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Sources and Fates of Sedimentary Organic Matter in the White Oak and Neuse River Estuaries

by

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DISCLAIMER STATEMENT

ABSTRACT

The question of the sources and fates of organic matter in coastal sediments has been addressed through the combined use of modern sediment chronology and carbon isotopic analysis (^{12}C, ^{13}C, ^{14}C) of sedimentary organic matter. The small, sparsely populated White Oak River estuary and the larger, more populous Neuse River estuary were selected as field sites. Sediment cores from one upriver and one downriver location in each river-estuary were studied in detail.

Modern sediment chronologies based upon excess ^{210}Pb and fallout $^{239,240}Pu$ were used to provide a deposition-age context in which to view the ^{14}C ages of sedimentary organic matter. In three of four cores deposition-age intervals were assigned as follows: 0-30 years for samples containing excess ^{210}Pb and plutonium; 30-100 years for samples containing excess ^{210}Pb but lacking plutonium. One of these locations (White Oak, downriver) may have experienced steady-state sediment accumulation at about 0.25 cm/yr; the other two locations (White Oak, upriver; Neuse, upriver), while not sites of steady-state sediment accumulation, have had average accumulation rates $< \sim 0.5$ cm/yr over the last 60-100 years. In the fourth sediment core (Neuse, downriver) excess ^{210}Pb and plutonium were very similarly distributed and were evidently transported by a common mixing process rather than by sediment accumulation.

Stable carbon isotopes in organic matter were generally heavier (^{13}C-enriched) in downriver (relative to upriver) sediments, consistent with increased inputs of marine organic matter at downriver locations. Vertical variations in stable isotopic composition within the sediment columns showed no consistent trends.

^{14}C analyses of sedimentary organic matter revealed the presence of bomb ^{14}C in core-top samples, but at concentrations which indicated the admixture of aged organic matter; thus organic matter inputs include both recently produced and aged material. Below the horizon of bomb ^{14}C contamination ^{14}C ages exceeded sediment deposition ages by about 100-1000 years. Old organic matter is therefore preserved in these sediments, but the issue of its preferential preservation, relative to recently produced organic matter, is unresolved because of non-steady-state in ^{14}C concentration of organic-matter inputs, both pre-bomb and post-bomb.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

As a substrate for microbial growth, organic matter in the sediments of rivers and estuaries represents a potential oxygen demand on, and nutrient source to, the overlying water. The actual impact of sedimentary organic matter on water quality depends upon the rates of the processes of microbial degradation. The sources (hence the composition) of the organic matter strongly influence these rates. Organic matter is supplied to coastal sediments from many sources. We have utilized carbon isotopes (^{12}C, ^{13}C, ^{14}C) as tracers for distinguishing the sources of organic matter to the sediments of the White Oak and Neuse river estuaries and for examining the differential preservation of various components of the organic matter through microbial decomposition within the sediments. Our hypothesis was that organic matter supplied to the river-estuary systems from aged reservoirs (soils, sediments, etc) should be preferentially preserved over recently produced organic matter. A consequence of this would be an increase in ^{14}C age of sedimentary organic matter with depth in the sediment column, at a rate more rapid than the increase in deposition age of the sediment. The goal of our study was to demonstrate this relationship through the determination of deposition ages in sediment cores and of ^{14}C ages on organic matter from those cores.

The White Oak and Neuse river-estuary systems were selected as representative of different degrees of watershed development and probable human impact on organic-matter loading. The watershed of the White Oak is small and sparsely populated, approaching a "natural" system, while that of the

Neuse is larger, more populous, and more diversely used. Two sediment cores from each river-estuary system have been studied; upriver and downriver locations were chosen in each case to maximize the potential influences of continental and marine sources of organic matter, respectively.

Sediment deposition ages were studied through the use of excess ^{210}Pb and fallout ^{239,240}Pu as tracers of the vertical transport of sediment particles in the sediment column. In three of the four cores studied (WORH1 = White Oak River estuary, downriver; WORF1 = White Oak River estuary, upriver; NRC1 = Neuse River estuary, upriver) deposition-age intervals were assigned to horizons in the sediment: 0-30 years for horizons containing both fallout plutonium and excess ^{210}Pb, 30-100 years for horizons containing excess ^{210}Pb and lacking plutonium. In one of these cores (WORH1) the tracer data were compatible with steady-state sediment accumulation as a dominant sediment-transport process: the sediment accumulation rate was about 0.25 cm/yr. Based upon the deposition-age intervals average sediment accumulation rates for cores WORF1 and NRC1 appeared to be $<$ 0.5 cm/yr. In core NRH1 (Neuse River estuary, downriver) excess ^{210}Pb and fallout plutonium were very similarly distributed; thus mixing was determined to be the dominant sediment-transport process at this site, and the average sediment accumulation rate was relatively low (and possibly zero) during the last $\sim$ 100 years.

The stable carbon isotopic composition of the sedimentary organic matter provided an index of the relative importance of terrestrial (C_3-plants and products thereof) and marine (plankton, salt-marsh grasses) sources of organic matter. Most of the isotopic data were compatible with purely

terrestrial organic matter sources. An offset in isotopic composition between upriver and downriver locations, however, suggests an increasing contribution from marine sources in the downriver direction. Vertical changes in stable carbon-isotopic composition of organic matter within the sediment columns were variable from location to location and probably resulted from variable composition of source materials over time.

The ^{14}C determinations on organic matter from the sediment cores further constrain the sources and fates of sedimentary organic matter. Newly deposited organic matter is a mixture of recently produced and aged material: bomb ^{14}C was present in core-top samples, but at concentrations lower than would be expected if only plant materials produced during the last 25 years were present. Where sediment deposition ages could be estimated, samples from below the depth of bomb ^{14}C influence were found to have ^{14}C ages in excess of deposition ages by about 100-1000 years. This shows clearly that aged organic matter was preserved in these sediments. Whether the aged material was preferentially preserved, relative to recently produced organic matter, was unclear, owing to non-steady-state in ^{14}C age of the organic-matter inputs. At the core tops, where rapid microbially-mediated decomposition of organic matter was expected, any resulting changes in ^{14}C age were masked by bomb ^{14}C. But ^{14}C age was not found to increase monotonically with depth in the sediment even in horizons below those affected by bomb ^{14}C; this implies that variation of the average ^{14}C age of the organic source materials to the sediments may be a chronic feature in these estuaries. Under such conditions reasonable modelling of the effect of microbial degradation processes upon ^{14}C age of organic matter in sediment cores is not possible.

Recommendations

1. The results of our study and of studies performed in other locations are consistent with the notion that microbial decomposition processes act to preferentially remove recently produced organic matter from a mixture of young and aged material. If this is true, the potential impact of organic matter introduced to North Carolina estuaries depends upon its age. Loadings of recently-produced, untreated or partially treated organic materials are likely to substantially increase sediment oxygen demand and the rate of nutrient regeneration, thereby increasing the vulnerability of the estuaries to water-column anoxia and nuisance algal blooms. Sediment accumulation rates are too low to rapidly remove these materials from the zone of intense microbial activity. Discharges of these susceptible organic materials must therefore be controlled. Aged organic materials are more inert and are therefore less likely to cause serious oxygen depletion or nutrient enhancement. From this viewpoint the aged material may be relatively innocuous. [We emphasize, however, that aged materials may have more subtle impacts on water quality and productivity (e.g., through interactions with micronutrient elements) and that no increase in organic-matter loading can be assumed to be free of the risk of environmental deterioration.]

2. Differential preservation of aged and recently produced organic matter would also dictate refined approaches to the assessment of potential hazards to water quality from existing sediments. Measurements of gross organic carbon content alone may be very misleading: the susceptibility of

the organic matter to microbial degradation must also be considered. One approach to this goal is through the use of carbon isotopes (including ^{14}C), but other aspects of the composition of sedimentary organic materials should be investigated for their relevance to rates of microbial degradation.

3. The research goals of this project were frustrated in part by non-steady-state in the carbon isotopic composition of organic matter inputs to the estuarine sediments. Further studies of depth profiles of carbon isotopes in these sediments would meet with the same difficulties. Two alternative approaches, both beyond the scope of the present project, might be considered:

(i) a comparison of carbon isotopic compositions in surficial sediments and in source materials. A large number of samples would be desirable, and the source materials should include numerous samples collected in suspension in the water column. An age difference between sources and sediments might be directly demonstrated in this way.

(ii) microcosm (jar) studies. Sediment samples would be incubated in the laboratory, and changes in the carbon isotopic composition would be followed over time. This is an experiment on a larger scale than the foregoing, in that large amounts of sediment and long incubations would be required.

I. INTRODUCTION

General

Particulate organic matter enters rivers and estuaries through several processes: erosion of soils and sediments, organic productivity in the water column, disposal of wastes (sanitary, agricultural, industrial). Because the organic solids are of low density, they are transported in and through sedimentary environments with the fine-grained (silt + clay) fraction of inorganic particles. Deposition of this material from quiescent waters produces organic-rich mud accumulations. These muds support intense biogeochemical activity which exerts a profound influence on the chemistry of both the sediments and, through nutrient regeneration and oxygen consumption, the overlying water. Improved models for the biogeochemical interactions in riverine and estuarine sediments are therefore essential to the understanding of both present patterns and future changes in water quality.

Several factors interact to control the types and rates of biogeochemical reactions which occur at a given location. Here we consider one of these: the effect of composition and provenance of the sedimentary organic matter on the biogeochemical processes. Evidence of the importance of this factor is very clear. In a typical coastal mud both the concentration of organic matter and the rates of processes of microbial degradation of organic matter decrease with increasing depth in the sediment column. Below a few tens of centimeters' depth, the concentration of organic matter levels off at a finite value, and the rate of further degradation is too slow to be readily detectable. These patterns in organic matter and microbial activity are thought to result from variations in the susceptibility of organic matter to microbial degradation: newly deposited organic matter is rich in easily-metabolized components ("reactive," "juicy"), but selective removal of this material leaves a residue of "refractory" organic matter which is resistant to decomposition. Berner (1971; 1974; 1980) has emphasized the importance of the nature of the organic substrates to the rates of microbial degradation in early diagenesis.

Although they are of paramount importance, the distinctions in composition between "metabolizable" and "refractory" organic matter are very poorly understood. It seems likely, however, that the metabolizable and refractory fractions in a contemporary mud may correlate in a simple way with the proximal sources of organic matter to the deposit. Organic matter derived by erosion from an aged reservoir (soil, sediment, peat, coal, petroleum, etc) is a residue from an earlier cycle of degradation, during which metabolizable components have been at least partly re-mineralized; such material may be expected to resist further degradation when re-deposited in contemporary sediments. In contrast, a substantial fraction of newly produced organic matter, with no previous history of degradation, should undergo rapid degradation in contemporary sediments. To test this hypothesis it is necessary to discriminate, in the complex mixture of organic materials in muds, among the various sources of organic matter. In this project we have utilized carbon isotopes as source tracers for organic matter in muds from the White Oak and Neuse River-estuaries, North Carolina.

Carbon Isotopes as Source Tracers for Organic Matter

Natural carbon consists of the stable isotopes ^{12}C (98.89%) and ^{13}C

(1.11%) and the radioactive isotope ^{14}C (half-life 5,730 years). Our use of ^{14}C as a tracer depends upon age differences among the various reservoirs which contribute organic matter to riverine and estuarine sediments. With the stable isotopes we exploit the well-studied fractionation of ^{12}C and ^{13}C in natural processes.

Isotope fractionation. The mass difference between ^{12}C and ^{13}C causes the atoms of these isotopes to react chemically at slightly different rates and so to distribute themselves differentially (i.e., to fractionate) between reactants and products. Useful summaries of fractionation mechanisms and effects are contained in Hoefs (1980). At environmental temperatures the fractionations produced are small, so they can be expressed on an expanded ("per mil," or parts per thousand) scale:

$$\delta^{13}C_{sample} = \frac{(^{13}C/^{12}C)_{sample} - (^{13}C/^{12}C)_{standard}}{(^{13}C/^{12}C)_{standard}} \times 1000\ 0/00$$

The usual standard is the PeeDee belemnite, a fossil of Cretaceous age composed of calcium carbonate; all $\delta^{13}C$'s in this report are relative to this "PDB" standard. Materials which are relatively enriched in ^{12}C are said to be isotopically "light" and those relatively enriched in ^{13}C are said to be "heavy".

We are concerned here with the carbon-isotopic composition of organic matter, which derives ultimately from photosynthesis. The process of photosynthesis involves a substantial isotopic fractionation between the inorganic carbon source reservoir (CO_2, gaseous or dissolved) and the organic matter produced: organic matter is isotopically light compared to the inorganic carbon. The magnitude of the isotopic fractionation depends upon the photosynthetic pathway employed. Plants employing the Calvin cycle (C_3 plants: most higher plants) produce organic matter which is lighter, on average, by about 17-27 0/00 than the source carbon. Plants which photosynthesize by the Hatch-Slack pathway (C_4 plants: mainly grasses, including corn and some salt-marsh species) are lighter than the source carbon by 0-12 0/00. CAM (crassulacean acid metabolism) plants (certain succulents) produce fractionations overlapping the ranges of C_3 and C_4 plants; these do not figure significantly in our field areas and are omitted from further discussion.

Added to the variability in the isotopic composition of plant carbon due to photosynthetic pathway is that which arises from variations in isotopic composition of the inorganic carbon sources which are utilized. Important source reservoirs, together with their isotopic compositions, include the following:

	$\delta^{13}C$, 0/00
Atmospheric CO_2	-7
Dissolved CO_2, marine	0.8 to 2.0
Dissolved CO_2, freshwater	-1 to -24
Marine carbonates	0 ± 3
Freshwater carbonates	-15 to +4

Dissolved CO_2 (chiefly HCO_3^- in most natural waters) is heavier that gaseous CO_2 due to isotope-exchange equilibria. Freshwater dissolved CO_2 and carbonates are generally isotopically lighter than their marine counterparts because of the greater influence of light plant carbon, added through respiration. Thus, for a given photosynthetic pathway, a marine plant, using HCO_3^- as carbon source, will be isotopically heavier than a terrestrial plant, using atmospheric CO_2. And in cases where the isotopic composition of the carbon source reservoir can fluctuate, due to variable inputs of atmospheric, marine and respired CO_2, corresponding fluctuations must be anticipated in the isotopic composition of newly-produced organic matter; estuaries may be particularly susceptible to variability of this sort (Spiker, 1980).

