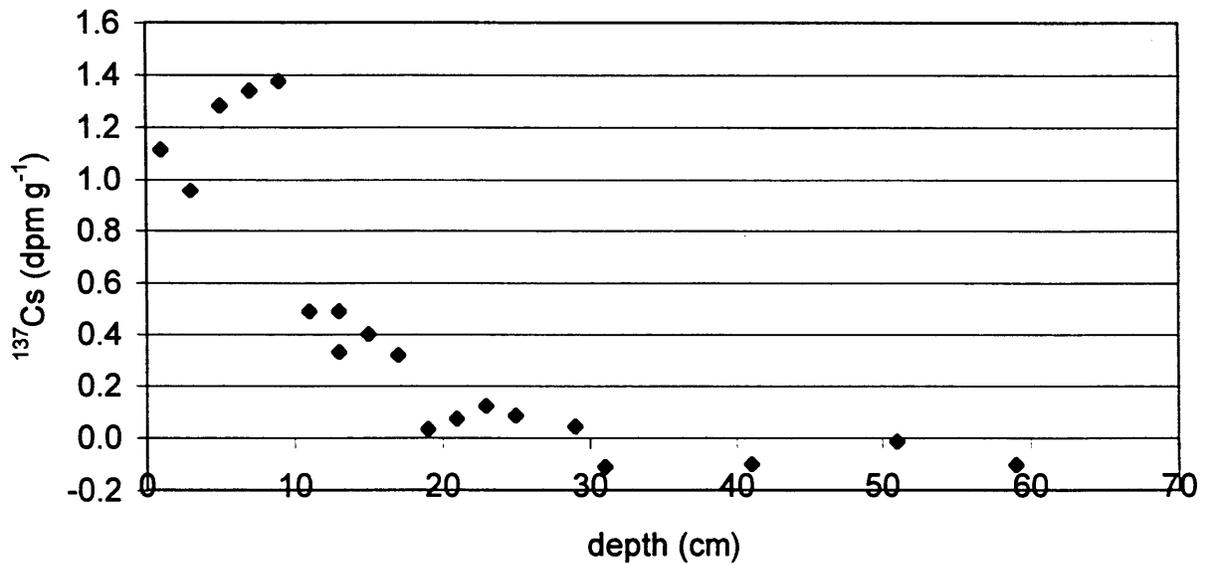
Pamlico Core BC ^{137}Cs activity vs. depth



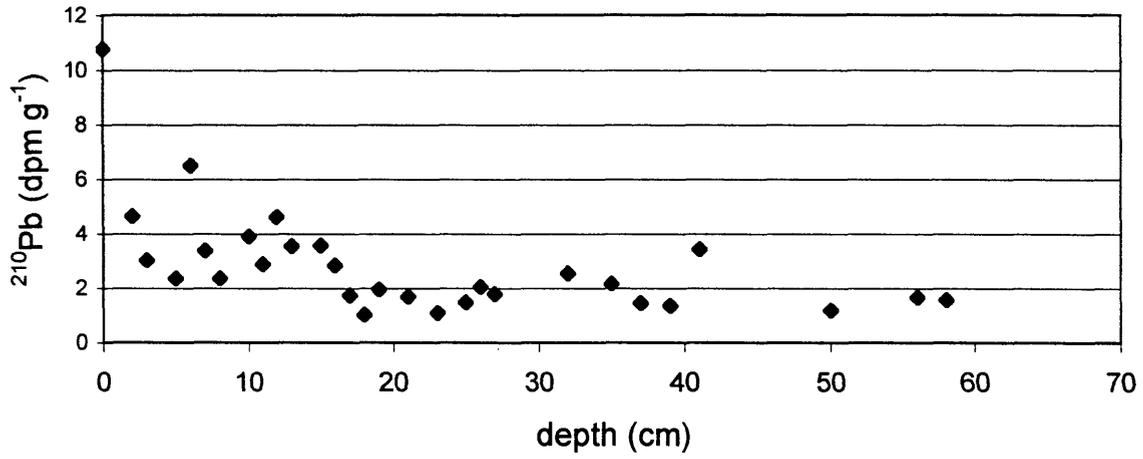
Pamlico Core BB ^{210}Pb activity vs. depth



