

# Records of Nutrient-Enhanced Coastal Ocean Productivity in Sediments from the Louisiana Continental Shelf

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**ABSTRACT:** Shelf sediments from near the mouth of the Mississippi River were collected and analyzed to examine whether records of the consequences of anthropogenic nutrient loading are preserved. Cores representing approximately 100 yr of accumulation have increasing concentrations of organic matter over this period, indicating increased accumulation of organic carbon, rapid early diagenesis, or a combination of these processes. Stable carbon isotopes and organic tracers show that virtually all of this increase is of marine origin. Evidence from two cores near the river mouth, one within the region of chronic seasonal hypoxia and one nearby but outside the hypoxic region, indicate that changes consistent with increased productivity began by approximately the mid-1950s when the inorganic carbon in benthic forams rapidly became isotopically lighter at both stations. Beginning in the mid-1960s, the accumulation of organic matter, organic  $\delta^{13}\text{C}$ , and  $\delta^{15}\text{N}$  all show large changes in a direction consistent with increased productivity. This last period coincides with a doubling of the load of nutrients from the Mississippi River, which levelled off in the mid-1980s. These data support the hypothesis that anthropogenic nutrient loading has had a significant impact on the Louisiana shelf.

## Introduction

The Mississippi River drains approximately 47% of the conterminous United States delivering an annual load of approximately  $2 \times 10^{14}$  g of suspended matter to the northern Gulf shelf (Meade and Parker 1985). River monitoring over the past 35 yr shows an approximate doubling of the an-

nual nitrate load, to approximately  $1 \times 10^{11}$  g, between the mid-1960s and the mid-1980s, with a subsequent decline (Turner and Rabalais 1991; Dinnel and Bratkovich In Press). It has been argued (Riley 1937; Turner and Kaswadji 1987) that anthropogenic increases in nutrient concentrations in the lower Mississippi River, with subsequent increased loads to the northern Gulf of Mexico, have resulted in higher coastal productivity, causing or contributing to the observed seasonal

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shelf hypoxia. Hypoxia on the shelf of the northern Gulf of Mexico was first observed in the early 1970s (Farrell 1974; Harper et al. 1981). Subsequent surveillance cruises (Rabalais et al. 1991, 1992) have established that this phenomena is extensive west of the delta and is a recurrent seasonal feature on the shelf, developing after thermal stratification of inshore waters during the spring and ending with autumn overturn.

Anthropogenic impacts to the water quality of the northern Gulf coastal region presumably began in the 19th Century with the beginning of significant river basin cultivation and population increase. The record of fertilizer consumption, although an imperfect surrogate for nutrient load, appears to be well correlated ( $p < 0.05$ ) with estimates of nitrogen flux from the Mississippi River (Turner and Rabalais 1991). Records of commercially-produced-fertilizer consumption in the United States extending back to 1895 (United States Department of Commerce 1975, 1982, 1989) imply that nutrient fluxes begin to increase above background level around 1930, with substantial increases beginning in the mid-1950s (Eadie et al. 1992; Nelsen et al. 1994).

Although detailed estimates of river nutrient concentrations and fluxes are available for more than 35 yr and sporadically before that (Riley 1937; Turner and Rabalais 1991; Dinnel and Bratkovich 1993), a long-term record of coastal productivity is unavailable. However, a record of local productivity may be contained in sediments from the shelf. These sediments have been shown to preserve recent anthropogenic effects such as a reduction in lead inputs due to regulation of gasoline additives (Trefry et al. 1985). Although sediments contain valuable information, deconvolving such records is an uncertain and challenging task. In addition, changes in river flow patterns, occasional sediment disruptions, and transport of sediments by severe storms, all contribute to complex sediment accumulation records in this region.

Organic matter in shelf sediments has two major sources. The Mississippi River delivers approximately  $2 \times 10^{12}$  g yr<sup>-1</sup> of particulate organic carbon (POC) to the Gulf (Malcolm and Durum 1976). In addition, these near-delta sediments receive materials from coastal primary production enhanced by terrestrial nutrient inputs. Near the river mouth, productivity is impeded by high turbidity (Riley 1937; Lohrenz et al. 1992) and does not reach a maximum (ca.  $10 \text{ g m}^{-2} \text{ d}^{-1}$ ; Lohrenz et al. 1992) until a salinity of 15–20‰. Within this mid-salinity region (a few kilometers from the mouth), extremely high levels of primary production consume the inorganic nutrients delivered by the river, while further along the shelf, intense nutrient re-

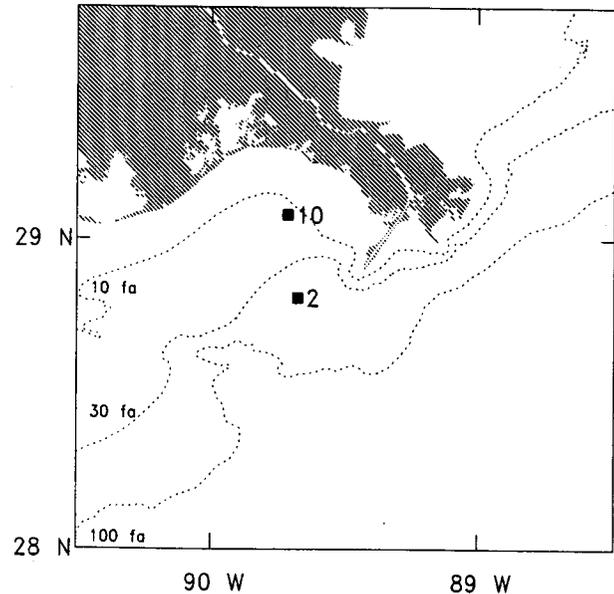


Fig. 1. Coring locations. Station 10 is within the region of chronic summer hypoxia, while station 2 is outside this region.

cycling provides the requirements for elevated productivity. During summer, when shelf waters are thermally stratified and circulation is predominately a longshore westward drift, settling of this organic material into stagnating bottom waters results in hypoxic and occasional anoxic conditions. Although extensive oxidation of organic matter occurs in the water column (Benner et al. 1992; Gardner et al. 1994), we present evidence in this manuscript that anthropogenic nutrient enhancement in the coastal zone has produced proportional enhancement of primary productivity recorded as increased carbon burial and deposition of biomarkers in the shelf sediments.

