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Paleoecological Evidence of Human Impacts on the Neuse and Pamlico Estuaries of North Carolina, USA

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ABSTRACT: Sediment cores were collected from the Neuse and Pamlico River estuaries, North Carolina, at seven different sites, and the data show strong anthropogenic influence on water quality. The sediments from these cores were dated using ^{210}Pb, ^{137}Cs, ^{14}C, and pollen horizon techniques. Specific parameters investigated include bulk density, sedimentation rates, diatom assemblage changes, nutrient and trace metal flux, and vegetation changes as recorded in the pollen record. The greatest increases in sedimentation, nutrient and metal flux, and changes in diatom assemblages have occurred in the past 50–60 yr in the Pamlico and Neuse. Diatom diversity has decreased and small planktonic forms have become dominant over time, most likely due to eutrophication and increased turbidity and sedimentation. Major changes occur before phytoplankton surveys and monitoring were initiated. Overall trends are similar to those found in Chesapeake Bay, although the time frame of major changes is more recent. Dominant small planktonic diatom species differ between Chesapeake Bay and the Neuse and Pamlico. Variance in paleoecological indicators between these mid-Atlantic estuaries may be due to geomorphology and land use history.

Introduction

There are numerous recent concerns about water quality in the Pamlico and Neuse River estuaries of North Carolina, as in many estuaries and coastal areas around the world. 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. Local and federally funded research on these North Carolina estuaries is growing, especially for the Neuse. A more complete appreciation of the historical processes that have contributed to estuarine water quality changes is essential to support these research and modeling efforts. In responding to these concerns, the research described here can also serve as a beginning model for other estuaries.

Historical information remains in the stratigraphic record of depositional environments (such as exist in these estuaries) and is accessible through the use of paleoecological methods. Although estuaries are very dynamic systems as compared to many lakes and have been less studied in this way, sites of constant sedimentation and minimal mixing can be found. It is possible to use a paleoecological approach to compare estuarine water quality proxies over hundreds to thousands of years as an alternate source of historical data in the absence of long-term monitoring. This type of approach has already played an integral part in providing scientific background for Chesapeake Bay research and watershed management plans (Brush 1986; Cooper and Brush 1991; Cooper 1995a; Zimmerman and Canuel 2002).

This research was undertaken to quantify the history of water quality in the Neuse and Pamlico, covering the past several hundred years. The primary organisms studied are diatoms. Principal water quality parameters investigated include eutrophication (nutrient flux), trace metal flux, sedimentation rates, and benthic versus pelagic habitat quality. The dominant algal groups in the Neuse and Pamlico are the diatoms, dinoflagellates, and cryptophytes (Mallin et al. 1991; Mallin 1994). Diatoms are particularly useful for paleoecological research because they grow a silica shell (frustules), the morphology of which is species specific. The frustules are preserved as fossil evidence in the stratigraphic record. Diatoms have a fairly well studied taxonomy and ecology (Stoermer and Smol 1999). Presence or absence of individual species and diatom assemblages are often interpreted as indicators of eutrophication, climate changes (temperature, sea level, and precipitation), land

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TABLE 1. Location, water depth, and labels given to sediment cores collected from the Pamlico (June 3, 1997) and Neuse (July 27–28, 1997) River estuaries, North Carolina.

Location and Core Label	Water depth (m)	Latitude	Longitude
Pamlico River estuary			
Mouth of Bath Creek (BC)	3.4	35°27′.01″N	76°49′.19″W
Channel marker 4, near Gum Point (M4)	5.4	35°24′.44″N	76°45′.51″W
Channel marker 7, near Maules Point (M7)	4.2	35°27′.07″N	76°55′.03″W
Blounts Bay (BB)	3.4	35°26′.51″N	76°56′.28″W
Neuse River estuary			
Near marker 7, Oriental (OR)	6.6	35°00′.38″N	76°40′.19″W
Near marker 9, off Whitakers Creek (WP)	7.0	34°57′.41″N	76°47′.91″W
Benninger's site, south of Beard's Creek (UNC)	4.0	34°58′.21″N	76°51′.49″W

clearance (turbidity), pH, and salinity changes (Cooper 1999; Korhola et al. 2000). Diatom assemblages are also used to assess changes in benthic versus pelagic environments, since different species indicate specific habitats as well as water quality. Responses of diatom communities to environmental changes can show which historical periods or events have most shaped recent changes to the North Carolina estuarine ecosystems.

Geochemical parameters that provide information on nutrient loading, primary productivity, and oxidation potential include total organic carbon (TOC), total nitrogen (TN), total phosphorus (TP), sulfur (S), iron (Fe), and biogenic silica (BSi). TN, TP, and Fe provide additional information on nutrient loading of coastal waters and sediments, and BSi measurements indicate diatom and other siliceous organism burial (Cornwell et al. 1996). 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 and Malone 1992; Dortch and 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.

Trace metals have been increasing in coastal systems due to human activity. The concentration of these metals in the sediments and the water column can be of concern to aquatic life and to humans (Mann et al. 2002), or they may act to increase eutrophication effects (Coale 1991). The trace metals measured in these estuarine sediments include arsenic (As), chromium (Cr), cadmium (Cd), copper (Cu), nickel (Ni), silver (Ag), lead (Pb), and zinc (Zn).

The results of this work help to clarify mechanisms by which different human activities and land uses affect North Carolina estuarine water quality. There are no published data on phytoplankton-related studies in the Pamlico before 1966 (Mallin 1994), which is after phosphate mining and effluent discharge to the estuary began in 1964 (Copeland and Hobbie 1972). 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.

Materials and Methods

STUDY SITES AND SAMPLE COLLECTION

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 U.S. Two of the major tributaries that contribute to this system are the Pamlico and Neuse River estuaries in eastern North Carolina, both drowned river valley coastal plain estuaries. Pamlico Sound is connected with the Atlantic Ocean through several relatively small openings in the Outer Banks (barrier islands) of North Carolina. 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. Residence time for water in the Pamlico averages about 24 d and varies between 10 d and 2 mo depending on freshwater flow (Stanley 1992). The Neuse residence time is on the order of 2–6 mo.

Two sediment cores of either 5.1 or 7.6 cm (2 or 3 inch) diameter were collected at each of seven sites in the Pamlico and Neuse on June 3 and July 27–28, 1997, respectively, using a modified Livingstone piston-coring device (Wright et al. 1965; Table 1). The smaller diameter cores were 117–147.5 cm in length and the larger diameter cores were 81.5–97 cm in length. Four sites in the Pamlico and three sites in the Neuse were chosen based on personal communications (Benninger 1997; McNinch 1997; Riggs 1997) as well as reports of sedimentation, circulation, and monitoring of bottom water oxygen in the estuaries (Garrett 1992, 1994; Riggs et al. 1992; Treece 1993; Bales and Robbins 1995;

Robbins and Bales 1995). The salinity of the overlying water (including bottom and surface salinities) as reported by U.S. Geological Survey (Garrett 1994) near the sites of core collection is variable, from $<$0.1–20.1‰ in the Pamlico and 0.3–32.8‰ in the Neuse for the period April 1989 to September 1992. The mean daily salinity for this time period at the same sites is reported to be 2.2–7.7‰ for the Pamlico and 5.7–10.2‰ for the Neuse (with $\geq$568–800 complete days of record; Bales and Robbins 1995; Robbins and Bales 1995).

X-radiographs were made of each core before extrusion. All cores were extruded and sectioned every 1–2 cm, and stored in airtight plastic bags in the dark at 4°C prior to analyses. Bulk density of sediments was determined immediately following extrusion and subsampling of the sediment cores by weighing 1 ml of wet sediment sample followed by drying at 70°C. Loss on ignition (LOI) was then determined by placing the dried sediment in a muffle furnace at 450°C for at least 24 h and comparing mass (Krom and Berner 1983).