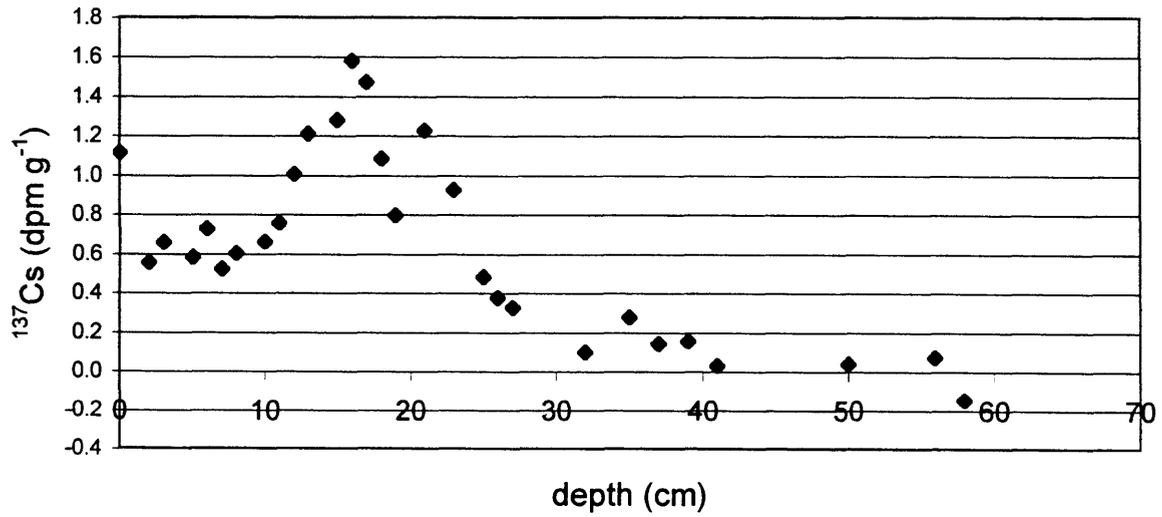
Pamlico Core BB ^{137}Cs activity vs. depth



Pamlico Core M7 ^{210}Pb activity vs. depth



Pamlico Core M7 ^{137}Cs activity vs. depth



Appendix B. List of diatom species identified from the seven cores collected in the Pamlico and Neuse estuaries with taxonomic authorities (in alphabetical order). The references used for these identifications include Hustedt (1927-30, 1955), Hendey (1964), Patrick and Reimer (1966, 1975), Krammer and Lange-Bertalot (1986-1991), Cooper (1993, 1995*b*), Tomas (1997), and Snoeijs *et al.* (1993-1998).

Acanthoceros sp.
Achnanthes cf. *amoena* Hustedt
Achnanthes af. *bioretii* Germain
Achnanthes af. *conspicua* Mayer
Achnanthes *curvirostrum* Brun
Achnanthes *delicatula* ssp. *hauckiana* (Grunow) Lange-Bertalot and Ruppel
Achnanthes *septentrionalis* (Østrup)
Achnanthes af. *elliptica* Schumann
Achnanthes *exigua* Grunow
Achnanthes af. *fogedii* Håkansson
Achnanthes af. *helvetica* (Hustedt) Lange-Bertalot
Achnanthes af. *laevis* Østrup
Achnanthes *lanceolata* (Brébisson) Grunow and varieties
Achnanthes *lemmermanii* Hustedt
Achnanthes *levanderi* Hustedt
Achnanthes *lilljeborgii* Grunow
Achnanthes *linkei* Hustedt
Achnanthes cf. *minuscula* Hustedt
Achnanthes *minutissima* Kützing
Achnanthes af. *oblongella* Østrup
Achnanthes af. *pericava* Carter
Achnanthes af. *petersenii* Hustedt
Achnanthes af. *punctulata* Simonsen
Achnanthes af. *reversa* Lange-Bertalot and Krammer
Achnanthes sp. Pamlico A
Achnanthes cf. *submarina* Hustedt
Achnanthes cf. *taeniata* Grunow
Actinocyclus *normanii* (Gregory) Hustedt
Actinocyclus *normanii* fo. *subsalsa* (Juhlin-Dannfeldt) Hustedt
Actinocyclus *octonarius* var. *crassus* (Wm. Smith) Hendey
Actinocyclus *octonarius* var. *tenellus* (Brébisson) Hendey
Actinocyclus sp.
Actinoptychus *senarius* (Ehr.) Ehrenberg
Amphipleura *pelucida* (Kützing) Kützing
Amphiprora *similis* Hustedt
Amphora af. *acutiuscula* Kützing
Amphora cf. *aequalis* Krammer
Amphora af. *amoena* Hustedt
Amphora af. *angusta* Gregory