Despite the evident complications, the regularities in stable isotopic composition suffice to permit some degree of discrimination among sources of organic matter (Hoefs, 1980: see Fig. 1a). Terrestrial macrophytes, which are mainly C_3 plants operating on atmospheric CO_2, are characteristically light (typically $-30 < \delta^{13}C < -24$ 0/00). The early stages of decomposition do not alter the isotopic signature (Brown et al, 1972; Haines and Montague, 1979), so that soil organic matter and sewage are also expected to be light. Diets rich in corn and sugar cane, both C_4 plants, would shift sewage toward a heavier isotopic composition (van der Merwe, 1982), but two sewage sludge samples from New York City were found to have $\delta^{13}C$'s of -25.7 0/00 and -26.0 0/00 (Burnett and Schaeffer, 1980). Coal and oil are not distinguishable from C_3 plants in the carbon-isotopic composition. Marine plankton collected from temperate and tropical waters are found to be relatively heavy ($-22 < \delta^{13}C < -18$ 0/00) (Sackett et al, 1974), though in culture experiments most of 17 taxa of phytoplankton produced isotopic fractionations as large as those of C_3 plants (Wong and Sackett, 1978); present knowledge of the physiology and ecology of the phytoplankton is inadequate to explain the apparent discrepancy between field samples and laboratory cultures. The field data form the basis of numerous studies of carbon isotopic composition of organic matter in coastal sediments (e.g., Sackett and Thompson, 1963;

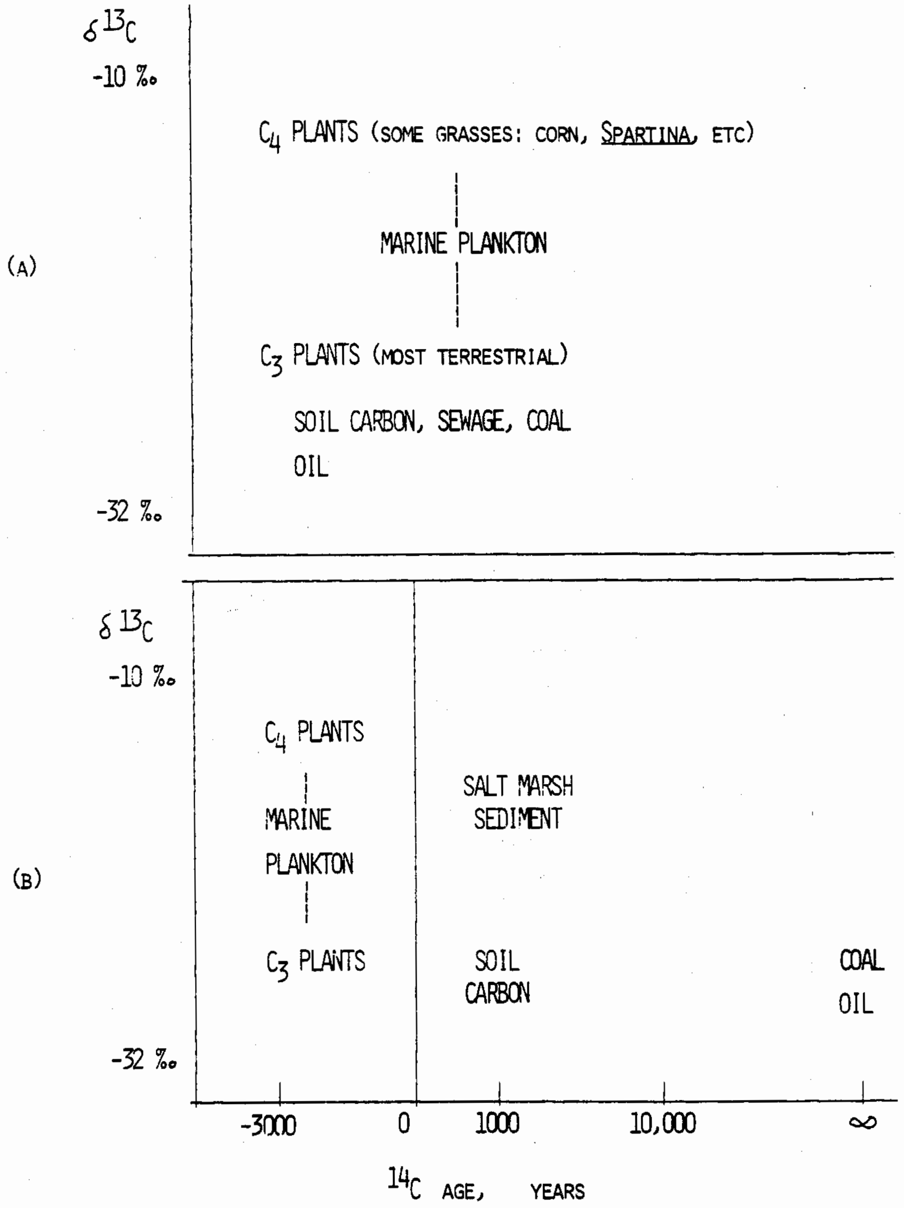

Figure 1. Carbon isotopic signatures of organic matter.
(A) Stable carbon isotopes ($\delta^{13}C$ relative to PDB standard).
(B) Stable carbon isotopes and ^{14}C age. Negative ^{14}C ages reflect contamination with bomb ^{14}C.

Hunt, 1970; Shultz and Calder, 1976; Gearing et al, 1977). Generally $\delta^{13}C$ of the organic matter increases rapidly with increasing distance from the coast (from $\delta^{13}C < -24$ 0/00 to $\delta^{13}C \simeq -20$ 0/00); this is interpreted as indicating that the carbon preserved in Recent sediments on the continental shelves is largely derived from marine photosynthesis.

^{14}C ages of carbon sources. With respect to our goal of characterizing the reactive or metabolizable fraction of organic matter in contemporary sediments, the stable carbon isotopes have the defect of not discriminating between organic matter from modern plants and from aged reservoirs (sediments, soils, coal, oil: Fig. 1a). This defect is remedied in part by adding ^{14}C (Fig. 1b). Coal and oil contain no ^{14}C ("infinite" ^{14}C age). The organic matter from the top one meter of soil profiles has average ^{14}C age varying between zero and thousands of years, with average age typically increasing with increasing depth in the profile (Campbell et al, 1967; Scharpenseel et al, 1969; Scharpenseel, 1970; Martel and Paul, 1974). A similar pattern of ^{14}C ages may be expected in salt-marsh sediments, although the vertical scale may be expanded (e.g., Bloom and Stuiver, 1963); stable carbon isotopes will be heavier than in soil profiles if C_4 salt-marsh plants contribute significantly to the sedimentary organic matter (Haines, 1976). Clearly the average ^{14}C age of organic matter derived from soils or salt-marsh sediments will depend upon the depth of active erosion, but this material will certainly be older than contemporary vegetation; peat exposed at low tide in a wave-cut bank facing Core Sound, North Carolina gave ^{14}C ages ($\delta^{13}C$-corrected, 5,730-year half-life) from 260 to 490 years (C.S. Martens, unpublished data).

Contemporary vegetation and immediate by-products are shown in Figure

1b as having formal negative age, that is, as containing excess ^{14}C. This excess has resulted from artificial ^{14}C production during the period of atmospheric testing of nuclear weapons ("bomb ^{14}C"). By convention the zero-age date for ^{14}C is taken as A.D. 1950, prior to contamination of the atmosphere with artificial ^{14}C. Contemporary vegetation contains bomb ^{14}C and thus has negative age on this scale.

Turekian and Benoit (1981) used carbon isotopes to constrain sources of organic matter to sediments of the inner New York Bight. In addition, several previous investigators have used ^{14}C age, alone or in combination with $\delta^{13}C$, as an indicator of provenance of organic matter in coastal sediments. Erlenkeuser et al (1974) presented carbon isotope data on recent sediments from the Baltic Sea. By extrapolating ^{14}C age from depth in long cores they showed a "recent age" (i.e., age at zero depth) of 850 years. This age is not obtained by direct measurements on core-top organic matter because of recent additions of fossil-fuel carbon (infinite ^{14}C age) and bomb ^{14}C. The 850-year "recent age" was interpreted as resulting from admixture of fossil organic matter eroded from nearby glacial sediments. Similarly, Benoit et al (1979) found an extrapolated "recent age" of 2310 ± 310 years for a sediment core from Long Island Sound. These investigators interpreted this as the age of that fraction of total carbon deposited which survives degradation and is buried (the non-metabolizable or refractory organic matter); soils were regarded as the probable source of this aged material. Baxter et al (1980) found an extrapolated "recent age" of 3000 years for a sediment core from the Firth of Clyde; in this case the aged fraction of organic matter was thought to be predominantly Carboniferous coal eroded from the nearby coastline.

Research Strategy

General approach. Previous investigations of carbon-isotopic composition of organic matter from coastal sediments support our presumption that the refractory fraction of organic matter in these sediments must be derived in part from aged reservoirs. It was our purpose to test this hypothesis in sediments from North Carolina estuaries. If it could be shown that the organic matter which survives microbial degradation in these sediments is dominated by refractory residues from soils or sediments, then the clear implication would be that increased inputs of modern wastes would increase microbial activity, potentially affecting water quality.

Our work has two major components. The determination of the carbon-isotopic composition of the organic fraction of sediment samples provides the basis for source discrimination and thus for distinctions between the metabolizable and refractory fractions. Modern sediment chronologies, based upon naturally-occurring excess ^{210}Pb and fallout $^{239,240}Pu$, have been used to establish a sediment-age context for interpretation of the ^{14}C ages on organic matter.

Field areas. In choosing field areas we recognized the necessity both to test our hypothesis in a relatively simple system and to attempt its application in a larger system of more immediate practical interest. Accordingly, we chose the White Oak and Neuse River estuaries as field areas for this study.

The drainage basin of the White Oak lies entirely within the Coastal Plain and is small enough to be quite homogeneous geologically. Population is sparse, and the major human impact is probably that associated with land use in agriculture. Background studies applicable to our research were available (Martens and Goldhaber, 1978 and unpublished data).

The Neuse River drains approximately 6,000 square miles of the North Carolina Piedmont and Coastal Plain (Billingsley, Fish and Schipf, 1957), an area large enough to encompass diverse geology and land use and which contains a significant fraction of the population of the state; industry is present, but the drainage basin is not heavily industrialized. Studies of sedimentary diagenesis in the Neuse estuary (M. Brinson and E. Matson, East Carolina University, with WRRI support) were in progress.

II. METHODS

Sampling

Sediment cores were collected in the White Oak River and estuary on 7 April 1982 with the collaboration of Jeffrey P. Chanton of the Curriculum in Marine Sciences, UNC-Chapel Hill and Norman H. Cutshall and Curtis R. Olsen of Oak Ridge National Laboratory. Sampling sites were selected to coincide with station F (here designated WORF) of Martens and Goldhaber (1978) and station H (here WORH) of Gruebel (1981) (Fig. 2). Station WORF was approximately 28 km upstream of the highway bridge at Swansboro, North Carolina (NC Highway 24). Sediment pore-water salinities at this site indicate no regular seawater intrusion (Martens and Goldhaber, 1978). Station WORH was located about 7.5 km upstream of the highway bridge at Swansboro. This site is within the estuary: pore-water salinities ranging from 2-26 0/00 have been reported (Gruebel, 1981). At both WORF and WORH water depth was less than two meters. Cores were taken in a six-inch diameter, stainless steel corer which was pushed manually into the sediment.

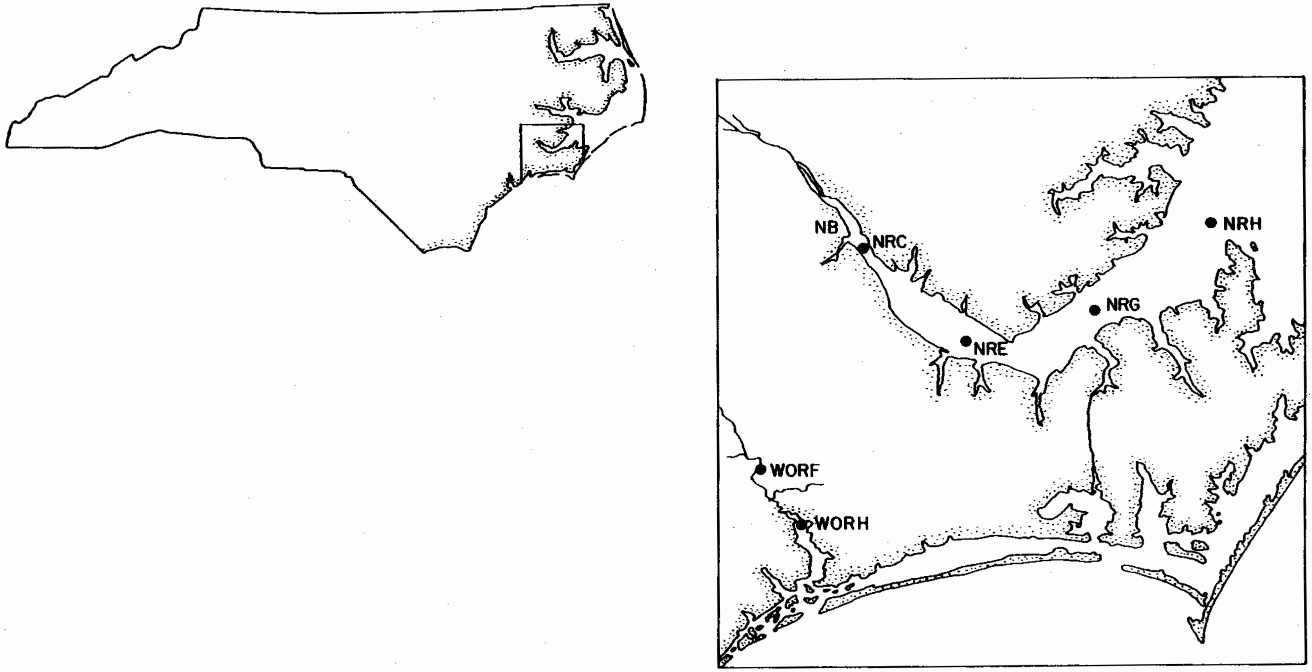

Figure 2. Station locations, eastern North Carolina: boxed area at left is enlarged at right. NB = New Bern, North Carolina. Neuse River estuary stations: NRC, NRE, NRG, NRH; results are presented on sediment cores from NRC and NRH. White Oak River estuary stations: WORF, WORH.

For convenience these cores are designated WORF1 and WORH1. The cores were subsampled in the field into two-centimeter depth intervals. All subsamples were frozen within one day of core collection and were maintained frozen until they could be dried in the laboratory in Chapel Hill.

Sediment cores were collected in the Neuse River estuary on 7 July 1982. Core samples were collected at stations H,G,E, and C of M. Brinson and E. Matson, East Carolina University. The cores from station H (here designated NRH) and C (NRC) were selected for detailed study; these cores are designated NRH1 and NRC1. Stations NRH and NRC were approximately in mid-channel, 60 km and 2.7 km, respectively, downstream from the Highway 17 bridge at New Bern, North Carolina. At the time of sampling the water depth at NRH was 6.7 m and salinities were 12 0/00 (surface water) and 13 0/00 (6 m depth); water depth at NRC was 3.4 m, and salinities were 0.9 0/00 (surface) and 3.8 0/00 (3 m depth). Cores were collected manually by divers (M. Brinson and E. Matson) using SCUBA. Four-inch polybutyrate tubes (1/8-inch wall) were pushed into the sediment and sealed top and bottom with rubber stoppers prior to withdrawal. Some core-shortening was observed: that is, the sediment-water interface within the core tube was visibly lower than in the surrounding sediment. About 1 cm shortening was observed in core NRH1, 4-5 cm in core NRC1. Cores were shielded from direct sunlight in the field and were returned to the shore laboratory (Pamlico Estuarine Laboratory, East Carolina University) for subsampling. All cores were subsampled in two-centimeter depth increments. The topmost two centimeters was in all cases very fluid and was sampled from the core tube with a plastic spoon; the remainder of the core was subsampled by extrusion from the core tube. Below 6-10 cm depth the sediment was sufficiently cohesive that the outermost ∿ 2 mm could be trimmed from each interval and discarded. Subsampling was completed in all cases within fourteen hours of core collection. The subsamples were sealed into plastic pouches and were stored frozen (including the top 12 cm of each core) or refrigerated until they could be dried in the laboratory in Chapel Hill.

Bulk Properties and Isotope Chemistry

All subsamples were dried at 90-100°C. Per cent water is the per cent mass lost (wet-mass basis) on drying. The dried subsamples were then ground in a ceramic mortar; to aid in homogenization the mortar used was large enough to contain the entire subsample as one charge. Except for the subsamples from core WORF1, the products of this grinding were powders which were visually homogeneous with respect to their major components. The WORF1 subsamples were visually inhomogeneous: polydisperse organic matter and silicate sand contributed, in varying proportions, to every subsample. There being no practical way to homogenize materials of such disparate density, aliquots of the WORF1 subsamples for all subsequent chemical measurements were taken with a riffle-type microsplitter.

One- to ten-gram aliquants of the dried subsamples were roasted in air for two days at 475°C. Loss-on-ignition (LOI) is the per cent mass lost (dry-mass basis) on roasting.

^{210}Pb was determined as the granddaughter ^{210}Po, which was assumed to exist in secular equilibrium with ^{210}Pb in these samples. One- to three-gram aliquants of the dried subsamples were totally dissolved by first treating with HNO_3 - HCl to oxidize organic matter, then attacking the silicate residue with a mixture of HF, HNO_3 and H_2SO_4 (300:100:50 by volume). Yield-tracer ^{208}Po was present throughout the dissolution process. Polonium isotopes were deposited onto silver disks from warm, stirred 1 $\overline{N}$ HCl and were determined by alpha spectrometry.

$^{239,240}Pu$ was determined using slight modifications of the procedure of Krishnaswami and Sarin (1976). One- to seventeen-gram (generally 3-10 gram) aliquants of dried sediment were moistened with 7 $\overline{N}$ HNO_3, then spiked with 0.84 dpm ^{242}Pu as yield tracer. Two leaches, with hot HNO_3 (60 ml) and hot HNO_3 (40 ml) + HCl (20 ml), were used to solubilize fallout plutonium. Plutonium was separated from the combined leachates by anion-exchange chromatography and electrodeposited on stainless steel planchets (Puphal and Olsen, 1972; Kressin, 1977) for determination by alpha spectrometry.