## Methods

### STATION SELECTION AND GEOCHRONOLOGY

Core locations for this study (Fig. 1) were carefully chosen based on available sediment accumulation rates for this area (Shokes 1976; Nelsen and Trefry 1986; McKee et al. 1990). Our objective was to carefully retrieve cores with relatively high temporal resolution covering 50–200 yr of accumulation; the period of potential anthropogenic influence. Sediment samples were collected by two coring methods: a  $25 \times 25 \times 60$  cm stainless-steel box corer, which was subcored with 2.6-inch diameter plastic core barrels; and with a 2.6-inch diameter benthos gravity corer. Stratigraphic integrity of the sediment column was visually examined on-board ship by slicing one of the sub-cores lengthwise. After passing preliminary on-

TABLE 1. Sediment sampling locations.

Station	N Latitude	W Longitude	Water Depth (m)	Core Length (cm)	Collection Date	<sup>210</sup> Pb Time Span
2	28°49.0	89°41.0	69	94	August 1982 <sup>a</sup>	1982–1760
10	29°05.22	89°43.48	29	51	February 1991 <sup>b</sup>	1991–1900

<sup>a</sup> Gravity core stored at 4°C prior to analysis; sectioned in 2-cm intervals.

<sup>b</sup> Box core sectioned (1-cm intervals) immediately after collection; stored frozen until freeze-dried.

board screening, subsamples were taken at 1-cm intervals from 2 to 3 subcores, combined, and homogenized to assure that all analyses would be made on the same sediment interval. Samples for chemical and biological analyses were freeze-dried and stored frozen until preliminary radiochemical interpretation assured that the core had a interpretable geochronology.

A number of cores were available or collected from this region. Two were selected (Table 1) for detailed analysis for this preliminary report. Station #10, located west of the delta was selected as representative of an area of chronic hypoxia. This location was determined from available information from several previous cruises (Rabalais et al. 1991, 1992). A gravity core from station #2, previously collected and dated from the same region but outside the zone of hypoxia, provided a basis for comparative analysis.

Sediment geochronology was determined using <sup>210</sup>Pb ( $t_{1/2} = 22.3$  yr) and <sup>234</sup>Th ( $T_{1/2} = 24.1$  d). Each interval was transferred to a hygroscopic vial (for water content determination) and subsequently weighed and dried. Yield tracers (<sup>228</sup>Th/<sup>209</sup>Po/<sup>232</sup>U) were added to the dried sediments and samples were then leached with a solution of HNO<sub>3</sub>, HCl, and H<sub>2</sub>SO<sub>4</sub>. Thorium and uranium were isolated and purified by ion exchange, extracted into thenoyltrifluoroacetone, evaporated onto stainless

steel planchets, and counted on a low-background beta counter (McKee et al. 1986). <sup>210</sup>Pb was measured via the polonium method (Nittrouer et al. 1979; McKee et al. 1986) by plating <sup>210</sup>Po (a direct daughter of <sup>210</sup>Pb) and <sup>209</sup>Po (yield tracer) onto silver planchets and counted by alpha spectrometry on a silicon barrier detection system. Samples were counted to an error of less than 3%.

A nonlinear Marquadt-Levenberg fit of cumulative mass accumulation versus the <sup>210</sup>Pb activity was used to estimate the activity of supported <sup>210</sup>Pb at the base of the core or below by extrapolation. A weighted least-squares of the log of excess <sup>210</sup>Pb versus the cumulative mass accumulation was then used to estimate the sediment accumulation rate. This approach takes sediment compaction and errors in sampling intervals into consideration. Both sediment profiles (Fig. 2) were well behaved, resulting in mass accumulation rates of 0.28 g cm<sup>-2</sup> yr<sup>-1</sup> and 0.38 g cm<sup>-2</sup> yr<sup>-1</sup> for stations 2 and 10, respectively. These convert to average linear accumulation rates of 0.43 cm yr<sup>-1</sup> and 0.56 cm yr<sup>-1</sup>.

#### CARBON, NITROGEN AND STABLE ISOTOPE ANALYSES

Samples for organic carbon and nitrogen analysis were ground, acidified with 1 N HCl to remove CaCO<sub>3</sub>, and mixed on a shaker table overnight. They were then oven-dried at 90°C and stored in a desiccator prior to analysis. Measurements were made using a Perkin-Elmer 2400 CHN analyzer. Accuracy was monitored through the analysis of known standards at regular intervals; precisions for a laboratory standard sediment were 2.1% for carbon and 4.1% for nitrogen.

Aliquots of these carbonate-free sediment samples were prepared for isotope analysis by high temperature combustion. The sediments were weighed into 9-mm Vycor tubes, which had been precombusted at 900°C. Precombusted CuO wire and Cu powder were added to the tubes, which were then evacuated and flame-sealed. The samples were combusted at 850°C for 2 h, cooled for 2 h to 600°C, then cooled to ambient temperature overnight. Gases were purified by cryogenic vacuum distillation; CO<sub>2</sub> was frozen into a sample tube immersed in liquid nitrogen and nitrogen-frozen into a sample bulb with evacuated molecular sieves

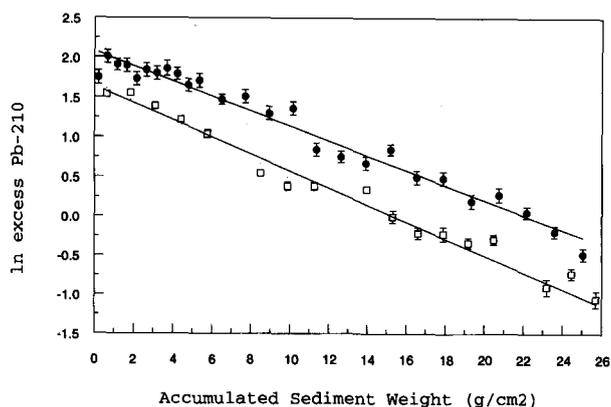


Fig. 2. Geochronologies based on excess <sup>210</sup>Pb. Average linear accumulation rates are 0.56 cm yr<sup>-1</sup> for station 10 (solid circle) and 0.43 cm yr<sup>-1</sup> for station 2 (open box). The same symbols are used for each core throughout the paper.

at liquid nitrogen temperature. Carbon quantified by manometry during this process agreed (to  $\pm 5\%$ ) with CHN results. Stable isotopes were analyzed using a VG PRISM mass spectrometer.