Amphora beaufortiana Hustedt
Amphora coffaeformis (Agardh) Kützing
Amphora cf. *commutata* Grunow
Amphora cf. *fogediana* Krammer
Amphora granulata Gregory
Amphora cf. *libyca* Ehrenberg
Amphora ostrearia var. *lineata* Cleve
Amphora ovalis Kützing
Amphora cf. *pediculus* (Kützing) Grunow
Amphora cf. *proteoides* Hustedt
Amphora sp. B
Amphora sp. S
Amphora af. *staurophora* Juhlin-Dannfelt
Amphora af. *subcuneata* Hustedt
Amphora tenerimma Hustedt
Amphora tenuissima Hustedt
Amphora veneta Kützing
Anaulus balticus Simonsen
Anorthoneis eurystoma Cleve
Anorthoneis excentrica (Donkin) Grunow
Anorthoneis cf. *tenuis* Hustedt
Ardissonia sp.
Asterionella formosa Hassall
Asterionella cf. *ralfsii* W. Smith
Attheya sp.
Aulacoseira cf. *distans* (Ehr.) Simonsen
Aulacoseira cf. *granulata* (Ehr.) Simonsen.
Aulacoseira af. *alpigena/subarctica*
Auliscus sp.
Bacillaria paxillifer (Müller) Hendey
Bacillariophyceae unknown sp. Pamlong A
Bacillariophyceae unknown sp. A
Bacillariophyceae unknown sp. BC
Biddulphia spp.
Brachysira vitrea (Grunow) R. Ross
Caloneis amphisbaena fo. *subsalina* (Donkin) Van der Werff and Huls
Caloneis bacillum (Grunow) Cleve
Caloneis westii (Wm. Smith) Hendey
Campylodiscus? sp.
Catenula adhaerens Mereschowsky
Centrics Unknown centric #1
Chaetoceros spore 5-1X or 3-5-like
Chaetoceros af. *affinis* Lauder (spore)
Chaetoceros cf. *decipiens* Cleve
Chaetoceros af. *diadema* (Ehr.) Gran
Chaetoceros spore 5-1X(2)

