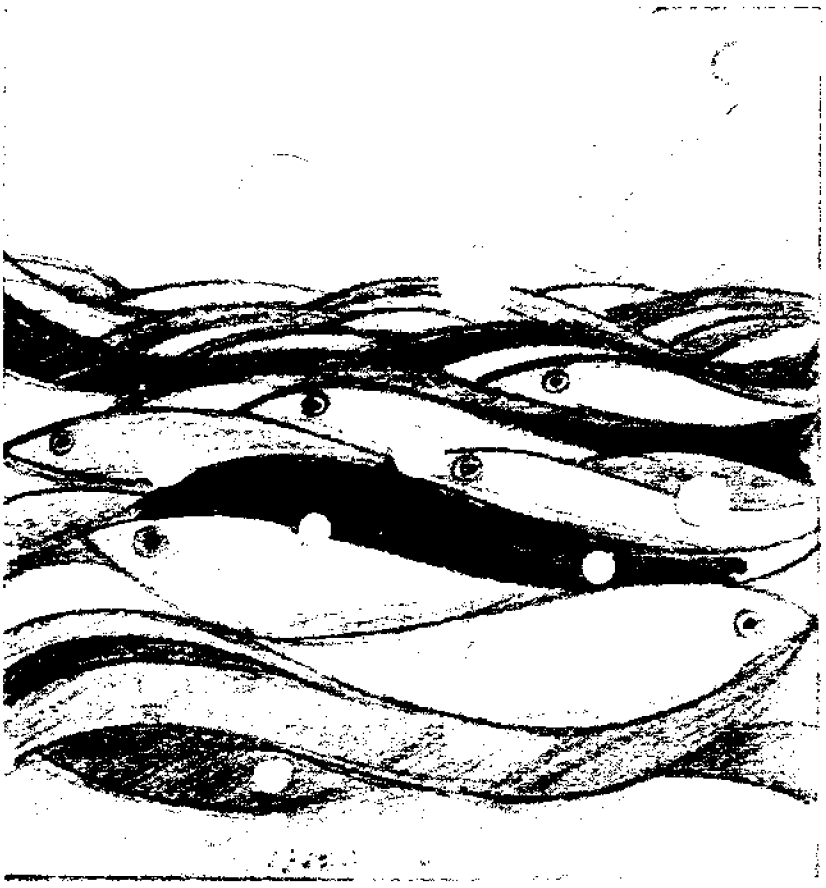
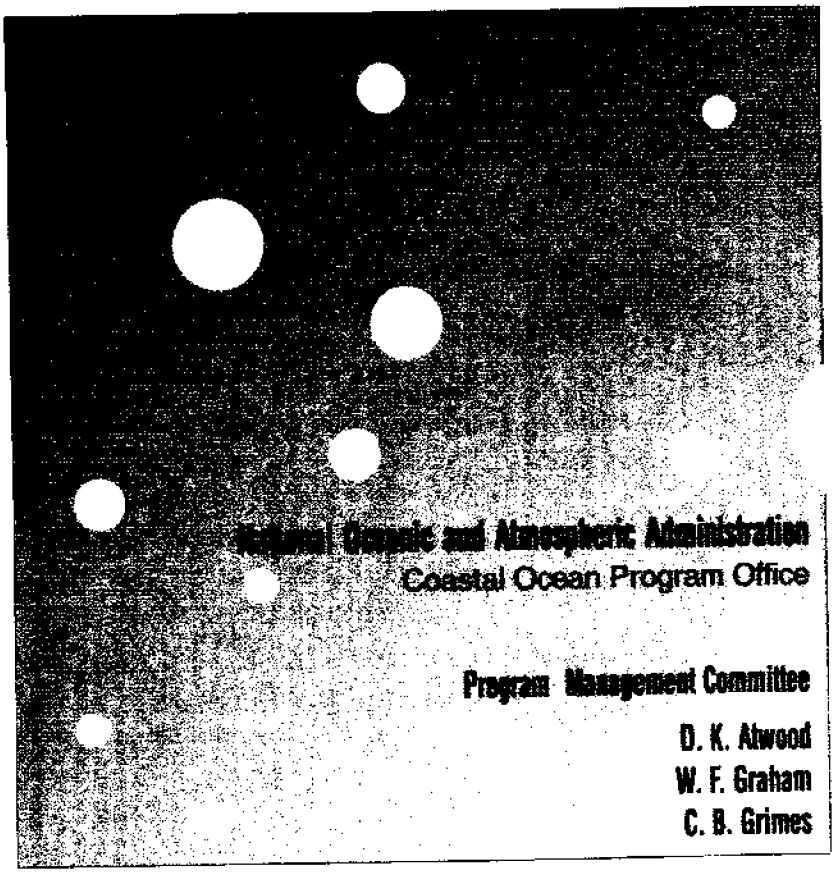
Proceedings of Synthesis Workshop

Nutrient-Enhanced Coastal Ocean Productivity



National Oceanic and Atmospheric Administration
Coastal Ocean Program Office

Nutrient-Enhanced Coastal Ocean Productivity



Produced by **Louisiana Sea Grant College Program**
Louisiana State University Baton Rouge, Louisiana 70803

1995

Contents

INTRODUCTION AND SUMMARY

The NOAA Nutrient Enhanced Coastal Ocean Productivity (NECOP) program started in 1990. It is sponsored, in part, by the NOAA Coastal Ocean Program in cooperation with the NOAA National Sea Grant Program and NOAA's Environmental Research Labs, i.e., the Atlantic Oceanographic and Meteorological Laboratory in Miami, FL, and the Great Lakes Environmental Laboratory in Ann Arbor, MI. The program is focused on the outflows of the Mississippi River and its tributary, the Atchafalaya River, and the impact of that outflow on the Northern Gulf of Mexico coastal waters. Given that the predominant coastal flow near the Mississippi Delta is to the west most of the NECOP effort has been directed to the area west of the outflow, and particularly on the Louisiana Inner Shelf. Monitoring since the mid 1980's has revealed that summer hypoxia develops on an annual basis over much of this shelf. Much of the NECOP investigation has dealt with this hypoxia, the extent and timing of its occurence, causal factors, impacts, and history through retrospective analysis.

On April 26 and 27, 1994 NECOP Principal Investigators, and Data and Program Managers met in Baton Rouge, LA to develop an initial synthesis of the program results and to make plans for a program final synthesis. This document constitutes a report of that meeting and, in itself, is one of the synthesis products from the NECOP program. In the following summary all references are to papers in this volume.

Over the last several decades 80% of all monthly-average Mississippi discharge rates have been within +10% of the long term (last 40 years) cycle (Dinnel, et al) with most outliers being due to phase shifts in the annual cycle. These flows are apt to be maximal in spring (April; ~22,000m3/s +10,000m3/s) and minimal in late summer (September; ~7,000m3/s +2,000m3/s). In 1992 the spring flow was below normal and in 1993 the flow was above normal all year with the highest flows in May. These flows bring an exceptionally high nutrient load into the Northern Gulf of Mexico, which has been increasing (by 2.5 times) during the last several decades. Typical nitrate concentrations at the outflow are 60 to 120μm. However, as the result of heavy flooding in the drainage basin in 1993, July 1993 values reached 150 to 200μm. Lopez-Veneroni et al report that this input accounts for about 30-70% of the N on the shelf with less than 10% of that being denitrified. This nutrient load stimulates coastal productivity, with maximal pigment concentrations several kilometers from the outflow where adequate light is available. Lohrenz et al have studied the optical properties of the outflow plume and adjacent waters measuring, among other parameters, attenuation spectra. A spectral attenuation model was able to reproduce these measured spectra very well over a range of one order of magnitude. Absorption and scattering were dominated by dissolved organic carbon and suspended particulate matter. Lohrenz, et al also used a photosynthesis-irradiance (P-I) model to estimate areal distributions of column-integrated primary productivity with some success, but, variability in ecological parameters, e.g., growth rate and cell size contributed to variations in pigment-specific photosynthesis-irradiance parameters. Dagg and Ortner report that the primary fate of phytoplankton production on this river dominated shelf is to be grazed by zooplankton. However, Dortch, et al note that while phosphate and nitrate inputs have increased, silicate inputs have declined with a potential for silicate limitation and alteration of the phytoplankton community. Such limitation was, in fact, pervasive in one spring cruise.

Rabalais, et al report on the distribution and characteristics of hypoxia resulting from the above described loading. Clear temporal and spatial linkages were evident between hypoxia and fresh water (nutrient) inputs. Given the magnitude of these inputs in 1993 summer hypoxia was maximal that year. Consequences of shifts in nutrient balances over the past several decades include changes in silica-based phytoplankton response and trophic structure, in phytoplankton community structure, in sediment carbon accumulation, and in bottom water oxygen stress. Rowe, et al reveal that in hypoxic areas the largest biomass is found in the bacterial component. Nelsen, et al report results from surface and cored sediments that show shifts in foraminifera assemblages and mineralogy (glauconite) indicating that this hypoxia became severe coincident with increases in river loading of nutrients due to increasing use of fertilizers in the drainage basin. Bierman, et al report on a sensitivity analysis of a deterministic, mass balance model for nutrients, phytoplankton, and dissolved oxygen. This analysis showed that in large part intra segmental processes were more dominant than inter segmental ones. In each segment bottom dissolved oxygen is very sensitive to changes in sediment oxygen demand, but, water column oxygen demand dominates.

CONTINUOUS UNDERWAY MEASUREMENT OF MICROBIAL ENZYME ACTIVITIES IN SURFACE WATERS OF THE MISSISSIPPI RIVER PLUME AND THE LOUISIANA SHELF

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Abstract

Cell-surface enzymes are crucial to the bacterial utilization of polymeric carbon and nitrogen sources, as well as of organic phosphates. Such enzymes are also important to phytoplankton, but bacteria appear to dominate most of cell-surface enzyme activities measured in the field with the possible exception of alkaline phosphatase. Bacterial ectoenzyme activities have been shown to be good indicators of the state of bacterial carbon, nitrogen, or phosphorus nutrition, depending on the enzyme assayed. However, like most other biochemical and molecular measurements, cell- surface enzyme activities have been limited to discreet water samples. We have recently developed a continuous underway method for measuring microbial enzyme activities using high-sensitivity fluorescent substrates. This method has been successfully applied to alkaline phosphatase measurements and peptidase measurements in the surface waters of the Mississippi River Plume and the Louisiana shelf. The alkaline phosphatase measurements demonstrate a large area of phosphate-deficient surface water in the plume region. Furthermore, since these enzyme activities can be measured continuously, we can achieve spatial and temporal coverage nearly comparable to physical oceanographic measurements.

Introduction

Since the development of bacterial growth rate measurement methods in the late 1970s and early 1980s, the importance of planktonic bacteria in carbon cycling in aquatic ecosystems has become clear. Bacteria are now thought to utilize about 50% of the carbon fixed by primary production in many pelagic ecosystems (Cole et al. 1988; Ducklow and Carlson 1992) and metabolize a large fraction of the carbon in continental shelf environments. Rather than exporting carbon offshore, as has been proposed (Walsh et al. 1981), continental shelf environments may be major sites of bacterial carbon degradation (Rowe et al. 1988).

Despite all the progress in bacteriological methods and concepts in the last fifteen years, there are still no methods for measuring bacterial biomass or growth which can be employed either continuously underway aboard ship or by remote sensing. This contrasts strongly with phytoplankton methods such as underway in vivo fluorescence measurements of chlorophyll (Lorenzen 1966), and remote sensing of chlorophyll (and eventually primary production) from satellites (Lewis 1992). Furthermore, presently available bacterial growth and metabolic measurements usually involve isotopes and require tedious processing.

Cell-surface (or extracellular enzymes) in aquatic microorganisms, especially phosphatases, have been studied for several decades. Though much of the work has been in freshwater, marine studies of phosphatases date back at least twenty years (Perry 1972). Recently there has been greatly increased interest in cell-surface enzymes, sometimes termed ectoenzymes (Chrost 1990). In a recent review, Chrost (1990) lists 18 different microbial ectoenzymes whose activities have been measured in natural waters and sediments. This list includes, in addition to phosphatases, enzymes which hydrolyze polymeric carbohydrates or proteins, such as glucosidases and peptidases. The activity of these latter enzymes, in particular, is dominated by the bacterial fraction in the plankton. Many ectoenzyme assays are done with fluorescent substrates, so that they avoid the handling problems associated with radioisotopes. The fluorescence method has been especially popular since the methylumbelliferyl substrates were introduced (Hoppe 1983), because so many different enzyme substrates are available. However, at least until the present, ecotoenzyme assays have been done only on discrete samples.

One of the best-studied cell-surface enzymes in aquatic ecosystems is alkaline phosphatase. Due to the potential for phosphate-limitation of phytoplankton and bacterial growth, mechanisms which increase the availability of phosphorus for uptake and incorporation into biomass may increase net primary and bacterial secondary production. Cell membranes of microorganisms are largely impermeable to phosphorylated organic compounds (Lugtenberg 1987) such as nucleotides. Alkaline phosphatase (AP) hydrolyzes orthophosphate (Pi) from wide variety of dissolved organic phosphates, thus making it available for uptake. The major substrates of AP are

phosphate-esters like sugar-phosphates, but also phospho-anhydrides such as nucleotides. AP activity has been measured in field samples by sensitive fluorometric techniques since the early 1970s (Perry 1972), and the extensive study devoted to its role in P-cycling has been reviewed (Cembella et al. 1984). AP activity is Pi-inhibited and AP synthesis is Pi-repressed, so AP activity is therefore usually low in waters with measurable Pi. AP activity is most often measured in low-P lakes, estuaries, and oceanic central gyres, and it is often interpreted as a sign of P limitation (Perry 1972). Most older studies attributed AP activity in natural waters to phytoplankton, though more recent studies have shown that a substantial portion of the AP activity is bacterial (Chrost 1991). Previous studies have shown that alkaline phosphatase activity is high in the Mississippi River Plume region (Ammerman 1992).

Materials and Methods

The impetus for developing this continuous assay has come from extensive studies of alkaline phosphatase activity, including "manual mapping" of surface activity in the Mississippi Plume region of the Gulf of Mexico and further downstream (Fig. 1). This figure was generated by measuring alkaline phosphatase activity on over 85 discrete surface samples during a one-week cruise in May of 1992. Since activity was high, incubations were could be kept as short as five minutes. Figure 1 is an unusually detailed surface map of ectoenzyme activity. The highest alkaline phosphatase activity, or shortest turnover time, was found near the Mississippi delta. The activity then decreased towards the west, with an exception near the Atchafalaya outflow. This enzyme data suggests that the plankton near the delta were phosphate-deficient because of the high nitrogen to phosphorus ratio in the inflowing river water. This conclusion is supported by radiotracer studies of phosphate uptake and nutrient concentration measurements (Ammerman 1992).

The system we have developed for continuous underway measurement of ectoenzyme activity is diagrammed in Fig. 2. A autoanalyzer-type peristaltic pump is connected to the ship's sea chest or flow-through system, such as is used for a SAIL system or in vivo fluorescence measurements. On the R/V Longhorn the intake was at approximately two meters of depth. The fluorescent substrate, 4-methylumbelliferyl phosphate (MUF-P; Sigma Chemical Co., St. Louis), which becomes fluorescent after enzyme hydrolysis, was continuously added and the sample was incubated in a loop immersed in a temperature-controlled water bath. The length of incubation with substrate was varied by the length of the loop and can vary from a few minutes to probably at least an hour, depending on the enzyme

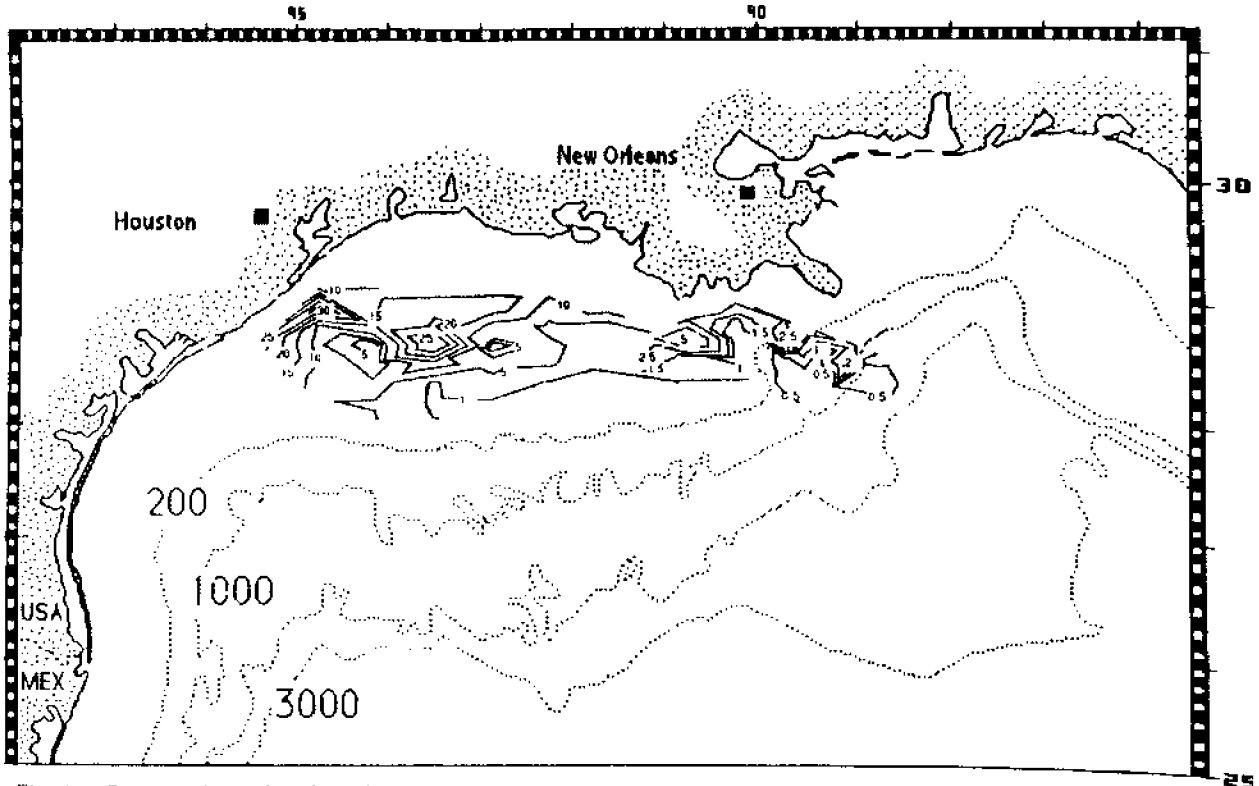

Fig. 1. Contour chart of surface alkaline phosphatase activity in the Gulf of Mexico during May 1992, showing turnover times in hours. Activity was measured manually at 85 stations, using 100 nM 4-methylumbelliferyl phosphate as the substrate. Depth contours in meters are also shown.

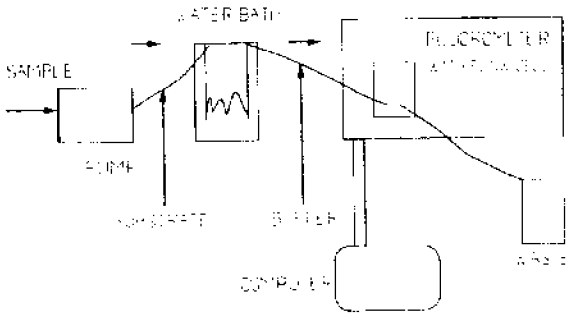

Fig. 2. Schematic diagram of continuous-flow system for measuring microbial cell-surface enzyme activities. Note the separate injection points for substrate and buffer. The total flow rate was 2 to 3 ml per min and the volume of the flow cell was 0.75 ml. The length of the incubation time in the water bath and the excitation and emission wavelengths for the fluorometer were specific for the enzyme being assayed.

activity. Obviously the incubation time or length of the loop must be predetermined and is specific for each enzyme in each environment. In the phosphate-deficient lake where we have made initial tests, a five minute incubation period was sufficient. This incubation time was also used in most of the Mississippi Plume sampling. However for peptidase measurements and phosphatase measurements along the western Louisiana shelf, a fourteen minute incubation was necessary. Before entering the flow cell in the fluorometer, 50 mM borate buffer was mixed with the sample in order to raise the pH above 10. This was necessary to achieve the maximum fluorescence of the methylumbelliferyl substrates (Chrost and Krambeck 1986). Finally the fluorescence was measured (excitation wavelength 360, emission wavelength 440), logged in the computer, and the sample discarded. The measurement parameters of the fluorometer were also controlled by the computer. The total flow rate was 2 to 3 ml per min and the volume of the flow cell was 0.75 ml. For details of reagents and preparation see the description of the manual alkaline phosphatase method described in Ammerman (1993).

Manual enzyme assays were used to measure initial activities so that the continuous method could be optimized and also to compare with the continuous assay. Killed controls and turbidity blanks were run routinely. Activity was demonstrated by an increase in fluorescence in live samples incubated with substrate over samples that had been boiled and cooled and then incubated with substrate. Turbidity blanks, which included live samples plus buffer but no substrate, were lower than the killed controls.

The major focus of this study was the continuous assay of alkaline phosphatase using the substrate 4-methylumbelliferyl phosphate, though we also measured continuous peptidase activity with this system, with l-leucine 7-amido-4-methyl coumarin (MCA-leucine; Sigma Chemical Co., St. Louis) as the substrate (excitation wavelength 380, emission wavelength 440). Since there are many methylumbelliferyl or closely-related fluorescent substrates available for cell-surface enzymes, many different enzymes could be measured continuously using this system.

Results

This continuous-flow system has been used many times in the laboratory to measure alkaline phosphatase activity on lake water samples and has also been taken out on Lake Travis, an oligotrophic to mesotrophic, phosphate-deficient lake west of Austin, Texas (data not shown). We employed this system on a cruise on the R/V Longhorn in July 1993 in the Mississippi River Plume area. We concentrated on measurements of alkaline phosphatase activity but also measured peptidase activity.

Locations where automated enzyme measurements were made covered roughly the same area as the May 1992 manual map (Fig. 1). Locations of specific runs of the continuous flow system shown or referred to in the results are shown in Fig. 3, with the direction of the ship's progress indicated by the arrows. All but section 3 were on the shelf, within the 200 m contour. Section 3, in contrast, was over the slope, crossing the 1000 m contour. More runs of this system completed during the July 1993 cruise are still being analyzed.

The annotated continuous alkaline phosphatase data record from location 2 (Fig. 3) is shown in Fig. 4 as an example of the data output from the continuous-flow system. This figure shows the data record from Stations 54 to 56. At the left side (Station 54) was a killed control (plus 1 uM MUF-P substrate and buffer) with a fluorescence value of 48. This was followed by a sample run with fluorescence values between about 80 and 95. The initial spike was due to the switch from killed control to sample, but some of the smaller spikes may be real variation in activity. At present we do not have enough enzyme data or ancillary information to distinguish such spikes from noise. This sample run is followed by another killed control which stabilized at 48 fluorescence units, just as the previous one. (Some records, in contrast, show an increase in

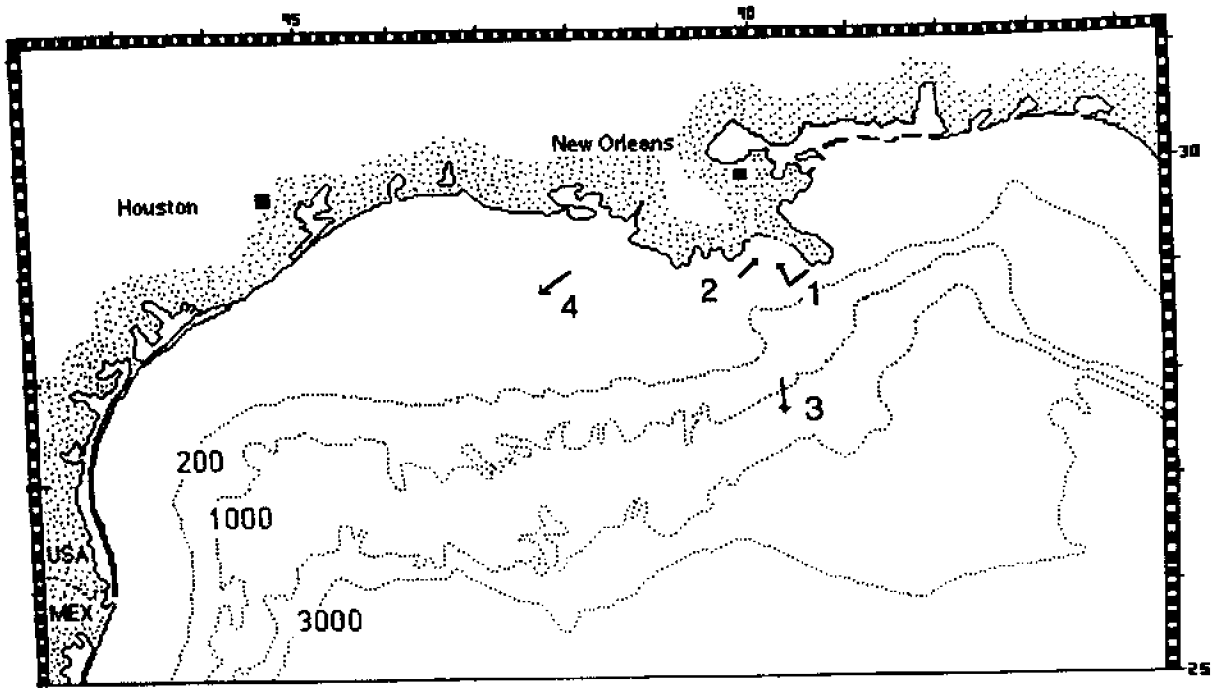

Fig. 3. Chart of locations of continuous-flow enzyme activity measurements in the Gulf of Mexico during July 1993. Arrow indicates the direction of the ship's track. Runs 1 through 3 were alkaline phosphatase measurements, run 4 was a peptidase section. Depth contours in meters are also shown.

the fluorescence values of the killed control over time.)

Fluorescence values then varied from 66 to 80 with numerous spikes early in the record, followed by another killed control which stabilized at 45. A final run near Station 56 was rather constant around a fluorescence value of 66. The minimum value at the right side (4) was a turbidity blank with sample and buffer as normal, but the substrate replaced with distilled water. Finally the peak at the extreme right was a 100 nM 4- methylumbelliferone (MUF) standard. The alkaline phosphatase activity calculated from Fig. 4 is discussed below.

The similar continuous record of peptidase activity from location 4 (Fig. 3) is shown in Fig. 5. The substrate (MCA-leucine), substrate concentration (10 uM), incubation time (14 min) excitation and emission wavelengths (380nm /440 nm), and fluorescence values are all different from the previous figure. The minimum fluorescence value (42) shown at the left was a turbidity blank, followed by a peptidase measurement run with fluorescence values between 935 and 1000 (instrument maximum). This was followed by a killed control which stabilized at about 868 and another peptidase run where fluorescence values varied between 920 and 940. At the right side is another turbidity blank, which reached a minimum value of 21, and a 100 nM 7-amido-4-methyl coumarin (MCA) standard, which yielded a fluorescence value of 200. The peptidase activity calculated from Fig. 5 is discussed below.

Enzyme assay results of the study locations shown in Fig. 3 are summarized in Table 1. Alkaline phosphatase activity was unmeasurable in the surface waters at the mouth of Southwest Pass (location no. 1)

Table 1. Range of alkaline phosphatase (AP) and peptidase (P) activities for selected transects measured with the continuous-flow system.

Enzyme Activity	Location # (on Fig. 3)	Turnover time (hours)	Rate (μmol l^{-1} h^{-1})
AP	1	∞ to 0.64	0 to 1.56
AP	2	6.58 to 2.60	0.15 to 0.38
AP	3	5.00 to 3.13	0.20 to 0.32
P	4	89.85 to 35.35	0.11 to 0.28

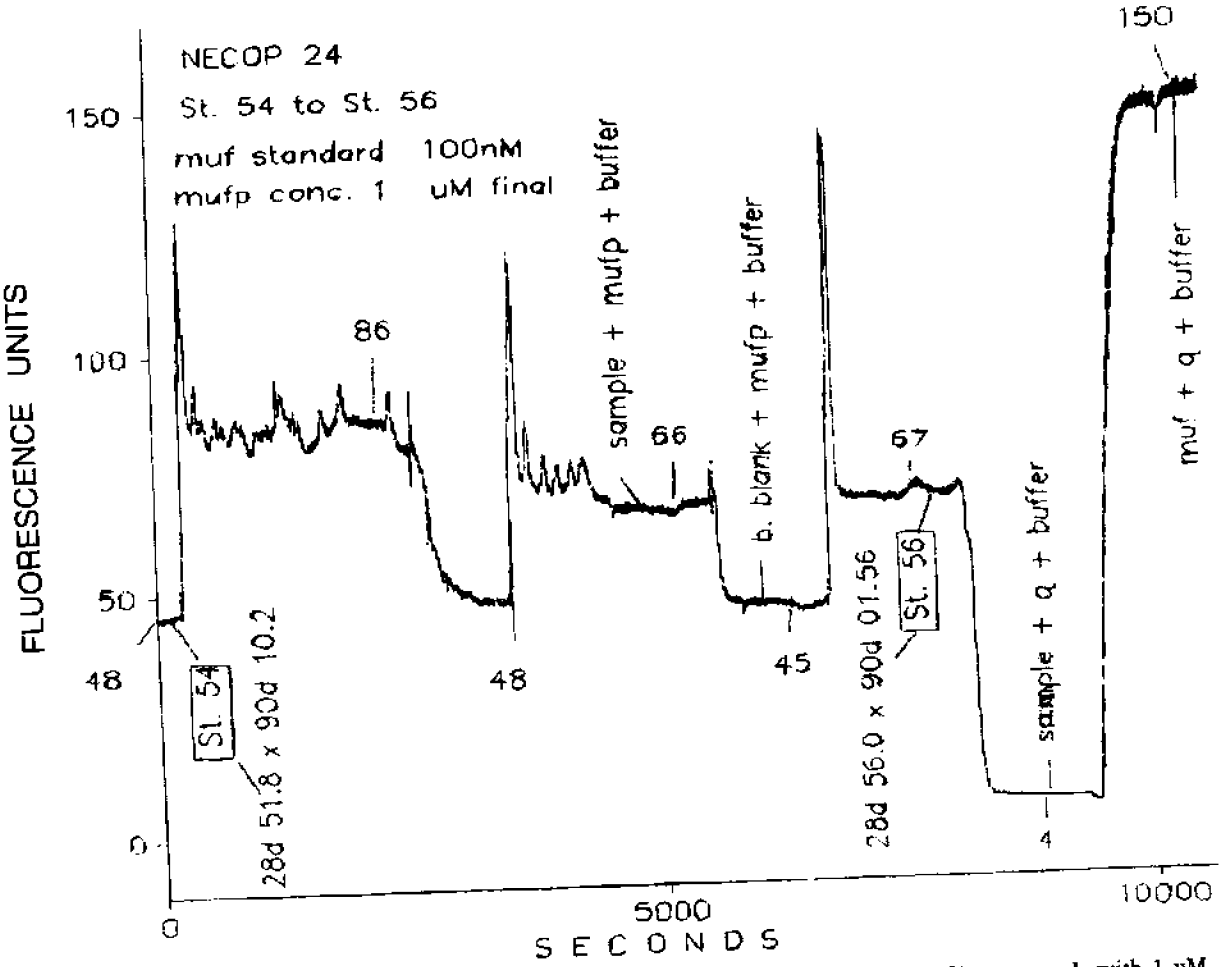

Fig. 4. Annotated continuous alkaline phosphatase data record from location 2 (Fig. 3), measured with 1 uM 4-methylumbelliferyl phosphate as the substrate, and expressed in fluorescence units vs. time. This data record is described in detail in the text.

but increased rapidly offshore once the turbidity decreased and plankton biomass and productivity increased. Activity reached very high rates, greater than 1 umol l-1 h-1, probably the highest of the cruise, before declining slightly toward the end of the section. Alkaline phosphatase activity in section 2, the one described in Fig. 4, was lower and less variable than in section 1, but with a greater than 50% decrease from west to east. This section was the most inshore of all four sections. Section 3 measured alkaline phosphatase activity offshore, going from north to south across the 1000 m contour line. Though activity was the lowest of the three alkaline phosphatase sections, the range of activity overlapped with the other two sections and was the least variable of the three.

Section 4 (shown in Fig. 5) was the only section of peptidase activity measured. This section started toward the middle of the shelf west of the Atchafalaya outflow and proceeded offshore towards the southwest. Though the fluorescence due to enzyme activity was less than 10% above the killed control, and turnover times were long, the actual rate of hydrolysis was similar to the phosphatase activity from sections 2 and 3, about 0.1 to 0.3 umol l-1 h-1. Much of the explanation for the long turnover times and high background result from the fact that the substrate concentration used (10 uM) was ten times higher then that used for alkaline phosphatase. Except for some peaks near the middle of the section, which may have been artifacts, no spatial trend in peptidase activity was observed in this section.

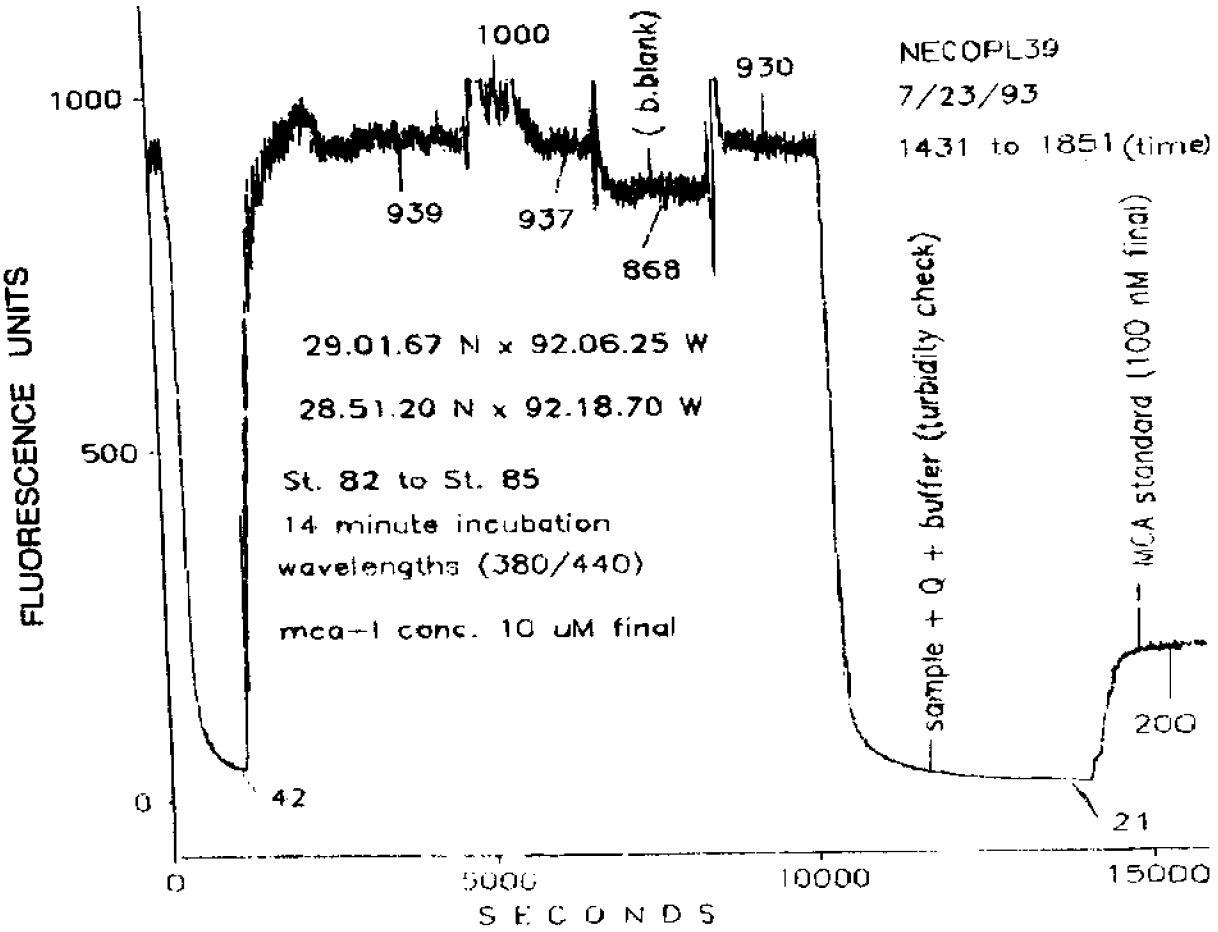

Fig. 5. Annotated continuous peptidase data record from location 4 (Fig. 3), measured with 10 uM 7-amido-4-methyl coumarin as the substrate, and expressed in fluorescence units vs. time. This data record is described in detail in the text.

Discussion

This study has demonstrated that microbial cell-surface enzyme activities can be measured continuously in the environment and that we can observe spatial variations in these activities which can be correlated other environmental parameters. In this study we concentrated on alkaline phosphatase activity, but also measured peptidase activity. The focus on phosphatase activity resulted from the goal of the project, which was to examine the role of phosphorus in nutrient limitation in the Mississippi Plume region. The peptidase measurements were to show that this continuous-flow system can be used for other enzyme activities as well.

Alkaline phosphatase activity is often used as an indicator of phosphorus deficiency, especially in lakes (Pick 1987), but also in estuaries (Fisher et al. 1992). Previous work during a high-flow summer season (1990) has shown that the inflowing surface water from the Mississippi River has a high nitrogen to phosphorus ratio (Ammerman 1992). The resulting phosphorus deficiency results in rapid uptake rates of inorganic phosphate and high alkaline phosphatase activity in the productive waters offshore from the river mouth and further to the west (Ammerman 1992). In contrast, the degree of phosphorus deficiency and the corresponding rates of activity were much lower in the fall, presumably due to decrease freshwater inflow and productivity (Ammerman 1992). Since alkaline phosphatase activity appears to be closely related to phosphate uptake rates in this region (Ammerman, unpublished), we have used measurements of this enzyme as a proxy for phosphate uptake.

The 1930-1992 average flow record for the Mississippi River shows a maximum flow in April and May and a minimum in September and October (Dowgiallo 1994). The continuous enzyme activity measurements reported here were made during July

1993, during the record flooding of the Mississippi River (Dowgiallo 1994). During July the flow is normally decreasing as it approaches the fall minimum. However, during July of 1993, the river flow was about 23,000 cubic meters per second, higher than the 1930-1992 average of about 14,000 cubic meters per second (Dowgiallo 1994). (From August 5th to September 10th the flows actually exceed the previous maximum flows recorded.) The manual measurements shown in Fig. 1, in contrast, were made in the normally high flow spring season in May. In 1992, however, the year they were made, the May flow was only about 15,000 cubic meters per second, less than the average of 21,000 cubic meters per second. Thus, both the spring 1992 and the summer 1993 seasons were anomalous, and the July 1993 flow actually exceed that of May 1992.

Regardless of the flow anomalies of particular years, the alkaline phosphatase data shown in Fig. 1 and Table 1 are both from relatively high-flow, productive seasons. The minimum turnover times were comparable from the two different methods, manual and continuous-flow, measured in two different seasons and years, May 1992 and July 1993. However, the continuous alkaline phosphatase measurements from July of 1993 (Table 1) were done with a ten-fold higher substrate concentration (1 uM vs. 100 nM) than the earlier measurements. Thus the actual substrate hydrolysis rate at a given turnover time was ten times higher in 1993. This suggests that the enzyme activity during the 1993 summer flood much higher than during the previous spring, which correlates with the unusually low surface salinity and high phytoplankton biomass reported during the summer flood period (Dowgiallo 1994). Undoubtedly, further data on microbial biomass and activity during the flood period will be available in the future. When the alkaline phosphatase data are coupled with these measurements, we should gain additional insights about microbial growth and phosphorus cycling.

With only three sections discussed, we are just beginning to determine the surface distribution of alkaline phosphatase activity during July of 1993. Due to the high turbidity, there was no activity at the mouth of Southwest Pass. The highest activity was found in section 1 (Fig. 3, Table 1), slightly offshore from Southwest Pass. This is the intermediate-salinity, highly- productive region of the river plume where the turbidity has decreased enough to allow light penetration, but nutrients are still available, though they are rapidly being utilized. Past work has shown that this high alkaline phosphatase activity, and rapid phosphate uptake, are limited to the upper 5 to 10 m of the water column with significant river input (Ammerman 1992). Surface alkaline phosphatase activity was readily measurable over a wide area, including at least as far south as the 1000 m contour line (section 3, Fig. 3; Table 1). This is not surprising in light of the large freshwater input and resulting reduced surface salinity during the flood period (Dowgiallo 1994), especially since river water usually has a high nitrogen to phosphorus ratio.

The peptidase measurements (section 3, Fig. 3; Fig. 5; Table 1) demonstrate that other microbial-cell surface enzymes can also be measured with this continuous underway system. Though the difference in fluorescence between sample and killed control was less than for phosphatase, the actual rate of peptidase activity was comparable to the lower range of phosphatase activities. We have insufficient peptidase data to see any spatial trends, but Chrost (1991) found that the specific activity (activity normalized to bacterial biomass) of both leucine aminopeptidase and beta-D-glucosidase and was highest during the late stages of a spring bloom in a lake, when algal cells were decaying. Peptidases and proteases are usually among the easiest enzymes to measure in natural aquatic environments, since they have among the highest activities of the ecotoenzymes. In studies of marine aggregates (Smith et al. 1992), "protease" activity, measured with the same peptidase substrate we used, was always the first or second most active of a series of ectoenzymes, phosphatase was the other highly active enzyme. Likewise in Australian ox-bow lakes, aminopeptidase and alkaline phosphatase were the most active of a series of ectoenzymes assayed (Boon 1991). Peptidases and proteases have been repeatedly measured by several different methods in a variety of marine coastal environments, including the Belgian coast of the North Sea (Billen 1991) and the mesotrophic Southern California Bight (Hollibaugh and Azam 1983; Rosso and Azam 1987). Therefore, they should be a good candidate for more extensive continuous-flow measurements in the future.

Acknowledgements

This work was supported by the following grants to the first author: NOAA NECOP (NA90AA-D-SG689), Texas Sea Grant (R/ES-34), and NSF OCE90-19415.

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PRIMARY PRODUCTION AND DISSOLVED OXYGEN IN THE MISSISSIPPI RIVER PLUME/INNER GULF SHELF REGION: COMPONENTS ANALYSIS AND SENSITIVITY TO CHANGES IN PHYSICAL TRANSPORT

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Abstract

A deterministic, mass balance model for phytoplankton, nutrients and dissolved oxygen was applied to the Mississippi River Plume/Inner Gulf Shelf (MRP/IGS) region. The model was previously calibrated to a comprehensive set of field data collected during July 1990 at over 200 sampling stations in the northern Gulf of Mexico. This study involved use of the calibrated model to conduct components analyses of gross primary production and dissolved oxygen, and sensitivity analyses of model responses to changes in physical transport. Gross primary production and losses due to intra-segment chemical-biological processes are much more important than inter-segment physical transport processes and net settling in controlling phytoplankton carbon dynamics. Zooplankton grazing, phytoplankton respiration, and DOC exudation account for approximately 50, 25 and 20 percent, respectively, of the immediate fate of gross primary production. Intra-segment chemical-biological processes are relatively more important than inter-segment physical transport processes in controlling bottom water dissolved oxygen dynamics. The estimated contribution of sediment oxygen demand to total oxygen depletion rates ranges from 22 to 30 percent. Salinity in surface waters is more responsive to changes in dispersive mixing than salinity in bottom offshore waters. Salinity responses to changes in seaward boundary dispersion are somewhat greater than responses to changes in vertical dispersion. Chlorophyll concentration is much less responsive to changes in dispersive mixing than salinity. Chlorophyll responses to changes in seaward boundary dispersion and vertical dispersion are very small in all model segments. Bottom water dissolved oxygen concentration is very sensitive to changes in dispersive mixing, especially to changes in seaward boundary dispersion. Bottom water dissolved oxygen concentration is also very sensitive to changes in sediment oxygen demand.

Introduction

The Mississippi-Atchafalaya River (MAR) system is the largest single source of freshwater and nutrient inputs to the coastal waters of the United States. An extensive and persistent zone of seasonal hypoxia (dissolved oxygen < 2 mg l-1) has been documented in the nearshore bottom waters of the Louisiana-Texas continental shelf (Rabalais et al. 1991; 1992). Turner and Rabalais (1991) speculated that increased nutrient inputs from the MAR system may have affected the extent and severity of hypoxia in this region by supporting enhanced levels of primary productivity. Justic et al. (1993) strengthened the evidence for this hypothesis through cross correlation analysis of MAR nutrient inputs, net productivity and hypoxia in the northern Gulf of Mexico.