DATING OF SEDIMENTS

Dating of sediment cores was accomplished through a combination of methods including radiocarbon (C) dating of sediments deposited before European settlement, ^{210}Pb dating, and ^{137}Cs dating for recent sediments (Binford 1990; Schelske et al. 1994). Pollen dating techniques were used for determination of the agricultural horizon (Brush 1989).

For ^{210}Pb and ^{137}Cs, sediments were dried, ground, sieved, and placed in petri dishes to achieve the same grain size and volume for all samples in order to minimize error due to any differences in sediment composition and self-absorption. Several samples were corrected individually for self-absorption according to Cutshall et al. (1983), which was minimal. The samples were taped and left to equilibrate for 2 wk before 24 h analysis on an EG&G Ortec planar gamma spectrometer. Peaks were counted as in Schelske et al. (1994), and include ^{210}Pb, ^{137}Cs, ^{214}Bismuth (Bi), and ^{214}Pb (295 and 352 keV photopeaks). ^{210}Pb data was corrected for radium activity as calculated from the Bi and Pb isotope activities. ^{210}Pb profiles were analyzed 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.

The CRS model was chosen because it allows for temporal variability in sedimentation rates, although the CRS model assumes that sediments are not significantly mixed by bioturbation. This assumption is more appropriate at deeper 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. C analyses were done by Beta Analytic, Inc., Miami, Florida. All but one sample (radiometric analysis) were analyzed 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* (ragweed) horizon was determined to be the point in each core where the percent *Ambrosia* pollen increased to 1% or above, and the pine:ragweed ratio showed a marked decrease (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 (Merrens 1964; Watson 1975; Reed 1981) and consultation with archaeologists and historians in the region by personal communication (Irwin 1999; Wood 1999). The uncertainty of this date is not known.

MICROFOSSIL ANALYSES

Diatoms were extracted using a modification of the method published by Funkhauser and Evitt (1959). A measured volume of the diatom residue for each sample was mounted on a glass slide with Naphrax and 400–500 diatom valves identified (except for one sample of 339). For statistical purposes, a minimum of 300 diatom valves identified per sample is recommended (van Dam 1982). Identifications were done using light microscopy (Leitz DM RB with Nomarski optics at 100×), according to available taxonomic references including Hustedt (1927–1930, 1955), Krammer and Lange-Bertalot (1986–1991), Snoeijs (1993), Snoeijs and Vilbaste (1994), Cooper (1995b), Snoeijs and Potapova (1995), Snoeijs and Kaperovičienė (1996), and Snoeijs and Balashova (1998).

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 is much less when more than 400 valves are counted. Digital images of representative diatoms were collected and archived. Diatom assemblage diversity was calculated for each sample using Shannon's H′ (Shannon and Weaver 1949).

Centric diatoms are generally planktonic forms in estuarine waters, and pennate diatoms are generally benthic, including epiphytic forms. Centric diatoms are more prevalent in eutrophic waters than pennate diatoms in certain areas (Cooper 1999). An increase in the centric to pennate ratio (c : p) may also be useful in determining changes from predominantly benthic to predominantly planktonic communities (Cooper 1995a).

Principal components analysis (PCA) using CANOCO for Windows 4.0 (ter Braak and Šmilauer 1998) was performed on the diatom data to summarize major trends in the diatom assemblages, as well as the influence of environmental variables. Detrended correspondence analysis (DCA) was used to provide a measure of the gradient length present within the assemblage data. A short gradient length (<2) suggests that a linear method of ordination such as PCA is suitable (ter Braak and Šmilauer 1998; McCure et al. 2002). Input for the CANOCO program included the percent abundance of diatom taxa that were present in at least 1% abundance. This reduced the diatom list from more than 430 to 84 taxa. Scaling was focused on intersample distances and the species data were square-root transformed. The data were centered and standardized by species. Supplemental data included with the PCA were LOI, [P], P flux, %TOC, TOC flux, %N, N flux, %BSi, BSi flux, %S, S flux, diversity of diatom assemblages, and c : p ratios.

Pollen was extracted from sediments following the methods of Faegri and Iverson (1989). 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 40×). Counts were made of at least 300 pollen grains per sample. Dinoflagellate cysts and foraminifera were also enumerated from the same slides but will not be discussed in this paper.

GEOCHEMICAL PROCEDURES

TOC was determined by the method described by Krom and Berner (1983). Dried and ashed sediment samples were measured for %C, %N, and %S on a Perkin/Elmer Series II CHNS/O Analyzer 2400 (Carter 1993). All analytical runs were evaluated using external reference standards obtained from the National Institute of Standards and Technology (NIST), procedural blanks, and laboratory replicates. Sediment digestions for P were done using a nitric-perchloric digestion (Carter 1993) and were measured colorimetrically on a Bran/Luebbe TRAACS 800 by ascorbic acid reduction (U.S. Environmental Protection Agency 1983). Methods for measurement of BSi in sediments are described in Conley (1988) and use a weak Na_2CO_3 base to dissolve BSi in a sediment matrix. Silica measurements were made on a Bran/Luebbe TRAACS 800 autoanalyzer. For biogenic silica analysis, four intralaboratory quality control samples were obtained from Conley (1998) that were routinely run with samples.

Acid-soluble Fe was measured on a Perkin/Elmer Model 5100 PC atomic absorption spectrophotometer, after samples were boiled in concentrated HCl for 1 min and diluted in known volume (Berner 1970). Trace metals were extracted using HCl and HNO_3, and then analyzed using an inductively coupled plasma-mass spectrometer (ICP-MS). NIST estuarine sediment standards, along with internal drift standards, were used for monitoring the accuracy of results. Analyses 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 and McLennan 1995).

HISTORICAL DATA

Historical data was collected from U.S. Census Bureau records (U.S. Census Bureau 1840–1992) 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 focused on the counties immediately adjacent to the estuaries. These include Beaufort and Hyde counties for the Pamlico, and Carteret, Craven, and Pamlico counties for the Neuse.

Results

SEDIMENT CORES

X-rays of the cores from both estuaries (Table 1) revealed uniform stratigraphy with no evidence of significant sand layers, areas of severe mixing, or 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. Depths of color changes within the sediments were noted.

The bulk density and LOI of the sediment subsamples were 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 varied from 4.1–26.2% in the Pamlico, and from 5.8–24.2% in the Neuse. Two core sites in the Pamlico (BC and M7) show a pattern of bulk density downcore that indicates more mixing of surface sediments or possible periods of excessive sedimentation or even scouring. Due to time constraints, core M7 was not analyzed for all indicators. In the Neuse, core site OR results indicate sedimentation of a higher percentage of inorganic material compared to the other sites in this estuary.