Stable isotope ratios were calculated as follows:

$$\delta^{13}\text{C}(\text{‰}) = \left[ \frac{\text{R}(\text{sample}) - \text{R}(\text{standard})}{\text{R}(\text{standard})} - 1 \right] \times 1,000$$

where  $\text{R} = \text{C}^{13}/\text{C}^{12}$ ; with an analogous formula for nitrogen. Data are reported relative to the PDB standard for carbon and air for nitrogen. Precision (1 SD) for triplicate analyses of split samples was  $<0.1\text{‰}$  for carbon and  $<0.2\text{‰}$  for nitrogen; similar to our replication of standard materials. Blanks were less than 1% of these samples.

Ground sediment samples (about 50 mg) to be isotopically analyzed for  $\text{CaCO}_3$  were roasted at  $300^\circ\text{C}$  for 2 h then weighed into side-arm flasks. Four ml of 100% phosphoric acid were added to the second arm, the flasks evacuated, and mixed. The reaction was held at  $25^\circ\text{C}$  for 16–24 h, then the  $\text{CO}_2$  was collected as above. Precision (1 SD) for triplicate analyses of split samples was  $<0.1\text{‰}$  for carbon and  $<0.3\text{‰}$  for oxygen (reported relative to SMOW). Carbon was quantified manometrically.

#### BIOMARKERS

Total lipids were extracted by weighing approximately 4 g of ground, freeze-dried sediment into a 50-ml glass centrifuge tube, adding 35 ml of (2:1) chloroform:methanol, and sonifying for 2 min with a 375-watt microprobe. The sample was then centrifuged, the supernatant collected, and the solvent replaced. This process was repeated three times, combining the supernatant extracts. The extracts were washed with 25 ml of pre-extracted water, separated, rotary-evaporated to dryness, and weighed. Carbon isotope analysis was carried out on 10% of this material redissolved in dichloromethane. The solvent was blown down under nitrogen, and prior to sealing, the sample tube was left under vacuum for several minutes until there was no observable change on a thermocouple vacuum gauge adjacent to the sample tube. The lipid carbon was quantified manometrically.

Sediment lignins were prepared by the method of Hedges and Ertel (1982); oxidized with  $\text{CuO}$  at  $170^\circ\text{C}$ , ether-extracted, derivitized, and quantified by capillary gas chromatography. The results are reported as lambda units (Hedges and Ertel 1982), the sum of syringyl and vanillyl compounds per 100 mg of sediment organic carbon. Lambdas calculated for replicate extraction and analysis of three split sediment samples agreed within 13%.

## Results

### GEOCHRONOLOGY

West of the delta, where the main river channel (Southwest Pass) presently delivers approximately one-third of the Mississippi River flow,  $^{210}\text{Pb}$  profiles at stations 2 and 10 were well behaved (Fig. 2), with linear accumulations of  $0.43 \text{ cm yr}^{-1}$  and  $0.56 \text{ cm yr}^{-1}$  respectively. These cores span periods of greater than 90 yr, allowing for an examination of the record through what we believe to be the period of anthropogenic impact.  $^{234}\text{Th}$  was detected only in the upper 1 cm of core 10, indicating limited bioturbation over periods (months) comparable to several half-lives of  $^{234}\text{Th}$ . This is significant since this core was collected in April, near the end of the well-mixed period and prior to the onset of hypoxia. This is the period of maximum benthic abundance (Rabalais and Harper 1992) and should correspond to maximum bioturbation. After the setup of hypoxic conditions, benthic biomass decreases dramatically.  $^{234}\text{Th}$  was not measured in the core from station 2. Close examination of the  $^{210}\text{Pb}$  profiles at stations 2 and 10 indicate that both cores were mixed down to approximately 4–6 cm, thus the temporal resolution at any depth in the cores is approximately  $\pm 10$  yr.

### $\text{CaCO}_3$

The benthic foram communities in sediments from this region are described elsewhere (Eadie et al. 1992; Nelsen et al. 1994). Their preservation deeper in the sediment allowed us to examine both the concentration of and carbon and oxygen isotope composition of  $\text{CaCO}_3$  as a potential indicator of the onset or intensification of hypoxia. There was no trend in the downcore profile of  $\text{CaCO}_3$  concentration; values were approximately constant at  $2.0 \pm 0.4 \text{ mg C g}^{-1}$  sediment for station 10 and  $1.6 \pm 0.4 \text{ mg C g}^{-1}$  sediment for station 2. At both stations, the  $\delta^{13}\text{C}$  was light near the surface (Fig. 3) and rapidly became about  $0.6\text{--}1.0\text{‰}$  heavier before the mid-1960s. The  $\delta^{18}\text{O}$  remained constant (no downcore trends) at  $27.2 \pm 0.4\text{‰}$  in both cores.

