

A retrospective analysis of nutrient enhanced coastal ocean productivity in sediments from the Louisiana continental shelf

Brian J. Eadie and John A. Robbins

NOAA/Great Lakes ERL, 2205 Commonwealth Blvd., Ann Arbor, Michigan 48105

Pat Blackwelder

University of Miami, Miami, Florida 33149

Simonne Metz and John H. Trefry

Florida Institute of Technology, Melbourne, Florida 32901

Brent McKee

Louisiana Universities Marine Consortium, Chauvin, Louisiana 70344

Terry A. Nelson

NOAA/AMOL/OCD, Miami, Florida 33149

Abstract

Sediments have been collected and analyzed to obtain evidence in support of the argument that anthropogenic nutrient loading has led to changes in coastal water quality and increased productivity. Cores representing approximately 100 years of input show unmistakable signs of increased accumulation of organic carbon beginning early in the 1900s. Organic tracers show that virtually all of this increase appears to be of marine origin. At two sites within the plume/hypoxia region, preliminary estimates are that 50 to 70 percent more organic carbon is presently accumulating than at the turn of the century. These preliminary interpretations provide strong support for the central themes of the NECOP program. Analysis and interpretation of further supporting information is continuing.

The central hypothesis of the NECOP program is that anthropogenically increased nutrient concentrations in the lower Mississippi River and subsequent increased loads to the northern Gulf of Mexico have resulted in higher coastal productivity and contributed to or caused the observed seasonal shelf hypoxia. Although estimates of nutrient concentrations and fluxes (Turner and Rabalais, 1991; Bratkovich and Dinnel, this issue) are available for 30+ years, the record for coastal productivity is not. A record related to productivity may be contained in sediments from the shelf that accumulate at a high rate (i.e. 0.1-10 cm/yr; Nelsen and Trefry, 1986) and 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).

Anthropogenic impacts on the coastal region presumably began in the 19th century with the beginning of significant cultivation of the Great Plains and population increase. Records of commercially produced fertilizer consumption in the U.S. extend back to 1895 (SAUS). The record of fertilizer consumption, although an imperfect surrogate for nutrient load, does appear to be correlated with the estimates of nitrogen flux from the Mississippi River (Fig. 1). This implies that anthropogenic nutrient increases extend back to the period 1900 to 1930. Although sediments contain information through this period and beyond, deconvolving such records is always an uncertain and challenging task. In addition, changes in river flow patterns, occasional disruptions and transport by severe storms and mass wasting of sediments all contrib-

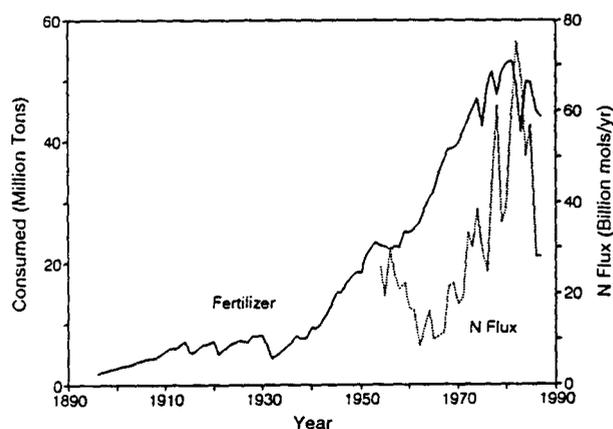


Figure 1. Commercial fertilizer consumption in the U.S. (SAUS) and nitrogen flux from the Mississippi River (Bratkovich and Dinnel, this issue). Note that although the use of fertilizer extends back to before 1895, substantial increases begin around 1930.

ute to complex sediment accumulation records in this region.

Our efforts in this program are to examine the following hypotheses through an analysis of the coastal sediment record:

1. Anthropogenic nutrient enhancement in the coastal zone has produced proportional enhancement of primary productivity and concomitant carbon burial in the shelf sediment depocenters;
2. observed riverine nutrient enhancement, together with silicon decline, has promoted a shift in plank-

tonic community structure on the Mississippi/Louisiana Shelf and this shift is preserved in the sediment record, and

3. byproducts of hypoxia/anoxia events have left characteristic markers that produce a time history of such events in the sediment record.

To test these hypotheses a multi-disciplinary approach was organized including stratigraphy, radiochemical-based geochronology, organic and inorganic chemical analyses and biostratigraphy including palynology. Results of a partial analysis of sediments selected from the AOML core library and collected on the first two NECOP cruises are presented in this report and clearly indicate increased carbon accumulation in this century accompanied by changes in the community structure.

Methods

Cores from study sites (Fig. 2) were carefully chosen based on two major criteria, critical geographic location and stratigraphic/geochronological integrity of the sediment column. The NECOP program objectives that our effort addresses include evaluating the sediment record for (1) historical increases in the burial of carbon, (2) organic/inorganic markers of historical hypoxic conditions, and (3) the offshore transport and deposition of carbon.