As part of the Nutrient Enhanced Coastal Ocean Productivity (NECOP) program, a study was initiated to synthesize information on physical, chemical and biological processes in the Mississippi River Plume/Inner Gulf Shelf (MRP/IGS) region within a mass balance modeling framework. This paper involves application of a coarse grid, deterministic model for phytoplankton, nutrients and dissolved oxygen to the Louisiana Inner Shelf portion of the MRP/IGS (Fig. 1). In a previous study (Bierman et al. 1994), the model was calibrated to a comprehensive set of field data collected during July 1990 at over 200 sampling stations in the northern Gulf of Mexico. The calibrated model was used to conduct diagnostic analyses and numerical experiments to better understand environmental processes controlling primary productivity and dissolved oxygen dynamics in the study area.

This paper contains results from use of the previously calibrated model as a tool for conducting additional diagnostic analyses, and sensitivity analyses

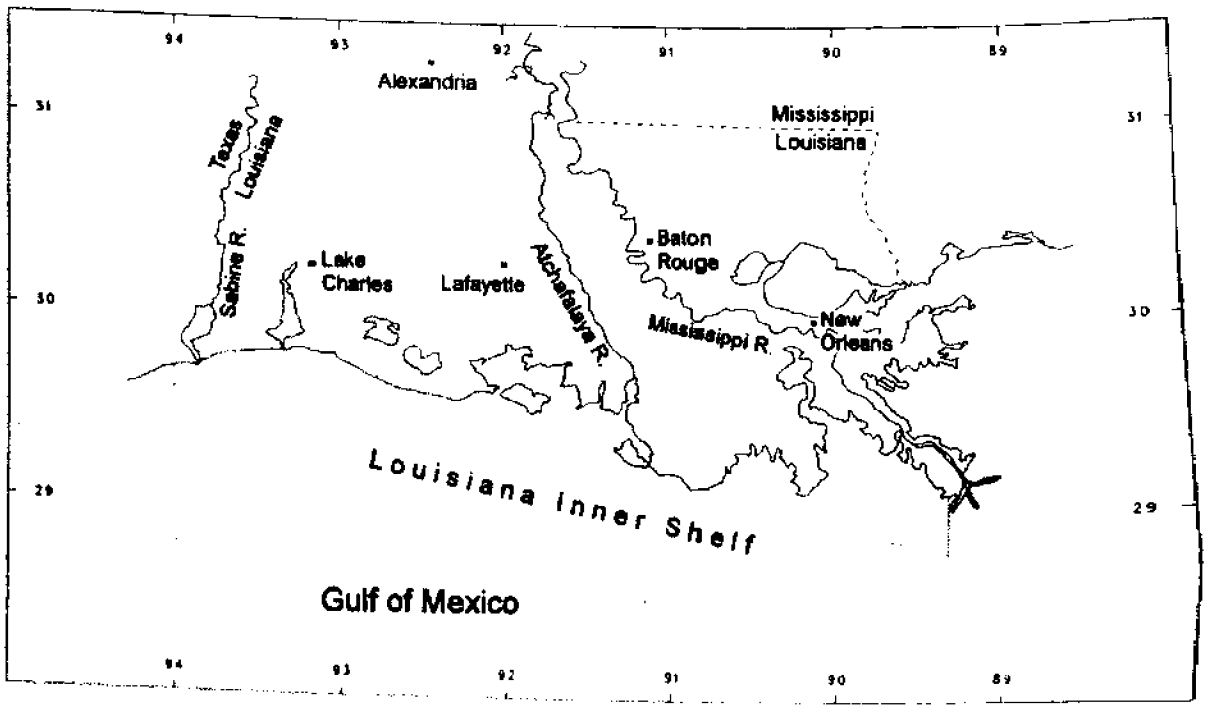


Fig. 1. Location map of study area.

of model responses to changes in physical transport. The diagnostic analyses include components analyses of the fate of gross primary production and of dissolved oxygen sources and sinks. The sensitivity analyses include determination of salinity, chlorophyll and dissolved oxygen responses to changes in physical transport and sediment oxygen demand.

Modeling Approach

The conceptual framework for the modeling approach is shown in Fig. 2. State variables in the model include salinity, phytoplankton carbon, phosphorus (dissolved phosphate and unavailable forms), nitrogen (ammonia, nitrate plus nitrite, and unavailable forms), dissolved oxygen and carbonaceous biochemical oxygen demand. 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. Sediment interactions are represented by user-specified values for net settling rates for particulate phase constituents, sediment-water diffusive fluxes for dissolved nutrients and sediment oxygen demand. Although this model contains only a moderate degree of chemical-biological complexity it requires a considerable amount of field data for specification of external forcing functions, as well as for comparison with model output.

This conceptual model was implemented for the MRP/IGS region using a modified version of the WASP4 computer coding framework. Ambrose et al. (1988) contains a complete description of WASP4 model theory, governing equations, and a user manual. There were two principal modifications to WASP4 for this application: first, use of a saturation kinetics mechanism for water column nutrient mineralization proposed by DiToro and Matystik (1979); and second, use of a saturation kinetics mechanism for phytoplankton decomposition proposed by Rodgers and Salisbury (1981).

Model Application

Spatial and Temporal Scales The spatial domain of the model is represented by 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 30-60 meter bathymetric contours (Fig. 3). The spatial segmentation grid includes one vertical layer nearshore and two vertical layers offshore. All of the spatial segments are assumed to be 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 depths of these bottom offshore segments range between 6.1 and 20.3 meters.

The temporal domain of this application represents only steady-state conditions for July 1990. The reason is that time-series data were not available at

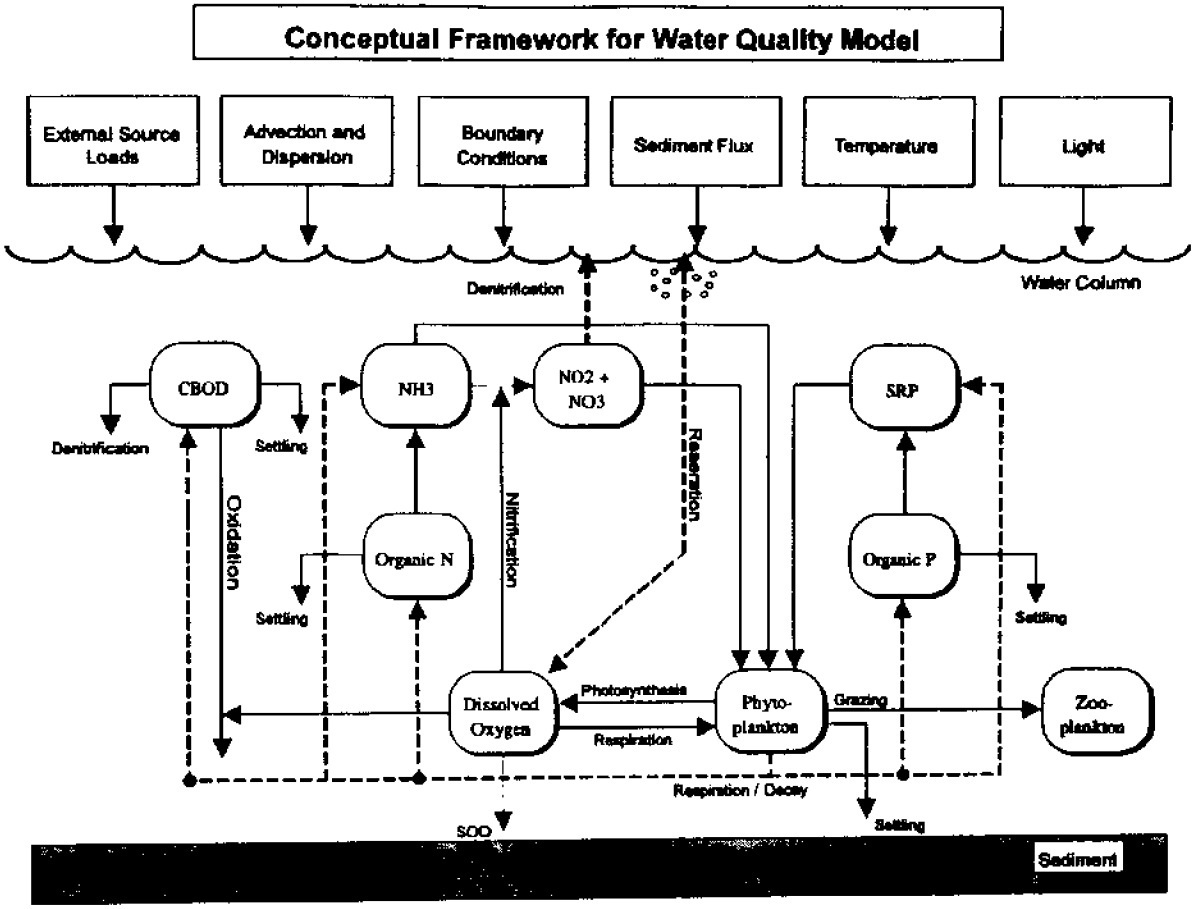


Fig. 2. Schematic diagram of principal model state variables and processes.

the shelfwide spatial scale. Typically, a single shelfwide monitoring effort is conducted during the July-August period to characterize the spatial extent of hypoxic conditions in the study area. Operationally, model forcing functions were assigned constant values that represented summer average conditions during 1990. The time-variable model was then run to steady-state and model output was compared with a combined field data set from three different sampling cruises conducted during mid-July. It was assumed that these combined data were synoptic and that they were in temporal equilibrium with the specified model forcing functions.

Field Data The combined field data set used for model calibration included the following groups of sampling stations (Fig. 4): (1) NECOP - NECOP90 shelfwide cruise that occupied 64 stations located primarily inside the model segmentation grid; (2) GYRE - GYRE90 cruise conducted by Texas A&M University that occupied 113 stations located both inside and outside the model segmentation grid; (3) NURC - NURC90 cruise conducted by Louisiana Universities Marine Consortium, Texas A&M University at Galveston and Texas Institute of Oceanography that occupied 38 stations located immediately west of the Mississippi Delta in the primary hypoxic region; and (4) River - U.S. Geological Survey stations in the Mississippi and Atchafalaya Rivers. The field data from all of these sampling stations (except River stations) reside in the NECOP data base management system and are subject to NECOP policies on quality control, archiving and distribution.

Physical Transport Physical transport in the model is represented by advective flow and bulk dispersion. Bulk dispersion is a lumped parameter that represents transport processes at scales smaller than the model spatial segments. These processes include molecular diffusion, turbulent eddy diffusion and shear flow dispersion. Because the model balances mass and not momentum, magnitudes and directions for advective flows must be externally specified. Dispersive mixing coefficients across all horizontal and vertical interfaces are calibration parameters determined by conducting a mass balance to salinity, a conservative tracer.

Water circulation on the Louisiana-Texas Shelf is strongly influenced by wind stress (Cochrane and Kelly 1986) and freshwater discharges from the Mississippi and Atchafalaya Rivers (Wiseman et al.

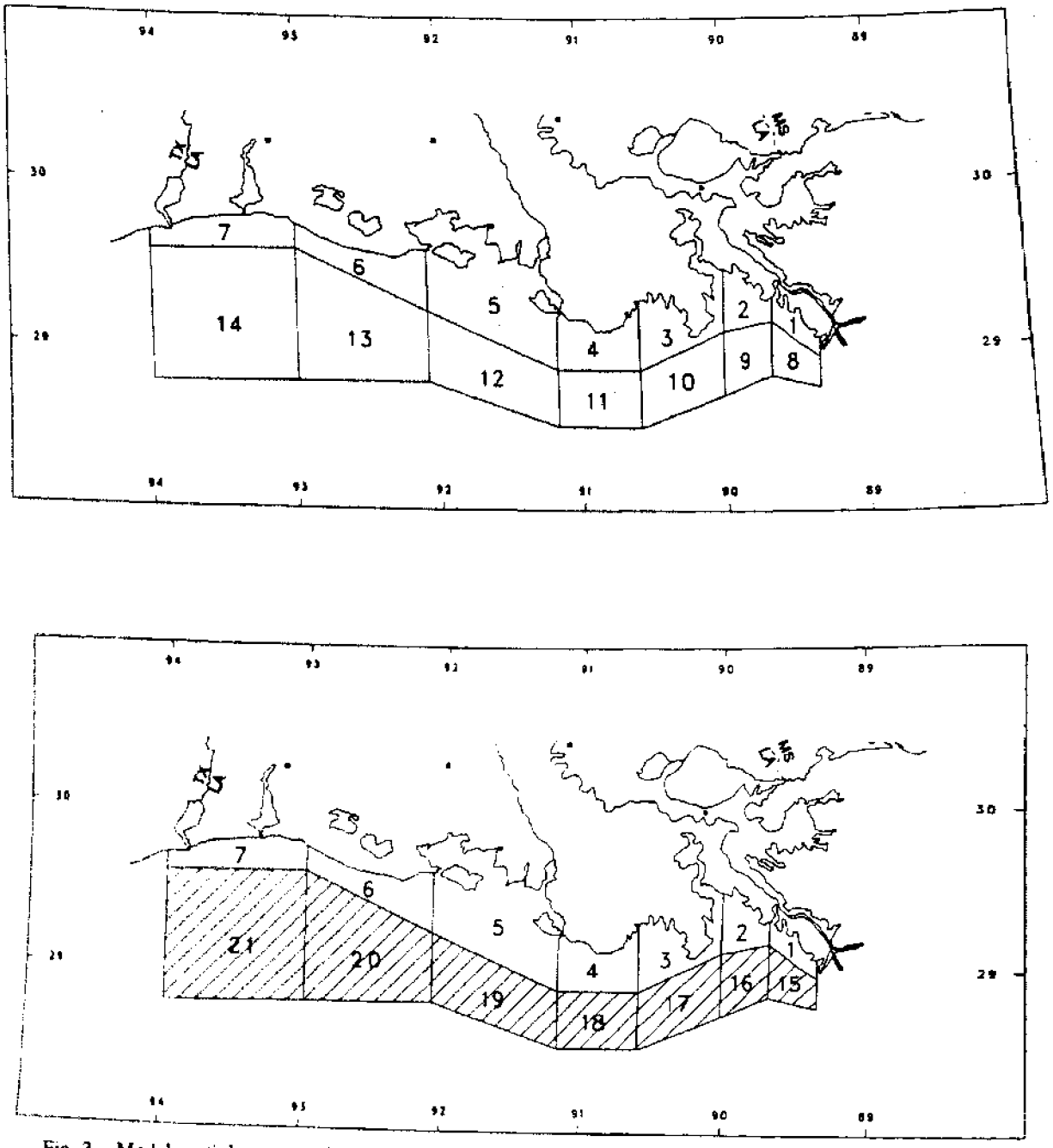


Fig. 3. Model spatial segmentation grid for Mississippi River Plume/Inner Gulf Shelf region. Top panel contains surface segments (Segments 1-7 nearshore; Segments 8-14 offshore) and bottom panel contains bottom segments (Segments 15-21).

1982; Dinnel and Wiseman 1986). It is believed that summer average conditions in the spatial domain of the model are typically represented by the Louisiana Coastal Current which has a net westward drift along the shelf bathymetry. This representation is supported by current meter measurements from a long-term mooring maintained by one of the co-authors (W.J. Wiseman, Jr.) at a location off Cocodrie (Segment 10) in 20 meters of water. Typical summer average current speeds are approximately 10 and 3 cm s-1, respectively, in surface and bottom waters.

Summer 1990 conditions were anomalous in that net eastward drift was observed in both surface and bottom waters at speeds of approximately 2 and 0.8 cm s-1, respectively. The freshwater advective flow fields in Fig. 5 represent our best judgment in synthesizing

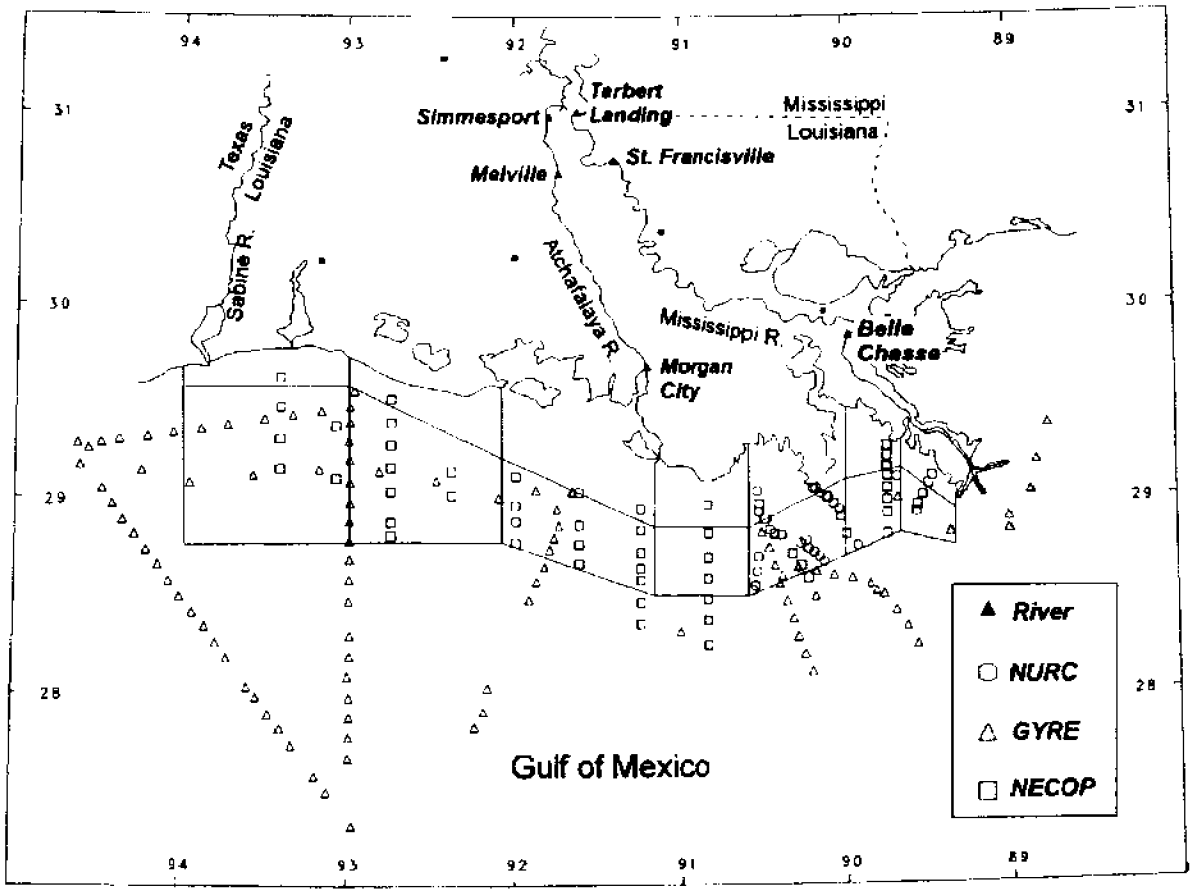


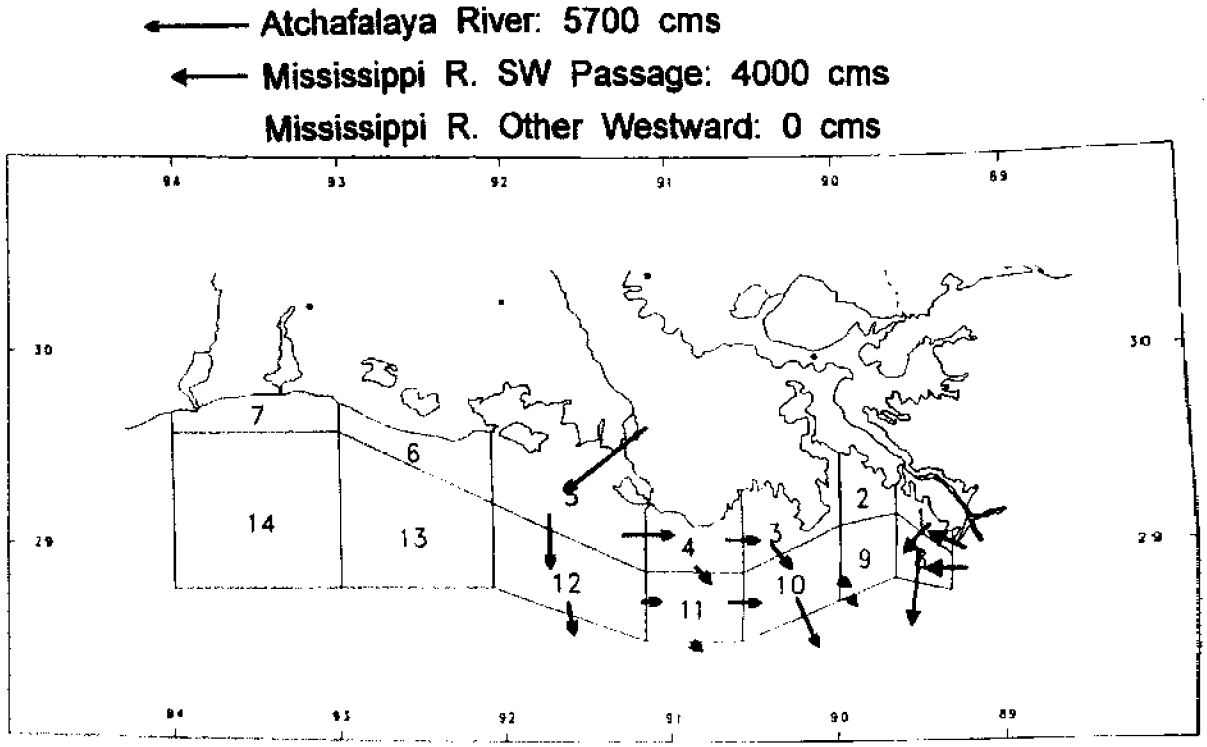
Fig. 4. Locations of field sampling stations used in model calibration for July 1990. River - USGS tributary loading stations, NURC - NURC90 cruise stations, GYRE - GYRE90 cruise stations, NECOP - NECOP90 shelfwide cruise stations.

available data for riverine discharges and observed current speeds and directions during July 1990. Values for discharges from the Southwest Pass of the Mississippi River into Segments 1 and 8 and from the Atchafalaya River into Segment 5 were based on measurements at Tarbert Landing and Simmesport (Fig. 4), respectively (U.S. Army Corps of Engineers, New Orleans District Office, personal communication). No freshwater flow from other Mississippi River passages was represented in this application because of the observed net eastward drift in the coastal current. In addition to these freshwater flows, net eastward flow fields of Gulf of Mexico water through the nearshore, surface offshore and bottom offshore model segments were also represented (not shown). Values for these Gulf of Mexico flows were constrained so that total flow through Segment 10 was consistent with current meter observations. The water circulation pattern in Fig. 5 is qualitatively consistent with a NOAA-11 AVHRR sea surface temperature map for July 25, 1990 (N.D. Walker, Coastal Studies Institute, Louisiana State University, personal communication).

Model Calibration After specification of external forcing functions, the model was calibrated using the above combined field data set. Observations for salinity, phytoplankton chlorophyll, dissolved oxygen and dissolved available nutrients were available for most of the 21 model spatial segments. In addition to concentrations for these model state variables, the model was also calibrated using various process rates and mass fluxes, and concentrations of phytoplankton carbon, dissolved organic carbon and dissolved organic nitrogen from specialized measurements conducted in the primary hypoxic region (Segments 10 and 17). Refer to Bierman et al. (1994) for a complete discussion of the model calibration approach and actual calibration results.

Diagnostic Analyses

Fate of Gross Primary Production An important research question in the NECOP program concerns the fate pathways for phytoplankton production



JULY 1990 ADVECTIVE FRESHWATER FLOW DISTRIBUTION

Fig. 5. Schematic diagram of freshwater advective flows used in model calibration for July 1990.

in the MRP/IGS region. The principal source and sink components for phytoplankton carbon are shown in Fig. 6 (top panel) for four representative surface offshore model segments. The magnitudes of gross primary production and total loss (due to intra-segment chemical-biological processes) are much greater than those of inter-segment advective-dispersive transport processes and net settling. Intra-segment chemical-biological processing accounts for approximately 95 percent of the immediate fate of gross primary production in all four segments.

Individual components of total chemical-biological losses for these same four model segments are shown in the bottom panel of Fig. 6. Zooplankton grazing (ingestion), phytoplankton respiration, and DOC exudation account for approximately 50, 25 and 20 percent, respectively, of total chemical-biological losses in each segment. Non-predatory mortality is very small in all four segments.

Analysis of Dissolved Oxygen Dynamics Another important research question in the NECOP program concerns the principal factors controlling dissolved oxygen and seasonal hypoxia on the Louisiana Inner Shelf. The total mass balance components of dissolved oxygen are shown in Fig. 7 (top panel) for four representative bottom offshore model segments. The magnitudes of intra-segment chemical-biological processes (photosynthesis and depletion) are greater than those of inter-segment advective-dispersive transport processes. Photosynthesis is the largest source of dissolved oxygen and depletion (water column plus sediment demand) is the largest sink of dissolved oxygen in all four segments. Furthermore, the magnitudes of these two processes increase with increasing distance from the Mississippi Delta.

Individual components of total oxygen depletion rates for these same four model segments are shown in the bottom panel of Fig. 7. Oxidation of carbonaceous material in the water column, phytoplankton respiration and sediment oxygen demand all contribute significantly to total oxygen depletion rates. Carbonaceous biochemical oxygen demand is the largest component in each of the four segments, and its relative contribution increases with increasing distance from the Delta. Nitrification is a relatively small component in all four segments. The computed contribution of sediment oxygen demand to total oxygen depletion rates ranges from 22 to 30 percent.

Sensitivity Analyses

Dispersive Mixing In terms of data requirements for mass balance modeling, there are two

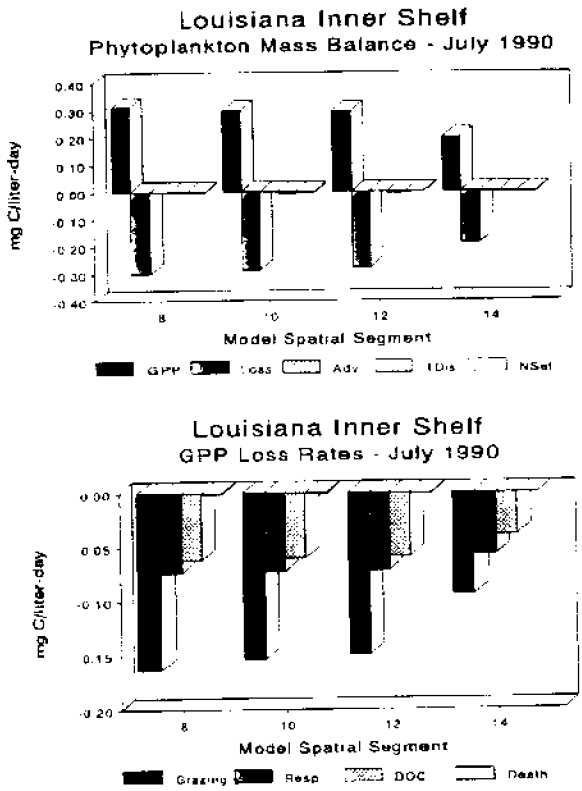


Fig. 6. Components analysis of phytoplankton carbon sources and sinks in the calibrated model for selected surface (offshore) segments. Total mass balance components (top panel): GPP - gross primary production, Loss - total loss due to chemical-biological processes, Adv - net advective exchange, TDis - total dispersive exchange, NSet - loss due to net settling. Chemical-biological loss components (bottom panel): Grazing - ingestion by zooplankton, Resp - phytoplankton respiration, DOC - DOC exudation, Death - non-predatory mortality.

major gaps in the overall NECOP program: first, lack of information on physical transport processes in the MRP/IGS region; and second, insufficient measurements of seaward boundary concentrations. Accordingly, it is important to determine the sensitivity of model results to changes in physical transport parameters, especially those which affect constituent mass fluxes across the seaward boundaries.

The sensitivity analyses involved changes of plus/minus 50 percent in the following three sets of calibration parameters: total dispersive mixing across all horizontal and vertical interfaces, dispersive mixing across only seaward boundaries and vertical dispersion between surface and bottom segments. Calibration values for horizontal dispersive mixing coefficients ranged between 400 and 600 m2 s-1. The calibration value for vertical dispersion was 5 x 10-6 m2 s-1. All advective flow magnitudes and directions, and all seaward boundary concentrations, were held constant at their calibration values. The model response parameters were salinity and chlorophyll concentrations in all 21 segments, and dissolved oxygen concentrations in bottom offshore segments.

Advective flow magnitudes and directions were not changed in the sensitivity analyses for the following reasons: first, calibration values for flow magnitudes were constrained to the extent that direct measurements were available for MAR inflows and for surface and bottom currents, albeit at only a single location; and second, except for MAR outflows across the seaward boundaries of Segments 8-12 (Fig. 5), there were no cross-shelf advective flows in the calibrated model. The principal cross-shelf transport component was bulk dispersive mixing. Consequently, the most straightforward and systematic way to conduct a transport sensitivity analysis of this model calibration was to vary bulk dispersion coefficients.

In general, salinity in surface segments is more responsive to changes in dispersive mixing than salinity in bottom offshore segments (Fig. 8). Responses to changes in seaward boundary dispersion (Fig 8., middle panel) are somewhat greater than responses to changes in vertical dispersion (Fig. 8., bottom panel). An increase in seaward boundary dispersion causes salinity increases in all segments, and a decrease in seaward boundary dispersion causes salinity decreases in all segments (Fig. 8, middle panel). An increase in vertical dispersion causes salinity increases in surface segments, but causes salinity decreases in bottom offshore segments (Fig. 8, bottom panel). This response pattern is reversed for a decrease in vertical dispersion.

It should be noted that salinity responses to changes in seaward boundary dispersion (Fig. 8, middle panel) and vertical dispersion (Fig. 8, bottom panel) do not completely account for salinity responses to changes in total dispersion (Fig. 8, top panel). This is because total dispersion also includes cross-shelf dispersive mixing between nearshore and offshore surface segments, and along-shelf dispersive mixing.

In general, chlorophyll concentration is much less responsive to changes in dispersive mixing than salinity (Fig. 9). Chlorophyll responses to changes in seaward boundary dispersion (Fig. 9, middle panel) and vertical dispersion (Fig. 9, bottom panel) are very small in all model segments. Chlorophyll is responsive to changes in total dispersion in nearshore surface segments (Fig. 9, top panel), thus indicating that nearshore-offshore dispersion and/or along-shelf dispersion are important.

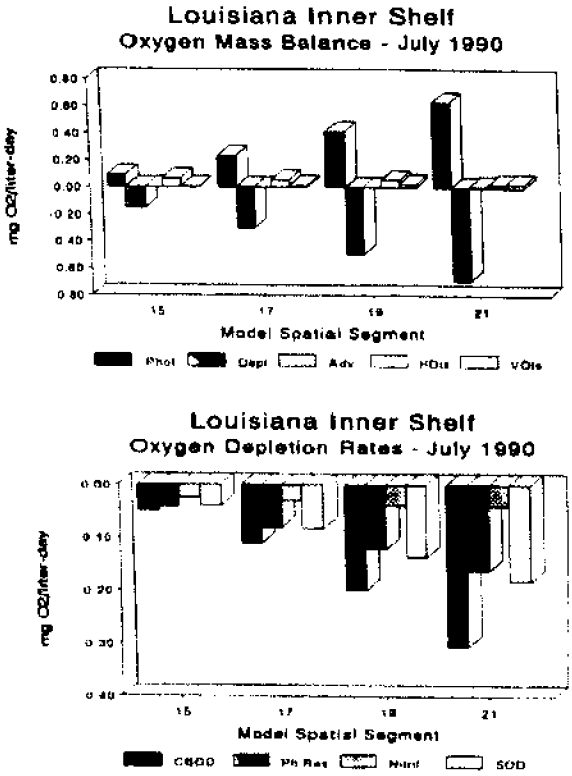


Fig. 7. Components analysis of dissolved oxygen sources and sinks in the calibrated model for selected bottom (offshore) segments. Total mass balance components (top panel): Phot - photosynthesis, Depl - depletion due to water column processes plus sediment oxygen demand, Adv - net advective exchange, HDis - net horizontal dispersive exchange, VDis - net vertical dispersive exchange. Depletion rate components (bottom panel): CBOD - carbonaceous biochemical oxygen demand in the water column, Ph Res - phytoplankton respiration, Nitrif - nitrification, SOD - sediment oxygen demand (areal rate expressed as a volumetric demand).

In contrast to salinity and chlorophyll concentration, bottom dissolved oxygen concentration is very sensitive to changes in dispersive mixing, especially to changes in seaward boundary dispersion (Fig. 10). Dissolved oxygen responses to changes in seaward boundary dispersion (Fig. 10, middle panel) account for most of the responses to changes in total dispersion (Fig. 10, top panel). Responses to changes in vertical dispersion are relatively small and occur primarily in the area of the Atchafalaya River discharge and further west (Fig. 10, bottom panel).

Sediment Oxygen Demand Sediment oxygen demand differs from advective-dispersive physical transport; however, it can be viewed as a mass flux of dissolved oxygen across the water-sediment boundary. The boundary condition for total sediment oxygen demand in the calibrated model included aerobic benthic respiration measured using in situ chambers (Rowe et al. 1992) plus an estimate of anaerobic metabolism (G.T. Rowe, personal communication). Although calibration values for sediment oxygen demand were constrained by direct measurements, it is appropriate to determine the sensitivity of model responses to changes in this important external forcing function.

Results in Fig. 11 indicate that bottom dissolved oxygen concentration is very sensitive to changes in sediment oxygen demand. Furthermore, the magnitudes of dissolved oxygen responses tend to increase with distance from the Mississippi Delta.

Discussion

The result that zooplankton grazing accounts for a large fraction of the immediate fate of gross primary production (Fig. 6, bottom panel) is consistent with experimental observations by Dagg and Ortner (1992). It should be noted that zooplankton grazing in this analysis represents only the immediate fate of phytoplankton carbon and does not represent the portion of gross primary production that ultimately settles in the form of fecal pellets.

It is not intuitively clear why photosynthesis should be a source of dissolved oxygen in bottom offshore waters, nor is it clear why this source should become progressively larger with increasing distance from the Delta (Fig. 7, top panel). This phenomenon is partly due to changes in water column depth along the inner shelf and the influence of light attenuation-depth relationships in the calibrated model. Refer to Bierman et al. (1994) for a more complete discussion.

The result that intra-segment chemical-biological processes are relatively more important than inter-segment advective-dispersive transport processes in controlling dissolved oxygen (Fig. 7, top panel) should be interpreted within the spatial-temporal scales of this model application. All results in this paper represent the coarse spatial scale of the model segmentation grid and summer average steady-state conditions. Potential responses of dissolved oxygen concentrations to meteorological events, shelf-edge upwellings and mesoscale shelf circulation are not represented.

Interpretation of model responses to changes in physical transport is straightforward for salinity because salinity is a conservative tracer and is not coupled to any of the other state variables in the model. In the analyses conducted, salinity responses are a direct

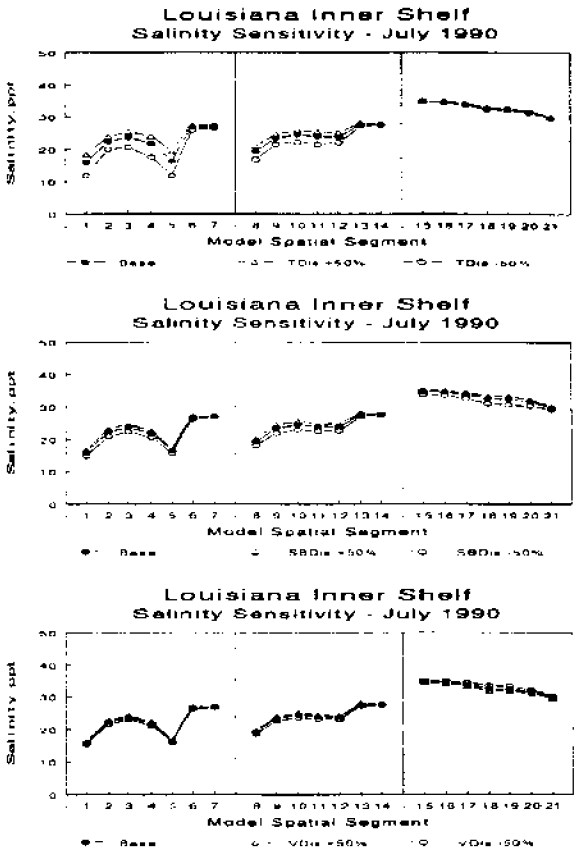


Fig. 8. Responses of salinity, relative to base calibration values, to changes of ±50 percent in dispersion across all horizontal and vertical interfaces (TDis, top panel), dispersion across seaward boundaries (SBDis, middle panel) and vertical dispersion (VDis, bottom panel).

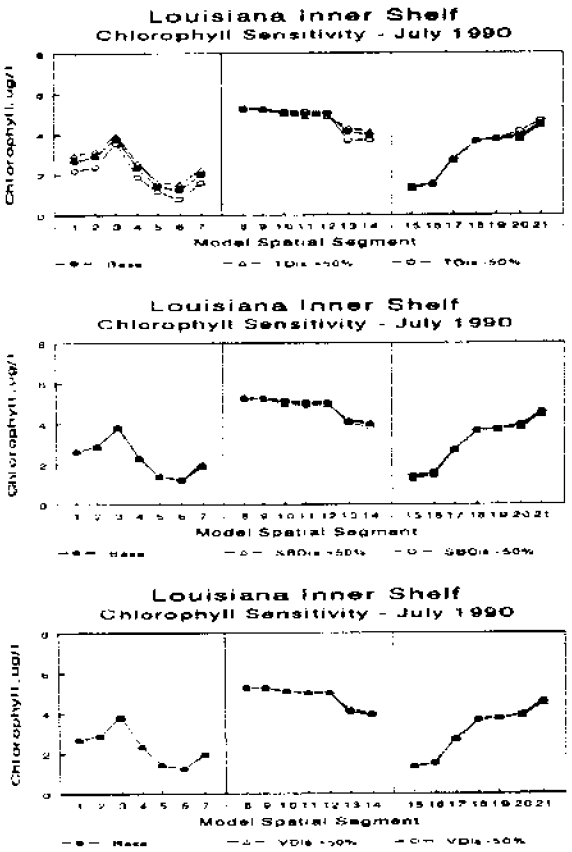


Fig. 9. Responses of chlorophyll concentration, relative to base calibration values, to changes of ±50 percent in dispersion across all horizontal and vertical interfaces (TDis, top panel), dispersion across seaward boundaries (SBDis, middle panel) and vertical dispersion (VDis, bottom panel).

indication of model sensitivity to changes in dispersive mixing coefficients. The sensitivity results in Fig. 8 are completely consistent with the fact that observed salinity increases in the seaward direction and with depth offshore.

Interpretation of chlorophyll and dissolved oxygen responses to changes in physical transport is more difficult because these variables are non-conservative and are each tightly coupled to other state variables in the model (Fig. 2). Chlorophyll responses are a function of changes in both chlorophyll and nutrient mass fluxes across model segment interfaces. Dissolved oxygen responses are a function not only of changes in oxygen mass fluxes, but of changes in mass fluxes of ammonia nitrogen, phytoplankton carbon, and carbonaceous biochemical oxygen demand.

It is interesting to note that chlorophyll concentration is less sensitive to changes in physical transport (Fig. 9) than salinity (Fig. 8). The lack of sensitivity of chlorophyll concentration to changes in inter-segment physical transport is consistent with results of the components analysis in Fig. 6 (top panel). This implies that temporal scales for primary productivity are much shorter than temporal scales for physical transport in this model application. It should also be noted that although chlorophyll is coupled to nutrient concentrations, phytoplankton growth rates in the calibrated model are more strongly controlled by underwater light attenuation than by nutrient limitation (Bierman et al. 1994).

In sharp contrast to results for chlorophyll concentration, dissolved oxygen concentration is much more sensitive to changes in physical transport (Fig. 10) than salinity (Fig. 8), especially to changes in seaward boundary dispersion. The strong sensitivity of dissolved oxygen to changes in inter-segment physical transport appears inconsistent with results of the components

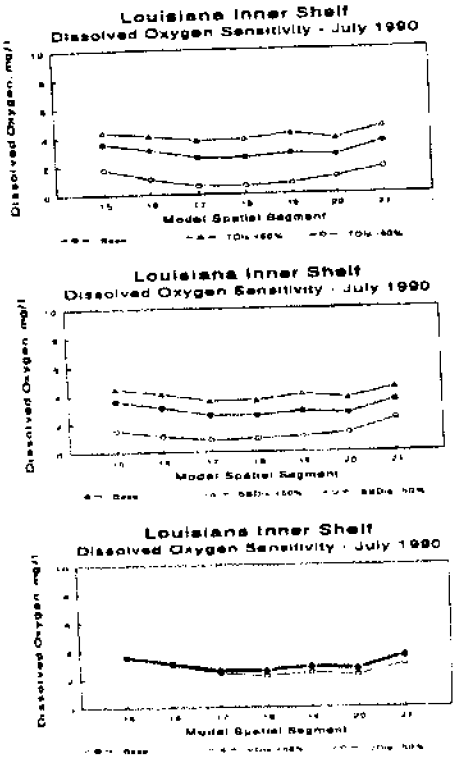


Fig. 10. Responses of dissolved oxygen concentration in bottom offshore waters, relative to base calibration values, to changes of ±50 percent in dispersion across all horizontal and vertical interfaces (TDis, top panel), dispersion across seaward boundaries (SBDis, middle panel) and vertical dispersion (VDis, bottom panel).

analysis in Fig. 7 (top panel). The reason for this behavior, however, is that dissolved oxygen depletion rates are tightly coupled to carbonaceous biochemical oxygen demand, phytoplankton carbon (through endogenous respiration) and ammonia nitrogen (through nitrification) (Fig. 7, bottom panel). Responses of dissolved oxygen to changes in seaward boundary dispersion represent the integrated effects of simultaneous changes in mass fluxes of dissolved oxygen and these other three model state variables.

The sensitivity of dissolved oxygen concentration to changes in sediment oxygen demand is yet another factor that complicates accurate representation of dissolved oxygen dynamics. Dissolved oxygen differs from other state variables in the model because it is strongly influenced by mass flux across the water-sediment boundary. Although boundary conditions for sediment nutrient fluxes are included in the model, responses to changes in these nutrient fluxes are insignificant because these loading sources are small relative to MAR mass loadings (Bierman et al. 1994).

Results of sensitivity analyses for seaward boundary dispersions are not independent of externally-specified seaward boundary concentrations. A more focused analysis of model sensitivity in response to changes in mass fluxes across seaward boundaries would involve systematic changes in seaward boundary concentrations for each model state variable. Such an analysis would isolate model responses for individual state variables, as opposed to responses for model state variables as a coupled system.

It should be noted that the advective flow magnitudes and directions in the calibrated model, although somewhat constrained by direct measurements, are not unique. Different flow routing schemes could be developed that would be consistent with the available physical data. A complete analysis of model sensitivity in response to changes in physical transport should include investigation of alternate advective flow fields.

Conclusions

The following conclusions are drawn from this diagnostic and sensitivity analysis of the calibrated water quality model for the MRP/IGS region:

1. Gross primary production and losses due to intra-segment chemical-biological processes are much more important than inter-segment physical transport processes and net settling in controlling phytoplankton carbon dynamics.
2. Zooplanktongrazing(ingestion),phytoplankton respiration, and DOC exudation account for approximately 50, 25 and 20 percent, respectively, of the immediate fate of gross primary production. Zooplankton grazing in this analysis does not represent the portion of gross primary production that ultimately settles in the form of fecal pellets.
3. Intra-segment chemical-biological processes are relatively more important than inter-segment physical transport processes in controlling bottom water dissolved oxygen dynamics.
4. Oxidation of carbonaceous material in the water column, phytoplankton respiration and sediment oxygen demand all appear to contribute significantly to total oxygen depletion rates in bottom waters. The estimated contribution of sediment oxygen demand to total oxygen depletion rates ranges from 22 to 30 percent.
5. Salinity in surface waters is more responsive to changes in dispersive mixing than salinity in bottom offshore waters. Responses to changes in seaward boundary dispersion are somewhat greater than responses to changes in vertical dispersion.
6. Chlorophyll concentration is much les responsive to changes in dispersive mixing than

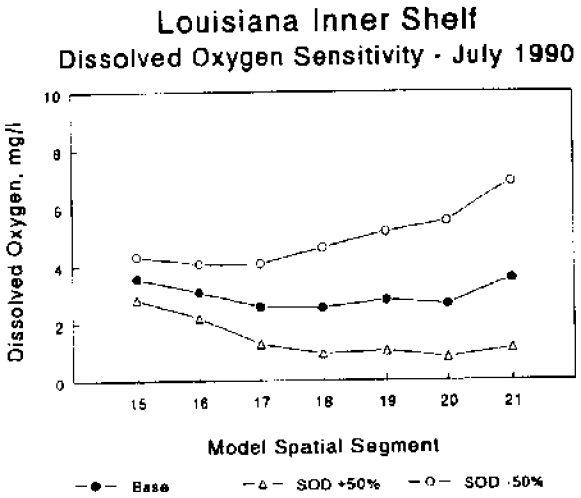


Fig. 11. Responses of dissolved oxygen concentration in bottom offshore waters, relative to base calibration values, to changes of ±50 percent in sediment oxygen demand (SOD).

salinity. Chlorophyll responses to changes in seaward boundary dispersion and vertical dispersion are very small in all model segments.

