

ABSTRACT

Lancen S. Tully. EVALUATION OF SEDIMENT DYNAMICS USING GEOCHEMICAL TRACERS IN THE PAMLICO SOUND ESTUARINE SYSTEM, NORTH CAROLINA. (Under the direction of Dr. D. Reide Corbett) Department of Geology, July 2004.

The purpose of this study was to characterize geochemically the sediment dynamics operating within Pamlico Sound and to quantify the significance of marsh erosion as a sediment source to Pamlico Sound. A total of fifteen sediment cores, seventeen marsh grabs, and one marsh core were collected from Pamlico Sound and the surrounding marshes in 2002 and 2003. The estuarine cores are characterized by organic-rich mud (ORM) of varying thickness. The marsh grabs were collected from mainland and barrier island sites and represent two broad peat categories including: 1) surface peat and 2) subsurface peat. The geochemical tracers employed in this study include radionuclides (^{210}Pb , ^{137}Cs , and ^7Be), carbon ($\delta^{13}\text{C}$) and nitrogen ($\delta^{15}\text{N}$) stable isotopes and C:N ratios, and metal abundances (Al, Fe, Zn, and Cu). Additionally, the estuarine sediments were analyzed for grain-size distribution. These parameters provided a geochemical and sedimentological basis for comparing the estuarine muds and marsh peats, assessing changes in sediment dynamics and sediment quality over time, and illustrating the modern pathways of organic matter transport and organic matter sources.

Sediment accumulation rates of ORM vary throughout Pamlico Sound (0.1 to 0.5 cm y^{-1}), and are generally the greatest in deeper portions of the central and southern sub-basins or in shallower water located in protected coves and embayments. Stable carbon and nitrogen isotopic data acquired from Abbene (2004) indicate that sediments are transported toward the center of the sound, in accordance with sediment accumulation

rates. The data show that a major shift in either sediment dynamics or sediment source occurred in the 1960's. Probable causes of this could be related to natural (storms) and anthropogenic (trawling) resuspension events and/or changes in sediment source (i.e., increases in marsh erosion) over time. Comparing estuarine shoreline erosion rates calculated by Riggs and Ames (2003) with excess ^{210}Pb modeled accumulation rates for Pamlico Sound sediments, estuarine shoreline erosion accounts for ~9 to 14% of sediment to the sound. This represents the first time that the marsh erosion portion of the sediment budget has been calculated for Pamlico Sound. Trace metal (Zn, Cu) data correspond well with previous studies in the region and show that Pamlico Sound is relatively unpolluted (with respect to Zn and Cu) compared to the neighboring Neuse and Pamlico Rivers, Albemarle Sound, and many other estuaries globally.

**EVALUATION OF SEDIMENT DYNAMICS
USING GEOCHEMICAL TRACERS
IN THE PAMLICO SOUND ESTUARINE SYSTEM,
NORTH CAROLINA**

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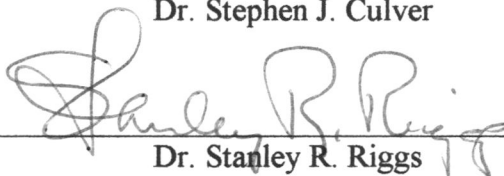
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DEDICATION

This thesis is dedicated to my parents, Brenda and Kenneth, and my wonderful girlfriend Kim. My parents have been a constant source of love and support throughout my life; without them I would have accomplished very little. Through their own hard work and sacrifice they have set an example, which has given me the fortitude to complete this manuscript. Kim has given me support, comfort, and the belief in myself that I could finish this undertaking. I look forward to our future together and I can only hope to repay her for all that she has given me.

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LIST OF ABBREVIATIONS

Radionuclides

⁷ Be	Beryllium-7
²⁰⁹ Po	Polonium-209
²¹⁰ Po	Polonium-210
²²⁶ Ra	Radium-226

¹³⁷ Cs	Cesium-137
²¹⁰ Pb	Lead-210
²²² Rn	Radon-222
²³⁸ U	Uranium-238

Elements

Al	Aluminum
Fe	Iron
Sc	Scandium

Cu	Copper
Li	Lithium
Zn	Zinc

Reagents

HNO ₃	nitric acid
NH ₄ OH	ammonium hydroxide

HCl	hydrochloric acid
HF	hydrofluoric acid

Units/Statistical Values

cm	centimeter
‰	parts per thousand (ppt)
μg	microgram
dpm g ⁻¹	disintegrations per minute per gram
psi	pounds per square inch

ppm	parts per million
mg	milligram
W	watt
r ²	correlation coefficient
nm	nanometer

INTRODUCTION

Prichard (1967) defined an estuary as “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 freshwater derived from land drainage”. Estuaries are perhaps the most studied, but often least understood of all coastal systems (Nichols and Biggs, 1978). The difficulty in understanding arises largely from the fact that estuarine systems are the meeting place between terrestrial and oceanic environments. As a result, the morphological nature of, and sedimentation within, a particular estuary are controlled by a mixture of numerous complex processes. Fairbridge (1980) delineated eight different estuarine physiographic types, each reflecting the way estuaries are modified by variations in tidal range, river discharge, and climate. In addition to these factors, antecedent geology plays a critical role in determining the modern state of coastal environments (Riggs et al., 1995). Although many estuaries are morphologically distinct, all modern estuaries were formed as a response to a rise in sea-level that began during the most recent deglaciation some 14,000 years ago. Since that time, sea-level has risen approximately 100 to 130 meters, drowning former river valleys and coastal lowlands (Nichols and Biggs, 1978).

Estuarine environments are very important to society. They function as natural harbors, places for recreation, and prominent nursery grounds for aquatic life (Korfmacher, 2002). It is important to maintain the integrity of estuaries because once they are damaged, remediation may be difficult to impossible (Birch and Taylor, 1999). Proper management and preservation of estuarine environments must begin with

thorough understanding of their dynamics. As estuaries act as a filter between terrestrial and marine environments, estuarine sediments are valuable repositories of information about the nature of coastal systems (Kranck, 1984). By examining in detail the sedimentological and geochemical characteristics of estuarine sediments, it may be possible to determine the past, present, and likely future health of the estuary. Some caution must be employed whenever interpreting estuarine deposits as they are the product of multiple sediment sources modified/reworked by biological (bioturbation) and physical (resuspension, erosion, and deposition) processes (Kniskern and Kuehl, 2003). Common sources of sediment to estuaries include river input, erosion of estuarine margins (marshes, swamps, and sediment banks), biogenic production, and continental shelf sediments via inlets (Wells and Kim, 1989).

Pamlico Sound is a bar-built estuary located in eastern North Carolina. It is an ideal nursery habitat for aquatic life, supporting more than 90% of North Carolina's commercial and 60% of recreational finfish and shellfish catches (Copeland and Gray, 1991; Paerl et al., 2001). Although Pamlico Sound is of great economic and ecologic importance, relatively little geochemical or sedimentological research has been conducted here (Paerl et al., 2001). Additionally, no attempts have been made to quantify the sediment sources listed above or amounts of sediment accumulating in the sound (Wells and Kim, 1989). Documentation of estuarine shoreline erosion shows that it is very extensive in the Pamlico Sound region (Riggs and Ames, 2003), suggesting that it is potentially a significant sediment source. It is the aim of this study to provide an interpretation of modern sediment dynamics and quantify the significance of marsh

erosion as a sediment source to Pamlico Sound using sedimentological (grain-size) information and a suite of geochemical tracers. The geochemical tracers employed for this task include radionuclides (^{210}Pb , ^{137}Cs , and ^7Be), percent organic matter (carbon and nitrogen), stable carbon ($\delta^{13}\text{C}$) and nitrogen ($\delta^{15}\text{N}$) isotopes and C:N ratios, and trace (Zn, Cu) and major (Al, Fe) metal distributions.

Objectives

The main objectives of this study are to 1) use geochemical tracers to determine the sediment dynamics operating within Pamlico Sound, and 2) quantify some of the sediment sources to Pamlico Sound.

Specific sub-objectives include:

1. Characterization of Sediment Dynamics

A) Relate the grain-size distributions of Pamlico Sound sediments to sediment dynamics;

B) Determine sediment accumulation rates, extent of sediment reworking, and establish a geochronology of sedimentation in Pamlico Sound using radionuclides;

C) Illustrate the modern pathways of sediment transport geochemically; and

D) Assess any natural or anthropogenic impacts reflected in the data that may have altered sediment quality and/or affected sediment dynamics;

2. Quantifying Marsh Erosion as a Sediment Source

E) Characterize and compare Pamlico Sound sediments geochemically with peats from adjacent marshes and lowlands; and

F) Compare Pamlico Sound sediment accumulation rates with estuarine shoreline erosion rates indicated in Riggs and Ames (2003) to establish its significance as a sediment source to the sound.

Study Area

Hydrography and Hydrology

Located in eastern North Carolina (Figure 1), Pamlico Sound is the largest bar-built estuary in the United States (Cooper, 1998). It is bounded by coastal lowlands to the north and west and the Outer Banks barrier island chain to the east and south. The sound is about 110-130 km long and 35-50 km wide covering an area of nearly 5300 km² (Pietrafesa et al., 1986). It is a relatively shallow water body with an average depth of approximately 4.8 m (Wells and Kim, 1989). The sound is separated into three broad basins: 1) a shallow upper basin in the north; 2) a deep mid-basin in the central portions of the sound; and 3) a deep southern basin (Riggs and Ames, 2003). The mid and southern basins are separated by Bluff Shoal, which extends southward from Bluff Point toward Ocracoke Inlet. Bluff Shoal is believed to represent a Pleistocene interstream divide (Zielinski, 1995). The break between the shoal and the basins is sharp, changing from ~2 to 6 m in depth in only a few kilometers (Wright, 1974). The maximum depth (7.3 m) occurs in the mid-basin, while the southern basin reaches a depth of 7 m (Wells and Kim, 1989). There are numerous shoals near the modern inlets and along the barrier islands which have been postulated to be relict inlet deltas (Fisher, 1962) in some cases,

or as part of a remnant barrier island system associated with the Hatteras Flats interstream divide (Riggs et al., 2002).

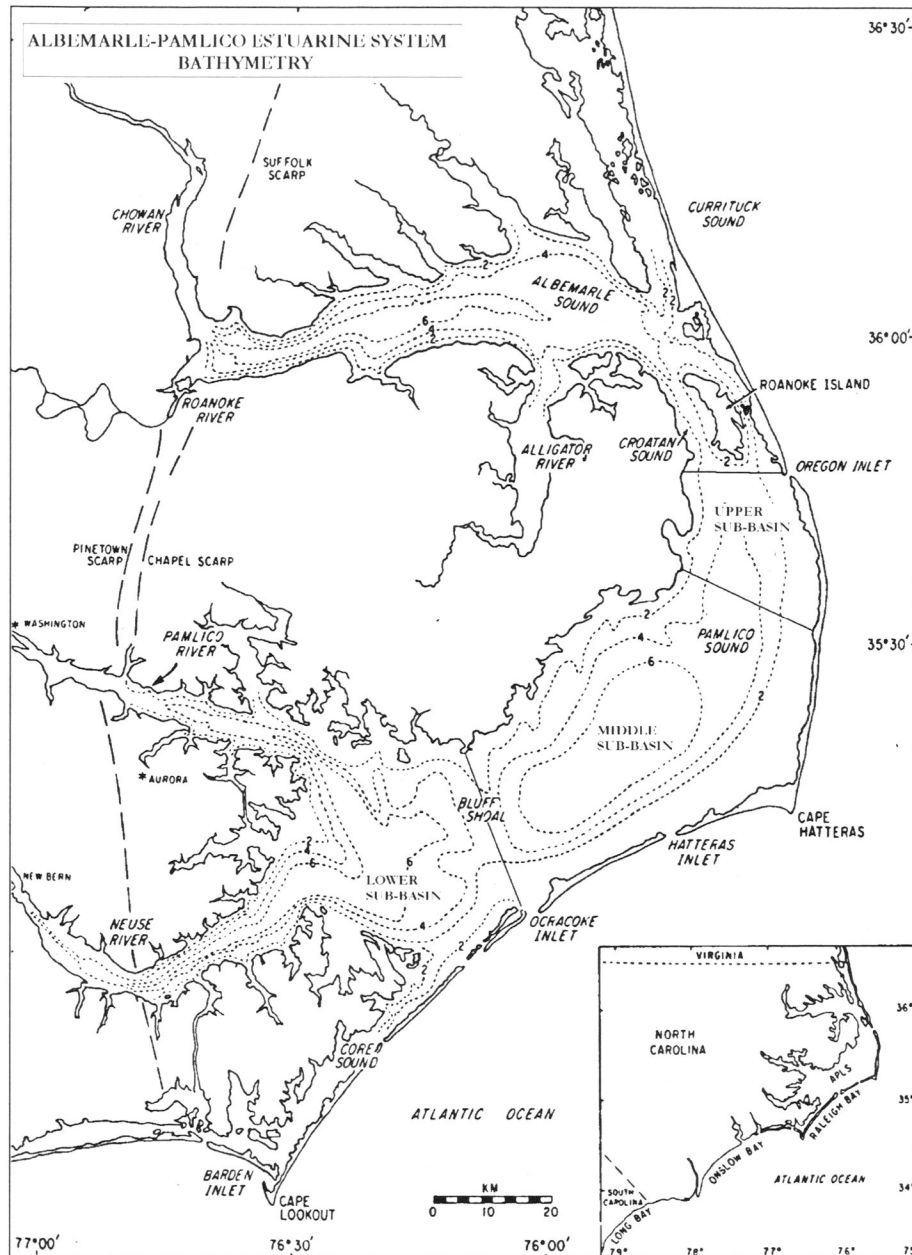


Figure 1: Pamlico Sound region bathymetry, sub-basins, and associated areas (modified from Wells and Kim, 1989).

The major river inflows into Pamlico Sound are the Neuse and Tar-Pamlico River systems, and the Chowan and Roanoke Rivers; the latter discharge indirectly into Pamlico Sound by way of the Albemarle, Croatan, and Roanoke sounds. These rivers flow over the Piedmont province consisting of a complex of igneous, metamorphic, and Triassic rocks, and then across Coastal Plain Cretaceous and Cenozoic sediments (Park, 1971). There are numerous other smaller Coastal Plain streams draining the abundant swamp forests and marshlands that virtually encircle the sound. Amein and Airan (1976) provided a summary of the major sources of water to the sound (Table 1). By comparing the ratio of the average annual inflow ($\sim 900 \text{ m}^3 \text{ s}^{-1}$) to the volume of the sound (~ 26 billion m^3) there is a theoretical freshwater replacement time of around 11 months (Giese et al., 1985; Paerl et al., 2001).

Table 1: Mean annual discharge (in $\text{m}^3 \text{ s}^{-1}$) from Pamlico Sound drainage basins (after Amein and Airan, 1976).

	Gauged Area	Discharge	Ungauged Area	Estimated Discharge	Total Discharge
Basin	km^2	$\text{m}^3 \text{ s}^{-1}$	km^2	$\text{m}^3 \text{ s}^{-1}$	$\text{m}^3 \text{ s}^{-1}$
Neuse River	9327	112	5281	35	147
Pamlico River	5783	69	5095	61	129
Roanoke River	21782	231	3160	34	264
Chowan River	583	9	11784	142	151
Marshes	0	0	10360	113	113

Three inlets (Oregon, Hatteras, and Ocracoke) provide an interaction between Pamlico Sound and the Atlantic Ocean. Two other inlets (Drum) exist in Core Sound, farther south. As a result of such a limited number of inlets, there are essentially no

perceptible astronomical tides in Pamlico Sound, except in the vicinity of the inlets (Posner, 1959; Amein and Airan, 1976). Despite the limited influence of astronomical tides, currents in Pamlico Sound can still reach significant velocities due to wind tides. The wind direction tends to vary depending on season; from April to August winds tend to blow from the south to southwest and from the north to northwest between September and February (Wells and Kim, 1989). In most directions Pamlico Sound is not fetch-limited, allowing wind setup to be the dominant short-term factor in currents (Giese et al., 1985; Riggs and Ames, 2003).

Seasonal and geographical salinity variations are controlled by changes in runoff, seasonal changes in rainfall and evaporation, proximity to inlets, and wind direction (Duane, 1962). Average salinities in Pamlico Sound range from about 15 near the mainland to 20 near the inlets (Williams et al., 1973). Salinities tend to be the highest in April and the lowest in December (Epperly and Ross, 1986). The persistent wind energies present in the sound cause the water column to remain relatively well-mixed and thus no significant salinity or thermal stratification can occur (Park, 1971). Temperature differences between surface and bottom waters are generally less than 1 to 2°C (Giese et al., 1985). Water temperatures are strongly coupled with the surface air temperatures and generally range from about 6°C to 30°C over the course of a year (Roelofs and Bumpus, 1953; Giese et al., 1985).

Estuarine Margins

Riggs and Ames (2003) defined two categories of shoreline that are most prevalent along North Carolina estuaries; sediment bank shorelines (approximately one-

third of all shorelines) and organic shorelines (approximately two-thirds of all shorelines). Sediment bank shorelines consist of three subdivisions including low bank (<1.5 m), high bank (1.5 to 6 m) and bluff (>6 m) that, when eroded by wave action, produce large amounts of sand. The organic shorelines are divided into swamp forests and marshes having peat sediments with varying amounts of sand and mud. The swamp forests and marshes occur throughout the mainland areas on the western shores of Pamlico Sound. Typically the swamps consist of cypress, gum, and swamp maple trees. Fringing the Outer Banks barrier islands on the eastern margin of the Pamlico are large expanses of brackish, irregularly flooded marshes (Pilkey et al., 1998). The marsh vegetation displays a zonation of species relative to the extent of inundation; inundation controls biologically important factors in the soil pore water such as nutrient concentrations, pH, and salinity (Bockelmann et al., 2002). This zonation typically involves a transition from emergent grasses such as *Spartina alterniflora*, *Juncus roemerianus*, and *Spartina patens* to transitional zone and scrub-shrub vegetation in more upland areas (Riggs and Ames, 2003). Some factors influencing the inundation of fringe marshes in the Pamlico Sound region are local wave activity, flushing by wind-influenced water level fluctuations, and globally rising sea-level (Brinson, 1989).

Pamlico Sound Sediments

Sediments within Pamlico Sound typically range in size from medium sand to clay, with the predominant fraction being fine sand. The sand-sized fraction consists of variable proportions of quartz (60-90%), heavy minerals (1-15%), shell and wood fragments (2-20%), and mica (up to 10%) (Pickett and Ingram, 1969; Park, 1971; Folger,

1972 a, b; Wells and Kim, 1989). The coarsest sediments are generally found on the shallow perimeter platforms near shoals, inlets, and shorelines (Riggs, 1996). The finest sediments tend to be confined to the deeper, central parts of the sound (Figure 2) and in quiet water environments, such as protected embayments along the mainland (Wells and Kim, 1989). The central basin sediments are organic-rich clayey silts with variable sorting (Pickett and Ingram, 1969). These sediments fall into the category of organic-rich mud (ORM). ORMs are generally characterized by less than 50% organic detritus and a large fraction of inorganic clay (Riggs, 1996). Duane (1962) suggested that the abundance of silt over clay is related to the nature of the source material and a large portion of the clays remaining in suspension due to disturbance. Pamlico Sound ORMs can also contain wood fragments, pollen, and seeds winnowed from coarser sediments in shallower waters (Park, 1971).

Geologic Setting

The mainland coastal lowlands adjacent to Pamlico Sound lie upon a gently sloping surface known as the Pamlico Terrace. This terrace is bounded on the west by the Pleistocene-aged Suffolk Scarp (Figure 1) and its more southern counterparts, the Pinetown and Chapel Scarps (Mixon and Pilkey, 1976). The scarps represent ancient shorelines stranded on the Coastal Plain following previous Pleistocene interglacial highstands (Riggs et al., 1995). Beneath the North Carolina continental margin is a seaward-thickening wedge of Jurassic to Holocene-aged sediments deposited on crystalline basement rock (Dubar and Solliday, 1963; Brown et al., 1972; Bellis et al.,

1975; Wells and Kim, 1989). The depth to basement is nearly 1000 m at Aurora, NC and approximately 3,000 m at Cape Hatteras (Wells and Kim, 1989).

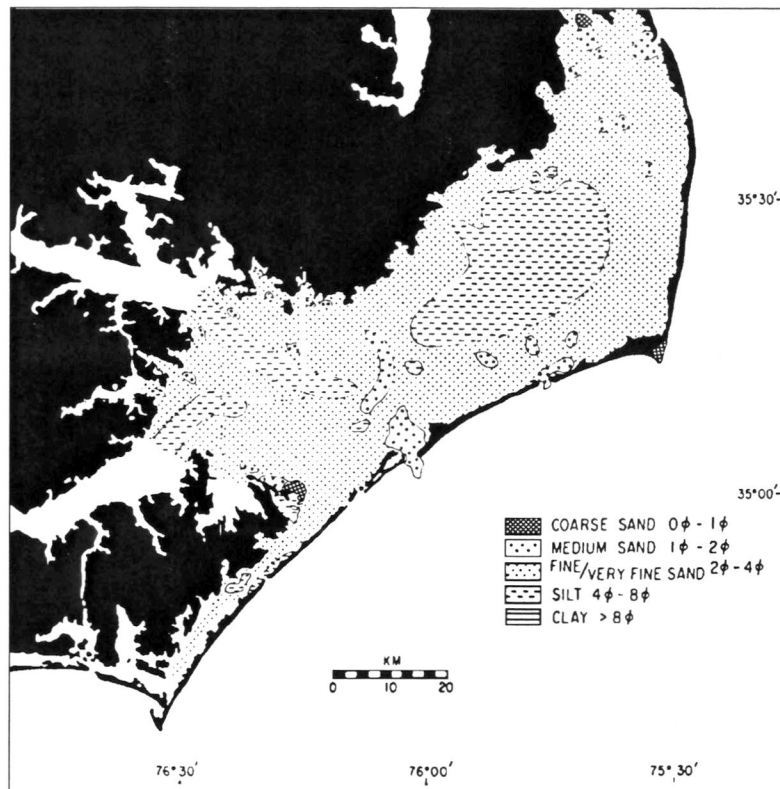


Figure 2: Grain-size distribution (in ϕ) of Pamlico Sound sediments (modified from Wells and Kim, 1989).

The thin veneer of Holocene mud and sand in Pamlico Sound occupy a portion of a regional depositional basin called the Albemarle Embayment (Ward and Strickland, 1985). It has been suggested that the embayment was produced by erosion of the surface of the Pliocene Yorktown Formation during the Plio-Pleistocene interval (Wells and Kim, 1989). The paleotopography of the Yorktown Formation influenced the infilling of Plio-Pleistocene and younger units during interglacial/glacial periods, respectively. The

bathymetric features of the modern Pamlico Sound are the direct erosional products of the Pamlico drainage system that was active during the last glacial episode that was active between 20,000 and 14,000 years ago. (Riggs et al., 1995; Riggs and Ames, 2003). Sediments in the Albemarle Embayment were deposited during a series of transgressive/regressive episodes throughout the Quaternary. These complex sequences of stacked channels represent multiple coastal environments including fluvial, estuarine, barrier island, and continental shelf (Riggs and Belknap, 1988; Ward et al., 1991; Riggs et al., 1992; Sager and Riggs, 1998; Parham, 2003). The thickness of these Quaternary sediments and the nature of paleodrainage (Figure 3) in coastal North Carolina are controlled by paleotopographic submarine and subaerial headlands (Riggs et al., 1995). Regionally, the Albemarle Embayment is bounded to the south by the Cape Lookout High and to the north by the Norfolk Platform (Riggs and Belknap, 1988; Ward et al., 1991).

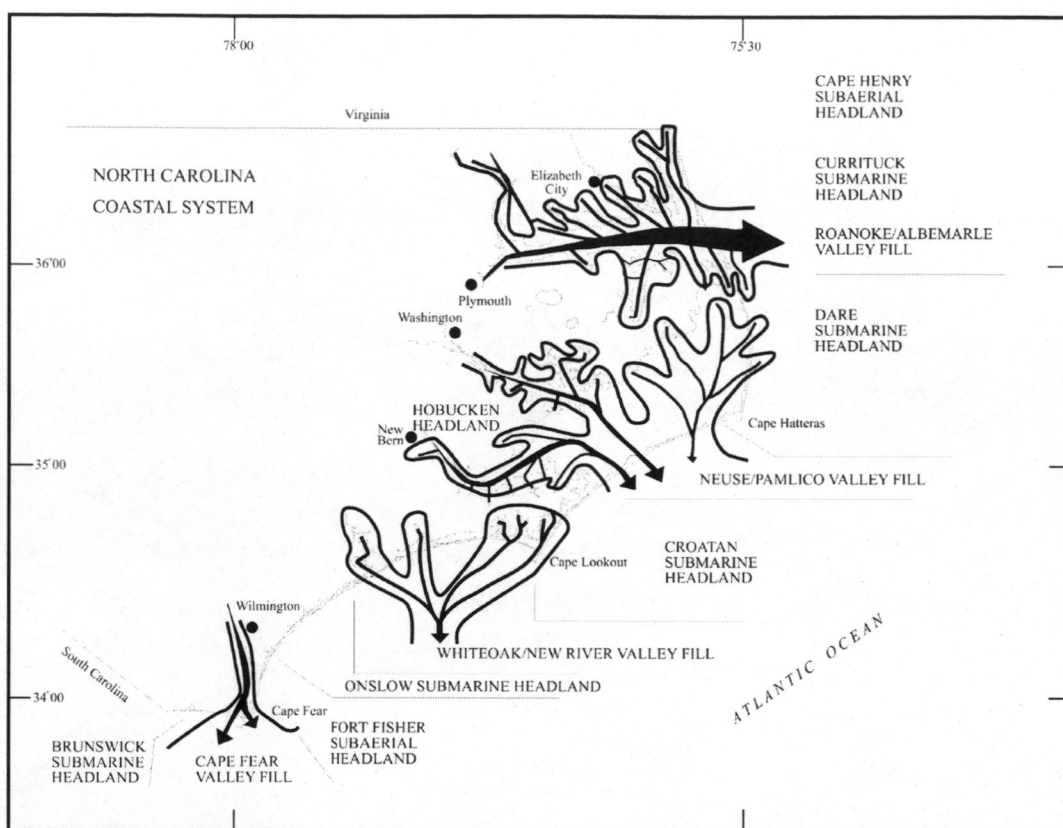


Figure 3: Paleodrainage patterns and valley fills related to submarine headlands of the North Carolina coast (modified from Riggs et al., 1995).

PREVIOUS WORKS

Pamlico Sound Studies

The earliest known scientific research conducted in the Pamlico Sound region was by Winslow (1886), who was interested in the potential of oyster cultivation. Trask (1932) described the nature of Pamlico Sound bottom sediments in a comprehensive report on source rocks of petroleum. Elements of the hydrology and hydrography of Pamlico Sound have been described by numerous sources over the years: (Marshall, 1951; Roelofs and Bumpus, 1953; Posner, 1959; Jarrett, 1966; Magnuson, 1967; Smallwood and Amein, 1967; Woods, 1967; Williams et al., 1973; Amein and Airan, 1976; Pietrafesa, et al., 1986). The authors found that Pamlico Sound was wind-dominated, microtidal, and had very slow currents with respect to riverine and tidal flow; however, currents related to wind and storm forcing can be intense and occur commonly. Some work on the clay mineralogy and other sediment properties have been studied by Duane (1962, 1964), Pickett (1965), Pickett and Ingram (1969), Nelson and Pierce (1971), Park (1971), and Folger (1972a, b). These authors found that Pamlico Sound sediment grain-size distributions showed distinct boundaries, which correlated strongly with water depth. Clay mineralogy varies with position in the estuary, although illite generally dominates over kaolinite in most cases. Sedimentary structures were highlighted by Katuna (1974). Wells and Kim (1989) provided a synopsis of many of the sediment studies to date.

Pamlico Sound Estuarine Shoreline Erosion

Riggs and Ames (2003) documented the effects of sea-level rise in coastal lowlands of eastern North Carolina and provided an excellent summary of the multiple processes that influence estuarine shoreline erosion. The authors used aerial photography and GPS to calculate erosion rates (Table 2) for numerous estuarine margin sites. Of particular interest to this study are the six sites surrounding Pamlico Sound (Figure 4). Riggs and Ames (2003) also listed nine major factors that control estuarine shoreline erosion: 1) fetch; 2) geographic location; 3) offshore bottom character; 4) shoreline geometry; 5) sediment bank height; 6) sediment bank composition; 7) abundance and type of fringing vegetation; 8) persistence of boat wakes; and 9) storms. At any given location, a combination of these factors acting in concert will determine the magnitude of shoreline erosion. Of the factors, Riggs and Ames (2003) cite storms, in particular storm frequency, intensity, and duration, as having the greatest effect on shoreline erosion.

Table 2: Net marsh platform shoreline erosion rates and average thickness of peat platforms for selected mainland and barrier island sites from Riggs and Ames (2003).

Location	Net Erosion Rate	Average Peat Thickness
Barrier Island Sites	<i>m y⁻¹</i>	<i>m</i>
Salvo	0.27	0.30
Buxton	0.79	0.45
Hatteras	0.15	0.60
<i>Barrier Island Average</i>	<i>0.40</i>	<i>0.45</i>
Mainland Sites	<i>m y⁻¹</i>	<i>m</i>
Point Peter Road	2.29	1.10 ¹
North Bluff Point	1.74	1.00 ¹
Swanquarter (bay)	0.37	2.70
Swanquarter (open)	0.88	2.70
Long Shoal Point	NA ²	1.10 ¹
<i>Mainland Average</i>	<i>1.32</i>	<i>1.60</i>

¹peat thicknesses derived from vibracores collected for the ECU-USGS-NCGS CGC database;

²NA indicates no data.

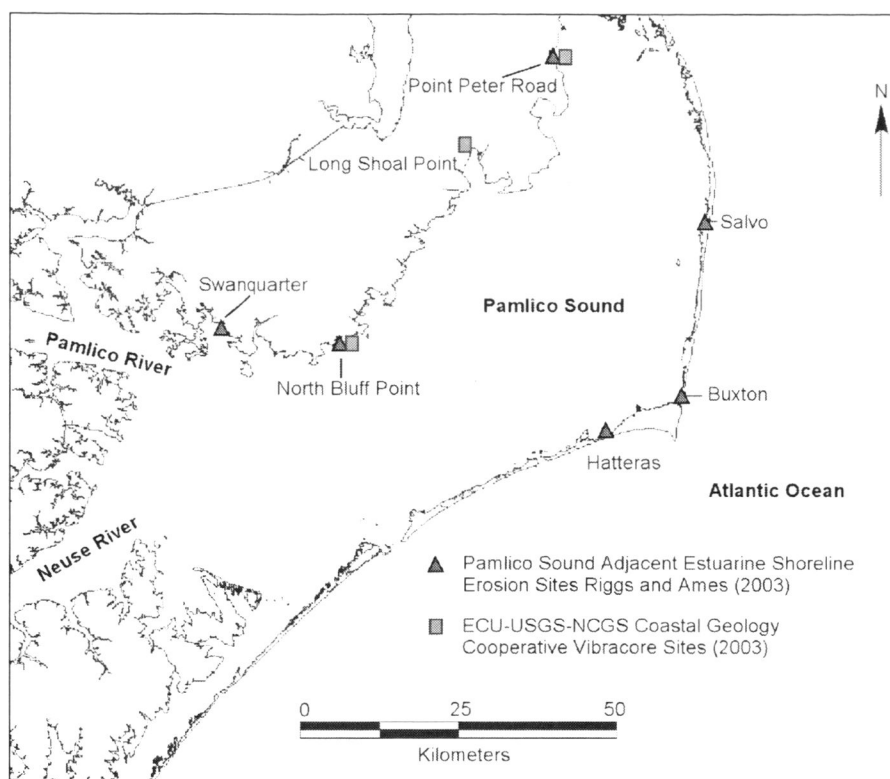


Figure 4: Location of Riggs and Ames (2003) estuarine shoreline erosion sites and ECU-USGS-NCGS CGC vibracore sites adjacent to Pamlico Sound (as indicated in Table 2).

Radionuclide Measurements in Recent Sediments

Several different radionuclides, each with different half-lives, can be used to provide a chronology for sediment deposition/accumulation rates and to examine the extent of sediment reworking. The radionuclides used in this study include ^{210}Pb , ^{137}Cs , and ^7Be .

Lead-210 (^{210}Pb)

Lead-210 is a naturally-occurring radioisotope often used for age dating of sediments that is part of the ^{238}U decay series (Krishnaswamy et al., 1971; Ravichandran et al., 1995a; Patchineelam et al., 1999; Lewis et al., 2002). A disequilibrium occurs

between ^{210}Pb and its parent isotope, ^{226}Ra ($t_{1/2} = 1602$ years), by diffusion of ^{222}Rn ($t_{1/2} = 3.84$ days). Some of the ^{222}Rn atoms that are formed by the decay of ^{226}Ra in soils diffuse into the atmosphere, eventually decaying to ^{210}Pb . The ^{210}Pb is removed from the atmosphere by precipitation or dry deposition, where it can be adsorbed onto sediments in water bodies (Appleby and Oldfield, 1992). By subtracting the ^{210}Pb activity supported by ^{226}Ra from the total ^{210}Pb , excess ^{210}Pb (or unsupported ^{210}Pb) activity can be determined. A half-life of 22.3 years allows ^{210}Pb to be used for dating sediments up to approximately 120 years of age.

Cesium-137 (^{137}Cs)

Cesium-137 is an anthropogenic radionuclide that is a by-product of fission reactions. Atmospheric ^{137}Cs ($t_{1/2} = 30.1$ years) derived from nuclear weapons testing was first detectable in 1953, with the maximum fallout occurring in 1963 in the northern hemisphere (Chumura and Kisters, 1994). This provides the possibility of two dated horizons (Figure 5), one reflecting the initial early 1950s increase and the other the 1963 peak in ^{137}Cs fallout. This allows ^{137}Cs to be a viable stratigraphic marker in lake, marsh, and estuarine sediments (Pennington et al., 1973; Chmura and Kisters, 1994; Nyman et al., 1995; Cearreta et al., 2000; Donnelly et al., 2001a, b; Neubauer et al., 2002).

Three assumptions must be made when using ^{137}Cs in the measurement of sediment accumulation in aquatic systems: 1) the ^{137}Cs entering the water body is quickly adsorbed to suspended material in the water column; 2) in cases where radiocesium is deposited in the catchment area of a water body, the radionuclide is firmly adsorbed on soil particles and any redistribution results chiefly from erosion and deposition; and

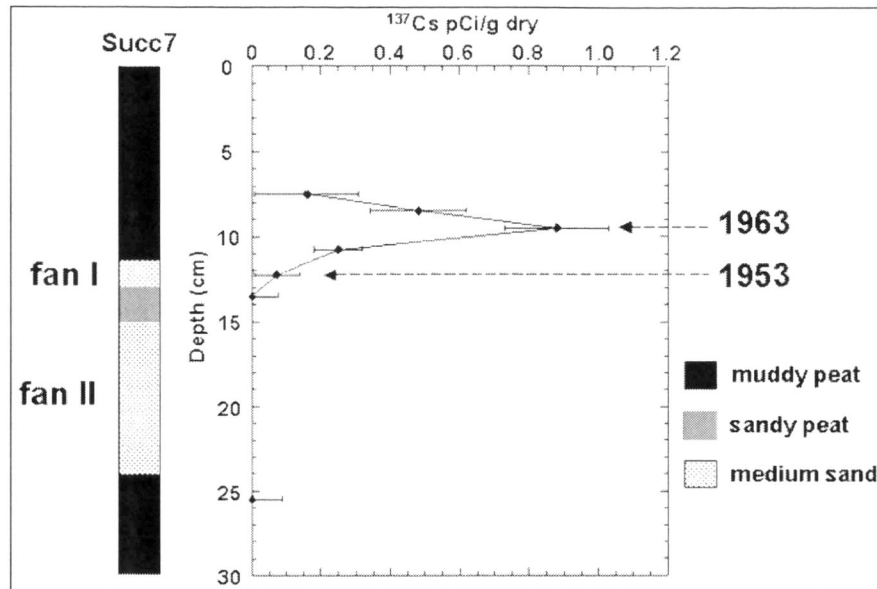


Figure 5: Cesium-137 profile from a marsh showing the 1953 onset of nuclear-bomb testing and the 1963 peak of nuclear-bomb testing activity (modified from Donnelly et al., 2001a)

3) once deposited in the sediment column the radionuclide is immobile and is not affected by reworking or diffusional movement up or down in the substrate (Hutchinson, 1995).

In anoxic sediments radionuclide mobility can be enhanced, invalidating assumption three.

Beryllium-7 (⁷Be)

Beryllium-7 ($t_{1/2} = 53.3$ days) is a naturally-occurring, particle-reactive radionuclide produced by cosmic ray spallation processes of nitrogen and oxygen within the Earth's atmosphere (Olsen et al., 1985). It is produced primarily in the stratosphere; however, due to the long residence times of stratospheric air masses, most of the ⁷Be delivered to the Earth's surface comes from the troposphere (Dutkiewicz and Husain, 1985; Canuel et al., 1990). Deposition on the Earth's surface occurs primarily through

precipitation and dry deposition of ^7Be associated with aerosols. Residence times of ^7Be in the water column can vary from a few days to several weeks depending on the amount of fine particles in suspension, sediment accumulation rates, and frequency of sediment resuspension (Olsen et al., 1986). The short half-life of ^7Be allows it to be a useful particle tracer for sediment dynamic activities on time scales of days to months (Giffin and Corbett, 2003).

Radionuclide Case Study (Ravichandran et al., 1995a)

A 1995 study by Ravichandran et al. (1995a) shows the utility of ^{210}Pb and bomb fallout radionuclides ($^{239,240}\text{Pu}$) in geochemical tracer studies and illustrates some inherent sedimentological and geochemical properties that can complicate interpretation of radionuclide data. The purpose of the study was to establish a geochronology that would put a timeline on sediment contamination in the anthropogenically impacted Sabine-Neches estuary of southeast Texas. In the Sabine-Neches estuary there is an excellent correlation between grain-size and ^{210}Pb activity in surface sediment samples, attesting to the particle-reactive nature of this radionuclide. The authors noted that the grain-size effect is important downcore in the estuary, where changes in the percentages of fines can appear to have the same effect on radionuclide profiles as intense mixing. In cases where the grain-size is highly variable within a core, the constant-flux constant-sedimentation (CF:CS) model for determining ^{210}Pb accumulation rates becomes invalidated and the constant-initial-concentration (CIC) model is more appropriate. ^{210}Pb profiles from the Sabine-Neches estuary were characterized by low activities and numerous irregularities that the authors attributed to the escape of some dissolved ^{210}Pb from the estuary,

sediment mixing, the grain-size effect, and the introduction of ^{222}Rn -rich groundwater to sediments at depth. All of these factors made ^{210}Pb modeling problematic; however, the $^{239,240}\text{Pu}$ peaks were well-defined in most cases, allowing sediment accumulation rates to be calculated. The average sediment accumulation rate varied from about 4 to 5 mm y^{-1} comparing well with local sea-level rise (6 mm y^{-1}) caused by subsidence from fluid withdrawal in the Gulf of Mexico region (Turner, 1991).

Carbon and Nitrogen Stable Isotopes and C:N Ratios

The differences that exist among natural abundances of stable carbon ($\delta^{13}\text{C}$) and nitrogen ($\delta^{15}\text{N}$) isotopes and atomic ratios of carbon to nitrogen in organic matter derived from different sources (i.e., terrestrial, anthropogenic, marine, etc.) make them valuable geochemical tracers (Matson and Brinson, 1990). When using stable isotopes in this manner, it is assumed that the isotopic distributions of organic matter are based on conservative isotopic ratios determined by physical mixing of end-member sources (Cifuentes et al., 1988). The isotopic value of carbon ($\delta^{13}\text{C}$ in ‰) is determined by

$$\delta^{13}\text{C} \text{ or } \delta^{15}\text{N} (\text{‰}) = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \times 1000 \quad (1)$$

where R is the atomic $^{45}\text{CO}_2/^{44}\text{CO}_2$ ratio and the standard is carbonate from *Belemnitella americana* from the Cretaceous Peedee Formation of South Carolina (Smith and Epstein, 1971). Similarly, the isotopic composition of nitrogen ($\delta^{15}\text{N}$ in ‰) in a sample is

expressed in EQ 1, where R is the atomic $^{15}\text{N}/^{14}\text{N}$ ratio and the standard is atmospheric N_2 (Heaton, 1986; Thornton and McManus, 1994).

Implications of $\delta^{13}\text{C}$ Signatures

Organic carbon can display a wide range of $\delta^{13}\text{C}$ values depending on the source of the organic matter. Materials enriched in ^{13}C relative to ^{12}C are isotopically heavy and have more positive $\delta^{13}\text{C}$ values, while materials depleted in ^{13}C relative to ^{12}C are isotopically light, and have more negative $\delta^{13}\text{C}$ signatures. Variations in the $\delta^{13}\text{C}$ signatures for terrestrial and marine plant matter (Figure 6) are related to the mechanism of CO_2 fixation used by the flora during photosynthesis (C_3 vs. C_4 photosynthetic pathway). Terrestrial plants tend to employ the Calvin-Benson (C_3) pathway, which produces an average $\delta^{13}\text{C}$ value of -27‰. The Hatch-Slack (C_4) pathway is used by many grasses and salt marsh plants and produces an average $\delta^{13}\text{C}$ value of -13‰ (Smith and Epstein, 1971; Waller and Lewis, 1979; Sherr, 1982; Benninger and Martens, 1983; Nordt et al., 1994; Hedges et al., 1997; Letrick, 2003). Studies have shown that the isotopic signature of carbon is not susceptible to significant alteration following deposition (Sherr, 1982; Nordt et al., 1994; Freudenthal et al., 2001; Letrick, 2003).

Implications of $\delta^{15}\text{N}$ Signatures

Isotopic nitrogen ($\delta^{15}\text{N}$) values can be indicative of the biogeochemical cycling of nitrogen in estuarine sediments. Multiple processes occurring in the water column and sediments including ammonification, nutrient assimilation, nitrification, and denitrification, function to enrich the substrate in ^{15}N (Owens, 1987; Thornton and McManus, 1994). This enrichment is due to a preferential removal of the lighter ^{14}N

relative to ^{15}N during organic matter degradation and assimilation processes. This is evidenced by food web observations which show greater enrichment at higher trophic levels (Freudenthal et al., 2001). Generally, $\delta^{15}\text{N}$ values for terrestrial nitrogen compounds range from -15 to +20‰ (Heaton, 1986). Salt marsh peats tend to have values ranging from -3 to 2‰. $\delta^{15}\text{N}$ values derived from anthropogenic activity can vary with the source. For example, nitrate from sewage and animal wastes is usually highly positive, while nitrate and ammonia from fertilizers has a $\delta^{15}\text{N}$ signature near zero ‰ (Figure 7).

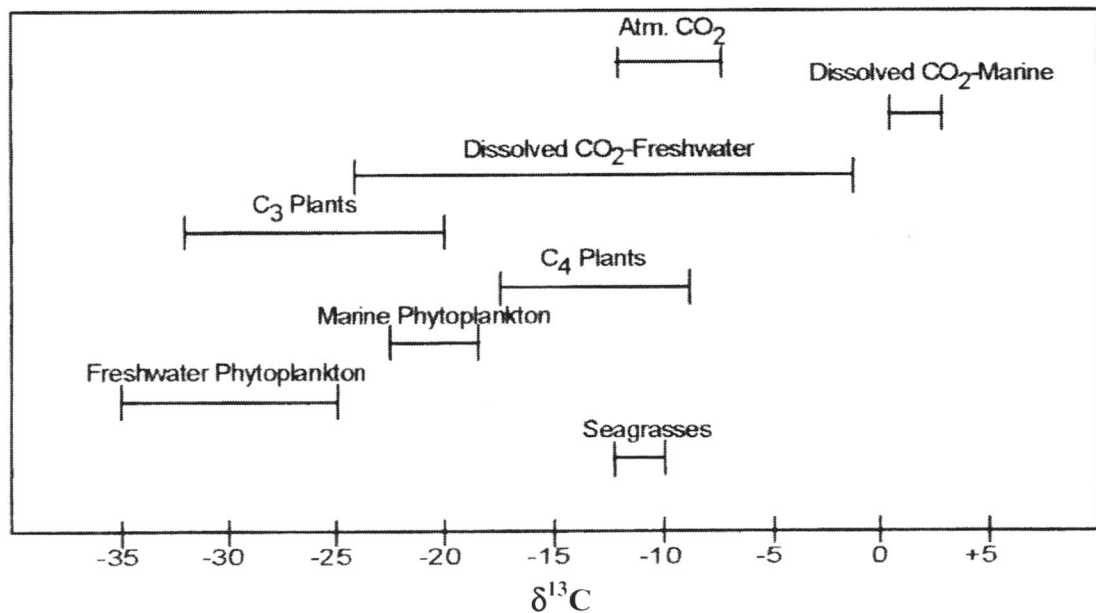


Figure 6: Isotopic carbon ($\delta^{13}\text{C}$) values of various species of carbon (in ‰) (modified from Letrick, 2003 after: Sackett, 1964; Smith and Epstein, 1971; Waller and Lewis, 1979; Sherr, 1982; Benninger and Martens, 1983; Fry and Sherr, 1984; Canuel and Martens, 1993; Nordt et al., 1994; Hedges et al., 1997; Maksymowska et al., 2000).