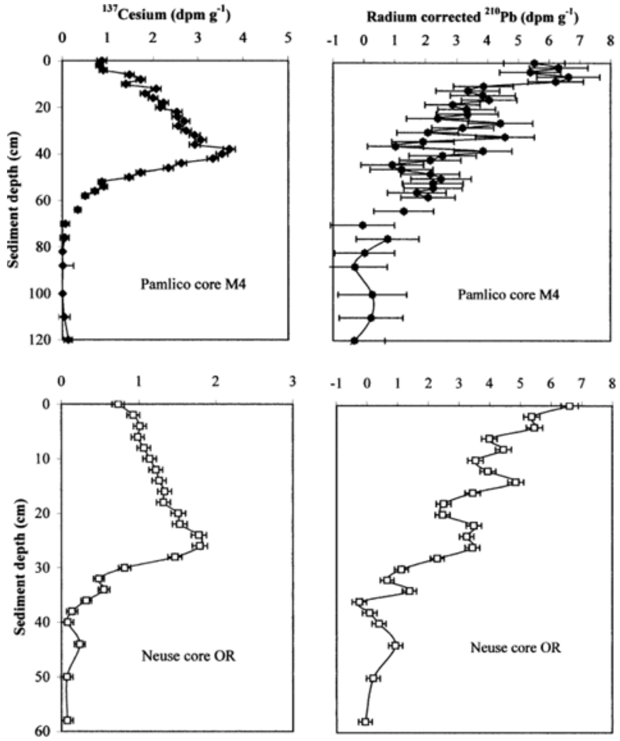

FIG. 1. ^{210}Pb and ^{137}Cs results for Pamlico core M4 and Neuse core OR. ^{137}Cs results are presented as disintegrations per minute per gram (dpm g^{-1}), and ^{210}Pb are presented as dpm g^{-1} after correction for radium levels in each sample.

DATING OF SEDIMENTS

The results of the ^{210}Pb and ^{137}Cs dating show clear ^{137}Cs peaks and reasonable declines in ^{210}Pb as shown for cores M4 and OR from the Pamlico and Neuse (Fig. 1). Total and excess ^{210}Pb activity decreased somewhat irregularly with depth (expected with variable sedimentation). The ^{137}Cs peak represents a date of approximately 1963 A.D. (Olsson 1986). The dates derived from the ^{210}Pb data according to the CRS model (Binford 1990) agree fairly well with the ^{137}Cs data (Table 2). Cs may be slightly mobile within the estuarine sediments as the peak for ^{137}Cs was consistently deeper than the associated ^{210}Pb model derived level. Average sedimentation rates and mass accumulation rates are shown in Table 2. The highest resolution (greatest sedimentation) in the past 100 yr occurred in core M4 for the Pamlico and core OR for the Neuse, both relatively deep-water sites. The two long cores from these sites will be the focus of this paper, although diatom data from 6 sites are included.

The *Ambrosia* horizon was determined from pollen counts for the same six sites as for diatom analysis (Table 2). C dates were obtained for a subset of samples including bottom sediments of cores from each site (Table 3). The C dates indicate that there is a component of old carbon present in the sediments. The date associated with the depth of the *Ambrosia* horizon is notably older than the date assigned to this horizon based on historical data. Benninger and Martens (1983) measured ^{14}C ages of approximately 1,000 yr for the organic matter in Neuse River sediments that contained finite ^{210}Pb (half-life = 22 yr). 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 C dates of the bottom sediments from the cores were not used directly, but the difference between the C 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 C date available, estimates based on cores in the same estuary were used to determine older average sedimentation rates and

TABLE 2. Summary of Pamlico and Neuse sediment core dating information. ALAR = average linear accumulation rate (cm yr^{-1}). AMAR = average mass accumulation rate (g cm^{-2} yr^{-1}). Depth is measured in centimeters.

	Pamlico			Neuse		
	BC	M4	BB	OR	WP	UNC
Depth of ^{137}Cs peak (~1963)	16	40	10	26	24	8
Depth of ^{210}Pb model 1963	14	38	8	22	20	7
Depth of excess ^{210}Pb presentation	36	110	30	60	58	40
Ragweed horizon (~1720) depth	40	121	34	76	72	48
Average resolution (years per 2 cm sample)						
last 35 years (1963–1997)	4.7	1.8	7.9	2.9	3.3	9.4
ALAR from 1947–1997	1.20	1.15	0.27	0.60	0.61	0.22
ALAR from 1850–1947	0.12	0.26	0.11	0.20	0.28	0.16
ALAR from 1720–1850	0.08	0.39	0.11	0.25	0.18	0.19
ALAR pre-1720	0.09	0.06	0.06	0.09	0.10	0.19
AMAR 1947–1997	0.83	0.49	0.092	0.24	0.18	0.06
AMAR 1850–1947	0.09	0.14	0.076	0.12	0.14	0.08
AMAR 1720–1850	0.06	0.23	0.073	0.19	0.09	0.10
AMAR pre-1720	0.08	0.033	0.036	0.08	0.05	0.09

TABLE 3. C dates assigned to sediments as provided by Beta Analytic Incorporated, Miami, Florida.

Core Site	Depth in Core Analyzed (cm)	Type of Analysis	Intercept Data	Calibrated Results (95% Probability)	Beta Analytic Lab Number
Pamlico BC	116–121	AMS	A.D. 885	A.D. 775 to 995	Beta-112739
Pamlico M4	114–118	AMS	A.D. 1265	A.D. 1205 to 1290	Beta-125232
Pamlico M4	130–137	radiometric	A.D. 1290	A.D. 1175 to 1420	Beta-112740
Pamlico BB	84–87	AMS	A.D. 370	A.D. 220 to 450	Beta-120394
Neuse OR	74–76	AMS	A.D. 995	A.D. 895 to 1030	Beta-125233
Neuse OR	140–148	AMS	A.D. 350	A.D. 225 to 430	Beta-112741
Neuse WP	132–136	AMS	A.D. 665	A.D. 600 to 780	Beta-120396
Neuse UNC	50–56	AMS	A.D. 70	B.C. 50 to A.D. 220	Beta-125234
Neuse UNC	124–130	AMS	B.C. 40	B.C. 180 to A.D. 70	Beta-112742

must be treated with caution. In this way, a chronology was developed for each core so that every sample was assigned a sedimentation rate and an average (approximate) date. Figure 3 shows sedimentation rates as determined for Pamlico core M4 and Neuse core OR and are representative of the two estuaries. Calculated sedimentation rates along with bulk density measurements of sediments were used for calculating and presenting accumulation of all geochemical and biotic indicators extracted from the sediments.

Diatoms

Diatoms are well preserved in the sediments of the Neuse and Pamlico, with approximately 1 to 5 million valves preserved in each milliliter of wet sediment. Over 430 taxa were identified from 49 subsamples in six cores, with a total of 22,099 diatom valves counted from the sediments of the Neuse and Pamlico. The 10 most abundant species identified (followed by their highest percent abundance in one sample) include: *Thalassiosira proschkinae* Makarova (44.1%), *Cyclotella meneghiniana* Kützing (30.6%), *Thalassiosira* sp. 1 (19%), *Cyclotella choctawhatcheeana* Prasad (17.6%), *Aulacoseira* aff. *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). A complete list of the diatom taxa identified in the sediments from these cores can be found in Cooper (2000).

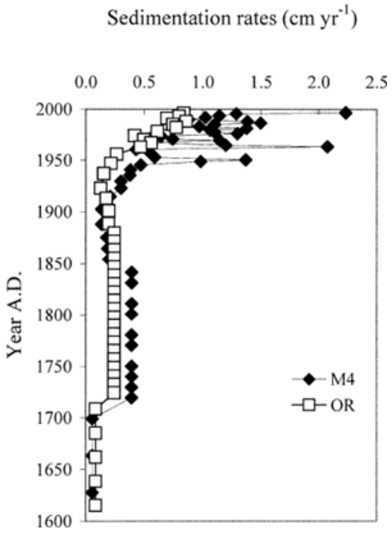

FIG. 2. Sedimentation rates by approximate date as calculated for Pamlico core M4 and Neuse core OR.

Changes in diatom species richness and diversity show a declining trend in all cores analyzed. All counts from the Neuse and Pamlico are combined to show this trend in diversity and the opposing increase in c : p ratios for these diatom assemblages through time (Fig. 3). Diatom abundance for selected species from core M4 in the Pamlico and core OR in the Neuse (cores for which diatoms were analyzed in most detail) are shown in Figs. 4 and 5.