Four sites are highlighted in this report. The first, east of the delta (Fig. 2, site 1) is in an area of high

productivity and rapid sediment accumulation, providing an opportunity for high resolution recent reconstructions. The second site, west of the delta (location 3) was selected as representative of an area of chronic hypoxia. Its location was determined from previous reports (Rabalais, pers. comm.). A set of cores (Fig. 2, sites 5-7) were selected as being from the same region, while outside the zone of hypoxia, and provides a basis for comparative analysis. Finally, prior work (Nelsen and Trefry, 1986) demonstrated a midwater offshore transport of detached nepheloid layers over areas of the Mississippi canyon. Core site 4 was selected as a representative that might contain a record of this process.

Sediment sampling was done with a 25 x 25 x 60 cm stainless steel box corer, which was subcored with 3-inch diameter plastic core barrels and a 3-inch diameter Benthos gravity corer. Because sediment mass transport, bioturbation and *in-situ* gas production can disrupt and bias the sediment historical record, a rigorous set of criteria were used to evaluate each core prior to radiochemical analyses for geostratigraphy. After preliminary on-board approval, subsamples were taken at one centimeter intervals from each subcore, and combined and homogenized to assure that all analyses were done on the same sediment interval. Samples for chemical and biological analysis were stored until preliminary radiochemical interpretation assured that the core had a coherent geochronology.

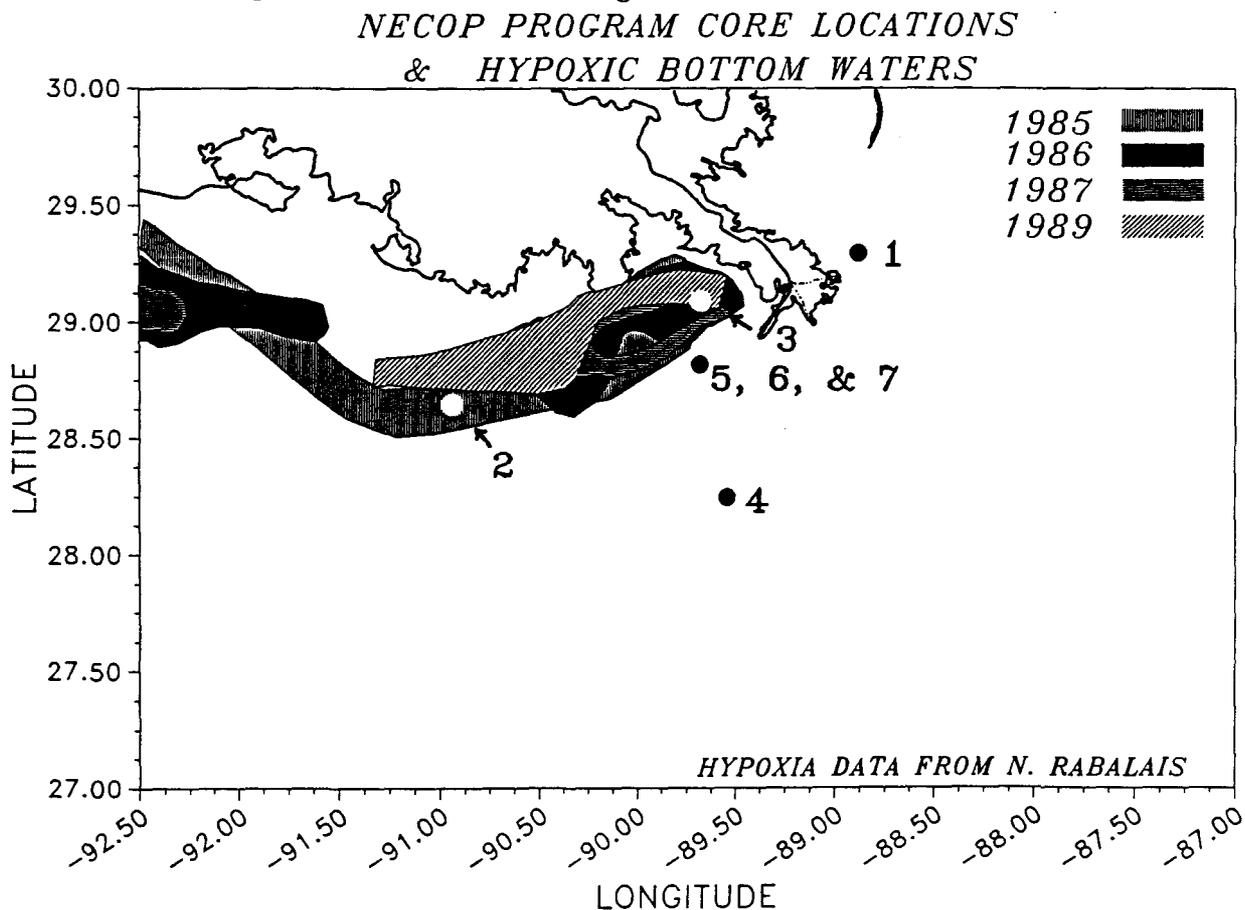


Figure 2. Coring locations.