### ORGANIC CARBON

Surface organic carbon concentrations were greater than 1%, similar to previously reported values for the northern Gulf shelf (Shokes 1976; Entzeroth 1982). At shelf stations 2 and 10, profiles of organic carbon decline throughout the record of this century until a relatively constant background level is reached (Fig. 4). There are two complementary processes that can account for this observation, an increasing rate of organic accumulation presumably associated with enhanced productivity

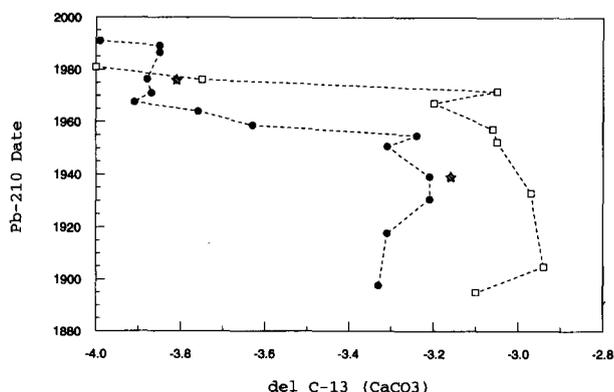


Fig. 3.  $\delta^{13}\text{C}$  for  $\text{CaCO}_3$  in the core from station 10 (solid) and station 2 (open). The filled stars are samples of *Bulliminella morgani* from station 10.

due to increased nutrient loading, or a diagenetic effect. The organic carbon profile at station 10 decreases steadily from 1.45% in the surface mixed layer, down to a constant (within experimental error) concentration of 0.75% below a depth corresponding to approximately 1930 (34 cm). Similarly, at station 2 the organic carbon concentration decreases from a surface value of 1.25% to a constant background value of approximately 0.90% below the 1925 horizon (26 cm) in the 94-cm-long gravity core. At the base of this core, corresponding to 1760 (assuming constant accumulation below the excess  $^{210}\text{Pb}$  cutoff at 50 cm and no compaction), organic carbon concentration was 0.85%.

#### STABLE ISOTOPE RECORDS

The organic carbon isotope ratio data for cores 2 and 10 are shown in Fig. 5. The surface intervals for both cores are isotopically light and may be contaminated or contain materials (such as labile, isotopically light lipids) that are rapidly remineralized near the sediment-water interface, and thus are not characteristic of the materials that are eventually consolidated. Below the first cm, the  $\delta^{13}\text{C}$  values from station 10 are heavier (more marine) near the surface, then get lighter downcore to a relatively constant value below the early 1960s horizon. The overall downcore change in  $\delta^{13}\text{C}$  is small, less than 1‰, but real. Triplicates (split sediment samples) of three depths for station 10 and two depths for station 2 provide an average standard deviation of 0.06‰. The decrease in  $\delta^{13}\text{C}$  at station 10 (within the region of recurrent hypoxia) is larger than that of station 2. At this station the  $\delta^{13}\text{C}$  peaks at the 1930s level, although the overall profile is virtually constant.

The nitrogen isotope records in both cores (Fig. 5) decrease downcore from heavier values to a rel-

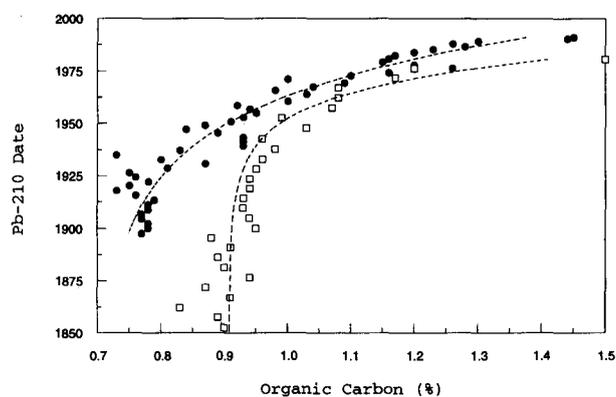


Fig. 4. Organic carbon concentrations for core 2 (open) and core 10 (solid). Lines are G-model fits (see Discussion and Table 3).

atively constant value below the mid-1960s. With this tracer, the decreases downcore were approximately the same for both cores, although the core from the hypoxic region was about 1‰ heavier throughout. Surface sediment values are somewhat lighter than values from materials collected in free-drifting sediment traps (Table 2) in the plume region (Redalje et al. 1992).  $\delta^{15}\text{N}$  has been used with success in identifying sources of sedimentary nitrogen (Coakley et al. 1992) and organism nitrogen (Van Dover et al. 1992).  $\delta^{15}\text{N}$  is also known to fractionate biologically (DeNiro and Epstein 1981), becoming heavier as it moves into higher organisms.

#### ORGANIC BIOMARKERS

The phenolic oxidation products of lignins were measured in seven segments below the interface in each of these two cores as a tracer of terrestrial woody plants. The concentration of the sum (per 100 mg organic carbon) of the syringyl and vanillyl derivatives ( $\lambda$ ; defined in Hedges and Ertel 1982) showed no downcore trend and was  $0.48 \pm 0.08$  in core 2 and  $0.63 \pm 0.21$  in core 10. The values of  $\lambda$  were similar to those reported for surface sediments from this region (Hedges and Parker 1976). Since lignins are more resistant to decay than total organic matter in sediments (Hedges and Mann 1979; Benner et al. 1984; Hedges 1992), these values provide a separate estimate of the terrestrial fraction of the material in these cores (assuming that terrestrial material behaves like lignins). The differences in the two cores support the carbon isotope evidence for more terrestrial material in the core from station 10.

Total extractable lipids were a significant fraction of the total sediment organic carbon, decreasing from >10% of the total sediment organic carbon to a relatively constant 7% below the 1980