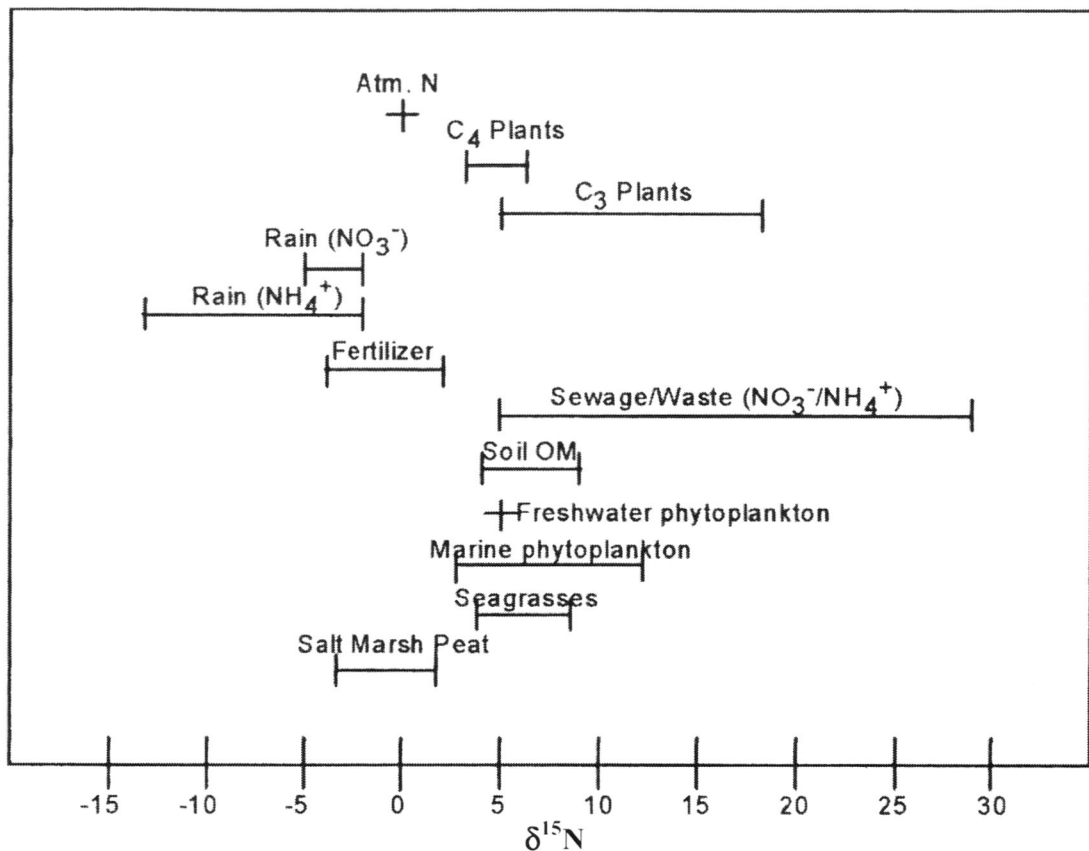


Figure 7: Isotopic nitrogen ($\delta^{15}\text{N}$) values (in ‰) of selected nitrogen species (modified from Letrick, 2003 after: Peters et al., 1978; Sweeny and Kaplan, 1980; Heaton, 1986; Owens, 1987; Chapelle, 1993; Howarth, 1998; Maksymowska et al., 2000).

Implications of C:N Ratios

As with $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, the molecular ratio of carbon to nitrogen is unique for many different types of organic matter. Generally, terrestrially-derived organic matter will have higher C:N ratios (12 or greater) than that of marine organic matter sources (10 or less) (Maksymowska et al., 2000). Much like $\delta^{15}\text{N}$, C:N ratios can be subjected to alteration by degradation processes during transport. The majority of the time nitrogen will be removed preferentially to carbon, increasing the C:N ratio. Comparisons between

suspended organic matter C:N ratios and surface sediment C:N ratios invariably show that surface sediments have higher C:N ratios (Andrews et al., 1998; Middelburg and Nieuwenhuize, 1998). After sediment deposition, alteration of the C:N ratio can continue. The greatest alteration in C:N ratios often occurs in coarser sediments where bacteria can more readily degrade particulate organic matter. A good correlation between C:N ratios and $\delta^{15}\text{N}$ values yields evidence that support a granulometric control over sediment diagenetic processes (Thornton and McManus, 1994).

Carbon and Nitrogen Isotope Case Study (Thornton and McManus, 1994)

Thornton and McManus (1994) examined carbon and nitrogen stable isotopes and C:N ratios in lacustrine and riverine sediments of the Tay River of Scotland in an attempt to illustrate organic matter provenance. The authors found that the $\delta^{13}\text{C}$ signatures between the estuarine and lake samples were compositionally distinct. Furthermore, the estuarine samples tended to have much greater $\delta^{13}\text{C}$ variability than the lake samples, attesting to a greater variability in source material. Thornton and McManus (1994) were unable to distinguish estuarine from lake samples with either $\delta^{15}\text{N}$ or C:N ratios due to their high variability, but they discovered that the two tracers covaried with respect to location. They attributed this covariance to degradation processes occurring during transport and the granulometric effect. This study shows the benefits of a combined geochemical tracer approach to illustrate organic matter provenance and the effects of degradation processes that occur during transport and following deposition.

Metal Distributions in Recent Sediments

Metal/Sediment Interactions

Trace and major metals in coastal environments are typically derived from the weathering of continental material or anthropogenic discharges. When introduced into aquatic systems, metals tend to admix or interact with sediments (Cearreta et al., 2000). Removal of the metals from the water column tends to occur by physicochemical (flocculation) or biological uptake processes, or by direct uptake at the sediment/water interface (Santschi, 1982). Although the amount of suspended sediment is the master variable in scavenging metals from the water column, water chemistry is critical. In situations where the pH, suspended sediment composition and suspended sediment concentrations are held the same, metals in a freshwater system will always be scavenged more efficiently than in an estuarine (more saline) system due to competition from other dissolved ions (Hatje et al., 2003). The following list from Riggs et al. (1993) summarizes many of the mechanisms by which metals can become incorporated into sediments in a coastal environment:

1. Dissolved in interstitial pore waters,
2. Adsorbed or chelated by organic matter, often as surface coatings,
3. Adsorbed or occluded with oxy-hydroxy precipitates of iron or manganese (occurring as discrete particles or surface coatings),
4. Precipitated as distinct metal salts (e.g., hydroxides, sulfides, carbonates, etc.) or other mineral species,

5. Adsorbed or occluded in carbonates of inorganic origin (calcite, aragonite, etc.) or of biogenic origin (shell hash),
6. Adsorbed at ion exchange or adsorption sites of mineral grains,
7. Bound at interlayer sites of clay minerals, and
8. Incorporated into the crystalline lattice of minerals.

Metal Mobility in Estuarine Systems

The metals are not necessarily fixed in the sediment, and can be released into the water column by physical reworking, resuspension, and early diagenetic processes (Beno and Gibbs, 1990; Cearreta et al., 2000). Metals reintroduced to the water column are often scavenged by fine-grained suspended sediments, causing them to be redeposited. Thus, the physicochemical properties of resuspension, aggregation and settling of particles, and hydrodynamic circulation can limit or enhance the distribution of metals in estuarine systems. Additionally, metal movement through an ecosystem may be related to the chemical forms in which the metals can occur, dictated by environmental conditions such as temperature, pH, and concentration (Santschi, 1982). Although metals are normal constituents of most estuarine systems, their presence can be elevated by anthropogenic activities, making them useful indicators of sediment source and sediment transport paths (Riggs et al., 1993).

Normalization of Metal Data

Typically the determination of metal abundances in sediments is done by sensitive instruments such as atomic absorption (AA) spectrometers or inductively coupled plasma (ICP) spectrometers, following an acid leach or total acid digestion. Results from acid

leach and total acid digestion studies have been found to be uncomparable (Swolsman et al., 1996). Metal concentrations can be diluted in estuarine sediments by coarse-grained materials that lack the affinity for metals as that of fine-grained sediments (Ravichandran et al., 1995b). In order to correct for this dilution effect, normalization procedures are often applied. Normalization is done by dividing the concentration of a particular metal by another parameter such as median grain-size (Birch and Taylor, 1999; Swolsman et al., 1996), organic matter (Swolsman et al., 1996), or by the concentration of a conservative metal in the sample. Numerous metals can be used for this including Sc (Grouset et al., 1995), Fe (Tam and Yao, 1998; Baptista Neto et al., 2000), Li (Aloupi and Angelidis, 2001) and Al (Benninger et al., 1993; Ravichandran et al., 1995b; Soto-Jimenez and Paez-Osuna, 2001). Of the conservative metals listed above, Al is perhaps the best choice for normalization. It represents the aluminosilicates which are the most important carrier phase for adsorbed metals, thereby compensating for both sediment grain-size and composition. Also, metal to Al ratios tend to be fairly constant in the Earth's crust and are not particularly susceptible to alteration by human activity (Ravichandran et al., 1995b).

Metal Distribution Case Study (Benninger and Wells, 1993)

A study that is of particular relevance to interpretation of trace and major metal distributions in Pamlico Sound sediments was conducted by Benninger and Wells (1993). They used Zn, Cu, and Al concentrations in sediments as well as Zn and Cu normalized to Al to examine sediment sources in the Neuse River estuary in eastern North Carolina. Benninger and Wells (1993) observed decreasing trends in Zn and Cu concentrations

downstream and downcore, suggesting that the source of the metals was near the head of the estuary and has increased over time. Aluminum concentrations deviated from this trend somewhat, with mid-estuary cores showing the highest values. However, the estuary mouth sediments still had the lowest metal concentrations. Aluminum normalization of Zn and Cu data showed that the highest ratios were near the surface, while the lowest values were found at depth. However, the difference between metal/Al ratios in surface sediments and metal/Al ratios in deeper sediments decreased with distance downstream (i.e., downstream cores showed less variation between surficial metal/Al ratios and metal/Al ratios with depth than those of more upriver stations). Benninger and Wells (1993) attributed decreases of metal concentrations and metal/Al ratios downstream to a combination of landward transport of sediments from Pamlico Sound, a decreased influence of riverine sedimentation, and a dilution of the sediment with coarser-grained sediments derived from marsh erosion.

METHODS

Sample Collection

Fifteen cores of varying lengths (20 to 54 cm) were collected for geochemical and sedimentological analysis from Pamlico Sound during the summers of 2002 and 2003. Additionally, in December 2002 one core and twenty peat grab samples were collected from marshes at seven sites surrounding Pamlico Sound. These particular marsh sites were chosen due to their high erosion rates and extent of peat development. Figure 8 shows the sample collection locations.

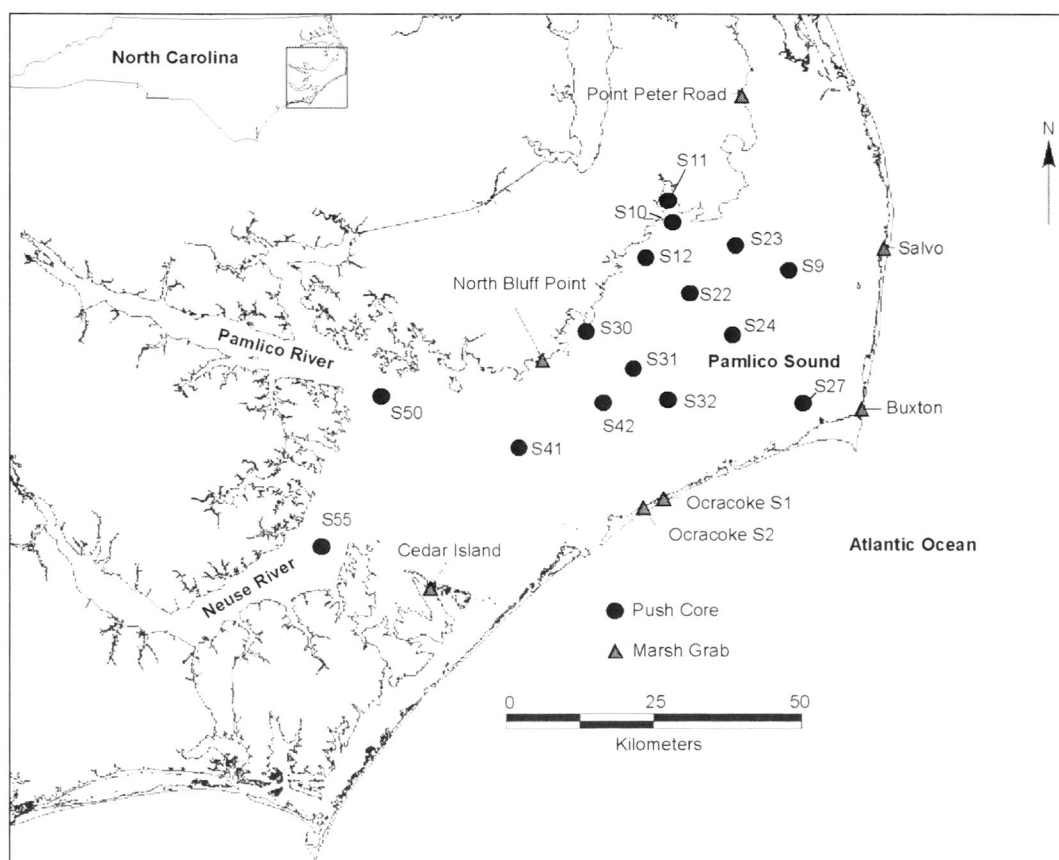


Figure 8: Location of estuarine cores and marsh peat grab samples collected for sedimentological and geochemical analyses during 2002 and 2003.

Marsh grab samples were selected based on changes in sediment type at each site, in order to have an adequate representation of the material that is currently eroding (i.e., surface marsh peat, older underlying peat, submerged peat platforms, etc.) (Riggs and Ames, 2003). The marsh peat grab samples were placed in plastic bags and stored in a cooler while in the field. The estuarine cores were collected from a small research vessel, the ECU Privateer, by diver or by using a PVC push-coring device containing a one-way flow valve attached to either a 10.2 or 15.2 cm diameter, 100 cm long piece of acrylic pipe. The peat core was collected by hand pushing a 7.6 cm diameter acrylic pipe into the marsh. The cores were extruded in the field and sampled at 2 cm intervals. Subsamples of each interval were collected in pre-weighed 7 ml plastic vials for determination of porosity and loss on ignition (LOI) and 20 ml plastic vials for carbon/nitrogen stable isotope and trace metal analyses. In general, the 7 ml vials were only collected for the intervals of 0-2 and 2-4 cm, then at alternating intervals beyond that. The 20 ml samples were collected at each interval. The 20 ml vials were stored on ice in the field and frozen upon return to the lab to prevent any alteration in the samples by biologic activity. The remaining sediment was placed into plastic sample bags for grain-size and radionuclide analyses.

Initial Sample Preparation

The 7 ml vials were weighed, oven-dried at 60°C for 3 days, and then reweighed to determine porosity. A small amount of wet sediment was removed from the plastic sample bags for grain-size determination. Each marsh peat grab was separated into three

different replicate samples (A, B, and C) to examine statistical variability in carbon and nitrogen stable isotopes, C:N ratios, and metal concentrations. The peat samples, along with the remaining Pamlico Sound samples collected from cores and the sediments in 20 ml vials, were oven dried at 60°C for at least 3 days. The sediments were then homogenized with a mortar and pestle, removing all visible shell and plant fragments. A sedimentological log was made for each of the intervals, noting any abundances of shell or plant material and any changes in grain-size or sediment texture.

Percent Organic Matter (Loss on Ignition)

Percent organic matter was determined by loss on ignition (LOI) for each marsh peat sample and estuarine sediment samples for intervals where porosity samples were collected. A small amount of dried, homogenized sample (10-20 g) was spooned in a pre-weighed ceramic crucible. The crucibles were placed in a desiccator containing drierite (anhydrite) overnight to remove any moisture that might have accumulated in the sediments during storage. The crucibles and sediments within were weighed and then combusted in a muffle furnace for 4 hours at 450°C. The crucibles were removed from the furnace and placed back in the desiccator to cool. Upon cooling, the crucibles were re-weighed to determine LOI by

$$\text{LOI (\%)} = \frac{\text{Initial Mass} - \text{Combusted Mass}}{\text{Initial Mass}} \times 100 \quad (2)$$

Grain-Size Sample Preparation and Analysis

Grain-size analysis was typically performed only on sample intervals where porosity vials were collected. Hydrogen peroxide (30% H_2O_2) was added to ~5-15 g of relatively shell-free, wet sediment and allowed to sit for several days to remove all organic matter. The sediments were then transferred into 50 ml centrifuge tubes. The tubes were spun at 4000 rpm for 20 minutes and then any remaining peroxide and excess water decanted. The sediments were stirred and about 20 ml of water was added to wash the sediments before they were centrifuged again at 4000 rpm for 20 minutes. The fluid was decanted and a mixture of the surfactant sodium hexametaphosphate (calgon) and water (0.6 g calgon/liter DI water) was added to the sediments to prevent flocculation of any clays. The calgon solution was added in an approximately equal volume as the quantity of sediment contained in the tubes. The samples were then shaken and remained in the solution for at least 24 hours prior to analysis.

The sample grain-size distribution and median grain-size were determined on a Coulter LS 230 grain-size analyzer in the ECU sedimentology lab. The instrument consists largely of 4 units: the optical module (houses the laser), the fluid module (sample well and sonicator), a 30 cell autosampler, and a computer. The LS 230 has the capability to measure particles in suspension from 0.4 to 2000 micrometers (μm) in size. A very small volume of sample (~ 3-6 drops) was loaded into a glass vial with an eyedropper, which was then inserted in the autosampler. The sample was emptied into the fluid module and sonicated. The optical module laser emitted a light with a wavelength of 750 nanometers (nm) into the sample cell, where particles suspended in

the liquid diffracted the incident light in characteristic patterns dependent on their sizes. Values were averaged over the duration of the measurement, resulting in the true particle size distribution of the sample (Coulter Corporation, 1994). The percentage of light scattered out of the beam by the particles (obscuration) needed to be between 8 and 12% for a run to be considered valid. Either increasing or decreasing the sample volume was necessary to achieve values within this range.

Radionuclide Preparation and Analysis

The potential of establishing a geochronology was evaluated by using short-lived radioisotopes including ^{210}Pb ($t_{1/2} = 22.3$ years) and ^{137}Cs ($t_{1/2} = 30.1$ years). Sediment resuspension and mixing rates were assessed with ^7Be ($t_{1/2} = 53.3$ days). The activities of the radioisotopes, with the exception of ^{210}Pb , were determined by direct gamma counting on a low-background, high-purity germanium detector. For ^{210}Pb , activities were obtained indirectly via alpha spectrometry counting of its granddaughter radionuclide ^{210}Po , under the assumption that the two were in secular equilibrium. Polonium-210 ($t_{1/2} = 138.4$ days) is the last radioactive member of the ^{238}U decay series (Hamilton and Smith, 1985). Counting followed an acid leach, an iron scavenge, and a spontaneous deposition of ^{210}Po from solution on a nickel disc.

Gamma Spectrometry (^{137}Cs and ^7Be) Sample Preparation and Parameters

For gamma spectrometry, a small volume of homogenized sediment was packed into tins (~25-40 grams) or vials (~4-9 grams), prior to analysis. The actual mass packed into a vial or tin was largely dependent on sample grain-size and density. To ensure that

sample geometries were uniform, after the addition of each spatula full of sediment, the vial or tin was tapped several times, causing the sediment to settle and compact. Once the appropriate volume was achieved, both the vials and tins were capped and sealed to prevent exchange with the atmosphere. The vials were sealed with a fast drying epoxy and the tins were sealed with electrical tape.

The packed vials and tins were then counted by gamma spectrometry in the ECU biogeochemical environmental radioactive measurement (BERM) facility. The BERM lab contains both a well and coaxial high-resolution, low-background, high-purity germanium detector, coupled with a multi-channel analyzer. The detectors are calibrated regularly against a number of natural matrix standards (IAEA-300, 312, and 314) at different energies of interest, with the exception of ^7Be . Efficiency of ^7Be was calculated by a linear regression of efficiency values for energies beyond 200 keV.

Samples were counted for ~24 hours on either the well or coaxial gamma detector, depending on sample geometry (well for vials and coaxial for tins). Peaks of interest included those for ^7Be at 477 keV and ^{137}Cs at 661 keV (Nie et al., 2001). As ^7Be activity was not expected to exceed 10 cm in depth, the top 10 cm of most of the cores were counted first. Three of the cores (S12, S22, and S23) were counted after ^7Be activity had become negligible, so no ^7Be data was acquired for these cores.

Alpha Spectrometry (Total ^{210}Pb) Sample Preparation and Parameters

An overview of the preparation and counting procedure for total ^{210}Pb by alpha spectrometry is provided here. For a detailed, step-by-step account see Appendix A. For the alpha procedure, a small amount of homogenized sediment (1.0-1.5 g), 15 ml 8M

nitric acid (HNO_3), and 1 ml ^{209}Po tracer spike ($\sim 11.1 \text{ dpm g}^{-1}$) were placed in a Teflon microwave vessel under a fume hood overnight. The mixture was then heated in an ESP 1500 Plus MARS 5 microwave for 50 minutes at 75 psi. The mixture was then cooled and centrifuged three times for 2 minutes at 3000 rpm, with an acid rinse between centrifuges. Following each centrifugation, the fluid was decanted into a 100 ml Teflon beaker. The solution was placed on a hot plate ($\sim 3\text{-}5$ hours) followed by the addition of ammonium hydroxide (NH_4OH) until a pH of 8 was reached to ensure that all of the iron contained within the sample would precipitate. It was assumed that this iron scavenging process would remove any of the ^{210}Po , as well as the ^{209}Po tracer spike, contained within the sample. The mixture was then centrifuged three times for 2 minutes at 3000 rpm, with an acid rinse between centrifuges. The remaining iron was put back into solution by adding 3.75 ml hydrochloric acid (HCl) and bringing the solution volume to 30 ml with deionized water. The solution was then transferred back into the 100 ml Teflon beaker containing a pre-prepared nickel disc inserted into a magnetic stirrer bar. Ascorbic acid was added until the solution became clear. Samples were placed on a stir plate and spun at 250 rpm for 24-40 hours in order to plate the discs with ^{210}Po and the ^{209}Po tracer.

The plated discs were counted on an Ortec EG&G Octete Plus, eight channel alpha spectrometer. Each of the eight sample chambers contains a high-resolution silicon dioxide-passivated, ion implanted detector (Perkin-Elmer, 2001). Efficiency of the instrument was measured every two months by running standards prepared from NIST traceable materials. Blank nickel planchets were run monthly to determine background levels in each vacuum chamber.

Samples were placed in the alpha spectrometer to determine the total ^{209}Po and ^{210}Po activities, with counting times ranging from about 24 to 72 hours. Counting did not cease until one of three criteria were met: 1) sample counts for the ^{210}Po peak at ~ 5300 keV = 1000; 2) the gross area for the ^{210}Po peak was greater than 1000; or 3) the samples were counted for 250,000 seconds. Once the total ^{210}Po was determined, and hence total ^{210}Pb , supported ^{210}Pb was estimated by averaging the activities at depth in each core where the change in ^{210}Pb was negligible. Excess ^{210}Pb was calculated by subtracting supported ^{210}Pb from total ^{210}Pb .

Lead-210 Modeling

A number of different models were used in trying to interpret the excess ^{210}Pb data. Similar to Lewis et al. (2002), the steady state sediment accumulation rate was calculated using the constant flux constant sedimentation model (CF:CS). This was done by applying a least-squares linear regression to the natural log of the ^{210}Pb activity. The slope of the regression divided by the ^{210}Pb decay constant (0.3108 yr^{-1}) gave the steady state accumulation rate in cm yr^{-1} . Similarly, mass accumulation rates ($\text{g cm}^{-2} \text{ yr}^{-1}$) were calculated by a regression of the natural log of excess ^{210}Pb with increasing cumulative sediment mass. For comparison to this “simple model”, the constant initial concentration (CIC) model was also applied to each core. When using the CIC model it is assumed that there is a constant initial unsupported ^{210}Pb activity that is unaltered by changes in the net accumulation rate (Appleby and Oldfield, 1992). Additionally, sediment accumulation rates relative to the depth of the ^{137}Cs peak were calculated whenever possible.

Carbon/Nitrogen Stable Isotope and C:N Ratio Sample Preparation and Analysis

Both estuarine and marsh peat samples were analyzed for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ stable isotopic ratios, organic carbon content, and nitrogen content by the Stable Isotope Laboratory at the University of California at Davis. Prior to sending samples to UC-Davis, the sediments were prepared by the acid fumigation method described in Harris et al. (2001). This procedure was necessary to remove any inorganic carbon that might otherwise lead to erroneous $\delta^{13}\text{C}$ values. This method involves an initial calculation of total carbon content in each sample, to ensure that the amount of carbon in the sample was within the acceptable working range for their instrument (800-1200 $\mu\text{g C}$). To obtain the correct sample weight for the procedure, it was assumed that total carbon content equaled 40% of the loss on ignition (Harris et al., 2001). Sample weights required varied from approximately 0.184 to 0.002 grams for marsh peat samples and 0.232 to 0.015 grams for estuarine samples. The necessary amount of sample was carefully weighed into 8 X 5 mm silver capsules, with the capsules then placed in a 96 well microtitre plate. The samples were wetted with 50 μl of deionized (DI) water. The microtitre plate was then placed in a 5-liter desiccator along with a 150 ml beaker containing 100 ml of 12.1 M HCl for 6 hours. After the fumigation process was complete, the capsules were oven dried at 60°C until the sediments were dry. The capsules were then placed in a crimper plate, closed, and shipped to UC-Davis for analysis. The samples were analyzed on a Europa Hydra 20/20 continuous flow mass spectrometer following combustion at 1000°C in a Europa ANCA-GSL CN analyzer (Harris et al., 2001). Standard gases injected into the mass spectrometer before and after sample peaks allowed $\delta^{13}\text{C}$ (expressed relative to

Vienna-Pee Dee Belemnite) and $\delta^{15}\text{N}$ (expressed relative to atmospheric N_2) values to be calculated.

Metal Abundance Analysis

Sample Preparation

Sediment samples and sediment standard reference materials (SRM) were completely digested prior to analysis on an atomic absorption spectrometer (AAS). The particular SRMs that were used as a comparison for sample metal abundances, were estuarine sediment standards (1646 and 1646a). The microwave assisted acid digestion techniques used were based on a modification of the method used by Balls et al. (1997). An overview of the procedure is provided here, for a step-by-step account see Appendix B. Approximately 0.5 grams of sediment (± 0.05 g), along with 7.5 ml of concentrated, trace metal grade HNO_3 (15.8 M) were placed in a Teflon microwave vessel under a fume hood overnight. The mixture was then heated in an ESP 1500 Plus MARS 5 microwave for 10 minutes at 180°C , following a 14-minute ramp to temperature at maximum power (1200 W). The samples were cooled, and 3 ml of concentrated, trace metal grade 50% hydrofluoric acid (HF) was added to facilitate the breakdown of silicates. The samples were microwaved again, holding at 180°C for 30 minutes following a 14-minute ramp to temperature at maximum power. Upon cooling, 20 ml of 0.65 M boric acid (H_3BO_3) was added to each of the samples to aid in complexing the HF.

The digested sediments, now in solution, were transferred into acid-washed centrifuge tubes. Deionized water was then used to rinse the vessels, bringing the volume in the centrifuge tubes to 40 ml. Samples were centrifuged for 3.5 minutes at 3000 rpm to separate out any particulates. The fluid was decanted into a 50 ml volumetric flask and 5.1 ml of concentrated, trace metal grade NH_4OH (20%) was added. The addition of the strong base was to reduce the acid percent of the solution to within acid-tolerance levels of the AAS ($< 5\%$ by volume). DI water was added to bring the solutions in each of the volumetric flasks to 50 ml. The flasks were shaken vigorously, and their contents placed into pre-labeled, acid-rinsed, 50 ml centrifuge tubes for storage until AAS analysis could be performed.

Dilution for Iron and Aluminum Determination

Due to the high concentrations of iron and aluminum in the samples and sediment standards, an additional 16:1 dilution was required to get their concentrations within the working range of the AAS. To obtain this dilution factor, 3.125 ml of the original digested 50 ml sample were removed and added to a 50 ml volumetric flask. Aluminum tends to ionize at high temperatures; however, this ionization is suppressed in the presence of 1000-2000 ppm K. Therefore, 5 ml of a 20000 ppm potassium chloride (KCl) solution was added to each flask. The volume of the solution was brought to 50 ml with DI water.

Atomic Absorption Spectrometer Parameters and Sample Analysis

Digested sediment samples and standards were analyzed for Zn, Cu, Fe, and Al by AA spectrometry on an Instrumentation Laboratory IL-457 atomic absorption

spectrometer. The AA spectrometer works by passing a beam of light from a source lamp to a detector through a flame. The source lamp emits a light of a wavelength characteristic of a particular metal. When a sample is aspirated into the flame it atomizes, and a portion of the light will be absorbed. The amount of energy absorbed at this characteristic wavelength is proportional to the concentration of the metal in the sample (Instrumentation Laboratory Inc., 1981). A summary of the instrumental parameters and analytical capabilities of the instrument are provided in Table 3.

Table 3: IL-457 AAS settings and analytical capabilities (after Sotera and Stux, 1979)

Element	Instrument Settings/Parameters				Analytical Capabilities	
	Wavelength (nm)	Bandpass (nm)	Lamp Current mA	Flame Type	Working Range (ppm)	Sensitivity (ppm)
Zn	213.9	1.0	3	air-acetylene	< 1	0.008
Cu	325.0	1.0	5	air-acetylene	< 4	0.03
Al	309.3	1.0	8	N ₂ O-acetylene	< 60	0.4
Fe	248.3	0.3	8	N ₂ O-acetylene	< 5	5

Prior to sample analysis, the quality of the readings from the AAS was assessed by aspirating a series of five or more elemental standards made from 1000 ppm reference solutions. If the coefficient of variation (r^2) value of the absorbance values plotted against concentration of the standards was 0.95 or higher, then analysis could proceed. The protocol for sample analysis was the same, regardless of element. First, one of the two estuarine sediment standards (Table 4) was aspirated. Next, ten or fewer samples were analyzed, followed by the estuarine standard. This pattern continued until all of the

samples for a particular site were complete. Typically two runs following this protocol were done for each site, with an aspiration of the elemental standards for quality control between each run. Values obtained for sample absorbance were referenced to the estuarine standard, with corrections being made for instrument drift, mass discrepancies, and percent recovery. The results for both runs were then averaged. Combined errors were calculated from metal errors of the standard reference materials (SRM) and instrumental errors, which associate an error of 1% of the concentration of the sample or standard (Sotera and Stux, 1979).

Table 4: Estuarine sediment standard reference material mass fractions and associated errors for Zn, Cu, Fe, and Al.

Estuarine Sediment Standard Name	Mass Fraction in ppm				Mass Fraction in %			
	<i>Zn</i>	(+/-)	<i>Cu</i>	(+/-)	<i>Fe</i>	(+/-)	<i>Al</i>	(+/-)
1646	138.0	6.0	18.00	3.00	3.350	0.100	6.250	0.200
1646a	48.9	1.6	10.01	0.34	2.008	0.039	2.297	0.018

RESULTS

Field Data

A total of fifteen cores were collected from Pamlico Sound and the mouths of the Neuse and Pamlico River estuaries for this study. Core lengths ranged from 22 to 54 cm with an average of 32 cm. Surface water salinities ranged from 22 to 30, averaging 25 in Pamlico Sound. Surface water salinity values were much lower at the sites located at the mouths of the Neuse and Pamlico River estuaries, 7 and 9, respectively. Water depths at the sites ranged from 1.5 m to 6.7 m and averaged 5 m. Table 5 summarizes the field data observations that were collected prior to core extraction at each site.

Table 5: Field data collected from Pamlico Sound study sites (see Figure 8 for site locations).

Site	Latitude	Longitude	Surface Salinity	Water Depth (m)	Core Length (cm)	Date Collected
S9	35.497	75.651	25	5.5	36	8/1/2002
S10	35.572	75.866	24	2.3	30	8/2/2002
S11	35.601	75.877	22	1.5	26	8/2/2002
S12	35.515	75.914	22	3.7	32	8/2/2002
S22	35.459	75.838	25	6.1	34	8/6/2002
S23	35.536	75.750	25	5.2	26	8/6/2002
S24	35.398	75.760	25	6.7	30	8/6/2002
S27	35.287	75.624	27	4.3	26	8/6/2002
S30	35.401	76.031	27	3.1	22	8/10/2002
S31	35.346	75.944	26	6.1	54	8/10/2002
S32	35.295	75.876	30	6.7	28	8/10/2002
S41	35.221	76.157	22	5.8	28	8/11/2002
S42	35.292	75.999	24	6.1	32	8/11/2002
S50	35.298	76.423	7	5.5	50	7/31/2003
S55	35.065	76.527	9	6.1	30	8/1/2003

Grain-Size and Organic Carbon Data

Surficial Grain-Size and Organic Carbon Distributions

Pamlico Sound sediments vary in grain-size distribution, median grain-size, and organic carbon content spatially and with depth. Surface sediment median grain-size has the lowest values in areas where the water depth is greatest or in shallower areas where irregularities in the mainland shoreline offer protection (Figure 9). Surface sediment median grain-size generally decreases from the estuary margins into the deep central basin. The highest observed surficial median grain-size was 196 μm at S12, while the lowest was 7 μm at S55.

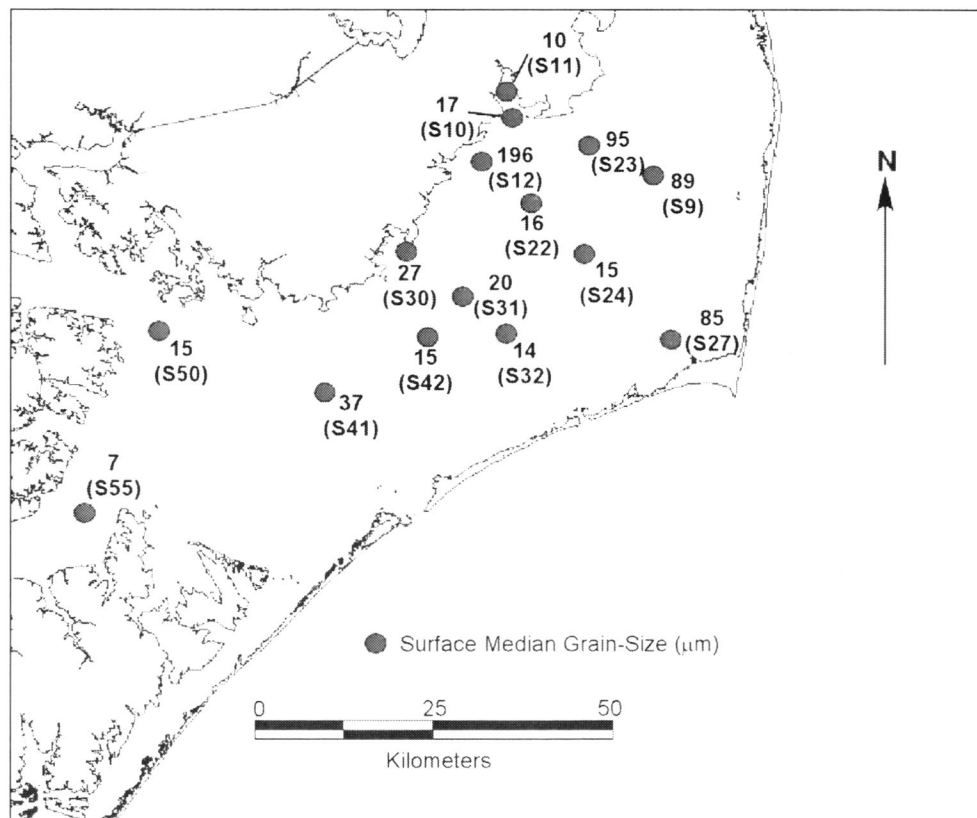


Figure 9: Median grain-size (in μm) distribution for Pamlico Sound surface sediments.

Surface organic carbon (OC) content shows a spatial distribution somewhat similar to surface median grain-size (Figure 10). The percentage of organic carbon tends to be the greatest wherever the median grain-size is the least. Thus, cores located in the deep central basin, at the Pamlico and Neuse River estuary mouths, and within protected embayments showed the greatest amount of organic carbon. Cores taken from shallower or more exposed sites tend to have the least amount of organic carbon. Surficial organic carbon content ranged from 0.51% (S12) to 3.52% (S50), the sites with the highest and lowest median grain-size, respectively.

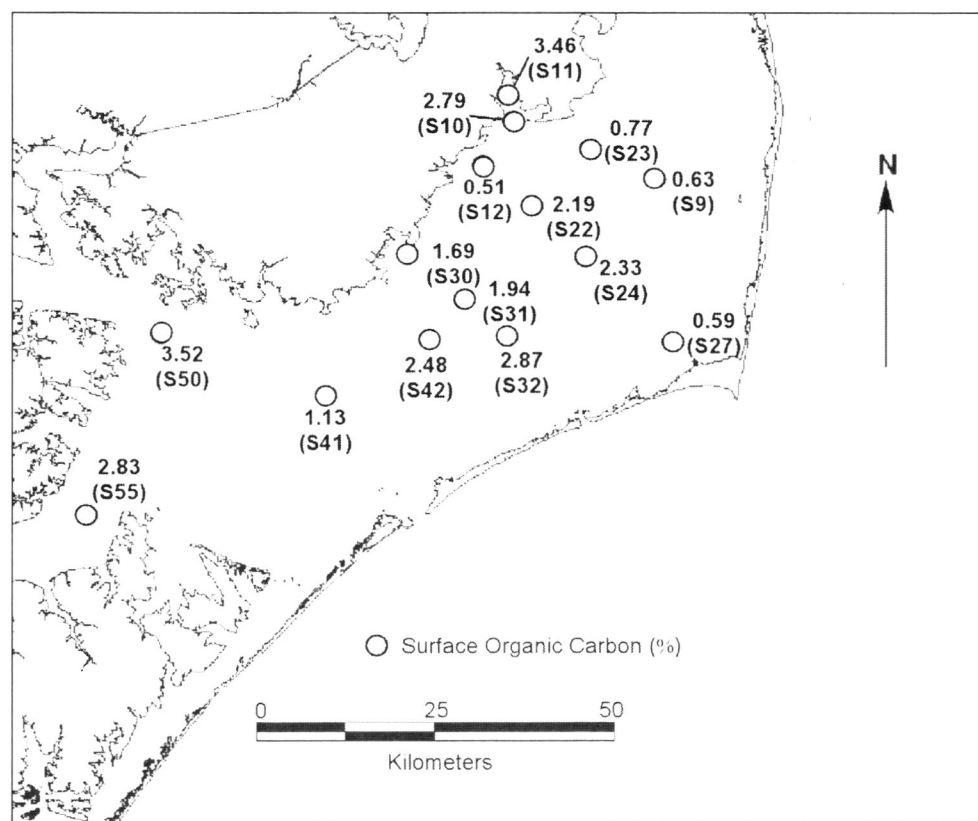


Figure 10: Organic carbon content (in %) distribution for Pamlico Sound surface sediments.

Downcore Grain-Size and Organic Carbon Distributions

In order to better compare observed grain-size trends between Pamlico Sound cores, it was useful to group the cores into different categories. The categories were based upon proximity to shoreline, water depth, and similarities in profiles of median-grain size, grain-size distribution, and organic carbon vs. depth in the cores. The categories include: 1) protected embayment; 2) perimeter platform (OC-rich); 3) perimeter platform (OC-poor); 4) central basin; and 5) estuary mouth (Figure 11). These environments were partially based upon Katuna (1974), who used a similar terminology in describing sedimentary structures in cores taken from various parts of Pamlico Sound.

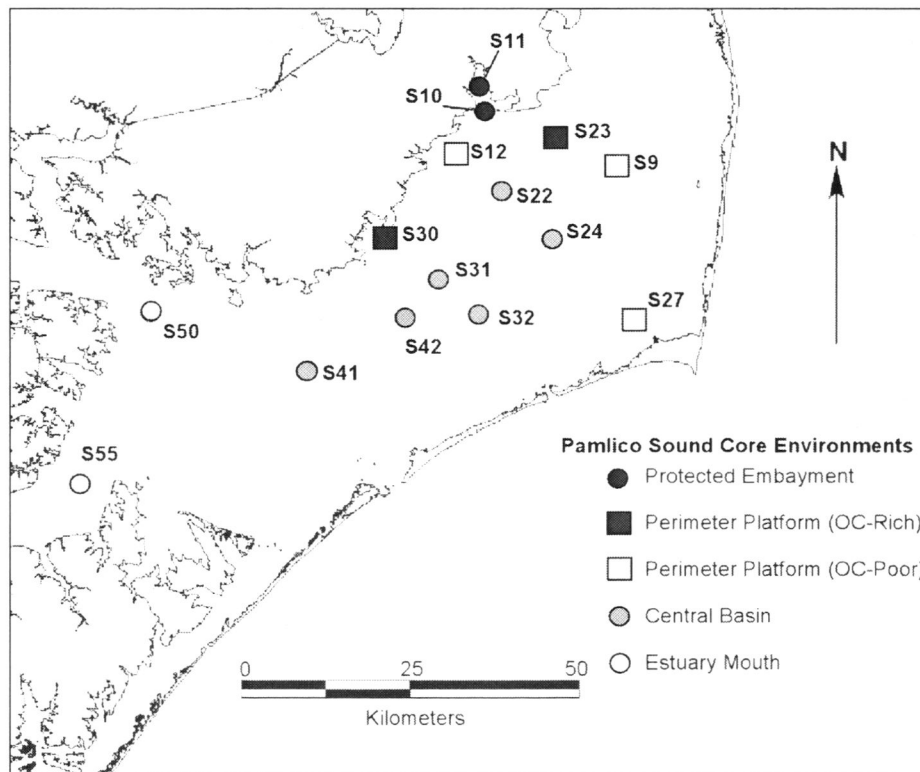


Figure 11: Map depicting environments within Pamlico Sound from which cores were collected.

Protected Embayment

Cores from S10 and S11 were collected from Long Shoal River, a shallow embayment (~1.5 m depth) located on the northwestern margin of Pamlico Sound (Figure 11). These sediments are characterized by an abundance of clayey silt in the upper regions of the cores, grading into a silty sand at depth (Figure 12). With the exception of a lens of sandier material at 3 cm depth, S11 contains an overall greater amount of finer material and a lower median grain-size, particularly at depth. Percent organic carbon is the greatest at the surface and decreases with depth to a value of about 1% at 5 cm in S11 and around 0.7% at 13 cm in S10. S11 shows a more rapid decline, and greater variation, with depth in percent organic carbon than S10.

Perimeter Platform (OC-Rich)

The cores that have been included in the organic carbon-rich perimeter platform category are those from S23 and S30 (Figure 13). These cores were grouped together due to their similar alternating pattern of finer and coarser material with depth and overall abundance of OC relative to other perimeter platform cores. Although this alternating pattern occurs at similar depths for each core, the sediments are generally much coarser in S23 (silty sand) than in S30 (sandy silt). Median grain-size shows the same alternating pattern with depth reflected in the grain-size distribution; however, S23 shows a general decrease in median grain-size with depth, whereas S30 generally maintains the same value (Figure 13). Percent organic carbon tends to follow a similar trend as median grain-size, with the higher organic carbon values occurring at the same depths as the lower median grain-size values. In both cores, a relatively similar pattern in organic

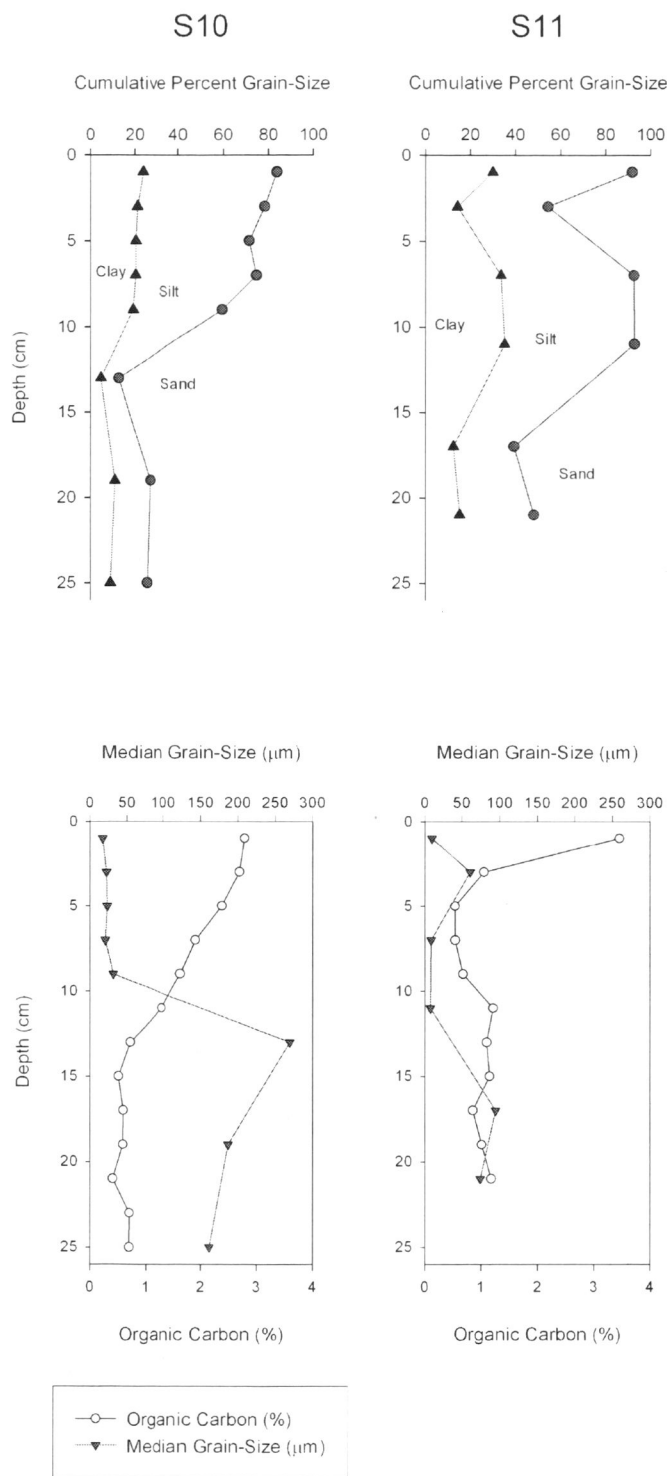


Figure 12: Upper graphs show grain-size distribution (cumulative %) for sites 10 and 11; lower graphs are of organic carbon (%) and median grain-size (μm) vs. depth for sites 10 and 11.