Chaetoceros spore #1
Chaetoceros spore #3b
Chaetoceros spore #5-1X(2)
Chaetoceros spore #6
Chaetoceros spore #8
Chaetoceros spore 10b
Chaetoceros spore type 3
Chaetoceros? spore #10
Cocconeis diminuta Pantocsek
Cocconeis disculoides Hustedt
Cocconeis neothumensis Krammer
Cocconeis peltoides Hustedt
Cocconeis placentula Ehrenberg (and varieties)
Cocconeis quarnerensis (Grunow) Schmidt
Cocconeis scutellum Ehrenberg
Cocconeis sp. 62
Cocconeis sp. R98
Cocconeis sp. T
Cocconeis cf. *stauroneiformis* (W. Smith) Okuno
Coscinodiscus af. *apiculatus* var. *ambigua* Grunow
Coscinodiscus oculus-iridis Ehrenberg
Coscinodiscus sp.
Cyclostephanos sp.
Cyclotella atomus Hustedt
Cyclotella af. *bodanica* Grunow
Cyclotella choctawhatcheeana Prasad
Cyclotella af. *comensis* Grunow
Cyclotella af. *comta* Kützing
Cyclotella af. *distinguenda* Hustedt
Cyclotella af. *glomerata* Bachmann
Cyclotella meneghiniana Kützing
Cyclotella ocellata Pantocsek
Cyclotella cf. *pseudostelligera* Hustedt
Cyclotella sp. 1
Cyclotella sp. 2
Cyclotella sp. Neuse
Cyclotella sp. Neusecyc
Cyclotella sp. OR8
Cyclotella sp. U
Cyclotella stelligera Cleve and Grunow
Cyclotella stelligeroides Hustedt
Cyclotella striata (Kützing) Grunow
Cyclotella af. *woltereckii* Hustedt
Cylindrotheca closterium (Ehr.) Reimann and Lewin
Cymatosira belgica Grunow
Cymatosira sp.?

Cymbella cf. *gracilis* (Ehr.) Kützing
Cymbella af. *reichardtii* Krammer
Cymbella minuta var. *silesiaca* (Bleisch) Reimer
Delphineis minutissima (Hustedt) Simonsen
Delphineis spp.
Delphineis surirella (Ehr.) Andrews
Denticula af. *kuetzingii/subtilis*
Detonula af. sp.
Dimeregramma minor (Greg.) Ralfs
Dimeregramma sp.?
Diploneis bombus Ehrenberg
Diploneis cf. *decipiens* var. *parallela* A. Cleve
Diploneis af. *elliptica* (Kützing) Cleve
Diploneis cf. *finnica* (Ehr.) Cleve
Diploneis cf. *litoralis* (Donkin) Cleve
Diploneis oblongella (Naegeli) Cleve-Euler
Diploneis oculata (Bréb.) Cleve
Diploneis af. *pseudovalis* Hustedt
Diploneis smithii (Bréb.) Cleve
Diploneis smithii var. *pumila* (Grunow) Hustedt
Diploneis sp. A
Diploneis stroemii Hustedt
Diploneis cf. *subovalis* Cleve
Diploneis cf. *weisflogii* (A. S.) Cleve
Ditylum af. *brightwelli* (West) Grunow
Ellerbeckia af. *arenaria* (Moore ex Ralfs) Crawford
Entonomeis paludosa (W. Smith) Reimer
Entonomeis pseudoduplex Osada and Kobayasi
Epthemia af. *adnata* (Kützing) Brébisson
Epthemia turgida (Ehr.) Kützing
Eunotia af. *formica* Ehrenberg
Eunotia af. *minor* (Kützing) Grunow
Eunotia cf. *naegelii* Migula
Eunotia cf. *soleirolii* (Kützing) Rabenhorst
Eunotia spp.
Eunotogramma spp.
Fallacia clepsidroides Witkowski
Fragilaria af. *amicorum* Witkowski and Lange-Bertalot
Fragilaria brevistriata Grunow
Fragilaria cf. *capucina* varieties
Fragilaria capucina var. *gracilis* (Østrup) Hustedt
Fragilaria cf. *construens* f. *subsalina* Hustedt
Fragilaria construens f. *venter* (Ehr.) Grunow
Fragilaria cf. *delicatissima* (W. Smith) Lange-Bertalot
Fragilaria cf. *elliptica* Schumann
Fragilaria cf. *exigua* Grunow

