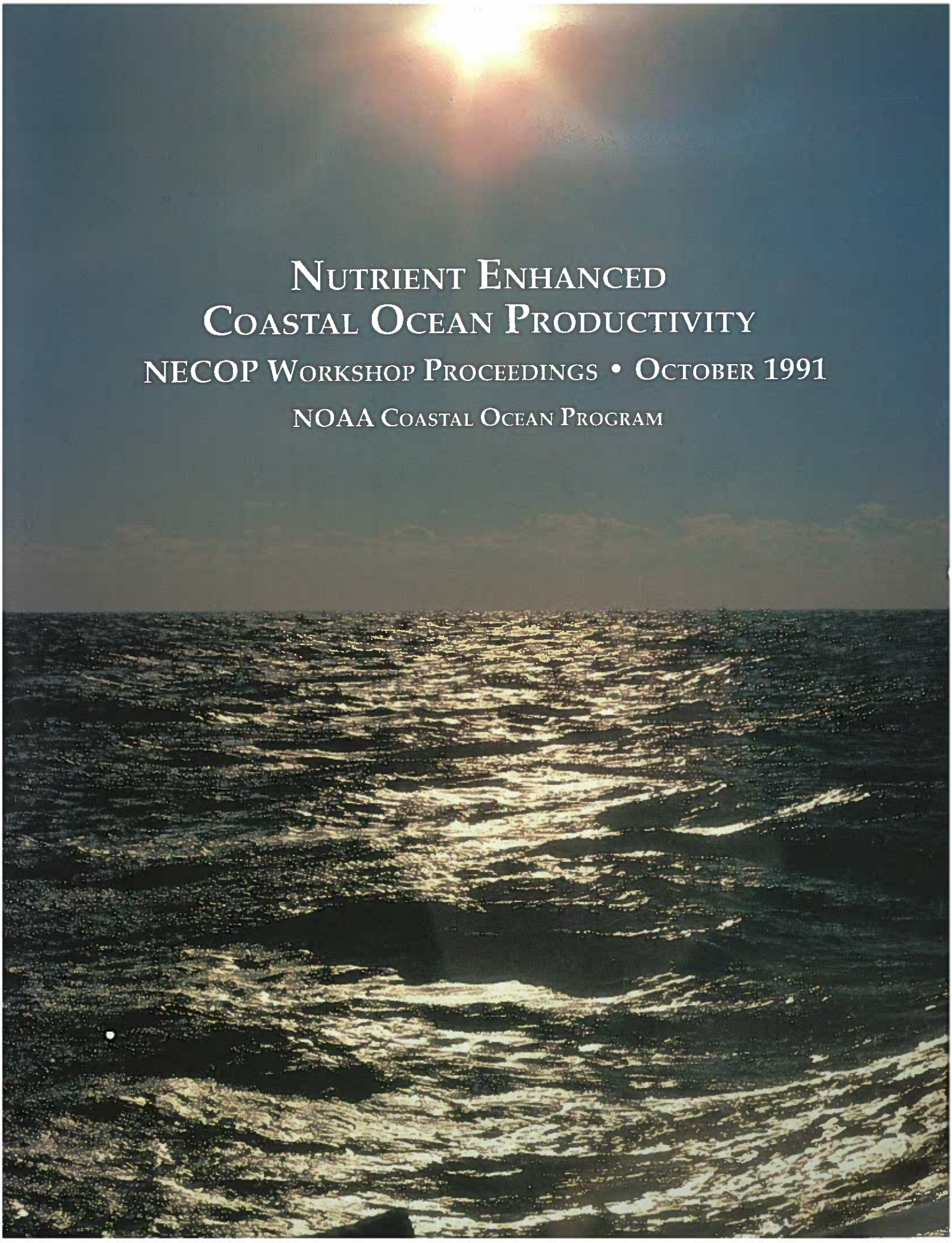

Nutrient Enhanced Coastal Ocean Productivity

NECOP Workshop Proceedings • October 1991

NOAA Coastal Ocean Program

National Oceanic and Atmospheric Administration
Coastal Ocean Program Office

Nutrient Enhanced Coastal Ocean Productivity

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Executive Summary

In 1989 the National Oceanic and Atmospheric Administration (NOAA) initiated the Nutrient Enhanced Coastal Ocean Productivity (NECOP) study as the first field effort of its Coastal Ocean Program. The long-term goal of NECOP is to conduct generic studies of nutrient loading to coastal ecosystems of the United States, and, in particular, to develop an improved understanding of the effects of anthropogenic nutrient loadings in these ecosystems. The specific objectives of NECOP are to:

- determine the degree to which coastal primary productivity has been enhanced in areas receiving terrestrial nutrient inputs;
- determine the impact of the resultant enhanced productivity on water quality, and;
- determine the fate of fixed carbon in coastal areas and its impact on living resources within the affected coastal ecosystems.

The initial NECOP field study is being conducted within the shelf waters of Louisiana and Texas influenced by the Mississippi/Atchafalaya River (MAR) system. The MAR system is the largest single source of nutrient input to the coastal waters of the United States. The resultant nutrient loading to the Lousiana/Texas shelf has been hypothesized as the source of enhanced productivity which, in turn, is believed to support widespread hypoxia (dissolved oxygen levels < 2.0 mg l^{-1}) observed in the subpycnocline waters of the Louisiana/Texas shelf in the summer.

Field work in NECOP began during the summer of 1990, i.e., only 15 months before the date of the review documented herein. In October of 1991 a workshop was held at the Louisiana Universities Marine Consortium to summarize progress to date. This report summarizes the observations and preliminary interpretations that were presented at that workshop.

Significant anthropogenic nutrient loading to the coastal waters of the northern Gulf of Mexico presumably began in the 19th century with the first significant cultivation of the Great Plains. Evidence for this hypothesis is provided by the fact that consumption of commercial fertilizer is correlated with nitrogen flux from the Mississippi River (Turner and Rabalais, 1991). Direct measurements of dissolved inorganic nitrogen indicate that nitrogen inputs to the northern Gulf of Mexico via the MAR system have dramatically increased since the turn of the century (Turner and Rabalais, 1991), although nitrate loadings have declined somewhat since 1983. There are strong annual cycles in riverine nitrate with highest concentrations observed during the spring discharge peak and minima during the period of lowest flow, in the autumn.

While the most reliable measurements of productivity in shelf waters have been limited to the past three decades, retrospective studies provide some insight into the past. These approaches have been instrumental in meeting the first two objectives of the program. Temporal records derived from sediment cores yield strong evidence that the increased nutrient flux over the past few decades has, in fact, enhanced coastal productivity. Isotope (Th^{234} and Pb^{210}) data from cores collected at several sites west of the Mississippi River Delta indicate burial rates ranging from 0.54 - 1.3 cm yr^{-1}. At these rates, the cores provide a historical record of up to 100 years. Organic matter concentrations in the surficial sediments are high (1.3 percent), declining back through time in undisturbed cores to a relatively constant level before 1900 (0.7 percent). While recognizing that diagenetic effects might be important, the temporal records suggest that the rate of accumulation of organic carbon has increased through this century. The record further suggests enhanced productivity in the overlying water column. Carbon isotope ratios show that the deposited carbon is primarily marine in origin, and that since 1920 the increased deposition is entirely marine. Carbon accumulation rates are very high, between 40 and 70 gC m^{-2} yr^{-1}, and present carbon accumulation is twice that at the turn of the century.

The distribution of inorganic materials in cores also suggests that nutrient loading has contributed to, or directly caused, the recently observed hypoxia in bottom waters during the summer. Glauconite is believed to form only in shallow, reducing environments which are rich in organic matter. The mineral phase glauconite was only observed in sediments from hypoxic areas and it declined downcore to the core bottom, dated at about the turn of the century. This suggests that within the last century hypoxia has become more frequent or is more prolonged during the summer.

A monitoring program has been included within the field effort to directly assess the extent of hypoxia on the Louisiana shelf; this project is central to meeting the second objective of the NECOP study. Widespread and persistent hypoxia on the Louisiana continental shelf covered 6200 km^2 and 7300 km^2 during the summer months of 1990 and 1991, respectively (Fig. 1 from Rabalais, Turner and Wiseman, this volume). Hypoxic conditions occur below the seasonal pycnocline, being generally confined to bottom waters between the 10 and 30 m isobaths. Patterns of distribution mapped during large-scale cruises in July of each year, when compared to similar data sets from previous years, indicate significant interannual variation. Monthly monitoring cruises along a single cross-shelf transect

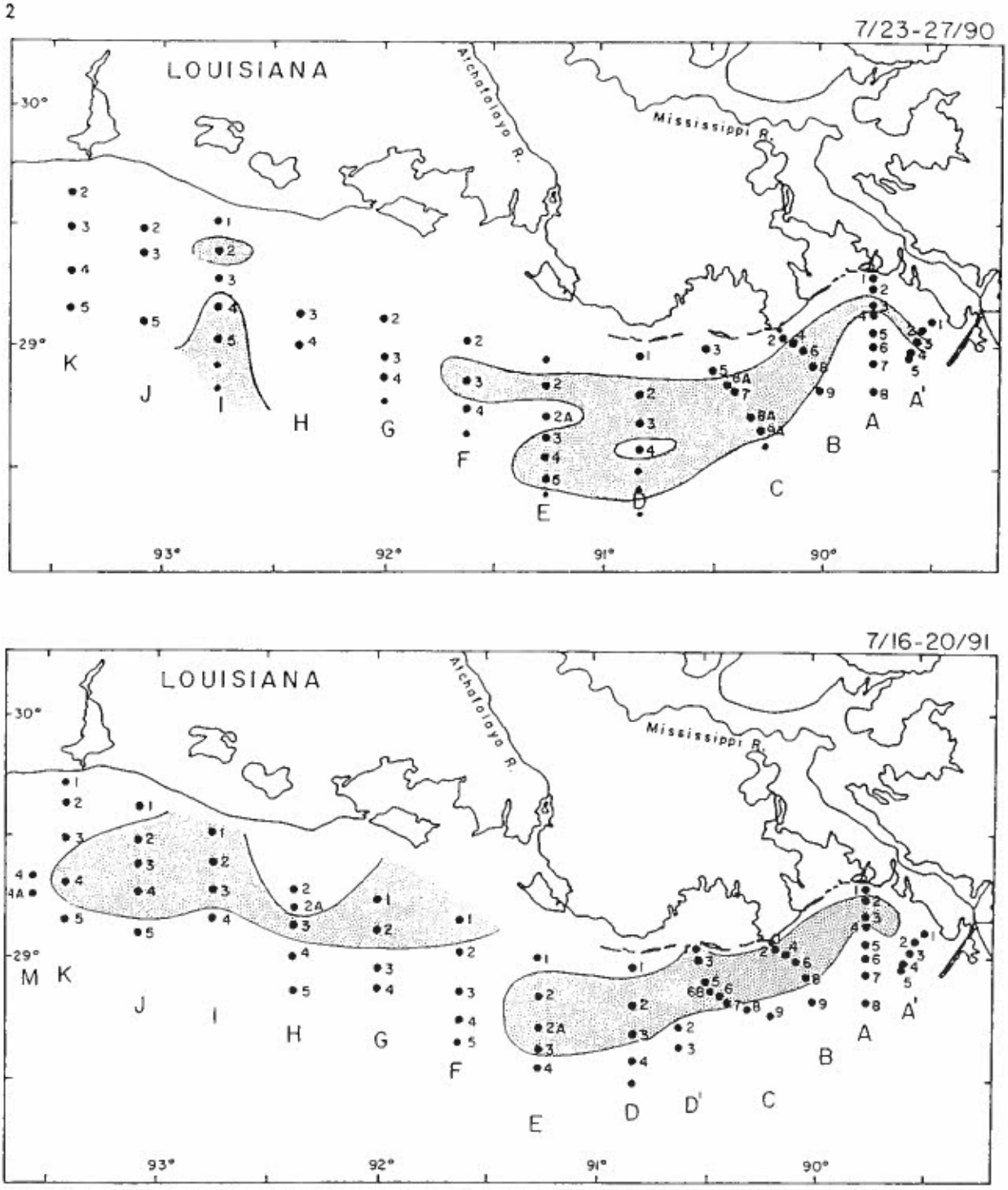

Figure 1. Areal distribution of dissolved oxygen concentrations at or below 2 mg l^{-1} in near bottom waters in 1990 (upper panel) and 1991 (bottom panel).

and continuous records from a single mooring (station C6A, Fig. 1) further show significant temporal variation at time scales from hours to months; these records do not, however, separate temporal and advective effects.

The number of species and abundance of individuals in the benthos is dramatically reduced during strong hypoxic events, but some macrofauna survive. Bottom waters are reaerated in the fall during wind-induced mixing events. Population levels and species diversity quickly return to "pre-hypoxic" levels in the fall, although it is not clear if this is by recruitment, migration, or both.

A primary thrust of the NECOP study is to conduct process studies designed to obtain an improved understanding of the environmental factors that regulate productivity and the development of hypoxia on the shelf. These are important in meeting the first and third objectives of NECOP (see above). Two important questions being addressed by these studies are:

- How is nutrient loading linked to hypoxia, and
- what is the ultimate fate of the enhanced coastal

productivity attributed to nutrient loading?

The plume area is highly dynamic. Large changes are observed in surface salinity, nitrate, extracted chlorophyll concentrations, and fluorescence over short temporal and spatial scales. Drifter data suggest that the spatial variability, and hence the material derivative of properties, is more important than local time rates of change. Nitrate from the river is utilized within 75 to 100 km of the Delta, indicating that recycling processes fuel productivity in the coastal current downplume from the delta. The highest surface pigment concentrations occur at salinities intermediate between the immediate river outflow and the open Gulf, i.e., downstream from regions of the highest surface nitrate concentrations within the plume, and at the edges of the plume. Within the hypoxic area, the temporal variability in surface properties is less than in the river plume.

Plots of surface nutrient concentrations as a function of salinity indicate that significant temporal variability exists, and that non-conservative processes are dominant factors regulating nutrient distributions. One or more of the major nutrients (nitrate, silicate and phosphate) often are depleted in surface waters at intermediate salinities (15-30 psu). There is considerable uncertainty regarding which, if any, of these nutrients are the most important in regulating, or limiting, phytoplankton production on the shelf (Turner and Rabalais, 1991; Dortch and Whitledge, in press). It is also unclear as to which specific factors control the temporal patterns of surface nutrients.

In the fall, nitrate concentrations are depleted within ca. 30 km of the river mouth, while ammonium concentrations remain at detectable levels (generally > 1 uM) over large distances. Nitrate uptake is highest in the zone of maximum phytoplankton biomass. Both nitrate and ammonium uptake appear higher in the spring than in the fall. The "f" ratio (Eppley and Peterson, 1979) is low in surface waters during both seasons (0.20 to 0.35), but highest in the spring. Ammonium regeneration rates exceed ammonium uptake rates by almost an order of magnitude and are highest in the fall. In total, these observations indicate a high dependance on recycled nitrogen, in spite of initial high nitrate concentrations within the low-salinity plume. Thus, except at the highest salinities in offshore waters, nitrogen availability may not limit the magnitude of phytoplankton production due to high rates of ammonium regeneration.

There are also indications that silicate is often limiting within the NECOP study region, and this limitation may influence the composition of the phytoplankton community, favoring species with lower silicate requirements. Generally, these species would be lesslikely to sink from the euphotic zone, and therefore less likely to serve as a carbon source to fuel hypoxia. This hypothesis is supported by the fact that in the low-salinity river plume the phytoplankton community is dominated by the chain-forming diatom *Skeletonema* while in the surface waters of the hypoxic region the less strongly silicified *Ceratulina* dominates. However, consistent patterns of silicate or nitrogen limitation were not found in either region.

Additional observations indicate rapid phosphate uptake and potential phosphate deficiency within the surface plume, particularly in the summer. Inorganic phosphate turnover times within the upper 5 to 10 m of the plume are on the order of 10 minutes, decreasing with depth. Alkaline phosphatase activity always shows a maximum within the surface plume, although turnover time for the organic phosphorus fraction is longer. This potential P deficiency has been related to a high N:P ratio in the Mississippi River source waters. In autumn, the phosphate deficiency is relatively weaker, with the shortest phosphate turnover times on the order of hours at depth > 15 m.

During summer the initial response of the shelf waters to large inputs of dissolved organic and inorganic nutrients is seen in very high growth rates of phytoplankton in the plume region, 2.7 d^{-1}; lower rates characterize the hypoxic region, 0.3 d^{-1}. Detailed measurements of growth rates of individual phytoplankton species are some of the highest *in situ* rates ever reported, 0.2 - > 3.0 d^{-1} for surface waters in the plume. Most taxa exhibit very high growth rates in surface waters, but rates decline rapidly with depth. Thus the average growth rates for the euphotic zone are lower than maximum growth rates for individual species. The exceptionally high growth rates in the summer are attributed to high water temperature (approximately 30°C) and high nutrient concentrations (e.g. NO_3 > 90 uM).

Integrated primary production (IPP) rates are much higher in the plume region during the summer (4 - 10 gC m^{-2} d^{-1}) than during early spring (0.4 - 0.7 gC m^{-2} d^{-1}). In the hypoxic region, rates are considerably lower: 2-4 gC m^{-2} d^{-1} in summer vs 0.1-0.5 gC m^{-2} d^{-1} in early spring. In spite of a wide range in phytoplankton community growth rates, based on the C^{14} labelled chlorophyll technique, there is relatively little variation in photosynthetic parameters (alpha, P_{max}) for the various communities within the study region. Estimates of production derived from a photosynthesis-irradiance model agree with observed patterns of low integral production at both high and low salinities, with high values at intermediate salinities (regions of mixing between plume and oceanic waters).

The high phytoplankton growth rates observed within the plume (2.7 d^{-1}) suggest that nutrients are not limiting primary productivity. A limited variation in photosynthetic characteristics (such as maximum and light-limited photosynthetic rates) further suggests that the major variation in the integral production can be attributed to variability in standing stock and the available irradiance. Phytoplankton stocks at intermediate salinities, although typically very high, are constrained by loss factors which potentially include sedimentation, grazing, loss of fixed carbon to the DOC pool, and physical transport from the region. These factors, considered further below, may regulate the

upper limit of productivity in the plume, while nutrient availability apparently constrains production only at higher salinities.

In order to link the observations of enhanced production to the development of hypoxia, it is essential to determine the fate of the organic carbon fixed on the shelf. Process studies examining the fate of carbon have concentrated on both the dissolved and particulate phases. These studies are also conducted in close cooperation with those investigators involved in the retrospective analysis of sediment cores. Several investigators have examined the role of sediment and particulate organic matter transport on the shelf. The concentration of suspended particulate matter (SPM) in the surface waters varies seasonally, and in all seasons decreases rapidly with distance from the river mouth (Wright, 1969, 1970). Not all the SPM that sinks to the bottom is buried; instead, the SPM is frequently resuspended and transported alongshelf, downshelf and offshelf by bottom currents.

The terrigenous load of particulate organic carbon (POC) inthe Mississippi River is on the order of 2 million metric tonsannually, approximately equal to that of dissolved organic carbon (DOC) (Malcolm and Durum, 1976). Since terrigenous particles rapidly sink to the bottom seaward of the river mouth, and the growth rates of biogenic particulates subsequently increase as light is no longer limiting, the organic fraction of the SPM increases from < 5percent of the total mass at the river mouth to > 90percent at distances exceeding a few km. Further downstream from the delta (> 70 km), POC concentrations subsequently decreased by nearly 5-fold in both summer and winter.

During summer, DOC concentrations decrease from 4 mg C l^{-1} in the river to 1 mg C l^{-1} in the open Gulf. In the summer enhanced DOC levels at intermediate salinities coincide with regions of high phytoplankton production, suggesting a biogenic source. Additionally, during the summer, nitrate from riverine sources is predominantly incorporated into phytoplankton biomass at intermediate salinities (15 to 30 psu). At these salinities, DOM characterized by high N^{15} values is released from phytoplankton, perhaps through grazing activities. DOC concentrations are lower in the winter, when no peak is observed at the intermediate salinities.

The direct sedimentation of particulate organic material,however, was highest during the early spring period when short term measurements from drifting sediment traps show that the vertical carbon flux was equivalent to 64 to 266 percent of integrated primary production (IPP). In contrast, during summer the vertical POM flux was equivalent to only 3 to 9 percent of IPP. Thus, in the plume region the direct sinking of POM (derived from phytoplankton production in the euphotic zone) to subsurface waters and the benthos does not appear to be significant during the summer. It is however, a significant loss factor during the early spring.

Ingestion by the mesozooplankton community (organisms > 200 um) accounts for a significant fraction of the daily phytoplankton production in both the plume and hypoxic regions in the summer. Ingestion rates of 230-1800 mg C m^{-2} d^{-1} were observed. Grazing is lower (150-600 mg C m^{-2} d^{-1}) in the less-productive hypoxic zone, but accounts for approximately the same fraction of phytoplankton production. Preliminary estimates indicate grazing rates during early spring are very low.

In addition, microzooplankton (organisms < 200 um) grazing is very high in surface waters of the plume, and much lower in the hypoxic region during summer. No data from the NECOP cruises are available for the spring, but work in previous years indicates moderately high rates in late April (Dagg unpublished). Detailed microscopic counts of microzooplankton grazing on specific phytoplankton species indicate this size fraction represents a major loss factor for phytoplankton biomass in both the plume and hypoxic regions in the summer. Furthermore, direct sinking appears to be an important loss factor for only one diatom (*Skeletonema*) at this time.

Clearly, the dominant initial fate of phytoplankton production during the summer is to be grazed by either the micro- or meso-zooplankton communities. This loss term appears to be much smaller during the spring, when direct sinking losses account for a large fraction of the phytoplankton production.

Maximum bacterial abundances and production rates occur at the intermediate salinities in the summer. In early spring, bacterial abundances are much less variable across the entire salinity gradient. This pattern in bacterial biomass corresponds to that of phytoplankton production. In summer bacterial production is equivalent to approximately 50percent of the C fixed by phytoplankton, while in the winter bacterial production exceeds phytoplankton production. This trend indicates that riverine-derived organic matter is an important substrate supporting bacterioplankton growth in the winter. Calculations indicate that bacterial oxygen demand alone could reduce oxygen concentrations in the bottom "hypoxic" zone from saturation levels to observed *in situ* levels within 13 to 28 days, assuming a 10 percent growth efficiency. Depletion times increase to 40 to 84 days assuming 30 percent efficiency, when more carbon is fixed into bacterial biomass. If the bulk of the carbon supporting bacterial growth originates from the spring bloom, the oxygen demand from growth of planktonic, heterotrophic bacteria in the subsurface waters is sufficient to establish hypoxic conditions by summer. There are also indications that the respiration rates increase as temperatures increase in the summer.

Other work suggests that most bacterial production is supported by dissolved, rather than particulate, materials. Nitrogen recently fixed by phytoplankton is rapidly recycled in the plume, at least during the summer, and subsequently released to the water column as labile DON. Turnover rates of this nitrogen pool are estimated to range from 0.12 d^{-1} to 0.48 d^{-1}.

All organic matter is not processed or recycled

within the water column however; a significant fraction reaches the benthos. Concentrations of phytoplankton pigments (chlorophyll and phaeopigments), biogenic silica, and organic carbon in benthic sediments are all correlated; this suggests that where high carbon sedimentation rates occur, the source is mainly biogenic carbon. Measurements of benthic community oxygen demand and sediment nutrient regeneration from the entire shelf region indicate a summertime remineralization rate of about 70 g C m^{-2} y^{-1} on the sea floor. Since benthic macrofauna are not abundant in this region, meiofauna and bacterial processes are likely to be the major components of this benthic recycling community.

While a large part of the NECOP study is devoted to monitoring and process studies, a modeling effort is also underway to consolidate and assist in the interpretation of the field observations. A central objective of the modeling effort is to provide a tool for environmental managers in order to assess future changes in nutrient inputs to the Louisiana Shelf ecosytem. Mass balance modeling efforts have produced a steady state "demonstration calibration" for data from a July 1985, shelf-wide survey (supplemented, when necessary, by data from NECOP cruises in 1990 and 1991). The results for model state variables agree with available field data within approximately a factor of 2. Model output for surface primary production and POC/PON settling fluxes compare favorably with measurements from the 1990 NECOP data. The model independently supports the conclusions from process studies regarding the importance of light as the dominant control on phytoplankton productivity and the importance of three separate processes — phytoplankton respiration, oxidation of carbonaceous material in the water column, and sediment oxygen demand — to oxygen depletion within the hypoxic region.

When all aspects of the NECOP study are considered together, significant progress is being made towards understanding the fates of nutrient enhanced production in this region, and the processes linking nutrient input to hypoxia on the inner shelf. Nevertheless, there remain important caveats that restrict the ability to draw definitive conclusions from work to date. Salinity gradients, for example, have been used as a surrogate for a downstream advective time scale, yet strong cross-stream salinity gradients are common in the study area. Direct measures of downstream velocities are to be provided by the LATEX program, which is just beginning its field work in 1992. Much of the process study work has been restricted to the outer edge of the region of most intense hypoxia because of the depth restrictions of research ships. The system is responsive to external forcing by storms and river discharge fluctuations; furthermore, significant interannual variability is known to exist. Brief, isolated cruises occurring over less than two years may not even properly define the seasonal patterns. Most of these problems are tractable, however, and are being addressed in the next two years of the program.

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

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Abstract

Sediments have been collected and analyzed to obtain evidence in support of the arguement 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 anthropogenicaly 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 contribute to complex sediment accumulation records in this region.

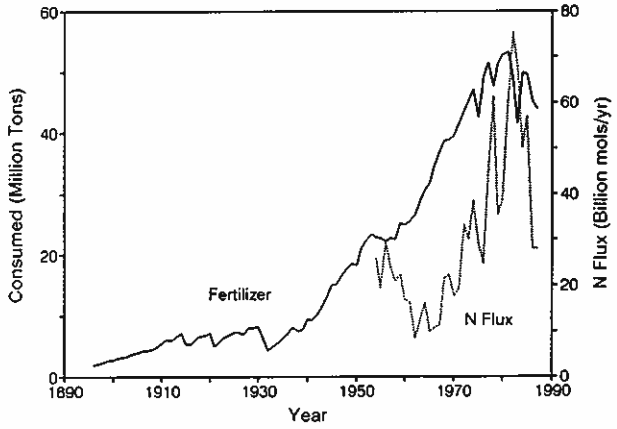


Figure 1. Commercial fertilizer consumption in the U.S. (SAUS) and nitrogen flux from the Mississippi River (Bratkovich and Dinnel, this issue). Note that although the use of fertilizer extends back to before 1895, substantial increases begin around 1930.

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 offshelf 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 interpertation assured that the core had a coherent geochronology.

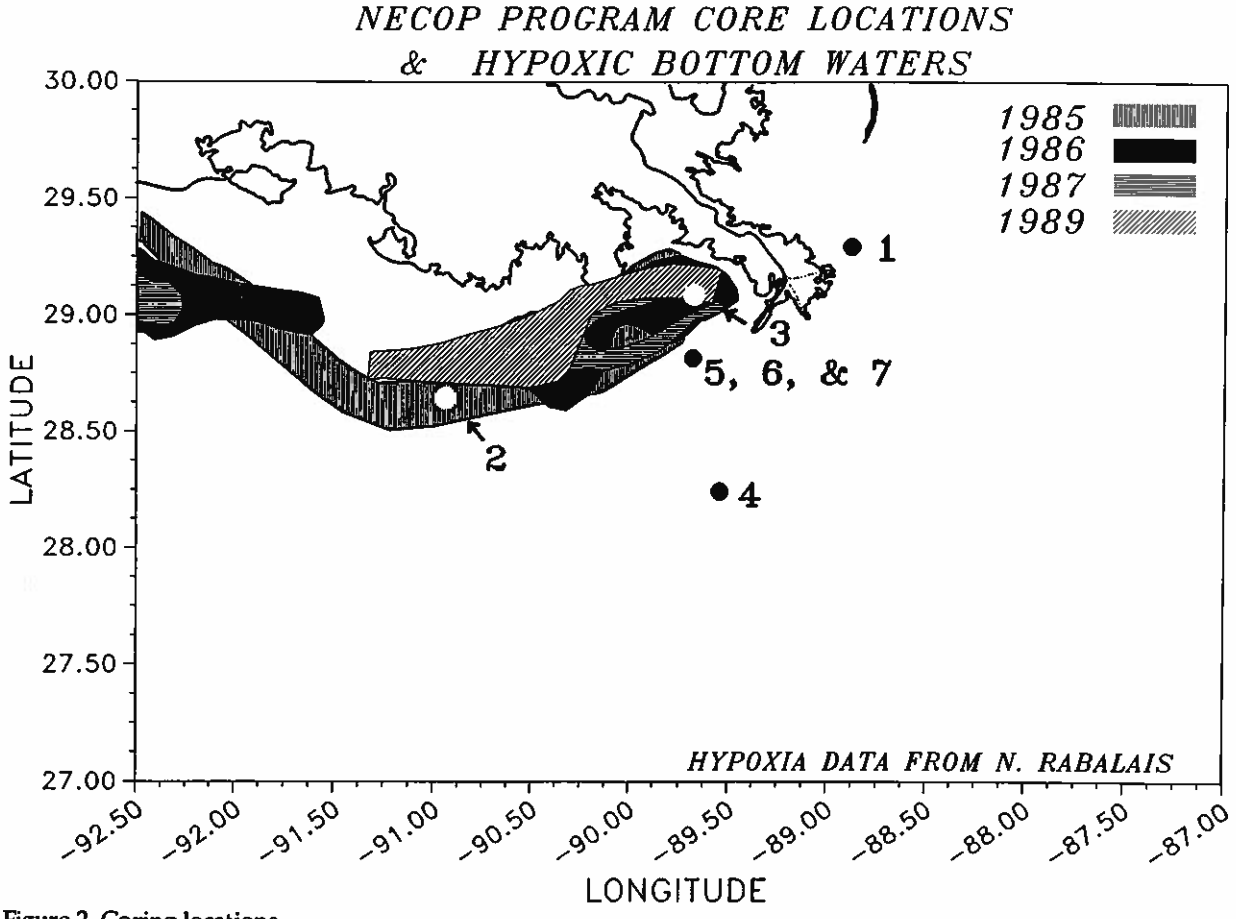


Figure 2. Coring locations.

Table 1. Current Status of Analyses

Core	Record (years)	Geochron	C,N and Metals	C and N Isotopes	Organic Biomarker	Palynology	Biostrat-igraphy
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

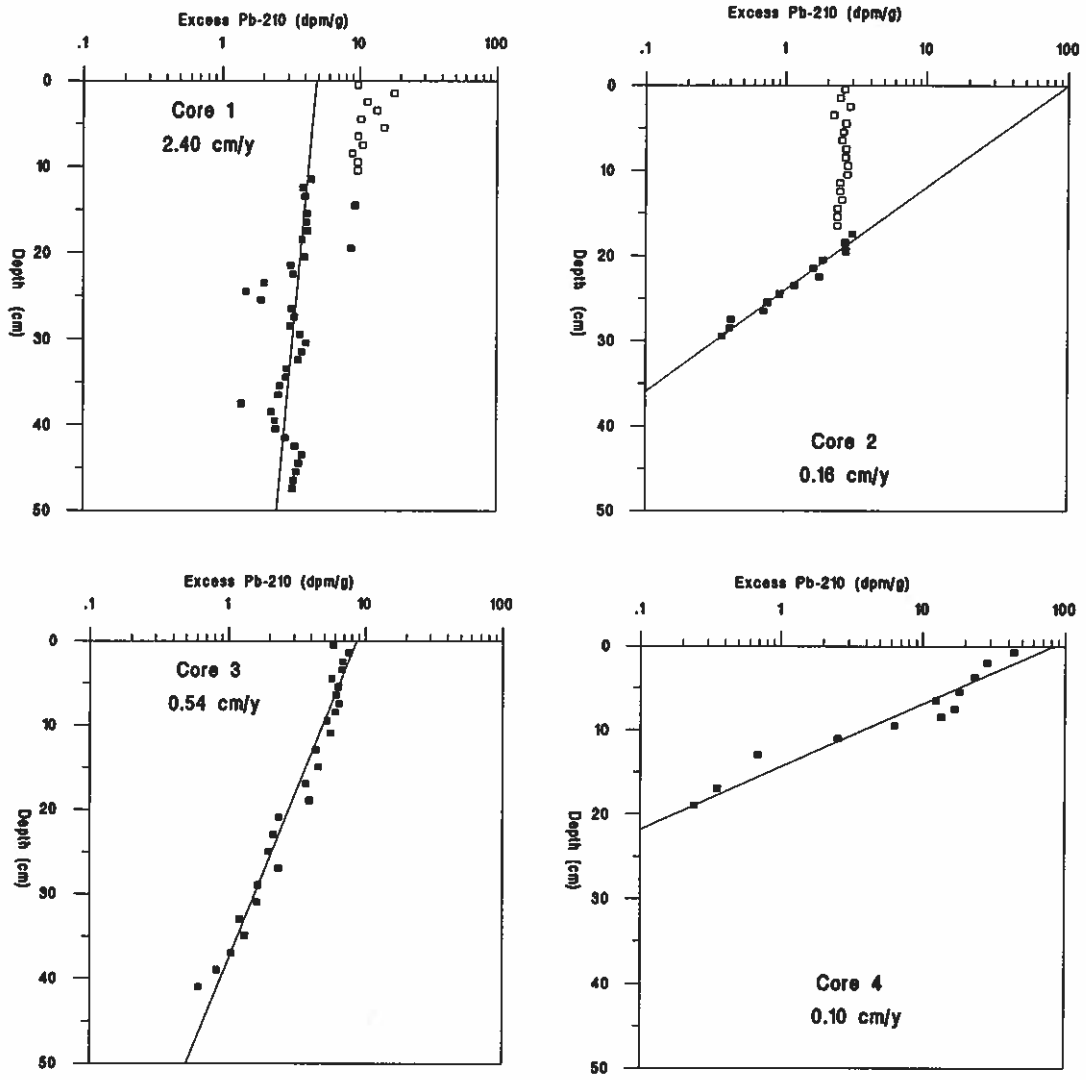
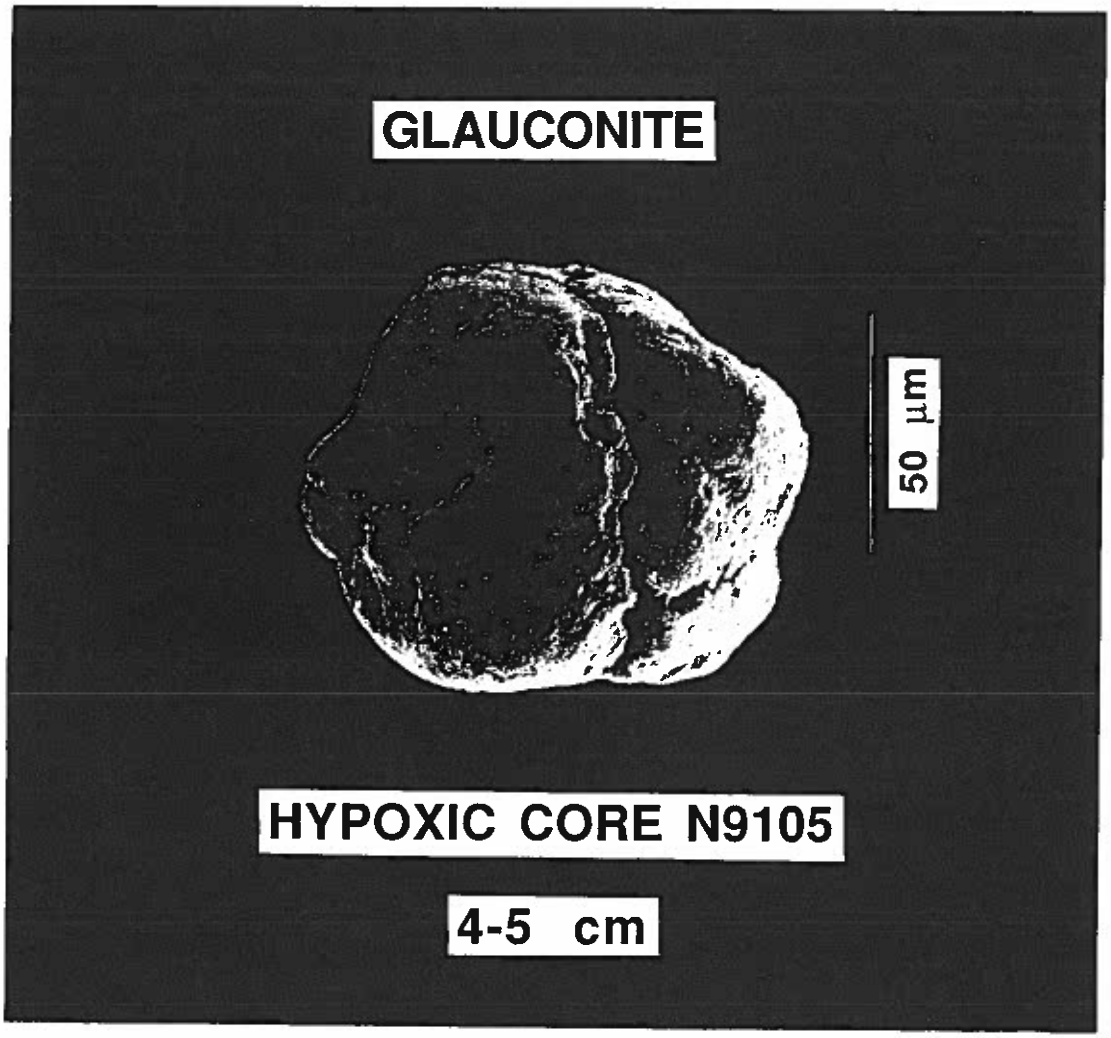


Figure 3. Excess Pb-210 in NECOP cores. Core 5 (not shown) had an accumulation rate of 1.3 cm/yr.



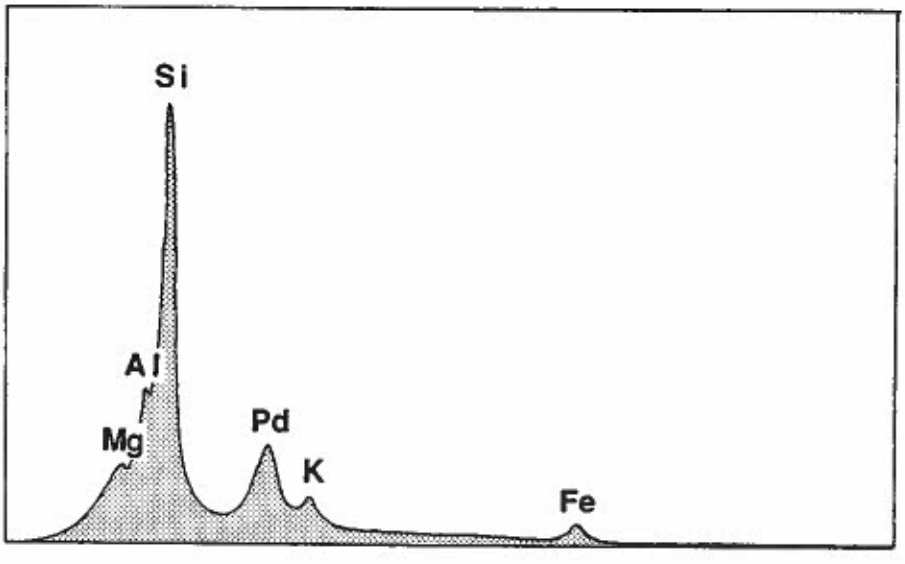


Figure 4. SEM of a grain identified as glauconite from NECOP core 3. The elemental composition of this grain is consistent with our tentative identification.

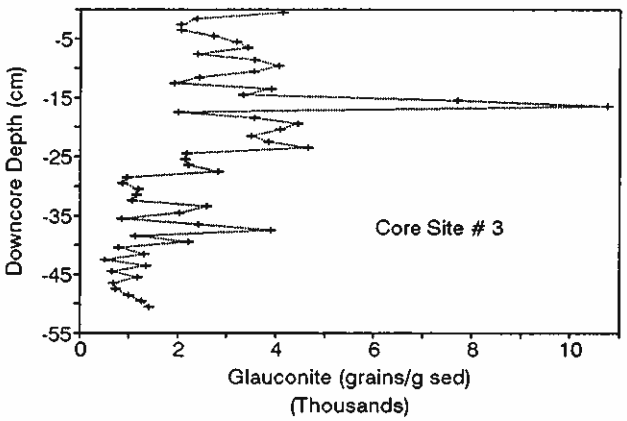


Figure 5. The downcore distribution of glauconite in the core from NECOP site 3, in the region of chronic hypoxia.

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.

Mineralology 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 identification, 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

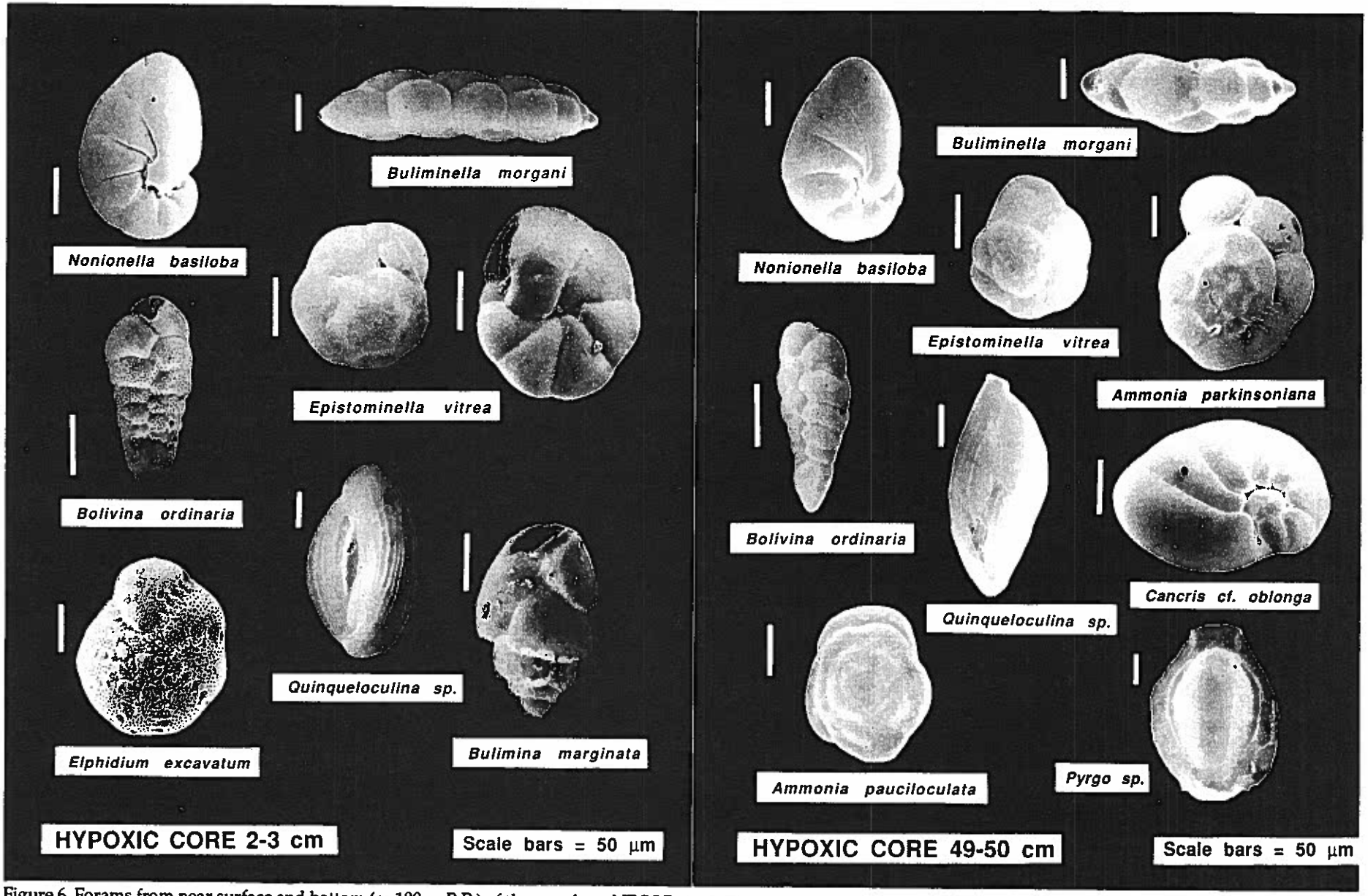


Figure 6. Forams from near surface and bottom (ca 100 yr B.P.) of the core from NECOP site 3. The visual integrity of the shells implies little dissolution, therefore species counts will provide useful information on community change.

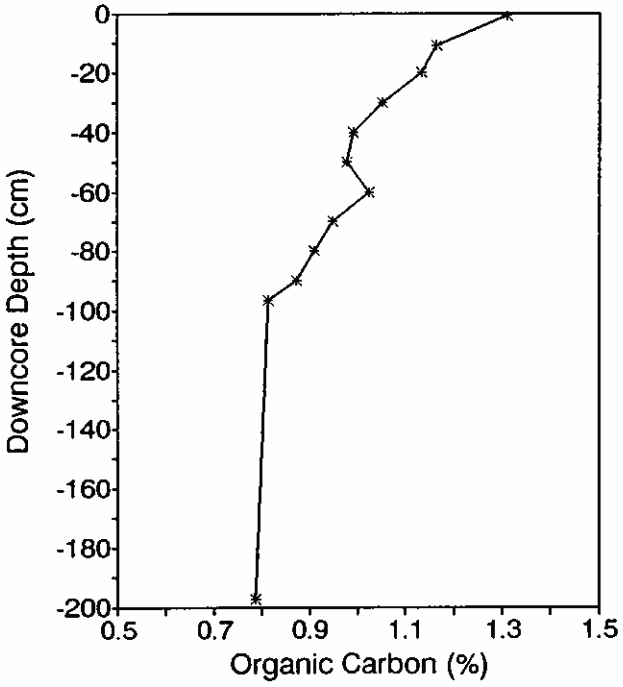


Figure 7. Carbon at site 5-7; box core (5) Pb-210 accumulation rate is 1.3 cm/yr.

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. Stoichiometricly 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

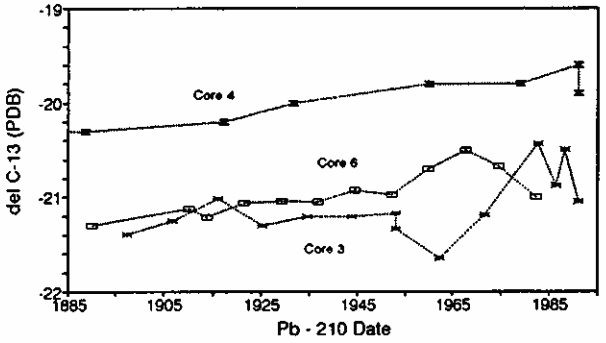


Figure 8. Organic carbon del C-13 for three NECOP cores. All get measurably lighter with depth, an indication of change in the source of the organic matter.

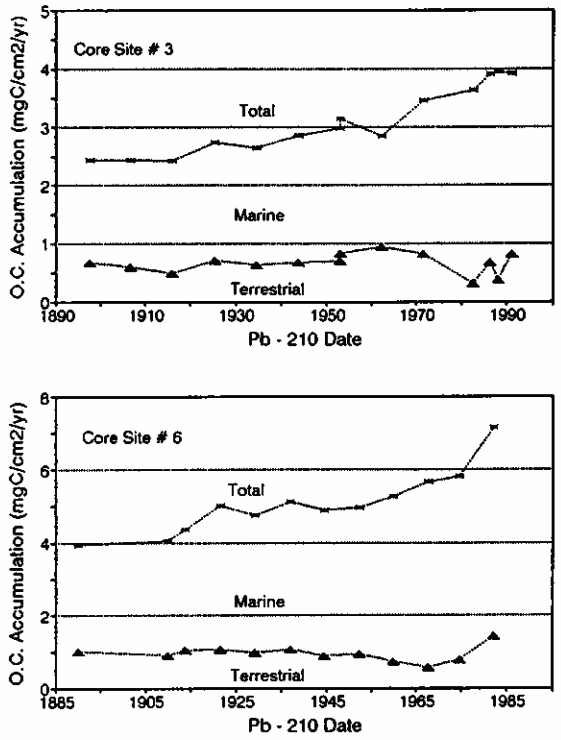


Figure 9. Organic carbon accumulation at 2 sites west of Southwest Pass. Partitioning into terrestrial and marine is based on carbon isotope composition; lignin distributions gave the same results.

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 del C-13 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 del N-15 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.

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Distribution and characteristics of hypoxia on the Louisiana shelf in 1990 and 1991

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Abstract

Hypoxia developed in mid-May and persisted through mid-October in 1990 along a transect across the southeastern Louisiana inner continental shelf. Continuous near-bottom water oxygen measurements indicated extended periods of anoxic or near-anoxic conditions at Station C6A. Oxygen meter recordings also showed limited periods in late May to early June and in mid to late August where the dissolved oxygen concentrations rose above 2 mg/l; otherwise, conditions were hypoxic and/or anoxic for the entire summer. The shelfwide distribution of hypoxia in mid-July 1990 was extensive off the southeastern Louisiana coast and more limited off the southwestern portion of the state. In 1991, near-hypoxic bottom waters were documented in February and March on monthly cruises, and hypoxia/anoxia recorded by an oxygen meter deployment during early March. Hypoxia, however, was ephemeral and not widespread until early July when stormy winter and spring weather conditions changed, winds calmed, and wind-induced mixing was decreased. Oxygen meter recordings for 1991 indicated a much more accurate representation of near-bottom dissolved oxygen conditions than the monthly monitoring cruises, but the monthly transect cruises provided valuable and comparative information concerning the extent of hypoxia. The mid-July 1991 shelfwide monitoring cruise documented widespread hypoxia on both the southeastern and southwestern Louisiana shelf.

An obvious manifestation of nutrient-enhanced productivity on the continental shelf influenced by the Mississippi and Atchafalaya Rivers is the extensive and seasonally prevalent zone of hypoxic bottom waters. Since the mid-1970s, hypoxia (operationally defined as concentrations less than 2 mg/l) has been observed in the nearshore bottom waters of coastal Louisiana during most summers. Oxygen-depleted bottom waters may cover areas as large as 8,500 to 9,500 km^2 of the Louisiana (and sometimes Texas) shelf (Rabalais *et al.*, 1991; Harper *et al.*, 1991). Variability within year and from year-to-year is influenced by riverine inflow, climatic events, wind-controlled physical structure and biological processes. During the period of our studies, 1985 to 1991, there have been dramatic differences in the annual river flow and seasonality of flood events. For example, 1988 was a 52-year record low flow; 1990 had peaks in river flow in March and June; 1991 had high flow the entire winter and spring, but was accompanied by unusually stormy and windy conditions well into the summer. We have also documented long-term changes in the water quality of the Mississippi and Atchafalaya Rivers (Turner and Rabalais, 1991). The consequences of these changes could be seen in changes in coastal food webs and carbon flux to the benthos. The data presented here are a preliminary compilation of information from a series of cruises and instrument deployments in 1990 and 1991.

Methods

Monthly monitoring cruises were conducted along Transect C (see Fig. 4) in April through November 1990 and February through November 1991. More frequent small boat trips were made to the site of the permanent instrument mooring to maintain various pieces of equipment. A shelfwide cruise (Transects A'-M in Fig. 4) was conducted mid-July in 1990 and 1991. Instrument packages were deployed at Station C6A, 20 m water depth from mid-March through mid-November in 1990 and at Station C6B, 21 m water depth from late February through mid-November in 1991 (see Fig. 4).

Hydrographic monitoring instrumentation for the monthly or small boat trips was usually a Hydrolab Surveyor II CTD unit and for the shelfwide cruises, a Sea-Bird CTD unit. The Hydrolab Surveyor II is laboratory-calibrated pre- and post-cruise; the Sea-Bird unit is factory-calibrated. Cross-calibration of oxygen measurements for both instruments is checked periodically with Winkler titrations (Parsons *et al.*, 1984). Cross-calibration of conductivity measurements is checked periodically with salinity determinations on an AGE salinometer. Water samples for chemical analyses were collected with 5-l Niskin bottles on a rosette sampler for the Sea-Bird CTD, on a cable deployed to

Acknowledgments

We thank the many research assistants and associates who helped with the collection of data and analysis of samples as well as the captains and crews of the R/V *ACADIANA*, R/V *PELICAN*, and LUMCON small boat fleet. Support for this research has been provided by the Louisiana Board of Regents Education Quality Support Fund LEQSF(1987-90)-RD-A-15 and a NOAA NECOP Grant NA90AA-D-SG691 Award MAR31.

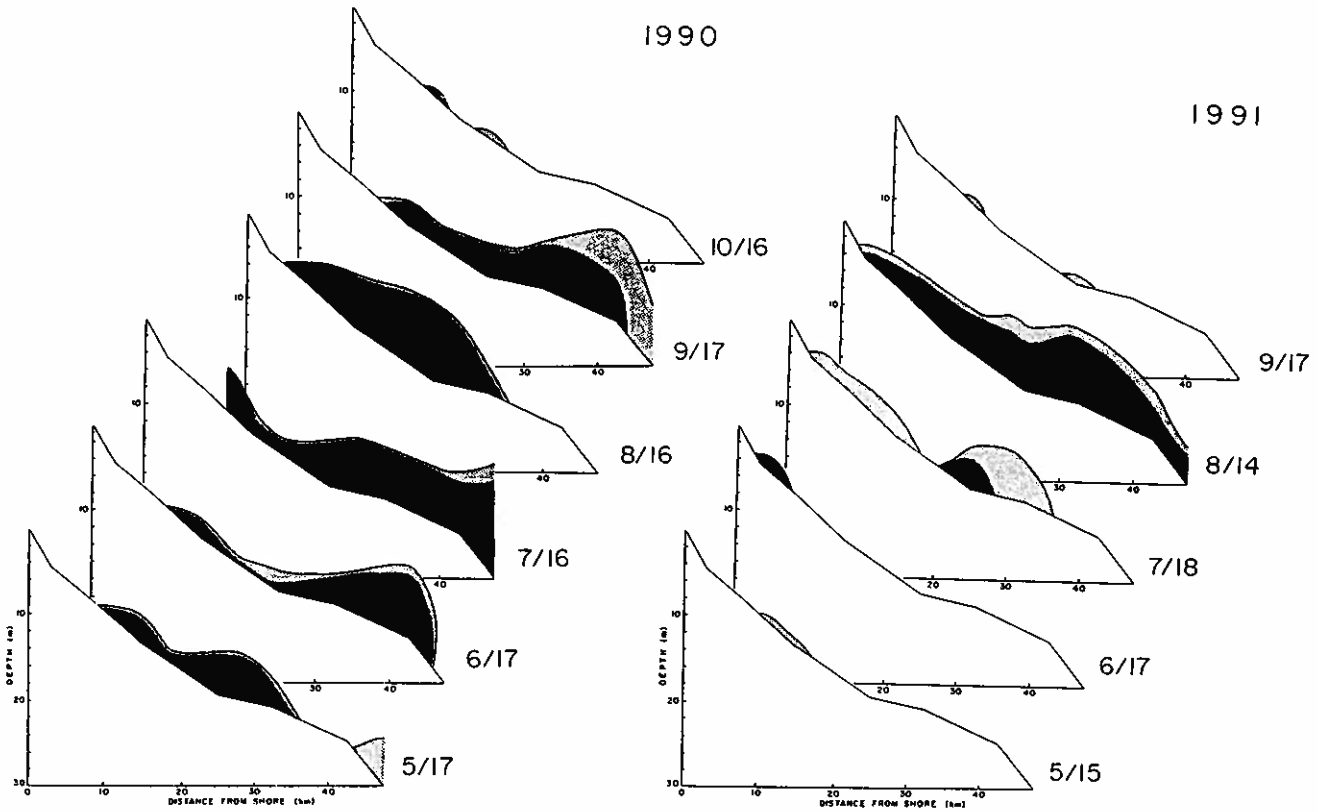

Figure 1. Cross-shelf contours along Transect C in 1990 and 1991 where water column dissolved oxygen concentrations decreased below 2 mg/l (stippled) and below 1 mg/l (black).

the bottom or at an appropriate depth as measured by the Hydrolab, or with a bucket for the surface.

Instrumentation on the mooring includes an upper water column current meter and particle trap (5-9 m) and a near-bottom current meter and particle trap (16-18 m). An Endeco 1184 oxygen meter is deployed within 1 m of the bottom. Oxygen probes for the Endeco meter are either factory- or laboratory-calibrated, and checked periodically with Winkler titrations or comparison to the Hydrolab Surveyor II.

Results

Monthly cruises along Transect C on the southeastern Louisiana continental shelf in 1990 documented widespread areas of lower water column hypoxia and very often anoxic or near-anoxic conditions in near-bottom waters from mid-May through mid-September (Fig. 1). Hypoxia occurred as late as mid-October. Hydrogen sulfide was detected in the near-bottom water samples on several occasions in June, July and August and at one or more stations along Transect C in 1990. By comparison, hypoxia in the lower water column was patchy and ephemeral along Transect C in 1991 from mid-May through mid-July, was extensive and severe in mid-August, and had diminished substantially by mid-September (Fig. 1). Near-bottom water dissolved oxygen concentrations approached anoxia on few occasions during the monthly cruises of 1991, and there were no instances when hydrogen sulfide was detected in the near-bottom waters.

Preliminary analyses of the Endeco oxygen meter recordings indicate that dissolved oxygen concentrations 1 m above the bottom were below 2 mg/l for most of the record between May 24, 1990, and Sept. 28, 1990, (Fig. 2). The few instances of re-aeration of the bottom waters above 2 mg/l in early June and late August-early September were associated with reductions in the density stratification as indicated by reduced water temperature differences recorded in near-surface and near-bottom water current meters. Unfortunately, a malfunction in the battery pack for the Endeco meter prevented the capture of the oxygen record from March 18, 1990, through May 24, 1990, when hypoxia was developing and becoming established along Transect C. A preliminary plot of the Endeco record in 1991 of dissolved oxygen concentrations 1 m above the bottom indicates a period in late February and early March when hypoxia occurred (Fig. 3). There were other much shorter periods of hypoxia in March-June followed by rapid re-aeration. For most of July and August and into early September, near-bottom waters were near-anoxic or anoxic. Beginning in early September, the water column was re-aerated by wind-induced mixing from the beginning of a series of strong cold front passages. The early part of the year (March-June) was also characterized by a fairly continuous series of strong weather fronts with strong winds and subsequent wind-induced mixing.

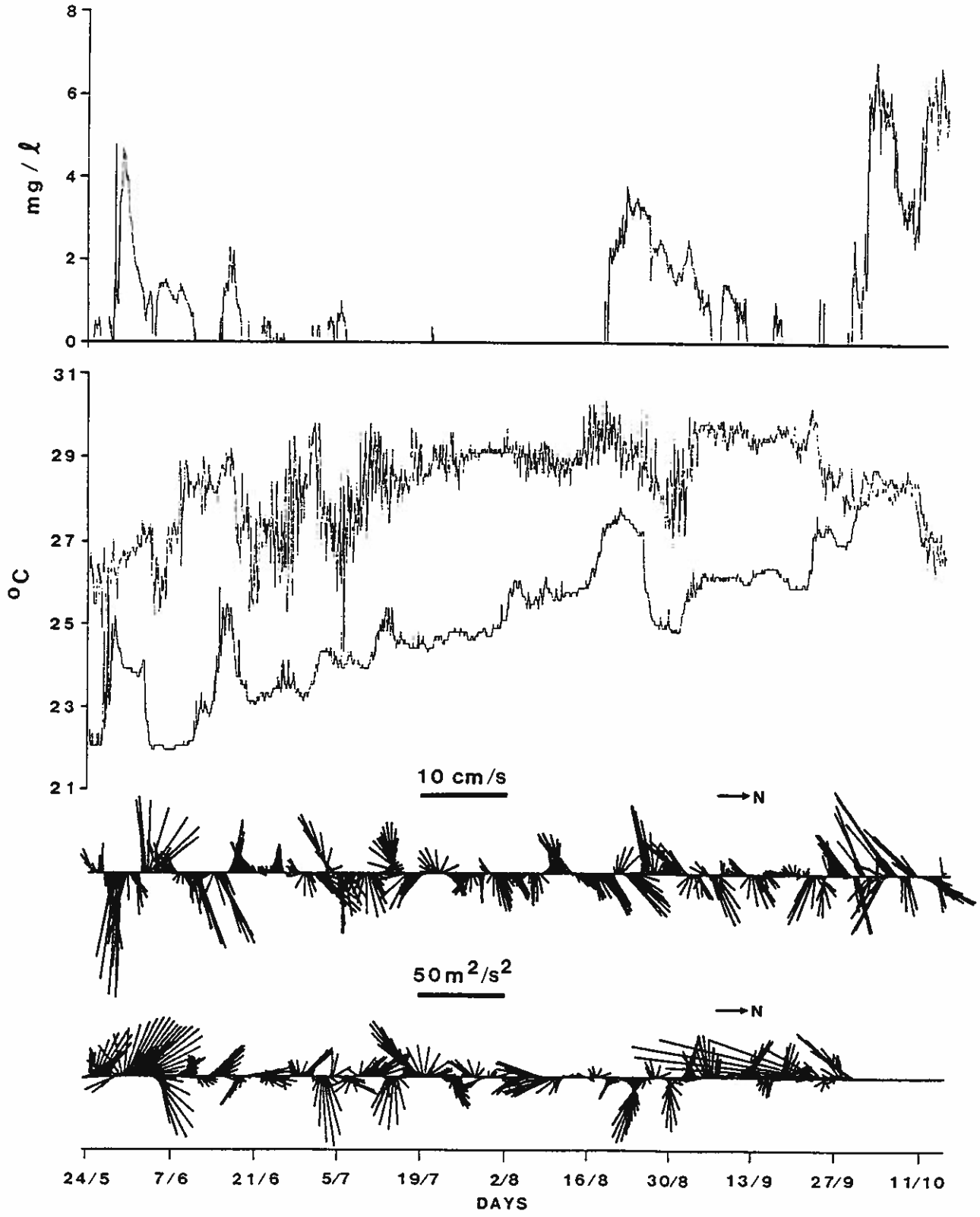

Figure 2. Time series (from top to bottom) of near-bottom dissolved oxygen, near-surface and near-bottom temperature, near-bottom currents, and wind pseudo-stress (u | u |). The stick diagrams have been rotated 90° clockwise. The period of record is May 24, 1990, through Oct. 15, 1990.

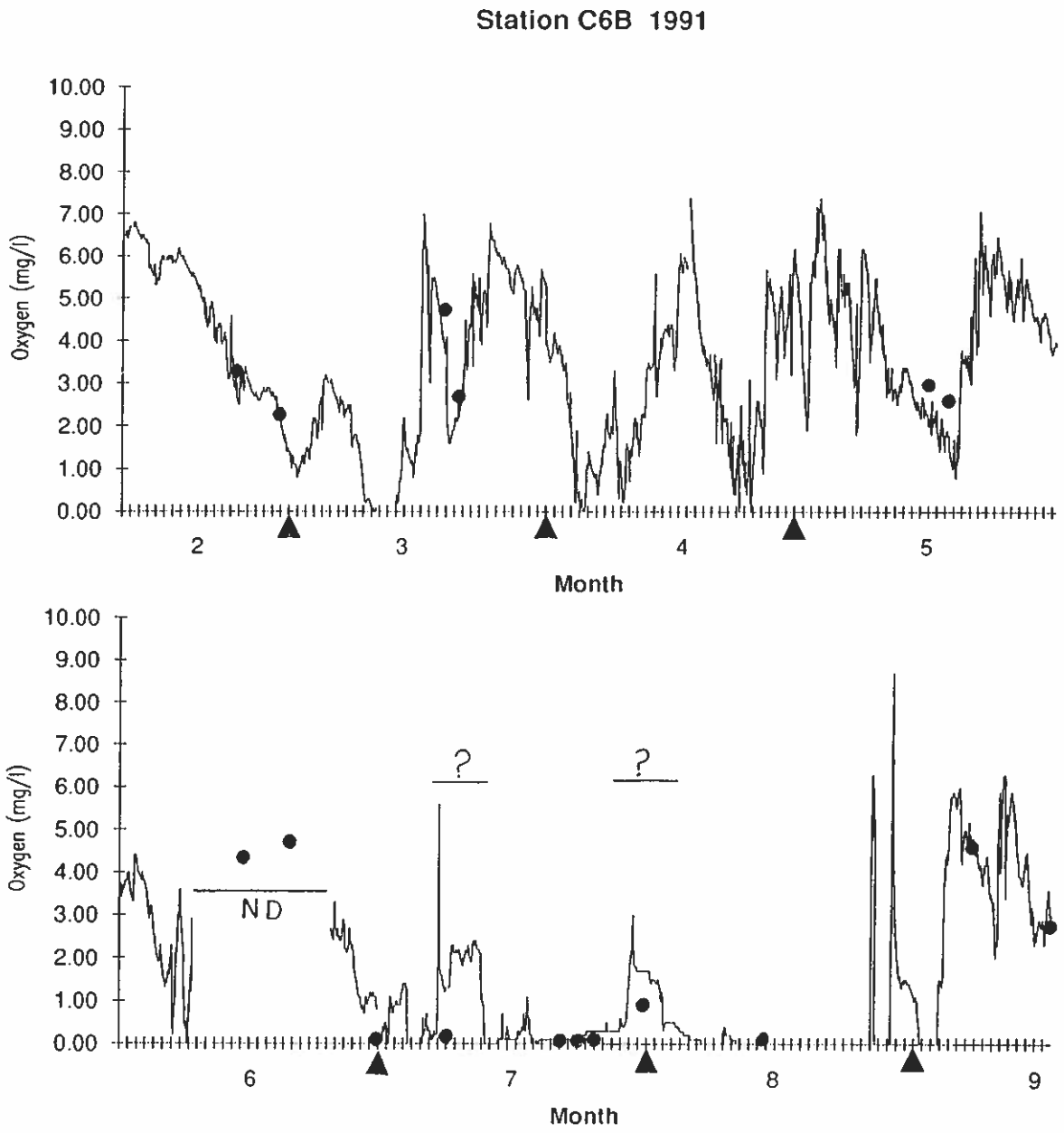

Figure 3. Preliminary plot of near-bottom dissolved oxygen for period of record March 18, 1991, through Sept. 17, 1991. Black dots indicated Hydrolab dissolved oxygen readings for the appropriate dates; lack of data indicated by ND; data problems indicated by "?."

A comparison of the areal extent of near-bottom water dissolved oxygen levels that fell below 2 mg/l in 1990 and 1991 is shown in Fig. 4. While the estimated total areal coverage is somewhat similar between the two years (6,200 km^2 and 7,300 km^2), the geographic configuration is very different. The extent of hypoxia on the southeastern Louisiana shelf in 1990 was much greater than most previous years sampled (1985 to 1989) and occurred in deeper water and farther offshore than normal. The extent of hypoxia on the southwestern shelf, however, was reduced compared to most previous years sampled. In 1991, similarly-sized areas were documented on both parts of the Louisiana shelf and conformed to the more normal pattern of hypoxia zones extending down-coast from the vicinity of Southwest Pass of the Mississippi River delta and the mouth of Atchafalaya Bay.

Discussion

The series of mapping cruises and mooring deployments have begun to define the scales of variability of hypoxia on the Louisiana shelf and its relationship to physical and biological processes. A band of nearshore hypoxia is found in the bottom waters of the Louisiana shelf during most summers (Rabalais *et al.*, 1991). A break in the longshore continuity of hypoxic bottom waters is often observed near the Atchafalaya Delta (Fig. 4). Spatial and temporal variability in the distri-

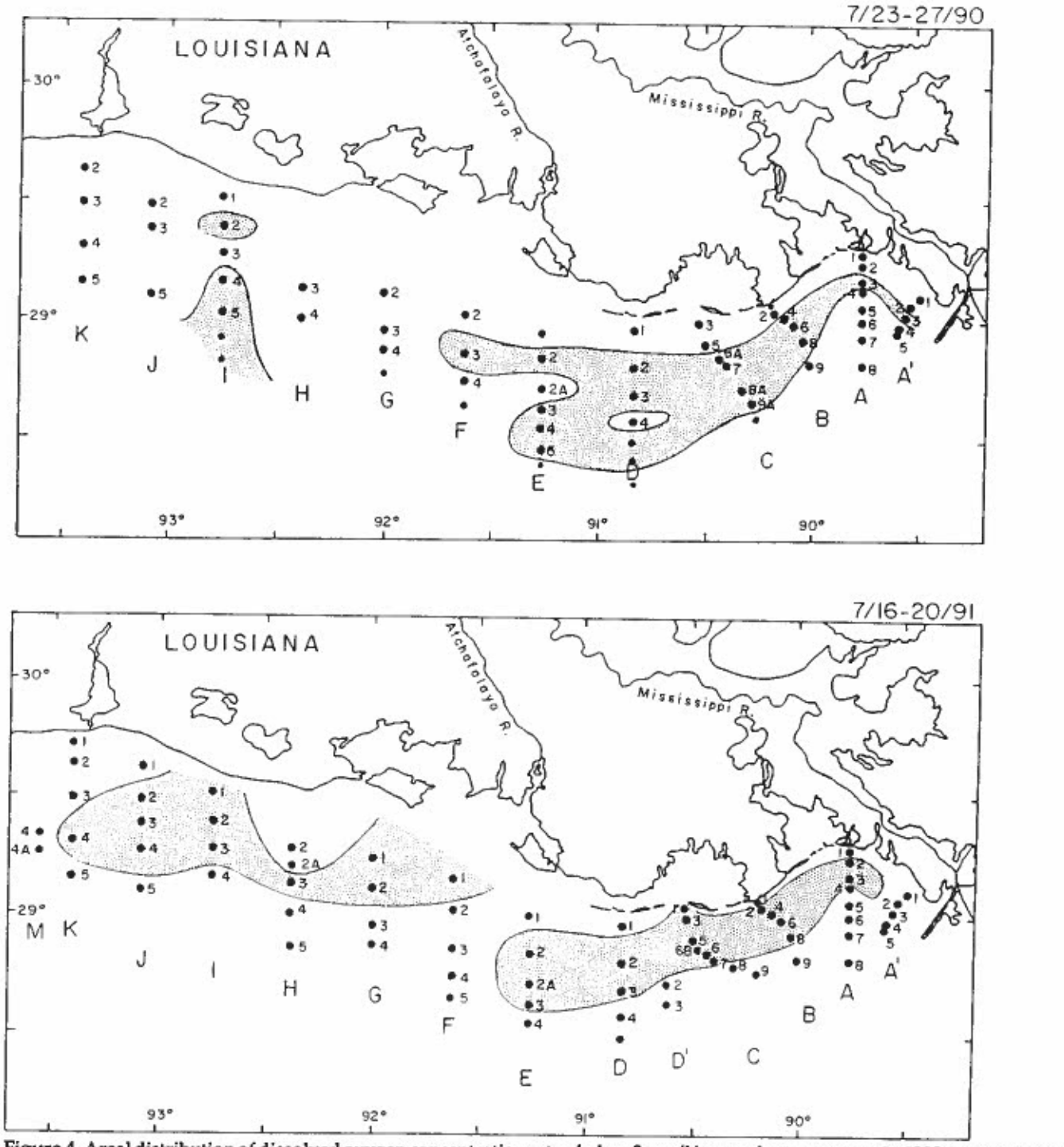

Figure 4. Areal distribution of dissolved oxygen concentrations at or below 2 mg/l in near-bottom waters in 1990 (upper panel) and 1991 (lower panel).

bution patterns exists and is, at least partially, related to the amplitude and phasing of Mississippi River discharge and, consequently, in nitrate flux to the coastal waters. The region of bottom hypoxia is generally confined to a nearshore band of waters between 10 and 30 meters water depth, although hypoxia has been observed in both deeper and shallower water (Fig. 1). The thickness of the hypoxic water column is variable, but may reach 15 m (Fig. 1). The data set from the shelfwide monitoring cruises is approaching a time series of sufficient length to be useful in resolving mini-climatic changes and long-term trends. Cruises along the cross-shelf transect show how variable the system is over a larger area on a coarse time scale, and how variable Transect C is from year to year with dramatically different river flow and climatic conditions. Until the deployment of the continuously recording oxygen meter, however, the real variability was not apparent. The near-bottom oxygen record is event dominated. Long periods of very low oxygen

concentration are interspersed with abrupt increases in dissolved oxygen content and followed by moderately rapid decay. The dissolved oxygen content does not reach saturation levels during these events nor does stratification break down completely. Full reoxygenation of the water column occurs only during strong vertical mixing events.

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Physical structure of the Louisiana shelf hypoxic region

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Abstract

The physical structure of the Louisiana inner shelf varies on time scales from the decadal, climatic scale to tidal time scales. The physical structure has long alongshore coherence length scales for some parameters, but short scales for others. The cross-shelf coherence scales are generally small. The vertical structure is complex and highly variable dependant upon the recent local mixing history. The character of summer hypoxia appears to vary on many of these same scales.

The regular summertime appearance of hypoxia and its apparent association with the strong stratification of the inner shelf waters suggest that the carbon source depleting the bottom water oxygen content is detritus from the spring bloom driven by riverine nutrients and that the stratification isolates the bottom waters from direct reaeration. The flow of the Louisiana Coastal Current redistributes the nutrients fueling the spring plankton bloom and the associated buoyancy flux contributes to maintaining the phytoplankton in the photic zone. This current exhibits variability on a variety of scales. Its dynamics, though, are poorly understood.

Large Scale Variability

We have been surveying the extent and strength of mid-summer (July) hypoxia since 1985 (Rabalais *et al.*, 1991). While depressed bottom oxygen concentrations were found over large areas nearly every summer, the patterns of hypoxic conditions (oxygen concentrations less than 2 mg/l) varied extensively during the seven-year period. The basic pattern appears to involve two plumes of hypoxia extending down-coast from the vicinity of Southwest Pass, Mississippi River Delta and the mouth of Atchafalaya Bay. They are centered roughly along the 20 meter isobath and extend approximately 50 km in the cross-shelf direction. The interannual variability is great (see Rabalais et al., this volume).

One suspects that the interannual variability is linked to that of the local weather or the river discharge. If the surface salinity at the mouths of coastal bays is used as a surrogate for coastal salinities, significant variations on decadal scales are observed (Wiseman et al., 1990). These variations are reflected in the stratification of the coastal current system.

Interannual variations in wind stress can cause important variations in coastal sea level (Blaha and Sturges, 1981) and, presumably, in the mean strength of the coastal current. Mixing associated with anomalous winds will also result in fluctuations in the reaeration rate of the bottom waters and the baroclinic pressure gradients driving the coastal flows. Anomalous current patterns occurred during spring 1989 when winds blew water consistently towards the east along the Louisiana inner shelf, opposite to the direction of normal flow. The mean current in the bottom waters during this hypoxia season was statistically indistinguishable from zero. Air-sea heat exchange will also influence metabolic rates in the hypoxic waters. All these proceses occur with random phases. Their relative timing will determine the observed effect on dissolved oxygen.

Seasonal Variability

If estuarine salinities are again used as surrogates for coastal current salinities, a strong seasonal correlation is apparent between Mississippi River discharge and coastal hydrographic variability. While this runoff directly accounts for the strongest stratification signal in the coastal current region, a secondary signal is also present. The large-scale shelf circulation and the summer insolation contribute to the generation of a seasonal pycnocline. The circulation redistributes some of the spring discharge from the Mississippi and Atchafalaya Rivers across the shelf. The result of this redistribution is seen in maps of excess fresh water over the shelf (Dinnel and Wiseman, 1986) and forms a seasonal halocline. The summer insolation contributes to a seasonal thermocline. Together, these form a seasonal pycnocline, much like that observed near the Islay front (Hill and Simpson, 1989). It is the morphol-

ogy of this seasonal pycnocline that best correlates with the structure of hypoxic water rather than the morphology of the near-surface halocline associated with the Louisiana Coastal Current proper. When all data we have collected from 1985 through 1988 are considered, the depth of the maximum oxycline and the maximum halocline (pycnocline) are correlated with an r^2 of 0.05 (0.16). When we compare the near-bottom, seasonal pycnocline with the oxycline, we obtain an r^2 of 0.743. One is then forced to ask why the hypoxia is limited in offshore extent. Is it because the layer below the seasonal pycnocline thickens seaward or because the benthic oxygen demand is reduced in the seaward direction as a result of decreased carbon loading and/or cooler temperatures?

The spectrum of near-bottom dissolved oxygen estimated from all available data at a single station offshore of Cocodrie using gappy data techniques shows a statistically significant annual peak and a marginally significant semi-annual peak. The data is sampled aperiodically and is noisy. Many environmental parameters possess annual cycles. Statistically reliable correlations between these signals are not yet available. Many more years of monitoring will be necessary before data sets will allow reliable estimation of even second order statistics (spectra, cross-spectra, coherences). More effort needs to be expended on process studies, if the mechanics of the system are to be understood.

Storm Scales

Most studies of the Louisiana Coastal Current system have produced time series less than a year in length. The spectra of the signals are red. They are dominated by storm systems that pass through the region at three- to ten-day periods in the fall, winter and spring. Summer storm systems are generally weaker, less frequent and have a longer return period. In response, the character of the time-varying flow field changes from winter to summer as does the associated vertical mixing. Storms affecting coastal Louisiana have large spatial scales. The alongshore flow response has similarly large scales. The coherence between eight-month records of longshore currents from offshore of Calcasieu, La., and Freeport, Tex., were statistically significant only at the storm frequencies, 0.3 and 0.1 cycles per day (F. Kelly, pers. comm.). The alongshore coherence scale for cross-shelf flow and the cross-shelf coherence scales are generally small (O(10 km)).

The importance of small spatial scales, even for steady wind forcing, is apparent in the numerical model results. Mixing, bathymetric steering and blockage all appear to be important processes affected by the topography.

Stratification over the inner shelf can be readily broken down by storm driven mixing (Wiseman *et al.*, 1986). This process effectively reaerates the deeper water and is one reason that hypoxia does not occur during winter months. In 1990, we observed the breakdown of stratification at the end of the hypoxic season and the associated reestablishment of oxygenated bottom water (Fig. 1). Weaker mixing events, which do not fully destroy the stratification, are also reflected as increased bottom oxygen concentrations.

Tidal scales

Tidal currents on the shelves of the northern Gulf of Mexico are generally weak and diurnal. They increase in amplitude and the semi-diurnal component becomes more important over the broadest parts of the shelf offshore of Atchafalaya Bay and western Louisiana. Tidal ellipses are generally oriented in the cross-shelf direction. Inertial currents and internal tides are also important in this region (Daddio *et al.*, 1976). Time series of near-bottom dissolved oxygen contain brief bursts of diurnal energy. These have not been of sufficient duration to determine if they were coherent with lunar or solar forcing. Coherence analysis of the longest available records suggests a statistically significant association in the diurnal frequency band with the cross-shelf currents being most coherent with the oxygen.

Louisiana Coastal Current Dynamics

Shallow, highly stratified coastal current systems are expected to be strongly wind-driven (Csanady, 1981). There are many analyses of current records from the Louisiana-Texas inner shelf that indicate that this is indeed the case, e.g. Crout *et al.* (1984), Cochrane and Kelly (1986). Nevertheless, simple linear model results are generally inconsistent with observations. Residuals are larger than anticipated. A momentum source or sink other than wind and bottom stress is needed. Internal friction (Lewis and Reid, 1985), pressure gradients generated by alongshelf variations in effective bottom friction (Cochrane and Kelly, 1986, Chuang and Wiseman, 1983), or pressure gradients generated by coastline morphology (Dinnel, 1988) have been proposed as the missing term.

Bottom-mounted pressure cells separated by 47.4 km were deployed along the 20 m isobath to investigate the role of longshore pressure gradients. A four-month record that recorded the onset of the spring flood and the build-up of coastal water level on both a seasonal scale and at storm periods has been obtained. Pressure variations were similar at the two stations. The recorded pressure variation range was 45 mb, but most variations were 7 to 15 mb (Fig. 2). The alongshore differences about the mean were as large as 9 mb with most variations being of order half this value (Fig. 3). The equivalent sea surface slopes are of order 10^{-6}, a value large enough to drive significant flow.

The pressure signals, near-bottom current meter data, u_b, and three-hourly wind data from New Orleans airport were filtered with a 40-hour low pass filter. Means were subtracted from the residuals and the fluctuating portion of the signal analyzed.