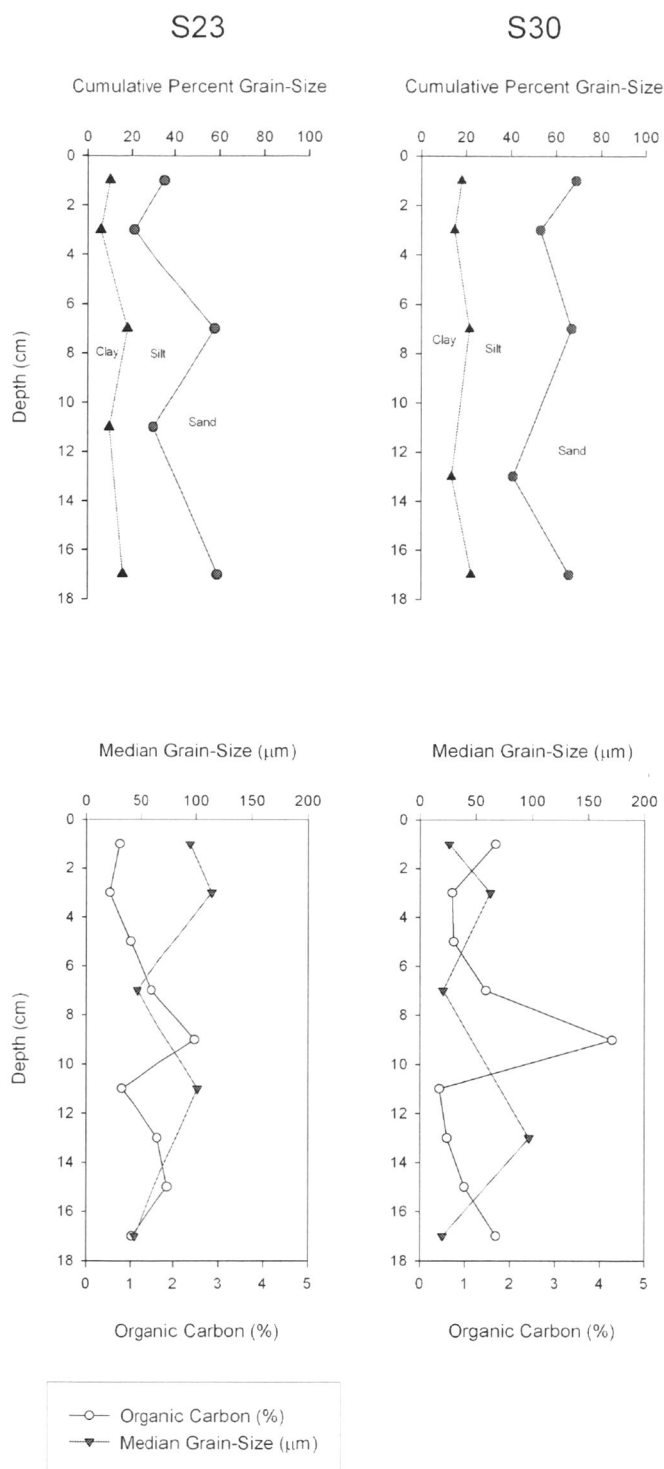


Figure 13: Upper graphs show grain-size distribution (cumulative %) for sites 23 and 30; lower graphs are of organic carbon (%) and median grain-size (μm) vs. depth for sites 33 and 30.

carbon content is observed, with a distinct peak at about 9 cm. Beneath this peak there is a general increase in percent organic carbon with depth.

Perimeter Platform (OC-Poor)

Cores collected from S9, S12, and S27 have been grouped into the organic carbon-poor perimeter platform category (Figure 14). These cores are typified by an abundance of sand over silt and clay. S9 and S12 have similar grain-size distribution profiles, with a small amount of mud at the surface and a muddy lens that occurs at about 20 cm. Of the three cores, S27 contains the largest portion of fine material and is characterized by silty sand, with the percentage of sand generally increasing at depth. Median grain-size tends to decrease in S9 and S12 until about 20 cm, and then it increases slightly toward the bottom of the cores. Median grain-size in S27 increases somewhat with depth. Each of these cores is relatively low in organic carbon content; however, organic carbon values are generally highest in the middle portions of the cores. Variations in median grain-size and organic carbon tend to correlate well, with the highest organic carbon values at intervals with the lowest median grain-size.

Central Basin

The central basin cores consist of S22, S24, S31 (Figure 15), S32, S41, and S42 (Figure 16). These cores are characterized by an abundance of silt (~50 to 60%), significant amounts of clay (~25%), and relatively little sand (generally <20% except for S41). S41, located just west of Bluff Shoal in the southern part of the sound, shows the highest percentage of sand (~25%) of any of the basin cores while S31 has the least

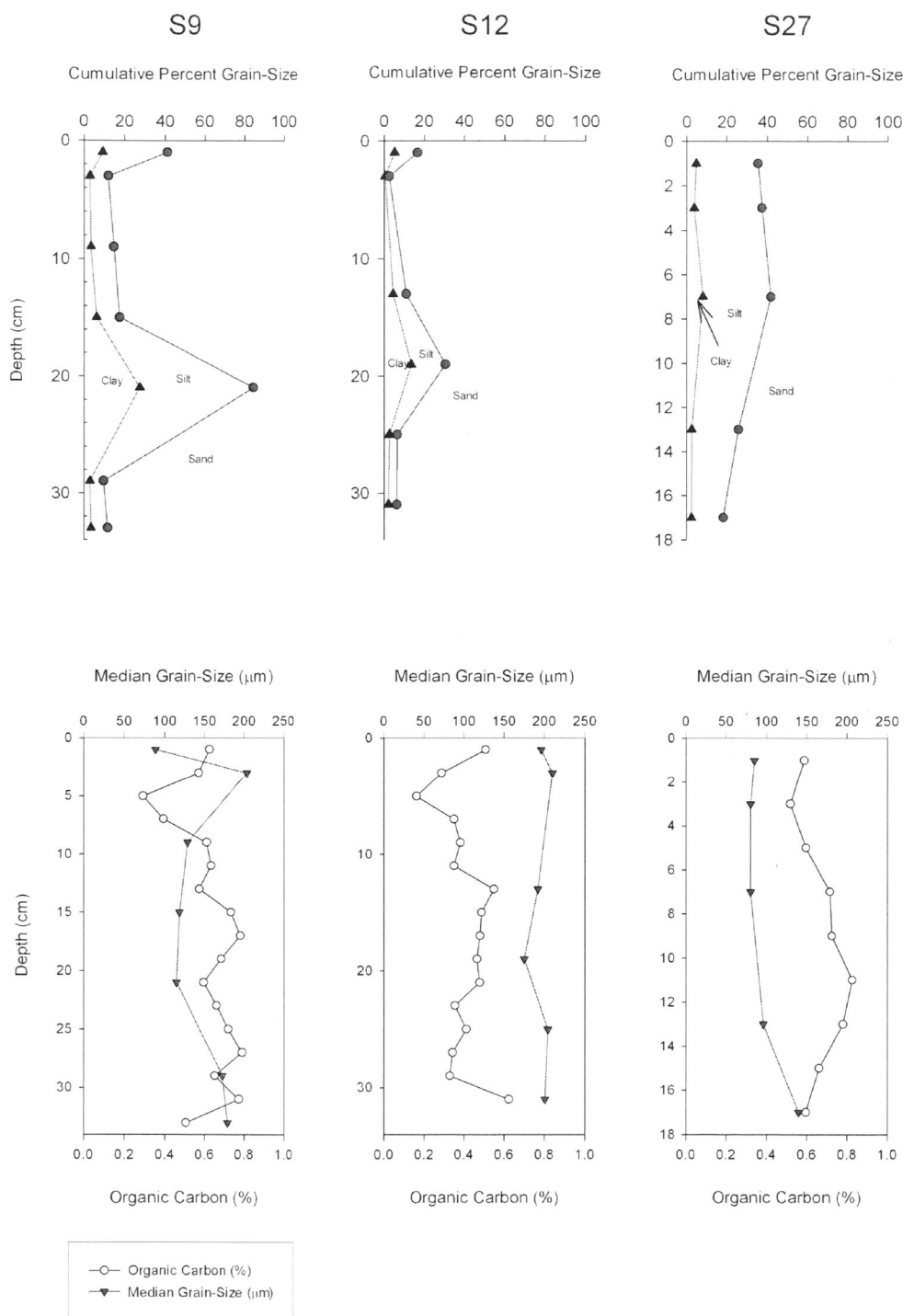


Figure 14: Upper graphs show grain-size distribution (cumulative %) for sites 9, 12, and 27; lower graphs are of organic carbon (%) and median grain-size (μm) vs. depth for sites 9, 12, and 27. *note the difference in scale for depth.

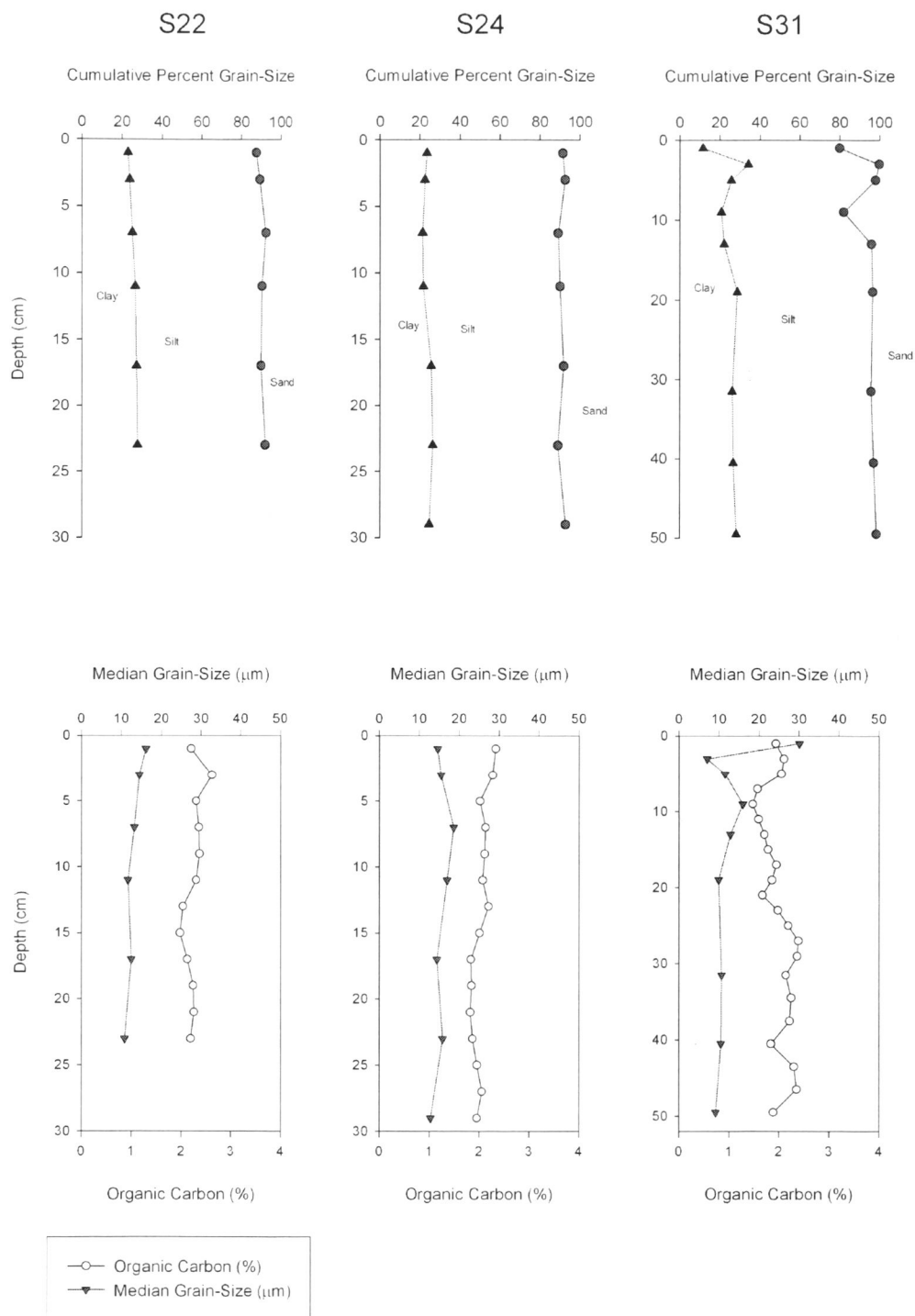


Figure 15: Upper graphs show grain-size distribution (cumulative %) for sites 22, 24, and 31; lower graphs are of organic carbon (%) and median grain-size (μm) vs. depth for sites 22, 24, and 31. *note the difference in scale for depth.

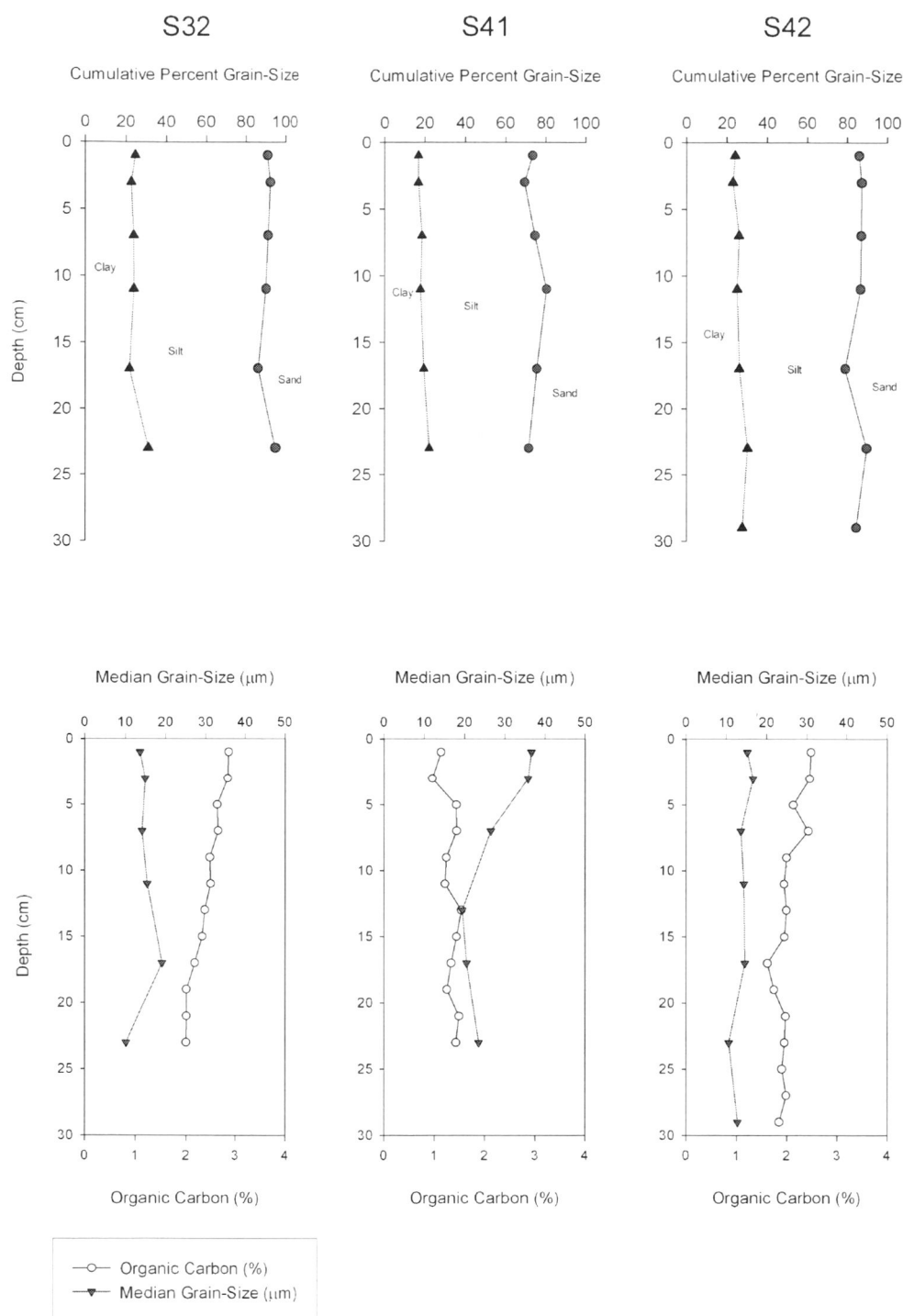


Figure 16: Upper graphs show grain-size distribution (cumulative %) for sites 32, 41, and 42; lower graphs are of organic carbon (%) and median grain-size (μm) vs. depth for sites 32, 41, and 42.

(<10%, excluding minor variations). Relative percentages of each component tend to remain fairly constant with depth in each core, with the only exception being at S31, which shows some additional sandy material near the surface and in a lens at about 9 cm depth. Median grain-size values range from ~40 μm (S41) to ~8 μm (S31) and generally decrease with depth. The organic carbon content of the sediments remains fairly constant with depth for about half of the cores; however, organic carbon in S41 tends to increase with depth, while S32 and S42 show a slight decrease with depth. Organic carbon content is approximately 2% for all cores excluding S41 (OC ~1.5%). There is slightly greater variation in the percent organic carbon than median grain-size with depth, particularly at S31.

Estuary Mouth

The estuary mouth cores include S50 collected at the mouth of the Pamlico River, and S55 collected at the mouth of the Neuse River (Figure 9). Similar to the central basin cores, these cores consist predominately of silt with varying amounts of sand and clay (Figure 17). S50 is almost devoid of sand, while S55 has a lens of sand at depth, changing from clayey silt to silty sand at about 13 cm. Median grain-size is generally lower for S55 than S50, excluding the sandy layer. Percent organic carbon decreases for both cores, although there is a slight increase in value at depth in S55. There appears to be little correlation with median grain-size and percent organic carbon in either core.

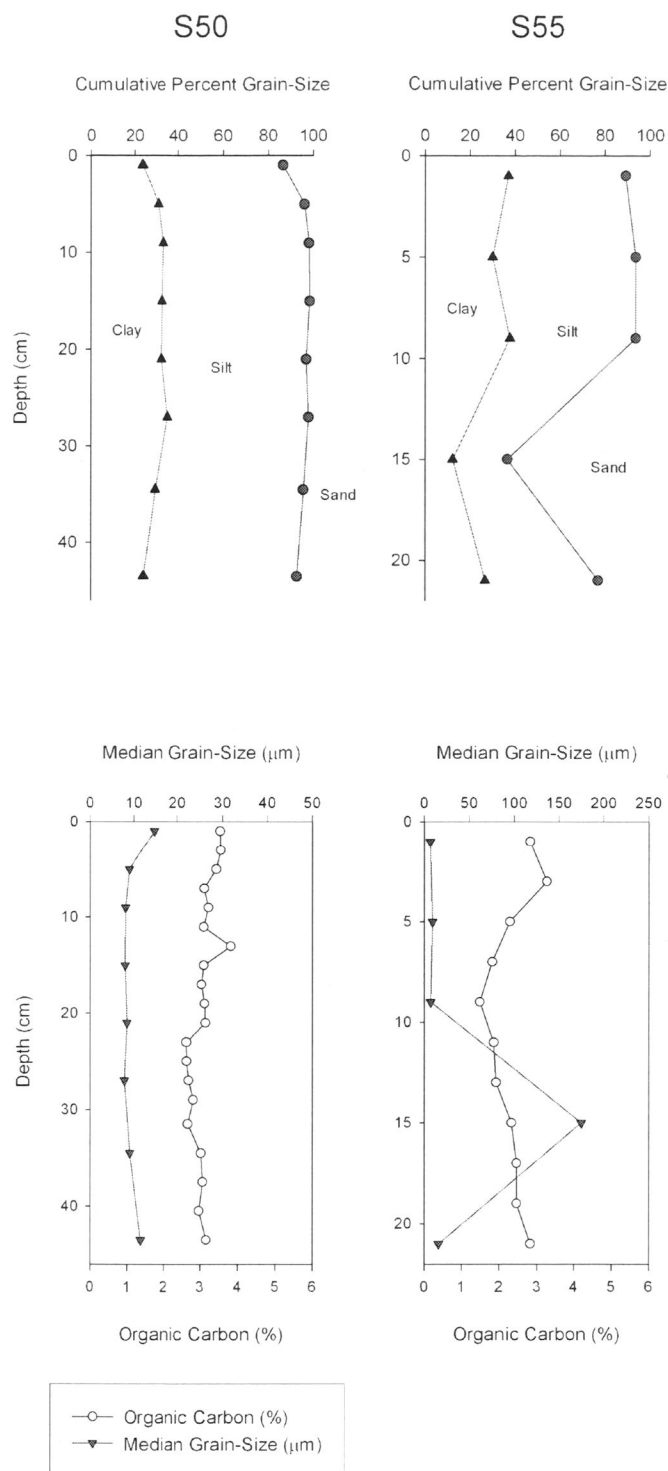


Figure 17: Upper graphs show grain-size distribution (cumulative %) for sites 50 and 55; lower graphs are of organic carbon (%) and median grain-size (μm) vs. depth for sites 50 and 55. *note the difference in scale for depth.

Radionuclide Data

Fifteen Pamlico Sound estuarine cores and one marsh peat core from North Bluff Point were analyzed for radionuclide activities in order to determine sediment accumulation rates with ^{210}Pb and ^{137}Cs and the extent of sediment reworking with ^7Be . Again, cores have been grouped by the same environments for comparative purposes. This portion of the results section discusses the shapes of the radionuclide profiles and presents modeling data for accumulation rates and depth of mixing. For a complete summary of all radionuclide data see Appendix C.

Downcore Radionuclide Profiles

Protected Embayment

Both S10 and S11 cores show similar excess ^{210}Pb activities at the surface ($\sim 8 \text{ dpm g}^{-1}$) and have no measurable excess ^{210}Pb at similar depths ($\sim 15 \text{ cm}$); however, the shapes of their profiles are somewhat different (Figure 18). The decrease in activity at S10 is fairly linear, while at S11 it is more logarithmic. The greatest ^{137}Cs activities occur at or near the surface, making the ^{137}Cs peak poorly-defined at S10 and undefined at S11. ^{137}Cs activity extends either to, or beyond the point in the cores where there is no excess ^{210}Pb activity. Significant ^7Be activity is only found in the top 2 cm at S10 and S11.

Perimeter Platform (OC-Rich)

S23 and S30 cores have significantly different surface excess ^{210}Pb activities ($\sim 2 \text{ dpm g}^{-1}$ at S23 and $\sim 4 \text{ dpm g}^{-1}$ at S30) and profile shapes (Figure 19). S23 shows excess ^{210}Pb activity to a slightly greater depth than S30, despite having a lower activity overall.

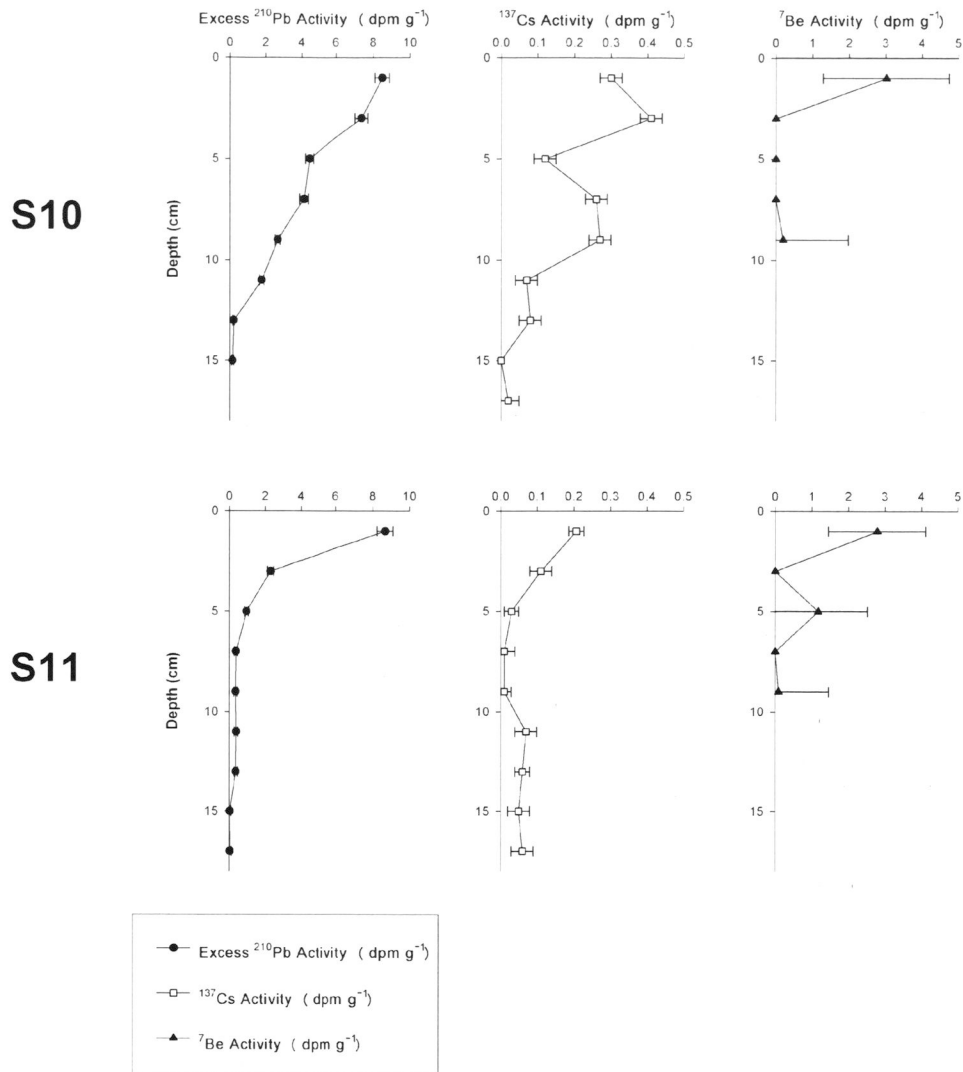


Figure 18: Profiles of excess ^{210}Pb , ^{137}Cs , and ^7Be activities (in dpm g^{-1}) vs. depth for protected embayment cores (S10 and S11).

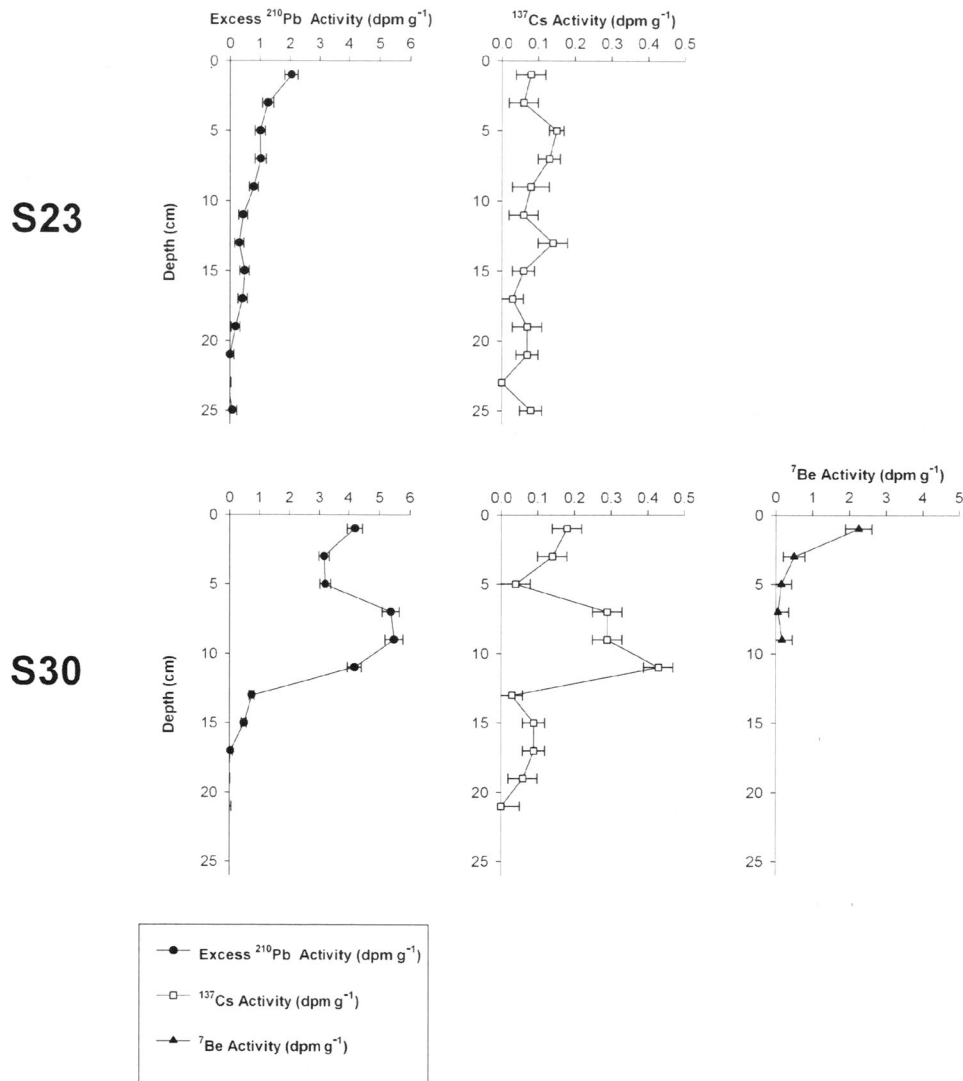


Figure 19: Profiles of excess ²¹⁰Pb, ¹³⁷Cs, and ⁷Be activities (in dpm g⁻¹) vs. depth for organic carbon-rich perimeter platform cores (S23 and S30).

The excess ^{210}Pb profile for S23 contains some minor inflections, but activities decrease rather linearly. The excess ^{210}Pb profile for S30 is much more complex, showing the highest activities ($\sim 6 \text{ dpm g}^{-1}$) in the middle of the core between 7 and 11 cm. As with excess ^{210}Pb , ^{137}Cs activities and profiles bear little resemblance to each other; S23 has very low ^{137}Cs activities (generally $< 0.1 \text{ dpm g}^{-1}$) and no clearly defined ^{137}Cs peak, while S30 has higher activities (generally $> 0.1 \text{ dpm g}^{-1}$) and a well-defined ^{137}Cs peak at 11 cm. ^{137}Cs activity extends either to, or beyond the point in the cores where there is no excess ^{210}Pb activity. At S30, ^7Be activity decreases to nearly zero by 6 cm.

Perimeter Platform (OC-Poor)

Excess ^{210}Pb activity at the surface is relatively low for each of the cores, varying from $\sim 3 \text{ dpm g}^{-1}$ at S9 to $\sim 1 \text{ dpm g}^{-1}$ at S27 with S12 falling in between at $\sim 2 \text{ dpm g}^{-1}$. The maximum depth of excess ^{210}Pb activity follows a pattern similar to relative activities, with S9 having activities to the greatest depth ($\sim 25 \text{ cm}$), followed by S12 ($\sim 19 \text{ cm}$) and S27 ($\sim 17 \text{ cm}$). Excess ^{210}Pb profiles are fairly similar for S12 and S27, exhibiting almost linear decreases in activity with depth and only minor inflections (Figure 20). Conversely, S9 shows a much higher excess ^{210}Pb activity in the upper 5 cm of the core compared to the remainder of the core. Cesium-137 data show similar overall activities for each core ($\sim 0.1 \text{ dpm g}^{-1}$); however, only at S9 is there a well-preserved ^{137}Cs peak (9 cm). In each case there is ^{137}Cs activity at the same or greater depths than which there is no excess ^{210}Pb activity. Both S9 and S23 show only negligible ^7Be activities with fairly large counting errors.

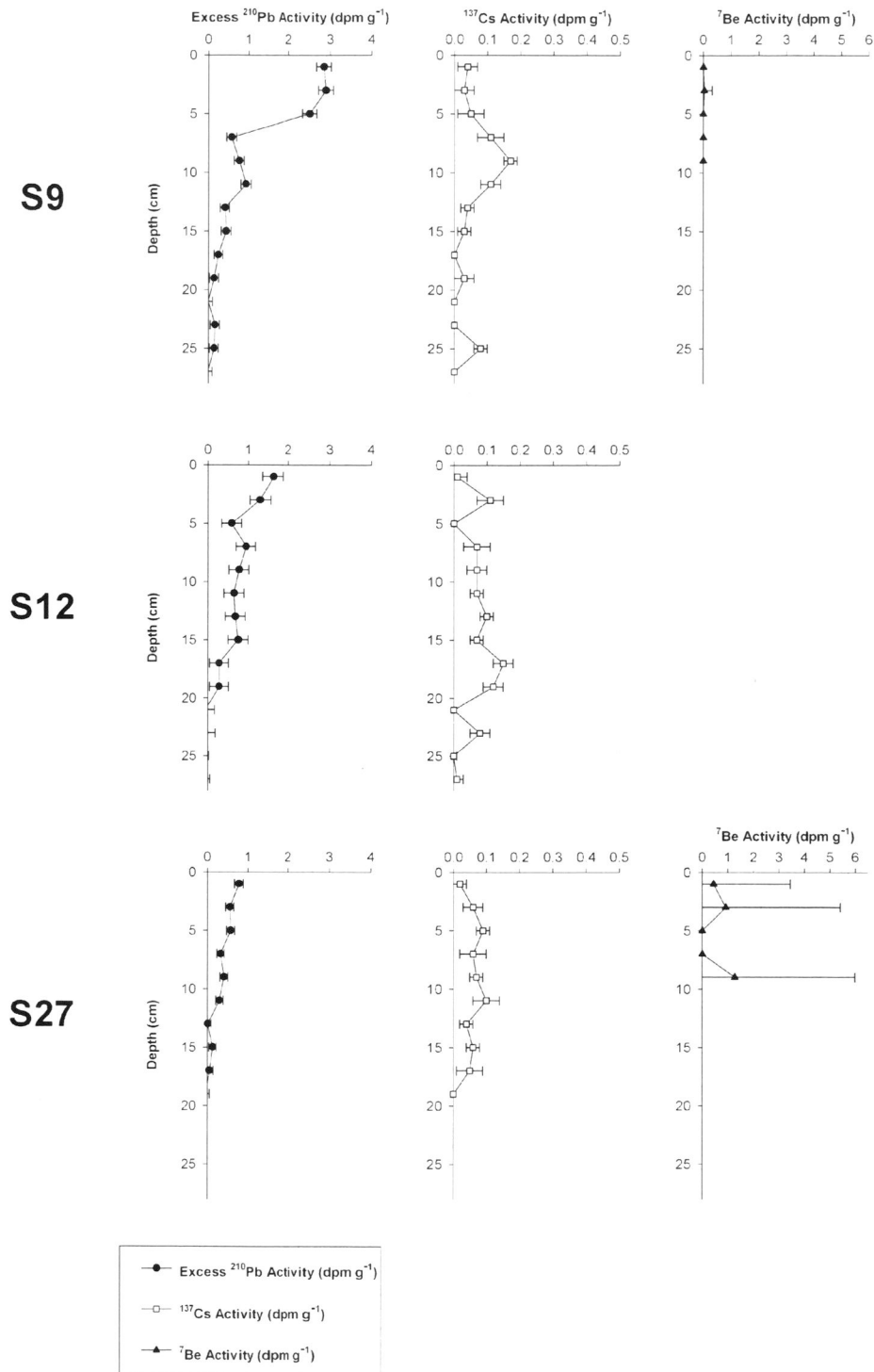


Figure 20: Profiles of excess ^{210}Pb , ^{137}Cs , and ^7Be activities (in dpm g^{-1}) vs. depth for organic carbon-poor perimeter platform cores (S9, S12, and S30).

Central Basin

These cores show a range of surface excess ^{210}Pb activities ($\sim 6 \text{ dpm g}^{-1}$ at S22 to $\sim 10 \text{ dpm g}^{-1}$ at S32), which are generally higher in the southerly cores. The upper 8-10 cm of the central basin profiles (excluding S24 and S31) are nearly vertical, often showing an alternating pattern of higher and lower excess ^{210}Pb activities (Figures 21 and 22). At S24 excess ^{210}Pb activity decreases linearly with depth and exhibits no irregularities or inflections in profile. The maximum depth of excess ^{210}Pb activity varies greatly within the central basin cores, ranging from $\sim 23 \text{ cm}$ at S41 to $\sim 52 \text{ cm}$ at S31. The depth of zero excess ^{210}Pb activity is unknown for S32, as the core did not penetrate to a sufficient depth to observe this horizon. Cesium-137 overall activities are fairly similar for the cores, ranging from about 0.2 to 0.4 dpm g^{-1} on average. Well-defined ^{137}Cs peaks exist for S31, S32, and S41; however, the peak is poorly-preserved for S22 and S42 and is essentially nonexistent for S24. In each case (excluding S32), the depth of ^{137}Cs activity equals or exceeds the maximum depth of excess ^{210}Pb activity. Depths of significant ^7Be activity in the central basin range from 2 to 4 cm.

Estuary Mouth

Excess ^{210}Pb activities are fairly similar at the surface of cores taken from S50 and S55; however, the excess ^{210}Pb profiles for these two cores bear little resemblance to one another (Figure 23). The profile for S50 resembles many of the central basin cores discussed previously, showing an alternating pattern of higher and lower excess ^{210}Pb activities in the upper 10 cm, with activity decreasing more regularly with depth. The excess ^{210}Pb profile from S55 is quite different from all other profiles. It is characterized

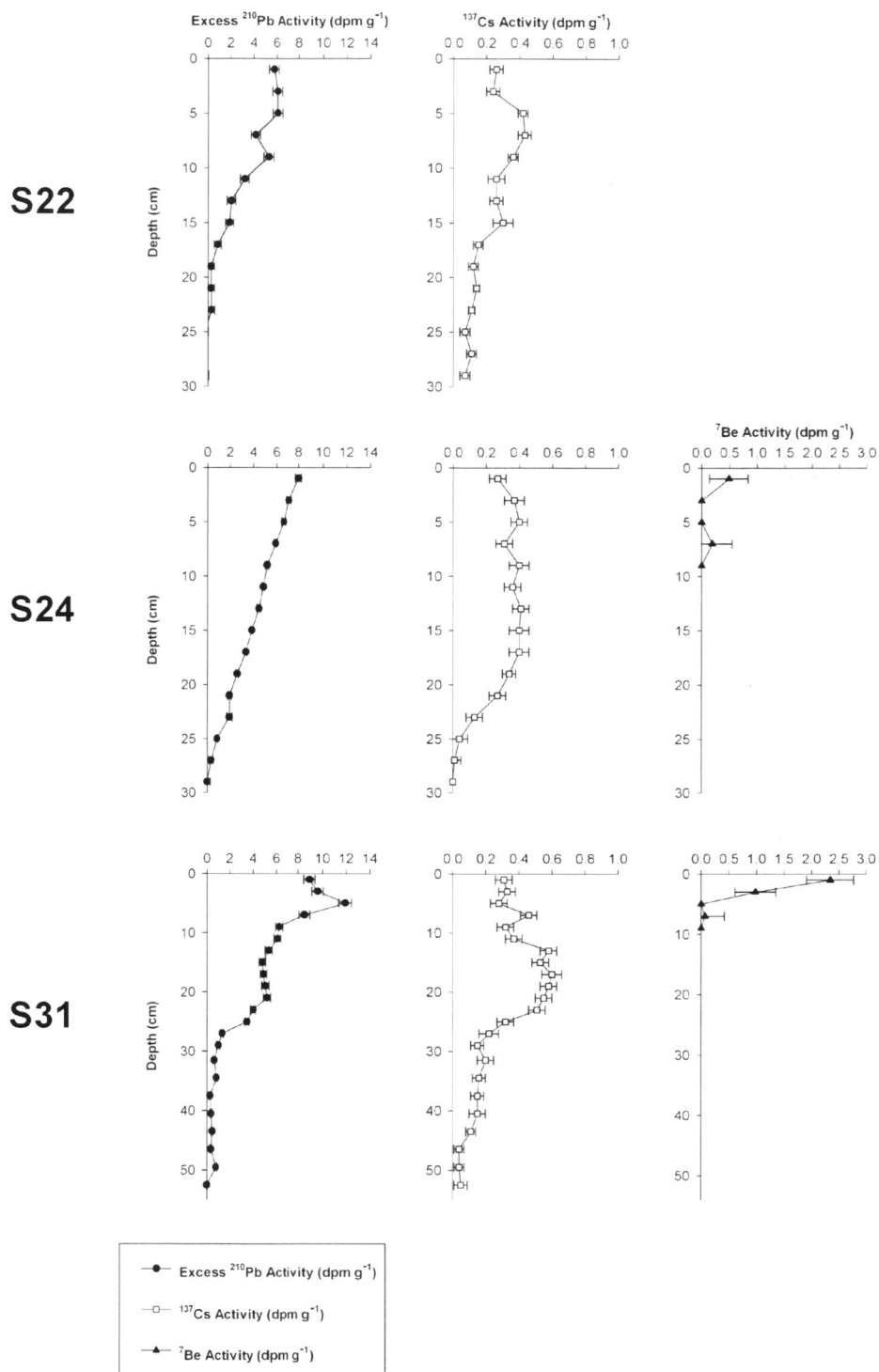
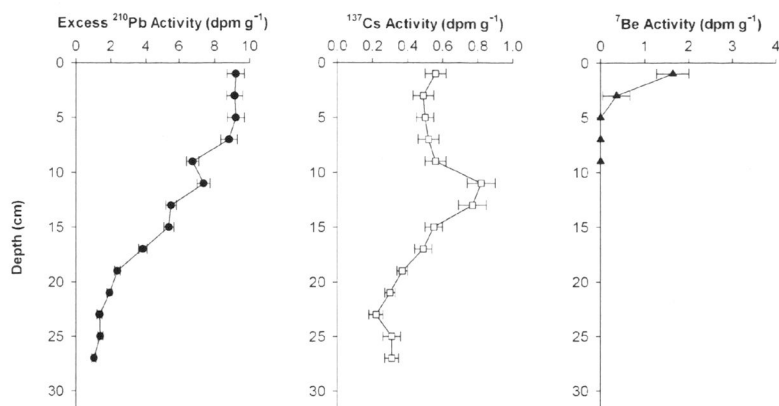
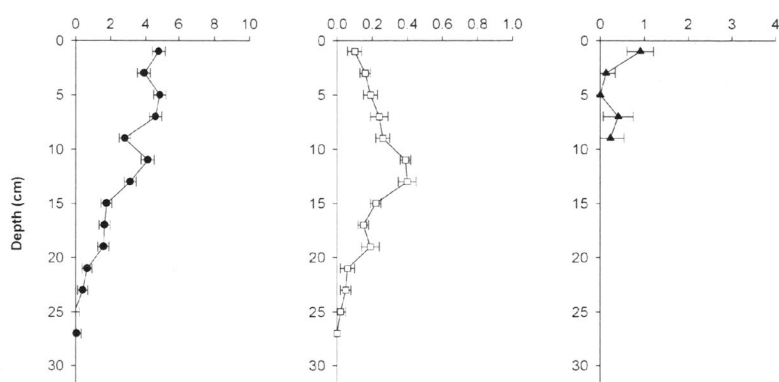


Figure 21: Profiles of excess ^{210}Pb , ^{137}Cs , and ^7Be activities (in dpm g^{-1}) vs. depth for central basin cores (S22, S24, and S31) *note the difference in depth scale for S31.

S32



S41



S42

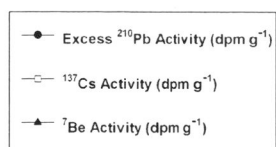
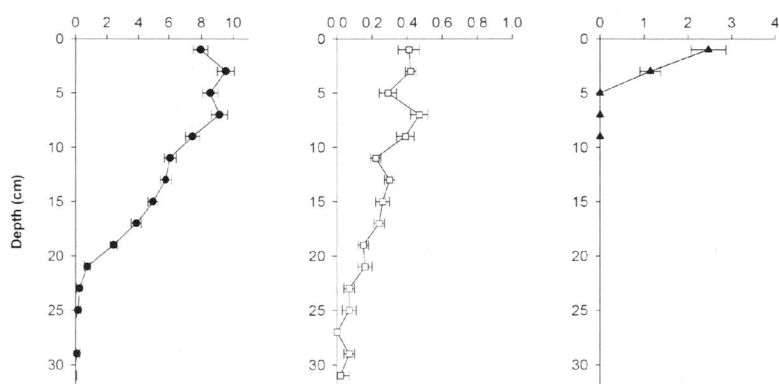


Figure 22: Profiles of excess ²¹⁰Pb, ¹³⁷Cs, and ⁷Be activities (in dpm g⁻¹) vs. depth for central basin cores (S32, S41, and S42).

by a rapid decrease in activity to zero at about 5 cm and remaining excess ^{210}Pb dead until about 17 cm where there is some slight activity that is generally within error. The ^{137}Cs profiles are also quite dissimilar, with a well-preserved peak at S50 (~17 cm) and no peak preservation at S55. S55 shows the highest ^{137}Cs activity at the surface. At S50 ^{137}Cs activity extends to the maximum depth of excess ^{210}Pb activity. The ^7Be profile for S55 displays activity only at the surface, while activity reaches ~4 cm at S50.