7. Bottom water dissolved oxygen concentration is very sensitive to changes in dispersive mixing, especially to changes in seaward boundary dispersion. Responses to changes in vertical dispersion are relatively small and occur primarily in the area of the Atchafalaya River discharge and further west.

8. Bottom water dissolved oxygen concentration is very sensitive to changes in sediment oxygen demand.

These conclusions should be considered preliminary because the model has not yet been validated to an independent set of field data. It should also be noted that the typical behavior of the Louisiana Coastal Current is believed to be represented by net westward flows, and that flow conditions for the present model application are considered to be anomalous. Future work in this NECOP modeling study will include application of the steady-state model to summer average conditions for different years, and application of a time-variable version of the model to field data from six different surveys representing spring and summer conditions in 1993.

Acknowledgments

This modeling research was supported by the NOAA Coastal Ocean Program Office through Grant No. NA90AA-D-SG691 to the Louisiana State University Sea Grant Program. Support to Limno-Tech, Inc. was provided through Subcontract No. R136643 from Louisiana State University.

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ZOOPLANKTON GRAZING AND THE FATE OF PHYTOPLANKTON IN THE NORTHERN GULF OF MEXICO

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Abstract

The copepod community consumes a significant fraction of the phytoplankton production that is stimulated by riverine nutrient inputs in the northern Gulf of Mexico. In addition, there is strong evidence that Appendicularians are important consumers of small particles (including pico-phytoplankton). The primary fate of phytoplankton production in this river dominated shelf is to be grazed by zooplankton.

Introduction

High production rates and large stocks of phytoplankton are commonly observed at intermediate salinities in discharge plumes of large rivers (e.g. Lohrenz et al. 1990 for the Mississippi; Demaster et al. 1986 for the Amazon). These blooms of phytoplankton occur because riverine waters, rich in nutrients, override and spread out over the receiving oceanic waters creating an environment with light and nutrient regimes ideal for high rates of phytoplankton growth. Phytoplankton losses, derived from advection, dilution, sinking, and mortality, are initially less than growth rates resulting in the accumulation of phytoplankton stock, a bloom. However, the temporal and spatial scales of the bloom-producing imbalance between growth and loss processes are small and the bloom dissipates as salinity increases and the plume community develops further. High rates of grazer-induced mortality have been observed in estuarine and coastal environments (e.g. Dagg and Turner 1982; Welschmeyer and Lorenzen 1985), and in some river plumes (e.g. Malone and Chervin 1979) but generally not much is known about the contribution of zooplankton grazing to the decline of phytoplankton blooms in river-dominated continental shelves.

The purpose of our work is to measure the ingestion of phytoplankton by the mesozooplankton community, the portion of the grazing community comprised of organisms > 200 um.

Methods

Field measurements of feeding were made during cruises in 9/91 and 5/92. Measurements were made at two locations: a series of stations near SW Pass and at a mid-shelf site. A free-floating array of sediment traps was deployed for 1 - 2 days in each study area (Redalje *et al.* 1994). CTD casts and zooplankton collections were made periodically near the array throughout each 1-2 day deployment. At 3-4 h intervals over 24-36 h, zooplankton were collected with a 1m closing net (202um mesh) from deep and surface depth strata. Immediately after the net came on board, an aliquot of the cod-end sample was poured through a filter apparatus containing a 47 mm piece of 150um mesh Nitex which was then frozen in liquid nitrogen. The remainder of the sample was preserved in a 10 % formalin-seawater solution.

In the shore laboratory, frozen samples were thawed and sorted copepods were analyzed for the amounts of phytoplankton pigments retained in their guts (Mackas and Bohrer 1976; Dagg *et al.* 1989). Gut contents were converted to ingestion rates by application of the gut residence time, determined from the generalized equation for copepods relating temperature to gut residence time (Dam and Peterson 1988). A correction was also made for the average 34 % destruction of pigment that occurs during ingestion/digestion (Kiorboe and Tiselius 1987; Dam and Peterson 1988). Subsamples from the formalin preserved sample were taken with a stempel pipette to determine the concentration of each numerically abundant organism. The ingestion of phytoplankton by each copepod taxon is determined from the product of ingestion rate per copepod and the abundance of that copepod. The sum of the contributions from all copepod taxa is termed copepod community ingestion in this paper but in reality this is a slight underestimate because rare copepods are not included.

Community grazing rates determined at specific sites can be scaled up to larger areas if information on water properties and zooplankton abundance and distribution is available. During a cruise in April 1993, zooplankton abundance was mapped on a series of transects along and across the shelf. A V-fin tow vehicle was towed continuously in the near surface. It simultaneously measured with temperature, salinity, chlorophyll fluorescence, visible (400-700nm) light transmittence and acoustic backscatter at six frequencies

Table 1. Ingestion of phytoplankton by the copepod community. Primary production rates are derived from 14C based incubations described in Redalje et al. (1994).

Site	Depth (m)	Ingestion (I) (mg chl/m2/d)	C:chlor	Ingestion (mg C/m2/d)	Prim Prod (PP) (mg C/m2/d)	I/PP (%)
plume	10 - 0	5.07				
	75 - 10	7.42				
	75 - 0	12.49	43(6)	537	860 - 1650	33 - 62
shelf	32 - 0	2.01	46(3)	92	170 - 360	26 - 54
plume	25 - 0	2.52				
	65 - 25	0.55				
	65 - 0	3.07	54(11)	166	3370 - 3860	4 - 5
shelf	12 - 0	1.46				
	34 - 12	1.42				
	34 - 0	2.88	51(7)	147	280 - 1070	14 - 53

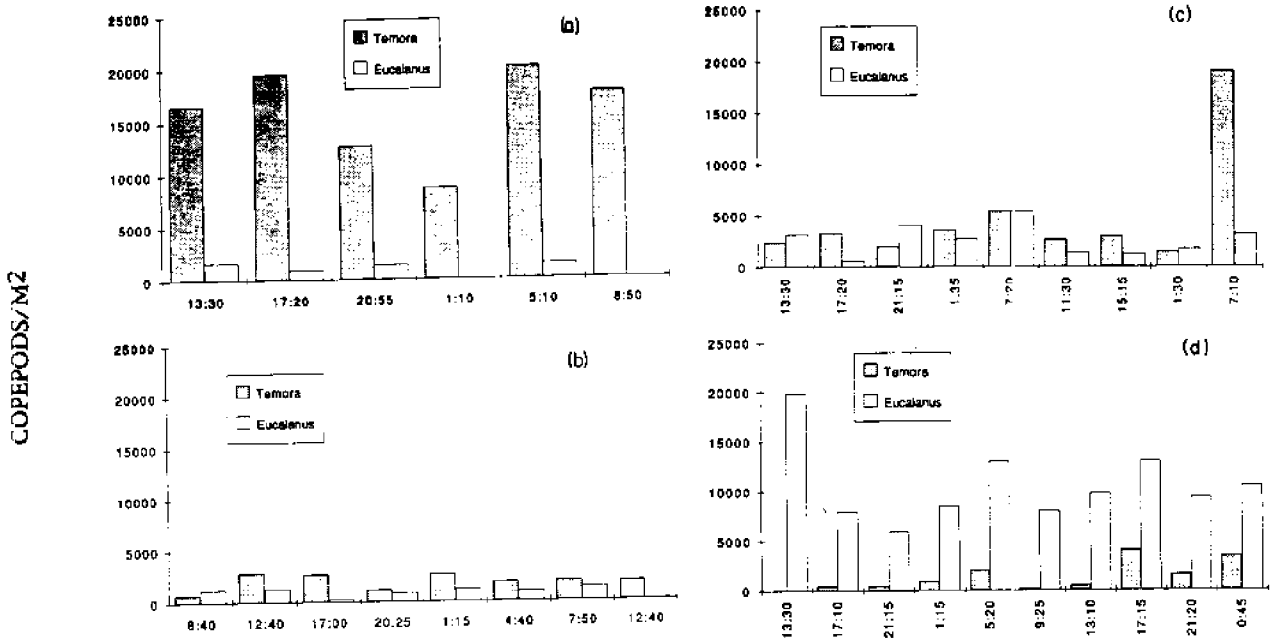

Fig. 1. Abundance of Temora turbinata C6 females and Eucalanus pileatus C6 females near the sediment trap array at (a) the plume site in 9/91, (b) the shelf site in 9/91, (c) the plume site in 5/92 and (d) the shelf site in 5/92.

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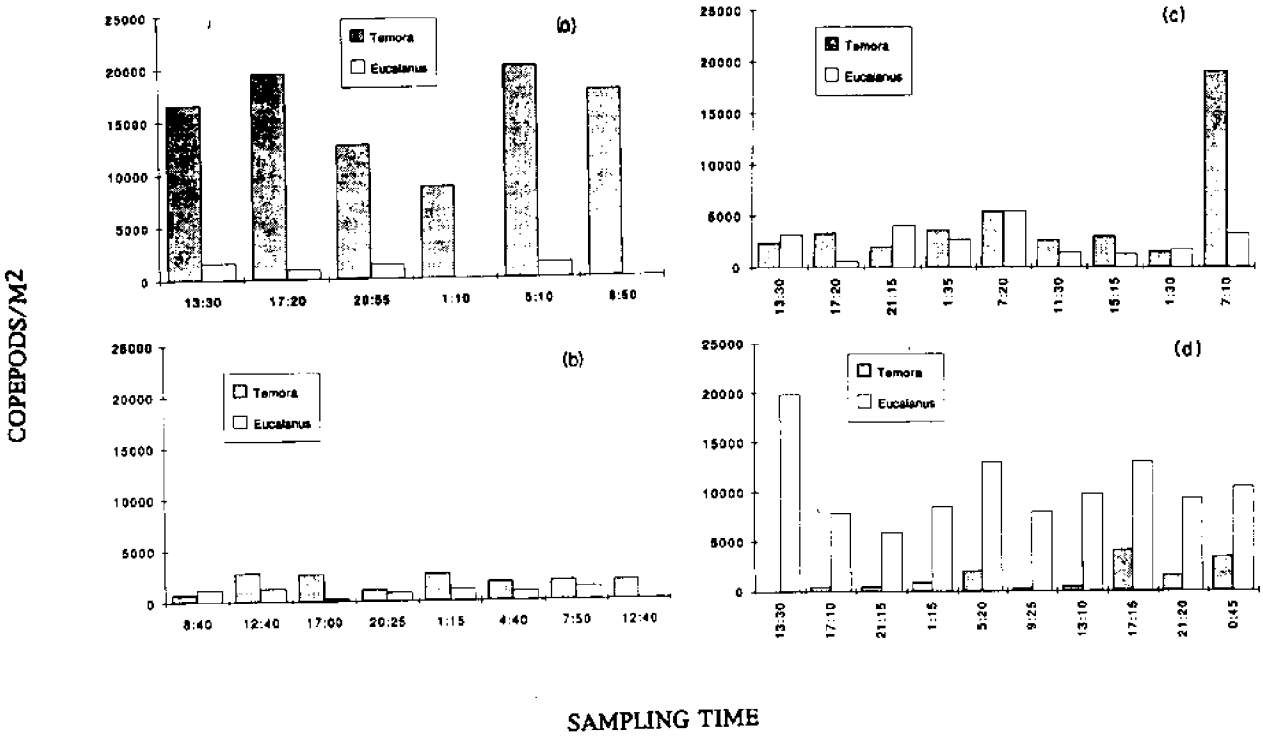

Fig. 1. Abundance of Temora turbinata C6 females and Eucalanus pileatus C6 females near the sediment trap array at (a) the plume site in 9/91, (b) the shelf site in 9/91, (c) the plume site in 5/92 and (d) the shelf site in 5/92.

ranging from 256KHz to 3.0MHz. The latter data will eventually be used to estimate particle size distribution (see Greenlaw, 1990). At the same time an optical particle counter/video system (Ortner *et al.*, submitted) was used to sample water continuously pumped aboard through the ship's MIDAS system. The data generated by the latter device facilitates identication of animal targets and direct comparision with acoustic data.

Results

Observations of zooplankton abundance and distribution from the net tows are consistent with those described previously (Ortner et al. 1989) and will not be presented at length here. There was however, considerable variation between cruises and sampling sites (e.g. Figure 1). In this example, the integrated water-column abundance of two important copepods, Temora turbinata females and Eucalanus pileatus females, is compared. Temora was much more abundant than Eucalanus in the plume area during 9/91 whereas Eucalanus predominated at the shelf site in 5/92.

In general, gut pigment levels were greater at the plume site than at the shelf site during each cruise. However, gut pigment levels within each site were higher during 9/91 and did not reflect the generally higher chlorophyll concentrations observed in the water during 5/92.

Ingestion rate by the copepod community is summarized in Figure 2. The contribution from each species is derived by summing the contributions from the late developmental stages. Rates are calculated separately for each depth stratum and combined in Figure 2. Analysis of variance indicated community ingestion rates were significantly ($p < 0.05$) different at the 9/91 plume site than at the other 3 sites. Temora turbinata and Eucalanus pileatus are important contributors to copepod grazing at all sites, accounting for 54 % and 43 % of the grazing by the copepod community at the plume and shelf sites respectively during 9/91, and 38 % and 86 % during 5/92 (Figure 2). Hourly rates (Figure 2) are integrated over 24h to obtain daily ingestion rates of phytoplankton by the copepod community (Table 1).

Comparison of the ingestion of phytoplankton with phytoplankton production can be made by applying carbon:chlorophyll ratios, determined using a modification of the chlorophyll labeling method originated by Redalje and Laws (1981). Conversions of

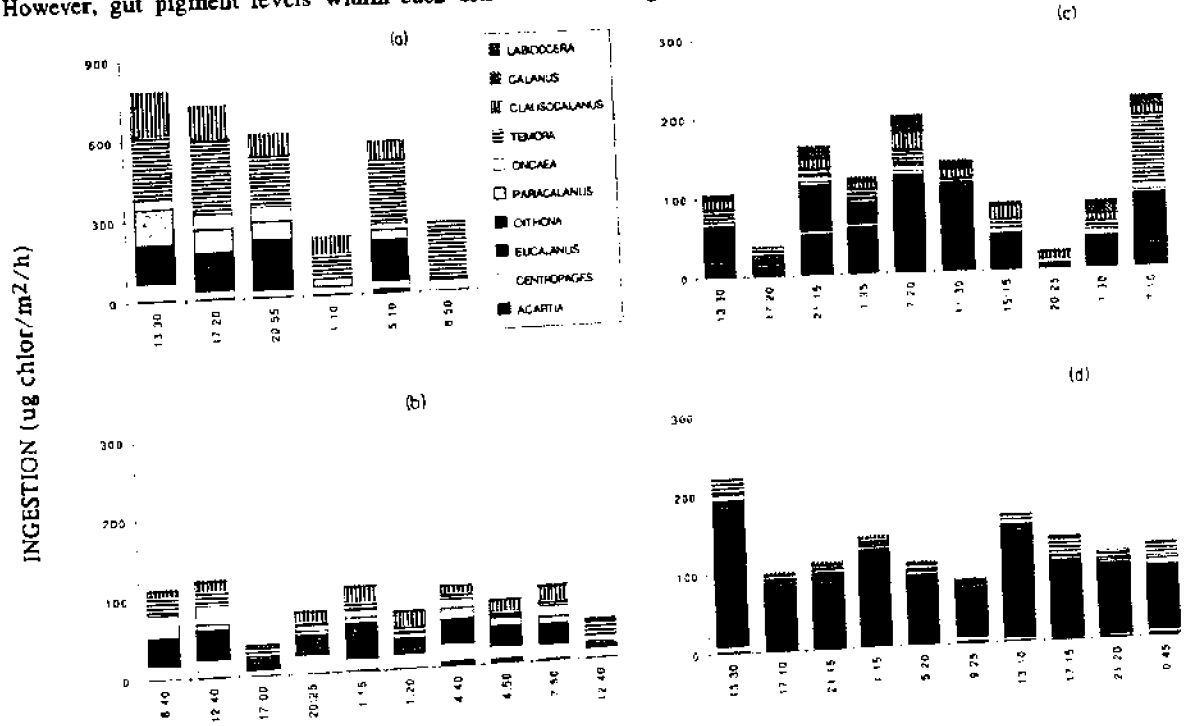

Fig. 2. The hourly ingestion of phytoplankton by the copepod community during each collection period at (a) the plume site in 9/91, (b) the shelf site in 9/91, (c) the plume site in 5/92 and (d) the shelf site in 5/92. Note the scale change for (a).

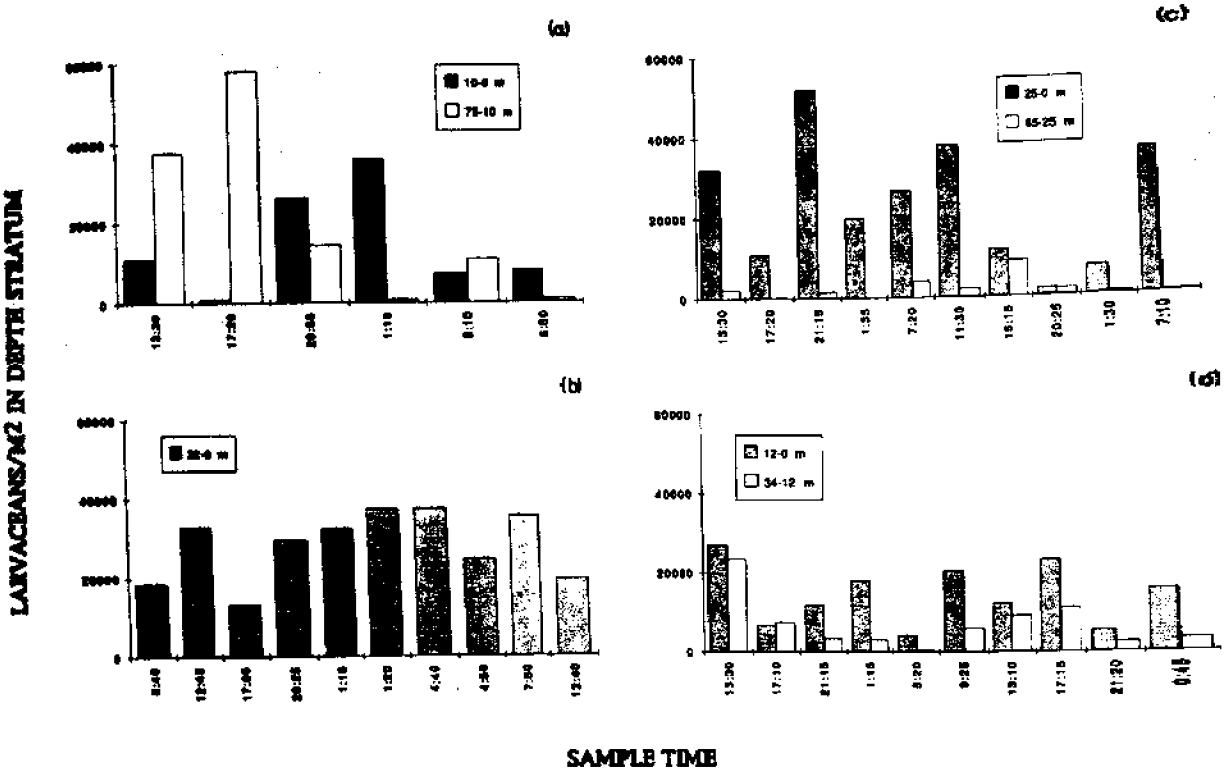

Fig. 3. The abundance of larvaceans near the sediment trap array at (a) the plume site in 9/91, (b) the shelf site in 9/91, (c) the plume site in 5/92 and (d) the shelf site in 5/92.

ingested chlorophyll to carbon are made accordingly and compared to phytoplankton production rates (Table 1) measured on these same cruises (Lohrenz *et al.* 1994). Except during 5/92 at the plume site, the copepod community ingested a significant fraction of the daily phytoplankton production.

Discussion

Grazing by the copepod community was only 4 - 5 % of daily phytoplankton production in plume waters during 5/92. This contrasts with higher rates, 14 - 62 %, in the plume during 9/91 and at the shelf site during both cruises. It is not possible to develop a clear understanding of patterns from only these two cruises but this observation appears consistent with the suggestion that copepods will not be an important component of the grazing community in the river plume until they have some time to numerically respond to the presence of phytoplankton food. In the plume region, copepod populations should increase throughout the spring in response to the spring maximum of riverine-stimulated phytoplankton production. Numerical response rates should also increase in the spring as water temperatures increase. Patterns observed in this study are consistent with these generalizations but more information is required to properly develop these arguments.

Other components of the zooplankton community may also ingest significant amounts of phytoplankton. Organisms less than 200um, including protozoans and small metazoans, may be important grazers but are not included in this analysis. High grazing rates by this microzooplankton community have been observed at both sites during other times of the year (Strom unpublished).

Another potentially important grazer is the larvacean Oikopleura dioica. Larvacans are typically abundant during spring, summer, and fall. For example, a detailed cross-shelf description of their abundance (Fig 6) and the associated physical and biological system parameters (Figs 4 and 5) was provided during April/93. The transect was run from slope waters directly north towards the inner shelf just south of the Atchafalya. Salinity, temperature and light transmission increased dramatically towards the inner shelf. Fluorescence was very low offshore and increased during the transect.

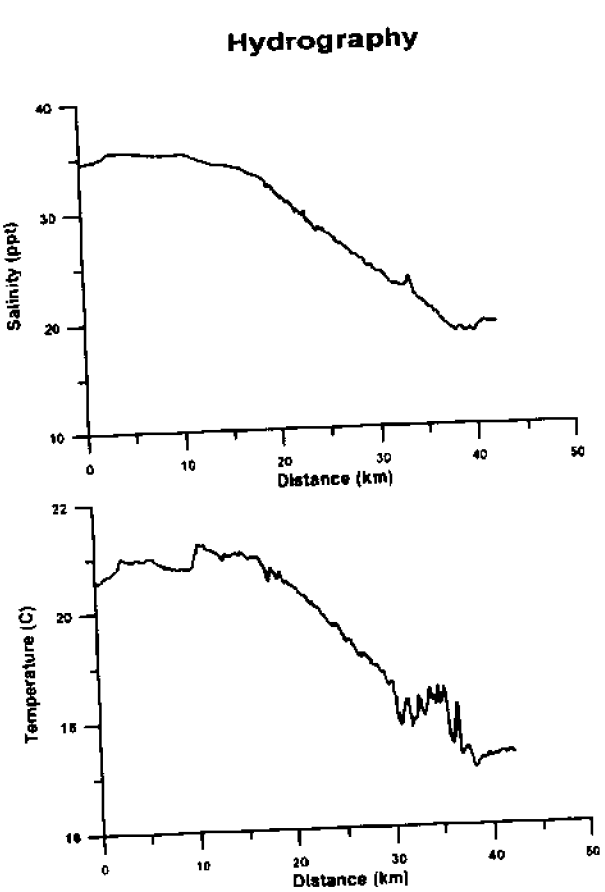

Fig. 4. Salinity (ppt) and Temperature (deg.C) continuously measured at 4m along a 42km shoreward transect south of the Atchafalya in April 1993.

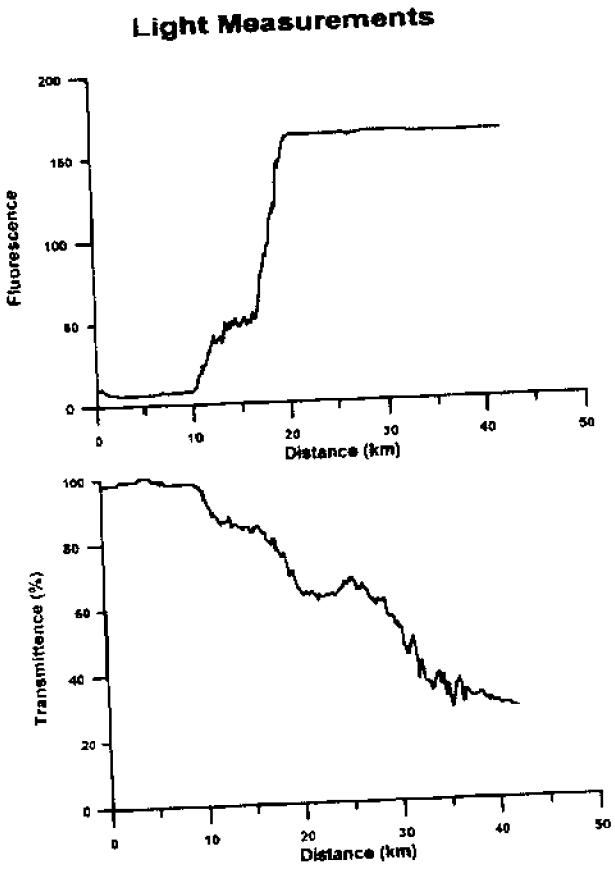

Fig. 5. Chlorophyll fluorescence (relative units) and visible light (400-700nm) transmittence continuously measured at 4m along a 42km shoreward transect south of the Atchafalya in April 1993. Fluorescence was offscale at values >162.

From about the 20km mark onwards, fluorescence was maximal for the instrument setting and the apparent plateau is not real. Since it appears to be closely correlated, albeit inversely, with transmittence it is likely fluorescence likely continued to increase shoreward. Larvaceans were abundant over most of the transect but especially so from km 25-35, attaining concentrations of several/liter at intermediate salinities and temperatures (ca. 25ppt and 19 deg.C). Lowest concentrations were at the innermost part of the shelf. Note that larvaceans were more abundant than small copepods except well offshore over the entire transect and that their changes in abundance were not well correlated. Moreover the larvacean distribution appears to be more patchy [at least on large spatial scales]. These differences are entirely consistent with larvacean biology since their rapid growth rate permits them to bloom and increase dramatically in abundance over periods as short as a few days (King *et al.*, 1980). Interestingly the dominant peak in larvacean (and small copepod) abundance are seen in acoustic returns at high frequencies but not at lower frequency (Fig 7).

The grazing impact of the larvacean population has not yet been not estimated for this transect but during the 9/91 and 5/92 cruises is estimated by calculating the carbon requirements for growth of the observed populations. These O. dioica were small, ranging between 200 and 600um trunk length (n=200 for each cruise). Calculated carbon requirements, which need not be met by phytoplankton only, are greater than requirements for the entire copepod community during 9/91 and only slightly less than requirements for the copepod community during 5/92 (Table 2).

A more direct estimate of phytoplankton removal by larvaceans can be obtained by applying the filtering rate of the larvacean community to the

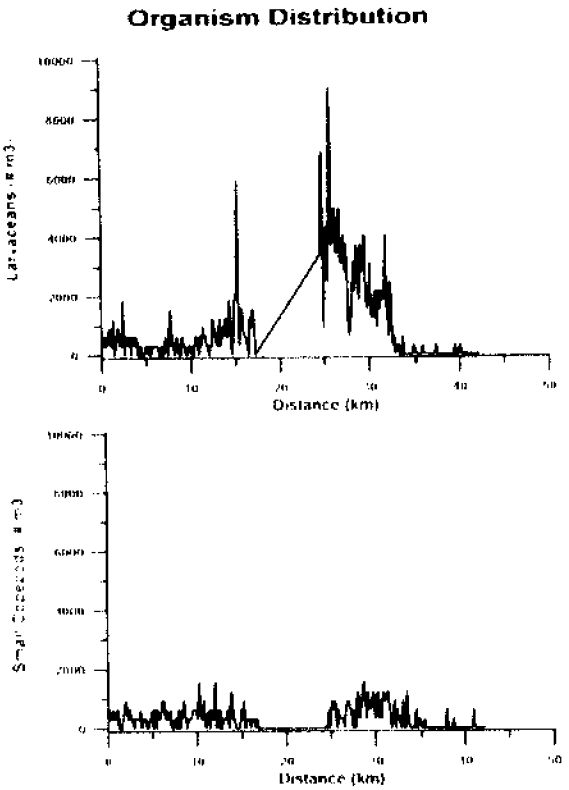

Fig. 6. Larvacean and small copepod abundance (#/m3) in unconcentrated pump samples collected at <1m depth along a 42km shoreward transect south of the Atchafalya in April 1993. Data were binned into 1 minute intervals (ca. 150m) that constitute 1800 individual video frames.

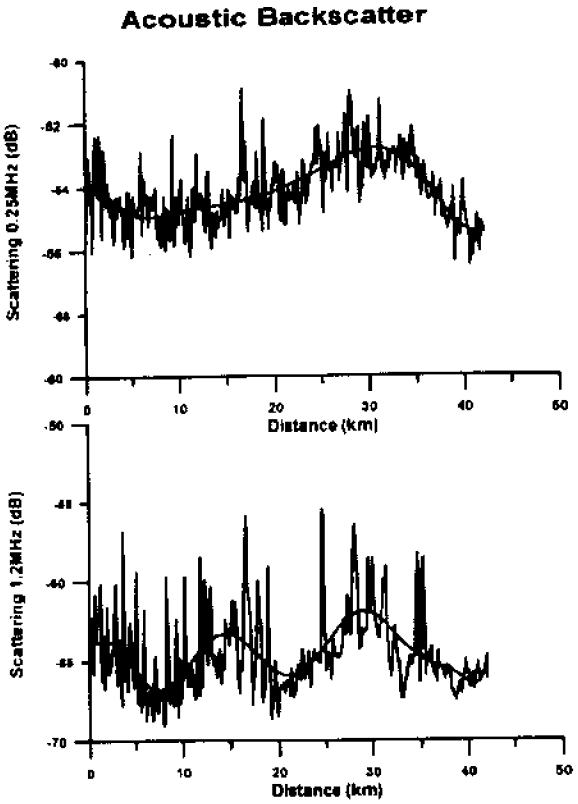

Fig. 7. Acoustic backscatter at 256KHz and 3.0MHz continuously measured at 4m along a 42km shoreward transect south of the Atchafalya in April 1993. Data were binned into 1 minute intervals (ca. 150m) that constitute 1800 individual video frames.

chlorophyll stock. Filtration rates are computed for each size of O. dioica from a relationship between filtration rate and trunk length (Alldredge 1981). Alldredge's measurements were made at 23.5oC and her relationship is applied directly to O. dioica for the 5/92 cruise. Resultant rates are similar to rates calculated by the energy demand method (Table 2). Estimates are not made with this method for the 9/91 cruise because of uncertainty in scaling up the calculation to the higher temperature. These high abundances and the calculated high ingestion rates support the argument that larvaceans are important grazers on phytoplankton in this region.

The input of new nutrients onto the continental shelf of the northern Gulf of Mexico greatly stimulates phytoplankton production, and large phytoplankton stocks are typically observed at intermediate salinities in plumes of the Mississippi River (Lohrenz *et al.* 1990). Grazing by the copepod community is an important

Table 2. Ingestion rates for the observed populations of *Oikopleura dioica* calculated from growth rates (1) and from filtration rates (2).

Date	Site	Depth (m)	Ingestion (1) (mg C/m2/d)	Ingestion (2) (mg C/m2/d)
9/91	plume	10 - 0	537.4	
		75 - 10	481.0	
		75 - 0	1018.4	
	shelf	32 - 0	1155.4	
5/92	plume	25 - 0	83.0	163.4
		65 - 25	8.5	17.1
		65 - 0	91.5	180.5
	shelf	12 - 0	50.8	83.7
		34 - 12	24.4	18.9
		34 - 0	85.2	102.6

source of mortality for this phytoplankton. Grazing from other components of the zooplankton community is as yet unquantified but indications are that protozoans and larvaceans can contribute significantly. If so, the primary fate of phytoplankton production in this plume system is to be grazed by zooplankton.

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BUOYANCY AND NUTRIENT EXCHANGE IN THE MISSISSIPPI RIVER OUTFLOW REGION

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Source Function Variability[1]

Daily-average water discharge values are plotted versus time for the lower Mississippi River (Figure 1). The time period shown spans the NECOP study period. Horizontal dashed lines near the top of the plot area correspond to NECOP-funded research cruise time windows. Asterisks are monthly averaged data points (per calendar month), and open octagons are annual average data points (per calendar year). Plotted sinusoid depicts the long-term (last forty years) annual average cycle of discharge with associated variation limits (shaded areas). Horizontal dashed line shows the long-term mean for the same period. Over the last several decades, approximately 80% of all monthly-average discharge values fall within the shaded region (10% above and 10% below). Most "outliers" are due to phase shifts in the annual cycle and do not exceed the absolute maximum or minimum of the shaded region. Note that the variation limits must be skewed in amplitude (~2:1) to account for the greater likelihood of

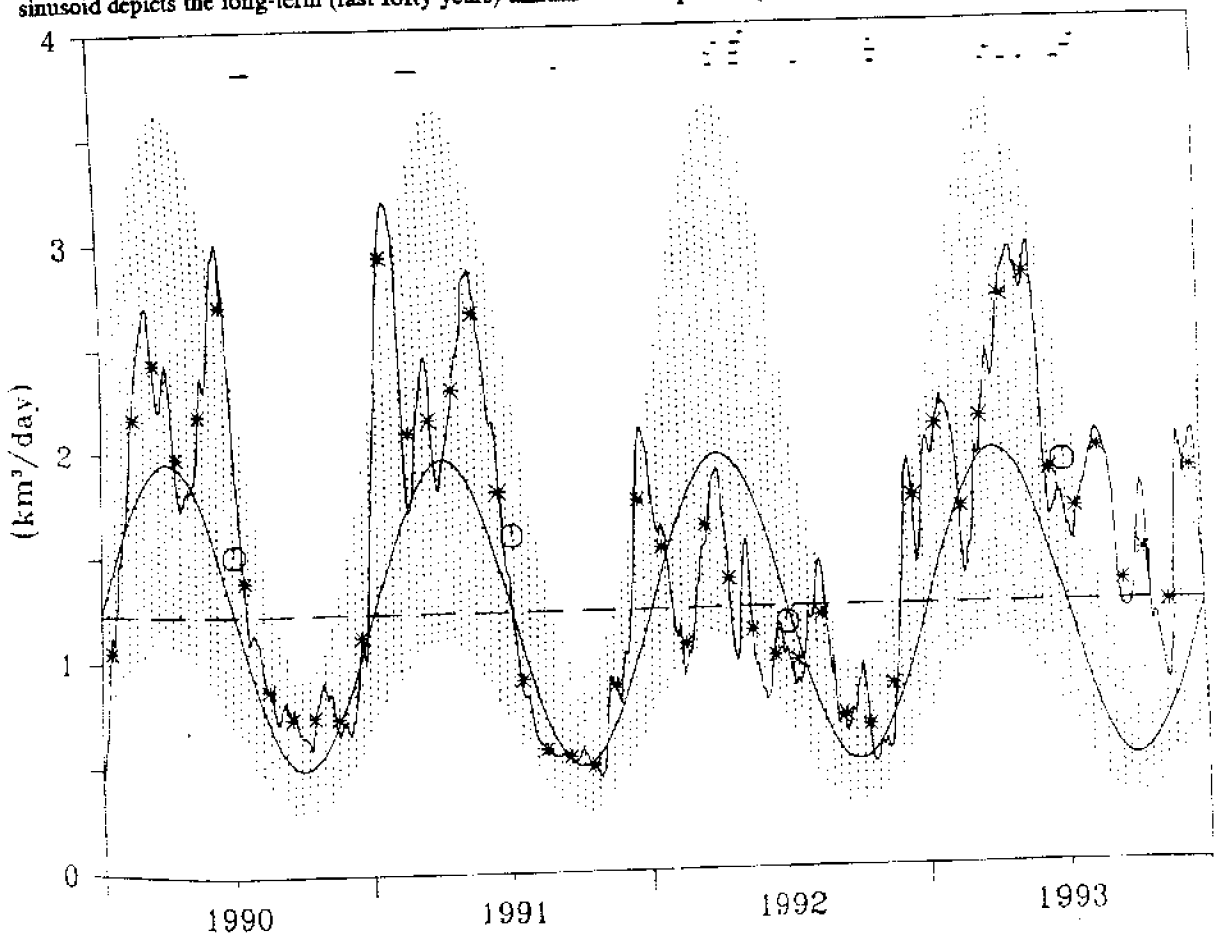

Fig. 1. Water discharge for the lower Mississippi River.

larger-than-average versus smaller-than-average flow events in a given month.

The annual average value for 1993 is about a 1-in-50 yr "event" based upon values observed since 1900. Elevated summer and fall flow is the anomalous aspect of this flow year as illustrated by the plot.

Hydrographic Fields and Fill Time Estimates[2]

Hydrographic survey data from four research cruises in the Mississippi River outflow region (Louisiana shelf) were analyzed. Data was collected for the NOAA Nutrient Enhanced Coastal Ocean Productivity (NECOP) program. Two cruises were aboard the Louisiana Universities Marine CONsortium (LUMCON) RV Pelican (12-19 April 1992 and 27 March-2 April 1993) and two were aboard the University of Texas RV Longhorn (14-21 May 1992 and 2-12 July 1993).

Louisiana shelf mean flow is generally westward from the Mississippi River Delta, and continuing past the Atchafalaya River Delta, over the winter and spring. Perturbations of this general flow are caused by east-to-west passage of cold fronts. Summer observations suggest possible flow reversal in the western portions of the region, with surface currents to the east.

The Mississippi River discharges into the northern Gulf of Mexico via the Mississippi Delta, of which an average 53% of the flow discharges directly to the west. Approximately 30% of the total Mississippi River System flow discharges via the Atchafalaya River 150 km to the west. Mississippi River daily discharge for the 1992 and 1993 NECOP survey cruise coverage was provided by the U.S. Army Corps of Engineers and was gauged at Tarbert Landing, MS, below the diffluence of the Atchafalaya River. Longterm monthly average flow have a maximum flow of ~22,000 m^3/s (±10,000 m^3/s) in April and a minimum flow of ~7,000 m^3/s (±2,000 m^3/s) in September. The 1992 flow was below average in the spring; while the 1993 flow was above average most of the year. At the time of the April 1992 survey daily discharges were ~15,000 m^3/s, ~6,000 m^3/s below the long-term average, but followed by three weeks the annual high flow of ~22,000 m^3/s. The May 1992 survey also followed a brief, relatively high flow period by two weeks, daily discharges were ~12,000 m^3/s, ~8,000 m^3/s below the annual average. The survey on April 1993 occurred before the annual high flow period; flows were ~27,000 m^3/s in April, ~5,000 m^3/s above the annual average. The highest flows in 1993 occurred in May and were ~35,000 m^3/s. For the July 1993 survey, flow was still ~5,000 m^3/s higher than the annual average, reaching ~18,000 m^3/s near the July cruise.

The general distribution of salinity had a fresher surface layer in the Mississippi Delta near-field (<100km) that evolved downcoast to meso-field (>100km) cross-shelf and vertical gradients. Surface salinities in 1992 had lowest values near the Mississippi Delta with strongest gradients gulfward. Low values extend <100 km to the west of the Mississippi Delta. Surface salinities >100 km to the west establish a parabathic pattern routinely seen on this shelf. Atchafalaya River outflow is seen against the coast west of the Atchafalaya Delta. Surface salinities in 1993 also had lowest values near the Mississippi Delta with the strongest gradients gulfward. There was an apparent surface freshening due east of the Mississippi Delta in April and due south in July. One hundred kilometers to the west the salinity contours again established a parabathic pattern. Atchafalaya River outflow was more readily observed on the inner shelf south and west of the Atchafalaya Delta.

The residence time of river discharge on the shelf is related to varying river discharge magnitudes. Residence times have been estimated for three regions for each of the four survey cruises. Region 1 corresponds to the near-field shelf west of the Mississippi Delta. Region 2 corresponds to the meso-field shelf at distances greater than 100 km from the Mississippi Delta outflow. Region 3 corresponds to the far-field shelf relative to the Mississippi Delta outflow but is the near-field shelf relative to the Atchafalaya Delta outflow.

Fill times are used to estimate the residence time of river water on the shelf. Fill time is defined as the length of time it took the river outflow to fill a volume of fresh water present on the shelf at any time.

The river outflows considered here are simply the Atchafalaya River discharge and that portion of the Mississippi River discharge flowing directly west. The volume of fresh water present on the shelf was determined as the volume sum of depth layers multiplied by the associated fresh water fraction, $f = (S_r-S)/S_r$, where S_r is a reference salinity chosen to be 36.3 °/oo, and S is the area weighted average salinity. Average salinity for each region was determined from area-weighted salinity fields produced from contoured cruise data at selected depths (1, 3, 5, 7, 9, 12.5, 17.5, 22.5, 27.5 and 32.5 m).

Regional fresh water volumes are presented in Table 1. In 1992 shelf freshwater volumes decreased from April to May. In 1993 shelf freshwater volumes increased from April to July. Both surveys in 1993 measured the greater volumes of fresh water on the shelf than surveys in 1992. The region proportion of freshwater volume was relatively constant for both surveys in 1992. In 1993 the proportions in the

Table 1. Fresh water volumes (in km^3) and proportion of total volume (in %) in the Mississippi and Atchafalaya Rivers outflow region.

Cruise	Region 1	2	3	Total
Apr 92	11.68	17.51	20.76	49.95
	23%	35%	42%	
May 92	8.14	12.55	14.04	34.73
	23%	36%	40%	
Apr 93	14.57	22.56	29.21	66.34
	22%	34%	44%	
Jul 93	17.05	25.66	46.63	89.34
	19%	29%	52%	

Mississippi Delta near- and meso-field regions decreased while the proportion in the Mississippi Delta far-field increased.

The vertical profiles of weighted salinity and fresh water fraction are similar, only the fresh water fraction is presented here for each region and cruise (Figure 2). The largest fresh water fraction in Region 1 is observed as a 10 m thick low salinity layer for each cruise. Region 2 again had most fresh water contained in a surface layer, but there is considerable more fresh water mixed to greater depths in the 1993 surveys. Although most of Region 3's fresh water is in a surface layer, the amount increases with depth.

Fill times can be determined for each region as if the riverine outflow discharged directly into the region itself (Table 2). This provides (and assumes a steady state in any upstream region) a lower limit estimate of residence time. In reality there will be a storage term (gain or loss of volume over time) for any upstream region. Although the limited data prevents a precise relationship, longer fill times (the fresh water is resident in a region longer) do occur during 1993, the higher discharge year. Region 3 appeared to be filled by the Atchafalaya River over approximately the same interval of time as Regions 1 and 2 were filled by the westward flowing Mississippi River flow. Using both flows the total regional freshwater volumes are filled in 1-1.5 months. Fill times for the Mississippi River near-field (Region 1) are < 2 weeks for moderate flows in 1992 and < 3 weeks for high flows in 1993. Fill times for the meso-field (Regions 2 and 3) are 30-50% longer during the high flows of 1993 than those for the moderate flows in 1992. Fill times in both years are very consistent between survey cruises.

Near-Field Variability of Nutrient and Bio-Optical Variables[3]

In order to understand the distributions of nutrient and hydrographic variables in the vicinity of the Mississippi River plume, relatively simple physical, nutrient, and biological model has been developed to test hypotheses resulting from the analysis of the hydrographic data sets. As part of the development of this model, multivariate analysis of several of the hydrographic data sets was performed to analyze the major components of variability within these data sets.

Intuitively and based on previous observations, one would expect several major components of variability associated with the Mississippi River plume. One major component would be the axis between the offshore relatively unmixed Gulf of Mexico water and the undiluted river water. It is expected that this component of variability would be correlated with salinity, nutrient concentrations, and suspended particulate matter concentrations. A second major component of variability is the vertical hydrographic gradients that are common to the coastal ocean. This component is often correlated with vertical gradients of temperature, salinity, and nutrients, and also with the distribution of phytoplankton biomass and pigments. A third component of the variability is likely to be correlated with phytoplankton productivity and biomass. This may be a part of the second component described or may be independent depending on the stratification and physical processes that determine the patterns of biomass and productivity. It is also common to have a

Table 2. Regional fill times (in days) using Mississippi and Atchafalaya River outflows.