Carbon isotope measurements were purchased from Beta Analytic, Inc., of Coral Gables, Florida. In most cases ^{12}C, ^{13}C and ^{14}C were determined on a single, large (35-100 grams) sample. To supplement these data and to test (at relatively low cost) for consistency within cores, some additional, smaller (2-4 grams) samples were analyzed for ^{12}C and ^{13}C only. Since determinations on the organic fraction were desired, sediment samples were pre-treated to remove $CaCO_3$; these pre-treatments were performed in our laboratories. The sediment was slurried in a large excess of 0.6 $\overline{N}$ HCl and stirred, either continuously or at frequent intervals, for a minimum of 30 minutes. Calcium carbonate was a minor constituent in our samples, and visible CO_2 release ceased in all cases within a few minutes. The treated sediment was collected by centrifugation and filtration under vacuum, with copious washing to remove excess acid; after washing, it was re-dried and ground for carbon-isotope analysis. At Beta Analytic the samples were combusted in O_2 to convert organic carbon to CO_2. $\delta^{13}C$ was measured mass-spectrometrically on the CO_2 gas. For the ^{14}C measurements the CO_2 was chemically converted to benzene, which was counted by liquid scintillation (Noakes et al, 1965; Polach and Stipp, 1967; Calvert et al, 1978).

III. RESULTS

General Core Descriptions

General descriptions of the field sites and of the sediments collected are given in Table 1. Stations WORH (White Oak estuary), NRH and NRC (Neuse estuary) were all in muddy (predominantly silt + clay) sediments. The mud from WORH1 was generally darker than that collected in the Neuse, except that a horizon in NRC1 (18-24 cm) was as dark as the White Oak sediment. Organic matter in these muds was mainly fine-grained; leaves and/or woody fragments were noted at the sediment-water interface at NRC and intermittently down core WORH1. Coal fragments were found at the base (38-42 cm) of core NRC1. All of these estuarine sediments contained minor shell material and, excepting those from NRC, all smelled of hydrogen sulfide.

As noted in Table 1, the sediment from core WORF1 (White Oak River) contained variable proportions of organic matter and silicate minerals. Both fractions were generally coarser than in the estuarine sediments, and the proportion of silicate sand increased noticeably with depth in the core. There was no macroscopic shell material, and a slight odor of hydrogen sulfide was detected only intermittently.

Table 1. Sample locations and core descriptions.

Station WORF, core WORF1. 34°49.6'N, 77°10.8'W. Collected near SE bank, offshore of rooted grasses nearest the bank. Variable proportions of relatively coarse organic matter and silicates with depth in the core, with conspicuous increase in sand content with depth. Slight smell of hydrogen sulfide intermittent.

Station WORH, core WORH1. 34°45'N, 77°7.2'W. Collected just south of channel marker 20. Dark mud with occasional macroscopic organic matter (leaves and/or wood fragments). Bivalve shell material visible throughout, but minor. Sulfidic.

Station NRC, core NRC1. 35°5.3'N, 77°1.0'W. Collected approximately mid-estuary. Dark mud; 18-24 cm depth appreciably darker than sediment above or below, with sharp interface between gray and black mud in interval 24-26 cm. Leaves, sticks on sediment surface. Oxidized layer > 1 cm, < 2 cm thick. Two articulated *Rangia* at 4-6 cm. Macroscopic coal fragments in 38-40 cm, 40-42 cm.

Station NRH, core NRH1. 35°5.7'N, 76°30.0'W. Collected approximately mid-estuary. Dark mud. Bottom was densely burrowed at this station. Oxidized layer approximately 0.5 cm. Minor shell material visible in top 20 cm; no intact valves. Sulfidic.

Bulk Properties and Isotopic Results

Bulk properties. Per cent water and per cent LOI (loss on ignition) for the four sediment cores are given in Table 2, and the LOI data are displayed in Figures 3-6.

Overall the nominal range in per cent water was about 32-86 %. Both extremes are suspect as true measures of *in situ* water content: the highest values were from core tops, where the precise location of the sediment-water interface was difficult to establish, the lowest from sandy horizons which may have drained during subsampling. Below the topmost samples and for water contents greater than about 45 %, however, the results should be free of sampling artifacts. In undisturbed sediments of uniform lithology water content should decrease slowly with increasing depth, due to compaction. This pattern was not observed in any of the sediment cores studies here. Rather, the large ranges in water content and the fluctuations with depth in the cores reflect variable lithology: mud has a higher water capacity than does sand.

Water content and LOI were positively correlated; this is often observed in sediments of variable lithology (e.g., Benninger and Krishnaswami, 1981). Linear correlation coefficients between these parameters were > 0.97 for cores WORF1 (2-40 cm, 44-48 cm), NRC1 (2-20 cm, 24-42 cm) and NRH1 (2-46 cm) and 0.81 for core WORH1 (0-44 cm). The data omitted in computing these correlations include those identified above as being suspect and, in addition, samples 20-22 cm and 22-24 cm from NRC1; these latter samples were among those found to be darker than the surrounding sediment (Table 1). In general, then, water content and LOI are redundant indicators of lithologic

Table 2. Bulk sediment properties, ^{210}Pb and ^{239,240}Pu

Station WORF, Core WORF1

Depth, cm	% H_2O[1]	% LOI[2]	^{210}Pb, dpm/g[3]	^{239,240}Pu, dpm/kg[3]
0-2	71.09	12.93	3.92 ± 0.12	27.3 ± 2.8
2-4	79.28	24.83	6.89 ± 0.17	53.9 ± 3.5
4-6	80.41	28.77	7.22 ± 0.13	72.2 ± 4.5
6-8	82.16	34.79	7.48 ± 0.16	91.7 ± 5.0
8-10	80.57	27.41	6.98 ± 0.12	118.8 ± 7.1
10-12	78.30	27.16	5.82 ± 0.12	90.5 ± 5.3
12-14	79.09	27.60	4.93 ± 0.11	79.8 ± 4.5
14-16	61.18	13.56	2.57 ± 0.06	37.0 ± 2.7
16-18	62.92	14.10	2.32 ± 0.07	10.8 ± 1.0
16-18(2)			2.19 ± 0.05	
18-20	58.85	11.30	1.68 ± 0.04	3.1 ± 0.4
20-22	61.73	14.23	2.04 ± 0.06	2.2 ± 0.4
22-24	67.72	17.58	2.57 ± 0.06	0.9 ± 0.2
24-26	64.85	16.29	2.42 ± 0.07	1.5 ± 0.5
26-28	72.09	21.75	2.74 ± 0.08	0.9 ± 0.3
26-28(2)			2.75 ± 0.06	
28-30	77.01	29.57	3.35 ± 0.09	1.4 ± 0.6
30-32	75.97	27.58	3.17 ± 0.11	1.0 ± 0.4
32-34	73.70	23.08	2.30 ± 0.05	
34-36	60.67	13.91	1.46 ± 0.05	
36-38	59.23	12.79	1.41 ± 0.05	
38-40	59.62	11.76	1.47 ± 0.05	
40-42	37.06	4.16	0.81 ± 0.03	
42-44	32.61	3.03	0.67 ± 0.03	
44-46	49.95	6.99	0.81 ± 0.03	
46-48	57.96	11.10	1.08 ± 0.04	

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1) Mass per cent of wet sediment
2) LOI = loss on ignition; mass per cent of dry sediment
3) dpm = disintegrations per minute. Errors are ± 1σ due to counting statistics.

Table 2, continued.

Station WORH, Core WORH1

Depth, cm	% H_2O[1]	% LOI[2]	^{210}Pb, dpm/g[3]	^{239,240}Pu, dpm/kg[3]
0-2	62.74	14.33	9.98 ± 0.18	122.7 ± 6.0
2-4	65.47	12.45	9.57 ± 0.25	113.5 ± 7.5
4-6	62.24	10.83	7.47 ± 0.20	103.4 ± 5.5
6-8	54.92	9.06	6.00 ± 0.17	71.9 ± 4.3
8-10	56.03	9.98	4.94 ± 0.18	27.2 ± 2.3
10-12	56.03	8.72	4.41 ± 0.17	23.2 ± 1.4
10-12(2)			4.35 ± 0.10	
12-14	53.05	8.78	3.67 ± 0.12	16.4 ± 1.4
14-16	57.49	10.86	2.72 ± 0.09	1.4 ± 0.4
16-18	65.72	12.68	2.92 ± 0.07	1.2 ± 0.4
18-20	62.06	10.39	2.54 ± 0.06	1.7 ± 0.5
18-20(2)				2.3 ± 0.6
20-22	61.18	10.25	2.46 ± 0.10	1.6 ± 0.3
20-22(2)			2.39 ± 0.08	
22-24	55.46	9.24	2.05 ± 0.07	1.2 ± 0.4
24-26	61.27	11.71	1.94 ± 0.06	0.5 ± 0.2
26-28	65.76	15.08	1.99 ± 0.07	0.3 ± 0.2
28-30	59.53	10.69	1.78 ± 0.06	
30-32	57.31	9.63	1.62 ± 0.06	
32-34	59.78	9.41	1.74 ± 0.05	
34-36	59.95	9.52	1.69 ± 0.07	
36-38	57.27	9.70	1.61 ± 0.06	
38-40	55.95	9.41	1.71 ± 0.06	
40-42	56.06	8.46	1.78 ± 0.06	
42-44	59.04	8.78	1.78 ± 0.06	

Table 2, continued.

Station NRC, Core NRC1

Depth, cm	% H_2O[1]	% LOI[2]	^{210}Pb, dpm/g[3]	^{239,240}Pu, dpm/kg[3]
0-2	86.13	18.57	9.41 ± 0.20	68.0 ± 5.8
2-4	80.41	17.91	9.54 ± 0.27	80.1 ± 6.1
4-6	75.48	17.18	7.58 ± 0.20	124.9 ± 15.6
4-6(2)				103.4 ± 6.4
6-8	74.36	15.24	7.45 ± 0.20	170.2 ± 9.9 159.3 ± 10.6
8-10	69.77	14.63	4.39 ± 0.11	48.9 ± 3.7
10-12	69.39	14.81	4.12 ± 0.10	5.5 ± 1.2
12-14	68.51	13.91	3.71 ± 0.08	1.7 ± 0.6
14-16	66.59	13.06	3.38 ± 0.10	1.5 ± 0.5
16-18	66.29	12.82	3.50 ± 0.10	3.2 ± 0.7
18-20	69.52	14.39	2.87 ± 0.08	0.9 ± 0.4
20-22	74.72	18.15	2.37 ± 0.06	1.6 ± 0.5
20-22(2)			2.44 ± 0.09	
22-24	76.69	19.71	2.60 ± 0.07	
22-24(2)			2.39 ± 0.08	
24-26	68.14	13.99	5.63 ± 0.15	1.0 ± 0.4
24-26(2)			4.04 ± 0.11	
24-26(3)			4.11 ± 0.11	
26-28	63.99	12.56	4.40 ± 0.13	
26-28(2)			4.35 ± 0.12	
28-30	62.70	12.55	4.27 ± 0.10	0.1 ± 0.1
30-32	60.88	12.43	4.79 ± 0.12	
32-34	58.41	12.09	3.84 ± 0.10	0.3 ± 0.2
32-34(2)			3.93 ± 0.10	
34-36	57.05	11.84	3.80 ± 0.09	
36-38	55.38	11.07	3.65 ± 0.08	0.2 ± 0.1
38-40	51.97	9.87	2.92 ± 0.09	
40-42	43.65	6.97	2.13 ± 0.06	

Table 2, continued.

Station NRH, Core NRH1

Depth, cm	% H_2O[1]	% LOI[2]	^{210}Pb, dpm/g[3]	^{239,240}Pu, dpm/kg[3]
0-2	86.47	14.67	10.21 ± 0.31	157.9 ± 5.8
2-4	81.79	14.52	10.99 ± 0.30	
4-6	80.73	14.79	11.27 ± 0.33	173.8 ± 8.7
6-8	76.78	12.52	10.14 ± 0.24	166.4 ± 10.8
8-10	73.92	11.55	9.76 ± 0.26	175.4 ± 10.0
10-12	72.35	10.99	9.31 ± 0.19	188.9 ± 8.4
12-14	67.64	9.96	6.52 ± 0.20	124.3 ± 7.9
14-16	66.33	9.97	3.17 ± 0.10	39.3 ± 2.0
16-18	64.89	9.36	1.81 ± 0.05	14.0 ± 1.2
18-20	62.42	8.46	1.59 ± 0.04	8.8 ± 1.0
18-20(2)			1.59 ± 0.05	
20-22	59.00	7.22	1.19 ± 0.04	4.4 ± 0.8
22-24	62.74	8.39	1.38 ± 0.04	3.8 ± 1.0
24-26	62.82	8.04	1.41 ± 0.05	4.7 ± 0.4
26-28	62.06	7.88	1.26 ± 0.04	1.7 ± 0.5
26-28(2)			1.19 ± 0.05	
28-30	61.84	7.42	1.16 ± 0.04	<0.2 ± 0.2
30-32	65.14	8.17	1.30 ± 0.04	1.4 ± 0.4
32-34	65.06	8.50	1.23 ± 0.05	
34-36	61.88	8.07	1.24 ± 0.04	
36-38	62.83	8.39	1.32 ± 0.05	
38-40	63.19	8.69	1.36 ± 0.05	0.1 ± 0.1
40-42	62.33	8.36	1.37 ± 0.05	
42-44	62.41	8.49	1.36 ± 0.04	
44-46	63.43	9.12	1.37 ± 0.05	

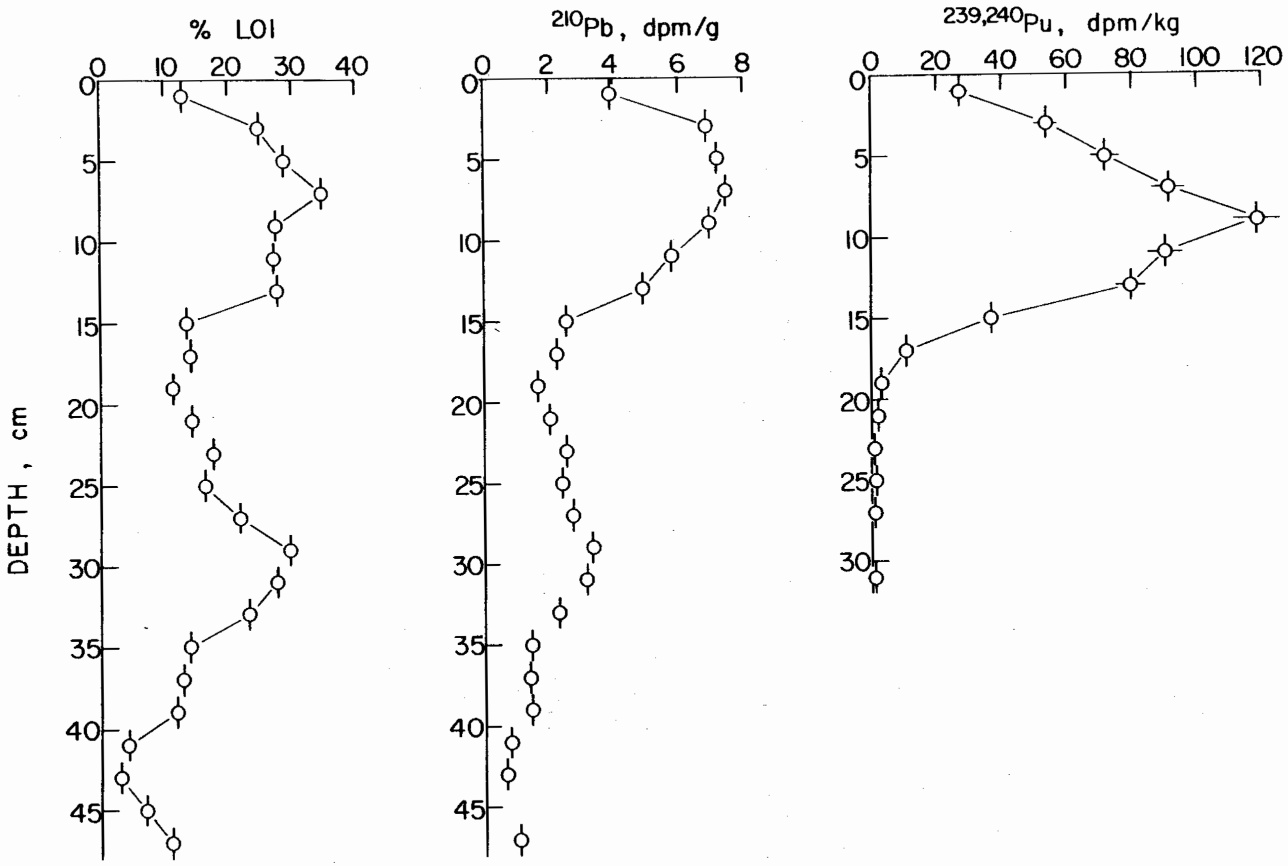

Figure 3. Loss on ignition (LOI) and chronometric tracer data, core WORF1. Total ^{210}Pb (excess- + ^{226}Ra-supported) is shown; excess ^{210}Pb was considered to terminate at 34 cm depth. ^{239,240}Pu was finite throughout 0-20 cm depth.