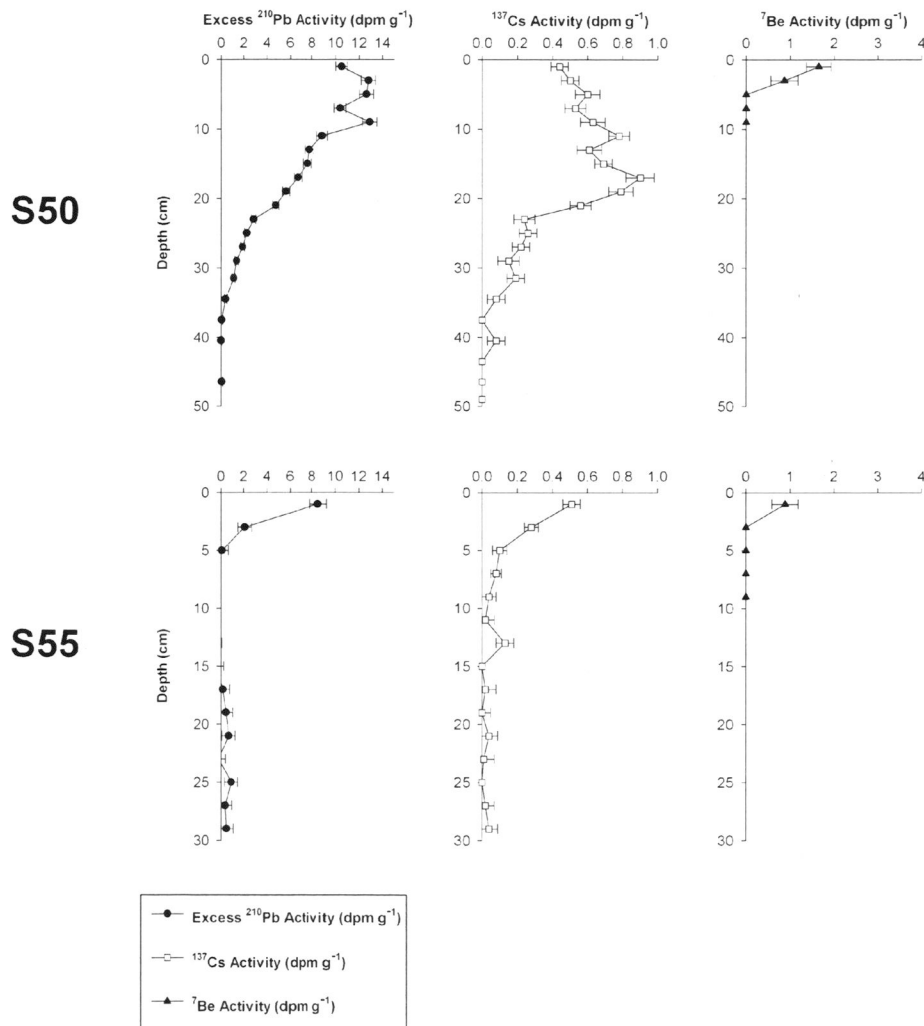


Figure 23: Profiles of excess ^{210}Pb , ^{137}Cs , and ^7Be activities (in dpm g^{-1}) vs. depth for estuary mouth cores (S50 and S55) *note the difference in depth scale for the profiles.

North Bluff Point

The excess ^{210}Pb profile for the marsh core at North Bluff Point displays three zones where the profile shape is fundamentally different (Figure 24). In the lower zone, extending from the maximum depth of excess ^{210}Pb activity (~ 37 cm) to about 25 cm, the excess ^{210}Pb profile increases regularly. The middle zone, extending from 25 cm to the position of the ^{137}Cs peak at 10 cm, is characterized by a nearly vertical profile. From the ^{137}Cs peak to the surface of the marsh excess ^{210}Pb activities generally decrease. The ^{137}Cs profile exhibits a well-preserved peak at about 10 cm, above which the activity decreases rapidly; however, below the peak, activities are significant and extend below the maximum depth of excess ^{210}Pb activity. The activity of the ^{137}Cs peak at North Bluff Point is approximately an order of magnitude greater than those of Pamlico Sound cores. No ^7Be activity was detected.

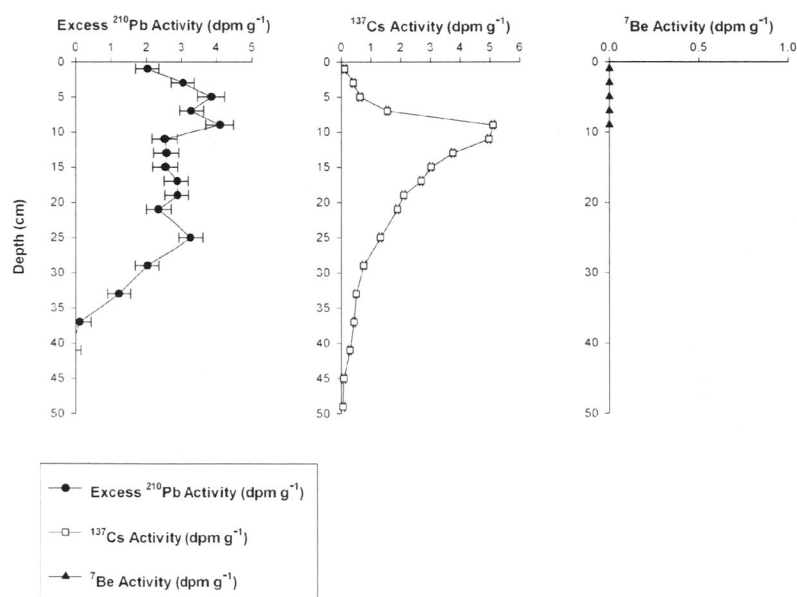


Figure 24: Profiles of excess ^{210}Pb , ^{137}Cs , and ^7Be activities (in dpm g^{-1}) vs. depth for the North Bluff Point marsh core.

Sediment Accumulation Rates and Excess ^{210}Pb Inventories

Sediment accumulation rates (cm y^{-1}) were calculated for each of the cores by a number of different methods: 1) the CIC model; 2) the CF:CS or “simple” model; and 3) relative accumulation rates using the ^{137}Cs peak (Table 6). For calculating accumulation rates relative to the ^{137}Cs peak, the depth of the peak was divided by either 39 or 40 years (year of core collection-1963) depending on the year in which cores were collected (2002 or 2003). Mass accumulation rates ($\text{g cm}^{-2} \text{y}^{-1}$) were calculated for both the CF:CS and CIC models. Mass accumulation rates were generally lower for the CF:CS model, but the values correlated rather well ($r^2 = 0.48$; $n=15$; $p=0.007$). Mass accumulation rates based on the CIC model ranged from 0.05 to 0.43 $\text{g cm}^{-2} \text{y}^{-1}$, averaging 0.26 $\text{g cm}^{-2} \text{y}^{-1}$. Mass accumulation rates based on the CF:CS mode ranged from 0.02 to 0.38 $\text{g cm}^{-2} \text{y}^{-1}$, averaging 0.16 $\text{g cm}^{-2} \text{y}^{-1}$.

Comparing the sediment accumulation rates from the CF:CS and CIC models yielded an r^2 value of 0.52 ($n=15$; $p=0.002$), showing that in general, there is a good correspondence. In most cases sediment accumulation rates predicted from the CIC model were highest, followed by those relative to the ^{137}Cs peak, with those based on the CF:CS model showing the lowest rates. CF:CS sediment accumulation rates range from 0.03 to 0.35 cm y^{-1} , with an average of 0.20 cm y^{-1} . CIC accumulation rates vary from 0.06 to 0.54 cm y^{-1} with an average of 0.32 cm y^{-1} . Accumulation rates based on the ^{137}Cs peak ranged from 0.18 to 0.44 cm y^{-1} , averaging 0.29 cm y^{-1} . In six of the fifteen estuarine cores, there was no well-defined ^{137}Cs peak; therefore, accumulation rates derived from the peak are based on limited data.

Table 6: Average sediment accumulation rates (in cm yr^{-1}) and mass accumulation rates (from CF:CS and CIC only, in $\text{g cm}^{-2} \text{yr}^{-1}$) based on CIC modeling of excess ^{210}Pb data, CF:CS modeling of excess ^{210}Pb data, and relative to the position of the ^{137}Cs peak. Also shown are total excess ^{210}Pb inventories (in dpm cm^{-2}) for each core.

	Excess ^{210}Pb Inventory	Constant Flux:Constant Sedimentation Model				Constant Initial Concentration Model				Accumulation Relative to ^{137}Cs peak	
		Deposition Rate	error	Mass Accumulation	error	Deposition Rate	error	Mass Accumulation	error	Depth of ^{137}Cs Peak	Depth/(39 years)
Site	dpm g^{-1}	cm yr^{-1}	(+/-)	$\text{g cm}^{-2} \text{yr}^{-1}$	(+/-)	cm yr^{-1}	(+/-)	$\text{g cm}^{-2} \text{yr}^{-1}$	(+/-)	cm	cm yr^{-1}
9	28.85	0.17	0.01	0.20	0.01	0.22	0.02	0.32	0.05	9.00	0.23
10	31.38	0.11	0.02	0.08	0.01	0.30	0.07	0.23	0.06	9.00	0.23
11	21.12	0.12	0.03	0.13	0.03	0.10	0.01	0.12	0.01	NA ¹	NA
12	16.86	0.31	0.02	0.38	0.02	0.39	0.06	0.43	0.06	NA	NA
22	35.35	0.16	0.02	0.09	0.01	0.41	0.11	0.23	0.03	7.00	0.18
23	12.47	0.24	0.02	0.17	0.01	0.22	0.01	0.21	0.01	NA	NA
24	64.73	0.32	0.04	0.18	0.02	0.54	0.06	0.36	0.05	NA	NA
27	7.31	0.09	0.02	0.10	0.02	0.25	0.02	0.36	0.05	NA	NA
30	42.36	0.14	0.04	0.11	0.04	0.33	0.10	0.27	0.07	11.00	0.28
31	98.79	0.35	0.03	0.20	0.01	0.33	0.04	0.19	0.01	17.00	0.44
32	81.63+	0.29	0.01	0.19	0.01	0.38	0.05	0.22	0.01	11.00	0.28
41	54.47	0.21	0.02	0.16	0.02	0.41	0.08	0.37	0.06	13.00	0.33
42	72.61	0.14	0.01	0.09	0.01	0.32	0.04	0.19	0.01	7.00	0.18
50	155.62	0.37	0.07	0.25	0.05	0.53	0.14	0.42	0.10	17.00	0.45 ²
55	11.00	0.03	0.01	0.02	0.00	0.06	0.00	0.05	0.00	NA	NA
NBP	25.18	0.42	0.03	0.10	0.00	0.32	0.06	0.26	0.01	9.00	0.24
AVG ³	46.64	0.20	0.11	0.16	0.08	0.32	0.13	0.26	0.11	11.22	0.29

¹ NA indicates no well-developed ^{137}Cs peak existed;

² for S50 the depth of the ^{137}Cs peak is divided by 40;

³ average parameter values do not include NBP.

Excess ^{210}Pb inventories for the cores ranged from 7.31 (S27) to 155.62 dpm cm^{-2} (S50) with an average inventory of 46.64 dpm cm^{-2} . The highest inventories tend to be found in the central basin; and the lowest generally in the protected embayment or in coarser sediments of the perimeter platform cores. The estuary mouth cores show the greatest variation in inventory, with S50 having the highest inventory of all cores (155.62 dpm cm^{-2}) and S55 close to the least (11.00 dpm cm^{-2}). The marsh peat core at NBP has an inventory that is lower than the majority of estuarine cores (25.18 dpm cm^{-2}). Expected excess ^{210}Pb inventories from atmospheric deposition in eastern North Carolina are ~ 26.5 dpm cm^{-2} (Benninger and Wells, 1993).

Marsh Grab Sample Descriptions

Sixteen grab samples were collected for geochemical analysis from seven (three mainland, four barrier island) marsh sites surrounding Pamlico Sound. The mainland sites included Point Peter Road (PPR) North Bluff Point (NBP), and Cedar Island (CI); the barrier island sites consisted of Salvo (SAL), Buxton (BUX), and two sites at Ocracoke (OCR S1, S2). The grab samples have been grouped into two categories (surface peat and subsurface peat) based on the particular area of the marsh that was sampled. Typically, surface peats were collected from marshes or marsh surfaces at depths no greater than 10 cm. Subsurface peat grabs were at least 10 cm beneath the marsh surface and were often underwater. It was later determined that the samples collected from PPR came from a dredge spoil pile from a ditching operation during the construction of Point Peter Road (S.R. Riggs, personal communication). Despite the fact

that these samples were not in-situ, it was possible to determine reasonably where they originated from based on their lithologies and vibracore data obtained from the ECU-USGS-NCGS Coastal Geology Cooperative database. The very organic-rich PPR G1 and PPR G3, are representative of the subsurface peat on which the modern marsh accumulates.

Table 7 gives a general description of the peat locations and peat grab types. The peat grabs generally consisted of a large amount of vegetation-derived organic matter decomposed to different extents, various amounts of sand and mud, and occasionally wood and shell fragments and in-situ mussels. The relative amounts of mud vs. sand were characterized by a cursory visual observation during sample processing. A very general scale of the amount of the particular constituent (mud or sand) was developed: abundant (~80% or greater of the constituent), predominantly (~60 to 80% of the constituent), and subequal (~40-60% of a particular constituent). This approximate scale applies in all cases unless otherwise specifically stated. It was found that some generalizations, particularly with stages of organic matter decomposition and relative grain-size distributions, could be drawn between the mainland and barrier island sites and between the subsurface and surface grab samples. In general, the mainland peats contained less sand and vegetative organic matter that was degraded to a greater extent than the barrier island peats. Additionally, subsurface peats generally showed a greater decomposition of organic matter and less sand, relative to surface peat grabs.

Table 7: General descriptions of dominant vegetation at each marsh site, marsh grab type (modern marsh and subsurface peat), and marsh grab characteristics (extent of decomposition, general grain-size, other constituents).

General Descriptions of Marsh Grab Samples		
Site	Grab	Description
PPR	G1	Grab Type: Subsurface peat beneath a modern <i>Spartina patens</i> and <i>Baccharis</i> dominated marsh Description: Very organic-rich, plant matter is very decomposed, abundant mud
PPR	G3	Grab Type: Subsurface peat beneath a modern <i>Spartina patens</i> and <i>Baccharis</i> dominated marsh Description: Very organic-rich, plant matter is very decomposed, abundant mud
NBP	G2	Grab Type: Subsurface peat beneath a modern <i>Spartina alterniflora</i> / <i>Spartina patens</i> marsh Description: Organic-rich, plant matter very decomposed, small wood fragments present, abundant mud
NBP	G3	Grab Type: Reworked organic detritus from the surface of a modern <i>Spartina alterniflora</i> / <i>Spartina patens</i> marsh Description: Organic-rich, contains small plant and shell fragments, abundant mud
NBP	G5	Grab Type: Surface sample of a <i>Spartina alterniflora</i> / <i>Spartina patens</i> marsh Description: Abundant undecomposed plant matter, in-situ mussels, predominantly mud
CI	G1	Grab Type: Subsurface peat beneath a modern <i>Juncus roemerianus</i> marsh Description: Plant matter predominantly undecomposed, predominantly sand
CI	G2	Grab Type: Subsurface peat beneath a modern <i>Juncus roemerianus</i> marsh (deeper than G1) Description: Plant matter is more decomposed than G1, predominantly sand
SAL	G1	Grab Type: Surface sample of a <i>Spartina alterniflora</i> marsh Description: Abundant undecomposed plant matter, shell fragments, subequal amounts of sand and mud
SAL	G2	Grab Type: Detached surface peat block from a <i>Spartina alterniflora</i> marsh Description: Similar to G1, with slightly less sand
SAL	G3	Grab Type: Subsurface peat beneath a modern <i>Spartina alterniflora</i> marsh Description: Organic-rich, plant matter very decomposed, small wood fragments present, predominantly mud
BUX	G1	Grab Type: Surface sample of a <i>Spartina alterniflora</i> / <i>Juncus roemerianus</i> marsh Description: Plant matter predominantly undecomposed, predominantly sand
BUX	G2	Grab Type: Surface sample of a <i>Spartina alterniflora</i> / <i>Juncus roemerianus</i> marsh Description: Greater plant matter decomposition than G1, subequal amounts of sand and mud
BUX	G3	Grab Type: Subsurface peat beneath a modern <i>Spartina alterniflora</i> / <i>Juncus roemerianus</i> marsh Description: Organic-rich, plant matter is very decomposed, predominantly mud
OCR S1	G1	Grab Type: Surface sample of a <i>Juncus roemerianus</i> marsh Description: Plant matter predominantly undecomposed, predominantly sand
OCR S1	G2	Grab Type: Surface sample of a <i>Spartina alterniflora</i> / <i>Spartina patens</i> marsh Description: Plant matter predominantly undecomposed, in-situ mussels, predominantly sand
OCR S2	G1	Grab Type: Surface sample of a <i>Juncus roemerianus</i> marsh Description: Plant matter predominantly undecomposed, abundant sand

Carbon and Nitrogen Stable Isotope and C:N Ratio Data

Excluding data from the marsh peat samples, all carbon and nitrogen data presented in this section were acquired from a parallel study by Abbene (2004).

Mainland Marsh Grabs

Table 8 displays $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, C:N ratio, percent organic carbon, and percent nitrogen for peat grab samples collected from the PPR, NBP, and CI mainland marsh sites. Within each grab from mainland marsh sites, there is very little variation in $\delta^{13}\text{C}$ ($< 0.7\text{‰}$), $\delta^{15}\text{N}$ (usually $< 0.5\text{‰}$), or C:N ratio (< 4); however, the percent organic carbon and percent nitrogen do vary somewhat. The PPR grabs tend to have the most depleted $\delta^{13}\text{C}$ signature and the greatest $\delta^{15}\text{N}$, C:N ratio, percent organic carbon, and percent nitrogen values of all the mainland sites. Conversely, the CI site grabs are the most enriched in $\delta^{13}\text{C}$, and have the lowest C:N ratio, percent organic carbon and percent nitrogen values of the mainland sites. In comparing the surface peats vs. subsurface peats, some trends are evident in the carbon and nitrogen data. Among the NBP grabs, the subsurface peat G2 has the lowest $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values and the highest percent nitrogen. The surface organic detritus NBP G3 has the highest C:N ratio and percent organic carbon. Finally, the surface marsh NBP G5 has the most enriched $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ signatures, and the lowest C:N ratio, percent organic carbon, and percent nitrogen values. At CI, both G1 and G2 are subsurface peats; however, G2, which is nearer to the surface, is characterized by enriched $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ signatures, as well as lower C:N ratios, percent organic carbon, and percent nitrogen.

Table 8: $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, C:N ratio, organic carbon (%), and nitrogen (%) values for mainland marsh grab samples.

Mainland Marsh Grabs											
Site	Grab	$\delta^{13}\text{C}$ (‰)	(+/-)	$\delta^{15}\text{N}$ (‰)	(+/-)	C:N Ratio	(+/-)	Organic Carbon (%)	(+/-)	Nitrogen (%)	(+/-)
Point Peter Road	G1 A	-29.00		2.36		40.67		48.14		1.18	
Point Peter Road	G1 B	-28.87		2.45		38.51		45.71		1.19	
Point Peter Road	G1 C	-28.70		2.24		39.54		45.17		1.14	
<i>Grab Average</i>		-28.86	0.15	2.35	0.11	39.57	1.08	46.34	1.58	1.17	0.02
Point Peter Road	G3 A	-27.98		1.56		24.89		45.45		1.83	
Point Peter Road	G3 B	-27.86		1.41		26.48		42.90		1.62	
Point Peter Road	G3 C	-27.80		1.48		23.56		43.82		1.86	
<i>Grab Average</i>		-27.88	0.09	1.48	0.08	24.98	1.46	44.06	1.29	1.77	0.13
Site Average		-28.37	0.69	1.92	0.61	32.28	10.32	45.20	1.62	1.47	0.42
North Bluff Point	G2 A	-26.78		-0.17		21.17		13.12		0.62	
North Bluff Point	G2 B	-26.56		-0.33		21.18		11.89		0.56	
North Bluff Point	G2 C	-26.91		-0.49		21.04		17.27		0.82	
<i>Grab Average</i>		-26.75	0.18	-0.33	0.16	21.13	0.08	14.10	2.82	0.67	0.14
North Bluff Point	G3 A	-26.04		1.90		25.71		12.40		0.48	
North Bluff Point	G3 B	-25.93		2.10		24.59		14.56		0.59	
North Bluff Point	G3 C	-26.03		2.15		26.48		18.58		0.70	
<i>Grab Average</i>		-26.00	0.06	2.05	0.13	25.59	0.95	15.18	3.13	0.59	0.11
North Bluff Point	G5 A	-23.96		4.82		17.13		9.89		0.58	
North Bluff Point	G5 B	-23.95		3.96		18.25		8.60		0.50	
North Bluff Point	G5 C	-24.08		4.96		16.98		13.01		0.77	
<i>Grab Average</i>		-24.00	0.08	4.58	0.54	17.45	0.69	10.50	2.27	0.61	0.14
Site Average		-25.58	1.42	2.10	2.45	21.39	4.08	13.26	2.45	0.62	0.04
Cedar Island	G1 A	-25.00		1.98		21.64		13.99		0.65	
Cedar Island	G1 B	-24.74		1.93		20.62		12.66		0.61	
Cedar Island	G1 C	-24.52		1.40		21.14		11.19		0.53	
<i>Grab Average</i>		-24.75	0.24	1.77	0.32	21.13	0.51	12.61	1.40	0.60	0.06
Cedar Island	G2 A	-20.76		2.11		17.76		11.51		0.65	
Cedar Island	G2 B	-21.12		2.45		15.99		10.77		0.67	
Cedar Island	G2 C	-20.47		2.33		19.42		12.95		0.67	
<i>Grab Average</i>		-20.78	0.32	2.29	0.17	17.72	1.72	11.74	1.11	0.66	0.01
Site Average		-22.77	2.81	2.03	0.37	19.43	2.41	12.18	0.62	0.63	0.05
Mainland Marsh Average		-25.57	2.70	2.03	1.45	23.94	7.58	22.08	15.88	0.87	0.45

Barrier Island Marsh Grabs

Table 9 displays $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, C:N ratio, percent organic carbon, and percent nitrogen for marsh grab samples collected from the four barrier island marsh sites. There is very little variation in $\delta^{13}\text{C}$ (usually $<0.5\text{‰}$) and $\delta^{15}\text{N}$ (usually $<0.6\text{‰}$) values and C:N ratios (usually <3) within the barrier island marsh grabs. As with the mainland marsh grabs, the parameters that tend to have the greatest variation in barrier island marsh grabs are percent organic carbon and percent nitrogen. At each of the barrier island sites, there will typically be at least one grab (usually either surface or subsurface) with a significantly depleted or enriched $\delta^{13}\text{C}$ signature compared to the other grabs. The exception to this is at SAL, where the surface and subsurface grabs have similar signatures. There seems to be no correlation to a particular $\delta^{13}\text{C}$ enrichment/depletion pattern vs. the grab type. At the majority of the sites, the subsurface peat grab has the most depleted $\delta^{15}\text{N}$ value. Where there is less extensive peat development, usually the more decomposed grab will have the most depleted $\delta^{15}\text{N}$ value. Organic carbon and nitrogen values vary; however, the relative values of each increase with increasing plant matter decomposition. In comparing the four barrier island sites Salvo has the isotopically lightest $\delta^{13}\text{C}$, and the greatest percent organic carbon and nitrogen. Ocracoke S1 has the highest C:N ratio and most enriched $\delta^{15}\text{N}$ value. Finally, Ocracoke S2 has the isotopically heaviest $\delta^{13}\text{C}$ and the isotopically lightest $\delta^{15}\text{N}$ value, as well as the lowest organic carbon and nitrogen percentages.

Table 9: $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, C:N ratio, organic carbon (%), and nitrogen (%) values for barrier island marsh grab samples.

Barrier Island Marsh Grabs											
Site	Grab	$\delta^{13}\text{C}$ (‰)	(+/-)	$\delta^{15}\text{N}$ (‰)	(+/-)	C:N Ratio	(+/-)	Organic Carbon (%)	(+/-)	Nitrogen (%)	(+/-)
Salvo	G1 A	-23.05		3.06		13.15		7.13		0.54	
Salvo	G1 B	-23.02		3.41		13.46		7.96		0.59	
Salvo	G1 C	-23.16		3.41		12.90		6.68		0.52	
Grab Average		-23.07	0.07	3.29	0.20	13.17	0.28	7.26	0.65	0.55	0.04
Salvo	G2 A	-23.67		3.05		13.66		7.66		0.56	
Salvo	G2 B	-24.03		2.97		14.24		7.23		0.51	
Salvo	G2 C	-23.20		2.96		13.43		7.53		0.56	
Grab Average		-23.63	0.42	2.99	0.05	13.78	0.42	7.47	0.22	0.54	0.03
Salvo	G3 A	-23.48		1.84		14.31		8.96		0.63	
Salvo	G3 B	-23.64		2.21		14.25		11.06		0.78	
Salvo	G3 C	-23.93		1.74		15.12		11.46		0.76	
Grab Average		-23.68	0.23	1.93	0.25	14.56	0.48	10.49	1.34	0.72	0.08
Site Average		-23.46	0.34	2.74	0.71	13.84	0.70	8.41	1.81	0.60	0.10
Buxton	G1 A	-15.88		2.36		12.48		2.63		0.21	
Buxton	G1 B	-16.24		1.73		13.47		1.11		0.08	
Buxton	G1 C	-15.95		2.05		13.69		3.35		0.24	
Grab Average		-16.02	0.19	2.05	0.32	13.22	0.65	2.36	1.14	0.18	0.09
Buxton	G2 A	-20.85		2.77		13.04		6.87		0.53	
Buxton	G2 B	-19.84		2.85		12.02		6.30		0.52	
Buxton	G2 C	-19.98		2.47		12.73		6.13		0.48	
Grab Average		-20.22	0.55	2.70	0.20	12.60	0.52	6.43	0.39	0.51	0.03
Buxton	G3 A	-16.54		1.44		11.95		7.24		0.61	
Buxton	G3 B	-16.41		1.80		11.39		5.41		0.47	
Buxton	G3 C	-16.48		1.24		11.78		6.89		0.58	
Grab Average		-16.48	0.06	1.49	0.28	11.71	0.28	6.51	0.97	0.56	0.07
Site Average		-17.57	2.30	2.08	0.60	12.51	0.76	5.10	2.37	0.42	0.21

Table 9 continued: $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, C:N ratio, organic carbon (%), and nitrogen (%) values for barrier island marsh grab samples.

Barrier Island Marsh Grabs											
Site	Grab	$\delta^{13}\text{C}$ (‰)	(+/-)	$\delta^{15}\text{N}$ (‰)	(+/-)	C:N Ratio	(+/-)	Organic Carbon (%)	(+/-)	Nitrogen (%)	(+/-)
Ocracoke S1	G1 A	-22.58		3.93		13.88		4.37		0.31	
Ocracoke S1	G1 B	-22.52		3.29		15.74		2.02		0.13	
Ocracoke S1	G1 C	-22.34		3.54		13.95		1.40		0.10	
<i>Grab Average</i>		-22.48	0.13	3.59	0.33	14.52	1.06	2.60	1.57	0.18	0.12
Ocracoke S1	G2 A	-16.78		2.12		15.59		1.52		0.10	
Ocracoke S1	G2 B	-16.31		2.34		13.00		1.04		0.08	
Ocracoke S1	G2 C	-16.61		2.52		12.65		0.59		0.05	
<i>Grab Average</i>		-16.57	0.23	2.33	0.20	13.75	1.61	1.05	0.47	0.07	0.03
Site Average		-19.52	4.18	2.96	0.89	14.14	0.55	1.82	1.09	0.13	0.08
Ocracoke S2	G1 A	-15.94		1.44		14.97		0.67		0.04	
Ocracoke S2	G1 B	-16.27		1.45		11.25		0.35		0.03	
Ocracoke S2	G1 C	-16.28		1.86		11.32		0.36		0.03	
Site Average		-16.16	0.20	1.58	0.24	12.51	2.13	0.46	0.18	0.04	0.01
Barrier Island Marsh Average		-19.81	3.17	2.44	0.63	13.31	0.86	4.96	3.55	0.37	0.26

Surface Mixed Layer $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and C:N ratios

Beryllium-7 showed that mixing was significant in Pamlico Sound for about half of the cores for which there were data (Figure 25). To ensure that the surface sediment samples considered for the various carbon and nitrogen tracers were coeval between cores, it was necessary to provide a temporal basis for comparison. This was done by examining the greatest depth of ^7Be activity in each of the cores. Thus the “surface mixed layer” is simply an average of all the values for the particular carbon and nitrogen tracers over the depth where significant (i.e., not within error of zero) ^7Be activity is present. Where there were no ^7Be data it was assumed that the maximum depth of ^7Be activity was equivalent to the average depth of activity for cores in similar environments.

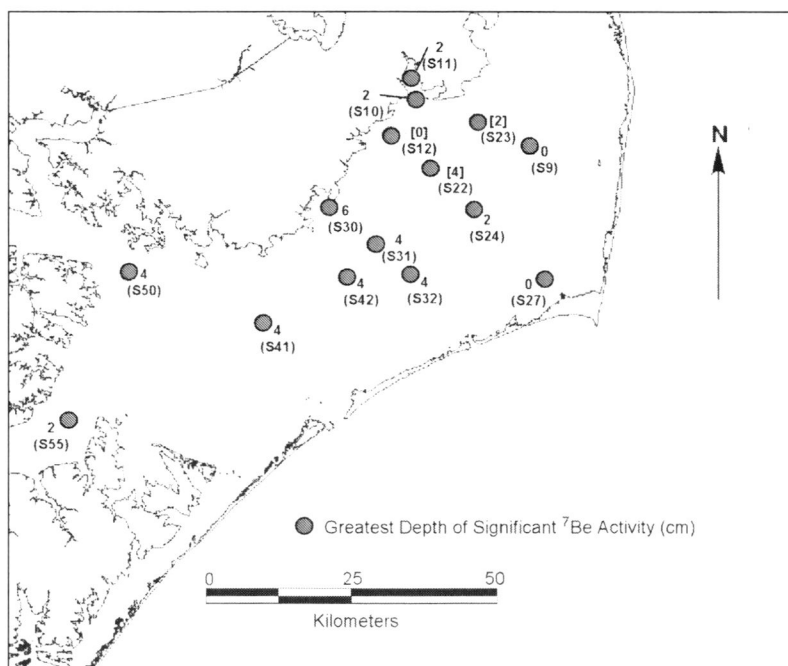


Figure 25: Depth of the surface mixed layer; represented by the greatest depth (in cm) of ^7Be activity (brackets indicate estimated depths in cores for which there are no ^7Be data).

The mainland marsh sites have a much more terrestrial (i.e., depleted) $\delta^{13}\text{C}$ value (avg. -25.57‰) than do the barrier island sites (avg. -19.81‰) (Figure 26). In Pamlico Sound, $\delta^{13}\text{C}$ ranges from -24.61‰ at the mouth of the Neuse River to -19.10‰ at S27 near Hatteras Island. $\delta^{13}\text{C}$ signatures generally become more enriched toward the center of the sound. Between the marsh sites the average $\delta^{15}\text{N}$ has a relatively small range (2.96 to 1.58‰), and all marsh sites are depleted relative to Pamlico Sound sediments in every case excluding S27 (Figure 27). $\delta^{15}\text{N}$ values in the surface mixed layer of Pamlico Sound sediments range from 2.62‰ at S27 near Buxton, to 6.03‰ at S31 at the center of Pamlico Sound. As with $\delta^{13}\text{C}$, isotopic nitrogen increases in value toward the center of the sound (S31). Average C:N ratios are much higher, and the overall abundance of organic matter greater, for mainland marsh grab samples compared to barrier island marsh grabs (Figure 28). C:N ratios from the marsh sites are greater than the majority of the estuarine surface samples. Within the estuarine surface sediments C:N ratios vary from 8.84 at S50 to 15.29 at S11. Although the trend is less well-developed, as with $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, C:N ratios generally decrease toward the central portions of the sound.

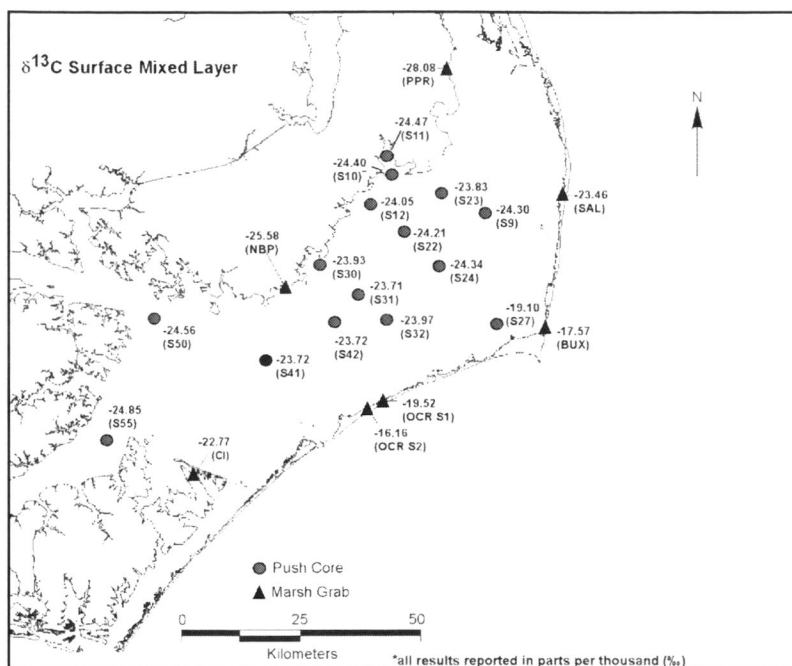


Figure 26: Spatial distribution of $\delta^{13}\text{C}$ (in ‰) for Pamlico Sound surface mixed layer sediments and marsh grab site averages.

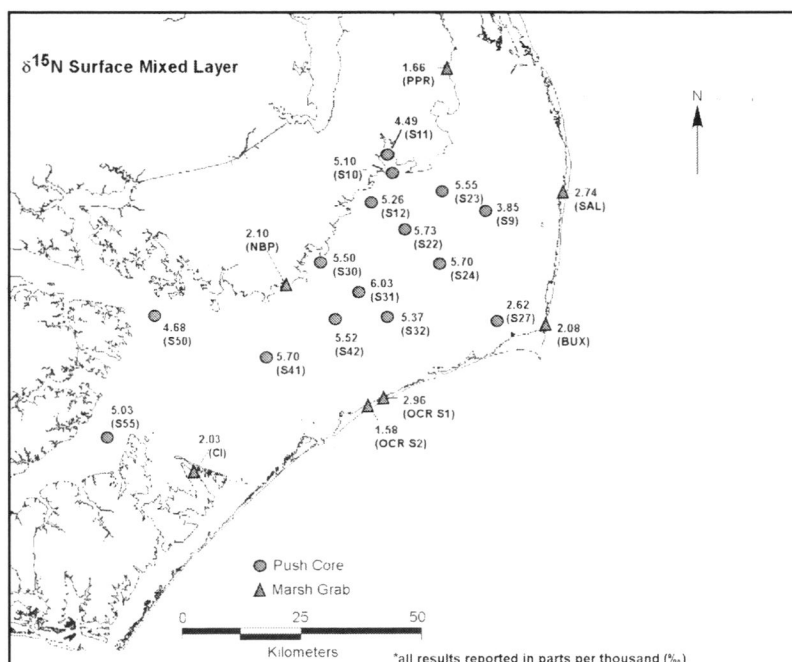


Figure 27: Spatial distribution of $\delta^{15}\text{N}$ (in ‰) for Pamlico Sound surface mixed layer sediments and marsh grab site averages.

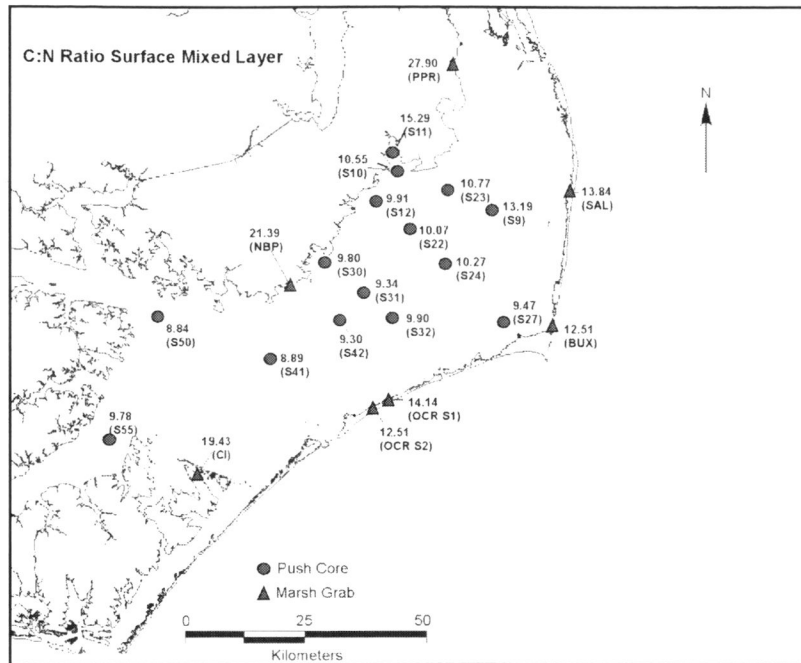


Figure 28: Spatial distribution of C:N ratio for Pamlico Sound surface mixed layer sediments and marsh grab site averages.

North Bluff Point Marsh Core

Figure 29 shows $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, C:N ratio, and percent organic carbon vs. depth for the marsh core collected at North Bluff Point. Also indicated are the positions of the ~ 1963 ^{137}Cs activity peak (solid line) and the maximum depth of excess ^{210}Pb activity representing ~ 120 ybp (dashed line). $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ have enrichment in their respective heavier isotopes through time from the maximum depth of excess ^{210}Pb activity until just near the ^{137}Cs peak. Above the ^{137}Cs peak, this trend reverses and $\delta^{13}\text{C}$ becomes isotopically lighter ($\sim -24\text{‰}$ at the surface), while $\delta^{15}\text{N}$ increases in value rapidly to $\sim 5\text{‰}$ at the surface. The C:N ratio and percent organic carbon generally increase downcore from the surface achieving their highest values below the extent of excess ^{210}Pb activity.

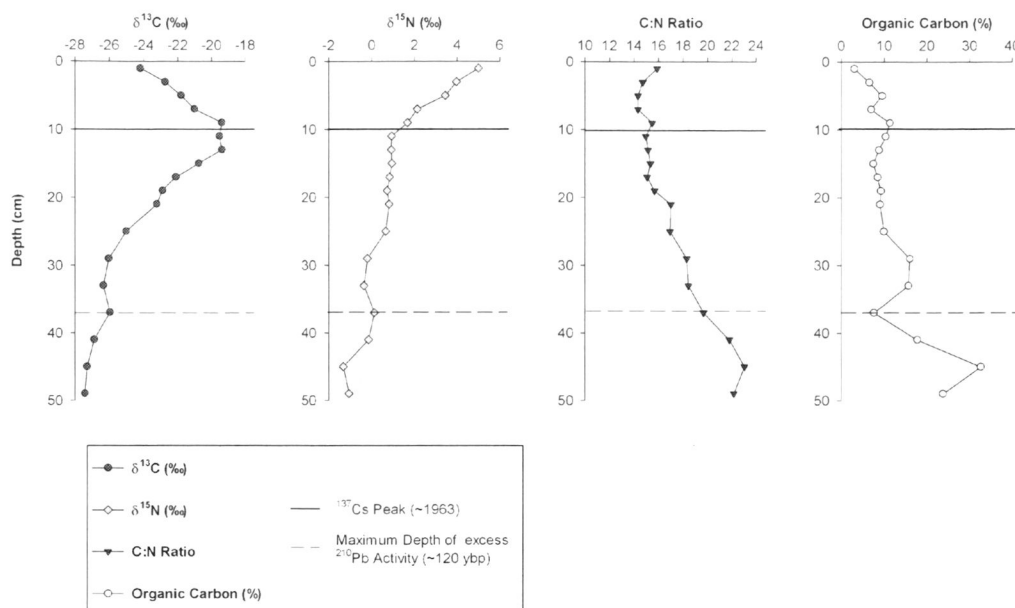


Figure 29: $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, C:N ratio, and percent organic carbon vs. depth for the marsh core collected at North Bluff Point (solid line indicates the position of the ^{137}Cs peak corresponding to ~1963; dashed line denotes greatest depth of excess ^{210}Pb activity representing ~120 ybp).

Pamlico Sound $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and C:N Ratios Downcore

Carbon and nitrogen stable isotope and C:N ratio data acquired from Abbene (2004) is presented for five Pamlico Sound cores to aid in interpretation of trace and major metal abundance data collected from the same cores in this study (Figure 30). Figures 31 and 32 depict downcore $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and C:N ratios from S12, S50, S31, S32, and S41. $\delta^{13}\text{C}$ generally decreases by ~0.5 to 1‰, $\delta^{15}\text{N}$ increases by ~1 to 2‰ and C:N ratios tend to decrease by 1 to 2 upcore. Profiles do not simply increase or decrease regularly; however, they are characterized by inflections in value. For example, at S31, S32, and S41 the profiles of $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and C:N ratio vs. depth are much different at

depths near or just below the ^{137}Cs peak than they are above the peak. There is a shift from enriched $\delta^{13}\text{C}$ and depleted $\delta^{15}\text{N}$ to a more depleted $\delta^{13}\text{C}$ and enriched $\delta^{15}\text{N}$ nearer to the surface. Additionally, the C:N ratio decreases rapidly toward the surface. These changes tend to be the most exaggerated in S31, nonetheless they are still evident at S32 and S41. Although no well-defined ^{137}Cs peak exists for S12, these same trends exist at what are probably equivalent depths.

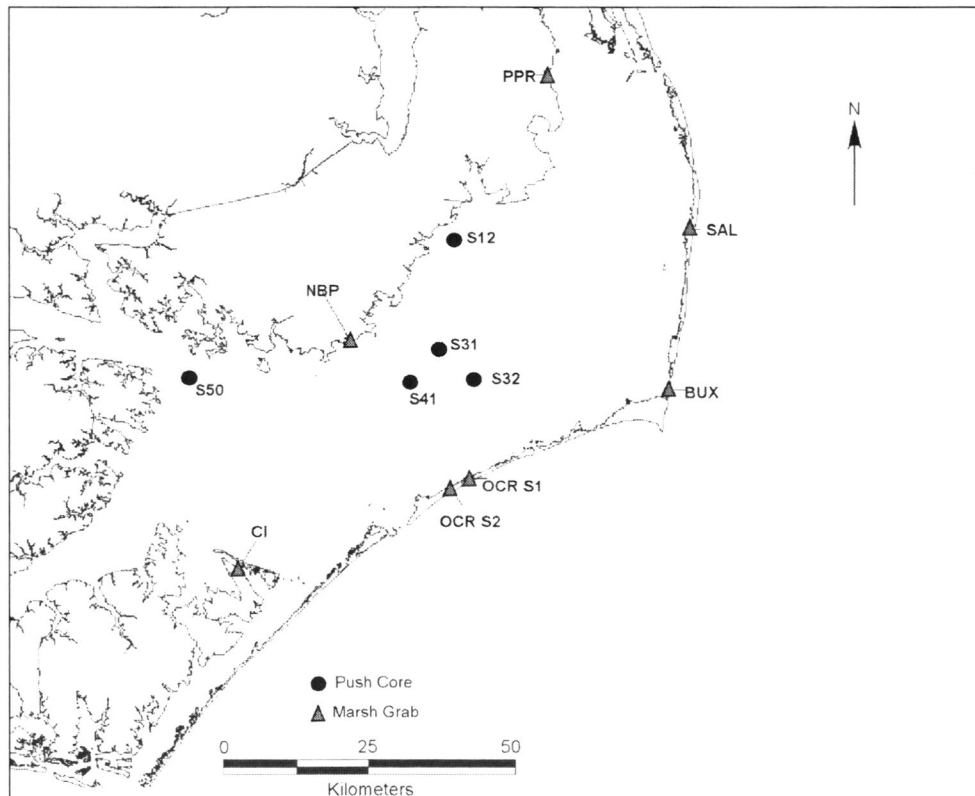


Figure 30: Locations of Pamlico Sound core and marsh grab samples analyzed for metals, (this study) carbon and nitrogen stable isotopes, and C:N ratios (Abbene, 2004).