Table 1. Current Status of Analyses

Core	Record (years)	Geochron	C,N and Metals	C and N Isotopes	Organic Biomarker	Palynology	Biostratigraphy
1	1970	C	C	C	0	C	IP
2	1925	C	C	0	0	0	0
3	1910	C	TBD	C	C	IP	IP
4	>1800	C	IP	C	0	IP	IP
5	1950	C	C	C	0	C	0
6	~1890	TBD	0	C	C	0	0
7	>1800	0	C	C	C	0	0

C = completed, IP = in progress, TBD = to be done, 0 = not planned

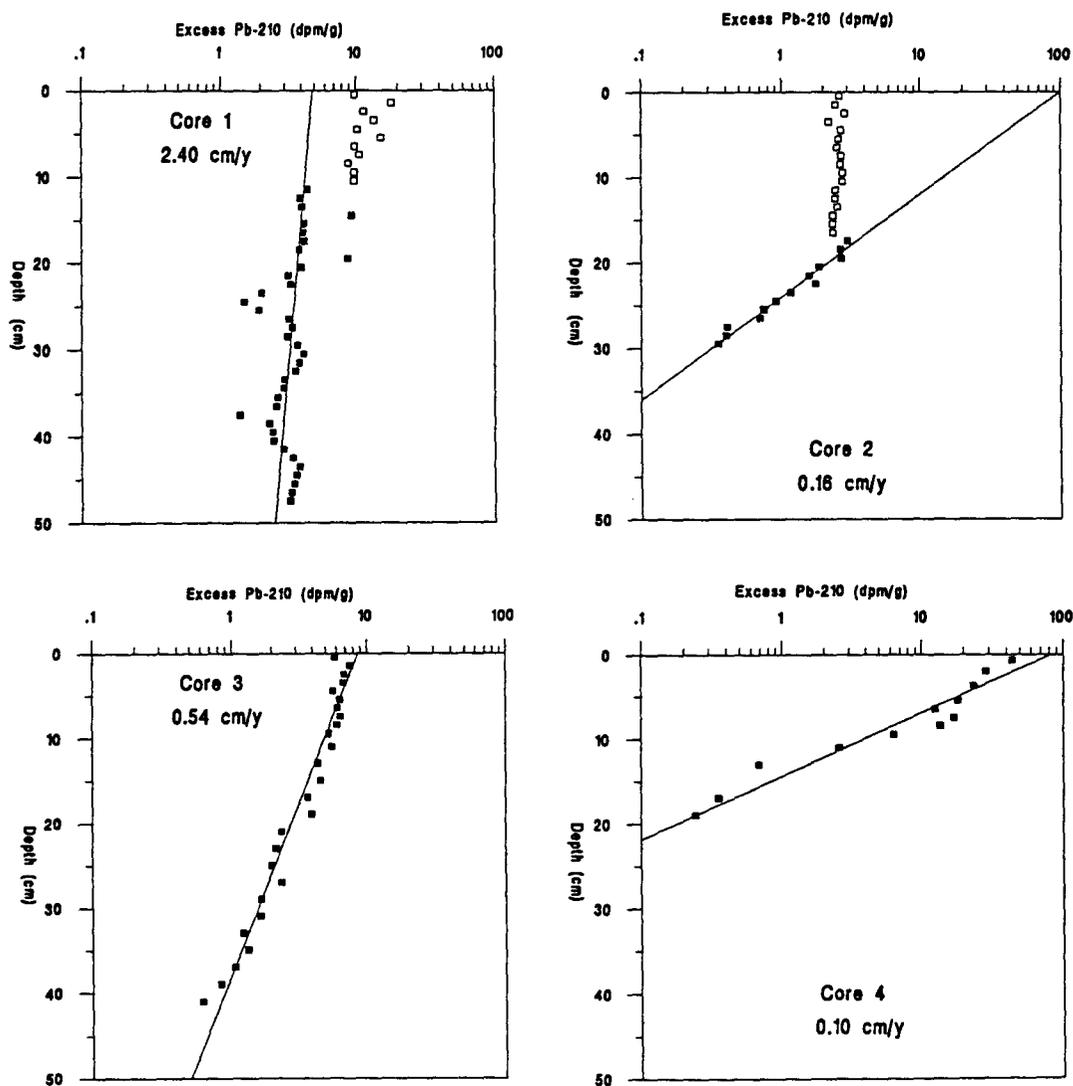
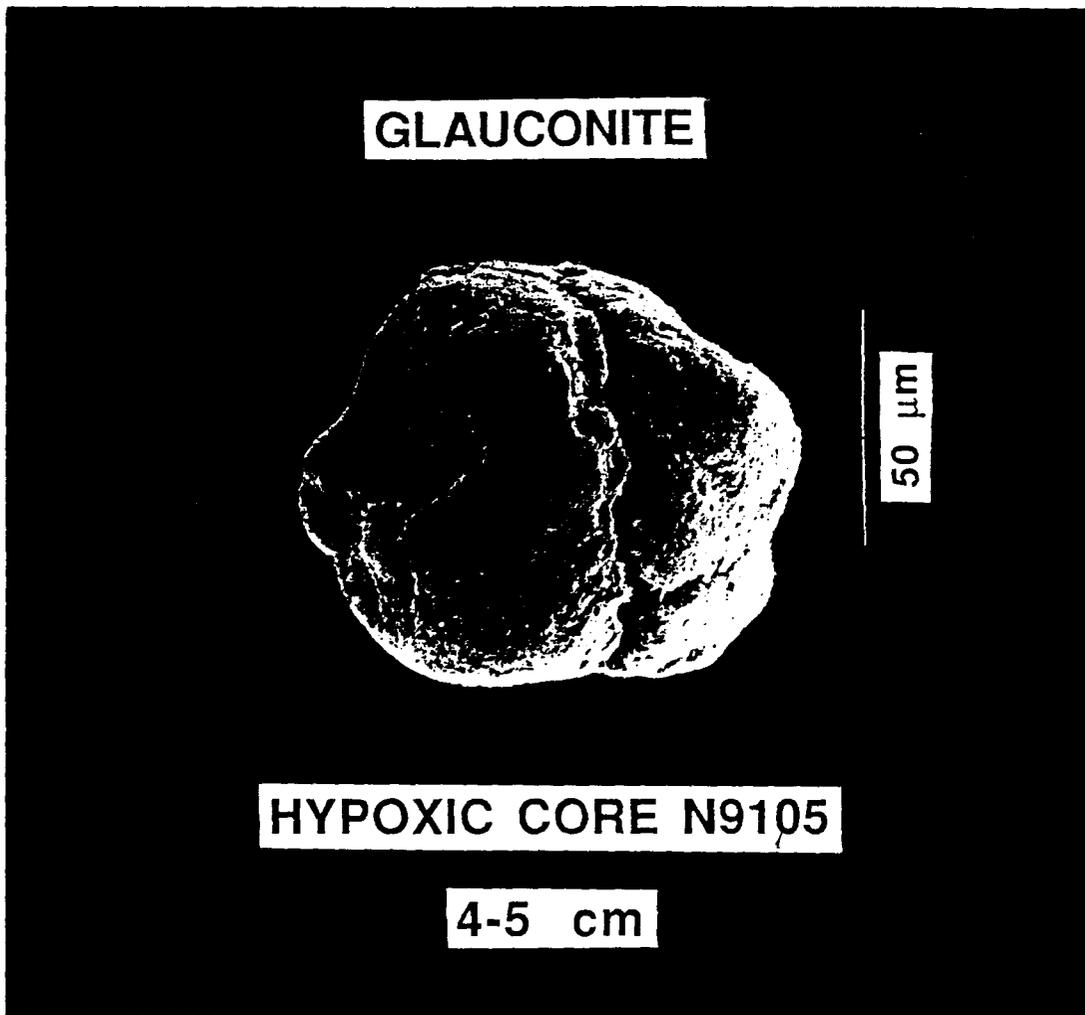
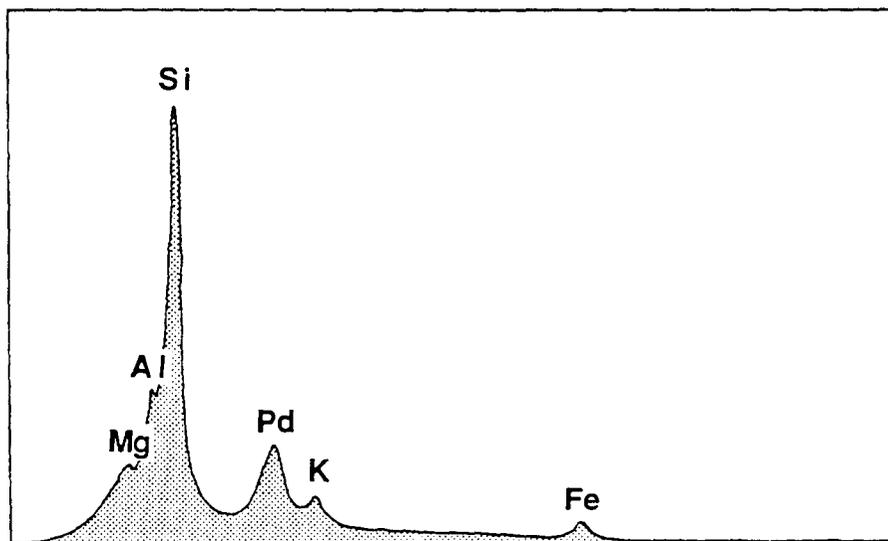


Figure 3. Excess Pb-210 in NECOP cores. Core 5 (not shown) had an accumulation rate of 1.3 cm/yr.