Inputs	Direct Mississippi River			Atch. River	Miss. River	Both Rivers
	Region			Region	Total	Regions
Cruise	1	2	3	3		
Apr 92	10	19	22	29	69	31
May 92	11	19	22	27	45	29
Apr 93	14	24	33	39	68	41
Jul 93	19	26	40	49	69	42

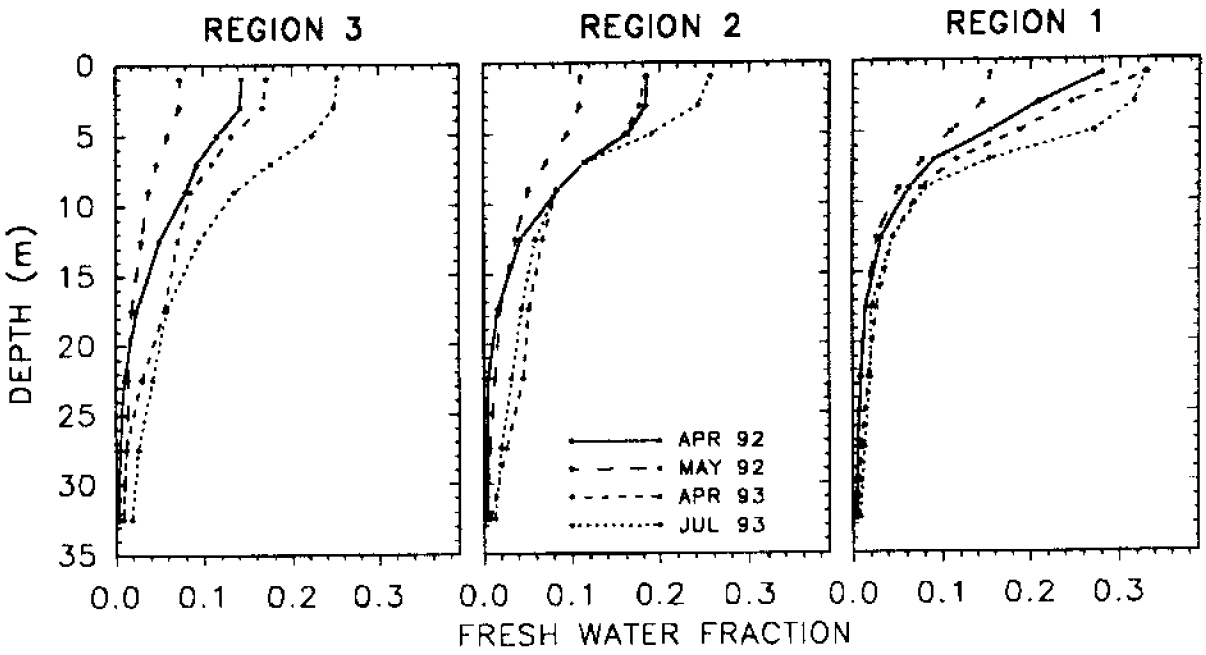

Fig. 2. Regional freshwater fraction for four survey cruises.

significant component of this variability dominated by ammonium and nitrite, indicative of nutrient regeneration processes.

In early July 1993 the R/V Longhorn hydrographic data set from that included relatively closely spaced stations in the vicinity of the Mississippi River outflow from Southwest Pass, the first three principal components accounted for 71% of the variability in the data set (Table 3).

Table 3. Results of principal components analysis of bottle variables.

	Principal component loading of each variable				
	1	2	3	4	5
% of variance	39.3%	21.8%	9.6%	7.3%	6.0%
Variable					
Temperature	-0.309	-0.739	-0.043	0.037	-0.211
Salinity	0.846	0.434	0.082	0.050	0.074
Sigma-t	0.811	0.522	0.083	0.037	0.104
Oxygen	-0.159	-0.598	0.086	0.086	0.432
Beam C	-0.878	-0.153	-0.073	-0.197	0.069
Chlor. Fluor.	-0.668	-0.474	-0.032	0.007	0.059
PO_4	-0.622	0.593	-0.045	-0.208	-0.064
SiO_4	-0.691	0.215	-0.142	-0.281	-0.144
NO_3	-0.703	0.544	-0.049	0.164	0.164
NO_2	-0.271	0.087	0.741	-0.425	-0.489
NH_4	-0.257	-0.049	0.743	0.358	0.397

The first component accounted for 39.3% of the variance, as expected it was dominated by salinity and beam c, indicative of high suspended particulate matter (SPM) concentrations. Other variables that contributed to this component include nitrate, phosphate, silicate, and chlorophyll fluorescence. The general trend of this component is that low salinity is correlated with high nutrients, SPM and chlorophyll fluorescence. The factor score for this component has the highest absolute value in the vicinity of Southwest Pass and decreases to the west and south.

The second component contained 21.8% of the variance in the data set. Temperature had the highest correlation with this component, suggesting that it may be related to the vertical structure in the water column. Oxygen and chlorophyll fluorescence were also correlated with this component, and nitrate was negatively correlated with this component. The trend in these variables are all consistent with the general pattern in vertical structure, but when mapped in the surface layer, highest absolute values are in the nearshore area and decrease offshore. In this particular component, the Mississippi River mouth and deep water appear to have similar values. So it appears that both the vertical structure and the biomass/productivity gradients are part of this component.

The third component accounted for less than 10% of the variance. It was strongly correlated with both nitrite and ammonium, indicating that it was

representative of nutrient regeneration processes in the system. In the surface layer it generally decreased from east to west, suggesting that there was a measurable input of both of these nutrients related to the Mississippi River plume. Either the plume contained elevated concentrations of these two nutrients, or the high organic load of the river was undergoing nutrient regenerative processes as it entered the coastal region. Oxygen concentration did not seem to have any relationship to this component in the July data set.

Another relationship of the variables in this analysis that has not been brought out in the above discussion is that beam c and silicate concentration, mapped closely with each other in principal component space. This may result from both beam c levels (SPM) and silicate being high in the Mississippi River. It may also suggest that there is significant regeneration of silicate occurring in relationship to high concentrations of SPM.

In this particular analysis, oxygen concentrations and temperatures are correlated with each other and with the second principal component. Both are relatively uncorrelated with the first principal component. This appears to be primarily correlated with the vertical hydrographic structure, and with primary productivity. One might infer from this result that low oxygen water is unrelated to the inputs from the Mississippi River water. However, the correlations that exist within a data set do not explain the pathways leading from one variable to another variable. Therefore, concluding that low oxygen water is not coupled to the nutrient input would not be warranted based on this analysis alone.

As in the source data, the gradients in the principal component scores are very large in the vicinity of the Mississippi River plume and indicate the spatial variability in this region is very large. In a study such as this, it is difficult to adequately resolve this variability.

Nutrient Concentrations in the Gulf of Mexico Resulting From Summer 1993 Mississippi/Atchafalaya River Outflows[4]

The discharge of the Mississippi/Atchafalaya Rivers (MAR) carries large quantities of dissolved nutrients of nitrogen, phosphorus and silicon and there are clear indications that their concentrations have increased in the river water over the past four decades as agricultural fertilizer application in the watershed have increased. The nutrients in the freshly discharged river are utilized rapidly by phytoplankton growth after entering the relatively low nutrient Gulf of Mexico waters. While dissolved silicon and phosphorus are important to support the phytoplankton growth, nitrogen in the form of nitrate is normally the most critical nutrient necessary to promote rapid plant growth. However, there are strong indications that the changing proportions of nitrogen, silicon and phosphorus in the river water have affected the amounts and types of plants that respond to the nutrient efflux.

The typical nitrate concentration observed at the mouth of the MAS ranges from 60 to 120 micromoles per liter. Values in the range of 150-200 micromoles per liter were measured in July 1993 during the period of flooding in the upper river basin. This corresponds closely to those values reported in the lower Mississippi River by Goolsby (in Dowgiallo, 1994) at that time. The excess water in 1993 that caused flooding appeared to mobilize more of the applied fertilizer than in a normal rainfall year and the higher than normal water speeds of the river may have increased turbidity and shortened transit time in the lower river which, in turn, reduced biological uptake and removal rates that occurred in the lower reach of the river proper.

The plume of the Mississippi River near Southwest Pass as defined by elevated nitrate concentrations was similar in size to the other summer periods from the previous six years, but the higher

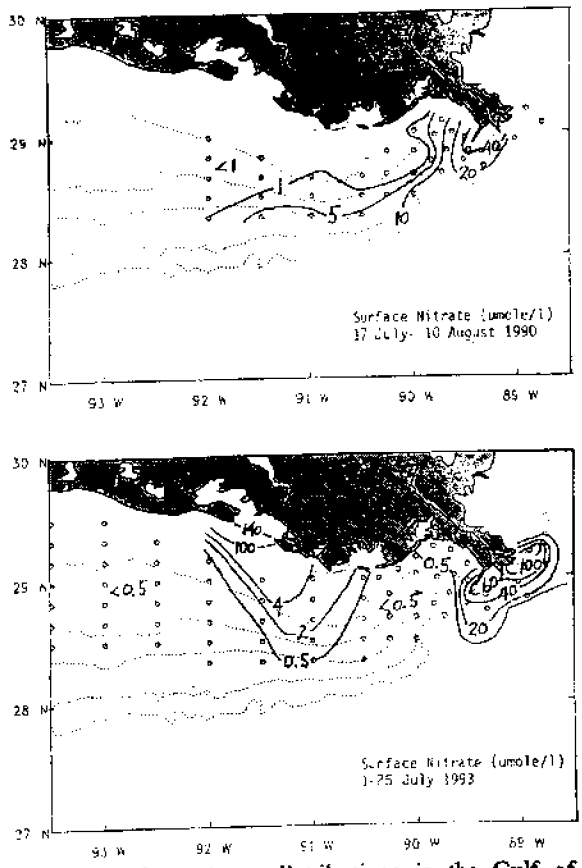

Fig. 3. Surface nitrate distributions in the Gulf of Mexico during July-August 1990 and July 1993.

initial concentrations meant that the horizontal gradients were also very large indicating rapid phytoplankton utilization (Figure 3). The uptake of nutrients was rapid enough to reduce concentrations to less than 1 micromole per liter within a 30 mile radius of the discharge point. Regenerated nutrients begin to become relatively important in this region since 40 to 80% of the available nitrogen is in the form of ammonium. As the discharged water moves even further away from the discharge points the regenerated nitrogen continues to be produced by microbial processes and maintains the enhanced productivity of the river water over a very large area. The total area affected as shown by enhanced chlorophyll concentrations during 1993 is still being assessed but it was certainly larger than normal.

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SILICATE LIMITATION ON THE LOUISIANA CONTINENTAL SHELF

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Abstract

Increased nitrogen and phosphorus but decreased silicon inputs to the Louisiana continental shelf from the Mississippi River may have increased the potential for Si limitation, changed the phytoplankton species composition and altered carbon flux and hypoxia. The occurrence of silicate limitation in the Louisiana coastal zone in the extended plume of the Mississippi River was assessed on one spring and one summer cruise, using four possible indicators, based on diatom silicon requirements, silicate uptake kinetics, and phytoplankton species composition. Three of the four indicators showed that Si limitation was pervasive during the spring cruise, but not the summer cruise. The fourth indicator, % diatoms/total autotrophs, was not found to be a reliable indicator of Si availability in this system.

Introduction

Nutrient enhanced coastal ocean productivity is often associated with large increases in dissolved inorganic nitrogen (DIN) and phosphorus (P) loading Ryther and Officer (1980) pointed out that since dissolved silicate (Si) either remains the same or decreases when the N and P loadings increase, the Si/N ratios can decrease substantially, leading to the potential for Si limitation of diatoms in the coastal zone. This in turn will lead to changes in phytoplankton species composition (Officer and Ryther 1980; Smayda 1989, 1990; Dortch et al. 1992), trophic structure, vertical carbon flux and hypoxia (Dortch et al. 1992 a,b, Conley et al. 1993).

Changes in nutrient availability and phytoplankton species composition have been observed recently in highly eutrophied coastal areas with large river inputs of nutrients (Conley et al. 1993), including the Louisiana continental shelf, which is impacted by the Mississippi River. Since 1950 DIN in the Mississippi River has increased while Si has decreased, so that the Si/N ratio of the water flowing onto the Louisiana shelf has decreased from approximately 4 to 1 (Turner and Rabalais, 1991). Based on nutrient concentrations and ratios from one spring and one summer cruise, Dortch and Whitledge (1992) concluded that at present Si limitation was more likely than other types of nutrient limitation. Justic' et al. (in press) have proposed that both the riverine nutrient inputs and concentrations are currently more balanced with regard to phytoplankton N, P, and Si requirements than they were 25 years ago, but that the potential for Si limitation in the coastal zone has increased. Supporting this hypothesis is evidence that Si uptake rates have increased over time and silicate reaches very low concentrations at much lower salinities now than in the past (Turner and Rabalais, in press). Rather than cause a species shift from diatoms to non-diatoms, Si limitation in this system appears to have so far only caused a shift to lightly-silicified diatoms (Dortch et al. 199 2a,b; Rabalais et al. submitted).

Several indicators of Si limitation can be used to determine the degree of Si limitation experienced by natural populations. Some of these would be more sensitive to Si limitation of uptake, whereas others would be a better indicator of limitation of growth.

1. *Ambient DIN and Si Concentrations and Ratios.*

Based primarily on data from phytoplankton culture experiments for nutrient uptake kinetics, nutrient uptake ratios, and ratios of particulate nutrients, Dortch and Whitledge (1992) proposed a series of criteria for distinguishing N, P, and Si limitation of natural populations based on ambient nutrient concentrations and ratios. The criteria for probable Si limitation are ambient Si/DIN ratios <1 and Si concentrations ≤ 2 μM.

2. *Degree of Limitation based on Si Uptake Kinetics.*

Si uptake as a function of Si concentration can be described by a rectangular hyperbola, represented by the following equation,

$$V = V_{max} \frac{Si}{Si + K_s} \quad (1)$$

where Si is the ambient Si concentration, V is the specific Si uptake rate (hr^{-1}) at that concentration, V_{max}

is the maximal uptake rate when the Si concentration is so high that Si uptake is independent of concentration, and K, is the Si concentration at 1/2 V_{max}. The K, and V_{max} are determined for any given population by measuring the Si uptake rate after the addition of increasing concentrations of Si to subsamples. We propose that if the Si uptake rate at ambient Si concentration is less than 75% of the V_{max} determined for that station and depth, then kinetic limitation of Si uptake is readily detectable. If V is > 75% V_{max} then assessing Si limitation kinetically is problematical (for example, Nelson and Tregeur 1992).

3. *Diatoms as a % of Total Autotrophs (% diatoms).*

Egge and Aksnes (1992) observed a hyperbolic relationship between % diatoms and silicate concentrations in mesocosm experiments, which suggest that the % diatoms may be a useful indicator of Si limitation.

4. *Phytoplankton, especially diatom, species composition.*

A shift from diatoms to non-diatoms would be the most obvious indication of Si limitation (Officer and Ryther 1980; Smayda 1989, 1990). However, in this system, which is nearly balanced with regard to availability of N, P, and Si (Justic' et al. in press), the abundance of specific diatoms may be a good indicator of Si limitation. For example, *Rhizosolenia fragilissima* is a very lightly silicified diatom (Conley et al. 1989), which has been observed at highest abundances at some distance from the river mouth when silicate concentrations are very low (Dortch et al. 1992 a & b).

As part of a larger study of Si cycling in the plume of the Mississippi River (Nelson and Dortch in prep.), we report here evidence of Si limitation from a spring and a summer cruise, using these indicators.

Materials and Methods

Cruises were conducted on the RV *Pelican* from April 24 to May 2, 1993 and July 24 to 29, 1992 in the area indicated in Figure 1. Standard hydrographic measurements were made at all stations with a SeaBird CTD system. Surface water samples were collected with a plastic bucket, due to the shallowness of the river plume at some stations, and at all other depths with Niskin bottles on a rosette.

Salinity was measured on bucket samples with an AutoSal salinometer. Nutrient concentrations were measured for all samples on frozen, unfiltered samples using EPA methods (No. 370.2, 353.2, 350.1, and 365.2, Anonymous, 1979). Chlorophyll *a*, corrected for phaeopigments, was measured fluorometrically (Parsons et al. 1984) on all samples.

Silicate uptake kinetics were measured using silicate labelled with the stable isotope ^{30}Si as a tracer,

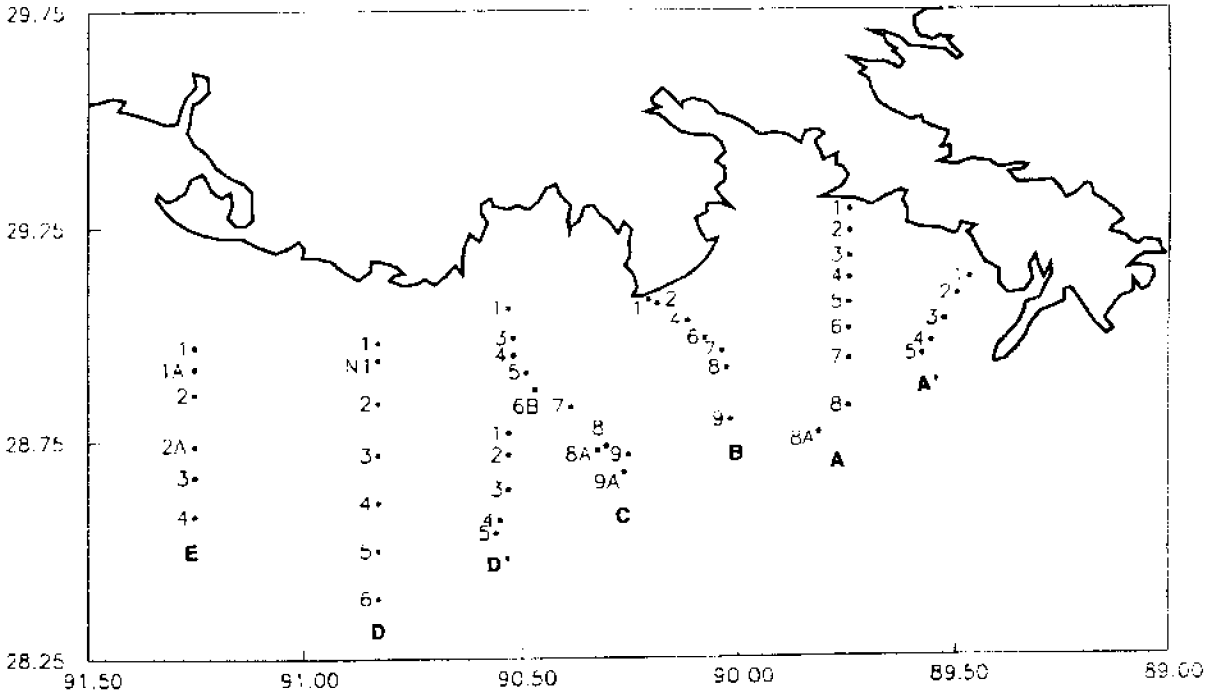

Fig. 1. Station locations on the Louisiana continental shelf, west of the Mississippi River Delta.

according to Nelson and Brzezinski (1990). These experiments were only run at selected stations, where rapid, high sensitivity silicate analyses (Brzezinski and Nelson 1994) indicated that ambient silicate was < 5 μM (1992: C9, C6B-7/25/, D2, D1 and 1993: B4, C3, C6B-4/27 and -5/2, D2, D4, D6, E2A, E4). Increasing concentrations of ^{30}Si were added to subsamples of seawater which were incubated on deck at simulated *in situ* temperature and light. Incubations were terminated by filtration after 1-4 hr, depending on biomass, and the samples were dried and stored for later analysis by mass spectrometry.

Phytoplankton were identified and counted (Dortch et al. 1992), using epifluorescence microscopy, on size-fractionated samples (0.2, 3, 8, and 20 μm) taken at approximately every other stations, including all Si uptake kinetics stations and at least one station at each end and in the middle of every transect (Fig. 1).

Results and Discussion

During the spring cruise salinities were significantly lower, whereas chlorophyll *a* was significantly higher than during the summer cruise (Table 1), as would be expected for high and low river flow periods. The order of magnitude higher phytoplankton numbers in summer reflects the shift from diatoms to cyanobacteria (Table 1). Since cyanobacterial size is much smaller than diatom size, the phytoplankton biomass maximum occurs in the spring, as indicated by the chlorophyll *a* data. DIN concentrations were also significantly higher during the spring cruise, as a result of the large riverine input (Table 1). Although the differences between these cruises are highly significant, there were strong gradients along the shelf (not shown).

There were no significant differences in either mean P or Si concentrations between the two cruises (Table 1). However, while P concentrations were quite uniform throughout the study area, Si concentrations showed strong gradients, especially during the spring cruise. The highest concentrations, besides those measured in the river, were observed near the river during the spring. Further, some of the lowest Si concentrations measured in any ocean, were measured on the western transects in the spring (Nelson et al. 1994). As a result of the high DIN and, frequently, low Si, the mean Si/DIN ratios were significantly lower in spring than summer.

All of the indicators (Table 2), except % diatoms (Table 1), showed that Si limitation was much more pervasive in spring than summer. Data for Si concentrations and ratios provided broad areal coverage and indicated that in spring Si was limiting at 50% of stations. Most of these were located on the C, D, D', and E transects (Fig. 1). The criteria, which were originally based on literature kinetic data, are supported by the kinetic data obtained in this system (Nelson et al. 1994). The kinetics experiments were run at stations where Si < 5 μM, so they tended to indicate more widespread limitation than the Si/DIN ratios and Si concentrations.

The occurrence of diatom indicator species suggested that growth as well as uptake was limited by Si availability during the spring. As had been observed in earlier data (Dortch et al, 1992 a, b), *Rhizosolenia fragilissima* tended to occur under conditions of low Si availability. It also varied inversely with the numbers of other more heavily silicified species, such as *Skeletonema costatum* (not shown). However, several species with which it tends to co-occur and which have also been proposed as indicators of low Si availability, occurred only infrequently on either cruise and could not be included. Instead *Chaetoceros socialis* was observed only on the spring cruise and only at stations with very low Si concentrations and very low numbers of diatoms with higher Si requirements, such as *S. costatum*. Although this had been observed earlier, it was never quantified (Dortch unpublished), but suggests it may be a good of Si limitation. Recent data from the Bay of Brest supports this hypothesis (Ragueneau et al. 1994). Obviously, many environmental factors besides Si availability determine the distribution and abundance of particular species. These data are part of an extensive 5 yr data set (approx. 2000 samples) for this region which is nearing completion and which will be analyzed more systematically for diatom species which will serve as indicators of Si availability for growth.

The highest % diatoms was found during spring when all other indicators suggested pervasive Si limitation. Given the conclusiveness of the other evidence, it seems unlikely that this discrepancy means that Si limitation is unlikely. Rather, for several reasons it suggests that the % diatoms is not a reliable indicator of Si limitation in this system.

The studies of Egge and Aksnes (1992), who first proposed the relationship between Si concentration and % diatoms, were conducted in large bags of natural populations, to which high nutrient seawater was added at frequent intervals. Thus, these bags represented quasi-steady state chemostats, making it easier to observe possible relationships. In the plume of the Mississippi River, growth is more similar to a batch culture where the highest concentrations of phytoplankton (or diatoms) are observed just as the limiting nutrient becomes depleted. Since riverine inputs of both N and Si are higher in the spring, the yield of diatoms is higher, but they are more likely to be Si limited.

Table 1.Comparison of environmental conditions and phytoplankton species composition from 0 to 5 m in study area (Fig. 1) during spring and summer. SD=standard deviation; n=number of samples, *=means significantly different. Student's t-test, $p<0.01$.

		Spring April 24-May2 1993		Summer July 24-29 1992
Salinity (°/oo)	Mean	23.48	*	27.56
	SD	4.564		3.805
	n	68		51
Chlorophyll *a* ($\mu g\ liter^{-1}$)	Mean	25.11	*	5.21
	SD	16.449		7.831
	n	68		51
Silicate (Si) (μM)	Mean	6.63		3.85
	SD	12.312		4.463
	n	67		50
Phosphate (μM)	Mean	0.33		0.25
	SD	0.338		0.173
	n	67		50
Dissolved Inorganic Nitrogen (DIN, μM)	Mean	10.36		1.37
	SD	16.550		2.112
	n	67		50
Si/DIN (by mole)	Mean	0.39	*	3.79
	SD	0.438		3.694
	n	67		50
Total Autotrophs (# cells $liter^{-1}$)	Mean	2.24×10^7	*	5.20×10^8
	SD	1.27×10^7		3.88×10^8
	n	56		40
Diatoms/Total Autotrophs (%)	Mean	61.28	*	0.28
	SD	22.951		0.689
	n	56		40
Cyanobacteria/Total Autotrophs (%)	Mean	26.06	*	99.10
	SD	18.877		1.266

In this system, which is nearly balanced with regard to N, P, and Si riverine inputs and availability in the coastal zone (Justic' et al. in press), the extreme consequence of Si limitation, dominance by flagellates, does not occur. Instead, there is a switch to diatoms with lower Si requirements, which would, of course, be included in % diatoms. Thus, % diatoms is not a sufficiently sensitive indicator to be reliable.

Diatom abundance may be affected by some other environmental factors, as well. The association of diatoms with spring blooms and pulses of nitrate suggests a high N requirement. However, during the summer flood of 1993, spring-like DIN concentrations were observed on the Louisiana shelf (Rabalais et al. 1994), Si concentrations exceeded 40 μM (Dortch unpublished), but diatom concentrations, although higher than normal for summer, were lower than the usual spring concentrations (Dortch 1994). The small coccoid cyanobacteria which usually dominate in summer were stimulated the most by enhanced nutrient availabilities

Table 2. Comparison of indicators of Si limitation during spring and summer. Specific criteria for Si limitation described in footnotes[1,2,3,4] and Introduction. %=number of stations meeting specified criterion for Si limitation/number of stations with specified data available; n=number of stations with specified data available.

Indicator of Si Limitation		Spring April 24-May2 1993	Summer July 24-29 1992
Si Concentration and Si/DIN ratio[1]	%	58.2	4.0
	n	67	50
Si Uptake Kinetics[2]	%	79	25.0
	n	9	4
Species Composition			
Rhizosolenia fragilissima[3]	%	33.0	10.0
	n	51	38
Chaetoceros socialis[4]	%	33.0	0.0
	n	51	38

[1]Si≤2 μM and Si/N<1
[2]Specific Si uptake rate (V, hr^{-1})<75% maximum specific Si uptake rate (V_{max}; hr^{-1})
[3]Si ≤2 μM and *R. fragilissima* (# cells $liter^{-1}$)/total diatoms (# cells $liter^{-1}$)*100 ≥ 10%
[4]Si ≤2 μM and *C. socialis* (# cells $liter^{-1}$)/total diatoms (# cells $liter^{-1}$)*100 ≥ 10%

in summer 1993 (Dortch 1994). Analysis of data from 1990-1993 indicates that cyanobacterial numbers are correlated with temperature, whereas diatoms reach a maximum at intermediate temperatures and then decrease (Parsons and Dortch, unpublished). Whether the controlling factor is temperature or some other related factor, it is clear that % diatoms is not sufficiently determined by Si concentrations in this system for the % diatoms to be an indicator of Si availability.

Conclusions

1. The spring, 1993 cruise was characterized by lower salinities and higher DIN, chlorophyll and diatom abundance than the summer, 1992 cruise.
2. Three out of four proposed indicators showed pervasive Si limitation in the plume of the Mississippi River in spring, 1993, but not in summer, 1992.
3. The fourth proposed indicator, % diatoms, was not found to be a reliable indicator of Si limitation in this system.

Acknowledgements

This research was supported by the NOAA Coastal Ocean Program OFfice, Nutrient Enhanced Coastal Ocean Producivity (NECOP) study grant no. NA90AA-D-SG691 to the Louisiana Sea Grant College Program, award nos. MAR 92-02, 31 and 92-07, and grant no. NA26RG0274-01 to the Oregon Sea Grant College Program. Invaluable technical assistance was provided by Julie Arrington, Ben Cole, Jim Lee, Dana Milsted, Tom Oswald, Suzan Pool, Randy Robichaux and Lorene Smith.

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ORGANIC MATTER DECOMPOSITION, NITROGEN RECYCLING, AND OXYGEN CONSUMPTION IN THE MISSISSIPPI RIVER PLUME/GULF SHELF REGION

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Introduction

The Mississippi River is one of the largest rivers in the world, ranking sixth in terms of discharge and seventh in terms of sediment load (Milliman and Meade 1983). The Mississippi drains an extensive area covering 41% of the contiguous continental USA (Turner and Rabalais 1991) that includes agricultural lands and major metropolitan centers. An understanding of the dynamics of materials introduced by the Mississippi into the Gulf of Mexico is necessary to quantify the impact of the River on the coastal ecosystem. The outflow of the River contributes more than 70% of the freshwater input into the Gulf of Mexico (Deegan et al. 1986) and is a major source of organic (Malcolm and Durum 1976) and inorganic materials (Fox et al. 1987; Turner and Rabalais 1991). The discharge of these materials into the Gulf is likely to significantly affect the productivity and trophic dynamics of coastal ecosystems. Riverborne inorganic nutrients appear to support the high rates of primary production measured on the Louisiana continental shelf (Sklar and Turner 1981; Lohrenz et al. 1990), and the subsequent decomposition of this freshly produced organic matter in addition to organic matter introduced by the river contributes to the observed hypoxic conditions during the summer in bottom waters near the Mississippi River delta (Rabalais et al. 1991).

Decomposition of organic matter, mediated by bacteria and other heterotrophic organisms, is critical to both nutrient supply and oxygen depletion in the Gulf of Mexico. Organic matter decomposition resupplies mineralized nutrients to primary producers and also exerts an oxygen demand that contributes to the development of hypoxia during the summer in bottom waters near the Mississippi River delta. Heterotrophic bacteria are the major consumers of dissolved organic matter (DOM) (Wright 1984) and dissolved oxygen (Williams 1984) whereas animals also contribute to the breakdown and mineralization of particulate organic matter (POM). Estimates of bacterial growth, total community respiration, and nutrient mineralization rates are therefore critical to understanding the cycling of key bioreactive elements, such as C, N, P, and O, in the Mississippi River Plume/Gulf Shelf (MRP/GS) region, and the development of hypoxia in certain regions.

The dynamics of organic matter decomposition depend on the chemical nature of the organic substrates that in turn reflects their sources. Results from the initial NECOP study indicate that "newly-produced" autochthonous organic material in the plume is often more important to nutrient mineralization and oxygen consumption than is organic matter delivered directly from the River. However, in the winter, organic matter delivered from the river accounted for much of the bacterial production. More seasonal studies were clearly needed to define the dynamics of organic matter mineralization and its effects on nutrient and oxygen dynamics in the MRP/GS.

Rates of degradation of organic matter by bacteria and other heterotrophs must be measured to understand the effects of the Mississippi River on the ecology of the MRP/GS and the development of hypoxia in regions offshore from the plume. Degradation of river-derived organic material may supply nutrients and cause an oxygen demand in the region. Nitrogen recycling by heterotrophic organisms in the pelagic (Dugdale and Goering 1967; Harrison 1978; Selmer 1988) and benthic regions (Rowe et al. 1975; Blackburn 1979) is a major process providing ammonium nitrogen to primary producers in coastal marine environments.

Our initial NECOP investigation (Benner et al., 1992) focused on respiration/ammonium regeneration experiments in large dark-bottle experiments and on comprehensive spatial studies of bacterial and DOM dynamics across the salinity gradient. In addition, several analytical and bioassay approaches were developed and evaluated to study DOM/bacterial dynamics (see above sections and Appendices). A

major conclusion was that nutrient recycling through DOM and POM via bacteria and other heterotrophs was a major factor providing nutrients to primary producers in the MRP/GS. Also, bacterial oxygen demand was sufficient to cause hypoxia in waters below the pycnocline in a matter of weeks. There is a clear need for more spatial and temporal coverage of heterotrophic bacterial dynamics in the MRP/GS, as we observed quantitatively large differences in process rates among the initial cruises at different seasons as well as among sites within a cruise. Using new approaches developed during NECOP-1, we have expanded these results to spatially and temporally quantify the importance of community and heterotrophic mineralization of organic matter to phytoplankton nitrogen demand and to oxygen depletion in the MRP/GS.

To achieve the above goal, we have examined the following hypotheses:

1. Remineralization of autochthonous organic matter is a major source of nitrogen for primary production in the euphotic zone and of oxygen demand in the bottom waters of the MRP/GS region.

2. Highest decomposition rates for autochthonous organic matter occur in the euphotic zone near the regions of maximum primary productivity.

3. Heterotrophic bacteria grow more efficiently in the plume than in the river.

4. River-derived organic matter provides a higher proportion of total bacterial substrate demand in the winter than in the summer.

These hypotheses are being examined by addressing the following objectives:

1. Determine nitrogen regeneration rates and oxygen consumption/carbon dioxide production rates seasonally at selected sites from the Mississippi outflow through the hypoxic region in the MRP/GS.

2. Determine the abundances, rates of production, and growth efficiencies of heterotrophic bacterioplankton and determine the importance of bacteria relative to total-community nitrogen cycling and oxygen consumption rates at selected sites.

3. Determine the seasonal concentration, chemical nature, and likely source of labile organic compounds, by bioassay and chemical/isotopic analyses, to estimate the relative contribution of compounds from different sources in removing oxygen from the region of hypoxia.

Herein, we report on our results for four major NECOP 'process' cruises (7-8/90, 2/91, 5/92, and 7/93) and a subset of these data from other NECOP cruises although, at this time, not all of the sample analyses are complete and data analyses are in-progress. During each 'process' cruise, detailed studies were conducted for several key stations: the river mouth, two plume regions, the hypoxic region, and open Gulf water (figure 1). Other, less detailed measurements, were made on transects covering the whole salinity gradient. Results, presented in summary graphs, include seasonally defined rates and mechanisms of organic matter mineralization/nitrogen regeneration by bacteria and other heterotrophs at different depths and regions in the plume and probes of the sources and composition of organic matter being mineralized. This information will be particularly critical to the NECOP Program's second and third main goals, i.e., to determine the impact of nutrient-enhanced coastal primary productivity on water quality (particularly dissolved oxygen demand), and to determine the fate of carbon fixed in highly-productive coastal areas of the outflow region.

Approach

We made the following three complementary types of measurements to examine organic matter degradation and nutrient regeneration in the MRP/GS:

1. Community nitrogen regeneration (ammonium production) and respiration (oxygen consumption/carbon dioxide production) rates in short-term bottle experiments, conceptually described in figure 2.

Determination of community metabolic rates by measuring concentration changes of specific compounds, such as ammonium, oxygen, or carbon dioxide, in closed bottles over time provides an integrative picture of the mineralization process and provides information that is directly relevant to nutrient supply and oxygen removal processes in the MRP/GS. Nitrogen regeneration is important in marine systems such as the MRP/GS because nitrogen supply rate is often the major factor limiting primary production (Ryther and Dunstan 1971). Quantification of nitrogen recycling rates in aquatic systems is hindered by the fact that long-lived radiotracers are not available for nitrogen. Instead, the stable isotope, ^{15}N, is used for isotope dilution studies. Analysis of ammonium regeneration by conventional emission or mass

spectrometry method requires that ammonium be removed from the water, dried, and converted to N_2 before analysis (Blackburn 1979; Caperon et al. 1979; Glibert et al. 1982). To simplify mineralization rate measurements, we have developed a new HPLC technique to directly fractionate and quantify the two isotopes of ammonium after direct injection of seawater filtrate from previously spiked (2-4 mM $^{15}NH_4$) experimental bottles (Gardner et al. 1991). Although not suitable for tracer level additions, that are required for waters with very low regeneration rates, the method has yielded measurable rates for MRP/GS plume waters. The small sample-volume requirements (5 ml) make it particularly suitable for measuring changes after experimental manipulations (e.g. bacteria additions, see below).

There are still surprisingly few direct measurements of respiration rates in the ocean (Williams 1984) because of the historical lack of precision in determining small changes in the concentration of dissolved oxygen or CO_2 in samples over short time periods. Although much progress has been made in the use of oxygen electrodes (Langdon 1984; Griffith 1988), we have found that they lack the needed reliability and precision. The precision of the classical Winkler method for oxygen measurements has been enhanced considerably by the use of photometric, amperometric, and potentiometric techniques to determine the end point of the titration (Williams and Jenkinson 1982; Culberson and Huang 1987; Oudot et al. 1988). The photometric method is the most precise of these techniques but it cannot be used on turbid samples. We used an automatic titration system with a potentiometric detector that can accurately and precisely determine oxygen consumption rates and heterotrophic carbon mineralization rates in the water column. In addition, we measured short-term respiration rates of labile DON using tritium-labeled amino acids. A high proportion of bacterial production can be supplied by amino acids in marine systems (Fuhrman 1990).

2. Bacterial abundances, production rates, and growth efficiencies.

Heterotrophic bacteria consume a large fraction (20-40%) of primary production, primarily as dissolved organic matter (DOM), and may be important components of food webs in aquatic ecosystems (Azam et al. 1983; Ducklow 1983). Bacteria are important to nutrient cycling and therefore affect the total productivity of a system. The measurement of bacterial production is a powerful approach for estimating the contributions of heterotrophic bacteria to overall metabolism in ecosystems. The supply of bacterial biomass potentially available to grazers can be determined from rates of bacterial production, and if the average growth efficiency of the bacterial population is known or estimated, production rates can be used to calculate the total utilization of organic carbon and consumption of oxygen by bacteria. In addition, rates of bacterial production can be used as a sensitive indicator of the response of bacteria to spatial and temporal fluctuations in environmental conditions. These measurements have allowed us to differentiate the bacterial component of the mineralization process from that of the total heterotrophic community. Comparison of bacterial demand for nitrogen, carbon, and oxygen at different sites also provided intra-site comparisons for bacterial turnover in different regions of the MRP/GS.

3. DOM (and DIC) characterization and activity measurements.

Examination of the concentrations and compositions (chemical and isotopic) of DOM as a function of salinity provides useful information about the reactivity and potential ecological role of DOM as the river water passes through the MRP/GS. Isotopic characterization and careful quantification of DIC (dissolved inorganic carbon) in relatively deep waters (isolated from atmospheric exchange) and in bottle experiments has provided insights on the origin of recently mineralized organic carbon. Examination of potential availability and turnover rates of specific labile components of the DOM (e.g. amino acids) allowed us to compare the activities of these known compounds at different sites. Bioassays of DOM by measuring process rates after addition of various levels of concentated bacteria provided further information about the nature of labile DOM at the different sites.

Results

Summary results are presented in the following figures complete with interpretative legends:

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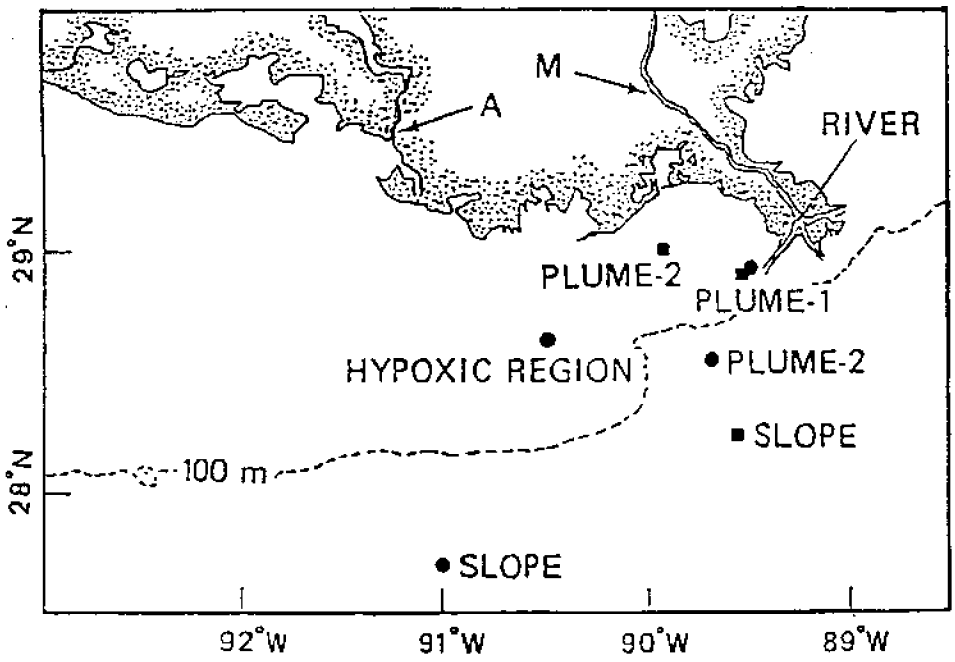

Figure 1. Generalized cruise plan. Each of the NECOP Process Cruises sampled along salinity transects from the Mississippi River (later including the Atchafalaya River) out to open Gulf water. Several mid-salinity stations were included. Major incubation studies were conducted at each site.

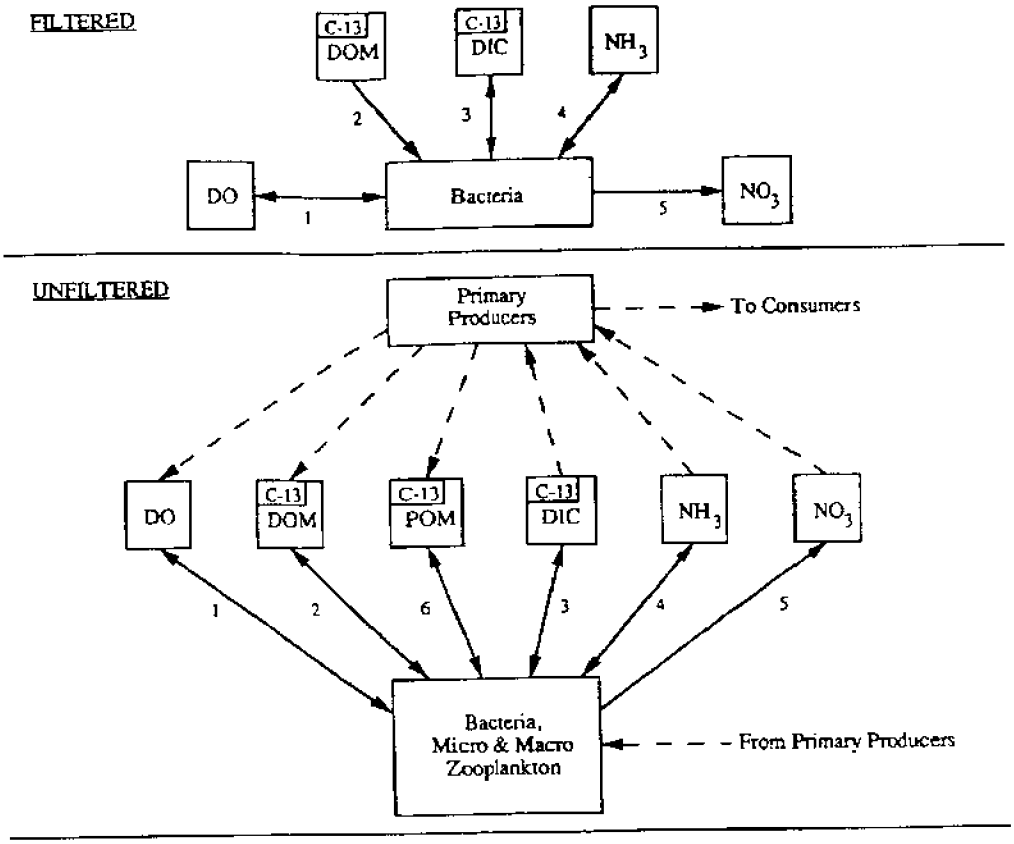

Figure 2. Conceptualized incubation experiments. On the July 1990 and Feb 1991 cruises, both filtered (1mm) and unfiltered incubation experiments were conducted. On later cruises only unfiltered incubations were run. Process rates measured and summarized in following figures included: 1) O_2 depletion, 2) DOC depletion, 3) remineralization of organic carbon, 4) NH_4 production and assimilation, 5) nitrification, 6) POC depletion and bacterial growth rates and abundance.