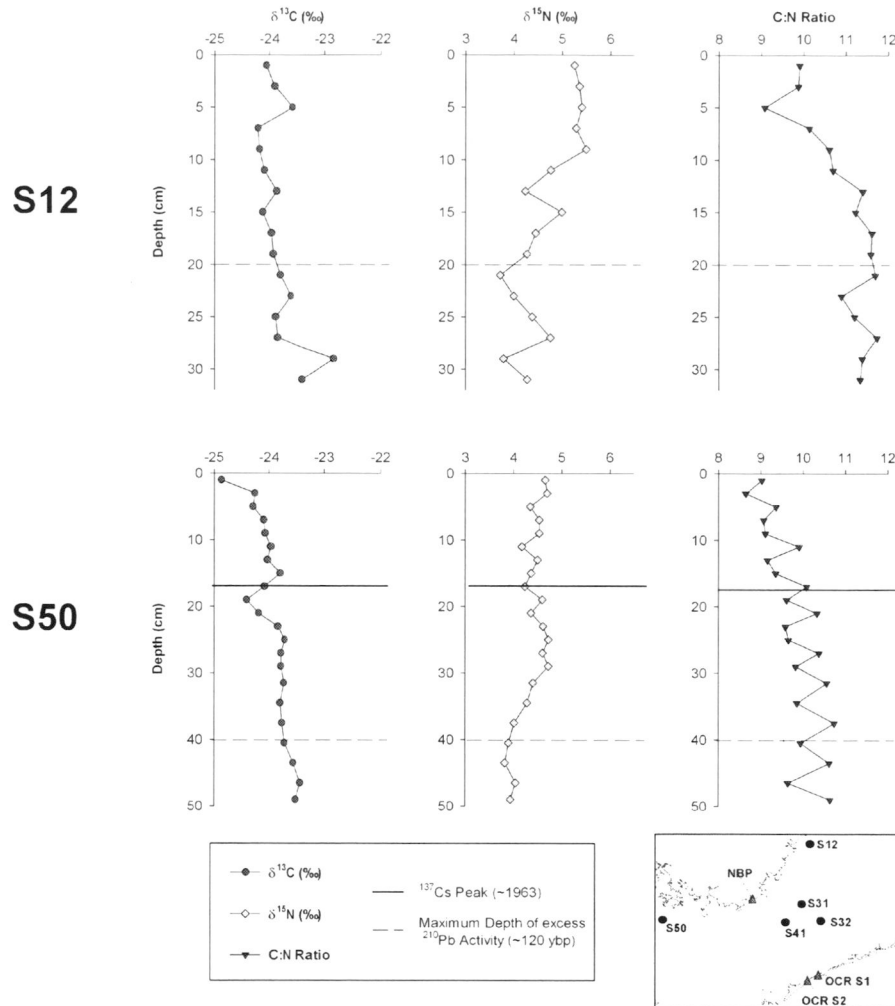


Figure 31: $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and C:N ratio vs. depth for Pamlico Sound cores collected from S12 and S50 (solid line indicates the position of the ^{137}Cs peak corresponding to ~1963; dashed line denotes greatest depth of excess ^{210}Pb activity representing ~120 ybp) *note the difference in scale for depth.

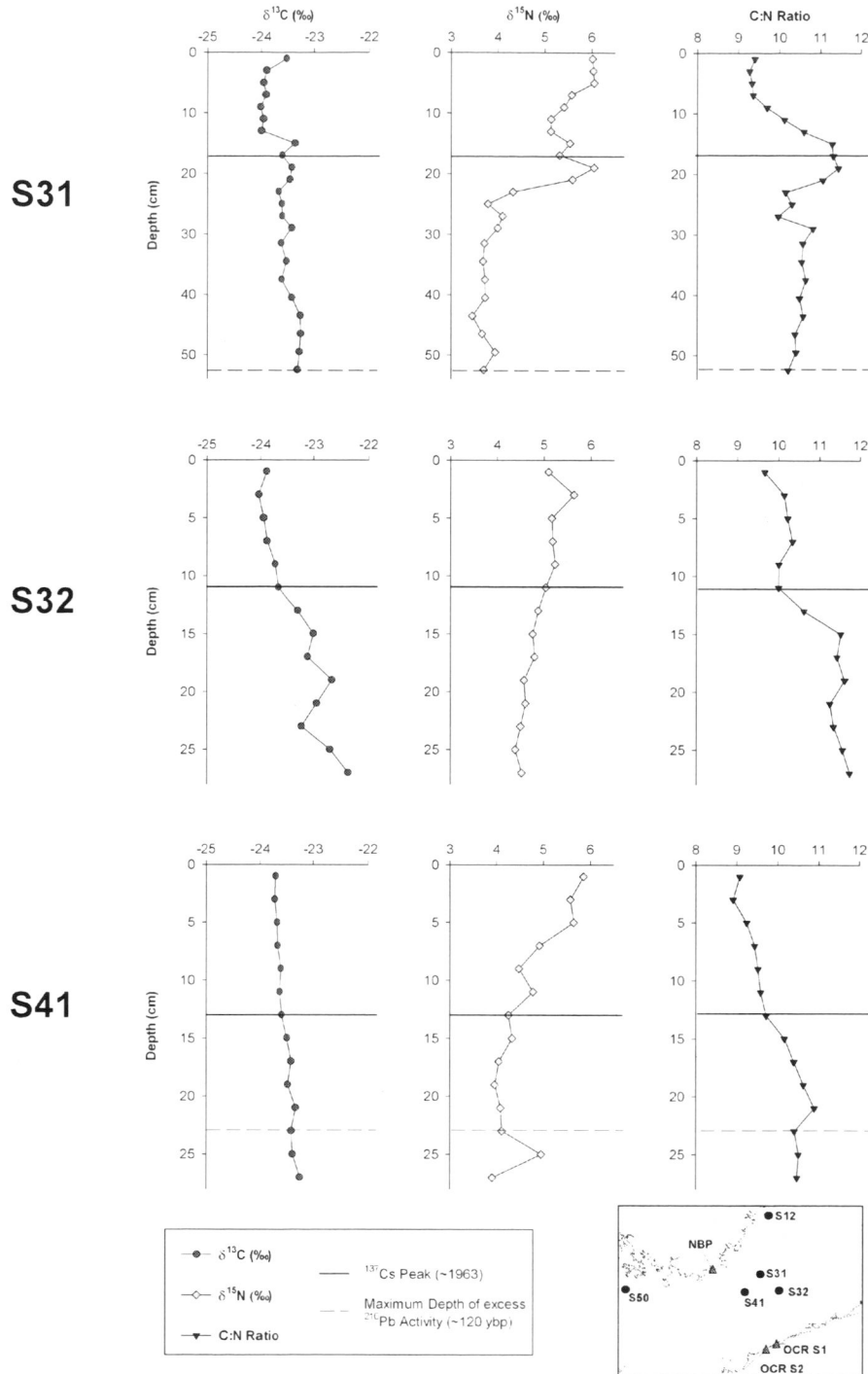


Figure 32: $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and C:N ratio vs. depth for Pamlico Sound cores collected from S31, S32, and S41 (the ^{137}Cs peak (~1963) is indicated by the solid line; the dashed line denotes greatest depth of excess ^{210}Pb activity representing ~120 ybp) *note the difference in scale for depth.

Metal Abundance Data

In addition to the carbon and nitrogen isotopes and C:N ratios, metal abundances (Zn, Cu, Fe, and Al) were used to characterize geochemically selected estuarine cores (S12, S50, S31, S32, and S42) and the marsh grab samples. It was found that, by comparing metal abundance values for standards made from stock solutions with those obtained from the estuarine sediment standard reference material, there was some incomplete extraction for all the metals. Generally Zn, Cu, and Fe showed good total metal recoveries (80% for Zn; 90% for Cu; and 75% for Fe); while, percent recovery for Al was considerably less (40%). The data presented here have been corrected for these percent recoveries. To correct for variations in sediment grain-size and composition, the Zn, Cu, and Fe metal data were normalized to Al. In the case of Zn and Cu the metal/Al ratio was multiplied by 1000 to make their values of a comparable magnitude to the Fe/Al ratio. As with the carbon and nitrogen data, replicate marsh grab samples (A and B only) were analyzed to examine natural variability within a sample. For complete summaries of metal abundance data and aluminum normalized metal data see Appendices D and E.

Mainland Marsh Grab Metal Concentrations

Table 10 shows concentrations of Zn, Cu, Fe, and Al in grab samples collected from the mainland marsh sites. Within individual grabs, metal distributions in samples A and B tend to correlate relatively well. By making a ratio between the maximum range of metal variation and the average metal concentration, an estimate of the relative amount of variation for each particular metal can be calculated. The range of variation vs. the

Table 10: Zn, Cu, Fe, and Al concentrations and associated errors (in ppm) for mainland marsh grab samples.

Mainland Marsh Grabs									
Site	Grab	Zn (ppm)	+/-	Cu (ppm)	+/-	Fe (ppm)	+/-	Al (ppm)	+/-
Point Peter Road	G1 A	5.98	1.60	3.34	0.34	1540	196	11604	110
Point Peter Road	G1 B	8.27	1.60	3.68	0.34	1596	196	11422	110
<i>Grab Average</i>		7.13	1.62	3.51	0.24	1568	40	11513	129
Point Peter Road	G3 A	20.08	1.61	2.02	0.34	4157	199	14029	119
Point Peter Road	G3 B	25.12	1.61	1.04	0.34	5684	201	17710	133
<i>Grab Average</i>		22.60	3.56	1.53	0.69	4921	1080	15870	2603
Site Average		14.86	10.94	2.52	1.40	3244	2371	13691	3081
North Bluff Point	G2 A	28.57	1.62	3.80	0.34	15447	229	42840	251
North Bluff Point	G2 B	27.67	1.61	3.32	0.34	15118	227	35415	214
<i>Grab Average</i>		28.12	0.64	3.56	0.34	15283	233	39127	5250
North Bluff Point	G3 A	41.89	1.63	6.38	0.34	17358	236	40641	240
North Bluff Point	G3 B	49.54	1.65	6.88	0.35	19417	245	44676	261
<i>Grab Average</i>		45.72	5.41	6.63	0.35	18388	1456	42658	2853
North Bluff Point	G5 A	55.16	1.66	7.18	0.35	16614	233	37146	223
North Bluff Point	G5 B	58.98	1.67	7.10	0.35	20454	250	30422	190
<i>Grab Average</i>		57.07	2.70	7.14	0.06	18534	2715	33784	4755
Site Average		43.64	14.59	5.78	1.94	17401	1836	38523	4468
Cedar Island	G1 A	101.97	1.79	27.28	0.42	16156	232	44641	261
Cedar Island	G1 B	83.93	1.73	21.31	0.39	16882	234	46346	269
<i>Grab Average</i>		92.95	12.76	24.30	4.22	16519	513	45494	1206
Cedar Island	G2 A	56.40	1.66	12.51	0.36	16013	231	35076	212
Cedar Island	G2 B	67.56	1.69	12.79	0.36	16473	233	33936	207
<i>Grab Average</i>		61.98	7.89	12.65	0.20	16243	325	34506	806
Site Average		77.47	21.90	18.47	8.23	16381	195	40000	7769
Mainland Marsh Average		45.08	31.34	8.47	8.43	13065	7896	31850	14781

average metal concentration are as follows: Zn (25%), Cu (25%), Fe (35%) and Al (20%), indicating that in the mainland marshes, Fe tends to show the greatest variability. These are, however, a measure of sample variability using the maximum range for a particular sample. Typically, there was much greater correlation between metal concentrations for samples A and B within each grab.

At PPR, the organic-rich subsurface peats have lower metal values than any other mainland site. CI grabs have the highest Zn and Cu values of the mainland grabs, and Al and Fe concentrations comparable to NBP. Among the mainland grabs, the subsurface peat grabs generally have lower metal concentrations than do the surface marshes; however, there was only one surface marsh grab which was in-situ (G5). A concentration gradient is seen for the majority of the metals in the three NBP grabs. The surface marsh peat (G5) has greater concentrations than the subsurface peat (G2); metal concentrations for the organic detritus grab (G3) is somewhere in the middle. At CI the deeper of the subsurface grabs (G1) has much higher Zn, Cu, and Al values than does CI G2, although the Fe concentrations are similar between the grabs.

Barrier Island Marsh Grab Metal Concentrations

Table 11 displays the concentrations of Zn, Cu, Fe, and Al in marsh grab samples taken from the four barrier island sites. Much like the mainland marsh sites, metal concentrations for samples A and B in barrier island grabs correlate well. Relative variabilities derived from the range of maximum variation vs. the average metal concentration are as follows: Zn (30%), Cu (40%), Fe (15%) and Al (40%). It is evident from this comparison that the barrier island marsh grabs have a greater variability in

Table 11: Zn, Cu, Fe, and Al concentrations and associated errors (in ppm) for barrier island marsh grab samples.

Barrier Island Marsh Grabs									
Site	Grab	Zn (ppm)	+/-	Cu (ppm)	+/-	Fe (ppm)	+/-	Al (ppm)	+/-
Salvo	G1 A	84.26	1.73	9.01	0.35	36709	340	40558	240
Salvo	G1 B	82.00	1.72	7.46	0.35	33019	318	50244	290
<i>Grab Average</i>		83.13	1.73	8.24	0.35	34864	329	45401	265
Salvo	G2 A	84.73	1.73	9.45	0.35	31102	307	41498	245
Salvo	G2 B	83.22	1.73	13.19	0.36	32300	314	57114	326
<i>Grab Average</i>		83.98	1.73	11.32	0.36	31701	310	49306	285
Salvo	G3 A	56.31	1.66	5.55	0.34	25695	276	47179	274
Salvo	G3 B	55.00	1.66	4.74	0.34	24897	272	38914	232
<i>Grab Average</i>		55.66	1.66	5.15	0.34	25296	274	43047	253
Site Average		74.25	16.11	8.23	3.09	30620	4875	45918	3162
Buxton	G1 A	43.34	1.64	5.18	0.34	13232	220	24256	161
Buxton	G1 B	35.43	1.62	3.67	0.34	10356	211	22109	151
<i>Grab Average</i>		39.39	1.63	4.43	0.34	11794	215	23183	156
Buxton	G2 A	70.26	1.69	64.51	0.68	20736	251	34663	210
Buxton	G2 B	79.75	1.72	65.01	0.68	23042	262	27835	177
<i>Grab Average</i>		75.01	1.71	64.76	0.68	21889	256	31249	194
Buxton	G3 A	62.31	1.67	8.90	0.35	23440	264	38050	227
Buxton	G3 B	67.72	1.69	10.46	0.35	26137	278	28999	183
<i>Grab Average</i>		65.02	1.68	9.68	0.35	24789	271	33525	205
Site Average		59.80	18.37	26.29	33.42	19491	6821	29319	5435
Ocracoke S1	G1 A	28.47	1.62	5.09	0.34	8861	207	33496	204
Ocracoke S1	G1 B	21.53	1.61	6.85	0.35	5772	201	33103	203
<i>Grab Average</i>		25.00	1.61	5.97	0.34	7317	204	33300	203
Ocracoke S1	G2 A	23.49	1.61	2.55	0.34	5326	200	17438	131
Ocracoke S1	G2 B	21.38	1.61	1.58	0.34	4369	199	19396	139
<i>Grab Average</i>		22.44	1.61	2.07	0.34	4848	199	18417	135
Site Average		23.72	1.81	4.02	2.76	6082	1746	25858	10524
Ocracoke S2	G1 A	31.41	1.62	2.75	0.34	8441	206	19227	139
Ocracoke S2	G1 B	28.05	1.62	3.49	0.34	10500	211	20493	144
Site Average		29.73	1.62	3.12	0.34	9471	209	19860	141
B. Island Marsh Average		53.26	24.13	12.75	10.81	19107	11049	33032	11159

metal abundances (excluding Fe) than do the mainland grab samples. In particular, Al and Cu show a much greater variability.

In comparing the barrier island marsh grab sites with one another, the OCR S1 and S2 collectively have the lowest average concentrations for each metal. SAL has the highest average metal concentrations, excluding Cu. Copper values are somewhat skewed for BUX G2 (~75 ppm Cu), which has a Cu concentration triple that of any other grab sample. An evaluation of the average metal abundances between the mainland and barrier island sites illustrates that all of the metals tend to be enriched in barrier island peats relative to the mainland peats; however, OCR S1 and S2 have the lowest metal abundances of any site. Comparing the surface marsh peats to the older subsurface peats shows that metal concentrations are generally higher in the more modern peats, however, this is not always the case (e.g. BUX G1).

Aluminum Normalization of Marsh Metal Data

Tables 12 and 13 show aluminum normalized Zn, Cu, and Fe data for mainland and barrier island marsh sites. At PPR, G1 has lower metal/Al ratios than G2, excluding Cu. At NBP, the metal/Al values all increase for G2, G3, and G5. At Cedar Island G1 has a greater Zn/Al and Cu/Al ratio than does G2, however Fe/Al is greater in G2. In comparing the three mainland sites, CI has a greater Zn/Al and Cu/Al ratio, and NBP has a slightly greater Fe/Al ratio. At Salvo, G1 generally has the highest metal/Al ratios, while the subsurface peat G3 has the least. At the Buxton site, G2 commonly has the greatest metal/Al ratio and the surface marsh grab at G1 has the lowest ratios. Among the Ocracoke sites, OCR S1 is more depleted in Zn/Al and Fe/Al, however values for Cu/Al

Table 12: Zn, Cu, and Fe concentrations normalized to Al concentrations for mainland marsh grab samples (Zn/Al and Cu/Al ratios have been multiplied by 1000).

Mainland Marsh Grabs							
Site	Grab	Zn/Al X 1000	+/-	Cu/Al X 1000	+/-	Fe/Al	+/-
Point Peter Road	G1 A	0.52	0.14	0.29	0.03	0.13	0.13
Point Peter Road	G1 B	0.72	0.14	0.32	0.03	0.14	0.12
<i>Grab Average</i>		<i>0.62</i>	<i>0.15</i>	<i>0.31</i>	<i>0.02</i>	<i>0.14</i>	<i>0.00</i>
Point Peter Road	G3 A	1.43	0.12	0.14	0.02	0.30	0.03
Point Peter Road	G3 B	1.42	0.09	0.06	0.02	0.32	0.05
<i>Grab Average</i>		<i>1.42</i>	<i>0.01</i>	<i>0.10</i>	<i>0.06</i>	<i>0.31</i>	<i>0.02</i>
Site Average		1.02	0.47	0.20	0.12	0.22	0.10
North Bluff Point	G2 A	0.67	0.04	0.09	0.01	0.36	0.02
North Bluff Point	G2 B	0.78	0.05	0.09	0.01	0.43	0.02
<i>Grab Average</i>		<i>0.72</i>	<i>0.08</i>	<i>0.09</i>	<i>0.00</i>	<i>0.39</i>	<i>0.05</i>
North Bluff Point	G3 A	1.03	0.04	0.16	0.01	0.43	0.01
North Bluff Point	G3 B	1.11	0.04	0.15	0.01	0.43	0.01
<i>Grab Average</i>		<i>1.07</i>	<i>0.06</i>	<i>0.16</i>	<i>0.00</i>	<i>0.43</i>	<i>0.01</i>
North Bluff Point	G5 A	1.48	0.05	0.19	0.01	0.45	0.02
North Bluff Point	G5 B	1.94	0.06	0.23	0.01	0.67	0.01
<i>Grab Average</i>		<i>1.71</i>	<i>0.32</i>	<i>0.21</i>	<i>0.03</i>	<i>0.56</i>	<i>0.16</i>
Site Average		1.17	0.47	0.15	0.06	0.46	0.11
Cedar Island	G1 A	2.28	0.04	0.61	0.01	0.36	0.02
Cedar Island	G1 B	1.81	0.04	0.46	0.01	0.36	0.02
<i>Grab Average</i>		<i>2.05</i>	<i>0.33</i>	<i>0.54</i>	<i>0.11</i>	<i>0.36</i>	<i>0.00</i>
Cedar Island	G2 A	1.61	0.05	0.36	0.01	0.46	0.02
Cedar Island	G2 B	1.99	0.05	0.38	0.01	0.49	0.02
<i>Grab Average</i>		<i>1.80</i>	<i>0.27</i>	<i>0.37</i>	<i>0.01</i>	<i>0.47</i>	<i>0.02</i>
Site Average		1.92	0.29	0.45	0.12	0.42	0.06
Mainland Marsh Average		1.34	0.55	0.25	0.16	0.38	0.14

Table 13: Zn, Cu, and Fe concentrations normalized to Al concentrations for barrier island marsh grab samples (Zn/Al and Cu/Al ratios have been multiplied by 1000).

Barrier Island Marsh Grabs							
Site	Grab	Zn/Al X 1000	+/-	Cu/Al X 1000	+/-	Fe/Al	+/-
Salvo	G1 A	2.08	0.04	0.22	0.01	0.91	0.01
Salvo	G1 B	1.63	0.04	0.15	0.01	0.66	0.01
<i>Grab Average</i>		<i>1.85</i>	<i>0.32</i>	<i>0.19</i>	<i>0.05</i>	<i>0.78</i>	<i>0.18</i>
Salvo	G2 A	2.04	0.04	0.23	0.01	0.75	0.01
Salvo	G2 B	1.46	0.03	0.23	0.01	0.57	0.01
<i>Grab Average</i>		<i>1.75</i>	<i>0.41</i>	<i>0.23</i>	<i>0.00</i>	<i>0.66</i>	<i>0.13</i>
Salvo	G3 A	1.19	0.04	0.12	0.01	0.54	0.01
Salvo	G3 B	1.41	0.04	0.12	0.01	0.64	0.01
<i>Grab Average</i>		<i>1.30</i>	<i>0.16</i>	<i>0.12</i>	<i>0.00</i>	<i>0.59</i>	<i>0.07</i>
Site Average		1.64	0.36	0.18	0.05	0.68	0.13
Buxton	G1 A	1.79	0.07	0.21	0.01	0.55	0.02
Buxton	G1 B	1.60	0.07	0.17	0.02	0.47	0.02
<i>Grab Average</i>		<i>1.69</i>	<i>0.13</i>	<i>0.19</i>	<i>0.03</i>	<i>0.51</i>	<i>0.05</i>
Buxton	G2 A	2.03	0.05	1.86	0.02	0.60	0.01
Buxton	G2 B	2.87	0.06	2.34	0.03	0.83	0.01
<i>Grab Average</i>		<i>2.45</i>	<i>0.59</i>	<i>2.10</i>	<i>0.34</i>	<i>0.71</i>	<i>0.16</i>
Buxton	G3 A	1.64	0.05	0.23	0.01	0.62	0.01
Buxton	G3 B	2.34	0.06	0.36	0.01	0.90	0.01
<i>Grab Average</i>		<i>1.99</i>	<i>0.49</i>	<i>0.30</i>	<i>0.09</i>	<i>0.76</i>	<i>0.20</i>
Site Average		2.04	0.49	0.86	0.97	0.66	0.17
Ocracoke S1	G1 A	0.85	0.05	0.15	0.01	0.26	0.02
Ocracoke S1	G1 B	0.65	0.05	0.21	0.01	0.17	0.04
<i>Grab Average</i>		<i>0.75</i>	<i>0.14</i>	<i>0.18</i>	<i>0.04</i>	<i>0.22</i>	<i>0.06</i>
Ocracoke S1	G2 A	1.35	0.09	0.15	0.02	0.31	0.04
Ocracoke S1	G2 B	1.10	0.08	0.08	0.02	0.23	0.05
<i>Grab Average</i>		<i>1.22</i>	<i>0.17</i>	<i>0.11</i>	<i>0.05</i>	<i>0.27</i>	<i>0.06</i>
Site Average		0.99	0.30	0.15	0.05	0.24	0.06
Ocracoke S2	G1 A	1.63	0.09	0.14	0.02	0.44	0.03
Ocracoke S2	G1 B	1.37	0.08	0.17	0.02	0.51	0.02
Site Average		1.50	0.19	0.16	0.02	0.48	0.05
Barrier Island Marsh Average		1.61	0.53	0.40	0.63	0.55	0.22

are similar. The barrier island subsurface peat grabs always have lower Zn/Al ratios, and often lower Fe/Al ratios and Cu/Al ratios than do the surface marsh grabs.

The barrier island grabs have greater metal/Al ratios on average than do the mainland marsh grabs; however, OCR S1 has the lowest metal/Al ratio of any site. Additionally, both the mainland and barrier island marshes show a dominance of metal/Al ratios decreasing from Fe/Al >> Zn/Al > Cu/Al. Ranges for the particular metal/Al ratios are as follows: Fe/Al (0.24-0.68), Zn/Al X1000 (0.99-2.04), and Cu/Al X 1000 (0.15-0.86).

In relation to the values given for the metal/Al ratios for the average shale by Turkeian and Wedepohl (1961) (Zn/Al X1000 =1.08; Cu/Al X1000 =0.51; Fe/Al = 0.54), the mainland sites are generally enriched in Zn/Al, and depleted in Cu/Al and Fe/Al. The barrier island sites show much greater variability in metal/Al ratios in comparison to the average shale. BUX, SAL, and OCR S2 all show an enrichment in Zn/Al, while OCR S1 is depleted. With the exception of G2 at BUX, all of the barrier island grabs are depleted in Cu/Al with respect to the average shale. Fe/Al is enriched in the BUX and SAL sites, but depleted in the two OCR sites.

Pamlico Sound Metal Concentrations

Figures 33 and 34 show the distributions of Zn, Cu, Fe, and Al vs. depth in five estuarine cores (S12, S50, S31, S32, and S41). As is the case for the marsh peats, the general abundance for the analyzed metals in decreasing order is Al>Fe>>Zn>Cu. Zinc concentrations generally increase from the ~120 year mark to about the position of the ¹³⁷Cs peak. Above the ¹³⁷Cs peak, Zn generally decreases, often showing an increase in

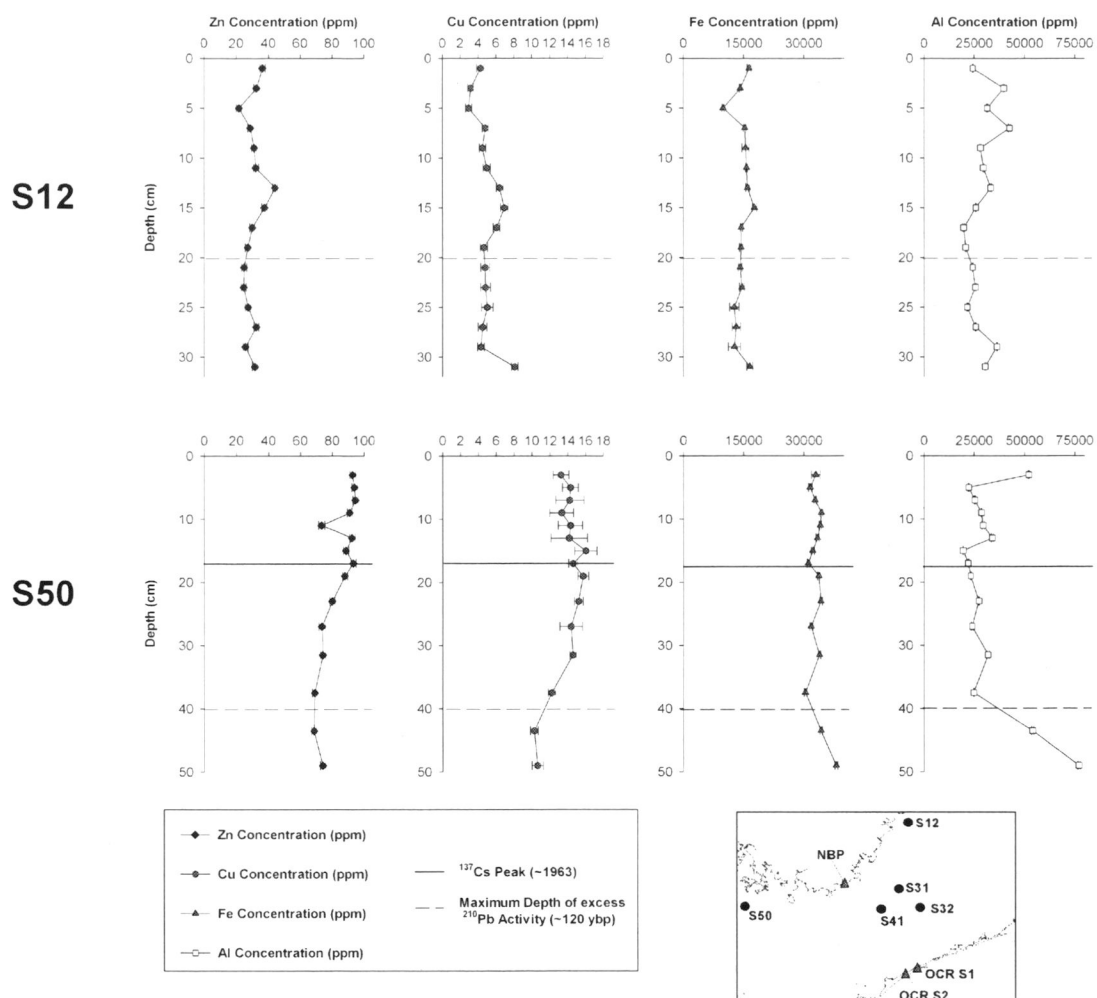


Figure 33: Concentrations of Zn, Cu, Fe, and Al (in ppm) vs. depth for S12 and S50 (solid line denotes the ~1963 peak of ^{137}Cs activity; dashed line indicates the maximum depth of excess ^{210}Pb activity) *note the difference in depth scale.

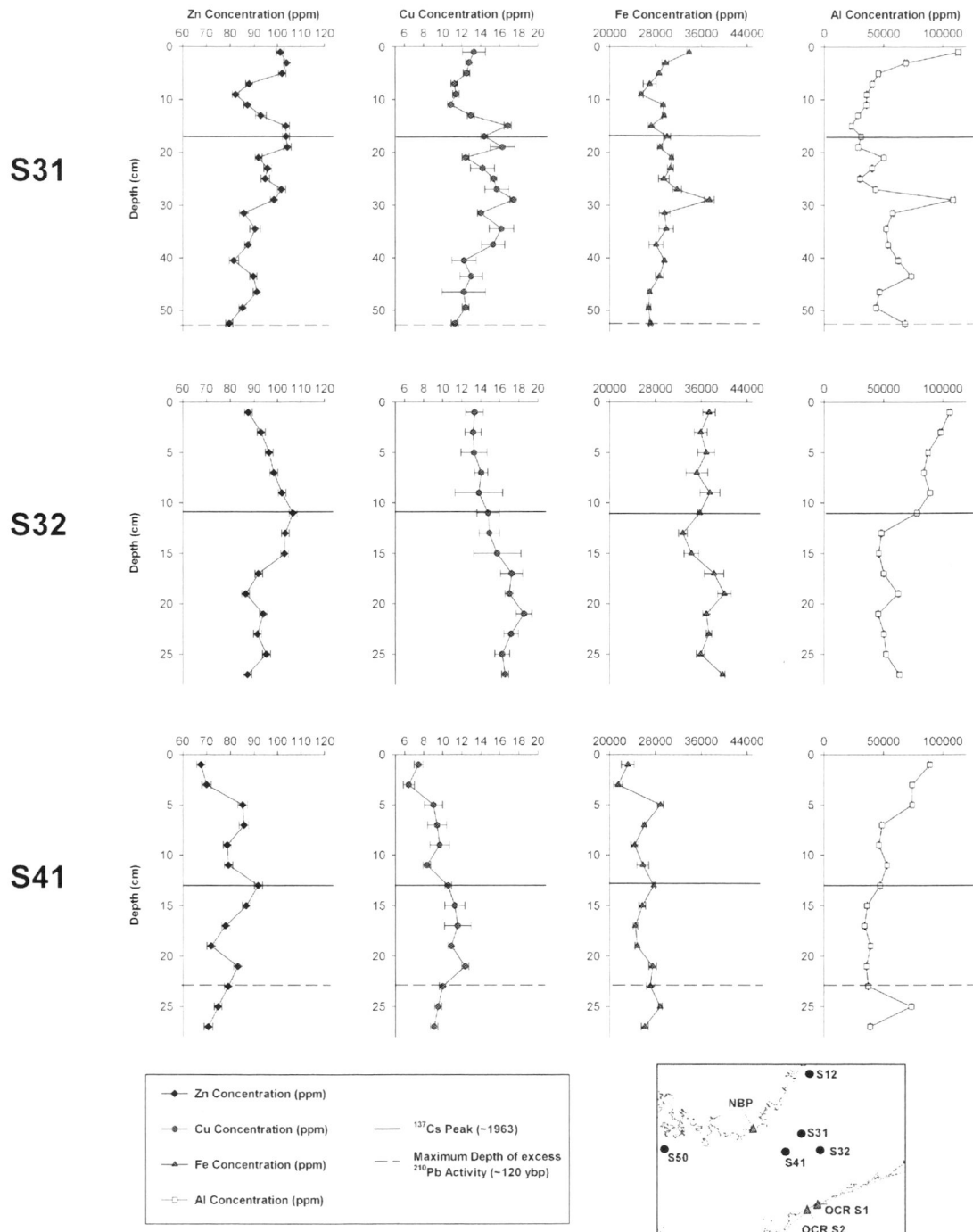


Figure 34: Concentrations of Zn, Cu, Fe, and Al (in ppm) vs. depth for S31, S32, and S41 (solid line denotes the ~1963 peak of ^{137}Cs activity; dashed line indicates the maximum depth of excess ^{210}Pb activity) *note the difference in depth scale.

concentration just at the surface. Copper concentrations increase in some of the cores before the ^{137}Cs peak, but in all cases concentrations decrease following 1963. Al and Fe vary more so, with some cores increasing in concentration to the peak and others decreasing; in the majority of the cores the Fe and Al increase after the ^{137}Cs peak. Average concentrations of metals throughout the cores tend to be the greatest for S31, S32, and S50, less for S41, and significantly less for S12. One exception to this is Al at S50, which is significantly lower in concentration than the majority of the other cores.

Aluminum Normalization of Pamlico Sound Metal Data

Figures 35 and 36 show the metal/Al distributions vs. depth for S12, S50, S31, S32, and S41. Also shown on the graphs are the metal/Al ratios (X 1000) for Zn (1.08), Cu (0.51), and Fe (0.54) taken from the average shale (Turekian and Wedepohl, 1961). The cores are generally enriched with respect to the average shale in Zn/Al and Fe/Al, and are largely depleted in Cu/Al. For the majority of the cores metal/Al ratios tend to increase upcore from the depth of no excess ^{210}Pb activity until the ^{137}Cs peak. At S31, S32, and S41 just below the ^{137}Cs peak a similar pattern of alternating metal/Al ratios exists that seem to be time coincident. Above the peak, metal/Al ratios tend to decrease rather regularly, with the exception of S50, which is characterized by a major decreasing inflection at ~10 cm. Taken as a whole, the majority of cores show an overall decrease in metal/Al ratio upcore. One exception to this is at S50, which shows the greatest metal/Al increase upcore. Overall values of metal/Al ratio tend to be the greatest for S50 and S41, decreasing in S31 and S32, and the least for S12.

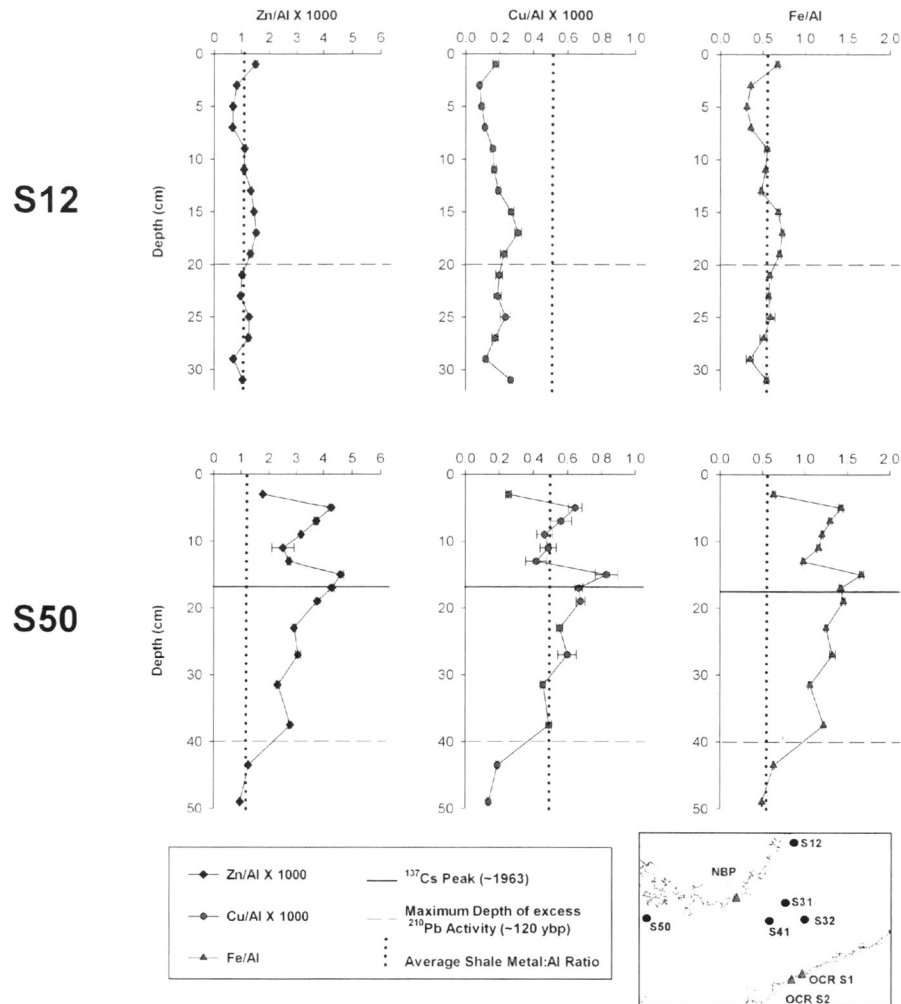


Figure 35: Al normalized concentrations of Zn, Cu, and Fe vs. depth for S12 and S50 (solid line denotes the ~1963 peak of ^{137}Cs activity; dashed line indicates the maximum depth of excess ^{210}Pb activity; vertical dotted line indicates metal/Al ratio for avg. shale).

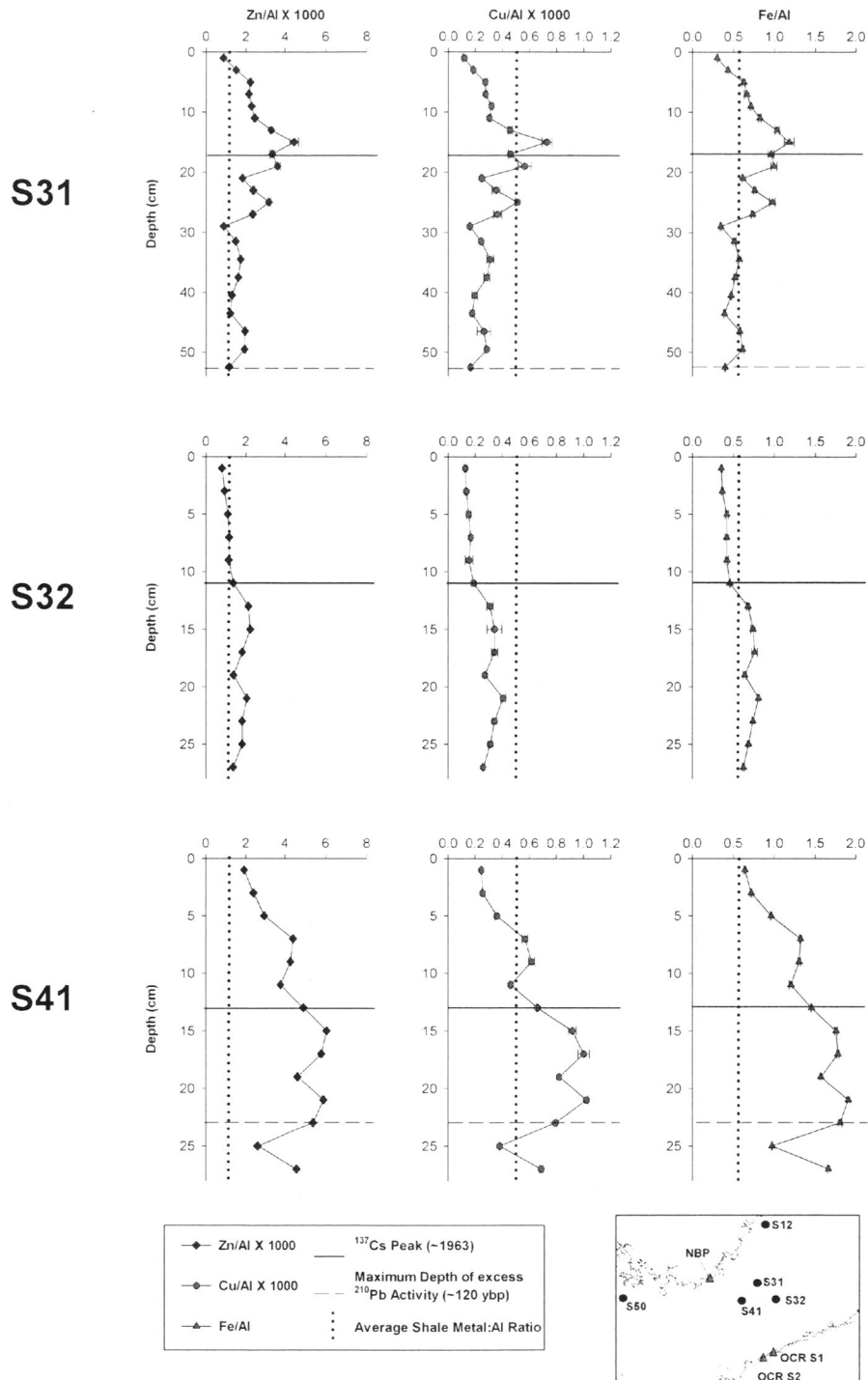


Figure 36: Al normalized concentrations of Zn, Cu, and Fe vs. depth for S31, S32, and S41 (solid line denotes the ~1963 peak of ^{137}Cs activity; dashed line shows the maximum depth of excess ^{210}Pb activity; vertical dotted line indicates metal/Al ratio for avg. shale).

DISCUSSION

Grain-Size Distributions

The grain-size data acquired from this study are significant as they represent the first time to the author's knowledge that Pamlico Sound sediment grain-size data have been analyzed downcore, on an interval-by-interval basis. Previous works, as summarized by Wells and Kim (1989), focused mainly on surficial grab samples for grain-size interpretation. The cores that were collected were either homogenized to get an average grain-size (Wright, 1974), or used for other purposes such as examining sedimentary structures (Katuna, 1974).

Factors Influencing Grain-Size Distributions

The spatial distributions of sediment grain-size found in this study were in excellent agreement with previous work summarized by Wells and Kim (1989). The finest sediments, dominated by clayey silt, tended to accumulate in two predominant settings: 1) in deep water in the central portions of the sound and at the mouths of the Neuse and Pamlico River estuaries; or 2) in relatively shallow water in embayments and tributary estuaries. Although the material accumulating in the central basin and estuary mouths is of a similar grain-size as the shallower embayments, the ORM deposits are far more extensive in deeper water. This is evidenced in cores from S10 and S11 that contain very fine material in the upper portions of the core, and grade to a sandier substrate at depth. In deeper portions of the sound where the ORMs are accumulating, fine-grained material was present throughout the cores. The shallower water embayments and tributary estuaries could be either limited by accommodation space,

have had insufficient time to develop significant ORM deposits, or they could have experienced some sediment removal. Cores located in the perimeter platform environment exhibited the greatest variability in grain-size. These cores also represented an intermediary in water depth between the shallower protected embayment and deeper estuary mouth and central basin core environments.

Thus, it appears that the grain-size distributions in Pamlico Sound are related to water depth. Equally as important though must be the relative protection from wave activity and the nature of and proximity to sediment source material. To illustrate the relative importance of these factors it is useful to compare and contrast the various cores from the perimeter platform environment. These cores exhibit differences in grain-size, with S30 and S23 (Figure 13) generally being finer than S9, S12, and S27 (Figure 14). Cores from S30 and S12 were collected from similar, relatively shallow depths (3.1 m at S30 and 3.7 m at S12); however, S30 is much closer to the mainland shoreline where marsh erosion is very significant ($\sim 1.3 \text{ m y}^{-1}$) (Riggs and Ames, 2003). S12 is somewhat farther away from the local dominant sediment source (marsh erosion), and consequently much of the fine material deposited is winnowed away, giving S12 a coarser grain-size overall than S30. This same trend is observed in deeper water at S23 (5.2 m) and S9 (5.5 m). Again, S23 is closer to the mainland shoreline than is S9, and as a result S9 is comparatively depleted in fines.

Grain-Size Controls on Geochemical Tracers

Excess ^{210}Pb Inventories

Grain-size effects on geochemical tracer values are evident in many of the cores, particularly the radionuclide and metal data. Grain-size does not seem to be a limiting factor in determining the depth of no excess ^{210}Pb activity. For example, in comparing S30 and S23 (both from the perimeter platform OC-rich environment), S30 has roughly twice the amount of mud and an excess ^{210}Pb inventory approximately four times as great as S23; however, excess ^{210}Pb activity goes about 4 cm deeper for S23 than S30. Comparing the average grain-size for Pamlico Sound cores with their inventories demonstrates a general logarithmic relationship, with inventories decreasing as average median grain-size increases (Figure 37). This may be a function of less sediment accumulation in areas of higher energy, or due to differences in adsorption properties of the sediment (Ravichandran et al., 1995).

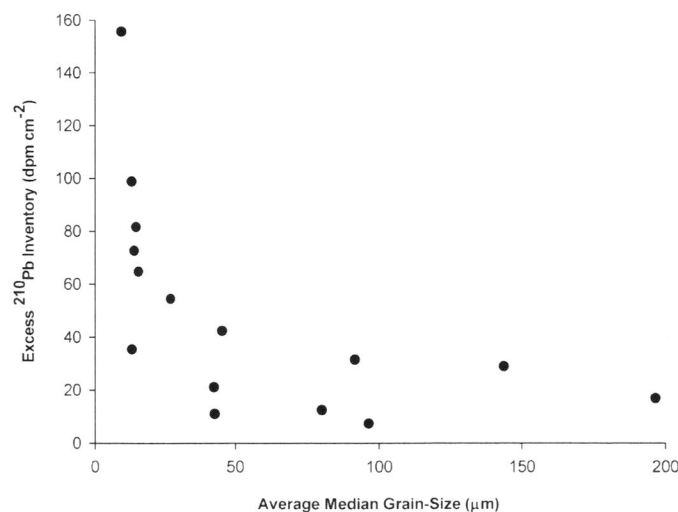


Figure 37: Relationship between excess ^{210}Pb inventories (in dpm cm⁻²) and average median grain-size (in μm) for Pamlico Sound cores.