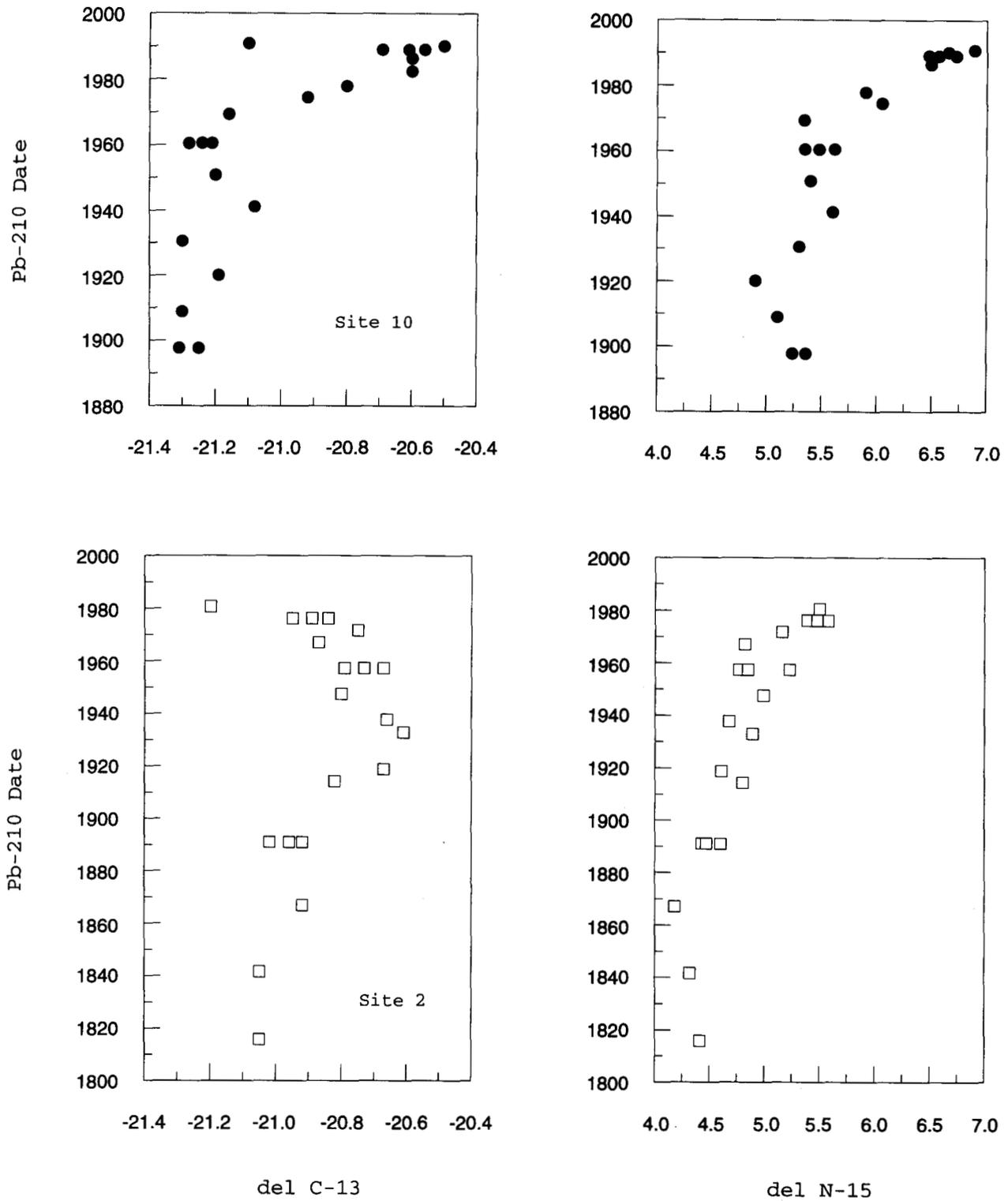


Fig. 5.  $\delta^{13}\text{C}$  (left) and  $\delta^{15}\text{N}$  (right) for the organic matter at station 10 (upper; solid circles) and station 2 (lower; open squares). Below the surface interval,  $\delta^{13}\text{C}$  for core 10 gets significantly lighter while core 2 remains approximately constant. The average standard deviation for five sets of triplicates was 0.06‰. The  $\delta^{15}\text{N}$  profiles are similar for both cores, with about a 1‰ offset. Precision was 0.16‰.

TABLE 2. Stable isotope values in the area of our sediment stations.

Type	Average NECOP	
	$\delta^{13}\text{C}$	$\delta^{15}\text{N}$
POM (sal = 0 ‰)	-25.5	6.2
POM (sal = 36 ‰)	-20.0	5.0
Net zooplankton	-18.1	7.9
Sediment trap <sup>a</sup>	-18.4	7.2

<sup>a</sup> Lorentz et al. (1994).

horizon (Fig. 6). This rapid decrease is most likely the result of microbial degradation of a labile fraction of the lipids. Although the decrease in lipid concentration was large (from 1.4 mg C g<sup>-1</sup> sediment to 0.8 mg lipid C g<sup>-1</sup> sediment) in the core from station 10, the lipid  $\delta^{13}\text{C}$  remained nearly constant ( $-25.7 \pm 0.2\text{‰}$ ) from the top of the core down through the 1900 horizon. The  $\delta^{13}\text{C}$  of the lipid-free organic matter shows a similar down-core profile to the  $\delta^{13}\text{C}$  of the total organic matter (Fig. 5), indicating that the rapid loss of some lipids near the surface had little overall effect on the isotopic composition of the preserved organic matter.

### Discussion

Our objective was to examine the solid-phase sediment organic matter to determine whether a record of anthropogenic effects on productivity or hypoxia was recorded and could be interpreted. To clarify and amplify the sediment signal, it was desirable (if possible) to separate the terrestrial organic component from the marine organic material. Terrestrial material is generally reported to be more refractory than marine organic matter, and there may have been changes in the accumulation of terrestrial organic material corresponding to river flow changes over the period of time represented by the cores. This partitioning required tracers of organic matter of terrestrial and marine origin. Numerous investigators have used stable carbon isotopes as a tracer of the dispersion of terrestrial organic matter into coastal oceans. Sackett and Thomson (1963), Parker et al. (1972), Hedges and Parker (1976), and Parker (1979) found a strong  $\delta^{13}\text{C}$  gradient for surface sediment organic carbon from a terrestrial value of  $-26\text{‰}$  to a more (temperate) marine  $-21\text{‰}$  a few km offshore of the Mississippi-Alabama coast. Similar results have been found near the mouths of other major rivers (Gearing et al. 1977; Showers et al. 1986) supporting the general argument of rapid deposition of coarse-grained terrestrial material near the mouth. In the case of the Mississippi River, biomarker lignins (Hedges and Parker 1976) and lipids (Gearing et al. 1976) have also provided evidence for the