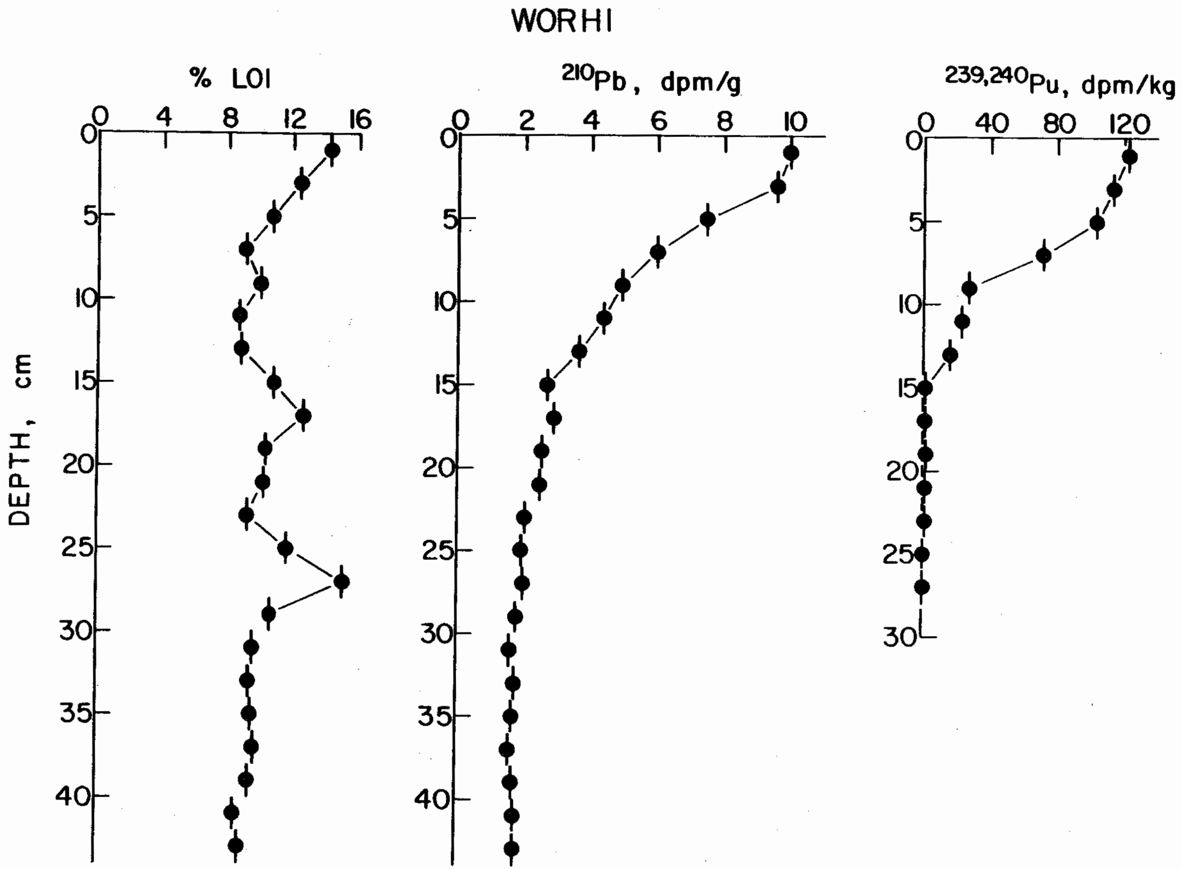

Figure 4. Loss on ignition (LOI) and chronometric tracer data, core WORH1. Total ^{210}Pb (excess- + ^{226}Ra-supported) is shown; excess ^{210}Pb was considered to extend to 28 cm depth. ^{239,240}Pu was finite throughout 0-14 cm depth.

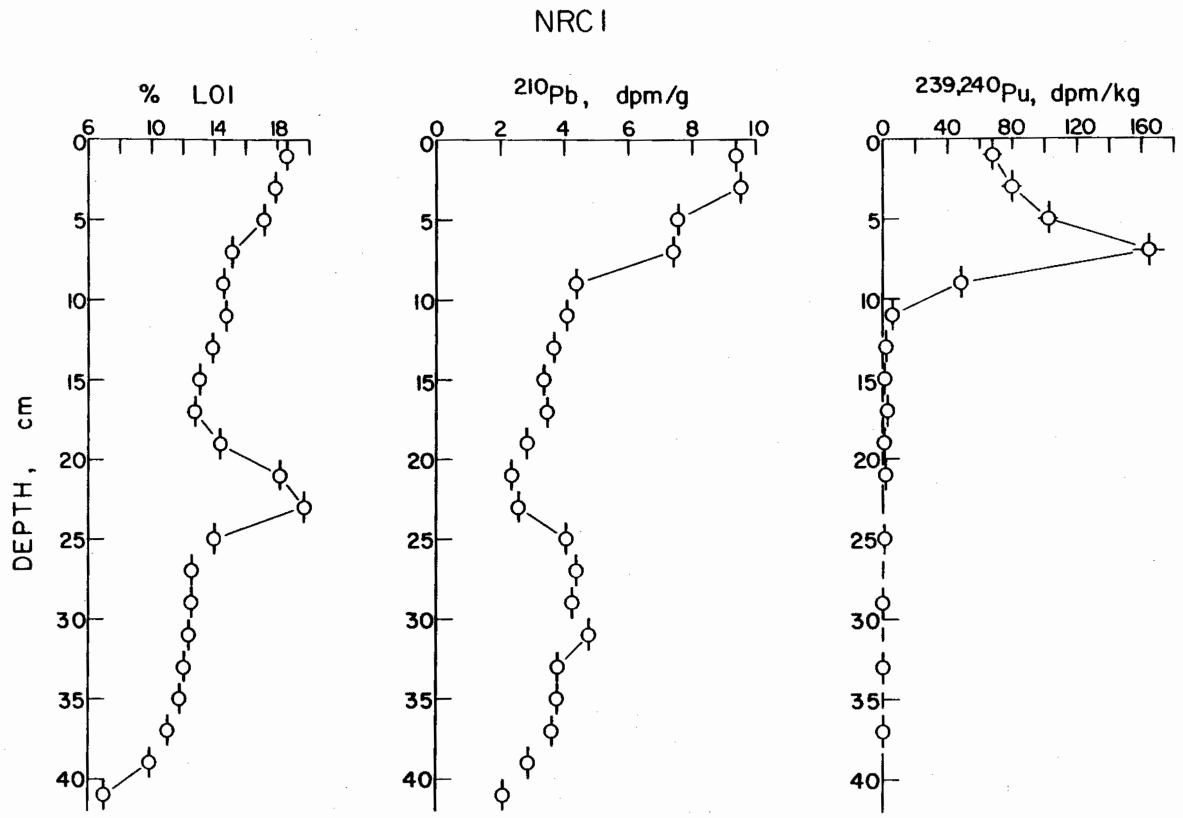

Figure 5. Loss on ignition (LOI) and chronometric tracer data, core NRC1. Total ^{210}Pb (excess- + ^{226}Ra-supported) is shown; the entire 0-42 cm interval probably contained excess ^{210}Pb. ^{239,240}Pu was finite throughout 0-12 cm and at 16-18 cm depth.

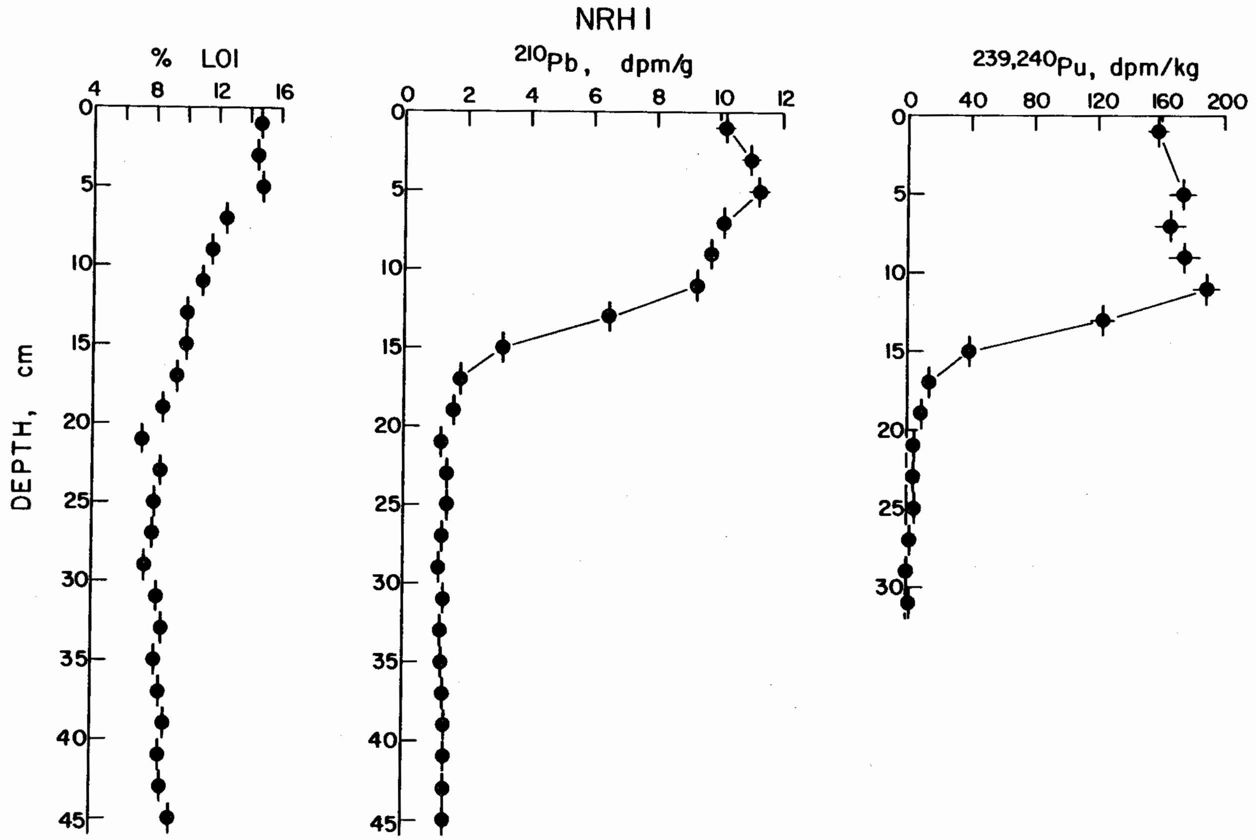

Figure 6. Loss on ignition (LOI) and chronometric tracer data, core NRH1. Total ^{210}Pb (excess- + ^{226}Ra-supported) is shown; excess ^{210}Pb extended to 20 cm depth. ^{239,240}Pu was finite to 26 cm depth.

variability in these sediments, and the plots, in Figures 3-6, of LOI *vs* depth show the patterns of variability.

^{210}Pb and excess ^{210}Pb. The concentrations of ^{210}Pb (as activities, dpm/g = disintegrations per minute per gram dry sediment) are given in Table 2 and plotted *vs* depth in sediment in Figures 3-6. The range of concentrations, roughly 0.7 dpm/g to 11.3 dpm/g, is typical of coastal sediments. Nine duplicate analyses were performed (see Table 2), and the average coefficient of variation was found to be 4.2 % (2.1 % if one outlier is excluded).

The use of ^{210}Pb in modelling vertical sediment transport due to sediment accumulation and mixing is based upon the shape of the ^{210}Pb concentration-depth profile. If the transport processes and the accumulation of excess ^{210}Pb (see below) have operated at steady-state in a location, the resulting ^{210}Pb concentration profile should be monotone non-increasing with increasing depth in the sediment. Significant deviations from this expectation were observed in two of the four cores studied here (WORF1, NRC1, Figures 3 and 5). These reversals of smoothly decreasing trends in ^{210}Pb are discussed in detail below, where the chronologic significance of the ^{210}Pb data is discussed.

Only the excess activity of ^{210}Pb (hereafter "excess ^{210}Pb"), relative to the activity of the progenitor nuclide ^{226}Ra, decays with the ^{210}Pb half-life of 22.3 years; this is because the long-lived ^{226}Ra (half-life 1600 years) produces ^{210}Pb as a decay product and so "supports," at secular equilibrium, a background ^{210}Pb activity equal to the ^{226}Ra activity. For chronology using ^{210}Pb, therefore, an estimate of ^{226}Ra in each sample is required. In the absence of direct ^{226}Ra determinations the self-defined

^{210}Pb background value (i.e., constant ^{210}Pb observed deep in sediment cores) is commonly used. As a check on such self-defined backgrounds, coastal sediments of widely varying lithology, when analyzed by total dissolution or gamma spectrometry, have been found to have ^{226}Ra concentrations of 0.4-2.1 dpm/g (Benninger et al, 1979; Benninger and Krishnaswami, 1981; DeVito, 1981); higher apparent background values would be suspect. Self-defined backgrounds were evident in the ^{210}Pb data for cores WORH1 (Fig. 4) and NRH1 (Fig. 6). In core WORH1 the eight analyses in the interval 28-44 cm defined a non-decreasing background of 1.71 ± 0.07 dpm/g ($\bar{x} \pm s$); excess ^{210}Pb therefore penetrated to 28 cm depth. In core NRH1 no decrease in ^{210}Pb was detectable below 20 cm, and the thirteen analyses in the interval 20-46 cm defined a background of 1.30 ± 0.08 dpm/g. Core NRC1 (Fig. 5) was apparently too short to penetrate through the zone of excess ^{210}Pb; a background (^{226}Ra) value of 1.50 ± 0.10 dpm/g was assumed here. Core WORF1 presented the difficulty of unusually large lithologic variations (Fig. 3: LOI): ^{226}Ra was probably not constant with depth. Based upon the analyses from 34-40 cm and 46-48 cm, it was assumed here that for samples having LOI > 10 %, the appropriate background (^{226}Ra) value was 1.35 ± 0.20 dpm/g.

$\underline{^{239,240}\text{Pu}}$. The concentrations of ^{239,240}Pu are given in Table 2 and plotted in Figures 3-6. Note that the concentrations (as activities) are expressed per kilogram of dry sediment. Thus the contribution of ^{239,240}Pu to the total activity of the sediment was very small: the maximum activity ratio, $^{239,240}\text{Pu}/^{210}\text{Pb}$, was 0.022. The concentrations observed, 0-190 dpm/kg, are typical of modern coastal sediments from northern temperate latitudes. Three duplicate analyses were performed (Table 2), and all duplicates agreed within the reported counting statistics.

In using fallout plutonium as a tool in modern-sediment chronology, it is important to define the maximum depth of penetration of plutonium into the sediment column. Ideally this should correspond to that depth at which the plutonium concentration, within counting statistics, is truly zero. If we choose 'zero within two standard deviations' as defining the zero level, it is apparent that few true zero concentrations of ^{239,240}Pu are reported in Table 2. The large number of concentrations between 0-2 dpm/kg would then pose severe problems of interpretation; while many of these samples probably contained ^{239,240}Pu, its presence may have resulted either from natural processes or as artifacts of sample handling and preparation. As a practical limit, therefore, any concentration which overlapped, at one standard deviation (Table 2), the range 0-2 dpm/kg was regarded as zero. With this definition the maximum depths of ^{239,240}Pu penetration into the sediment cores were found to be:

WORF1	20 cm
WORH1	14 cm
NRC1	18 cm (12 cm)
NRH1	26 cm

Two limits are shown for NRC1 because, while the interval 16-18 cm contained finite ^{239,240}Pu, continuous non-zero ^{239,240}Pu terminated at 12 cm in this core.