Excess ^{210}Pb Profiles

In the majority of the core environments (i.e., protected embayment, central basin, etc.), there is at least one excess ^{210}Pb profile that shows some effects of changes in grain-size (Figure 38). At S10, the excess ^{210}Pb activity decreases regularly with an increase in grain-size downcore. At depth, where the core lithology changes from a clayey silt to a fine sand, excess ^{210}Pb decreases to zero. The excess ^{210}Pb profile for S30 appears to be dominated by grain-size effects; depletions in excess ^{210}Pb near the surface and at depth correspond with the coarsest grain-sizes in the core. Finally, the upper portion of the excess ^{210}Pb profile at S31 shows a decrease in activity that is related to a layer of slightly sandy material at the surface.

Metal Abundances

Although the complexity of metal abundance profiles seems to suggest that mechanisms other than grain-size are the dominant control on their shapes, comparing the metal concentrations for each site shows the influence of grain-size on relative concentration (Figures 33 and 34). For instance S12, the sandiest of all the cores analyzed for metals, has the least concentration. S41, located near the flank of Bluff Shoal, contains more sand than any of the deeper water cores analyzed for metals. It has metal values intermediate between S12 and the deeper water cores. Finally, the deep water cores (S31, S32, and S50) all have similar percentages of fines and relatively similar metal concentrations.

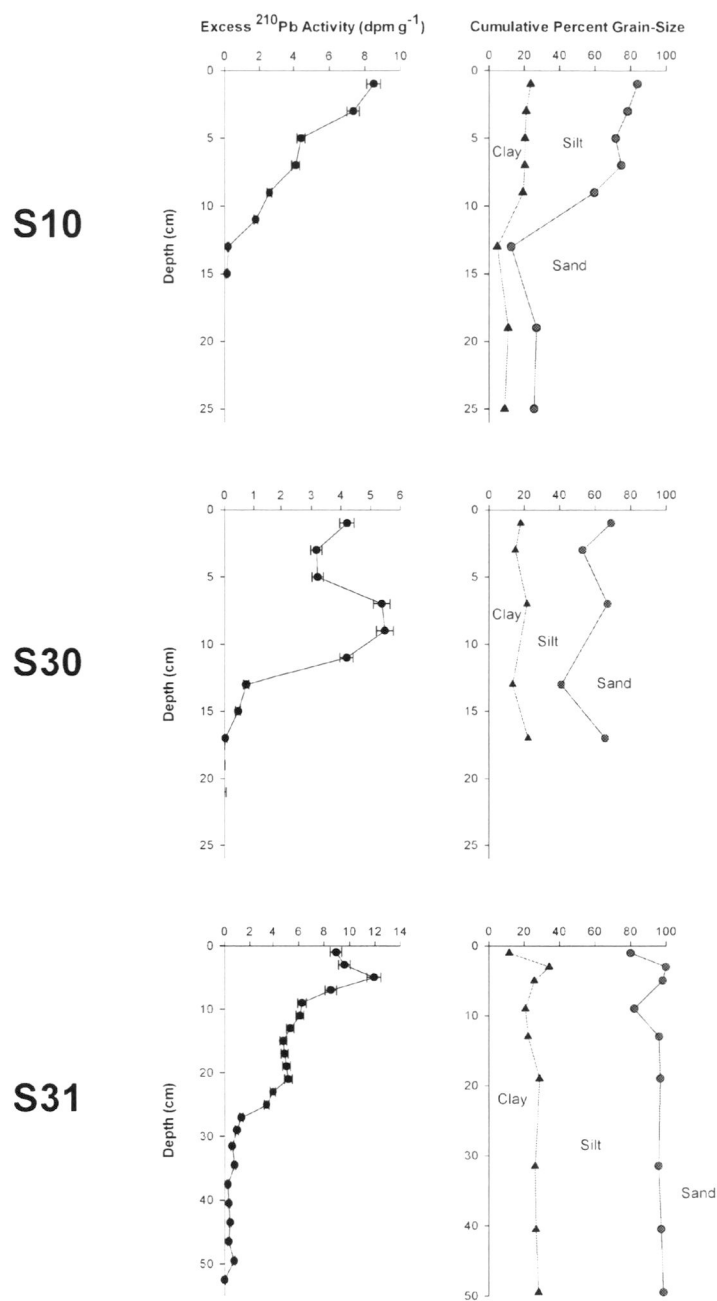


Figure 38: Grain-size related anomalies observed in excess ^{210}Pb profiles when compared with cumulative percent grain-size for S10, S30, and S31.

The apparent depletion in metal values with increasing grain-size could be more a function of the amount of organic carbon than grain-size alone. Wright (1974) was unsuccessful in teasing out which parameter (grain-size or organic carbon) was the dominant control on trace metal abundances in Pamlico Sound sediments. He found that the two parameters correlated so well ($r^2 = 0.905$), that it was impossible to determine which was dominant. Median grain-size in this study has a good agreement with organic carbon, and similar to the excess ^{210}Pb inventories listed above, the relationship is a logarithmic function (Figure 39). Thornton and McManus indicated that increases in enrichment of $\delta^{15}\text{N}$, and/or C:N ratios with increasing grain-size could occur; however, this phenomenon was not observed in the limited data acquired from Abbene (2004) for this study.

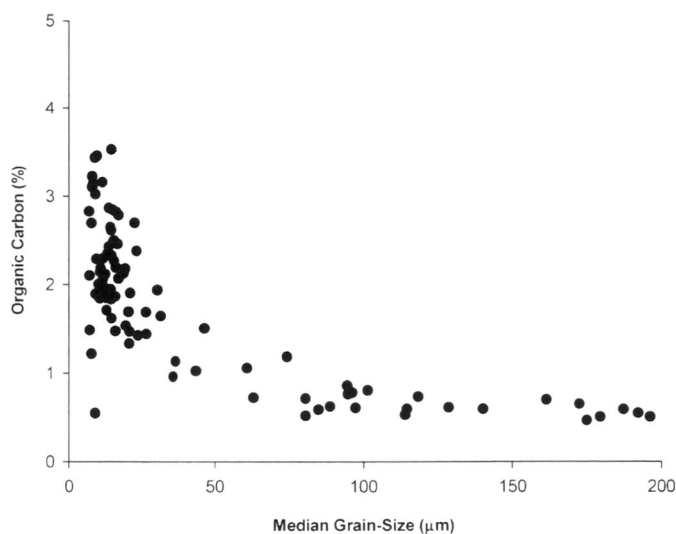


Figure 39: Relationship between organic carbon (in %) and median grain-size (in μm) for Pamlico Sound cores.

Geochemical Indicators of Pamlico Sound Sediment Dynamic Processes

Geochemical tracer data can be used to illustrate a multitude of factors within a particular system relating to both sediment provenance (e.g. Thornton and McManus, 1994) and sediment dynamics (e.g. Giffin and Corbett, 2003). Some of the processes documented in this study include sediment mixing, spatial sediment accumulation patterns, event related sediment deposition/erosion, modern sediment and organic matter transport/distribution pathways, and some possible changes in either sediment source or sediment dynamics since the 1960's.

Sediment Mixing

All three radionuclides (^7Be , ^{210}Pb , and ^{137}Cs) used in this study helped to illustrate the degree of mixing in Pamlico Sound. Beryllium-7 activity was present at depths ranging from ~0-6 cm, averaging approximately 3 cm (Figure 26). Beryllium-7 activity at depth could also be an indication of rapid deposition; however, the excess ^{210}Pb profiles, grain-size data, or observations of core logs did not show any evidence of this. There were two significant rain events that occurred within the six months prior to the sampling period in 2002 (Figure 40), that could have facilitated the deposition of some ^7Be . Additionally, the upper 8-10 cm of the excess ^{210}Pb profiles in many of the cores (especially those from the central basin), display nearly vertical activities or alternations in activities which help to corroborate mixing indicated by ^7Be (Figures 21, 22, 23).

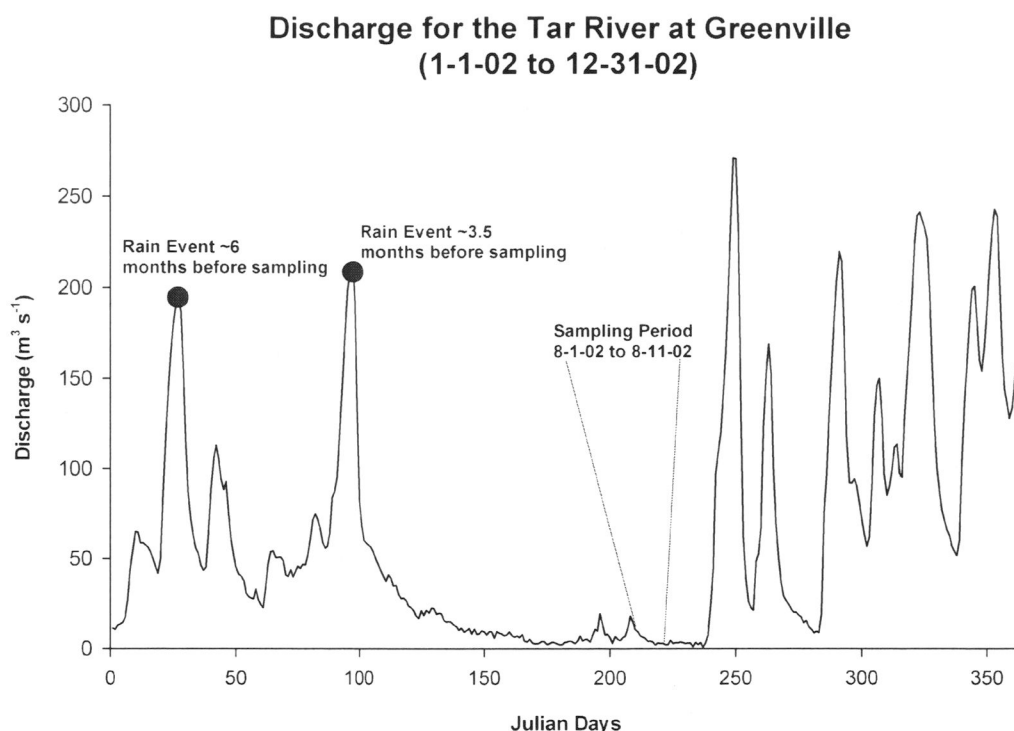


Figure 40: Discharge (in $\text{m}^3 \text{s}^{-1}$) for the Tar River at Greenville for the year of 2002. Indicated are two rain events (circles) occurring within about 6 months of the sampling period in early August, 2002 (data obtained from www.usgs.gov).

Of the three radionuclides used in this study, ^{137}Cs was perhaps the best indicator of sediment mixing and reworking. In almost half of the cores, ^{137}Cs peaks are poorly-developed or not present at all. This could represent an unconformity caused by sediment removal. However, in the majority of cases it is probably caused by the obliteration of the peak due to mixing. In every case where the ^{137}Cs peaks are well-defined, there is a tailing off of ^{137}Cs activity above and below the peak. If no mixing were occurring and sedimentation were rather constant, then there would be a horizon of no ^{137}Cs activity beneath the peak, reflecting a period before the onset of atmospheric bomb testing. Such a horizon is not present in any of the cores, as each of them have ^{137}Cs activity to, and

often beyond, the depth at which there is no excess ^{210}Pb activity. This sort of phenomenon could be expected in cases where sediment resuspension is very intense; however, ^{137}Cs can become mobile in anoxic sediments, which could cause some downward or upward migration of the radionuclide as well (Christiansen et al., 2002; Bondavalli, 2003). The fact that ^{137}Cs activity exists at some depths where there is no excess ^{210}Pb can be explained by the longer half-life of ^{137}Cs (30.1 years) in relation to ^{210}Pb (22.3 years) and mixing or diffusion following deposition. This greater half-life allows ^{137}Cs to persist even when excess ^{210}Pb activity has gone to zero.

Just as with the majority of the estuarine cores, mixing is evident in the ^{137}Cs profile of the marsh peat core at NBP. The ^{137}Cs peak is very well-constrained and distinct in this core. As would be expected in a case where there is little to no mixing, ^{137}Cs activity tends to tail off rapidly above the 1963 horizon; however, there is significant activity beneath the peak and at depth, which would not be expected in a case where there is no mixing. The mechanism that likely controls the distribution of ^{137}Cs activities at NBP is a downward transport of sediments and organic matter via physical reworking by roots. Another possible explanation could be ^{137}Cs diffusion downward through porewater as a response to anoxic conditions (Bondavalli, 2003); however, if this were the case it would seem like there would be upward diffusion during times of higher water, which would eliminate the distinctiveness of the ^{137}Cs peak.

Spatial Sediment Accumulation Patterns

In a system where there is no sediment removal or transport, no non-atmospheric sources of radionuclides exist, and radionuclide scavenging occurs at 100% efficiency.

Radionuclide inventories in sediment cores would be expected to equal the atmospheric input of radionuclides (Benninger and Wells, 1993). Thus, if an atmospheric inventory is known, it is possible to compare the relative efficiencies of scavenging in coastal environments, which might yield clues to sediment transport and deposition patterns. A record of excess ^{210}Pb inventories for eastern North Carolina is known from a soil core near Raleigh (Graustein and Turekian, 1986) and salt marsh cores at Cedar Island and North River (Benninger and Wells, 1993). The excess ^{210}Pb inventories of these cores average $\sim 26.5 \text{ dpm cm}^{-2}$ and are presumed to represent a record of only atmospheric deposition of excess ^{210}Pb (Benninger and Wells, 1993). The average value of these inventories compares extremely well with the inventory obtained from the marsh core at North Bluff Point ($\sim 25.2 \text{ dpm cm}^{-2}$).

An examination of the spatial distribution of excess ^{210}Pb inventories for Pamlico Sound cores (Figure 41) illustrates that the majority of the cores have inventories greater than the expected atmospheric inventory. From a standpoint of inventories alone, it appears that Pamlico Sound is largely an area where there is significant input, rather than export, of excess ^{210}Pb from some source. However, a direct comparison of atmospheric excess ^{210}Pb with those in the sediment cores is insufficient to illustrate sediment transport and deposition patterns, as there are other factors to consider. For instance, it has been shown that there is an inverse relationship (a function of particle-reactivity and energy levels) between grain-size and excess ^{210}Pb inventories (Figure 38). This relationship is observed in many of the cores in Figure 41, as the areas which have the highest inventories generally occur in the finest sediments.

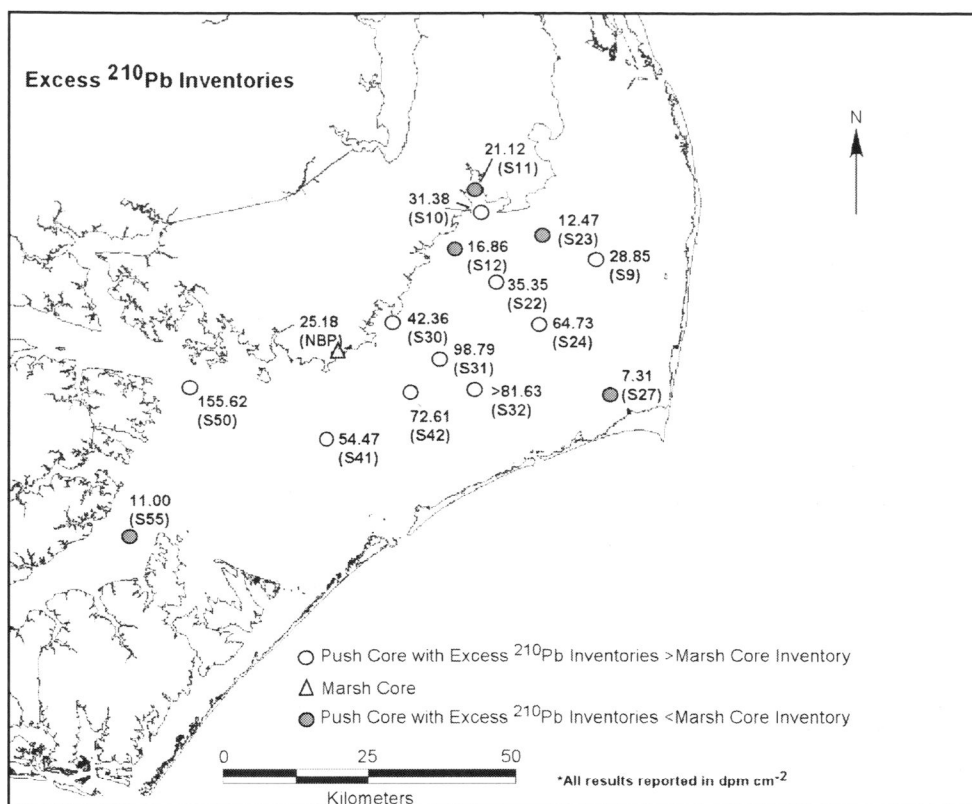


Figure 41: Excess ^{210}Pb inventories (in dpm cm^{-2}) for Pamlico Sound cores and the marsh core at NBP.

Event Related Sediment Removal/Deposition Processes

Two of the cores (S11 and S55) collected from areas of similar grain-size (clayey-silt) show inventories lower than the expected atmospheric excess ^{210}Pb inventory. In comparing the inventories of these individual cores with the other cores from their same environments, the protected embayment cores (S10 and S11) both have fairly similar excess ^{210}Pb inventories, while the estuary mouth cores (S50 and S55) have inventories with an order of magnitude difference. The minor differences in inventory at S10 and S11 can probably be attributed to small changes in lithology or minor sediment

transport/redistribution out of or within the protected embayment; however, the large differences in inventories between S50 and S55 seem to suggest a major sediment removal at S55.

Evidence for Sediment Removal at S55

Aside from the vast differences in excess ^{210}Pb inventories, other evidence exists in the radionuclide data at S55 that lend credence to the idea of considerable sediment removal at this location. Comparison of the excess ^{210}Pb profiles (Figure 23) from the estuary mouth cores shows that the activity extends to a much lesser depth at S55 than at S50 (< 10 and >40 cm, respectively). Additionally, calculated sediment accumulation rates from both the CIC and CF:CS models are much greater at S50 (0.53 (CIC) and 0.37 (CF:CS) cm y^{-1}) than S55 (0.06 (CIC) and 0.03 (CF:CS) cm y^{-1}).

Perhaps the most striking evidence in support of major sediment removal is found by comparing ^{137}Cs profiles for S55 with S50. At S55 the ^{137}Cs peak is truncated, with the maximum value near the surface, while at S50, the ^{137}Cs peak is well-preserved (~ 20 cm). By matching up the surface activity of ^{137}Cs at S55 with a similar activity in the profile at S50 at depth, there is an excellent correlation with both activity and profile shape (Figure 42). Assuming that under normal, non-erosional conditions the two estuary mouth sites had similar sediment accumulation rates, approximately 20 cm of sediment could have been removed from S55. The mechanism of this removal is unknown; however, recent studies in North Carolina estuaries have shown that significant amounts of sediments can be resuspended by both natural (wind events, storms, etc.) and anthropogenic (trawling) mechanisms (Benninger and Wells 2001a and b; Giffin and

Corbett, 2003; Corbett et al., 2004; Frank, 2004; Vance, 2004). In fact, some studies suggest that deeper water portions of the nearby Albemarle Sound may be characterized by sediment erosion rather than sediment accumulation as a function of limited accommodation space (Corbett et al., 2004; Vance, 2004).

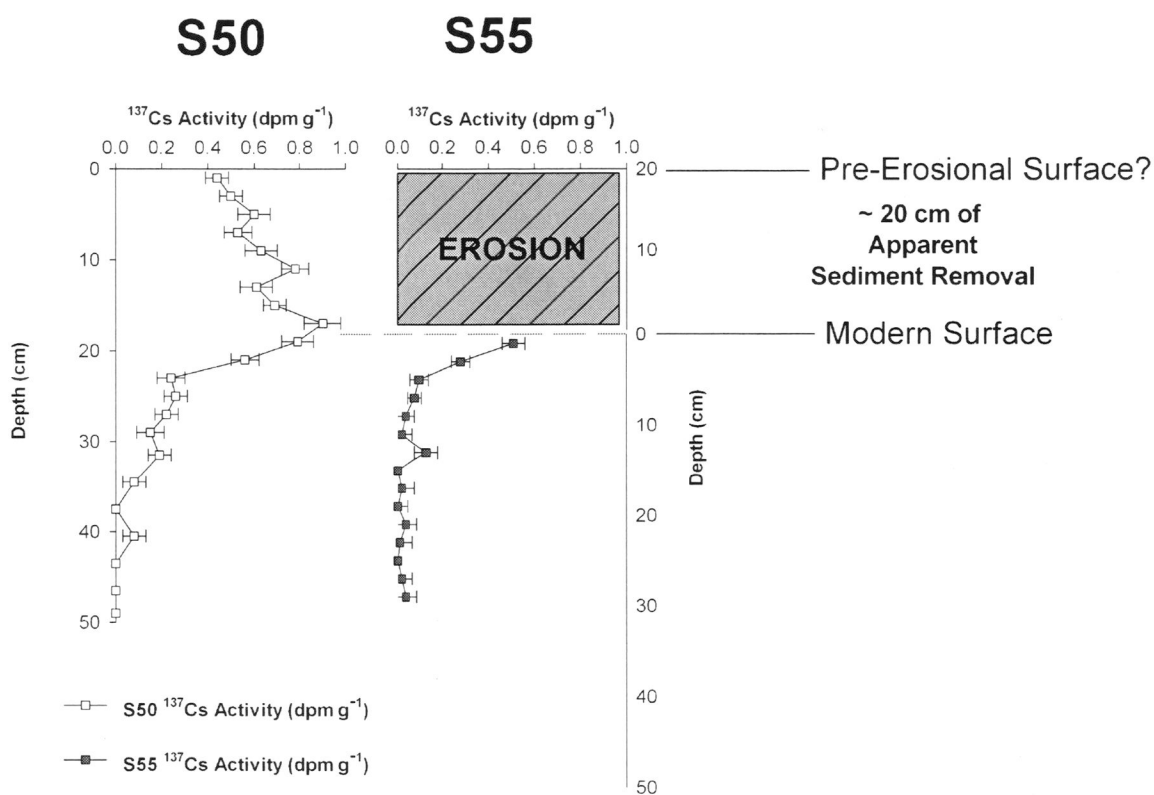


Figure 42: Apparent erosional event at S55 removing ~20 cm of sediment as is indicated by the truncated ^{137}Cs peak.

Mechanisms of Sediment Removal at S55

Cesium-137 profiles from two cores collected from the mouth of the Neuse River by Benninger and Wells (1993) do not display the same truncation of the ^{137}Cs peak as S55, although the cores were collected from the same area. The ^{137}Cs peaks in those cores, collected from the same site in 1982 and again in 1990, are well-preserved at depths of about 13 cm (1982) and 21 cm (1990), respectively. Increases in the depth of the ^{137}Cs peak over time in the Benninger and Wells (1993) cores seem to indicate that this area, at least prior to 1990, was characterized by sediment accumulation.

Therefore, the cause of the sediment removal S55 is probably not a result of an erosive trend or limitation in accommodation space as is observed in the Albemarle Sound, and may be event related (Corbett et al., 2004). One significant nor'easter, with hurricane force winds that persisted for over 24 hours struck the North Carolina coast in 1993 (Barnes, 2001). Little precipitation was associated with this event, possibly increasing its potential for eroding estuarine sediments rather than depositing them. The fact that the highest ^{137}Cs activities occur right at the surface, rather than a few cm beneath it (to account for ~ 10 years of sediment accumulation from 1993-2003) seems to suggest that the removal occurred more recently.

There were numerous hurricanes that impacted the North Carolina coast during the late 1990's that could have resuspended and transported significant amounts of sediment locally. Some recent studies have suggested that storms such as these with great precipitation and shoreline erosion potential can lead to net sediment accumulation in portions of some of the North Carolina estuaries, rather than erosion (Benninger et al.,

2001a and b; Corbett et al., 2004). In response to the three 1999 hurricanes (Dennis, Floyd, Irene) impacting the NC coast, Benninger et al. (2001a and b) noted that both the upper and lower portions of the Neuse River estuary experienced some erosion; however, the lower portions of the estuary near Oriental, NC also showed a net deposition. S55 was located farther down the Neuse River estuary than the site at Oriental, so it is possible that the sediment removal observed here is related to these storms. One might expect that if this removal were related to some major storm events affecting eastern North Carolina, then perhaps a similar ^{137}Cs profile would occur in other Pamlico Sound cores, particularly at the other estuary mouth site S50. However, the impacts of these storms vary regionally and are dictated by many variables including the track and intensity of the storm, estuarine shoreline geometry, and estuarine orientation (S.R. Riggs, personal communication).

Sediment Deposition Related to Mid-20th Century Storms

During the 1950's and early 1960's the North Carolina coast experienced one of the most storm active periods on record. Some nine hurricanes and one of the most famous nor'easters in history struck during this time span, costing hundreds of millions of dollars and dozens of lives (Barnes, 2001). It appears that in at least one of the Pamlico Sound cores (S31 in the depocenter of the sound), there is some signature retained in the sediment record of this climatically active time period. Figure 43 shows profiles of excess ^{210}Pb , ^{137}Cs , $\delta^{15}\text{N}$, C:N ratio, and Zn/Al. Highlighted (box) is the core interval stretching from about 12-20 cm, showing the region where some of the geochemical tracers have anomalous values, roughly corresponding to the ^{137}Cs peak. Over this

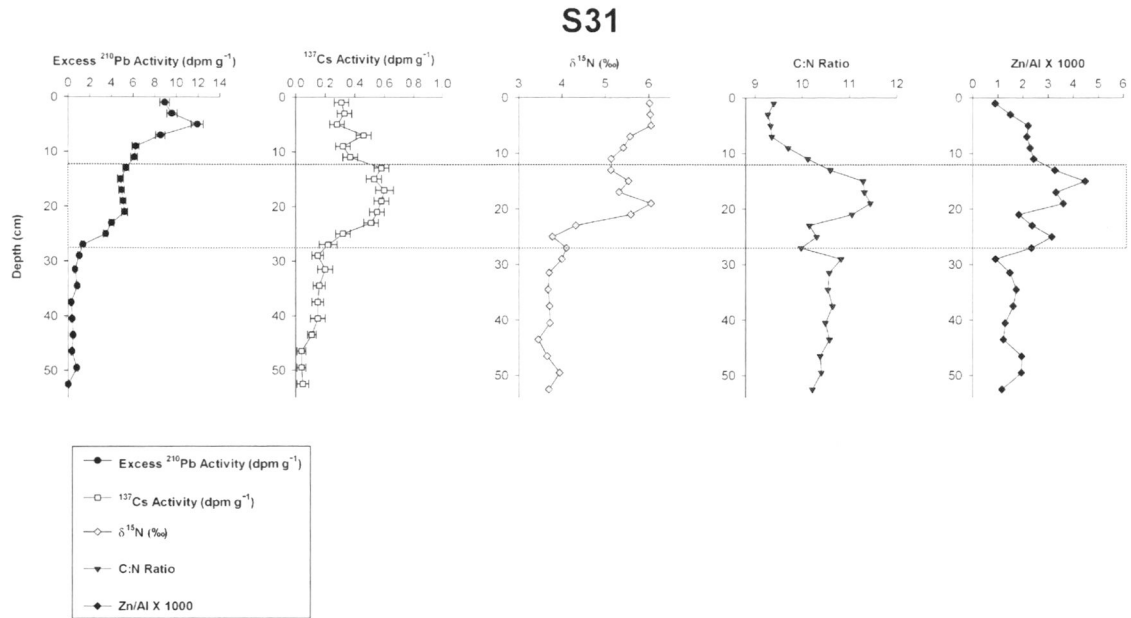


Figure 43: Multiple geochemical profiles for S31 indicating apparent storm influences from the 1950's and 1960's on sedimentation. (box indicates section of interest)

portion of the profiles, activities for excess ^{210}Pb and ^{137}Cs are both nearly vertical, which may suggest a period of intense mixing and/or rapid sedimentation that would be expected with major storm events. At the base of this apparent mixing/rapid sedimentation zone of the core, there is a distinct layer of small, well-preserved, disarticulated *Rangia cuneata* shells immediately overlain and underlain by muds barren of shells. The *Rangia cuneata* clams cannot tolerate the anoxic nature of Pamlico Sound central basin sediments, preferring instead to dwell in the shallower waters of the perimeter platform environment (S.R. Riggs, personal communication). Their presence here must indicate some sort of transport mechanism capable of depositing the shells. If this unit is storm related it could result from the preferential settling of the heavier shells

over the muddy sediments during periods of resuspension, or a winnowing of fines leaving the shells as a lag deposit. If either of these were the case, the shells could concentrate in a distinct layer, accounting for the lack of shells above and below this interval. Another possibility that could explain the distinctiveness of this unit is related to the decomposition of the *Rangia* clams following their death. It has been observed that the smaller clams can become buoyant as their shells fill with gases released during the decomposition process (S.R. Riggs, personal communication). If these clams experienced a massive die off in response to eutrophication or increased turbidity following a major storm, then the buoyant decomposing clams could be transported to the center of the sound, becoming deposited in distinct layers. This could explain the well-preserved nature of the shells.

There is also an abrupt increase in $\delta^{15}\text{N}$ and C:N ratio in this section of interest. One likely response of all of the storms during this time period would be an increase of organic matter deposition from runoff. This could directly effect the C:N ratio by introducing large amounts of organic carbon into the system. Increases in $\delta^{15}\text{N}$ and the C:N ratio could result from an increase in biological degradation as a response to organic matter loading in the estuary or simply an increased influx of enriched $\delta^{15}\text{N}$ organic matter from urban areas. The metal/Al ratios all show a similar increase during the time period of interest; however, only Zn/Al is shown for comparison. The enrichment of Zn could result from a transport of metal-rich sediments from one of the major tributary estuaries or, less likely but possibly, the Albemarle Sound as a response to flushing. Both

the Neuse River and Albemarle Sound have been documented to have higher metal concentrations (Benninger and Wells, 1993; Riggs et al., 1993) than Pamlico Sound.

Modern Sediment Transport Paths and Apparent Organic Matter Sources

In order to elucidate the modern sediment transport paths and apparent sediment sources, it was useful to examine the surface mixed layer as defined by the greatest depth of significant ^7Be activity. By looking at this surface layer rather than an individual surface sample, sediment mixing was accounted for. Surface mixed layer $\delta^{15}\text{N}$ values (Figure 44) show that all of the average marsh peat grabs are depleted relative to the

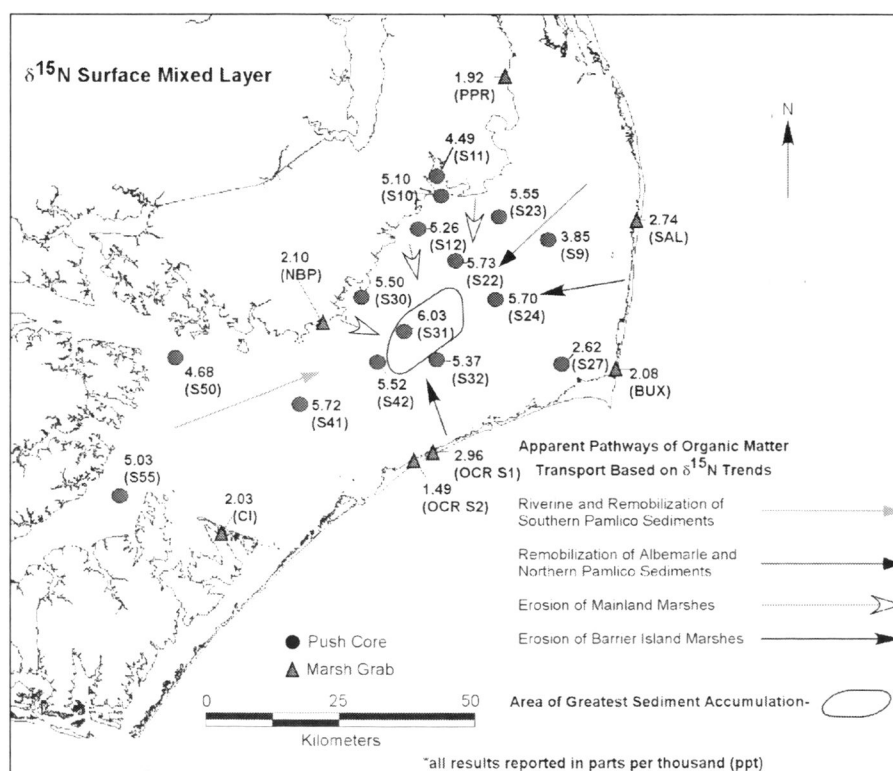


Figure 44: Apparent pathways of organic matter transport based on $\delta^{15}\text{N}$ trends (in ‰). Enrichment in $\delta^{15}\text{N}$ is seen in all directions toward the center of Pamlico Sound (S31), the area of greatest sediment accumulation (ellipse).

estuarine samples. Also, there is an enrichment in the $\delta^{15}\text{N}$ signature toward the center of the sound (S31) in every direction. Thus, it appears that organic matter associated with sediments is being continuously enriched in $\delta^{15}\text{N}$ during multiple periods of transport, before coming to rest in the center of the sound. This is supported by the fact that S31 has excess ^{210}Pb activity to the greatest depth (~50 cm) of any core collected. Since this area is the depocenter of the sound, organic matter here is probably derived from a number of sources including riverine, remobilization of Pamlico Sound and Albemarle Sound sediments, mainland marsh erosion, barrier island marsh erosion, and autochthonous biogenic production.

Mixed layer $\delta^{13}\text{C}$ values (Figure 45) and C:N ratios (Figure 46) illustrate some of the apparent sources of organic matter. The mainland marsh peats show a terrestrial $\delta^{13}\text{C}$ signature typical of C_3 plants, while the barrier island marshes show values more typical of an intermix of C_3 and C_4 plants. Pamlico Sound samples don't exhibit a very wide range of $\delta^{13}\text{C}$ values. Typically the sediments at the mouths of the Pamlico and Neuse River estuaries, near the mainland shoreline, and in the northern Pamlico Sound in general show slightly more terrestrial $\delta^{13}\text{C}$ values than those in the middle of the sound.

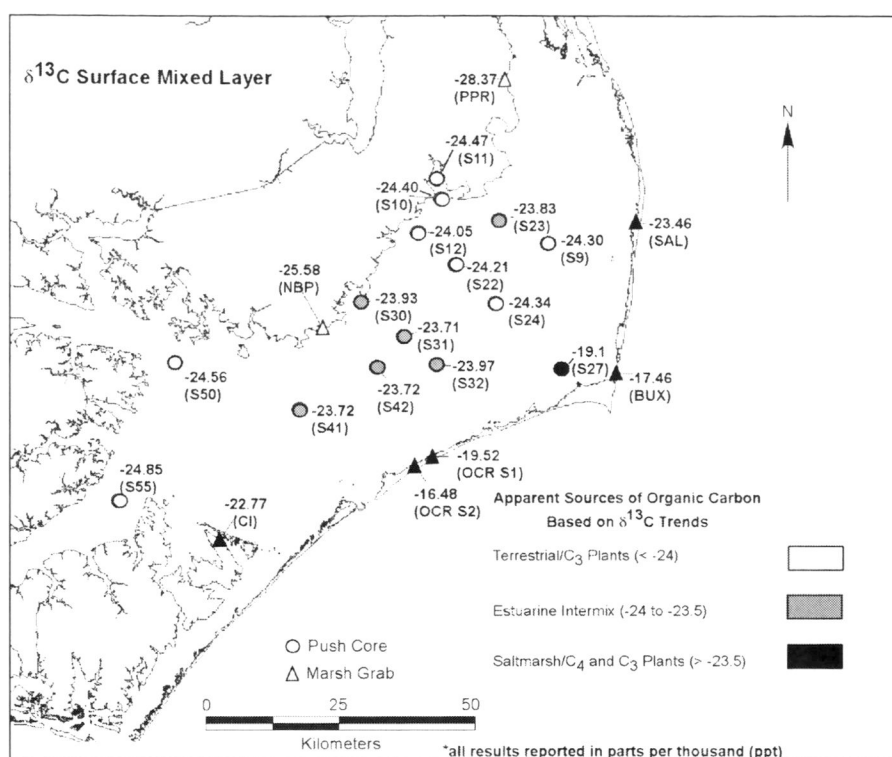


Figure 45: Apparent sources of organic matter based on $\delta^{13}\text{C}$ trends (in ‰). Values generally increase toward the depocenter of the sound (S31). Values less than -24‰ are representative of more terrestrial sources, while values of -23.5‰ or greater indicate a mixture of C₄ and C₃ plants.

For the C:N ratios, values of 11 or greater have been defined as dominantly terrestrial, 11 to 9 as a terrestrial marine intermix, and 9 or less as dominantly marine. The marsh grabs generally reflect a terrestrial source, although it is much greater in the organic carbon-rich mainland marsh grabs than the barrier island grabs. Although most of the estuarine samples have very similar values, there is a general decrease in C:N ratio toward the center of the sound. This seems to concur with the $\delta^{15}\text{N}$ transport paths, showing a preferential removal of carbon over nitrogen during sediment transport and/or resuspension.

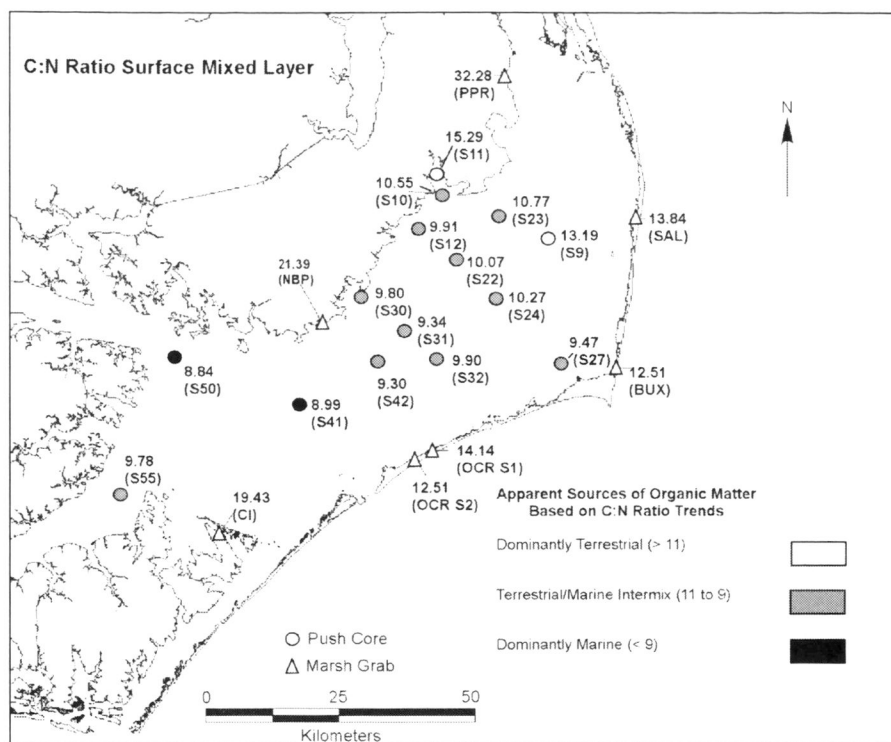


Figure 46: Apparent sources of organic matter based on C:N trends. Values of 11 or greater have been defined as dominantly terrestrial, while values of 9 or less are indicative of organic matter that is dominantly marine.

In order to better confirm that the organic matter sources indicated by the individual tracers ($\delta^{13}\text{C}$ and C:N ratios) in the figures above were actually distinct, a comparison of the individual tracers to one another was necessary. By plotting the tracers against one another, different suites of organic matter related to source can be identified (Thornton and McManus, 1994). The upper portion of Figure 47 shows a plot of the average C:N ratios vs. the average $\delta^{13}\text{C}$ values for the mainland and barrier island sites and the surface mixed layer for Pamlico Sound sites. There is significant scatter in the marsh values, but the mainland peats are generally characterized by higher C:N ratios and more terrestrial $\delta^{13}\text{C}$ signatures than are the barrier island peats. The majority of the

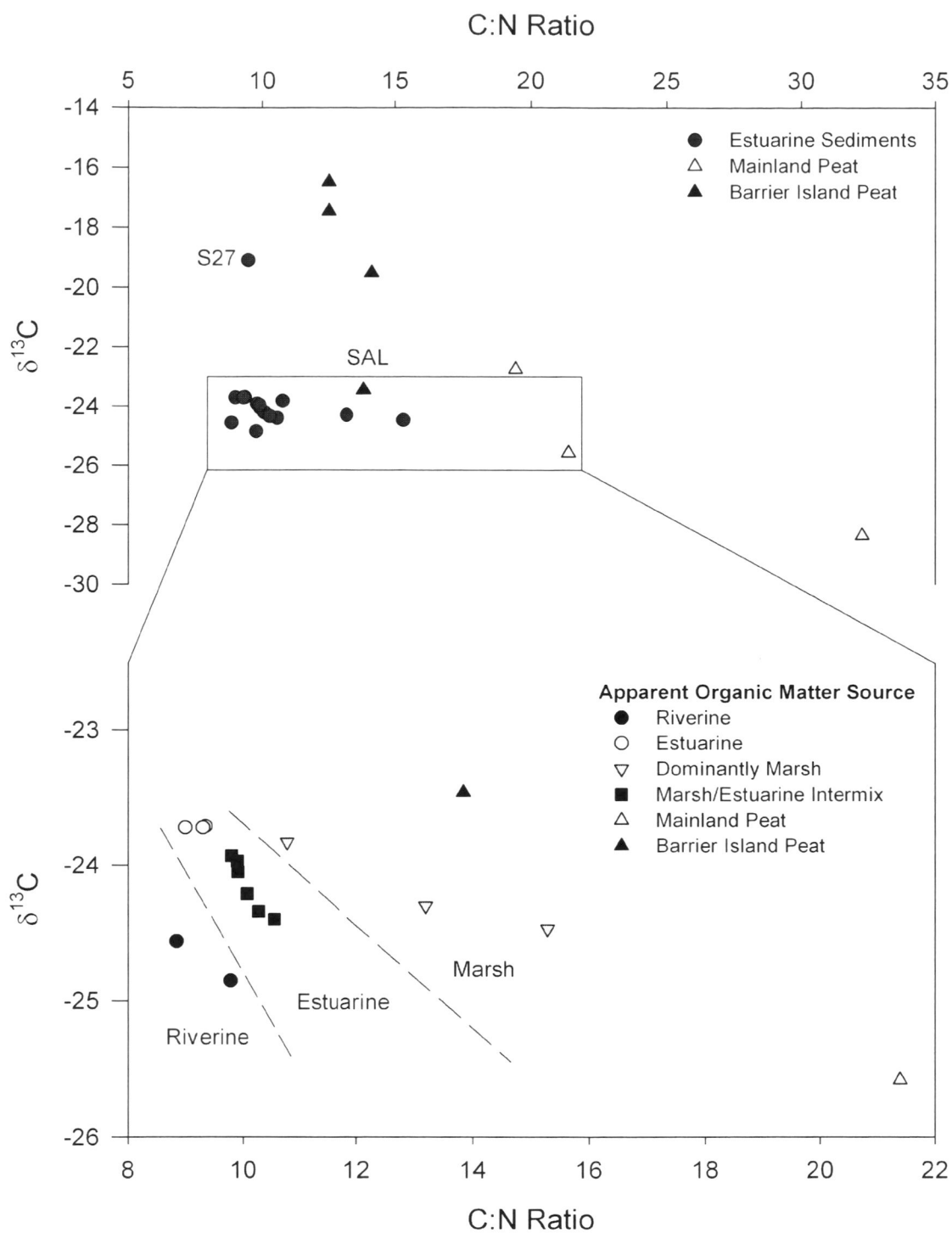


Figure 47: C:N ratio vs. $\delta^{13}\text{C}$ for mainland and barrier island peat grabs and Pamlico Sound surface mixed layer sediments. Also highlighted are apparent organic matter sources for the estuarine sediments.

estuarine samples plot in the same general area; however, upon closer examination (lower portion of Figure 47) it becomes apparent that the estuarine data fall into distinct regions. These regions appear to be representative of the dominant organic matter source in that location (marsh, marsh/estuarine intermix, estuarine, riverine). A spatial examination of these sources (Figure 48) shows that the influence of a marsh source is greatest in the northeastern part of Pamlico Sound, and generally decreases toward the center of the sound, becoming more estuarine. This agrees well with the organic matter sources indicated in Figures 45 and 46.

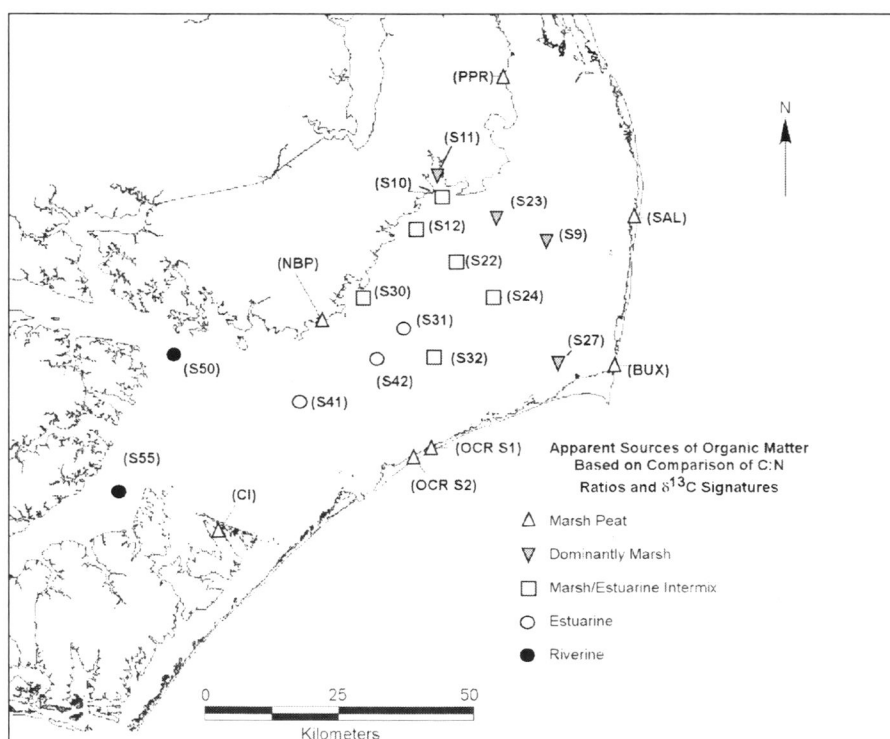


Figure 48: Apparent sources of organic matter based on comparison of C:N ratios and $\delta^{13}\text{C}$ signatures. Marsh influence decreases from the northeast to southwest toward the center of Pamlico Sound.