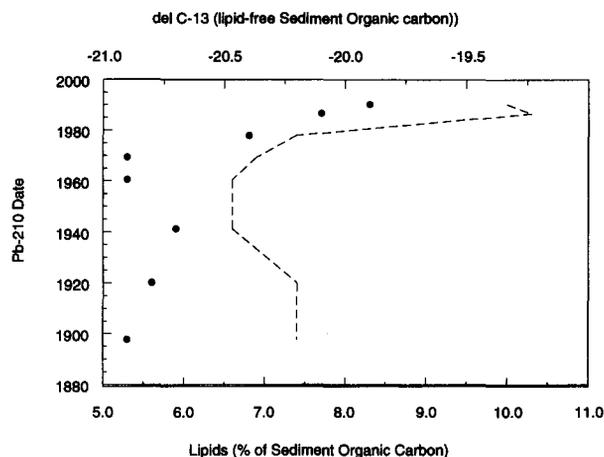


Fig. 6. The lipid content of the sediment organic matter for core 10 (dashed line) and the  $\delta^{13}\text{C}$  of the lipid-free sediment organic matter (solid circles). The  $\delta^{13}\text{C}$  of the lipid material showed no downcore trend and averaged  $-25.7\text{‰}$ , while the lipid-free organic matter had a  $\delta^{13}\text{C}$  profile similar to that of the total sediment organic carbon from this site.

rapid deposition of substantial terrestrial material within a few km of the delta.

If diagenesis is assumed to not significantly alter the isotopic composition of carbon (Fenton and Ritz 1988; McNichol et al. 1988; McArthur et al. 1992), then the relative contributions of terrestrial and aquatic carbon to the sediments can be partitioned. The isotopic composition of river particulate organic carbon measured on the NECOP cruises averaged  $-25.5\text{‰}$ , and for marine end-member POC in this region we use a value of  $-19.5\text{‰}$  (Table 2), agreeing with earlier measurements (Eadie and Jeffrey 1973; Eadie et al. 1978; Parker 1979; Thayer et al. 1983; Macko et al. 1984). Using a simple linear mixing model for carbon isotopes

$$\delta^{13}\text{C}_{\text{measured}} = x(-25.5) + (1 - x)(-19.5)$$

where  $x$  is the terrestrial fraction. Thus defined, the accumulation of terrestrial and marine organic carbon at stations 2 and 10 was calculated and are shown in Fig. 7. Below the questionable first sediment section, the terrestrial input has remained virtually constant for these two stations, with more material accumulating at station 10, implying more river influence at this station. This isotopic tracer indicates that a majority of the carbon being deposited is of marine origin and that the increase in accumulation over the past 50–75 yr is almost exclusively marine. The lack of any downcore trend in the value of  $\lambda$  and the higher concentrations at station 10 support this interpretation.

Do these sediment records support the argu-

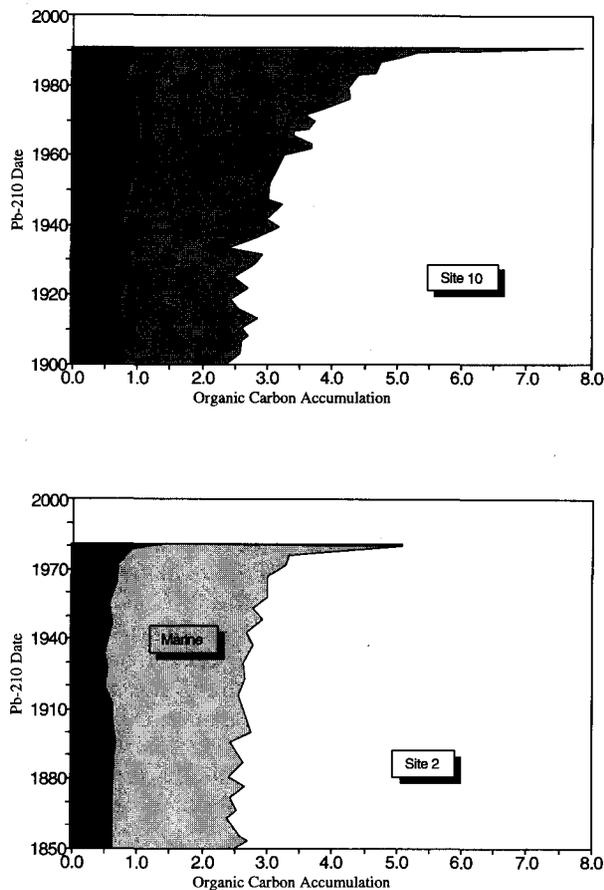


Fig. 7. Organic carbon accumulation rates  $\text{mg (C cm}^{-2} \text{ yr}^{-1})$  at stations 2 and 10. The partitioning of the organic matter into terrestrial (black) and marine (gray) fractions is based on  $\delta^{13}\text{C}$ . The recent increase in organic accumulation is much larger in the core within the region of hypoxia. Accumulation of terrestrial organic matter is also larger at station 10, implying it receives more river influence than station 2.

ment for increased productivity or can the observed changes be accounted for by in situ diagenesis? Distinguishing between these processes using sedimentary evidence is complicated by the fact that many of the changes that should be produced are similar or complementary, such as the down-core profile of organic matter. Because early diagenesis of organic matter is an important component of the carbon cycle, extensive work has been done on this topic over the past 20 yr (see Henrichs 1992 for a recent review). The apparent rates of decomposition of organic matter determined in these cores (Table 3) are within the range reported (Henrichs 1992), although most estimates of decomposition assume a constant input. In many cases for anthropogenically-impacted near-coastal sediments (such as ours), this assumption is weak. Although the accumulation record for organic

TABLE 3. Decomposition rates of organic matter based on the model  $G = G_0 + G_1 e^{-kt}$  (Westrich and Berner 1984).

	Core 10			Core 2		
	$G_0$	$G_1$	$k(\text{yr}^{-1})$	$G_0$	$G_1$	$k(\text{yr}^{-1})$
Total organic (Fig. 4)	0.71	0.67	0.030	0.87	0.39	0.028
Marine organic	0.53	0.77	0.049	0.62	0.59	0.12
Lipids	0.050	0.097	0.039			

matter can be interpreted by either process, the stable isotope profiles and other correlative evidence primarily or uniquely support increased production.