Data from previous years suggest that much of the low frequency current variability occurs in a single

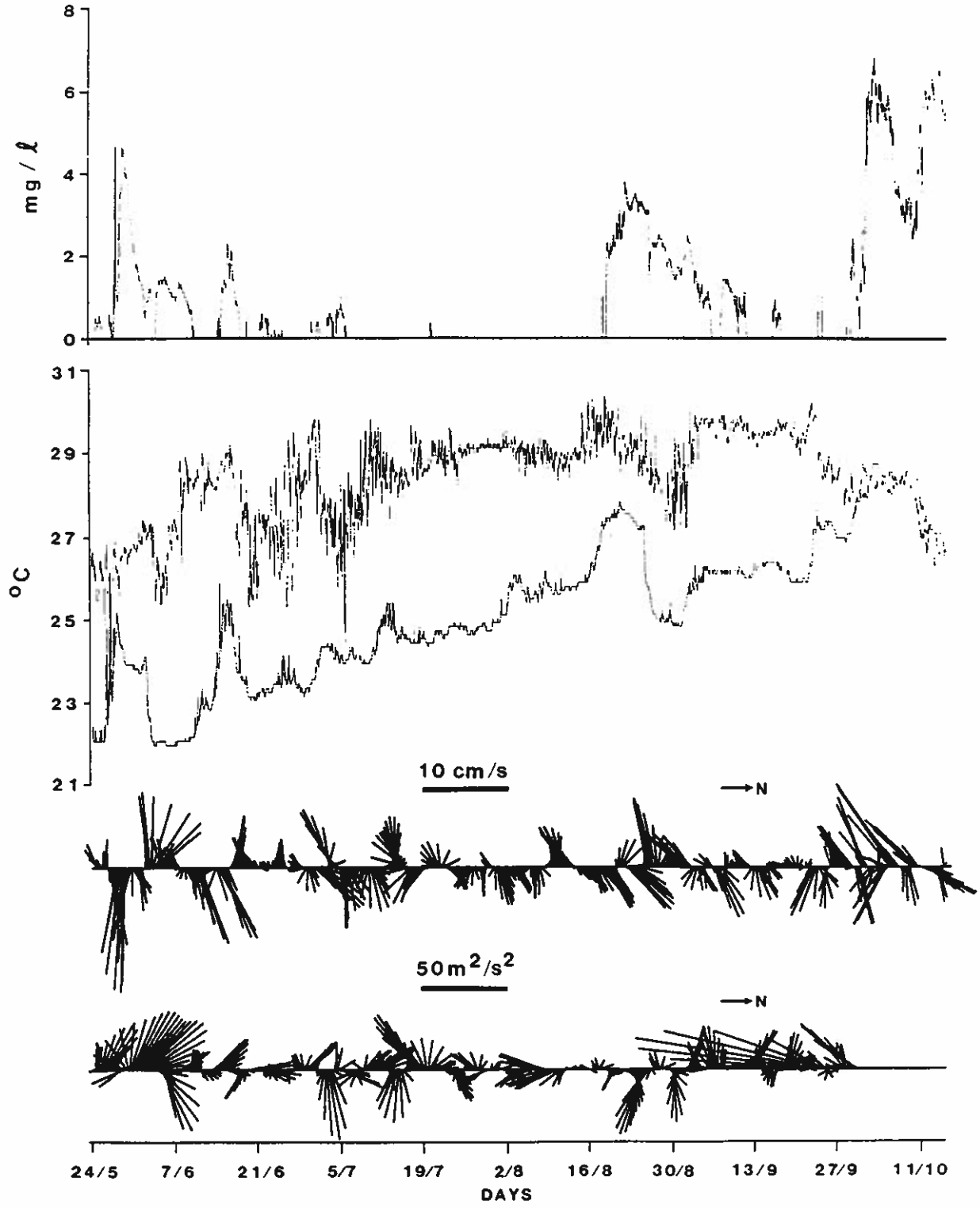

Figure 1. Time series of (from top to bottom) near-bottom dissolved oxygen, near-surface and near-bottom temperature,low-passed near-bottom currents and wind pseudo-stress (u | u |). Note that the stick diagrams have been rotated 90° clockwise. The dissolved oxygen record is clearly event dominated. The period of record is May 24, 1990, through October 15, 1990.

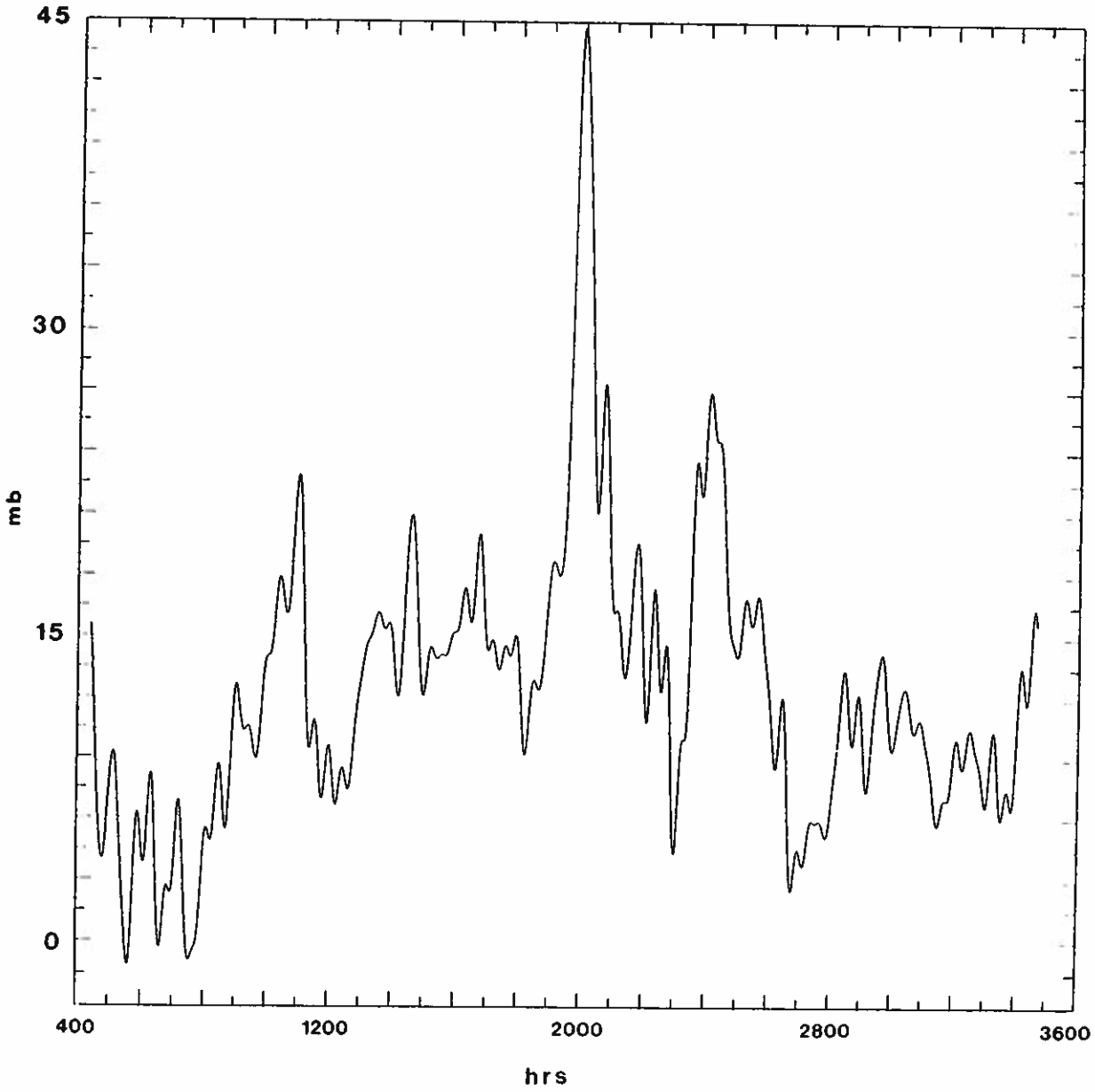

Figure 2. Time series of bottom pressure relative to an arbitrary datum. The gauge is in roughly 20 m of water. The record begins on March 19, 1991. The time origin is 0000 on March 1, 1991.

empirical orthogonal mode. Thus, we write

$$u(z,t) = k(z)u_b(t).$$

We begin with a simple assumed balance for the alongshore currents

$$du/dt = - \text{grad } p + d\tau/dz - fv.$$

Integrating yields

$$du_b/dt \times \int Ik(z)dz = -h \times \text{grad } p + \tau_W - C_D \times u_b$$

We have used the coastal constraint to eliminate the Coriolis term. A least squares fit for the surface and bottom drag coefficients and the vertical integral of k(z) yields a model that accounts for only 20 percent of the variability in the pressure gradient. The pressure is the external signal most coherent with the alongshore current and accounts for 50 to 60 percent of the current variance across the spectrum and up to 80 percent in the most energetic band. If we assume that the pressure field is 'hinged' at the shelf break, coastal pressure is a surrogate for cross-shelf pressure gradient.

Cross-shelf currents show the greatest coherence with the alongshore pressure gradient. The associated phase relations, though, are inconsistent with a geostrophic balance.

Many causes contribute to the lack of a good local model. Drag coefficients and stratification will vary with wind stress and wave height. Furthermore, there is weak evidence that wave-like signals propagate along the west Louisiana shelf. Interannual variability is also a problem. The one-month record analyzed

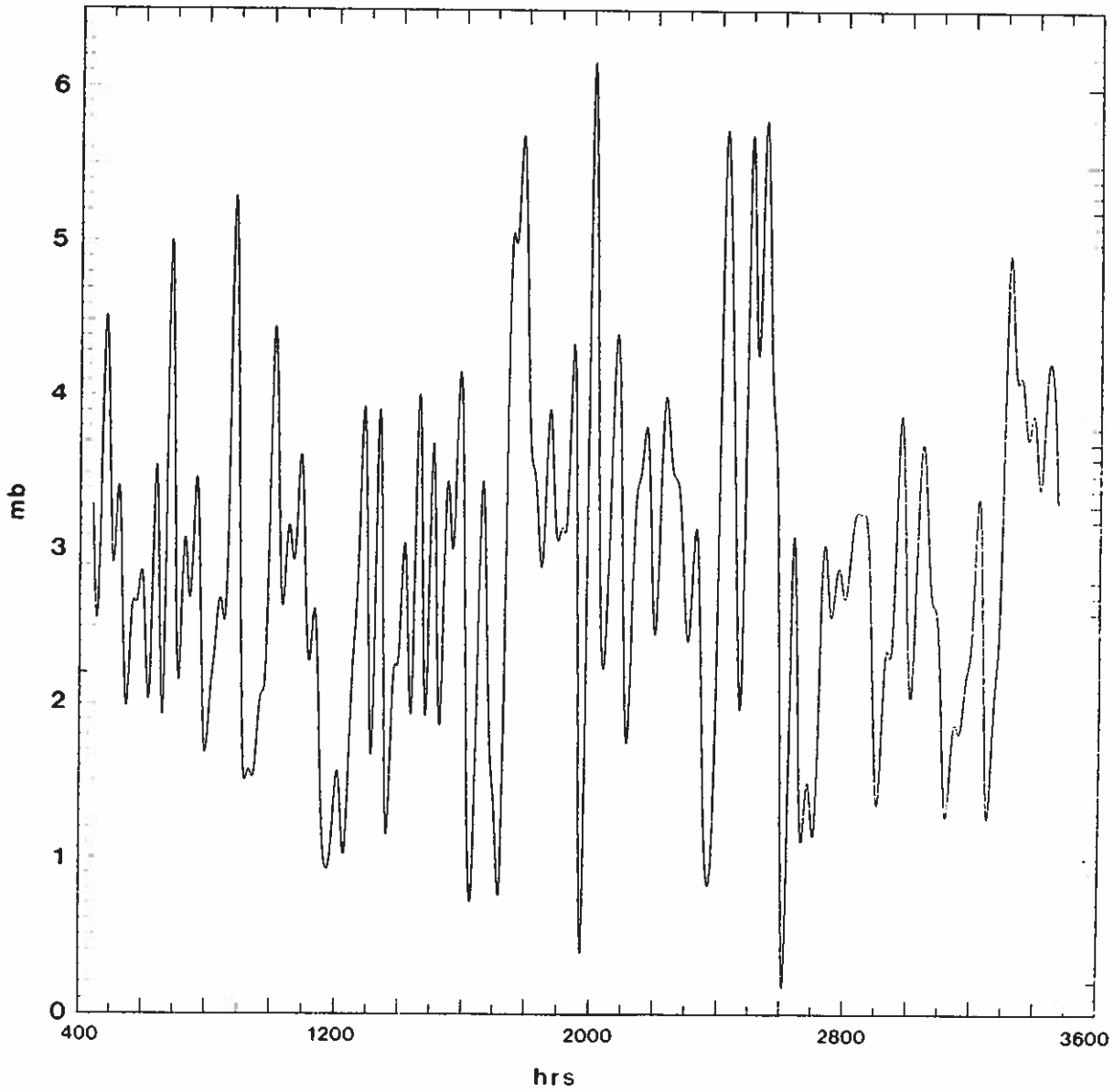

Figure 3. The fluctuating portion of the pressure difference between two bottom pressure gauges separated by 47.4 km in the alongshore direction. The datum is arbitrary. The time origin is 0000 March 1991.

from 1991 had a low-frequency variance ellipse aligned nearly cross-shelf while the variance ellipse from prior years was aligned alongshelf.

Conclusions

The current and stratification patterns over the west Louisiana-Texas inner shelf exhibit variability on time and length scales ranging from tidal periods and tidal excursions up to interannual periods and alongshelf scales as large as the distance from the Mississippi River Delta to the Mexican border. Much of the variability occurs on the scale of storms. Non-stationarities and propagating disturbances appear to preclude the validity of simple dynamic models.

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Mass balance modeling of water quality constituents in the Mississippi River plume/inner Gulf shelf region

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Abstract

A preliminary calibration was conducted with a mass balance water quality model using shelfwide synoptic data representing summer average conditions in the MRP/IGS region. State variables in the model included salinity, phytoplankton, phosphorus, nitrogen, dissolved oxygen and carbonaceous biological oxygen demand. Model output compared with available data for state variable concentrations, surface primary production and POC/PON settling fluxes to within approximately a factor of 2. The calibrated model was used as a preliminary diagnostic tool to investigate the relative importance of environmental processes controlling primary production and dissolved oxygen depletion. Temporal scales for primary production were shorter than those for advective-dispersive transport. Underwater light attenuation was relatively more important than nutrient limitation in controlling phytoplankton growth rates. Nitrogen was relatively more limiting than phosphorus in controlling phytoplankton growth rates in most of the study area. Phytoplankton respiration, oxidation of carbonaceous material in the water column and sediment oxygen demand all contributed significantly to total oxygen depletion rates. Sediment oxygen demand accounted for approximately 25 percent of the total oxygen depletion rate in the principal hypoxia region.

The overall goal of this study is to synthesize the best current understanding of physical, chemical and biological processes influencing hypoxia and related water quality in the MRP/IGS within a quantitative, mass balance modeling framework. The specific objectives are the following:

1. Develop a primitive equation model with simple kinetics to reproduce seasonal patterns of transport, stratification and dissolved oxygen.
2. Develop a coarse grid mass balance model with more sophisticated kinetics to describe dynamics of primary production, dissolved oxygen and organic carbon fate.
3. Apply the models to available historical data and to NECOP-generated field data.
4. Use the calibrated models as diagnostic tools to investigate cause-effect mechanisms that lie behind the data.
5. Use the calibrated models to estimate system responses to changes in anthropogenic nutrient loadings and river discharge.

Acknowledgments

We thank S.E. Lohrenz, D.G. Redalje, G.T. Rowe, W. Phoel and S.P. Dinnel for contributing portions of their unpublished field data to this modeling study.

This paper describes preliminary results from the initial phase of work with the coarse grid water quality model. The principal emphasis is on application to available historical data. Results are presented from a "demonstration calibration" and from use of the model as a preliminary diagnostic tool to investigate the relative importance of environmental processes controlling primary production and dissolved oxygen depletion.

Approach

Conceptual framework — A coarse grid, deterministic mass balance model was developed and applied to the study area. State variables in the model include salinity, phytoplankton carbon, phosphorus, nitrogen, dissolved oxygen and carbonaceous biological oxygen demand (Fig. 1). User-specified external forcing functions include constituent mass loadings, advective-dispersive transport, boundary conditions, sediment fluxes, water temperature, incident solar radiation and underwater light attenuation. Although this model contains only a moderate degree of chemical-biological complexity, it requires a considerable amount of field data for comparison with model output, as well as for specification of external forcing functions.

Application framework — This conceptual model was implemented using the WASP4 computer coding

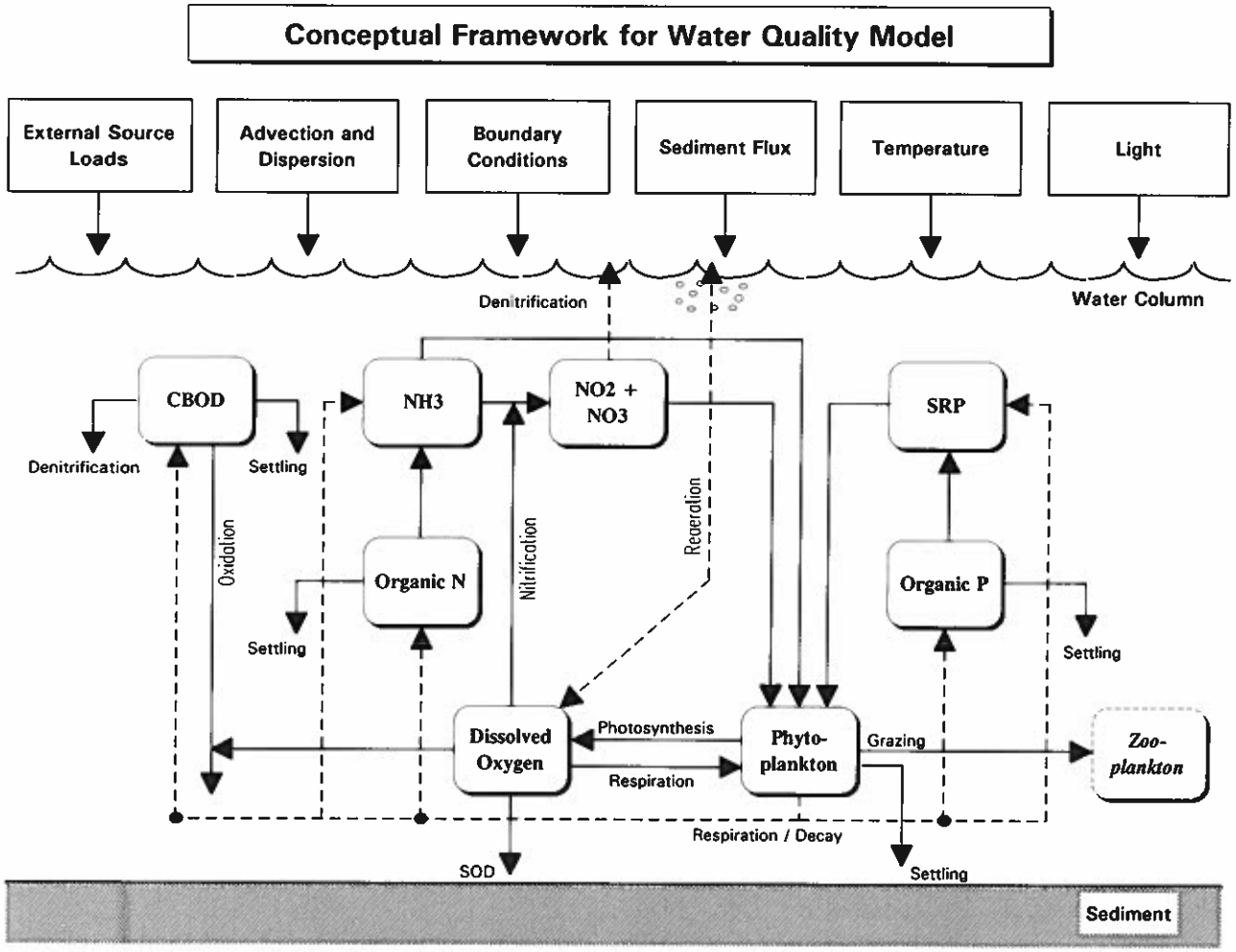


Figure 1. Schematic diagram of principal model compartments and interaction pathways.

framework (Ambrose *et al.*, 1988). WASP4 is a dynamic compartment modeling system that can be used to analyze a variety of water quality problems in a diverse set of water bodies. The model processes are represented in special kinetic subroutines that are either chosen from a library or written by the user. WASP4 is structured to permit easy substitution of kinetic subroutines into the overall structure to form site-specific models.

Spatial-temporal scales — The model was applied to a 21-segment water column grid extending from the Mississippi River Delta west to the Louisiana-Texas border, and from the shoreline seaward to the 30- to 60-meter bathymetric contours (Fig. 2). The spatial segmentation grid includes one vertical layer nearshore and two vertical layers offshore. All of the spatial segments are completely mixed. The nearshore segments have an average depth of 5.6 meters. The surface offshore segments are completely mixed in the vertical to a fixed pycnocline depth of 10 meters. The bottom offshore segments are completely mixed from 10 meters to the seabed.

The model consists of a coupled system of ordinary, non-linear, time-dependent, differential equations. Due to the limited available shelfwide field data, only steady-state model simulations were conducted. Model forcing functions were assigned constant values that represented summer average conditions. The model was then run to steady-state and output was compared with field data that were assumed to be in equilibrium with the forcing functions.

Model Application

Historical field data — The most extensive historical data base for water quality constituents on the Louisiana Inner Shelf was collected during 1985-1989 by Louisiana Universities Marine Consortium (LUMCON) (Rabalais *et al.*, 1991). The relationship between principal cruise transects from these surveys and the model spatial segmentation grid is shown in Fig. 3. The preliminary model calibration presented herein was restricted to data from the shelfwide cruise conducted in July 1985 (Rabalais *et al.*, 1986). Data from this cruise were the most comprehensive in terms of spatial coverage relative to the model grid. Furthermore, available physical formation indicated that summer conditions in 1985 corresponded to "typical" behavior of the Louisiana Coastal Current.

Physical transport — Because the model balances only mass and not momentum, magnitudes and direc-

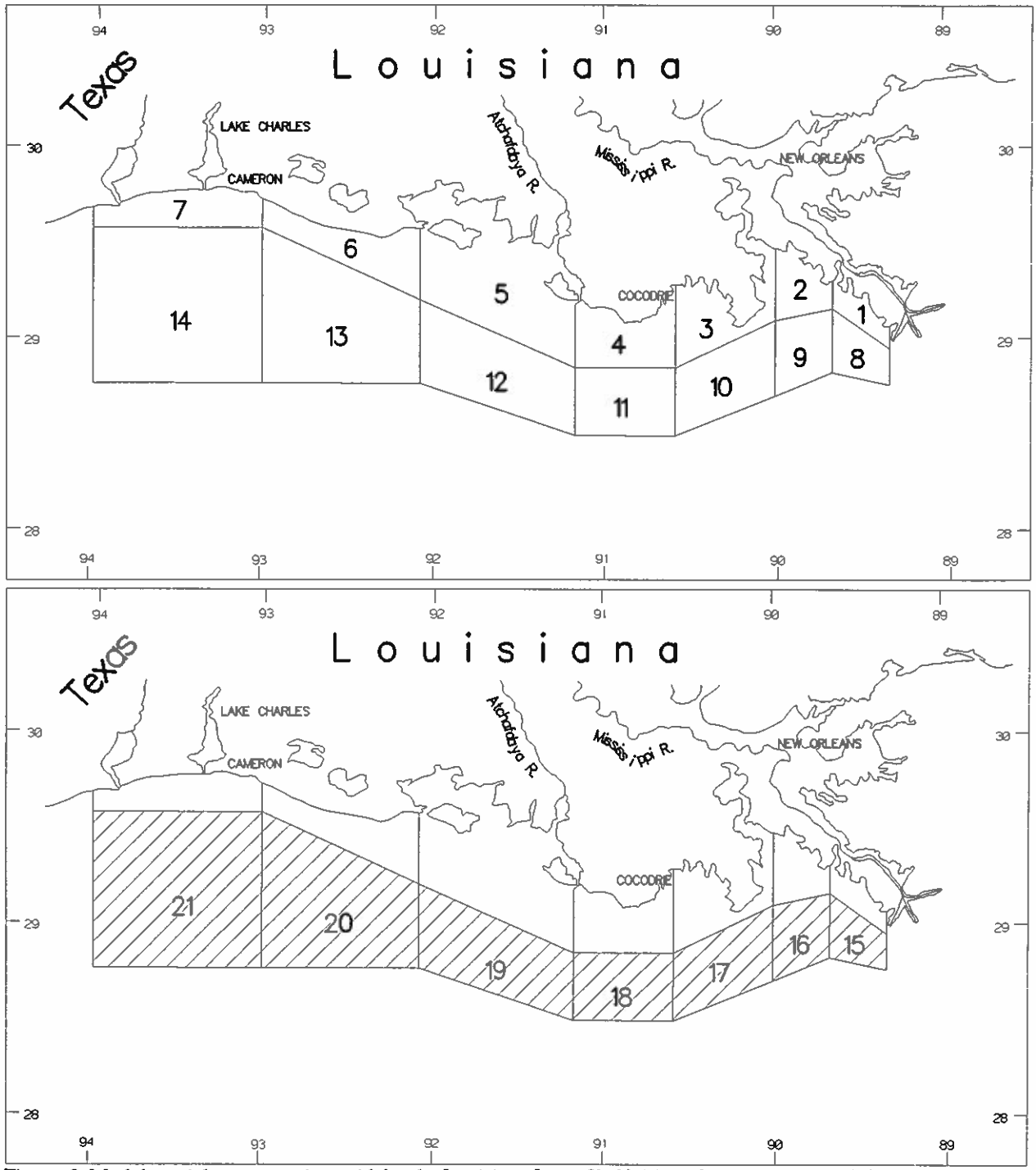


Figure 2. Model spatial segmentation grid for the Louisiana Inner Shelf. (a) surface segments and (b) bottom segments.

tions for advective flows must be externally specified by the user. The three freshwater flow fields represented in this particular application are shown in Fig. 4. These flows were quantified using discharge measurements taken by the U.S. Geological Survey at Tarbert Landing on the Mississippi River, and estimates of flow distribution from U.S. Army Corps of Engineers (1984) and Dinnel and Wiseman (1986). In addition to these freshwater flows, net westward flows of Gulf of Mexico water were added to the model grid such that current speeds of 10 and 3 cm/sec, respectively, were maintained in the surface and bottom spatial segments. These constraints were based on summer averages of current meter data from a long-term mooring located at Station 6 on Transect "C" (Fig. 3). Dispersion coefficients across the model interfaces were determined by mass balances for salinity, a conservative tracer.

Chemical-biological variables — Although the LUMCON shelfwide surveys were extremely compre-

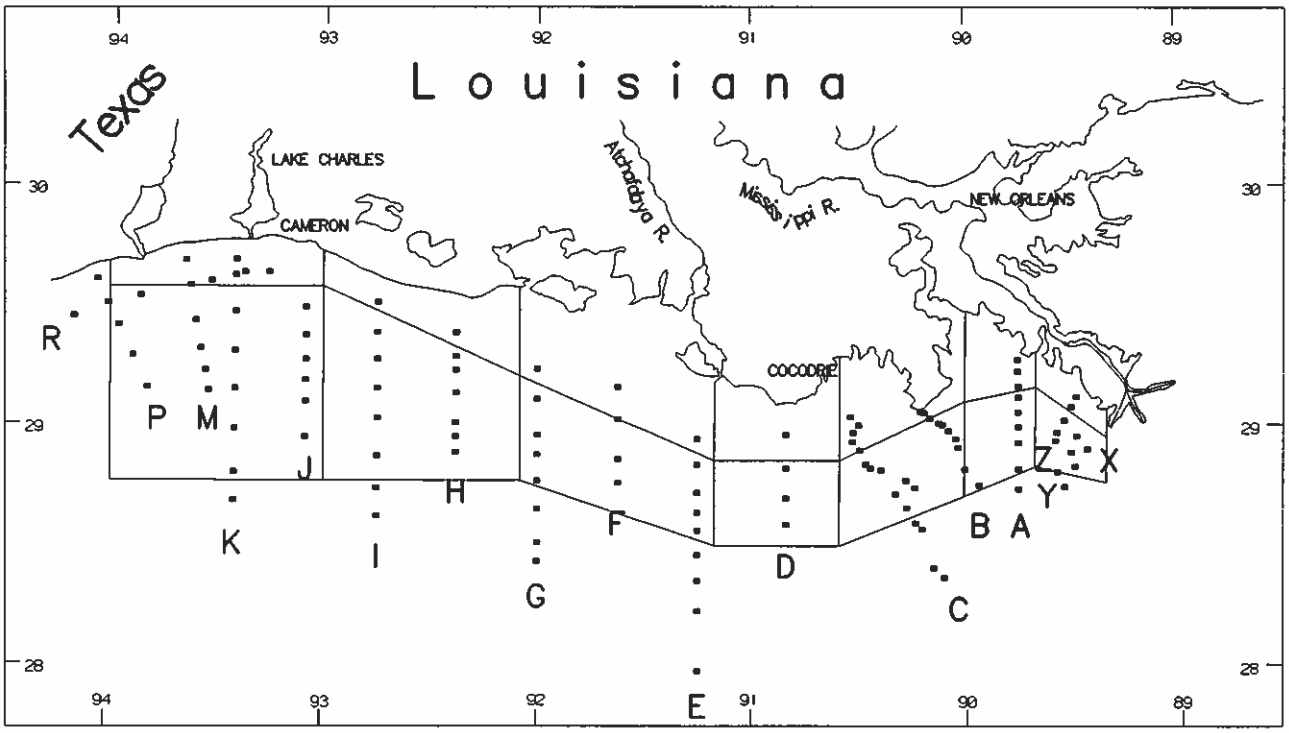


Figure 3. Relationship between LUMCON cruise transects and model spatial segmentation grid.

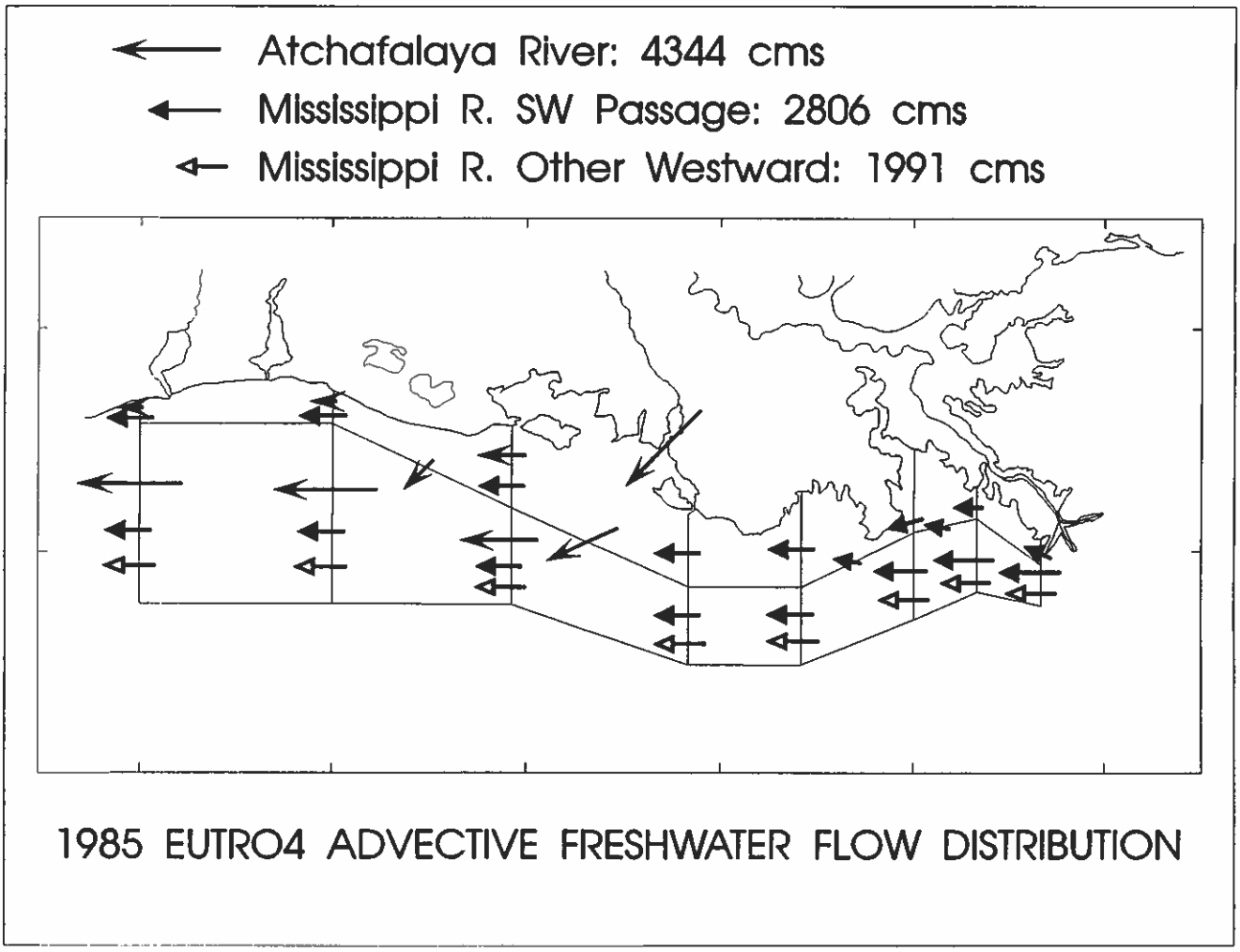


Figure 4. Schematic diagram of freshwater advective flow fields used in the model calibration.

hensive from an assessment standpoint, they were not designed to provide field data for a water quality mass balance model. Consequently, there are data gaps that precluded a comprehensive model calibration. In addition to the steady-state restrictions discussed above, other obstacles included no field data for organic carbon, phosphorus or nitrogen, no direct measurements of underwater light attenuation, and no field data for water depths less than 5 meters. Mindful of these circumstances, the model application presented herein should be viewed only as a "demonstration calibration."

Mass input loadings from the Mississippi and Atchafalaya Rivers were specified using the above freshwater inflows and constituent concentrations from Turner and Rabalais (1991) and from the U.S. Geological Survey NASQAN station at St. Francisville on the Mississippi River (S.P. Dinnel, personal communication). Underwater light attenuation was estimated from observations of Secchi depth using an empirical regression model (Effler, 1985). Sediment oxygen demand and sediment nutrient fluxes (ammonia and phosphate) were specified using measurements from the GOMEX benthic lander (G.T. Rowe, personal communication). Boundary concentrations and water temperature were specified directly from the LUMCON field data.

Calibration results for phytoplankton concentrations are displayed in terms of chlorophyll *a* concentrations (Fig. 5). Internally, the model computes phytoplankton biomass in terms of organic carbon. A carbon:chlorophyll ratio is then assigned solely for the purpose of comparing model output with available field data. This ratio has been observed to vary by an order of magnitude in the study area (D.G. Redalje, personal communication). A carbon: chlorophyll ratio of 100 was used for this particular calibration. Model output for chlorophyll concentration compares with the field data to within approximately a factor of 2.

Calibration results for nitrate-nitrogen concentrations are shown in Fig. 6. There is good agreement between model output and field data. Model output for ammonia-nitrogen (Fig. 7) is consistently lower than the data in the surface spatial segments, and agrees approximately with the data in the bottom segments offshore. The reasons for the systematic discrepancies in the surface waters are not known.

Results for dissolved oxygen concentrations in the bottom segments are shown in Fig. 8. There is reasonably good agreement between model output and field data, with both showing significant degrees of undersaturation. Model output tends to overestimate the field data for spatial segments located farther west of the Delta.

Apart from comparisons between model output and field data for state variable concentrations, comparisons for process rates and mass fluxes are crucial in helping to establish the credibility of a model calibration. Although not available in the historical data base, measurements of surface primary production and

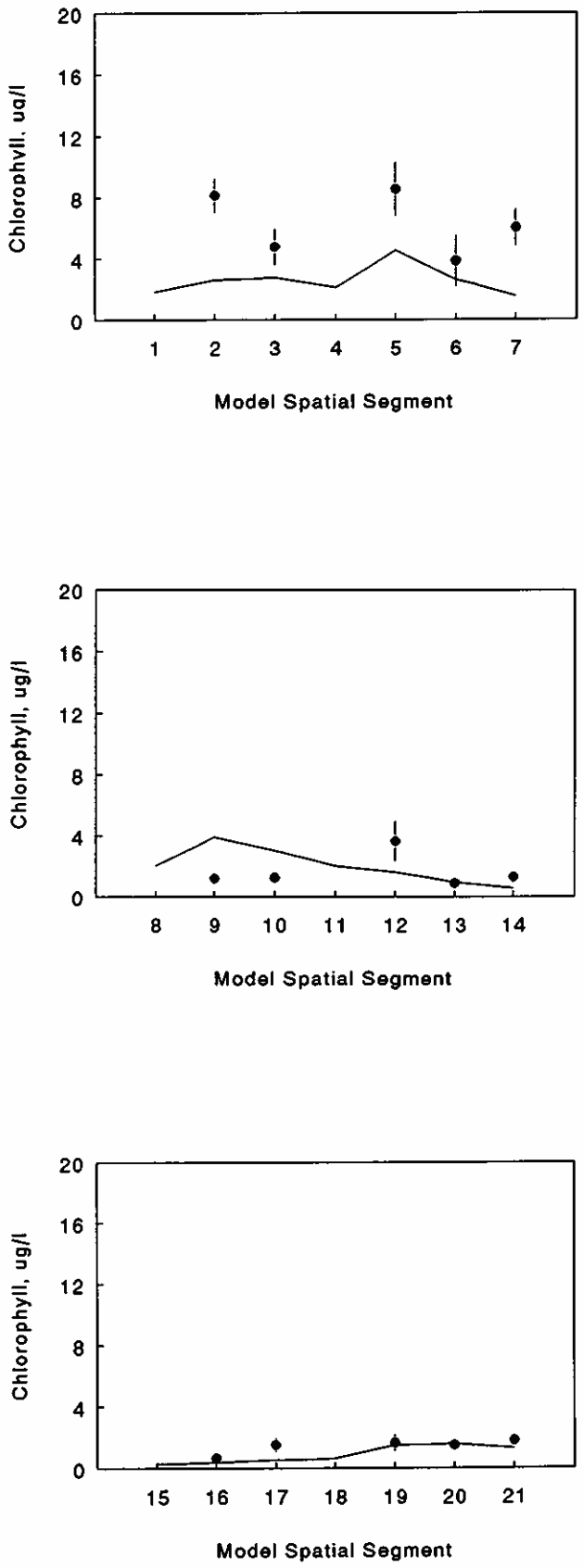
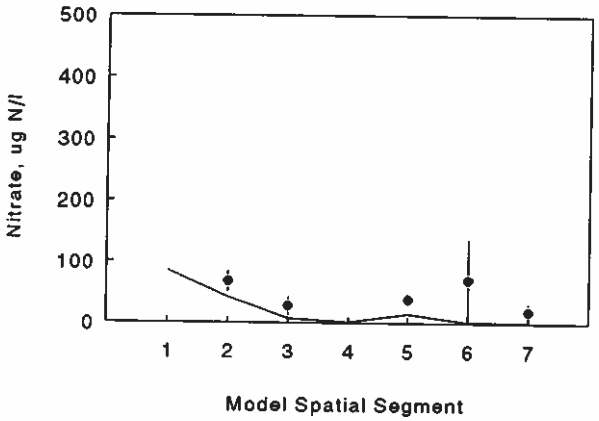
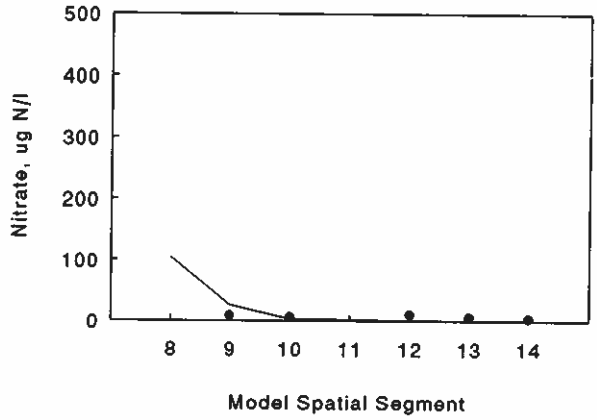


Figure 5. Relationship between model output and field data for chlorophyll *a* concentrations in July 1985. Solid line is model output and data are segment means ± one standard error.





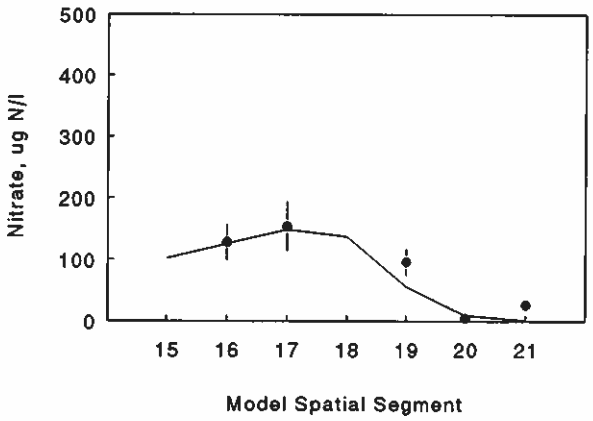
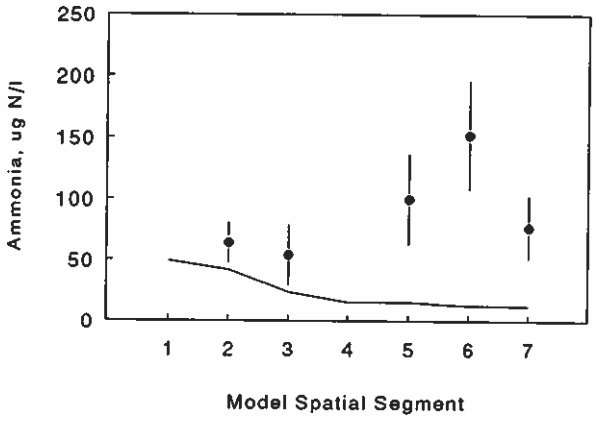
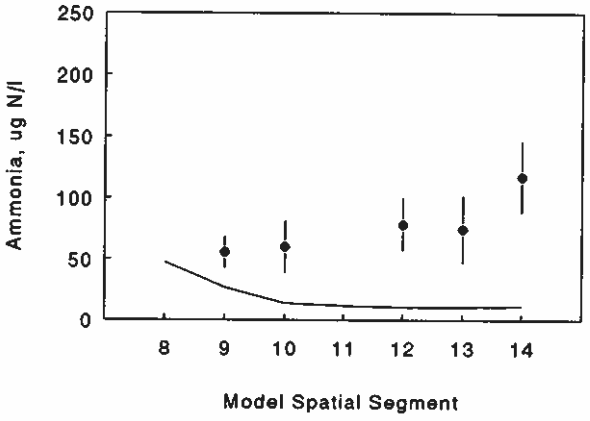


Figure 6. Relationship between model output and field data for nitrate-nitrogen concentrations in July 1985. Solid line is model output and data are segment means ± one standard error.





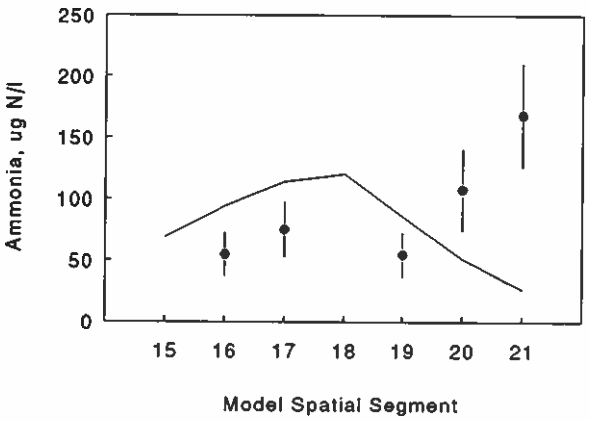


Figure 7. Relationship between model output and field data for ammonia-nitrogen concentrations in July 1985. Solid line is model output and data are segment means ± one standard error.

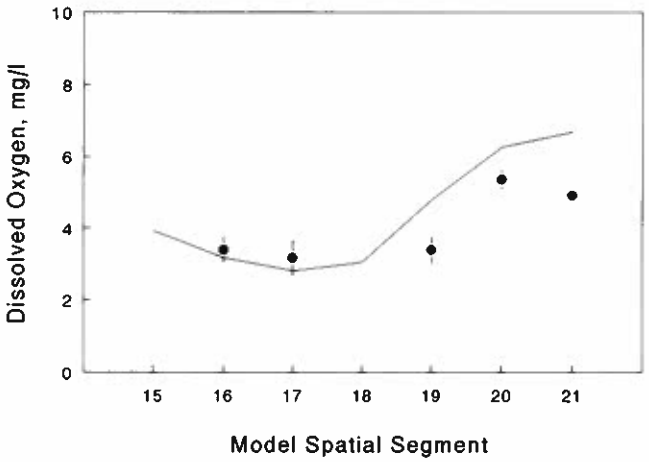


Figure 8. Relationship between model output and field data for dissolved oxygen concentrations in the bottom waters in July 1985. Solid line is model output and data are segment means ± one standard error.

POC/PON settling fluxes were available from the July-August 1990 NECOP cruise (D.G. Redalje, personal communication). These measurements compared favorably with corresponding model output from the July 1985 calibration.

Summarizing to this point, a steady-state "demonstration calibration" has been conducted for the July 1985 shelfwide field data. Results for model state variable concentrations compare with available field data to within approximately a factor of 2. Model output for surface primary production and POC/PON settling fluxes compares favorably with measurements from the July-August 1990 NECOP cruise. It is concluded that the model calibration is at least intuitively reasonable.

Discussion

Temporal scales for production and physical transport — A critical question in the NECOP study relates to the scales of physical and biological variability. For example, the relative importance of primary production versus physical transport will significantly influence the potential relationship between anthropogenic nutrient inputs and hypoxia in the bottom waters. The relative magnitudes of organic carbon sources and sinks due to primary production and physical transport in the calibrated model are shown in Fig. 9 for selected spatial segments. Gains in organic carbon due to primary production are substantially larger than

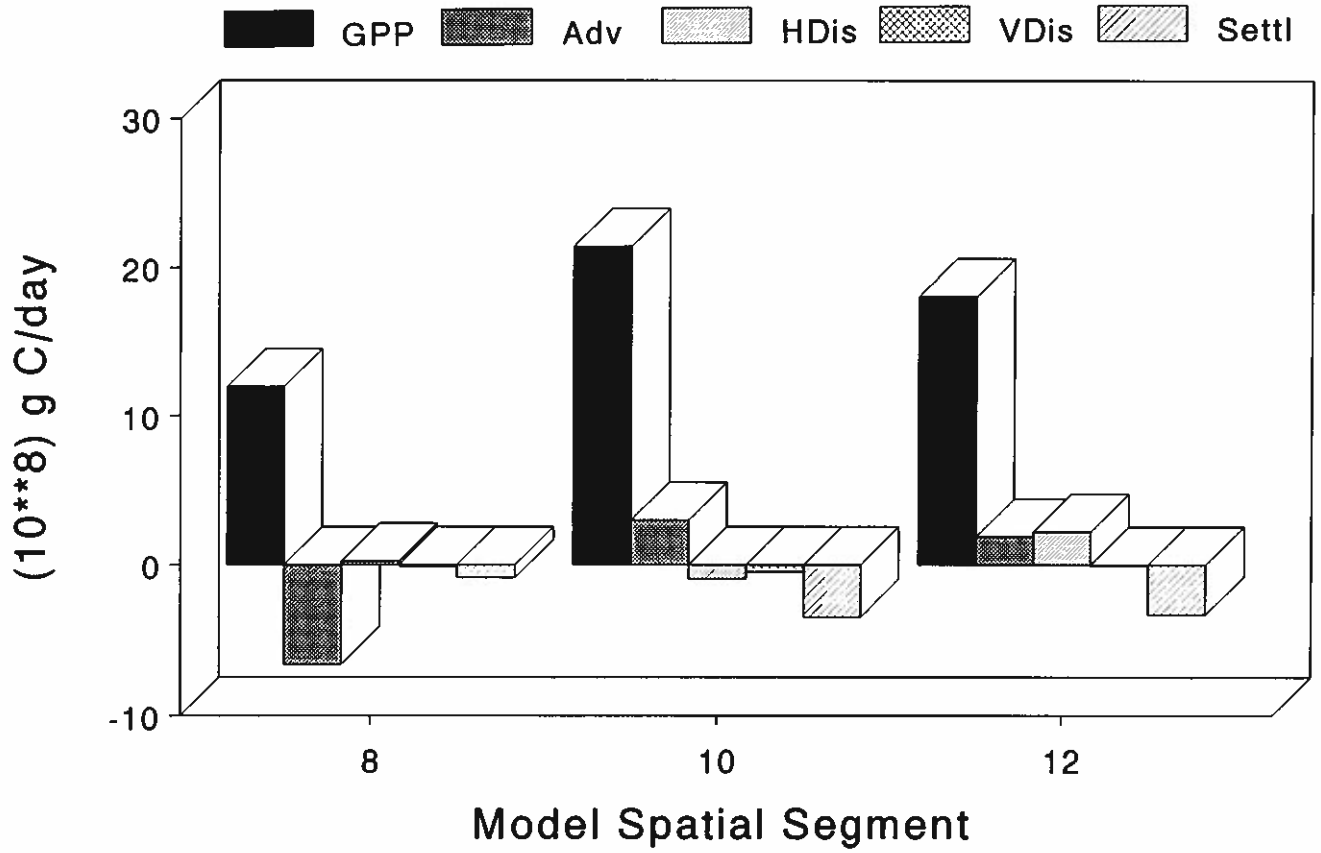


Figure 9. Relative magnitudes of organic carbon sources and sinks in the calibrated model. GPP — gross primary production. Adv — net advective transport. Hdis — net horizontal dispersion. Vdis — net vertical dispersion. Settl — net settling.

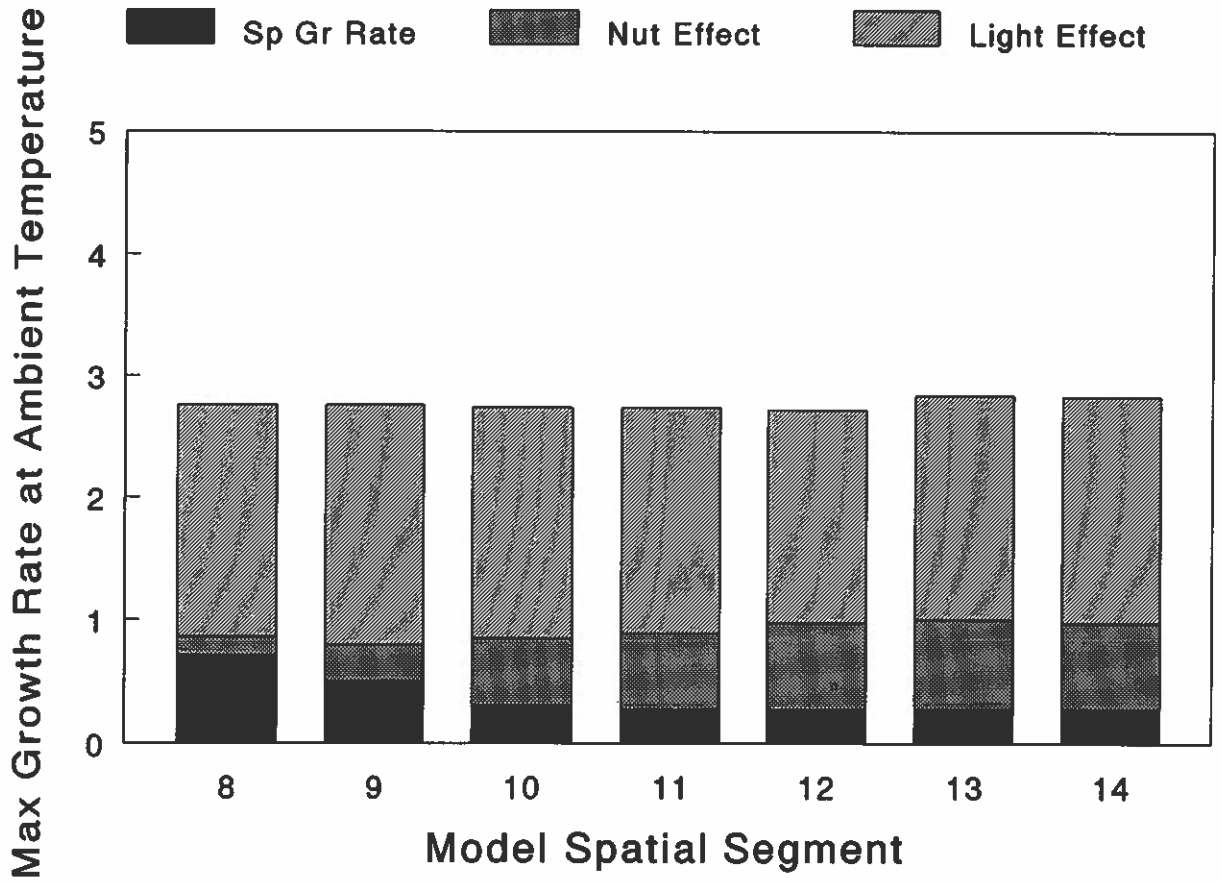


Figure 10. Components of phytoplankton growth rates in the calibrated model. Sp Gr Rate — actual specific growth rate. Nut Effect — nutrient reduction effect. Light effect — light reduction effect.

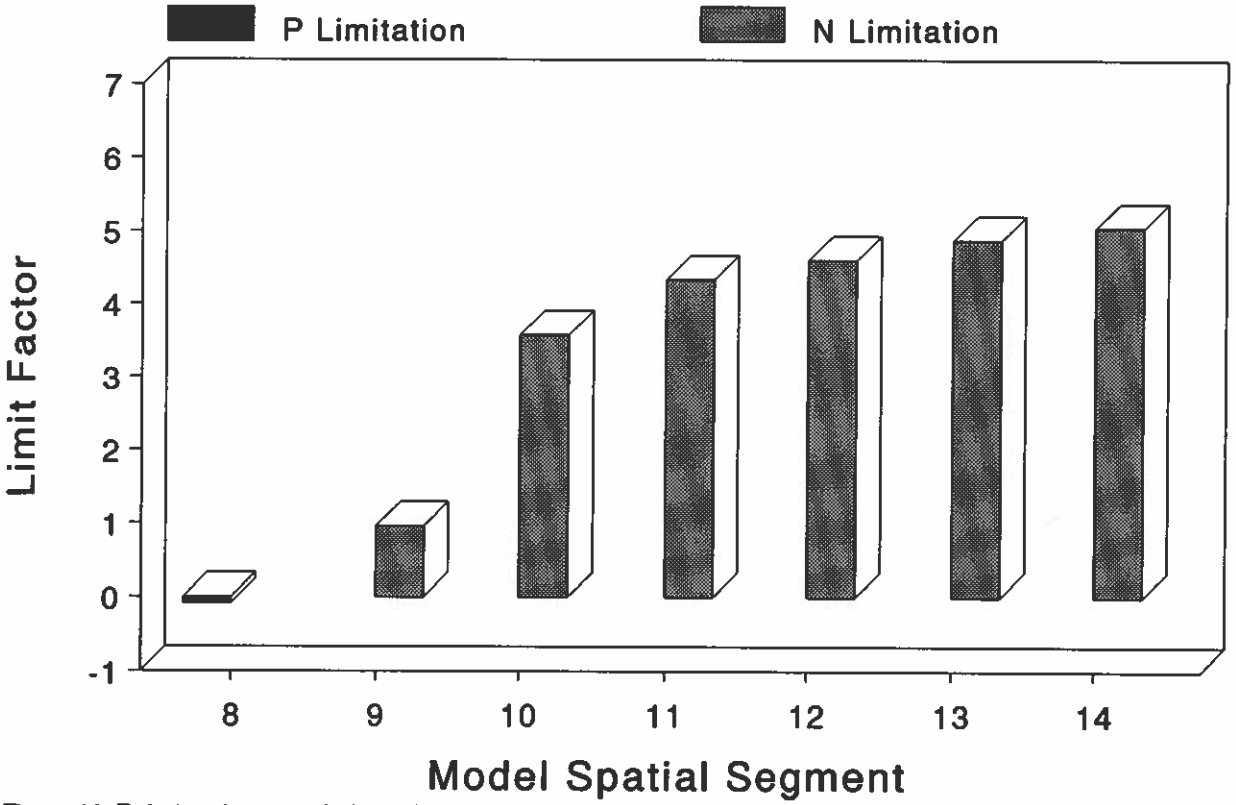


Figure 11. Relative degrees of phytoplankton growth rate limitation by phosphorus and nitrogen in the calibrated model. Magnitude of the "limit factor" is grossly indicative of the relative degree of limitation.

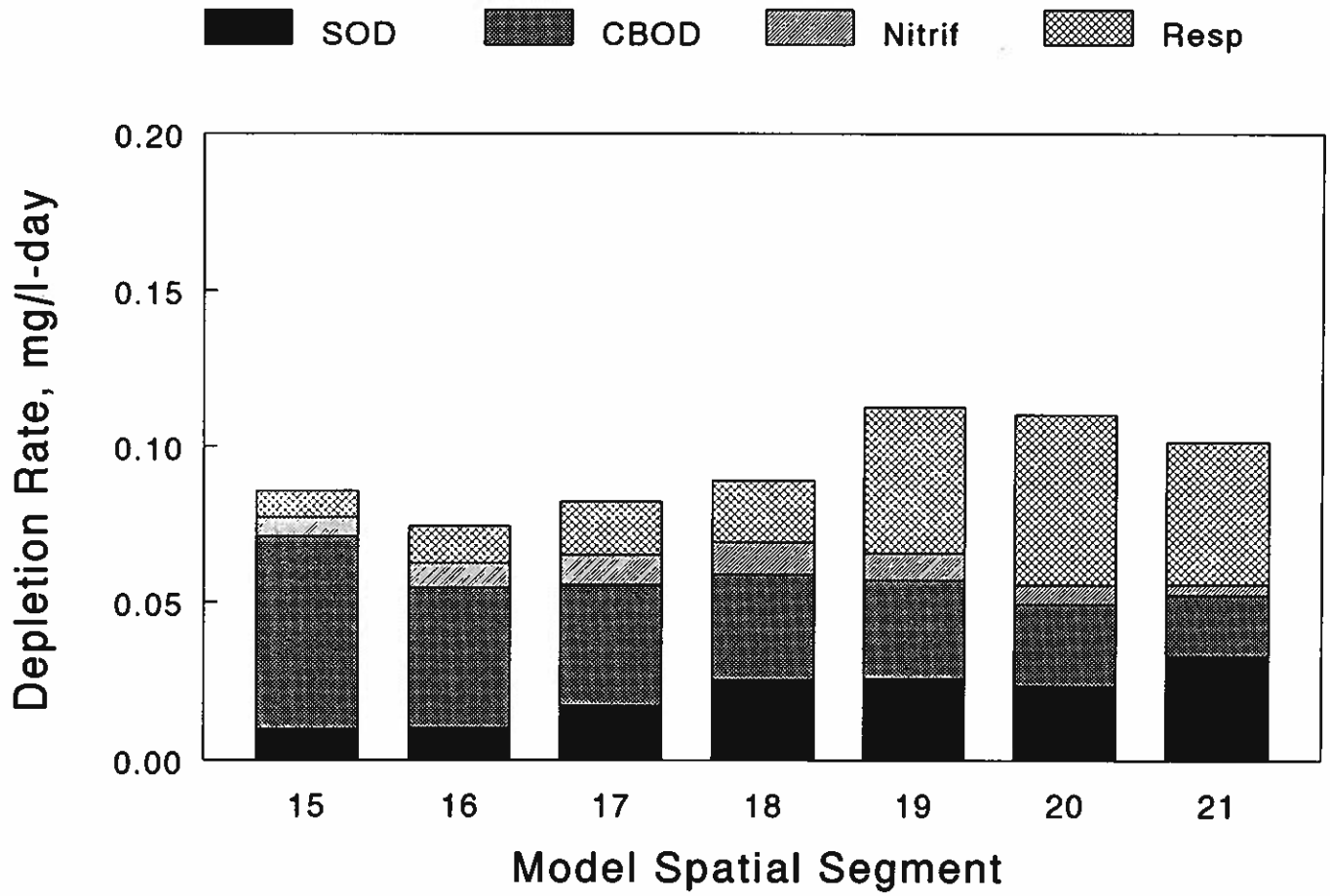


Figure 12. Components of total oxygen depletion rates in the calibrated model. SOD — sediment oxygen demand. CBOD — oxidation of carbonaceous material in the water column. Nitrif — oxygen consumption due to nitrification in the water column. Resp — oxygen consumption due to phytoplankton respiration in the water column.

gains or losses due to physical transport processes.

The most important physical processes appear to be advection and net settling. Advection is a net loss for Segment 8 due to dilution by upstream boundary flows. Advection is a net gain for Segments 10 and 12 because phytoplankton carbon concentrations are higher in their respective upstream model segments. Net settling is a relatively more important loss process in Segments 10 and 12 than in Segment 8 because the hydraulic residence times in Segments 10 and 12 are much longer than that in Segment 8.

Phytoplankton growth rate components — Another aspect of the relationship between physical and biological processes is the degree to which nutrients versus underwater light attenuation control phytoplankton growth rates. Under conditions of optimal temperature, light and nutrients, phytoplankton growth rates are limited solely by physiology. Under ambient conditions, water temperature generally dictates upper bound maximum growth rates. Specific growth rates actually realized depend on potential limiting effects due to underwater light attenuation and/or nutrient limitation.

The components of phytoplankton growth rates in the calibrated model due to temperature, light and nutrient effects are shown in Fig. 10. It should be understood that all rates represent vertical averages in the 10-meter deep surface mixed layer. Maximum growth rates at ambient temperatures are relatively high (approximately 2.8 per day) due to high water temperatures in the Gulf of Mexico. Growth rate limitation due to underwater light attenuation is substantially greater than growth rate limitation due to non-optimal nutrient concentrations in all spatial segments. Furthermore, the magnitude of growth rate limitation increases with distance from the Mississippi Delta (Segment 8). This analysis emphasizes the importance of direct measurements of attenuation coefficients for downwelling irradiance of photosynthetically active radiation (PAR).

Limiting nutrients — Another important question in the NECOP study is the relative importance of phosphorus and nitrogen as potentially limiting nutrients. The relative degrees of phytoplankton growth rate limitation by these two nutrients in the calibrated model are shown in Fig. 11. The indicated "limit factor" is an engineering unit that has no inherent physical meaning. A positive value indicates nitrogen limitation and a negative value indicates phosphorus limitation. The magnitude of the limit factor is grossly indicative of the relative degree of limitation.

Nitrogen is more important than phosphorus in controlling phytoplankton growth rates in most of the study area. The degree of nitrogen limitation increases with distance from the Delta. Phosphorus is relatively more limiting than nitrogen in Segment 8, the area immediately west of the Delta.

Dissolved oxygen depletion rates — A crucial question in the NECOP study relates to the principal factors controlling dissolved oxygen dynamics and seasonal hypoxia on the Louisiana Inner Shelf. An important part of this question is the relative importance of water column processes versus sediment oxygen demand (SOD). The components of total oxygen depletion rates in the bottom spatial segments in the calibrated model are shown in Fig. 12. CBOD represents oxidation of carbonaceous material in the water column. Respiration represents only consumption of oxygen due to phytoplankton respiration.

In general, water column processes and SOD both contribute significantly to total oxygen depletion rates. Near the Delta, CBOD is relatively more important than phytoplankton respiration; however, the inverse occurs at greater distances as more phytoplankton biomass is produced and advected westward along the shelf. The contribution of SOD to total oxygen depletion rates ranges from 12 to 33 percent, with an average of approximately 25 percent in the principal hypoxia region.

The importance of purely morphometric factors in influencing hypoxia on the Louisiana Inner Shelf is illustrated by the spatial structure of the magnitudes (not the relative contributions) of the SOD contributions to total oxygen depletion rates. In the calibrated model, a spatially constant SOD value was specified in terms of an areal rate. The magnitudes of the SOD components in Fig. 12 are simply inversely proportional to the depths of the respective model segments.

Conclusions

The following preliminary conclusions can be drawn from the water quality mass balance modeling conducted to date:

1. A "demonstration calibration" has been obtained for summer average conditions on the Louisiana Inner Shelf as represented by the July 1985 shelfwide synoptic cruise.
2. Temporal scales for phytoplankton production appear to be shorter than those for advective-dispersive physical transport.
3. Underwater light attenuation appears relatively more important than nutrient limitation in controlling phytoplankton growth rates.
4. Nitrogen appears to be relatively more important than phosphorus in controlling phytoplankton growth rates in most of the study area. Phosphorus may be more controlling than nitrogen in the near-field region west of the Mississippi Delta.
5. Phytoplankton respiration, oxidation of carbonaceous material in the water column and sediment oxygen demand all appear to contribute significantly to total oxygen depletion rates in the hypoxic region.

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Lower Mississippi River historical nitrate flux and Mississippi River outflow buoyancy flux

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Abstract

Results from an analysis of 35-year time sequences of Lower Mississippi River water discharge, nitrate concentration and nitrate flux are discussed. The potential predictability of these quantities is evaluated. Results indicate a large amplitude, very-low-frequency cycle in the nitrate concentration that is not observed in the water discharge. A decrease in average nitrate concentration from a peak in 1983 to the present confirms that this variability is more cyclic than trend-like. River-water discharge variation is greatest in association with the annual cycle. The annual water discharge and nitrate concentration cycles are similar, high nitrate concentrations usually occur near the spring freshet and low concentrations usually occur along with autumn low flow conditions. Nitrate flux variations exhibit a low amplitude, very-low-frequency modultation of a dominant, annual cycle. A predictor-hindcastor analysis indicates that truly skilled forecasts of all three fields are feasible.

Shelf stratification and nutrient field conditions respond to forcing by riverine source functions. Hydrographic data in the Mississippi River outflow region from two NECOP cruises are presented. Spatial distributions of Cruise 1 (summer 1990) and Cruise 2 (winter 1991) hydrographic data are compared seasonally and with historical data. Shelf stratification conditions are examined based on NECOP cruise data, and these conditions are discussed in the context of riverine and other forcing functions.

The Mississippi River system drains approximately 41 percent of the contiguous United States, with an average water discharge that ranks first in North America and seventh in the world (van der Leeden et al., 1990). Nitrate concentration in the lower Mississippi River has increased by a factor of two over the last 35 to 40 years (Walsh *et al.*, 1981; Turner and Rabalais, 1991). Monthly nitrate concentration values also progress through a less distinct annual cycle with high values in the spring and lows in the fall. This annual cycle is similar to the characteristic annual Mississippi River water discharge cycle. The ecological implications to the coastal waters of the northern Gulf of Mexico are many, some of which are changing primary production (Lohrenz *et al.*, 1990), possible association with near-bottom, low dissolved oxygen regions in the adjacent shelf regions (Turner *et al.*, 1987), and species succession due to changes in nutrient levels (Turner and Rabalais, 1991). In this work we examine the relationship of water discharge and nitrate concentration over a 35-year time period using linear correlation and time series analyses. We also examine the predictability of nitrate flux, nitrate concentration and water discharge using linear optimal estimator analysis (Dinnel and Bratkovich, 1990 and manuscript submitted).

Mississippi River nitrate data was extracted from U.S. Geological Survey (USGS), Surface Water Quality Reports for the station at or near St. Francisville, La., (U.S. Department of the Interior, 1964-1990), data from 1954-1963 was reported by Walsh *et al.*, (1981). Samples were begun in 1954 and continued through September 1990. St. Francisville is approximately 450 km upstream from the Mississippi River Delta. Mississippi River water discharge data at Tarbert Landing, 480 km upstream from the Mississippi River Delta, was reported by the U.S. Army, Corps of Engineers (USACOE). There are no major tributaries downstream of this gauging station on the Mississippi River.

The nitrate concentrations used were essentially instantaneous values, sampled at approximately monthly intervals; water discharge data were monthly averages of daily values. We have paired the nitrate concentrations with the water discharge for each month. Although we expect nitrate concentrations to fluctuate over short periods, we cannot describe these variations and, therefore, assumed that the instantaneous concentrations were reasonably characteristic for the entire month. The monthly average water discharge data are relatively accurate estimators of a given month's discharge. Standard deviations of daily values range from 5 to 20 percent of the monthly means. The monthly nitrate flux is the arithmetic product of instantaneous nitrate concentrations and the monthly average water discharge.

Analysis and filtering of time series were performed using a Fast Fourier Transform (FFT) algorithm. Filtering was performed in the frequency domain. Three frequency bands were chosen based on analyses of the autospectra: a sub-annual band, with frequencies <0.075 cycles per month (cpm) (periods greater than 13.33 months), an annual band, with frequencies between 0.075 and 0.1875 cpm (periods between 13.33 and 5.33 months), and a supra-annual band, with frequencies

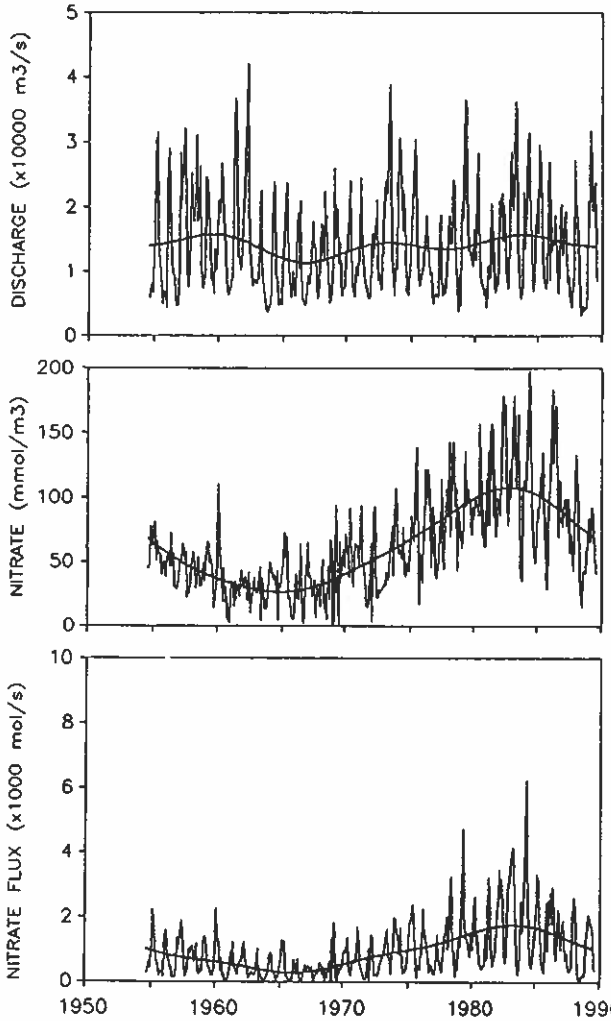

Figure 1. Monthly and very-low-passed times series of Mississippi River water discharge, Tarbert Landing, Miss. (upper), Mississippi River nitrate concentration near St. Francisville, La. (center), and associated nitrate flux (lower) (Dinnel and Bratkovich, submitted).

between 0.1875 and 0.5 cpm (periods between 5.33 and 2.0 months). The sub-annual band was further divided into narrower frequency bands to help delineate spectral peaks. The very-low-frequency band (VLF), with frequencies <0.004 cpm (periods greater than 250 months), is defined as the long-term trend.

A predictor/hindcastor analysis was performed using linear optimal estimation theory following Davis (1976). This approach is often used as a self-consistent method of determining the degree to which a specific 'signal' can be predicted or hindcast. For this particular application, we examine the effectiveness of hindcastors for river water discharge, nutrient concentration and nutrient flux variations about their long-term temporal average values. Motivated by the need to predict the above fields with a known degree of skill and the fact that the historical data seemed to be dominated by identifiable temporal cycles, we constrained the hindcastor using time varying sinusoids as input data. This form for the input data has the advantages of analytical simplicity, orthogonality, and direct relevance to spectrally derived results.

Time series of monthly Mississippi River water discharge, nitrate concentration and associated nitrate flux are presented in Fig. 1. Monthly water discharge has a prominent annual cycle and smaller-amplitude VLF cycle (~12 year period). The nitrate concentration has a pronounced VLF cycle (~36 year period). This VLF cycle has a minimum near 1965 and a maximum near 1983; a definite decrease occurred over the earliest decade and the last six years of the record. The nitrate concentration also has an definite annual cycle. The annual cycle common to both nitrate concentration and water discharge is also observed in the nitrate flux (Fig. 2).

Linear regression of detrended nitrate concentration against detrended water discharge indicates a statistically significant, positive relationship at the 95 percent level; scatter is large, R^2=0.07. A linear regression using the annual-band data also shows a significant but marginal relationship (R^2=0.19).

Monthly water discharge, nitrate concentration and nitrate flux are not normally distributed about their annual means (Fig. 3). All three probability density functions (PDFs) are biased toward low values, lowest values are within two standard deviations below the annual mean, while highest values exceed three standard deviations above the annual mean. Skewness values are 0.98, 0.90, and 1.85 for water discharge, nitrate concentration and nitrate flux, respectively.

The water discharge, nitrate concentration and nitrate flux auto-spectra are dominated by statistically significant peaks at the annual frequency (at the 90 percent level). Cross-spectral analysis between water discharge and nitrate concentration indicates statistically significant (at the 95 percent level), coherence-squared values near the annual band, where the water discharge leads the nitrate concentration by approximately one month.

More than 60 percent of the water discharge total variance is contained within the annual band, with only 25 percent contained in the sub-annual bands and a lesser amount in the supra-annual band (Table 1). More than 67 percent of the nitrate concentration total variance is contained in the sub-annual band, with 54 percent of the total variance contained in the VLF band associated with the long-term cycle. The nitrate flux band-limited variances reflect both the water discharge and the nitrate concentration variance patterns.

Results of the linear optimal estimator analysis are presented in Table 2. The specific form of the estimator used is $P = \alpha_1\cos(\omega_1 t+\phi_1)+\alpha_2\cos(\omega_2 t+\phi_2)$. The indices (1 and 2) refer to the annual and the very low-frequency cycles, respectively, with associated amplitudes, α_i, frequencies, ω_i, and phases, ϕ_i. The cycle period selection was motivated by the results of the spectral analysis and by qualitative examination of the time series themselves.

The estimator skill values, shown in Table 2, indicate the hindcastor skills are greatest for water dis-

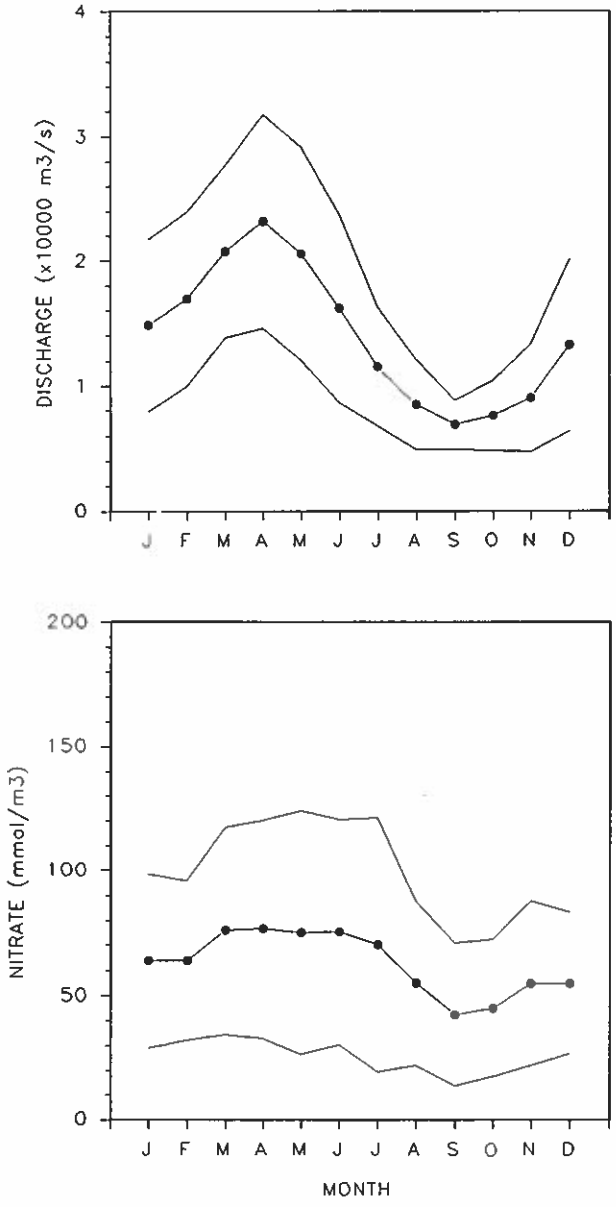

Figure 2. Annual cycle of average monthly Mississippi River water discharge, Tarbert landing, Miss. (upper) and Mississippi River nitrate concentration near St. Francisville, La. (lower), plus and minus one standard deviations are shown.

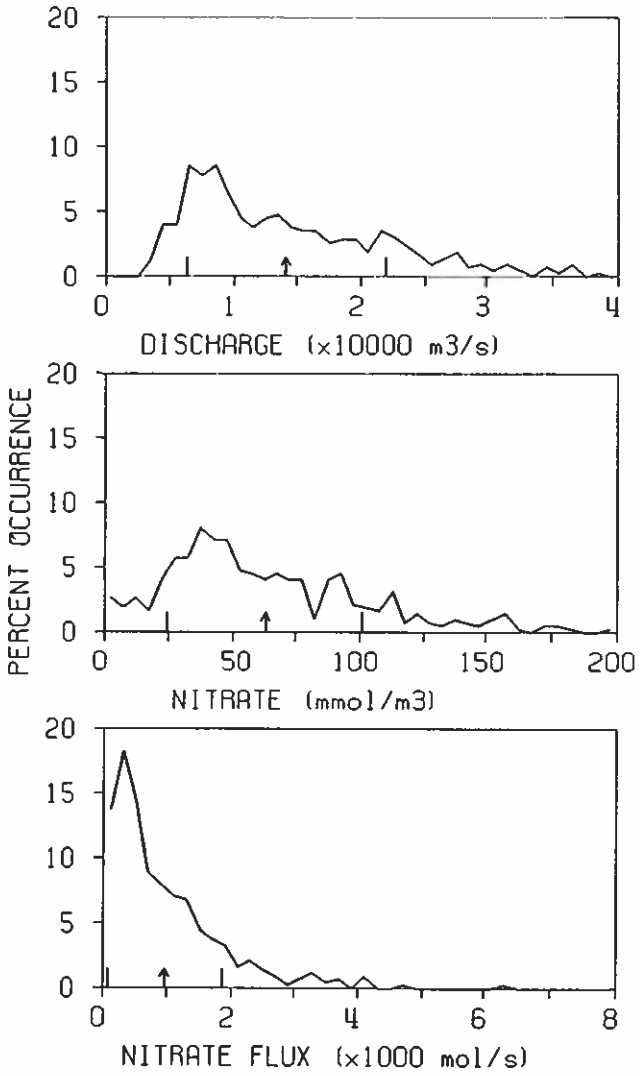

Figure 3. Probability density functions of Mississippi River water discharge (upper), Mississippi River nitrate concentration (center), and associated nitrate flux (lower). Arrow and vertical bars represent sample annual means and one standard deviation, respectively (Dinnel and Bratkovich, submitted).

charge and nitrate concentration if a single component estimator is employed; i.e. the annual cycle for the water discharge and the long-term cycle for the nitrate concentration. The nitrate flux estimator skill is equally partitioned between annual and the long-term components. The best estimator for all the quantities account for 40 to 50 percent of the variance in the signal. These are substantial skill levels considering the point that the 95 percent confidence limit for non-zero skill is conservatively estimated to be 0.1 on one- to five-year time scales.

We have analyzed 35 years of monthly sampled, time-sequence data of lower Mississippi River water discharge, nitrate concentration and nitrate flux. We have also explored the degree to which predictions of water discharge, nitrate concentration and nitrate flux can be made. These results indicate a large amplitude, dominant very-low-frequency (VLF) cycle in the nitrate concentration that is not observed in the water discharge, a decrease in average nitrate concentration from the 1983 peak to the present confirms that this variability is more cyclic than trend-like. River water discharge variation is greatest in association with the annual cycle. The annual cycles are similar in water discharge and nitrate concentration, high nitrate concentrations usually occur during the spring freshet and low concentrations usually occur along with autumnal low-flow conditions.

Despite this qualitative similarity, a linear regression analysis revealed that the quantitative covariability

Table 1. Variance of monthly mean Mississippi River water discharge (Tarbert Landing, Miss.) and monthly sampled Mississippi River nitrate concentration (St. Francisville, La.) from August 1954 through December 1990 (Dinnel and Bratkovich, submitted).

	Water Discharge Variance ($10^7 m^6 s^{-2}$)	Percent Total	Nitrate Variance ($10^{-7} mol^2 m^{-6}$)	Percent Total	Nitrate Flux Variance ($10^5 mol^2 s^{-2}$)	Percent Total
Total	6.084		146.228		7.937	
Total Sub-annual Band (>0.075 cpm)	1.521	25.0	98.190	67.1	3.517	44.3
Separate Sub-annual Bands (>0.004 cpm)	0.144	2.4	77.895	53.3	2.213	27.9
(0.004-0.01 cpm)	0.297	4.9	4.310	2.9	0.280	3.5
(0.01-0.03 cpm)	0.648	10.7	5.478	3.7	0.455	5.7
(0.03-0.045 cpm)	0.136	2.2	3.628	2.5	0.118	1.5
(0.045-0.075 cpm)	0.296	4.9	6.879	4.7	0.451	5.7
Annual Band (0.075-0.1875 cpm)	3.663	60.6	29.020	19.8	3.568	45.0
Supra-annual Band (<0.1875 cpm)	0.864	14.3	19.014	13.0	0.852	10.7

Table 2. Means, standard deviations (S_d), coefficients of variation (CV), and hindcastor skills for time series of water discharge (Tarbert Landing, Miss.), nitrate concentration (St. Francisville, La.) and associated nitrate flux. Hindcastor skill are presented for predictions using the annual (A), very-low-frequency (VLF), and both the annual and the very-low-frequency cycles. Estimated skills below the threshold (~0.1) associated with random correspondence or artificial hindcastor skill are indicated by **** (Dinnel and Bratkovich, submitted).