HYPOXIC CORE N9105
GLAUCONITE ELEMENTAL COMPOSITION



4-5 cm

Figure 4. SEM of a grain identified as glauconite from NECOP core 3. The elemental composition of this grain is consistent with our tentative identification.

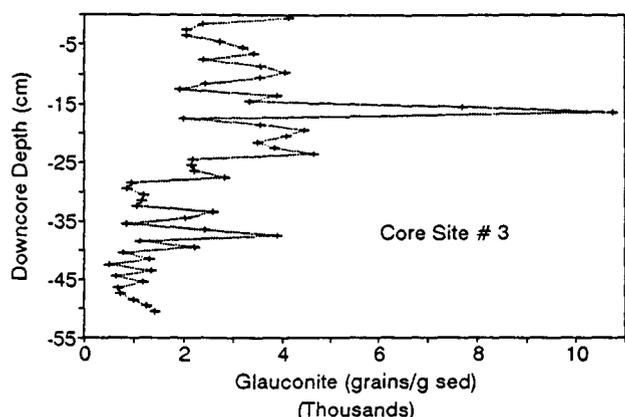


Figure 5. The downcore distribution of glauconite in the core from NECOP site 3, in the region of chronic hypoxia.

X-radiographs and photographs have been taken and interpreted for all cores. The status of other analyses are listed in Table 1. Analytical procedures are not described for the sake of brevity.

Results and Discussion

Geochronology — Preliminary interpretation of the radiochemical data indicates that three of the five stations yielded cores with relatively simple geochronologies (Fig. 3). East of the delta (station 1), the accumulation rate was very high (2.4 cm/y) below a 10 cm thick region of sediments deposited within the past few months (based on Th - 234). Although this core only represents the past two decades of accumulation, it offers an opportunity to examine short-term events. West of the delta (stations 3 and 5-7), accumulation was within the range we were seeking (0.54 and 1.3 cm/y, respectively) and the cores spanned periods of approximately 100 years allowing for an examination of the record through what we believe to be the period of anthropogenic impact. The core from station 3 was recovered from an area of chronic hypoxia while cores 5-7 were recovered from a nearby shelf site of similar depth but without documented hypoxic events. The other two cores exhibited a more difficult geochronology. Core 2, from a region of apparent anoxia during cruise 1, has a 20 cm thick overlay of material that has a constant excess Pb - 210 activity, implying intense mixing or a recent massive deposit. Core 4 from the head of the Mississippi Canyon (990 m) also presented an apparent discontinuous accumulation pattern. The length of the record for this core extends far beyond the turn of the century and along with the 5+ meter piston core from station 5-7 will provide samples for background.

Mineralogy and Biostratigraphy — Early results from one core taken within an area of demonstrated chronic hypoxia (site 3) indicate that signals critical to the overall interpretation of the sediment record are present and preserved in this region.

The mineral phase glauconite is only observed in our sediments from hypoxic areas. Phase identifica-

tion, at present, is based on color (green) and chemical composition (Fig. 4) with more detailed chemical analysis presently in progress. Current knowledge of the genesis of glauconite indicates formation in shallow marine environments rich in organic matter, reducing conditions and relatively low sediment accumulation rate all of which are known, or implied, to exist at this coring site. The general downcore trend in the distribution of glauconite, as seen in Fig. 5, indicates a general decline toward the core bottom, dated (Pb-210) to about the turn of the century. Both the smoothed and raw data show initial correlation to river events from the decadal to essentially the yearly scale. Continued work is expected to refine these initial results.

Sediment biostratigraphy of the hypoxia-area core indicates temporal variability in overall abundance counts of benthic forams. Representative species from near the core top (2-3 cm) and bottom (49-50 cm), spanning about the last 9-10 decades, are shown in Fig. 6. Because post-depositional processes have not dissolved or corroded any foram tests, excellent downcore preservation will permit continued work on foram species identification and diversity studies. These studies are currently in progress and will allow evaluation of population shifts with time and the contribution thereof to the historical investigation of hypoxia in the program study area. Benthic forams may also provide a valuable isotopic signature for the onset or intensity of hypoxia.

Organic Carbon — The concentration of organic matter in the surficial sediments is greater than the measured background (pre-1900) for the cores we have analyzed. Profiles of organic carbon decline throughout the record of this century until a relatively constant background level is reached. This is illustrated in Fig. 7, the organic carbon concentration of the sediments from the box and piston cores at site 5-7. There are two possibilities for this observation, increased rate of organic accumulation presumably associated with enhanced productivity or a diagenetic effect. We are proceeding on the assumption that the former effect is much greater than the latter and we are examining geochemical information that will allow us to estimate the magnitude of these effects. In the subsequent discussion of our preliminary data interpretation we make the assumption that the effect of diagenesis is small below sediment depth of approximately 10 cm in this area.