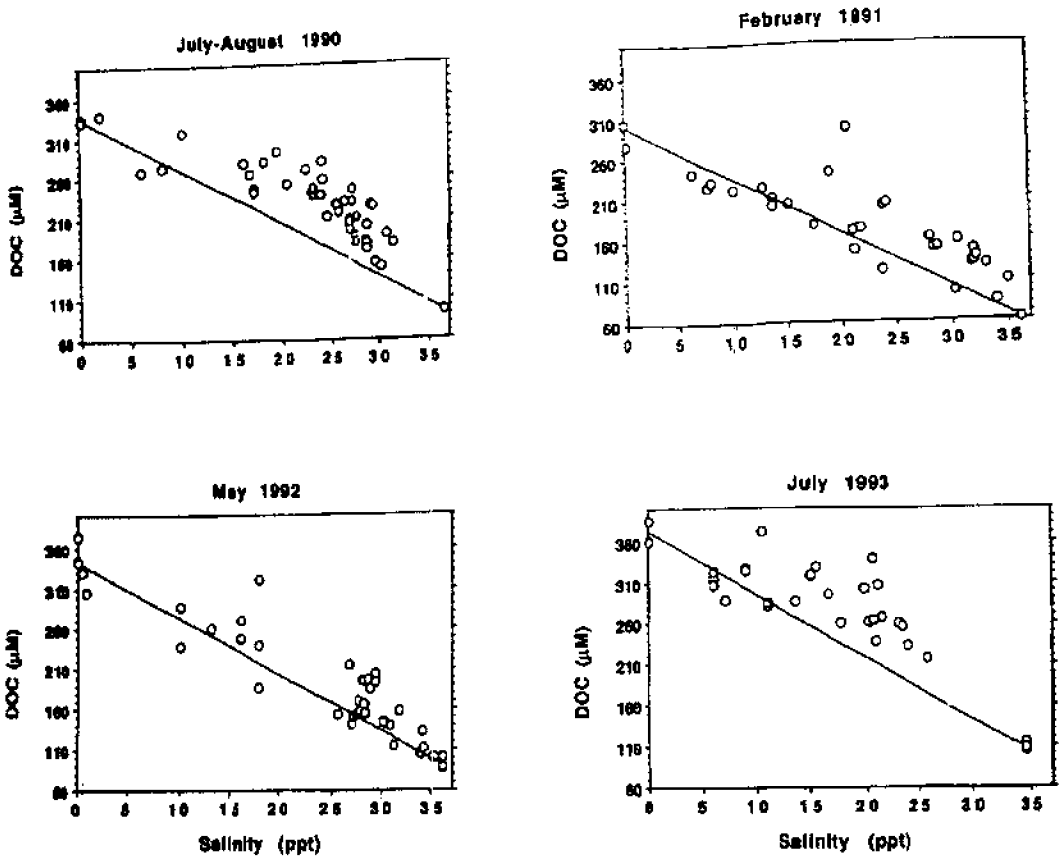

Figure 3. DOC results from four cruises are presented as concentration vs salinity. The lines represent a conservative mixing model, data above the line indicates local production. All cruises show mid-salinity DOC production, presumably from phytoplankton. River and open Gulf DOC concentrations remained within a narrow range for all of the cruises

Concentrations of DOC were measured by high- temperature combustion using a Shimadzu TOC 5000 analyzer and a Pt catalyst (Sugimura and Suzuki 1988). Water and instrument blanks were be measured daily, and DOC measurements were blank-corrected as described by Benner and Strom (1991). Water samples for the measurement of DOC were filtered (combusted GF/F filter) and acidified (pH=2) immediately following collection using procedures that have been shown to be noncontaminating (Benner and Hedges 1991). Note, there is considerable controversy over the measurement of DOC (see Williams and Druffel 1988), and a workshop, sponsored by the National Science Foundation, the National Oceanographic and Atmospheric Administration and the Department of Energy, on the measurement of DOC and DON was recently held in Seattle, Washington, to discuss recent developments in the field. As a part of this workshop, the results from a large comparison of the DOC content of four different natural water samples were presented to help determine the magnitude and sources of variability in DOC measurements by different laboratories. A total of 34 independent laboratories using 20 different types of insturments participated in the DOC comparison. A major conclusion from that comparison was that operator-dependent factors, such as blank determination and treatment, are more important sources of measurement variability than instrument design (Hedges et al. 1991).

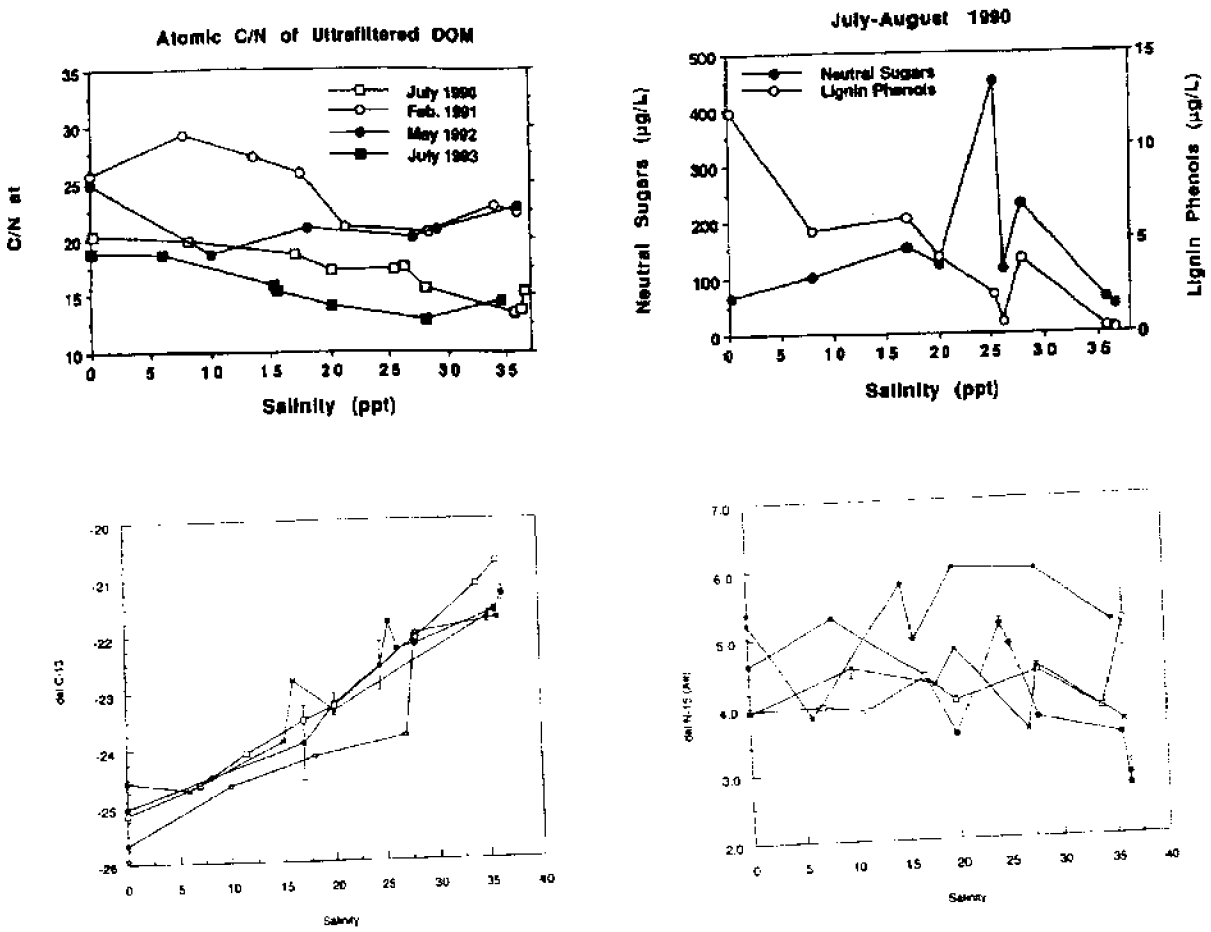

Figure 4. Chemical characterization of high molecular weight (HMW)DOM. HMWDOM was isolated from large volumes (200 l) for thorough chemical and isotopic characterization (Benner 1991). Water samples were prefiltered through 0.2 mm pore-size polycarbonate cartridge filters followed tangential-flow ultrafiltration system with 1000 Dalton cutoff. The concentrated DOM was then diafiltered to remove salts and freeze-dried for chemical and isotopic analysis. The high molecular weight DOC constituted between 25 and 50% of the total DOC.

Some summary analyses are presented as quantity vs salinity plots. The atomic C/N ratio of the HMWDOM are high compared with POM (C/N ~ 9) and seasonally variable. Neutral sugar analyses were measured because carbohydrates appear to be a major component of ultrafiltered DOM isolates and may carry information about the biological sources and diagenetic stage of this material (Cowie and Hedges 1984b). Lignin determinations (Hedges and Ertel 1982; Benner et al 1990b) provides sensitive characterization of these biomarkers of vascular land plants. Stable carbon and nitrogen isotopes for the four cruises show the characteristic C-13 shift across salinity gradients, but much less change in the N-15. The values are within a relatively narrow range across time.

Although not presented, we have applied a bioassay approach to estimate the relative availabilities of DON in the river and in the plume. Bacterial-concentration/addition experiments have provided information on the importance of bacteria relative to other heterotrophs in community mineralization/respiration and on the amount of "labile" DON that is available relative to microbial community growth requirements.

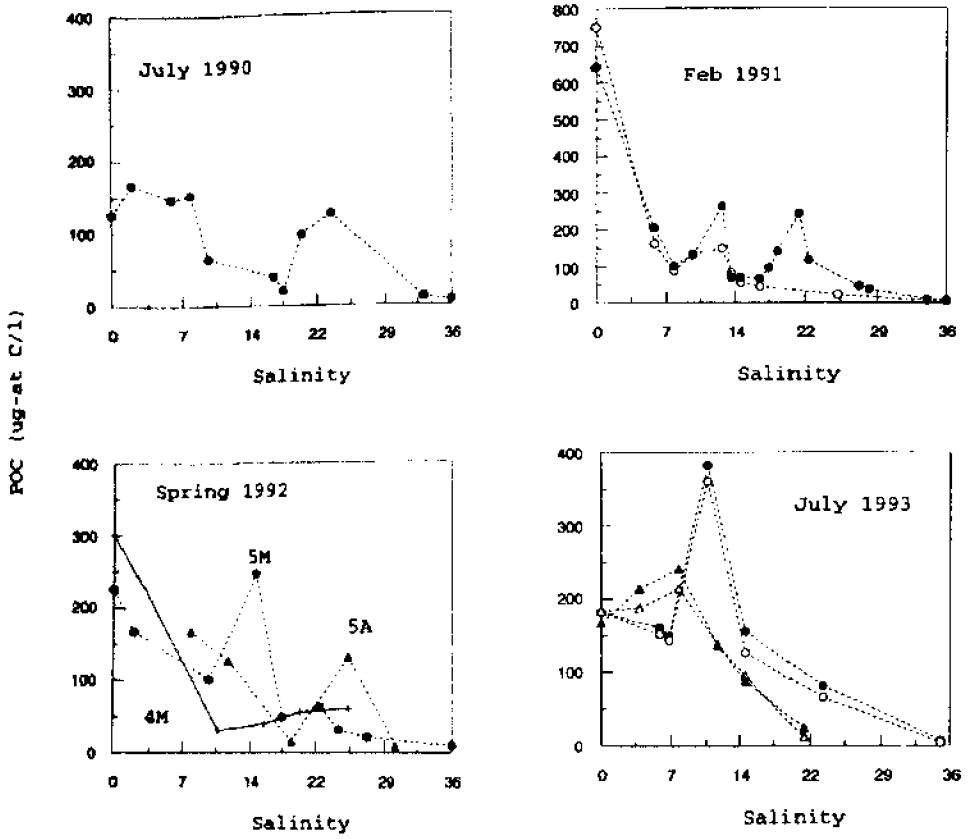

Figure 5. The concentrations of particulate organic carbon (POC) for five NECOP cruises are presented vs salinity. Filled circles represent samples from transects of the Mississippi River, open symbols represent samples of POC less than 20um (pre-screened). Triangles represent samples from transects from the Atchafalaya River. The lower left panel contains data from two spring 1992 cruises, April (4M) and May (5A and 5M), where the M indicates samples from transects of the Mississippi River and A from the Atchafalaya River. Note that the scale for Feb 1991 is twice the other three panels. Several of the transects have a mid-salinity peak, presumably due to plume productivity. River concentrations are relatively high and seasonally variable, ranging from approximately 1/3 to twice the river DOC concentrations at the same times. The POC concentrations were measured by capacitance manometry as part of stable isotope sample preperation.

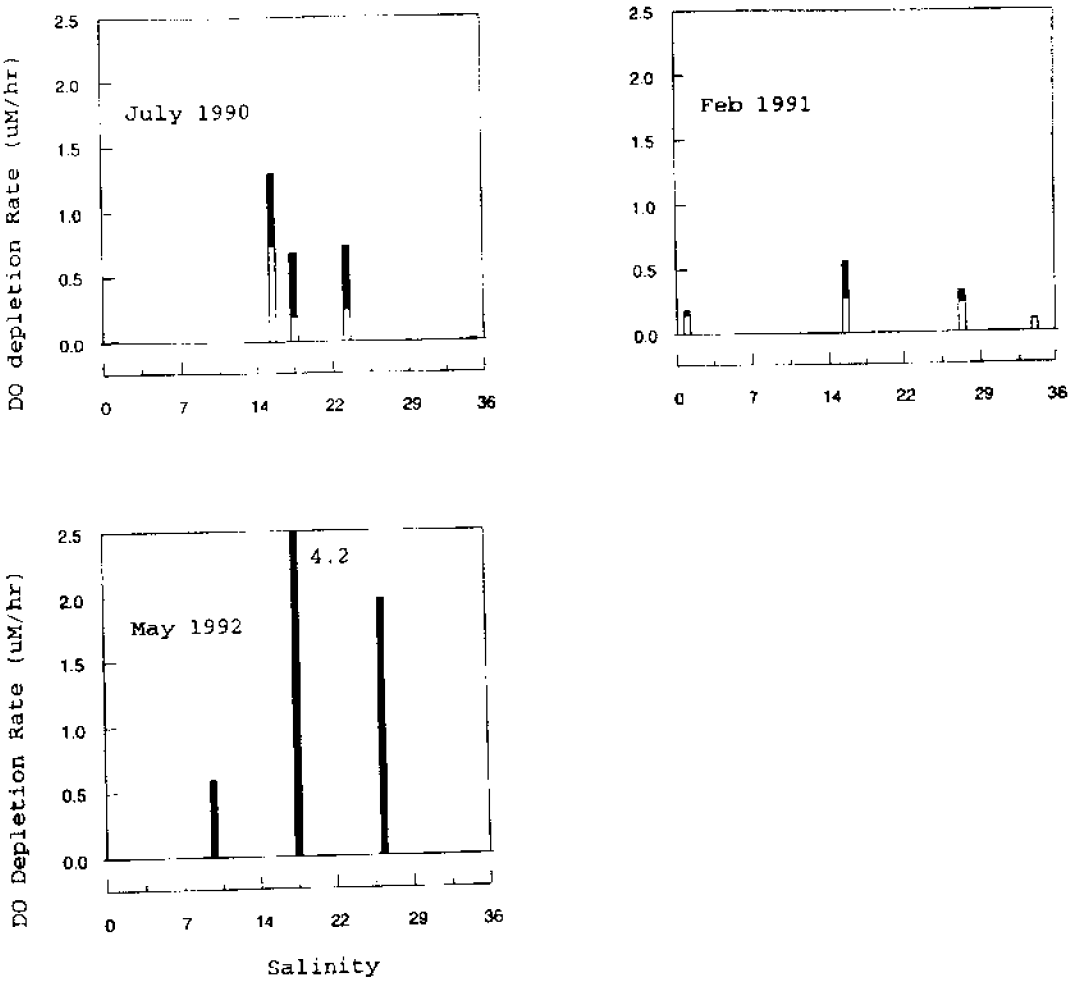

Figure 6. Oxygen consumption. Community oxygen consumption was measured by a precise and sensitive automatic titrating system (Mettler DL-21) for potentiometric end point determination of Winkler oxygen titrations. Respiration rate determinations were conducted in conjunction with determinations of bacterial growth and DOC flux to estimate the flux of carbon through the bacterioplankton. Time course experiments were run to monitor the kinetics of oxygen consumption during short-term incubations (3-12 h) in the dark. Triplicate 250-ml BOD bottles were analyzed at 3h intervals over a 12 h period (24 hours at 0 and 36 ppt salinity where rates are low). Respiration rates are derived from the linear portion of the oxygen consumption curve and oxygen consumption converted to carbon units assuming a respiratory quotient (RQ=dCO2:dO2) of 1.0. Several experiments will utilize prefiltered (1.0 mm pore size) samples to estimate the contribution of heterotrophic bacteria to community oxygen consumption.

The calculated rates for three cruises are presented vs salinity. The open section of each bar represents the contribution from dissolved materials (incubations using filtered water), while solid bars or sections are values measured in unfiltered waters. River and open Gulf rates are low for all periods. Maximum rates are at mid-salinity, where primary production is high and organic substrate is 'fresh'. Rates in May were the highest measured to date.

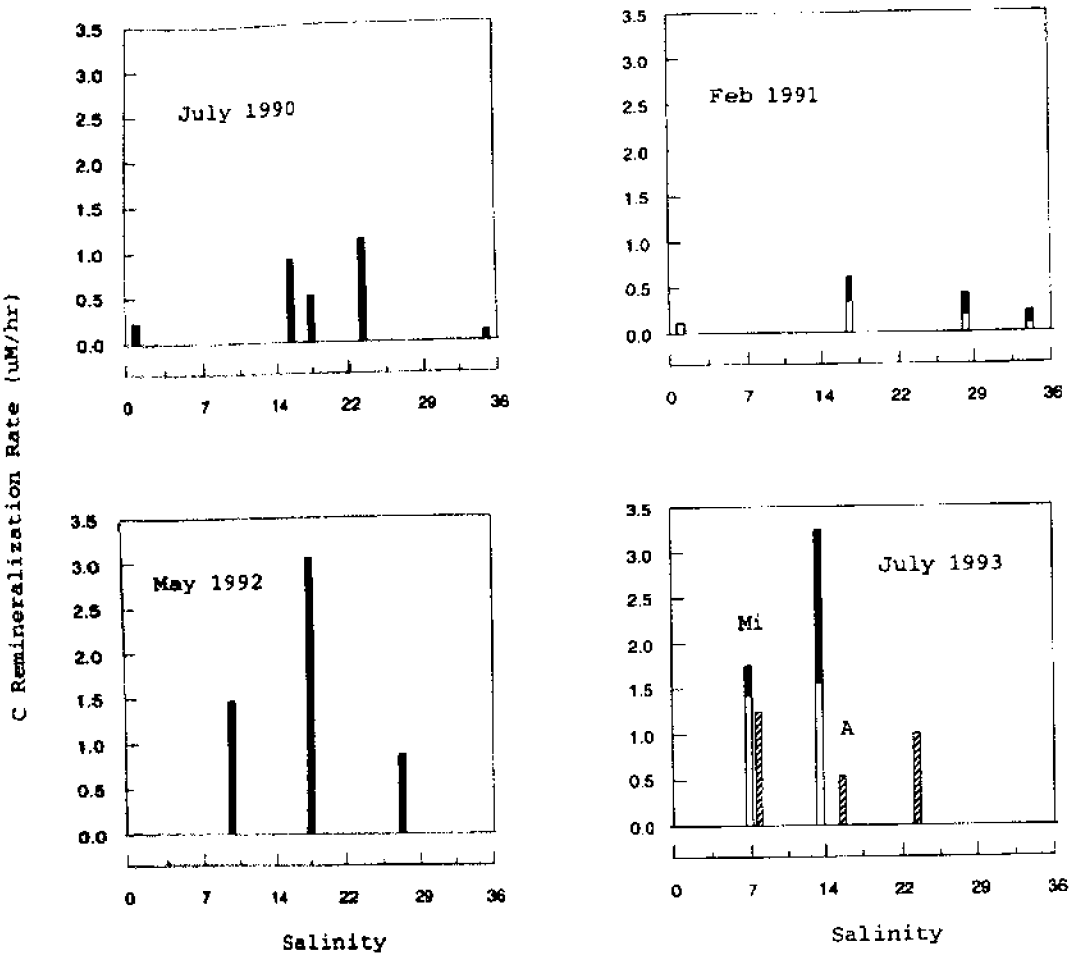

Figure 7. Carbon remineralization rates were calculated by measuring increased concentrations of dissolved inorganic carbon in the incubation bottles. Coulometric measurements allowed us to measure changes with a precision of 2uM of DIC. Twelve to twenty four incubations were sufficient for accurate rate measurements at all but the river and open Gulf end member stations. These latter rates were usually not significantly different from zero. Carbon isotopes were measured on the DIC in the initial and final incubation bottles to provide information on sources of the organic matter being mineralized.

The calculated rates for all four cruises are presented vs salinity. The open section of each bar represents contribution from the DOM as these were measured in dark, filtered water bottles. The filled bars represent total rates measured in unfiltered dark bottles. Maximum rates are at mid-salinity where primary production is high and much of the organic matter is 'fresh'. Rates were highest in May and July, 1993. The July, 1993 panel also contains rates from a salinity transect from the Atchafalaya (hatched) as well as from the Mississippi.

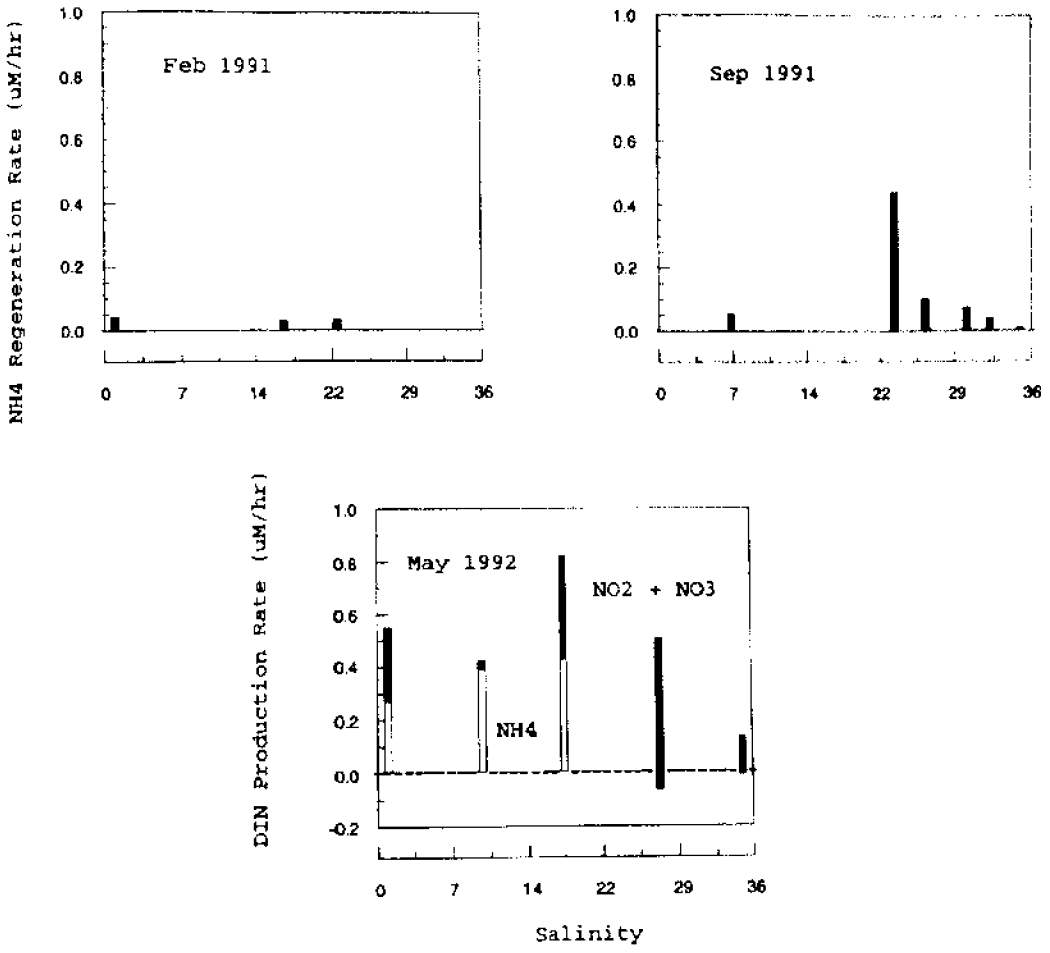

Figure 8. Nitrogen regeneration. Community organic-nitrogen mineralization rates were estimated by measuring isotope dilution of $^{15}NH_4$ added to water samples using the Blackburn/Caperon model (Blackburn 1979; Caperon et al. 1979). The ammonium concentrations and isotope ratios were measured directly using a new HPLC technique (Gardner et al., 1991). The isotope dilution experiments were done on 60 ml samples held under natural light for 2 to 12 hours. At some stations, experiments were also done on prefiltered (1 mm pore size) water to estimate the fraction of regeneration produced by unattached bacteria.

The calculated rates for three cruises are presented vs salinity. Maximum rates are at mid-salinity where primary production is high and much of the organic matter is 'fresh'. Rates were highest in May 1992 and lowest in winter. The rates for May 1992 were measured by autoanalyzer; the isotope dilution data are not yet available. The panel for May shows the rates for NH_4 production (open boxes) as well as significant production of NO_2+NO_3 (filled boxes). There appeared to be a significant amount of nitrification occuring in the mid-salinity water column (Pakulski et al., submitted).

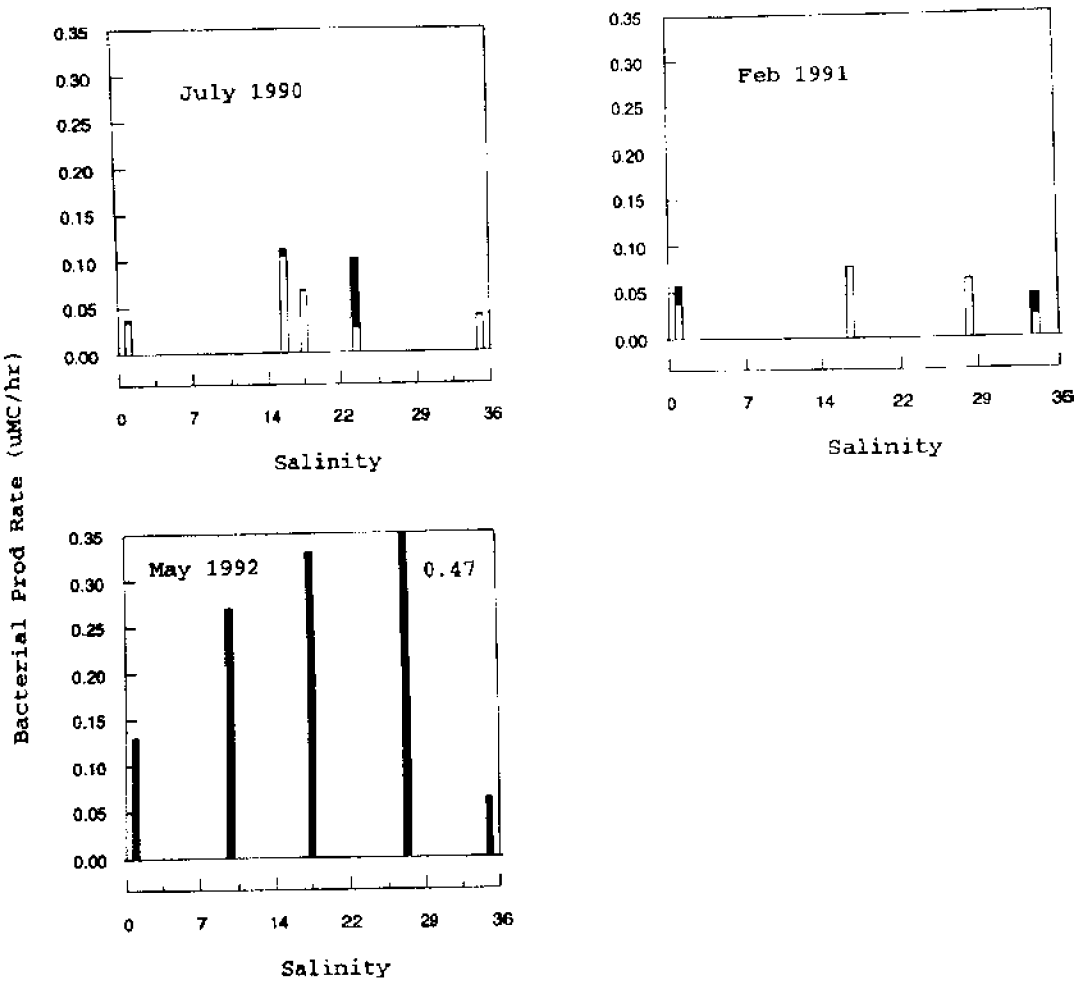

Figure 9. Bacterial abundances were measured by epifluorescence of DAPI stained samples (Porter and Feig, 1980). Bacterial production rates were estimated from rates of DNA and protein synthesis as measured by the rate of labelled thymidine (TdR)(Fuhrman and Azam, 1982) and leucine (Leu)(Kirchman et al. 1985), respectively. A duel-label method (Chin-Leo and Benner 1991a) was used to facilitate simultaneous determination of these independent measures of growth. Rates for July and Feb are from Chin-Leo and Benner (1991b).

The calculated rates for three cruises are presented vs salinity. Maximum rates are at mid-salinity where primary production is high and much of the organic matter is 'fresh'. Rates were highest in May 1992 and lowest in winter. Open boxes represent rates measured on filtered water, thus the contribution from DOM.

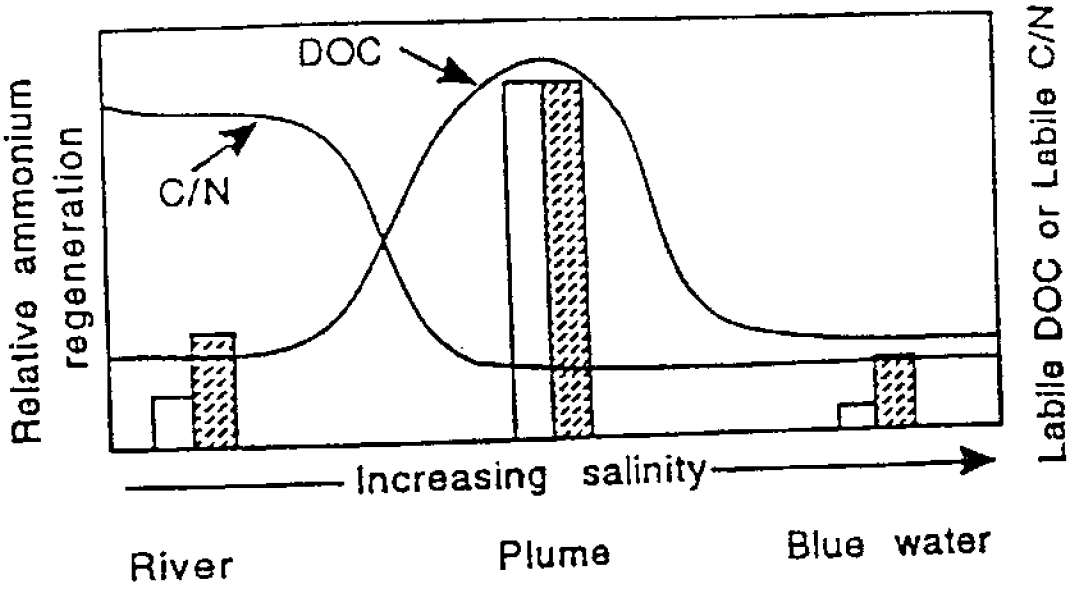

Figure 10. Conceptual model of nutrient and labile DOM cycling in the NECOP region: a qualitative summary of the information presented in the previous figures. River water DOM, with a high C/N ratio, is a poor substrate for recycling and rates are low. At intermediate salinities, primary production is high and the fresh DOM is rapidly recycled by heterotrophs (open bars) and other organisms (hatched bars). Open Gulf DOM concentrations are low and have a low C/N ratio; grazing may control bacterial production in these offshore waters. Figure from Cotner and Gardner, 1993.

PHYTOPLANKTON RATE PROCESSES IN COASTAL WATERS OF THE NORTHERN GULF OF MEXICO AND RELATIONSHIPS TO ENVIRONMENTAL CONDITIONS

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Abstract

Research describing phytoplankton rate processes and their relationship to environmental conditions is summarized. Relationships between P-I parameters and environmental variables in the region of study were significant in some cases, but variation between cruises made it difficult to generalize. Variability in ecological variables such as growth rate and cell size appeared to contribute to variations in pigment-specific photosynthesis-irradiance parameters. Our findings did support the view that a limited set of observations may be adequate to characterize P-I parameter distributions in a given region within a restricted period of time. Available data on photosynthetic parameters, in conjunction with irradiance and biomass (chlorophyll), provided input for a model to estimate areal distributions of primary production in relation to characteristics of the Mississippi River outflow plume and adjacent waters. Areal distributions of daily water column-integrated primary production (mg C m^{-2} d^{-1}), estimated using the P-I model, were spatially and temporally variable. Variability in magnitude, timing and circulation pattern of river discharge influenced the observed distributions of primary production. Productivity maxima occurred at intermediate salinities, presumably a consequence of increased light availability and decreased mixing/dilution rates. Highest productivities were observed during periods of warming and stratification in spring and late summer. Low productivities were attributed to low temperatures and relatively high rates of mixing in March 1991 and to reduced supply of river-borne nutrients in September 1991. An ocean color model to estimate primary production was evaluated. The model used an approach outlined in Morel and Berthon (1989), but with site-specific empirical relationships to estimate the integrated pigment in the water column from satellite detectable chlorophyll (C_{sat}) and site-specific trophic categories (oligotrophic to eutrophic) based on pigment concentration in the water column. Observed primary production versus production estimated by by the satellite algorithm compared well. Sinking rates of particulate organic carbon (POC) from the photic zone showed no significant relationship to integrated primary production, but was strongly correlated with suspended particulate matter concentration. In addition, the ratio of primary production to POC export from the photic zone was highly variable. This was attributed, in part, to variations in phytoplankton species composition and grazing activities of microzooplankton and mesozooplankton. Taxon-specific growth and sedimentation rates of dominant phytoplankton provided evidence that in the northern Gulf of Mexico, phytoplankton rate processes proceeded very rapidly with growth rates primarily controlled by the supply of nutrients via the Mississippi River and the fate controlled primarily by size and density (silicification). Incorporation of ^{14}C into protein as well as analyses of chemical composition supported the idea that phytoplankton in the plume and shelf were growing at high relative growth rates and were adapted to low light levels.

Introduction

Primary production on the Louisiana continental shelf has been shown to be enhanced by nutrient-rich outflow from the Mississippi-Atchafalaya river system (Riley, 1939; Thomas and Simmons, 1960; Lohrenz et al., 1990). Nitrate concentrations in the lower Mississippi River have doubled since 1950 (Turner et al., 1987; Turner and Rabalais, 1991) leading to concerns that increases in primary production of fixed carbon coupled to increased nutrient loading (*cf.* Nixon et al., 1984) could result in significant perturbation of the northern Gulf of Mexico coastal ecosystem. 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 (Rabalais et al., 1992; Justic et al., 1993) and associated reduction in living resource yields. The impact of increased nutrient loading on carbon burial and shelf/sea transport could also have implications for studies of the global carbon cycle (*e.g.*, Walsh et al., 1981, 1989).

Prediction of the coupling between nutrient loading, primary production, and export of organic matter from the photic zone requires quantification of

Table 1. Means and standard deviations (S.D.) of midday (1000-1400 h) values of photosynthetic parameters in the upper mixed layer. Units were as follows: P^B_{max} (gC g Chl a^{-1} h^{-1}), α^B (g C [g Chl a h]$^{-1}$ [µmol quanta m^{-2} s^{-1}]$^{-1}$), I_k (µmol quanta m^{-2} s^{-1}). N=number of samples.

	P^B_{max}		α^B		I_k		
Cruise	Mean	S.D.	Mean	S.D.	Mean	S.D.	N
September 1989	9.0	3.6	0.032	0.010	284	59	9
April 1990	10.4	3.4	0.041	0.014	281	127	7
July-August 1990	10.0	3.8	0.033	0.010	349	231	17
October 1990	11.3	5.3	0.049	0.024	246	74	10
March 1991	6.1	2.0	0.022	0.009	303	142	13
September 1991	23.0	5.5	0.055	0.015	429	83	7
April 1992	8.4	2.3	0.028	0.011	370	213	16
May 1992	5.4	2.8	0.018	0.004	325	221	5

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. Taxon-specific variations in phytoplankton production, growth and sinking may affect the quantity and quality of organic material reaching the sediments.

In 1990, the National Oceanic and Atmospheric Administration Coastal Ocean Program initiated the Nutrient Enhanced Coastal Ocean Productivity Program (NECOP) with a goal of understanding mechanisms of coupling between nutrient loading, magnitude and distribution of primary production, and formation of hypoxic bottoms waters on the Louisiana shelf. Here we present a summary of our work investigating phytoplankton rate processes and their relation to environmental conditions.

Spatial and Temporal Variations of Photosynthetic Parameters in Relation to Environmental Conditions in Northern Gulf of Mexico Coastal Waters

The variable nature of primary production in this region has complicated efforts to discern temporal and spatial patterns of regional productivity and their relation to possible controlling factors. Improved temporal and spatial resolution of primary production distributions has been achieved by using photosynthesis-irradiance models (*e.g.*, Fee, 1973a,b; Harrison et al., 1985). Such approaches require knowledge of the relationship of rates of pigment-specific photosynthesis to light, *i.e.*, the photosynthesis-irradiance curve (*e.g.*, Jassby and Platt, 1976, Platt et al., 1980). Estimates of primary production can then be made from information about biomass and irradiance distributions, thereby allowing for more detailed sampling.

Environmental variability can act at the level of physiology within phytoplankton species as well as through effects on species composition to cause variations in photosynthesis-irradiance relationships. Such variation contributes to uncertainty in estimates of primary production derived using photosynthesis-irradiance models. Previous studies have demonstrated that photosynthetic parameters may vary over a wide range of temporal and spatial scales, with temperature and light being the most commonly observed environmental covariates (Platt and Jassby, 1976; Harrison and Platt, 1980; Malone and Neale, 1981; Falkowski, 1981; Cote and Platt, 1983). Diel periodicity (MacCaull and Platt, 1977; Harding et al., 1981, 1982) and species composition and cell size (Malone and Neale, 1981; Gallegos, 1992) have also been implicated as factors contributing to variability.

While variation in photosynthetic parameters in other coastal ecosystems has been examined, little is

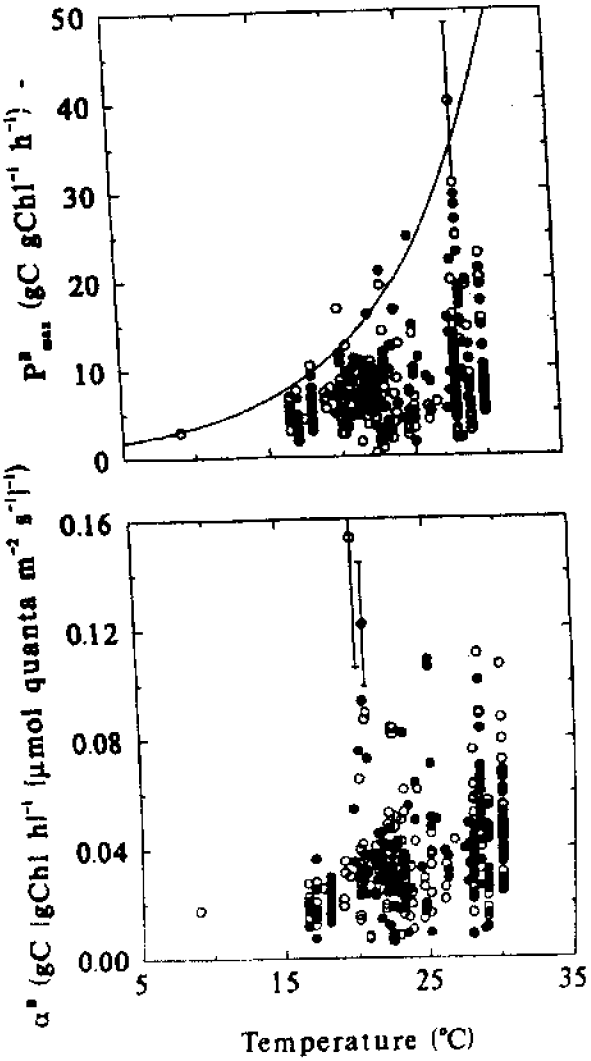

Fig. 1. Combined data for P^B_{max} and α^B from all cruises plotted as a function of temperature (T). Closed symbols indicate results from measurements conducted during midday (1000-1400 h). Curved line is a subjective fit to the high values and is described by the equation, $P^B_{max} = \exp(0.125\ T)$. P^B_{max} and α^B transformed to their natural logarithms were both significantly correlated with temperature (r^2=0.157, P<0.001, N=363 for $\ln(P^B_{max})$ and r^2=0.153, P<0.001, N=363 for $\ln(\alpha^B)$). Error bars indicate ±1 standard error of the estimate and are shown only for the highest values.

known about their spatial and temporal variation in the northern Gulf of Mexico. Such data can be used in the generation of modeled distributions of primary production over seasonal temporal scales and regional spatial scales (Lohrenz et al., 1992 and in prep.) and may facilitate understanding mechanisms of control at the ecosystem level. In addition, information about the distributions of photosynthesis-irradiance relationships may be incorporated into larger scale predictive models of primary production (*e.g.*, Platt and Sathyendranath, 1988).

On a series of 8 cruises conducted in the northern Gulf of Mexico, efforts were made to characterize temporal and spatial variability in parameters of the photosynthesis-irradiance saturation curve (P^B_{max}, α^B, I_k) and to relate the observed variations to environmental conditions (Lohrenz et al., in review). Experiments to examine the importance of diel variation in upper mixed layer populations were conducted in July-August 1990 and March 1991. During July-August 1990, P^B_{max} and I_k showed significant increases and α^B decreased during the photoperiod in both river plume and shelf/slope populations. During March 1991, no consistent covariance of P-I parameters with local time was found, although highest values of α^B in the river plume were observed in early morning. Seasonal variation in P^B_{max} and α^B (Table 1) were correlated with temperature (Fig. 1). Spatial variations of photosynthetic parameters in the upper mixed layer ranged 2-3 fold within any given cruise. For example, during the July-August 1990 cruise, values of P^B_{max} and carbon-specific growth rates were higher in the river plume than in shelf waters (Fig. 2). In an effort to identify environmental regulatory factors, variations of photosynthetic parameters in the upper mixed layer were related to principal components derived from environmental variables including temperature, salinity, nutrients, mixed layer depth, attenuation coefficient and daily photosynthetically available radiation (PAR). Greater than 70% of the variation in the environmental variables could be accounted for by two principal components; the majority of this variation was associated with the first principal component, which was generally strongly correlated with salinity, nutrients, mixed layer depth, and attenuation coefficient. Correlations of P^B_{max}, α^B, and I_k with the first principal component were found to be significant in some cases, an indication that spatial variability in P-I parameters was related to river outflow. Variation of P-I parameters in relation to depth and PAR were evaluated by regressions with principal components derived from depth, temperature and mean daily PAR. For most cruises, P^B_{max} and I_k were negatively correlated with the first principal component, which was strongly positively correlated with depth and negatively correlated with daily PAR. This was consistent with a decrease in P^B_{max} and I_k with depth that could be related to decreasing daily PAR. Positive correlations of α^B with the first principal

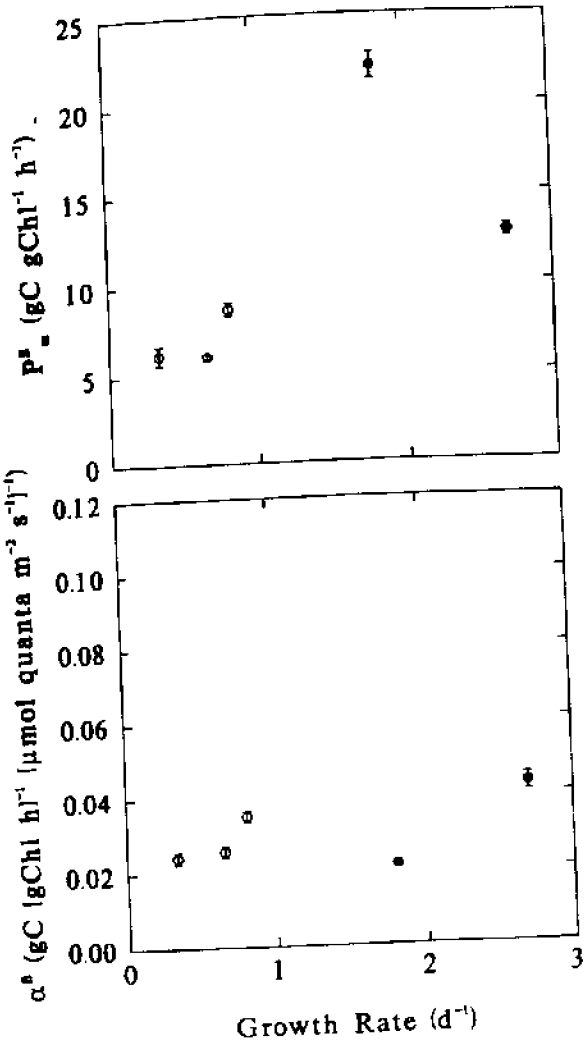

Fig. 2. Relationship of midday (1000-1400 h) values of P^B_{max} and α^B to growth rate. Filled symbols indicate samples from the plume and open symbols were from shelf waters. Error bars designate ±1 standard error.

component on two cruises, March 1991 and April 1992, indicated an increasing trend with depth. In conclusion, relationships between P-I parameters and environmental variables in the region of study were significant in some cases, but variation between cruises made it difficult to generalize. We attributed this variation to the physically dynamic characteristics of the region and the possible effects of variables that were not included in the analysis such as species composition. Our findings do support the view that a limited set of observations may be adequate to characterize P-I parameter distributions in a given region within a restricted period of time.