Fragilaria fasciculata (Agardh) Lange-Bertalot
Fragilaria af. *gedanensis* Witkowski
Fragilaria gessneri Hustedt
Fragilaria lapponica Grunow
Fragilaria af. *nanana* Lange-Bertalot
Fragilaria af. *nitzschiodes* Grunow
Fragilaria af. *oldenburgiana* Hustedt
Fragilaria pinnata Ehrenberg
Fragilaria pulchella (Ralfs) Lange-Bertalot
Fragilaria af. *robusta* (Fusey) Manguin
Fragilaria schulzii Brockmann & *F. subsalina* (Grun.) Lange-Bertalot
Fragilaria sp. L
Fragilaria sp. Unk
Fragilaria sp. Tre
Fragilaria spp.
Fragilaria ulna (Nitzsch) Lange-Bertalot
Fragilaria zeilerii Héribaud
Fragilariopsis cf. *cylindrus* (Grunow) Krieger
Frustulia rhomboides var. *crassinervia* (Bréb.) Ross
Frustulia cf. *vulgaris* (Thwaites) De Toni
Frustulia spp.
Gomphonemopsis exiguum Medlin & Round
Grammatophora macilenta Wm. Smith
Gyrosigma balticum (Ehr.) Cleve
Gyrosigma fasciola (Ehr.) Griffith and Henfrey
Gyrosigma spp.
Hantzschia amphioxys (Ehr.) Grunow
Leptocylindrus? cf. *danicus* Cleve (spores)
Lunella cf. *bisecta* Snoeijs
Mastogloia braunii Grunow
Mastogloia elliptica (C. A. Agardh) Cleve
Mastogloia exigua Lewis
Mastogloia cf. *patrickae* Hustedt
Mastogloia pumila (Grunow) Cleve
Mastogloia pusilla Grunow
Mastogloia cf. *smithii* Thwaites
Mastogloia spp.
Mastogloia sp. BC
Mastogloia sp. OR74
Melosira af. *monoliformis* (Müller) Agardh
Melosira? sp.
Minidiscus spp.
Navicula abunda Hustedt
Navicula aequorea Hustedt
Navicula amphipleuroides Hustedt
Navicula af. *arvensis* Hustedt

Navicula cf. *bipustulata* A. Mann
Navicula af. *bottnica* Grunow
Navicula *brachium* Hustedt
Navicula af. *bryophila* Petersen
Navicula *cancellata* Donkin
Navicula *capitata* var. *hungarica* (Grunow) Ross
Navicula *capitata* var. *lueneburgensis* (Grunow) Patrick
Navicula af. *cari* Ehrenberg
Navicula *clamans* Hustedt
Navicula unknown clear valves
Navicula *clementis* Grunow
Navicula *clipeiformis* König
Navicula *confervaceae* Kützing
Navicula af. *consentanea* Hustedt
Navicula *cruciculoides* Brockmann
Navicula *cryptocephala* Kützing
Navicula *cryptolyra* Brockmann
Navicula *cryptotenella* Lange-Bertalot
Navicula *digitoradiata* (Gregory) Ralfs
Navicula *diploneioides* Hustedt
Navicula *dissipata* Hustedt
Navicula *eidrigiana* Carter
Navicula cf. *erifuga* Lange-Bertalot
Navicula af. *flanatica/praeterita*
Navicula *forcipata* Greville
Navicula cf. *fossalis* Krasske
Navicula cf. *fossalis* var. *obsidialis* (Hustedt) Lange-Bertalot
Navicula cf. *gastrum* (Ehr.) Kützing
Navicula af. *gerloffii* Schimanski
Navicula *germanopolonica* Witkowski and Lange-Bertalot
Navicula *granulata* Bailey
Navicula *gregaria* Donkin
Navicula *halophila* (Grunow) Cleve
Navicula af. *ignota* Krasske
Navicula cf. *incertata* Lange-Bertalot
Navicula af. *joubaudii* Germain
Navicula af. *kuelbsii* Lange-Bertalot
Navicula cf. *lucinensis* Hustedt
Navicula 'lyra group' spp.
Navicula af. *margaritiana* Witkowski
Navicula *marina* Ralfs
Navicula *menisculus* Schumann
Navicula af. *meniscus* Schumann
Navicula cf. *minima* Grunow
Navicula af. *minuscula* var. *muralis* Lange-Bertalot
Navicula af. *molestiformis* Hustedt