Carbon isotopes. The complete carbon isotope data are collected in Table 3. Examination of this table reveals serious inconsistency in $\delta^{13}C$ between those samples which were analyzed for $\delta^{13}C$ only and those which were analyzed for both ^{14}C and $\delta^{13}C$; the former samples yielded $\delta^{13}C$ significantly lighter (more negative) for cores WORH1, NRC1 and NRH1. The cause of this

Table 3. Carbon isotopes in sedimentary organic matter

Station WORF, Core WORF1

Depth, cm	$\delta^{13}C$, 0/00[1]	$\Delta^{14}C$, 0/00[2]	^{14}C age, years[3]
0-2	-27.61	112 ± 14	-880 ± 105
4-6	-29.94		
8-10	-26.84	115 ± 6	-900 ± 45
12-14	-26.99		
18-20	-29.79	-53.1 ± 7.6	450 ± 65
28-30	-25.99	-26.2 ± 7.3	220 ± 60
40-42	-23.31	-73.8 ± 6.8	630 ± 60

Station WORH, Core WORH1

Depth, cm	$\delta^{13}C$, 0/00[1]	$\Delta^{14}C$, 0/00[2]	^{14}C age, years[3]
0-2	-29.07		
2-4	-27.61		
2-4	-25.25	-51.1 ± 8.8	430 ± 75
4-6	-25.35	-7.0 ± 9.0	60 ± 75
8-10	-25.39	-119.8 ± 8.5	1050 ± 80
16-18	-26.17	-112.9 ± 9.3	990 ± 90
22-24	-29.44		
28-30	-26.61	-77.0 ± 9.4	660 ± 85
34-36	-31.30		
40-42	-23.31	-153.4 ± 9.5	1380 ± 95

Table 3, continued.

Station NRC, Core NRC1

Depth, cm	δ^{13}C, 0/00[1]	Δ^{14}C, 0/00[2]	^{14}C age, years[3]
0-2	-30.35		
2-6	-28.59	73.3 ± 6.2	-580 ± 50
8-12	-29.39	-113.6 ± 8.1	1000 ± 75
16-20	-29.08	99.5 ± 6.1	-780 ± 45
22-24	-31.20		
24-26	-31.96		
24-28	-28.34	-136.2 ± 8.7	1210 ± 85
34-38	-28.01	-116.5 ± 8.2	1020 ± 75

Station NRH, Core NRH1

Depth, cm	δ^{13}C, 0/00[1]	Δ^{14}C, 0/00[2]	^{14}C age, years[3]
0-2	-28.84		
2-4	-31.32		
2-6	-25.43	14.5 ± 9.9	-120 ± 80
8-12	-23.59	-9.0 ± 9.0	75 ± 75
16-18	-29.60		
22-26	-26.01	-135.6 ± 10.5	1200 ± 100
30-34	-25.41	-193.6 ± 10.8	1780 ± 110
40-44	-24.17	-213.5 ± 11.9	1990 ± 130

1) δ^{13}C relative to the PDB standard

2) Δ^{14}C = $((A_{sn}/A_{abs}) - 1) \times 1000$ 0/00, where A_{sn} = sample activity, normalized to δ^{13}C = -25 0/00; A_{abs} = absolute international standard activity (see Stuiver and Polach, 1977).

3) Ages are δ^{13}C-corrected and calculated using the 5,730-year half-life.

offset is presently unknown, but it seems clear that a systematic error has been introduced in sample preparation and/or isotopic measurement. Beta Analytic Inc. is working with us to discover the nature of the problem. For the present we regard the combined isotopic measurements (^{12}C, ^{13}C, ^{14}C on the same sample) as the more reliable, for two reasons: (i) the $\delta^{13}C$'s from the combined analyses showed comparatively smooth trends (excepting core WORF1) which were consistent with previous measurements on sediments from these locations (C. Martens and M. Goldhaber, unpublished data; M. Brinson and E. Matson, unpublished data); (ii) the $\delta^{13}C$'s reported without ^{14}C determinations were very light compared to published values for organic matter in coastal sediments. The data plotted in Figures 7 and 8 and discussed in this report are therefore only those which were obtained from measurement of ^{12}C, ^{13}C and ^{14}C on the same sample.

Carbon-isotope data for the White Oak River and estuary cores are displayed in Figure 7. Core WORF1 had generally lighter carbon ($\delta^{13}C$ more negative) than core WORH1, consistent with a greater proportion of terrestrial (C_3) organic matter at the upriver location (WORF); the carbon at WORH was not fully marine (or from C_4 plants), however, as it was too light ($\delta^{13}C$ mainly < -25 0/00) and was observed to consist in part of leaves and wood fragments. The ^{14}C age of the organic matter did not increase monotonically with depth in either core WORF1 or core WORH1. Core WORF1 was younger at all horizons sampled and showed a much stronger influence of bomb ^{14}C (negative ages at 0-2 cm, 8-10 cm); despite the finite ages at all depths sampled in core WORH1, however, the upper samples were probably also contaminated with bomb ^{14}C (see discussion below).

Carbon-isotope data for the Neuse River estuary cores are displayed in

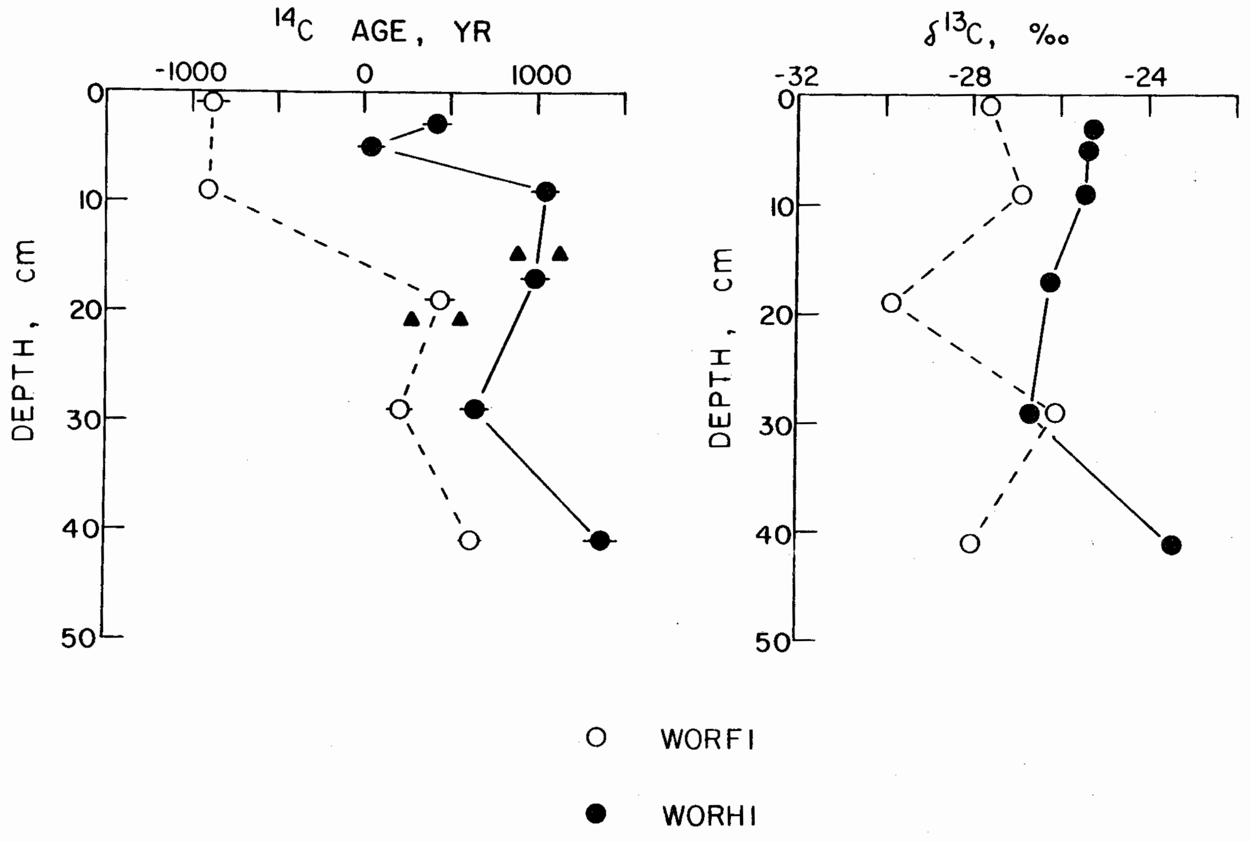

Figure 7. Carbon isotope data, White Oak River estuary cores WORF1 (upriver) and WORH1 (downriver). Stable isotopes (right): $\delta^{13}C$ relative to PDB. ^{14}C age (left): age is $\delta^{13}C$-corrected and based upon the 5,730-year half-life. Filled triangles show maximum depths of penetration of $^{239,240}Pu$.

Figure 8. Once again the upriver core (NRC1) had consistently the lighter carbon (a more terrestrial average source), but the downriver core (NRH1) was too light isotopically to contain organic matter only from marine or C_4-plant sources. Core NRC1 showed no trends in ^{14}C age; bomb ^{14}C was abundant at 2-6 cm and 16-20 cm, but a sample from intermediate depth, as well as two deeper samples, gave ^{14}C ages $\geq$ 1000 years. Core NRH1 was the only one to yield a profile of smoothly increasing ^{14}C age with increasing depth, from -120 years at 2-6 cm to 1990 years at 40-44 cm.

IV. DISCUSSION

Sediment Chronologies

Introduction. Robbins (1978) clearly sets forth the principles underlying the use of radionuclides as tracers for determining rates of sediment accumulation and mixing. To be a useful tracer a radionuclide must attach irreversibly to sediment particles, so that it does not move independently of them, and it must be supplied at a known rate to the sediment-water interface. Under these conditions the depth distribution of the radionuclide in the sediment column is a product of those processes which transport particles in the sediment column. Sediment accumulation is one such process: relative to the sediment-water interface, sediment particles are transported downward by the accumulation of sediment. In shallow-water sediments especially, the transport due to true sediment accumulation is normally confounded with that due to mechanical disturbance, whether biological (bioturbation) or physical (re-suspension, erosion). To sort out these

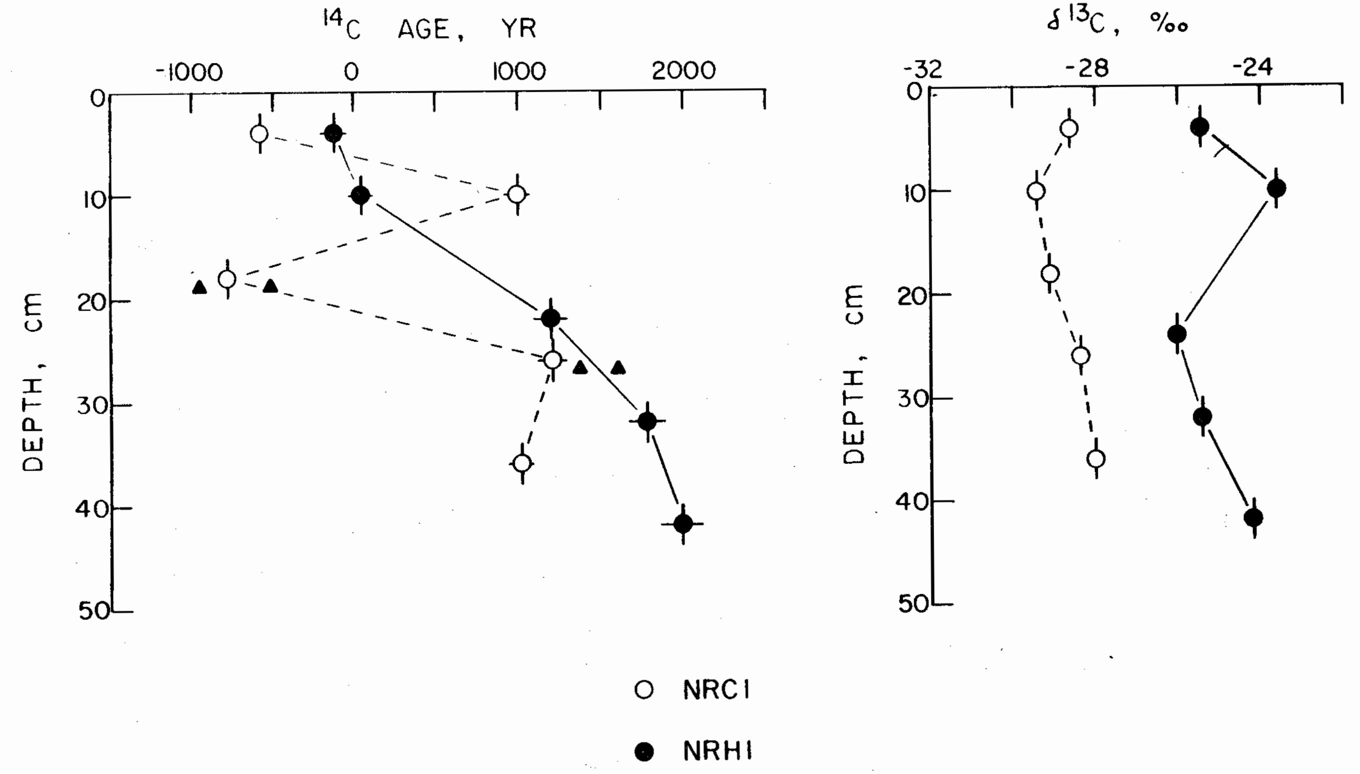

Figure 8. Carbon isotope data, Neuse River estuary cores NRC1 (upriver) and NRH1 (downriver). Stable isotopes (right): $\delta^{13}C$ relative to PDB. ^{14}C age (left): age is $\delta^{13}C$-corrected and based upon the 5,730-year half-life. Filled triangles show maximum depths of penetration of $^{239,240}Pu$.

effects more than one tracer is needed. Here we have employed as tracers natural excess ^{210}Pb and fallout ^{239,240}Pu. We follow conventional practice in assuming that these nuclides are true particle tracers (that is, do not show chemical mobility) in the sediment column.

The principal supply of both excess ^{210}Pb and ^{239,240}Pu to most coastal sedimentary environments is by atmospheric deposition. ^{210}Pb (half-life 22.3 years), a member of the ^{238}U decay series, is produced in the atmosphere by radioactive decay of ^{222}Rn and its short-lived daughters (Turekian et al, 1977). The deposition flux of ^{210}Pb to the earth's surface is not influenced by human activities and may be assumed to be constant at any particular location. Usually a sediment chronology based upon ^{210}Pb extends over 4-5 half-lives (88-110 years) and is limited by the necessity to distinguish excess ^{210}Pb relative to the ^{226}Ra-supported background. Atmospheric ^{239,240}Pu was a product of the above-ground testing of nuclear weapons. It was not measured systematically in fallout collections, but its history of deposition is assumed to follow that of ^{90}Sr, which is well known: the earliest measurable deposition occurred during the early 1950's, and the peak deposition at most locations occurred during 1963 (HASL, 1977).

Both in soils and in natural waters ^{210}Pb and ^{239,240}Pu sorb strongly onto sediment particles. We assume here that this sorption is irreversible, but the sorption process is not indiscriminate. Both tracers sorb preferentially onto fine-grained, organic-rich (mud) particles. As is illustrated below, significant variation in lithology within a core must be taken into account when interpreting the tracer data.

The distributions of excess ^{210}Pb and fallout ^{239,240}Pu in the sediment column carry information about different, but overlapping, time scales, the last ∿100 years for excess ^{210}Pb and the last ∿30 years for ^{239,240}Pu. In the simplest situation the only vertical sediment transport is due to steady-state sediment accumulation, and the only supply of either tracer is by direct atmospheric deposition. Then excess ^{210}Pb should decrease exponentially with increasing depth into the sediment, with the shape of the profile governed by the rate of sediment accumulation and the half-life for radioactive decay. ^{239}Pu (half-life 24,390 years) and ^{240}Pu (half-life 6,540 years) have not undergone significant decay since their production, so in this simple situation (supply by atmospheric deposition, transport by sediment accumulation) the ^{239,240}Pu profile should peak at a depth corresponding to 1963, and the concentration should fall to zero at a depth corresponding to the early 1950's. More realistically, the top of the sediment column is usually mixed biologically or physically, and the chronometric tracers may be supplied by lateral transport as well as by direct atmospheric deposition. Then both excess ^{210}Pb and ^{239,240}Pu may show homogeneous concentrations in a surficial, rapidly-mixed zone. Concentrations decrease with depth below this zone of rapid mixing, but the concentration profiles may still be influenced by mixing as well as by sediment accumulation. If true sediment accumulation, at steady-state, has contributed significantly to the vertical transport of excess ^{210}Pb and ^{239,240}Pu in the sediment column, however, the two tracers should show different maximum depths of penetration; in this case various models can be used to extract rates of steady-state sediment accumulation (e.g., Benninger et al, 1979).