Significant changes in taxonomic composition of assemblages have occurred in the recent past in both estuaries. While small planktonic forms such as *T. proschkinae* 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. *T. proschkinae* shows ≥37% abundance at some time since 1970 in five of the six sites (BC, M4, UNC, WP, and OR) and >28% abundance at the lowest salinity upriver site (BB) in the 1990s. *T. proschkinae* is a tiny planktonic form also found in the Chesapeake Bay, but not with the same increase in abundance. This species is reported as a truly brackish water *Thalassiosira* (Muylaert and Sabbe 1996) and has been reported in high nutrient waters from Hong Kong (Lee and Liu 2002) to the southern Baltic Sea (Monitoring Long-term Trends in Eutrophication and Nutrients 1996–2003; Stachura-Suchoples 2001). The reports of large blooms of this species in Hong Kong are from eutrophic

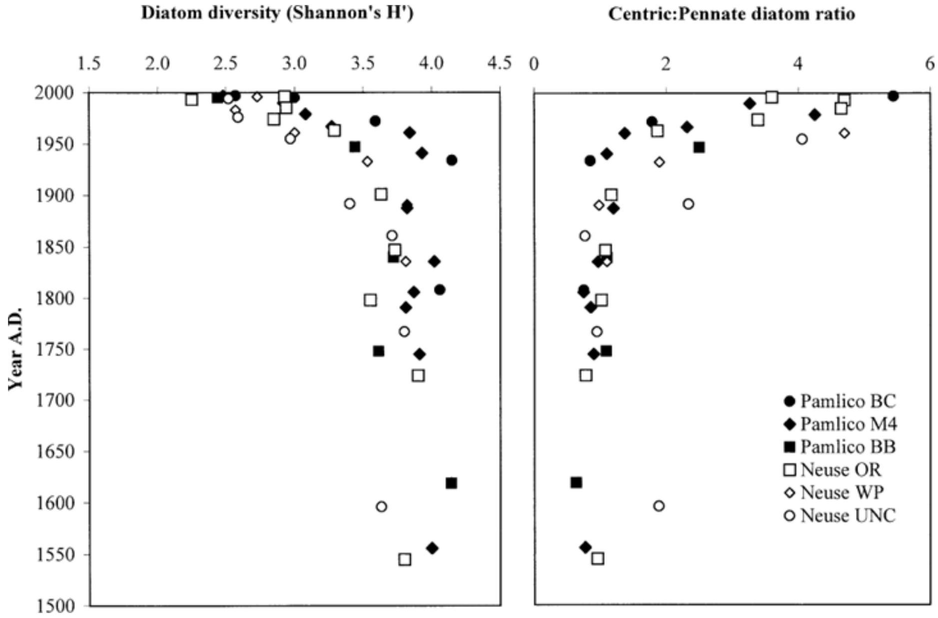

FIG. 3. On the left is a graph of diatom assemblage diversity as Shannon's H′ (Shannon and Weaver 1949). On the right is a graph of centric to pennate (c:p) diatom ratio changes. These results include data collected from all sediment core samples analyzed for diatoms. All dates along the y-axis are approximate.

coastal lagoons with very low tidal flushing. In the Baltic Sea it is a common taxon and thrives well in turbid waters with varying, but generally quite high nutrient concentrations (e.g., TN of 400–2,000 $\mu g\ l^{-1}$). Another small planktonic diatom, tentatively identified as *Thalassiosira* sp. 1, shows higher abundance since the 1960s in both the Neuse and Pamlico.

Other species show differences between the two North Carolina estuaries. *C. meneghiniana,* a small centric diatom known to occur in lower salinity water with high nutrient content (Monitoring Long-term Trends in Eutrophication and Nutrients 1996–2003; Clarke 2001), shows a clear trend of increasing abundance with time in the samples from the Pamlico sediment cores, mostly after 1950. This same species shows increases in the Neuse after initial European settlement and then again in the past 50 yr. Recent abundances of *C. meneghiniana* in the Pamlico are as high as 30.6% at the most upriver site, but are never higher than 15.3% in the Neuse cores. This difference is most likely due to salinity differences at the core collection sites (lower salinity sites in the Pamlico). N:P ratios may also be a factor, since *C. meneghiniana* shows higher TN optima than *T. proschkinae* (Monitoring Long-term Trends in Eutrophication and Nutrients 1996–2003). *N. palea, Diploneis* sp. A, and *C. belgica* show greatest abundances in sediments from the Pamlico dated between 1750 and 1850, but show highest abundances in the Neuse from 1900 to 1970. *C. belgica* is a species known to occur in high nutrient waters (increasing N and P) with higher salinity (Clarke 2001). *N. palea* is also known from eutrophic waters (Krammer and Lange-Bertalot 1988; Monitoring Long-term Trends in Eutrophication and Nutrients 1996–2003).

DCA indicated that the gradient length of the species data was ≤1.7, so PCA was appropriate. Biplots of the samples along the first two PCA axes (using diatom assemblage data) and the supplemental variables are shown in Figs. 6 and 7. The first two axes explain 18.3% and 11.3%, respectively, of the variance in the species data. Two main clusters are evident for the samples from all cores. Cluster a includes all surface and recent samples and cluster b includes all of the deeper and oldest samples analyzed from the cores. Cores M4 and OR show a shift from cluster a to b around the early 1960s A.D. This date coincides with initiation of phosphate mining operations on the Pamlico. The biplot indicates that both estuaries are showing similar changes in diatom assemblages through time. Cores BB and BC in the Pamlico deviate along axis 2 from the other cores; this may be related to their location in lower salinity waters. The biplot of supplemental data (Fig. 7) confirms the increase in nutrients and c:p ratio and a decline in diatom diversity along the same axis of major changes in diatom assemblages through time.

The results of calculated flux of diatom valves

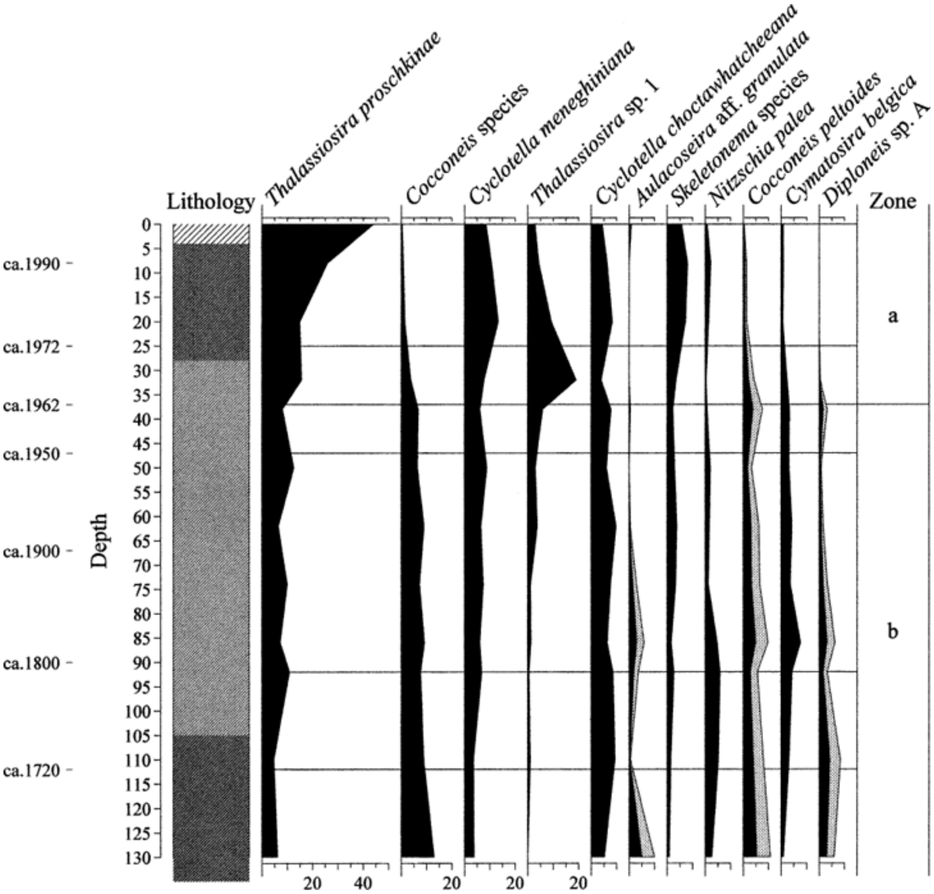

FIG. 4. Percent abundance of selected diatom species from subsamples analyzed for Pamlico core M4. Zones listed at the right correspond to principal components analysis (PCA) performed on the diatom assemblage data (see Fig. 6). The lithology indicates sediment color changes downcore from uniform brown to black-brown to dark gray-brown to dark gray-black.