	Mean	S_d	CV	Hindcastor Skill		
				A	VLF	A+VLF
Water Discharge (m^3/s)	14100	7800	0.55	0.44	****	0.46
Nitrate Concentration ($mmol/m^3$)	62.8	38.1	0.60	****	0.50	0.48
Nitrate Flux (mol/s)	961.84	890.55	0.93	0.27	0.26	0.49

Note: Perfect estimators have skill = 1.0; skill cannot be less than zero.

between these two fields was weak (R2<0.15), even if filtered versions of the data sequences were used. Variability in nitrate flux time history reflected the combined influences of the dominant VLF cycle in nitrate concentration and the dominant annual cycle in water discharge. Low amplitude modulation in the annual cycle was evident.

A linear optimal estimator analysis showed that there was significant hindcastor (and forecastor) skill for water discharge, nitrate concentration, and nitrate flux. Since the estimator constructs consist of one or two simple sinusoids with offset frequencies, there is reason to believe that truly skilled forecasts of all three fields are feasible over times scales of several months to several years.

Daily Mississippi River discharge for 1990 and 1991 is presented to define the discharge environment of the two field sampling cruises. Cruise I followed the spring freshet discharge decline by approximately one month. The outflow region was associated with discharge values near the long-term mode, approximately 10,000 $m^3 s^{-1}$, less than one standard deviation below the annual mean. Cruise II occurred during the 1991 spring freshet. The outflow region was associated with the smaller of three peaks in the spring flood, discharge values were approximately 25,000 $m^3 s^{-1}$, slightly greater than one standard deviation above the annual mean (see Fig. 3).

Using historical hydrographic data from the RV GUS, Bureau of Commercial Fisheries, shelfwide surveys in the early 1960s, we have been able to estimate the fill time of the Louisiana Bight region (Fig. 4). This region is defined as the shelf (depth <100 m) west of the delta to approximately 90.5°W. Fill time represents a time-dependent estimate of residence time. It is determined by summing the fresh water inputs backward in

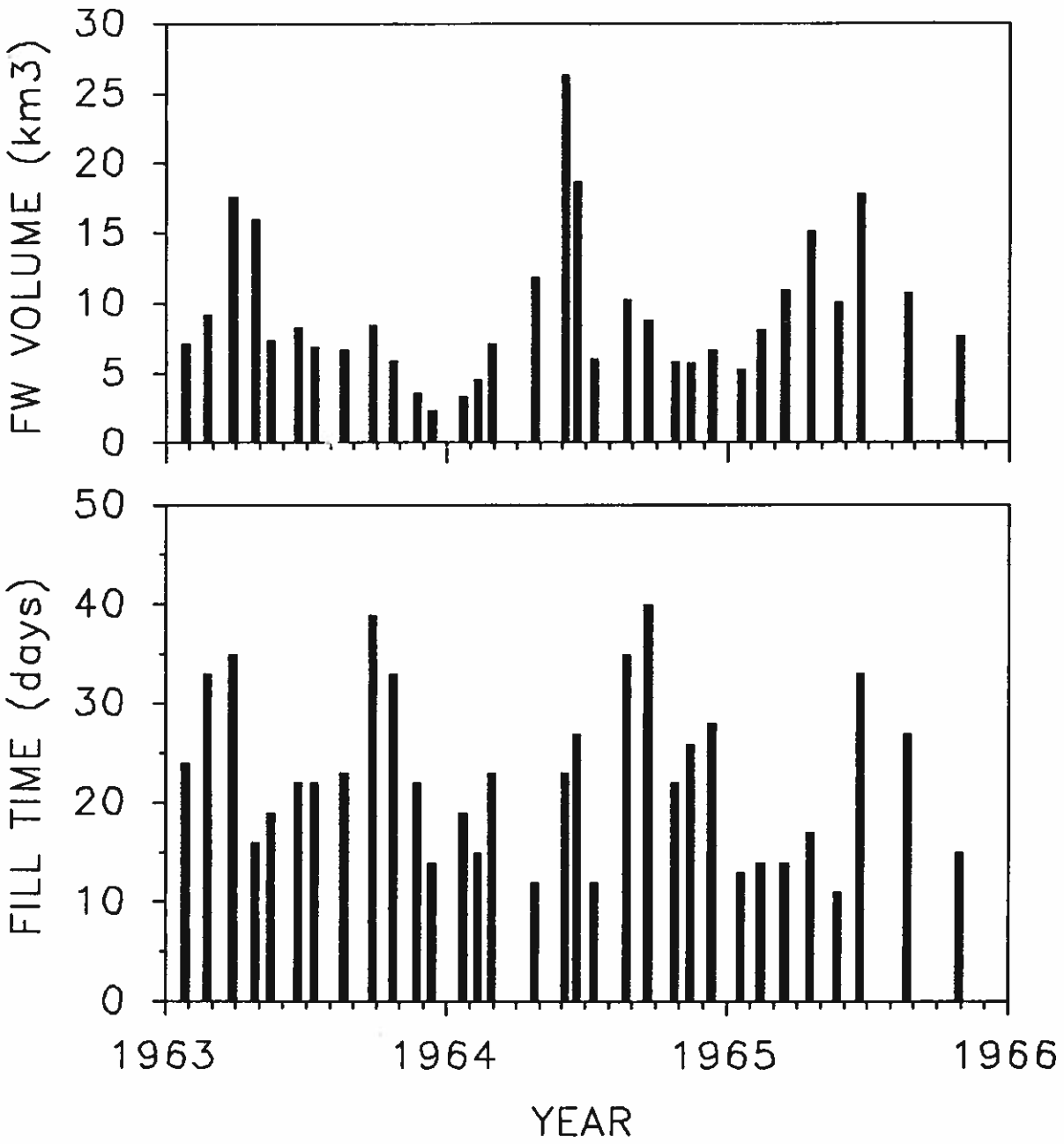

Figure 4. Louisiana Bight fresh water volume and fill times 1963-1965, based on upper 37.5 m of water column.

time to account for an estimated shelf freshwater volume (Dinnel and Wiseman, 1986). Freshwater volume in the upper 37.5 m of the Louisiana Bight is closely tied to discharge levels. Fill times were short, between 15 and 40 days, with an average less than one month. This implies that the outflow region has, at times a very short residence time (0.5 month) of Mississippi River discharge when the river is in flood; and an approximate one-month memory of past discharge at times of lower flow.

Salinity fields for NECOP Cruise I and II were presented. During Cruise I (lower river discharge), the surface (1 m) salinities were lowest (~17‰) near mouth of Southwest Pass, graded to open-Gulf of Mexico values (>36‰) 50 km offshore, and to upper 20's in the western portion of the sampled region (100 km west). Salinities at 10 m depth showed similar distributions but were 8 to 10‰ greater. Salinity fields during the first leg of Cruise II show a very similar surface pattern as Cruise I, with almost identical salinity values. Lowest salinity values were nearest the delta and graded to less than open Gulf values offshore and westward (~32‰). Over the shelf, salinities at 10 m graded from low to higher values seaward, and also never reached open Gulf values.

In the immediate future we intend to estimate freshwater volume and fill times for NECOP Cruise I and II data and to relate them to the historical analyses. Based

on comparisons to RV GUS data and on time series data we expect freshwater volume and fill times to range from 5 to25 km^3 and 15 to 30 days, respectively.

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Nutrient/pigment variability in the Mississippi River plume and adjacent waters

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Abstract

The spatial distribution of salinity, temperature, pigments and nutrients was examined in the vicinity of the Mississippi River Delta and contiguous coastal waters in Summer 1990 and Spring 1991. The objectives were to document spatial distributions by mapping parameters, and contrast these distributions with temporal patterns near the mouth of Southwest Pass and to the west, near hypoxic bottom waters. The temporal patterns are also compared to observations taken while following a drifting surface instrument package (with a sediment trap array). The mesoscale surface distributions in Summer 1990 and Spring 1991 show that localized regions of high nitrate exist west of Southwest Pass. Additionally, a maximum in surface chlorophyll was consistently southwest, or downplume, of the highest surface nitrate concentrations. The surface salinity pattern, however, was not consistent from summer to spring. In the summer observations there was no coherent pattern of low-salinity waters emanating from Southwest Pass; the position of the low-salinity plume was too variable in time to derive a persistent spatial pattern. This was supported by large variations (> 10 psu in 6 hours) in surface salinity while at a fixed position (28°55'N, 89°29'W) near the mouth of Southwest Pass. Temporal variations in surface properties within the plume, while following an instrumented surface drifter, show less variability. The large-scale movement of the plume appears to be the dominant factor determining the temporal and spatial variability in surface properties in the Louisiana Bight. The observed time scales of the plume and drifter motions suggest factors such as tides and inertial motions are forcings mediating the variability in surface properties near Southwest Pass.

The large volume of freshwater discharged by the Mississippi River, coupled with high ambient concentrations of inorganic nutrients, has been hypothesized as a major factor influencing the productivity of the Louisiana-Texas shelf ecosystem (Riley, 1937). There is now evidence that the rate at which nutrients are delivered to the shelf is increasing, primarily due to anthropogenic inputs within the watershed of the Mississippi River. During the past four decades the concentration of nitrate in the lower Mississippi River has doubled, silicate has decreased, and phosphate concentrations, in contrast, have exhibited no clear trends (Turner and Rabalais, 1991). In assessing the potential impact of nutrient loading on the Louisiana - Texas Shelf ecosystem, assumptions have generally been made as if nutrients were uniformly distributed over the Louisiana-Texas shelf area west of the Mississippi Delta. If the discharge rates are extrapolated to a 'total' shelf area of 1.06×10^5 km^2 (Dinnel and Wiseman, 1986), for example, the subsequent estimates of enhanced "new" production on the Shelf range from 23 (Turner and Rabalais, 1991) to 30 gC m^{-2} yr^{-1} (Dagg and Whitledge, 1991).

While the potential impact of anthropogenic nutrient loading undoubtedly influences the whole Shelf to an unknown extent, the initial utilization of river-born nutrients likely occurs within surface plumes. When the low salinity waters are discharged onto the shelf they expand as broad, thin, highly-turbid plumes, often with a well-defined optical front at the periphery. In both Summer 1987 and Spring 1988, for example, sharp salinity gradients occurred at the plume front, which coincided with a visual color boundary. In one transect across the plume emanating from Southwest Pass salinity increased by >20 psu over a horizontal distance of only 7 km (Dagg and Whitledge, 1991). The highest productivity rates and pigment biomass on the shelf also are known to occur about the periphery of the plume from Southwest Pass, where enhanced production occurs in response to increased light availability (Lohrenz *et al.*, 1990).

Prior studies of the spatial distribution of nutrients and plankton biomass surrounding the Delta have generally presented "composite" maps of surface distributions, which are non-synoptic. Thus, in order to determine the relevant time scales over which the "new" nutrients from riverine sources are utilized, the distribution of the nutrients and pigments must be resolved at time scales characteristic of the time for water parcels to transit from the Mississippi River to the Shelf. We have conducted a series of surveys about the Mississippi River Delta and the western Louisiana Shelf that have attempted to determine these scales and suggest the dominant forcings that regulate the spatial and temporal variability in surface properties.

Materials and Methods

Surveys — Surface distributions of salinity, temperature and fluorescence were taken from cruises in the Summer (17 July to 10 August) 1990 and Spring (19

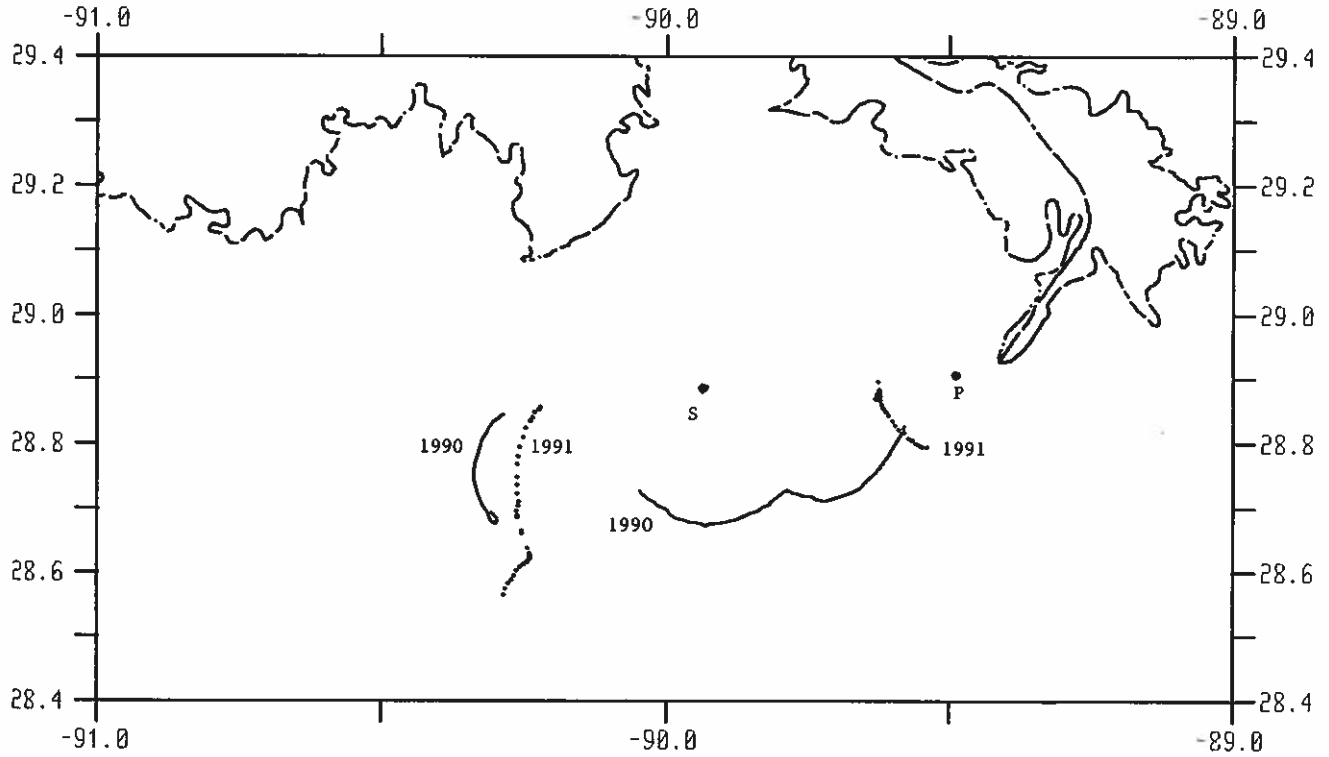

Figure 1. Position of anchor stations (P = plume; S = shelf) and tracks of drifting instrument package in the 'plume' region, east of 90°W, and in the "shelf" region, west of 90°W. Solid lines indicate drifter trajectories for Summer 1990 and dashed lines indicate drifter trajectory for Spring 1991.

February to 10 March) 1991 on the N/S *Malcolm Baldrige*. A 'flow-through' system recorded salinity (Sea Bird SBE 4-02/0 sensor), temperature (SeaBird SBE 3-01F sensor) and *in vivo* fluorescence (Turner Designs fluorometer) from seawater taken through a PVC fitting in the ship's bow at ca. 4 meters depth, with the instruments mounted in the bow bubble. Transit time from the bow fitting to the sensors was less than 20 seconds, with flow rates adjusted for 4 l min^{-1}. Sensors were polled at 3-second intervals and voltages recorded on the ship's computer (VAX) system. The sensors were calibrated with salinity and pigment samples taken at periodic intervals. Individual salinity samples were collected and analyzed by means of an Autosal salinometer. At selected stations discrete samples were taken with Go-Flo bottles mounted on the Neil Brown package at selected depths. Each survey period consisted of CTD profiles, from either a Neil Brown Mk III CTD or a hand-lowered Sea Bird Instruments Seacat, run on transects in three general areas.

On each cruise an initial survey was run about the Mississippi River delta to document the mesoscale variation in salinity. The second area surveyed was selected on the basis of the distribution of bottom hypoxic waters in July 1991 (courtesy of N. Rabalais) and spanned the area bordered by 89.5°W to 92.0°W, and 28.3°N to 29°N. A third region, encompassing stations over the Slope, covered the region between 91°W to 90°W and 28.5° to 27.5°N. The surveys were interspersed with anchor stations located near the mouth of Southwest Pass (28°54.7'N, 89°29.4'W) and in Shelf waters further west (28°53.2'N, 89°56.1'W). During each cruise a drifting instrument package was also deployed in the "plume" region to the west of Southwest Pass, and on the Shelf, west of 90°W (Fig. 1).

Nutrients were measured by means of automated techniques with a Technicon AAII. The techniques described in Whitledge *et al.* (1981) were employed, with all analyses conducted onboard during the cruises. The analytical methods are based upon those of Murphy and Riley (1962) for PO_4^{3-} and Armstrong *et al.* (1977) for SiO_3^- and NO_3^-. The NH_4^+ analyses were run according to the phenolhypochlorite method adapted for automated techniques by Slawyk and MacIssac (1972).

Pigments, as chlorophyll *a* and phaeopigment *a*, were assayed in duplicate on particulate matter filtered onto Whatman GF/F filters at a reduced vacuum (< 50 mm). The individual filters were placed into 5 ml of a DMSO:acetone (60:40) solution and extracted in the dark for one hour before the samples were centrifuged. The fluorescence was then recorded before and after acidification on a Turner Designs fluorometer with a red-sensitive photomultiplier. The methodology was based upon that of Holm-Hansen *et al.* (1965) with the machine calibrated by Sigma chlorophyll *a*. An examination of the chlorophyll *a* stock solution by means of HPLC revealed the material was essentially pure chlorophyll *a* with no detectable phaeopigments (courtesy of Dr. G. Kleppel). For the flow-through system in the bow, discrete pigment samples were

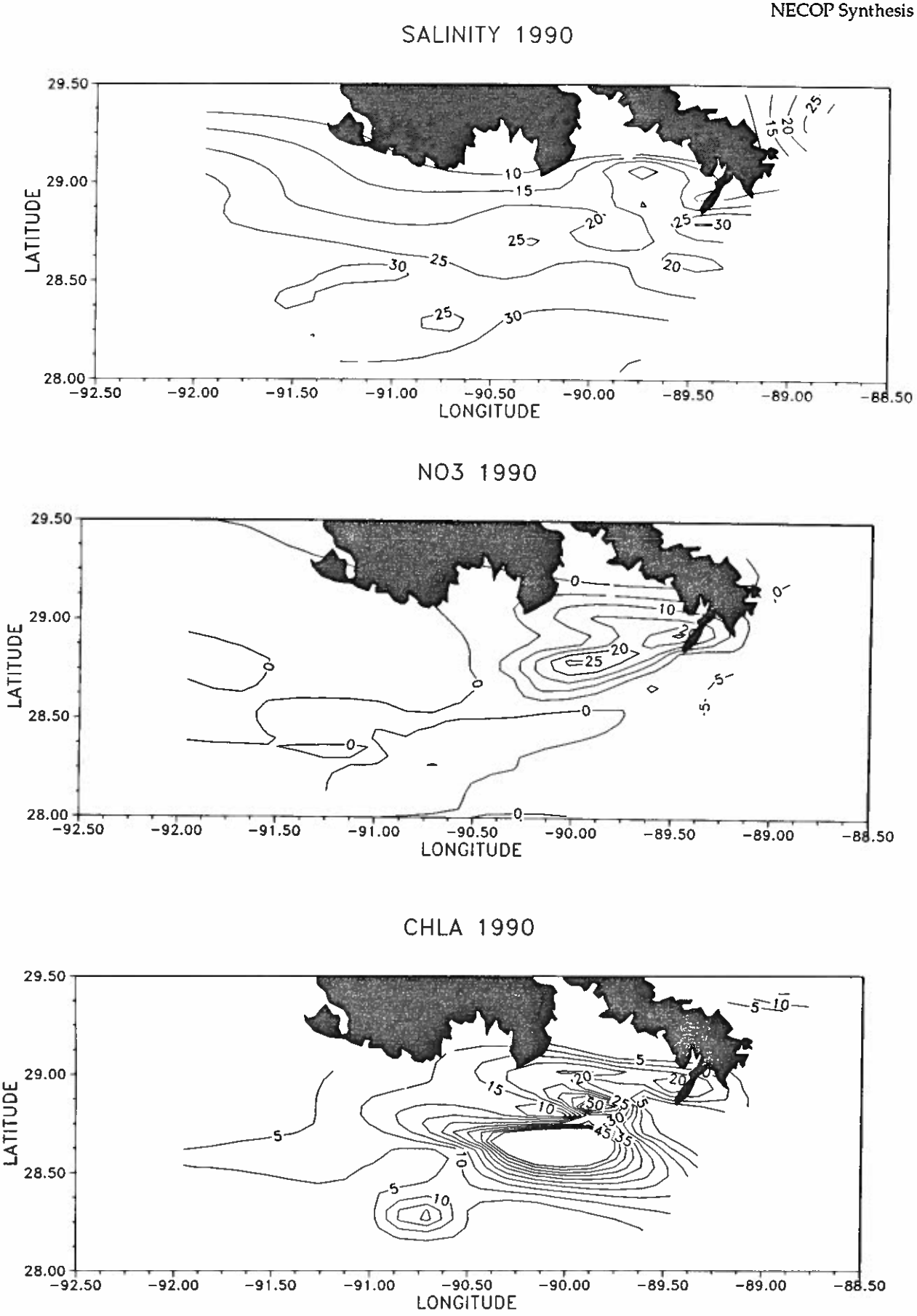

Figure 2. Surface distribution of salinity (psu), nitrate (μM) and total chlorophyll *a* (μg l^{-1}) from 89 discrete stations on the Louisiana Shelf. Data collected during the Summer1990 N/S *BALDRIGE* cruise and contoured with a "smoothing spline" routine.

taken periodically with the corresponding fluorescence values recorded (scale, door factor).

Drifter Studies — A surface instrumentation package provided records of the temporal variation in nitrate and chl *a* fluorescence as the package transited the plume and hypoxic regions. The package was constructed of epoxy-coated metal and four plastic floats. A set of two Vertex sediment trap arrays were attached to the float at 5 and 15 m (see Lohrenz *et al.* this volume). The float was tracked by recording range and bearing at 15- to 30-minute intervals relative to the ship position. A strobe light and radar reflector aided tracking. CTD profiles were conducted within 100 meters of the float at various times to ascertain changes in subsurface properties.

Nitrate was measured *in situ* by a newly developed chemical analyzer employing wet chemistry (Whitledge and Liljestrand, in press). The sample rate and data storage was controlled by a Tattletale model 6 microprocessor system, which is programmed in Basic. The instrument was programmed to collect samples (6 hour^{-1}) and periodically insert standards (1 hour^{-1}), with a prelaunch calibration of five standard concentrations run to determine initial chemical factors. The internal standards run during the deployment were used to correct for any baseline drift. Reagents and standards were contained in sterile plasma bags in sufficient quantity for five to seven days' operation. Power was provided by D cells (later from sealed 6V lead/acid batteries) that could operate the system for two weeks. The detection level for nitrate was about 0.2 μmole l^{-1}, with an operational range of 0.2 to 200 μmole l^{-1}.

Results

Surface Distributions — The distribution of surface properties west of Southwest Pass was examined by contouring salinity, nitrate and total chlorophyll *a* (sum of chlorophyll and phaeopigment *a* from extracted samples). The contouring scheme is based upon the "smoothing spline" approach (Wahba and Wendelberger, 1980) and developed at AOML by J. Festa and C. Thacker. For the Summer 1990 cruise a total of 89 discrete observations were used to derive surface contour plots, while in the Spring 1991 cruise 68 discrete points were used. The surface distributions present an integrated set of observations over the course of approximately two to three weeks, and are, therefore, not synoptic. They are intended to show the broad distributions of surface properties.

In 1990 discharge rates from the Mississippi River were high, reflecting intense summer rainfall in the watershed. The surface salinity distribution over the study region revealed that surface isohalines paralleled the coast, with the 20 psu isohaline extending northwest of the mouth of Southwest Pass (Fig. 2). Further offshore the 25 psu isohaline tended northwest, with surface waters >30 psu generally south of 28°30'N. Surface distributions of both nitrate and silicate, however, showed that the highest concentrations occurred west of the Southwest Pass. Relatively high surface concentrations of nitrate (>20 μM) were at 90.3°W and north of 28.50°N (Fig. 2). Highest silicate concentrations, in contrast, were limited to the region within 30 km of the Delta (not shown). The influence of the Mississippi River discharge from the Delta was also clearly evident east of Southwest Pass. At a station near the mouth of Pass a Loutre (29.21°N, 89.88°W), for example, surface salinity was ca. 3 psu, while both surface nitrate (>70 μM) and silicate (>60 μM) concentrations were high.

The surface distribution of extracted Chl *a* indicated that a relatively large area, southwest of the region of highest nitrate and silicate, was characterized by high pigment concentrations. The surface map of total chlorophyll *a* contained a localized maxima (>40 μg l^{-1}) centered near 28.9°N, 89.9°W to the north of the highest nitrate concentrations. A larger area existed south of the nitrate maximum, between 28.5° and 28.65°N, 89.8° and 90.5°W. Highest concentrations wihtin this area were 75 μg l^{-1}. Surface pigment concentrations decreased to the west. Along a line of stations at 92°W, for example, surface concentrations ranged from 1 to 5 μg l^{-1}. In general, however, the highest pigment values occurred about the region of highest nitrate concentrations.

Surface properties in the spring of 1991 suggest that while the low salinity waters emanating from Southwest Pass were more well-defined than in the summer of 1990, corresponding gradients in surface nutrients and pigments were weaker. The salinity distribution in the spring clearly showed the low salinity plume, with a tongue of surface water <25 psu extending west from the mouth of Sothwest Pass to 90°W (Fig. 3). The highest surface nitrate values generally coincided with the distribution of surface waters <25 psu. The highest nitrate concentration was found at the mouth of Southwest Pass, 74 μM, while the seasonal maximum in surface silicate, 48.1 μM, was observed just north of the mouth. As in the summer, the highest silicate concentrations tended to be restricted about the Delta.

The surface pigment distribution in the spring of 1991 differed from that found in the previous summer in terms of both the magnitude of the pigment biomass and spatial distribution. The highest surface pigment concentration observed in spring 1991 (31.9 μg l^{-1}) was almost half the summer maximum. The spatial distribution of highest pigment concentrations (>5 μg l^{-1}) encompassed a smaller area than that in August 1990 (cf. Fig 2, 3). The spring pigment distribution, however, was similar to that in the summer in that the maximum was displaced south of the highest surface nitrate concentrations.

Anchor Station and Drifter Observations — While the mesoscale distributions of surface salinity, nitrate and pigment serves to delineate the shelf area directly influenced by the low salinity plume, the non-synoptic surface maps obscure a high degree of short-term variability in the surface properties. The temporal variation in surface hydrographic properties on July

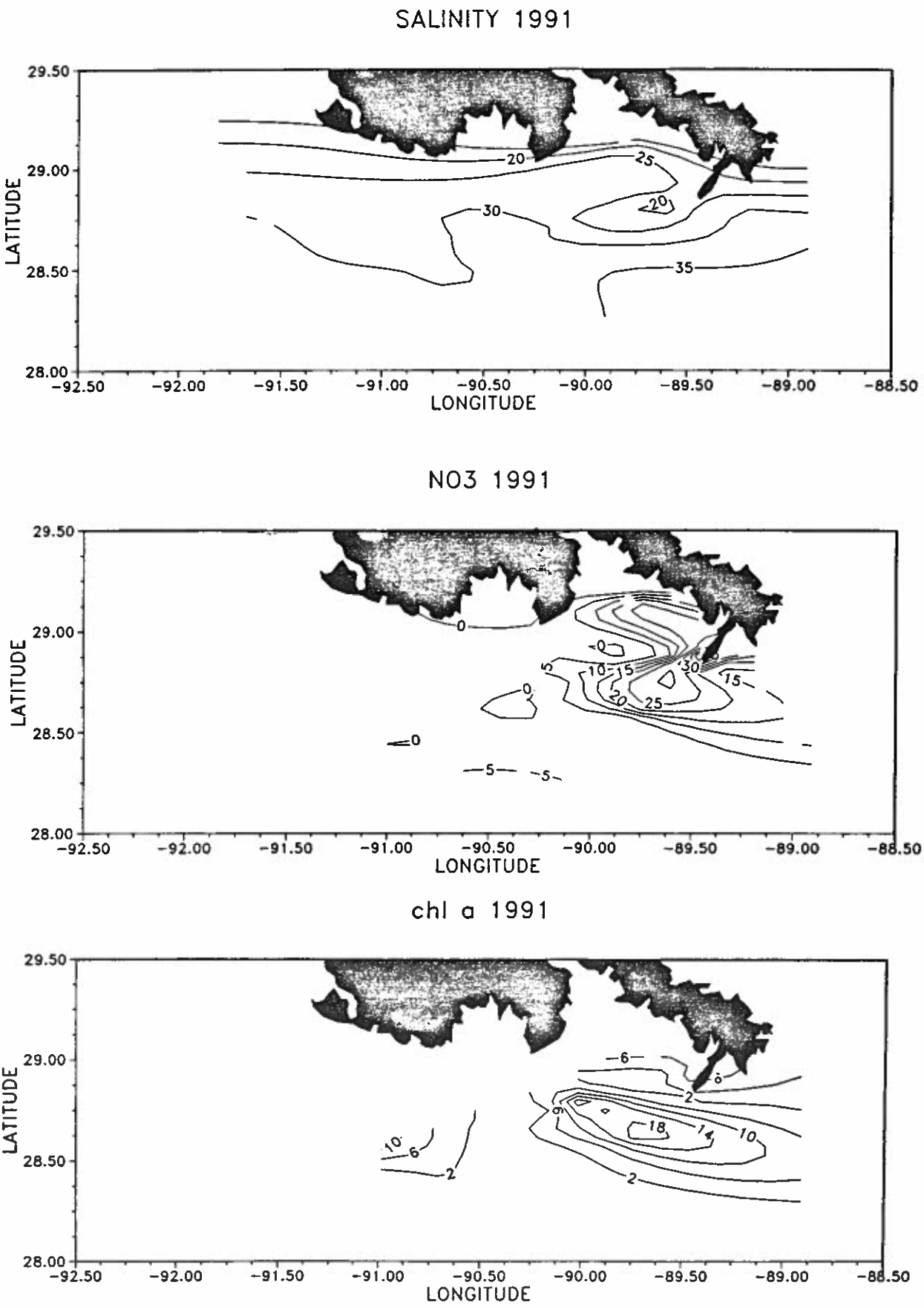

Figure 3. Surface distributions of salinity (psu), nitrate (μM) and total chlorophyll *a* (μg l^{-1}) from 68 discrete stations on the Louisiana Shelf. Data collected during the Spring 1991 N/S *BALDRIGE* cruise. Contouring as in Fig. 2.

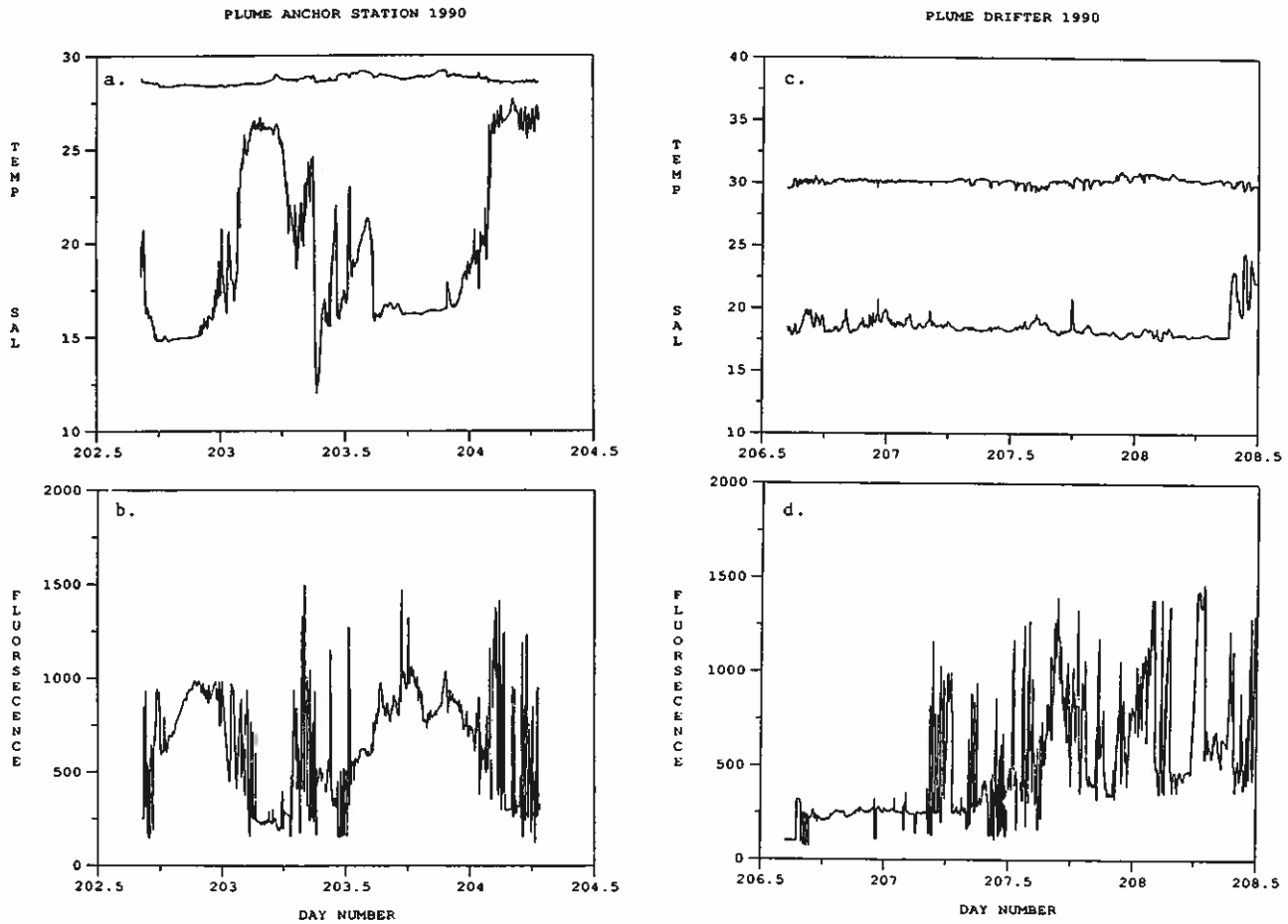

Figure 4. Temporal record of salinity, temperature (a) and relative fluorescence (b) from continuous flow system while at anchor at the "plume" station, July 21-23, 1990. Record of salinity, temperature (c) and relative fluorescence (d) while following the drifter in the plume, July 25-27, 1990. See Fig. 1 for position of anchor stations, drifter trajectory.

21-23, 1990, at the "plume" anchor (28.91 °N, 89.49 °W), 6.7 km west of Southwest Pass, shows that over two days near-surface salinity values ranged from <15 to >25 psu in time periods of less than six hours (Fig. 4a). Relatively less variation was evident in the surface temperature record, as the plume and shelf waters were uniformly warm. Relatively constant periods of salinity minima or or maxima extended at the anchor station for five to seven hours. Individual nitrate samples taken from the bow bubble at these times ranged from 8 µM to >40 µM.

Chl *a* fluorescence exhibited two distinct trends; a diel periodicity with a maximum near local noon, and periods of extreme short-term (3- to 10-minute) variability when the surface salinity altered from one extreme to another (Fig. 4b). These periods of 'higher frequency' salinity and fluorescence variations coincided with the passage of the low-salinity plume by the ship. This passage was also evident in the passage of the surface water optical front, as recorded by the bridge watch.

Although the motion of the plume has a major influence on the magnitude and temporal variation of surface properties near Southwest Pass, the temporal record of surface properties sampled within the plume exhibited less variability. During the deployment of the surface instrument drifter in July 1990, for example, the surface temperature remainded relatively constant over the course of nearly 48 hours (Fig. 4c). Surface salinity values also exhibited little variation during the initial 36 hours of deployment, increasing only towards the final hours as the float transited towards the western end of the highly turbid, low-salinity surface lens.

During the first 12 hours of deployment chlorophyll *a* fluorescence also exhibited relatively less temporal variation than at the anchor station (Fig. 4d). Thereafter, chlorophyll *a* fluorescence gradually increased, although shorter-term variations (3 to 30 minutes) effectively masked the longer term increase in pigment fluorescence as the instrument package drifted south and west, into the region of higher surface pigemnt concentrations. The discrete, extracted pigment samples taken while following the surface drifter revealed that surface concentrations increased from ca. 10 to >60 µg l^{-1} as the float drifted west. Thus the time-dependent increase in pigment observed within the plume confirms the mesoscale surface distribution (e.g., Fig. 2).

In contrast to the high degree of variability in sur-

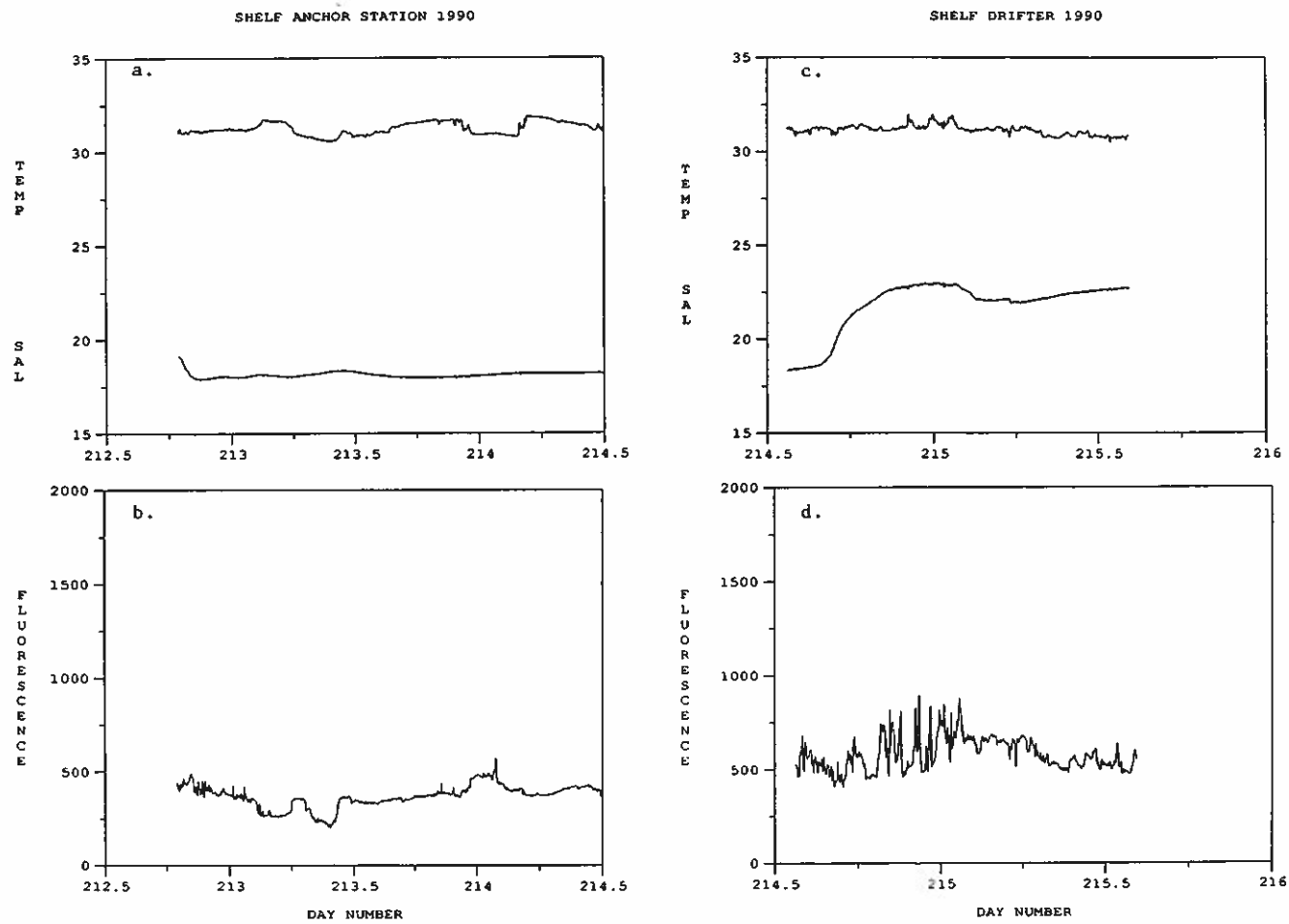

Figure 5. Temporal record of salinity, temperature (a) and relative fluorescence (b) from continuous flow system while at anchor at the "shelf" station, July 30-August 2, 1990. Record of salinity, temperature (c) and relative fluorescence (d) while following the drifter on the shelf, August 2-3, 1990. See Fig. 1 for position of anchor stations, drifter trajectory.

face properties near the mouth of Southwest Pass, there was less temporal variation in surface parameters on the shelf, near hypoxic bottom waters. During the summer, 1990 shelf anchor station, for example, temperature ranged from ca. 30° to 31 °C, while salinity remained <20 psu over 40 hours (Fig. 5a). There was also relatively less variation in the chl *a* fluorescence on the shelf than in the "plume" region, with fluorescence values at the shelf station spanning a two-fold range (Fig. 5b). During the shelf drifter deployment surface temperature ranged from 31° to 32°C. The surface salinity pattern during the drifter deployment increased from ca 17 psu (as the instrument package was launched near the western periphery of the plume), to >22 psu as it transited north, toward the coast (Fig. 5c). After the first 10 hours of deployment, the salinity of surface waters about the drifter was relatively constant. The fluorescence during the drifter deployment increased as the package passed from low to higher salinity waters. However, as in the deployment in the plume region, there was considerable higher-frequency variations with periods on the order of tens of minutes (Fig. 5d).

In Spring 1991 the temporal records of surface salinity and temperature from the anchor station near Southwest Pass, and the subsequent drifter deployment in the plume, exhibited less variability in properties than was seen the previous summer. At the anchor station surface temperatures varied from 23° to 24°C, while salinity ranged from only 17.5 to 18.3 psu over the course of the day-long station (Fig. 6a). During the drifter deployment the surface temperature range was slightly greater (24° to 26°C), probably reflecting the mixing of warmer shelf water with the cooler river water. Salinities were also slightly higher, ranging from 18 to 19 psu (Fig. 6b). However, neither parameter exhibited either the wide range or the short-term variability which was evident in the Summer 1990 records. During the deployment the *in situ* nitrate meter revealed that nitrate concentrations initially started near 18 µM, increased to almost 20 µM and declined to 16 µM within the first eight hours of the deployment (Fig. 7a).

Discussion

The observed patterns in the surface distributions of nitrate and chlorophyll *a* in Summer 1990 and Spring 1991 suggest that there is relatively little variability in spatial distributions of maximum nitrate and pigment on the Louisiana Shelf on a seasonal time scale. The

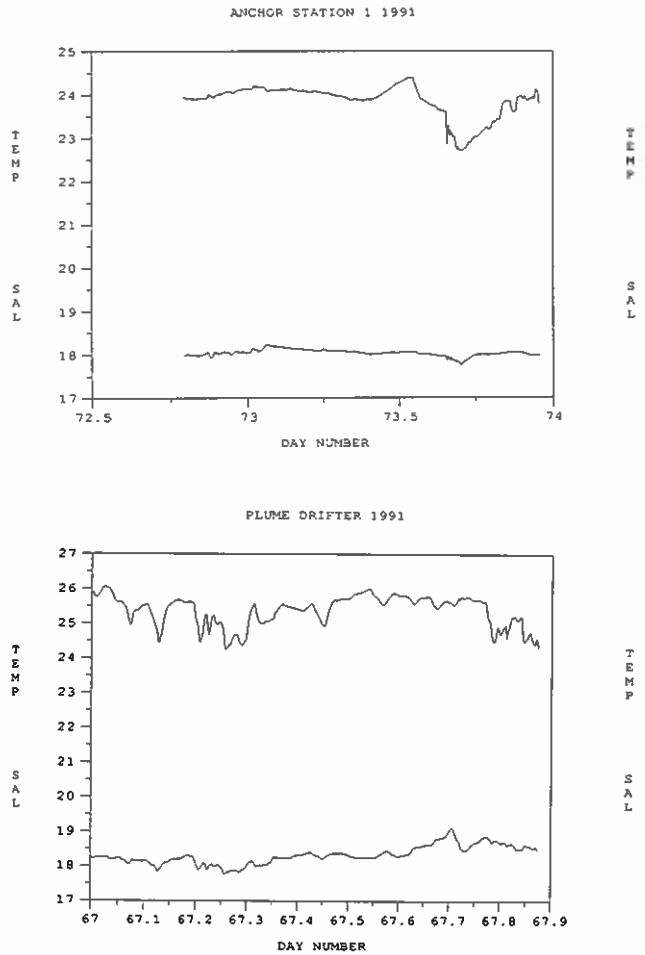

Figure 6. Temporal record of salinity, temperature from continuous flow system at anchor in "plume" waters, April 1991 (a), and following the drifter, April 1991 (b). The computer-based recording system for the fluorometer was inoperable at these times.

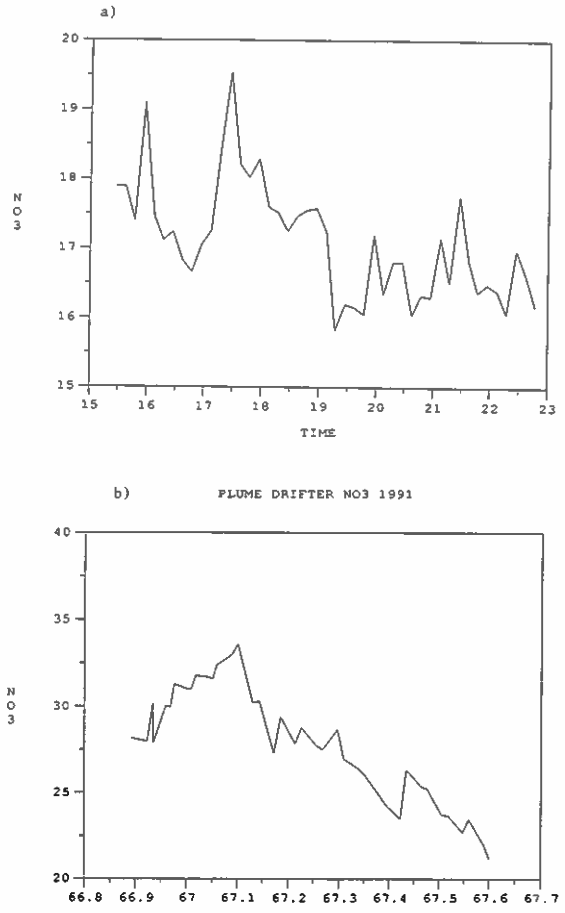

Figure 7. (a) Temporal record of *in situ* nitrate (μmole l^{-1}) at 2 m depth as a function of time (local) while at anchor in plume waters in April 1991. The data corresponds to initial eight hours of the deployment record in Fig. 6a. (b) Temporal record of *in situ* nitrate (μmole l^{-1}) on the near-surface drifter deployed in plume waters in the spring of 1991; x-axis corresponds to decimal Year Days 66 to 67. See text for details.

area over which the highest pigment concentrations were found was consistently "downplume" from that of the highest nitrate concentrations in both seasons. This pattern is consistent with previous observations that the region of highest productivity on the Shelf occurs at the periphery of the plume from Southwest Pass (Lohrenz *et al.*, 1990). As the suspended particulate load in the plume is reduced, phytoplankton productivity increases in response to increased available light. As productivity increases, the nutrient (nitrate) standing stock declines and biomass (as chlorophyll *a*) increases. Hence, the mesoscale patterns in surface nitrate and pigment in both the summer and spring suggest that there is little seasonal variation in this sequence of events in the plume from Southwest Pass.

The observations from the drifter deployments in the plume verify this sequence of events. Nitrate concentrations were observed to increase during the first five hours, then decreased monotonically to ca. 10 μM during the next 10 hours. Smaller-scale variations (Fig. 7b) were also noted in the nitrate record, which is probably related to the variable dispersive nature of the freshwater plume. Pigment concentrations and fluorescence records show an increase over one-to-two-day periods (Fig. 4d). The length of the deployment in Spring 1991 (shortened by a storm event) was, however, too short to reveal a corresponding increase in pigment biomass.

While the mesoscale surface nitrate and pigment distributions were similar in the summer and spring, the surface salinity distributions differed between seasons. This was due, in part, to the short-term (diel) variability in the motion of the surface plume in the summer. The rapid transistion from "shelf" to "plume" salinity signatures within surface waters at the anchor station 7 km west of Southwest Pass in July 1990 readily indicates the time scale over which this surface property can alter. The corresponding temporal change in pigment fluorescence suggests that optical properties can also vary on these time scales. The periodicity (ca. a day) in the salinity record at the anchor station and the "cyclic" motion of the drifting instrument package over each 24-hour period (Fig. 1) indicates that forcings on these time scales (inertial, tidal) are

mechanisms mediating the observed variability in surface property distributions.

Although the motion of the surface drifter reinforces the suggestion that inertial and tidal factors are important factors on the shelf, it is important to recognize that the drifter was not a quasi-Lagrangian device. The sediment trap array extended below the surface layer, across a level of horizontal velocity shear. This design was necessary to combine the measurements of vertical particulate flux, from the sediment traps, with the temporal records of nutrient and pigment changes in the overlying surface layer. Nevertheless, it restricts any interpretation of the drifter trajectory to qualitative observations.

There was less variation in surface properties, particularly salinity, during the spring than during the summer near Southwest Pass. This "limited variability" could have arisen from an absence of motion in the plume, or, alternatively, the plume may have covered a wider area in the spring than in the summer. Hence, the apparent "lack" of diel-scale changes in the position of the plume during the spring could have arisen from the fact that the periphery of the feature did not pass the ship during the course of the anchor station. The motion of the brief drifter deployment in Spring 1991 suggests the cumulative forcings were, as in the summer, similar.

The variability in surface properties in the "hypoxic" region shows that surface waters are less variable, in terms of the temporal variation of temperature, salinity and pigments, than about the plume from Southwest Pass. This generalization was true from the perspective of the anchor station and the drifter in both seasons. Thus while the discharge of the Mississippi River exerts a strong influence on the salinity of coastal waters along the Louisiana-Texas Shelf, the highest degree of variability in surface waters occurs at the fronts of the surface plumes. This relationship may also hold for nutrient utilization: the initial utilization of the "new" nutrients exported to the Shelf from the river appears to occur within the plume. Further west, beyond approximately 75 to 100 km, the influence of the Mississippi River on the shelf ecosystem is likely to be mediated by the recycling of these inorganic nutrient sources. The next objective of our research is to validate or reject this hypothesis by exmaining the individual, submesoscale distributions from individual transects at various locations about the plume and shelf regions.

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Nitrogen uptake and regeneration in surface waters of the Louisiana continental shelf influenced by the Mississippi River

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Abstract

Several lines of evidence have led to the hypotheses that ammonium uptake and regeneration are much higher in waters influenced by the Mississippi River than would be expected for a continental shelf with such a high input of nitrate and that these high rates greatly amplify the impact of the nitrate input on productivity and hypoxia. As a preliminary test of the first hypothesis, some of the data for the Louisiana continental shelf on water column nitrate and ammonium uptake and ammonium regeneration have been compiled. Although nitrate (new production) and ammonium (regenerated production) uptake rates are very high, water column regeneration rates are even higher. Consequently, N availability only occasionally limits productivity in this system and the effect of the riverine nitrogen input is spread out over the entire shelf. In addition, because of the amplification of the effect of riverine N input by water column regeneration, it will take large reductions in riverine input to reduce eutrophication and hypoxia along the Louisiana continental shelf.

The Mississippi and Atchafalaya Rivers supply large amounts of nitrogen to the Louisiana coastal zone, which is thought to be responsible for the high productivity and, perhaps, hypoxia in the region. Most of the nitrogen supplied by the rivers is in the form of nitrate, although the importance of dissolved organic nitrogen and particulate nitrogen cannot be discounted. Much of this "new N" (Dugdale and Goering, 1967) is completely depleted within a short distance of the river mouth, but productivity is high across the entire Louisiana shelf. Several lines of evidence suggest that the high productivity is maintained by nitrogen recycling within the water column.

1. Mass balance calculations of nitrogen on the shelf indicate that N recycles within the surface layer almost four times before it is lost from the system (Turner and Rabalais, 1991). This is twice the usual value for other coastal areas (Harrison et al., 1983).
2. Ammonium concentrations are rarely <1 μM in surface waters (Dortch and Whitledge, in press).
3. The proportion of heterotrophic biomass to total biomass is unusually high on the Louisiana shelf (Dortch, unpubl.), suggesting a high dependence on recycled nutrients.
4. Finally, some preliminary measurements of ammonium uptake and regeneration, both in the coastal zone (Twilley, unpubl.) and in an estuary of the Atchafalaya River (Fourleague Bay; Table 2), were extremely high.

Consequently, it appears that the impact on productivity of the large input of new nitrogen from the river is greatly amplified in the coastal zone by regeneration.

To test this hypothesis nitrate uptake (new production), ammonium uptake (regenerated production), and ammonium regeneration were measured on a shelfwide cruise (LaSER 6, Oct. 23-29, 1990) and in the spring (February-March 1991) at one station in the core of the hypoxic zone (Station C6B). On the monthly cruises size-fractionated (>20, 3-20, and <3 μm) nitrate and ammonium uptake were also measured. Although the data are not reported here, the work has been continued with an additional shelf-wide cruise (July, 1991) and monthly sampling through September 1991.

Methods

^{15}N-nitrate and ^{15}N-ammonium were added to water samples, which were incubated under simulated *in situ* conditions for up to four hours around noon (Dugdale and Goering, 1967; Glibert *et al.*, 1982). On samples taken at time intervals, the ratio of ^{14}N/^{15}N in the particulate and dissolved phases was measured by emission spectroscopy (Lipschultz, 1984). Uptake and regeneration were calculated according to Harrison and Harris (1986). Nutrient concentrations were measured with an Alpkem RFA-2 Nutrient Analyzer. Chlorophyll concentrations were measured fluorometrically, after extraction with 40:60 (by volume) dimethyl sulfoxide:acetone (Lohrenz *et al.*, 1990).

Acknowledgements

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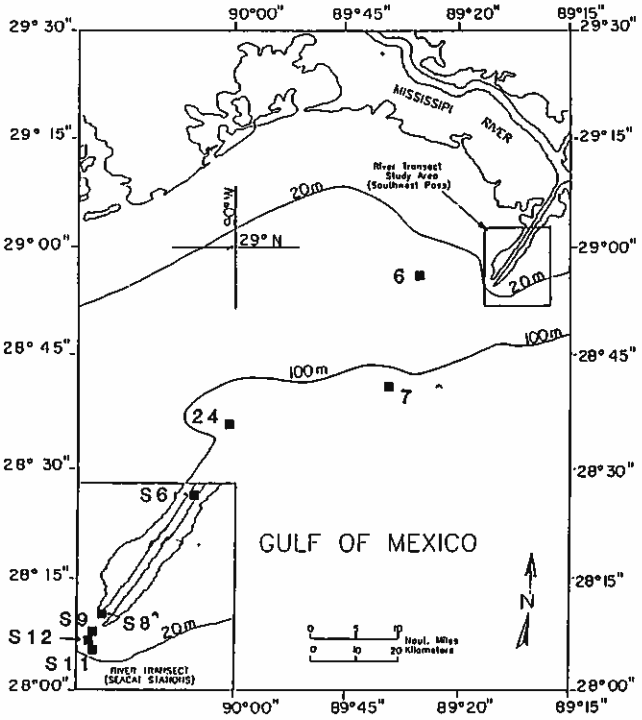


Figure 1. Station locations off the Louisiana coast, October 23-29, 1990.

Results and Discussion

Spatial Variation in Nitrogen Uptake and Regeneration — Nitrate and ammonium uptake and ammonium regeneration was measured at nine stations (Fig. 1) along a salinity gradient starting in the channel of the Mississippi River. It was necessary to start within the river because of the low river flow. Nitrate was depleted within 32 km of the river mouth, but ammonium concentrations ranged between 0.4 and 3.6 µM (Fig. 2). The chlorophyll concentration reached a peak before the nitrate was depleted and, then, showed a sharp drop. This pattern is quite typical of the outflow of the Mississippi River, although the salinity at which the peak chlorophyll is reached and the nitrate is depleted is variable with season (Lohrenz et *al.*, 1990; Dortch and Whitledge, in press).

Nitrate uptake (Fig. 2) was highest in the zone where the biomass maximum develops and the nitrate is depleted, which indicates that high biomass is associated with nitrate utilization. Ammonium uptake (Fig. 2) rates were high at all locations, but maximal in the biomass maximum.

Ammonium regeneration rates (Fig. 2) were extremely high and exceeded uptake rates by an order of magnitude. They were highest at high salinities.

Seasonal Variation in Nitrogen Uptake and Regeneration Rates — The data from three experiments conducted at station C6B in February and March 1991 are compared with that from the three experiments at similar salinities from the October 1991 shelfwide cruises (Table 1). Both nitrate and ammonium uptake were higher in the spring than in the fall, despite the

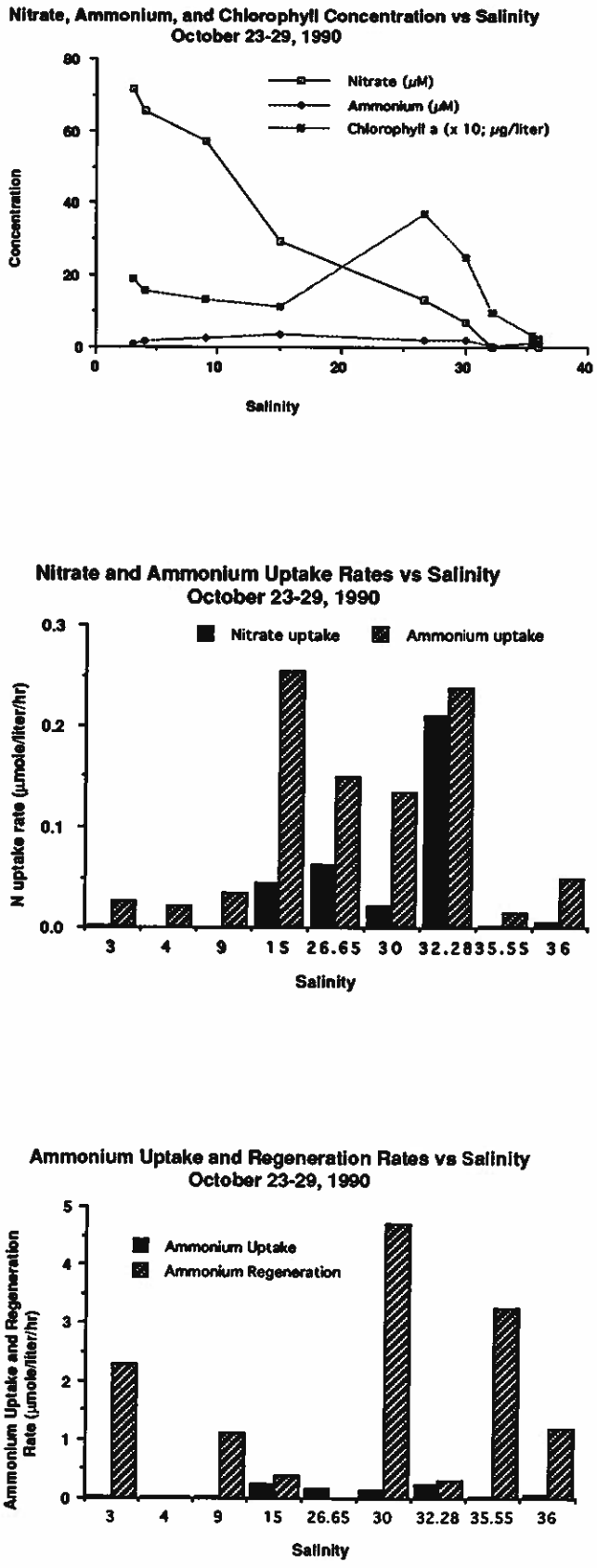
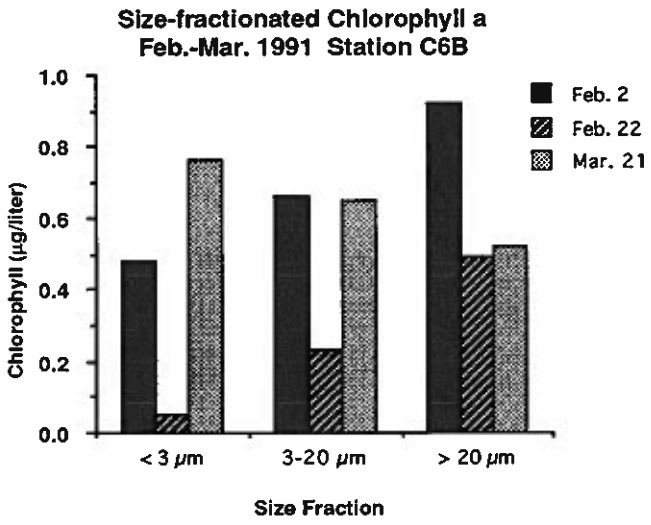
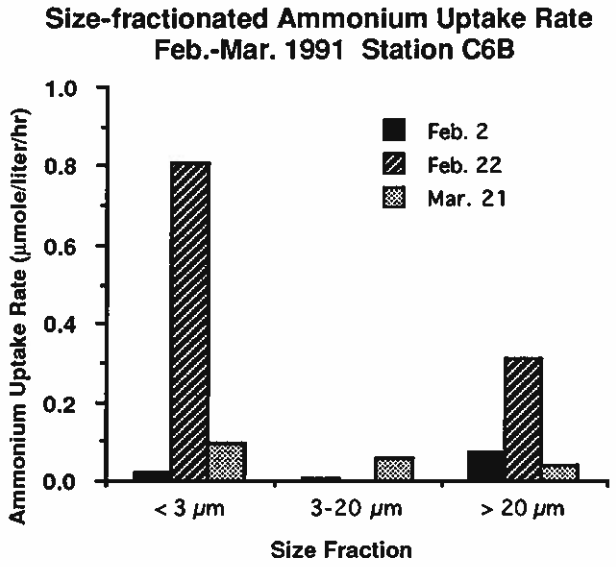


Figure 2. Nitrate, ammonium, and chlorophyll concentrations, and nitrate uptake, ammonium uptake, and ammonium regeneration rates along a salinity gradient from the Mississippi River, October 23-29, 1990.





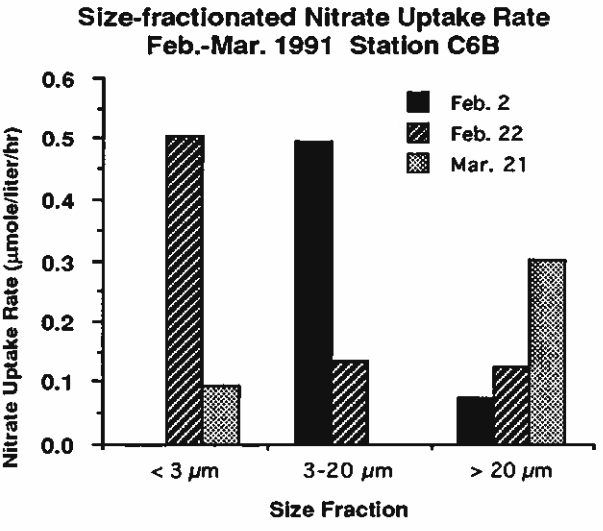


Figure 3. Size-fractionated chlorophyll a concentrations and nitrate and ammonium uptake rates in the spring at Station C6B in the core of the hypoxic region on the Louisiana shelf.

higher biomass, and similar nitrogen concentrations, in the fall. However, ammonium regeneration was much higher in the fall than in the spring.

The f ratio, which is the ratio of nitrate uptake/total nitrogen uptake, is used as an indication of reliance on "new" vs. "regenerated" ammonium or as an indicator of "new" vs. "regenerated" production (Eppley and Peterson, 1979). The f ratio was much lower in the fall than in the spring, but in general it was low. This indicates that despite the high input of nitrate, the system is highly dependent on ammonium and regeneration.

Effect of Size on Nitrogen Uptake — It is generally believed that nitrate is taken up preferentially by large phytoplankton and ammonium is taken up by small phytoplankton and bacteria (e.g., Glibert et *al.*, 1982; Harrison *et al.*, 1983; Harrison and Wood, 1988; Kokkinakis and Wheeler, 1988). Thus, small phytoplankton are usually associated with a system dependent on regeneration. Such a pattern was not observed in the spring at a single station in the core of the hypoxic region (Fig. 3). However, these studies have been continued monthly through September and a clearer pattern is expected to emerge. In spring 1990, there were relatively low concentrations of small phytoplankton and high concentrations of large phytoplankton, whereas by fall the small phytoplankton were several orders of magnitude more numerous and large ones had decreased significantly (Dortch et *al.*, this volume).

Comparison of Regeneration Rates in Different Environments — The most significant result of these experiments is the very high regeneration rates that were obtained. When they are compared with those from other regions, they are among the highest values observed (Table 2). The only higher water column values were obtained in an estuary of the Atchafalaya River, Fourleague Bay. This explains why ammonium concentrations remain high through much of the region and why N limitation is only occasionally observed (Dortch and Whitledge, in press).

Conclusion

Nitrate and ammonium uptake rates are high along the Louisiana continental shelf, but ammonium regeneration rates are even higher. The effect of the high riverine nitrate input on primary production is greatly amplified by the extraordinarily high rates of ammonium regeneration. As a result, nitrogen should limit productivity in this system only at the highest salinities. Furthermore, it will take large reductions in riverine N input to alter the course of eutrophication along the Louisiana continental shelf substantially.

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Table 1. Seasonal variation in nitrogen uptake and regeneration.

Season	Nitrate Uptake Rate (µmol/l/hr)	Ammonium Uptake Rate (µmol/l/hr)	f Ratio	Ammonium Regeneration Rate (µmol/l/hr)	Nitrate (µM)	Ammonium (µM)	Chlorophyll (µg/l)
Spring, 1991*	0.580	0.470	0.35	0.070	16.80	1.26	1.59
Fall, 1990**	0.043	0.180	0.19	1.700	16.44	2.48	2.44

*Data from February and March size-fractionation experiments
**Data from three stations from Fall 1990 whose salinities bracket those of spring, 1991

Table 2. Comparison of ammonium regeneration rates from different areas. Adapted from Rivera-Monroy 1988.

Environment	Location	Rate (µmol/liter/hr)	Reference
Lakes	Smith Lake	0.09-4.8	Alexander, 1970
	Ace Lake	0-4.8	Alexander, 1970
	Castle Lake	0.004-0.037	Axler *et al.*, 1981
	Lake Calado, Brasil	0.58-2.0	Morrisey and Fisher, 1988
Estuary	Chesapeake Bay, USA	0.11-1.95	Glibert *et al.*, 1982
	Oslofjord, Norway	0.012-0.061	Paasche and Kristiansen, 1982
	Delaware River, USA	0.15-0.34	Lipschultz *et al.*, 1985
	Estuaries	0.009-3.9	Fisher, unpubl. from Morrisey and Fisher, 1988
	Fourleague Bay, USA	0.1-15.7	Rivera-Monroy, 1988
Coastal Waters	**Louisiana continental shelf**	**0.030-4.702**	**This Study**
	Vineyard Sound, USA	0-0.31	Glibert, 1982
	Continental shelf, southeastern USA	0.060-0.723	Hanson and Robertson, 1988
	Bedford Basin, Canada	0.056	La Roche, 1983
	Southern California Bight, USA	0.0006-0.0091	Harrison, 1978
	Middle Atlantic Bight, USA	0.008-0.029	Harrison *et al.*, 1983
	Davies Reef, Australia	0.00013-0.0112	Hopkinson *et al.*, 1987
Open Ocean	Sargasso Sea	0.0020-0.0646	Glibert *et al.*, 1982
	subartic Pacific	0.0023-0.0193	Wheeler and Kokinakis, 1990

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Dissolved organic nitrogen distribution and transport in the continental shelf of the northwest Gulf of Mexico

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Abstract

As part of NOAA's NECOP program, dissolved organic nitrogen (DON) concentrations were measured in the Mississippi-Atchafalaya plume region and in two transects across the Texas and Louisiana shelf in July, 1990. Measurements by high-temperature combustion and chemiluminescent detection showed that DON became the dominant dissolved nitrogen species in the river-ocean mixing zone. Furthermore, DON (advected from the river and generated *in situ*) was the principal nitrogen species transported by the westward-drifting low-salinity plume.

At the plume region, DON concentrations varied from 12 to 50 μM N. Over the Texas-Louisiana shelf, the average DON concentration inside the plume (< 36 ppt) was 9.7 μM N, whereas the mean DON concentration in oceanic shelf water was 5.5 μM N. Unit DON stocks were similar for both shelf transects, although the relative content of DON carried by low-salinity (<32 ppt) upper water compared to the total DON in the plume was greater in the transect farthest away from the source water. This difference can be accounted for by intrinsic DON contents of the plume at different times of formation, by *in situ* DON cycling within the westward-drifting plume, or by diffusive mixing of plume waters with adjacent oceanic water.

A net advection of DON nitrogen exists along the NW Gulf of Mexico's continental shelf, which can account for the transport of an important fraction of nitrogen derived from the Mississippi River. Questions remain as to the nature and lability of these DON compounds, and, thus, its influence to the shelf's primary production.

The Mississippi-Atchafalaya River (MAR) contributes about two-thirds of the annual freshwater input into the Gulf of Mexico (Moody, 1967) and has an estimated average nitrogen loading of 1.3×10^{11} g N/y (Turner and Rabalais, 1991). In spite of this large nitrogen loading, the observed riverine nutrient signature disappears at the freshwater and ocean water mixing zone within a few miles from the outflow (e.g., Dagg, 1988; Lohrenz *et al.*, 1990; Turner and Rabalais, 1991). A major objective of the NECOP program is thus to trace the cycling, transport and fate of these riverine nutrients.

The impact of MAR nutrient load on the adjacent shelf's production is evident. Productivity is two to three times greater within the plume compared to the adjacent surface shelf waters (4 to 5 *vs* < 2 g C/m^2/d; Lohrenz *et al.*, 1990). There is evidence that nutrient inputs from MAR have been increasing, most likely as a result of anthropogenic activity (e.g., from fertilizers and sewage). For example, a doubling in NO_3 concentration has been observed during the last 50 years compared with the first half of the century (Turner and Rabalais, 1991). Seasonal hypoxic events, which intensify during summer water stratification, have been connected with an increase in biogenic particulate matter generated in the nutrient-rich plume's mixing zone. The degradation of this organic matter eventually depletes oxygen concentrations below the pycnocline (Rabalais *et al.*, 1991).

Owing to reported values of dissolved organic nitrogen (DON) of up to 40 μM N in Pacific Ocean surface waters (Suzuki *et al.*, 1985), the interest in DON standing stocks and DON cycling has been revived. Earlier estimates for coastal and oceanic waters range from 5 to 10 μM N (Sharp, 1983; Walsh, 1989). Analyses with different techniques show that *ca* 10 to 20 percent of the total DON pool has been identified (Sharp, 1983). Characterized labile compounds (*e.g.*, those readily determined by biochemical methods) include dissolved free amino acids (0.04-2.2 μM N), dissolved combined amino acids (3 times higher than the free forms), urea (0.1-1.0 μM N), dissolved DNA, vitamins, and amino sugars (Sharp, 1983). Jackson and Williams (1985) demonstrated that if DON is taken into account, the dissolved nitrogen to phosphorus ratio of oceanic surface waters increases and approaches the Redfield ratio, and concluded that DON should be a nitrogen source in oligotrophic waters. It follows that DON is an important nitrogen reservoir which needs to be considered in studies of ocean and coastal nitrogen cycling.

The distribution of DON in the Mississippi-Atchafalaya plume (MAP) region and in two transects

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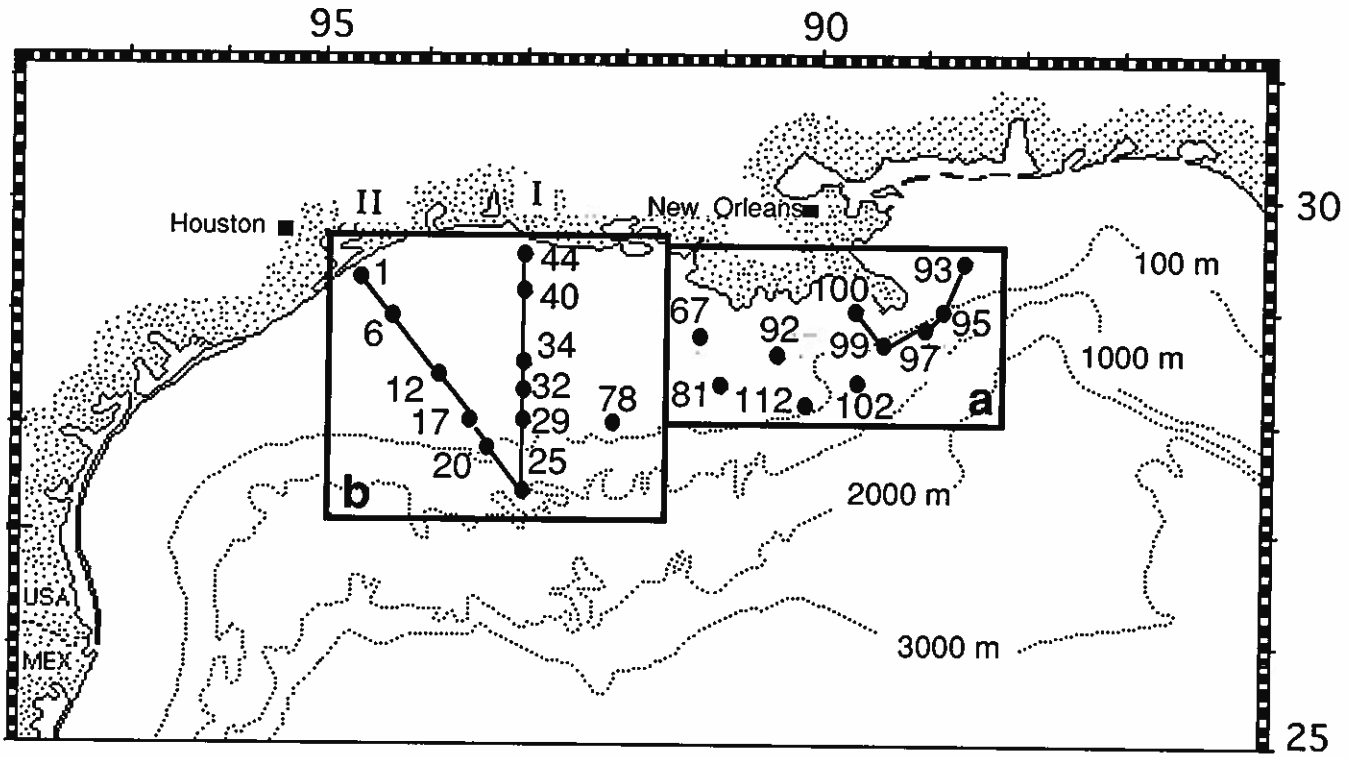

Fig 1. Station position for Cruise 90G-10, July 11-25, 1990. (a): MAP sampling region (east of 92°W); (b): Texas and Louisiana sampling region (I: Midshelf Transect; II: Galveston Transect). Only those stations with DON data are shown, but other stations within the transect lines were also used for contour maps and scatter-plots.

perpendicular to the Louisiana and Texas continental shelf are documented for the summer of 1990. DON concentrations are then compared to other nitrogen reservoirs in the water column, and it is shown that this is the most important nitrogen species transported from the MAP region in the westward-flowing plume. Estimates of DON transport are given, and the possible causes of the different unit DON stocks at the two Louisiana and Texas shelf transects are discussed.

Methods

Cruise 90G-10 of Texas A&M University, in collaboration with NOAA and the Texas Sea Grant Program and within the context of the NECOP program, surveyed the MAP region and the Louisiana-Texas continental shelf in July 1990 (Fig 1). This cruise represented an intensive sampling effort since 113 stations were surveyed over the shelf, giving a relatively high resolution in both spatial (*ca* 10 nmi horizontal; 5-10 m vertical) and temporal (two-week sampling period) dimensions for the analysis of the distribution of physical and nutrient parameters (Texas A&M University, 1990).

The DON data presented in this paper was obtained at 22 stations distributed in three regions (refer to Texas A&M University, 1990): Galveston Transect (stations 1-25) along a NW-SE heading from Galveston Bay to the upper slope (27°18'N, 93°00'W); Midshelf Transect (stations 25-44) along 93°00'W, in E Louisiana; and the MAP region, between longitudes 91°30'W and 88°30'W which includes NECOP'S study area (stations 67-112).

Salinity and temperature profiles were measured with a Seabird SBE-09 conductivity-temperature-depth profiler (CTD); bottle salinity samples were also obtained at discrete depths and analyzed on board. Samples for nutrients were taken from Niskin bottles every 5 to 30 m depth and analyzed on-board with a Technicon AA-II auto-analyzer (Biggs *et al.* 1982). Particulate organic nitrogen (PON) was sampled by vacuum-filtering 1 L of seawater through a 25 mm GF/F filter (heated at 450°C for 2 h). The filters were oven-dried for 24 h at 60°C and stored in a vacuum desiccator prior to analysis. Samples were analyzed on a Carlo-Erba NA1400 CNS analyzer.

Stations that included DON measurements had an average spacing of 30 nmi between them at Midshelf and Galveston Transects and a shorter horizontal separation at the MAP region. Samples were obtained from Niskin bottles at near-surface, near-bottom, and at several intermediate depths in the water column. Some surface samples were also obtained by pumping water directly to the ship's laboratory. The samples were filtered through 25 mm GF/F filters (heated at 450°C for 2 h). The filtrate was placed in ampules, sealed, frozen immediately, and stored at -20°C prior to analysis.

DON was measured with a modified Shimadzu TOC-5000 high-temperature combustion (HTC) analyzer coupled to an ANTEK-720 chemiluminescent

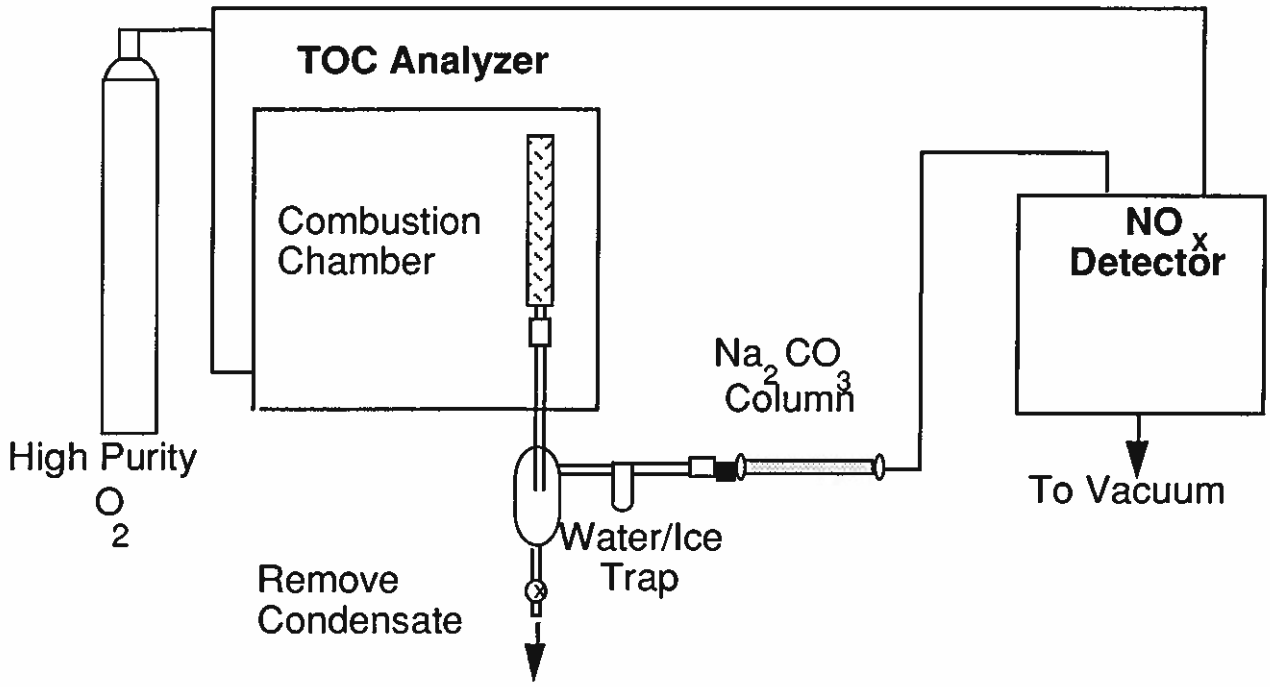

Fig 2. Instrumentation used for DON analysis. The sample is injected into the high-temperature combustion chamber of a total organic carbon (TOC) analyzer where it is combusted to oxides of nitrogen. Vapor is removed in a water trap and a sodium carbonate column, and the oxides are determined by chemiluminescence when reacted with ozone.

detector (Fig 2). 50 µL of sample were injected into the HTC combustion column (alumina support coated with platinum catalyst) using high-purity oxygen as carrier gas. The generated nitrogen oxides (NOx) travel through a purge and trap device similar to that described by Garside (1982). Inside the chemiluminescent detector, NOx reacts with O_3 producing metastable nitrogen dioxide (NO_2*). When the NO_2* relaxes, its chemiluminescence is sensed by a photomultiplier tube. The emitted light is proportional to the concentration of total dissolved nitrogen (TDN: DON plus dissolved inorganic forms) allowing easy quantification. DON was calculated by difference.