Recent Changes in Sediment Dynamics or Sediment Source

In Pamlico Sound central basin cores, Zn and Cu concentrations generally decreased above the ^{137}Cs peak toward the surface, particularly when normalized to Al (Figure 36). This seems to indicate that metal sources have either reduced in recent history, the sources have been diluted, or the metals are being removed by some mechanism. If it is indeed a reduction in metal input to the estuary over time, one would expect a similar decrease in metal values for surface sediments in the Neuse River. However, Benninger and Wells (1993) show the highest metal concentrations and metal/Al ratios at or near the surface in Neuse River sediments. Point sources of Zn and Cu to the Neuse River have been identified by Riggs et al. (1991) as being from the Bridgeton/New Bern area of Craven County as well as the Cherry Point Marine Corps Air Station. According to the US Census Bureau, Craven County has had an increase in population from 81,613 in 1990 to 91,436 in 2000 (~10% increase) (US Census 1990 SFT1; US Census 2000 SF1). Considering this population increase, with the assumption that the majority of Zn and Cu is sewage effluent related, it seems highly unlikely that there has been an overall reduction of Zn or Cu input into the system.

Another possibility is that perhaps there has been some sort of dilution in Pamlico Sound sediments with metal-poor sediments. The grain-size data for central Pamlico Sound cores show that relative percentages of clay, silt, and sand remain virtually unchanged throughout the cores and median grain-size changes are insignificant (Figures 15 and 16). The fact that the grain-size data remain unchanged with depth for these cores eliminates any grain-size effect as a cause for upcore metal depletion. One possible

explanation for the depletion of metals in near surface sediments is an increase in marsh erosion as a sediment source over time. It has already been established that marsh sediments are relatively depleted in metals compared to estuarine sediments (above). Erosion rate data over multiple time intervals indicate that marsh erosion rates have increased over time (Riggs et al., in preparation).

Table 14 shows aluminum normalized Zn and Cu average data for mainland and barrier island marsh grabs, as well as the surface mixed layer and total core data for central Pamlico Sound cores (S31, S32, and S41). It is evident that the metal/Al ratios in the surface mixed layer of Pamlico Sound cores more closely resemble the average marsh grab values than averages for the total core. Mainland marshes consist of thicker peats eroding at a faster rate than barrier island marshes. It would then be expected for $\delta^{13}\text{C}$ values to become more terrestrial (i.e., more negative) over time, and indeed this trend is observed in the central basin cores (Figure 33) and in virtually all other cores analyzed by Abbene (2004).

Table 14: Average Zn/Al and Cu/Al (X 1000), $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and C:N ratio values for mainland and barrier island marsh grab samples and Pamlico Sound central basin surface mixed layer and total core.

Ratio	Marsh Grab Average		Pamlico Sound Central Basin Average	
	Mainland	Barrier Island	Surface Mixed Layer	Total Core
Zn/Al X 1000	1.92	1.61	2.65	3.77
Cu/Al X 1000	0.45	0.40	0.36	0.63
$\delta^{13}\text{C}$	-25.57	-19.81	-23.81	-23.48
$\delta^{15}\text{N}$	2.03	2.44	5.08	4.74
C:N Ratio	23.94	13.31	9.66	10.37

There is another possibility that might explain decreases in metal concentrations above the ^{137}Cs peak of ~1963. Perhaps there has been a change in sediment dynamics, such as an increase in sediment resuspension related to natural or anthropogenic influences. Trace metals adsorbed to sediment surfaces can become mobile to the water column if there is any sediment resuspension, although their particle-reactive nature makes them re-adsorb to sediments quickly (Beno and Gibbs, 1990; Riggs et al., 1989; Cearreta et al., 2000). Pamlico Sound is not fetch limited and is fairly shallow (generally <6m), so any significant storm has the potential to resuspend sediments. Hurricanes, in particular can cause a lot of sediment remobilization, in fact it has been suggested that over just a few hours of hurricane force winds, several years worth of sediment deposition and transport can occur (Riggs et al., 1993; Riggs et al., in preparation). Following the hurricane-active 1950's there was a period of general quiescence with respect to hurricane landfalls in North Carolina. North Carolina did not experience any significant hurricanes until the mid 1990's (Barnes, 2001). The last decade, however, has been the most intense storm period on record with over 12 major storms (Riggs and Ames, 2003). Therefore, it seems likely that this reduction in metal activity since the 1960's could be the result of hurricane-related storm activity.

Another possible sediment dynamics-related explanation could be anthropogenic effects related to shrimp trawling. Shrimp trawling in Pamlico Sound began in the early 20th century; and by the 1960's record numbers of boats were on the water. Advances in technology in the years since have reduced the number of shrimp boats, but have increased the number of trawl nets that a single boat can pull, increasing productivity

(NCFA, 2001). Increased trawling over the years could resuspend sediments multiple times during a season, potentially releasing any adsorbed metals into the water column. Additional geochemical evidence in $\delta^{15}\text{N}$ and C:N ratio data (Figure 33) provided by Abbene (2004) seems to support this explanation. As organic matter associated with particulate matter typically goes through the greatest nitrogen fractionation during sediment transport, enrichment of the $\delta^{15}\text{N}$ signature is expected with any sediment resuspension (Owens, 1987; Thornton and McManus, 1994). In S31, S32, and S41 there is a marked increase in $\delta^{15}\text{N}$ following the ^{137}Cs peak. Additionally, the C:N ratio shows a decrease in value above the ^{137}Cs peak. This could result from a preferential removal of carbon relative to nitrogen during the resuspension process. Alternatively, or in concert with preferential organic carbon removal, sediment resuspension by trawling could induce nutrients into the water column, increasing the marine phytoplankton biomass. Although marine phytoplankton typically have a low C:N ratio (Matson and Brinson, 1990), which would explain the upcore decrease in the C:N ratio, organic carbon derived from marine phytoplankton is usually isotopically heavier (i.e., more positive) than terrestrial derived organic carbon. Since the $\delta^{13}\text{C}$ values become more terrestrial upcore, an increased marine phytoplankton organic carbon source over time seems unlikely.

Alteration of metal activities and carbon and nitrogen data is most likely a function of some combination of the factors above. The steady increase of $\delta^{13}\text{C}$ observed in Pamlico Sound cores over time is probably a function of increased terrestrial input from mainland marsh erosion over time. The nature and timing of the reduction of metal activities, C:N ratios, and increase in $\delta^{15}\text{N}$ values, could all be explained by the effects of

increased sediment resuspension related to shrimp trawling from the 1960's until the present.

Marsh Peat Geochemistry

Stable Nitrogen $\delta^{15}\text{N}$

The $\delta^{15}\text{N}$ signatures for subsurface peat grabs are depleted relative to surface marsh grabs, at every site where both grab types are present. In cases where there is not significant marsh peat thickness developed, such as the Ocracoke sites, the more degraded peats have the most depleted signature. This same decreasing $\delta^{15}\text{N}$ trend with depth/peat degradation is observed in the marsh core from NBP (Figure 30). Kalbitz and Geyer (2002) noted a similar phenomenon when comparing stages of humification in peat deposits with the behavior of nitrogen and carbon. They attributed this decrease of $\delta^{15}\text{N}$ with increasing peat degradation to the preferential removal of isotopically light ^{14}N by bacterial activity. The mainland peat grabs are lighter on average than are those of the barrier island marshes, which is to be expected as the mainland peats in general show a much greater degree of degradation.

Stable Carbon $\delta^{13}\text{C}$

There is a general trend of $\delta^{13}\text{C}$ depletion with increasing peat degradation among the mainland peats. Kalbitz and Geyer (2002) documented an opposite trend, suggesting that peats became enriched in $\delta^{13}\text{C}$ with increasing humification. They believed that this was a result of a decrease in the abundance of ^{13}C depleted lignin-derived aromatics during the degradation process. Therefore, the apparent correlation of

organic matter degradation with $\delta^{13}\text{C}$ signature observed in the mainland marsh grabs is probably related to a change to a more terrestrial OM source (i.e., greater C_3 plant dominance) over time. In some of the highly decomposed subsurface peat grabs large pieces of wood were found, suggesting that perhaps these peats, may have originated from swamp forest type environments. This would be in accordance with the lateral progression model of marsh migration, as a response to rising sea-level (Brinson, 1989; Riggs and Ames, 2003).

The barrier island marsh grabs show no definitive $\delta^{13}\text{C}$ pattern with either organic matter degradation or grab type. The three Salvo grabs, for example, have nearly identical $\delta^{13}\text{C}$ signatures, while at Buxton, there is a difference of $\sim 5\text{‰}$ between the two surface grabs alone. The Salvo signatures seem to indicate a marsh peat that has been dominated by the same vegetation type, or perhaps the same relative mixture of plant types, for an extended period of time, relative to the Buxton site. Conversely, the $\delta^{13}\text{C}$ signatures from the Buxton site imply a situation where plant OM sources, or at least the relative dominance of C_3 and C_4 plant types, have changed over time. Trying to deduce the timing of such events, or even a relative order of succession is difficult to do with only the grab samples collected for this study.

C:N Ratio

The influence of more terrestrial organic matter sources is apparent in the C:N ratios of the mainland peat grabs. C:N ratios for mainland grabs are generally higher than those of barrier island grabs and tend to increase with increasing peat degradation. As with the $\delta^{13}\text{C}$ signatures, this could be a function of an increased terrestrial influence in

the older mainland peats as terrestrial macrophytes are typically rich in carbon and depleted in nitrogen (Thornton and McManus, 1994). The C:N ratios of barrier island grabs show far less correspondence with organic matter degradation than the mainland grabs. The deeper peats at Salvo have greater C:N ratios than those peats above them; however, the subsurface peat at Buxton has a lower C:N ratio than the surface grabs there, despite having a greater percent organic carbon.

Metal Distributions

The surface marsh grabs of both the mainland and barrier island marshes tend to be enriched in metals (particularly Zn and Cu) compared to the subsurface peat grabs. Additionally, the barrier island marsh grabs tend to be metal-enriched relative to the mainland grabs. Elevated levels of metals (particularly Zn) in the younger surface peats could be indicative of increases in air pollution over time (Shotyk, 1990; Swolsman et al., 1996). It is somewhat unexpected to find elevated levels of trace metals in the barrier island grabs, as they are generally sandier than the mainland peats. One possible explanation for this could be an anthropogenic source related to the proximity of North Carolina highway 12. Heavy metals associated with the wear of automobile parts such as tires, brake pads, engine components, and body rusting; as well as the combustion of fossil fuels, can be deposited on road surfaces. The barrier island marshes were sampled in places relatively close to the road. And the barrier island marshes are much closer to this main road than are the mainland marshes to a road of comparable automobile activity. It is possible that runoff associated with rain events could be introducing metals into these peats. Another possibility could be related to the sands themselves. There are

several portions of the barrier island where heavy mineral placer deposits accumulate; however, heavy mineral studies of North Carolina barrier island, estuarine, and shelf environments document no minerals that would be enriched in either Zn or Cu (Duane, 1962; Guy, 1964; Grosz et al., 1990; Nickerson et al., 1993).

Iron and Aluminum Variability

The barrier island peats tended to show the greatest variation in Al, while the mainland peats had the greatest variation in Fe. Mud content has been documented to be a very important factor controlling the Al concentration, and metal concentrations in general, in marsh peats (Velde et al., 2003). Thus, the barrier island Al distribution is probably related to the highly variable grain-size that is present in these grab samples. Iron has been shown to be a very redox sensitive metal in marsh systems. In anoxic and acidic conditions, often present at depth in peats, Fe becomes mobile (Shotyk et al., 1992). The subsurface peat grabs from the mainland had some of the lowest Fe values of all the grabs, so perhaps the variability in Fe is related to these redox conditions.

Copper and Zinc Anomalies

Two of the grabs (CI G1; BUX G2) had anomalous trace metal concentrations in comparison with the other grab samples. Zn was elevated somewhat and Cu was elevated significantly (2x at CI; 5x at BUX) above the barrier island grab average. There are no particular trends in Al or Fe concentrations or the general character (i.e., elevated percentages of muds) of the samples that would indicate these elevated trace metal values. Elevated levels of Cu associated with ore deposits have been documented in peat bogs in Canada (Shotyk et al., 1990); however, no such deposits are known to exist in the

Coastal Plain. The Cedar Island site was relatively close to a home (~ 100 m). Cedar Island is a fairly remote area away from any urban centers that possess municipal sewage, so it is almost certain that the homeowner near the grab collection site disposed of waste via a septic tank. Thus the elevated levels of Zn and Cu could possibly be related to some sort of sewage effluent discharging from a local septic system. This is pure speculation based on limited data, but the proximity of the residence and the fact that the grab site was at lower elevation than the home make the scenario plausible. The reason for the extremely high Cu concentrations at Buxton is somewhat more difficult to explain. Many of the Buxton residents are on septic systems; however, no homes were in close proximity to the site. Velda et al. (2003) attributed increased levels of Cu in marsh sediments in the vicinity of Delaware Bay to bioaccumulation in the roots of *Spartina*.

Significance of Marsh Erosion as a Sediment Source to Pamlico Sound

In order to quantify the significance of marsh erosion as a sediment source to Pamlico Sound, it was necessary to relate the volume of eroding marsh sediment to the amount of sediment accumulating in the sound. A number of assumptions were made in the following calculations including: 1) average peat thicknesses from vibracores obtained from the ECU-USGS-NCGS Coastal Geology Cooperative database and those estimated by Riggs and Ames (2003) are representative of peat thicknesses for the remainder of Pamlico Sound shorelines; 2) average erosion rates for six Pamlico Sound sites studied by Riggs and Ames (2003) are representative erosion rates for the remainder of Pamlico Sound shorelines; 3) the average sediment accumulation rates as determined

by CIC and CF:CS modeling of ^{210}Pb data are representative of accumulation rates throughout the sound; and 4) the shallow ~2 km wide Hatteras Flats that extend from approximately Oregon Inlet to Ocracoke Inlet is an area of non-deposition due to the high energy environment that exists there.

Amount of Sediments Liberated from Marsh Erosion

The volume of sediment derived from marsh erosion in the Pamlico Sound region was assessed by comparing the average peat thicknesses determined from vibracores obtained from the ECU-USGS-NCGS CGC database and Riggs and Ames (2003) and average erosion rates (Table 3) from the six marsh sites studied by Riggs and Ames (2003) with measured shoreline lengths. It was assumed that the average mainland and barrier island peat thicknesses (1.6 and 0.45 m, respectively) and average mainland and barrier island erosion rates (1.32 and 0.40 m y^{-1} , respectively) were representative of peat thicknesses and erosion rates for the remainder of Pamlico Sound shorelines.

Approximately 1000 km of mainland estuarine shoreline and 250 km of barrier island estuarine shoreline were measured over the reaches indicated by digitizing the shorelines in Mapinfo™ (Figure 49). Shorelines of any small islands or tributary estuaries were also included in this calculation.

Thus, 1000 km of a 1.6 m thick mainland peat, eroding at 1.32 m y^{-1} would generate a sediment volume of approximately $2.11 \times 10^6\text{ m}^3$ per year. Similarly, the 250 km of barrier island shoreline eroding a 0.45 m thick peat at 0.40 m y^{-1} would generate a

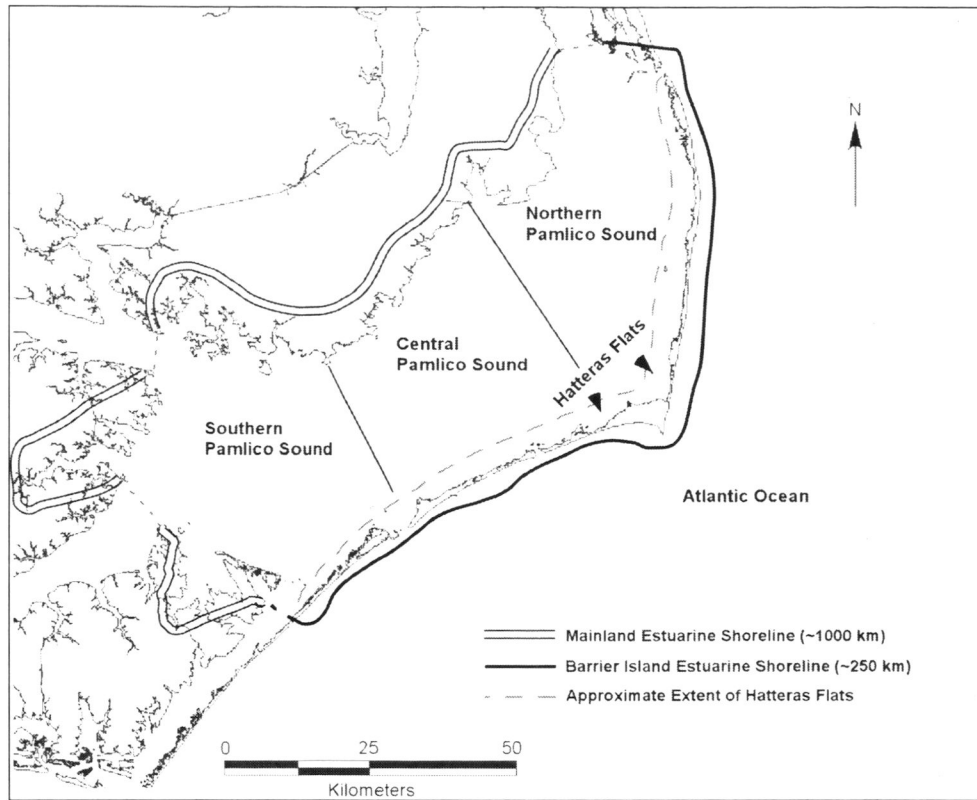


Figure 49: Calculated shoreline lengths (in km) of estuarine shorelines fringing Pamlico Sound (double line indicates areas included in calculating mainland shoreline lengths; bold line indicates areas used for calculating barrier island shoreline lengths). Also indicated is the approximate extent of Hatteras Flats (dashed line).

sediment volume of nearly $4.50 \times 10^4 \text{ m}^3 \text{ y}^{-1}$. The total volume of sediments liberated by marsh erosion each year is then approximately $2.16 \times 10^6 \text{ m}^3$.

Average organic carbon values in Pamlico Sound estuarine sediments (1.73%) are less than average organic carbon values for mainland marsh grabs (22.08%) and barrier island marsh grabs (4.96%). Since the marsh grabs contain more organic carbon than the estuarine sediments, it is apparent that some organic matter (OM) is either being oxidized prior to incorporation within the sediments or is being diluted with inorganic constituents. As such, a certain weight of the marsh grabs can be subtracted out in order to correct for

this dilution/oxidation factor. Obviously not all of the OM contained within Pamlico Sound sediments is derived from marsh erosion; however, it is likely that some of it is. Since the exact amount is unknown, making calculations assuming that either 100% or 0% of OM results from the marsh erosion ensures that the true value will lie within this range.

It is generally assumed that total organic matter is double the amount of organic carbon for any soil or peat (Mitsch and Gosselink, 2000). Therefore, the average organic matter contained in the mainland and barrier island peats, as well as the estuarine sediments can be calculated from the organic carbon content (average estuarine (3.5%); average mainland grab (44.2%); average barrier island grab (9.9%)). Mainland marsh grab organic matter represents approximately 78% of the total organic matter liberated by marsh erosion and barrier island marshes account for 22%. Under the assumption that Pamlico Sound sediment OM is all derived from marsh erosion, approximately 2.7% of the OM in the estuarine sediments is representative of mainland marsh erosion, and 0.8% of the OM can be accounted for by barrier island marsh erosion. Calculating the percent of organic matter lost to oxidation/dilution is a matter of simple subtraction. Assuming 100% of Pamlico Sound OM originates in marshes, about 41.5% of the mainland marsh and 9.1% of the barrier island marsh erosion volumes can be subtracted out. Assuming that no OM from marsh erosion is retained in Pamlico Sound sediments requires subtracting the entire OM content (44.2% mainland; 9.9% barrier island).

If all of the OM in the estuarine sediments originates from marsh erosion, then the volume of sediment contributed by the mainland marshes is $1.23 \times 10^6 \text{ m}^3 \text{ y}^{-1}$, while

sediments derived from barrier island erosion account for $4.09 \times 10^4 \text{ m}^3$ per year. Under the assumption that none of the OM in Pamlico Sound sediments results from marsh erosion, the volumes of sediments eroding from mainland and barrier island marshes each year are $1.18 \times 10^6 \text{ m}^3$ and $4.06 \times 10^4 \text{ m}^3$, respectively. Based on these two end-members, marsh erosion would contribute between 1.22 - $1.27 \times 10^6 \text{ m}^3$ annually. By comparing these two numbers, it is evident that relative to the total volume of sediment there is very little difference ($\sim 4\%$) obtained by correcting for OM oxidation or dilution.

Pamlico Sound Sediment Accumulation

In order to assess the total volume of sediment accumulating in the sound, the two critical parameters to assess were: 1) the area of the sound where sediments are actively accumulating and 2) the average sediment accumulation rates for different regions of the sound. The area of Pamlico Sound is about 5300 km^2 (Wells and Kim, 1989); however, the area encompassing Hatteras Flats (approximately 2 km wide by 200 km long) and Bluff Shoal ($\sim 100 \text{ km}^2$) may be subtracted since these are shallow, high-energy environments with little deposition. Thus, the approximate total area of the sound in which sediment is actively accumulating is 4800 km^2 .

The average sediment accumulation rates were determined by the CIC and CF:CS modeling of excess ^{210}Pb data for the northern, central, and southern portions of Pamlico Sound (Figure 49). The division between the northern and central regions was based on differences in sediment accumulation rates; the division between the central and southern region was based upon the position of Bluff Shoal. In order to gain a better understanding of accumulation rates in the southern region of Pamlico Sound,

preliminary unpublished data were used from a number of push cores that were not analyzed for this study. Table 15 shows the approximate areas and modeled average sediment accumulation rates for each of the three regions. With each model, the central region shows the greatest annual sediment accumulation (3.92 to $6.30 \times 10^6 \text{ m}^3 \text{ y}^{-1}$), followed by the northern (2.03 to $3.03 \times 10^6 \text{ m}^3 \text{ y}^{-1}$) and southern (3.55 to $4.26 \times 10^6 \text{ m}^3 \text{ y}^{-1}$) regions, respectively.

Table 15: Sediment accumulation rates and annual sediment accumulation volumes for northern, central, and southern Pamlico Sound.

	Area	Constant Flux: Constant Sedimentation		Constant Initial Concentration	
		Accumulation Rate	Sediment Volume	Accumulation Rate	Sediment Volume
Region	km^2	cm y^{-1}	$\text{m}^3 \text{ y}^{-1}$	cm y^{-1}	$\text{m}^3 \text{ y}^{-1}$
Northern	1390	0.15	2.03×10^6	0.22	3.03×10^6
Central	1630	0.24	3.92×10^6	0.39	6.30×10^6
Southern	1780	0.20	3.55×10^6	0.24	4.26×10^6
Total	4800		9.0×10^6		13.6×10^6

Marsh Erosion Volumes vs. Pamlico Sound Sediment Accumulation Volumes

Comparing the estimated eroded marsh sediment volume to the volume of sediment accumulating in the sound gives an idea of the relative importance of marsh erosion as a sediment source to Pamlico Sound. As noted above, the annual volume of sediments liberated by marsh erosion is $\sim 1.25 \times 10^6 \text{ m}^3$. The annual volume of sediment accumulating in Pamlico Sound varies depending on the accumulation model, with the CIC model yielding greater sediment volumes ($\sim 13.6 \times 10^6 \text{ m}^3$) than the CF:CS model ($\sim 9.0 \times 10^6 \text{ m}^3$). This causes the marsh sediment contribution to be greater for the CF:CS

model (~13.9% of total volume) than the CIC model (~9.2% of total volume). It is likely that the true total and regional contributions are somewhere in between the values listed for the two sediment accumulation models, making the sediment contribution to Pamlico Sound from marsh erosion approximately 12%.

Pamlico Sound Sediment Quality

Although the primary objective for using trace metal abundances was to examine sediment sources to Pamlico Sound, trace metals can also be used to examine sediment quality. Zn and Cu are natural constituents of rocks and minerals; however, elevated levels of these two metals can be indicative of anthropogenic contamination most often associated with sewage effluents, industry, boating activity, and mining (Riggs et al., 1991; Perin et al., 1997; Baptista Neto et al., 2000). In order to assess the degree to which central Pamlico Sound ORMs are or are not contaminated, with respect to Zn and Cu, metal concentrations were compared to trace metal studies that have been done both in the region and globally. For the purpose of this discussion, only cores from the central part of the basin (S31, S32, and S41) were considered. As indicated above, S12 exhibited some strong grain-size effects and S50 was located at the mouth of the Pamlico River and as such could be affected by local contamination.

Average trace metal values for central Pamlico Sound cores are ~90 ppm Zn and ~13 ppm Cu. These values compare favorably with values from the 1974 study on Pamlico Sound metal distributions by Wright, who found ~75 ppm Zn and ~30 ppm Cu in bulk sediment digestions of entire cores. Discrepancies in the Cu data are probably

related to problems with data reproducibility Wright (1974) experienced, which resulted from poor atomic absorption spectrometer sensitivity. Also Wright (1974) made no reference to any sort of recovery correction that would be necessary if exactly 100% of the metals were not liberated by the digestion procedure. It is generally expected to achieve metal recoveries less than 100% due to matrix effects and other inefficiencies in digestion methodologies (Beck and Sneddon, 2000). Therefore, it is likely that there was at least some small amount of unrecovered metals in Wright's (1974) digestion, and non-recovery corrected Zn values obtained from this study are comparable to Wright's 1974 data (non-recovery corrected average Pamlico Sound Zn = ~73 ppm).

Some regional sediment trace metal studies include those by Riggs et al. (1989) in the Pamlico River, Riggs et al. (1993) in the Albemarle Sound, and Neuse River studies by Riggs et al. (1991), Benninger and Wells (1993) and Balthis et al. (2002). Riggs et al. (1989, 1991, 1993) used acid extractions to determine the concentrations of loosely bound, bioavailable metals that could be easily taken up by biota. It was found that average extractable Zn concentrations were ~234 ppm and average Cu values were ~38 ppm in ORMs from the Pamlico River (Riggs et al., 1989). In Albemarle Sound sediments, Riggs et al. (1993) found average Zn and Cu concentrations of ~56 and ~13 ppm, respectively, each with 60% recovery. Therefore, total average metal concentrations for Albemarle Sound sediments can be expected to be ~90 ppm for Zn and ~22 ppm for Cu. Benninger and Wells (1993) found that Zn concentrations ranged from 54 to 228 ppm (~140 ppm on average) and Cu values ranged from 11-41 ppm (~26 ppm on average) in cores taken from the Neuse River. Zn and Cu concentrations were

generally the highest at the tops of the cores, and values tended to decrease monotonically with distance down the estuary. These trends are also observed in the other Neuse River studies by Riggs et al. (1991) and Balthis et al. (2002). Zn and Cu concentrations of Pamlico Sound ORMs are comparable to muds at the mouth of the Neuse River and progressively less than Zn and Cu concentrations further upstream. The decreases in Zn and Cu concentrations toward Pamlico Sound from the Neuse River could be a function of dilution from metal-poor sediment sources such as marsh erosion and a decreasing influence of contaminant point sources located farther upstream.

In comparison with other estuaries that have been heavily impacted by man, concentrations of Zn and Cu in Pamlico Sound muds tend to be significantly lower. This can be attributed to the open nature of the estuary and the relative lack of close proximity point sources for contamination (Hyland et al., 2000). Table 16 shows Zn and Cu concentrations from selected metal contamination studies in estuarine environments throughout the world. It is apparent that Pamlico Sound sediments could be considered “pristine” with respect to Zn and Cu compared to most of the estuaries listed below. Wright (1974) suggested that Zn and Cu concentrations in Pamlico Sound sediments could be used as background values in future estuarine studies assessing metal contamination. Although Pamlico Sound is relatively unpolluted with respect to Zn or Cu, these metals represent only a fraction of the contaminant metals and compounds often found in estuarine environments. Additional analyses for multiple other contaminants would need to be done to provide an accurate assessment of sediment quality in Pamlico Sound.

Table 16: Zn and Cu concentrations (in ppm) for selected estuaries throughout the world.

Study	Location	Average Zn (ppm)	Average Cu (ppm)
Bellucci et al. (2002)	Venice Lagoon, Italy	~1000	NA
Aloupi and Angelidis (2001)	Lesvos Harbor, Greece	~140	~40
Baptista Neto et al. (2000)	Jurujuba Sound, Brazil	~158	~51
Cearetta et al. (2000)	Bilbao Estuary, Spain	>1000	>160
Perin et al. (1997)	Gunabara Bay, Brazil	~384	~88
Benninger and Wells (1993)	Neuse River, USA	~140	~26
Ravichandran et al. (1995b)	Sabine-Neches Estuary, USA	~77	~11
Hornberger et al. (1997)	San Francisco Bay, USA	~77	~33
This Study	Pamlico Sound, USA	~90	~13

CONCLUSION

Pamlico Sound is a prominent nursery habitat for numerous forms of aquatic life; despite its economical and ecological importance it is relatively unstudied with respect to sediment geochemistry (Pilkey et al., 1998). This study, in conjunction with the parallel study by Abbene (2004), represents an attempt to rectify this, by producing a sizeable geochemical database for Pamlico Sound using multiple geochemical tracers.

The patterns of grain-size distributions derived from this study are in excellent agreement with previous sedimentological studies performed in Pamlico Sound as summarized by Wells and Kim (1989). The grain-size data acquired from this study are significant, as they represent the first time that interpretations of core sections have been done for grain-size in Pamlico Sound. It has been observed that the finest sediments (predominantly silty clay) tend to accumulate in either deep water in the center of the sound and at the mouths of the Neuse and Pamlico River estuaries, or in shallow water in protected embayments and coves. The five environments defined for the core locations (protected embayment, OC-rich perimeter platform, OC-poor perimeter platform, central basin, and estuary mouth) were useful in illustrating the relationship of position within the basin with sediment grain-size distributions. The major controls on grain-size distributions in Pamlico Sound appear to be related to energy level (a function of water depth), proximity to and nature of sediment sources, and (particularly in shallow water) the extent of protection from shorelines. Additionally, sediment grain-size has been shown to have a great effect on a number of the geochemical tracers employed in this study, most notably radionuclides, trace metals, and organic carbon.

The downcore distribution of radionuclides (^7Be , ^{137}Cs and excess ^{210}Pb) and the shapes of the radionuclide profiles with depth, indicate that mixing is significant for Pamlico Sound. Excess ^{210}Pb inventories of Pamlico Sound cores are generally greater than the expected atmospheric deposition indicated in the marsh core at North Bluff Point. This seems to suggest that the basin is actively accumulating sediments, as opposed to neighboring Albemarle Sound, which appears to be exporting sediments rather than accumulating them due to a limits in accommodation space (Corbett et al., 2004; Vance, 2004). Although the deeper water portions of Pamlico Sound are accumulating fine-grained sediments overall, some event-related erosion and deposition processes were documented in this study. A truncated ^{137}Cs peak at S55 showed a loss of potentially 20 cm of sediment. The mechanism for this is unknown; however, a well-defined peak at the counterpart estuary mouth core (S50) seems to indicate that this removal is local rather than regional.

There has been a major change in either sediment source or sediment dynamics since the 1960's. Trace metal data (Zn and Cu normalized to Al) show a reduction in value above the ^{137}Cs peak. Studies by Riggs et al. (1993) in Albemarle Sound and Benninger and Wells (1993) in the Neuse River indicate the most polluted sediments occur at or near the surface, suggesting that the decreases in trace metal values observed in Pamlico Sound are not a function of decreased metal source. Further evidence for another process at work is provided by a decreasing C:N ratio, a slight depletion of $\delta^{13}\text{C}$, and an enrichment $\delta^{15}\text{N}$ above the ^{137}Cs peak. The conclusion based on these several lines of geochemical tracer evidence is that both trawling, which began in earnest in the

1960's (NCFA, 2001), and dilution from marsh sediments are the dominant factors in recent Pamlico Sound sediment dynamics.

The marsh grabs show that geochemical tracer distributions can generally be correlated with grab type (surface marsh grab vs. subsurface peat) and location (barrier island marsh vs. mainland marsh). The control on this correlation is largely related to the relative amount of organic matter degradation, grain-size (specifically, the amount of fines), the particular source of the organic matter (C_3 vs. C_4), and potentially anthropogenic input. Surface marsh grabs of the barrier island sites tend to be the most enriched in trace metals, which could possibly be a response to anthropogenic input, while subsurface peat grabs of the mainland are generally the most depleted. This appears to relate to the composition and relative age of the peat, as well as the proximity to any potential contaminant sources.

By carefully measuring the Pamlico Sound estuarine shoreline and using erosion rates and peat thicknesses from Riggs and Ames (2003) and the ECU-USGS-NCGS database, it was possible to calculate an average volume of sediment that would result from marsh erosion over a years time. Comparing this with average sediment accumulation rates acquired by the CIC and CF:CS excess ^{210}Pb models showed that between ~9 and 14% of Pamlico Sound sediments could be contributed from marsh erosion. This provides an important part of the overall sediment budget of Pamlico Sound, which was previously unknown.

Pamlico Sound sediments are relatively unpolluted in relation to Zn and Cu. Average concentrations generally fall within those ranges indicated for unpolluted

estuaries, and well below those which are considered polluted. Relatively speaking, Pamlico Sound sediments are much less polluted than sediments from the neighboring Neuse and Pamlico Rivers or Albemarle Sound. Further studies with additional metals; however, are needed to ascertain the exact level of contamination.

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APPENDIX A: ALPHA SPECTROMETRY SAMPLE PREPARATION AND ANALYSIS PROCEDURES

Description: Contains a detailed account of the methodology used in all phases of sample preparation for the ^{210}Po leach method of determining ^{210}Pb activity. Also included are step-by-step instructions for sample analysis by alpha spectrometry.

Polonium-210 Leach Methodology

1. Assemble 14 Teflon microwave vessels, liners, and caps.
2. Place 1 gram (+/- 0.25 g) of sediment into the vessel, recording the sediment weight, vessel number, and site information in a logbook.
3. Add 1 ml of ^{209}Po tracer ($\sim 11.1 \text{ dpm g}^{-1}$) to each vessel.
4. Add 15 ml of 8M HNO_3 to each vessel.
5. Place caps and liners on vessels and put under a fume hood for at least 10 hours.
6. Assemble the vessels by attaching the blue pressure release caps and safety membranes, inserting them into their respective carriages, and placing them in the microwave carousel.
7. Insert the temperature and pressure gauges into the control vessel.
8. Place the carousel into the microwave and turn the microwave on.
9. Plug in the temperature and pressure gauges, rotate carousel to check for clearance.
10. Run the microwave program "PO LEACH 14 VES".
Microwave Parameters:
 - a. 15 minute ramp to pressure (75 psi) at 100% power and 1200W
 - b. 50 minute hold at 75 psi
 - c. 5 minute cool down.
11. Once the vessels have cooled to at least 60°C , remove the carousel from the microwave and place the carriages under the fume hood.
12. Slowly open the blue caps to allow the vessels to vent, releasing any excess pressure.
13. Remove the temperature and pressure gauges and disassemble the carriages.
14. Assemble 14 pre-labeled 50 ml centrifuge tubes.
15. Transfer the contents of each vessel into the appropriate centrifuge tube then rinse the vessel with 20-30 ml of DI water to ensure the vessel is empty.
16. Bring all the liquid in the centrifuge tubes to an equal volume by adding DI water.
17. Centrifuge samples for 2 minutes at 3000 rpm to separate sediments from the fluid.

18. Assemble 14 pre-numbered 100 ml Teflon beakers.
19. Pour the fluid from the tubes into the appropriate Teflon beaker, being careful not to remove any sediment from the tubes.
20. Rinse the sediments by adding 5 ml of 8M HNO_3 to each centrifuge tube and shaking.
21. Centrifuge again for 2 minutes at 3000 rpm.
22. Pour the fluid from the tubes into the appropriate Teflon beaker.
23. Add 5 ml of 8M HNO_3 to each centrifuge tube and shake.
24. Centrifuge again for 2 minutes at 3000 rpm.
25. Pour the fluid from the tubes into the appropriate Teflon beaker.
26. Discard the sediment from the centrifuge tubes and thoroughly rinse the tubes with DI water.
27. Place the 14 fluid-filled Teflon beakers on a hot plate set at 3-4 (33% power) under the fume hood.
28. After about 10 minutes slowly add 2-3 ml of 30% hydrogen peroxide to each beaker to facilitate the breakdown of organics.
29. The samples should remain on the hot plate until their volume has reached approximately 10 ml (3-5 hours).
30. Once the samples reach 10 ml pour them into their appropriate centrifuge tubes and rinse the beaker with DI water to ensure that all its contents are in the tube.
31. Bring the volume of the centrifuge tubes to 25 ml with DI water.
32. Slowly add concentrated ammonium hydroxide to the tubes with a disposable pipette; iron will begin to precipitate out.
33. Check the pH of the fluid, once a pH of 8 is reached stop adding ammonium hydroxide (usually 3-5 pipettes full of NH_4OH (~ 6-10 ml) is sufficient).
34. Bring all the tubes up to an equal volume (40-45 ml) with DI water.

35. Centrifuge the tubes for 2 minutes at 3000 rpm to separate the precipitated iron from the solution.
36. Decant the fluid into a high-volume (at least 1L) waste container under the fume hood, being careful not to lose any iron.
37. Rinse the iron by adding 5 ml HNO_3 to each tube and shaking.
38. Centrifuge again for 2 minutes at 3000 rpm.
39. Pour off the excess fluid into the waste container.
40. Add 5 ml HNO_3 to each tube and shake.
41. Centrifuge again for 2 minutes at 3000 rpm.
42. Pour off the excess fluid into the waste container.
43. Dilute the waste container fluid thoroughly with tap water and empty the container into the drain.
44. Add 3.75 ml of 12.1 M HCl to each centrifuge tube to get the iron to go back into solution.
45. Add DI water to each tube, bringing the total volume to 30 ml.
46. Assemble pre-prepared nickel discs, magnetic disc holders, and the Teflon beakers.
Preparing nickel discs:
 - a. Place nickel discs into a 500 ml bottle.
 - b. Add a small amount (20-30 ml) of 15.8 M HNO_3 and cap bottle.
 - c. Shake the bottle for about 10 minutes, occasionally venting under the fume hood by opening the cap.
 - d. Pour off the HNO_3 into a waste container and rinse the discs with DI water.
 - e. Dry the discs and paint one side with high-temperature enamel.
 - f. Allow the discs to dry for at least 6 hours.
47. Label the nickel discs, insert them into the magnetic disc holders with the painted side down, and place them into the appropriate Teflon beaker.
48. Pour the contents of the centrifuge tubes into the beaker.
49. Rinse the tubes and caps to ensure that all of the fluid is transferred from the centrifuge tubes to the beaker.

50. Place the solutions on a magnetic stirrer plate at 250 rpm and add ascorbic acid until the solution becomes clear.
51. Cover the beakers with a Teflon watchglass and let the samples spin for 20-40 hours to complete the plating process.
52. Once 20-40 hours have passed, remove the discs from the solution, rinse them with DI water, and allow them to dry. They are now ready to be counted.

Counting Procedures

1. Record sample information in the logbook noting filename, detector number, sample weight, and sample location.
2. On the detector turn each of the 8 chambers to “vent”.
3. Place the plated discs into their appropriate detector, painted side down.
4. Close the chambers doors and switch the knob from “vent” to “pump”.
5. Once the chamber pressure has dropped to about 15 torr, the samples can be counted.
6. Open the Maestro program
7. For each detector, select Services/Sample Description and enter sample name, weight, and filename.
8. Select Services/Job Control and click “Bias On”, the bias lights on each detector should illuminate.
9. Select Services/Job Control and “Start Cycle” to begin the counting process.
10. Samples should be counted until there are 1000 counts for ^{210}Po , the gross area of the ^{210}Po peak (at ~5304.33 keV) is 1000, or the sample has counted for 250,000 seconds. Samples should not be counted longer than 250,000 seconds.
11. Once one of the above parameters has been fulfilled, the samples can be removed from the detector.
12. Select Services/Job Control and “Stop All” to stop counting.
13. Select Services/Job Control and “Bias Off”, the bias lights should go out.

14. Select the region of interest (ROI) for the ^{209}Po (at ~ 4880.8 keV) and ^{210}Po (at ~ 5304.33 keV) peaks and save the file.
15. Select File/ROI Report and “Print” for each detector to obtain copies of the data.
16. Turn the knob on each detector chamber to vent and remove the samples.

APPENDIX B: TOTAL ACID DIGESTION AND SAMPLE DILUTION PROCEDURES

Description: Contains step-by-step procedures for the total microwave-assisted acid digestion method used in this study. Additional information provided on the dilutions used for determination of Al and Fe.

Total Acid Digestion Procedure

1. Assemble 14 Teflon beakers, caps, and liners.
2. Place 0.5 grams (+/- 0.05 g) of dried, homogenized sediment in each of the vessels, recording the sediment weight, vessel number, and site information in a logbook.
3. Under the fume hood, add 7.5 ml of trace metal grade 15.8 M HNO₃ to each vessel.
4. Place caps and liners on vessels and leave under a fume hood for at least 10 hours. This will facilitate the breakdown of any organic matter in the sample.
5. Assemble the vessels by attaching the blue pressure release caps and safety membranes, inserting them into their respective carriages, and placing them in the microwave carousel.
6. Insert the temperature and pressure gauges into the control vessel.
7. Place the carousel into the microwave and turn the microwave on.
8. Plug in the temperature and pressure gauges, rotate the carousel to check for clearance.
9. Run the microwave program "EPA 3051 MOD".
 - Microwave Parameters:*
 - a. 14 minute ramp to temperature (180°C) at 100% power and 1200W
 - b. 10 minute hold at 180°C
 - c. 5 minute cool down.
11. Once the vessels have cooled to at least 60°C, remove the carousel from the microwave and place the carriages under the fume hood.
12. Slowly open the blue caps to allow the vessels to vent, releasing any excess pressure.
13. Remove the temperature and pressure gauges and disassemble the carriages.
14. Discard used safety membranes and replace with new ones.
15. Add 3 ml concentrated trace metal grade HF to each of the vessels.
16. Reassemble microwave vessels by attaching the blue pressure release caps and safety membranes, inserting them into their respective carriages, and placing them in the microwave carousel.

17. Insert the temperature and pressure gauges into the control vessel.
18. Place the carousel into the microwave and turn the microwave on.
19. Plug in the temperature and pressure gauges, rotate the carousel to check for clearance.
20. Run the microwave program "EPA 3051 MOD".
 - Microwave Parameters:*
 - a. 14 minute ramp to temperature (180°C) at 100% power and 1200W
 - b. 30 minute hold at 180°C
 - c. 5 minute cool down.
21. Once the vessels have cooled to at least 60°C, remove the carousel from the microwave and place the carriages under the fume hood.
22. Slowly open the blue caps to allow the vessels to vent, releasing any excess pressure.
23. Remove the temperature and pressure gauges and disassemble the carriages.
24. Discard used safety membranes.
25. Add 20 ml of 0.65 M H_3BO_3 to each of the vessels to complex the HF.
26. Allow the solution to remain under the fume hood for at least 30 minutes.
27. Assemble 14 acid-rinsed, labeled 50 ml centrifuge tubes.
28. Transfer the contents of each vessel into the appropriate centrifuge tube by rinsing with 17.5 Ωm deionized water.
29. Bring each the contents of each tube to 40 ml with DI water.
30. Centrifuge the tubes for 3.5 minutes at 3000 rpm to remove any particulates.
31. Assemble 14, 50 ml volumetric flasks.
32. Decant the fluid into a 50 ml volumetric flask and discard the centrifuge tubes.
33. Add 5.1 ml of concentrated, trace metal grade, NH_4OH to each volumetric flask. This will reduce the weight percent acid in the sample to acceptable levels for atomic absorption analysis later.
34. Place parafilm over the volumetric flasks and shake repeatedly.

35. Assemble 14 acid-rinsed, labeled 50 ml centrifuge tubes.
36. Transfer the contents of the volumetric flasks into the appropriate centrifuge tubes. The samples are now ready to be analyzed for Zn and Cu.

Diluting Samples for Fe and Al Analysis

1. A 16:1 dilution is required to get the Fe and Al concentrations to within the working range of the instrument.
2. Pipette 3.125 ml of the digested sediment sample into a 50 ml volumetric flask.
3. Add 5 ml of the 20,000 ppm KCl (K suppressant) solution to the flask to give the solution 2,000 ppm K.
4. Add deionized water (17.5 Ω m) to the flask and bring the volume to 50 ml.
5. Cover the flask with parafilm and shake vigorously.
6. Transfer the solution into an acid-washed, labeled 50 ml centrifuge tube for storage. The contents are now ready to be analyzed for Fe and Al.

APPENDIX C: RADIONUCLIDE DATA SUMMARIES

Description: Contains downcore radionuclide data (^7Be , ^{210}Pb , and ^{137}Cs) for Pamlico Sound estuarine cores and the marsh core at North Bluff Point.