(from slide counts) to the sediments and the flux of measured sediment BSi show similar increasing trends through time (Fig. 8). This evidence supports the assumption that BSi represents primarily diatom valve delivery and preservation in the sediments.

POLLEN

Pollen grains appear to be well preserved in the sediments of the Neuse and Pamlico. Pollen assemblage changes include an increase in *Ambrosia* pollen over the past several hundred years, signifying increased land disturbance by humans. Counts also show an increase in nut tree pollen (*Juglans* and *Carya*), and an increase in *Liquidambar styraciflua* (sweetgum) tree pollen in the past 50 yr. Human cultivation of nut trees is especially evident on farms and plantations in eastern North Carolina, while sweetgum is considered an ornamental tree. A significant increase in % *Ambrosia* along with a large drop in the pine:ragweed ratio was discernable in each core (Fig. 9). This change in the pollen stratigraphy is interpreted as the agricultural horizon, or the time at which land disturbance by European settlers became identifiable. This agricultural horizon was less clear for core M4 from the Pamlico with only two samples at the bottom of core showing a drop to close to 1% *Ambrosia*.

GEOCHEMICAL ANALYSES

The results of analyses of REE show that downcore sediments in all cores are from the same crustal material and are of recent origin. All the cores show TOC content of 1.3–7.5% of sediment dry mass (0.1–10.5 mg cm^{-2} yr^{-1}), and P concentration varied from 149–1,852 μg g^{-1} (12.7–1,699 μg cm^{-2} yr^{-1}). P in recent sediments was highest in core M4. P measurements for Neuse sites averages about half that of Pamlico sites. N levels were measured at <0.1–3.5% (<0.01–0.75 mg cm^{-2} yr^{-1}), BSi measurements varied from 1.9–17.7% of sediment dry mass (0.2–4.0 mg cm^{-2} yr^{-1}), and S varied from 0.2–4.6% of dry mass (0.03–8.0 mg cm^{-2} yr^{-1}). Variability in all geochemical parame-

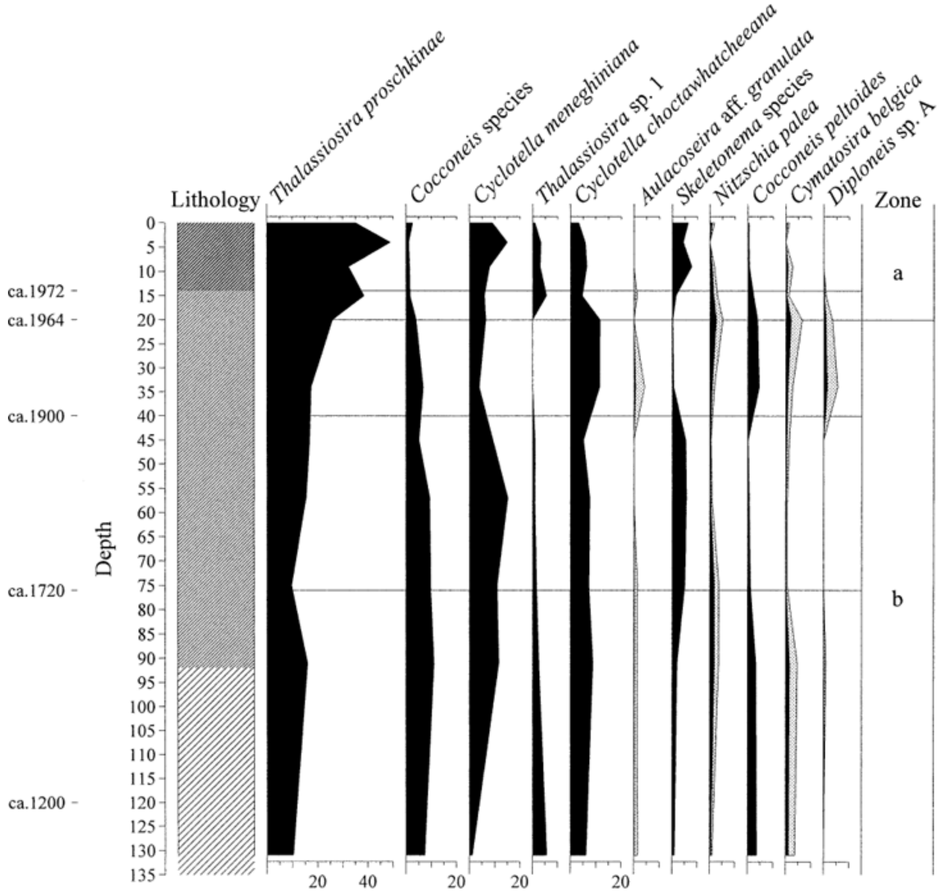

FIG. 5. Percent abundance of selected diatom species from subsamples analyzed for Neuse core OR. Zones listed at the right correspond to PCA performed on the diatom data (see Fig. 6). The lithology indicates sediment color changes downcore from uniform black to dark brown to brown.

ters was higher in the Pamlico samples than in the Neuse samples. Graphs of these data for core M4 in the Pamlico and core OR in the Neuse are shown in Figs. 10 and 11. These two cores have the highest resolution and the most data of all the cores.

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. Levels of most trace metals found in surface samples of the cores collected from the Neuse and Pamlico exceed U.S. Environmental Protection Agency (Environmental Protection Agency 1997) published Threshold Effects Levels (TEL) for sediments at several sites. Levels of Cd were highest (and more than double the TEL) in the M4 core collected in the Pamlico nearest the phosphate mining operations. Levels of most trace metals, including Zn, Cu, Cr, Ag, As, and Ni, are generally higher in the Neuse sediments. Results for Fe, Pb, As, and Cd are presented for samples from core M4 in Fig. 12. Additional data and graphs of trace metals are available in Cooper (2000) and Kim (1998).

HISTORICAL DATA

Historical data on increasing human population, cropland, fertilizer use, and swine populations in the counties directly adjacent to the Neuse and Pamlico are shown in Fig. 13.

Discussion

SEDIMENT CORES

Results show that sediment cores collected from the Neuse and Pamlico contain valuable information about past and present water quality. Cores of approximately 1 m in depth record the history of the estuaries back hundreds of years to over a thousand years before present. These sediments can be dated, and although sedimentation rates vary from site to site, good resolution of recent sediments can be obtained.