All data were corrected with a distilled water blank, which was generally < 1 µM N. The samples were originally calibrated with a urea standard according to Suzuki *et al.* (1985) and later with a nitrate standard following the recommendation of Hopkinson *et al.* (1992). However, samples analyzed using both standards showed no statistical difference between them. This modified HTC method had a high yield for most nitrogen standards (Table 1) and a precision of ±3 to 4 percent was obtained for triplicate runs (of TDN; lower for DON). The instrument responded linearly in the concentration range of the samples.

Results and Discussion

MAP region — The MAP region stations that included DON measurements are shown in Fig 1. The grid of stations for this region consisted of an arc parallel to and 15-30 nmi away from the Mississippi River delta, and it also included shelf and slope stations to the east of 92°W within the fresh and ocean water mixing zone.

Stations forming the arc off the Mississippi outflow

Table 1. Percentage Recovery of Nitrogen Standards, and Comparison with Published Results

Compound	N[1]	Percent Recovery	Cited Recovery[2]
Ammonium	1	96	-
Antipyrine	2	74	100
Caffeine	4	99	98
Quinoline	1	97	102
Sulfathiazole	3	93	38
Thiourea	2	94	98
Urea	2	93	-

[1] N atoms in the molecule
[2] Suzuki *et al.* (1985)

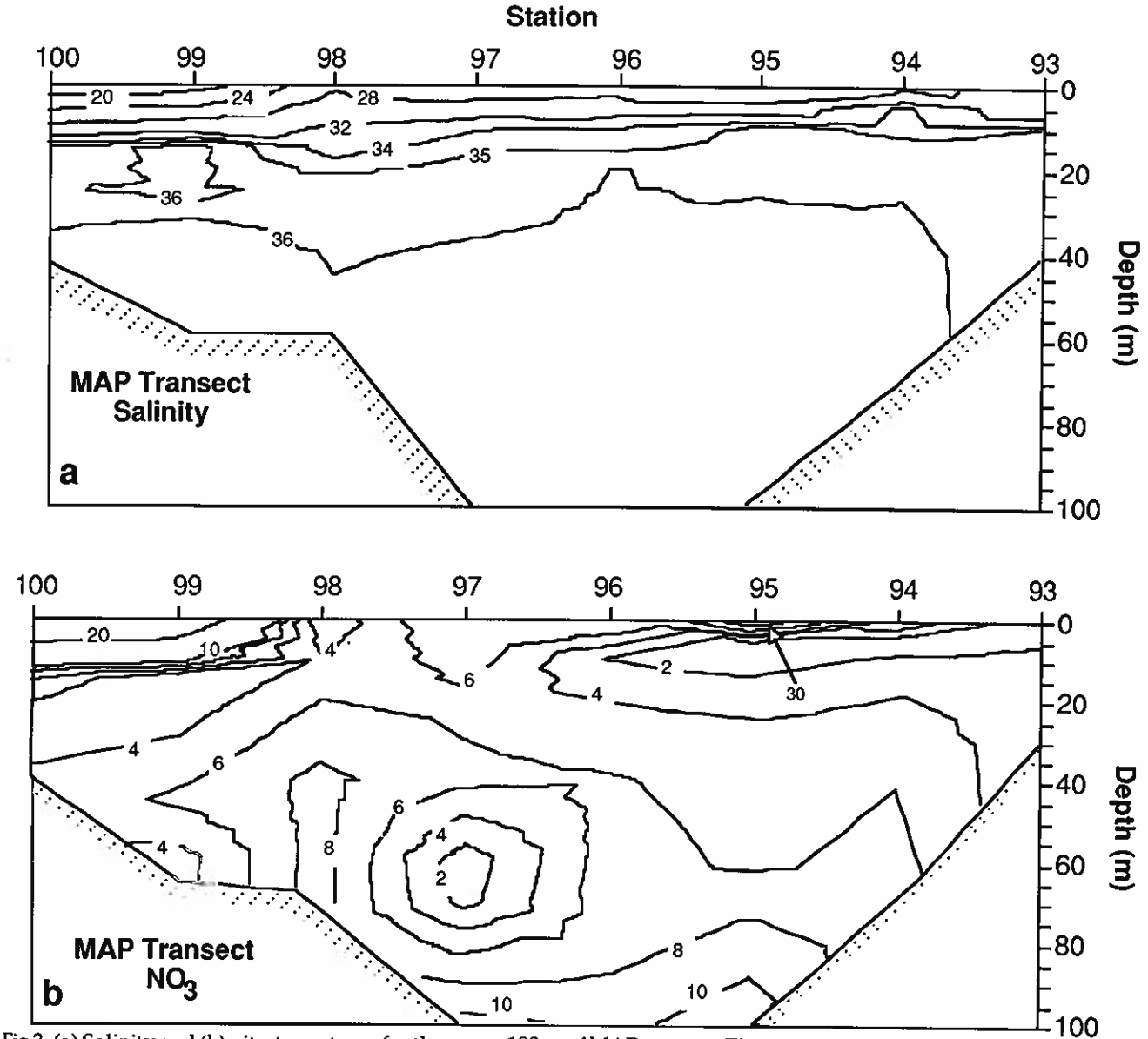

Fig 3. (a) Salinity and (b) nitrate contours for the upper 100 m of MAP transect. The transect is a two-dimensional projection of the arc of stations joined by a line off the Mississippi River delta (see Fig 1a).

were directly influenced by two freshwater discharge regions: off South Pass and off Southwest Pass. The salinity distribution for the upper 100 m in this arc (Fig 3a) shows two relatively freshwater surface lenses (down to 17 ppt) with a lateral spread throughout the arc and a strong halocline in the upper 10 m of the water column. Ocean salinities (>36 ppt) were encountered below 30 m depth.

Concentrations of up to 30 μM nitrate occurred in the upper layers of the arc (Fig 3b). This nutrient was associated with the freshwater input, and decreased to a minimum at the base of the halocline. High concentrations of chlorophyll a (up to 8 μg/L) and PON (up to 23 μM N, see Figs 4a and 5b) were also found in the upper layers of the arc, which suggested that high biological activity was also associated with freshwater input. Below the halocline, nitrate increased to 10 μM at a depth of 100 m. Corresponding chlorophyll and PON at these depths were an order of magnitude smaller compared with surface waters.

The DON vertical distribution for the upper 100 m in the MAP region is shown in Fig 4a. Similar to nitrate, DON concentrations were high in the upper 10 m and decreased with depth. Although the values were somewhat scattered, near-surface maxima of about 50 μM N occurred off Southwest Pass and at the eastern end of the arc. These values contrast with those for subsurface oceanic waters, where DON decreased to < 10 μM N below 30 m. However, a horizontal gradient was also evident throughout the subsurface oceanic waters where DON increased from the eastern to the western end of the arc (from < 10 to > 40 μM N). Vertical profiles from stations proximal to the outflow suggest that *in situ* N transformations occurred near the freshwater

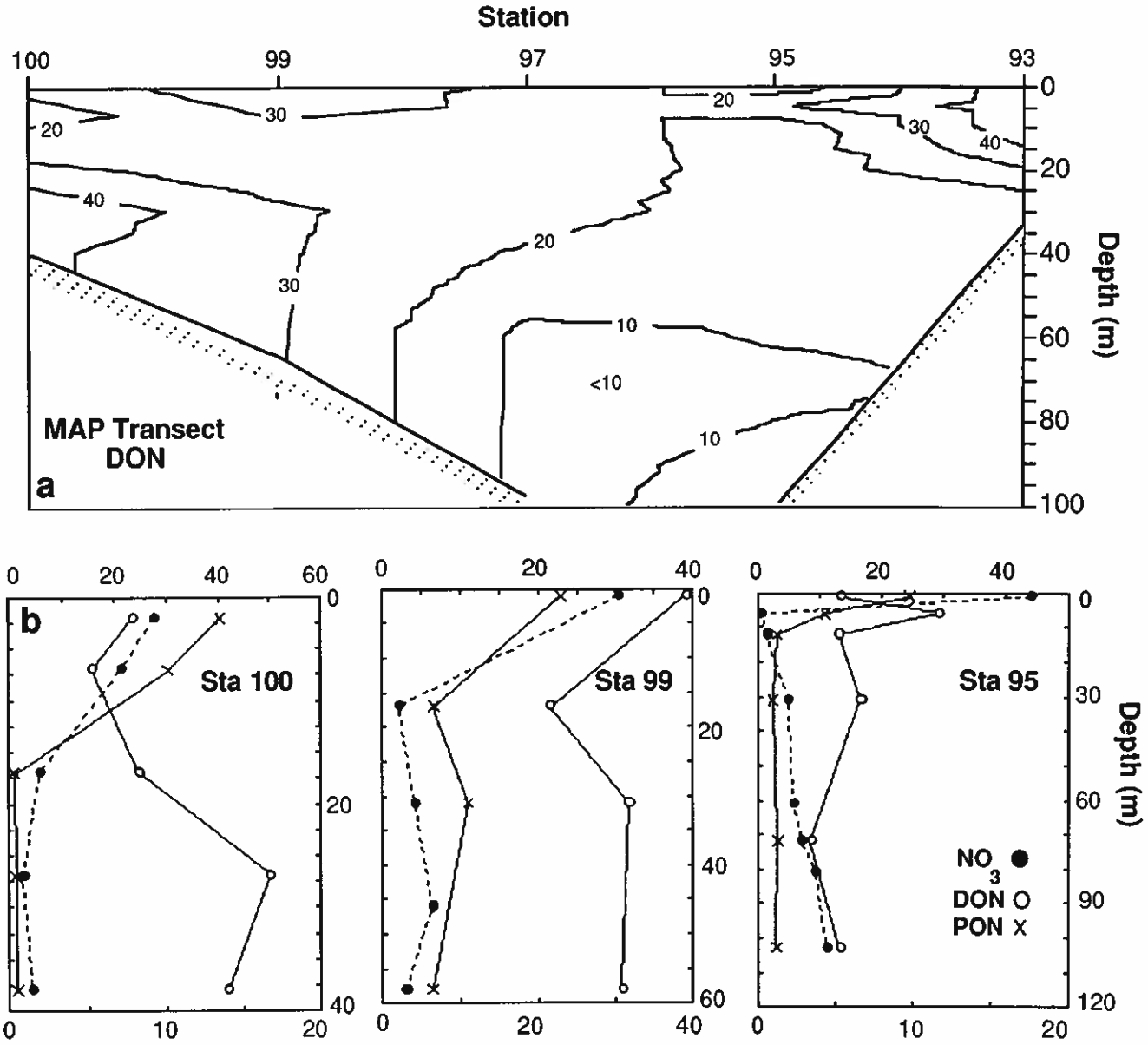

Fig 4. (a) DON (μM N) contour for the upper 100 m of MAP transect. Horizontal axis not to scale. (b) Vertical distribution of DON and DIN (upper scale), and PON (bottom scale) for MAP transect. Concentrations of nitrogen species are in μM N.

source, as evidenced by the inverse profiles between DON and NO_3 on the one hand, and PON on the other (Fig 4b).

Dissolved inorganic nitrogen (DIN = Σ NO3 + NO_2 + NH_4) and DON are plotted against salinity for the upper 10 m of the MAP region in Fig 5a. DON constituted *ca* 40 percent of the total dissolved nitrogen at the lowest encountered salinities (15 ppt), which was similar to Turner and Rabalais' (1991) estimate for the DON contribution to the total dissolved nitrogen budget in the Mississippi River. The high DIN concentrations associated with riverine inflow became undetectable at salinities above 25 ppt. A distinct DON increase was observed downstream at salinities between 30 and 35 ppt where PON and chlorophyll *a* decreased to near detection limits (Fig 5b). Here, DON became the most important dissolved nitrogen species and accounted for more than 90 percent of the total dissolved nitrogen in the MAP region's upper shelf waters (Fig 5c).

The observed increase in DON and the concomitant DIN decrease supports Benner *et al.*'s (1992) contention that riverine nitrate is transformed into DON within the plume. It appears that DIN assimilation by phytoplankton and its subsequent cycling to DON was rapid because sharp changes in these nitrogen components were observed within a small salinity gradient. Cycling of DIN through PON seemed to be transient in the MAP region, as evidenced by a sharp decrease in particulate nitrogen at oceanic salinities, which contrasts with the consistent increase of DON concentrations. Furthermore, these nitrogen transformations can be associated with intense heterotrophic activity mediated by bacterioplankton at intermediate salinities (Chin-Leo and Benner, 1992). Gardner *et al.*

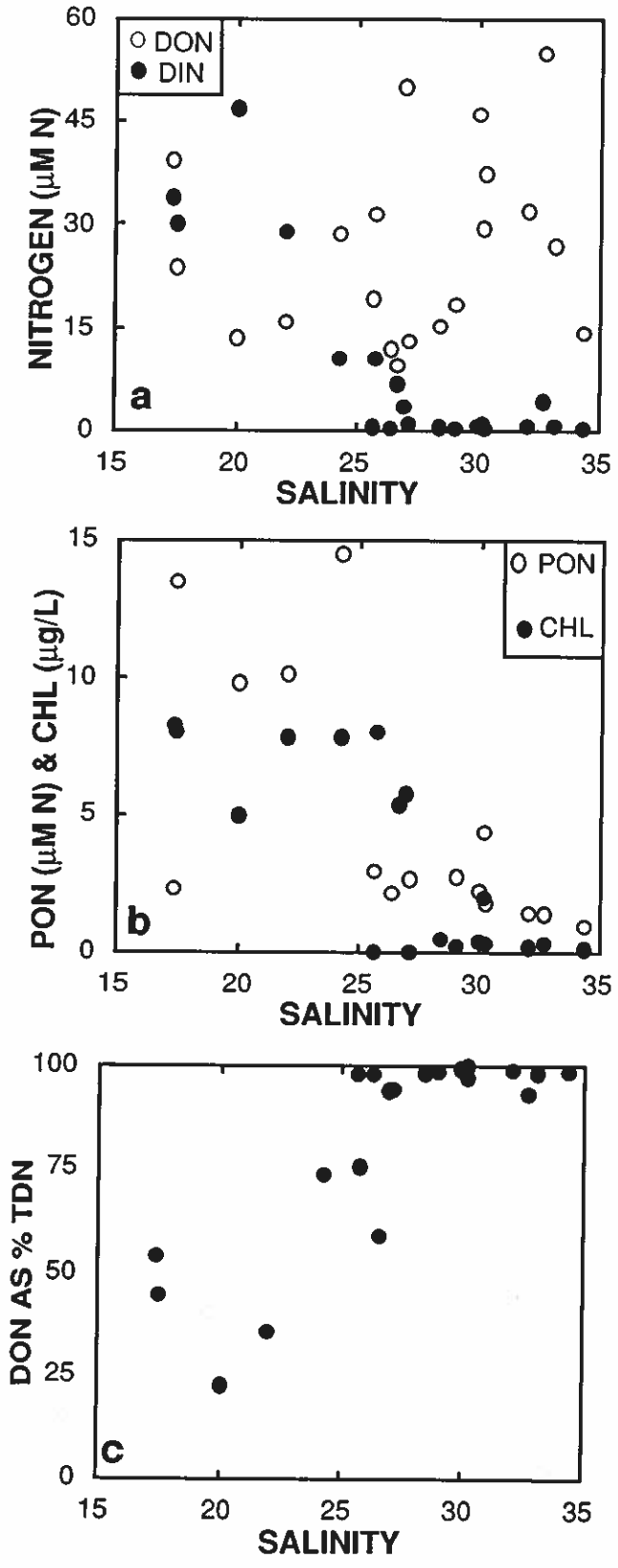

Fig 5. Scatter plots for the upper 10 m at MAP region showing: (a) DON and DIN *vs* salinity; (b) PON and chlorophyll *a* vs salinity; and (c) DON as percentage of total dissolved nitrogen (DIN+DON) *vs* salinity. The data includes all sample pairs from the numbered stations in Fig 1a.

(1992), for example, found high nitrogen mineralization rates for particles > 1 μm in these transition waters. DIN transformation also seemed to occur at depth in the western end of the MAP arc, where low DIN and high DON values off Southwest Pass indicated nitrogen cycling within oceanic waters under direct particulate nitrogen fallout (Fig 4b). Finally, DON accounted for an important fraction of DIN loss within the plume and was the major dissolved nitrogen pool transported out of the MAP region into adjacent waters.

Texas-Louisiana shelf —

Physical setting — Circulation in the NW Gulf of Mexico continental shelf is dominated by a cyclonic cell with a westward-flowing inshore limb and an offshore eastward flow at the shelf break (Cochrane and Kelly, 1986). The strong coherence between alongshore current and wind stress shows that wind is a major cause of the circulation along much of the shelf. Surface flow varies throughout the year in response to the wind and the relation of both is especially strong to the west of 92.5°W. The extent of the westward current migrates seasonally (coinciding with the displacement of coastal wind convergence) and reaches its southernmost position in the fall. In July and August, this gyre is normally absent, and an anticyclone develops due to high insolation of surface waters and a reversal in the alongshore wind stress component. Reversal of flow occurs at some locations during this season (Cochrane and Kelly, 1986; Dinnel and Wiseman, 1986; Rabalais *et al.*, 1991). In late summer, coastal westward flow is reestablished.

Contours of thermosteric anomaly ($\Delta_{S,T}$) calculated from the cruise's CTD data suggest a somewhat sluggish westward-drifting flow along most of the length of the two Texas-Louisiana Transects during the sampling period (Fig 6). This contrasts with stronger flow observed at other seasons (as determined by $\Delta_{S,T}$, e.g., Fig 12 from Cochrane and Kelly, 1986). Furthermore, evidence for flow reversal at Galveston Transect's inner shelf (94.5°W) is suggested by the $\Delta_{S,T}$ distribution and salinity signature of coastal stations (see below), in agreement with Cochrane and Kelly's (1986) upcoast surface flow for July off Freeport, TX. At the outer shelf's subsurface waters, low $\Delta_{S,T}$ isolines (< 300 x 10^{-8} m^3/kg) had a gentle down-slope in the seaward direction that suggests an eastward subsurface flow. This shelf break's eastward flow has been observed throughout the year by both hydrographic and current-meter data (see Cochrane and Kelly, 1986; and references therein).

Dinnel and Wiseman (1986) analyzed a two-year data set and estimated the freshwater content distribution in the Texas and Louisiana continental shelf. They found an annual freshwater cycle dominated by the MAR spring flood. In contrast to the winter, when its volume is low and its highest content appears as an inner shelf band, a high freshwater content in the summer appears as an isolated region in the center of the shelf (92°-94°W). In late summer, this high region

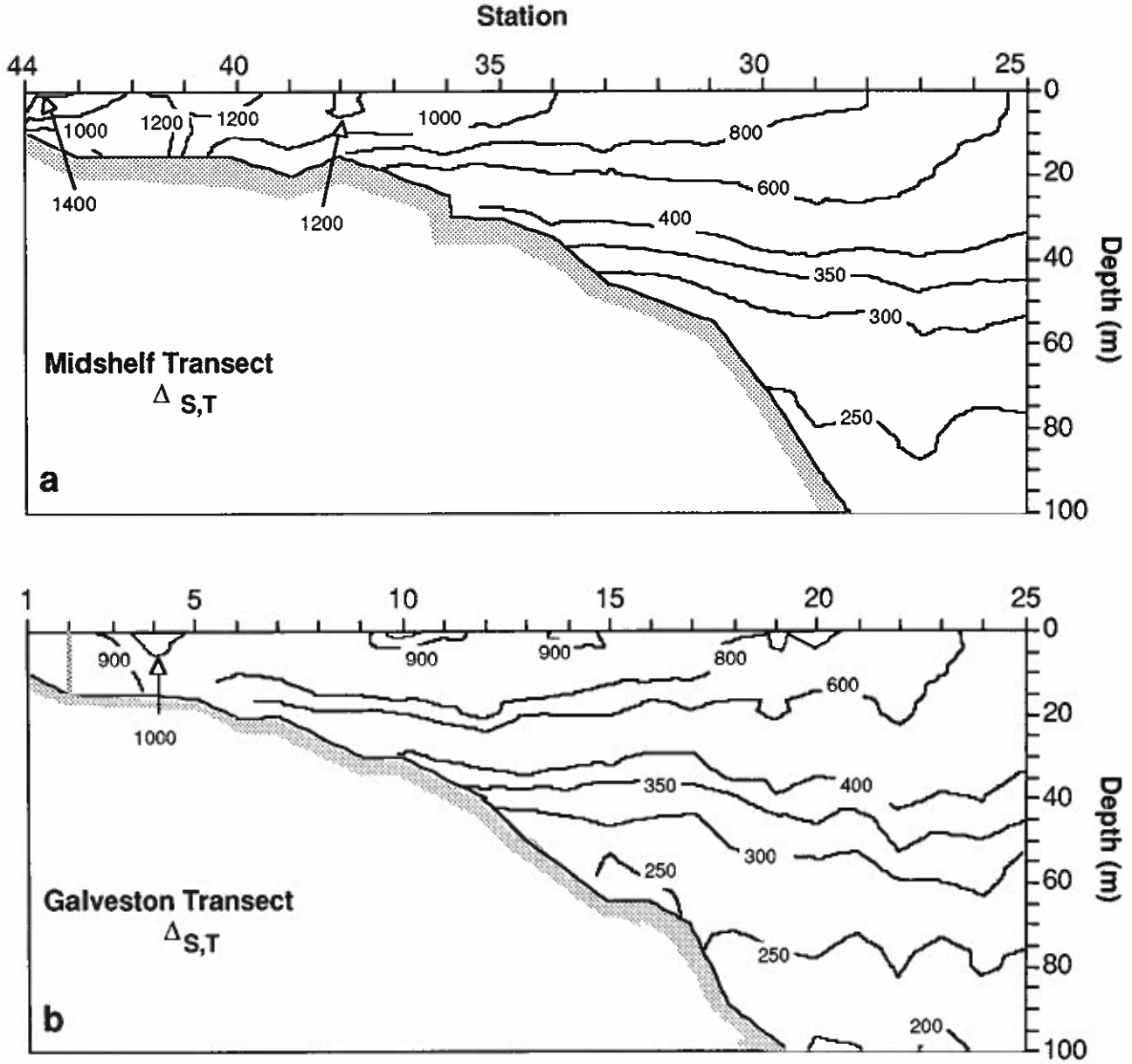

Fig 6. Thermosteric anomaly (10^{-8} m^3/kg) contours for the upper 100 m at (a) Midshelf Transect, and (b) Galveston Transect. No temperature data was available for Sta 1. Note change of scale for isoline intervals. Horizontal axis not to scale.

dissipates and migrates to the SE.

Along Midshelf Transect a low-salinity plume (< 36 ppt) was observed throughout the upper 40 m of the inner shelf which extended seaward to the shelf break (Fig 7a). Near-surface waters < 32 ppt occurred in the inner shelf's upper 10 m and extended 100 nmi seaward from the innermost station. The 30 ppt isohaline intersected the surface at 28°N and a surface salinity front was evident throughout the outer shelf and into the slope. A strong vertical gradient separated the low-salinity waters from oceanic salinities (> 36 ppt below 40 m at the outer shelf stations).

Off Galveston Transect the plume also extended offshore throughout the shelf (Fig 7b); however, the lens <32 ppt had a shorter extension (60 nmi) and had been displaced from the inner shelf by an intrusion of relatively higher salinity waters (31-33 ppt), possibly originating from Galveston Bay. In contrast to Midshelf Transect, the salinity front was not as intense, and the outer shelf's surface waters were ca 1 ppt more saline. The shelf's low-salinity distribution for the summer of 1990 suggests a similar pattern to that proposed by Dinnel and Wiseman (1986). The low-salinity plume extended from the inner shelf to the slope, and surface ocean salinities were encountered only at the most offshore station (Sta 25).

DON distribution — DON inside Midshelf Transect's low-salinity plume varied from 5.2 to 15.2 µM N (mean [DON] = 10.2 µM N; Fig 8a). Although DON sampling had a rougher resolution than that for salinity (in both vertical and horizontal realms), a similar trend in isoline contours was evident for both

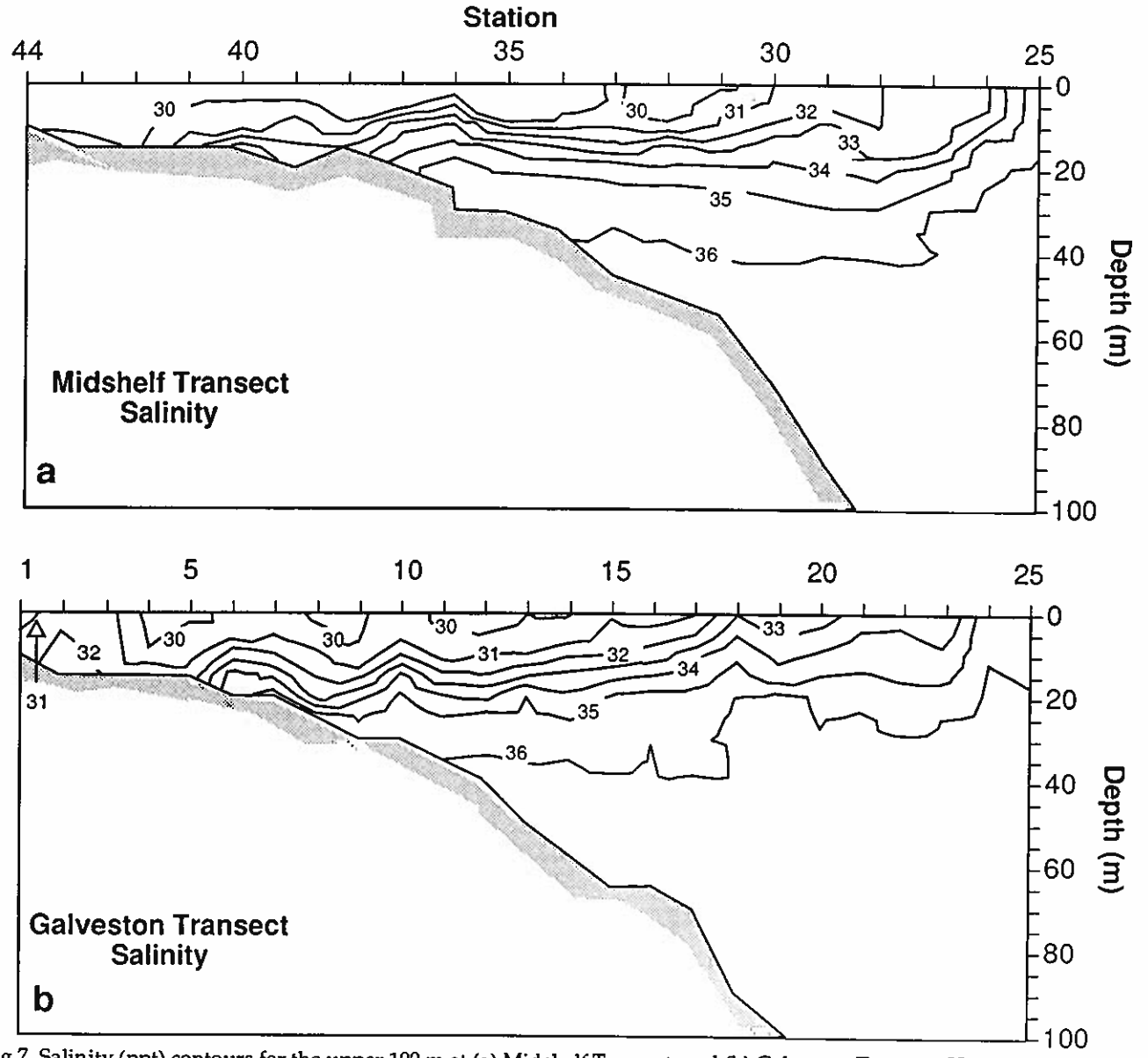

Fig 7. Salinity (ppt) contours for the upper 100 m at (a) Midshelf Transect, and (b) Galveston Transect. Horizontal axis not to scale.

data sets. Highest DON concentrations occurred at innermost stations and in the upper waters inside the plume (Fig 8a). In contrast, DON outside the plume was generally lower with an average of 5.9 μM N in the outer shelf oceanic waters.

DON inside Galveston Transect plume had an average concentration of 9.3 μM N. Outside the plume it decreased by half (mean [DON] = 5.0 μM N; Fig 8b). The innermost stations, which appeared to have their own salinity signature, also showed lower DON (6-8 μM N) in contrast to plume waters. As in Midshelf Transect, Galveston Transect offshore oceanic waters (> 40 m depth, and > 36 ppt) were lower in DON.

DON and salinity within the Midshelf Transect plume correlated inversely with a negative slope of -0.84 μM N/ppt ($r = -0.84$; Fig 9a). A greater scatter was evident in the DON-salinity scatter plot in Galveston Transect compared with Midshelf Transect (Fig 9b). At low salinities, both high and low DON concentrations were observed. If only plume waters are considered, a steeper slope (-1.2 μM/ ppt) relative to Midshelf Transect's plume existed. Some inner shelf samples fell outside the regression curve and suggest that the northward flow of water, probably originating from minor freshwater sources along the Texas coastline (*e.g.*, Galveston Bay) had a different salinity and DON signature from that originating at MAR. This distribution appears to reflect DON transport by low-salinity waters from the MAP region and a progressive mixing of plume and ocean waters as the water is advected westward.

In contrast to the relative high DON concentrations in plume waters, the outer shelf of both transects had a minimum DON region below 20 m, which coincided

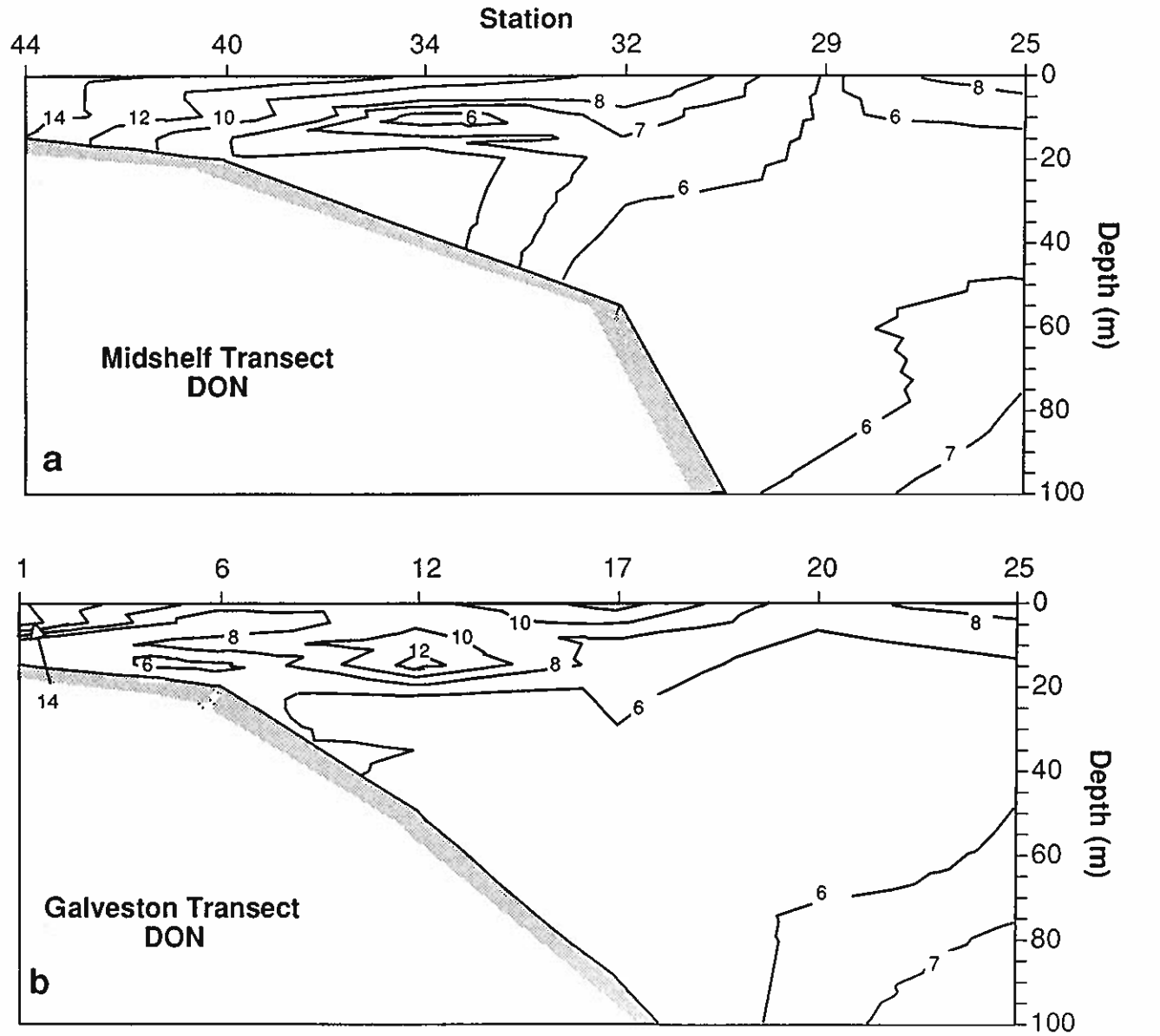

Fig 8. DON (μM N) contours for the upper 100 m at (a) Midshelf Transect, and (b) Galveston Transect. Horizontal axis not to scale.

with the chlorophyll maximum zone above the thermocline depth. This correspondence indicates that either the base of the thermocline is a DON sink, or that there are eastward-flowing subsurface waters that are DON-depleted.

NO_3 distribution — Compared to the relatively high DON encountered over parts of the shelf's upper waters, NO_3 approached near-detection-limit concentrations (Fig 10). At the inner shelf, however, localized values of 0.5 to 2.5 μM N-NO_3 near the bottom, along with relatively high NH_4 and NO_2 (not shown), suggest active *in situ* nitrogen cycling. The nitracline occurred at 80 m over the outer shelf and intersected the shelf's bottom at the 40 m isobath. If the encountered NO_3 distribution is representative for summer conditions, then new production seems to be confined to the outer shelf (*e.g.*, 50 m isobath) where the nitracline lies at the base of the euphotic zone. Therefore nutrient-nitrogen availability for the Texas-Louisiana inner shelf's production appears to depend on the active cycling of labile N compounds, possibly including some less-refractory DON transported by the coastal plume.

DON fluxes — The high DON signature inside the plume waters of Midshelf and Galveston Transects compared to oceanic background concentrations provides evidence of DON transport out of the MAP region and into the Louisiana and Texas shelf. Although the DON sampling pattern had a lower resolution relative to salinity and nutrient measurements, a unit DON stock at each transect can be roughly estimated.

For each transect, DON was vertically integrated at each station in the plume (S < 36 ppt), averaged for

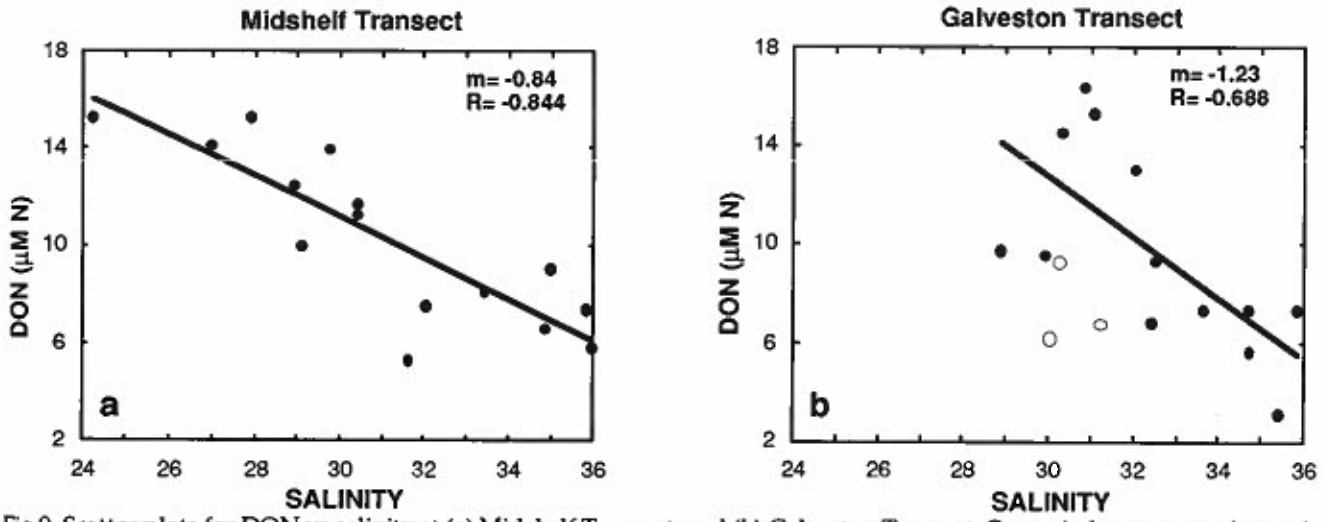

Fig 9. Scatter plots for DON vs salinity at (a) Midshelf Transect, and (b) Galveston Transect. Open circles are coastal samples that were not used in the regression (see text). The data includes all sample pairs with ≤ 36‰ in the upper layers of each transect.

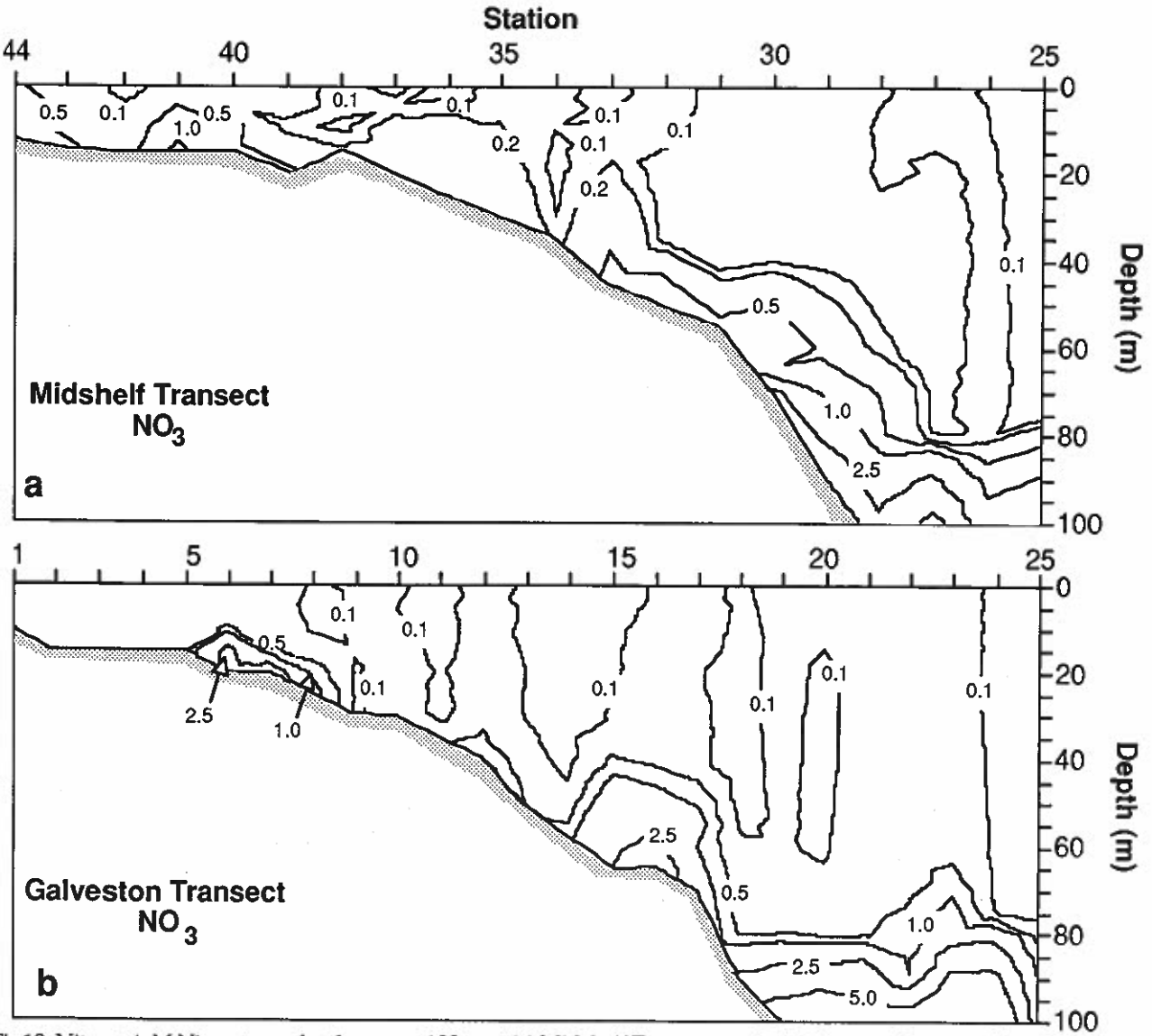

Fig 10. Nitrate (μM N) contours for the upper 100 m at (a) Midshelf Transect, and (b) Galveston Transect. Note change of scale in nutricline region. Horizontal axis not to scale.

Table 2. Volume of Water and Unit Nitrogen Stock in Midshelf and Galveston Transects for the Summer of 1990

Transect	Length[1]	V_{32}[2]	V_{36}[2]	N_{32}[3]	N_{36}[3]	Percent H_20[4]	Percent N[4]
Midshelf	254970	2.49	6.72	3.65	8.01	37.1	45.57
Galveston	269160	2.60	7.04	3.57	6.76	37.0	52.81

[1]Transect distance (m)
[2]Volume of water less than 32 or 36 ppt (m x 10^6)
[3]Nitrogen unit stock in water less than 32 or 36 ppt (g N/m x 10^5)
[4]Percent of water or nitrogen in water < 32 ppt relative to 36 ppt

adjacent stations and integrated throughout the transect's length. These estimates indicate that a unit DON stock of about 8.0 x 10^5 g N/m occurred at Midshelf Transect, and *ca* 6.8 x 10^5 g N/m were present at Galveston Transect (Table 2). When only water < 32 ppt is considered, the estimates are 3.7 x 10^5 g N/m, and 3.6 x 10^5 g N/m, respectively; that is, about the same mass per unit length of N-DON was found in the less saline waters of both transects. Although water < 32 ppt constituted 37 percent of the total plume's volume in both transects, it contained more DON at Galveston Transect relative to the total plume's volume.

The above estimates show that there was a difference in DON content between the two transects. These differences can be accounted for by different initial DON concentrations between the plume's waters at their time of formation; by *in situ* DON transformations; or by mixing processes between the plume and adjacent oceanic waters. These possibilities are considered next.

The discharge rates of the Mississippi and Atchafalaya Rivers varied considerably between late spring and mid-summer. Between mid-June and late July, for example, the average daily discharge decreased by 38 percent from a peak discharge of 34 x 10^3 m^3/s to 12.7 x 10^3 m^3/s (U.S. Army Corps of Engineers, 1991). The average longitude difference between Midshelf and Galveston Transects was 48 nmi (~ 55 mi). Considering a mean flow between 10 and 100 cm/s, a water parcel would require 1 to 10 days to transit between both transects. Thus the 4.5 percent greater volume of plume water in Galveston Transect relative to Midshelf Transect is consistent with the Mississippi River discharge decrease (assuming equal evaporation, precipitation and mixing rates).

Due to its dynamic nature, the MAP region shows large salinity and nutrient gradients in space and time. In estuaries of the MAP deltaic plain, Madden *et al.* (1988) reported tidal and seasonal nutrient variations. Lohrenz *et al.* (1990) found higher NO_3 at intermediate salinities relative to the river end-member within the MAP region, attributable to *in situ* transformation processes, variable riverine inputs, and different mixing dynamics. Likewise, riverine and *in situ*-generated DON could also vary, considering its coupling to the DIN pool. It is then possible that the intrinsic DON content of the waters leaving the plume region may have been different at the time of formation.

Based on reported DON and DIN concentrations, and productivity rates from the oligotrophic North Pacific, Jackson and Williams (1985) estimated DON degradation rates of 0.005/d. Bronk and Glibert (1991) measured phytoplankton DON production rates in the range 0.05 to 0.20 µM N/hr. Assuming DON on the order of 10 µM N, a conservative estimate of DON turnover would range from 0.12 to 0.48/d. Although relatively labile DON compounds of short residence time are continually generated and degraded in the nitrogen cycle, a fraction of the transported DON could be lost by in *situ* processes during the plume's westward transit.

Oceanic fronts are regions of intense biological activity (Bowman and Iverson, 1978). The co-occurrence of low NO^3 and DON at the salinity front of both transects suggests that DON could be a nitrogen source for both primary producers and bacterioplankton. A net DON loss to other nitrogen reservoirs within the plume is unlikely, however, as the average PON between both transects was statistically similar (1.72 *vs* 1.75 µM N), and DIN did not increase from one transect to the other.

Dinnel and Wiseman (1986) attributed a significant fraction of shelf freshwater volume decrease to diffusive mixing with offshore oceanic waters. This mechanism is another likely explanation for DON loss. Even if the DON pool was relatively inert in the time-scales considered, its signature would eventually disappear by a Fickian process as a function of the DON gradient between the plume and oceanic end-members. The DON-salinity scatter plots for both transects show a steeper negative DON change in the Galveston Transect plume that implies faster DON diffusion across the salinity gradient.

Conclusion

The application of recent DON techniques to studies of nitrogen cycling in MAP and NW Gulf of Mexico is useful in accounting for the disappearance of nutrients within the plume region. The data presented in this paper demonstrate that DON and DIN are coupled at the MAP salinity gradient, and suggest a westward N transport into the NW continental shelf.

Further studies in the region should include DON freshwater end-member characterization, its time-dependent variations within the plume area, its lability (e.g., as a N source and sink), and bottom layer and pore water DON cycling.

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Seasonal variation in phosphate turnover in the Mississippi River plume and the inner Gulf Shelf: rapid summer turnover

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Abstract

Studies of phosphate cycling in the Mississippi River Plume and the Inner Gulf Shelf were undertaken in July 1990 and September 1991 in association with the NECOP program. These studies included isotopic measurements of inorganic and organic phosphate turnover and fluorometric measurements of alkaline phosphatase activity, along with conventional nutrient and biomass measurements. In July the lower salinity waters in the upper 5 to 10 m showed very rapid inorganic phosphate turnover times of ten minutes or less, but these rates declined steeply in deeper waters. Organic phosphate turnover and alkaline phosphatase activity displayed a similar pattern, although turnover times were slightly longer. In September the freshwater flow from the river was reduced and the plume was much smaller. Phosphate turnover and related parameters were slower than in July, although turnover times of a few hours were common. In contrast with July, the greatest phosphate uptake (minimum turnover time) and alkaline phosphatase activity were consistently found at depths of 15 m or below. These measurements suggest a phosphate deficiency in the surface waters in July. This deficiency apparently resulted from the high nitrogen/phosphorus ratio of the inflowing Mississippi River water and extended a considerable distance into the Gulf in association with the river plume. In September this phosphate deficiency was weaker, apparently greatest at depth, and not associated with the plume.

The Mississippi River is the largest river in the U. S., drains 40 percent of the continental U. S. land area, and accounts for 65 percent of the freshwater runoff into the Gulf of Mexico. The Mississippi River Plume/ Inner Gulf Shelf (MRP/IGS) region has a clear anthropogenic nutrient signal resulting in significant nutrient-enhanced productivity. This enhanced productivity also has a clear impact on the coastal environmental quality. The MRP/IGS has valuable living marine resources that could be adversely affected by a decrease in environmental quality.

Both light and nutrients limit phytoplankton primary productivity in the MRP/IGS region (Sklar and Turner, 1981). Light-limitation is most apparent near shore and nutrient-limitation increases offshore as the turbidity declines. Although nitrogen (N) is widely agreed to be the major limiting nutrient in marine waters, there are several important reasons why other potentially limiting nutrients, such as phosphorus (P), silica (Si), and perhaps others, should also be studied (see below).

Hecky and Kilham (1988) conclude in a recent review that the severity and extent of N limitation in marine waters remains unclear. Unlike P-limitation in lakes, which has been rigorously demonstrated at many levels from algal cultures [level 1 or 2 experiments; (Hecky and Kilham, 1988)] to mesocosms (level 3) and whole lakes (level 4), N-limitation in marine waters has generally been demonstrated only at the level of single-species cultures (level 1) or community algal cultures (level 2). The few mesocosm-level experiments (level 3) done in estuaries have shown either a lack of strong nutrient limitation [in contrast with level 1 studies from the same estuary; (Nixon *et al.*, 1984)] or a seasonal alternation between N and P limitation (D'Elia *et al.*, 1986). Hecky and Kilham (1988) note that though many coastal areas have very low N:P ratios, the particulate N:P ratios in these areas differ little from the Redfield value of 16:1, suggesting no strong deficiency of N or P. Since phytoplankton growth rates are controlled by internal nutrient concentrations and are often difficult to relate to external concentrations, they suggest a greater reliance on measurements of particulate matter composition and biomass-normalized physiological rates to infer nutrient limitation.

There is little direct published evidence for N-limitation of phytoplankton in the MRP/IGS region. The evidence cited is either inferences made from N:P ratios (Sklar and Turner, 1981) or references to unpublished data (Turner *et al.*, 1987). R. E. Turner (personal communication) has done numerous short-term nutrient addition and deletion experiments with water samples from the MRP/IGS that are currently unpublished. These are equivalent to level 1 or 2 experiments described above, and assessed the effects of N, P, Si, trace metals, and other nutrients. Many of these experiments suggest N-limitation, but 10 percent or less suggest P-limitation, and there is some scatter in the data (R. E. Turner, personal communication). Similar but less rigorous experiments in estuarine and

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nearshore waters of the northeastern Gulf of Mexico showed that P limited phytoplankton productivity more often that N (Meyers and Iverson, 1981). Dortch and Whitledge (1992) measured an intracellular indicator of N deficiency and ratios of nutrient concentrations in water samples. They concluded that N limitation was not widespread and that Si limitation may be as likely as N limitation.

As discussed above, nutrient limitation in the MRP/IGS may be difficult to infer solely from external nutrient concentrations and N:P ratios, or from the N:P loading ratio in the lower Mississippi. Nonetheless, these concentrations and ratios are the most frequently cited evidence for N-limitation (Sklar and Turner, 1981). Even if such nutrient ratios were easily interpretable, the data available for the MRP/IGS do not uniformly favor N-limitation. Figure 5 (Sklar and Turner, 1981) shows that the average ratio of inorganic N to P for six stations seaward of Barataria Bay was exactly the Redfield value of 16:1, with higher ratios in the winter and lower ratios in the summer. Similarly, a compilation of N and P data from the USGS by G. A. Jackson (personal communication) shows that the ratio of total N to total P exceeds the Redfield ratio in much of the fall and winter, but falls below it in spring and summer. A simple interpretation of these data would suggest N-limitation in the spring and summer and P-limitation in the fall and winter.

Concentrations of nitrate in rivers and the nitrate load to coastal areas have clearly increased in the last few decades, both in the Mississippi (Turner *et al.*, 1987; Turner and Rabalais, 1991) and in the nation as a whole (Smith *et al.*, 1987). Total P loads, in contrast, have decreased in many areas, due at least partly to increased point source control (Smith *et al.*, 1987). The long-term trend in P in the Mississippi is unclear (Turner and Rabalais, 1991), the fact that the load of suspended sediments in the river has decreased suggests a P decline (Turner *et al.*, 1987), but other sources show an increase in total P inputs to the Gulf (Smith *et al.*, 1987). If we assume that the N:P ratio in the river is increasing with time, this suggests that even if N were limiting at present, P-limitation would become more likely with time.

The factors discussed above suggest that N is not the only anthropogenically-enriched nutrient that may impact the productivity of the MRP/IGS system. While they do not necessarily establish a case for P limitation, they suggest that P, Si, and perhaps other nutrients should be considered as part of any effort to study nutrient enhanced productivity in this area.

Methods

Sampling — Phosphate studies were made on two cruises to the Mississippi Plume region and the Gulf of Mexico. The summer cruise took place from July 11-25, 1990, aboard the R/V *GYRE*, and the fall cruise from September 11-18, 1991, aboard the R/V *PELICAN*. Both cruises were carried out as part of or in association with the NOAA NECOP (Nutrient-enhanced Coastal Ocean Productivity) Program. Water samples were collected with Niskin bottles on a CTD-rosette system.

Turnover of dissolved inorganic phosphate (DIP) — Carrier-free ^{32}P-labeled orthophosphate (^{32}Pi) was added to replicate water samples to measure inorganic phosphate turnover. Samples were incubated in a temperature-controlled incubator in the lab. Incubation temperatures were maintained at 27° to 29°C during the summer and 29° to 30°C in the fall. Incuba-

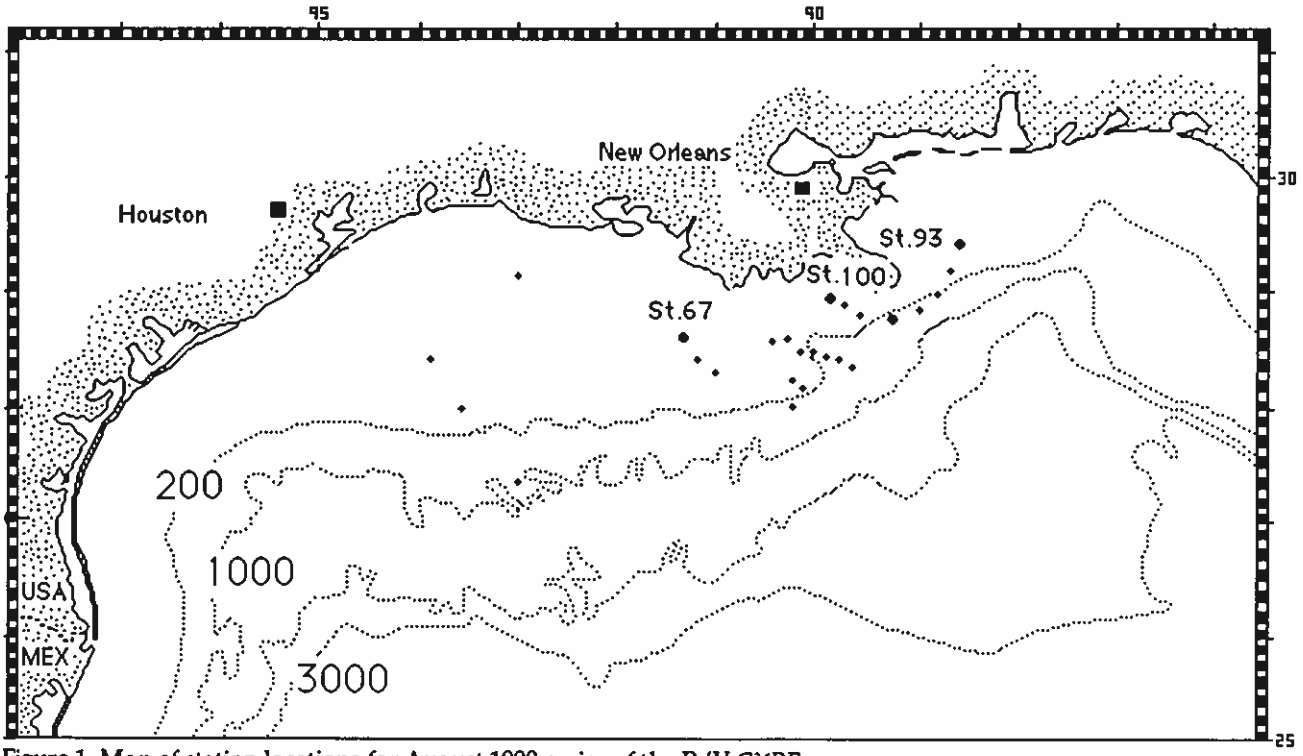

Figure 1. Map of station locations for August 1990 cruise of the R/V *GYRE*.

Table 1. Data from transect around the mouth of the Mississippi River, Stations 93-100.

Station	Depth (m)	Salinity (ppt)	DIP turnover (min)	Nitrate/DIP
93	2	30.00	9	6
93	12	34.98	6022	11
94	1	26.68	8	611
94	22	35.91	1153	11
95	1	20.06	817	47
95	12	35.39	1825	13
96	1	25.80	10	44
96	22	36.02	10809	13
97	1	24.28	6	49
97	21	35.76	4651	13
98	2	27.01	6	31
98	26	35.86	2787	18
99	1	17.33	6	168
99	17	35.50	3335	13
100	2	17.48	7	550
100	17	35.38	3719	17

tion times ranged from one minute to one hour, depending on activity. Uptake rates were calculated from ^{32}P incorporation into particulate matter on 0.22 µm Millipore or 0.2 µm Nuclepore filters.

Turnover of dissolved organic phosphate (DOP) — This was measured by determining the hydrolysis rate of [γ-^{32}P]ATP added to water samples at tracer concentrations, as well as the uptake rate of released phosphate. Details of the assay are described in Ammerman and Azam, 1991. Incubation conditions were the same as those above, although incubation times were slightly longer. ATP is a substrate for the microbial cell-surface enzymes alkaline phosphatase and 5'-nucleotidase and is assumed to act as a model dissolved organic phosphate compound (Ammerman and Azam, 1991).

Alkaline phosphatase (AP) assay — AP activity was determined by the fluorometric method of Hoppe (1983) and greater detail is provided elsewhere (Ammerman and Azam, 1991). AP activity was measured by following the increasing fluorescence of the substrate analog, 4-methylumbelliferyl phosphate, with time. Substrate concentrations used were 100 nM in spring and 1 µM in the fall, and incubation conditions were the same as described above, although incubation times up to four hours were required in the fall.

Other methods — Dissolved inorganic phosphate (DIP, sometimes also referred to as orthophosphate or Pi) and other nutrients were determined by autoanalyzer aboard ship by standard methods (Strickland and Parsons, 1972). Chlorophyll *a* was measured by fluorescence aboard ship (Strickland and Parsons, 1972); bacteria were counted by epifluorescence using DAPI (Porter and Feig, 1980).

Results and Discussion

The location of stations where at least inorganic P turnover was measured in the surface water are shown by the dots marked on Fig. 1. Station 67, off the Atchafalaya, is also marked on this chart. I will use this station as representative of the plume water because it was well-characterized, even though it was farther offshore than some of the others. Station 67 may also receive more freshwater input from the Atchafalaya than the Mississippi itself. The temperature and nutrient distributions at station 67 are shown in Fig. 2A. The important feature is the lower salinity water in the upper 15 m. This was a very common feature found at many stations during the July cruise. Some of the inshore stations near the mouth of the Mississippi had surface salinities of less than 20 ppt.

Nutrient distributions at station 67 are show in Figures 2B and 2C. Phosphate was low but detectable; at some stations it was zero in surface waters. All nutrient concentrations increased with depth, especially ammonia, nitrate and nitrite. Nitrite concentrations showed an unusual layered profile, but other stations showed similar patterns, suggesting that this profile was not an artifact. The ratio of dissolved inorganic nitrogen (DIN) plus urea to dissolved inorganic phosphate (DIP) at station 67 was very close to the Redfield Ratio (16:1, N:P) in the upper 15 m, which suggests neither N nor P were in short supply. Below 15 m, however, this ratio decreased, indicating possible excess P. Chlorophyll *a* and bacterial numbers at station 67 are shown in Fig. 2D. The chlorophyll concentration was below 1 mg l^{-1} and decreased slowly with depth until increasing in the bottom sample. Bacterial numbers were high in the upper 6 m and decreased sharply with depth, showing a much greater change with depth than chlorophyll *a*.

Turnover of DIP is shown in Fig. 2E. Turnover times were very rapid in the surface water, less than 20 minutes in the upper 2 m and less than 30 minutes at 5 m (see inset in Fig. 2E). Below 5 m, the DIP turnover

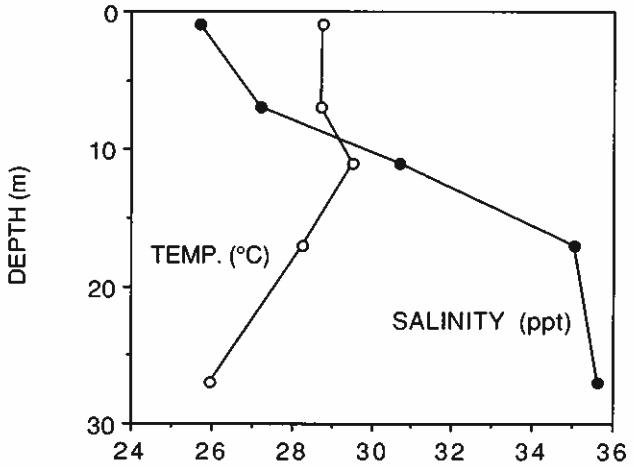

Figure 2a. Vertical profiles of properties of Station 67 from the August 1990 cruise. A. Temperature and salinity.

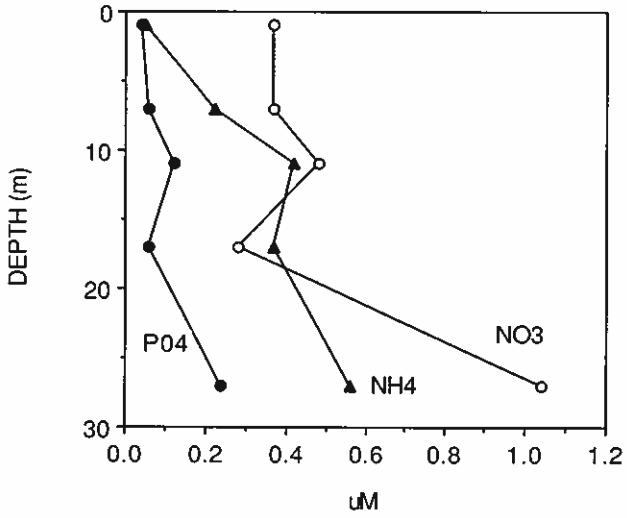

Figure 2B. Ammonium, nitrate, and phosphate concentrations.

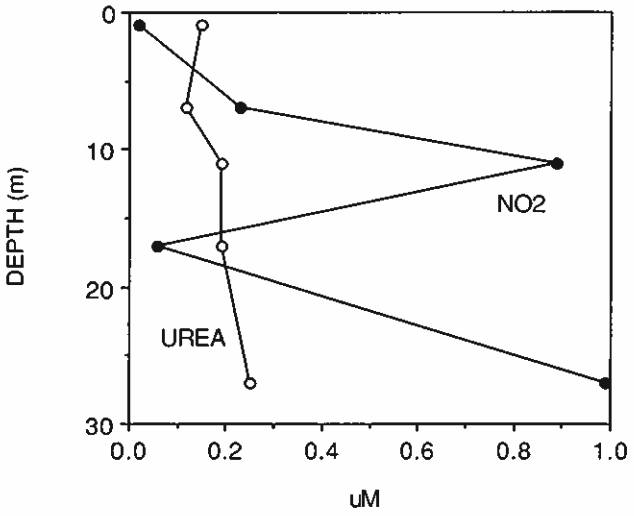

Figure 2C. Nitrite and urea concentrations.

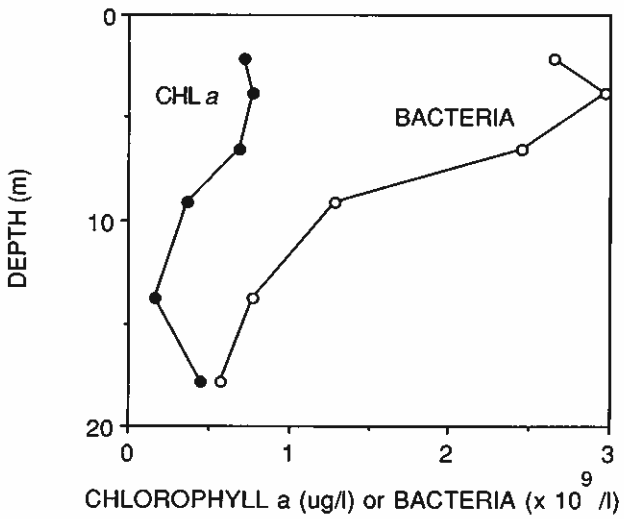

Figure 2D. Bacterial numbers and chlorophyll a concentrations.

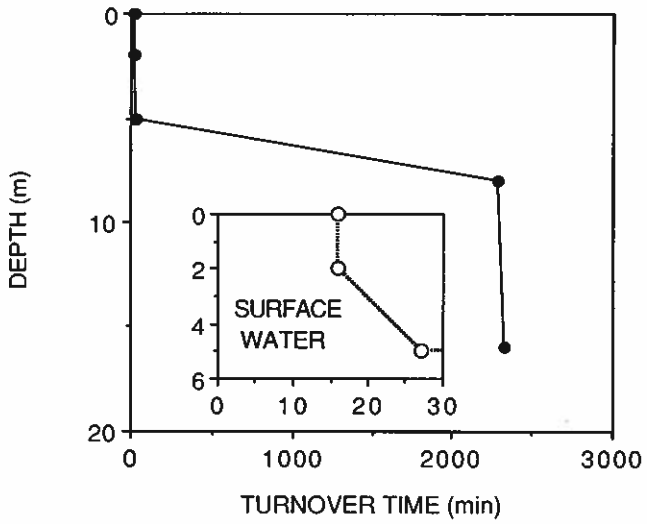

Figure 2E. Pi turnover time, see inset for surface waters.

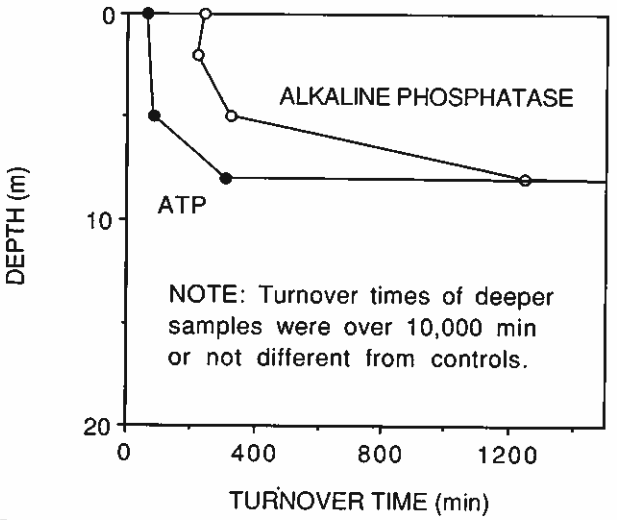

Figure 2F. Turnover times of alkaline phosphatase substrate and radiolabeled ATP.

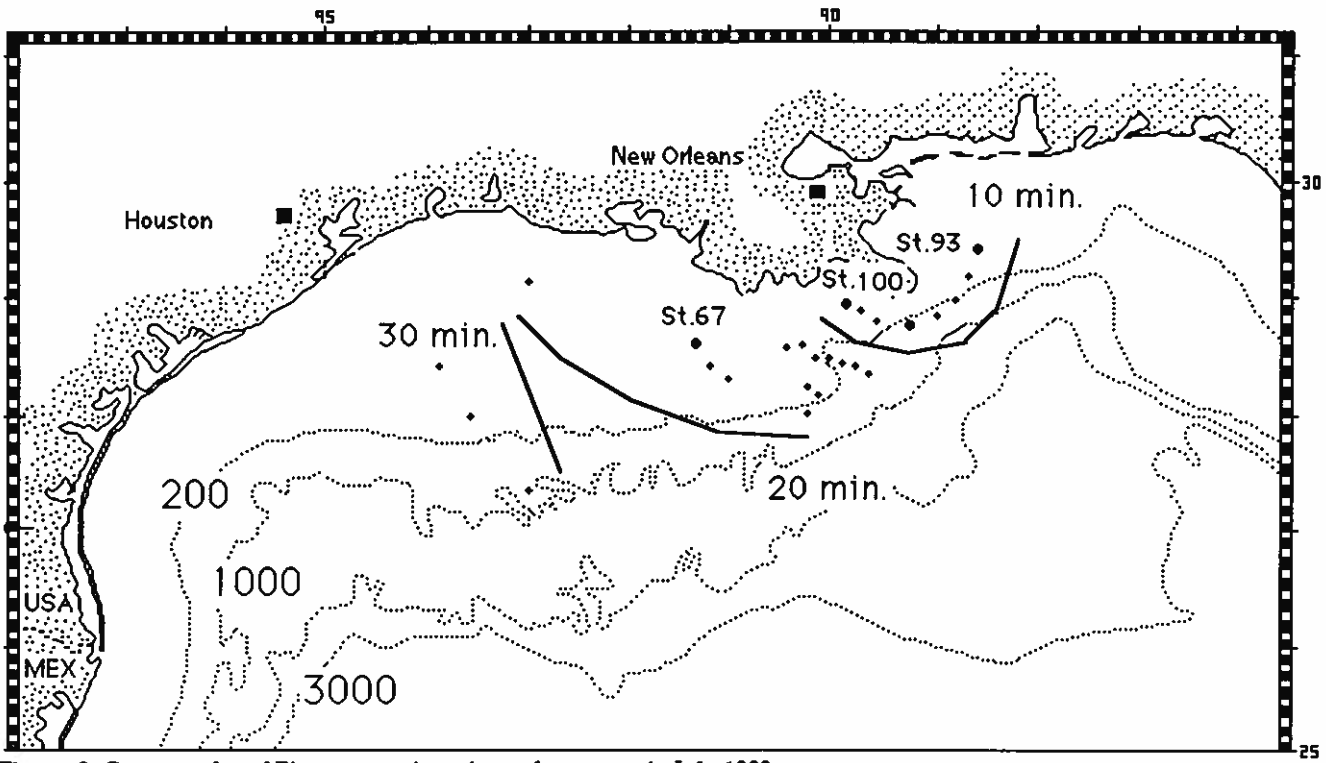

Figure 3. Contour plot of Pi turnover times in surface water in July 1990.

time increased rapidly to more than 1,000 minutes. Thus, the layer of rapid Pi turnover coincided with the surface low-salinity layer.

Dissolved organic phosphate turnover, as measured by the hydrolysis rate of [γ-^{32}P]ATP, showed a similar vertical pattern (Fig. 2F) of rapid turnover in the surface waters. DOP turnover times were longer than for DIP, but were still less than 100 minutes in surface waters. Substrate turnover of the enzyme alkaline phosphatase (AP), an indicator of P-deficiency (Cembella *et al.*, 1984), also displayed a similar vertical profile (Fig. 2F). However, AP substrate turnover was slower than for DOP, probably because a higher substrate concentration was required for assay. When considered together, these data suggest that the surface waters at station 67 were probably P-deficient.

Table 1 shows similar data from stations 93 to 100 around the mouth of the Mississippi River in July (see Fig. 1 for locations). At each station, samples were collected near the surface and at the first depth with a salinity of 35 ppt. With one exception, the nitrate/DIP ratio in the surface water was above 30 and sometimes much higher, suggesting strong P-deficiency. (Note: This is not the same N/P ratio discussed above for station 67 because only nitrate is included here, if other forms of N were added the ratio would be even higher.) In the deeper waters this ratio was always close to or less than the Redfield Ratio. The apparent P-deficiency in the surface water is clearly shown in the Pi turnover times. All but one of the surface turnover times was 10 minutes or less, whereas the shortest turnover time in the deep samples was more than 1,000 minutes.

Fig. 3 shows the spatial distribution of DIP turnover times in surface waters in July. The contour lines drawn on this chart show that large areas of the MRP/IGS had inorganic phosphate turnover times less than 30 minutes; even stations at considerable distances from the Mississippi or Atchafalaya inflows displayed low turnover times. From the limited data presented here, however, it appears that the fastest Pi turnover was in the stations sampled closest to the mouth of the Mississippi (the data in Table 1).

The situation in the September cruise was considerably different. (Much of the data are currently unavailable since the cruise just returned Sept. 18, 1991.) DIP turnover was generally much slower, with fastest turnover times of an hour or more. As shown in Fig. 4, stations in the plume (station 9) and in the often hypoxic area (station 32), showed similar profiles of DIP turnover, with the fastest turnover often occurring at depth. (The "hypoxic" area, including stations 29, 32, and others, was generally not hypoxic during this cruise.) These two profiles were taken four days and many kilometers apart and their similarity suggests minimal influence of the freshwater plume on phosphate cycling in September.

Station 29 showed a similar subsurface minimum of Pi turnover time in a more detailed vertical profile (Fig. 5). Alkaline phosphatase activity had a corresponding profile of substrate turnover (Fig. 5), although the actual turnover times were ten times longer. Part of the reason for the much longer turnover times is the higher substrate concentration used (1 μM) in order to detect activity.

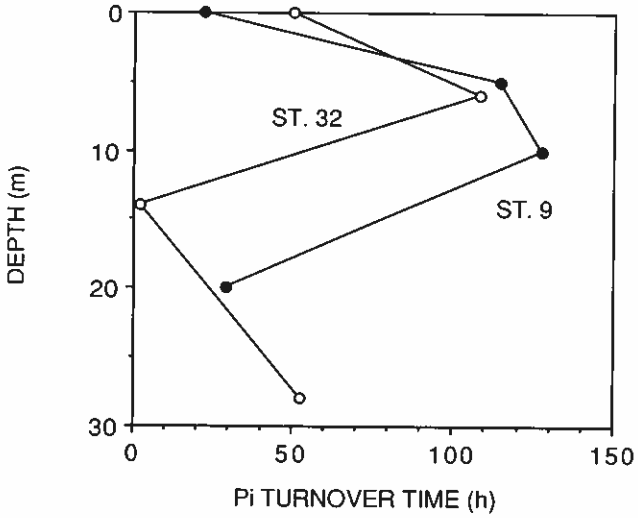

Figure 4. Vertical profiles of Pi turnover times at a "plume" station (9) and a "hypoxic" station (32) taken on the September 1991 cruise.

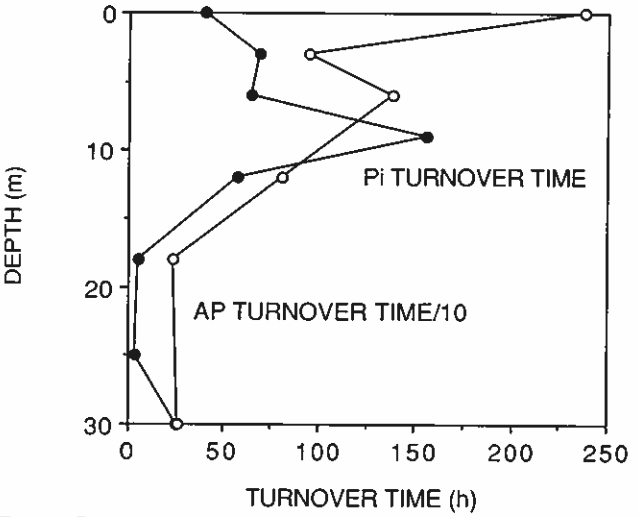

Figure 5. Vertical profiles of Pi turnover and AP substrate turnover at station 29 on the September 1991 cruise.

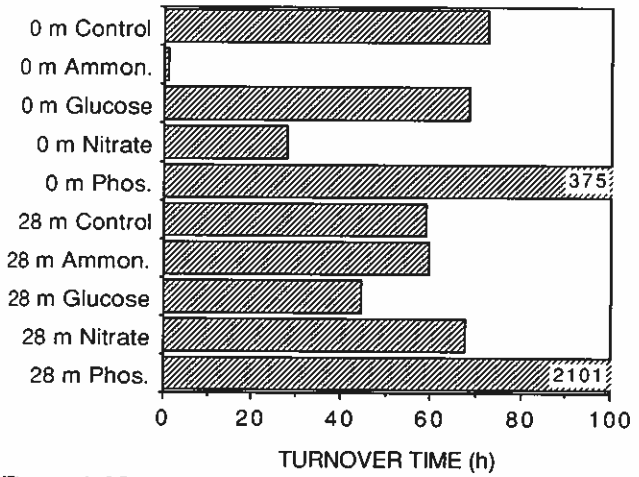

Figure 6. Nutrient addition experiment done with surface and 28 m water from station 32 on the September 1991 cruise.

A nutrient addition experiment was conducted on the September cruise in collaboration with J. Cotner. The purpose of this experiment was to assess which nutrient was likely to be limiting. Surface and 28 m samples were taken from station 32 (Fig. 4) in the hypoxic region and incubated with 10 μM added ammonium, glucose, nitrate, phosphate or no addition (control). Samples were incubated at 50 percent surface light intensity for 26 hours and then analyzed. The most dramatic effect was the ammonium addition to the surface water, the Pi turnover time dropped from a control value of 70 hours to less than 2 hours (Fig. 6), a value similar to the original Pi turnover time for the 14 m sample from this station. This ammonium addition apparently shifted the community in the surface sample towards P deficiency, since the fastest alkaline phosphatase activity was also found in this sample (data not shown). There was a smaller decrease in the Pi turnover time in the surface sample with added nitrate, but no effect of either ammonium or nitrate addition to the 28 m sample. This deep sample showed a small decrease in Pi turnover time with glucose addition only, and both surface and deep samples showed the expected large increase in Pi turnover time with Pi addition.

In lakes, Pi turnover times of 10 minutes or less are thought to be good evidence for Pi deficiency (Lean *et al.*, 1987). In July 1990, the Mississippi River Plume and Inner Gulf Shelf exhibited rapid inorganic phosphate turnover times that were 10 minutes or less near the mouth of the Mississippi. This suggests an apparent phosphate deficiency in surface waters, despite the presence of measurable phosphate in some samples. Organic phosphate and alkaline phosphate substrate turnover times also suggested that organic phosphates were being rapidly utilized. This P-deficiency apparently results from the high N/P ratio of inflowing Mississippi and Atchafalaya River water, and extends a considerable distance into the Gulf coincident with the river plume. In September 1991, preliminary data show that phosphate turnover was slower and apparently independent of the plume. The peak of activity was found at depth over a large area. Nutrient addition experiments showed that ammonium addition could quickly lower Pi turnover times.

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Role of silicate availability in phytoplankton species composition and the fate of carbon

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Abstract

It has been hypothesized that hypoxia and the fate of carbon are determined in part by phytoplankton size and species composition, which are influenced by many environmental factors, but especially the supply of N and Si. In particular, when N and Si concentrations are high, the predominant algal species are large, heavily to moderately silicified diatoms. While these may be grazed at rapid rates and fuel productivity at higher pelagic trophic levels, a large proportion either sinks below the pycnocline directly or in fecal pellets, perhaps leading to hypoxia. When N concentrations are not limiting and Si concentrations are low, as often happens on the Louisiana continental shelf, either lightly silicified diatoms or non-diatoms, usually small, flagellated algal species, predominate. These organisms yield less vertical flux of organic matter to the bottom, because most sinking phytoplankton is made up of only a few heavily or moderately silicified diatom species. Thus, silicate availability determines the vertical flux of directly sinking phytoplankton and influences the severity and extent of hypoxia. Any changes in riverine silicate input will affect hypoxia by this mechanism.

The large area of hypoxic water on the Louisiana continental shelf has been hypothesized to result from eutrophication induced by the high inputs of nutrients from the Mississippi and Atchafalaya Rivers (Rabalais *et al.*, 1991). Until recently, riverine N inputs were increasing, while silicate inputs were decreasing (Turner and Rabalais, 1991). More recently, however, it appears that N inputs have leveled off but silicate levels are increasing (Turner and Rabalais, 1991). While N may limit the overall productivity of the system (Turner and Rabalais, 1991), Dortch and Whitledge (in press) have shown that silicate is often more limiting than N. Si availability will strongly affect phytoplankton size and species composition by determining the abundance of large diatoms with high Si requirements. These diatoms are associated with high vertical carbon flux, both by direct sinking or via grazing and fecal pellet flux and, thus, may play a major role in causing hypoxia. Consequently, changes in silicate input from the river may have a direct effect on the extent and severity of hypoxia through changes in the abundance of large diatoms

The data from four shelf-wide cruises (1989 and 1990), a monthly transect through the core of the hypoxic region (1990), and two sediment trap experiments (1990) have been compiled to address two questions.

1. What is the relationship between silicate concentrations and the abundance of large diatoms?
2. What is the relationship between silicon availability, diatoms, and phytoplankton flux?

This is a preliminary report after only partial analysis of the data. A more complete publication will be forthcoming.