At site 5-7, the organic carbon concentration decreases from a surface value of 1.3 percent to a level of less than 1 percent over about 50 years and reaches a background value of approximately 0.7 percent below 100 cm in the piston core. This temporal change in concentration is consistent with increases in river borne nutrients and fertilizer consumption (Fig. 1). Similar time trends have been observed for cores from stations 3 and 4. Surface organic carbon concentrations at all sites analyzed are greater than 1 percent, a very high value for shelf sediments.

A number of studies in this region have successfully

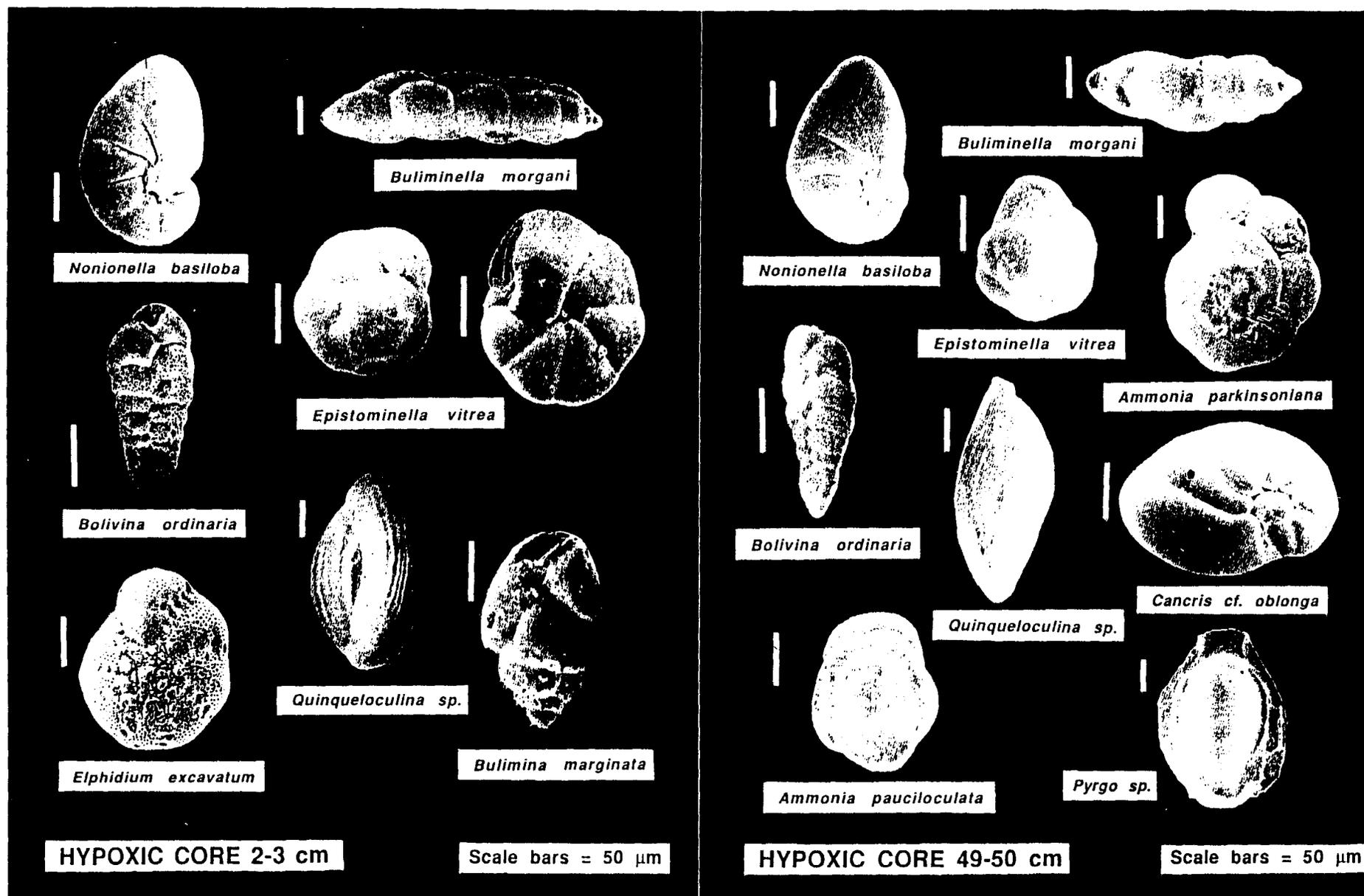


Figure 6. Forams from near surface and bottom (ca 100 yr B.P.) of the core from NECOP site 3. The visual integrity of the shells implies little dissolution, therefore species counts will provide useful information on community change.