The models for extracting rates of sediment accumulation and/or sediment mixing from chronometric tracer data generally assume steady-state; in particular the rates of accumulation of excess ^{210}Pb and of sediment and the rate of sediment mixing are assumed to be constant. These assumptions cannot be defended in detail, and they are certainly not equally plausible in every situation. It is important to understand that the assumption of steady-state is a constraint imposed by the limited number of tracers available and not a statement as to the true nature of the processes which operate in the sedimentary environment.

If it is once admitted that chronometric tracer profiles may have resulted from non-steady-state transport processes, the significance of the profiles to the true deposition age of the sediment is evidently uncertain. For example, since the tracers and their carriers could represent a negligible mass fraction of the sediment, it is possible that modern tracer levels could be stirred into an old sediment column without detectable true sediment accumulation. When two or more tracers are employed the possibility of misidentifying transport processes is reduced because an acceptable transport model must be consistent with multiple constraints; we exploit this advantage here. Below we have assumed, except as noted, that our tracer ages are true deposition ages for the sediments with which the tracers were associated.

It was not our purpose here to develop detailed models of vertical sediment transport for our stations in the White Oak and Neuse river estuaries. Rather, our principal goal was to establish a sediment-age context within which to interpret ^{14}C ages on organic matter: was the organic matter older, as expected, than the deposition age of the sediment which contained it? In addition we have used the ^{239,240}Pu as an index of the penetration of bomb ^{14}C into the sediment: we have assumed that there was no significant bomb ^{14}C below the maximum depth of plutonium penetration.

Core WORF1. As noted above ^{239,240}Pu was found to a depth of 20 cm in this core; using the estimated ^{210}Pb background (^{226}Ra) value of 1.35 ± 0.20 dpm/g, excess ^{210}Pb was found to 34 cm. The separation between these depths of maximum penetration implies that the tracer profiles were not products of recent mixing alone. We can say crudely that the top 20 cm of the core had an age of $\leq \sim 30$ years (Pu time-scale), the top 34 cm an age of 70-90 years (^{210}Pb time-scale; a longer interval could not be detected with certainty here because of the low ^{210}Pb concentrations). These are, in effect, maximum sediment "ages" for these depths because we have assumed that the establishment of the profiles took all of the time available.

In order to determine whether a steady-state transport model could be fit to these data it was first necessary to correct for the apparent (Fig. 3) correlation between LOI and tracer concentrations. LOI, ^{210}Pb and, to some extent, ^{239,240}Pu were positively correlated because all were associated with the mud fraction of the sediment, which was variable down the length of the core. A simple way to view this problem is to assume that mud, carrying excess ^{210}Pb and ^{239,240}Pu, and sand, devoid of tracers, accumulated independently. Then the tracer nuclides would carry no information about the rate of accumulation of the sand. But if the mud accumulated at steady-state, the tracers could be used to determine its rate of accumulation, and this information, together with the vertical distribution of mud in the core, would define an age-depth relationship for the core.

In the foregoing 'mud' was used as a shorthand designation for the carrier of excess ^{210}Pb and $^{239,240}Pu$. To apply the two-component ('mud'-'sand') model, it is necessary to identify an index of this carrier whose concentration profile can be determined. Per cent LOI has proved to be a useful index in some situations (Benninger and Krishnaswami, 1981).

Application of the two-component model to core WORF1 is illustrated in Figure 9. The assumption underlying the model is that excess ^{210}Pb and LOI (as an index of the tracer carrier) accumulated at a constant rate. The excess ^{210}Pb data were normalized to LOI, and depth in the sediment was transformed to cumulative mass of LOI (g LOI/cm^2). For the model to be plausible the data should define a straight line on a semi-logarithmic plot (Fig. 9). This was clearly only approximately true; the least-squares line through the data has only a moderate correlation coefficient ($r = -0.825$), and the residuals are not randomly scattered about the line. The slope of this line yields an accumulation rate of 39.5×10^{-3} g LOI/cm^2-yr; the corresponding age at 34 cm is about 57 years.

Despite the doubtful semi-logarithmic fit of Figure 9, this accumulation model is reasonably consistent with $^{239,240}Pu$. For Figure 9, the plutonium data were also normalized to LOI; relative to Figure 3 the subsurface maximum was reduced in amplitude, but its position was unchanged, as was the maximum depth of penetration. Using the above model the $^{239,240}Pu$ peak (9 cm depth $\simeq$ 0.53 g LOI/cm^2) dates 1968-1969, the maximum depth of penetration (20 cm $\simeq$ 1.236 g LOI/cm^2) 1950-1951. The latter is compatible with the history of plutonium fallout, and the former offset (peak fallout

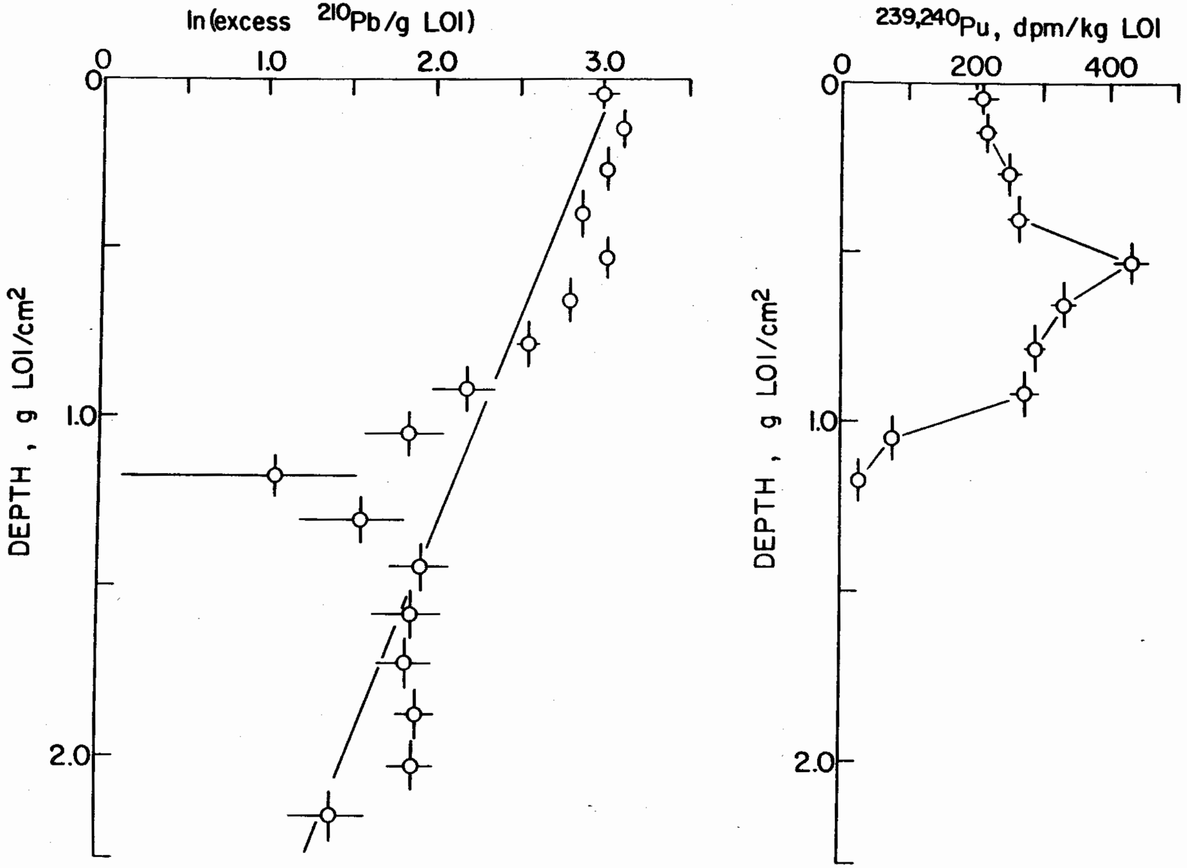

Figure 9. Sediment chronologic model, core WORF1. Data have been normalized to LOI to correct for lithologic variability. ^{210}Pb model assumes constant rates of accumulation of excess ^{210}Pb and LOI; slope of line gives accumulation rate = 39.5 x 10^{-3} g LOI/cm^2-yr. (Calculation assumes density of sedimentary solids to be 2.2 g/cm^3)

occurred in 1963) may be due to inputs other than from direct fallout.

In summary, for core WORF1 the ^{210}Pb and ^{239,240}Pu data are compatible with a sediment age of about 60 years at 34 cm. The depth interval 0-34 cm in this core may be viewed as the product of steady-state sediment accumulation, although the data do not compel this interpretation. Samples from below 34 cm depth appeared to contain neither excess ^{210}Pb nor ^{239,240}Pu; this horizon may therefore represent an unconformity (absence of deposition or loss of sediment by erosion), and ages below this depth are probably $\geq \sim$80 years.

Core WORH1. In core WORH1 ^{239,240}Pu was found to a depth of 14 cm, excess ^{210}Pb to a depth of 28 cm. As in core WORF1 the maximum depths of penetration for the two tracers are well separated, and it is reasonable to assume that the sediment had age $\sim$30 years at 14 cm depth and age $\sim$100 years at 28 cm depth.

Application of a steady-state transport model to the tracer data for core WORH1 is illustrated in Figure 10. In this case the variation in lithology down the core, as reflected in LOI (Fig. 4) was not large, and no correction for lithology was necessary. A mass-depth scale (g dry sediment/cm^2) was used in Figure 10 to avoid the effects of variable porosity on the simple centimeter scale. Both excess ^{210}Pb and ^{239,240}Pu were homogeneous in the interval 0-4 cm (0-1.8 g/cm^2), indicating rapid mixing to this depth. Below this horizon the excess ^{210}Pb data fit an exponential decrease very well (straight line on semi-log plot: $r = -0.989$); the top point was excluded from the fit because of mixing, and the bottom three points (depth > 11.7 g/cm^2) were excluded because of the relatively

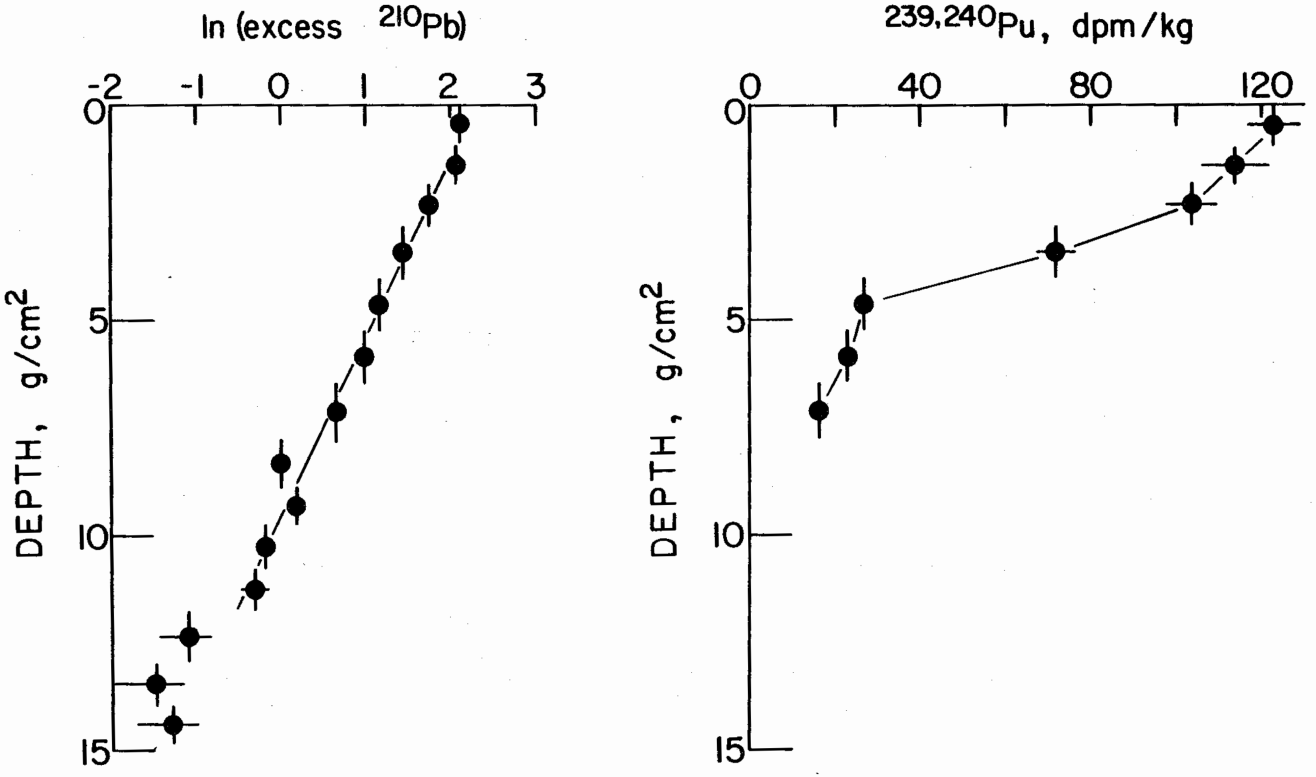

Figure 10. Sediment chronologic model, core WORH1. ^{210}Pb model assumes constant rates of accumulation of excess ^{210}Pb and sediment; slope of line gives sediment accumulation rate = 0.13 g/cm^2-yr. (Calculation assumes density of sedimentary solids to be 2.5 g/cm^3)

large uncertainties in excess ^{210}Pb. The slope of the line in Figure 10 yields a steady-state sediment accumulation rate of 0.13 g/cm^2-yr. To calculate the maximum depth of penetration of ^{239,240}Pu compatible with this accumulation rate one must add the thickness of the mixed layer (4 cm ≃ 1.83 g/cm^2) to the integrated accumulation of the period 1950-1982 (32 yr x 0.13 g/cm^2-yr); this gives 5.99 g/cm^2 as the expected maximum penetration. The actual maximum penetration lay in the interval 6.4-7.7 g/cm^2. Thus a more complete transport model would have to allow for some transport by mixing below 4 cm (1.83 g/cm^2). In such a model the rate of steady-state sediment accumulation would be reduced slightly, but the difference would not be significant here.

Applying the steady-state accumulation rate of $\leq$0.13 g/cm^2-yr to core WORH1 yields an age of $\geq$ 114 years at 28 cm, where excess ^{210}Pb went to zero. If the same rate is applied to deeper horizons, the calculated age at the core bottom (42 cm ≃ 22.7 g/cm^2) is $\geq$ 175 years. These ages are shown as lower limits because the true rate of sediment accumulation may be slightly less than 0.13 g/cm^2-yr; "corrected" ages would not exceed these figures by more than 25 %.

<u>Core NRC1</u>. It is apparent from Figure 5 that core NRC1 is not representative of steady-state sediment accumulation and mixing. LOI was found to reverse the trend of a general decrease with depth in the interval 18-24 cm; sediment from this interval was darker in color than that above or below (Table 1), and it was probably derived from a different source. ^{210}Pb was low in this interval of high LOI (18-24 cm) and increased again at depths below 24 cm; indeed, ignoring the 18-24 cm interval, ^{210}Pb showed

little tendency to decrease over the entire 8-38 cm interval and probably did not reach the background (^{226}Ra-supported) level even at the core bottom (42 cm). This pattern in ^{210}Pb (excluding the 18-24 cm interval) would be consistent with very rapid sediment accumulation, but the distribution of ^{239,240}Pu indicates that sediments from above and below the 18-24 cm interval are of different ages: ^{239,240}Pu was found in the interval 0-12 cm and possibly in 16-18 cm, but at no greater depth.

For present purposes adequate chronometric resolution is obtained from the maximum observed penetrations of the tracers: the top 18 cm has a deposition age $\leq \sim 30$ years, and the entire core has a deposition age $\leq \sim 90$ years.

Core NRH1. In core NRH1 excess ^{210}Pb and ^{239,240}Pu were detected to the same maximum depth (Fig. 6); indeed, probably because the zero background for plutonium is better defined than the ^{226}Ra-support level for ^{210}Pb, ^{239,240}Pu was demonstrably finite to 26 cm, while excess ^{210}Pb could not be detected below 20 cm. The lack of vertical separation of excess ^{210}Pb and ^{239,240}Pu in this core implies that both profiles were shaped by a common mixing process; the true rate of sediment accumulation was low enough, relative to the mixing rate(s), to leave no record, and it could have been zero. In such a case the deposition age of the sediment is indeterminate; we can only say that the top 26 cm of the sediment column has been open to particle transport within the last 30 years.