Methods

Cruises were conducted on the Louisiana continental shelf as outlined in Table 1. Floating sediment traps were deployed as described by Knauer *et al.* (1979) and moored sediment traps by Prior *et al.* (1987). Chloro-

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Table 1. Cruises on which phytoplankton in the water and sediment traps were enumerated.

Area	Dates	Funding
Mississippi River plume and adjacent shelf	April 10-22, 1989	LASER
Southeast Louisiana shelf	Aug. 4-8, 1989	LEQSF, NURC
C transect across Southeast Louisiana shelf	1 per month Mar-Nov. 1990	LEQSF, NECOP
Southeast Louisiana shelf	July 16-21, 1990	NURC
Louisiana shelf	July 23-27, 1990	LEQSF, NECOP
Mississippi River plume and adjacent shelf	July 20-Aug.7, 1990	NECOP

phyll and nutrients were measured according to Toon and Dagg (1990) and Parsons *et al.* (1984). Surficial sediments were obtained from syringe cores taken from large box cores.

Phytoplankton in the water were preserved in 0.5 percent glutaraldehyde and refrigerated for 1 to 24 hours. They were then size-fractionated into 0.2 to 3, 3 to 8 and >8µm fractions, with 0.03 percent proflavine hemisulfate used to stain the latter two fractions, and mounted in immersion oil (Murphy and Haugen, 1985; Shapiro *et al.*, 1989). The 0.2-3 µm fraction was counted immediately on shipboard, the 3-8 µm fraction was counted immediately, if possible, and, if not, as soon as possible after returning. The >8 µm fraction was frozen and counted later. All samples were counted using an Olympus BH2-RFCA epifluorescence microscope with blue and green excitation light. Phytoplankton in the floating sediment trap were treated the same as those in the water. The moored sediment traps included so much material that they were split 10 or 11 times with a small plankton splitter before filtration. To obtain surficial sediments, the top 2 mm was removed using a core extruder, preserved in 2.5 percent glutaraldehyde and split in the same manner as the moored sediment trap samples.

Results and Discussion

Relationship of diatoms and silicate concentration — To test the hypothesis that the distribution of diatoms would be related to silicate availability, the percent diatoms >8 µm was calculated for each of four cruises (Table 1, except July 20-Aug. 7, 1990) and the C transect (Table 1) and compared with the dissolved Si/N ratios. The Si/N ratio was chosen becuse it is an indicator of potential N or Si limitation (Dortch and Whitledge, in press). Values <1 indicate potential Si limitation and >1 indicate potential N limitation. The abundance of diatoms relative to other autotrophs is lowest at low Si/N (Fig.1), implying silicate limitation. A major flaw of this analysis is that phytoplankton <8µm are excluded and these are ususally the non-diatoms that grow when silicate or Si/N is low (see results for

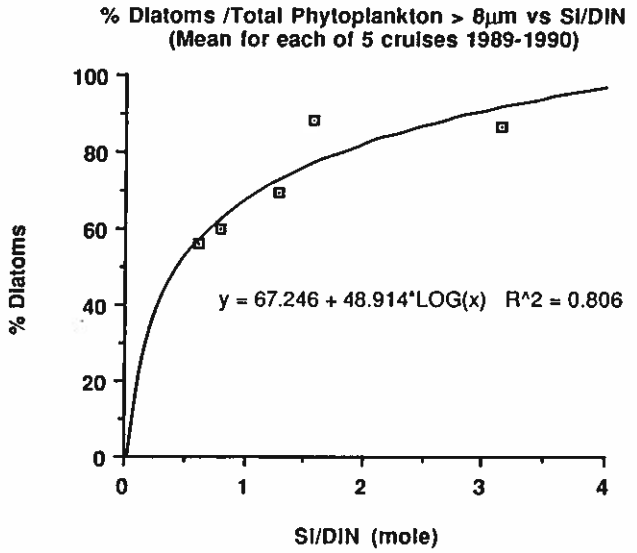


Figure 1. Average percent diatoms/total autotrophs >.8 µm vs. average Si/N for cruises on the Louisiana continental shelf.

mooored sediment trap). Thus, when all size fractions are included, the relationship between percent diatoms and Si/N will be strengthened.

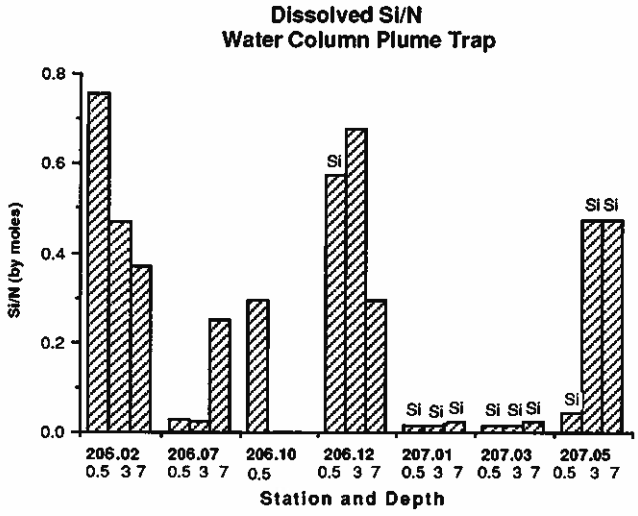
Direct sinking of phyto plankton

Floating Sediment Traps — Floating sediment traps were deployed in the plume region (two days, one trap at 15 m and one at 25 m) and the hypoxic region (one day, one trap at 15 m). While the traps were in the water, phytoplankton and nutrient samples were collected at three depths at intervals over the daylight hours.

In the plume region, N never reached limiting concentrations, although Si did on the second day (Fig. 2). However, the dominant phytoplanker, *Skeletonema costatum* (Table 2), did not show the morphology typical of Si limitation (Harrison et al. 1977) unti the very end. In the hypoxic region either Si or N was limiting much of the time, with Si limitation being more likely (Fig.2). The species composition was quite

Table 2. Dominant phytoplankton (>8μm) in the water column and in sediment traps and phytoplankton flux (cells/m²/d) for floating sediment traps, July and August 1990.

		Plume	Hypoxic
Water		*Skeletonema costatum*	*Ceratulina pelagica* *Rhizosolenia fragilissima*
Trap		*Skeletonema costatum*	*Skeletonema costatum*
Flux	**15 m**	1.5×10^9	6.5×10^8
	25 m	2.7×10^9	



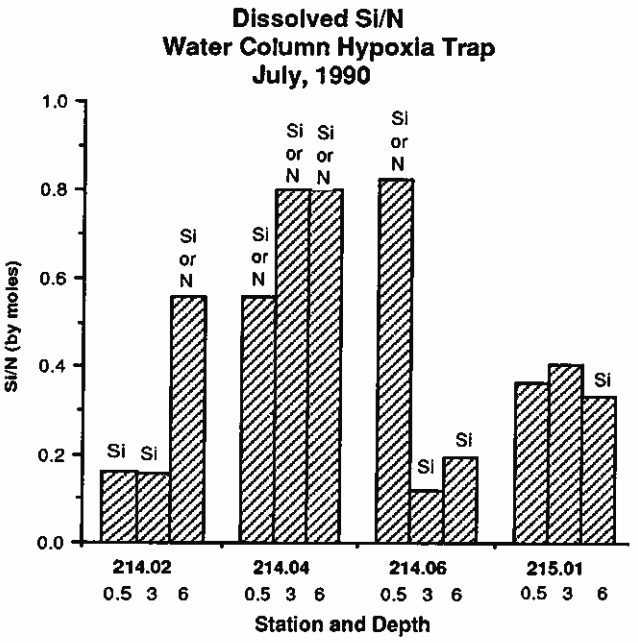


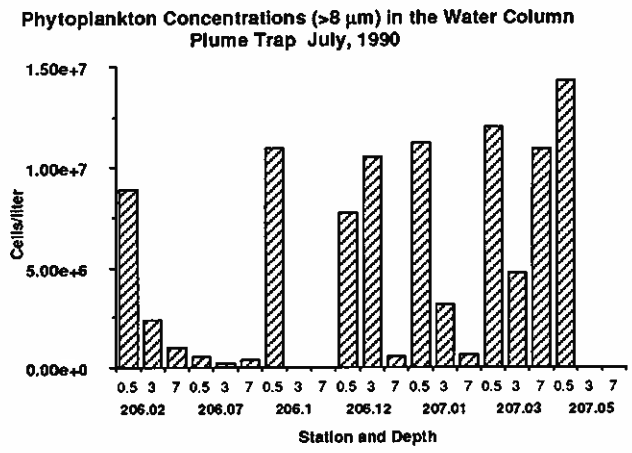
Figure 2. Dissolved Si/N ratios in the water while following the floating sediment traps in the plume and hypoxic regions. Si/N <1 indicates potential Si limitation. Si indicates that dissolved silicate concentration < 2 μM and N indicates that total dissolved inorganic N < 1 μM, the thresholds for Si and N limitation respectively.

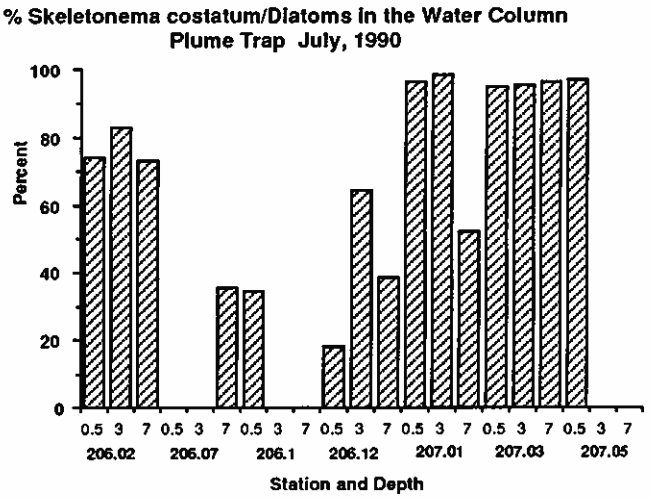
different from the plume region, with no *Skeletonema costatum*, which is moderately silicified, and was instead dominated by very lightly silicified phytoplankton (Table 2), such as *Ceratulina pelagica* and *Rhizosolenia fragillisima*.

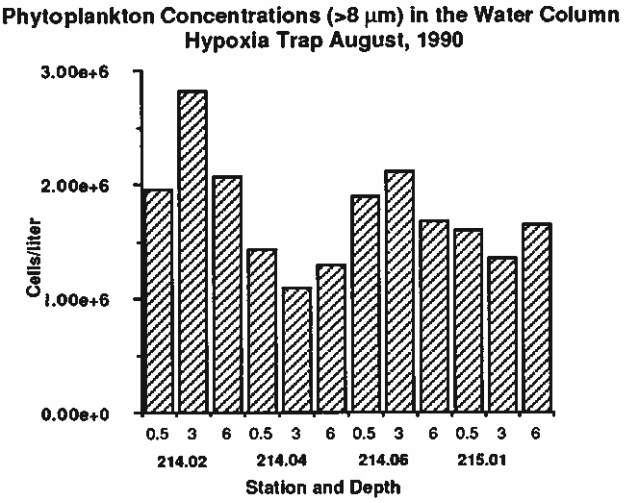
As a result of the nutrient limitation, the phytoplankton concentrations (>8μm) were an order of magnitude less in the hypoxic region, compared with the plume (Fig. 3). Similarly, the phytoplankton flux was also an order of magnitude less. Most of the flux consisted of diatoms, despite the low silicate concentrations. Furthermore, most of the diatom flux was *Skeletonema costatum*, even in the hypoxic region where there was virtually no *Skeletonema costatum* present in the water (Fig.4). Thus, it is clear that when Si is most limiting, the phytoplankton flux is much less, but still consists primarily of moderately silicified diatoms.

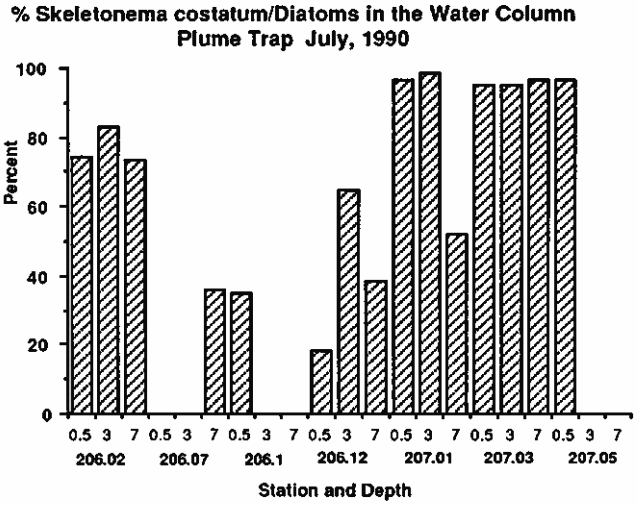
Moored Sediment Trap — Moored sediment traps were deployed from March through November 1990 at two depths at a station in the core of the hypoxic region (Station C6A, kRabalais *et al.*, unpubl.). The contents of the traps were removed at a three-week/one-week interval with water column sampling the day the contents of the three-week deployment were removed and the one-week deployment was begun. Except for chlorophyll and nutrients, the data for only the three-week/one-week deployments in May and the three-week deployment in September are shown. These dates were chosen because (1) they represent spring and late-summer periods, (2) the deployments had no problems, and (3) the fecal pellets in these traps are reported elsewhere (Qureshi *et al.*, this volume).

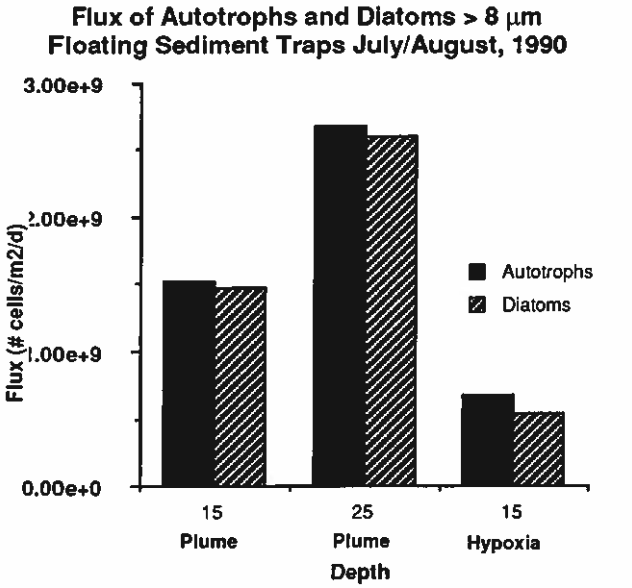
In this highly variable environment, chlorophyll and nutrients do not show a simple seasonal variation (Fig. 5), although the highest values of both occur in the spring. Silicate limitation (Si/N<1; Si <2; N >1) occurred toward the end of the three-week April/May deployment, during the one-week May deployment, and during the August/September three-week deployment (Fig. 5). This is clearly reflected in the phytoplankton species composition and size (Fig. 6, Table 3). The numbers of large phytoplankton (>8 μm) decreased drastically, while that of the small phytoplankton (0.2-3 μm and 3-8 μm) increased. The species composition changed from primarily large heavily and moderately silicified diatoms to non-diatoms and











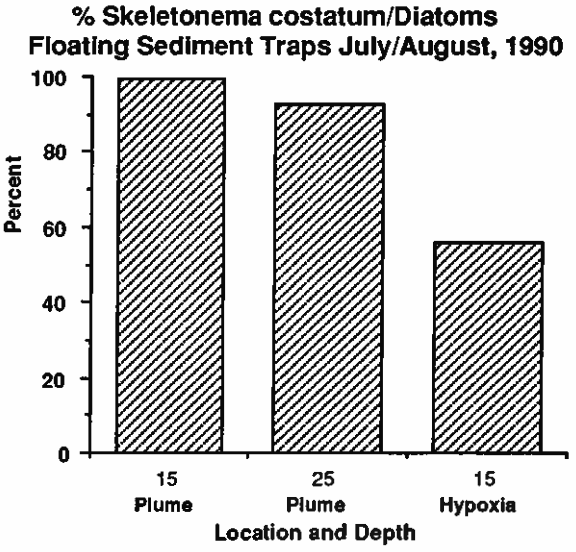


Figure 3.Phytoplankton abundance (>8 µm) in the water column while following floating sediment traps in the plume and hypoxic regions and phytoplankton and diatom flux into the traps.

Figure 4. Percent *Skeletonema costatum* / diatoms >8 µm in the water column while following floating sediment traps in the plume and hypoxic regions and in trap material.

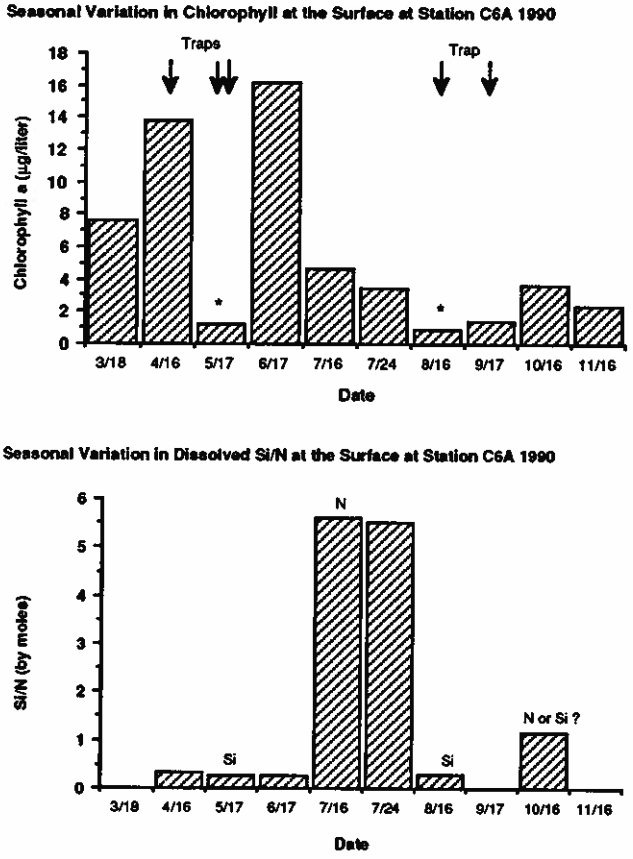


Figure 5. Seasonal variation of chlorophyll concentrations and Si/N ratios in surface waters at station C6A. Arrows indicate period of trap deployment. * indicates periods of Si limitation. Other symbols and ratios defined in Fig. 2.

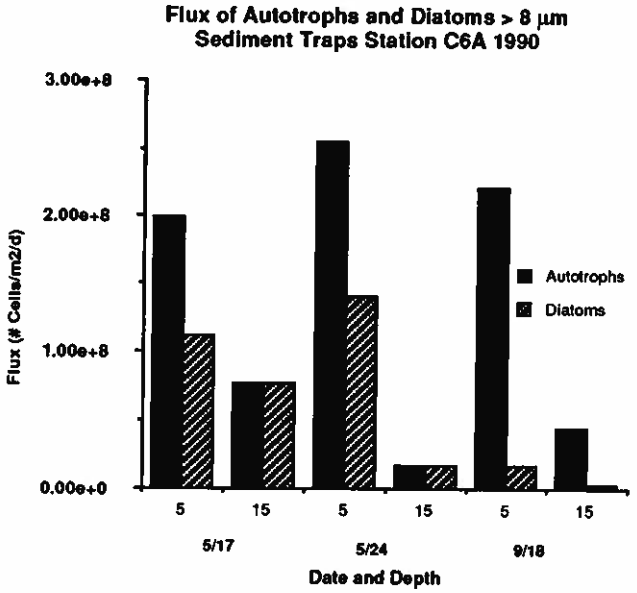


Figure 7. Phytoplankton and diatom (>8µm) flux into moored sediment traps at station C6A.

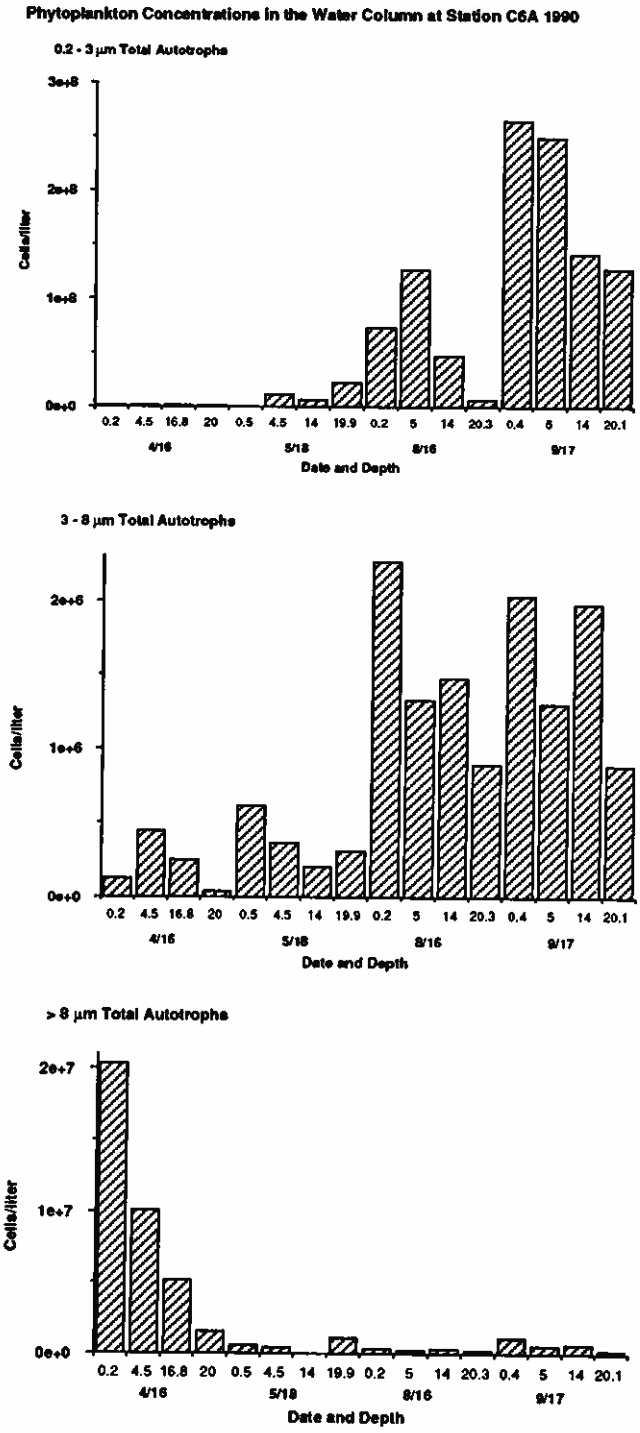


Figure 6. Phytoplankton abundance in the water (0.2-3 µm; 3-8 µm; >8 µm) on dates closest to moored sediment trap collections.

Table 3. **Dominant phytoplankton (>8μm) in the water column, sediment traps, and sediment and phytoplankton flux (cells/m^2/d) for the sediment trap moored at Station C6A in 1990.**

Date	4/16	5/17-18	5/24	8/16	9/17
Water	*Skeletonema costatum* *Chaetoceros* spp. *Nitzschia pungens* *Asterionelopsis glacialis*	Small non-diatoms *Bacteriastrum* sp. *Chaetoceros* spp. *Nitzschia pungens* *Asterionelopsis glacialis* *Skeletonema costatum*		Cyanobacteria small non-diatoms *Rhizosolenia fragilissima*	Cyanobacteria small non-diatoms *Rhizosolenia* spp. ? centrics
Trap		*Thalassionema nitzschioides*	Cyanobacteria		Cyanobacteria
		Nitzschia pungens ? pennates *Skeletonema costatum* *Chaetoceros* spp. *Ceratium* sp.	*Thalassionema nitzschoides* ? pennates *Asterionelopsis glacialis* *Skeletonema costatum*		? centrics *Thalassionema nitzschioides* *Hemiaulas* sp. *Chaetoceros* spp *Skeletonema costatum*
Sediment		*Thalassionema nitzschioides* ?centrics ? pennates *Chaetoceros* spp.			Cyanobacteria ? centrics ? pennates *Chaetoceros* spp.
Flux					
5 m		2.0×10^8	2.5×10^8		2.2×10^8
15 m		0.8×10^8	0.2×10^8		0.4×10^8

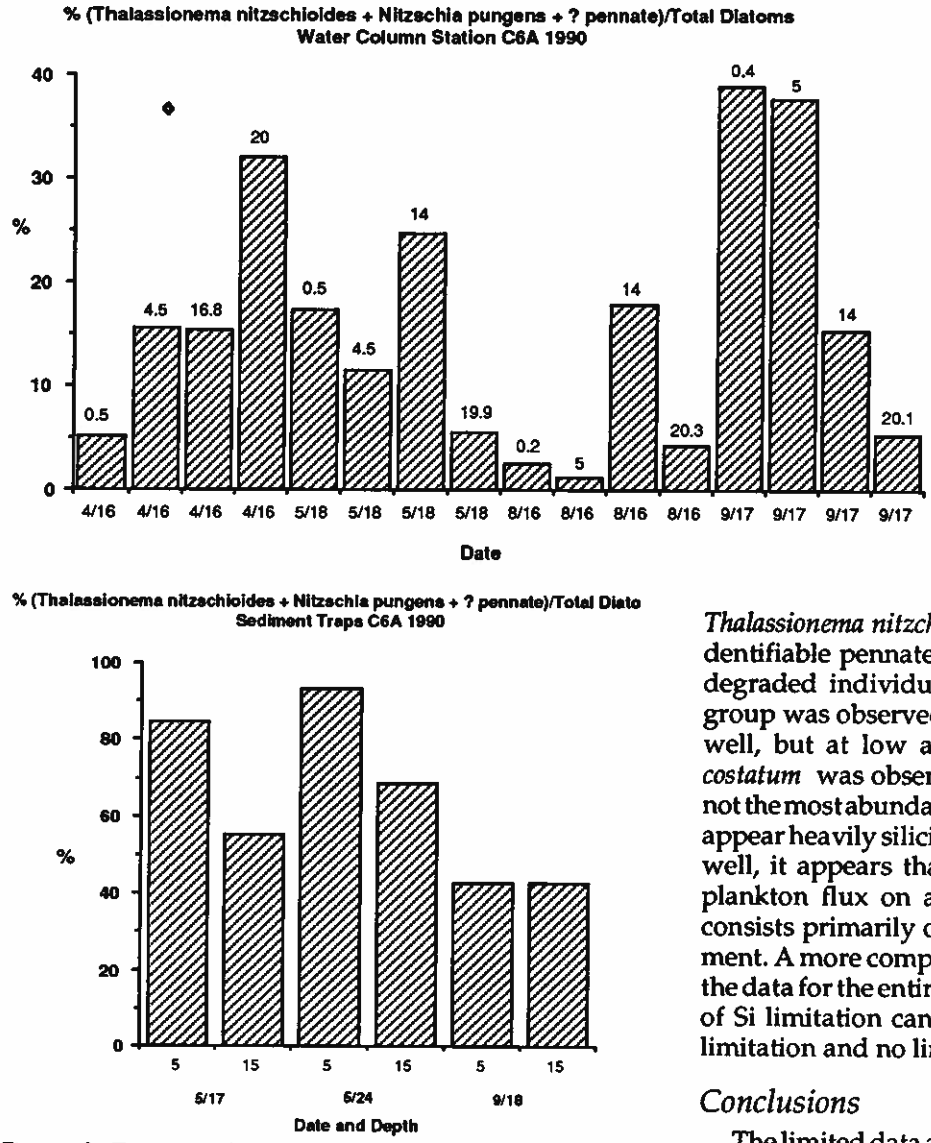


Figure 8. Percent (*Thalassionema nitzschioides* + *Nitzschia pungens* + ? pennate)/total diatoms > 8 µm in the water column and in the sediment traps.

lightly silicified diatoms, especially in the surface layers. In fact, the species composition suggests that Si limitation was more severe in the August/September period than in May.

The phytoplankton flux reflects the changed species composition (Fig. 7, Table 3). In the spring most of the flux, based on cell numbers, was diatoms, whereas in the late summer it was cyanobacteria, and the fluxes were similar. However, if the fluxes could be computed on the basis of carbon, the diatoms, which have much more C/cell than the tiny coccoid cyanobacteria, would dominate the flux and the flux would be much greater in the spring than the late summer. As with the floating sediment traps, the diatoms which comprised most of the material in the sediment traps were not necessarily the dominant organisms in the water column, although they were always present at some level (Fig. 8). This group consisted of three types, *Thalassionema nitzchioides, Nitzschia pungens* and unidentifiable pennates, which may have been partially degraded individuals of the first two species. This group was observed in the floating sediment traps as well, but at low abundance. Similarly, *Skeletonema costatum* was observed in the moored traps, but was not the most abundant. Microscopically, these pennates appear heavily silicified. Thus, in these experiments as well, it appears that Si is most limiting, the phytoplankton flux on a carbon basis is lower, but still consists primarily of diatoms with a high Si requirement. A more complete picture will be obtained when the data for the entire year are analyzed so that periods of Si limitation can be compared with periods of N limitation and no limitation.

Conclusions

The limited data available now for 1990 suggest that silicate limitation may have been widespread in the Louisiana coastal zone. As a result, the phytoplankton species composition was altered, especially when limitation was severe. First, there is a switch to lightly silicified diatoms. Later, small, non-diatoms predominate. The vertical flux of carbon due to phytoplankton sinking is lower during periods of low silicate availability. For the most part certain heavily or moderately silicified diatoms are responsible for most of the flux, even when Si is limiting. Most other diatoms are never found in traps. However, small coccoid cyanobacteria in clumps of sediment and detritus can also contribute to the vertical flux when Si concentrations are low and they dominate in the water column.

These results lead to several new predictions.

1. From simultaneous measurements of phytoplankton flux and phytoplankton species composition and the factors that regulate both, it may be possible to predict phytoplankton flux from phytoplankton distributions.
2. The magnitude of phytoplankton flux appears to be related to the presence of certain large, moder-

ately to heavily silicified diatoms. Since they probably have a high Si requirement, their abundance will be determined by Si availability. If the silicate input from the river continues the increase of the last several years (Turner and Rabalais, 1991) hypoxia may increase in intensity and/or duration.

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The fates and effects of riverine and shelf-derived DOM on Mississippi River plume/Gulf shelf processes

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Abstract

A variety of chemical and biological measurements provided complementary information on the dynamics of dissolved organic matter (DOM) during summer and winter cruises in the Mississippi River Plume/Gulf Shelf region. Non-conservative mixing of dissolved organic carbon (DOC) between the River and open Gulf was observed during the summer cruise, indicating a substantial input of DOC at intermediate salinities (15-30‰). Stable nitrogen isotope compositions of DOM isolated by ultrafiltration also indicated a source of freshly produced DOM at intermediate salinities during the summer, suggesting that phytoplankton were an important source of DOM in the plume. DOC mixing appeared to be fairly conservative during the winter cruise.

Calculation of areal bacterial demand for carbon indicated that bacteria consumed a substantial portion of the total carbon fixed by primary production in this region. The oxygen demand from growth of bacterioplankton in subsurface waters was sufficient to explain the occurrence of hypoxic conditions during the summer at stations where low oxygen levels were observed in bottom waters. Although more temporal data are needed to define seasonal trends accurately, bacterial activity, community respiration and nutrient regeneration rates were higher during the summer cruise than during the winter cruise. Rates of bacterial production, nitrogen regeneration and community respiration were highest at intermediate salinities in the plume, particularly during the summer. During both cruises, the proportion of total respiration and nutrient regeneration that were not accounted for by bacteria were consistently higher in the plume regions, where zooplankton grazing of particles may be relatively more important for nutrient regeneration than in regions where primary production was low.

Processes controlling the remineralization and fate of dissolved organic matter (DOM) in the Mississippi River Plume/Gulf Shelf (MRP/GS) region were studied to gain a fundamental understanding of the factors controlling productivity, hypoxia development and carbon transport and to fulfill the primary objectives of the Nutrient Enhanced Coastal Ocean Productivity (NECOP) program. The Mississippi River discharges ~2×10^{12} g of dissolved organic carbon (DOC) annually to the coastal waters of the Gulf of Mexico (Malcolm and Durum, 1976). In addition to this large load of dissolved organic materials the River also discharges dissolved inorganic nutrients that stimulate algal blooms in the plume region (Turner and Rabalais, 1991). Our studies in the MRP/GS region were focused on five primary objectives:

1. to determine the concentrations and origins of dissolved organic matter (DOM);
2. to determine the biological reactivity of DOM;
3. to determine the rates of ammonium regeneration and organic nitrogen utilization;
4. to determine the abundance and rates of production of heterotrophic bacteria; and
5. to estimate hetrotrophic bacterial carbon, nitrogen and oxygen demand.

Acknowledgements

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Materials and Methods

Study site and sampling procedures — An area of the northern Gulf of Mexico near the discharge of the Mississippi River was surveyed during two cruises of the NOAA vessel *MALCOLM BALDRIDGE* from July 18 to August 8, 1990, and from February 19-28, 1991. Nearly 70 percent of the river's discharge flows out of the Mississippi River delta. The remaining 30 percent enters the Gulf of Mexico through the Atchafalaya River, a large distributary of the Mississippi that flows into the Gulf west of the main delta. Samples were obtained near the outflows of the four major channels on the delta — the Southwest Pass, the South Pass, the Pass à Loutre and the Main Pass, and at stations to the west and to the south of the delta on the Louisiana Shelf. Water samples were collected with a clean plastic bucket or with Niskin bottles mounted on a Neil Brown Mk III CTD rosette.

DOM isolation and characterization — Concentrations of dissolved organic carbon (DOC) were measured using a Shimadzu TOC 5000 analyzer with a Pt catalyst (0.5 percent Pt on alumina) at 680 °C (Sugimura and Suzuki, 1988). Samples were filtered through a Whatman GF/F filter, acidified and purged with ultra-high purity oxygen immediately prior to analysis.

Standards were run several times each day, and the instrument and water blanks were evaluated during each cruise as described by Benner and Strom (1992).

Cross-flow ultrafiltration was used for the concentration and isolation of DOM from water samples (Benner, 1991). Water samples (100-200 l) were prefiltered through 0.2 µm pore-size filters and then through 1000 Dalton cutoff spiral wound polysulfone filters using an Amicon DC 10L ultrafiltration system. Concentrated DOM samples were diafiltered to remove sea salts and dried under vacuum in a Savant SpeedVac system. Stable carbon and nitrogen isotope compositions of the ultrafiltered DOM were measured using a sealed tube combustion method (Sofer, 1980). The isotope composition of a sample is defined as:

$$\delta^{h}I = [(R_{sample}/R_{standard}) - 1] \times 10^{3},$$

where ^{h}I is the heavy isotope of an element (^{13}C or ^{15}N) and R is the ratio of ^{13}C:^{12}C or ^{15}N:^{14}N in the sample and the standard. The standard for $\delta^{13}C$ was PDB (0.0‰), and the standard for $\delta^{15}N$ was air (0.0‰).

Bacterial abundance and production — Bacterial abundance was measured using epifluorescence microscopy of DAPI stained samples (Porter and Feig, 1980). Samples were analyzed in duplicate, and bacteria in at least 10 fields were counted for each microscope slide. Bacterial production was estimated from rates of DNA and protein syntheses as measured by a dual-label method using [^{3}H]Thymidine (TdR) and [^{14}C]Leucine (Leu) (Chin-Leo and Kirchman, 1988). Triplicate water samples (10 ml) were incubated with 10 nM (final concentration) [^{3}H]TdR (specific activity of 84.1 Ci mmol-1), and 20 nM (final concentration) [^{14}C]Leu (specific activity of 328.5 mCi mmol-1) for 30 min. All radioactive substrates were from New England Nuclear (Boston, Mass.). The nucleic acid and protein fractions were separated in all samples as described by Chin-Leo and Benner (1991) to test for the possible non-specific incorporation of TdR into protein. Replicate measurements of bacterial abundance and bacterial production (TdR and Leu incorporation) differed by <10 and <5 percent, respectively. Abiotic absorption of the labeled substrates was estimated by measuring the incorporation of radiolabeled substrates in samples previously fixed with formaldehyde (10 percent final concentration). All samples were corrected for abiotic incorporation by subtracting the radioactivity in the formalin-killed controls.

Bacterial parameters were measured in surface waters and with depth. Depending on the depth of the water column, between three to eight samples were collected to sample surface waters, the pycnocline and bottom waters. In shelf waters (<100 m), rates of TdR and Leu incorporation were integrated over the depth of the water column to estimate bacterial production on an areal basis. A step-wise rectangular integration method that does not require interpolating between points was used to obtain conservative estimates. Rates of TdR incorporation were converted to rates of C production using factors determined empirically by comparing isotope incorporation with increases of bacterial numbers and using a cell to C conversion value of 20 fg C cell^{-1} (Lee and Furhman, 1988). Experiments to determine empirical conversion factors were performed in duplicate using Mississippi River plume water. Estimates of bacterial C production were also determined from rates of Leu incorporation using a conversion factor of 3.1 kg C mol^{-1} of Leu (assuming an internal isotope dilution of 2) derived by Simon and Azam (1989), which is based on empirical confirmation of the assumptions of the Leu method and does not require a cell to C conversion factor.

Mesocosm experiments — Closed bottle incubations were conducted in the dark to differentiate heterotrophic processes from autotrophic ones and to compare the relative magnitude of heterotrophic activities at the respective sites. These experiments were conducted in 9-L glass bottles that were closed to the outside atmosphere and incubated for three to five days at *in situ* temperatures. For each experiment, duplicate bottles were set up for both filtered and unfiltered water samples. The filtered samples were prepared either by removing particles with a 1 µm pore-size filter (summer cruise) or by diluting (1:5) 3 µm pore-size filtered water with 0.2 µm pore-size filtered sea water from the same site (winter cruise). Both approaches decreased the quantitative importance of large organisms, i.e. zooplankton, large phytoplankton and detrital particles, relative to bacterial-sized particles. A second small reservoir, attached to each experimental bottle, provided makeup water for samples removed from the bottles without leaving an airspace. Each bottle was sampled at intervals of one or two times per day over the two- to five-day incubation interval. Concentrations of ammonium, dissolved oxygen, and carbon dioxide were monitored over time for each set of samples to provide an estimate of net mineralization rates for organic carbon and organic nitrogen in samples from the various sampling sites. Comparisons among sites, discussed here, are for accumulation or removal rates obtained over the whole incubation interval. In addition to measuring changes in dissolved organic components and mineralization products in the large dark bottles, additional indicators were used to assess organic matter turnover in the winter experiments, including: amino acid turnover, ammonium regeneration rates (as measured by isotope dilution), and process rate changes caused by bacterial manipulations (see below).

Ammonium and amino acid (and primary amine) concentrations were measured fluorometrically, after separation by cation exchange chromatography and reaction with o-phthalaldehyde/2-mercaptoethanol reagent (Gardner, 1978; Gardner and St. John, 1991). Amino acid turnover rates were determined by adding tracer amounts of a mixture of ^{3}H-labeled amino acids from algal protein hydrolysate (Amersham) to sea water and filtering 5 ml of sample through a 0.2 µm pore-size Millipore GS filter. After radioisotope addition, samples were filtered at various intervals from 0 to 30 minutes and dried. Biocount scintillation cocktail

(RPI) was added and samples were analyzed for radioisotope uptake on a LKB Model 1217 Rackbeta liquid scintillation counter. Counts were corrected to disintigrations per minute by calibration with quench curves and an external standard. Rates were calculated in the linear range of uptake as: [DPM(t1) - DPM(t0)] / Total DPM * 60 / (t1-t0).

Ammonium regeneration rates were estimated from changes in ammonium concentration and in isotope ratios of added $^{15}NH_4$ using the Blackburn/Caperon Model (Blackburn, 1979; Caperon *et al.*, 1979). Isotope ratios for ammonium in N-15 isotope dilution experiments were measured with a new HPLC technique that was developed to determine isotope ratios directly on filtrates of experimental water (Gardner *et al.*, 1991).

For bacterial manipulations, microbes less than 1 μm in size were concentrated to examine the effect of these microbes on amino acid turnover rates and on ammonium regeneration rates (as measured by isotope dilution of added $^{15}NH_4$). Ten liters of seawater, from the sites where large bottle experiments were conducted, were pre-filtered through a Gelman Polypure TDC capsule filter (nominal pore-size 1 μm). The filtrate was placed in a Gelman 3.8 L stainless steel pressure vessel and pumped through Gelman Acroflux capsule (0.2 μm pore size) at 100 psi. The retentate was collected and passed through the filter 4-6 times to further concentrate microbes. This concentrate was added back to treatments, for amino acid turnover rate and ^{15}N-NH_4 regeneration measurements, to increase heterotrophic bacterial concentrations from 7 to 29 percent above ambient concentrations.

Results and Discussion

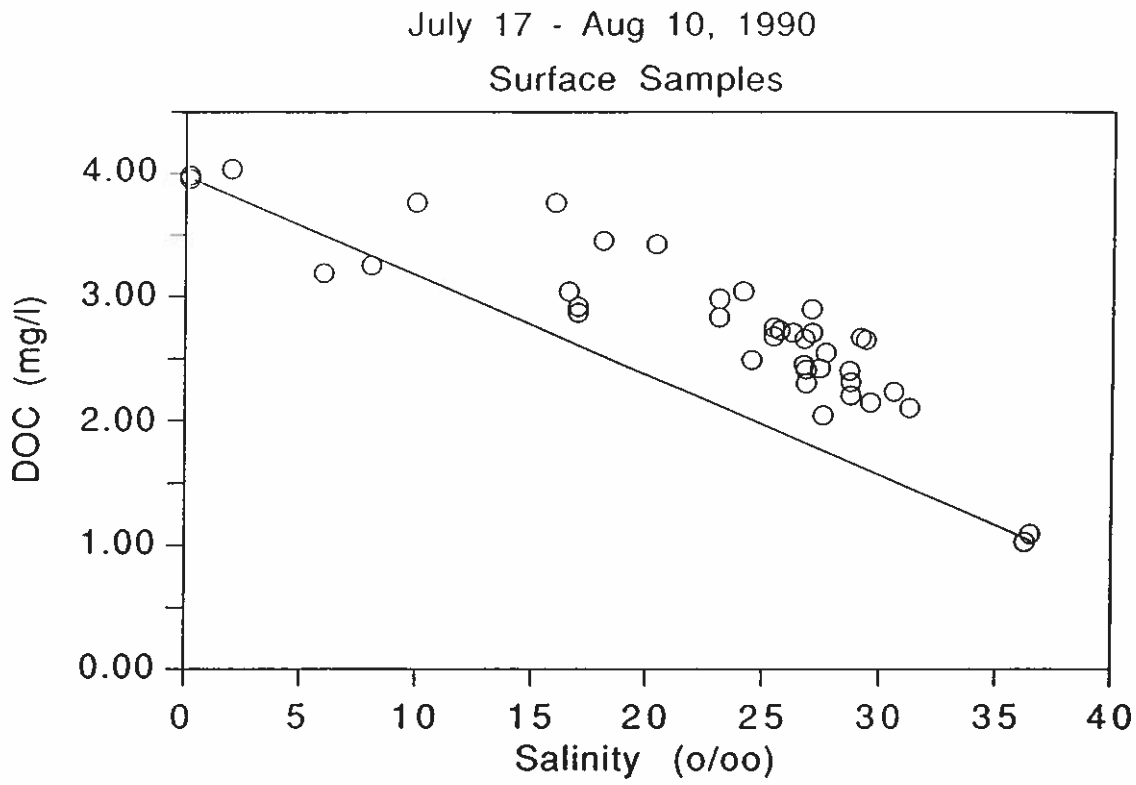
Dissolved Organic Matter — During both the summer and winter cruises, concentrations of DOC were measured at the Head of Passes in the Mississippi River and across a salinity gradient extending in a westerly direction from Southwest Pass on the Mississippi Delta to shelf and slope waters of the Gulf of Mexico. During the summer, DOC concentrations ranged from 4 mg C l^{-1} in the River to 1 mg C l^{-1} in surface waters of open Gulf water (Fig. 1a). Mixing between these two end members was not conservative, as DOC concentrations were enhanced at intermediate salinities (15-30‰). Enhanced DOC concentrations at intermediate salinities coincided with high phytoplankton production in surface water (Lohrenz *et al.*, 1991 NECOP Workshop Abstract) indicating that primary production was a potentially significant source of DOC during the summer in this region of the plume. DOC concentrations were lower during the winter in both the river (3.25 mg C l^{-1}) and the open Gulf (0.75 mg C l^{-1}). Mixing between these two end members was linear during the winter (Fig. 1b), indicating a fairly conservative behavior of DOC.

Dissolved organic matter (DOM) was isolated from water samples during the summer and winter cruises by cross-flow ultrafiltration with 1000 Dalton cutoff filters (Benner, 1991). The isolated material was subjected to a variety of isotopic and chemical analyses to study the fate of riverine DOM and to characterize the sources of DOM in shelf waters. The percentage of total DOC isolated by ultrafiltration decreased linearly from 45 percent in the river to ~27 percent in open Gulf waters. These spatial changes in the fraction of DOM recovered by ultrafiltration indicate that the average molecular size of riverine DOM is considerably greater than that of marine DOM. The percentage of DOC isolated at a given salinity was similar in summer and winter indicating that the average molecular size of the DOM did not vary temporally.

The completed analyses of stable carbon and nitrogen isotope compositions of the DOM samples collected during the summer cruise (Fig. 2) showed that stable carbon isotope ratios ($\delta^{13}C$) of DOM ranged from -25‰ in the river to -21.3‰ in the open Gulf. These ratios for ultrafiltered DOM are similar to ratios reported previously for bulk DOC in the river (-26 to -28‰) and the open Gulf (-22‰; Eadie *et al.*, 1978). Mixing between these two end members was approximately linear across the salinity gradient (Fig. 2a). The data for total DOC concentrations indicated a significant algal source of DOC at intermediate salinities, but the stable carbon isotope data do not indicate a significant input of algal-derived DOC above that expected for conservative mixing. However, we have preliminary data indicating that the inorganic carbon pool at intermediate salinities is depleted in ^{13}C by several parts per thousand relative to marine bicarbonate (~0‰), and the incorporation of this carbon into algal biomass would result in material that was isotopically "light" (-22 to -24‰) for algal-derived carbon. We therefore do not interpret the linear increase in stable carbon isotope ratios for DOC as completely conservative mixing between end members.

The stable nitrogen isotope ratios for the DOM isolated during the summer cruise demonstrate a strikingly different pattern across the salinity gradient (Fig. 2b). The $\delta^{15}N$ values for DOM from the River and the open Gulf were both near 3‰. No significant changes in isotopic composition across the salinity gradient would be expected if isotopic values resulted from conservative mixing between these two end members. Instead, $\delta^{15}N$ values increased significantly at intermediate salinities with maximal values near 9‰. It is evident that another source of organic nitrogen is contributing to the DOM pool at intermediate salinities. Cifuentes (1990 NECOP meeting, Miami, Fla.) reported a $\delta^{15}N$ value of ~10‰ for nitrate in the Mississippi River during the summer of 1990. It appears that riverine nitrate is incorporated into phytoplankton biomass at intermediate salinities and that DOM with a high $\delta^{15}N$ value (~10‰) is released from phytoplankton. We speculate that zooplankton grazing is the mechanism for the release of this DOM.

Heterotrophic bacterial abundance and production — Bacterial abundance and production were measured in water samples during the summer and winter



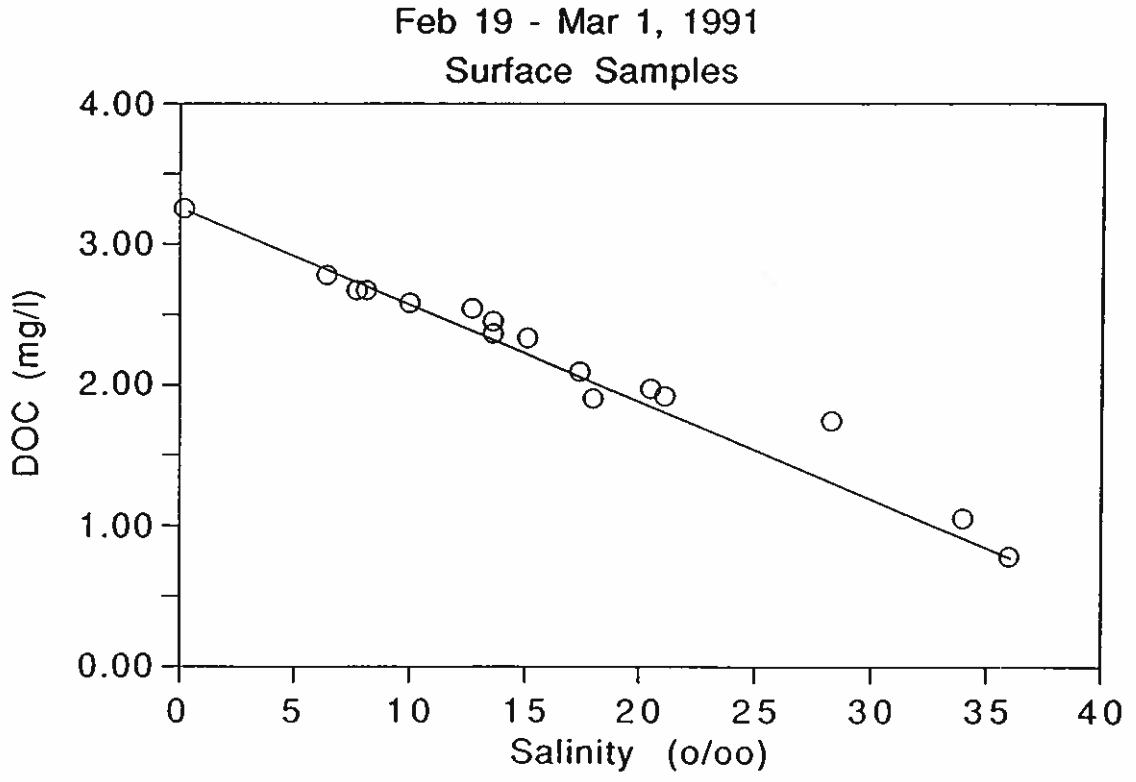


Figure 1. Concentrations of dissolved organic carbon (DOC) in surface water samples of varying salinity during the summer and winter NECOP cruises. The lines represent expected DOC values given conservative mixing between the freshwater and marine end members.

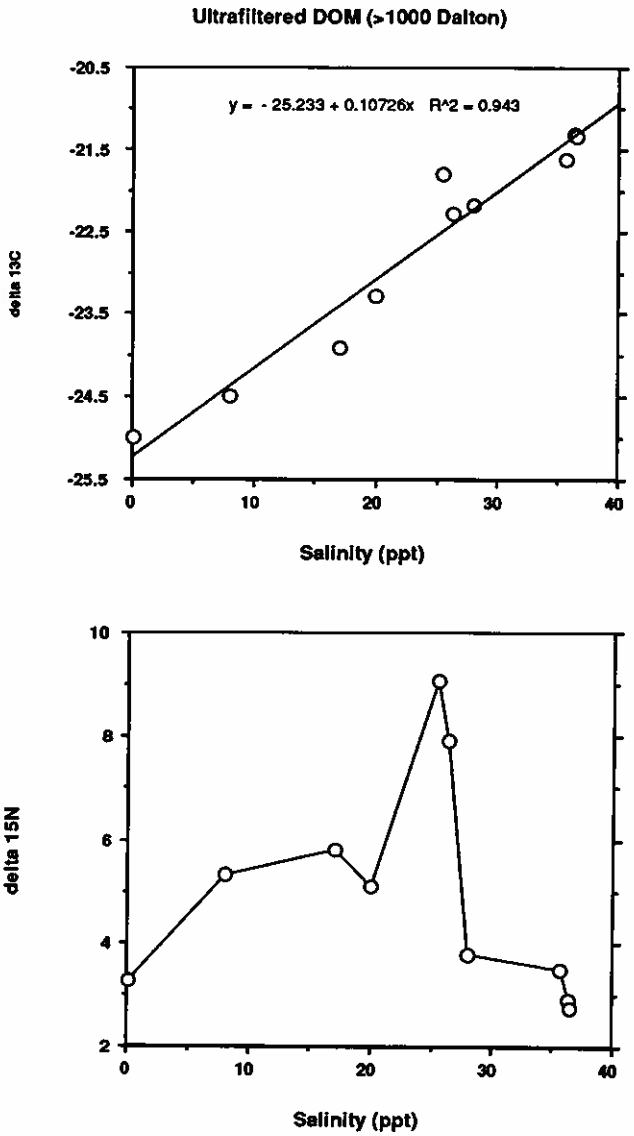


Figure 2. Stable carbon and nitrogen isotope compositions for ultrafiltered dissolved organic matter (DOM). A linear regression is shown for the stable carbon isotope data.

NECOP cruises. These data have been submitted for publication (Chin-Leo and Benner, 1991) and are summarized herein. Bacterial abundance ranged from 0.25 to 3.34 x 10^9 cells l^{-1} during summer and 0.36 to 1.09 x 10^9 cells l^{-1} in winter (Fig. 3a,d). During summer, maximal bacterial abundances occurred at intermediate salinities whereas during winter abundances were much less variable across the salinity gradient. Two independent indices of bacterial production, based on rates of DNA (thymidine incorporation) and protein synthesis (leucine incorporation), were measured. The magnitude of thymidine (TdR) and leucine (Leu) incorporation rates varied over the salinity gradient during summer and winter with maximal values occurring at intermediate salinities (Figs. 2b,c,e,f). Rates of TdR and Leu incorporation were significantly correlated during summer ($p = 0.0001$) and winter ($p = 0.0001$). The regions of maximal rates of TdR and Leu incorporation in surface water coincided with regions of enhanced phytoplankton production (Lohrenz *et al.*, 1991 NECOP Workshop Abstract) and phytoplankton-derived DOM. Overall, rates of TdR and Leu incorporation were several-fold higher in summer than in winter, particularly at intermediate salinities.

Depth profiles of rates of TdR and Leu incorporation were measured at 12 locations on the Louisiana shelf during the summer and four locations during the winter. Depth-integrated estimates of bacterial production were derived from rates of TdR incorporation using an empirically-derived conversion factor (1.89 x 10^{18} cells $mole^{-1}$) and a cell to C conversion factor of 20 fg C $cell^{-1}$ (Lee and Fuhrman, 1988). Depth-integrated rates of Leu incorporation were converted to estimates of bacterial production using the conversion factor (3.1 kg C mol^{-1}) determined by Simon and Azam (1989). During summer, integrated bacterial production on the shelf based on TdR incorporation varied from 238 to 740 mg C m^{-2} d^{-1} with a mean value of 443 mg C m^{-2} d^{-1} (Table 1). The corresponding estimates based on Leu incorporation ranged from 234 to 789 mg C m^{-2} d^{-1} with a mean value of 462 mg C m^{-2} d^{-1} (Table 1). Estimates of bacterial production during winter were about half of those during the summer with a mean value of 226 mg C m^{-2} d^{-1} based on TdR incorporation and 277 mg C m^{-2} d^{-1} based on Leu incorporation (Table 1).

Bacterial carbon metabolism and oxygen utilization — The potential role of bacteria in the cycling of C can be estimated from rates of bacterial production if the average bacterial growth efficiency is known. Mean integrated bacterial production in the Mississippi River plume based on TdR incorporation was 0.44 g C $m^{-2}d^{-1}$ in summer and 0.23 g C m^{-2} d^{-1} in winter. Using the range of bacterial growth efficiencies (10 to 30 percent) determined during the NECOP cruises (see below), the amount of C necessary to sustain these rates of bacterial production was 1.48 to 4.43 g C m^{-2} d^{-1} in summer and 0.75 to 2.26 g C m^{-2} d^{-1} in winter. Estimates of phytoplankton production during July and August 1990 ranged from 2 to 10 g C m^{-2} d^{-1} and during March 1991 ranged from 0.1 to 0.5 g C m^{-2} d^{-1} (Lohrenz *et al.*, 1991 NECOP Workshop Abstract). It is obvious from a preliminary analysis of these data that bacterial production on the Louisiana shelf consumed a substantial fraction of the C fixed by phytoplankton during the summer of 1990. Using median values for algal and heterotrophic bacterial production we estimated that ~50 percent of the total phytoplankton production was consumed by bacterioplankton. During the winter of 1991 phytoplankton production alone could not support the estimated bacterial carbon demand, indicating that riverine-derived organic matter was an important source of substrate supporting bacterioplankton growth.

A recurrent feature of the Mississippi River plume ecosystem is the presence of low oxygen concentrations in bottom waters west of the main river delta during summer (Turner and Allen, 1982). These hypoxic conditions probably result from the heterotro-

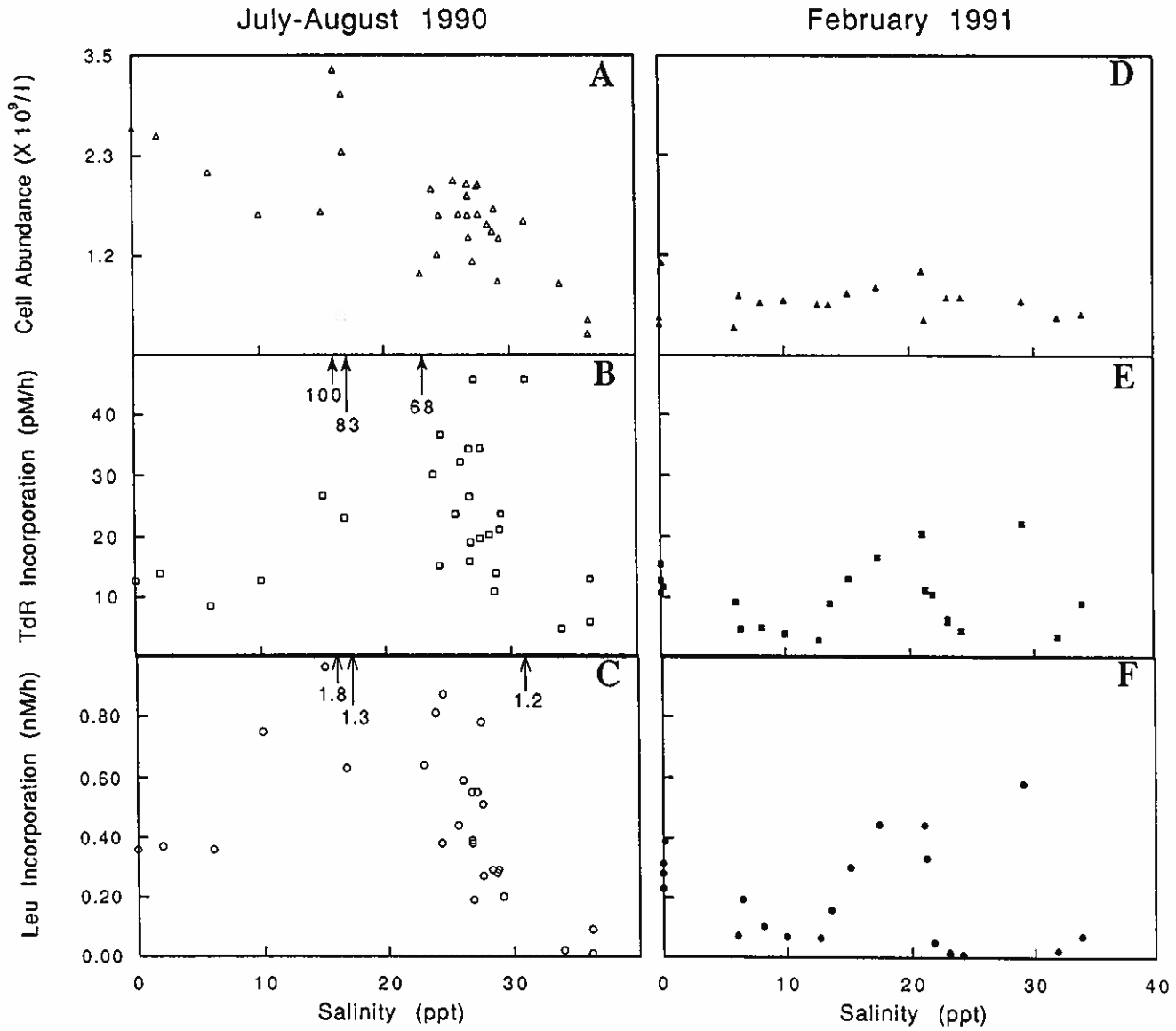


Figure 3. Scatter plots of surface water distributions during July and August 1990 of (A) cell abundance, (B) rates of TdR incorporation and (C) rates of Leu incorporation, and during February 1991 of (D) cell abundance, (E) rates of TdR incorporation and (F) rates of Leu incorporation.

phic utilization of organic matter in the water column and sediments and the lack of vertical mixing due to stratification. Rates of bacterioplankton C production can be used to estimate the O_2 demand by bacteria if bacterial growth efficiencies and respiratory quotients (RQ) are known. During the summer cruise four stations were surveyed where oxygen concentrations in bottom waters were <1 ml l^{-1}. At these stations, we estimated the possible role of planktonic bacteria in the establishment of these hypoxic conditions by calculating the time that would be required for bacteria below the pycnocline to reduce the oxygen concentration from a saturated value (4.51 ± 0.13 ml l^{-1}) to the *in situ* levels. We assumed: (1) the pycnocline prevented any gas exchange with overlying waters and horizontal mixing was negligble; (2) a bacterial respiratory quotient of 1; (3) a range of bacterial growth efficiencies from 10 to 30 percent. Using a 10 percent growth efficiency, bacterial oxygen demand would have reduced the concentration of oxygen from saturation to *in situ* levels in 13 to 28 d. Using a 30 percent growth efficiency, the range was from 40 to 84 d. If the bulk of the C supporting bacterial growth originates from the spring bloom, the oxygen demand from growth of planktonic heterotrophic bacteria in subsurface waters was sufficient to establish hypoxic conditions by summer.

Mesocosm experiments — Rates of dissolved oxygen consumption and carbon dioxide production (winter only) were measured during the mesocosm experiments to determine the total amount of organic matter that was oxidized and the relative lability of organic matter at various locations in the MRP/GS region. Rates of oxidation were usually higher in bottles with

Table 1 Depth integrated bacterioplankton C production on the Louisiana continental shelf. Estimates were calculated using rates of thymidine incorporation and an empirically determined conversion factor. Leucine incorporation rates were converted to rates of C production using the conversion factor determined by Simon and Azam (1988).

Date	Station	Latitude(W)	Longitude(N)	Surface Salinity (‰)	Depth (m)	Integrated Bacterial Production (mgC m^{-2} d^{-1}) TdR*	Leu#
27-Jul-90	HT-2	28° 50'	89° 49'	16	54	588	789
31-Jul	Anchor-2	28° 53'	89° 56'	18	36	399	591
29-Jul	HT-18	28° 48'	91° 31'	23	21	509	458
27-Jul	HT-8	28° 40'	90° 30'	24	18	362	441
21-Jul	J	28° 50'	89° 10'	24	99	740	719
29-Jul	HT-12	28° 36'	91° 00'	26	21	353	518
20-Jul	H	29° 17'	88° 52'	27	36	303	269
21-Jul	K	28° 50'	89° 22'	27	63	434	365
29-Jul	HT-20	28° 54'	91° 53'	27	20	238	328
21-Jul	I	28° 55'	89° 02'	28	75	614	374
29-Jul	HT-14	28° 27'	90° 59'	29	55	360	234
27-Jul	HT-10	28° 18'	90° 29'	29	56	411	457
					Mean ± SD =	443 ± 144	462 ± 170
23-Feb-91	Anchor-1	28° 54'	89° 29'	6	29	102	148
26-Feb	HT-18	28° 40'	90° 29'	18	17	143	192
24-Feb	Miss. Can.-1	28° 41'	89° 40'	21	92	363	487
22-Feb	C	28° 46'	89° 30'	22	84	299	279
					Mean ± SD =	226 ± 124	277 ± 151

*Estimated using a conversion factor of 1.89 X 10^{18} cells $mole^{-1}$ of thymidine and 20 fg C $cell^{-1}$ (Lee and Furhman 1987)
#Estimated using a conversion factor of 3.1 kg C $mole^{-1}$ of leucine (Simon & Azam 1988).

Table 2. Summary of rates of bacterial production, community respiration, and estimated bacterial growth efficiencies during mesocosm experiments conducted on the June/July 1990 NECOP cruise. Water samples were unfiltered (whole) or prefiltered through a 1 μm pore-size filter (filtered). Each number represents the mean of two replicate bottles.

Salinity (ppt)	Temperature (C)	Treatment	Bact. Production (μM C/h)	Respiration (μM O2/h)	Bact. Growth Efficiency (%)
0	28	whole	0.038	NA	NA
		filtered	0.034	NA	NA
17	28	whole	0.112	1.30	8
		filtered	0.105	0.74	13
17	30	whole	0.062	0.35	15
		filtered	0.067	0.19	26
23	31	whole	0.102	0.74	12
		filtered	0.027	0.24	10
36	24	whole	0.033	0.06	35
		filtered	0.038	0.01	82

Table 3. **Summary of rates of bacterial production, community respiration, carbon mineralization and estimated bacterial growth efficiencies during mesocosm experiments conducted on the February 1991 NECOP cruise. Water samples were unfiltered (whole) or diluted (1:5) with 0.2 µm pore-size filtered water (filtered). Each number represents the mean of two replicate bottles.**

Salinity (ppt)	Temperature (C)	Treatment	Bact. Production (µM C/h)	Respiration (µM O2/h)	Mineralization (µM C/h)	Bact. Growth Efficiency (%)
0	9	whole	0.058	0.19	0.11	24
		filtered	0.038	0.14	0.12	22
17	16	whole	0.065	0.56	0.61	10
		filtered	0.077	0.27	0.34	22
28	17	whole	0.059	0.33	0.43	15
		filtered	0.063	0.23	0.19	22
34	20	whole	0.047	0.10	0.23	32
		filtered	0.024	0.09	0.09	20

unfiltered water than in bottles containing filtered water (Tables 2, 3), indicating that detrital particles were important substrates for oxidation or that attached microflora and larger organisms were responsible for a significant fraction of the total respiration. Respiration rates ranged from 0.01 to 1.30 µM O_2 h^{-1} and were highest in plume waters of intermediate salinities (17 - 28‰) during both the summer (Table 2) and winter (Table 3). During the winter cruise both O_2 consumption and CO_2 production were measured as independent indicators of organic matter oxidation. Rates of O_2 consumption and CO_2 production were comparable and the overall mean respiratory quotient ($\Delta CO_2/\Delta O_2$) was 0.99 (excluding the data for the unfiltered bottle at 34‰ salinity).

Integrated estimates of bacterial carbon production did not show a consistent pattern of significantly higher rates of production in unfiltered water samples as was demonstrated with respiration rates (Tables 2,3). These results suggest that most bacterial production was supported by dissolved organic matter rather than particulate materials. As with respiration rates, bacterial production was highest in plume waters of intermediate salinities. Estimates of bacterial growth or carbon conversion efficiencies were calculated as:

Growth efficiency = bacterial production/(bacterial production + respiration)

assuming that the average respiratory quotient (RQ) was 1.0. Calculated growth efficiencies ranged from 8 to 35 percent (Tables 2, 3), excluding the high value of 82 percent determined for filtered Gulf water (36‰ salinity) during the summer. We did not observe any consistent spatial or temporal patterns in bacterial growth efficiencies. The average bacterial growth efficiency was 19 percent.

The patterns and rates of ammonium accumulation in the dark provided insights on the lability and chemical nature of dissolved organic nitrogen in the water samples from the respective sites and also provided information about whether bacteria and other heterotrophic organisms in the samples were net producers or users of dissolved ammonium. Results from the filtered and unfiltered samples were compared to provide insights on the relative importance of bacteria and larger heterotrophic organisms, respectively, in the mineralization process at the different sites and to provide comparisons between DOM and POM as substrate sources for the production of mineralized end products.

Three patterns of net ammonium accumulation or removal were observed — an increase in ammonium concentrations with time of incubation, no change in ammonium concentrations, or a decrease in ammonium concentrations. In experiments where accumulation of ammonium was observed, the rates of ammonium accumulation in the dark bottle experiments were generally linear with time of incubation. Samples showing no change in ammonium levels generally had no measureable ammonium either at the beginning or during the course of the experiments.

Duplicate-bottle ammonium regeneration rate results were generally in good agreement with each other (see SE bars on Figure 4) and results from duplicate treatments at each station were averaged to compare ammonium regeneration trends with salinity and to compare summer and winter trends (Fig. 4).

In July and August 1990, rates of ammonium accumulation for the river and offshore samples were generally <10 nM h^{-1}, as compared to rates of about 30 to 150 nM h^{-1} at the plume stations (salinities of 17 to 23‰) (Fig. 4a). These results are consistent with the hypothesis that organic nitrogen recently fixed by phytoplankton is rapidly recycled in the plume. The relatively low rates at the other stations may reflect low concentrations and fluxes of organic nitrogen substrates because temperatures were similar at all the stations in the summer. Alternatively, low net rates at high salinity stations could reflect a greater microbial demand for inorganic nitrogen than was observed at the low salinity stations.

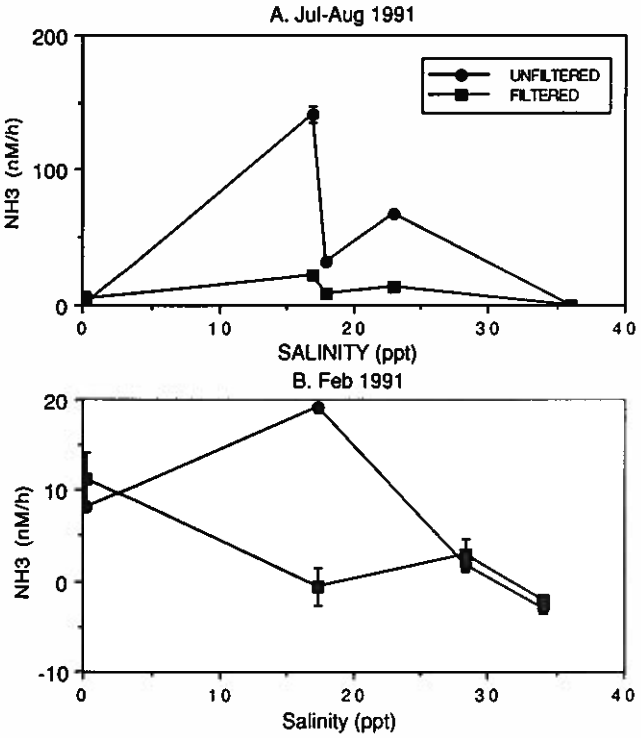


Figure 4. Net ammonium accumulation rates in the dark in water collected from different sites during the July and August 1990 and February 1991 cruises. For filtered treatments, water was either prefiltered through a 1 μm pore-size filter (July and August) or filtered (3 μm pore-size) water was diluted (1:5) with 0.2 μm pore-size filtered water (February). Error bars represent one standard error of the mean.

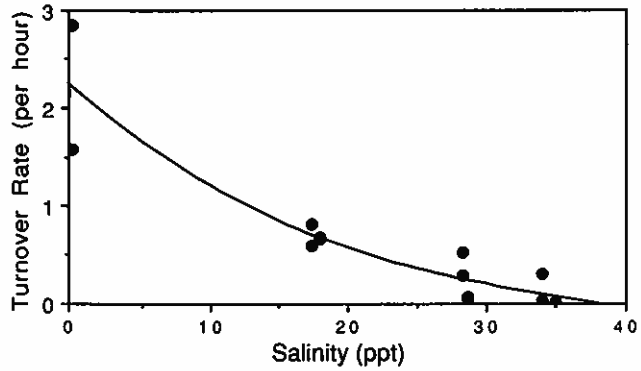


Figure 5. Amino acid turnover rates at different sites in the Mississippi River plume/Gulf shelf system during the February cruise.

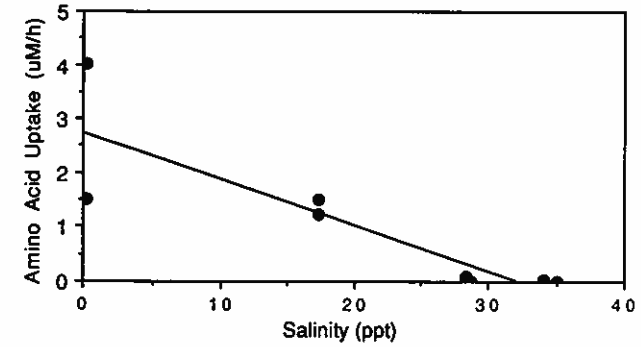


Figure 6. Amino acid uptake rates at different sites in the Mississippi River plume/Gulf shelf system during the February cruise. Uptake rates were determined by multiplying measured amino acid concentrations by turnover rates.

In contrast to results from the river and coastal plume samples, the samples from high-salinity stations (e.g. blue water station, and bottom water from hypoxic region) did not accumulate any ammonium during the course of our incubations. This result indicates either that ammonium was not produced in these waters or that that any ammonium produced in the bottles was quantitatively removed by microbes. For example, if the bacteria use organic substrates with a high molar C:N ratio, i.e. greater than 7, they could be net consumers of ammonium. Alternatively, autotrophic nitrifiers may have used ammonium as an energy source and quantitively removed it from solution.

The relative importance of the bacterial-sized fraction compared to larger particles in mineralizing organic nitrogen was dependent on the site of sampling. Ammonium accumulation rates in bottles containing filtered and unfiltered water samples were similar to each other in both the river and offshore stations. In contrast, the <1 μm size fraction accounted for only a relatively small fraction (20 to 25 percent) of total ammonium accumulation at the plume stations (Fig. 4). At stations where organic nitrogen mineralization was relatively high, only a small fraction of the total mineralization was attributed to microbes in the filtered bottles (Fig. 4). Thus, an important interaction was observed between sampling sites and the proportion of total ammonium regeneration accounted for by bacterial-sized particles. These results agree with those for respiration in the mesocosms and suggest that micro- or meso-zooplankton may account for a substantial portion of total nitrogen remineralization at the plume sites where primary production is relatively high.

Ammonium accumulation rates in the winter cruise (February 1991) ranged from negative values at the offshore station to near 20 nM h^{-1} for the unfiltered water at the near-river plume station (salinity = 17‰). Although rates at some stations were comparable to those sampled in the summer, those in the near-river plume were an order of magnitude lower (Fig. 4b). As was observed in the summer, differences between the unfiltered and filtered treatments were small in all samples except for the near-river plume station that had a relatively high ammonium accumulation rate in the unfiltered sample but a net uptake of ammonium (near zero) in the filtered sample.

In contrast to results from the summer cruise, water sampled from the river yielded ammonium accumulation rates (about 10 nM h-1) that were higher than those from the high salinity (>20‰) stations. Except for the plume station (salinity = 17‰), which showed a large discrepency in dark ammonium accumulation rates between the unfiltered and filtered samples, the rate of ammonium accumulation tended to decrease with increased salinity (Fig. 4b). Examination of amino acid turnover and uptake rates indicated patterns of bacterial activity consistent with the dark-ammonium accumulation rates in the diluted bottles. Amino acid turnover rates were highest in the river and decreased with

increasing salinity in the plume (Fig. 5). This result implies that the river had greater organic carbon demand than the plume if the assumption is made that DON composition and isotope dilution were comparable at all sites. The relationship of total amino acid uptake rate to station salinity (Fig. 6) generally resembled that for amino acid turnover (Fig. 5), indicating that the results from most of the sites were not influenced by isotope dilution during measurements. Amino acid turnover rates were also normalized for bacterial numbers, but again similar decreases were observed with increasing salinity (Fig. 7). These results imply that bacteria have a greater demand for amino acids in the river than in the plume and, if it is assumed that amino acids are representative of labile DON, they suggest that bacteria in the river and near-shore plume have the greatest DON demand of the sites examined.

These results imply that, at least in the winter, bacteria in the river and nearshore plume are more likely to remineralize available DON than are bacteria from offshore sites. However, DON cannot be remineralized to ammonium if it is not available for bacterial utilization. We examined the effect of increasing microbial concentration on amino acid turnover rates and on ammonium regeneration rates to get a relative idea of the size of of the labile DON pool at three different sites. In these experiments, amino acid turnover and ammonium regeneration rates were likely indicative of the size of the labile organic nitrogen pool because changes in rates with changes in bacterial concentrations were consistent with results from the bottle experiments. In the river and at the second anchor station (salinity = 28‰), neither amino acid turnover rates (Fig. 8) nor total ammonium regeneration rates, measured in $^{15}NH_4$ isotope dilution experiments (Fig. 9), increased with increasing microbe concentrations. These results suggest that ambient DON concentrations were turning over at maximal rates and that ambient concentrations of labile DON were low. At the near-river plume station, however, the amino acid turnover rates (Fig. 8) and ammonium regeneration rates (Fig. 9) both increased hyperbolically with increased bacterial concentrations. These results indicate that ambient labile DON concentrations were sufficiently high to support greater microbial uptake rates than were observed at this site. The close agreement between the patterns of amino acid turnover (Fig. 8) and ammonium regeneration (Fig. 9) with increased bacterial abundances at the different sites is consistent with the idea that both of these measurements reflect the relative turnover of DON at the different sites.

In conclusion, the results suggest that heterotrophic bacterial production and nutrient regeneration processes in the study region both depend strongly on the recycling of fresh organic material produced by phytoplankton in the near-river plume. Organic matter delivered from the river may also support a significant fraction of bacterial activity, particularly in the winter when primary productivity in the plume is relatively low.

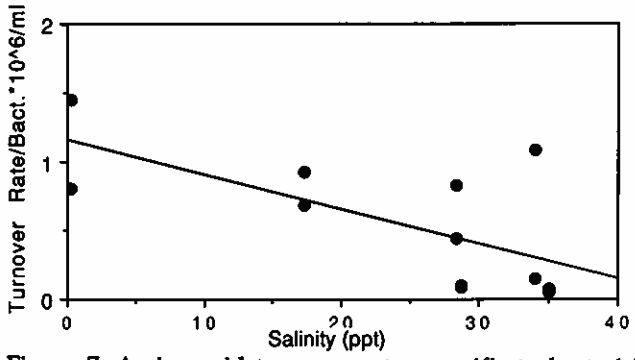


Figure 7. Amino acid turnover rates specific to bacterial numbers. Turnover rates were divided by ambient bacterial concentrations (cells per ml) to obtain y-values.

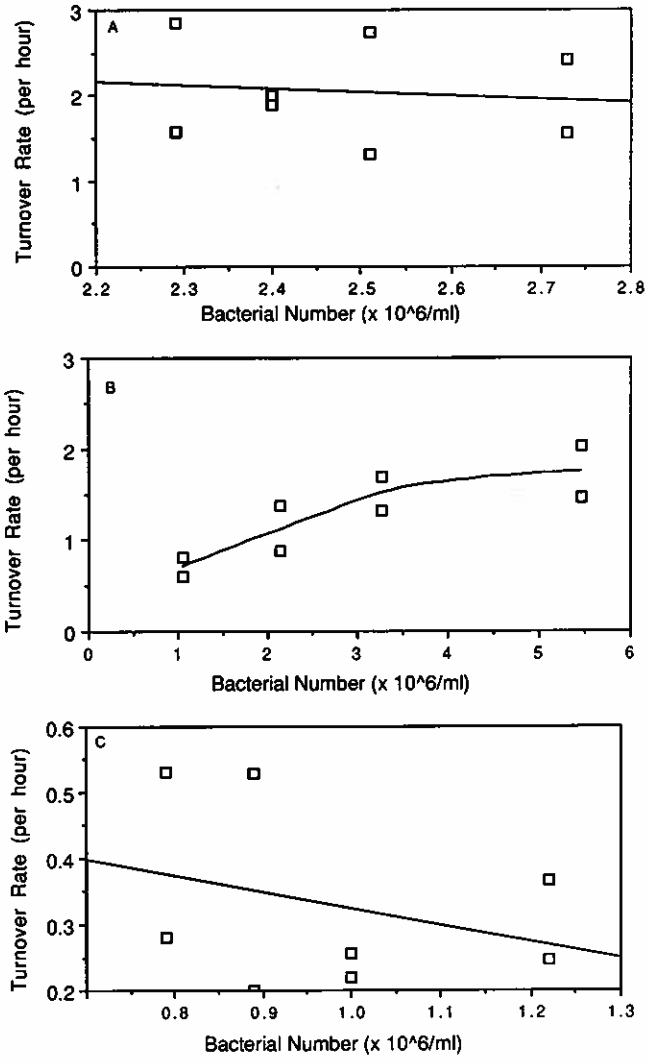


Figure 8. Amino acid turnover rates as a function of bacterial concentrations at the river site (A, salinity 0.3‰), first anchor station (B, salinity 17.3‰), and second anchor station (C, salinity 28.3‰) during the February 1991 cruise.