Because of the variable sedimentation within

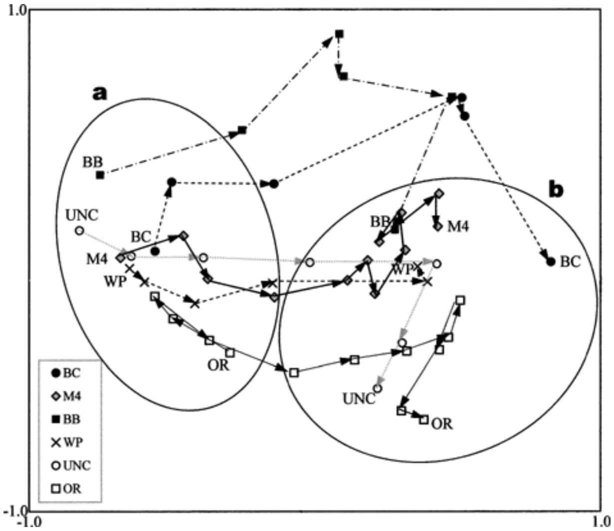

FIG. 6. Biplot of principal components analysis (PCA) of diatom assemblage data by sample using the first two axes. The first axis (x-axis) eigenvalue is 0.183, and the second axis (y-axis) eigenvalue is 0.113. The surface sediment samples for each core are labeled with the appropriate core label on the left of the biplot. Lines with arrows connect successively deeper (older) samples in each core. The bottom samples analyzed for each core are again labeled by core on the right of the biplot. Two clusters of data have been identified as a and b, referred to in the text.

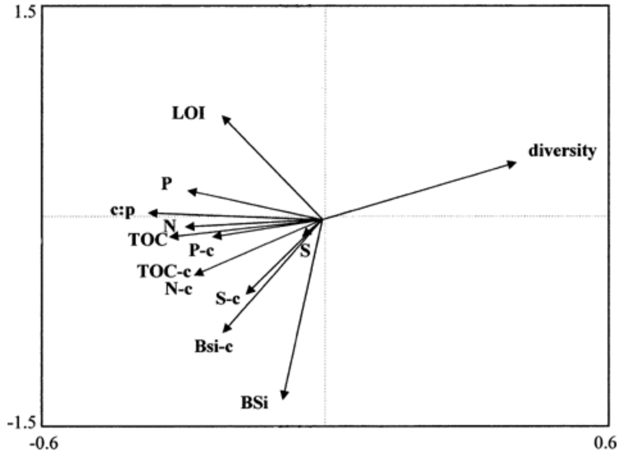

FIG. 7. Biplot of supplementary data included in the PCA according to the first two axes. Nitrogen (N), sulfur (S), biogenic silica (BSi), total organic carbon (TOC), phosphorus (P), loss on ignition (LOI), centric : pennate diatom ratio (c : p), and Shannon's H′ (diversity; Shannon and Weaver 1949) are shown. N-c, S-c, BSi-c, TOC-c, and P-c indicate corrected flux of these parameters to the sediments as compared to weight percent of the dried sediment. For example, N is measured in mg g^{-1}, while N-c (expressed as mg cm^{-2} yr^{-1}) is calculated by multiplying N by the appropriate bulk density and sedimentation rate determined for that sample.

these estuarine systems, not only in space but also in time, it is important to correct concentration of parameters measured in the sediment to account for periods of high or low relative sedimentation. Reporting measurements by concentration only or by depth only (as opposed to date of deposition) can be misleading or confusing if sedimentation rates are variable or have indeed increased over the past 50 yr, as appears to be the case for these estuarine sediments. Bulk density as well as total sedimentation will influence the concentration of geochemical parameters within the sediments and would not accurately reflect mass flux over time. TOC, P, N, and S have been shown both as concentration by depth and as mass flux in this paper

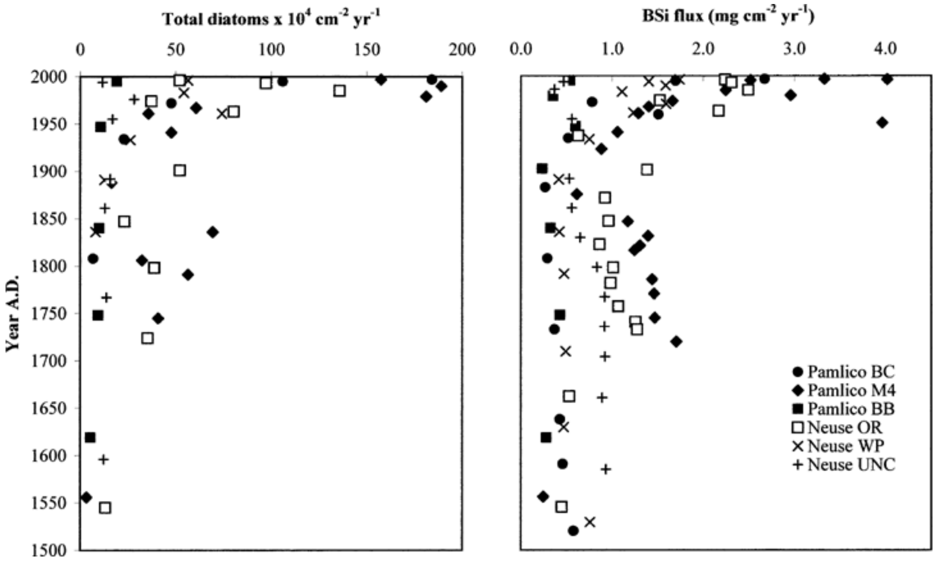

FIG. 8. Calculated diatom valve flux and biogenic silica (BSi) flux for Pamlico core M4 and Neuse core OR.

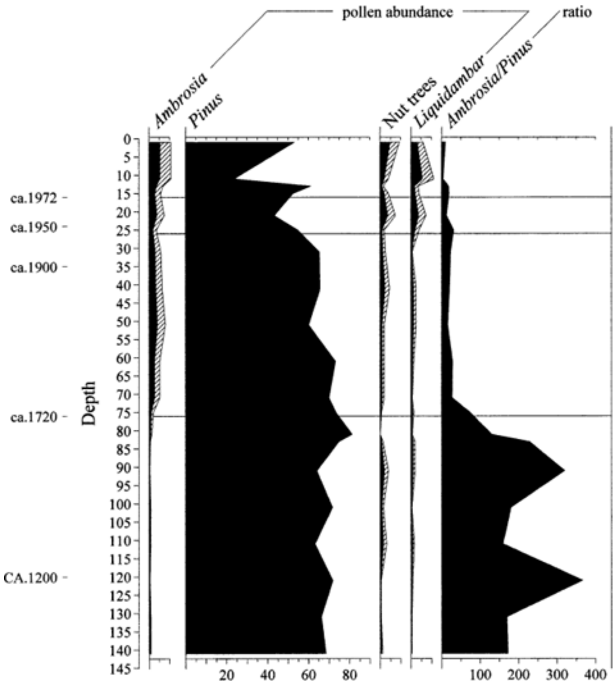

FIG. 9. Percent abundance of selected pollen types and one pollen ratio from subsamples analyzed for Neuse core OR.

along with calculated decay rate of surface TOC (Figs. 10 and 11).

DIATOMS

In the past 50 yr in all cores analyzed from the Pamlico and Neuse diatom assemblages have become increasingly composed of small planktonic forms, species that are often found in large blooms in higher nutrient waters. Assemblages found in sediments deposited before the 1940s and 1950s in both estuaries are composed of many more pennate benthic (including epiphytic) species and cluster together by site (depth) with PCA (Fig. 6). These data also show an increase in the c : p ratio of diatom assemblages (Figs. 3 and 7). The decline in epiphytic diatoms such as *Cocconeis* and *Mastogloia* species may be related to documented declines in submerged aquatic vegetation in the 1970s and 1980s in the Pamlico Sound and estuaries (Stanley 1992). Recent diatom assemblages also show significant declines in diversity compared to older (pre-1950) samples, yet with higher numbers of valves being deposited to the sediments (Fig. 3). These diatom flux and assemblage changes likely reflect eutrophication as well as increased turbidity and sedimentation.