Navicula af. *monoculata* Hustedt
Navicula af. *muraliformis* Hustedt
Navicula oculiformis Hustedt & *N. florinae* Möller
Navicula oestrupii Schulz
Navicula cf. *patrickae* Hustedt
Navicula pavillardii Hustedt
Navicula peregrina (Ehr.) Kützing
Navicula perminuta Grunow
Navicula phyllepta Kützing
Navicula cf. *platystoma* Ehrenberg
Navicula af. *praeterita* Hustedt
Navicula af. *pseudoarvensis* Hustedt
Navicula cf. *pseudoforcipata* Hustedt
Navicula af. *pseudolanceolata* Lange-Bertalot
Navicula pseudolitoricola Håkansson
Navicula cf. *pupula* Kützing
Navicula pygmaea Kützing
Navicula cf. *ramosissima* (C. A. Agardh) Cleve
Navicula rhynchocephala Kützing
Navicula cf. *salinicola* Hustedt
Navicula schroeterii Meister
Navicula af. *seminulum* Grunow
Navicula af. *soehrensensis* Krasske
Navicula sovereignae Hustedt
Navicula sp. 2
Navicula sp. 3-9
Navicula sp. A
Navicula sp. OR32
Navicula sp. pseudolyrata
Navicula sp. staurophora-like
Navicula spp.
Navicula subinflata Grunow
Navicula cf. *subminuscula* Manguin
Navicula af. *submolesta* Hustedt
Navicula af. *submuralis* Hustedt
Navicula af. *subrotundata* Hustedt
Navicula subryncocephala Hustedt
Navicula sulcifera Hustedt
Navicula tenelloides Hustedt
Navicula tenera Hustedt
Navicula tenelloides Hustedt
Navicula af. *vanhoeffenii* Gran
Navicula viminoides Giffen
Navicula viridula (Kützing) Ehrenberg
Neidium spp.
Neodelphineis pelagica Takano

Nitzschia acuminata (Wm. Smith) Grunow
Nitzschia af. *aequorea* Hustedt
Nitzschia cf. *angustata* (Wm. Smith) Grunow
Nitzschia af. *ardua* Cholnoky
Nitzschia cf. *aurariae* Cholnoky
Nitzschia brevissima Grunow
Nitzschia cf. *capitellata* Hustedt
Nitzschia af. *closterium* (Ehr.) W. Smith
Nitzschia af. *commutata* Grunow
Nitzschia constricta (Greg.) Grunow
Nitzschia dissipata (Kützing) Grunow
Nitzschia cf. *distans* Gregory
Nitzschia af. *flexa* Schumann
Nitzschia cf. *fonticola* Grunow
Nitzschia af. *fossilis* Grunow
Nitzschia frustulum (Kützing) Grunow
Nitzschia grossestriata Hustedt
Nitzschia hungarica Grunow
Nitzschia inconspicua Grunow
Nitzschia laevis Hustedt
Nitzschia af. *lanceola* Grunow
Nitzschia levidensis Grunow
Nitzschia cf. *linearis* Wm. Smith
Nitzschia lorenziana Grunow
Nitzschia cf. *marginata* Hustedt
Nitzschia marginulata Grunow
Nitzschia microcephala Grunow
Nitzschia af. *nana* Grunow
Nitzschia cf. *palea* (Kützing) Wm. Smith
Nitzschia cf. *paleaceae* Grunow
Nitzschia panduriformis Gregory
Nitzschia panduriformis var. *delicatula* Grunow
Nitzschia af. *parvula* W. Smith
Nitzschia cf. *perminuta* (Grunow) M. Peragallo
Nitzschia proxima Hustedt
Nitzschia punctata (Wm. Smith) Grunow
Nitzschia cf. *pusilla* Grunow
Nitzschia cf. *scalaris* (Ehr.) W. Smith
Nitzschia sigma (Kützing) Wm. Smith
Nitzschia spp.
Nitzschia sp. Neuse
Nitzschia sp. paleaPAM
Nitzschia sp. PamA
Nitzschia sp. Tiny
Nitzschia af. *subacicularis* Hustedt
Nitzschia sublinearis Hustedt