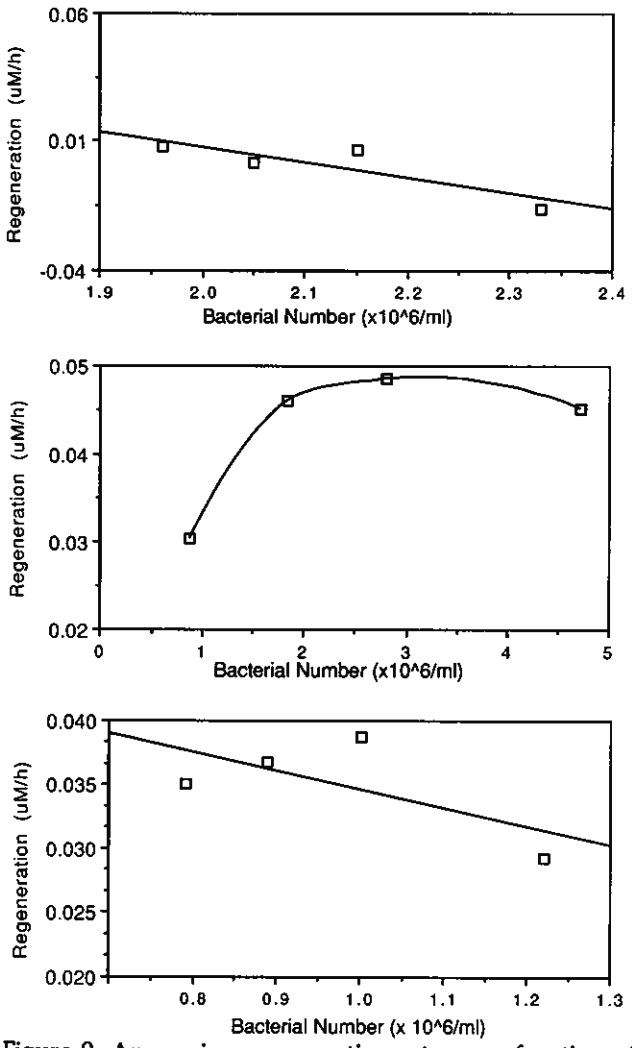


Figure 9. Ammonium regeneration rates as a function of bacterial concentrations at the river site (A, salinity 0.3‰), first anchor station (B, salinity 17.3‰), and second anchor station (C, salinity 28.3‰) during the February 1991 cruise.

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Regulation and distribution of primary production in the northern Gulf of Mexico

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Abstract

As part of the NOAA Nutrient Enhanced Coastal Ocean Productivity program, we are examining the degree to which elevated levels of nutrients in coastal Gulf of Mexico waters associated with the Mississippi River affect phytoplankton production, growth, and photosynthesis-irradiance (P-I) properties. Here, we present results obtained from three cruises including September 1989 and April and July-August 1990 in which we examined (i) the relationships between phytoplankton community physiology, photosynthetic properties and environmental conditions, and (ii) the temporal and spatial patterns of primary production in the northern Gulf of Mexico. Horizontal variations in photosynthetic properties (P^B_{max}, α) were relatively small, despite large differences in phytoplankton community growth rates between the nutrient rich plume waters and low nutrient shelf waters. We concluded that variations in photosynthetic properties were constrained by compensatory changes in carbon-to-chlorophyll ratios. Estimates of integral production from a photosynthesis-irradiance model agreed well with *in situ* and simulated *in situ* incubations. Areal integral production in the vicinity of the river outflow region was apparently coupled to riverine nutrient fluxes.

The primary biological process acting on nutrients introduced into coastal waters is uptake by phytoplankton. Nutrients (e.g. Riley, 1937; Ryther and Dunstan, 1971; Jaworski, 1981; Boynton *et al.*, 1982) and light (e.g. Cole and Cloern, 1984; Pennock, 1985; Pennock and Sharp, 1986; Cloern, 1987) are thought to be the principal factors regulating phytoplankton dynamics. Factors other than light and nutrients (e.g. physical processes and food web interactions) may also contribute to regulation of phytoplankton production and biomass in the complex ecosystems characteristic of estuaries, river plumes and coastal waters. The dynamic and heterogeneous nature of the Mississippi River plume (Thomas and Simmons, 1960; Sklar and Turner, 1981; Lohrenz *et al.*, 1990) has led to uncertainty about the factors controlling primary production in the eutrophic areas of the Mississippi River plume and adjacent shelf waters. Observations of initial limitation of production by light and subsequently by nutrient supply along decreasing turbidity gradients in estuaries might be expected to apply to river plumes (e.g. Xiuren *et al.*, 1988). Indeed, the spatial pattern of high production and biomass at intermediate salinities in the northern Gulf of Mexico (Sklar and Turner, 1981; Lohrenz *et al.*, 1990) encourages such speculation.

Nutrient concentrations associated with freshwater inputs into our estuarine and coastal ocean environments appear to have increased with population growth and industrial development. For example, nitrate concentrations in the lower Mississippi River have doubled since 1950 (Turner *et al.*, 1987; Turner and Rabalais, 1991). Eutrophication processes have also been demonstrated in Chesapeake Bay (Price *et al.*, 1985) and Altamaha River, Georgia (Walsh *et al.*, 1981). The potential increase in primary production of fixed carbon due to increased nutrient loading could result in significant perturbation of coastal ecosystems (e.g. Nixon *et al.*, 1984). Possible consequences of this nutrient enhanced production include increased sedimentation of organic matter (e.g. Hargrave, 1973, 1975; Smetacek, 1984) resulting in greater likelihood for development of hypoxic conditions in benthic environments and associated reduction in living resource yields. The impact of increased nutrient loading on carbon burial and shelf/sea transport could also have an impact on the global carbon cycle (e.g. Walsh, 1981, 1989).

Prediction of the coupling between nutrient loading, primary production, and export of organic matter from the photic zone requires quantification of these processes and the environmental and ecological factors which regulate them. Large environmental gradients characteristic of river-impacted coastal waters lead to significant variation in phytoplankton community production, growth and the vertical flux of particulate organic matter. The Mississippi River plume and inner Gulf shelf was selected as the initial study area for the Nutrient Enhanced Coastal Ocean Productivity Program (NECOP), part of the NOAA Coastal Ocean Program. As part of this effort, we examined temporal and spatial variation in phytoplankton production, growth and photosynthetic properties. The

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objectives of this portion of our study were as follows:

1. Characterize photoautotrophic community physiology and photosynthesis-irradiance properties in relation to optical conditions, nutrient inputs, and other aspects of the physical/chemical environment.
2. Describe temporal and spatial patterns in primary production using a predictive model based on irradiance and biomass distributions.

Materials and Methods

Data were collected during three cruises in September 1989 and April 1990 aboard the R/V *PELICAN* and July-August 1990 aboard the N/S *BALDRIGE*. Sampling locations for each cruise period are shown in Fig. 1. For R/V Pe*LICAN* cruises, hydrographic measurements, including profiling of CTD, *in situ* fluorescence, transmissometry, chlorophyll, nutrients and suspended particulate matter were conducted as described in Lohrenz *et al.* (1990) and Dagg *et al.* (1991). Nutrient analyses during the N/S *BALDRIGE*. cruise were performed using a Technicon autoanalyzer as described by Whitledge *et al.* (1981). Salinities were determined using an Autosal Model 8400.

Continuous measurements of surface photosynthetic photon flux density (PPFD) were recorded using a Li-Cor system including LI-1000 data logger and a LI-190SA quantum sensor. For underwater profiling during the R/V *PELICAN* cruises, a LI-192SA underwater quantum sensor was used. During the N/S *BALDRIGE* cruise, irradiance profiles were obtained using a Biospherical Instruments QSP-200 underwater quantum scalar irradiance sensor.

Both *in situ* and simulated *in situ* ^{14}C primary production incubations were conducted. Simulated *in situ* incubations were performed using temperature and irradiance quality/quantity controlled deck incubators (cf. Lohrenz *et al.*, 1988 and 1992). For simulated *in situ* incubations, light levels were adjusted to correspond to *in situ* levels. Samples for simulated *in situ* measurements were incubated in 1 L polycarbonate bottles. After incubation, samples were filtered onto GF/F filters using gentle vacuum, and filters acidified with 0.5 mL 1 N HCl to eliminate inorganic ^{14}C (Lean and Burnison, 1979). For selected samples, determinations were also made of carbon specific growth rates and carbon biomass (labeled chlorophyll technique; Redalje and Laws, 1981; Redalje, 1983; Laws, 1984). Activities of productivity samples were determined by liquid scintillation analysis (Packard Tri-Carb 2000CA). Liquid scintillation counts were corrected for quenching by external standard. Dissolved inorganic carbon samples for specific acitivity calculations were collected in serum stoppered bottles and preserved with sodium azide (final conc. 0.001 M). Acid-volatilized CO_2 concentrations were determined by infrared absorption spectroscopy (Horriba).

Photosynthesis-irradiance measurements were conducted using a photosynthetron (e.g. Lewis and Smith, 1983). Incubations were less than 1 hour. Samples from the photosynthetron incubations were acidified directly (final conc. 0.3 N H_2SO_4) and counted by liquid scintillation analysis as previously described. The resulting photosynthetic rates, normalized to chlorophyll, were used to construct photosynthesis-irradiance curves. The data were fit to the following equation (Platt *et al.*, 1980):

$$P = B * P^{B}_{s} * (1 - \exp(-\alpha * I/P^{B}_{s})) * (\exp(-\beta * I/P^{B}_{s}))$$

where P is the primary production rate (mg C m^{-3} h^{-1}), B is biomass concentration (mg chl m^{-3}), P^{B}_{s} is the saturated rate of photosynthesis in the absence of photoinhibition (mg C mg chl^{-1} h^{-1}), α is the photosynthetic efficiency (mg C mg chl^{-1} $(E\ m^{-2})^{-1}$), and β is the photoinhibition constant (mg C mg chl^{-1} $(E\ m^{-2})^{-1}$). The photosynthetic capacity (P^{B}_{max}, mg C mg chl^{-1} h^{-1}) was calculated as described by Platt *et al.* (1980). Data were fit using a nonlinear least squares estimation (Systat). In many cases, the photoinhibition parameter was not necessary to adequately model P-I data.

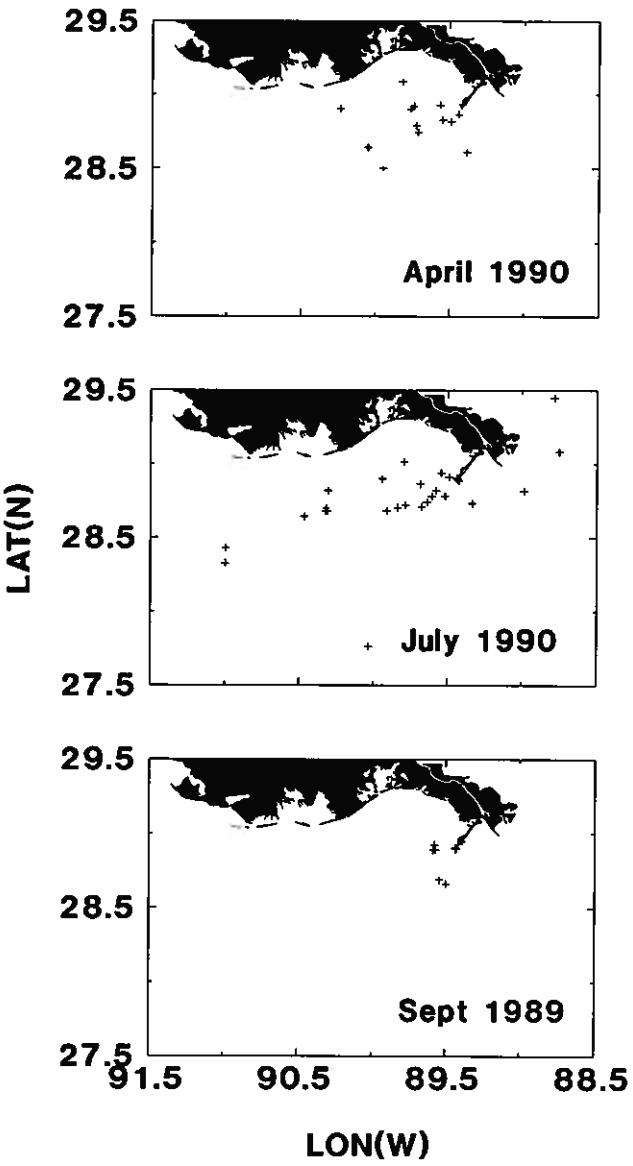

Figure 1. Maps showing station locations during cruises.

Table 1. Near surface photosynthesis-irradiance parameters and statistics

Period	P^B_{max}	Standard Deviation	N	α	Standard Deviation	N
September 1989	9.0	3.4	10	8.6	3.2	11
April 1990	7.9	3.8	20	20	14	20
July-Aug 1990	8.9	3.8	40	14	3.5	40

A second model was used to estimate daily integral primary production. Using an approach modified from Fee (1973), the Great Lakes Primary Production Model (GLM) accounted for diel variations in surface irradiance, and depth variations in P-I parameters, extinction coefficients, and chlorophyll concentrations (cf. Fahnensteil *et al.*, 1989). A version of this model has been used to evaluate the effect of internal waves on primary production (Fahnenstiel *et al.*, 1988).

Results

Relationship between photosynthetic properties and environmental parameters — The photosynthesis-irradiance curve provides an operational model for quantifying effects of environmental conditions on phytoplankton photosynthesis (Cote and Platt, 1984). In general, variation in near surface photosynthetic parameters within and between cruises was relatively small (Table 1). An exception was the variability observed in α in April 1990, possibly due to higher river discharge conditions leading to greater environmental variability. For the periods sampled, highest flow occurred in April and lowest flow in September (Fig. 2).

Near surface P-I parameters revealed no obvious patterns in relation to salinity in September 1989 (Fig. 3) and April 1990 (Fig. 4). However, there were some consistent trends in nutrient-salinity and light-salinity relationships. In September 1989, nitrate-salinity relationships showed some nonconservative behavior with evidence of depletion occurring around a salinity of 25. Both phosphate and silicate were detectable at all salinities, although there was nonlinearity in the relationships with salinity. The average light level in the mixed layer (expressed as a fraction of surface irradiance) was lowest at low salinity, and became higher and increasingly variable as salinity increased. Nutrient-salinity relationships for nitrate and silicate in April 1990 (Fig. 4) showed evidence of nutrient depletion at salinities greater than 30. Characterisitics of the nutrient-salinity relationships were very similar to those reported by Lohrenz et al. (1990) for April 1988. Again, the average light level in the mixed layer was lowest at low salinity, and higher and variable as salinity increased.

P^B_{max} and α were negatively correlated with salinities in surface waters during July-August 1990 (P^B_{max}

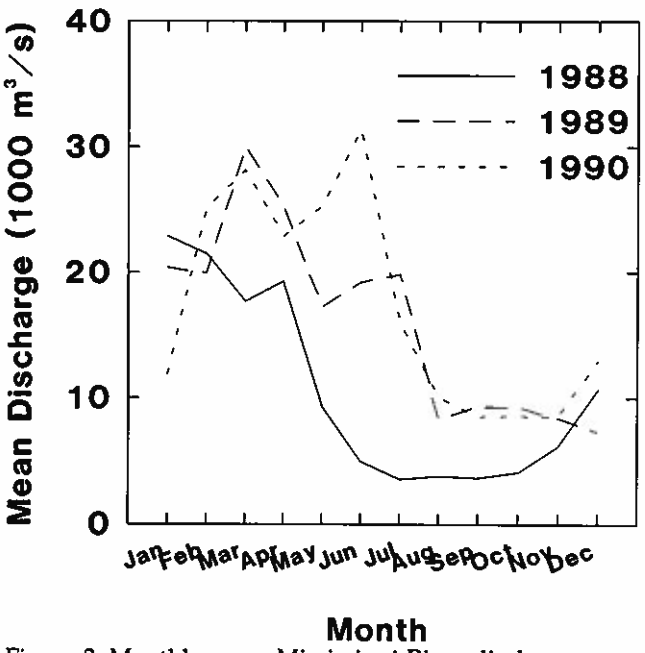

Figure 2. Monthly mean Mississippi River discharge measured at Tarbert Landing, Miss.. (Courtesy Army Corps of Engineers).

Table 2. Near surface growth rates and carbon-to-chlorophyll (C/chl) ratios.

Region	Salinity	Growth rate (d^{-1})	C/chl
Plume	12	2.7	12
Inner Shelf	25	0.34	125

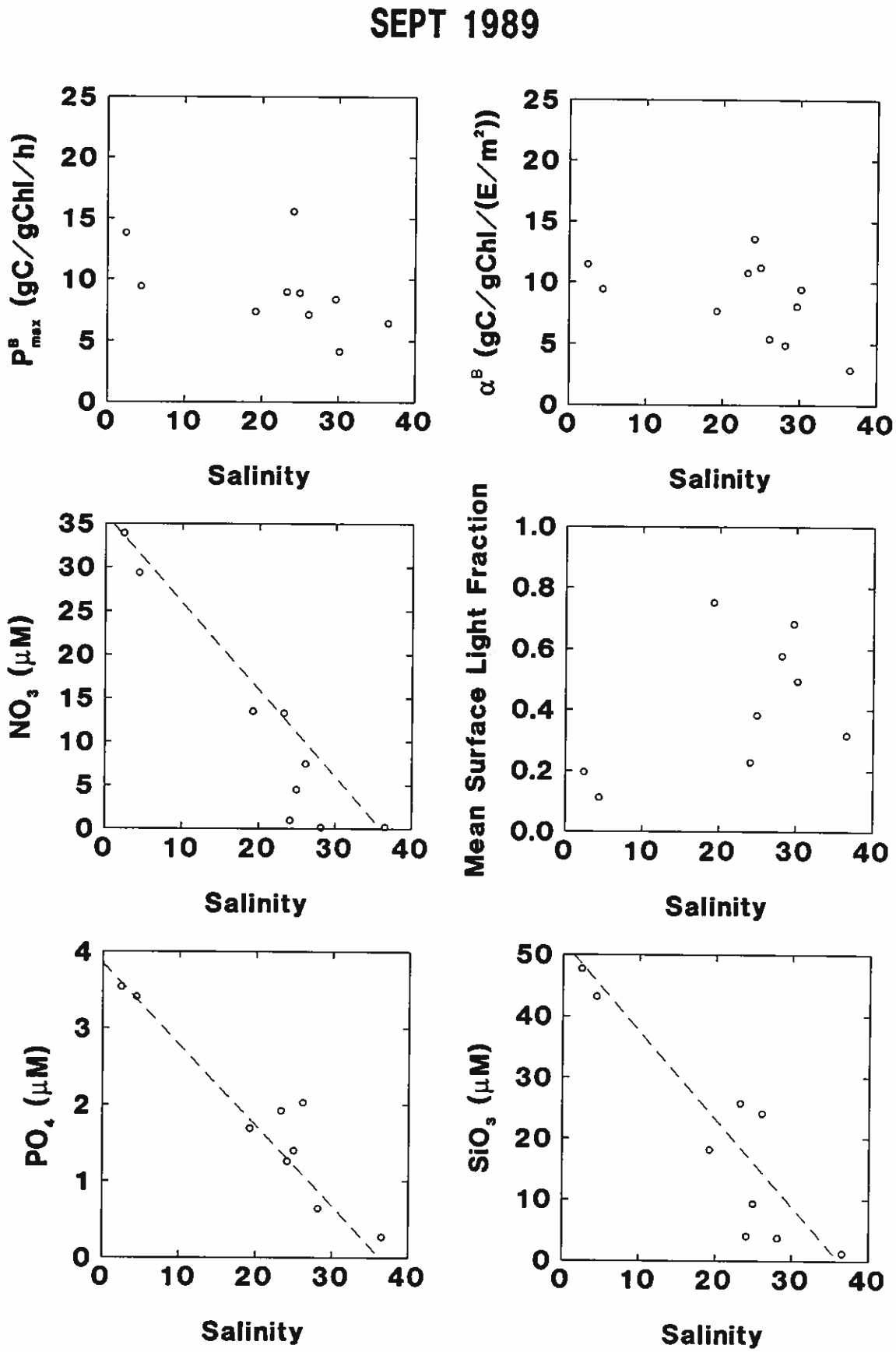

Figure 3. Near surface property-salinity relationships for September 1989. Dotted lines indicate possible conservative mixing relationship between river and Gulf of Mexico endmembers.

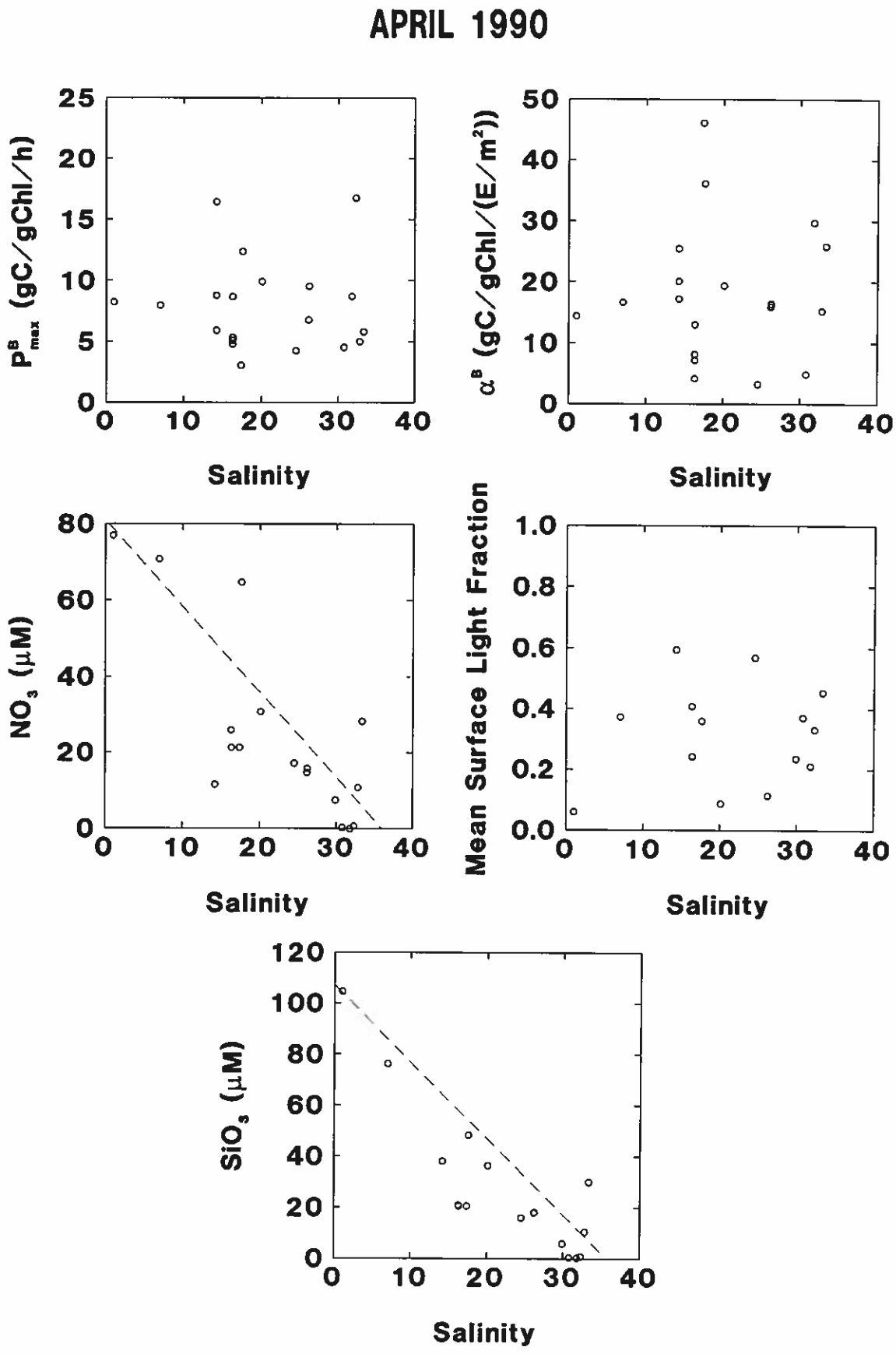

Figure 4. Near surface property-salinity relationships for April 1990.

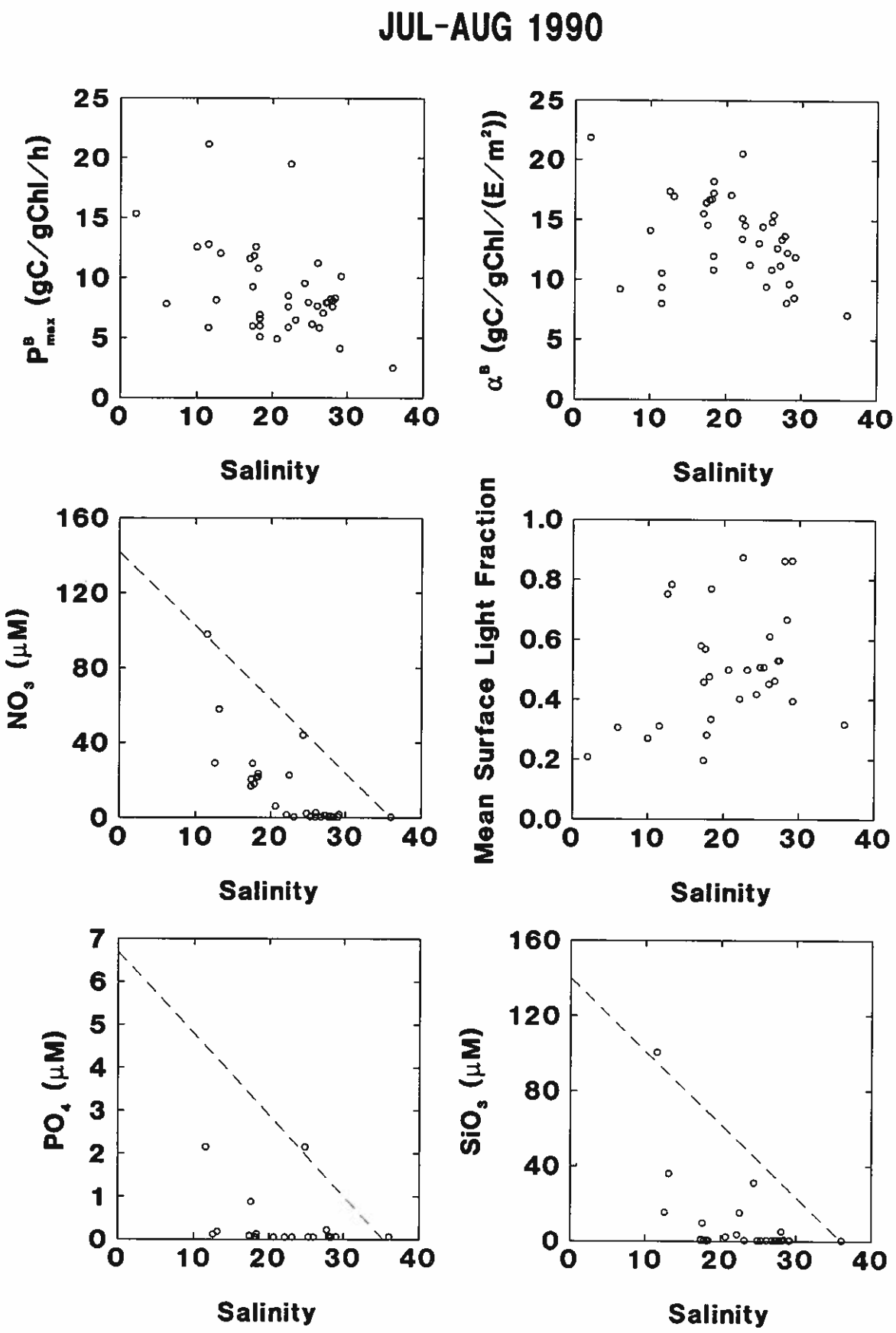

Figure 5. Near surface property-salinity relationships for July-August 1990.

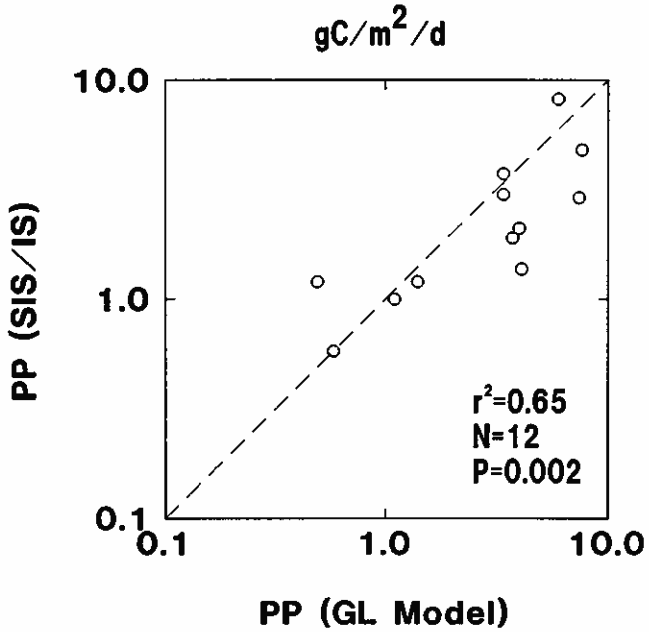

Figure 6. Comparison of integral production estimated using the Great Lakes Model with estimates from simulated *in situ* and *in situ* (SIS/IS) incubations.

versus salinity: r^2=0.20, P=0.004, N=40; α versus salinity: r^2=0.13, P=0.022, N=40; see Fig. 5). P^B_{max} was also negatively correlated with temperature (r^2=0.21, P=0.003, N=40) and positively correlated with nutrient concentrations (r^2>0.13, P<0.03, N>25). It was during the July-August 1990 period that strongest evidence of nutrient depletion was observed. Nitrate, phosphate and silicate all deviated from conservative mixing lines. In fact, phosphate and silicate were found to be at or below detection limits at salinities between 15 and 20. The pattern of light availability was similar to that observed on the other cruises, although the maximum levels were higher.

Despite the large environmental gradients in surface light and nutrients, variations in P-I parameters (Table 1 and Figs. 3-5) were generally small relative to variations in primary production (see below). In contrast, we observed substantial differences in phytoplankton community growth rates (Table 2), with highest growth rates observed in the river plume and lower growth rates in the inner Gulf shelf region. The relatively small differences in P-I parameters could be partially attributed to compensating differences in carbon-to-chlorophyll ratios between regions (Table 2).

Using photosynthesis-irradiance relationship to model primary production: the Great Lakes Model — The fact that variations in P-I parameters were relatively small justified the use of a photosynthesis-irradiance modeling approach to estimation of primary production. A comparison of integral production estimated by *in situ* and simulated *in situ* techniques with estimates obtained using the Great Lakes Primary Production Model (GLM) indicated good agreement (Fig. 6). Relationships between integral production and surface salinity were similar for all periods examined (Fig. 7). Low

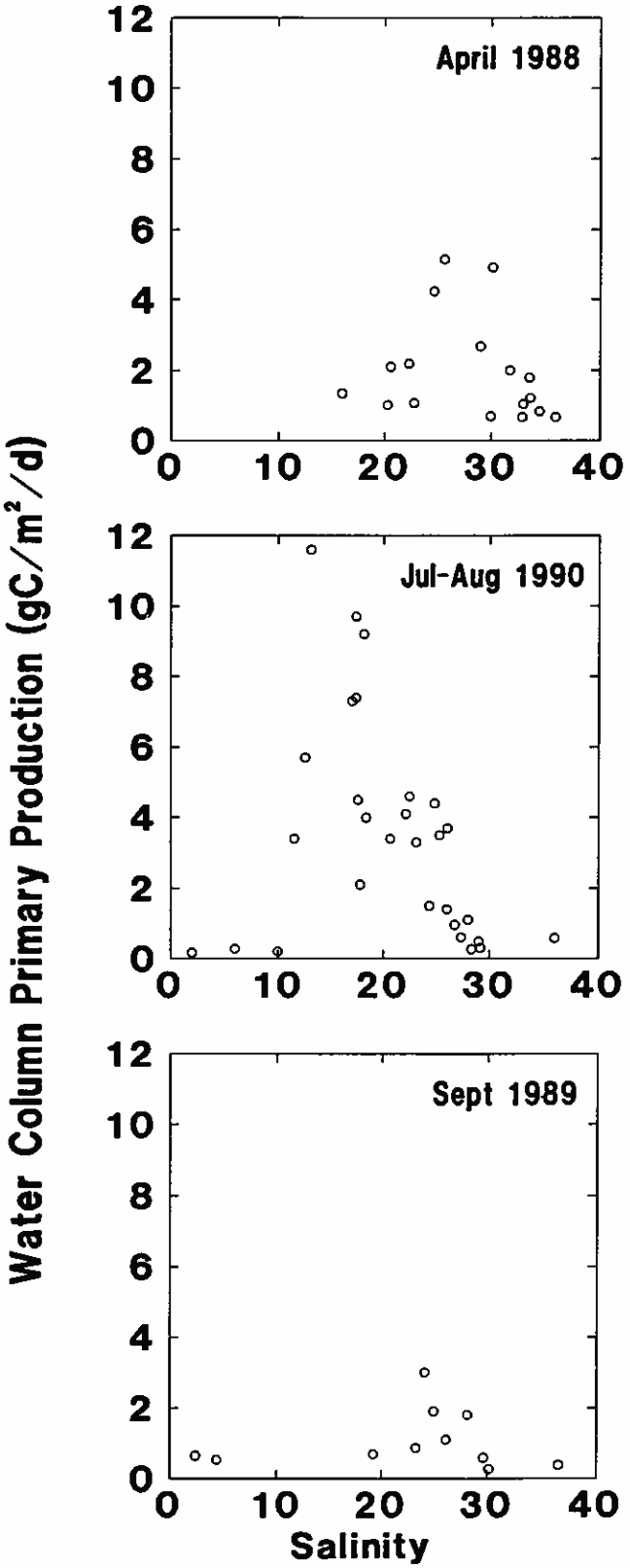

Figure 7. Relationship of integral production versus salinity. The Great Lakes Model was used to estimate integral production for September 1989 and July-August 1990. As model output was not yet available for April 1990, simulated *in situ* data from April 1988 (Lohrenz *et al.*, 1990) were used instead for comparison.

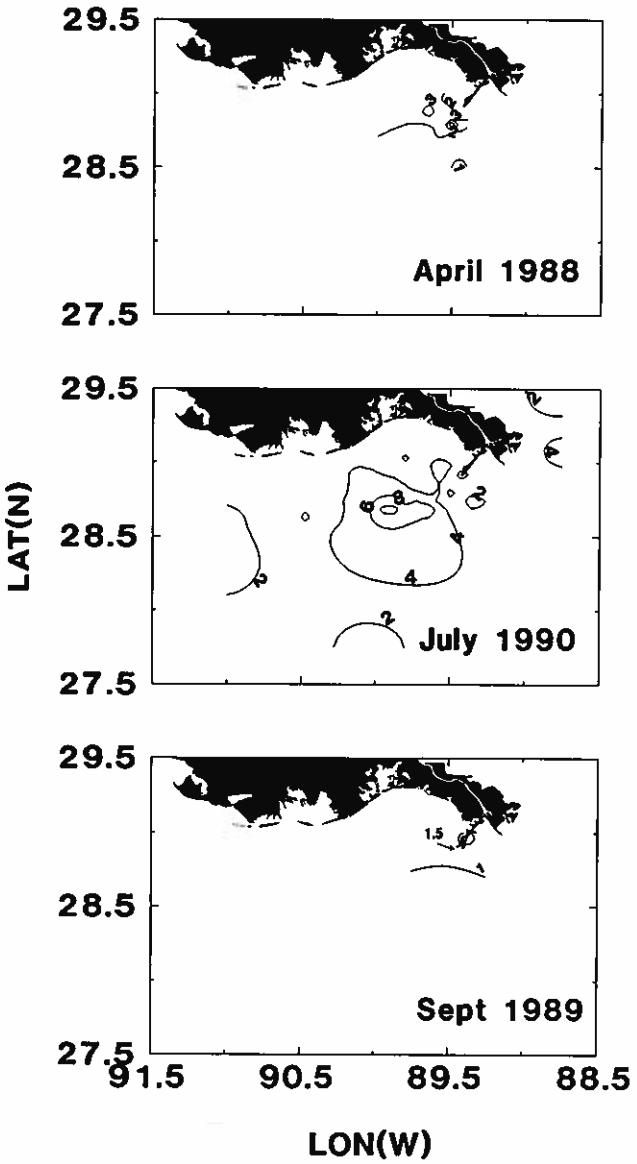

Figure 8. Contour maps of areal integral production using production data as described in Fig. 7.

integral production was generally observed at high and low salinities with highest values occurring at intermediate salinities. The salinity region of high integral production generally also corresponded to the region where depletion of nutrients was observed (cf. Figs. 3-5). Highest integral production values among cruises were observed in July-August 1990. Consistent with the results in Fig. 7, contour maps of areal integral production (Fig. 8) show localized regions of high primary production in regions of mixing of plume and oceanic waters.

Discussion

High growth rates of the phytoplankton community in the plume region (Table 2 and Fahnenstiel *et al.*, 1992) are evidence that populations were able to efficiently utilize available light. Thus, it may be necessary to re-evaluate the hypothesis that primary production is primarily light-limited in the plume. The relatively high growth rates in the plume suggested that growth rates were neither light nor nutrient limited. The lack of large variations in photoadaptive characteristics (Figs. 3-5) implies that much of the variation in photosynthetic rates can be explained on the basis irradiance and biomass distributions (cf. Lohrenz *et al.*, 1990; Cullen *et al.*, 1991). Thus removal mechanisms which constrain biomass, such as sedimentation, grazing, and advective and diffusive losses, may place an upper limit on rates of primary production. Lohrenz *et al.* (1990), using a light-limitation model (Wofsy, 1983), inferred high loss rates of phytoplankton in the Mississippi River plume. Scavia and Fahnenstiel (1987) found that sedimentation and zooplankton grazing were the major losses accounting for approximately 70 percent of phytoplankton growth in a Lagrangian study in Lake Michigan. However, phytoplankton losses due to sinking were generally small for most species in the Mississippi River plume in July-August 1990 (Fahnenstiel *et al.*, 1992). In contrast, microzooplankton grazing losses may have been important (Fahnenstiel *et al.*, 1992). Other evidence that grazing may be important in the northern Gulf of Mexico comes from estimates of mesozooplankton grazing (Dagg and Ortner, 1992) and high zooplankton abundance (Dagg *et al.*, 1987; Ortner *et al.*, 1989; Dagg *et al.*, in press). Losses of fixed carbon to the dissolved organic carbon pool, either through direct release from phytoplankton (e.g. Mague *et al.*, 1980) or through mediation by zooplankton (e.g. Corner *et al.*, 1984; Jumars *et al.*, 1990) may represent a significant flux. Some of the dissolved organic carbon would be available for consumption by microheterotrophs (e.g. Williams, 1984), thus re-entering the particulate carbon pool. Evidence that this may have been occurring during July-August 1990 comes from measurements of high dissolved organic matter concentrations and high rates of bacterial production at intermediate salinities (Benner *et al.*, 1992). Advective losses also may have been important. Lohrenz *et al.* (1990) estimated a mean turnover time of two days for Mississippi River plume waters, based on river flow volume and observed salinity distributions during April 1988. Although the calculation is approximate, it nonetheless illustrates that physical transport of materials can be significant in these waters.

Although phytoplankton community growth rates were high in the plume, it is likely that the supply of nutrients constrained growth rates at higher salinities. We observed lower growth rates in the inner Gulf shelf region, and concentrations of dissolved nitrate, phosphate and silicate were near detection levels at intermediate salinities (Figs. 3-5). The importance of each of these nutrients as limiting to phytoplankton along the plume/oceanic gradient has been suggested (Sklar and Turner, 1981; Thomas and Simmons, 1960; Dortch and Whitledge, in press; Dortch *et al.*, 1992; Ammerman *et al.*, 1992).

Spatial and temporal patterns of primary production — In addition to supporting the view that anthropogenic nutrient inputs from the Mississippi River produce

elevated levels of primary production in the northern Gulf of Mexico (cf. Riley, 1937; Thomas and Simmons, 1960; Sklar and Turner, 1981; Lohrenz *et al.*, 1990), our results suggest large temporal and spatial variability in the distribution of primary production in the northern Gulf of Mexico (Fig. 8). This is not surprising in view of the large changes in river flow and corresponding nutrient outputs. Previous investigators have suggested that seasonal variations in the extent of the river-influenced region were likely to be substantial (e.g. Sklar and Turner, 1981). To compare areal primary production in Fig. 8 to riverine nutrient inputs, we computed the approximate fluxes of nutrients at Southwest Pass, assuming a discharge of 30 percent of that measured at Tarbert Landing (Fig. 2). River endmember concentrations were extrapolated from the conservative mixing lines (Figs. 3 and 5 and Lohrenz et al., 1990). We estimated nitrate fluxes of 3×10^7 mol N d^{-1} for April 1988, 5×10^7 mol N d^{-1} for July-August 1990, and 0.8×10^7 mol N d^{-1} for September 1989. Comparison to Fig. 8 reveals that trends in areal production appeared to be closely related to riverine nutrient inputs. Based on these preliminary data, it is expected that the ecosystem of the plume environs will be eutrophic, with an abundant supply of new nutrients and production limited by other factors. As distances from the outflow region increase, the role of heterotrophic nutrient regeneration will become more important. Turner *et al.* (1987) noted that primary production beyond the plume was primarily nitrogen-limited, and hypothesized that increases in riverine nutrient inputs will result in increased inputs of phytoplankton carbon to bottom waters in those areas. However, Redalje *et al.* (1992) found that the relationship between primary production and the sinking of particulate organic matter may be quite variable. Thus, it may not be appropriate to assume a constant relationship between areal primary production and inputs of organic matter to the bottom.

Conclusions

1. Variations in near surface values of P^B_{max} and α were relatively small both within and between cruises. In contrast, there were large differences in growth rates between the plume and inner Gulf shelf regions.
2. Surface nutrient concentrations displayed nonconservative mixing patterns, with evidence of depletion at higher salinities.
3. There was large variability in the spatial and temporal patterns of integral primary production. This could at least partially be related to riverine nutrient fluxes.

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The relationship between primary production and the export of POM from the photic zone in the Mississippi River Plume and inner Gulf of Mexico shelf regions

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Abstract

As part of the NOAA Nutrient Enhanced Coastal Ocean Productivity program we examined the relationship between rates of primary production and the vertical export of POM out of the photic zone in the Mississippi River plume and inner Gulf of Mexico shelf regions. The study was conducted during both high (March 1991) and low (July/August 1990) river discharge periods. July/August rates of production were 4-10 $gCm^{-2}d^{-1}$ in the plume and 2-4 $gCm^{-2}d^{-1}$ on the shelf. During March, production rates were 0.4-0.7 $gCm^{-2}d^{-1}$ and 0.1-0.5 $gCm^{-2}d^{-1}$ for the plume and shelf regions, respectively. During July/August, 3-9 percent of the POC production was exported out of the photic zone in both regions, while during March, 64-266 percent was exported. We attribute the observed export differences to temporal variability in phytoplankton species composition and in the activities of zooplankton grazers.

The Mississippi River drains more than 40 percent of the continental United States. In the past 35-40 years there has been a two-fold increase in the observed concentrations of NO_3^- measured in river waters near the modern "birdsfoot" delta (Turner and Rabalais, 1991; Dinnel and Bratkovich, submitted). Examination of monthly records have led Dinnel and Bratkovitch (submitted) to conclude that seasonal variation in dissolved N concentrations, which are superimposed on a generally increasing trend, are linked with seasonal trends in river discharge. Higher nutrient concentrations are associated with higher river discharge rates (e.g. in winter and spring). Conversely, low river discharge appears to be correlated with lower nutrient concentrations in the river waters. It has been suggested that the observed increasing trend in dissolved inorganic nutrient concentrations could result in increased levels of primary production in the coastal regions of the Gulf of Mexico (Sklar and Turner, 1981; Lohrenz *et al.*, 1990). Further, it has been suggested that the increased levels of primary production would give rise to increased sedimentation of particulate organic matter (POM) and possibly contribute to the frequently observed episodes of hypoxia on the inner Gulf shelf (Turner *et al.*, 1987). One of the objectives of our study has been to examine temporal variability in primary production relative to variations in river flow for two regions: the Mississippi River plume and the inner Gulf of Mexico shelf (cf. Lohrenz *et al.*, 1992). It is the goal of this study to examine the temporal variability in the relationship between primary production and the export of POM from the euphotic zone in the study regions.

Materials and Methods

Two research cruises were conducted in the study regions onboard the NOAA ship *MALCOLM BALDRIGE*, one during a low river flow season (July/August 1990; Fig. 1a) and another during a high river flow season (March 1991; Fig. 1b). During each cruise studies were conducted in the Mississippi River plume and the inner Gulf shelf to measure primary production using simulated *in situ* incubations conducted in temperature, light quality and light quantity controlled deck-top incubators (Lohrenz *et al.*, 1991). Also, during each cruise free-floating MULTITRAP sediment trap arrays (Knauer *et al.*, 1979) were deployed, generally for one to two days, in both study regions to quantify the export of POM from the euphotic zone. Productivity experiments were coordinated with the sediment trap deployments; production experiments were generally conducted at sunrise of both days 1 and 2 of each trap deployment.

Water samples were collected prior to sunrise using either acid washed 10 L Niskin bottles or 30 L Go-Flo bottles from three depths corresponding to the 50 percent, 12 percent and 1.4 percent light depths. Samples were placed in 1 L polycarbonate bottles, inoculated with $H^{14}CO_3^-$ and incubated from sunrise to sunrise. Trace metal clean procedures, as recommended by Fitzwater *et al.* (1982), were employed throughout the study. Zero time blanks were used to correct particulate ^{14}C activities (Morris et al., 1971). After the

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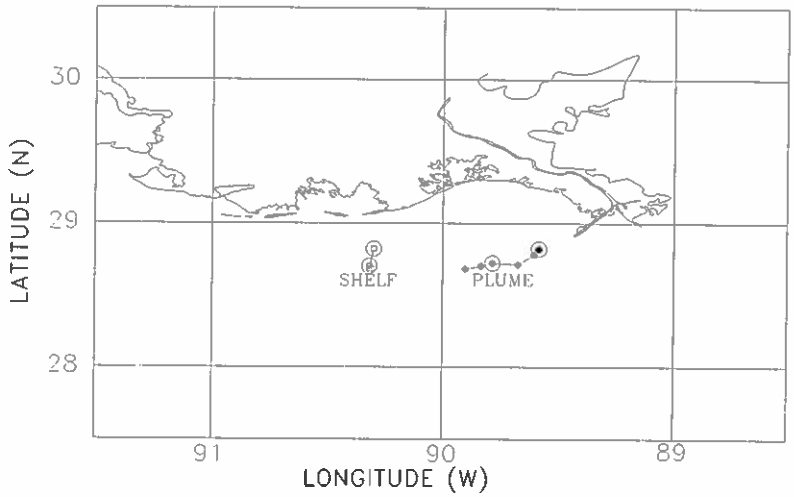

Figure 1a. Drift track of the free-floating sediment trap arrays deployed during the July/August 1990 cruise in the Mississippi River plume (filled circles) and the inner Gulf of Mexico shelf (open squares). The circled stations indicate the locations where primary production experiments were conducted.

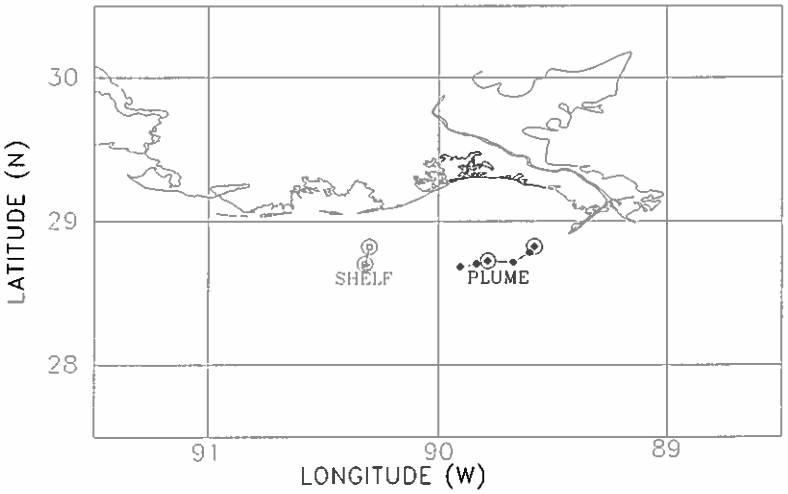

Figure 1b. Drift track of the free-floating sediment trap arrays deployed during the March 1991 cruise in the Mississippi River plume (filled circles) and the inner Gulf of Mexico shelf (open squares). Primary production experiments were conducted at the stations located at the beginning and end of the drift tracks.

incubations were complete, replicate subsamples were filtered onto Whatman GF/F filters to determine particulate ^{14}C activity. In most instances, post-incubation size-fractionation techniques (using Poretics 8 µm filters) were employed on replicate productivity bottles to determine the production for that portion of the phytoplankton community which was < 8 µm in diameter. Subsamples were also taken to determine the total amount of $H^{14}CO_3^-$ added to each bottle by combining 500 µL of sample with 500 µL of a 50 percent (v/v) mixture of ethanol and ethanolamine. Particulate ^{14}C activity filters were treated as suggested by Lean and Burnison (1979) to remove residual $H^{14}CO_3^-$. Sample ^{14}C activities were determined using SafetySolve liquid scintillation cocktail with a Packard Liquid Scintillation Analyzer.

Replicate (3-8) MULTITRAP sediment traps were attached to trap holder crosses and deployed at 15 m on free-floating arrays for each study region on both cruises (Fig. 1 a and b). Deployments were one to two days in duration. Prior to deployment, each sediment trap was filled with a brine solution (final density = 1.08 g kg^{-1}, to prevent loss of collected materials upon recovery) containing 2 percent (v/v) formalin as a preservative. After recovery, trap contents were examined microscopically to remove any "swimmer" zooplankton which would contaminate the collected POM (Karl and Knauer, 1989; Knauer *et al.*, 1984; Lee *et al.*, 1988). The concentration of particulate organic carbon (POC) and particulate organic nitrogen (PON) collected in each trap were determined using a Carlo Erba NA1500 Nitrogen-Carbon Analyzer.

Results

The results of the productivity studies are shown in Fig. 2 for the July/August 1990 cruise and Fig. 3 for the March 1991 cruise. In general, integrated primary production (IPP) rates were an order of magnitude greater in July/August 1990 than during March 1991. The <8 µm components of the phytoplankton community were responsible for 65 percent of the total IPP in the Mississippi River Plume and 60 percent in the shelf region during July/August 1990. During March 1991, the <8 µm size fraction was responsible for 68 percent of the total IPP in the plume region. The patchy nature of the study region is demonstrated by the results of production experiments for the shelf region during March 1991 (Fig. 3). IPP varied by more than a factor of 3 from day one to day two.

Tables 1 and 2 show the results of the sediment trap

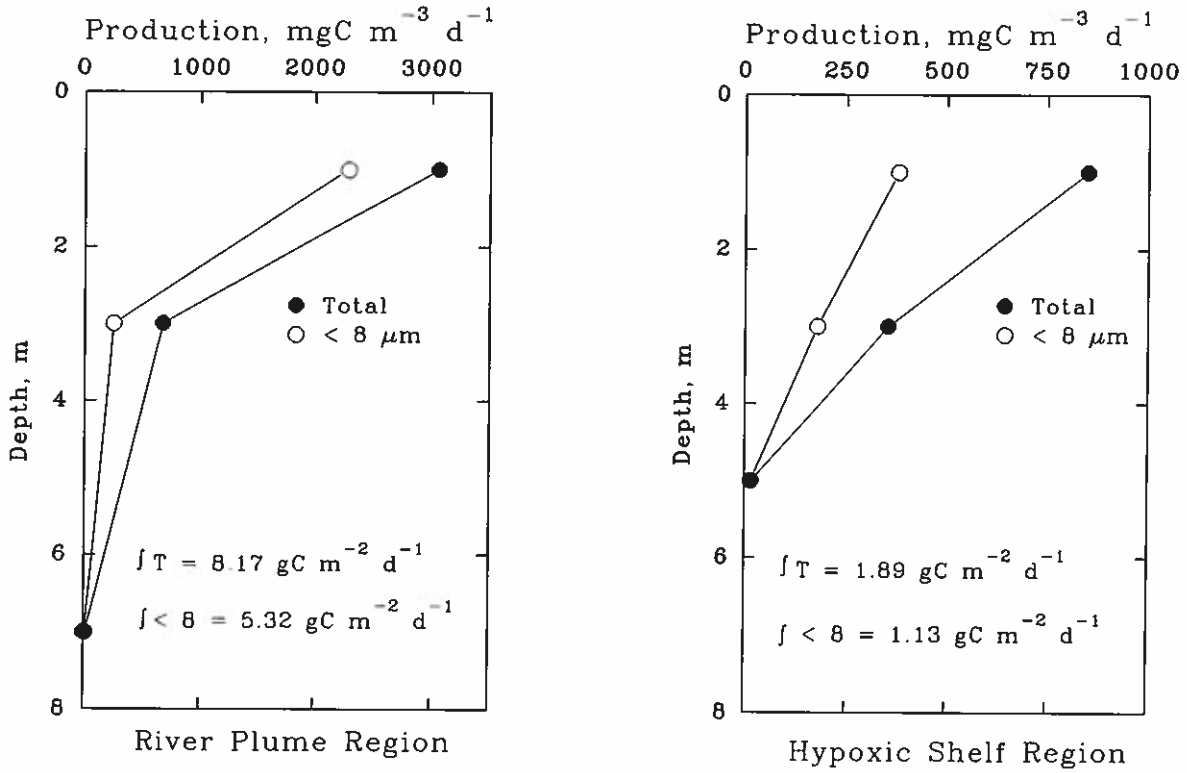

Figure 2. Simulated *in situ* primary production experiments conducted during the July/August 1990 research cruises in the Mississippi River plume and the inner Gulf of Mexico shelf. Post incubation size fractionation studies were conducted to determine the production of the <8 μm components of the phytoplankton community. Values for production integrated from the surface to the base of the photic zone are indicated.

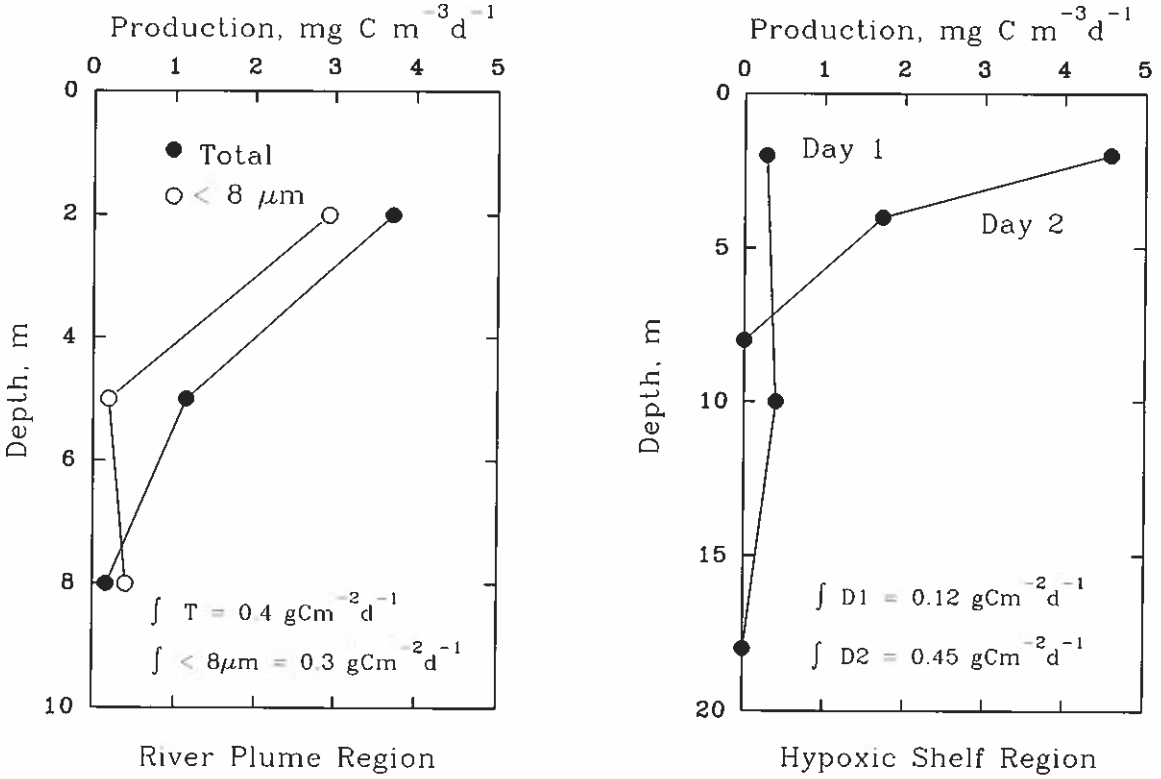

Figure 3. Simulated *in situ* primary production experiments conducted during the March 1991 research cruises in the Mississippi River plume and the inner Gulf of Mexico shelf. Post incubation size fractionation studies were conducted to determine the production of the <8 μm components of the phytoplankton community in the Mississippi River plume only. Values for production integrated from the surface to the base of the photic zone are indicated.

Table 1. **Integrated primary production (IPP) and the vertical export of POC and PON from the photic zone collected at 15 m in free floating sediment traps for both the Mississippi River plume (plume region) and the inner Gulf of Mexico shelf (hypoxic shelf region) from the July/August 1990 research cruise.**

	Plume Region	Hypoxic Shelf Region
Integrated Primary Production (IPP)	4-10 $gCm^{-2}d^{-1}$	2-4 $gCm^{-2}d^{-1}$
Vertical Export of POC and PON		
POC	0.29 $gCm^{-2}d^{-1}$	0.18 $gCm^{-2}d^{-1}$
(Standard Error, n)	(0.02, 3)	(0.007, 4)
Percent of IPP	2.9-7.3 %	4.5-9.0 %
PON	0.06 $gNm^{-2}d^{-1}$	0.03 $gNm^{-2}d^{-1}$
(Standard Error, n)	(0.002, 7)	(0.002, 8)

Table 2. **Integrated primary production (IPP) and the vertical export of POC and PON from the photic zone collected at 15 m in free floating sediment traps for both the Mississippi River plume (plume region) and the inner Gulf of Mexico shelf (hypoxic shelf region) from the March 1991 research cruise.**

	Plume Region	Hypoxic Shelf Region
Integrated Primary Production (IPP)	0.4-0.7 $gCm^{-2}d^{-1}$	0.1-0.5 $gCm^{-2}d^{-1}$
Vertical Export of POC and PON		
POC	0.95 $gCm^{-2}d^{-1}$	0.32 $gCm^{-2}d^{-1}$
(Standard Error, n)	(0.01, 3)	(0.02, 3)
% of IPP	136-237 %	64-266 %
PON	0.16 $gNm^{-2}d^{-1}$	0.05 $gNm^{-2}d^{-1}$
(Standard Error, n)	(0.01, 6)	(0.002, 6)

experiments in the two study regions for the July/August 1990 and the March 1991 cruises, respectively. The vertical flux rates of both POC and PON out of the photic zone were two- to three-fold greater during the March 1991 cruise than for the July/August 1990 cruise. During July/August 1990, a relatively small portion of the IPP (2.9 - 9.0 percent) was collected in the sediment traps, while a much larger portion (64 - 266 percent) of the IPP was collected in the traps in March 1991.

Discussion

It appears that the rates of primary production, the vertical export of POM from the photic zone and the relationship between the production and export of POM vary with time in both study regions. It is generally expected that high river discharge rates and seasonally high nutrient concentrations would occur during late winter and early spring, when incident irradiance is low, leading to lower rates of IPP. During summer, when expected river discharge and the input of dissolved N are both relatively low and incident irradiance is higher, rates of IPP should be high. Conventional wisdom suggests that higher levels of IPP are associated with higher rates of vertical export of POM from the photic zone (Eppley and Peterson, 1979; Walsh *et al.*, 1989. It appears that our July/August 1990 cruise may have been at variance with long term average conditions (cf. Dinnel and Bratkovitch, submitted) in that our cruise was preceded by a period of higher than normal river discharge and concentrations of NO_3^- >20 μM in the river plume. These environmental conditions were not generally very different from those encountered during the March 1991 cruise. Thus, the differences in our observed rates of IPP and export of POM are likely not due to variability in the nutrient fields. Temporal variation in the irradiance field com-

bined with the absorption and scattering properties of the dissolved and suspended materials in the plume and shelf areas may contribute to the observed variation in primary production (Lohrenz *et al.*, 1990; 1992). However the differences in the ratio of the vertical POC flux to IPP cannot be explained solely on the basis of differences in IPP which result from heterogeneity in the physical and chemical environment. It appears that at least two additional factors contribute to temporal differences in the fraction of the organic matter produced in the photic zone that is exported to the sediments: differences in phytoplankton communities present and differences in the activities of both microzooplankton and macrozooplankton grazers.

Our data indicate that the >8 μm components of the phytoplankton community, mostly composed of diatoms, were of lesser importance than smaller organisms in terms of their contribution to IPP during both the July/August 1990 (Dortch *et al.*, 1992; Fahnenstiel *et al.*, 1992) and March 1991 (Dortch *et al.*, 1992) cruises for the river plume and shelf regions. However, more diatoms, principally *Skeletonema costatum*, were found in the sediment traps deployed in the plume than in those deployed in the shelf region during the July/August 1990 cruise (Dortch *et al.*, 1992; Fahnenstiel *et al.*, 1992). It is possible that the lower salinity and higher nutrient concentrations observed in the plume by Lohrenz *et al.* (1992) may have contributed to diatoms being more important in the material collected in the plume sediment traps than for those deployed in the shelf region.

Another factor that can help to explain the observed differences in the proportion of the POM produced in the photic zone that is exported to the sediments is zooplankton grazing activity. One would expect that grazing by macrozooplankton would be dominant in a coastal environment such as that examined here (Ortner *et al.*, 1989). Dilution experiments that can be used to examine the grazing activity of microzooplankton (Landry and Hassett, 1982) were employed on both cruises (Dagg and Ortner, 1992; Fahnenstiel *et al.*, 1992). Their results suggest that microzooplankton grazing, which resulted in more tightly coupled production and regeneration of POM, was more intense during July/August 1990 than in March 1991. Our POM export results support this suggestion in that the fraction of IPP exported to the sediments is much lower when intense microzooplankton grazing was observed. The results of Benner *et al.* (1992) also support the idea that regeneration of organic matter was more important during July/August 1990 than in March 1991. Their bacterial production studies indicate that regeneration rates were an order of magnitude greater in the summer than in the following winter. Conversely, when macrozooplankton grazing activity was more intense (e.g. March 1991), rates of bacterial regeneration were much lower (Benner *et al.*, 1992; Dagg and Ortner, 1992). Thus, it seems likely that decreased regeneration by bacteria and lower rates of microzooplankton grazing allowed for a larger portion of the IPP to be exported from the photic zone, as is seen in our sediment trap results.

Conclusions

Our data from the NECOP program studies in the Mississippi River plume and the inner Gulf of Mexico region suggest that during July/August 1990, the production and regeneration of POM were tightly coupled giving rise to a low rate export of POM to the sediments. Conversely, during March 1991, production and regeneration were relatively uncoupled, allowing for a greater fraction of the IPP to be exported from the photic zone. Differences in phytoplankton species composition also contributed to the variability in the ratio of POM export to IPP.

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High growth and microzooplankton-grazing loss rates for phytoplankton populations from the Mississippi River plume region

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Abstract

During the July/August 1990 NECOP cruise, taxon-specific growth, and microzooplankon grazing and sedimentation loss rates were measured on dominant phytoplankton populations in the plume/hypoxia region. Taxon-specific growth rates (μ) ranged from <0.1 to >3.0 d^{-1} with highest rates (>2 d^{-1}) in the plume region. Many surface growth rates in the plume were close to or exceeded previously published μ_{max} values. For most taxa, including diatoms and non-diatoms, growth rates decreased in the hypoxia region. Significant microzooplankton grazing loss rates were noted only for small phytoplankton (< 15 μm); rates for these taxa were high (>1.0 d^{-1}) in the plume region and decreased in the hypoxia region. Sedimentation was an important loss only for a few diatoms. Our data suggest that during the summer in the plume region phytoplankton production rates are high and most of this production is recyled within the surface layer.

Anthropogenic nutrient inputs from the Mississippi River may produce enhanced primary productivity in the northern Gulf of Mexico (Riley 1937; Thomas and Simmons 1960; Sklar and Turner 1981; Turner and Rabalais 1991). However, the dynamics and heterogeneous nature of the Mississippi River plume have complicated attempts to relate changes in levels of riverine nutrient inputs to corresponding changes in regional production and phytoplankton growth (Thomas and Simmons 1960; Sklar and Turner 1981; Lohrenz *et al.* 1990). Furthermore, significant questions still remain regarding the nutrient(s) controlling primary production in this region (Schiller and Boyle 1987; Dortch and Whitledge 1991; J. Ammerman, pers. comm.). Phytoplankton dynamics within this region are also poorly understood.

Because of the complexities of this region and because rate processes occur at the species-level, we proposed to examine the growth, sedimentation and microzooplankton grazing loss rates of dominant individual species in the Mississippi River Plume/Inner Gulf Shelf region as part of the the NECOP program. In this paper, we present our preliminary data from the first NECOP cruise conducted in July/August 1990 in order to (1) compare taxon-specific ^{14}C-autoradiography and dilution estimates of growth, and (2) provide estimates of sedimentation and microzooplankton grazing loss rates.

Methods

Sampling was conducted at three stations during the July/August 1990 NECOP cruise aboard the RV *BALDRIDGE*. These three stations followed a transect from the river mouth at Southwest Pass to the inner part of the hypoxia region (Fig. 1). The first two stations, which will be referred to as plume stations, were sampled on July 22 and July 25; the third station, which will be referred to as the hypoxia station, was sampled on August 2-3.

All water samples were collected early in the morning, generally before dawn, with modified acid-washed Niskin bottles and a nylon rope. In order to avoid chemical contamination, all rubber parts of the Niskin bottle (o-rings, closure tubing, etc.) were replaced with silicone parts. Collected water was immediately transferred to 20-L polyethylene carboys for sample processing.

A Sea-Cat CTD with transmissometer and PAR sensor was used to measure vertical profiles of temperature, conductivity, PAR, and percent light transmission. Inorganic carbon concentrations were determined by infrared absorption spectroscopy.

The ^{14}C technique was used for estimating carbon uptake. Experiments were performed on July 22, July 25 and August 2. Briefly, 1-L polycarbonate bottles were gently filled with raw water, inoculated with

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$NaH^{14}CO_3$, and incubated in a deck-simulated in situ incubator (Lohrenz *et al.* 1990). Samples from 0.5m, 3m and 6m were incubated at 50 percent, 12 percent and 3 percent of surface irradiance using neutral density screens. Incubations started near dawn and terminated at dusk (15- to 16-hour incubation) or the following dawn (24-hour incubation). Following incubation, aliquots from the sample bottles were preserved with Lugol's solution, immediately filtered onto 0.22 µm Millipore filters, and transferred onto gelatin-coated slides. These gelatin-coated slides were then frozen for track autoradiographic analysis.

Track autoradiography was used to estimate the specific activity (dpm $cell^{-1}$) of individual cells (Carney and Fahnenstiel 1987). Gelatin-coated slides were dipped in filtered subbing solution (Knoechel and Kalff 1976) and then dipped in NTB-3 photographic emulsion at 29 °C. Slides were allowed to dry and then were developed as described in Carney and Fahnenstiel (1987). Tracks per cell were enumerated and activity (dpm $cell^{-1}$) was calculated (Knoechel and Kalff 1976). For this paper only 50 to 80 cells were counted for each taxa; therefore, these results should be viewed as preliminary.

We estimated taxon-specific growth rates from ^{14}C-autoradiography experiments by making simple assumptions about cell growth. The approach is first order and it is described in various ways throughout the literature (e.g., Welschmeyer and Lorenzen (1984), Li (1984), and Li and Goldman (1986)). Let C^* = specific activity of cellular ^{14}C (dpm $cell^{-1}$), U = uptake rate of C (C $cell^{-1}$ d^{-1}), t = time (d), µ = growth rate (d^{-1}), and a = isotope discrimination factor. Then the instantaneous time rate of change of cellular C^{14} is

$$\frac{dC^*}{dt} = \alpha U - \mu C^*. \quad (1)$$

Note that when growth is referenced to a cellular framework it represents a loss term reflecting the transfer of carbon due to cell division. At time t = 0, the initial value of C^* is 0. The solution of (1) is

$$C^* = \frac{\alpha U}{\mu} (1-e^{-\mu t}). \quad (2)$$

Equation 2 is further simplified by recognizing that

$$C_{asy} = \frac{\alpha U}{\mu} \quad (3)$$

where C_{asy} is the asymptotic activity of C^* and moreover

$$C_{asy} = C_m C_c \quad (4)$$

with C_m = activity of the inorganic medium, which for all practical purposes remains approximately constant throughout the experiment and C_c = cell carbon content. Thus C^* can be related to µ at any time t by parameters that can be directly measured (C^*, t, and C_m) or by approximating C_c through estimates of cell volume.

$$C^* = C_{asy} (1-e^{-\mu t}) \quad (5)$$

Finally, the growth rate µ is calculated from (5) and

$$\mu = -\frac{1}{\Delta t} \ln \frac{C_{asy}-C^*}{C_{asy}} \quad (6)$$

where, Δt is the incubation time interval corresponding to C^*. All of the ^{14}C-growth rates reported herein were calculated according to (6) and will be referred to as ^{14}C-autoradiography growth rates.

The dilution method also provided another independent estimate of phytoplankton growth as well as an estimate of the grazing loss rate by the microzooplankton community (Landry and Hassett, 1982). In these experiments microzooplankton abundances were manipulated through a series of dilutions with filtered seawater, and changes in abundances of phytoplankton populations were noted. These bottle dilutions were performed by mixing appropriate volumes of prescreened seawater (<200 µm) with filtered seawater (GF/F filtered water) in 2-L polycarbonate bottles. Bottles were incubated for 24h in a temperature controlled deck incubator. Because increasing bottle dilution alleviates grazing pressure, the slope of phytoplankton growth rate (dependent variable) across dilution treatments (independent variable) is an estimate of the microzooplankton grazing loss rate, and the intercept is an estimate of the phytoplankton growth rate. These dilution experiments were done either simultaneous (July 25) or a day later (August 3) than the ^{14}C experiments.

Phytoplankton sedimentation rates were determined from enumeration of a preserved phytoplankton sample collected from a free-floating MULTITRAP design sediment trap (Knauer *et al.*, 1979; Knauer *et al.*, 1990). These traps were deployed at 15m for a period of 1-2 days on July 25 and August 2.

In all cases, phytoplankton samples were preserved with Lugol's solution. These samples were then stored in amber vials until phytoplankton preparations were made. These phytoplankton samples were then either filtered onto slides and cleared (Dozier and Richerson, 1975) or settled onto coverslips. Phytoplankton were enumerated under low magnification (200-300X) and high magnification (600-1200X). A minimum of 1000 cells were enumerated. Phytoplankton volumes were estimated by determining the average cell dimensions from a a minimum of 30 randomly chosen individuals of each taxon from each sampling date. Because only 30 individual were measured, these volume estimates should be regarded as preliminary. The average dimensions were then applied to the geometric configuration which best approximated the shape of the taxon (e.g. spheres, prolate spheres). These cell volumes were then converted to carbon concentrations using the conversions of Strathman (1967) for diatoms and non-diatoms.

Results

Ambient conditions — Environmental conditions at the three stations suggest that we did sample along the plume/shelf gradient. The surface mixed layer was relatively shallow (< 4m) at stations 1 and 2 and surface salinity, nitrate, and temperature values were approxi-

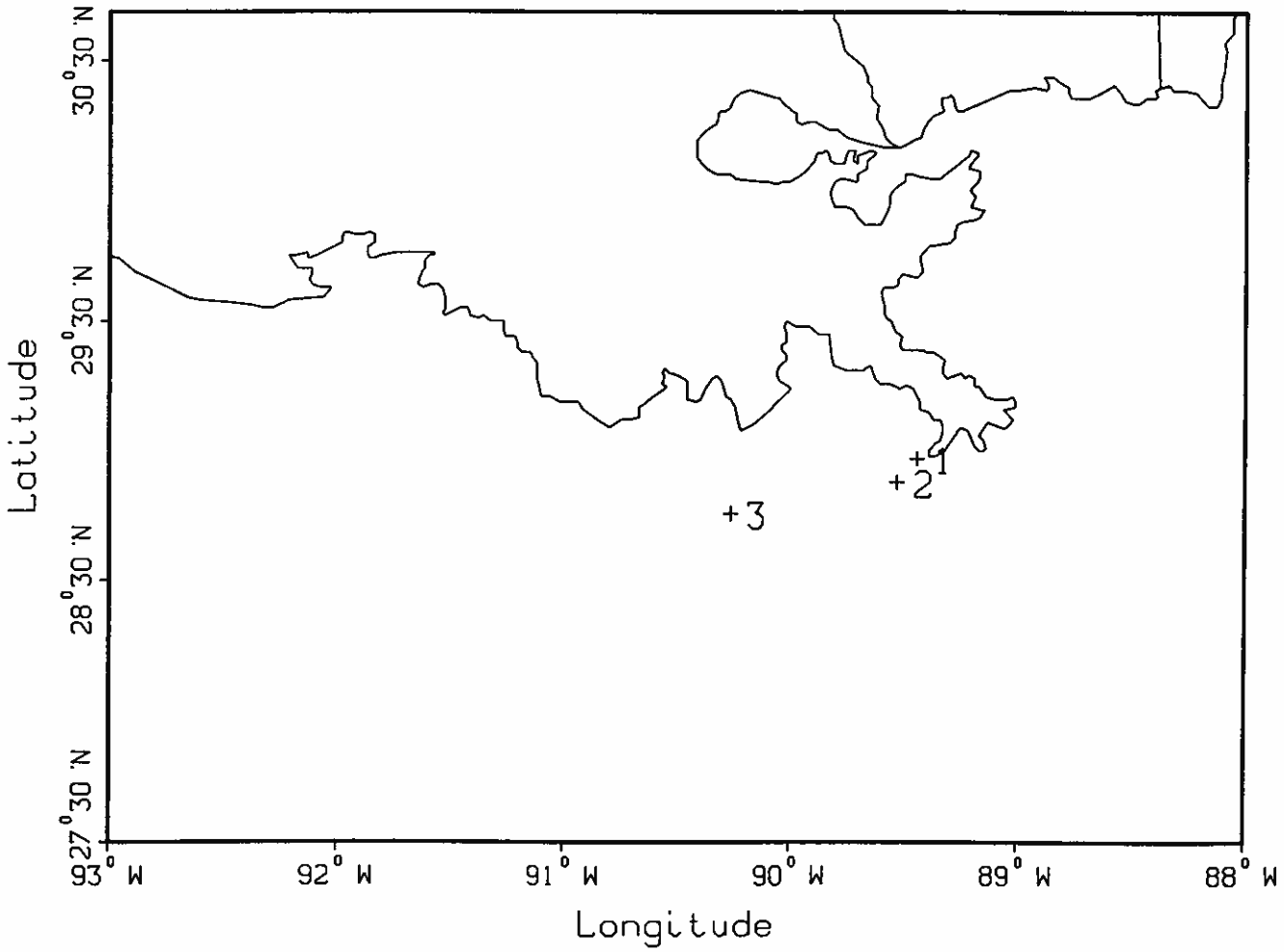

Fig. 1. Location of sampling stations (+) during the July/August 1990 NECOP Cruise. The two plume stations, 1 and 2, were sampled on July 22 and 25, respectively. The hypoxia station (3) was sampled on August 2-3.

Table 1. List of abundant taxa from surface waters on July 25 and August 2-3 and inventory of rate process data for these taxa. Abundances (cells ml^{-1}) are listed in order from most abundant on each date and rate process estimates were made where indicated (x).

Date	Taxa	Abundance	C-14 G[1]	Dil. G[2]	MG[3]	Sed[4]
July 25	*Cyclotella caspia*	1191	X	X	X	X
	Rhodomonas spp.	891	X	X	X	X
	Skeletonema costatum	766	X	X	X	X
	Small monads (e.g. *Ochr.*)	544	X			
	Gymnodinium sp. large	197				
	Cryptomonas sp.	165				
	Katodinium rotunda	147	X	X	X	X
	Cyclotella striata	41	X	X	X	X
	Total phytoplankton abundance	4047				
Aug. 2-3	Small monads (e.g. *Ochr.*)	1523	X	X	X	X
	Rhizosolenia fragilissima	676	X	X	X	X
	Rhodomonas spp.	429	X	X	X	X
	Nitzschia pungens	387	X	X	X	X
	Cerataulina pelagica	352	X	X	X	X
	Cymnodinium sp.-small	94	X	X	X	X
	Total phytoplankton abundance 3605					

[1] ^{14}C-autoradiography growth rate
[2] Dilution growth rate
[3] Microzooplankton grazing loss rate
[4] Sedimentation loss rate

Table 2. Growth (^{14}C-autorad. and dilution), microzooplankton grazing and sedimentation losses rates (d^{-1}) of representative taxa from the July/August 1990 NECOP Cruise.

Date	Taxa	Z (m)	^{14}C-auto.	Dil. Growth	Micro. Graz.	Sed
July 22	*Skeletonema cost.*	0.5	2.1	—	—	—
		5.0	0.2	—	—	—
July 25	*Skeletonema cost.*	0.5	1.0	1.7	0.3*	—
		3.0	0.5	—	—	—
		6.0	0.1	—	—	—
		0-15				0.3
July 25	*Cyclotella caspia*	0.5	3.0	2.5	0.6	—
		0-15				0.03
Aug. 2-3	*Nitzschia pungens*	0.5	0.6	0.9	0.2*	—
		3.0	0.3	—	—	—
		6.0	0.2	—	—	—
		0-15				<0.01
Aug. 2-3	*Rhizosolenia frag.*	0.5	0.4	0.6	0.4*	—
		3.0	0.3	—	—	—
		6.0	0.1	—	—	—
		0-15				<0.001
July 25	*Ochromonas* sp.	0.5	2.2	—	—	—
		3.0	2.8	—	—	—
		6.0	0.5	—	—	—
Aug. 2-3	*Ochromonas* sp.	0.5	1.6	1.0	1.0	—
		3.0	0.8	—	—	—
		6.0	0.1	—	—	—
		0-15				<0.001
July 25	*Katodinium rot.*	0.5	2.4	2.4	1.5	—
		3.0	2.1	—	—	—
		6.0	0.2	—	—	—
		0-15				<0.001
Aug. 2-3	*Gymnodinium* sp.-small	0.5	1.1	0.5	0.4	—
		3.0	0.3	—	—	—
		6.0	0.1	—	—	—
		0-15				<0.001
July 25	*Rhodomonas lac.*	0.5	2.7	2.0	1.4	—
		3.0	1.0	—	—	—
		6.0	0.1	—	—	—
		0-15				0.01
Aug. 2-3	*Rhodomonas lac.*	0.5	1.0	1.6	1.5	—
		3.0	0.5	—	—	—
		6.0	0.1	—	—	—
		0-15				<0.001

mately 15-18 ppt, >25 μM l^{-1}, and 29-30°C, respectively. These two stations will be referred to as plume stations. Conversely, station 3 was located in the hypoxia region of the inner shelf and environmental conditions were markedly different than those reported for stations 1 and 2. The surface-mixed layer was approximately 5 m and salinity and nitrate concentrations in this layer were 26 ppt and <3 μM l^{-1}, respectively. Surface temperature was 31°C.

Growth and loss rates — Growth rates were determined for at least 13 of the most abundant taxa on the three dates sampled (Table 1). Because of the overwhelming dominance of *Skeletonema costatum* on July 22, growth rates were determined for only two taxa, *Skeletonema* and *Cyclotella*. However, on July 25 and August 2-3 growth rate estimates were determined for at least six of the more abundant taxa.

At the three stations, surface growth rates varied from 0.2 to >3.0 d^{-1}. There was a general pattern of decreasing growth rates with greater distance from the river mouth; mean surface growth rates for diatoms and non-diatoms were higher on July 25 than on August 2-3. The mean diatom growth rate decreased from 1.6 d^{-1} on July 25 to 0.5 d^{-1} on August 2-3 whereas the non-diatoms decreased from 2.3 d^{-1} to 1.2 d^{-1}. Most taxa exhibited very high surface-growth rates (> 2 d^{-1})

on July 25 including some diatoms, dinoflagellates, cryptophytes and other small flagellates (Table 2). Growth rates generally decreased with depth; rates at the 1 percent light level (ca. 5-7 m) were generally 0.1-0.2 d^{-1} (Table 2). Thus, euphotic zone average growth rates are much lower than the high near-surface values.

Although there were some differences among taxa, overall surface ^{14}C autoradiography growth rates were not significantly different from dilution growth rates ($p > 0.25$, $n = 14$; Table 2). Likewise, comparisons on the individual dates also were not significantly different (July 25, $p > 0.5$, $n = 6$, August 2-3, $p > 0.3$, $n = 8$). Thus, ^{14}C and dilution techniques provide similar estimates of growth.