Carbon Isotopes

Deposition age vs ^{14}C age. The foregoing discussion has established

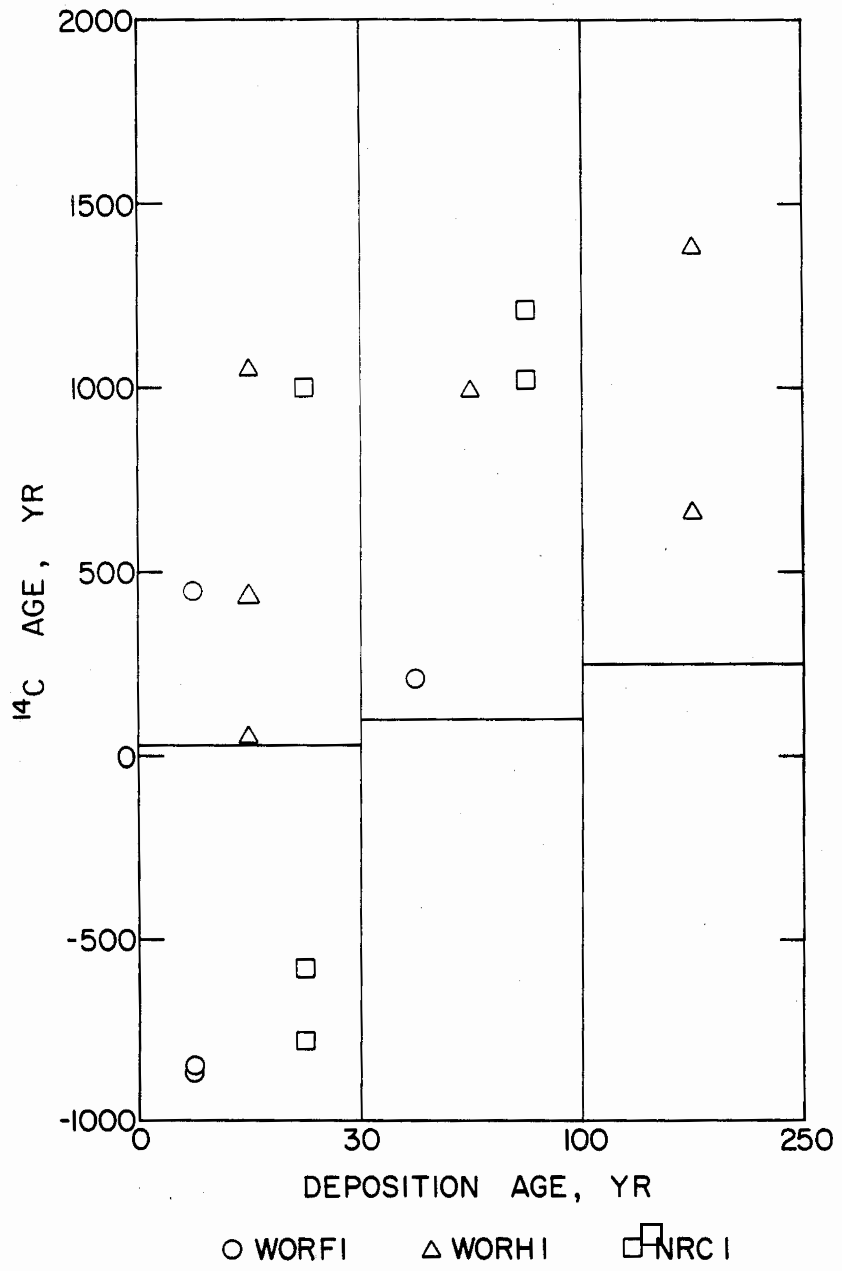

Figure 11. ^{14}C age of organic matter vs sediment deposition age, cores WORF1, WORH1, NRC1. Deposition age is resolved only into three intervals: 0-30 years (excess ^{210}Pb and Pu present); 30-100 years (excess ^{210}Pb, no Pu); 100-250 years (extrapolation of chronologic model).

rough deposition ages for depth horizons from cores WORF1, WORH1 and NRC1. The deposition ages are combined with ^{14}C ages on the organic fractions of these cores in Figure 11. No effort has been made to assign an absolute deposition age to any sample on which ^{14}C age has been determined. Rather, deposition age has been divided into three intervals:

0-30 years, based upon depth of penetration of $^{239,240}Pu$;
30-100 years, based upon depth of penetration of excess ^{210}Pb;
100-250 years, based upon extrapolation of the steady-state accumulation + mixing model.

We have assumed that the 100-250 year interval is sufficiently well-defined only for core WORH1 and that none of the intervals could be distinguished in core NRH1 (where $^{239,240}Pu$ and excess ^{210}Pb were not separated in the sediment column).

Despite the noise in the ^{14}C-age profiles (Figs. 7,8) a very simple picture emerges from Figure 11. All of the samples of deposition age > 30 years gave ^{14}C ages significantly greater than deposition age. Only for deposition ages in the interval 0-30 years was the ^{14}C age as young as (or younger than) the deposition age; this was true of about half the samples from the interval and was clearly due to the influence of organic matter contaminated with bomb ^{14}C. Probably all of the samples from the 0-30 year deposition-age interval contained both bomb ^{14}C and aged carbon. The likely presence of bomb ^{14}C, even where a negative age was not obtained, may be inferred from the presence of fallout plutonium; the presence of aged carbon in samples of negative age is inferred from the fact that pure "modern" (post-1957) carbon would give significantly more negative ages (see, e.g., Nydal et al, 1979; Barrette et al, 1980).

These results confirm the expectation that the organic matter flux to the sediments in the White Oak and Neuse river estuaries includes both recently produced and aged organic matter. Our hypothesis was that the recently produced organic matter should undergo more rapid decomposition, leading to preferential preservation of the aged, processed material. To demonstrate this we would need to show a systematic increase in ^{14}C age with depth in the sediment which is more rapid than the increase in deposition age. No such trend can be demonstrated from the present data. Near the core tops, where rapid, microbially-mediated changes in the composition of organic matter might have been expected, any resulting shift in ^{14}C age was masked by bomb ^{14}C; that is, while ^{14}C age showed abrupt increases between some horizons (Figs. 7,8), part or all of the observed increases could be ascribed to fluctuations in the input of organic matter contaminated with bomb ^{14}C.

In principle, it might have been possible to separate, by calculation, the contribution of bomb ^{14}C to the observed changes in ^{14}C age. Such a separation was not feasible here, for two reasons. First, 'bomb ^{14}C' cannot be characterized by any unique ratio of $^{14}C/C$. In northern temperate latitudes, tropospheric and contemporary terrestrial plant ^{14}C increased from about 110 % Modern in 1957 to about 200 % Modern in 1963-1965, then declined slowly to about 140 % Modern by 1978 (Nydal et al, 1979; Barrette et al, 1980; 'Modern' in this context refers to the international ^{14}C zero-age reference activity, specified as of 1950.). Increases in ^{14}C in surface ocean waters lagged the tropospheric increases and levelled off at about

120 % Modern (Nydal et al, 1979). Thus $^{14}C/C$ in organic matter contaminated with bomb ^{14}C would depend strongly on the date and place (land vs ocean) of its production. A second complication was that the organic matter in the sediments studied here represented inputs from a combination of sources, in proportions which varied significantly over time. This is shown by the oscillations in ^{14}C age which were found even below the depths of plutonium penetration: ^{14}C age increased monotonically with depth only in core NRH1. In contrast with the results reported by previous investigators (Erlenkeuser et al, 1974; Benoit et al, 1979; Baxter et al, 1980), there is evidently no constant "recent age" of the non-metabolizable fraction of organic matter in these shallow estuaries.

A range of "recent ages" can be calculated from those samples for which deposition ages could be estimated by simply computing the excesses of ^{14}C ages over deposition ages. This is most straightforward for samples which contained no plutonium and presumably, therefore, no bomb ^{14}C. In core WORH1, for example, samples from 16-18 cm and 28-30 cm contained no plutonium and had deposition ages $\leq \sim 100$ years; their ^{14}C ages were, respectively, 1120 ± 70 years and 640 ± 80 years. A sample from 40-42 cm in core WORH1 had a ^{14}C age of 1340 ± 80 years and a probable deposition age of < 250 years. The average excess ^{14}C age for these samples was thus about 880 ± 300 years. Similar calculations for core NRC1, where all deposition ages were < 100 years, yield an excess ^{14}C age of 1015 ± 135 years (two samples), and for core WORF1 a single sample (28-30 cm) yields an excess ^{14}C age of about 120 years. Additional minimum "recent ages" can be similarly calculated for those samples which had finite ^{14}C age despite the probable presence of bomb ^{14}C contamination. Excess ages, relative to a 30-year deposition age, for such samples are sometimes as large as, or larger than, those calculated above (420 years for WORF1, 18-20 cm; 1020 years for WORH1, 8-10 cm; 970 years for NRC1, 8-12 cm); presumably this is due to temporal fluctuations in the average ^{14}C age of the organic-matter input.

In sediments of the White Oak and Neuse river estuaries, therefore, the average pre-bomb "recent age" of organic matter which has escaped decomposition during burial to a depth of tens of centimeters has been in the range of one hundred to about one thousand years. Aged organic matter has certainly persisted in the sediments. To learn whether it has persisted preferentially, relative to recently produced organic matter, we would need to know the average pre-bomb ^{14}C age of the total organic matter flux; this information is not available either from the sediments or from analysis of modern sources, which are clearly contaminated with bomb ^{14}C.

Sources of organic matter. The combined carbon isotopic data are useful in constraining the sources of the organic matter which has been preserved in the sediments of the White Oak and Neuse river estuaries. In Figures 12 and 13 the carbon isotope data are plotted together with fields representing the carbon isotopic composition of potential source materials (diagram modified from Turekian and Benoit, 1981). For these figures ^{14}C has been expressed as the activity ratio A/A_o, where A is the present ^{14}C activity and A_o is the international radiocarbon-dating reference activity (A_o is a construct, roughly the ^{14}C specific activity in pre-bomb, pre-industrial wood produced in 1950). The value $A/A_o = 1$ thus corresponds

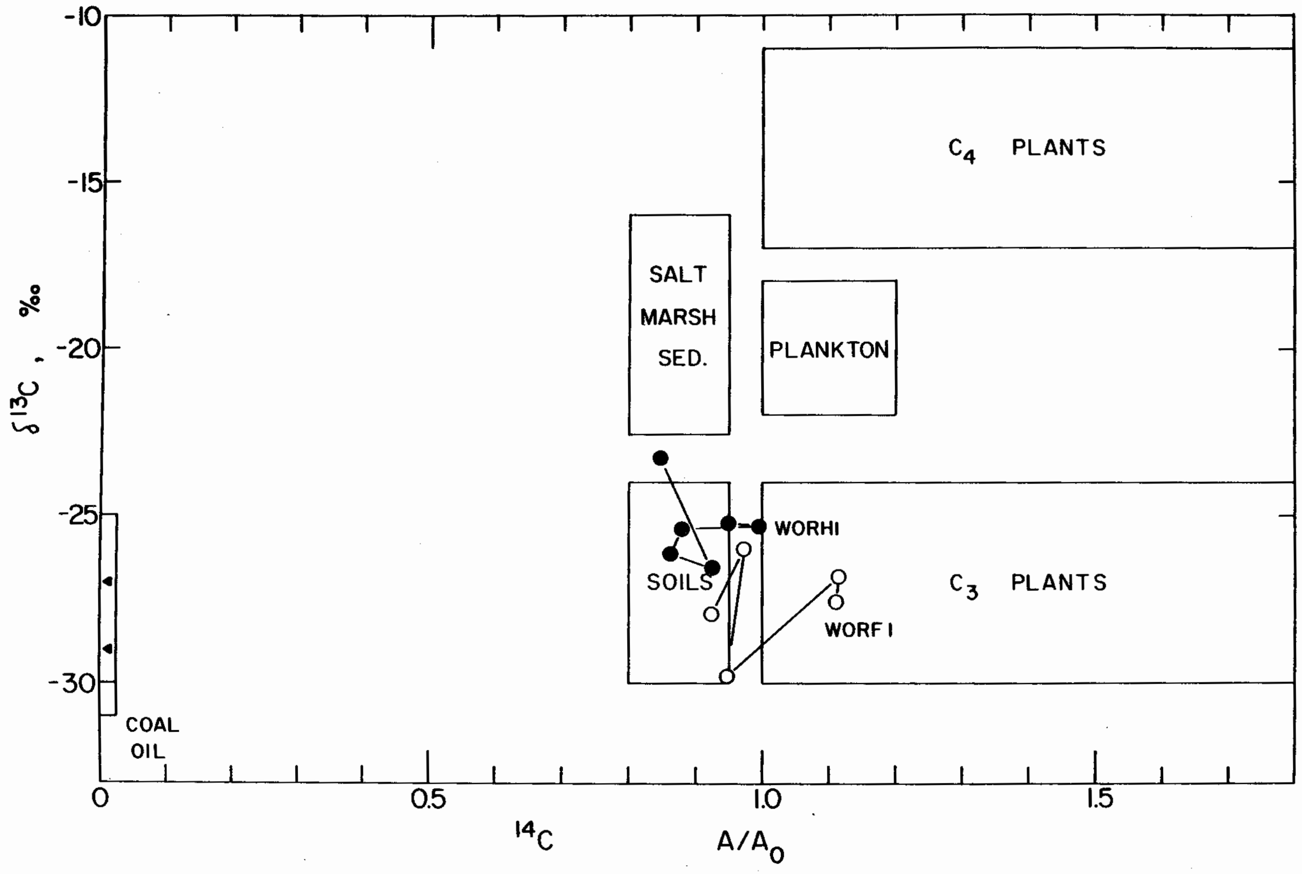

Figure 12. Carbon-isotopic composition of sedimentary organic matter and potential sources, White Oak River estuary cores WORF1, WORH1. $\delta^{13}C$ relative to PDB standard. ^{14}C: A = sample ^{14}C activity; A_0 = international radiocarbon dating reference activity.

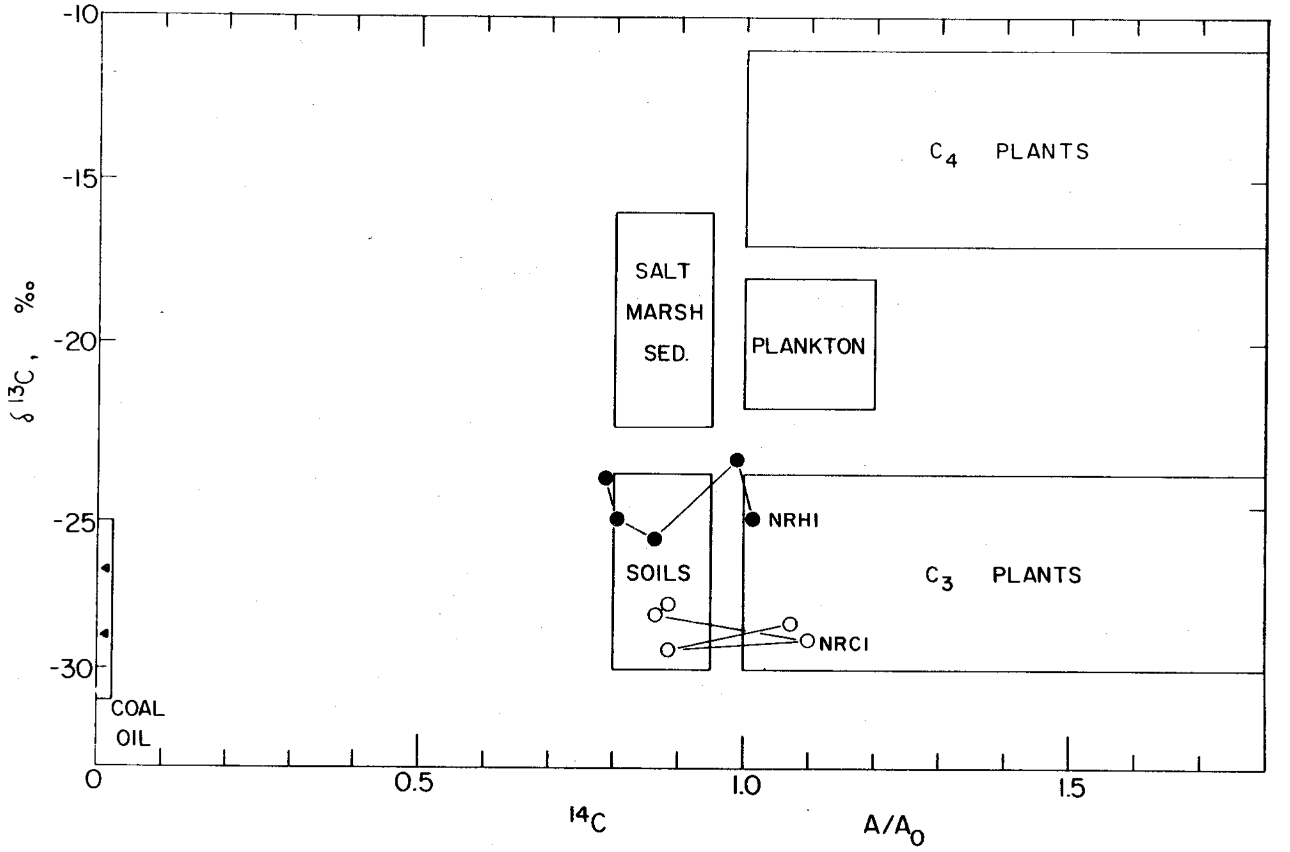

Figure 13. Carbon-isotopic composition of sedimentary organic matter and potential sources, Neuse River estuary cores NRC1, NRH1. $\delta^{13}C$ relative to PDB standard. ^{14}C: A = sample ^{14}C activity; A_0 = international radiocarbon dating reference activity.

approximately to zero-age carbon as of 1950; actual zero-age carbon in 1950 had A/A_o slightly less than 1.0, due to the Suess effect (Damon et al, 1978), but the difference is only a few per cent and so does not affect the arguments here.