Seasonal Variability in Coupling Between Primary Production and Outflow of the Mississippi River on the Louisiana Continental Shelf

Information about the spatial and temporal distributions of primary production in the Mississippi River plume and adjacent waters is required for an understanding of the extent to which distributions of productivity are coupled to nutrient inputs from the river and the importance of control by other factors. 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). However, isolating seasonal patterns from time-series assessments of primary production of limited spatial extent are complicated by the dynamic and spatially heterogeneous nature of primary production in this region (Thomas and Simmons, 1960; Lohrenz et al., 1990), a consequence of the strong and variable gradients in physical and chemical properties.

Available data on photosynthetic parameters (Lohrenz et al., in review), in conjunction with irradiance and biomass (chlorophyll), provided input for a model to estimate areal distributions of primary production in relation to characteristics of the Mississippi River outflow plume and adjacent waters. Areal distributions of daily water column-integrated primary production, estimated using the P-I model, were spatially and temporally variable and exhibited varying degrees of coupling to riverine inputs (Fig. 3). Highest productivity was observed in July-August 1990 (Fig. 3a) and regions of elevated primary production were highest at intermediate salinities (Fig. 4a). Productivity was uniformly low in March 1991 with the exception of one area to the west of the low salinity outflow water (Fig. 3b). Productivity was also low during September 1991, with the exception of a limited region of enhanced productivity in the vicinity of the restricted plume (Fig. 3c) corresponding to intermediate salinities (Fig. 4c). Finally, in April-May 1992 productivity was again higher (Fig. 3d) in the region of intermediate salinities (Fig. 4d).

Variability in magnitude, timing and circulation pattern of river discharge influenced the observed distributions of primary production. The pattern of high productivity at intermediate salinities (Fig. 4) has been observed previously in the Mississippi River outflow region (Lohrenz et al., 1990) and other coastal ecosystems, and presumably reflects increased light availability and decreased mixing/dilution rates. Highest productivities were observed during periods of warming and stratification in spring and late summer. Low productivities were attributed to low temperatures and high rates of mixing in March 1991 and to reduced supply of river-borne nutrients in September 1991.

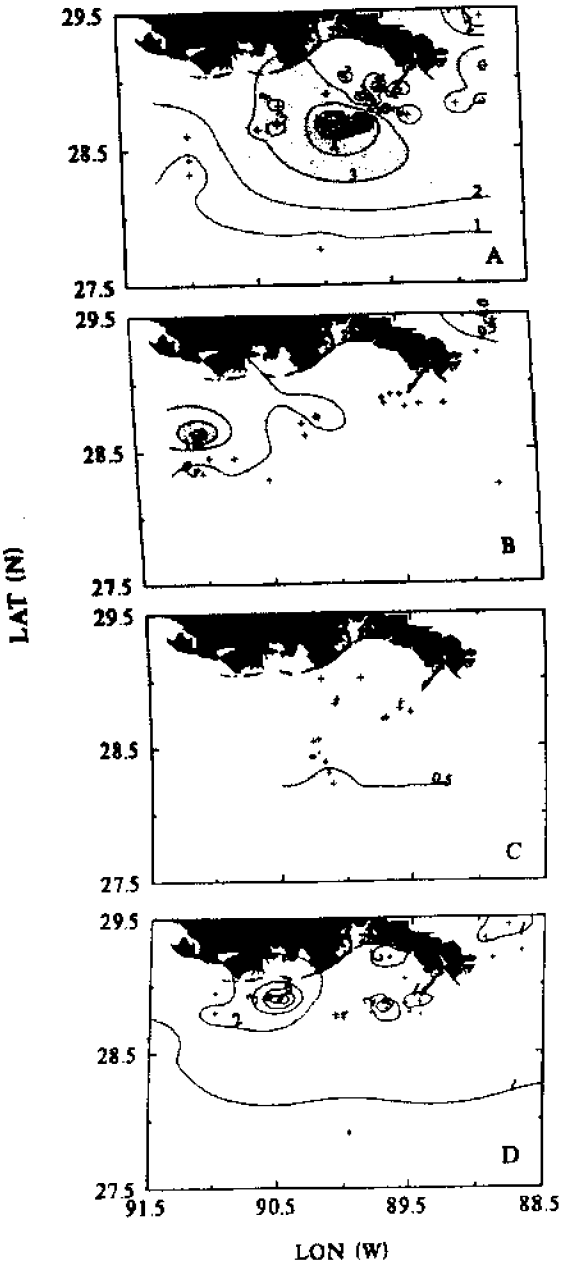

Fig. 3. Areal distributions of water column-integrated primary production estimated using a nonspectral photosynthesis-irradiance model (Lohrenz et al., 1992, and in prep.). A) July/August 1990, B) March 1991, C) September 1991, D) April/May 1992. Units are gC m^{-2} d^{-1}.

Primary Production in the Gulf of Mexico Coastal Waters Based on a Remote Sensing Algorithm

Attempts to derive ocean-color based estimates of pigment and primary production in coastal waters have been complicated by the contributions of signals from non-pigment materials to the water leaving radiance. An ocean color model to estimate primary production was evaluated for coastal waters of the northern Gulf of Mexico (Prasad et al., in press). The model utilizes C_{sat} (mg m^{-3}) (a variable that accounts for the pigment sensed by the satellite sensor), photosynthetically available radiation (PAR, J m^{-2} d^{-1}) and a parameter, ψ^* (g Chl)$^{-1}$, the water column chlorophyll specific cross-section for photosynthesis. C_{sat} and PAR were treated as variables while ψ^* was a site-specific parameter in the model. The model uses the approach outlined in Morel and Berthon (1989), but with site-specific statistical relationships to estimate the integrated pigment in the water column from C_{sat} and site-specific trophic categories (oligotrophic to eutrophic) based on pigment concentration in the water column. Observed production versus estimated production (mg C m^{-2} d^{-1}) for the pooled data compared very well (Fig. 5). ψ^* varied between 0.054 to 0.063 m^2 (g Chl)$^{-1}$, a range comparable to that observed in other regions.

The Relationship Between Primary Production and the Vertical Export of Particulate Organic Matter in a River Impacted Coastal Ecosystem

One of the objectives of our study was to examine temporal variability in primary production relative to variations in rates of sinking of particulate organic matter from the euphotic zone in two regions: the Mississippi River plume and the inner Gulf of Mexico shelf (Redalje et al., in review). Observations during four research cruises, July/August 1990, March 1991, September 1991 and May 1992, revealed that photic zone integrated primary production varied significantly in both the river plume and shelf study regions, with greatest variability observed in the river plume region (Table 2). In the river plume and the adjacent shelf, highest production occurred during July/August 1990 (8.17 $gCm^{-2}d^{-1}$ for the plume and 1.89-3.02 $gCm^{-2}d^{-1}$ for the shelf) and the lowest during March 1991 (0.40-0.69 gCm^{-2} d^{-1} for the plume and 0.12-0.45 $gCm^{-2}d^{-1}$ for the shelf). The vertical export of POC from the euphotic zone, determined with free-floating MULTITRAP sediment trap systems, also varied temporally in both study regions (Table 3), with highest values occurring in May 1992 (1.80±0.04 $gCm^{-2}d^{-1}$ for the plume and 0.40±0.02 $gCm^{-2}d^{-1}$ for the shelf) and lowest values occurring during July/August 1990 (0.29±0.02 $gCm^{-2}d^{-1}$ for the plume and 0.18±0.01 gCm

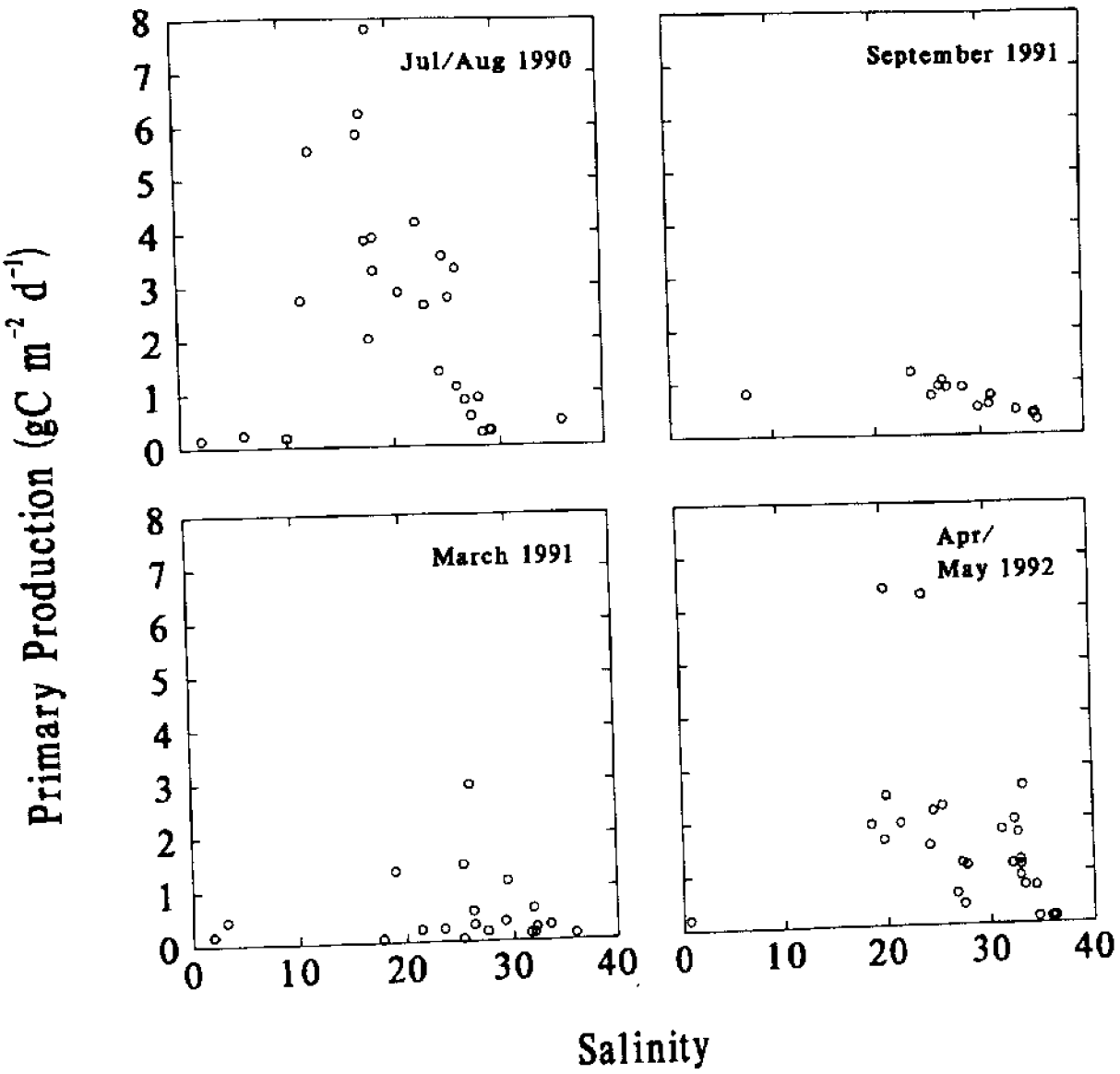

Fig. 4. Relationship of water column-integrated primary production to salinity.

$^{2}d^{-1}$ for the shelf). Vertical export of POC showed no significant relationship to integrated primary production, but was strongly correlated with suspended particulate matter concentration (Table 5). In addition, the ratio of primary production to POC export from the photic zone was highly variable. This was attributed, in part, to variations in phytoplankton species composition and grazing activities of microzooplankton and mesozooplankton.

Taxon-Specific Growth and Loss Rates for Dominant Phytoplankton Populations from the Northern Gulf of Mexico

Taxon-specific growth and sedimentation rates of dominant phytoplankton were measured during two cruises (summer 1990 and spring 1991) in the northern Gulf of Mexico as part of NOAA's NECOP program (Fahnenstiel et al., 1992, and in review). Microzooplankton grazing rates were measured during the summer cruise. During each of the cruises, a series of stations from the Mississippi River mouth to the hypoxia region (located ca. 50-100 km west) were

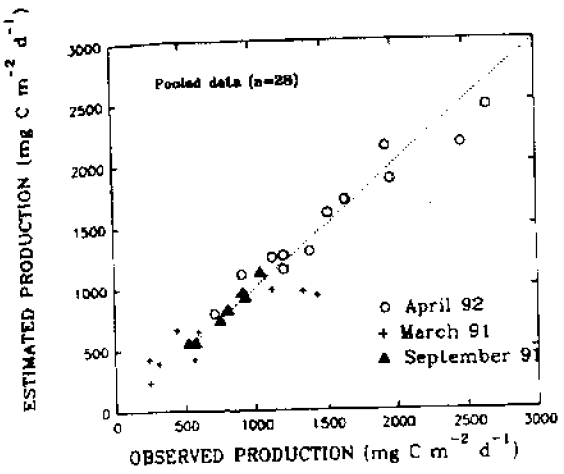

Fig. 5. Comparison of observed water column-integrated primary production versus that estimated by satellite algorithm. Estimated production was computed as (1/39)*PAR*IC*ψ^*, where ψ^* (g Chl)$^{-1}$ is the chlorophyll specific cross-section under each trophic category and the appropriate value of water column-integrated chlorophyll (IC, g m^{-2}) (Prasad et al.., in press). PAR is expressed in units of J m^{-2} d^{-1} and the factor 1/39 accounts for the fact that the fixation of 1 mg of carbon corresponds to a storage of 39 J of PAR.

sampled to examine variability of growth and loss processes along a strong environmental gradient. Significant taxa- and group specific differences were noted for both growth and loss rates. Growth rates ranged from <0.1-3.0 d^{-1} with highest rates in the plume region during the summer cruise where surface rates were close to or exceeded previous μ_{max} values for several taxa. For all taxa, growth rates were lower in the hypoxia region than in the plume region and soluble nitrogen concentrations explained over 50% of the variability in growth rates. Diatom growth rates were similar to non-diatoms in the plume region but were significantly lower in the hypoxia region suggesting that silica limitation may exist in this region. The fate of phytoplankton appeared to be controlled by size and the degree of silicification. Significant microzooplankton grazing loss rates were noted only for small taxa (<20 µm). For microflagellates, microzooplankton grazing rates averaged 82% (range 42-214%) of the growth rate and sedimentation rates were always <1% of the growth rate. Sedimentation was an important loss for several diatoms with significant taxon-specific and seasonal differences noted. Large colonial diatoms, such as *Skeletonema costatum* and *Thalassiosira rotula* exhibited the highest sedimentation rates in the plume region during the spring cruise(0.2-1.0 d^{-1}) whereas the lowest rates (<0.01 d^{-1}) were noted for *Rhizosolenia fragilissima* and *Ceratulina pelagica* in the hypoxia region during the summer cruise. Our results suggest that in the northern Gulf of Mexico, phytoplankton rate processes proceed very rapidly with growth rates primarily controlled by the supply of nutrients via the Mississippi River and the fate controlled primarily by size and density (silicification).

The Effects of Environmental Factors on Phytoplankton Physiological State and Chemical Composition

In addition to their impact on photosynthesis-irradiance parameters and the relationship between

Table 2. Photic zone integrated primary production (IPP; gC m^{-2} d^{-1}) for the simulated in situ primary production experiments conducted on each cruise in both the river plume and adjacent shelf study regions. Values are given for those experiments associated with the free-floating sediment trap array deployments. In addition, IPP results for the whole phytoplankton population and for the < 8 µm size fraction determined with post-incubation size fractionation procedures are presented. n.d. = no data.

Cruise	Plume Region		Shelf Region	
	Total	< 8 µm	Total	< 8 µm
July/August 1990	8.17	5.32	1.89 - 3.02	1.13
March 1991	0.40 - 0.69	0.27	0.12 - 0.45	0.11
September 1991	0.86 - 1.65	0.67 - 0.99	0.17 - 0.36	0.16 - 0.39
May 1992	3.37 - 3.86	n.d.	0.31 - 1.07	n.d.

Table 3. Vertical flux of POC (gC m^{-2} d^{-1}) and PON (gN m^{-2} d^{-1}) out of the photic zone for the four NECOP cruises completed thus far. The standard error and number of replicate samples are given in parentheses.

Cruise	Plume Region	Shelf Region
Jul/Aug 90		
POC Flux	0.29 (0.02; n=3)	0.18 (0.01; n=4)
PON Flux	0.06 (0.003; n=6)	0.03 (0.002; n=8)
March 91		
POC Flux	0.95 (0.01; n=3)	0.32 (0.02; n=3)
PON Flux	0.16 (0.009; n=6)	0.05 (0.002; n=6)
Sept 91		
POC Flux	0.69 (0.02; n=12)	0.19 (0.01; n=6)
PON Flux	0.12 (0.003; n=12)	0.03 (0.001; n=6)
May 92		
POC Flux	1.80 (0.04; n=8)	0.40 (0.02; n=10)
PON Flux	0.27 (0.008; n=16)	0.07 (0.004; n=10)

primary production and the vertical export of POM, changing environmental conditions can lead to variability in the chemical and biochemical composition of the phytoplankton present in the river plume and shelf regions. Seasonal variability in river discharge, and thus input of nutrients to the plume and shelf regions led to changes in the patterns of incorporation of ^{14}C into the major endproducts of photosynthesis - proteins, lipids, small molecular weight intermediates, and polysaccharides (Arwood, 1992). Predominate environmental conditions in the river plume (*e.g.*, either nutrient-sufficient or phosphate-limited growth and low light adaptation) permitted phytoplankton populations to grow at or near their maximum growth rates, as indicated by high relative incorporation of ^{14}C into protein (DiTullio and Laws, 1983; 1986; Arwood, 1992). As the nutrient fields become depleted with distance from the plume, phytoplankton respond by increasing the incorporation of ^{14}C into lipids and small molecular weight intermediate compounds. However, even under relatively nutrient-depleted conditions, phytoplankton maintained the capacity to utilize the available nitrogen and synthesize protein.

Our results support the view that phytoplankton in the river plume and adjacent shelf waters appear to be limited by the availability of PO_4, which is in agreement with the suggestions of Ammerman (1992) and Smith and Hitchcock (1994). Samples obtained from the river plume and adjacent shelf waters were

Table 4. The Pearson Correlation matrix for mean values of selected rate processes (integrated primary production, IPP; vertical export of POC, F_{POC}; vertical export of PON, F_{PON}; surface concentrations of NO_3^-, $PO_4^{=}$, $SiO_3^{=}$ and chl *a*; mass of suspended particulate matter, SPM; diffuse attenuation coefficient over photosynthetically available radiation, K_{PAR}; surface salinity, SAL; units are the same as in Table 3). Correlation coefficient values which exceed 0.707 (6 degrees of freedom) are considered to be significant at the 5% level.

	IPP	F_{POC}	F_{PON}	NO_3	PO_4	SiO_3	Chl a	SPM	K_{PAR}	SAL
IPP	1.000									
F_{POC}	0.068	1.000								
F_{PON}	0.091	0.996*	1.000							
NO_3	0.934*	0.163	0.192	1.000						
PO_4	0.397	0.832*	0.802*	0.375	1.000					
SiO_3	0.968*	0.073	0.099	0.948*	0.349	1.000				
Chl a	0.865*	-0.008	-0.001	0.748*	0.433	0.753*	1.000			
SPM	0.387	0.883*	0.881*	0.440	0.900*	0.376	0.362	1.000		
K_{PAR}	0.576	0.471	0.484	0.661	0.576	0.468	0.591	0.506	1.000	
SAL	0.068	-0.029	-0.338	-0.233	0.114	-0.011	0.335	-0.065	-0.401	1.000

given various nutrient enrichment treatments (including the addition of PO_4, NO_3, SiO_3, trace metals and vitamins in various combinations which included or excluded each of the components in standard f/2 medium concentrations; Chen, 1994). The phytoplankton responded with an increase in *in vivo* fluorescence when PO_4 had been added. The *in* vivo fluorescence response of treatments without added PO_4 were not different from that of the control treatments (e.g. no nutrient additions).

Chemical composition has frequently been used as an indicator of the physiological state of marine phytoplankton. Ratios of composition, such as C/chl a and C/N also provide useful information on environmental impacts on phytoplankton physiology. We investigated the responses of C/chl *a* and C/N for cultures of *Skeletonema costatum* and *Chaetoceros* sp. (which was isolated from the Mississippi River plume on cruise PE920412) to variation in light and dilution rate in semi-continuous cultures in the laboratory. Under strongly light limited growth conditions, such as those encountered by population in the river plume, cells were able to maintain high rates of growth and production through adjustment of cellular C and chl *a* content (Chen, 1994). C/N ratios decreased with light and with increased growth rates. The ratios which were encountered in the field (*e.g.*, approximately 7-8, by atoms) were similar to those which we found for the higher dilution rates and lowest light levels. This lends support to the idea that phytoplankton in the plume and shelf were growing at high relative growth rates and were adapted to low light levels (Chen, 1994).

Acknowledgements

This research was supported by NOAA/Mississippi-Alabama Sea Grant No. NA90AA-D-SG688, Project No. R/LR-25, and by the Board of Regents of the State of Louisiana through Contract no. 86-LUM(1)-083-13. We are grateful for the technical assistance of D. Taylor, H. Carrick, J. Cavaletto, and R. Krest. We also thank the captains and crews of the R/V *Pelican* and the N/S *Malcolm Baldrige*. USM/CMS Contribution No. .

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OPTICAL PROPERTIES OF MISSISSIPPI RIVER PLUME AND ADJACENT WATERS DURING MARCH 1991

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Abstract

Variations in attenuation of irradiance (total photosynthetically active radiation and downwelling spectral irradiance) were related to other optical measurements (beam c, solar-stimulated fluorescence) and to concentrations of particulate and dissolved materials determined from analyses of discrete samples. Four sampling locations were studied representative of conditions ranging from very turbid low salinity plume water to very oligotrophic water over the slope. Highest values of K_{par} (over 2.5 m^{-1}) were observed at the surface in a low salinity plume station, although there was considerable scatter in the values. Lowest values were observed at a slope water station (< 0.8 m^{-1}). The utility of measurements of L_u683 as an index of chlorophyll concentrations was found to be limited. Extracted chlorophyll concentrations tended to be overestimated in near surface waters and underestimated at depth. Profiles of beam c revealed high values (> 3 m^{-1}) in surface waters of the shelf stations. Spectral attenuation minima at shelf stations were in the vicinity of 540-580 nm. Lowest values of attenuation were observed at the slope water station where the attenuation minimum was around 490 nm. A spectral attenuation model reproduced measured spectra remarkably well considering variations in attenuation spanned over an order of magnitude. It was evident that in shelf waters during this period, absorption and scattering were dominated by dissolved organic carbon and suspended particulate matter.

Introduction

Light is known to be a critical parameter regulating primary production in turbid waters of the Mississippi River plume (Lohrenz et al., 1990). Optical properties in coastal waters are complex and variable, due to the high levels of terrestrially derived constituents that contribute to absorption and scattering of irradiance. Information about the irradiance field can be obtained by direct measurements with irradiance sensors. Spectral resolution of irradiance can provide an indication of the type of constituents that contribute to attenuation of irradiance. In addition, other optical instrumentation (transmissometer, fluorometers) can provide information about distributions of optically active materials with greater spatial resolution than is possible using discrete sampling techniques. Such information may be useful in the development of models (*e.g.*, Gallegos et al., 1990) that permit the characterization of irradiance field on the basis of selected input variables.

Here we describe a series of data collected in conjunction with the NOAA Nutrient Enhanced Coastal Ocean Program (NECOP) during March 1991 in the vicinity of the Mississippi River plume. Our efforts focused on the description of variations in attenuation of irradiance as related to other optical measurements (beam c, solar-stimulated fluorescence) and as related to concentrations of particulate and dissolved materials determined from analyses of discrete samples. The objectives of this research included the following: 1) to understand the predominate factors that mediate attenuation of irradiance in coastal waters of the northern Gulf of Mexico, and 2) to develop predictive models for irradiance attenuation as input in photosynthesis-irradiance models.

Methods

Data from four general locations occupied during the 4-17 March 1991 cruise aboard the N/S *Malcolm Baldrige* were examined. Locations of stations along with the type of measurement profile were given in Table 1.

Profiles of the diffuse attenuation coefficient of photosynthetically active radiation, K_{par} (400-700 nm), and temperature were determined using a Biospherical Instruments PNF300. This instrument also measured upwelling radiance at 683 nm, L_u683. Based on assumed values of the absorption coefficient of light at 683 nm (a(683), 0.48 m^{-1}), spectrally averaged pigment-specific absorption (a^*_{pb}, 0.04 m^{-1}) and quantum yield of fluorescence (ϕ_f, 0.045 (mol quanta)$^{-1}$), an estimate of chlorophyll concentration can be derived from L_u683 (Chamberlin et al., 1990).

An instrument system was used to provide profiles of conductivity, temperature, pressure/depth (Neil Brown CTD) and beam attenuation coefficient (beam c, m^{-1}) (SeaTech 10 cm path transmissometer). Data were provided courtesy of T. Nelsen. Beam c data were not available at Station D.

Table 1. Times and locations of optical stations. UT=universal time, Op# is an event identification number

Station	UT	Op#	Lat(N)	Lon(W)	Remarks
A	1608	91067238	28.881	89.620	Spectroradiometer
	1630	91067239	28.883	89.619	PNF-300
	1707	91067240	28.886	89.631	CTD 82
B	1720	91069296	28.750	90.129	PNF-300
	2043	91069302	28.791	90.156	Spectroradiometer
	2303	91069308	28.755	90.138	CTD 104
C	1624	91073380	28.909	89.490	Spectroradiometer
	1650	91073381	28.909	89.491	PNF-300
	1708	91073382	28.909	89.491	CTD 119
D	1557	91074405	28.244	88.812	PNF-300
	1631	91074406	28.240	88.822	Spectroradiometer
	1644	91074407	28.238	88.824	CTD 124

Samples for analysis of suspended particulate matter and photosynthetic pigments were collected in conjunction with CTD profiling using a rosette sampler (General Oceanics) fitted with 10 L Niskin bottles. Total suspended particulate material was determined by passing a known volume through a pre-rinsed, pre-weighed 47 mm GF/F filter followed by rinsing, drying and re-weighing the filter. Chlorophyll *a* and phaeopigment analyses were performed on board ship using an extraction technique modified from Shoaf and Lium (1976). Samples were filtered on Whatman GF/F glass fiber filters, which were then immersed in 5 ml of DMSO/acetone (40/60) and allowed to extract in darkness for 1 h. After extraction, samples were centrifuged and fluorescence was measured before and after acidification using a Turner Model 10 fluorometer (Holm-Hansen et al., 1965). Calibrations were made using a Sigma chlorophyll *a* standard.

Downwelling spectral irradiance was determined using a Li-Cor LI-1800-UW underwater spectroradiometer. The instrument was deployed at times and locations given in Table 1. A series of scans (2 nm resolution) were made at selected depths in the upper mixed layer and spectral attenuation at each wavelength band was calculated as follows:

$$(1) \quad k(\lambda,z) = \ln [I(\lambda,z_{i-1}) / I(\lambda,z_i)] / (z_i - z_{i-1})$$

where $I(\lambda, z_i)$ is the irradiance at wavelength λ and depth z_i.

Measurements of diffuse spectral attenuation were compared to estimates derived from a spectral attenuation model. The diffuse spectral attenuation coefficient, k, was calculated for all wavebands using the relation of Kirk (1984) as described in Gallegos et al. (1990). The model required that total spectral absorption ($a_t(\lambda)$, m^{-1}) and scattering coefficients ($b(\lambda)$, m^{-1}) be determined. The total spectral absorption coefficient, $a_t(\lambda)$, was estimated by summation of absorption due to individual constituents. The spectral absorption coefficient for particulate matter, $a_x(\lambda)$, was estimated by substituting the suspended particulate matter concentration for total suspended solids in Eq. 6 of Gallegos et al. (1990). The coefficient for absorption due to phytoplankton was determined by multiplying the chlorophyll-specific absorption coefficient, $a^*_{pb}(\lambda)$, that was obtained from Table 4 of Gallegos et al. (1990) by the measured chlorophyll *a* concentration. Values of spectral absorption of dissolved matter were estimated by substituting dissolved organic carbon concentrations (DOC) into Eq. 5 from Gallegos et al. (1990). DOC concentrations at our sampling locations were estimated from salinity based on a salinity-concentration relationship determined by R. Benner (unpublished) on the cruise leg immediately preceding ours. Estimated values were 1.2 mg l^{-1} (Station A), 1.1 mg l^{-1} (Station B), and 1.9 mg l^{-1} (Station C). The absorption by dissolved organic matter at the slope water Station D was taken as zero because Eq. 5 from Gallegos et al. (1990) was applicable only for higher concentrations as encountered in shelf waters. The scattering coefficient, $b(\lambda)$, was assumed to be invariant with wavelength and was calculated by assuming that the only significant absorbing substance in the 720 nm waveband was due

Table 2. Water sample data from optical stations. Symbols: Chl=chlorophyll, Phaeo=phaeopigments, SPM=suspended particulate matter, Sal=salinity, n.d.=no data available due to high salt blank, absorption due to suspended matter at Station D was assumed to be negligible.

Station (m)	Depth (mg m-3)	Chl (mg m-3)	Phaeo (g m-3)	SPM	Sal	REMARKS
A	2	1.37	0.28	0.540	25.4	cloudy skies, variable light
	5	1.53	0.36			some wind and waves
	8	0.69	0.49			plume water
B	2	3.37	1.79	1.4	26.3	clear skies, some wind and waves
	8	3.78	2.36			good ship angle
	14	2.60	2.35			shelf water
	16	2.09	1.28			
	27	0.34	0.81			
	32	0.54	0.92			
C	2	3.30	4.14	16.1	19.5	cloudy skies, some light variation,
	4	2.76	5.69	2.61		calm seas with some ship roll
	6	0.70	0.68			plume water
	9	0.26	0.34			
	17	0.23	0.50			
	26	0.35	0.67			
D	2	0.31	0.26	n.d.	36	cloudy gray skies, seas 1-2 m
	20	0.36	0.16			offshore, blue water
	34	0.57	0.29			
	50	0.56	0.29			
	95	0.08	0.13			

to water (*i.e.*, $a_t(720)=a_w(720)=1.002\ m^{-1}$, *cf.* Gallegos et al., 1990). The scattering coefficient, b(720), was then calculated from measured values of k(720) by rearranging Eq. 2 in Gallegos et al. (1990) and the resulting value was used for all wavebands. In the case of Station D, detection limits of the spectroradiometer did not permit an assessment of k(720). Instead, b(550) was estimated from chlorophyll *a* concentrations using Eq. 18 of Morel (1988). This equation was derived for case I waters. The resulting values of b were 2.19, 2.56, 33.7 and 0.152 m^{-1} for Stations A, B, C and D respectively. The diffuse spectral attenuation, k, was calculated for all wavebands using the relation of Kirk (1984) as described in Gallegos et al. (1990).

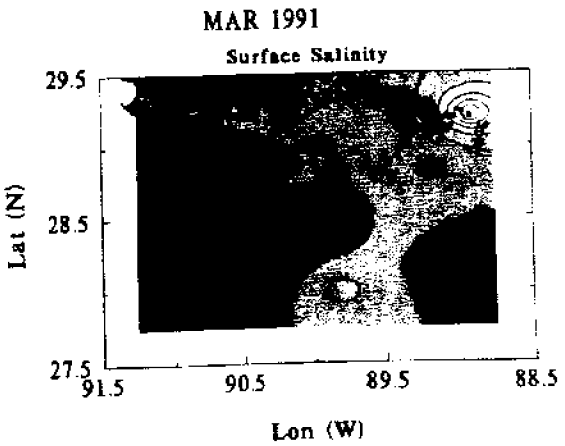

Fig. 1. Location of optical stations in relation to surface salinity based on available data collected during the 4-17 March 1991 cruise aboard the N/S *Malcolm Baldrige*.

Results

The four sampling locations (Fig. 1) included conditions ranging from very turbid low salinity plume water (Station C) to very oligotrophic water over the slope (Station D). Extracted chlorophyll *a* concentrations

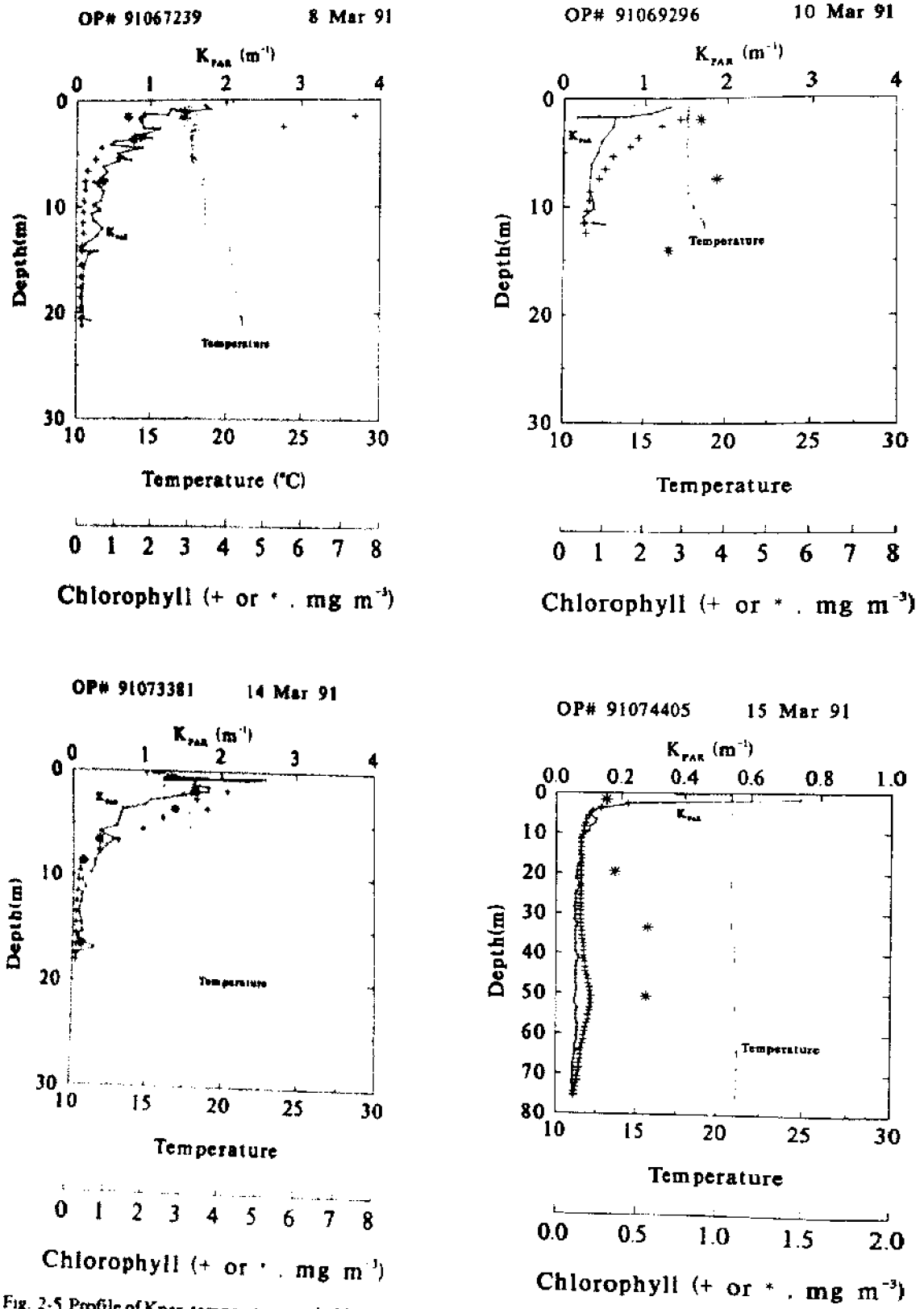

Fig. 2-5 Profile of Kpar, temperature, and chlorophyll estimated from Lu683 (+) and discrete analyses (*) at Station A (upper left), Station B (upper right), Station C (lower left) and Station D (lower right).

(Table 2) exceeded 3 mg m^{-3} at Stations B and C, while at Station D values were always less than 1 mg m^{-3}. Highest values of suspended particulate matter and lowest salinities were encountered at Station C, presumably strongly impacted by river outflow.

Profiles of K_{par} (Figs. 2-5) exhibited high values in the upper water column and decreased with depth. This was attributed to both the spectral shift in irradiance with depth (*e.g.*, Kirk, 1983) as well higher turbidity in the surface layer (*e.g.*, Station C, Table 2). Highest values of K_{par} were observed at Station C (Fig. 4), although there was considerable scatter in the values. Lowest values were observed at the slope water Station D (Fig. 5).

Chlorophyll estimated from L_u683 (Figs. 2-5) was generally highest near the surface and decreased with depth. At Station A, chlorophyll estimated from L_u683 exceeded extracted chlorophyll concentrations in surface waters, but underestimated extracted chlorophyll concentrations at depth (Fig. 2). At Stations B, C and D, chlorophyll estimated from L_u683 was similar to extracted chlorophyll concentrations in surface waters (Figs. 3-5). However, at both Stations B and D, values estimated from L_u683 underestimated extracted chlorophyll concentrations at depth. At Station C, both estimated and extracted chlorophyll showed similar decreases with depth (Fig. 4).

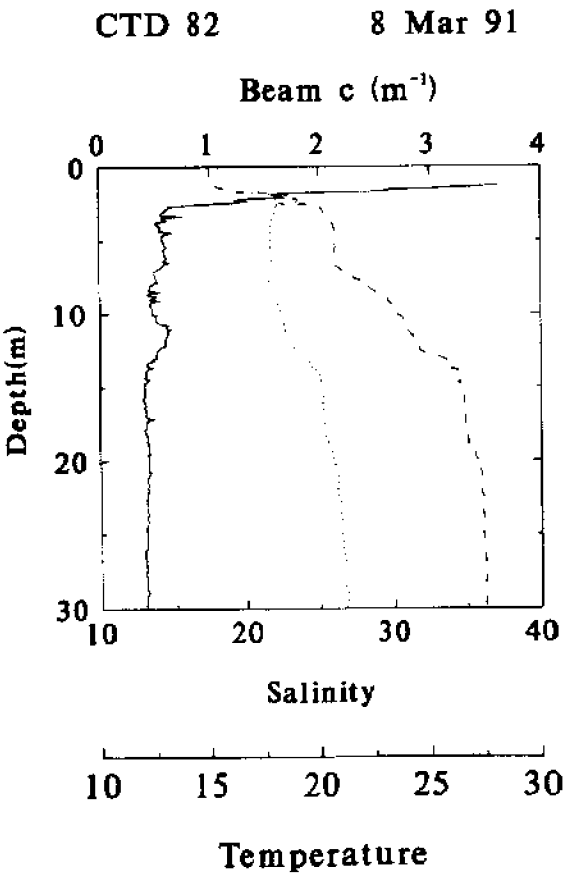

Fig. 6. Profile of salinity (dashed line), temperature (dotted), and beam c (solid) at Station A.

Profiles of beam c revealed high values in surface waters at Stations A, B and C (Figs. 6-8 respectively). Highest values of beam c were observed at Stations A and C. Sampling limitations of the instrument package precluded resolution within the upper 2-3 m, and there was a possibility that values were higher there. At Stations B and C, subsurface layers of high turbidity were observed that were apparently associated with a benthic nepheloid layer. Intermediate peaks in beam c were observed at Station C that did not reflect pigment maxima (*cf.* Fig. 4).

Average attenuation coefficient spectra (solid lines in Fig. 9) were similar at Stations A and B. High attenuation at short wavelengths was evident in the spectrum determined at Station C. Spectral attenuation minima at Stations A, B and C were in the vicinity of 540-580 nm. Lowest values of attenuation were observed at the slope water Station D where the attenuation minimum was around 490 nm. The spectral attenuation model performed well (dashed lines in Fig. 9). At Station D, there was a tendency of the modeled values to underestimate measured attenuation, particularly at either end of the spectrum.

Discussion

A wide range of water conditions were encountered in this study. Evidence of high turbidity in river plume was demonstrated by the high values of K_{par} (Fig. 4) and high spectral attenuation (Fig. 9) at Station C. Sharp vertical changes in optical properties were evident and attributed both to high concentrations of optically active constituents and heterogeneous vertical distributions. Spatial variation in irradiance attenuation characteristics was evident from the comparison of the different sampling locations, and underscored the complex nature of the optical environment in this coastal ecosystem.

The utility of measurements of L_u683 as an index of chlorophyll concentrations was found to be limited. Extracted chlorophyll *a* concentrations tended to be overestimated in near surface waters and underestimated at depth. Surprisingly, the station where the best agreement was found was Station C, the most turbid of our sampling locations. The discrepancies observed between estimated and extracted chlorophyll concentrations in the surface waters was likely due to a significant source of scattered L_u683 that did not originate from chlorophyll fluorescence. Underestimates

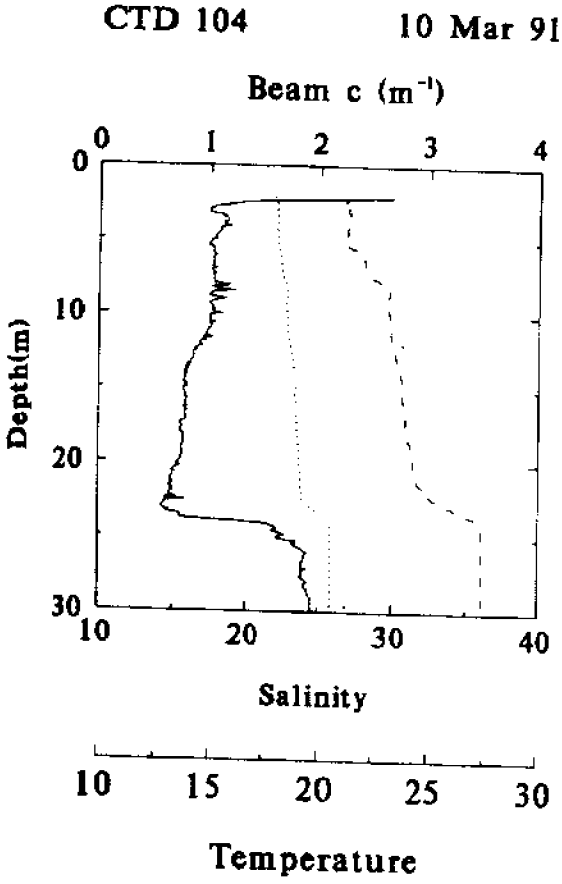

Fig. 7. Profile of salinity (dashed line), temperature (dotted), and beam c (solid) at Station B.