Nitzschia af. *thermaloides* Hustedt
Nitzschia cf. *tubicola* Grunow
Nitzschia valdestriata Aleem & Hustedt
Nitzschia vitrea var. *salinarum* Grunow
Opephora cf. *angusta* Cholnoky
Opephora af. *marina* (Gregory) Petit
Opephora martyi Heribaud
Opephora olsenii Møller
Paralia sulcata (Ehr.) Cleve
Pinnularia af. *appendiculata* (Agardh) Cleve
Pinnularia af. *viridis* (Nitzsch) Ehrenberg
Pinnularia af. *subrostrata* (A. Cleve) Cleve-Euler
Plagiogramma minimum Salah
Plagiogramma cf. *tenuistriatum* Cleve
Plagiotropis lepidoptera (Gregory) Kuntze
Plagiotropis spp.
Plagiotropis vanheurckii Grunow in Van Heurck
Pleurosigma aestuarii (Brébisson ex Kützing) W. Smith
Pleurosigma af. *angulatum* (Quekett) W. Smith
Pleurosigma af. *elongatum* Wm. Smith
Pleurosigma spp.
Pleurosigma af. *strigosum* Wm. Smith
Pseudonitzschia spp.
Pseudonitzschia multiseries (Hasle) Hasle
Rhabdonema adriaticum Kützing
Rhabdonema af. *minutum* Kützing
Rhabdonema spp.
Rhizosolenia af. *hebetata* Bailey
Rhizosolenia af. *longiseta* Zacharias
Rhizosolenia spp.
Rhopalodia acuminata Krammer
Rhopalodia spp.
Skeletonema spp.
Stauroneis phoenicenteron (Nitzsch) Ehrenberg
Stauroneis sp. *didyma*
Stauroneis sp. Neuse
Stauroneis sp. *Spiculasigma*
Stauroneis? sp.
Stauropsis? sp.
Stephanocostis cf. *chantaicus* Genkal and Kuzmin
Stephanodiscus cf. *hantzschii* Grunow
Stephanodiscus minutulus (Kützing) Cleve & Møller
Stephanodiscus spp.
Surirella cf. *brebissonii* Krammer and Lange-Bertalot
Surirella fastuosa var. *recedens* (A. Schmidt) Cleve
Surirella cf. *minuta* Brébisson in Kützing

Surirella spp.
Surirella cf. *visurgis* Hustedt
Synedra cf. *gaillonii* (Bory) Ehrenberg
Tabellaria cf. *ktenoeides* Kuylenstierna
Thalassionema nitzschiodes Grunow
Thalassiosira baltica (Grunow) Ostenfeld
Thalassiosira decipiens (Grunow) Jørgensen
Thalassiosira eccentrica (Ehr.) Cleve
Thalassiosira af. *guillardii* Hasle
Thalassiosira levanderi Van Goor
Thalassiosira lineata Jousé &? *Coscinodiscus lineatus* Ehrenberf
Thalassiosira nordenskioldi Cleve
Thalassiosira oestrupi (Ostenfeld) Proschkina-Lavrenko
Thalassiosira proschkinae Makarova
Thalassiosira pseudonana Hasle and Heimdal
Thalassiosira sp. 10 af
Thalassiosira sp. 11
Thalassiosira sp. 2
Thalassiosira sp. 7
Thalassiosira sp. Neusecyc
Thalassiosira sp. new
Thalassiosira sp. Pamlico
Thalassiosira tenera Proschkina-Lavrenko
Thalassiosira unknowns
Thalassiosira weisflogii (Grunow) Fryxell and Hasle
Trachyneis aspera var. *vulgaris* Cleve
Trachysphenia acuminata Peragallo
Unknowns