Microzooplankton grazing was a major loss for phytoplankton in the plume and hypoxia region (Table 2). Smaller phytoplankton (<15 μm) exhibited higher grazing loss rates than larger organisms. The mean microzooplankton grazing loss rate for small cells, e.g. *Rhodomonas* spp., *Ochromonas* sp., small monads, *Katodinium rotunda*, and *Gymnodinium* sp.-small (*Cyclotella* spp. included on July 25), was 1.0 d^{-1} (range 0.6-1.5 d^{-1}) on both dates. The mean growth rates for these same taxa on the same dates were 2.2 d^{-1} and 1.4 d^{-1}, respectively. Because the growth and loss rates were both measured in the surface-mixed layer they are comparable. However, in contrast, the microzooplankton grazing loss rates for larger phytoplankton, *Skeletonema costatum*, *Nitzschia pungens*, *Rhizosolenia fragilissima*, *Cerataulina pelagica*, and *Gymnodinium* sp-large, were never significantly different from zero.

Unlike microzooplankton grazing loss rates which were measured in the upper 1 m of the water column, sedimentation loss rates were an integrative measure over the upper 15 m. In this case, they are not directly comparable to surface growth and grazing loss rates because of the strong gradients that existed in the water column; however, they are useful for examining the relative role of sedimentation. With the exception of several diatoms, *Skeletonema costatum*, *Cyclotella caspia* and *C. striata*, all sedimentation loss rates were <0.01 d^{-1}.

Discussion

The growth rates measured in the plume region (stations 1 and 2) are some of the highest growth rates reported for marine phytoplankton assemblages (Furnas, 1990). Furthermore, despite limited comparative data, many of our taxon-specific growth rates (Table 2) are the highest reported for a given species under field conditions and/or are close to or exceed the maximum reported growth rate (μ_{max}) for the species under optimal culture conditions. For example, *Katodinium rotunda* has a μ_{max} of 1.5 d^{-1} at 20°C (Throndsen, 1976) and has a maximum reported field growth rate of 1.0 d^{-1} (Owens *et al.*, 1977). Our growth rate for *Katodinium rotunda* of 2.4 d^{-1} in the surface waters on July 25 exceeds both of the previous values (Table 2). Likewise, *Skeletonema costatum* has a carbon-specific μ_{max} of 1.7 d^{-1} at 25°C (Langdon, 1988). Maximum reported field growth rates for *Skeletonema costatum* were as high as 4.0 d^{-1} (Furnas, 1982), but carbon-specific values would be much lower and probably around 2.5 d^{-1} (Langdon, 1988). In this study the highest growth rate for *Skeletonema costatum* was 2.1 d^{-1} (Table 2).

The good agreement that we found between surface ^{14}C-autoradiography and dilution growth rate estimates ($p > 0.25$) supports our high growth rate estimates. Rarely in the past have species-specific growth rates been measured with two independent techniques (Furnas, 1990). Because neither technique actually measures growth or cell division, this type of collaboration is needed and should be more common in future studies.

The exceptionally high growth rates found in this study should be of little surprise given the environmental conditions present in the surface waters of the Mississippi River Plume during the summer. Water temperatures were approximately 30 °C and ambient dissolved nitrate concentrations exceeded 90 μM l^{-1} on July 22 and 25 μM l^{-1} on July 25. Thus, given the high temperatures and saturating light levels (50 percent of I_o) of a near surface incubation, it is not surprising that many species were growing at/near μ_{max}.

Silica may occasionally be an important limiting nutrient in the Mississippi plume region (Dortch and Whitledge, 1991) and our preliminary growth rate data can be used to assess the degree of silica limitation during our study. Clearly, silica or any other nutrient were not severely limiting growth in the surface waters at our plume stations (stations 1 and 2) where diatom growth rates were high and close to μ_{max}. In the hypoxia region (station 3), however, there is the potential for strong nutrient limitation as growth rates decreased (Table 2). But, the decrease in growth was found for both diatoms and non-diatoms suggesting that the limiting nutrient was not silica. The growth rate decrease for diatoms was greater than for non-diatoms, but because the composition of the diatom community also changed along this gradient, it is difficult to interpret these subtle shifts in growth rate without direct comparisons of relative growth rates for the same species. Further evidence for the lack of strong silica limitation can be found in the dissolved nutrient ratios at these stations. Silica:nitrogen ratios of <1 have been used to indicate possible silica limitation (Dortch and Whitledge, 1991). In the surface waters at the three stations, Si:N ratios varied from approximately 1-6, suggesting that silica was not strongly limiting diatom production.

Our data cannot be used to rule out the possibility of silica limitation for some diatom species nor does it suggest that silica is unimportant in this region. Because diatom composition does change as we move to the hypoxia region, differential silica limitation (competition for silica) among diatoms may be an important process. At this point, we simply have too little data to evaluate the role of silica. However, because

silica is a good indicator of eutrophication (Schelske *et al.*, 1986), it is important to determine its role, both presently and historically.

One major objective of the NECOP program was to determine the fate of phytoplankton carbon in this region. Our data suggests that much of the surface algal production appears to be recycled within the surface-mixed layer. For many species, particularly small phytoflagellates, microzooplankton-grazing loss rates in the surface waters were comparable to growth rates. Microzooplankton-grazing was not a major process affecting populations of large diatoms (Table 2). These results are consistent with the role of micrograzers in other environments (Fenchel, 1988).

Although it is difficult to compare sedimentation loss rates quantitatively with other processes in this study because sedimentation rates were measured at 15 m, sedimentation only appears to be an important fate for one diatom, *Skeletonema costatum*, and possibly two others *Cyclotella caspia*, and *C. striata*. Sedimentation rates were extremely low for all other taxa, including small flagellates and some large diatoms (*Rhizosolenia fragilissima, Cerataulina pelagica*).

When considering the significance of our results to the broad objectives of the NECOP Program, it should be remembered that these preliminary measurements have many spatial inconsistencies which prevent us from thoroughly evaluating the importance of growth and loss processes. Microzooplankton grazing rate measurements were confined to the upper 1 m as were the greatest density of growth rate measurements. On the other hand, sedimentation rates were determined at 15 m where no other processes were measured. In the Mississippi River Plume the surface-mixed layer is very shallow and strong environment and growth gradients exist within the water column. Mean euphotic zone or water column growth rates would be much lower than surface rates and the factor(s) controlling phytoplankton growth and dynamics below the upper 1 m of the surface-mixed layer are poorly understood. Future studies should include measurements on the same spatial scale and more intensive vertical rate process measurements.

To summarize, in the plume region during the July/August NECOP cruise surface phytoplankton growth rates for most taxa were high (>2 d^{-1}) and much of this growth was recycled within the surface-layer by microzooplankton grazing. In the hypoxia region growth rates were lower, but still most of this carbon was recycled within the surface-layer by microzooplankton grazing. Sedimentation was only an important loss for several diatoms.

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Mesozooplankton grazing and the fate of carbon in the Northern Gulf of Mexico

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Abstract

Grazing of the mesozooplankton community (organisms >200 um) on phytoplankton was measured in two regions of the continental shelf west of the Mississippi River delta. Grazing by individual organisms was measured experimentally, and scaled to the community by application of abundance and distribution data collected on several temporal and spatial scales by various methods. One of the principal fates of phytoplankton production stimulated by nutrient enrichment from the Mississippi River is to be grazed by the mesozooplankton community.

Mechanisms affecting interactions between the community of organisms >200 um, the mesozooplankton and phytoplankton are complex.

In some coastal environments, such as the continental shelves of the Bering Sea and the northeast United States, grazing by the mesozooplankton community has little impact on the phytoplankton during the spring bloom (Dagg *et al.*, 1982; Dagg and Turner, 1982). In these systems, the initial fate of most of the spring bloom is to sink to the bottom. At other times of year in these systems, phytoplankton growth and zooplankton grazing are more in balance but the microzooplankton community typically dominates as a grazing force.

In other coastal environments such as the northwest of the United States, the dominant fate of phytoplankton blooms is to be grazed by the mesozooplankton community (Landry and Lorenzen, 1989; Dagg, unpublished).

The objective of this work is to measure the grazing of the mesozooplankton community on the phytoplankton community. We are addressing one of the fates of the phytoplankton production stimulated by the river discharge.

Methods

We are using a hierarchal approach to address this question. First, we measure the feeding rates of each of the important individual organisms at a specific point in time and space, for example *Acartia tonsa* adult females. Second, the abundance of that taxonomic category is measured at that same location and time. The product of these two values is the grazing by the population of that taxonomic category at that specific location and time. Summing the grazing by all of the important taxonomic categories yields the community grazing.

Repeating this exercise at a variety of temporal and spatial scales provides information on the temporal and spatial patterns of community grazing. Relating grazing by individual organisms to environmental variables such as temperature, salinity, chlorophyll fluorescence and light transmission allows us to calculate community grazing from measurements of these variables and zooplankton community structure. This approach allows us to determine community grazing over a wide range of temporal and spatial scales. Here we report initial results from a cruise in July and August 1990.

We worked in waters of the continental shelf of the northern Gulf of Mexico, west of the Mississippi River delta. This continental shelf is heavily influenced by river discharge. In particular, two regions were selected for study. The plume region near the delta is heavily influenced by freshwater discharge from Southwest Pass, which carries approximately 30 percent of the total river flow, and from the generally westward-flowing freshwater that discharges as a halo around the delta (Wiseman and Dinnel, 1988). The hypoxia region is farther to the west, off Terrebonne Bay, in waters that are typically hypoxic (<2 ml/l oxygen) during the summer (Renaud, 1986; Leming and Stuntz, 1984).

Zooplankton samples were collected with a 0.75 m diameter net with 153 um mesh, towed vertically from a specified depth to the surface. Logistical considerations did not allow the net to be closed, therefore hauls were always made to the surface. The volume of water filtered by the net was determined from a General Oceanics flow meter attached to the inside of the net ring. Tows from two depths were made at intervals of approximately three hours over a 24- to 36-hour period while the vessel was on station.

Immediately after the net was brought on deck, a small aliquot of the contents was poured through a funnel that contained a pre-cut disk of 153 um mesh nitex. The nitex disk was placed in a petri dish and immediately stored in liquid nitrogen for later analysis in the laboratory. This preservation procedure effectively prevented gut evacuation of copepods after they were collected, and stabilized the phytoplankton pigments in the gut for later analysis. The remainder of the

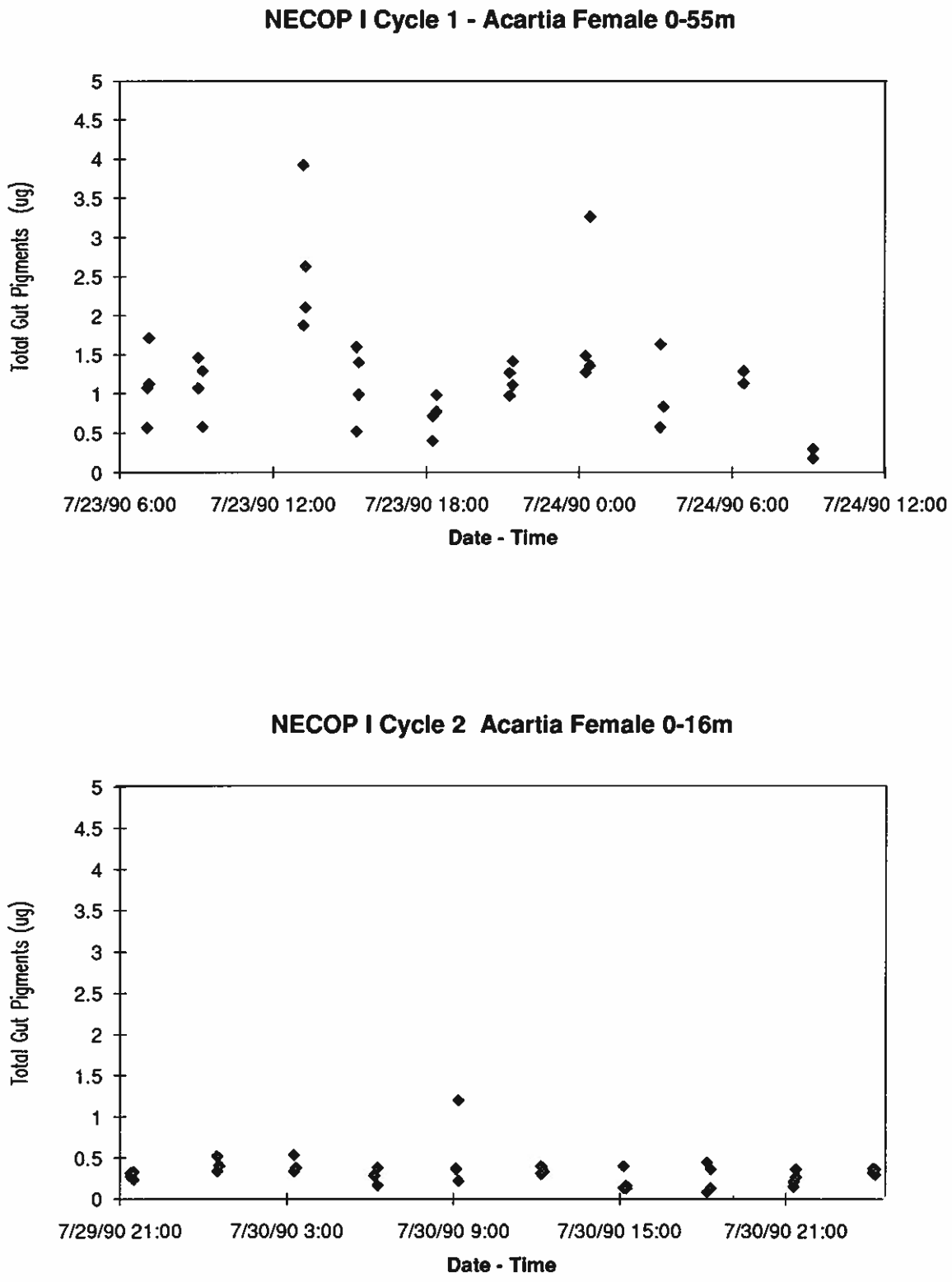

Figure 1. Gut pigment contents of *Acartia tonsa* adult females during an approximately 30-hour sampling period in the plume region (upper panel) and in the hypoxia region (lower panel). Each point represents several copepods.

sample was preserved in dilute formalin/seawater solution and returned to the laboratory.

In the laboratory, each nitex disk was removed from the liquid nitrogen and a portion of the sample was broken off and placed into filtered seawater. Zooplankton were immmediately sorted under red light by appropriate taxonomic category into disposable fluorometer cuvettes containing 5 ml of 40:60 DMSO:acetone solution. Samples were allowed to extract in the dark overnight then analyzed for their content of chlorophyll and pheopigments.

Portions of the frozen sample that were not used for the analysis of gut pigment contents were returned to the formalin preserved sample. These samples were then analyzed by first splitting with a Folsom plankton splitter, then subsampling one of the splits with a stempel pipette. Duplicate pipette samples were counted. After computing the total number of each taxonomic category in each sample, a correction was made for the number of individuals that had been removed for the gut pigment analyses, then the concentration (number m^{-3}) was computed.

In addition to measuring the abundance and distribution of mesozooplankton with net hauls, the latest version of an optical sensing system for zooplankton, first described in Ortner *et al.* (1981), was deployed. Modifications to the described system include full microprocessor control of all operations, the addition of a removable net door to prevent premature net-clogging and the incorporation of environmental sensors that acquire data at a rate of three times per second. Variables measured include temperature, conductivity, chlorophyll fluorescence and light transmittence. The output from these is graphically displayed in real-time aboard ship and is used to guide camera data acquisition.

Results and Discussion

Gut pigment contents were measured in 12 taxonomic categories of mesozooplankton (Table 1). In addition, analyses of preserved samples indicated that *Oikopleura dioica* was very abundant at most stations. Literature-based information was used to estimate larvacean feeding rates.

Gut pigment contents of *Acartia tonsa* females over both sampling cycles showed no significant diel variability (Fig. 1). Mean pigment contents were higher in the plume region (1.28 ng pigment•copepod^{-1}) than in the hypoxia region (0.33 ng pigment•copepod^{-1}). Similar patterns were observed in other taxa.

Gut contents were converted to ingestion rates by application of the relationship between gut evacuation rate and temperature (Fig. 2) derived by Dam and Peterson (1988). Unfortunately, there is little data available at the temperatures of our study region during this cruise. We made one measurement with *Acartia* at 28 °C and measured a K that was higher than the value resulting from the extrapolation of Dam and Peterson (1988), so we use the extrapolation for now. This yields a K of 0.0637, equivalent to a gut passage time of 15.7 minutes. Thus, each gut content represents the feeding that has occurred during the previous 15.7 minutes. From this and another correction for a partial destruction of pigment during digestion (mean of 34 percent, Dam and Peterson, 1988), the amount of phytoplankton pigment found in each copepod was converted to an ingestion rate.

Table 1. Taxonomic categories analyzed for gut pigment contents.

Acartia tonsa adult females
Acartia tonsa adult males
Acartia tonsa copepodid stg V
Centropages furcatus adults
Centropages furcatus copepodid stg V
Corycaeus spp. adults
Eucalanus pileatus adults (mostly females)
Eucalanus pileatus copepodid stg V
Oithona spp. adults
Oncaea spp. adults
Paracalanus sp. adults
Paracalanus sp. copepodid stg V

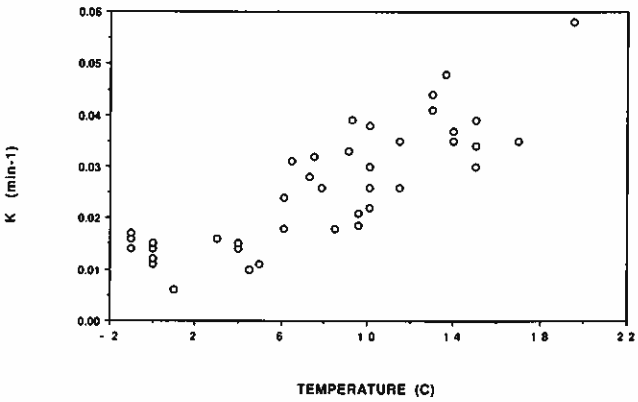

Figure 2. Gut clearance constant (K) vs. temperature for all copepods, as summarized by Dam and Peterson (1988). Extrapolation of this relationship to 29 °C (see text) yields a K of 0.0637 min^{-1}.

These rates were then applied to the abundances of organisms in each of the taxonomic categories, and the ingestion of all categories was summed to determine the community ingestion. Ingestion by the mesozooplankton community was greater in the plume region than in the hypoxia region (Fig. 3). In the plume region, community ingestion ranged between 11.6 and 89.4 mg chl•m^{-2}•d^{-1} (mean = 28.3) whereas in the hypoxia region the range was between 2.5 and 10.1 mg chl•m^{-2}•d^{-1} (mean = 5.6). In terms of carbon, the regional differences were smaller (Fig. 4) because the C:CHL ratio in the plume region was much lower than the C:CHL ratio in the hypoxia region (20 vs. 60, Redalje and Lohrenz, this volume). Ingestion by the mesozooplankton community varied between approximately 230-1800 mgC•m^{-2}•d^{-1} in the plume region and 150-600 m^{-2}•d^{-1} in the hypoxia region. In comparison, phytoplankton production was 4-10 gC•m^{-2}•d^{-1}

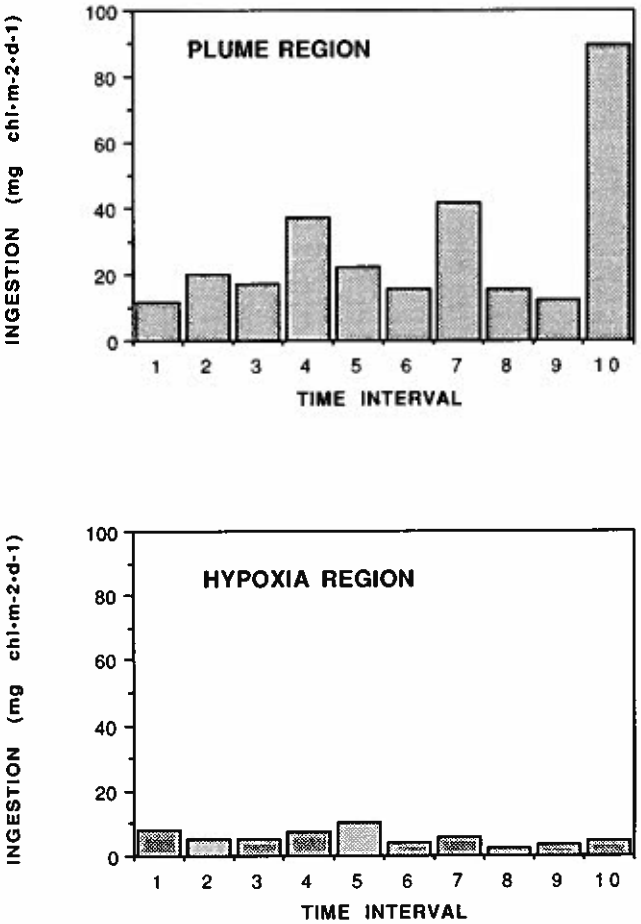

Figure 3. Ingestion of phytoplankton chlorophyll by the mesozooplankton community in the plume region (top panel) and in the hypoxia region (bottom panel) during each 30-hour sampling cycle.

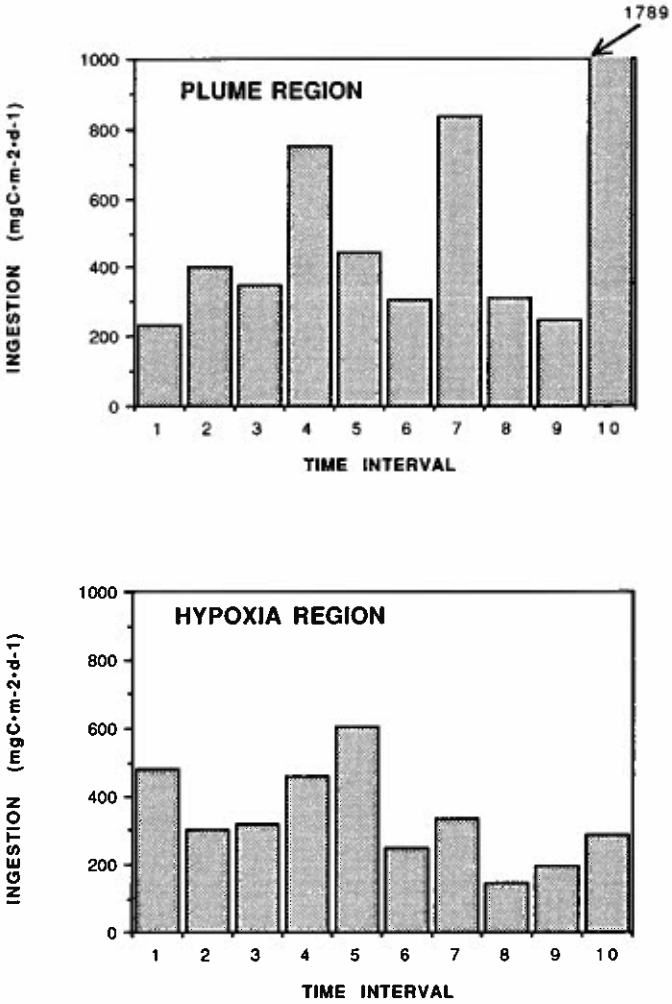

Figure 4. Ingestion of phytoplankton carbon by the mesozooplankton community in the plume region (top panel) and in the hypoxia region (bottom panel) during each 30-hour sampling cycle.

in the plume region and 2-4 $gC \cdot m^{-2} \cdot d^{-1}$ in the hypoxia region (Lohrenz and Redalje, this volume). Ingestion by the mesozooplankton community is the initial fate of a significant fraction of phytoplankton production.

Conditions of temperature, salinity, light transmittence and fluorescence during our sampling cycle at the hypoxia region were obtained from the towed optical system (Fig. 5) The water column is a strongly stratified two-layered system. This is reflected in the vertical distribution patterns of copepods and larvaceans (Fig. 6), and in the resultant pattern of community grazing. Integrated rates derived from these data (Fig. 6) are comparable to rates shown in Figs. 3 and 4.

Ultimately we plan to produce large scale detailed maps of zooplankton community grazing, based on acoustically derived abundances and relationships between grazing and readily monitored environmental variables such as temperature, salinity, transmittence and fluorescence. On the cruise in September 1991, the ship's 1200 khz towed sled was successfully used to map backscatter in the shallow plume waters but, unfortunately, the acoustic device on the optical system malfunctioned.

In conclusion, one of the principal fates of phytoplankton production stimulated by nutrient enrichment from the river is to be grazed by the mesozooplankton community. Amounts ingested are larger in the plume region than in the hypoxia region but the proportion of phytoplankton production ingested in each region is approximately the same in each region. However, microzooplankton grazing rates measured on this cruise were very high in the plume region (Dagg, poster) and lower in the hypoxia region. Summing the two components of the zooplankton community grazing indicates that the dominant initial fate of phytoplankton production in these regions during the summer is to be grazed.

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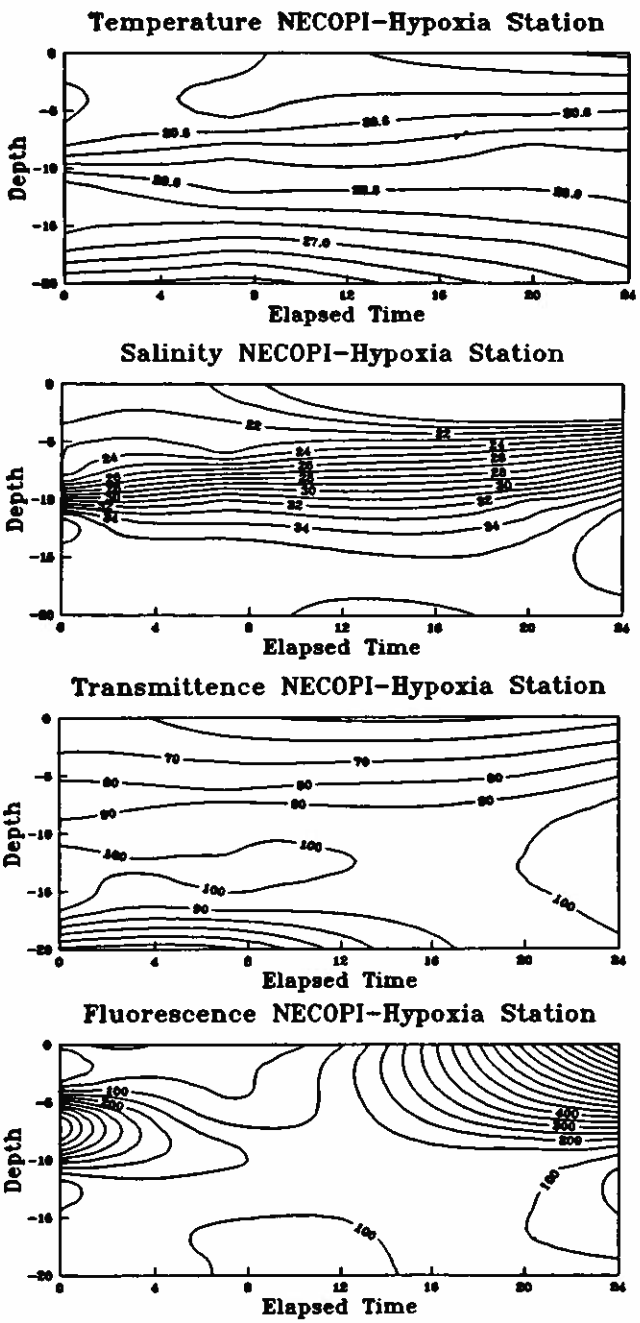

Figure 5. Water properties measured by the towed optical array during the sampling cycle at the hypoxia region.

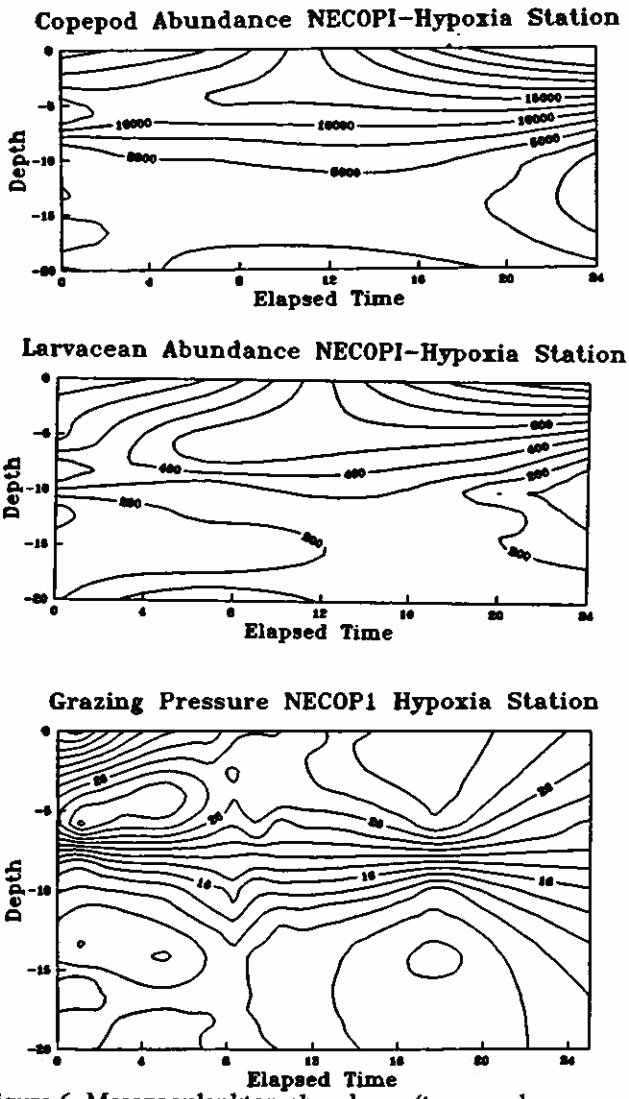

Figure 6. Mesozooplankton abundance (top panel, copepods; mid panel, larvaceans) and community grazing as $mgC \cdot m^{-3} \cdot d^{-1}$, during the sampling cycle at the hypoxia region.

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Seasonal differences in the sedimentation of zooplankton fecal pellets in the northern Gulf of Mexico

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Abstract

The origin of biogenic particles and their flux were studied by examining material collected in particle traps on a permanent mooring in the northern Gulf of Mexico within the core of the hypoxic area. Traps were located above the usual position of the pycnocline and near the bottom. Concomitant surficial sediment samples were examined. Preliminary results on particle trap samples collected in 1990 indicate the presence of amorphous fecal material as well as intact fecal pellets. More intact fecal pellets were found in the sediments than in either traps, although the time period of deposition is unknown for the surficial sediments. Amorphous fecal material was more abundant in the top trap compared to the bottom trap and sediments. More amorphous fecal material was collected in fall than in spring, whereas there were more intact fecal pellets in spring than in fall. Average fecal pellet length was smaller in fall samples than in spring. This difference may be due to different zooplankters or the amount of food present. The amount of fecal material, amorphous as well as intact fecal pellets, collected in a one-week period was higher than in a three-week period in May. Work on identification of the source of fecal pellets is in progress.

Fecal pellets play a significant role in the transfer of carbon to the benthos (Wiebe *et al.*, 1976; Honjo and Roman, 1978; Honjo, 1979; Turner and Ferrante, 1979; Angle, 1984). Fecal pellet flux to the seabed is related to the amount of pellets produced in the water column and their rate of sedimentation (Angle, 1984), the extent of coprophagy (Bathmann and Liebezeit, 1986), and their degradation in the water column (Lampitt *et al.*, 1990).

The amount of organic material reaching the seabed is important in the distribution and dynamics of oxygen-depleted bottom waters (< 2 mg O_2/l). Our working hypothesis is that hypoxia on the Louisiana shelf is fueled by carbon transported to the bottom waters by zooplankton fecal pellets. We investigated the sedimentation of fecal pellets during spring (high river flow) and fall (low river flow) and compared particle trap collections to the accumulation of fecal pellets in surficial sediments.

Methods

Field collections — Particle traps similar to those described by Prior *et al.* (1987) were deployed on a permanent instrument mooring at station C6A of Transect C (see Rabalais *et al.*, this volume) during March through November 1990. Particle trap tubes were collected and replaced at one-week and three-week intervals. The particle traps were located at 5 m water depth (above the usual position of the pycnocline) and near the bottom (15 m in a 19-m water column). Additional instrumentation on the mooring included near-surface and near-bottom current meters with temperature probes and a near-bottom pulsed sensor recording oxygen meter (Endeco 1184). A 3.5-cm diameter subcore of surface sediments (3-5 cm) was removed from a larger Ekman box corer deployed from the ship at the same location at monthly intervals.

Preparation of samples — Each particle trap sample was split five to eight times in a Folsom plankton splitter (the day it was retrieved or the next day). The last split was preserved in 5 percent glutaraldehyde and refrigerated. The top 2 mm of the sediment core was removed from the vertical core tube with a precision core extruder and placed in a vial of 3.5 cc of water immediately overlying the sediment-water interface. The sample was brought to a total volume of 20 ml by adding filtered seawater and 5 percent glutaraldehyde and then refrigerated.

Laboratory analyses — Additional splits were made on the preserved and refrigerated samples to dilute them enough for preparation of slides. Samples were stained with 1 drop/25 ml of proflavin for 5 minutes. Samples were than size-fractionated through a series of 294 (additional for sediments), 63, 20, and 8 µm filters. Cleared slides were examined under transmitted light and epifluorescence.

Counts and measurements were made of intact fecal pellets and converted to volume, assuming the

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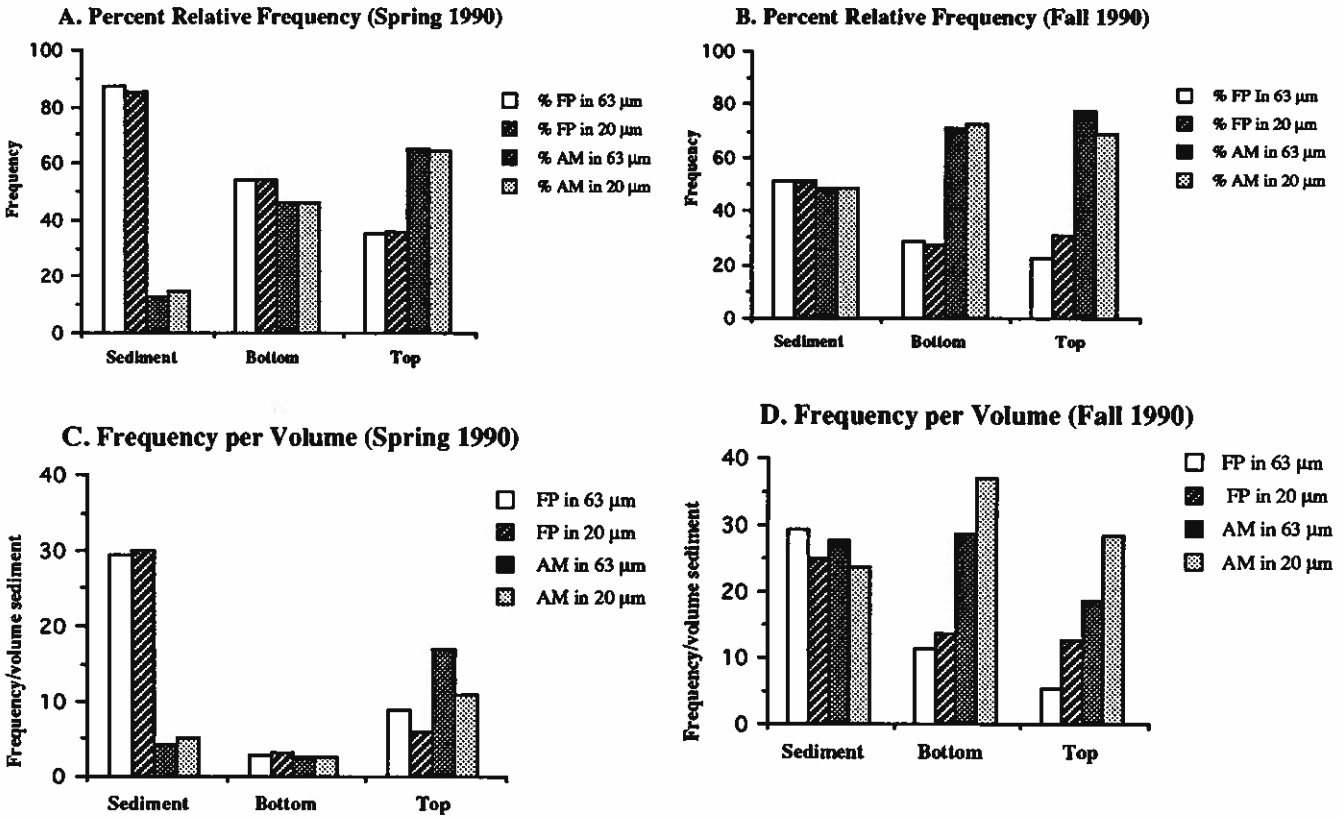

Figure 1. Comparison of relative percent frequency and frequency per volume of sediment for fecal pellets (FP) and amorphous fecal material (AM) in three-week particle trap collections in spring and fall 1990 for two size fractions.

pellets were prolate spheroids. Size, shape, composition and, if possible, source of fecal pellets were determined. Considerable amorphous material, resembling fecal pellets but not membrane-bound, was collected, making it impossible to quantify fecal material by only counting and measuring intact fecal pellets. Assuming a uniform distribution of all material on the filter, we used a modified method of quadrat unit analysis to calculate the relative frequency of intact fecal pellets (FP) and amorphous fecal material (AM). In order to compare different collections, a dilution factor for the number of splits made and the total volume of particles collected were used to calculate a frequency per volume of particles collected.

Data presented — The samples analyzed and presented in this preliminary treatment of the 1990 particle trap collections represent the following:

- Spring = 3 weeks ending May 17
  - 3 week May = 3 weeks ending May 17
  - 1 week May = 1 week ending May 24
- Fall = 3 weeks ending September 18

Results

Amorphous fecal material was found in all samples along with membrane-bound intact fecal pellets (FP). Amorphous fecal material (AM) resembled fecal pellets but lacked peritrophic membranes. Amorphous material contained mostly different sizes of centric and pennate diatoms without fluorescing pigments. A few broken fecal pellets were found with centric and pennate diatoms. It was usually difficult to discern anything in the intact fecal pellets. A few fecal pellets as well as amorphous material were also observed to have some fluorescent particles in them.

In spring the relative percent of AM to FP differed slightly between bottom and top traps but FP greatly exceeded AM in the sediments (Fig. 1A, 1B). In fall the relative percent of AM to FP was greater in both traps whereas it was nearly equal in the sediments. The relative frequency of AM to FP differed between spring and fall collections most dramatically in the sediments and bottom trap and less so in the top trap. The relative amount of amorphous fecal material exceeded intact fecal pellets in most trap samples, both spring and fall (the exception is the spring bottom trap) (Fig. 1C, 1D). More intact FP were present in the sediments than in either top or bottom trap collections in both seasons. In the trap collections, more fecal material (FP and AM) were collected in fall than spring. Differences in the two size fractions (>63 µm and >20 µm; FP and AM) were apparent in both spring and fall trap collections.

There were no differences in the relative frequency of AM to FP in the one-week versus the three-week sample. The amount of fecal material in the one-week sample was greater than the three-week sample in spring. This difference could be due to differential production and/or differential flux of fecal pellets. Similarities in the relative percent of AM to FP in the one-week versus three-week samples, as well as a greater amount of AM in the one-week collection,

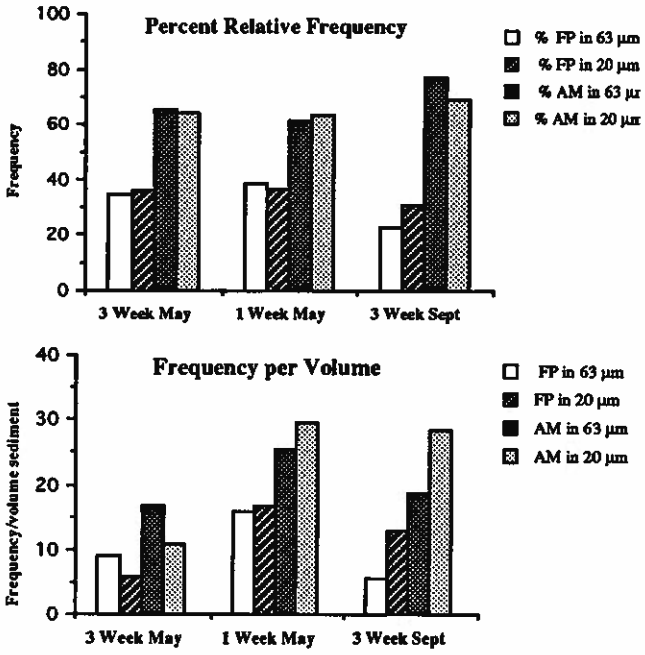

Figure 2. Comparison of relative percent frequency of fecal pellets (FP) and amorphous fecal material (AM) in one-week and three-week spring collections and a three-week fall collection in top trap samples for 1990.

indicate that degradation of FP in the trap is probably not the primary source of AM.

The average fecal pellet length ranged between 93.7 to 134.6 µm for size fraction >63 µm and 65.0 to 78.8 µm for >20 µm. The average fecal pellet volume was 1.35×10^5 to 4.5×10^5 µm³ for the >63 µm size fraction and ranged from 4.08×10^4 to 5.23×10^4 µm³ in >20 µm (Fig. 3). Average length of intact fecal pellets and average FP volume was greater in spring than in fall in both traps and in the sediments, even though the amount of AM and FP were both higher in the fall (Fig. 1C, 1D). There was more variation in the length and volume of fecal pellets between the two seasons for the >63 µm size fraction.

Discussion

The amorphous material differed from the intact fecal pellets in the absence of peritrophic membranes that bind fecal pellets. The amount of amorphous fecal material in the traps could not be attributed to the length of deployment of the particle traps so degradation in the trap is not a likely source. A possible mechanism for their production is coprorhexy, whereby copepods break up their own fecal pellets. Whatever the mechanism, the higher concentration of amorphous fecal material in the fall suggests greater water column remineralization of fecal pellets at that time.

The period of deposition of fecal material to the sediments is not known as compared to the time period for materials collected in the traps. The sediment fecal material is similar in size, shape, and appearance to the traps. Thus, although benthic organisms cannot be ruled out as a source, fecal materials appear to come from zooplankton. Early, prolonged and severe hypoxia/anoxia in 1990 (see Rabalais *et al.*, this volume) may have contributed to the preservation of fecal pellets in the sediments.

The presence of smaller size fractions of fecal pellets in the fall is comparable to the results of Bathmann and Liebezeit (1986). Fecal pellets produced by copepods can vary considerably in relation to the availability of food, which, in turn, is reflected in the flux to the sediments (Bathmann and Liebezeit, 1986).

Any decrease in food availability will also decrease the production of fecal pellets (Paffenhofer and Knowles, 1979). This occurs with a decrease in primary production following a zooplankton bloom. The utilization of fecal pellets as food, i.e. coprophagy, is likely to occur and can account for a decrease in the volume of fecal pellets, as "ghost pellets" may be produced that are of smaller size and volume. These FP are fragile, less compact and have lower sinking rates (Small *et al.*, 1979), and this will also increase the residence time of fecal pellets in the water column (Dagg and Walser, 1986).

The difference in the volume can also be due to differences in the composition and community structure of the zooplankton. Different organisms or species of copepods are producing the fecal pellets col-

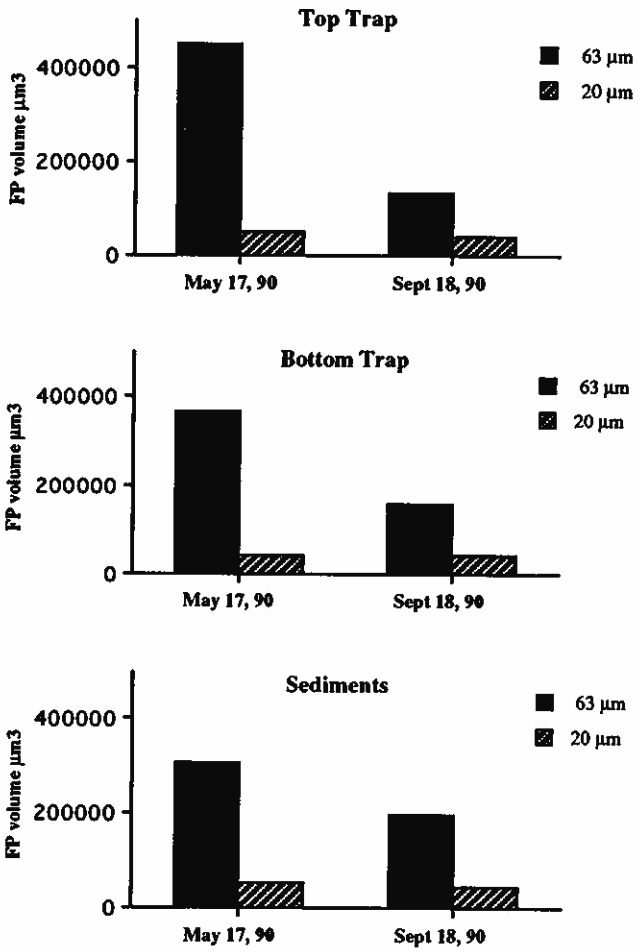

Figure 3. Average fecal pellet volume for three-week spring and fall collections for two size fractions.

lected in our traps. The producers of fecal pellets are not known for the period of our trap collections, but laboratory experiments are being conducted to identify fecal pellets produced by specific zooplankton. There are dramatic changes in the composition and structure of the resident zooplankton community in the vicinity of the instrument mooring (Qureshi *et al.*, unpubl. data).

Differences in the amount of fecal material collected in the traps (e.g., one-week versus three-week, or spring versus fall) may be attributed, among other factors, to differences in surface primary production, fecal pellet production rates, zooplankton community changes, and physical structure of the water column.

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Suspended particulate matter on the Louisiana shelf: Concentrations, composition and transport pathways

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Abstract

The concentrations, composition and transport pathways of suspended particulate matter and particulate organic carbon (POC) have a direct bearing on the development and persistence of shelf hypoxia as well as on the global cycling of carbon. More than 120 CTD-transmissometer profiles and >400 particle samples were collected from the Mississippi River and adjacent Gulf of Mexico on cruises during July-August 1990 and February 1991. River-flow is a dominant factor in controlling particle distributions; however, time-series data show that tides and weather fronts can greatly influence concentrations and movement of suspended matter. Results from chemical analyses show that concentrations of POC range from >80 μmol/L (>1 mg/L) at near-river locations to <0.8 μmol/L (<0.01 mg/L) in some deep offshore waters. The organic fraction of the suspended matter increases from <5 percent of the total mass near the river mouth to >90 percent along the shelf at about 10 km from the river. The C/N molar ratio in suspended particles from throughout the shelf is near uniform at 6. Plumes of particle-rich water at outer shelf depths of about 100 m, along with transport in near-bottom nepheloid layers, carry a POC burden that can be traced tens of kilometers offshore.

Suspended particles are a landmark feature of the Mississippi River and its seaward plume. These particles are important to both the production and transport of biogenic carbon and nitrogen because:

1. Particulate carbon and nitrogen, either brought in by the river or fixed in shelf waters, may be transported to other locations on the shelf or offshore to the continental slope.
2. The concentrations of suspended particulate matter (SPM) may limit the amount of available light and thereby reduce the amount of photosynthesis in a given area of the Mississippi Delta.
3. Decomposition of particulate organic carbon plays a role in the creation and persistence of hypoxia.

Suspended particles in the Mississippi River typically contain 1 to 2 percent organic carbon and 0.15 to 0.3 percent nitrogen with a C/N ratio commonly ranging from 6 to 9 (Trefry and Presley, 1976; and this study). Thus, the terrigenous load of particulate organic carbon (POC) for the Mississippi River is on the order of 2 million metric tons per year, about the same as that for dissolved organic carbon (DOC). Terrestrial inputs of POC and particulate nitrogen (PN) are, of course, greatly augmented by production of marine POC and PN along the Louisiana shelf.

Concentrations of SPM in river plumes can inhibit primary productivity by reducing light penetration and are sometimes modeled as inversely related to plankton biomass. Some field data suggest that an SPM value of about 10 mg/L is a threshold for primary production. For example, Demaster *et al.* (1986) showed that diatom uptake of silica in the Amazon River plume begins when levels of SPM fall below 10 to 20 mg/L, with most of the silica uptake occurring at SPM values of <10 mg/L. The Amazon study also showed that changes in river flow and plume dynamics can displace the critical SPM boundary by as much as 20 km or more on a daily to seasonal scale. The massive and dynamic plume of the Mississippi River can have a similar effect.

The SPM component of the NECOP Program was designed to determine the concentration and composition of suspended particles on the Louisiana shelf as a function of depth and location as well as to determine the importance of bottom resuspension and lateral transport to movement of organic and inorganic particles. Within this context, our study has focused on identifying the spatial (3-D) and temporal distribution of SPM, POC and PN along the Louisiana shelf and how this relates to dissolved oxygen distribution, apparent oxygen utilization (AOU) and the onset and persistence of hypoxia. Particulate carbon and nitrogen serve as tracers of biogenic material and particulate aluminum, iron and manganese trace detrital particles and resuspended sediment. Knowledge of the transport and fate of biogenic carbon has a direct bearing on our understanding of the development and persistence of shelf hypoxia as well as on the global cycling of carbon.

Methods

To achieve our objectives, more than 50 stations were occupied on each of the two NECOP cruises, NECOP I (July-August 1990) and NECOP II (February

1991). The stations shown in Fig. 1 were sampled using a rosette equipped with a Neil Brown CTD system, transmissometers and Teflon-lined Go-Flo water sample bottles. As a conceptual framework, the sample sites were grouped into the following five subgroups: (1) a circum-Delta arc; (2) a river mouth to shelf edge transect, referred to as the Mississippi Canyon transect; (3) a transect from the head of the Mississippi Canyon to the area of chronic hypoxia; (4) the hypoxia area; and (5) offshore stations. In addition to the sample sites described above, two anchor stations (AN-1 and AN-2) were occupied on both cruises for approximately 36 hours at each site per cruise. Anchor Site 1 was chosen to characterize temporal variations in the concentrations and composition of SPM within hundreds of meters of the river mouth at Southwest Pass. Anchor Site 2 was situated within an area of chronic hypoxia as established by the ongoing monitoring of Rabalais and co-workers. At each anchor station, a current meter record was obtained in the near-bottom flow field. The CTD and transmissometer data provided detailed snapshots of the distribution of SPM throughout the delta, outer shelf and slope.

To complement the data obtained by CTD/transmissometer, we collected more than 400 samples of SPM on both glass fiber and polycarbonate filters during the July-August 1990 and February 1991 cruises for chemical analysis and scanning electron microscopy. The water samples were collected with 10-L Go-Flo bottles or by pumping. All filtrations were carried out immediately after collection in a clean van aboard ship. Concentrations of suspended matter along with particulate Al, Fe, Si, Ca, Mn, Pb and Cd were determined using samples collected on 0.4 µm polycarbonate filters. Analysis was by flame or flameless atomic absorption spectrophometry following complete digestion with HF-HNO_3 in a sealed tube. Concentrations of POC and PN were determined using samples collected on glass fiber filters and analyzed with a Carlo Erba NA1500 CNS system.

Results and Discussion

Initial results from both NECOP cruises will be presented in this report. The distribution of SPM will be considered first and then a picture of chemical composition will be developed. The goal of this paper is to provide preliminary results of the spatial and temporal changes in the concentrations and composition of the suspended particles in the Mississippi River, on the Louisiana shelf and in offshore waters.

Seasonal differences in the concentrations of suspended matter in the Mississippi River are demonstrated by the SPM values at Head of Passes for July-August 1990 (NECOP I) of 44 mg/L versus 180 mg/L for February 1991 (NECOP II). A sharp decrease in SPM values to <10 percent of river levels occurred within 5 to 10 km of the river mouth at Southwest Pass on both cruises. A further decrease in SPM to <3 mg/L occurred by 15 to 30 km from the river in July and 30 to 80 km in February. These seasonal variations in the

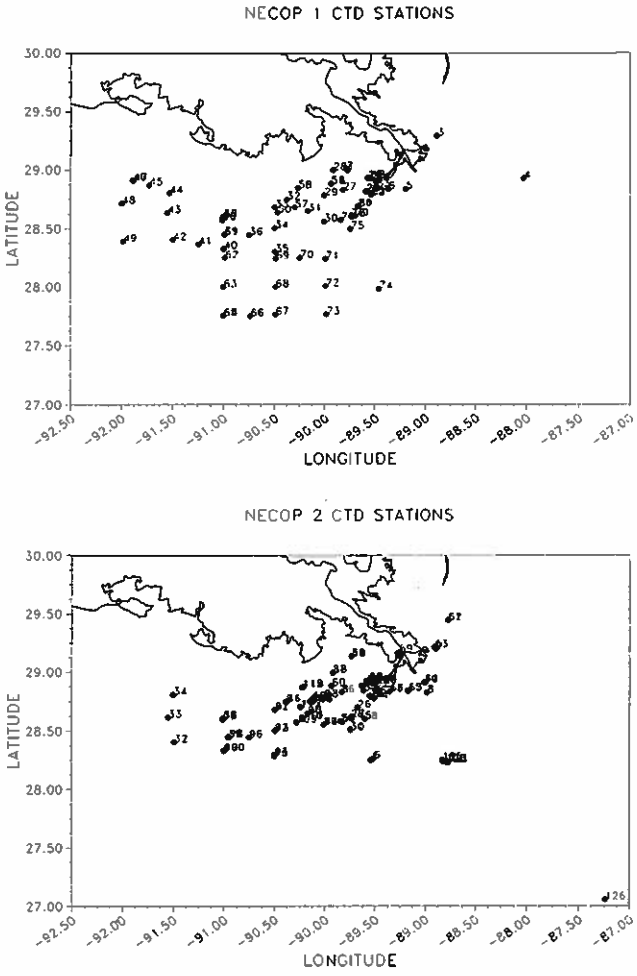


Fig. 1. Maps showing station locations for CTD, transmissometer and water samples during NECOP I (July-August 1990) and NECOP II (Leg 1, February 1991).

concentrations of suspended matter near the river mouth contribute to shifts in the location of areas of maximum productivity.

Examples of short-term (hours to days) shifts in the concentrations of suspended particles were observed at the anchor stations. Anchor stations 1 (28°54.4'N, 89°29.8'W) and 2 (29°08.3'N, 89°44.1'W) were located adjacent to the mouth of Southwest Pass and within the core of chronic hypoxia, respectively. One noteworthy example of rapid changes in SPM occurred at AN-1 during February 1991. Over a 30-hour period, surface salinity varied from <5 parts per thousand (ppt) to 18 ppt with SPM concentrations varying indirectly with salinity. This observation is common in this area and is related to tidal effects. Within the near-bottom nepheloid layer salinity remained at about 36 ppt; however, sizeable variations in SPM values were observed. These changes in concentrations of SPM in near-bottom water can be directly related to passage of a short-duration weather front over the site. As the front passed, bottom current speeds increased from about 5 cm/sec (about 0.1 knot) to a peak of about 35 cm/sec (0.7 knot) with an order-of-magnitude increase in the concentrations of SPM (Fig. 2). The amount of

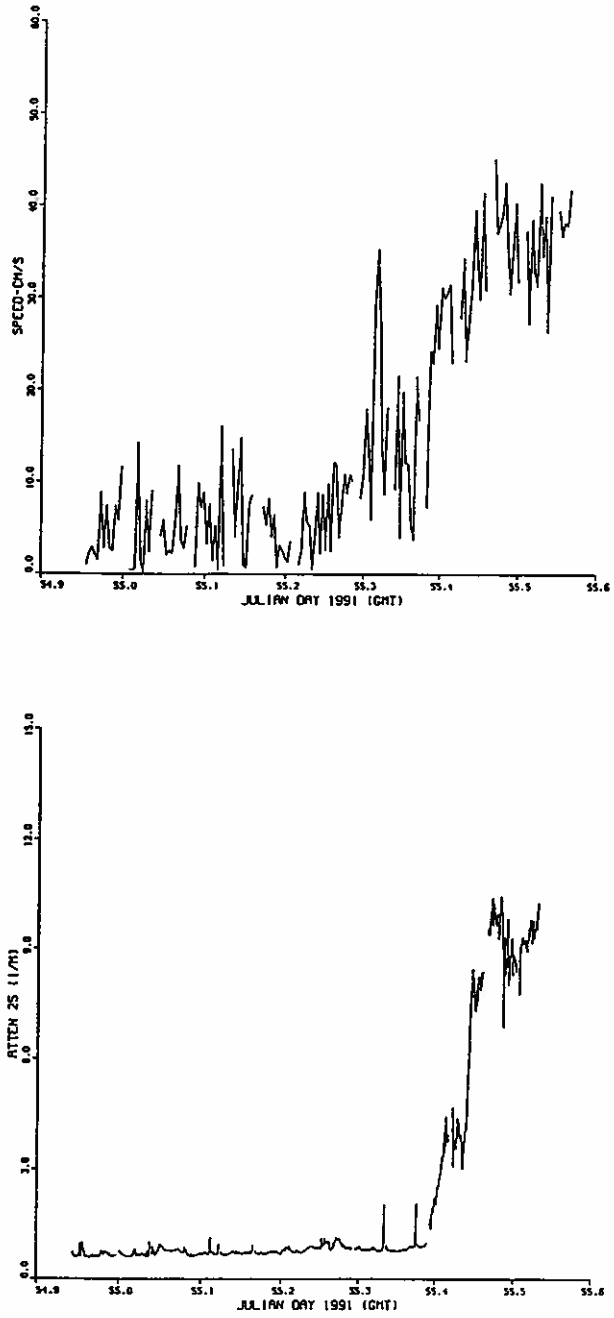


Fig. 2. Graphs showing (a) light attenuation for 25-cm path length transmissometer versus time and (b) current speed versus time for Feb. 24, 1991, at Anchor Station 1.

particulate matter as well as POC and PN transport along the shelf thus increased greatly. These changes in particle loading can have a direct effect on oxygen depletion as pulses of increased POC and PN move toward the area of chronic hypoxia. Detailed calculations of transport as well as temporal and spatial variations in concentrations of SPM and dissolved oxygen are ongoing.

From a chemical perspective, concentrations of particulate organic carbon and particulate nitrogen also show spatial and temporal changes. The POC value for the Mississippi River was 110 μmol/L (1.3 mg/L) for July-August and 220 μmol/L (2.6 mg/L) for February. Even though the Summer particles contained more organic carbon (3.1 percent) than the Winter particles (1.6 percent), the river carried twice as much POC during the February period.

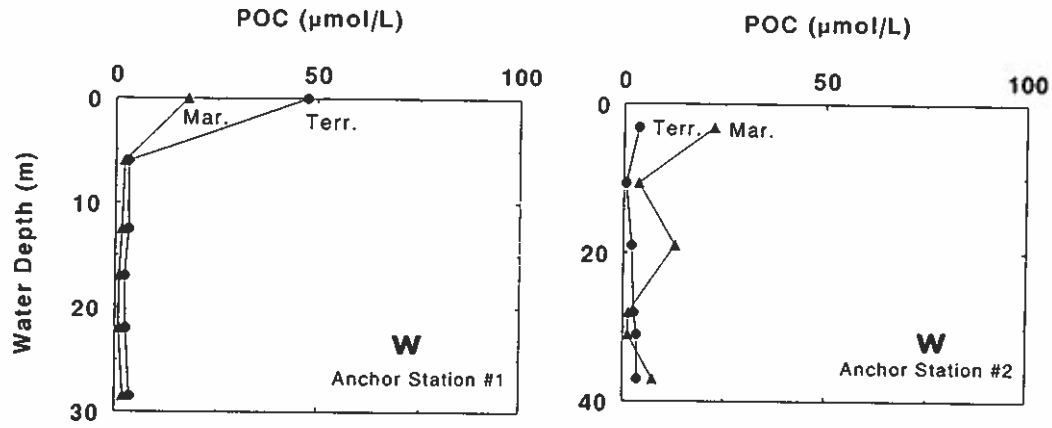
Further delineation of the spatial and temporal trends in POC can be seen in Fig. 3, which shows POC values for Anchor Stations 1 and 2 for the Summer and Winter cruises. The POC values (Fig. 3) have been divided into terrestrial and marine components using both δC-13 and the POC/Al ratio. Values for the δC-13 of terrestrial POC in the river are about -25 per mil, increasing to -20 per mil in marine POC (Eadie, person. comm.). The POC/Al ratio at Head of Passes varies seasonally and was 0.44 for NECOP I and 0.20 for NECOP II. The POC/Al ratio decreases to as low as 0.01 when the terrigenous material settles out of the plume and production of marine POC begins. By using end-member values for both the δC-13 and the POC/Al ratio, we can estimate the fraction of terrestrial and marine organic matter that comprise a given POC sample. Agreement between the two approaches is good in most instances; however, when questions arise the δC-13 values were considered more reliable.

At Anchor Station 1, the terrestrial POC is almost 50 μmol/L in February 1991 relative to 20 μmol/L in July 1990 (Fig. 3). This difference is in response to the increased particle load of the river during the NECOP II cruise. The difference in marine POC is equally dramatic; however, the trend is reversed with the higher marine component occurring in Summer (Fig. 3). Yet, the greater runoff was in Winter. Although somewhat preliminary, the observed differences at Anchor Station 1 show the combined effects of concentrations of SPM (light penetration), nutrient loading (river flow), and temperature on the levels of terrestrial and marine POC in the near-river-mouth area.

At Anchor Station 2, some 30 km away, the terrestrial POC values (Fig. 3) are markedly lower than at Anchor Station 1 during both cruises with <5 μmol/L in mid-water samples during the July 1990 period. Values for marine POC are similar for both the Summer and Winter cruises at Anchor Station 2.

A primary focus of the NECOP program is on the development of seasonal hypoxia. One means to assess trends in oxygen distribution is by the apparent oxygen utilization (AOU). Actual values for AOU at Anchor Station 1 in February are similar to those for July (Fig. 4); however, the Summer trend of increasing AOU with depth is clearer. The AOU values of 100 μmol/L represent utilization of about 60 percent of the dissolved oxygen. During both time periods, values for AOU increase between AN-1 and AN-2.

The trends for POC and AOU observed between Anchor Stations 1 and 2 can be followed farther west into an area of more intense seasonal hypoxia. At Station 26 (28°36.4'N, 91°00.8'W) during NECOP II, POC values were 6 to 26 μmol/L, essentially all marine and similar to concentrations observed at Anchor Station 2 (Fig. 3). Levels of AOU at Station 26 of 100 μmol/



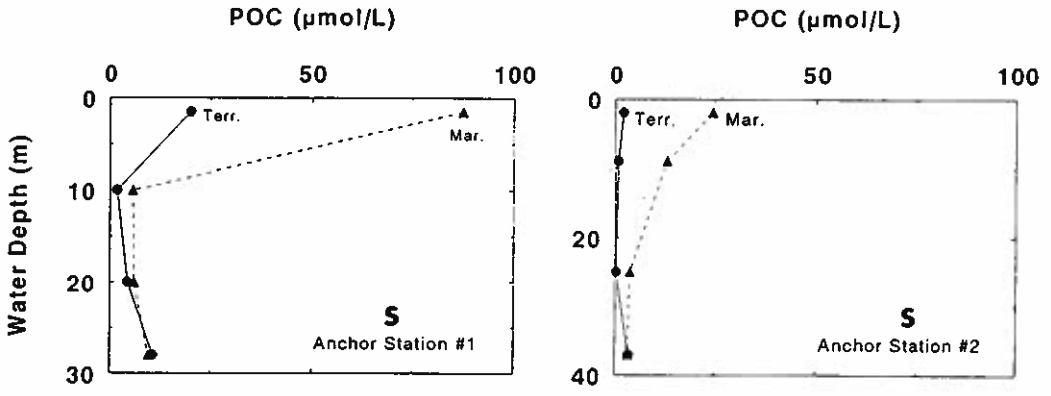
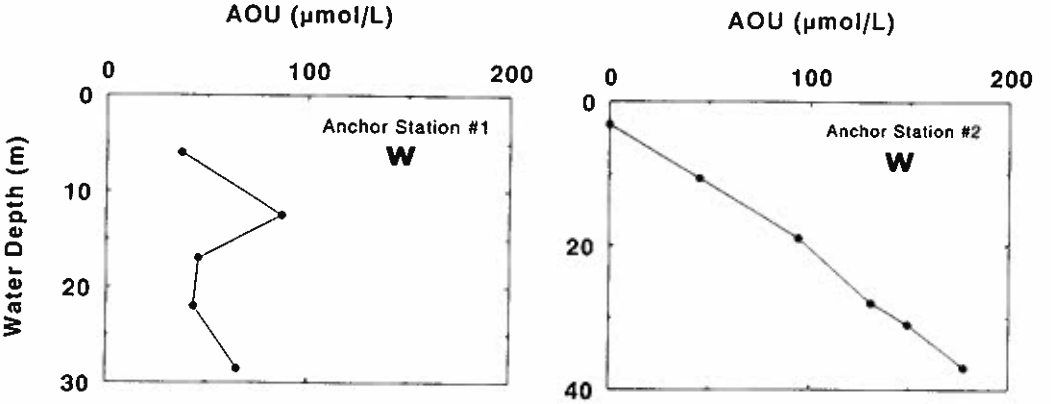


Fig. 3. Graphs showing values for particulate organic carbon (POC) versus depth for Anchor Stations 1 and 2 during NECOP I (S=Summer, July-August 1990) and NECOP II (W=Winter, February 1991).



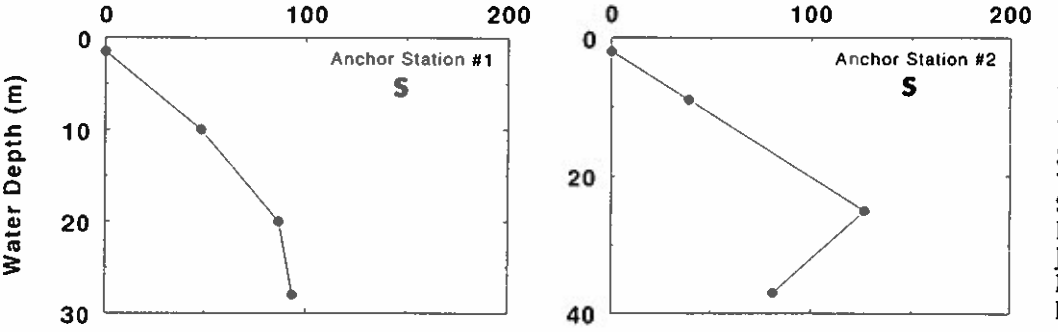


Fig. 4. Graphs showing values for apparent oxygen utilization (AOU) versus depth for Anchor Stations 1 and 2 during NECOP I (S=Summer, July-August 1990) and NECOP II (W=Winter, February 1991).

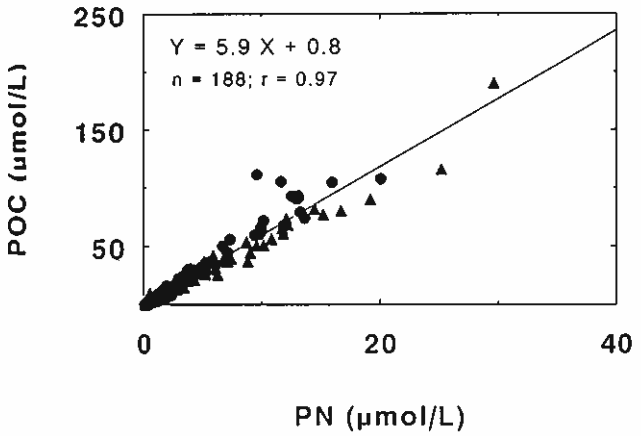


Fig. 5. Graph showing concentrations for particulate organic carbon (POC) versus particulate nitrogen (PN) for samples from both NECOP I and II cruises.

L were somewhat lower than AN-2 during this time of year. In contrast to the February 1991 observations, POC values during July-August in the western area around 91°W were 6 to 50 µmol/L, levels of AOU approached 200 µmol/L and dissolved oxygen values were as low as 0.4 mg/L. As our data processing continues, we are evaluating the seasonal and spatial trends of POC and AOU along and across the Louisiana shelf.

In addition to the POC data, we have carried out chemical analyses for particulate nitrogen, aluminum, silicon, calcium, manganese and selected trace elements. Our analyses for both NECOP cruises are complete and data interpretation is underway. Within the data set, we find that the C/N molar ratio for the entire NECOP I and II suspended matter data sets averages 5.9 (Fig. 5). This ratio is close to the classic Redfield ratio. Values for particulate manganese are elevated to as high as 5 percent in near-bottom water, especially during the Summer, as a result of release of dissolved Mn from the sediment interstitial water and subsequent oxidation of manganese oxides in the overlying water. Particulate Pb values (expressed as µg/g) decrease offshore as Pb-bearing river particles settle out of the water column. Particulate Cd values (expressed as µg/g) tend to increase offshore in response to increased biological uptake.

Conclusions

More than 120 CTD-transmissometer profiles and >400 particle samples were collected from the Mississippi River and adjacent Gulf of Mexico during July-August 1990 and February 1991 cruises. In addition to river-flow dependent variations in particle distributions, time-series data show the importance of tides and weather fronts on the concentrations of suspended matter. Results from chemical analyses show that concentrations of POC range from >80µmol/L (>1 mg/L) at near-river locations to <0.8 µmol/L (<0.01 mg/l) in some deep offshore waters. The organic fraction of the suspended matter increases from <5 percent of the total mass near the river mouth to >90 percent along the shelf at about 10 km from the river. The C/N molar ratio in suspended particles from throughout the shelf is near uniform at 6. Plumes of particle-rich water at outer shelf depths of about 100 m and in near-bottom nepheloid layers carry a POC burden that can be traced tens of kilometers offshore.

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Louisiana continental shelf sediments: Indicators of riverine influence

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Abstract

Sediments from the Louisiana continental shelf have been analyzed over the past six years for sediment chlorophyll *a*, phaeopigments, biogenic silica (BSi), phytoplankton, and fecal pellets. Sediment pigments are primarily phaeopigments (85 to 95 percent of total pigments). Sediment total pigments ranged over two orders of magnitude from approximately 1 μg/g dry sediment to more than 100 μg/g. There was an east-west gradient in sediment total pigments with higher values being associated with sediments in the Mississippi River Delta Bight. Sediment BSi ranged from 0.003 to 0.55 percent by weight. Concentrations of sediment pigments were greater in the spring and less in the summer and fall and correlated positively and strongly with sediment BSi and TOC. Diatoms were more numerous in sediments in the spring than in summer and fall 1989. Total autotrophs and fecal pellet volume, however, were greater in the summer collections. Sediment pigment concentrations mirrored upper and lower water column phytoplankton biomass measurements through a year, but the relationships were not strong.

The Mississippi River, which empties into the northern Gulf of Mexico, ranks eighth among the world's rivers in freshwater discharge and sixth in sediments delivered (Milliman and Meade, 1983). One-third of the river's effluent is discharged via the Atchafalaya River and the remainder through the current birdsfoot delta. Currents and circulation patterns on the Louisiana shelf west of the Belize delta are such that much of the freshwater delivered by these two rivers is retained on the shelf and a stratified system predominates most of the year.

The influence of the Mississippi and Atchafalaya Rivers on the physical and biological oceanography of the Louisiana shelf is dramatic with high primary and secondary production evidenced in the water column near the Mississippi River delta (Lohrenz *et al.*, 1990) and to great distances from it (Sklar and Turner, 1981). The amount of carbon reaching the benthic system, the source of the carbon, and the mechanism of transport is a concern, because of its contribution to the phenomenon of widespread, severe and persistent oxygen-deficient bottom waters during most of the summer. Various configurations of bottom water hypoxia have been documented on the Louisiana shelf since 1985, but the areal coverage ranges between 8,500 and 9,500 km² (Rabalais *et al.*, 1991).

The purpose of our investigations for the data presented in this report was to characterize the sediments with regards to indicators of phytoplankton production and determine if there was a signal in the sediments that could be linked to surface waters or the influence of the Mississippi River. The freshwater inputs of the Mississippi River can be identified to some distance from the delta, depending on the time of year and volume of river flow. Suspended particles fall out fairly close to the delta and much of the sediment load is delivered to deeper waters of the outer continental shelf and upper slope. There is a peak in phytoplankton production and biomass and bacterial biomass and production in the vicinity of the plume and downfield of the plume. Phytoplankton biomass peaks near 20 to 25 ppt salinity (Sklar and Turner, 1981), where water column clarity increases, but where sufficient nutrients remain. A peak in larger phytoplankton, most likely diatoms, can be seen at an optimum salinity range and somewhat removed in distance from the river (R.E. Turner, unpubl. data). We suspect that diatoms are a significant source of carbon that moves into the benthic layer, either via direct sinking, through fecal pellets, or advection downfield, especially within the direct influence of the river. Accord-

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Table 1. Sedimentary characteristics (and associated water column) for Louisiana continental shelf.

	Mean	Range
Depth (m)	29.5	12.0 - 95.0
Sediment Total Pigments (μg/g dry weight)	28.1	1.0 - 108.7
Sediment Chlorophyll *a* (μg/g dry weight)	3.6	0.12 - 74.2
Sediment Total Pigments (μg/cm^2)	5.4	0.6 - 24.0
(mg/m^2)	54	60 - 240
Sediment Total Pigments (Percent Phaeopigments)	89.1	44.0 - 97.0
Sediment Biogenic Silica (weight percent)	0.3	0.01 - 0.6
Sediment Percent Total Organic Carbon	1.0	0.3 - 1.4
Surface Water Total Pigments (μg/l)	10.2	0.2 - 74.5
Bottom Water Total Pigments (μg/l)	5.4	0.5 - 33.8

ing to the formula of Suess (1980), most of the phytoplankton produced in surface waters where depths are <100 m is likely to reach the bottom.

Methods

Surface sediments were collected from within the upper 5 mm using a syringe; cores were collected with a spade or Ekman box corer.

Sediment pigment analyses were done fluorometrically on acetone-extracted samples, with phaeopigments determined after acidification (e.g., Robertson *et al.*, 1980). Because there is considerable variability in the distribution of detritus or fecal material on the surface of the sediments, complicated by the recovery of relatively undisturbed cores, analyses require replication of at least four. Values shown are means of the four replicates. Calculations of chlorophyll *a* and phaeopigments were made based on the volume of the sample, on the surficial area of the sample, and by dry weight of the sediments extracted. There was a good relationship between the measurements based on weight versus area and weight versus volume, but the least amount of variability among the replicates was in units based on dry weight. These values are used throughout this paper.

Biogenic silica (BSi) was determined by methods outlined in DeMaster *et al.* (1983) and Krause *et al.* (1983), with some modifications. The method is basically a timed digestion of biologically-bound silica with the dissolved Si being measured by the molybdate blue spectrophotometric method. Standard techniques were used for sediment TOC (Control Equipment Elemental Analyzer) and sediment grain size analysis (Coulter Multisizer).

Results

Representative values, averaged for stations in depths of 12 to 95 m to avoid complications of shallow, high energy environments and non-representative upper slope stations, are listed in Table 1. Sediments

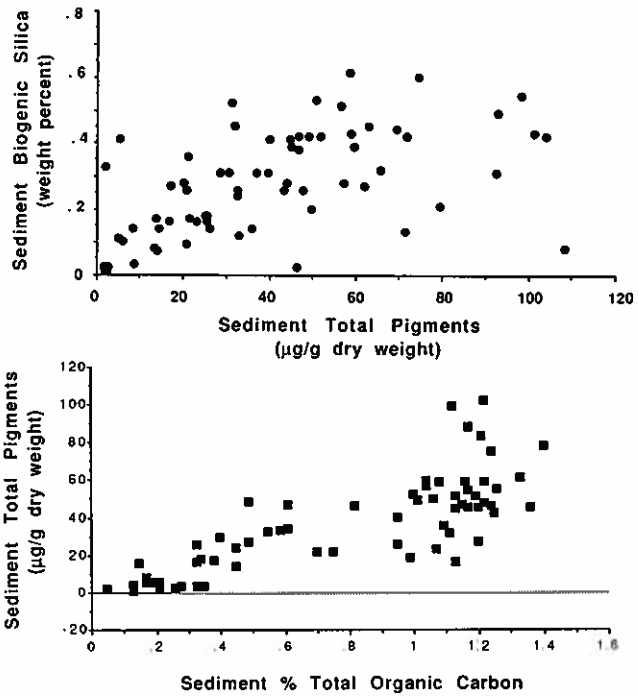

Figure 1. Comparisons of surficial sediment biogenic silica, total pigments, and percent total organic carbon for a series of stations from the Louisiana continental shelf as shown in Figure 2.

are primarily silty muds; >80 percent of the samples are 85 percent silt. The total organic content averages 1 percent, with a small range of 0.3 to 1.4 percent. These characteristics indicate fairly uniform sediment characteristics that could otherwise confound relationships with sediment pigments. Approximately 89 percent of the sediment pigments are composed of phaeopigments, but more frequently >95 percent. Exceptions to this general rule do occur. The total pigments per dry weight sediments averaged 28 μg/g but ranged over two orders of magnitude, with some values of 150 μg/g to >200 μg/g. These values are in the range of those reported for continental shelf envi-

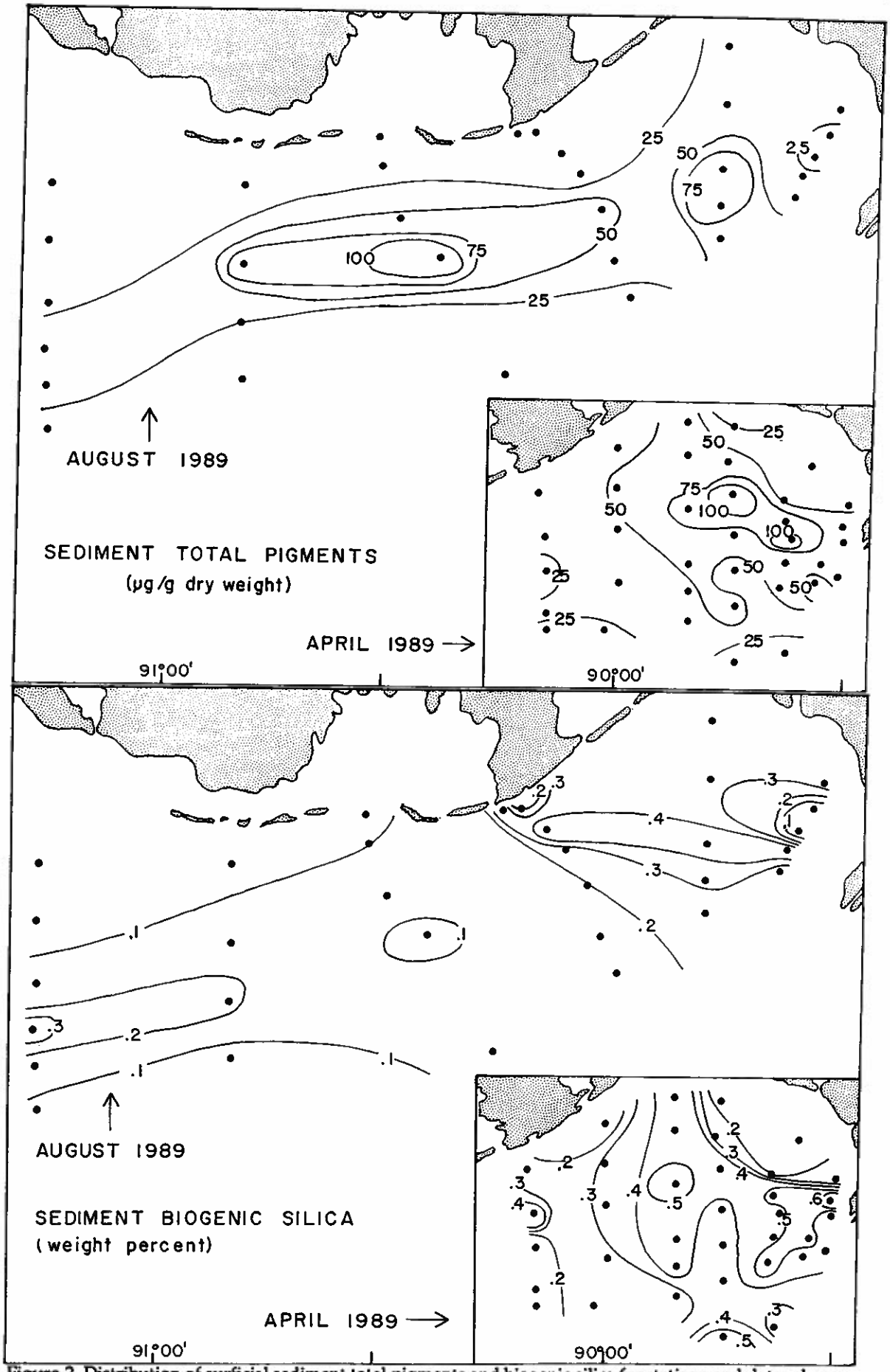

Figure 2. Distribution of surficial sediment total pigments and biogenic silica for stations and dates shown.

Table 2. Seasonal variation in phytoplankton and fecal pellets in surface sediments.