First, there is the change in isotopic composition of the organic matter. The  $\delta^{13}\text{C}$  change is small (but in the right direction) in core 10 (Fig. 5) and does not change significantly (below the surface interval) in core 2, thus this signal is small. As we showed above, an increase in the marine-derived fraction of the sediment organic carbon would support the observed profiles. In addition, we expect to observe heavier carbon isotopes being incorporated into biomass when productivity is increased (Schelske and Hodel 1991). There are two reasons for this, the rapid removal of light  $\text{CO}_2$  during photosynthesis can be faster than  $\text{CO}_2$  replacement by air-water exchange or chemical re-equilibration within the inorganic carbon cycle. This results in a depleted pool of available  $\text{CO}_2$  that is heavier than equilibrium values. In addition, high productivity modestly raises the ambient pH, shifting the equilibrium toward lower  $\text{pCO}_2$ . Both of these lead to a smaller pool of available  $\text{CO}_2$ , which will result in plankton with heavier carbon isotopic signature.

A change in the species composition of primary producers, in response to changing nutrient loads, might also systematically alter the isotopic composition of sediment organic matter. The  $\delta^{13}\text{C}$  of diatoms from Georges Bank was found to be several per mil heavier than ambient particulate organic matter (Fry and Wainright 1991). Since the load of silicate from the Mississippi River has actually gone down over the past 25 yr while both nitrogen and phosphorus have increased (Turner and Rabalais 1991), we expect a reduction in the proportion of diatoms to other primary producers. Thus the sediment  $\delta^{13}\text{C}$  that we observe is in the wrong direction to support his hypothesis.

The literature on carbon isotope fractionation during early diagenesis generally shows little or no change (McArthur et al. 1992) except in an extremely organic-rich mangrove sapropel (Spiker and Hatcher 1984). One of the most interesting comparisons to our data is a suite of cores from the Texas shelf (depths from 18 m to 285 m) where

there was no carbon isotope change between sediment sections from 0 cm to 4 cm and 15 cm to 20 cm (Entzeroth 1982). This environment is similar to the sediments examined here except that they are beyond the influence of the Mississippi River and any other significant anthropogenic influence, thus there has probably been little change in productivity. Although there is a relatively rapid decrease in the (isotopically light) extractable lipid fraction of the organic matter from station 10, the isotopic composition of the lipid-free residue retains the same general profile (Fig. 6). The implication is that the change in  $\delta^{13}\text{C}$  that we observed in the organic matter at station 10 is due to increased local productivity.

Second, the recent increase in  $\delta^{15}\text{N}$  observed in both cores (Fig. 5) also provides a strong indication of greater productivity and/or a more complex foodweb. As with carbon, higher productivity would result in more depletion of the nitrogen supply, forcing the algae to consume nutrients from an isotopically heavier pool. Although the  $\delta^{15}\text{N}$  change in the cores occurred during a period of a doubling of the load of nitrogen (with an increasing N:P ratio) into the region (Turner and Rabalais 1991), in the mid salinity waters of maximum productivity where these cores were collected, nitrogen is still the nutrient most responsible for limiting production (Turner et al. 1987). Another possible contribution to the increased  $\delta^{15}\text{N}$  that we measured in these sediments could come from increased nitrification-denitrification, processes that remove light nitrogen from the organic matter in the near-surface sediments. Although there are several factors that influence these processes, there is some evidence that rates are highest in regions of high nitrogen loading (Seitzinger 1990). Thus we might expect that these process rates have increased with increasing nitrogen input from the Mississippi River.

With the doubling of nitrogen loading from the river over the past 25 yr there are two other possibilities that might influence the sediment organic  $\delta^{15}\text{N}$  that we measured. The isotopic composition of the increased nitrogen is unknown, although it is presumably chemical fertilizer nitrogen with a smaller contribution of municipal and industrial waste. Chemical fertilizers are generally depleted in  $^{15}\text{N}$  with values within  $\pm 2\text{‰}$  of the air standard of zero (Heaton 1986; Wada and Hattori 1991). While municipal (sewage) waste can be isotopically heavy,  $-1.1\text{‰}$  to  $+7.8\text{‰}$  (Eganhouse and Kaplan 1988; Coakley et al. 1992; Van Dover et al. 1992), based on the small and relatively constant component of terrestrial organic matter in these cores, the contribution of any changes in this material to the observed change in  $\delta^{15}\text{N}$  must be small. These

arguments imply that the changes in the isotopic composition of the river material are probably small and in the direction of lighter, not heavier, nitrogen. The evidence for postdepositional nitrogen isotope fractionation (Velinsky et al. 1991) indicates that it is small and would not significantly alter the solid phase  $\delta^{15}\text{N}$ . Eganhouse and Kaplan (1988) used the  $^{13}\text{C}$  and  $^{15}\text{N}$  changes in sediments from nearshore southern California, covering a period of more than 30 yr, to isolate the fraction of organic matter derived from a sewage treatment plant. The results compared favorably with source-partitioning estimates using carbon isotopes and other biomarkers, implying that there was little isotope fractionation over this period in their cores. Thus, the substantial change in the  $\delta^{15}\text{N}$  that we observe over a similar interval is primarily due to a change in the isotopic composition of the source organic matter caused by increased productivity.