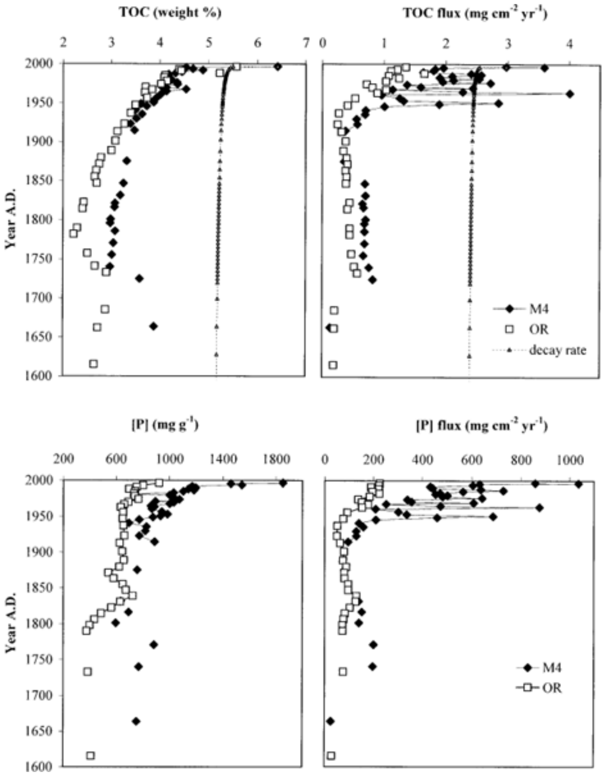

FIG. 10. Measured levels of total organic carbon (TOC) and phosphorus (P) concentration (on the left) next to calculated flux of TOC and P (on the right) to the sediments as measured for Pamlico core M4 and Neuse core OR. The degradation pattern calculated according to the decay rate published in Zimmerman and Canuel (2002) for surface concentrations of TOC is shown as small triangles. All dates along the y-axis are approximate.

Nutrient enrichment of the Pamlico and Neuse estuarine waters and blooms of noxious phytoplankton have been well documented over the past several decades (Paerl 1983; Paerl et al. 1998). Some of the most notable blooms have occurred in the Neuse in the last two decades. According to Mallin (1994), all phytoplankton related studies on the Pamlico were established since 1966, after phosphate mining and effluent discharge to the Pamlico was initiated in 1964. There are no baseline data available on species abundance and community structure prior to this major change in the watershed of the Pamlico. In the Pamlico, dinoflagellates are currently the dominant phytoplankton species (Hobbie 1971; Stanley 1992), with diatoms becoming dominant in higher salinity waters (Mallin 1994). In the Neuse, noxious blooms of blue-green algae became problematic in the oligohaline reaches of the estuary several decades ago (Paerl 1983), with eutrophication and algal blooms continuing to be a problem to the present (Paerl et al. 1998). Diatoms dominate phytoplankton in the lower Neuse in summer and early spring (Mallin 1994).

Overall trends in diatom diversity and c : p ratio changes as seen in the cores from the Pamlico and

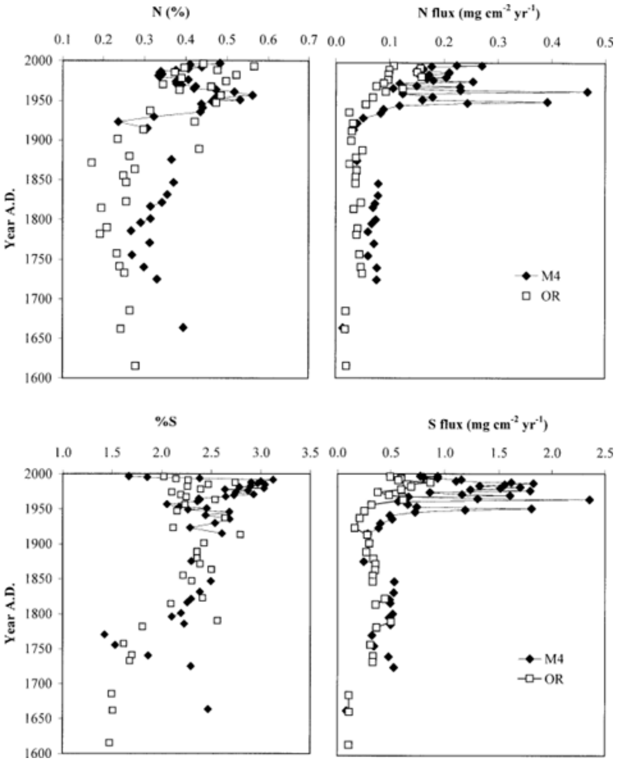

FIG. 11. Measured levels of nitrogen (N) and sulfur (S) concentration (on the left) next to calculated flux of N and S (on the right) to the sediments as measured for Pamlico core M4 and Neuse core OR. All dates along the y-axis are approximate.

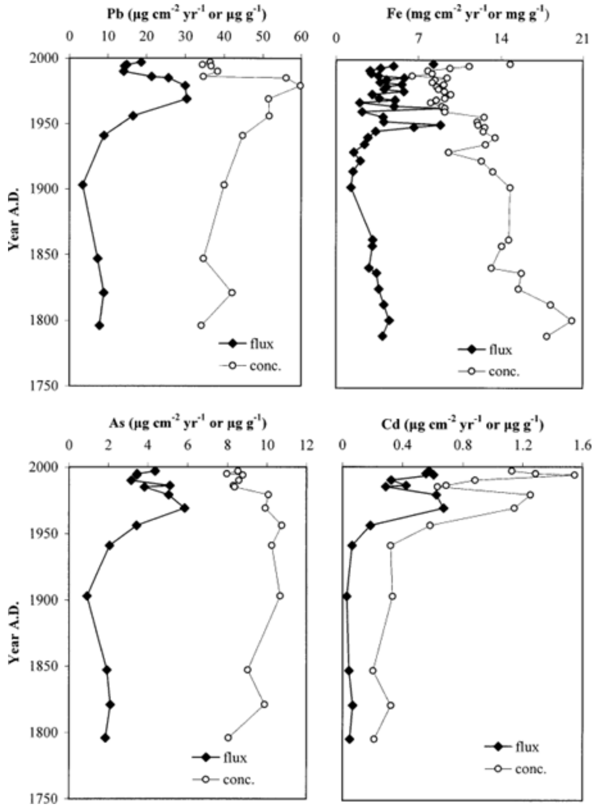

FIG. 12. Calculated flux of Pb (Pb), cadmium (Cd), arsenic (As), and acid-soluble iron (Fe) from Pamlico core M4 from sediment samples dated approximately 1700 to 1997 A.D.