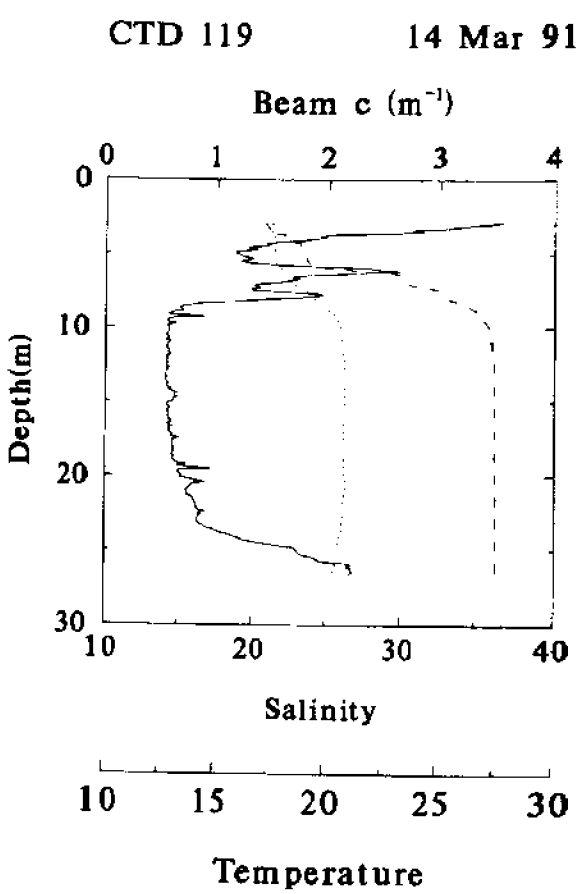

Fig. 8. Profile of salinity (dashed line), temperature (dotted), and beam c (solid) at Station C.

at depth were apparently due to errors in the assumed values of coefficients. For example, decreases in either the spectrally averaged pigment-specific absorption (a^*_{ph}) or the quantum yield of fluorescence (ϕ_f) would increase the estimated chlorophyll (*cf.* Chamberlin et al., 1990).

The spectral attenuation model performed remarkably well (Fig. 9) considering variations in attenuation spanned over an order of magnitude. Estimates of the relative contribution of individual constituents to total spectral absorption (data not shown) revealed that absorption at wavelengths less than 600 nm was dominated by DOC at Stations A and B, and by DOC and SPM at Station C. It was also evident from consideration of Eq. 18 from Morel (1988) that the scattering coefficients that were derived for Stations A, B and C were substantially higher than could be attributed to the observed chlorophyll *a* concentrations. We thus concluded that attenuation of PAR in shelf waters during this period was controlled primarily by factors other than pigment concentrations. In slope water (Station D), attenuation was underestimated by the model. This could be attributed to the fact that effects of both SPM and DOC terms were not quantified at this location. SPM estimates were not available at Station D because a high salt blank interfered with the measurement and the empirical relationship to estimate a_d from DOC was applicable only in regions of higher concentrations as encountered in coastal waters. Another factor that may have caused the model to underestimate attenuation at Station D was that the Kirk (1984) relation was intended to provide an average over the euphotic zone (to 1% light level). Our data were from upper 20 m where attenuation may have been slightly higher due to more rapid attenuation of longer wavelengths (*cf.* Fig. 5).

The spectral attenuation model required input of SPM, DOC, and chlorophyll. In addition, an estimate

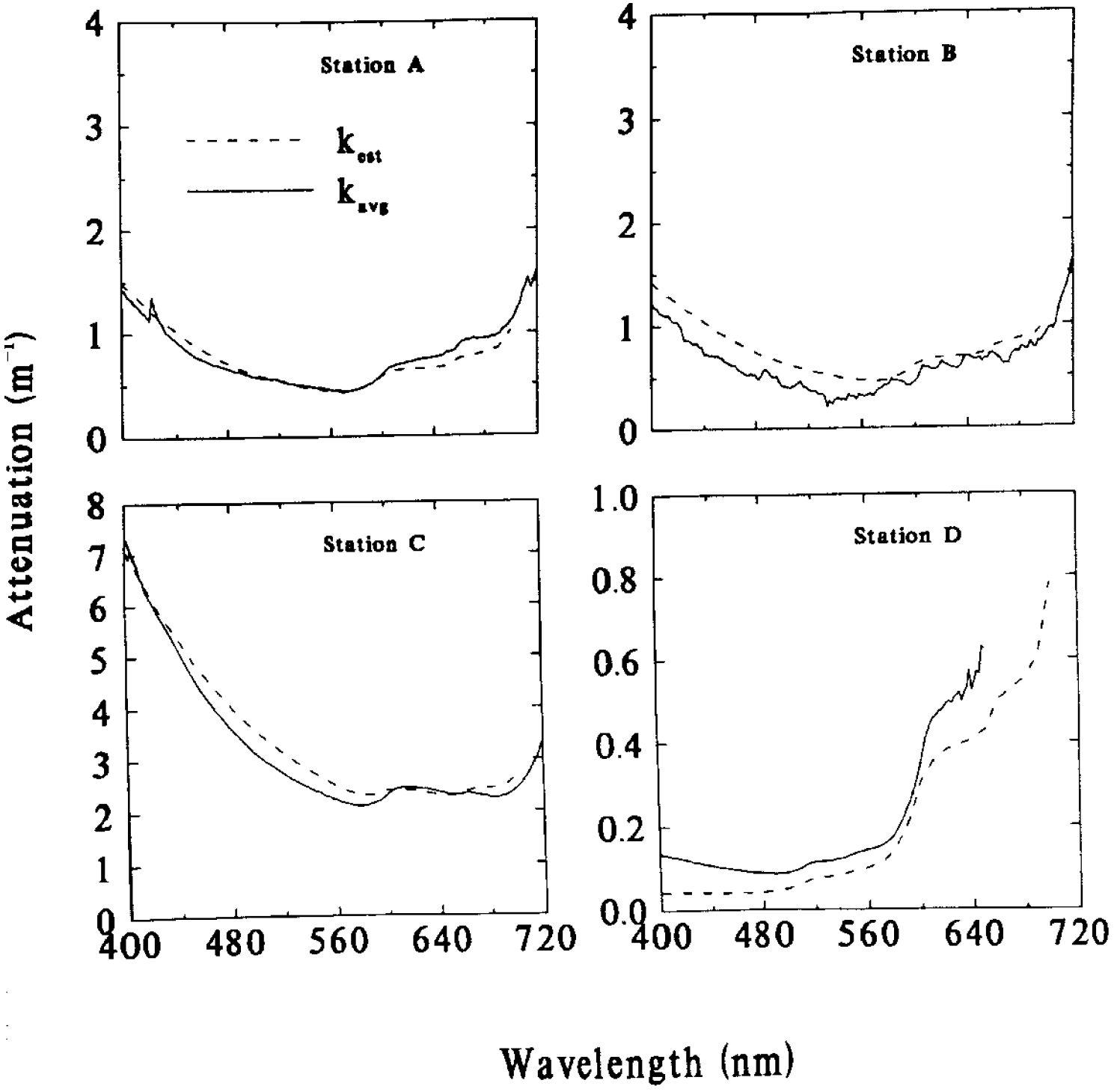

Fig. 9. Attenuation coefficient spectra calculated (Eq. 1) from measured spectral irradiance (solid lines). Scans were averaged from the upper 8 m (Station A), the upper 2 m (Stations B and C) or the upper 20 m (Station D). Dashed lines represent spectral attenuation estimated from a spectral attenuation model as described in Methods.

of k(720) was used to derive the scattering coefficient, b. Ideally, it would be possible to obtain information about these variables using high resolution sampling techniques. For example, empirical relationships have been found to exist between DOC and salinity (Benner, 1994 and unpublished). Thus, a limited set of samples across the salinity gradient may be adequate to characterize DOC on the basis of salinity mapping. It should be noted, howeveurer, that the relationship between DOC and salinity has been shown to be nonconservative during periods of high primary production (Benner, 1994). Improved vertical resolution of beam c may provide a convenient means of estimating SPM (*cf.* Spinrad, 1986). Such estimates would be useful for the assessment of particulate absorption, $a_x(\lambda)$. In addition, empirical relations between SPM and the scattering coefficient, b, may be derived (*cf.* Gallegos et al., 1990). Such a relation would eliminate the need for determining k(720).

As new instrumentation becomes available, it may be possible to better assess inputs required by this and other spectral models. In view of the strong impact of irradiance on primary production in this ecosystem, advances in the ability to characterize the optical environment should improve our ability to estimate and predict productivity.

Acknowledgements

This research was supported by NOAA/Mississippi-Alabama Sea Grant No. NA90AA-D-SG688, Project No. R/LR-25. LUMCON provided the use of the LI-1800-UW. R. Benner and T. Nelsen provided data. We are grateful for the technical assistance of D. Taylor, H. Carrick, and J. Cavaletto. We also thank the captain and crew of the N/S *Malcolm Baldrige*. USM/CMS Contribution No.

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AN ISOTOPICALLY-CONSTRAINED MODEL FOR DENITRIFICATION AND NITROGEN BURIAL IN THE CONTINENTAL SHELF OF THE NW GULF OF MEXICO

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Abstract

Nitrogen isotope ratios of suspended particulate matter, dissolved inorganic nitrogen, and sedimentary organic nitrogen were used to estimate the relative fractions of riverine and upwelled nitrogen inputs, and the advected, denitrified and buried nitrogen losses in the NW Gulf of Mexico continental shelf. Different cases were tested: ignoring and including riverine and shelf dissolved organic nitrogen (DON), and assuming different isotopic signatures for shelf DON. Our results indicate that DON needs to be considered in the nitrogen mass balance of the NW Gulf of Mexico continental shelf because this is the major nitrogen species advected out of the region. Depending on the considered scenarios, the Mississippi-Atchafalaya River system contributes 30-70% of the shelf's nitrogen. Our gross estimates suggest that less than 10% of the incoming nitrogen is denitrified throughout the shelf, but this value could possibly vary if spatial gradients or seasonal fluctuations were to be considered in the model.

Introduction In recent years considerable attention has been drawn to the effects of the Mississippi-Atchafalaya Rivers' nutrient loading onto the northern Gulf of Mexico continental shelf. Major aspects of these studies include nutrient transfers into biomass (Sklar and Turner 1981; Lohrenz et al. 1990; Dortch et al. 1992), the development of hypoxic zones in the region resulting from enhanced production (e.g. Rabalais et al. 1991; Turner and Rabalais 1991), and the ultimate loss of these riverine nutrients via burial (Walsh 1981; Eadie et al. 1992) or denitrification (Rowe et al. 1992).

Most research efforts under the NECOP program have been focused on the vicinity of the Mississippi and Atchafalaya Rivers outflow region where enhanced biological activity and physicochemical reactions occur. However, the influence of this freshwater source on the northern Gulf of Mexico continental shelf can be traced by a distinctive westward-drifting low-salinity plume that extends along the Texas coastline (Dinnel and Wiseman 1986; Dagg et al. 1990). The overall direct and indirect effects of this major nutrient inflow on the NW Gulf of Mexico continental shelf remain to be assessed.

In this study we combine measurements of stable nitrogen isotope ratios and concentrations of different nitrogen pools with other mass fluxes to estimate the relative influence of the Mississippi-Atchafalaya Rivers' nitrogen loading onto the NW Gulf of Mexico. Our results represent a preliminary approach to applying stable nitrogen isotopes to mass balance nitrogen inputs and outputs in the region; thus a range of results are obtained under several constraints used in our model.

Methods

Study zone The samples used were collected at different locations and seasons, between the Mississippi River outflow region and 97°W longitude. Table 1 shows the body of data sampled for the stable nitrogen isotope ratios of particulate organic nitrogen (PON), dissolved inorganic nitrogen (as NO_3), and sedimentary organic nitrogen (SON); the station locations of the samples are shown in Fig. 1.

Stable Nitrogen Isotope Ratio Measurements. Samples for PON were collected by pressure-filtering 5-15 L of seawater through a 47 mm GF/F filter inside an inline stainless steel filter holder. In the laboratory the samples were combusted inside an evacuated quartz tube with CuO and Cu to convert all PON into N_2.

Samples for ^{15}N-NO_3 were collected by filtering 1 L of seawater through a GF/F filter. The NO_3 in the sample was reduced to NH_3 using Devarda's reagent, distilled under basic conditions (pH 9-10) and trapped in zeolite (Velinski et al. 1989). The NH_3 adsorbed to the zeolite was then dried and combusted as described previously.

Sediments were collected with a boxcore and the top 10 cm were subsampled, sliced into 2.5 cm sections and frozen. In the laboratory, the samples were ground to a fine powder and ca 100 mg were combusted by the Dumas method for nitrogen isotopic measurements of SON.

Table 1. Number of locations and samples collected for isotopic analyses of particulate organic nitrogen (PON), nitrate (NO_3), and sedimentary organic nitrogen (SON) in the Northwest Gulf of Mexico continental shelf and slope.

Parameter	Cruise	Date	Locations (samples)
^{15}N-PON	90G-10	July 1990	22(79)
	92G-05	May 1992	24(91)
	92G-10	October 1992	23(39)
^{15}N-NO_3	89G-15	November 1989	4 (4)
	90G-04	February 1990	1 (2)
	90G-07	May 1990	3 (6)
	90G-10	July 1990	2 (3)
	91G-02	March 1991	4 (25)
^{15}N-SON	89G-15	November 1989	3 (12)
	90G-04	February 1990	2 (2)
	90G-10	July 1990	10(21)
	91G-02	March 1991	7 (15)

Nitrogen isotope ratios were measured in a Nuclide RMS-60 stable isotope ratio mass spectrometer against a nitrogen standard (99.999% purity). The values are expressed in δ notation which is the permile deviation relative to atmospheric nitrogen ($\delta^{15}N = 0‰$):

$$\delta^{15}N = (R_u/R_s - 1) \times 1000$$ where:

R_u $^{15}N/^{14}N$ of the sample, and

R_s $^{15}N/^{14}N$ of atmospheric dinitrogen.

Dissolved Organic Nitrogen Concentrations Dissolved organic nitrogen was measured by injecting the sample into a combustion column packed with an alumina support coated with 0.5% platinum as catalyst, and oxidized at 680ºC with high purity oxygen as carrier gas inside a Shimadzu TOC-5000 carbon analyzer. The generated nitrogen oxides were then reacted with ozone and quantified against KNO_3 standards of known concentrations. This system measures total dissolved nitrogen, and DON was calculated by difference (Lopez-Veneroni and Cifuentes 1992).

Salinity and Nutrients In each cruise, samples for salinity and nutrients (NO_3^-, NO_{2^-}, NH_4^+) were drawn at discrete depths and analyzed on board following the methods described in Biggs et al. (1982).

Results and Discussion

Data Reduction The study zone was divided into plume and shelf compartments by the 33 psu isohaline from each cruise and further separated by the 92ºW and 94ºW longitudes. Average values for salinity, nutrients, DON and a weighted average for ^{15}N-PON were obtained for each bin, and an overall weighted average (which considers the area of each compartment) was then

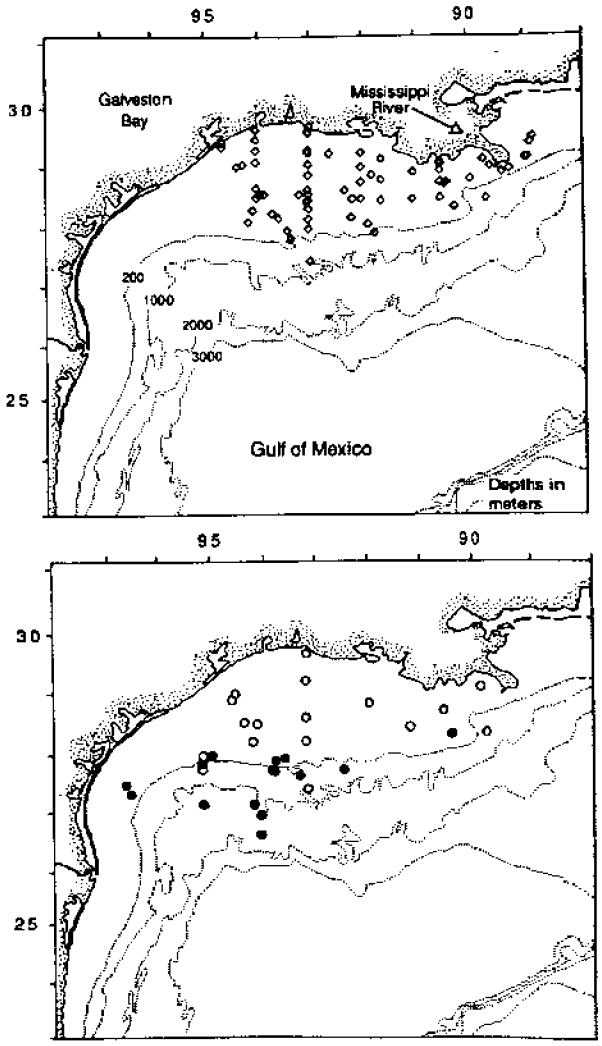

Fig 1. Location of stations sampled for stable nitrogen isotopes. Top panel: Stations sampled for water column particulate organic nitrogen. Bottom panel: Stations sampled for water-column nitrate (E) and organic nitrogen in sediments (J).

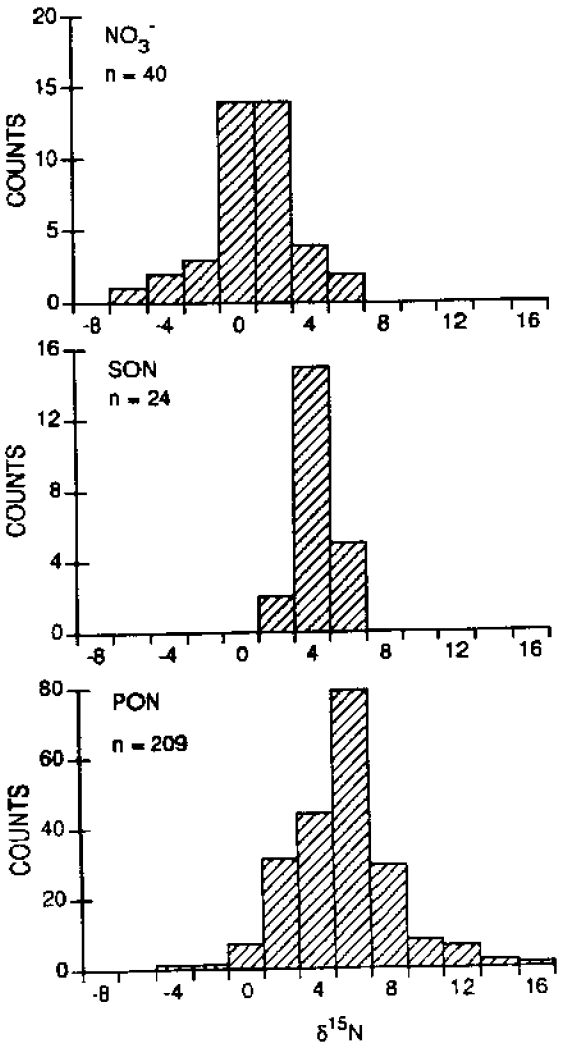

Fig 2. Frequency distribution of the stable nitrogen isotope ratio of NO_3 (top panel), SON (middle panel) and PON (bottom panel) in the NW Gulf of Mexico.

calculated (Table 2).

Frequency histograms for the isotopic ratios of the nitrogen pools that are considered here are shown in Fig. 2. The nitrogen isotopic signature for NO3- collected off the slope between 100 and 200 m depth had an average value of 2.0 ± 2.9‰ (weighted average of 2.1‰), with extreme values between -4.4 to +7.8‰. This contrasts with ^{15}N-enriched values of the riverine NO_3^- endmember ($\delta^{15}N$ = 8.8 ± 1.7‰, n = 9) at the outflow of the Mississippi River in the summer of 1990.

The 2.5 cm slices of each core were averaged for each location, and then an average $\delta^{15}N$ for SON was obtained for the upper 10 cm of the sampled sediments (5.1 ± 1.2‰). The range of isotopic values for SON varied from 3.5 to 7.2‰. (Fig 2).

The average stable nitrogen isotope ratio for water column PON over the continental shelf was 6.4 ± 2.8‰ (weighted average of 6.7‰) with a range of values that varied from -2.2 to +19.2‰. As with the isotope ratio distribution for NO_3^- and SON, the frequency distribution of $\delta^{15}N$-PON followed a normal curve suggesting that our samples are representative of the nitrogen isotope distribution from the different nitrogen pools of the study zone.

Model Equations The following equations were used to obtain salt, water, nitrogen and stable nitrogen isotope balances for the NW Gulf of Mexico continental shelf. The water balance for the shelf (Qs) was calculated from:

$$Q_s = Q_u + Q_r \quad (1)$$

In equation (1) the shelf's water flux is the sum of riverine Q_r and upwelled/offshore (Q_u) inputs. Evaporation predominates over precipitation in the NW Gulf of Mexico (Dinnel and Wiseman 1986; Cochrane and Kelly 1986), but the difference between the two is on the order of 103 $m^3 S^{-1}$, which is negligible when compared to the annual riverine inflow of about 3.7 x 104 $m^3 S^{-1}$ (Cochrane and Kelly 1986; Turner and Rabalais 1991).

The salt balance for the shelf (Ss) was obtained from:

$$Q_s S_s = Q_u S_u + Q_r S_r \quad (2)$$

In Equation (2) the shelf's salinity flux is balanced by offshore upwelling/advection (Su) because the second term of the right-hand side is zero.

The nitrogen balance in the shelf (N_s) was given by:

$$Q_s N_s = Q_r N_r + Q_u N_u - V_d k_d N_s - V_b k_b N_s \quad (3)$$

Equation (3) is a nitrogen balance for shelf waters with riverine and upwelling inputs, and denitrification (N_d) and burial (N_b) losses. The k_d and k_b terms are rate constants (t^{-1}), and V_d and V_b have units of volume.

The stable nitrogen isotope balance was calculated from:

$$Q_s N_s \delta_s = Q_r N_r \delta_r + Q_u N_u \delta_u - V_d k_d N_s \delta_d - V_b k_b N_s \delta_b \quad (4)$$

Equation (4) is the stable nitrogen isotope ratio balance in the shelf (δ_s), with upwelling and riverine

Table 2. Average values for salinity and for several water-column nitrogen pools in the NW Gulf of Mexico continental shelf during cruises 90G-10, 92G-05 and 92G-10.

	Region[a]						
Parameter	1p	1s	2p	2s	3p	3s	Average[b]
% Area	5	7	23	49	7	9	-
Salinity	28.92	35.68	29.84	35.69	30.86	35.59	33.66
^{15}PON[c]	6.52	7.37	7.64	5.94	8.38	6.45	6.68
DIN	5.92	2.99	1.52	1.14	0.40	1.07	1.54
PON	3.08	1.06	2.10	0.68	2.67	0.77	1.30
TDN	25.83	17.44	16.32	14.05	12.14	9.18	14.83
NO_3	4.38	2.23	0.71	0.86	0.20	0.82	1.05
DON	19.61	14.76	14.11	13.09	11.66	8.32	13.24
SN[d]	26.93	15.74	18.53	12.80	14.31	10.96	14.97
PON+DIN	8.47	3.42	3.94	1.75	3.10	2.03	2.83

[a]Regions divided latitudinally by the 33 psu isohaline where p is < 33 psu and s is > 33 psu. Region 1 is to the E of 92°W, Region 2 is between 92°W and 94°W, and Region 3 is to the W of 94°W
[b]Weighted average of all compartments into which the study zone was divided
[c]Weighted average = $S([PON] * {}^{15}PON)_i / S[PON]_i$
[d]SN = TDN + PON

inputs, and outputs from denitrification and burial. Here δ_d is the result of PON denitrification, that is: $\delta_d = \delta_s - \partial$, where ∂ is the fractionation factor associated with denitrification (ca -25‰, Mariotti et al. 1981).

Finally, the fractions (f) of buried, denitrified and exported nitrogen and isotope ratios are the only outputs considered here:

$$f_s + f_d + f_b = 1 \qquad (5)$$

Model Variables We considered an annual average riverine input of 1.4 x 104 m^3 S^{-1}, which results from 53% of the Mississippi and 100% of the Atchafalaya Rivers' flux into the NW Gulf of Mexico continental shelf (Dinnel and Wiseman 1986). The rivers' NO_3^- input was considered as 111 uM from the Mississippi and 77 uM from the Atchafalaya (who's average is 69% of the Mississippi's annual average, Turner and Rabalais 1991), and total riverine nitrogen was calculated from Turner and Rabalais' (1991) empirical equation (from their Fig 5). The difference between total nitrogen and nitrate was considered as riverine DON.

The stable nitrogen isotopic composition of the high molecularweight fraction of DON was provided by Dr Brian Eadie (unpublished data). These data were collected from four NECOP cruises along the salinity gradient, but only the riverine and oceanic endmembers were used in our calculations.

Our slope water salinity and NO3- average concentrations were estimated from 0 - 200 m depth observations at those stations where $\delta^{15}N\text{-}NO_3^-$ was collected (Fig. 1 and Table 1). This salinity (36.02 psu) and NO_3^- (5.5 uM) averages represent the offshore advection/upwelled component onto the continental shelf. The vertical salinity and NO_3^- distribution profiles for these stations is similar to those presented by Sahl et al. (1993) at various transects along the Texas-Louisiana continental shelf.

From the given water and nitrogen riverine fluxes, and the average NO_3^- concentration for slope thermocline waters, different scenarios were tested to estimate the advected, buried and denitrified losses in the region. These are discussed below and the results are summarized in Table 3.

Case 1. *Riverine and shelf DON are ignored.* In this case, NO_3^- is the only nitrogen species input considered to affect the shelf's nitrogen budget. Here, a combined average concentration of 94.6 uM NO_3^- enter via the Mississippi-Atchafalaya River system, 5.5 uM NO_3^- -

Table 3. Advected, denitrified and buried nitrogen for the NW Gulf of Mexico continental shelf, estimated under different assumptions.

Case	Nitrogen inputs		Nitrogen outputs		
	% upwelled	% riverine	% denitrified	% buried	% advected
1: DON is ignored	46	54	1	74	25
2: Same 15N-DON in shelf and river	33	67	-2	5	97
3. Different ^{15}N-DON for shelf and river	34	66	9	19	71

enter from the slope via upwelling/advection, and the nitrogen concentration exiting is 2.8 uM (weighted average for shelf PON and DIN, Table 2). In this scenario over 70% of the nitrogen needs to be buried, 1% would be denitrified, and about 25% of the incoming nitrogen would be advected out of the region, mostly as PON.

Case 2. *Riverine and shelf DON are considered, both with the same isotopic ratio.* In this case the DON pool is included, with an invariant δ ^{15}N value of 4.5%. (average at 0 and 33 psu) in both the shelf and river waters. The riverine total nitrogen input would increase to 158 uM with an isotopic signature of 7.1%. (40% DON and 60% DIN). The nitrogen concentration advected out of the shelf is 15 uM (DIN + PON + DON) with an isotopic value of 4.9%.. Under these constraints, 5% of the incoming nitrogen is buried, no denitrification occurs, and an external source is required to balance the nitrogen flux and the isotopic signature.

Case 3. *Riverine and shelf DON are included, each with different isotopic values.* In this case the DON riverine, shelf and offshore pools of varying isotopic signatures are included. No method to isolate DON from the salt matrix in oceanic samples is currently available, thus δ ^{15}N values of bulk oceanic DON are inexistent. Reported values for the isotopic composition of this pool consist of specific molecules (Benner et al. 1989) or of the high molecular-weight fraction (Eadie unpublished). From the previous two cases, however, it is evident that DON needs to be considered to balance the nitrogen fluxes in the region.

To estimate the isotopic signature of DON we assumed that a fraction of the incoming riverine DON is labile (e.g. 20%, Sharp 1983), thus the riverine nitrogen input is increased from 96 uM to 110 uM. Measurements of stable isotope values for NH_4^+ in the plume region averaged 9.8 $\pm$ 4.0%. (n = 8). The mean δ ^{15}N for bacteria (collected by both the bioassay and nucleic acid methods, Coffin and Cifuentes 1993) was 8.2 $\pm$ 3.2%. (n = 18). If it is assumed that bacterial nitrogen sources include DON and NH_4^+, and that 15-20% of their nitrogen requirements are met by DON (Wheeler and Kirchman 1986), then a δ ^{15}N of 6-7 %. for DON would isotopically balance the bacteria. This estimate is similar to the δ ^{15}N of shelf PON. Under these assumptions about 9% of the nitrogen would be denitrified and 19% would be buried.

These preliminary estimates obtained using the above approach throughout the NW Gulf of Mexico continental shelf are based on somewhat general and simplistic assumptions. Furthermore, these preliminary results do not consider spatial gradients nor seasonal variations which have been shown to occur in a variety of biological (e.g. Lohrenz et al. 1990), physical (Cochrane and Kelly 1986; Dinnel and Wiseman 1986), and chemical (Rabalais et al. 1991) parameters. Our results, however demonstrate the utility of measuring stable nitrogen isotopes of different reservoirs, and reinforce the concept that DON has to be considered as a major nitrogen pool in the region.

Acknowledgements

This work was partially funded by NOAA NECOP project 404514. We thank Dr Brian Eadie for providing his riverine and oceanic data set of δ ^{15}N-DON, and for collecting riverine DIN samples.

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DIET AND FEEDING ECOLOGY OF STRIPED ANCHOVY, Anchoa hepsetus, ALONG ENVIRONMENTAL GRADIENTS ASSOCIATED WITH THE MISSISSIPPI RIVER DISCHARGE PLUME

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Introduction

Inadequate understanding of the factors regulating recruitment, the process through which eggs are spawned and fish hatch, survive, and grow to a harvestable size, is a major obstacle to improved fishery management (Sissenwine 1984; Anderson 1988). It is generally accepted that fish recruitment is regulated during the early life history with three main factors, transport, predation and feeding success, interacting to determine recruitment success. Environmental features in the sea like the Mississippi River discharge have major consequences for all three of these factors, either by influencing the distribution and concentration of suitable food (Lasker 1978; Sherman et al. 1984; Govoni et al. 1989; Grimes and Finucane 1991) or by transporting larvae to areas of good or bad food supply and predator fields (Fortier and Leggett 1983; Frank and Leggett 1982; Leggett et al. 1985; Crecco and Savoy 1984). For example, with less than 40 copepod nauplii or 10 copepodites per liter (Blaxter 1965; May 1974; Arthur 1977; Hunter 1981), prey densities in the open ocean are low compared to concentrations encountered in the Mississippi discharge plume, which has up to 1000 copepod nauplii l^{-1} in surface frontal waters (Dagg and Whitledge 1991). The variables most affected by such changes in food supply are probably growth rates and larval stage duration (Cushing 1975; Werner and Gilliam 1984). While direct starvation might cause recruitment failure under some circumstances, increased predation on larvae during a longer larval period is the more likely consequence of reduced food supply (Houde 1986; Anderson 1988).

The northern Gulf of Mexico in the vicinity of the Mississippi River is the most productive region in the Gulf of Mexico. Portions of the continental shelf affected by the river have long been noted as regions of high phytoplankton stocks and productivity (Riley 1937; El-Sayed 1972), and more recently Lohrenz et al. (1990) reported extraordinarily high phytoplankton production (>5 g C $m^{-2}d^{-1}$) in the immediate vicinity of the discharge plume. Copepod naupliar densities off the Mississippi Delta have been reported to be 28-150 l^{-1}, up to 10 times greater than densities observed off Florida or Texas (Dagg et al. 1987). In the immediate vicinity of the discharge plume, Dagg and Whitledge (1991) found naupliar densities up to 1000 l^{-1} during summer. Similarly, average larval fish densities around the Mississippi River discharge (Govoni et al. 1989; Ditty 1986; Grimes and Finucane 1991) are up to 20 times greater than densities reported along Loop Current fronts in the open Gulf of Mexico (Richards et al. 1989). Among the nation's most productive fishing grounds, these rich waters annually yield approximately 2.4 billion pounds of fish valued at more than $780 million at dockside (estimated total economic impact of $2.34 billion). This harvest represents 40 percent of the total domestic harvest of fish (O'Bannon, 1993). In addition, this region is also a major recreational fishing area, providing 35% (in number) of the total U.S. recreational catch (Essig et al. 1991).

The biological production associated with the plume varies along environmental gradients. The highly productive 6-8 km wide frontal zone where plume and shelf waters meet is characterized by a strong salinity gradient and hydrodynamic convergence which may account for observed concentrations of fish larvae (Govoni et al. 1989; Grimes and Finucane 1991; Govoni and Grimes 1992). The frontal zone also contains concentrations of phytoplankton (Grimes and Finucane 1991; Lohrenz et al. 1990), copepod nauplii (Dagg and Whitledge 1991) and fish larvae (Govoni et al. 1989; Grimes and Finucane 1991) well above the already high ambient levels encountered in adjacent plume and shelf waters. Observations of this elevated biological activity are consistent with fronts in other regions (Yoder et al. 1981; Paffenhofer et al. 1984; Sakamoto and Tanaka 1986).

Several factors suggest that the Mississippi River is the ultimate source of much of this biological productivity. The river discharge is large and much of it remains on the broad shallow shelf for several months. River waters contain high concentrations of dissolved nutrients, and the open Gulf does not appear to be a significant source of shelf nitrogen (Dagg et al. 1991).

Due to this high biological production, it has been hypothesized that fish larvae in the vicinity of the discharge plume in general, and the frontal zone in particular, would utilize potentially rich food resources and consume a superior diet, grow faster, and thus experience a shorter stage duration, and survive better. However, the same biological and physical factors that concentrate larval fish prey may also concentrate their predators.

Studies conducted specifically to evaluate the growth and mortality elements of this hypothesis suggest that there may be a growth effect. Observed growth rates of king mackerel, Scomberomorus cavalla (DeVries et al. 1990) and Atlantic bumper, Chloroscombrus chrysurus, (Loeffler 1990) were higher off the Mississippi Delta than elsewhere in the Gulf. While DeVries et al. (1990) could not demonstrate similar growth differences for Spanish mackerel, Scomberomorus maculatus, more recent results show that Spanish mackerel (Grimes and DeVries, unpublished) and yellowfin tuna, Thunnus albacares, (Lang et al. 1994) grow faster at intermediate salinities (28-31%), i.e., in the frontal waters, as compared to adjacent shelf and plume waters. Daily instantaneous mortality rates for both king and Spanish mackerel larvae have been found to be higher in the vicinity of the discharge plume as compared to other Gulf of Mexico locations (Grimes and DeVries, unpublished), supporting the element of the hypothesis that larval fish predators as well as prey may be concentrated in the vicinity of the discharge plume.

Recent results have indicated that the positive growth effect may be at least partially artifactual, i.e., an upward bias in observed growth rate due to the effect of size-selective mortality. Grimes and Isely (in press) back-calculated growth histories of wild king mackerel and wild and lab-reared gulf menhaden larvae (Brevoortia patronis) using otolith microstructure. Back-calculated sizes at age were larger for older larvae, possibly the effect of selective mortality on the smallest larvae at age. Furthermore, the analysis demonstrates that for the king mackerel example the selective mortality effect may bias observed growth rates upward by as much as 25%.

There is little published information relevant to the diet and feeding ecology element of the proposed hypothesis. Govoni and Chester (1990) investigated the diet of spot, Leiostomus xanthurus, but were unable to demonstrate a trophic advantage for larvae in the plume. Powell et al. (1990) used morphological, gut content volume and recent growth criteria to evaluate the nutritional condition of spot larvae and could not consistently demonstrate an advantage for larvae in the plume.

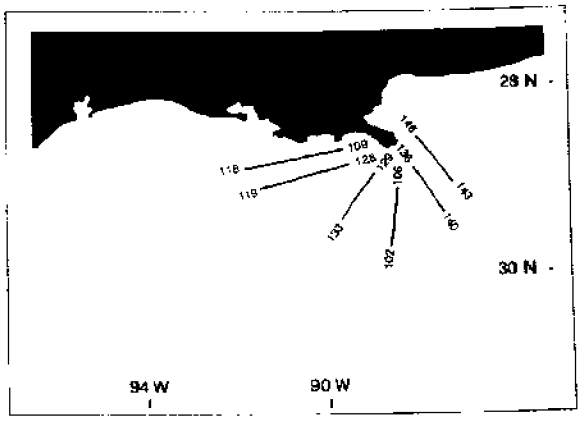

Fig. 1. Map of the Gulf of Mexico in the vicinity of the Mississippi River discharge plume. Solid lines represent transects sampled from 4 to 13 May 1992. Numbers indicate first and last stations along each of the six transects.

The purpose of this study is to thoroughly evaluate the larval fish feeding element of the hypothesis. In this paper we report results of analyses to determine diet; time of feeding; diet differences among plume, front and shelf water masses; and diet overlap and diversity among water masses for the striped anchovy Anchoa hepsetus.

Materials and Methods

We conducted a cruise to the Mississippi River discharge plume aboard the NOAA R/V Chapman from 4 to 13 May 1992. Fifty-two stations were sampled along six 15-25 km long transects off the major passes in the river system to allow us to examine diet and feeding differences at different time and space scales (Figure 1). Two of these transects, which began near Southwest Pass and extended westward, were designed to measure downstream differences (permanent time scale and farfield/km spatial scale). The other four transects were North-South transects designed to measure differences at the turbidity fronts (ephemeral/hrs and nearfield/m), as well as variations among water masses in the vicinity of the plume (permanent and nearfield/km).

Ichthyoplankton samples were collected in 10 minute surface tows with a 1 X 2 m neuston net (0.947 mm mesh) and a 1 X 1 m Tucker trawl (0.335 mm mesh). All samples from one East-West transect were preserved in 95% ethanol for 24 hours (for growth and mortality estimations) and then replaced with fresh ethanol. All other samples (for gut content microscopic analysis) were preserved in 10% buffered formalin solution for 24 hours, after which the solution was drained and replaced with 95% ethanol. Microplankton

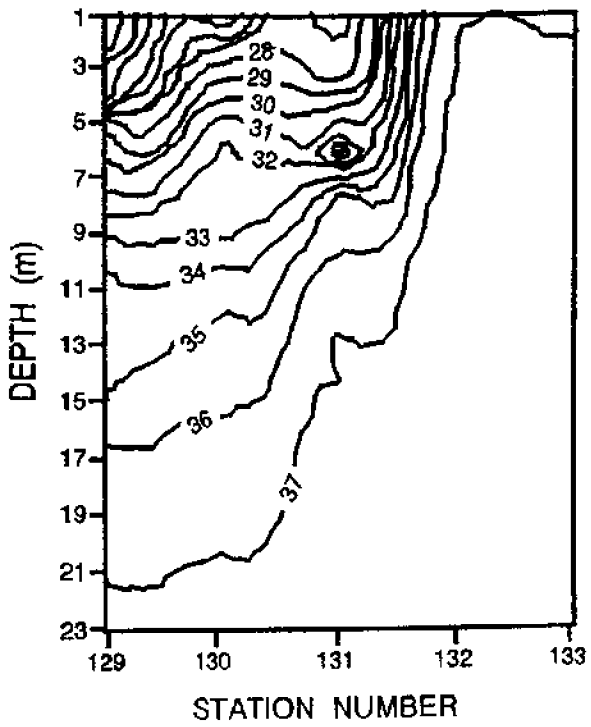

Fig. 2. Surface salinity profile for a North-South transect sampled during May 1992 off the Mississippi River plume. Stations 129 and 130 were labeled at plume water stations, 131 as a frontal water station, and 132 and 133 as shelf water stations.

(which represent food availability for diet selectivity estimations) were collected at each station with Niskin bottles. They were filtered through a 35 um sieve and then preserved in 10% buffered formalin solution. Surface water samples for chlorophyll a determination were collected with Niskin bottle casts, and environmental data for hydrographic profiles were determined with CTD casts. These data were used to create salinity profiles of each sampling transect, and samples from each station were designated as belonging to plume, front, or shelf waters based upon these profiles (Figure 2).

In the laboratory ichthyoplankton were sorted and identified using standard taxonomic references (Fahay 1983; Lippson and Moran 1974; Hildebrand and Shroeder 1928; Hildebrand 1943). The engraulid Anchoa hepsetus (striped anchovy) was the most abundant larval fish in the samples. In addition, striped anchovy are particularly important prey species in the Gulf of Mexico (Finucane, et al. 1990). Consequently, it was chosen for diet analyses. Larval striped anchovies were measured to 0.1 mm standard length (SL) with the aid of a dissecting microscope (50x) and an ocular micrometer. The gastrointestinal tracts of the larvae were removed, with no more than 30 larvae examined from any one station. Food items were teased from the gastrointestinal tracts and identified to the lowest possible taxonomic level using various zooplankton identification references (Smith 1977; Owre and Foyo 1967; Newell and Newell 1963; Omori and Ikeda 1984; Fraser 1962). They were then counted using a dissecting and compound microscopes (160x-320x).

For both qualitative and quantitative analyses of larval feeding patterns, percent by number and frequency of occurrence were calculated for consistently recognized taxonomic categories in each water mass using all food items. These two values were then plotted against one another to determine the relative importance of different prey items. A chi-square contingency test was calculated for the most important prey items to evaluate the statistical significance of spatial variations in diet contents among plume, front, and shelf waters (Windell and Bowen 1978).

To measure the degree of diet similarity between water masses, three pair-wise comparisons were made to measure diet overlap using Horn's (1966) modification of Morisita's Index (1959):

$$C_\lambda = \frac{2\left(\sum_{i=1}^{S} P_{ij}P_{ik}\right)}{\left(\sum_{i=1}^{S} P_{ij}^2\right) + \left(\sum_{i=1}^{S} P_{ik}^2\right)}.$$

In this equation P_{ij}^2 represents the relative frequency of prey category i in water masses j and k, while S is the total number of prey categories found in the two water masses being analyzed. The values for C_λ range from 0 (no overlap in diets between the two regions) to 1 (complete overlap).

To measure diet breadth (diversity) within each water mass, Levins' (1968) index for diet diversity,

$$B = \frac{1}{\sum_{i=1}^{S} P_i^2}$$

was calculated for plume, front, and shelf water masses. This diversity coefficient (B) varies between 0 (least

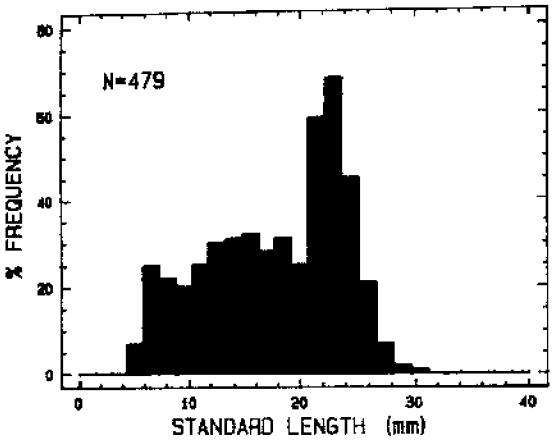

Fig. 3. Length-frequency histogram for larval striped anchovies, Anchoa hepsetus, collected in and around the Mississippi River discharge plume in May 1992.

diverse assemblage of prey) and S (most diverse assemblage). To analyze the evenness component of the distribution within a region, B was divided by the S prey categories available in the diet. These scaled values range from 0 (the most uneven distribution of prey items) to 1 (the most even distribution).

Results

A total of 479 larval striped anchovy were examined in this study. The lengths for all water masses combined ranged from 5.0 to 29.9 mm SL, with a mean of 17.7 mm SL. Plume larvae were 7.4 to 27.0 mm SL (mean = 18.5 mm SL); frontal larvae were 5.2 to 29.9 mm SL (mean = 17.5 mm SL); and shelf larvae were 5.0 to 26.0 mm SL (mean = 17.9 mm SL) (Figure 3).

To determine the time of day of striped anchovy feeding, the percent number of stomachs with food for each station was plotted against the time at which the station was sampled. The highest percentage of larvae with food in the stomachs was consistently found in the morning hours between 0600 to 0800 hours, suggesting that most feeding occurs at that time (Figure 4).

Overall the diet consisted of a wide array of prey items. Prey categories included various crustaceans (amphipods, cladocerans, copepods, ostracods, etc.), diatoms, eggs, larvaceans, and polychaete larvae. Several food items were found only in the plume, i.e., chaetognaths, amphipods, and mysids. Tintinnids were found only in the frontal zone. All prey categories in the shelf, however, were also in at least one of the other two water masses. The larvae in shelf waters ate half as many prey items as did those in the plume or frontal waters. Shelf anchovies ate primarily diatoms, while anchovies in the other two water masses consumed mainly diatoms and copepods (Table 1).

Using both quantitative measures of the diet, frequency of occurrence and number of prey items, copepods and diatoms were the predominant foods consumed. These two categories occurred in 83.34% of the guts and accounted for 60.64% of the total prey in plume waters, occurred in 71.28% of the guts and accounted for 69.49% of the total prey in frontal waters, and 87.51% of the guts and 81.17% of the total prey in shelf waters.

There were clear differences in the quantities of the major prey categories by water mass (Table 1). Diatoms occurred more frequently (42.86% of the guts) and were more abundant (39.36% of total prey items) at plume stations. They were also more frequent (71.88%) and more abundant (75.29%) in the shelf. At frontal stations copepods were the most frequent (48.51%) and the most abundant (48.02%) prey items found. We used chi-square contingency analysis to evaluate differences in the two major prey categories among water masses. The analysis indicated that the frequency of prey in the two categories was not independent of water mass, i.e., the frequencies were significantly different ($X^2 = 20.68$; df = 2; p = 0.00003).