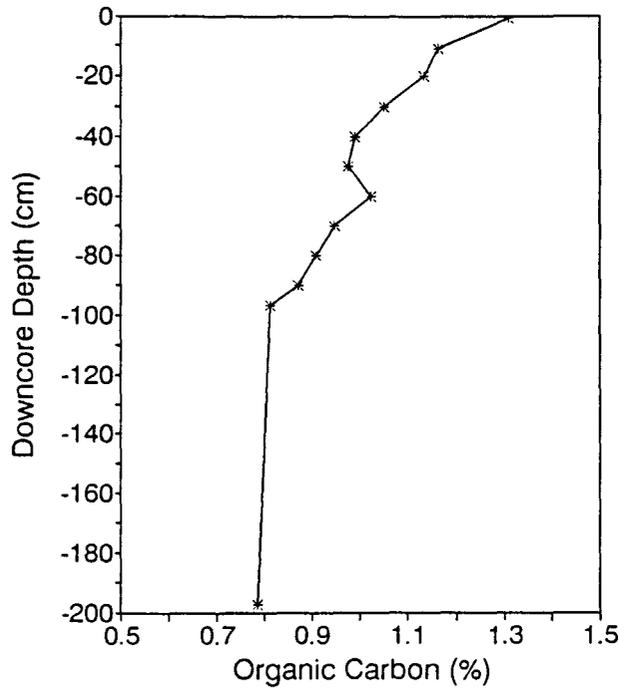


Figure 7. Carbon at site 5-7; box core (5) Pb-210 accumulation rate is 1.3 cm/yr.

used stable carbon isotopes (Parker, 1979) and lignin oxidation products (Hedges and Parker, 1976) as tracers of the source of surface sediment organic matter. Both of these tracers of sediment organic carbon show a rapid decrease in terrestrial organic matter with increased distance offshore. In Fig. 8 we present the carbon isotope ratio data for three cores. The common features are that they are heavier (more marine) at the surface, then get lighter down to approximately the 1920 horizon and remain relatively constant below this depth. The inflection near the 1920 horizon is consistent with the significant increase in fertilizer consumption at about this time.

Based on Pb-210, surface organic carbon accumulation rates for cores 3 and 5-7 are approximately 40 and 70 gC/m²/y respectively. These rates are extremely high, and represent a substantial fraction of local primary production (estimated at > 500 gC/m²/y in this area from NECOP cruise 1 data; Greg Lang, pers. comm.) and river input of carbon. For comparison, Turner and Rabalais (1991) report that the nitrogen load to the Louisiana shelf approximately doubled to 120 million kilograms per year from 1954 to 1987. Stoichiometrically converted to carbon (N x 6.75) and evenly distributed over the affected shelf, they estimate an increase of approximately 40 gC/m²/y; within the immediate vicinity of the river mouth the increase must be much larger.

The isotopic composition of river particulate organic carbon measured on the NECOP cruises is -25‰, while marine POC and sediments in this region have a composition of -20‰ (Parker, 1979). If diagenesis is assumed to be insignificant, then the relative contributions of terrestrial and aquatic carbon to the sediments

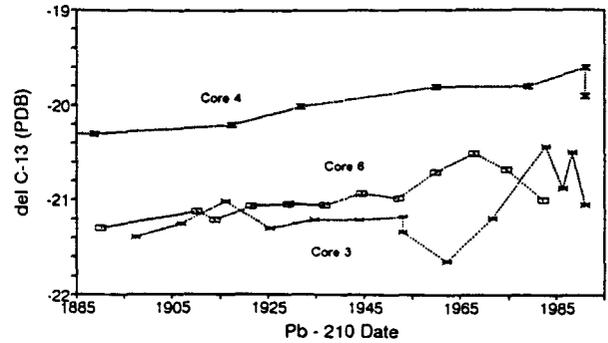


Figure 8. Organic carbon del C-13 for three NECOP cores. All get measurably lighter with depth, an indication of change in the source of the organic matter.

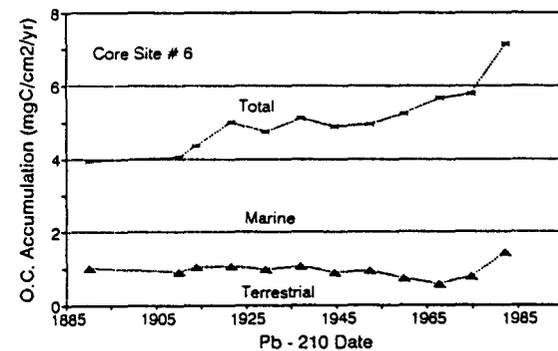
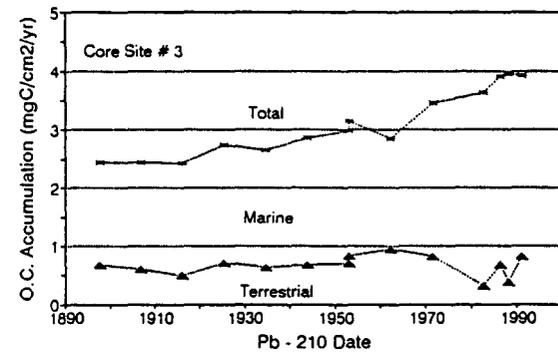