CRUISE	LaSER III	NURP	LaSER IV
DATES	Apr 14-20, 1989	Aug 4-10, 1989	Sept 20-27, 1989
Stations	All	Transects A & A'	All
n	11	10	3
PHYTOPLANKTON			
Diatoms (#/m^2)	9.75E+07	2.25E+08	1.40E+08
SD	1.42E+08	1.88E+08	9.46E+07
Total Autotrophs (#/m^2)	2.73E+08	5.04E+08	3.27E+08
SD	5.75E+08	4.81E+08	2.26E+08
FECAL PELLETS			
Number (#/m^2)	5.09E+06	1.50E+08	3.70E+07
SD	2.86E+06	1.15E+08	2.69E+07
Total Volume (cm^3/m^2)	1.63	8.75	10.22
SD	1.63	6.83	10.97

ronments, but in the upper end. The mean weight percent biogenic silica content of Louisiana shelf surficial sediments is 0.3 percent but ranges from negligible to 0.6 percent. The mean for the Amazon shelf is 0.25 percent, but values do not exceed 0.3 percent there (DeMaster *et al.*, 1983).

There are strong positive relationships between surface sediment biogenic silica, total pigments, and total organic carbon (Fig. 1). This indicates that sediment pigment levels are a good indicator of surface production (in the form of diatoms) that has reached the bottom. [Because of the strong relationships between the three variables, we will plot many of the remaining figures for total pigments only (our most complete data set).]

Sediment characteristics of the benthos, based on total pigments and biogenic silica, indicate that there is a signal of the river plume that can be identified on the seabed (Fig. 2). In April 1989, there were high concentrations of sediment pigments and biogenic silica removed in space somewhat down-plume of the delta, with decreases to the west and lower values inshore and offshore. It is not known whether the high biogenic silica near the river is a freshwater diatom signature or marine; freshwater diatoms have a 10X greater silica concentration per unit volume than marine (Conley et al., 1989). The eventual determination of the phytoplankton taxonomy will verify this. Carbon stable isotope studies indicate a rapid loss of the terrestrial signal from the river plume, but the 0.6 BSi value is from a station with a delta-C13 terrestrial signal (Rabalais and Fleeger, unpubl. data). In August 1989, a greater areal coverage of surface sediments indicated an east-west trend in biogenic silica (Fig. 2). During the August sampling adjacent to the Mississippi River delta, a similar pattern for total pigments was seen as in April. Downfield of the delta, however, high sediment pigment concentrations were not paralleled by high biogenic silica levels. This signal indicated high

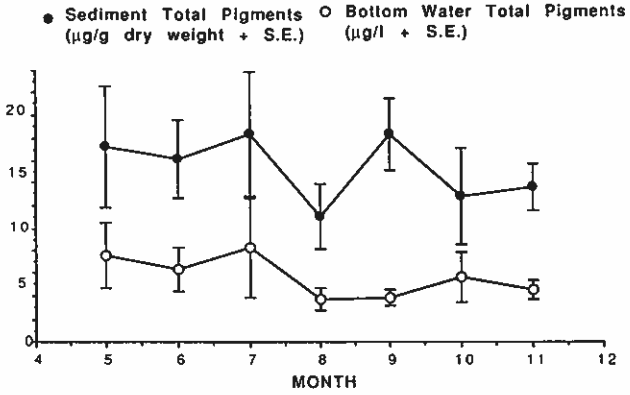

Figure 3. Average values for bottom water total pigments and surficial sediment total pigments for stations C5, C6 and C7 on a transect off Terrebonne Bay for the months shown in 1986.

levels of degradation products of non-diatom phytoplankton.

We have also documented variability in sediment total pigments at a series of stations along a transect off Terrebonne Bay (means for C3, C5, and C7, 12 to 20 m, 1986, in Fig. 3). There is a slight decrease through season, but no statistical difference; however, no data are available prior to May. A similar analysis showed no seasonal trend in 1990. There is surprisingly little temporal variation at stations C5-7 (in 1986) and C6A (in 1990), given that the variability in surface water chlorophyll *a* is 10-fold.

Bottom water pigments and surficial sediment pigments should not, however, necessarily track surface water pigment concentrations. The surface distribution of water masses including phytoplankton biomass responds to freshwater inflow, currents, and wind over short time periods. For example, near-surface currents at station C6A from mid-April to June in 1989 were 15 cm/s to the west and 0.5 cm/s and non-

directional near-bottom. Biological processes in surface waters are likely to change over short periods as well, as salinity and light conditions change, nutrients are depleted or regenerated, and phytoplankton community composition changes.

For many of the same sediments analyzed for pigments and biogenic silica, we also enumerated phytoplankton species and abundance, and fecal pellet abundance and volume (Table 2). There were no relationships between either diatoms or total autotrophs and either sediment total pigments or biogenic silica. This may not be unexpected, however, given the methodology and less than quantitative resuspension and subsampling of the sediments. Phytoplankton counts were of whole epifluorescent organisms, and as such we missed the frustules of dead diatoms that should contribute substantially to the biogenic silica. Despite these methodological problems, there are some differences, especially between spring and summer. Diatoms are much more numerous in sediments in spring than summer; and are more numerous in both these seasons than fall. Other autotrophs dominated in summer (sediments). On the other hand, the volume of fecal pellets in summer was considerably greater in summer than spring and also high in fall (see also Qureshi *et al.*, this volume).

Discussion

Several mechanisms exist for transfer of surface water phytoplankton biomass to the sediments. Direct sinking or advection of diatoms is likely near the river delta. *Skeletonema costatum*, which is found in the surface waters, can be identified in the sediments. Diatoms are more likely found nearer the river, and more likely to be present in spring than in summer. Diatoms found some distance from the river are not as heavily silicified. Phytoplankton counts showed no correlation with either sediment pigments or biogenic silica. However, as noted above, these were counts of whole organisms. Biogenic silica is a better measure and indicates diatoms as a major carbon source to the seabed. Biogenic silica in sediments, however, does not necessarily represent a direct sinking of diatoms; they could be incorporated in fecal pellets. Fecal pellets are numerous and voluminous in surface sediments and near-bottom particle traps in the summer (see Qureshi *et al.*, this volume).

We propose a combination of two mechanisms, differing in relative importance with distance from direct riverine influence, and with season. Where adequate water clarity, appropriate salinity (20 to 25 ppt), and adequate silicate occur, the phytoplankton community is diatom-dominated. This is less likely to occur with distance from the river and less likely in summer than in spring. Thus, direct sinking of larger diatoms is more likely to contribute to the carbon load of the sediments in the spring and closer to the river. Repackaging of phytoplankton, including diatoms, is a more likely mechanism later in the year. Mesozooplankton populations have become more diverse and numerous by mid-summer and there is an increase in fecal pellets in summer sediment samples.

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Benthic community oxygen demand and nutrient regeneration in sediments near the Mississippi River plume

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Abstract

Benthic community oxygen consumption and nutrient regeneration have been measured in recovered multiple cores incubated aboard ship (at 16 locations) and in paired *in situ* benthic chamber incubations (at 11 locations) in the NW Gulf of Mexico. The two approaches were used at six common locations, providing a direct comparison of the two techniques. Average oxygen demand (at stations unaffected by hypoxia or methodological artifacts) was equivalent to a remineralization of ca. 194 mg CO_2-C $m^{-2}d^{-1}$ (assuming an RQ of 0.85). Total nitrogen remineralization based on the chamber data was ca. 7 mg N $m^{-2}d^{-1}$, suggesting from comparison to the Redfield ration that ca. 5 mg N $m^{-2}d^{-1}$ was lost to denitrification within the sediments. Five *in situ* paired light and dark chamber incubations were conducted across a gradient of hypoxic conditions, thus providing a measure of the depression of oxygen consumption caused by limiting oxygen concentrations.

In shallow coastal ecosystems, the sediment biota plays an integral role in the cycling of carbon and nitrogen. The purpose of the present study has been to quantify net carbon and nitrogen remineralization by incubating bottom sediment and its contained community with bottom water. Additionally we wanted to identify any peculiar processes that characterize a shallow ecosystem being affected by a major river (the Mississippi) typified by substantial nutrient (nitrogen) loading.

Methods

Two traditional but distinct ecological approaches were employed in this study: the shipboard incubation of recovered multiple cores at *in situ* temperatures (pioneered by Mario Pamatmat, e.g., 1971) and the *in situ* incubation of the biota and sediments with overlying bottom water in chambers, an approach initiated in saltmarshes by Teal and Kanwisher (1961). The benthic chamber method utilized divers to emplant and sample chambers in shallow water (less than ca. 40 m depth), but for deeper work an autonomous "benthic lander" was employed (Smith *et al.*, 1976; Berelson *et al.*, 1984).

The shipboard incubations were made on sets of 4 to 8 fiberglass cores maintained in water baths at *in situ* temperatures. Oxygen consumption rate per unit area of sea floor was determined by intermittently subsampling the water overlying the sediment for oxygen and nutrients. See Rowe and Phoel (1991) for details. The *in situ* paired chambers were constructed of plexiglass. A volume of 7.5 L of water in each covers an area of 0.09 m^2, with a collar on the outside of each to assure precise penetration depth into the sediments. A stirring motor was utilized to slowly circulate the water in the chambers as well as to maintain rapid flow over the YSI oxygen electrodes used to monitor oxygen concentration in the chambers. The output from the electrodes was recorded internally on a data logger contained in a pressure-resistant, waterproof housing on an aluminum frame supporting the chambers. The water within the chambers was subsampled intermittently using 50 cc syringes for analyses of dissolved organic nitrogen (DON), volatile fatty acids (VFA's), inorganic nutrients ($Si(OH)_4$, PO_4, NH_4, NO_2 and NO_3) and in some cases O_2. The chambers emplanted by divers were transported to the bottom in a rectangular aluminum frame attached to a marker buoy to the surface. The remote lander used in deep water was also constructed of an aluminum frame. It carried (1) acoustic-controlled disposable anchors, (2) floatation spheres, (3) acoustically commanded release mechanism, (4) electronic timed release system, (5) power supply, (6) 8 mm videocamera, recorder and deep-sea light source, (7) oxygen electrode sensing and data recording system, and (8) a set of six 50 cc syringes used to sample each chamber (3 syringes in each chamber) over time. The syringes pulled chamber water through 0.2 micron filters during sampling to prevent bacteria from affecting the samples. On return to the surface all the samples were frozen or fixed immediately.

Acknowledgments

This work was supported by the NOAA NECOP program. Gratitude also goes to the officers, crew and marine technicians aboard the R/V GYRE who helped make this work a success. Ship time was paid for by the Texas Institute of Oceanography and the Department of Oceanography, Texas A&M University.

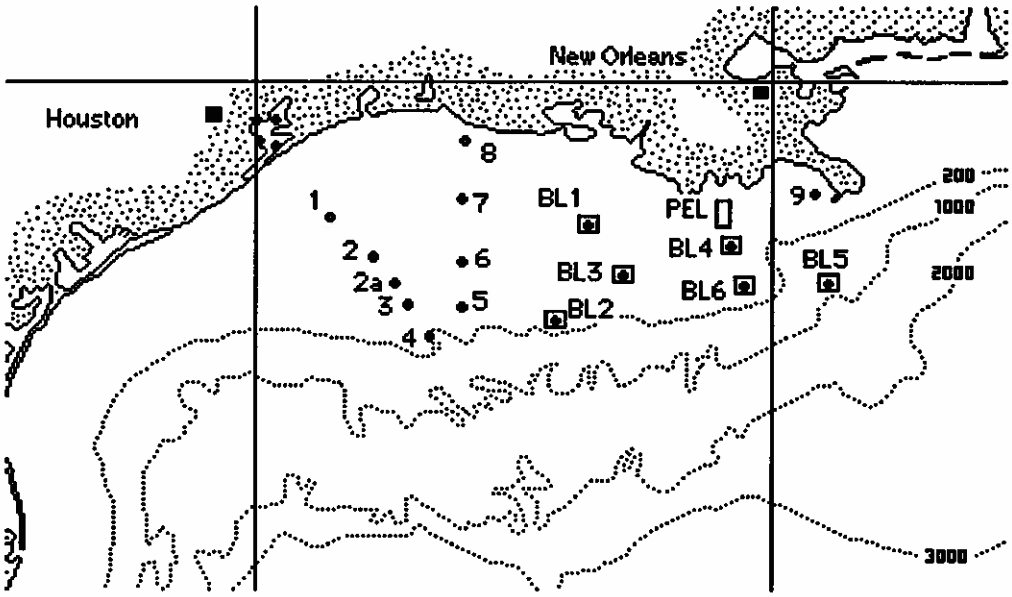

Figure 1. Map of locations of sediment oxygen demand measurements during NECOP study. Solid dots are recovered core incubations. Dots in boxes are recovered cores and benthic lander deployments. PEL is location of five paired chamber deployments in hypoxic bottom water. Four solid dots in Galveston Bay (near Houston) are paired benthic chambers.

Results

Oxygen demand in this study can be reported at 25 locations so far. As indicated in Fig. 1, this includes four locations in Galveston Bay, 15 locations on the continental shelf between the Mississippi River and a transect off Galveston, Tex., five locations in "hypoxic" areas just west of the Mississippi River plume, and one on the continental slope (900 m depth) due south of the river plume. The Galveston Bay and hypoxic area data are all based on diver-placed paired light and dark *in situ* chambers, whereas the other 16 shelf and slope locations were multiple core shipboard studies, six of which are also represented by lander (*in situ*) paired chamber flux estimates, as indicated.

An initial assessment we have attempted is a comparison of the two techniques. One conclusion we have made is that if recovered cores are taken in hypoxic water, the rates that are measured aboard ship will be artificially high if the water in the core is re-oxygenated. Secondly, if the chambers are clear plastic rather than opaque and the incubations are well within the euphotic zone, then the rates in these incubations will be low, because photosynthesis as well as respiration will be occurring within the chambers. At BL1, for example, the average core oxygen demand was 44.4 ml $m^{-2}h^{-1}$, compared to a lander rate of only 6.3 ml $m^{-2}h^{-1}$; but the station was well above the 1 percent light level, the bottom water was not hypoxic and the clarity of the water was relatively high, based on percent light transmission (Sanchez, in preparation; GYRE Unpubl. Data Rept., 90G-10). We, therefore, reject the lander rate and accept the core rate. On the other hand, at BL4 the multicore incubation rate was again high compared to

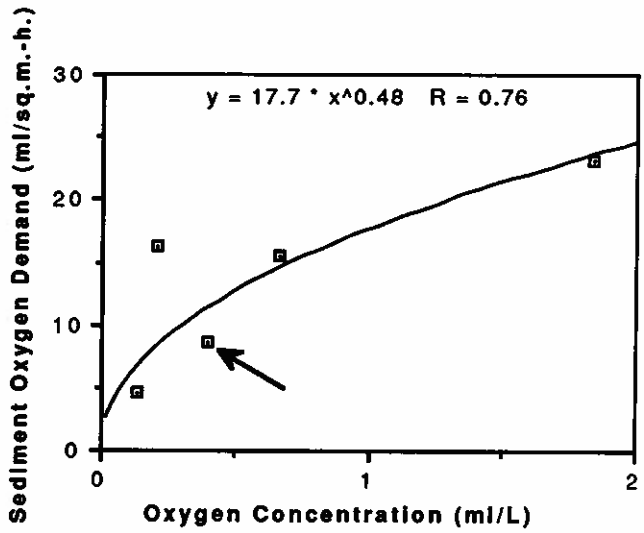

Figure 2. Relationship between oxygen demand in *in situ* opaque benthic chambers in relation to ambient oxygen concentrations in the bottom water. The data point identified by the arrow is the mean of two clear chambers used on a benthic lander deployment.

the lander chamber rate (37.1 vs. 8.6 ml $m^{-2}h^{-1}$), but here the bottom water was very turbid and the bottom oxygen concentration was only 0.4 ml L^{-1}. We, therefore, accept the lander value and reject that of the recovered cores, because we could not prevent the latter from being oxygenated on the surface between the time of recovery and the initiation of the incubations. The other values agree fairly well. Their lack of agreement is probably a reasonable estimate of the

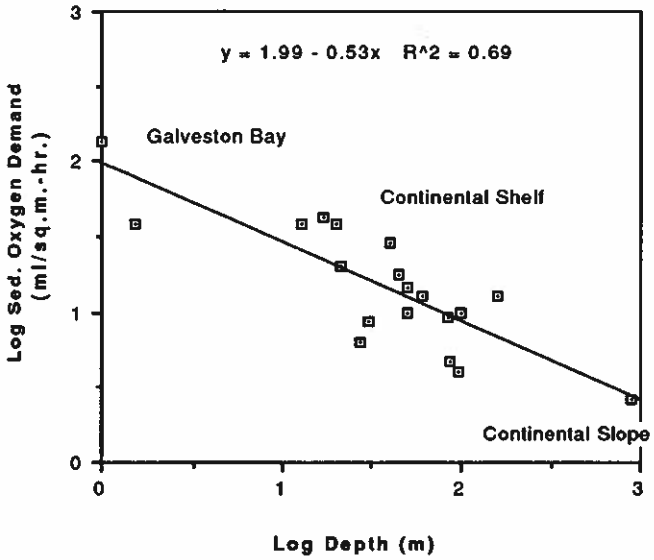

Figure 3. Sediment oxygen demand as a function of depth, Gulf of Mexico data. Includes both ship-board incubated cores and *in situ* chamber incubations.

variability that might be expected normally on the time and space scales of the measurements. Note that in every case the shipboard incubations are higher than the *in situ* rates. This difference ranges from a few percent to a factor 2 or 3.

The effects of low oxygen on rates of oxygen demand can be seen in Fig. 2. Four of these data points come from the opaque chambers used in shallow water under varying conditions of hypoxia. The other (as indicated) is the average of a pair of clear chambers on the lander, but in very turbid water. This illustrates the circumstances under which the measure of oxygen demand alone underestimates total heterotrophic metabolism.

All the data can be plotted relative to depth (Fig. 3). This regression includes the rates in Galveston Bay at the shallow end and the single slope station at 900 m at the deep extreme, but dependence on depth is not impressive. This relationship is significant only because the rates in Galveston Bay are so high.

The average for 18 rate measurements on the continental shelf, including data from both methods (but excluding known artifacts), was 17.7 ml m-2h-^{1} (0.79 mM $O_2 m^{-2}h^{-1}$). This is equivalent to the remineralization of ca. 194 mg $C0_2$ - C $m^{-2}d^{-1}$, assuming a respiratory quotient (RQ) of 0.85. This amounts to about 70 gm C m^{-2} being remineralized on the sea floor per year.

Total nitrogen remineralization into the lander chambers (as ammonium, nitrate and nitrite) averaged 7.4 mg N $m^{-2}d^{-1}$, while the carbon remineralization averaged 75 mg C $m^{-2}d^{-1}$. The expected remineralization, based on the Redfield ratio (6 mg of carbon remineralized for every 1 mg of nitrogen), would be approximately 12, however, and therefore the chamber studies suggest that ca. 5 mg N $m^{-2}d^{-1}$ is lost to denitrification within the sediments.

Discussion

Methodological artefacts may be important in explaining some of the average two-fold difference in rates measured by the lander and the recovered cores. Higher rates are measured by cores from hypoxic areas if the bottom incubation water is oxygenated. By pairing opaque and clear chambers we can now differentiate between bottom boundary photosynthesis and respiration. An artefact induced by the lander that might lower rates is "blowing" away the highly reactive "floc" layer on deployment or when the chambers are lowered to the bottom, although the lander video does not suggest that this is appreciable.

Similar studies with either chambers, recovered cores, or both, have been conducted on other continental shelves, and it is instructive to compare those areas with our study off the Mississippi River. A study south of New England (Shelf Edge Exchange Processes, or SEEP) recorded an average of approximately 10 ml O2 $m^{-2}h^{-1}$ in both sandy and muddy areas of the shelf (Rowe, et al., 1988), or about 1.7 times less than we have measured in the Gulf of Mexico. This may be biased by higher temperature in the Gulf, with greater numbers of stations in close proximity to shore, however. The Bering Sea shelf oxygen demand was even lower, averaging only 6 ml O2 $m^{-2}h^{-1}$ (Rowe and Phoel, in press).

It is tempting to attribute the differences in the above areas to temperature, and indeed there is a range of greater than 20 °C between the three areas (the Gulf of Mexico, the New England shelf to the Bering Sea shelf) during the summer months when most of these measurements were made. But a number of co-varying factors, including the decline in temperature with depth, sediment grain size and the seasonally-varying input of organic matter to the bottom, make this generalization difficult to demonstrate. The Bering Sea shelf is very wide and was suspected to retain considerable organic production after the spring bloom rather than exporting it. Although Hargrave (1978) has demonstrated how the freshness or quality of organic matter can over-ride temperature effects, the effects of any accumulation of fresh detrital matter in the Bering Sea was not reflected in our data.

The greatest deficiency in our study so far is our inability to estimate total rates that include anaerobic metabolism. In other areas, including those referred to above, it has been assumed that oxygen demand is also a good estimator of sulfate reduction because the sulfide produced is oxidized by free dissolved oxygen. Burial rates in sediments near the plume are extremely high (see Blackwelder *et al.*, this volume), reaching as much as 40 g C $m^{-2}y^{-1}$. This suggests that the ratio of metabolized to buried carbon is greater than 0.5, or far higher than that found in most marine ecosystems. We suspect that this massive, rapid sequestering of carbon below the surface due to burial is removing reactive compounds from the oxidized layers, and any further degradation must occur through anaerobic pathways, utilizing metal oxides, nitrate and sulfate as terminal

electron acceptors instead of oxygen, at rates that are not adequately accounted for using oxygen demand alone. In other words, loss of organic carbon to the bottom may be far higher than we originally suspected.

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Respiration rates in bottom waters of the Louisiana shelf

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Abstract

In order for bottom waters along the Louisiana coast that are influenced by the Mississippi and Atchafalya Rivers to become hypoxic, respiration rates of the water column and/or the benthos must be higher than rates of reaeration. Water column respiration rates were measured enzymatically (Electron Transport System activity, ETS) on samples obtained in May, June and July on a transect south of Cocodrie, La., through the core of the hypoxic region west of the Mississippi River and on samples obtained on a shelfwide cruise in July. Bottom water respiration rates were four times higher in July, when hypoxia was most intense, than in May and June, despite similar average temperatures. In general respiration rates are among some of the highest measured (25 to 1681 $mgO_2/m^3/d$). At hypoxic stations in July the oxygen below the oxycline would be completely depleted in 1.2 to 24 days from water column respiration alone. Since anoxia is not common or persistent, rapid resupply mechanisms must exist.

Introduction

Large areas (up to 9,500 km^2) of the Louisiana continental shelf can become hypoxic ($O_2 < 2mg/l$) during the summer months (Rabalais *et al.*, 1991). It is hypothesized that the hypoxia results because carbon produced by primary production in surface waters, due to high nutrient input from the Mississippi River, falls below the pycnocline and is respired during the warm months when salinity stratification prevents reaeration (Rabalais *et al.*, 1991). Such large scale hypoxia is of special concern in this region because of the possible impact on economically important fisheries and the possibility that changing nutrient loadings from the Mississippi River could exacerbate hypoxia (Turner and Rabalais, 1991).

Both benthic and water column respiration will contribute to oxygen depletion below the pycnocline. While benthic respiration is currently being measured (Rowe, pers. comm.; Twilley, pers. comm.), there are only a small number of water column respiration rate measurements from July and November 1976 (Turner and Allen, 1982) and the method used may underestimate the rate (Turner, pers. comm.). To understand and predict hypoxia, it is necessary to know the spatial and temporal variation of water column respiration in relation to benthic respiration and environmental conditions.

Water column respiration has been measured from changes in oxygen concentrations in bottles or in a confined body of water or by calculation from advection-diffusion models (see references Table 2). An alternate method involves measurement of the activity of enzymes associated with respiration in all organisms, the electron transport system (ETS) and calculation of respiration rates, using factors (R/ETS) that relate enzyme activity to respiration rate under different environmental conditions (Packard, 1985). The advantage to this method is that many samples can be collected quickly and the analysis gives an instantaneous rate without incubations. The disadvantage is the assumptions made in the choice of factors to convert from activity to respiration.

In May, June and July 1991 ETS activity was measured at the surface and in bottom waters on an across-shelf transect (C; Fig. 1) through the core of the hypoxic zone. In July ETS activities were measured on an alongshore transect down the axis of the plumes of both the Mississippi and Atchafalaya Rivers (Fig. 1). The purpose was to conduct a preliminary study of the spatial and temporal variability of water column respiration rates on the Louisiana continental shelf.

Methods

Samples were collected in 5-liter Niskin bottles on cruises on the R/V *ACADIANA* (C transects, May 15,1991, and June 17, 1991) and the R/V *PELICAN* (C transect, July 17, 1991; alongshore transect July 16-20,1991). They were filtered immediately onto GF/F filters, frozen in liquid N_2, and later analyzed, according to Packard and Williams (1981). Enzyme activities were determined at 25 °C and converted to *in situ* temperatures using the method of Packard *et al.* (1975). Activities were converted to respiration rates, using an R/ETS of 0.15 in the euphotic zone (assuming phytoplankton dominate the biomass), 0.49 below the euphotic zone with $O_2 > 2$ mg/liter (assuming non-bacterial heterotrophs dominate), and 1.10 below the euphotic zone with $O_2 < 2mg/liter$ (assuming bacteria

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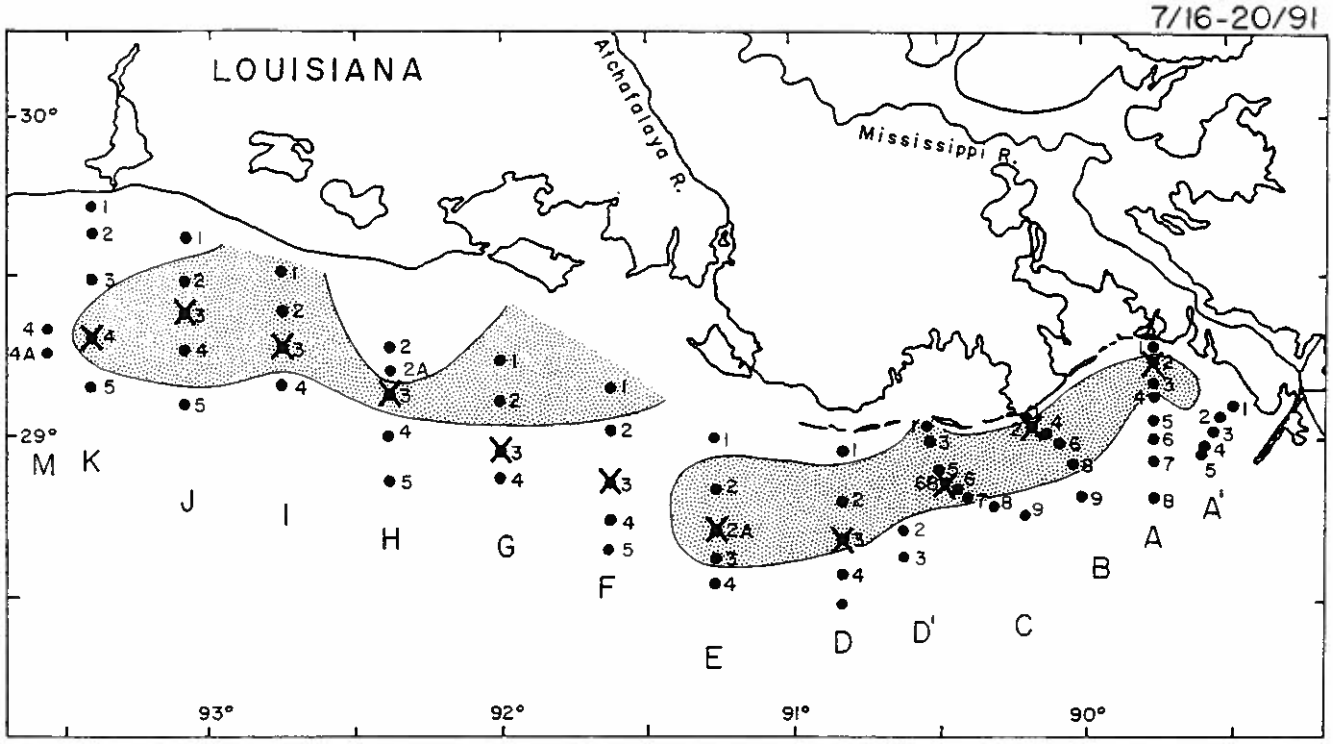

Figure 1. Location of sampling stations for O_2 (o), ETS (x), and hypoxia (stippled area; bottom O_2 concentrations ≤ 2 mg/liter) on the Louisiana continental shelf.

dominate), based on data in Packard (1985). At five stations in July, respiration rates in deep water were also calculated from changes in oxygen consumption, measured by the Winkler method (Parsons *et al.*, 1984) during 24-hour dark bottle incubations. Although there were not enough measurements to calculate R/ETS for this data set, the two methods gave similar rates (see Table 2).

Oxygen and temperature were measured with a Hydrolab Surveyor II on *ACADIANA* cruises and with a Seabird CTD with a Seabird dissolved oxygen sensor (S/N 13106) on the *PELICAN* cruise.

Results and Discussion

In May and June, although hypoxia was observed at one station on each C transect (Fig. 2), it was not widespread. By July, however, hypoxia was widespread, both on the C transect and along the entire Louisiana continental shelf. Respiration rates were generally much higher in July than in the two previous months (Figs. 2 and 3). In fact, in the near-bottom water at the four stations, which were sampled in all three months and became hypoxic by July, the respiration rates had increased by a factor of approximately four (Table 1). This was not due to increases in bottom water temperatures since those remained approximately the same from June to July (Table 1). Thus, the increased respiration must have been due to some combination of increased C flux, heterotrophic biomass or stratification. The water column respiration rates obtained in this study are near the upper end of rates obtained for any estuarine or coastal region (Table 2).

The days to oxygen depletion in the water below the oxycline were calculated for stations on the July cruise from integrated respiration rates and oxygen concentrations, assuming that no oxygen was resupplied. Values ranged from 1 to 24 days at hypoxic stations and 8 to 138 days at non-hypoxic stations (Figs. 4 and 5).

Benthic respiration was measured, using in *situ* chambers, one week later at or near five of the stations at which water column respiration was measured (Rowe, pers. comm.). Water column respiration averaged 75 percent of the total benthic and water column

Table 1. Mean respiration rates (mg O_2/m³/da), days to O_2 depletion, and temperature in the water just above the bottom on three dates at four stations on the C transect that were hypoxic by July.

Date	5/15/91	6/17/91	7/17/91
Respiration rate	94	60	376
Days to O_2 depletion	66	59	15
Temperature (°C)	24.19	26.01	26.40

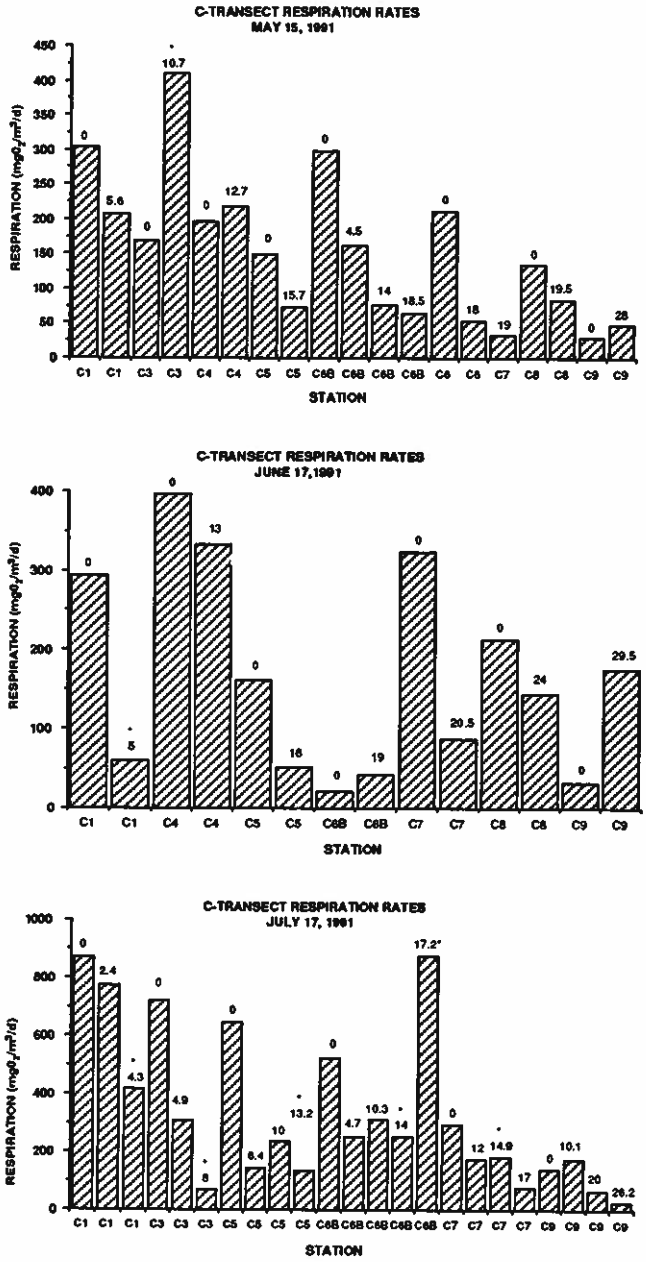

Figure 2. Respiration rates on C transect (see Fig. 1) on May 15, June 17 and July 17, 1991. Numbers above bars indicate depth from which samples were obtained. * indicates samples in which $O_2 \leq 2$ mg/liter.

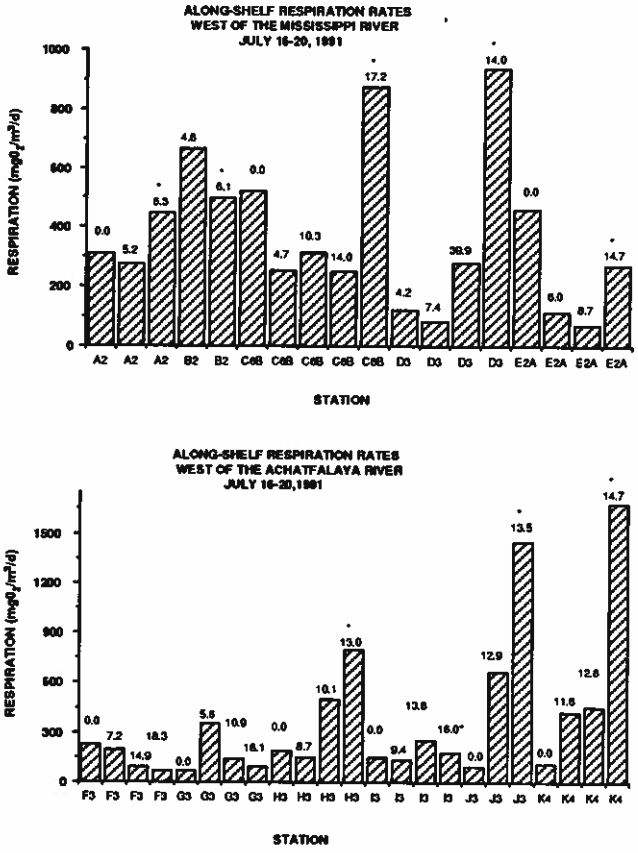

Figure 3. Respiration rates along the axis of the Mississippi and Atchafalaya Rivers at approximately 20 m depth. Symbols as in Fig. 2.

respiration below the oxycline. However, the predominance of water column respiration decreased at the deeper, and especially, non-hypoxic stations.

Since both water column and benthic respiration rates are so high, it becomes difficult to explain why anoxia, which occurs only occasionally (Rabalais, pers. comm), does not occur more frequently. Obviously, oxygen must be resupplied at substantial rates in order to prevent anoxia, although the mechanisms are currently unclear.

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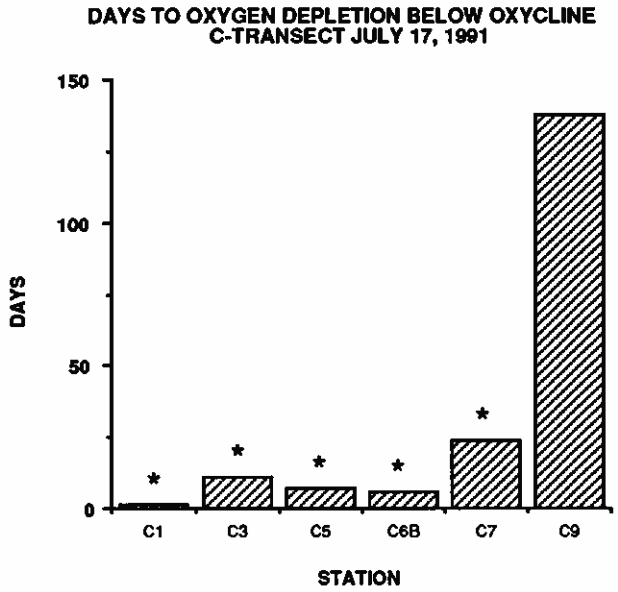

Figure 4. Days to oxygen depletion below the oxycline on the C transect on July 17, 1991. Symbols as in Fig. 2.

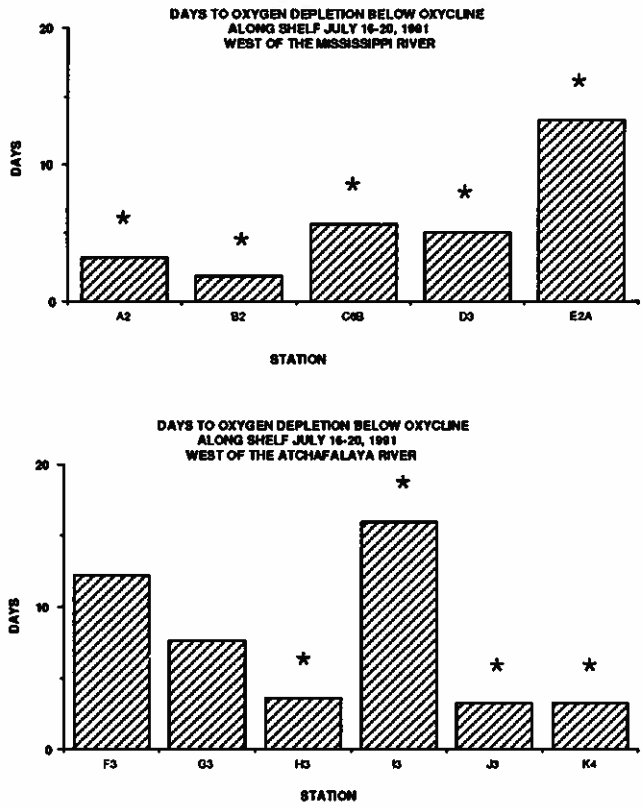

Figure 5. Days to oxygen depletion below the oxycline on the along-shore transect, July 16-20, 1991. Symbols as in Fig. 2.

Table 2. Respiration rates (mg $O_2/m^3/da$) in a variety of marine environments (adapted from Hopkinson, 1985).

Environment	Site	Rate	Reference
Estuarine	Chesapeake Bay, MD	210-2,100	Kemp and Boynton 1980
	Chesapeake Bay, MD	800-1,700	Taft et al. 1980
	Core Sound, NC	368	Williams 1966
	Doboy Sound, GA	620	Ragotzkie 1959
	Huizache-Caimanero Lagoon, Mexico	7,440	Edwards 1978
	Loch Eve, U.K.	100-250	Williams 1981
	Narragansette Bay, RI	457	Smayda 1957
	Port Hacking Estuary, Australia	80	Bulleid 1983
	Raritan Bay, NJ	360-2,100	Patten 1961
	Raskilde Fjord, Denmark	540-1,429	Jensen et al. 1990
	Southampton, U.K.	142-357	de Souza Lima and Williams 1981
	Wassau Sound, GA	440	Turner 1978
Coastal	Georgia Bight	38	Turner 1978
	Georgia Bight	713	Hopkinson 1985
	LA continental shelf 1976	2.4-192	Turner and Allen 1982
	LA continental shelf 1991	25-1,681	This study
	LA continental shelf 1991	5.6-1,059	Turner unpubl.
	New York Bight	90	Garside and Malone 1978
	Puget Sound	21	Christensen and Packard 1976
	Peru upwelling (euphotic) 1969	141	Packard 1969
	Peru upwelling (euphotic) 1977	34	Setchell and Packard 1978, 1979
	Peru upwelling (>2000 m) 1969	0.014	Packard et al. 1971
	Peru upwelling (>2000 m) 1976	0.025	Garfield and Packard 1979
Open Ocean	Mediterranean	0.137-0.178	Packard et al. 1988
	N. Atlantic	118-152	Riley 1939
	N. Atlantic	3-324	Pomeroy and Johannnes 1966
	N. Pacific (>2000 m)	0.016-0.075	Packard 1985

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Benthic biomass gradients on the Texas-Louisiana shelf

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Abstract

Macrofauna and bacterial biomass were studied in relation to depth, distance from the Mississippi River, primary productivity and concentration of organic carbon in the sediments. Preliminary results suggest that combined benthic biomass was relatively low in the Gulf of Mexico compared to that off New England. Low benthic biomass is thought to be a function of sediment load, unpredictable hypoxic events and trawling pressure, counteracting positive effects of high primary productivity, fine grain size and relatively high concentrations of organic matter in the sediments.

Organic carbon is a source of energy for all marine heterotrophic organisms. A complete understanding of the organic carbon cycling by the benthic community is of utmost importance in determining the carbon storage capacity of sediments and the role of this ecosystem in the global carbon cycle.The objective of this research is to describe the fate of organic carbon once it has reached the sediment community and to explain the role of the benthic fauna in the cycling of carbon, with particular attention to the Texas-Louisiana shelf.

The Texas-Louisiana shelf is a region of the Gulf of Mexico that extends from the Mississippi River Delta to the Rio Grande, covering an area of 2.1×10^5 km^2 (Walsh, 1988). One of the most conspicuous features of this area is the Mississippi River that discharges into the Gulf about 3×10^9 kg yr^{-1} of dissolved and particulate organic carbon (Defenbaugh, 1990). Understanding the fate of organic carbon in this area is necessary in order to evaluate the impact of the Mississippi River discharge on the carbon cycle, particularly in the benthic community of this area. The first step to reaching this objective is to study the biomass distribution of benthic organisms together with the environmental factors that may affect it.

Here we report preliminary results of macrofauna and bacterial biomass and environmental factors that affect them, such as depth, distance from the Mississippi River and primary productivity.

Materials and Methods

The data used in this study come from three cruises between May 1989 to May 1990, in an area on the continental shelf from the Mississippi River to Port Aransas, Tex. (Fig. 1).

A GOMEX box core (Rowe and Boland, 1991) was used to obtain sediment, macrofauna, meiofauna and bacteria samples. Macrofauna was separated using a 250μm mesh size sieve. Further separation was carried out with a dissecting microscope. The wet preserved weight was measured directly. The organic carbon content of the organisms was estimated using the relationship given by Rowe (1983), which assumes that organic carbon corresponds to 4.3 percent of wet preserved weight.

Bacterial abundances were measured through Flourescence Microscopy Enumeration using DAPI (4'-6-diadimidino-2-phenylindole dihydrochloride) to stain the cells (Hobbie Daley and Jarper, 1977; Porter and Feig, 1980). Biomass in g C m^{-2} was calculated using the Williams and Carlucci (1976) assumption that there are 10^{-14}g C per bacteria cell.

The results were then compared with those reported by Rowe and Menzel (1971) for the Campeche Escarpment and Rowe, and Polloni and Horner (1974) for Galveston and eastern Mississippi shelf region. Data from Sanchez and Biggs (1991) were used to compare primary production with benthic biomass.

Results and Discussion

Macrofauna biomass in the Gulf of Mexico ranged from 0.001 g C m^{-2} in the Campeche Escarpment (Rowe and Menzel, 1971) to a high of 1.82 g C m^{-2} in the northwestern shelf. One station located in the Atchafalaya River was totally devoid of macrofauna and only exosqueletal remains of insects (order Hemiptera) were encountered. The highest biomass was found, consistently throughout the three cruises, on the continental shelf off Texas.

Macrofauna biomass tended to decrease gradually with depth (Figures 2 and 3), reaching its lowest on the continental slope and the abyssal plain. This pattern was consistent with that found in other studies (Rowe *et al.*, 1988; Rowe *et al.*, 1990) and it is presumed to be associated with a diminished food supply (Rowe, 1981).

In spite of the great amount of nutrients discharged by the Mississippi River, benthic biomass in the Gulf of Mexico appears to be lower than that reported for the continental shelf of New England (Rowe *et al.*, 1988). They showed that biomass in that area varied from 7 g C m^{-2} at the inner shelf to 0.6 g C m^{-2} on the slope. A similar situation has been presented for the shelf region off the Amazon River. Aller and Aller (1986)

Acknowledgment

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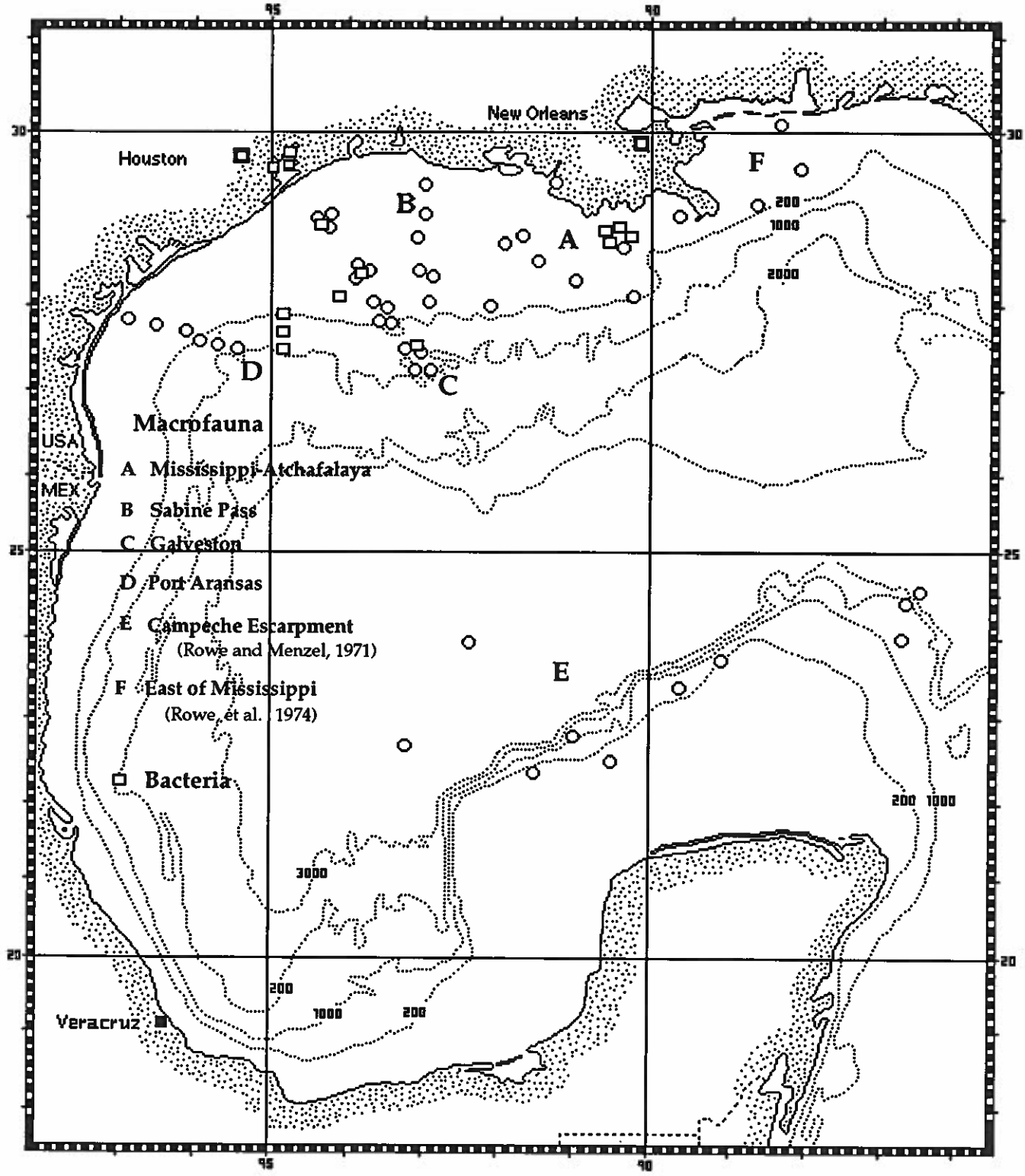

Figure 1. Sampling sites.

found that the abundance and diversity of benthic organisms in that area were very low and attributed that to the tremendous physical disturbance caused by the high concentration of sediments in the river discharge.

The conditions of the benthic community in the Gulf are further complicated by the hypoxic events occurring along the Louisiana inner shelf (Rabbalais, Turner and Weiseman *et al.*, this volume), fishing pressure and the effect of sediments and nutrients discharged by the Atchafalaya River. Factors known to influence the benthic biomass are primary productivity and organic carbon concentration in the sediments. Fig. 4 suggests there is a close relationship between macrofauna bio-

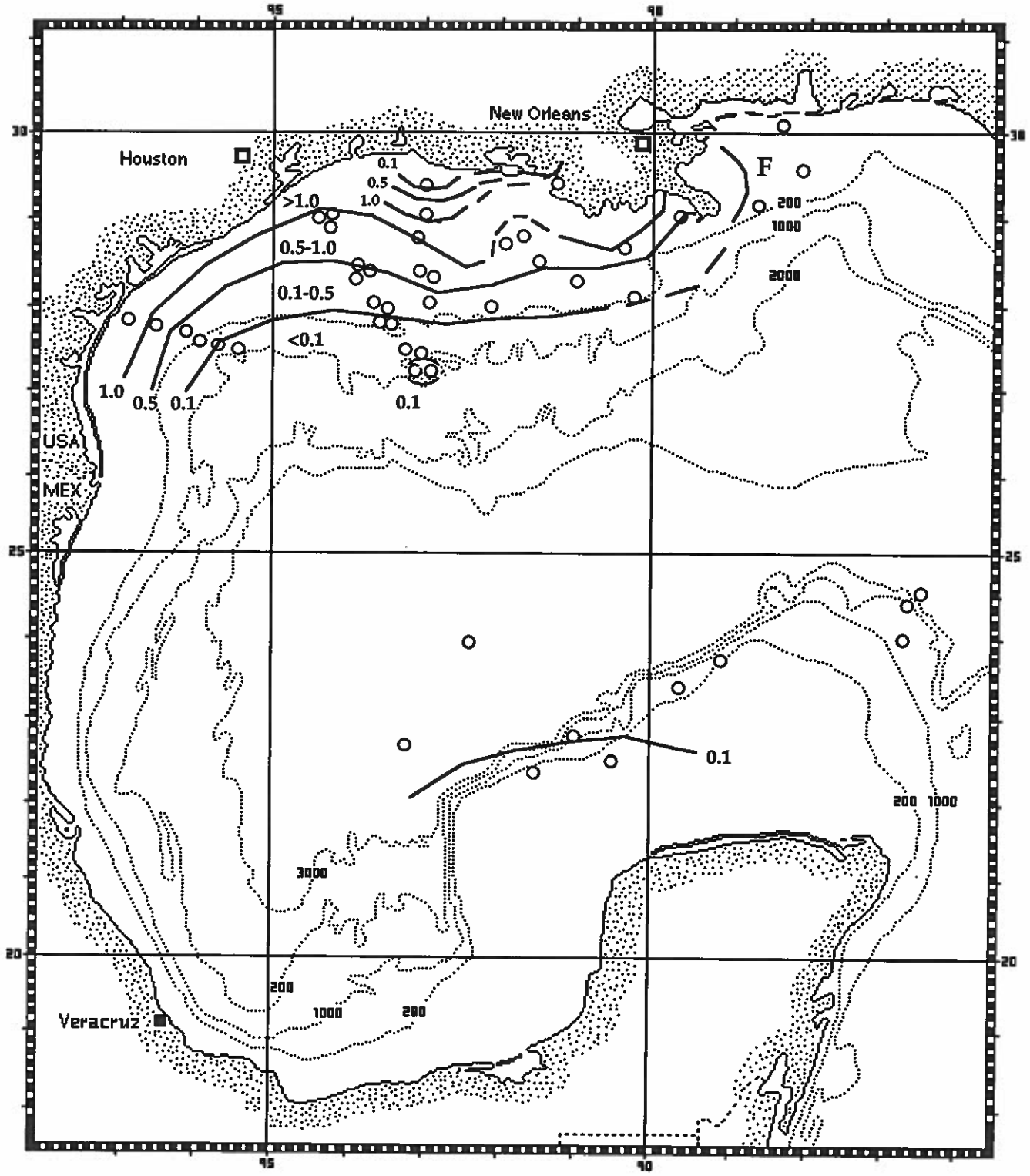

Figure 2. Contours of macrofauna biomass (g C m^{-2}) in the western Gulf of Mexico.

mass and primary productivity.We could document no linear gradient in macrobenthic biomass with distance from the Mississippi River (Fig. 5), in spite of the high organic loading near the river mouth (Blackwelder *et al.*, this volume).

The few stations analyzed for bacteria suggested that biomass in this group was higher in Galveston Bay and on the continental slope than on the continental shelf. More data will be necessary before reaching definite conclusions about the contribution of bacteria to benthic metabolism. The distribution pattern presented in Fig. 6, however, may indicate an export of organic carbon from the shelf to the slope.

In the locations where macrofauna and bacterial

data are both available so far, bacterial biomass was higher than macrofauna biomass (Fig. 7). In site A this is probably attributable to hypoxic events. Harper *et al.*, (this volume) reported extensive bacterial mats, and obvious stress and mortality among the macrobenthic populations due to the low concentration of oxygen in the water just above the sediments. High bacteria biomass would also support the idea of a high mineralization rate in the Texas-Louisiana shelf. Several authors, working in diverse deep-sea environments, have demonstrated the importance of bacteria in the remineralization of sedimentary organic carbon. Alongi (1990) showed that bacteria remineralized an average 40 percent of the detrital carbon in Solomon and Coral Seas. Rowe *et al.* (in press) suggested that of the total benthic biomass in the Hatteras abyssal plain, bacteria accounted for 81 percent of the total.

The results presented here are preliminary and further research is needed in bacteria and meiofauna populations, sediment structure, particle flux and organic carbon concentration in the sediments. Nevertheless, these results show that benthic biomass in the Texas-Louisiana shelf is relatively low in spite of high primary production. The causes for low biomass are probably high sediment

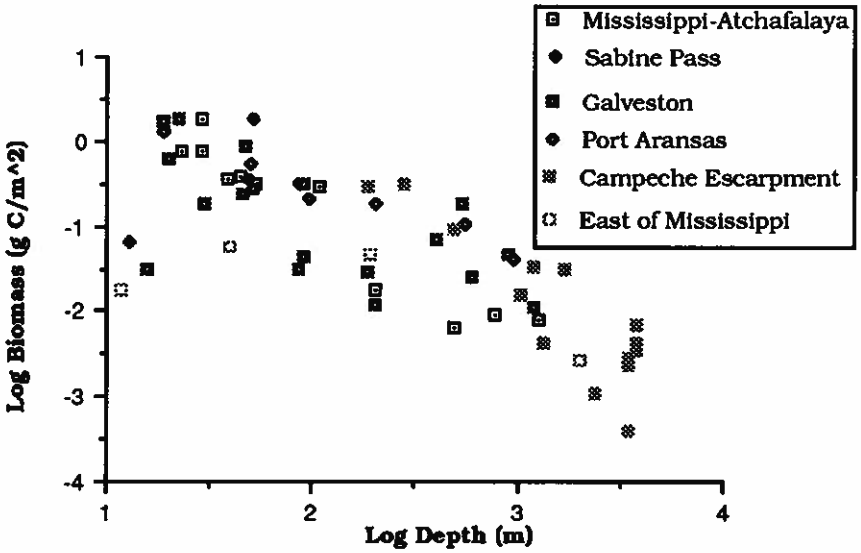

Figure 3. Macrofauna Biomass (g C m^{-2}) in the Gulf of Mexico vs. Log water depth in areas corresponding to those identified in Fig. 1.

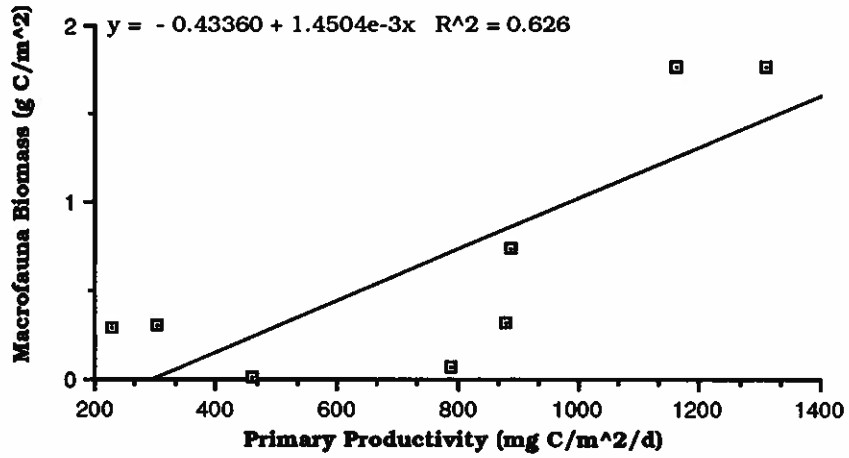

Figure 5. Macrofauna Biomass (g C m^{-2}) vs. Distance from the Mississippi river.

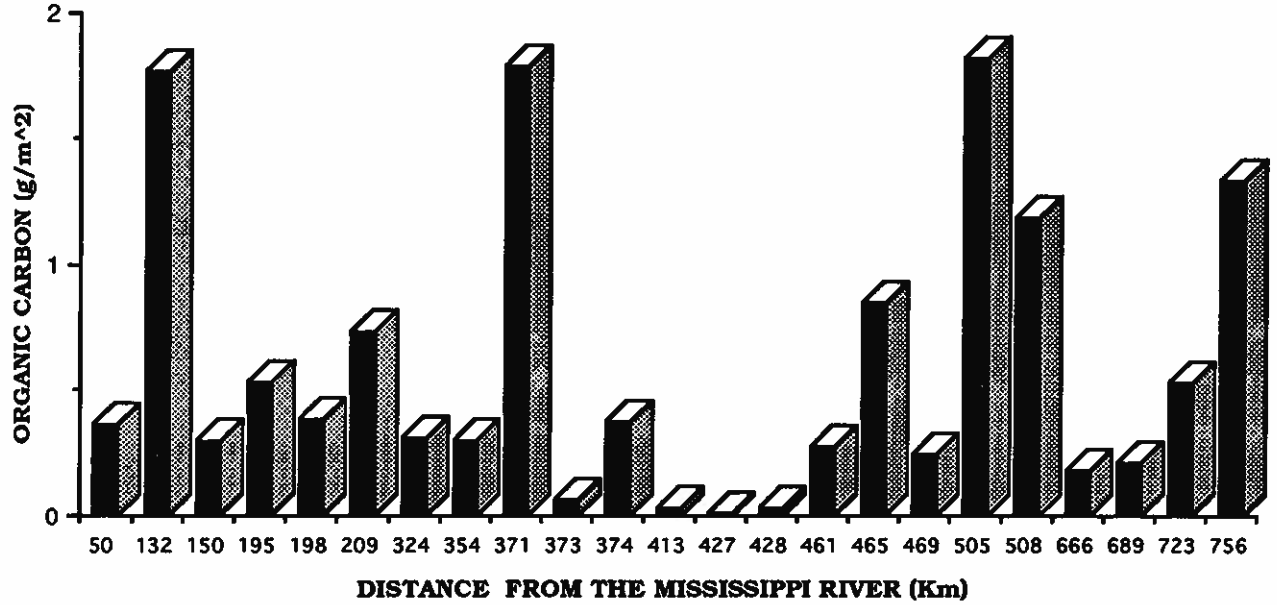

Figure 4. Log macrofauna biomass (g C m^{-2}) vs. Primary Productivity (mg C m^{-2} hr^{-1}) on the Texas-Louisiana shelf. (Productivity data taken from Sanchez and Biggs, 1991)

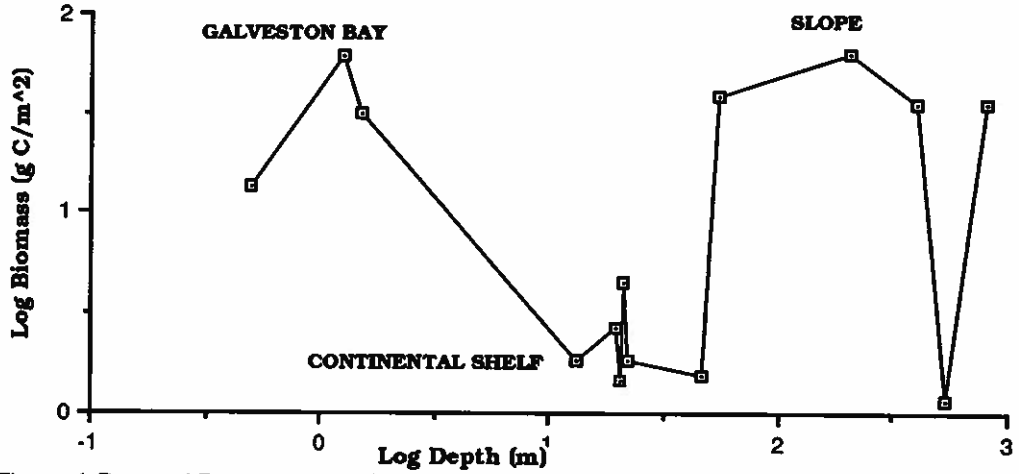

Figure 6. Bacterial Biomass (g C m^{-2}) vs. Water depth (m).

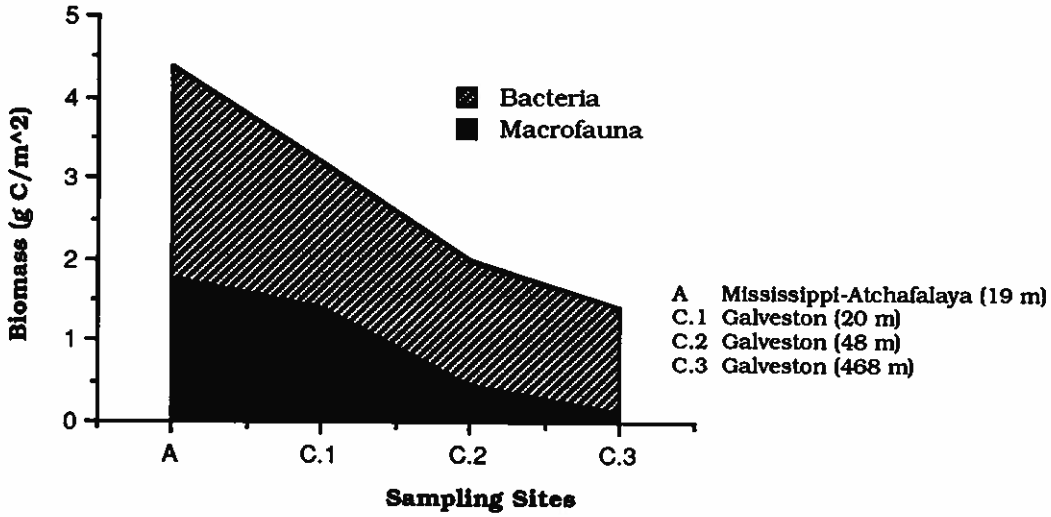

Figure 7. Macrofaunal and Bacterial Biomass (g C m^{-2}) vs. Sampling sites.

concentration discharged by the Mississippi-Atchafalaya River complex and intermittent hypoxia caused by stratification and high respiration rates.

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Studies of benthic biota in areas affected by moderate and severe hypoxia

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Abstract

Studies of macrobenthic assemblages impacted by hypoxia were conducted during monthly cruises from February through October in 1990 and in one-week cruises in the summers of 1990 and 1991. Preliminary results from Station C6A indicated healthy benthic communities in April and May with high species richness and abundance of individuals, a drop in these values in June, and drastic reductions in the fauna in July, with some recovery of the macroinfauna in September and October. Videotapes of demersal and benthic communities documented differences in abundance and composition of larger, motile organisms in varying levels of bottom water oxygen, widespread bacterial mats, dead and decaying benthic organisms, and behavioral adaptations of benthic organisms to oxygen stress.

The Louisiana continental shelf is the location of the largest, most severe, and most persistent zone of hypoxia in the United States coastal waters. Oxygen-depleted bottom waters may cover areas as large as 8,500 km^2 of the Louisiana (and sometimes Texas) shelf in mid-summer. Equal to or larger than similar phenomena off the northeastern coast of the U.S. (Garside and Malone, 1978; Swanson and Sindermann, 1979; Falkowski *et al.*, 1980; Officer *et al.*, 1984), these hypoxic zones occur at the terminus of the largest river in North America and amidst the nation's richest and most extensive fishing grounds. The area impacted by, and duration of, hypoxia on the Louisiana shelf is of considerable concern since Louisiana fisheries landings are 28 percent of the U.S. total. Fish, shrimp and benthic animal densities are depressed in these hypoxic zones (Harper *et al.*, 1981, 1991; Pavela *et al.*, 1983; Leming and Stuntz, 1984; Gaston, 1985; Renaud, 1986; Boesch and Rabalais, 1991).

We have investigated the areal extent, frequency of occurrence, and effects of hypoxic events in the northern Gulf of Mexico since 1979 (Harper *et al.*, 1981, 1991; Rabalais *et al.*, 1991; Boesch and Rabalais, 1991). We have shown that large-scale hypoxia occurs virtually every year, benthic macroinfaunal populations are drastically reduced in species richness and abundance of individuals, but that recovery from this defaunation occurs rapidly. High percentage of juveniles in the population and reduced biomass indicate that the populations are maintained in an early successional state by the annually recurring hypoxia. Significant discoveries were made during the hypoxic periods of 1990 and 1991, however, that have increased our understanding of the effects of hypoxia on the benthos.

Methods

Area of study — Benthic macroinfaunal samples were collected from several stations on the southeastern Louisiana shelf in 1990 and 1991, but analyses presented here are limited to Station C6A in 20 m water depth for 1990 (Fig. 1). Videotaping by the NOAA/NURC SuperPhantom ROV (remotely operative vehicle) or direct observations by divers were concentrated on many of the stations shown in Fig. 1.

Sampling and analysis — Hydrographic data were collected with a Sea-Bird CTD unit, a Sea-Cat CTD unit mounted on the ROV, a Hydrolab Surveyor II, and water samples collected by either diver, rosette-mounted 5-l Niskin bottles, or singly deployed 5-l Niskin bottles. Factory calibration and/or laboratory calibration of the various CTD units were corroborated with Winkler titrations (Parsons *et al.*, 1984).

Benthic macroinfauna were collected from 0.1-m^2 Ekman-type box corer and subsampled with a 0.02-m^2 Ekman grab or a 7.6-cm diameter core tube. Standard macroinfaunal analysis included sieving over a 0.5-mm mesh screen, preservation in 10 percent buffered formalin stained with Rose Bengal, and subsequent enumeration to lowest possible taxon in the labora-

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We thank the many research assistants who have helped in the collection and identification of benthic organisms, the captains and crews of the R/V *ACADIANA* and R/V *PELICAN*, and personnel of the NOAA National Undersea Research Center at the University of North Carolina at Wilmington. Support for our research has been provided by the Louisiana Board of Regents Education Quality Support Fund Grant No. LEQSF(1987-90)-RD-A-15, Minerals Management Service University Initiative Grant No. 17, NOAA NECOP Grant NA90AA-D-SG691 Award MAR24, the Louisiana Sea Grant College Program Grant R/HPX-1-PD, NOAA National Undersea Research Center Grant Nos. 90-OR-SCU/ROV-RABALAIS and 91-OR-SCU/ROV-RABALAIS, Texas Institute of Oceanography, Louisiana Universities Marine Consortium, and Texas A&M University at Galveston.

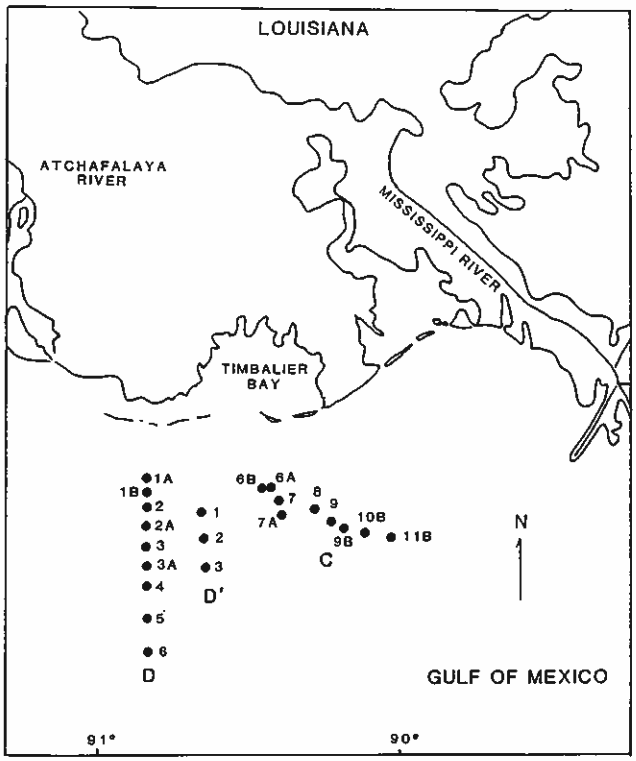

Figure 1. Map of study area on the southeastern Louisiana continental shelf showing Station C6A and the area of intensive sampling during mid-summer NURC cruises of 1990 and 1991.

tory. Random specimens of seemingly dead or moribund benthic fauna were collected, placed in containers of ambient water, and returned to the ship for examination after reoxygenation of the ambient water. Experiments were conducted in 1991 to document the percentage of living and dead benthic macroinfauna compared to the results obtained from standard benthic techniques. Sediment cores (8.2-cm diameter) were taken and sieved underwater through 0.5-mm mesh screen, placed in containers of ambient water, and returned to the ship for examination after reaeration. All living and dead organisms were identified and counted before standard benthic sample preservation.

To determine the distribution of various groups of benthic and demersal organisms, we conducted surveys across a range of bottom-water oxygen concentrations with shipboard CTD units and the ROV coupled with its Sea-Cat CTD unit and videotaping capabilities. The videotapes documented the condition of the benthic habitat with respect to presence/absence of a nepheloid layer, presence/absence of bacterial mats, and absence/presence and abundance of larger motile organisms or macroepifauna.

Results described below are preliminary in all instances, and will be refined with completion of replicate samples, statistical analyses, and quantification of videotape results.

Results

Benthic macroinfaunal communities — During 1990, there were extended periods from mid-May through

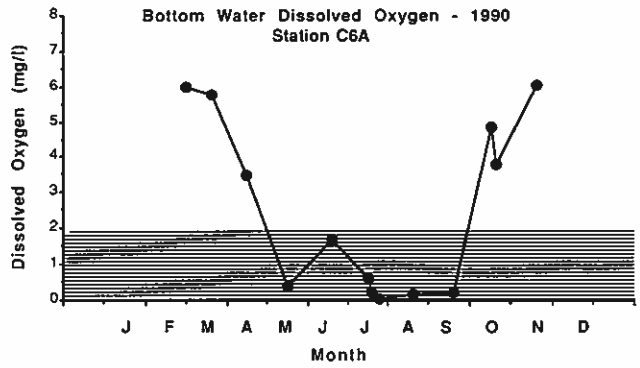

Figure 2. Concentration of near-bottom water dissolved oxygen at Station C6A during monthly and mid-July cruises of 1990.

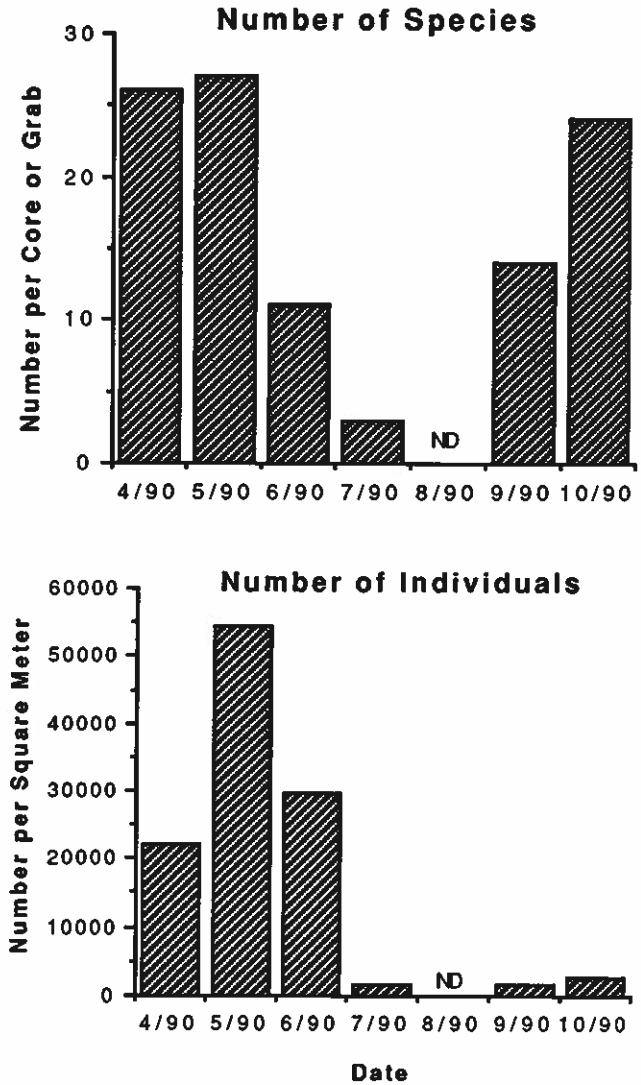

Figure 3. Benthic community parameters of either 3-cm core or 0.02-m² Ekman grabs at Station C6A in 1990.

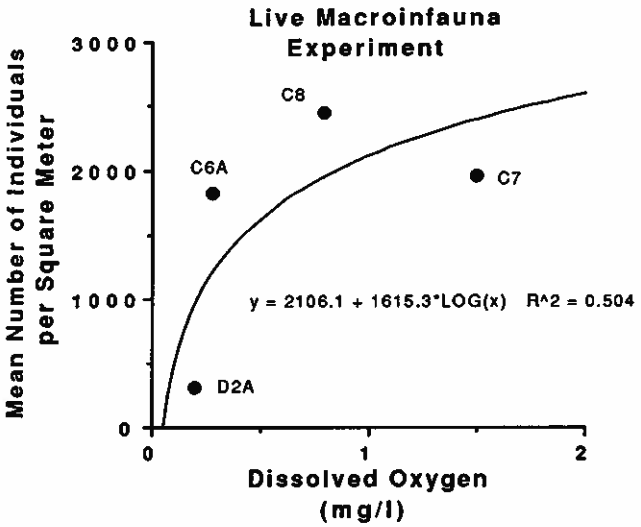

Figure 4. Number of live macrofauna per square meter for representative stations according to the dissolved oxygen content of the overlying water mass for 1991.

the end of September when oxygen levels decreased below 2 mg/l and extended periods from mid-June through mid-August when oxygen levels approached 0 mg/l. Fig. 2 depicts the oxygen concentration in near-bottom waters during cruises when benthic macroinfauna samples were collected (see Rabalais *et al.*, this volume for continuous oxygen concentration recordings). The number of species per core or grab sample at C6A averaged 26 to 27 for April and May 1990 (Fig. 3), dropped to 11 for June and 3 in July. The number of individuals per square meter (converted from either 3-cm core tubes or 0.02-m^2 Ekman grabs) was high and typical of northern Gulf of Mexico continental shelf benthic communities in April through June. Abundance of macroinfauna in September and October was somewhat higher than in the July samples but not substantially. Notable differences in the September/October samples and the April/May samples, however, were that the community was composed primarily of juveniles in April/May and primarily of adults in September/October. This indicates early successional stage recruiting individuals in the spring and a more mature community in the fall with individuals that had survived the period of hypoxia/anoxia.

Live versus dead experiment — Small living infaunal organisms were present in all core samples sieved *in situ* and returned to the surface in ambient water. At the most severely impacted station (D2A in 1991) a total of 4 polychaetes (2 *Magelona* sp. H, and 1 each of *Paraprionospio pinnata* and *Sigambra tentaculata*) were found alive in sediments that smelled of hydrogen sulfide; nemertean fragments were also found. These findings suggest that the "recolonization" of presumed defaunated benthic habitats may be due, in part, to organisms which survive the hypoxic event. Limited and preliminary data suggest that the curve described by infaunal abundance versus dissolved oxygen is nearly logarithmic, with the steep part of the curve occurring at very low oxygen conditions (Fig. 4). One sample from D2A also contained a dead sipunculid worm, the only dead, but intact, infaunal organism found in any of the small core samples; this sipunculid fixed and stained as a living organism would. Similar fixation of living and dead organisms could affect the interpretation of samples collected according to standard benthic techniques.

Condition of benthic habitats — ROV images, diver observations, and photography have documented that some larger invertebrates display very obvious signs of stress in hypoxic areas. In 1989, we observed several hermit crabs clustered atop shells lying on the bottom, gastropod mollusks moving about the surface with their siphons extended straight up into the water column, and ophiuroids out of their burrows with the disk elevated by standing on the proximal portion of their arms. In 1990, we again observed many of the same behaviors, as well as numerous young starfish on top of burrow mounds, and moribund gastropods, mud crabs and polychaetes.

Stress behavior was not as prevalent in 1991 as in 1990. The bottom at D2A was covered with an almost continuous sheet of bacterial mat, beneath which was black silty sediment that smelled of hydrogen sulfide when returned to the surface. Hydrogen sulfide was not detected in the overlying water. No organisms were seen at D2A. The other stations sampled (C6A, C6B, C7 and C8) had patches of bacterial mats of various sizes on the sediments, and most had at least a few large infaunal organisms lying on the surface of the sediments. Cerianthid anemones were very abundant at C8. Many of these were partly, or completely, extended from their tubes and were lying on the substrate; some were decomposing and many were flaccid. Station C7 had many immobile worms and clumps of decaying *Sargassum* sp. seaweed lying on the bottom. One small living stomatopod crustacean was observed in the entrance to its burrow. No demersal fish or living nektonic crustaceans were observed on the bottom at any of the above stations.

Photographs made in 1990 of "dead" organisms lying on the bottom revealed that many of these animals, which appeared colorless to the divers, contained pigments expected in living organisms. In particular, polychaetous annelids were found to have opalescent integuments, bright red coloration or red blood in the dorsal vessel. In 1991, several polychaetes, one hemichordate, one ophiuroid and several cerianthid anemones that appeared lifeless on the bottom became active when they were brought to the surface in sealed containers of ambient water and then placed in oxygenated water.

Discussion

While the number of species and abundance of individuals is dramatically reduced in hypoxic/anoxic benthic habitats on the Louisiana continental shelf, we have documented that some individuals of macroinfauna survive these conditions. Researchers

have noted rapid recolonization of infauna in benthic environments impacted by hypoxia/anoxia. Because many individuals collected were young or juveniles, recruitment of planktonic larvae has been suggested as a principal means of repopulating an affected bottom, although immigration of adults and reproduction of survivors have also been suggested (Harper *et al.*, 1981; Gaston, 1985; Gaston *et al.*, 1985). Our investigation indicates that even in the presence of hydrogen sulfide, the sediments may not be completely defaunated and that survivors, especially opportunists, have the potential to reproduce and provide recruits as soon as hypoxia abates.

Infaunal organisms have previously been collected from severely impacted bottoms, including areas where hydrogen sulfide was in the overlying water (Harper *et al.*, 1981, 1991; Boesch and Rabalais, 1991), and it has been questioned whether these benthos were alive or dead at the time of collection. Our research shows that at least some infaunal organisms are present even in apparently anoxic sediments. The five individuals collected at Station D2A in 1991 extrapolates to numbers per square meter obtained under similar conditions in May and June off Freeport, Tex., in 1979 (Harper, unpubl. data). Our research also demonstrates that infaunal abundances obtained in low oxygen concentrations are probably accurate, unless sediments are anoxic. In the latter instance, counts may be erroneous because of dead, undecomposed organisms being fixed, preserved and counted as living members of the benthic assemblage.

The combination of remote instrumentation, ROV and diver-observer-collector has proven a great value in rapidly assessing occurrences and effects of hypoxia on the Louisiana continental shelf. Stress reactions in larger motile invertebrates were reported by Jørgensen (1980) in Denmark and photodocumented by Stachowitsch (1984) in the Gulf of Trieste. Our research has confirmed this behavior in the northern Gulf of Mexico. It is evident that dissolved oxygen concentrations below 2.0 but not yet 0.0 ppm produce a rather consistent reaction in organisms capable of moving, i.e., an attempt to get at least part of their body higher into the water column. Our research has also confirmed the observation of Jørgensen (1980) that many of the organisms seen lying on the bottom in hypoxic areas are moribund, not dead. If these organisms survive, they probably re-enter the sediment and may partially account for the apparent recolonizaton of sediments when hypoxia abates. The presence of large, soft-bodied invertebrates on the bottom also indicates the exclusion of large bottom-feeding predators.

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