PAM02S9												
Midpoint	⁷ Be			Total ²¹⁰ Pb			Excess ²¹⁰ Pb			¹³⁷ Cs		
cm	dpm g ⁻¹			dpm g ⁻¹			dpm g ⁻¹			dpm g ⁻¹		
1	0.00	±	0.00	3.30	±	0.14	2.88	±	0.18	0.04	±	0.03
3	0.04	±	0.28	3.35	±	0.14	2.93	±	0.18	0.03	±	0.03
5	0.00	±	0.00	2.96	±	0.13	2.54	±	0.17	0.05	±	0.04
7	0.00	±	0.00	1.03	±	0.05	0.61	±	0.12	0.11	±	0.04
9	0.00	±	0.00	1.21	±	0.06	0.79	±	0.12	0.17	±	0.02
11	0.00	±	0.00	1.38	±	0.08	0.96	±	0.13	0.11	±	0.03
13	0.00	±	0.00	0.87	±	0.05	0.45	±	0.12	0.04	±	0.02
15	0.00	±	0.00	0.90	±	0.05	0.48	±	0.12	0.03	±	0.02
17	0.00	±	0.00	0.71	±	0.04	0.29	±	0.11	0.00	±	0.00
19	0.00	±	0.00	0.60	±	0.04	0.18	±	0.11	0.03	±	0.03
21	1.18	±	0.71	0.44	±	0.03	0.03	±	0.11	0.00	±	0.00
23	0.44	±	0.56	0.62	±	0.04	0.20	±	0.11	0.00	±	0.00
25	0.08	±	0.41	0.59	±	0.04	0.17	±	0.11	0.08	±	0.02
27	0.00	±	0.00	0.44	±	0.03	0.02	±	0.11	0.00	±	0.00
29	0.10	±	0.46	0.39	±	0.03	-0.03	±	0.11	0.00	±	0.00
31	0.00	±	0.00	0.31	±	0.03	-0.11	±	0.11	0.02	±	0.03
33	0.00	±	0.00	0.37	±	0.03	-0.05	±	0.11	0.04	±	0.03
35	0.00	±	0.00	0.42	±	0.03	0.00	±	0.11	0.00	±	0.00
	Supported ²¹⁰ Pb			0.45	±	0.11						

PAM02S10												
Midpoint	⁷ Be			Total ²¹⁰ Pb			Excess ²¹⁰ Pb			¹³⁷ Cs		
cm	dpm g ⁻¹			dpm g ⁻¹			dpm g ⁻¹			dpm g ⁻¹		
1	3.02	±	1.73	9.03	±	0.39	8.50	±	0.39	0.30	±	0.03
3	0.00	±	0.00	7.89	±	0.35	7.36	±	0.35	0.41	±	0.03
5	0.00	±	0.00	4.96	±	0.22	4.44	±	0.22	0.12	±	0.03
7	0.00	±	0.00	4.66	±	0.22	4.14	±	0.22	0.26	±	0.03
9	0.20	±	1.78	3.19	±	0.15	2.67	±	0.15	0.27	±	0.03
11	0.67	±	1.73	2.32	±	0.12	1.80	±	0.13	0.07	±	0.03
13	0.00	±	0.00	0.75	±	0.05	0.23	±	0.06	0.08	±	0.03
15	0.00	±	0.00	0.69	±	0.05	0.17	±	0.06	0.00	±	0.00
17	0.00	±	0.00	0.38	±	0.04	-0.14	±	0.04	0.02	±	0.03
19	0.00	±	0.00	0.50	±	0.04	-0.03	±	0.04	0.00	±	0.00
21	0.00	±	0.00	0.54	±	0.04	0.01	±	0.05	0.02	±	0.03
23	0.00	±	0.00	0.53	±	0.04	0.00	±	0.05	0.00	±	0.00
25	0.00	±	0.00	0.50	±	0.04	-0.02	±	0.04	0.00	±	0.00
27	0.00	±	0.00	0.52	±	0.04	0.00	±	0.05	0.00	±	0.00
29	0.00	±	0.00	0.56	±	0.04	0.04	±	0.05	0.00	±	0.00
	Supported ²¹⁰ Pb			0.52	±	0.02						

PAM02S11												
Midpoint	^7Be			Total ^{210}Pb			Excess ^{210}Pb			^{137}Cs		
<i>cm</i>	<i>dpm g⁻¹</i>			<i>dpm g⁻¹</i>			<i>dpm g⁻¹</i>			<i>dpm g⁻¹</i>		
1	2.79	±	1.34	9.35	±	0.44	8.68	±	0.44	0.21	±	0.02
3	0.00	±	0.00	2.97	±	0.16	2.30	±	0.17	0.11	±	0.03
5	1.17	±	1.35	1.63	±	0.09	0.96	±	0.11	0.03	±	0.02
7	0.00	±	0.00	1.04	±	0.07	0.37	±	0.09	0.01	±	0.03
9	0.09	±	1.37	1.02	±	0.07	0.35	±	0.09	0.01	±	0.02
11	0.00	±	0.00	1.05	±	0.08	0.38	±	0.10	0.07	±	0.03
13	0.26	±	1.07	1.04	±	0.08	0.37	±	0.09	0.06	±	0.02
15	0.00	±	0.00	0.70	±	0.06	0.03	±	0.08	0.05	±	0.03
17	0.00	±	0.00	0.71	±	0.06	0.04	±	0.08	0.06	±	0.03
19	0.00	±	0.00	0.60	±	0.05	-0.07	±	0.08	0.00	±	0.00
21	0.00	±	0.00	0.73	±	0.05	0.06	±	0.08	0.02	±	0.04
23	0.00	±	0.00	0.67	±	0.05	0.00	±	0.08	0.00	±	0.00
25	0.00	±	0.00	0.60	±	0.06	-0.07	±	0.08	0.00	±	0.00
	Supported ^{210}Pb			0.67	±	0.06						

PAM02S12												
Midpoint	^7Be			Total ^{210}Pb			Excess ^{210}Pb			^{137}Cs		
<i>cm</i>	<i>dpm g⁻¹</i>			<i>dpm g⁻¹</i>			<i>dpm g⁻¹</i>			<i>dpm g⁻¹</i>		
1	0.00	±	0.00	2.11	±	0.10	1.61	±	0.25	0.01	±	0.03
3	0.00	±	0.00	1.79	±	0.09	1.30	±	0.25	0.11	±	0.04
5	0.00	±	0.00	1.09	±	0.06	0.60	±	0.24	0.00	±	0.00
7	0.00	±	0.00	1.44	±	0.07	0.94	±	0.24	0.07	±	0.04
9	0.00	±	0.00	1.27	±	0.07	0.78	±	0.24	0.07	±	0.03
11	0.00	±	0.00	1.15	±	0.06	0.65	±	0.24	0.07	±	0.02
13	0.00	±	0.00	1.18	±	0.06	0.69	±	0.24	0.10	±	0.02
15	0.00	±	0.00	1.25	±	0.07	0.76	±	0.24	0.07	±	0.02
17	0.00	±	0.00	0.78	±	0.05	0.29	±	0.24	0.15	±	0.03
19	0.00	±	0.00	0.79	±	0.05	0.29	±	0.24	0.12	±	0.03
21	0.00	±	0.00	0.43	±	0.03	-0.06	±	0.23	0.00	±	0.00
23	0.00	±	0.00	0.45	±	0.04	-0.04	±	0.23	0.08	±	0.03
25	0.00	±	0.00	0.30	±	0.03	-0.20	±	0.23	0.00	±	0.01
27	0.00	±	0.00	0.32	±	0.03	-0.18	±	0.23	0.01	±	0.02
29	0.00	±	0.00	0.54	±	0.04	0.04	±	0.23	0.04	±	0.02
31	0.00	±	0.00	0.93	±	0.05	0.44	±	0.24	0.00	±	0.00
	Supported ^{210}Pb			0.50	±	0.23						

PAM02S22												
Midpoint	⁷ Be			Total ²¹⁰ Pb			Excess ²¹⁰ Pb			¹³⁷ Cs		
cm	dpm g ⁻¹			dpm g ⁻¹			dpm g ⁻¹			dpm g ⁻¹		
1	0.00	±	0.00	7.28	±	0.35	5.74	±	0.46	0.26	±	0.04
3	0.00	±	0.00	7.61	±	0.37	6.06	±	0.47	0.24	±	0.04
5	0.00	±	0.00	7.61	±	0.36	6.07	±	0.47	0.42	±	0.03
7	0.00	±	0.00	5.70	±	0.28	4.16	±	0.41	0.43	±	0.04
9	0.00	±	0.00	6.82	±	0.33	5.28	±	0.45	0.36	±	0.03
11	0.00	±	0.00	4.74	±	0.24	3.19	±	0.39	0.26	±	0.05
13	1.08	±	1.61	3.60	±	0.19	2.06	±	0.36	0.26	±	0.04
15	0.00	±	0.00	3.45	±	0.18	1.90	±	0.35	0.30	±	0.06
17	0.99	±	1.78	2.42	±	0.13	0.87	±	0.33	0.15	±	0.03
19	0.00	±	0.00	1.83	±	0.09	0.29	±	0.31	0.12	±	0.03
21	0.00	±	0.00	1.83	±	0.09	0.29	±	0.31	0.14	±	0.02
23	0.00	±	0.00	1.86	±	0.09	0.31	±	0.31	0.11	±	0.02
25	0.00	±	0.00	1.30	±	0.07	-0.24	±	0.31	0.07	±	0.03
27	0.00	±	0.00	1.17	±	0.06	-0.37	±	0.31	0.11	±	0.03
29	0.00	±	0.00	1.33	±	0.06	-0.21	±	0.31	0.07	±	0.03
31	0.00	±	0.00	1.26	±	0.06	-0.28	±	0.31	0.07	±	0.03
33	0.00	±	0.00	1.76	±	0.08	0.22	±	0.31	0.04	±	0.03
Supported ²¹⁰ Pb				1.54	±	0.30						

PAM02S23												
Midpoint	⁷ Be			Total ²¹⁰ Pb			Excess ²¹⁰ Pb			¹³⁷ Cs		
cm	dpm g ⁻¹			dpm g ⁻¹			dpm g ⁻¹			dpm g ⁻¹		
1	0.00	±	0.00	3.43	±	0.19	2.05	±	0.23	0.08	±	0.04
3	0.00	±	0.00	2.65	±	0.13	1.26	±	0.18	0.06	±	0.04
5	0.00	±	0.00	2.40	±	0.13	1.01	±	0.17	0.15	±	0.02
7	0.00	±	0.00	2.41	±	0.15	1.03	±	0.19	0.13	±	0.03
9	0.00	±	0.00	2.18	±	0.10	0.79	±	0.16	0.08	±	0.05
11	0.00	±	0.00	1.82	±	0.09	0.44	±	0.15	0.06	±	0.04
13	0.00	±	0.00	1.69	±	0.09	0.31	±	0.15	0.14	±	0.04
15	0.00	±	0.00	1.87	±	0.10	0.48	±	0.16	0.06	±	0.03
17	0.00	±	0.00	1.80	±	0.10	0.42	±	0.15	0.03	±	0.03
19	0.00	±	0.00	1.58	±	0.09	0.19	±	0.15	0.07	±	0.04
21	0.00	±	0.00	1.39	±	0.08	0.00	±	0.14	0.07	±	0.03
23	0.00	±	0.00	1.29	±	0.07	-0.09	±	0.14	0.00	±	0.00
25	0.00	±	0.00	1.47	±	0.08	0.09	±	0.15	0.08	±	0.03
Supported ²¹⁰ Pb				1.38	±	0.12						

PAM02S24												
Midpoint	^7Be			Total ^{210}Pb			Excess ^{210}Pb			^{137}Cs		
cm	dpm g $^{-1}$			dpm g $^{-1}$			dpm g $^{-1}$			dpm g $^{-1}$		
1	0.49	±	0.35	9.14	±	0.40	7.99	±	0.25	0.27	±	0.05
3	0.00	±	0.00	8.29	±	0.36	7.13	±	0.24	0.37	±	0.06
5	0.00	±	0.00	7.81	±	0.34	6.65	±	0.21	0.40	±	0.05
7	0.19	±	0.36	7.04	±	0.31	5.88	±	0.09	0.31	±	0.05
9	0.00	±	0.00	6.33	±	0.30	5.18	±	0.11	0.40	±	0.06
11	0.38	±	0.42	6.03	±	0.27	4.87	±	0.09	0.36	±	0.05
13	0.04	±	0.39	5.64	±	0.28	4.48	±	0.15	0.41	±	0.05
15	0.00	±	0.00	5.02	±	0.23	3.86	±	0.10	0.40	±	0.06
17	0.00	±	0.00	4.49	±	0.22	3.34	±	0.10	0.40	±	0.06
19	0.48	±	0.29	3.76	±	0.20	2.60	±	0.09	0.34	±	0.04
21	1.14	±	0.99	3.11	±	0.15	1.95	±	0.16	0.27	±	0.05
23	0.00	±	0.00	3.11	±	0.15	1.95	±	0.24	0.13	±	0.05
25	1.31	±	1.19	2.01	±	0.11	0.86	±	0.10	0.04	±	0.05
27	0.04	±	0.88	1.50	±	0.09	0.34	±	0.17	0.01	±	0.04
29	0.00	±	0.00	1.16	±	0.07	0.00	±	0.30	0.00	±	0.00
Supported ^{210}Pb				1.16	±	0.07						

PAM02S27												
Midpoint	^7Be			Total ^{210}Pb			Excess ^{210}Pb			^{137}Cs		
cm	dpm g $^{-1}$			dpm g $^{-1}$			dpm g $^{-1}$			dpm g $^{-1}$		
1	0.44	±	3.01	1.62	±	0.08	0.74	±	0.10	0.02	±	0.02
3	0.92	±	5.74	1.40	±	0.07	0.52	±	0.10	0.06	±	0.03
5	0.00	±	0.00	1.42	±	0.07	0.54	±	0.10	0.09	±	0.02
7	0.00	±	0.00	1.18	±	0.06	0.30	±	0.09	0.06	±	0.04
9	1.28	±	4.71	1.26	±	0.07	0.38	±	0.10	0.07	±	0.02
11	0.00	±	0.00	1.15	±	0.06	0.26	±	0.09	0.10	±	0.04
13	0.00	±	0.00	0.85	±	0.05	-0.03	±	0.09	0.04	±	0.02
15	0.00	±	0.00	0.97	±	0.05	0.09	±	0.09	0.06	±	0.02
17	0.00	±	0.00	0.90	±	0.05	0.01	±	0.09	0.05	±	0.04
19	0.00	±	0.00	0.81	±	0.05	-0.07	±	0.09	0.00	±	0.00
Supported ^{210}Pb				0.88	±	0.07						

PAM02S30												
Midpoint	⁷ Be			Total ²¹⁰ Pb			Excess ²¹⁰ Pb			¹³⁷ Cs		
cm	dpm g ⁻¹			dpm g ⁻¹			dpm g ⁻¹			dpm g ⁻¹		
1	2.25	±	0.36	4.98	±	0.24	4.20	±	0.24	0.18	±	0.04
3	0.50	±	0.29	3.95	±	0.18	3.18	±	0.19	0.14	±	0.04
5	0.15	±	0.29	4.00	±	0.19	3.22	±	0.20	0.04	±	0.04
7	0.06	±	0.30	6.15	±	0.28	5.38	±	0.28	0.29	±	0.04
9	0.17	±	0.29	6.26	±	0.29	5.49	±	0.30	0.29	±	0.04
11	0.00	±	0.00	4.97	±	0.22	4.19	±	0.22	0.43	±	0.04
13	0.00	±	0.00	1.52	±	0.08	0.75	±	0.09	0.03	±	0.03
15	0.00	±	0.00	1.26	±	0.07	0.48	±	0.08	0.09	±	0.03
17	0.00	±	0.00	0.81	±	0.05	0.04	±	0.06	0.09	±	0.03
19	0.00	±	0.00	0.74	±	0.05	-0.04	±	0.06	0.06	±	0.04
21	0.00	±	0.00	0.77	±	0.05	0.00	±	0.06	0.00	±	0.00
	Supported ²¹⁰ Pb			0.78	±	0.04						

PAM02S31												
Midpoint	⁷ Be			Total ²¹⁰ Pb			Excess ²¹⁰ Pb			¹³⁷ Cs		
cm	dpm g ⁻¹			dpm g ⁻¹			dpm g ⁻¹			dpm g ⁻¹		
1	2.34	±	0.43	9.86	±	0.45	8.93	±	0.45	0.31	±	0.05
3	0.98	±	0.37	10.52	±	0.47	9.60	±	0.47	0.33	±	0.05
5	0.00	±	0.00	12.85	±	0.55	11.93	±	0.55	0.28	±	0.05
7	0.07	±	0.35	9.46	±	0.43	8.54	±	0.43	0.46	±	0.05
9	0.00	±	0.00	7.18	±	0.33	6.25	±	0.33	0.32	±	0.05
11	0.00	±	0.00	7.02	±	0.32	6.10	±	0.33	0.37	±	0.05
13	0.38	±	0.40	6.26	±	0.29	5.34	±	0.29	0.58	±	0.05
15	0.00	±	0.00	5.75	±	0.27	4.83	±	0.27	0.53	±	0.05
17	0.20	±	0.50	5.85	±	0.27	4.92	±	0.28	0.60	±	0.06
19	0.00	±	0.00	5.99	±	0.28	5.07	±	0.28	0.58	±	0.05
21	0.00	±	0.00	6.13	±	0.28	5.21	±	0.29	0.55	±	0.05
23	0.00	±	0.00	4.94	±	0.23	4.01	±	0.24	0.51	±	0.05
25	0.00	±	0.00	4.39	±	0.21	3.47	±	0.21	0.32	±	0.05
27	0.00	±	0.00	2.28	±	0.12	1.36	±	0.13	0.22	±	0.06
29	0.00	±	0.00	1.93	±	0.10	1.01	±	0.11	0.15	±	0.04
31.5	0.00	±	0.00	1.56	±	0.08	0.64	±	0.10	0.20	±	0.05
34.5	0.00	±	0.00	1.75	±	0.09	0.83	±	0.10	0.16	±	0.04
37.5	0.00	±	0.00	1.21	±	0.06	0.28	±	0.08	0.15	±	0.04
40.5	0.00	±	0.00	1.30	±	0.07	0.37	±	0.09	0.15	±	0.05
43.5	0.00	±	0.00	1.40	±	0.07	0.47	±	0.09	0.11	±	0.03
46.5	0.00	±	0.00	1.28	±	0.07	0.36	±	0.09	0.04	±	0.03
49.5	0.00	±	0.00	1.72	±	0.08	0.80	±	0.10	0.04	±	0.03
52.5	0.00	±	0.00	0.92	±	0.05	0.00	±	0.08	0.05	±	0.04
	Supported ²¹⁰ Pb			0.92	±	0.05						

PAM02S32												
Midpoint	⁷ Be			Total ²¹⁰ Pb			Excess ²¹⁰ Pb			¹³⁷ Cs		
cm	dpm g ⁻¹			dpm g ⁻¹			dpm g ⁻¹			dpm g ⁻¹		
1	1.64	±	0.37	10.31	±	0.48	9.31	±	0.49	0.56	±	0.06
3	0.36	±	0.31	10.23	±	0.44	9.23	±	0.45	0.49	±	0.06
5	0.00	±	0.00	10.31	±	0.48	9.31	±	0.49	0.50	±	0.05
7	0.00	±	0.00	9.92	±	0.46	8.92	±	0.47	0.52	±	0.06
9	0.00	±	0.00	7.83	±	0.34	6.83	±	0.35	0.56	±	0.06
11	0.00	±	0.00	8.47	±	0.37	7.47	±	0.37	0.82	±	0.08
13	0.67	±	0.72	6.64	±	0.29	5.64	±	0.29	0.77	±	0.08
15	0.00	±	0.00	6.51	±	0.29	5.51	±	0.29	0.55	±	0.05
17	0.00	±	0.00	4.93	±	0.23	3.93	±	0.24	0.49	±	0.05
19	0.00	±	0.00	3.48	±	0.15	2.48	±	0.17	0.37	±	0.03
21	0.00	±	0.00	3.02	±	0.14	2.02	±	0.16	0.30	±	0.03
23	0.00	±	0.00	2.45	±	0.12	1.45	±	0.14	0.22	±	0.04
25	0.00	±	0.00	2.49	±	0.12	1.49	±	0.14	0.31	±	0.05
27	0.00	±	0.00	2.14	±	0.10	1.14	±	0.12	0.31	±	0.04
	Supported ²¹⁰ Pb			1.00	±	0.07						

PAM02S41												
Midpoint	⁷ Be			Total ²¹⁰ Pb			Excess ²¹⁰ Pb			¹³⁷ Cs		
cm	dpm g ⁻¹			dpm g ⁻¹			dpm g ⁻¹			dpm g ⁻¹		
1	0.91	±	0.30	5.87	±	0.30	4.82	±	0.41	0.10	±	0.04
3	0.13	±	0.21	4.98	±	0.26	3.92	±	0.37	0.16	±	0.03
5	0.00	±	0.00	5.94	±	0.29	4.89	±	0.39	0.19	±	0.04
7	0.41	±	0.34	5.67	±	0.29	4.61	±	0.39	0.24	±	0.05
9	0.23	±	0.31	3.89	±	0.20	2.84	±	0.33	0.26	±	0.04
11	0.00	±	0.00	5.20	±	0.26	4.14	±	0.38	0.39	±	0.03
13	0.00	±	0.00	4.21	±	0.21	3.16	±	0.34	0.40	±	0.05
15	0.00	±	0.00	2.83	±	0.15	1.78	±	0.31	0.22	±	0.03
17	0.00	±	0.00	2.72	±	0.15	1.66	±	0.31	0.15	±	0.03
19	0.30	±	0.91	2.66	±	0.15	1.61	±	0.31	0.19	±	0.05
21	0.00	±	0.00	1.73	±	0.10	0.67	±	0.29	0.06	±	0.04
23	0.12	±	0.64	1.47	±	0.09	0.42	±	0.28	0.05	±	0.03
25	0.16	±	0.66	1.00	±	0.06	-0.05	±	0.27	0.02	±	0.03
27	0.00	±	0.00	1.11	±	0.06	0.05	±	0.28	0.00	±	0.00
	Supported ²¹⁰ Pb			1.06	±	0.07						

PAM02S42												
Midpoint	⁷ Be			Total ²¹⁰ Pb			Excess ²¹⁰ Pb			¹³⁷ Cs		
cm	dpm g ⁻¹			dpm g ⁻¹			dpm g ⁻¹			dpm g ⁻¹		
1	2.47	±	0.40	9.15	±	0.43	7.96	±	0.46	0.41	±	0.06
3	1.14	±	0.23	10.73	±	0.50	9.54	±	0.53	0.42	±	0.03
5	0.00	±	0.00	9.76	±	0.45	8.57	±	0.48	0.29	±	0.05
7	0.00	±	0.00	10.34	±	0.49	9.14	±	0.51	0.47	±	0.05
9	0.00	±	0.00	8.65	±	0.41	7.45	±	0.44	0.39	±	0.05
11	0.00	±	0.00	7.28	±	0.35	6.08	±	0.39	0.22	±	0.03
13	0.00	±	0.00	6.99	±	0.34	5.79	±	0.38	0.30	±	0.03
15	0.00	±	0.00	6.10	±	0.30	4.90	±	0.34	0.26	±	0.04
17	0.18	±	0.31	5.06	±	0.25	3.86	±	0.30	0.24	±	0.03
19	0.00	±	0.00	3.60	±	0.16	2.40	±	0.23	0.15	±	0.03
21	0.00	±	0.00	1.96	±	0.10	0.76	±	0.19	0.16	±	0.04
23	0.00	±	0.00	1.45	±	0.07	0.25	±	0.18	0.07	±	0.03
25	0.00	±	0.00	1.36	±	0.07	0.17	±	0.18	0.07	±	0.04
27	0.00	±	0.00	1.00	±	0.06	-0.20	±	0.18	0.00	±	0.00
29	0.00	±	0.00	1.30	±	0.07	0.11	±	0.18	0.07	±	0.03
31	0.03	±	17.69	1.12	±	0.06	-0.08	±	0.18	0.02	±	0.05
	Supported ²¹⁰ Pb			1.20	±	0.17						

PAM03S50												
Midpoint	⁷ Be			Total ²¹⁰ Pb			Excess ²¹⁰ Pb			¹³⁷ Cs		
cm	dpm g ⁻¹			dpm g ⁻¹			dpm g ⁻¹			dpm g ⁻¹		
1	1.65	±	0.28	11.72	±	0.50	10.51	±	0.50	0.44	±	0.05
3	0.87	±	0.31	14.00	±	0.60	12.80	±	0.60	0.50	±	0.05
5	0.00	±	0.00	13.84	±	0.60	12.63	±	0.60	0.60	±	0.07
7	0.00	±	0.00	11.59	±	0.51	10.38	±	0.51	0.53	±	0.06
9	0.00	±	0.00	14.11	±	0.60	12.90	±	0.61	0.63	±	0.07
11	0.00	±	0.00	10.08	±	0.43	8.87	±	0.44	0.78	±	0.06
13	0.00	±	0.00	8.96	±	0.39	7.76	±	0.40	0.61	±	0.07
15	0.00	±	0.00	8.79	±	0.38	7.58	±	0.39	0.69	±	0.05
17	0.00	±	0.00	7.91	±	0.34	6.70	±	0.35	0.90	±	0.08
19	0.00	±	0.00	6.88	±	0.30	5.67	±	0.31	0.79	±	0.07
21	0.00	±	0.00	6.00	±	0.27	4.79	±	0.28	0.56	±	0.06
23	0.00	±	0.00	4.04	±	0.18	2.84	±	0.19	0.24	±	0.06
25	0.00	±	0.00	3.46	±	0.16	2.25	±	0.17	0.26	±	0.05
27	0.00	±	0.00	3.11	±	0.14	1.90	±	0.16	0.22	±	0.05
29	0.00	±	0.00	2.57	±	0.12	1.37	±	0.14	0.15	±	0.06
31.5	0.00	±	0.00	2.31	±	0.11	1.11	±	0.13	0.19	±	0.05
34.5	0.00	±	0.00	1.60	±	0.08	0.40	±	0.11	0.08	±	0.05
37.5	0.00	±	0.00	1.27	±	0.07	0.06	±	0.10	0.00	±	0.00
40.5	0.00	±	0.00	1.21	±	0.06	0.01	±	0.10	0.08	±	0.05
43.5	0.00	±	0.00	1.13	±	0.06	-0.07	±	0.09	0.00	±	0.00
46.5	0.00	±	0.00	1.28	±	0.07	0.07	±	0.10	0.00	±	0.00
49	0.00	±	0.00	1.14	±	0.06	-0.07	±	0.09	0.00	±	0.00
	Supported ²¹⁰ Pb			1.21	±	0.07						

PAM03S55												
Midpoint	⁷ Be			Total ²¹⁰ Pb			Excess ²¹⁰ Pb			¹³⁷ Cs		
cm	dpm g ⁻¹			dpm g ⁻¹			dpm g ⁻¹			dpm g ⁻¹		
1	0.89	±	0.30	10.00	±	0.44	8.53	±	0.72	0.51	±	0.05
3	0.00	±	0.00	3.55	±	0.17	2.08	±	0.60	0.28	±	0.04
5	0.00	±	0.00	1.54	±	0.08	0.07	±	0.58	0.10	±	0.04
7	0.00	±	0.00	0.79	±	0.05	-0.68	±	0.57	0.08	±	0.03
9	0.38	±	0.24	0.71	±	0.05	-0.76	±	0.57	0.04	±	0.04
11	0.00	±	0.00	0.88	±	0.05	-0.59	±	0.57	0.02	±	0.05
13	0.39	±	0.65	0.97	±	0.06	-0.50	±	0.57	0.13	±	0.05
15	0.00	±	0.00	1.14	±	0.06	-0.33	±	0.57	0.00	±	0.00
17	0.00	±	0.00	1.64	±	0.08	0.17	±	0.58	0.02	±	0.06
19	0.00	±	0.00	1.91	±	0.09	0.44	±	0.58	0.00	±	0.05
21	0.00	±	0.00	2.13	±	0.11	0.66	±	0.58	0.04	±	0.05
23	0.00	±	0.00	1.27	±	0.07	-0.20	±	0.58	0.01	±	0.06
25	0.00	±	0.00	2.36	±	0.12	0.89	±	0.58	0.00	±	0.00
27	0.00	±	0.00	1.83	±	0.09	0.36	±	0.58	0.02	±	0.05
29	0.00	±	0.00	1.94	±	0.10	0.47	±	0.58	0.04	±	0.05
	Supported ²¹⁰ Pb			1.47	±	0.57						

North Bluff Point												
Midpoint	⁷ Be			Total ²¹⁰ Pb			Excess ²¹⁰ Pb			¹³⁷ Cs		
cm	dpm g ⁻¹			dpm g ⁻¹			dpm g ⁻¹			dpm g ⁻¹		
1	0.00	±	0.00	2.81	±	0.13	2.30	±	0.34	0.12	±	0.03
3	0.00	±	0.00	3.83	±	0.17	3.32	±	0.36	0.41	±	0.05
5	0.00	±	0.00	4.65	±	0.20	4.14	±	0.37	0.64	±	0.05
7	0.00	±	0.00	4.08	±	0.18	3.57	±	0.36	1.55	±	0.06
9	0.00	±	0.00	4.89	±	0.22	4.37	±	0.38	5.11	±	0.10
11	0.00	±	0.00	3.30	±	0.16	2.79	±	0.35	4.97	±	0.13
13	0.00	±	0.00	3.35	±	0.16	2.83	±	0.35	3.76	±	0.10
15	0.04	±	0.01	3.32	±	0.16	2.80	±	0.35	3.02	±	0.05
17	0.08	±	0.01	3.65	±	0.17	3.13	±	0.36	2.69	±	0.05
19	0.00	±	0.00	3.66	±	0.17	3.15	±	0.36	2.10	±	0.08
21	0.00	±	0.00	3.13	±	0.15	2.62	±	0.35	1.89	±	0.07
25	0.00	±	0.00	4.07	±	0.19	3.55	±	0.36	1.32	±	0.06
29	0.13	±	0.09	2.81	±	0.13	2.30	±	0.34	0.76	±	0.06
33	0.04	±	0.09	2.01	±	0.10	1.50	±	0.33	0.51	±	0.05
37	0.17	±	0.07	0.91	±	0.05	0.39	±	0.32	0.44	±	0.04
41	0.00	±	0.00	0.63	±	0.04	0.11	±	0.32	0.30	±	0.05
45	0.00	±	0.00	0.27	±	0.03	-0.24	±	0.31	0.10	±	0.05
49	0.00	±	0.00	0.25	±	0.03	-0.26	±	0.31	0.07	±	0.04
	Supported ²¹⁰ Pb			0.51	±	0.31						

APPENDIX D: METAL ABUNDANCE DATA SUMMARIES

Description: Contains downcore metal abundance data (Zn, Cu, Fe, and Al) for selected Pamlico Sound estuarine cores (S12, S31, S32, S41, and S50).

PAM02S12												
Midpoint	Zn			Cu			Fe			Al		
cm	ppm			ppm			ppm			ppm		
1	36.45	±	1.63	4.27	±	0.43	16361	±	505	24195	±	138
3	32.78	±	1.62	3.17	±	0.35	14191	±	239	39683	±	308
5	21.71	±	1.61	2.94	±	0.35	9906	±	274	31414	±	367
7	29.00	±	1.62	4.79	±	0.34	15318	±	359	42582	±	530
9	31.26	±	1.62	4.50	±	0.37	15510	±	922	28094	±	339
11	32.40	±	1.62	4.95	±	0.40	15755	±	271	29513	±	238
13	44.35	±	1.64	6.41	±	0.39	15988	±	454	33206	±	364
15	37.62	±	1.63	6.92	±	0.42	17719	±	533	25833	±	138
17	30.07	±	1.62	6.05	±	0.36	14408	±	273	19643	±	388
19	27.23	±	1.62	4.62	±	0.41	14364	±	440	20539	±	135
21	24.93	±	1.61	4.78	±	0.48	14132	±	489	24237	±	158
23	24.73	±	1.61	4.81	±	0.57	14566	±	612	25628	±	315
25	27.42	±	1.62	5.02	±	0.66	12674	±	1175	21405	±	183
27	32.53	±	1.62	4.48	±	0.49	13132	±	1048	25830	±	176
29	25.87	±	1.61	4.31	±	0.38	12708	±	1504	36390	±	209
31	31.81	±	1.62	8.07	±	0.38	16553	±	720	30426	±	296

PAM02S31												
Midpoint	Zn			Cu			Fe			Al		
cm	ppm			ppm			ppm			ppm		
1	101.13	±	1.65	13.29	±	1.20	33858	±	422	113008	±	2406
3	104.02	±	1.55	12.78	±	0.36	29682	±	612	68620	±	999
5	101.97	±	1.57	12.52	±	0.36	28588	±	504	45589	±	1187
7	87.87	±	1.48	11.23	±	0.36	26966	±	1143	40557	±	605
9	82.22	±	1.46	11.40	±	0.36	25463	±	342	35732	±	198
11	87.17	±	1.59	10.86	±	0.35	29314	±	461	35624	±	320
13	92.98	±	2.40	12.96	±	0.36	29495	±	335	28472	±	593
15	103.57	±	1.58	16.86	±	0.37	27244	±	557	23081	±	1061
17	103.66	±	1.55	14.36	±	0.36	30019	±	595	31288	±	966
19	104.30	±	1.55	16.30	±	1.29	28761	±	430	28881	±	1037
21	92.03	±	1.52	12.41	±	0.36	30788	±	330	50097	±	447
23	95.89	±	1.62	14.20	±	1.28	30594	±	550	40202	±	480
25	94.87	±	1.77	15.37	±	0.37	29418	±	942	30128	±	502
27	101.69	±	1.80	15.71	±	1.25	31765	±	777	43200	±	396
29	98.57	±	1.61	17.45	±	0.38	37420	±	835	108617	±	1529
32	85.71	±	1.94	14.01	±	0.36	29566	±	961	57524	±	970
35	90.49	±	2.35	16.19	±	1.29	29850	±	1282	52111	±	654
38	87.34	±	1.50	15.31	±	1.22	28085	±	1199	53845	±	373
41	81.51	±	1.97	12.24	±	1.27	29534	±	298	62457	±	456
44	89.68	±	1.57	12.99	±	1.18	28654	±	651	73266	±	419
47	91.25	±	1.71	12.23	±	2.29	26972	±	346	46523	±	505
50	85.13	±	1.56	12.41	±	0.36	26790	±	430	43651	±	865
53	79.55	±	1.45	11.26	±	0.36	27133	±	288	67996	±	306

PAM02S32											
Midpoint	Zn			Cu			Fe			Al	
cm	ppm			ppm			ppm			ppm	
1	87.53	±	1.65	13.35	±	0.92	37357	±	1106	105630	± 808
3	93.09	±	1.77	13.19	±	0.85	35919	±	1133	98226	± 667
5	96.50	±	1.65	13.30	±	1.38	36886	±	1500	87591	± 1538
7	98.42	±	1.66	14.06	±	0.68	35243	±	1904	83930	± 698
9	101.94	±	1.66	13.80	±	2.52	37525	±	1722	89198	± 738
11	106.67	±	1.68	14.78	±	1.20	35714	±	356	78092	± 1168
13	103.33	±	1.67	14.91	±	1.09	32801	±	772	48194	± 558
15	103.03	±	1.69	15.75	±	2.47	34298	±	1279	46158	± 436
17	92.04	±	1.70	17.25	±	1.14	38241	±	1717	50276	± 415
19	86.35	±	1.64	16.99	±	0.42	40051	±	1186	62464	± 450
21	94.09	±	1.65	18.55	±	0.82	36918	±	687	45688	± 279
23	91.53	±	1.81	17.21	±	0.77	37346	±	485	50367	± 418
25	95.37	±	1.66	16.27	±	0.77	35903	±	720	52313	± 514
27	87.18	±	1.89	16.57	±	0.37	39770	±	380	63533	± 1029

PAM02S41											
Midpoint	Zn			Cu			Fe			Al	
cm	ppm			ppm			ppm			ppm	
1	67.64	±	1.72	7.45	±	0.46	23167	±	1118	89043	± 853
3	69.95	±	1.94	6.42	±	0.59	21485	±	794	73957	± 1036
5	85.12	±	2.05	9.03	±	0.96	28854	±	544	74082	± 993
7	85.63	±	2.05	9.40	±	1.00	26060	±	327	48828	± 902
9	78.63	±	1.67	9.68	±	1.02	24373	±	650	46297	± 584
11	79.18	±	1.78	8.33	±	0.41	25801	±	1037	53116	± 227
13	91.90	±	1.76	10.56	±	0.36	27700	±	297	47219	± 214
15	86.63	±	1.68	11.25	±	1.06	25694	±	593	36235	± 148
17	77.99	±	1.78	11.57	±	1.41	24490	±	422	34111	± 291
19	71.94	±	1.82	10.89	±	0.36	24827	±	412	39148	± 152
21	83.06	±	1.81	12.36	±	0.38	27521	±	702	35738	± 298
23	79.09	±	1.70	10.00	±	0.38	27102	±	741	37220	± 321
25	74.78	±	1.65	9.50	±	0.39	28825	±	347	73377	± 644
27	70.68	±	1.76	9.08	±	0.40	26132	±	606	38859	± 297

PAM02S50												
Midpoint	Zn			Cu			Fe			Al		
cm	ppm			ppm			ppm			ppm		
3	93.18	±	1.98	13.25	±	0.89	32932	±	1109	52155	±	258
5	94.36	±	1.73	14.29	±	0.89	31548	±	424	22132	±	224
7	94.98	±	1.68	14.22	±	1.57	32797	±	317	25306	±	261
9	91.24	±	1.67	13.31	±	1.32	34384	±	346	28574	±	142
11	73.55	±	1.86	14.29	±	1.36	34084	±	310	29340	±	519
13	92.90	±	1.80	14.16	±	2.06	33380	±	365	34025	±	527
15	88.82	±	1.71	16.02	±	1.25	32195	±	435	19310	±	122
17	93.65	±	1.68	14.58	±	0.49	31113	±	297	21859	±	242
19	88.10	±	1.66	15.73	±	0.60	33738	±	340	23188	±	262
23	80.14	±	1.65	15.21	±	0.49	34262	±	311	27397	±	266
27	73.80	±	1.92	14.37	±	1.27	31790	±	428	23979	±	503
32	74.36	±	1.64	14.59	±	0.37	33906	±	314	31897	±	552
38	69.24	±	1.65	12.21	±	0.41	30361	±	290	24826	±	150
44	68.75	±	1.63	10.24	±	0.44	34291	±	314	54056	±	576
49	74.28	±	1.64	10.61	±	0.63	38032	±	335	76987	±	555

APPENDIX E: ALUMINUM NORMALIZED METAL ABUNDANCE DATA SUMMARIES

Description: Contains downcore aluminum normalized metal abundance data ($\text{Zn}/\text{Al} \times 1000$, $\text{Cu}/\text{Al} \times 1000$, and Fe/Al) for selected Pamlico Sound estuarine cores (S12, S31, S32, S41, and S50).

PAM02S12									
Midpoint	Zn/Al X 1000			Cu/Al X 1000			Fe/Al		
cm									
1	1.51	±	0.07	0.18	±	0.02	0.68	±	0.02
3	0.83	±	0.04	0.08	±	0.01	0.36	±	0.01
5	0.69	±	0.05	0.09	±	0.01	0.32	±	0.01
7	0.68	±	0.04	0.11	±	0.01	0.36	±	0.01
9	1.11	±	0.06	0.16	±	0.01	0.55	±	0.03
11	1.10	±	0.06	0.17	±	0.01	0.53	±	0.01
13	1.34	±	0.05	0.19	±	0.01	0.48	±	0.01
15	1.46	±	0.06	0.27	±	0.02	0.69	±	0.02
17	1.53	±	0.09	0.31	±	0.02	0.73	±	0.02
19	1.33	±	0.08	0.23	±	0.02	0.70	±	0.02
21	1.03	±	0.07	0.20	±	0.02	0.58	±	0.02
23	0.97	±	0.06	0.19	±	0.02	0.57	±	0.02
25	1.28	±	0.08	0.23	±	0.03	0.59	±	0.06
27	1.26	±	0.06	0.17	±	0.02	0.51	±	0.04
29	0.71	±	0.04	0.12	±	0.01	0.35	±	0.04
31	1.05	±	0.05	0.27	±	0.01	0.54	±	0.02

PAM02S31									
Midpoint	Zn/Al X 1000			Cu/Al X 1000			Fe/Al		
cm									
1	0.89	±	0.02	0.12	±	0.01	0.30	±	0.01
3	1.52	±	0.03	0.19	±	0.01	0.43	±	0.01
5	2.24	±	0.07	0.27	±	0.01	0.63	±	0.02
7	2.17	±	0.05	0.28	±	0.01	0.66	±	0.03
9	2.30	±	0.04	0.32	±	0.01	0.71	±	0.01
11	2.45	±	0.05	0.30	±	0.01	0.82	±	0.01
13	3.27	±	0.11	0.46	±	0.02	1.04	±	0.02
15	4.49	±	0.22	0.73	±	0.04	1.18	±	0.06
17	3.31	±	0.11	0.46	±	0.02	0.96	±	0.04
19	3.61	±	0.14	0.56	±	0.05	1.00	±	0.04
21	1.84	±	0.03	0.25	±	0.01	0.61	±	0.01
23	2.39	±	0.05	0.35	±	0.03	0.76	±	0.02
25	3.15	±	0.08	0.51	±	0.01	0.98	±	0.04
27	2.35	±	0.05	0.36	±	0.03	0.74	±	0.02
29	0.91	±	0.02	0.16	±	0.00	0.34	±	0.01
32	1.49	±	0.04	0.24	±	0.01	0.51	±	0.02
35	1.74	±	0.05	0.31	±	0.02	0.57	±	0.03
38	1.62	±	0.03	0.28	±	0.02	0.52	±	0.02
41	1.31	±	0.03	0.20	±	0.02	0.47	±	0.01
44	1.22	±	0.02	0.18	±	0.02	0.39	±	0.01
47	1.96	±	0.04	0.26	±	0.05	0.58	±	0.01
50	1.95	±	0.05	0.28	±	0.01	0.61	±	0.02
53	1.17	±	0.02	0.17	±	0.01	0.40	±	0.00

PAM02S32									
Midpoint	Zn/Al X 1000			Cu/Al X 1000			Fe/Al		
cm									
1	0.83	±	0.02	0.13	±	0.01	0.35	±	0.01
3	0.95	±	0.02	0.13	±	0.01	0.37	±	0.01
5	1.10	±	0.03	0.15	±	0.02	0.42	±	0.02
7	1.17	±	0.02	0.17	±	0.01	0.42	±	0.02
9	1.14	±	0.02	0.15	±	0.03	0.42	±	0.02
11	1.37	±	0.03	0.19	±	0.02	0.46	±	0.01
13	2.14	±	0.04	0.31	±	0.02	0.68	±	0.02
15	2.23	±	0.04	0.34	±	0.05	0.74	±	0.03
17	1.83	±	0.04	0.34	±	0.02	0.76	±	0.03
19	1.38	±	0.03	0.27	±	0.01	0.64	±	0.02
21	2.06	±	0.04	0.41	±	0.02	0.8 1	±	0.02
23	1.82	±	0.04	0.34	±	0.02	0.74	±	0.01
25	1.82	±	0.04	0.31	±	0.02	0.69	±	0.02
27	1.37	±	0.04	0.26	±	0.01	0.63	±	0.01

PAM02S41									
Midpoint	Zn/Al X 1000			Cu/Al X 1000			Fe/Al		
cm									
1	0.76	±	0.02	0.08	±	0.01	0.26	±	0.01
3	0.95	±	0.03	0.09	±	0.01	0.29	±	0.01
5	1.15	±	0.03	0.12	±	0.01	0.39	±	0.01
7	1.75	±	0.05	0.19	±	0.02	0.53	±	0.01
9	1.70	±	0.04	0.21	±	0.02	0.53	±	0.02
11	1.49	±	0.03	0.16	±	0.01	0.49	±	0.02
13	1.95	±	0.04	0.22	±	0.01	0.59	±	0.01
15	2.39	±	0.05	0.31	±	0.03	0.71	±	0.02
17	2.29	±	0.06	0.34	±	0.04	0.72	±	0.01
19	1.84	±	0.05	0.28	±	0.01	0.63	±	0.01
21	2.32	±	0.05	0.35	±	0.01	0.77	±	0.02
23	2.12	±	0.05	0.27	±	0.01	0.73	±	0.02
25	1.02	±	0.02	0.13	±	0.01	0.39	±	0.01
27	1.82	±	0.05	0.23	±	0.01	0.67	±	0.02

PAM02S50									
Midpoint	Zn/Al X 1000			Cu/Al X 1000			Fe/Al		
<i>cm</i>									
3	1.79	±	0.04	0.25	±	0.02	0.63	±	0.02
5	4.26	±	0.09	0.65	±	0.04	1.43	±	0.02
7	3.75	±	0.08	0.56	±	0.06	1.30	±	0.02
9	3.19	±	0.06	0.47	±	0.05	1.20	±	0.01
11	2.51	±	0.41	0.49	±	0.05	1.16	±	0.02
13	2.73	±	0.07	0.42	±	0.06	0.98	±	0.02
15	4.60	±	0.09	0.83	±	0.07	1.67	±	0.02
17	4.28	±	0.09	0.67	±	0.02	1.42	±	0.02
19	3.80	±	0.08	0.68	±	0.03	1.46	±	0.02
23	2.93	±	0.07	0.56	±	0.02	1.25	±	0.02
27	3.08	±	0.10	0.60	±	0.05	1.33	±	0.03
32	2.33	±	0.07	0.46	±	0.01	1.06	±	0.02
38	2.79	±	0.07	0.49	±	0.02	1.22	±	0.01
44	1.27	±	0.03	0.19	±	0.01	0.63	±	0.01
49	0.96	±	0.02	0.14	±	0.01	0.49	±	0.01