Figure 9. Organic carbon accumulation at 2 sites west of Southwest Pass. Partitioning into terrestrial and marine is based on carbon isotope composition; lignin distributions gave the same results.

can be partitioned. Using a simple linear mixing model for carbon isotopes, the accumulation of organic carbon at sites 3 and 5-7 are shown in Fig. 9. A similar calculation using lignins gave very similar results. Either tracer indicates that a majority of the carbon being deposited is of marine origin and that the increase in accumulation over the past 50 to 75 years is almost exclusively marine. The terrestrial input has remained virtually constant for these two sites. This is powerful evidence supporting the argument that carbon accumulation is increasing in response to nutrient-enhanced coastal productivity.

In addition to developing evidence of rapid and increasing accumulation near the mouth of the river, we collected a core at the head of the Mississippi Canyon at a depth of 990 m in order to examine the offshore transport of organic matter. Sediment from station 4 had high carbon content (1.4 percent) with a marine isotope signature (Fig. 8). POC collected at 5 m above the bottom at this site exhibited a $\delta^{13}C$ that contained a significant fraction of terrestrial material. It is apparent that terrestrial/coastal organic matter is reaching offshore but, without any measurement of transport, calculations of fluxes are not possible.

Summary of ongoing work — This report has focused primarily on the first of the hypotheses that we planned to examine, enhanced accumulation of organic matter in sediments. We feel that we have presented, although briefly, some strong supporting evidence. The second hypothesis relates to changes in community structure and some preliminary results of biostratigraphy have been presented. Additional data on pollen, micropaleontology, biogenic silica, nitrogen concentrations and $\delta^{15}N$ are not yet completed, but initial results are encouraging. We are also examining the sediment record for specific evidence of the record of hypoxia. When critical sample analyses are completed a more comprehensive modeling effort will be conducted to interpret the records better.

References

- GEARING, P., F.E. PLUCKER AND P.L. PARKER. 1977. Organic carbon stable isotope ratios of continental margin sediments. *Marine Chem* 5: 251-266.
- HEDGES, J.I. AND P.L. PARKER. 1976. Land-derived organic matter in surface sediments from the Gulf of Mexico. *Geochim Cosmochim. Acta* 40: 1019-1029.
- NELSEN, T.A. AND J.H. TREFRY. 1986. Pollutant-particle relationships in the marine environment: A study of particulates and their fate in a major river-delta-shelf system. *Rapp. P.-v. Reun. Cons. Int. Explor. Mer*, 186: 115-127
- PARKER, P.L. 1979. Organic geochemistry in the natural setting of the Gulf of Mexico. *Proc. Research Needs in the Gulf of Mexico, Key Biscayne, Fla., and references therein.*
- SAUS. Statistical Abstracts of the U.S.; 1989, 1982 and 1975 editions; U.S. Dept of Commerce, Bureau of Census, Washington, D.C.
- TREFRY, J.H., S. METZ, R.P. TROCINE AND T.A. NELSEN. 1985. A decline in lead transport by the Mississippi River. *Science* 230: 439-441
- TURNER, R.E. AND N.N. RABALAIS. 1991. Changes in Mississippi River water quality this century. *BioScience* 41: 140-147

National Oceanic and Atmospheric Administration
Coastal Ocean Program Office
Nutrient Enhanced Coastal Ocean Productivity

Proceedings of Workshop
Louisiana Universities Marine Consortium October 1991

TAMU-SG-92-109
June 1992



Publication of this document supported in part by the National Oceanic and Atmospheric Administration Nutrient Enhanced Coastal Ocean Productivity Program and by Institutional Grant NA16 RG0457-01 to Texas A&M University Sea Grant College Program by the National Sea Grant Office, National Oceanic and Atmospheric Administration, U.S. Department of Commerce.



Nutrient Enhanced Coastal Ocean Productivity Program

The NECOP Program is part of NOAA's Coastal Ocean Program and is conducted through the NOAA Office of Oceanic and Atmospheric Research through

The Atlantic Oceanographic and Meteorological Laboratory
The Great Lakes Environmental Research Laboratory
The Florida Sea Grant Program
The Louisiana Sea Grant Program
The Mississippi/Alabama Sea Grant Consortium
The Texas Sea Grant Program

Additional copies available from:
Sea Grant Program
Texas A&M University
P.O. Box 1675
Galveston, Texas 77553-1675

TAMU-SG-92-108
500 June 1992
NA16RG0457-01
A/I-1