Definition of the source-material fields in Figures 12 and 13 was straightforward; the boundaries were for the most part derived from references cited above. Modern vegetation which withdraws its carbon from the atmospheric CO_2 reservoir has shown the bomb effect ($A/A_o > 1.0$) more strongly than has marine plankton because bomb ^{14}C has entered the oceans slowly and has been diluted by the large pool of bicarbonate in surface waters (Nydal et al, 1979; Stuiver, 1980). The $\delta^{13}C$ boundaries for salt-marsh sediment are based upon the data of Haines (1976) and reflect contributions from both C_3 and C_4 plants. An aged plankton component would clearly fall in this same field. The cutoffs for aged source reservoirs, $0.8 \leq A/A_o \leq 0.95$, are to some extent arbitrary; the corresponding ^{14}C age (5,730-year half-life) limits are $424 \leq {}^{14}C \text{ age} \leq 1845$ years.

None of our sediment isotopic compositions fell into the plankton, salt-marsh sediment, or C_4-plant source fields, and the organic matter in most of our samples could be viewed as simple mixtures of the C_3-plant (+ sewage), soil, and coal + oil sources. Since the stable carbon isotopes were consistently heavier in the cores from the downriver locations (WORH, NRH), however, it is probable that the organic matter from cores WORH1 and NRH1 contained some contribution from plankton and/or C_4 plants. We can approximate this contribution by assuming that the difference in average $\delta^{13}C$ between upriver and downriver locations has resulted from addition, at the downriver sites, of a plankton component ($\delta^{13}C$ = -20 0/00) which is missing upriver. Taking the average $\delta^{13}C$ in cores WORF1 and NRC1 as a purely terrestrial, C_3-plant signal, then, the contribution of carbon from the hypothetical plankton source is about 30 % in core WORH1 and about 40 % in core NRH1. Lesser amounts of C_4-plant carbon would be required to produce the same isotopic shifts between the upriver and downriver cores. Given the scatter in the stable isotopic compositions, both in our sediments and in source materials, any such calculated proportions are necessarily highly uncertain (± 50-100 %).

Mixing along the ^{14}C axes of Figures 12 and 13 is likewise not unambiguously resolved. None of the measured A/A_o's was significantly < 0.8, so that the aged carbon in our samples might all have come from reservoirs, like soils and salt-marsh sediments, of relatively young ^{14}C age. At the same time the presence of small amounts of coal and/or petroleum ($A/A_o = 0$) cannot be excluded; indeed, macroscopic coal fragments were found in core NRC1 (Table 1), albeit only from a horizon deeper than any in which ^{14}C was determined. The contrast between the Neuse and White Oak affords a basis for the estimation of the effect of coal and petroleum, in that the White Oak is certain to be less affected. For a fair comparison of ^{14}C Concentrations, it would be necessary to compare samples of the same deposition age. This is not possible because of the uncertainties in the sediment chronologies. However, the differences in ^{14}C A/A_o between deep samples (below plutonium) from cores NRH1 and WORH1 and from NRC1 and WORF1 are compatible with the addition of at most a few per cent (< 5 % of total carbon in all cases) coal or petroleum carbon to the Neuse River estuary samples.

Summary and Implications for Water Quality

Sediment chronological studies in combination with carbon isotope analyses on the organic fraction from sediment cores from the White Oak and Neuse river-estuary systems have revealed two simple patterns:

(i) stable isotope analyses suggest that marine (plankton, salt marsh) sources of organic matter increase in importance in the downriver direction but that terrestrial (C_3-plant) sources may predominate throughout the estuaries;

(ii) ^{14}C analyses show that the flux of organic matter to the sediments includes both recently produced and aged material and that, at depths below the influence of bomb ^{14}C, the ^{14}C age of organic matter is greater than the deposition age of the sediment.

We have not been able to demonstrate directly that microbial degradation has preferentially removed the recently produced fraction of the organic-matter influx. The predicted consequence of this process was that the proportion of aged material in the total organic matter would increase and that, therefore, the ^{14}C age of the organic matter would increase more rapidly than sediment deposition age. Since the intensity of microbial activity is greatest near the sediment-water interface, this model must be tested by careful measurements near core tops. In the case of our sediment cores the expected effect, if present, was masked by bomb ^{14}C.

Previous studies (Erlenkeuser et al, 1974; Benoit et al, 1979; Baxter et al, 1980) have demonstrated the existence of a non-metabolizable, aged organic matter input to coastal sediments by extrapolating ^{14}C age measurements from pre-industrial and pre-bomb horizons in sediment cores to the sediment-water interface: the finite (850-3000 years) "recent age" obtained in this way was interpreted as the ^{14}C age, at deposition, of organic matter which was not subsequently re-mineralized within the sediments. In cores from the Neuse and White Oak ^{14}C ages on samples from depths below the horizons contaminated by bomb ^{14}C generally did not increase monotonically with depth, probably because the sources of organic matter to these locations have varies. In three of four cores, however, the average ^{14}C ages on these pre-bomb samples, when corrected for deposition age, ranged between 100 and 1000 years. Based upon this we know that aged organic matter is preserved in sediments of the Neuse and White Oak river estuaries. Considering likely sources of organic matter, we believe, although we have not proved, that the aged organic matter is preferentially preserved.

We could not uniquely determine the sources of aged organic matter to the Neuse and White Oak. A significant input of organic matter of infinite ^{14}C age (coal, petroleum, etc) to the White Oak is improbable, however, because the watershed is sparsely populated and little developed. Greater development in the Neuse basin makes coal and oil pollution more plausible, and, relative to White Oak samples, the Neuse samples may have contained a 0-5 % component of infinite-age carbon in total sedimentary organic carbon. For both river-estuary systems it is probable that most of the aged organic matter was derived from reservoirs having ^{14}C ages of hundreds to a few thousands of years (soils, salt marshes, pre-existing sediments).

If recently produced organic matter is preferentially decomposed in estuarine sediments, as we have argued, the implications for water quality are clear. Increased loadings of aged, refractory organic matter, while possibly objectionable on other grounds, would carry a relatively small penalty in water-quality deterioration due to increased primary productivity or oxygen depletion; a large fraction of the aged organic matter would ultimately be buried in the sediment column. In contrast a large fraction of recently produced organic matter would undergo decomposition in surface sediments, consuming oxygen and returning nutrients to the water column. Increased loadings of this material would intensify these processes and increase the frequency of oxygen-depletion events. The fraction of recently produced organic matter that would ultimately be buried would probably vary with source. Given the low-moderate rates of sediment accumulation which we have found, however, burial is not an efficient means of removing sedimented organic matter from the near-interface zone of intense microbial activity.

REFERENCES

Barrette, L., Lasalle, P., Martel, Y. and C. Samson, 1980, Variations of ^{14}C in oats grown from 1957 to 1978 in Quebec, Radiocarbon 22, 410-414.

Baxter, M.S., Stenhouse, M.J. and N. Drndarski, 1980, Fossil carbon in coastal sediments, Nature 287, 35-36.

Benninger, L.K., Aller, R.C., Cochran, J.K. and K.K. Turekian, 1979, Effects of biological sediment mixing on the ^{210}Pb chronology and trace metal distribution in a Long Island Sound sediment core, Earth Planet. Sci. Lett. 43, 241-259.

Benninger, L.K. and S. Krishnaswami, 1981, Sedimentary processes in the inner New York Bight: Evidence from excess ^{210}Pb and $^{239,240}Pu$, Earth Planet. Sci. Lett. 53, 158-174.

Benoit, G.J., Turekian, K.K. and L.K. Benninger, 1979, Radiocarbon dating of a core from Long Island Sound, Estuarine Caostal Mar. Sci. 9, 171-180.

Berner, R.A., 1971, Principles of Chemical Sedimentology, McGraw-Hill, New York, 240 pp.

Berner, R.A., 1974, Kinetic models for the early diagenesis of nitrogen, sulfur, phosphorus, and silicon in anoxic marine sediments, in E.D. Goldberg, ed., The Sea, Vol. 5, Marine Chemistry, John Wiley and Sons, New York, 427-450.

Berner, R.A., 1980, Early Diagenesis: A Theoretical Approach, Princeton Univ. Press, Princeton, N.J., 241 pp.

Billingsley, G.A., Fish, R.E. and R.G. Schipf, 1957, Water resources of the Neuse River basin, North Carolina, U.S. Geol. Surv. Water-Supply Paper 1414, U.S. Government Printing Office, Washington, D.C., 89 pp.

Bloom, A.L. and M. Stuiver, 1963, Submergence of the Connecticut coast, Science 139, 332-334.

Brown, F.S., Baedecker, M.J., Nissenbaum, A. and I.R. Kaplan, 1972, Early diagenesis in a reducing fjord, Saanich Inlet, British Columbia - III. Changes in organic constituents of sediment, Geochim. Cosmochim. Acta 36, 1185-1203.

Burnett, W.C. and O.A. Schaeffer, 1980, Effect of ocean dumping on $^{13}C/^{12}C$ ratios in marine sediments from the New York Bight, Estuarine and Coastal Mar. Sci. 11, 605-611.

Calvert, M., Rudolph, K. and J.J. Stipp, 1978, University of Miami Radiocarbon dates XII, Radiocarbon 20, 274-282.

Damon, P.E., Lerman, J.C. and A. Long, 1978, Temporal fluctuations of atmospheric ^{14}C: Causal factors and implications, Ann. Rev. Earth Planet. Sci. 6, 457-494.

DeVito, C.M., 1981, Radionuclides as tracers of sediment transport processes in North Carolina continental slope sediments, M.S. Thesis, Univ. North Carolina - Chapel Hill, 60 pp.

Erlenkeuser, H., Suess, E., and H. Willkomm, 1974, Industrialization affects heavy metal and carbon isotope concentrations in recent Baltic Sea sediments, Geochim. Cosmochim. Acta 38, 823-842.

Gearing, P., F.E. Plucker and R.L. Parker, 1977, Organic carbon stable isotope ratios of continental margin sediments, Marine Chemistry 5, 251-266.

Gruebel, K.A., 1981, Radon sediment-water exchange in the White Oak River estuary, North Carolina, M.S. Thesis, Univ. North Carolina - Chapel Hill, 72 pp.

Haines, E.B., 1976, Stable carbon isotope ratios in the biota, soils and tidal water of a Georgia salt marsh, Estuarine Coastal Mar. Sci. 4, 609-616.

Haines, E.B. and C.L. Montague, 1979, Food sources of estuarine invertebrates analyzed using $^{13}C/^{12}C$ ratios, Ecology 60, 48-56.

HASL, 1977, Health and Safety Laboratory Environmental Quarterly: Final tabulation of monthly ^{90}Sr fallout data: 1954-1976, Health and Safety Laboratory, USERDA, New York, 405 pp.

Hoefs, J. 1980, Stable Isotope Geochemistry, Springer-Verlag, New York, 208 pp.

Hunt, J.M., 1970, The significance of carbon isotope variations in marine sediments, in G.D. Hobson and G.C. Speers, eds., Advances in Organic Geochemistry 1966, Pergamon Press, New York, 27-35.

Kressin, I.K., 1977, Electrodeposition of plutonium and maericium for high resolution alpha spectrometry, Anal. Chem. 49, 842-845.

Krishnaswami, S. and M.M. Sarin, 1976, The simultaneous determination of Th, Pu, Ra isotopes, ^{210}Pb, ^{55}Fe, ^{32}Si and ^{14}C in marine suspended phases, Anal. Chim. Acta 83, 143-156.

Martens, C.S. and M.B. Goldhaber, 1978, Early diagenesis in transitional sedimentary environments of the White Oak River estuary, Limnol. Oceanogr. 23, 428-441.

Noakes, J.E., Kim, S. and J.J. Stipp, 1965, Chemical and counting advances in liquid scintillation age dating, Proc. 6th International Conf. on Radiocarbon and Tritium Dating, Pullman, WA, 7-11 June 1965, 68-92.

Nydal, R., Lövseth, K. and S. Gulliksen, 1979, A survey of radiocarbon variation in nature since the Test Ban Treaty, in Berger, R. and H.E. Suess, eds., Radiocarbon Dating, Proc. Ninth Internat. Conf., Los Angeles and LaJolla, 1976, 313-323.

Polach, H.A. and J.J. Stipp, 1967, Improved synthesis techniques for methane and benzene radiocarbon dating, International Jour. Appl. Radiation Isotopes 18, 359-364.

Puphal, K.W. and D.R. Olsen, 1972, Electrodeposition of alpha-emitting nuclides from a mixed oxalate-chloride electrolyte, Anal. Chem. 44, 284-289.

Robbins, J.A., 1978, Geochemical and geophysical applications of radioactive lead, in J.O. Nriagu, ed., The Biogeochemistry of Lead in the Environment, Elsevier/North Holland, New York, 285-393.

Sackett, W.M. and R.R. Thompson, 1963, Isotopic organic carbon composition of recent continental-derived clastic sediments of eastern Gulf of Mexico, Bull. Am. Assoc. Petrol. Geol. 47, 525-531.

Sackett, W.M., Eadie, B.J. and M.E. Exner, 1974, Stable isotope composition of organic carbon in recent Antarctic sediments, in B. Tissot and F. Bienner, eds., Advances in Organic Geochemistry 1973, Editions Technip, Paris, 661-671.

Shultz, D.J. and J.A. Calder, 1976, Organic carbon $^{13}C/^{12}C$ variations in estuarine sediments, Geochim. Cosmochim. Acta 40, 381-386.

Spiker, E.C., 1980, The behavior of ^{14}C and ^{13}C in estuarine water: effects of in situ CO_2 production and atmospheric exchange, Radiocarbon 22, 647-654.

Stuiver, M., 1980, ^{14}C distribution in the Atlantic Ocean, Jour. Geophys. Res. 85, 2711-2718.

Stuiver, M. and H.A. Polach, 1977, Discussion: Reporting of ^{14}C data, Radiocarbon 19, 355-363.

Turekian, K.K. and G.J. Benoit, 1981, Radiocarbon in New York Bight sediments and the use of carbon isotopes in delineating carbon sources, in U.S. Dept. of Energy Report CONF-8009140, Flux of Organic Carbon by Rivers to the Ocean, 315-330.

Turekian, K.K., Nozaki, Y. and L.K. Benninger, 1977, Geochemistry of atmospheric radon and radon products, Ann. Rev. Earth Planet. Sci. 5, 227-255.

van der Merwe, N.J., 1982, Carbon isotopes, photosynthesis, and archaeology, Amer. Scientist 70, 596-606.

Wong, W.W. and W.M. Sackett, 1978, Fractionation of stable carbon isotopes by marine phytoplankton, Geochim. Cosmochim. Acta 42, 1809-1815.