Further support for an increase in productivity is supplied by the change in the  $\delta^{13}\text{C}$  of the sediment  $\text{CaCO}_3$ . Although there have been some species shifts in the forams in the core from station 10, Nelsen et al. (1994) report that *Bulliminella morgani* and *Epistomenella vitrea* have been the predominant benthic forams, averaging 42% and 23% respectively of the total populations throughout the core's length. Less than 5% of the biogenic carbonates could be attributed to pelagic forams and virtually no nonbiogenic carbonates were observed (Hood and Blackwelder personal communication). Beginning around 1940, the  $\delta^{13}\text{C}$  of this carbonate material became lighter by approximately  $0.6\text{‰}$ , with a similar change at station 2. The  $\delta^{13}\text{C}$  of *Bulliminella morgani*, picked from two depths at station 10 show a similar shift. If primary production increased in the past century, we would expect to see lighter carbonate carbon as more isotopically light organic matter decomposed in the bottom waters and was incorporated into benthic foram tests. Using a box model, an estimate can be made of the minimum (no mixing) steady-state amount of increased organic matter that was delivered to the bottom waters at station 10 for remineralization. Assuming no change in the isotopic fractionation by the forams over this period and a background of  $2,200 \mu\text{mol l}^{-1}$  DIC, the amount of organic matter with a  $\delta^{13}\text{C}$  of  $-21\text{‰}$  (an average for this region) needed to change the  $\delta^{13}\text{C}$  of the DIC pool by  $0.6\text{‰}$  is

$$(2,200 + x)(-0.6) = -21x$$

$$x = 65 \mu\text{mol l}^{-1} \text{ of organic carbon}$$

Using the respiration and remineralization rates measured and reported in Gardner et al. (1994) of approximately  $0.1\text{--}1 \mu\text{mol l}^{-1} \text{ h}^{-1}$ , this could be

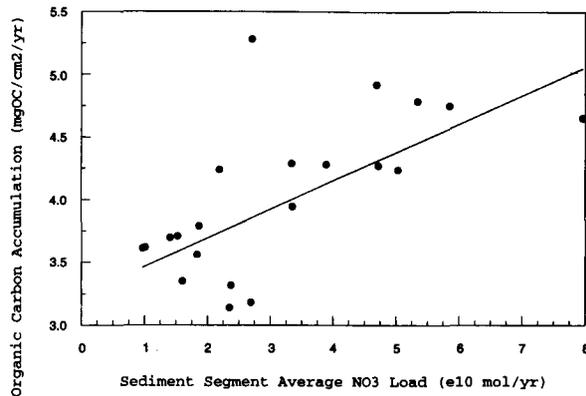


Fig. 8. The correlation of the organic carbon accumulated in each sediment section versus the Mississippi River nitrate flux for the same (Pb-210) interval. The least-squares fit for core 10 is  $y = 3.3 + 0.22x$  ( $r^2 = 0.65$ ).

accomplished in days. Conversion of this organic carbon to  $\text{CO}_2$  (assuming organic matter with a Redfield composition) requires approximately  $2 \text{ ml O}_2 \text{ l}^{-1}$ . This is a significant enhancement to the  $\text{O}_2$  depletion in these bottom waters during the period of stagnation.

Finally, in support of the productivity change argument, monitoring records of the Mississippi River show that there has been substantial increase in nitrate and changes in other nutrient fluxes to the Gulf over the past 30 yr (Turner and Rabalais 1991). Using our  $^{210}\text{Pb}$  measurements, we were able to calculate the time interval represented by the 1-cm sediment sections that we have analyzed. We used these dates and the Mississippi River monthly nitrate flux data provided by Dinnel and Bratkovich (1993) to calculate the total nitrate flux during each sediment interval and compared that with the organic carbon accumulated over the same interval. The result is shown in Fig. 8. A correlation with the data from station 10 yields  $r^2 = 0.65$  (0.77 without the surface interval), significant at  $p < 0.01$ . The river nitrate flux data only goes back to the mid-1950s. The core from station 2, collected in 1982 and sectioned into 2-cm intervals, yielded insufficient pairs of data to be analyzed in the same way.

The rate of commercial fertilizer usage in the United States began to increase in the late 1930s (United States Department of Commerce 1975, 1982, 1989), along with an increase in the load of nutrients to the shelf from the Mississippi River (Turner and Rabalais 1991; Eadie et al. 1992; Nelsen et al. 1994). Based on the data from these cores, we believe that increased productivity began at approximately the same time, with an increase in the rate of delivery of organic matter to the sediments at both stations. While it is likely that dia-

genesis alters the organic carbon profiles, we argue that the preponderance of evidence from the solid-phase of these sediments supports a record of increased primary production and rate of burial of organic matter in the sediments. The organic matter in these cores appears to be composed of three fractions: a nearly constant and refractory terrestrial component, a marine component that is rapidly lost within the surface sediment mixed layer, and a more resistant marine organic fraction that retains source information. Beginning in the mid-1950s to early 1960s, the sediment inorganic carbon (predominantly benthic forams) became isotopically lighter until about 1970 when it leveled off. In the thermally-stratified, coastally-trapped bottom waters of station 10, this change was due to the remineralization of organic matter contributing an increased  $\text{O}_2$  depletion of approximately  $2 \text{ ml l}^{-1}$ . From this time on, the flux of organic matter delivered to these bottom waters continued to grow, but after the mid-1960s, the increased flux began to accumulate more in the sediments rather than remineralize in the water column. It could be that water-column remineralization rates had reached a maximum for the prevailing conditions (T,  $\text{O}_2$ , mixing). Beginning about 1964, the organic accumulation, organic  $\delta^{13}\text{C}$ , and  $\delta^{15}\text{N}$  show large changes until the mid-1980s. This last period coincides with a doubling of the load of nutrients from the Mississippi River (Turner and Rabalais 1991), which also leveled off in the mid-1980s. These conclusions support the hypothesis that anthropogenic nutrient loading has had a significant impact on the Louisiana shelf, and the data provide information on the timing of water quality changes.

#### ACKNOWLEDGMENTS

We would like to thank the captain and crew of the National Oceanic and Atmospheric Administration (NOAA) ship *Malcolm Baldrige*. We also thank Terry Nelsen and Evan Forde for their assistance in collecting the cores, Terry Hood and Pat Blackwelder for providing samples of *Bulliminella morgani* from station 10 sediments, and Ron Woo, Dae-Hung Kim, and Amy Nelson for assistance in sample analysis. Partial support for this study was provided by the Coastal Ocean Program Office of NOAA. GLERL contribution # 869.

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Received for consideration, June 4, 1993  
Accepted for publication, December 14, 1993