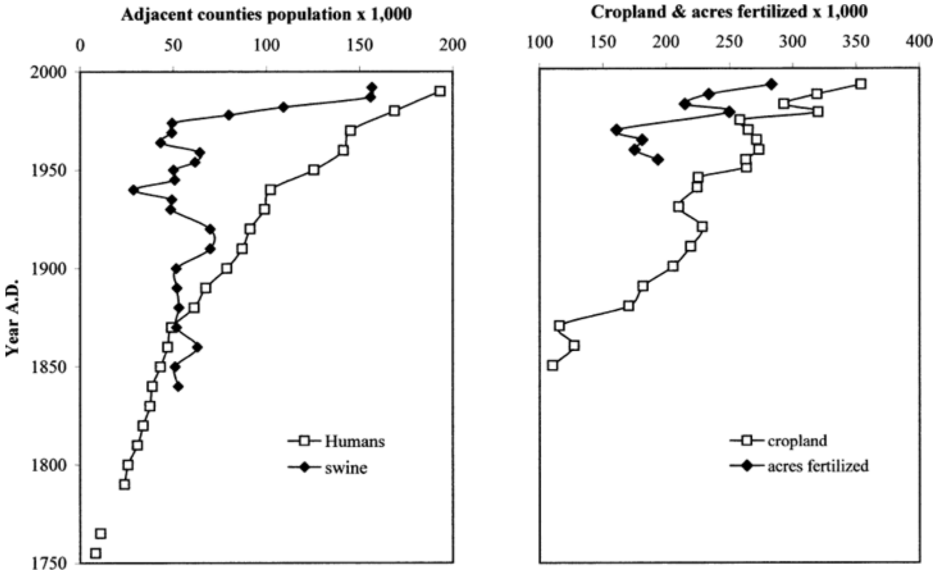

FIG. 13. On the left are human and swine population estimates for counties adjacent to the Pamlico River estuary (Beaufort and Hyde county data only) and the Neuse River estuary (includes data for Craven, Carteret, and Pamlico counties). Human population data for 1790–1990 are taken from Andriot (1993), while data for 1755 and 1765 are from Saunders (1887, Volume 5, p. 575 and Volume 4, p. 145) and include "White Taxables" and "Blacks" only (no white women or white men under 18 were counted). The swine population data is collected from U.S. Census Bureau Reports, (1840–1992). On the right are cropland and fertilizer use data collected from U.S. Census Bureau Reports, (1850–1992).

Neuse are similar to those found in Chesapeake Bay (Cooper 1995a), although the time frame of major changes is different. In Chesapeake Bay, the decline in diatom diversity and increase in c:p ratios began around 1760–1800 A.D. compared to 1900–1960 A.D. in the Neuse and Pamlico. All three estuaries have experienced a major shift from a diatom community composed of relatively even numbers of benthic and planktonic diatom species to one dominated by small planktonic forms with a major decline in abundance of benthic species. The dominant small planktonic species that became prevalent in the Chesapeake (Cooper 1995a,b) are not the same as the dominant species found in the Pamlico and Neuse of North Carolina. These mid-Atlantic estuaries are also different in total human population, land use history, geomorphology (including salinity patterns), water depth, and circulation patterns.

Shifts in phytoplankton production have often been attributed to changes in nutrient supply ratios. The ratios most often implicated are changes in N:P or N:Si. Data collected in this study does not accurately reflect the water column ratios of these nutrients at the time of sediment deposition. Most of the P and BSi measured in the sediments are inorganic, whereas the N is primarily organic. P also tends to be more mobile within the sediments. All three elements will undergo very different diagenesis patterns over time.

Dominant diatom species do show trends that may be interpreted as changes in nutrients, turbidity, and loss of benthic habitat (Figs. 4 and 5). *T. proschkinae* and *C. meneghiniana* in particular can be considered indicators of turbid waters with high nutrient content. Many benthic species show declining abundance in the most recent sediments (with increasing sedimentation).

GEOCHEMISTRY

The BSi results from this study show that much more BSi is being deposited to the sediments in recent years, a trend similar to that seen in Chesapeake Bay (Cooper 1995a; Colman and Bratton 2003). This indicates higher diatom production, most likely due to eutrophication. As production increases, dissolved silica in the waters may become limiting, especially if diatom frustules are not recycled, but preserved in the sediments. This phenomenon has been studied in Chesapeake Bay (Conley and Malone 1992). As silica becomes limiting in the water column, diatoms may be outcompeted by other algal species, including dinoflagellates, which are currently dominant in the Pamlico. The diatom community may be dominant for shorter periods of time than in the past, possibly contributing to the lower diversity seen in the sediment cores.

Measurements of C, P, and N for this study indicate higher accumulation of these elements in the sediments in the past 50 yr, especially at deeper sites. Sedimentation rates and trace metal fluxes to the sediments appear to have increased significantly in this time frame as well (by as much as an order of magnitude). The higher organic content of the most recent sediments is much more than would be expected based on diagenetic models (see Fig. 10). More detailed study of the organic composition of the sediments from the Pamlico and Neuse, including lipid biomarkers and stable isotope studies such as those done by Zimmerman and Canuel (2000, 2002) for Chesapeake Bay, would be very informative.

The highest overall P content is found in Pamlico core M4, which was collected at a location closest to the phosphate mining operations on the Pamlico. Previous research on these estuaries has shown that P loadings in the Pamlico are unusually high in comparison with other U.S. river basins, due primarily 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 officially began in 1964 (Copeland and Hobbie 1972). Total annual P loadings to the Neuse are estimated to have increased 60% in the last century, mostly in the past 40 yr, due to increased sewage discharge (Steel 1991). Generally, nutrient loadings to these estuaries and the Pamlico Sound are considered high (Quinn et al. 1989).

This study also shows large increases in N flux to the sediments of these estuaries in recent years, which may be more important in terms of eutrophication of these brackish water systems (Howarth et al. 2002). During the 1980s, point source N loadings were highest in the Neuse, and accounted for about 20% of the TN load (Stanley 1992), although it was estimated that point source N inputs could account for as much as 60–70% of TN during summer months when nonpoint source N is at its lowest levels (Steel 1991). N deposition from the atmosphere may account for an additional 15–32% of new N loadings to the Pamlico and Neuse (Paerl et al. 2002).

Most recorded 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 in these estuaries. For the Pamlico, hypoxia has become an important environmental issue. Hypoxia was first documented in the

Pamlico in the late 1960s (Hobbie et al. 1975). Many fish kills in the estuary have been attributed to hypoxia or anoxia. As in other estuarine systems such as 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).

Many metals occur naturally in seawater and are essential to marine organisms. The high levels of trace metals in the surface sediments of these estuaries (exceeding EPA's TEL) are of concern. Estuarine fine sediments are often the depositional environment of metals from many different sources. Because of the nature of the estuarine environment (e.g., variable salinity and redox potential) desorption and reabsorption of metals from particulates may occur at different times. The results of this study confirm previous research on metal deposition within the Pamlico and Neuse (Riggs et al. 1989, 1991) and provide a temporal framework for these changes. The high surface sediment concentrations of As, Cr, Cu, Ni, and Pb found in the Neuse may be associated with industrial and military operations. Cd and Ag levels in Pamlico core M4 most likely result from phosphate mining operations effluent discharges. The downcore Cd measurements appear to mirror the history of releases from the plant, although more sampling and analyses are needed to complete the record. The Pb profiles from the core samples show correlation with leaded gasoline use patterns through time (Fig. 12).

HISTORY

Historically, land use in the Albemarle-Pamlico region includes agriculture but mostly forest. According to Stanley (1992), forests recently comprised 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 growing. During the mid 1980s, 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 expanded rapidly between 1991 and 1995 with an average annual growth rate of nearly 30% (Legislative Research Commission 1996).

This paleoecological study of the sediments of the Pamlico and Neuse shows that many water quality changes have occurred in these estuaries in the past 50–60 yr. Although there are some interesting differences between the two estuaries that may be related to salinity and nutrient ratios, overall trends are the same. With apparent changes having occurred more recently than in Chesapeake Bay, the North Carolina estuaries are experiencing relatively new water quality problems related to anthropogenic sources. The overall trends in paleoecological indicators are very similar. The primary differences in diatom species appear to be due to differences in geomorphology (depth, salinity, and tidal flushing), land use history, and total human population. These data may be used for hindcasting of water quality models now being developed and used for the Neuse (Reckhow 1996). As research and management actions aimed at increasing water quality of the estuaries continue, knowledge of water quality changes related to human activities in the past is essential.

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