Diet overlap measures (C_λ) indicated that plume and frontal striped anchovy possessed more similar diets, while shelf and frontal larvae had the most dissimilar diets (Table 2). The value for the plume-front comparison was quite high (0.91), indicating almost total overlap in prey categories for these two areas. Similarly, the value for the plume-shelf comparison was

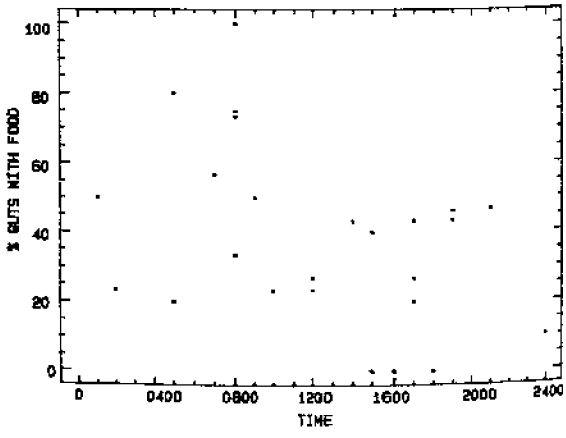

Fig. 4. Plot of percent number of striped anchovy guts with food for each station versus the time at which each station was sampled.

high (0.75), indicating a high degree of similarity of diet. The front-shelf comparison (0.55) showed the least amount of overlap between water masses.

The two measures of diet diversity (B and B/S) were consistent in showing that larvae in the plume consumed a more diverse assemblage of prey than those in either the shelf or the front (Table 3). Striped anchovy larvae in the plume consumed many more prey types than larvae in front or shelf waters, resulting in a high B (richness) value, however the evenness measure of diversity (B/S) was proportionately lower because of the relatively inequitable distribution of prey among categories.

We plotted percent frequency of occurrence on percent by number for all prey categories to obtain an index of relative importance of the different food categories in larval anchovy diets. In all three water masses, copepods and diatoms were the two major prey items, with diatoms most important in plume and shelf waters and copepods most important in frontal waters (Figure 5). All other food categories were much lower in importance when their percent frequency of

Table 1. Percent frequency of occurrence and percent number of prey categories for larval striped anchovy (N=42 guts with food in the plume; N=101 guts with food in the front; N=32 guts with food in the shelf).

Prey Item	%FO			%N		
	Plume	Front	Shelf	Plume	Front	Shelf
Chaetognatha	4.76			2.13		
Crustacea	69.05	64.35	18.76	38.30	57.62	7.06
Amphipoda	2.38			1.06		
Cladocera	4.76	0.99		2.13	1.13	
Copepoda	40.48	48.51	15.63	21.28	48.02	5.88
Mysidacea	2.38			1.06		
Ostracoda	2.38	1.98	3.13	2.13	1.13	1.18
Unidentified	16.67	12.87		10.64	7.34	
Diatoms	42.86	22.77	71.88	39.36	21.47	75.29
Centric	4.76	0.99		3.19	1.13	
Pennate	38.10	21.78	71.88	36.17	20.34	75.29
Dinoflagellates	7.14	1.98	3.13	3.19	1.13	4.71
Eggs	7.14	2.97	9.38	4.25	1.69	5.88
Hydromedusae	2.38	2.97		2.13	1.69	
Larvaceans	7.14	2.97		4.26	1.69	
Plant Material		0.99			0.56	
Polychaete Larvae	7.14	6.93	6.25	3.19	3.95	2.35
Radiolarian	2.38			1.06		
Salp	2.38			1.06		
Tintinnids		0.99	6.25		0.56	2.35

Table 2. Diet overlap (similarity) between water masses for larval striped anchovy.

Comparison	C_λ
Plume-Front	0.91
Plume-Shelf	0.75
Front-Shelf	0.55

occurrence and percent by number were plotted.

Discussion

The analysis to determine time of feeding suggests that most feeding occurs in the early morning hours 0600 to 0800 and falls off rapidly afterward. Since the gut contents we analyzed came from surface (neuston) samples, our conclusion regarding feeding time is not unequivocal. Subsurface larvae, if present, could have been actively feeding at other times.

Although the diet in general consisted of quite a wide variety of prey types (Table 1), it was clear that two types, copepods and diatoms, comprise the bulk of the diet. Combined, these two prey types alone accounted for 70% of the number of prey consumed. Frequency of occurrence data show a similar predominance of diatoms and copepods, occurring in 37 and 41% of guts, respectively. Furthermore, plots of percent frequency of occurrence on percent by number for copepods for each of the three water masses clearly

Table 3. Diet diversity (B) and evenness (B/S) of distribution of prey among categories. Values were calculated using numbers of prey.

Water Mass	B	B/S
Plume	5.11	0.23
Front	3.50	0.16
Shelf	1.73	0.08

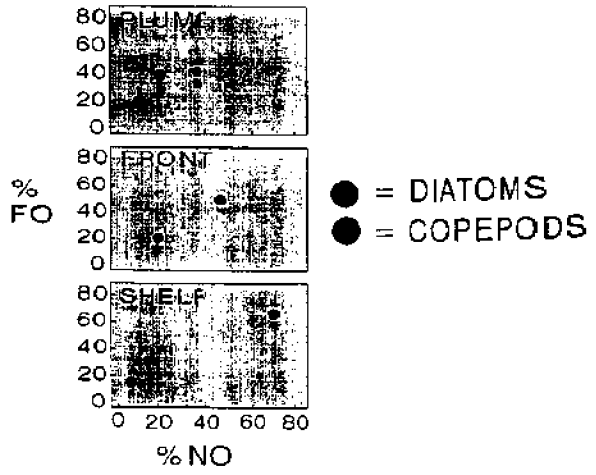

Fig. 5. Plot of percent frequency of occurrence versus percent number for the two major prey items found in the stomachs of larval striped anchovy. Diatoms are represented by the darker dots and copepods by the lighter dots.

showed that copepods were most important in the diet of larvae in the front.

We believe our results suggest that the diet consumed by larval striped anchovy in the frontal zone may be superior to the diet of plume and shelf larvae. The ratio of C:N in diatoms is approximately 4:1 (Vinogradov 1953), which is only slightly less than the ratio in copepods (Durbin and Durbin 1984; Stoecker and Govoni 1984). However, the copepods recovered in the diet were much larger than the diatoms, and copepods occurred most frequently and were numerically most abundant in the front. Consequently, we believe that larval anchovy in frontal waters were consuming a more nutritional diet than those in plume or shelf waters.

That similarity statistics show nearly complete diet overlap (and the highest among the three water mass comparisons) between plume and front samples is not surprising. This interface is the region of strongest horizontal density gradients which, along with wind and tidal shear, create strong hydrodynamic convergence (Govoni and Grimes 1992), an active mixing force that would promote similarity of prey assemblages.

Earlier work did not demonstrate that the potential trophic advantage is actually conferred to larvae associated with the Mississippi plume. Spot larvae collected in plume waters ate twice as many food organisms as did larvae in shelf waters (Govoni and Chester 1990). However, organisms consumed within the plume were mostly small (tintinnids, copepod

nauplii, pelecypod veligers and invertebrate eggs), whereas organisms eaten in shelf waters were larger (copepodites and adult copepods). Because the volume and nutritional quality of gut contents of larvae from the two areas were roughly equivalent, Govoni and Chester concluded that larvae in the plume gained no trophic advantage. Furthermore, Powell et al. (1990) used morphological, gut content volume and recent growth criteria to evaluate the nutritional condition of spot larvae, Leiostomus xanthurus, associated with the plume and could not consistently demonstrate an advantage, finding only a minimal association between instantaneous growth rates, gut content, volume and degree of starvation.

It may be that these studies were unable to conclusively demonstrate a trophic advantage to larvae in the Mississippi discharge plume and/or turbidity fronts because a full understanding of plume hydrography had not been developed. Salinity, temperature and sigma-t sections from 15-25 km transects made during both high and low flow regimes show that the discharge plume area contains three distinct water masses, a shallow lens of low salinity Mississippi plume water, Gulf of Mexico shelf water and frontal waters, a mixture of the former two (Grimes and Finucane 1991; Govoni and Grimes 1992). Turbidity fronts (with a scale of 5-50 m) form, disperse and reform at tidal frequencies and are nested within the broad frontal zone. Perhaps incomplete knowledge of the existence and scale of the frontal zone and its nested turbidity fronts resulted in inappropriate diet comparisons, i.e., larvae may not have been correctly assigned to plume or shelf waters.

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RETROSPECTIVE ANALYSIS OF NECOP AREA SEDIMENTS: BIOGENIC, INORGANIC AND ORGANIC INDICATORS OF ANTHROPOGENIC INFLUENCES SINCE THE TURN OF THE CENTURY

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Abstract

Surface and cored sediments from the NECOP study area were analyzed for physical (coarse-grain texture, composition), biological (foraminifera) and chemical (organic and inorganic) properties. Results of analyses for surface samples indicated spatial patterns of benthic foraminifera dictated by sediment accumulation rate and regions of seasonal hypoxia. The latter also correlated well with the distribution of surface authigenic glauconite. Temporal variability, determined from core samples, indicated transitions in benthic foraminifera community structure with upcore increases in hypoxia tolerant assemblages. Transitions in glauconite abundance, organic carbon, and other chemical parameters strongly correlated temporally with increases in fertilizer application in the United States.

Introduction.

The Mississippi River basin drains approximately 41% of the contiguous United States and with it comes the byproducts of both natural continental weathering and anthropogenic activities. Basinwide, these signals coalesce and transition seaward entering the Gulf of Mexico at two point sources, the Mississippi Birdfood Delta and the mouth of the Atchafalaya River. With the development of farming in America's heartland, agricultural runoff has also been transported seaward and perhaps the most significant has been enhanced nutrient loading, primarily as a byproduct of man's increasing use of artificial fertilizer. Recent measurements of Mississippi River water indicate rising levels of nutrient concentrations and fluxes (Bratkovich and Dinnel, 1992) that are implied to result from agricultural sources. Within the Louisiana/Texas continental shelf, recent observations of declining water quality have suggested linkage between river and continental shelf water qualities. To test this, the NECOP Program's central hypothesis was formulated to address this potential linkage, specifically:

Hypothesis: *ANTHROPOGENIC NUTRIENT INPUTS HAVE ENHANCED COASTAL OCEAN PRODUCTIVITY WITH SUBSEQUENT IMPACTS ON COASTAL OCEAN WATER QUALITY AND YIELDS OF LIVING RESOURCES.*

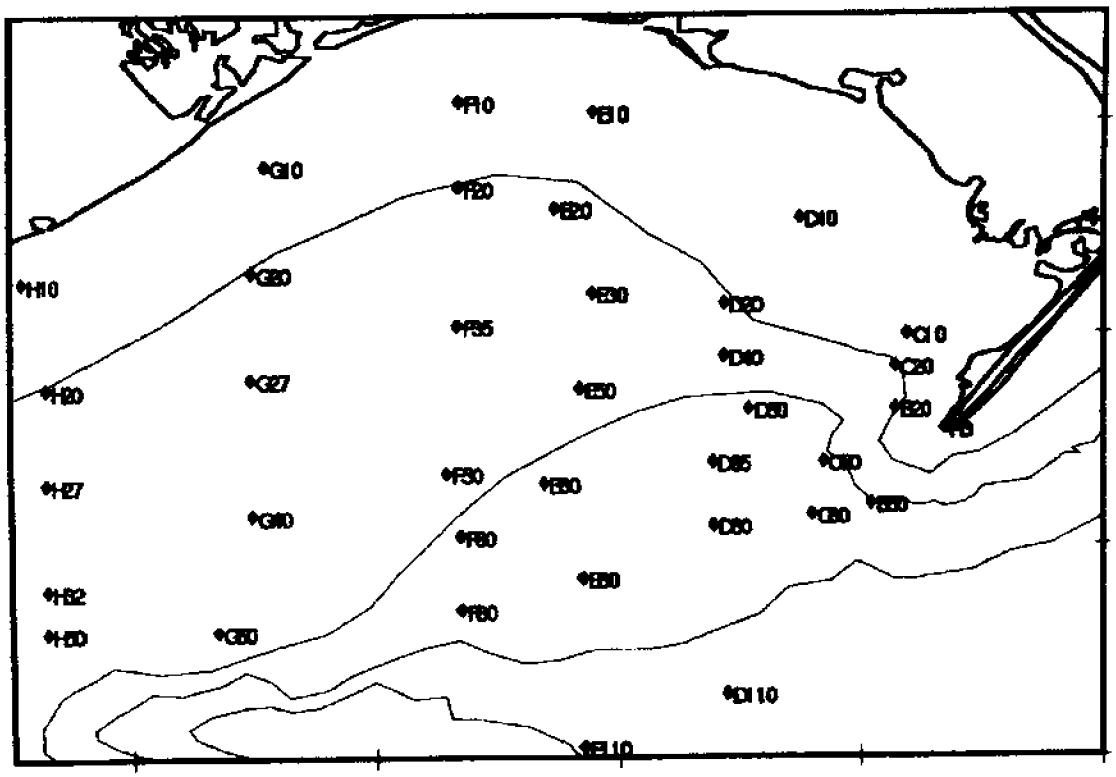
Unfortunately, measurements of Mississippi River water quality only go back for a few decades and coastal water quality less than a decade, and as such fall short of the time history of continental agricultural influences. The sediments however can potentially provide a record over decadal to century time scales and therefore act in a manner analogous to a long time-series record of natural and anthropogenic influences. Within the Louisiana shelf environment, this has been conclusively shown for anthropogenic lead (Trefry et al., 1984). To assist in addressing the NECOP central hypothesis, the Retrospective Analysis Group has tested the following hypotheses relative to the sediment record:

Hypothesis 1: *COMMUNITY STRUCTURE - OBSERVED RIVERINE NUTRIENT ENHANCEMENT, TOGETHER WITH SILICON DECLINE, HAS PROMOTED A SHIFT IN THE BENTHONIC COMMUNITY STRUCTURE OF THE MISSISSIPPI/LOUISIANA SHELF AND THIS SHIFT IS PRESERVED IN THE SEDIMENT RECORD.*

Hypothesis 2: *HYPOXIA INDICATORS - BY-PRODUCTS OF HYPOXIA/ANOXIA EVENTS HAVE LEFT CHARACTERISTIC MARKERS WHICH PRODUCE A TIME HISTORY OF SUCH EVENTS IN THE SEDIMENT RECORD.*

Hypothesis 3: *CARBON ACCUMULATION ANTHROPOGENIC NUTRIENT ENHANCEMENT IN THE COASTAL ZONE HAS PRODUCED PROPORTIONAL ENHANCEMENT OF PRIMARY PRODUCTIVITY AND CONCOMITANT CARBON BURIAL IN THE SHELF SEDIMENT DEPOCENTERS.*

A



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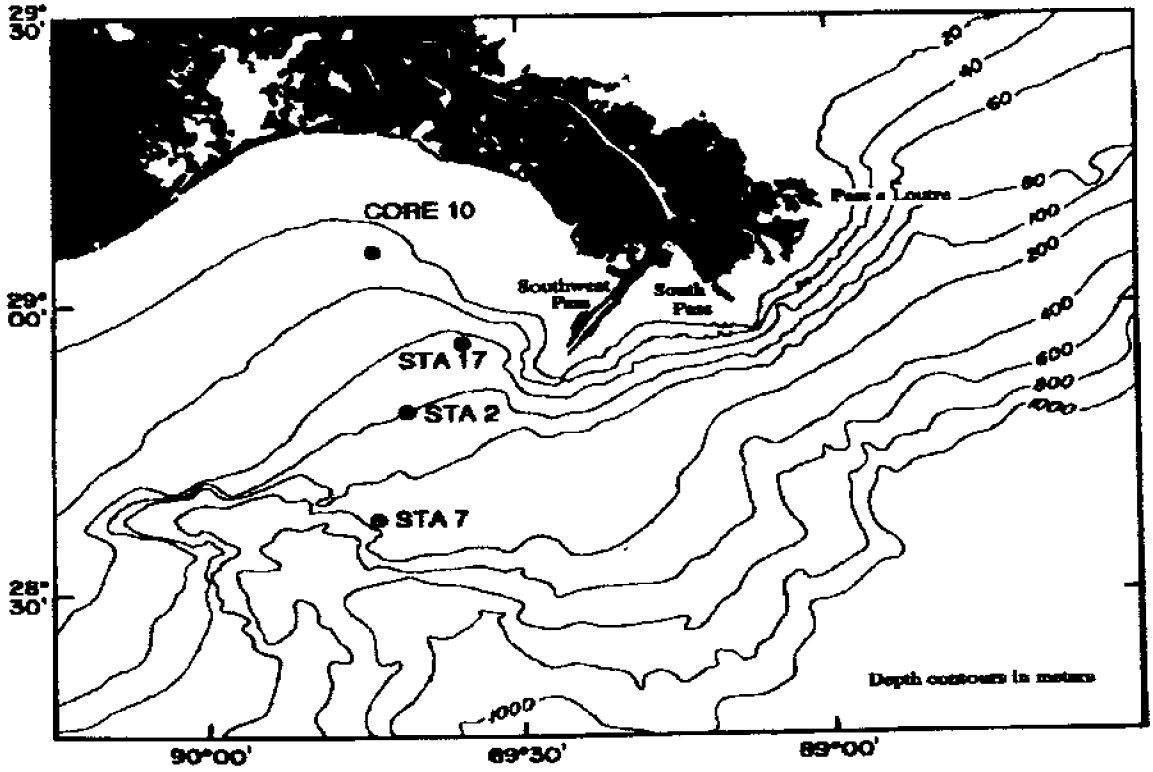

Fig. 1. A. Locations of surface grab samples examined in the study. B. Locations of cores recovered and analyzed in this study.

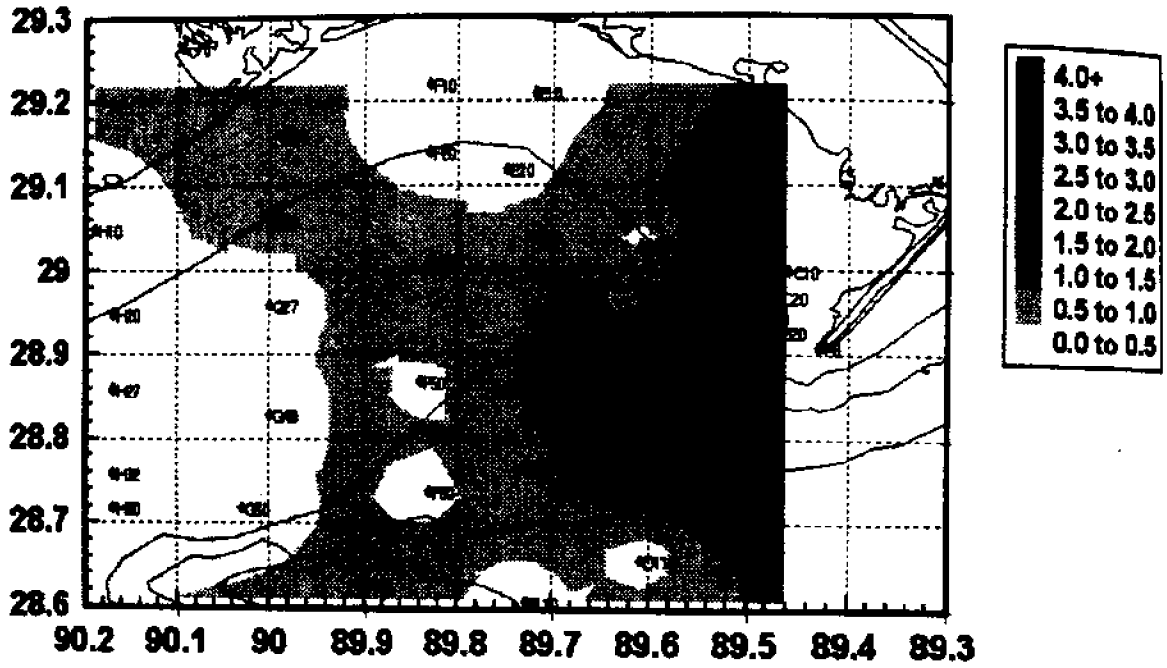

Fig. 2. Surface sediment accumulation rates (cm yr^{-1}) determined during the LASER Program.

Our progress to date, in testing these hypotheses, will be reported for both surface and cored sediments. The locations of surface sediment grab samples are shown in Fig. 1A and cored sediments in Fig. 1B.

Surface Sediments.

The grab-sample network (Fig. 1A) occupies prior LASER sites for which sediment accumulation rates have already been measured. The collection of surface sediments had the goal of evaluating the most recent sediment record for comparison to current environmental conditions such as sediment accumulation rates and seasonal hypoxia. The overall objective however was to take the results of these comparisons and apply them to downcore trends under the premise that "the present is a key to the past". Investigated parameters included benthic foraminifera distributions, organic carbon and glauconite distribution.

Sediment accumulation rate patterns reflect the large input from the Mississippi River, specifically from Southwest Pass, as shown in Fig. 2. The highest accumulation rates (4 cm yr^{-1}) are not directly adjacent to Southwest Pass but westward and centered at ~89.6 W and ~28.9 N. From this major depocenter, accumulation-rate gradients decline steeply to <1 cm yr^{-1} over most of the study area.

To test our hypothesis concerning benthic community structure in the sediment record, and its shift with time, if any, we studied the foraminifera community at each grab site (Fig. 1A). Approximately 300 benthic and planktic foraminifera were picked for each station and identified to the species level. In order to evaluate shifts in benthic foraminifera biodiversity, the Shannon-Wiener Information Function was utilized (Patrick, 1983). This index incorporates a measure of species evenness as well as number of species such that communities with many species of equal-size populations have the highest index. The index of diversity (H) is computed from the following expression:

$$H = -\sum_{i=1}^{N} p_i \ln p_i$$

where N is the number of species, and p_i is the proportion of the total number of individual species which belong to the i^{th} species (MacArthur, 1983). In

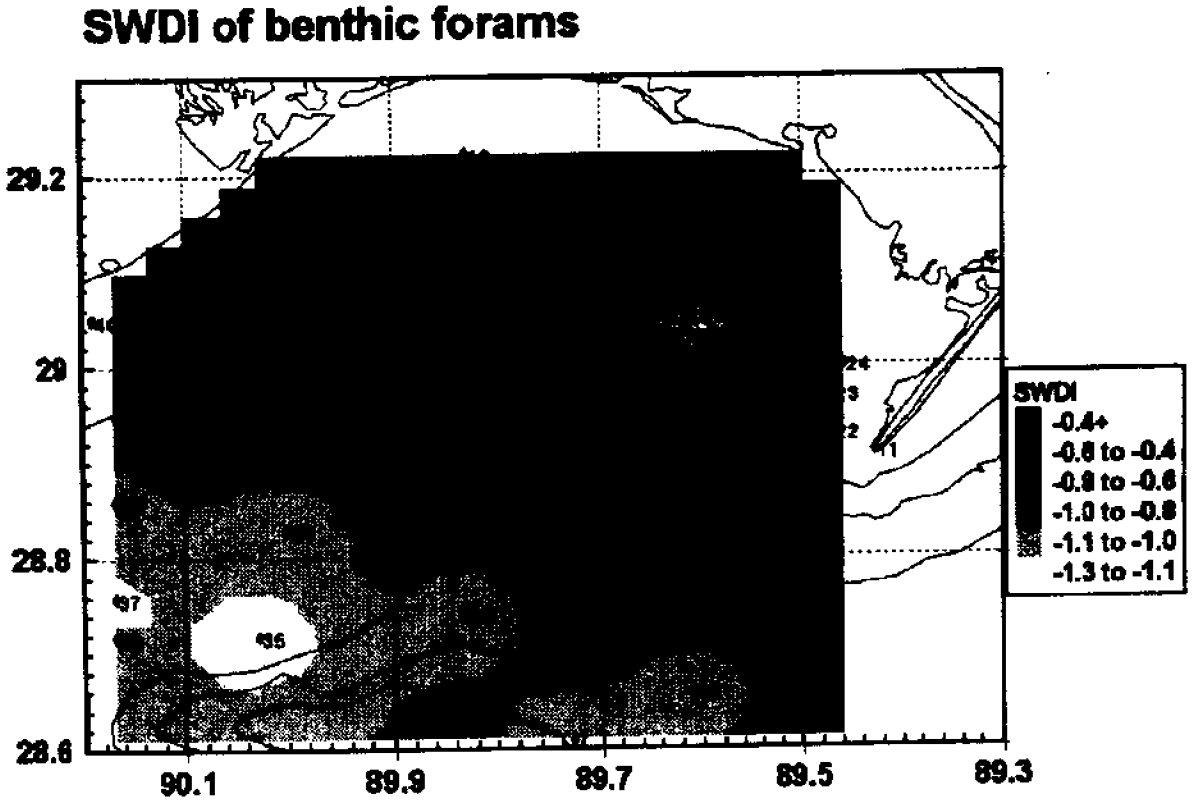

Fig. 3. Map of the diversity (SWDI, see text) of benthic foraminifera from the surficial sediments in the study area. Lower values (e.g. -0.4) indicate lower foraminifera-community diversity and visa versa.

this text, H will be referred to as the Shannon-Wiener Diversity Index (SWDI). Smaller values (e.g. -0.4) indicate lower diversity and visa versa.

Results indicate that the lowest values of the SWDI (Fig. 3) coincide with sediment accumulation-rate highs (Fig. 2) thus suggesting that diversity may be strongly influenced by sedimentation patterns. Spatial plots of all the identified foraminifera species indicated only a coherent pattern between accumulation rates and Epistominella vitrea (Fig. 4). As suggested by comparison of this distribution and that of sediment accumulation rate (Fig. 2), Epistominella vitrea strongly correlates ($r = 0.69$, $n = 38$) with sediment accumulation rate indicating a tolerance for such environmental conditions. Although spatial coherence between accumulation rates and Epistominella vitrea is high, the relatively low abundance of this species along the northern edge of the study area cannot help account for the relatively low SWDI values in this region.

Comparison of the surface distribution of the benthic foraminifera Buliminella morgani (Fig. 5) with sediment accumulation rate patterns (Fig. 2) show low correlation ($r = 0.01$, $n = 38$) indicating that the distribution of Buliminella morgani is not directly controlled by this process. However, the areas where Buliminella morgani comprise the dominant (i.e. ~50>65%) species of the foraminifera population corresponds to the highest occurrences of hypoxia (i.e. 69 out of nine years, Fig. 6) while offshore, where hypoxia has never been observed, Buliminella morgani percentages rapidly diminish. As such, these data clearly establish the present-day association between the benthic foraminifera Buliminella morgani and seasonally hypoxic environments.

In addition to community structure, we tested our hypothesis on characteristic markers of hypoxia/anoxia within the sediment and found evidence which supported the trends established by benthic foraminifera. During microscopic analysis of the 63μm fractions, a grain type was observed whose very-high abundance was limited to the 63μm fraction. These grains exhibited coloration in various shades of green and ranged from 63-200μm in diameter. Initial chemical analysis indicates a composition consistent with the solid-phase glauconite. Analyses, using SEM/EDA, indicate a major-element composition of Si, Al, Fe, K,

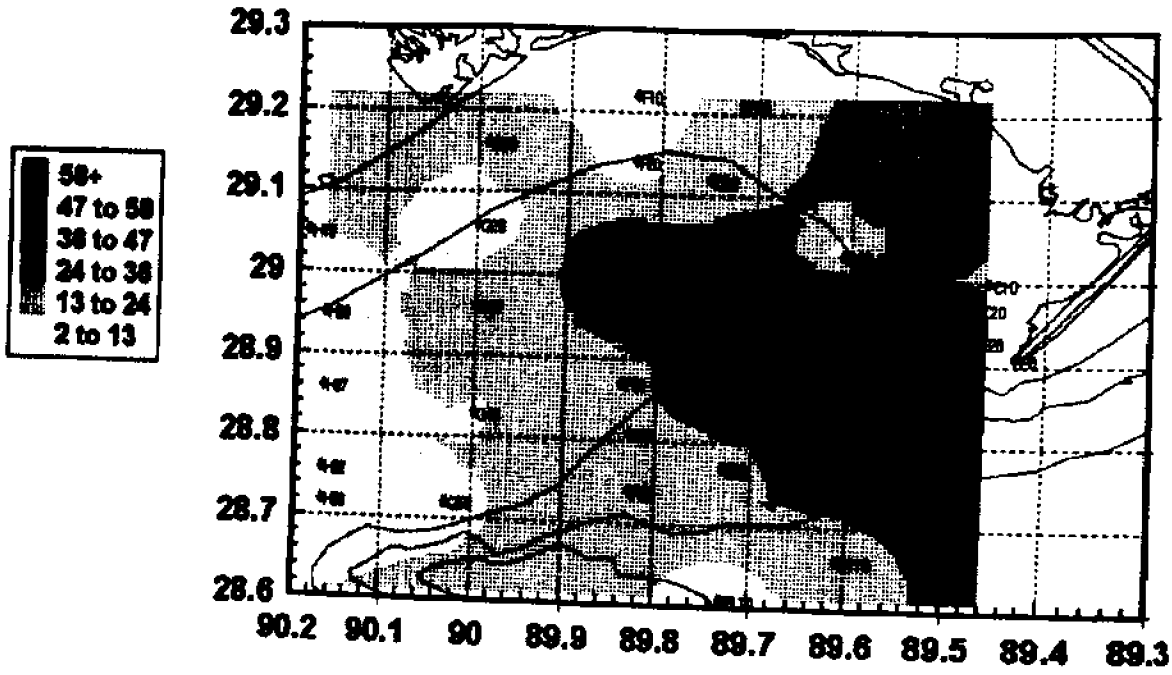

Fig. 4. This figure illustrates the surface distribution of the benthic foraminifera Epistominella vitrea expressed as percentage of the total benthic foraminifera population in each station sample.

and Mg, which corresponds well with the known major element composition of glauconite, which has the general formula of :

$K_{(x+y)}(Si_{4-x}Al_x)_4(Fe^{+3}Al,Mg,Fe^{+2})_2O_{10}(OH)_2$ (Odin, 1988)

This ongoing chemical and physical study of glauconite, from the shelf region adjacent to the Mississippi River, is based on our network of grab samples (38) uniformly covering the area of Fig. 7 as well as at the Mississippi River mouth and upriver (Hood et. al, in prep). Results to present indicate that shelf glauconite is chemically and physically (size) distinct from the river-borne population and enriched in Fe, Mg, and K relative to normal shelf sediments. Moreover, comparison of this figure with Fig. 6 indicates the highest percentage of surface glauconite is observed in areas of documented hypoxia (Nelsen et al., 1994). Glauconite grain-size-distribution data indicate that the river-derived component accounts for only 15%. The latter observation implies that while changes in discharge, channelization, and damming of the Mississippi River may induce modifications in the detrital fraction of glauconite present on the shelf, such would constitute a only a minor change in the current population.

Surface sediment concentrations of organic carbon range from 0.57% at station H-10 (nearshore at western edge of sample grid) to 1.91% at station F-10 (nearshore northern edge of grid at ~89.8 N). For comparison, Mississippi River suspended matter averages about 1.5-1.8% organic carbon. The trend for organic carbon values, seen in Fig. 8, shows a path of more organic-rich sediments along an hypothesized transport pathway from the mouth of Southwest Pass to the northwest as observed during lagrangian drifter studies. Lower levels of organic carbon to the west are found in somewhat coarser-grained sediments. Trends for sediment N and P are comparable with those for organic carbon.

Cored Sediments.

While surface samples allow spatial relationships to be evaluated, age-dated cores provide the temporal context of primary interest to the NECOP Program. Coring objectives were to recover interpretable sedimentary sequences from both the areas of seasonal hypoxia and areas outside the seasonal hypoxia. The former allowed study of time history of hypoxia indicators while the latter provided a control condition for comparison. Investigated parameters included coarse-fraction (>63μm) abundances of quartz,

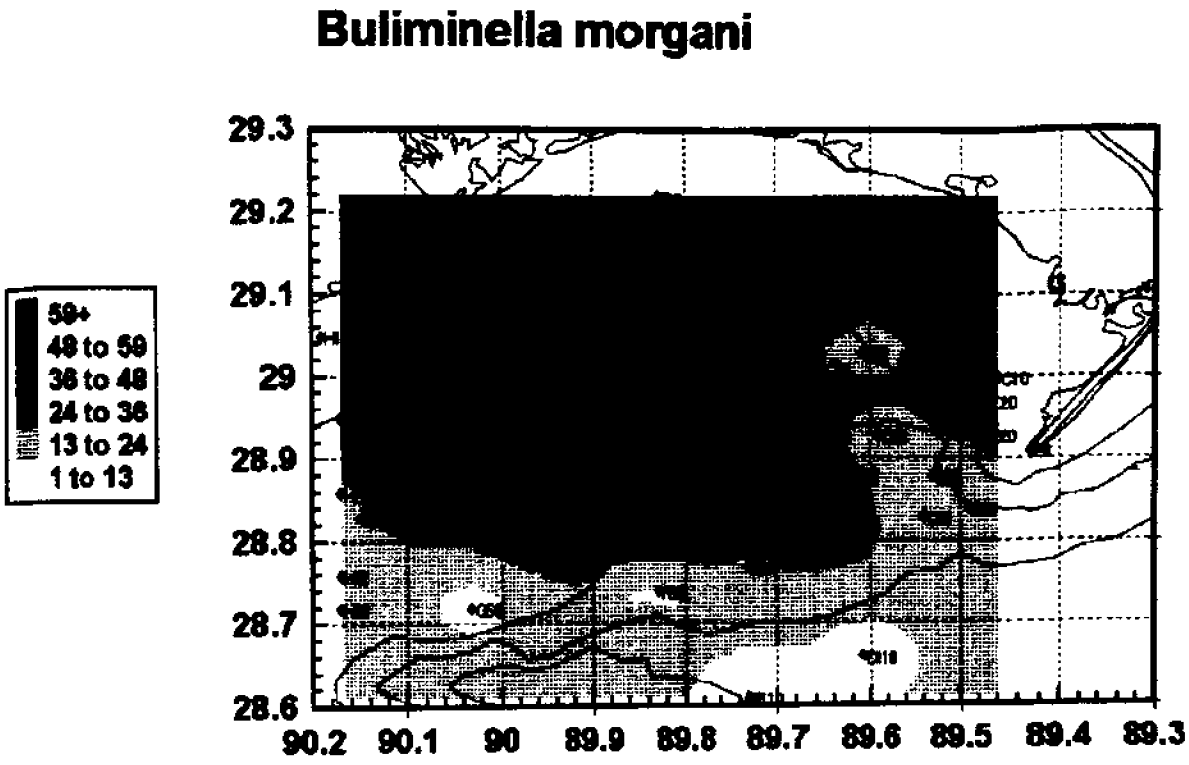

Fig. 5. This figure illustrates the surface distribution of the benthic foraminifera Buliminella morgani expressed as

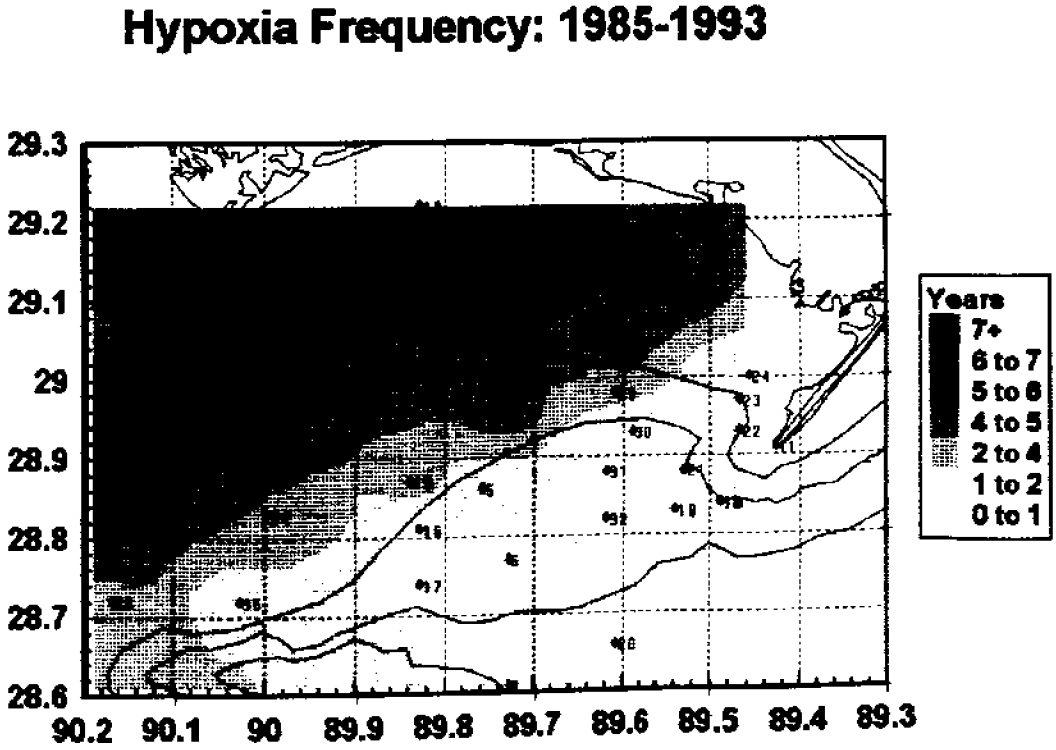

Fig. 6. These data illustrate the frequency and distribution of hypoxia that has occurred at each sampling station over approximately the last decade (1985-1993) based on existing hypoxia monitoring data (N. Rabalais, personal communication and seasonal hypoxia distribution maps).

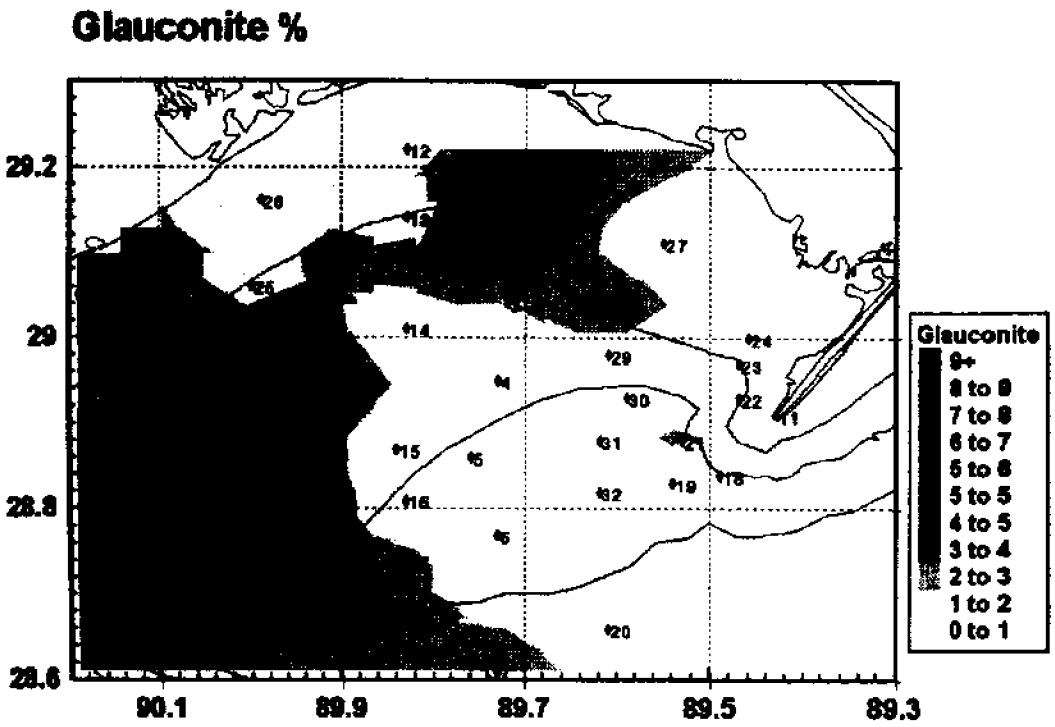

Fig. 7. The surficial distribution of authigenic glauconite expressed as a percentage of the coarse (63m) sediment fraction.

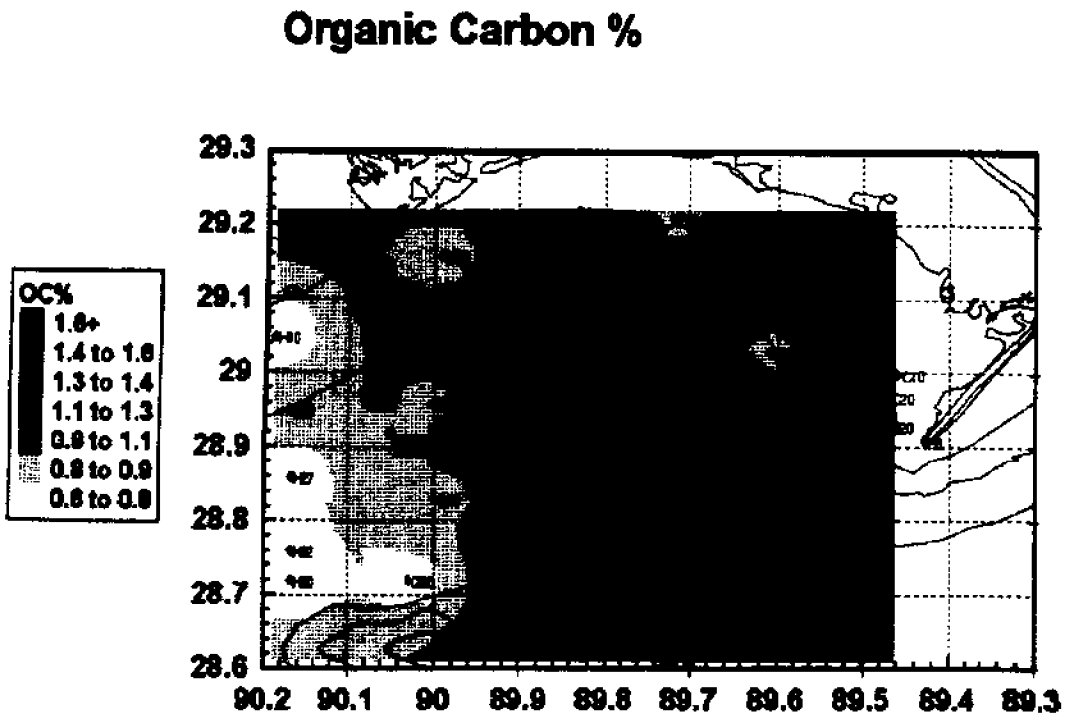

Fig. 8. A contour map showing concentrations of organic carbon (%) in surficial sediments (0-2 cm) from the Louisiana continental shelf.

glauconite, and benthic foraminifera community composition, community shifts and diversity changes as well as organic carbon, stable carbon isotopes and organic tracers. These parameters provided a data base for understanding environmental changes from ~1900~1990.

Core site selection was based on two criteria: 1) areas known for the presence and absence of documented seasonal hypoxia and, 2) a region in which sediment accumulation rates are adequate to allow decadal to century time-scale resolution. Sediment geochronology was done by ^{210}Pb to both establish an intact and interpretable sedimentary sequence and, once established, provide a temporal framework for subsequent analyses.

Core 10 (Fig. 1B) is the closest to a distributary mouth (~33 km), and in an area of documented persistent seasonal hypoxia (Rabalais et al., 1991). A sediment accumulation rate of 0.55 cm yr^{-1} (i.e. Fig. 9A: 1 cm 2 years) at this core site allowed analysis back to about the turn of the century. Thus, it was ideal for observing changes, if any, in sediment components due to anthropogenic influences during the last ~90 years. The Station 7 core was recovered near the shelfedge ~42 km from the mouth of S.W. Pass (Fig. 1B). It has an established geochronology of ~1900-1980 (Fig. 9B) and was therefore ideal for comparison of non-hypoxic (Station 7) with seasonally-hypoxic (Core 10) shelf conditions since just after the turn of the century.

Detailed (1 cm intervals) analysis of the sediment's coarse fraction (63m) indicated a complex and variable record of quartz within Core 10 (Fig. 10A). A linear trend analysis of these data indicates an upcore decline (-8267%) in lithogenic quartz abundance that is consistent with declining trends of sand transport for the Mississippi River (Meade and Parker, 1984). In contrast, the total coarse fraction displays an increasing upcore trend (Fig. 10A) indicating that the abundance changes of this portion of total sediment is controlled by factors other that lithogenic quartz.

A plot of glauconite abundance in Core 10 (Fig. 10B), along with a linear trend analysis of these data, indicates an upcore increase in this component consistent with the trend in total coarse percent and antithetical to the lithogenic quartz trend (Fig. 10A vs B). Conditions at the Core 10 site are known to be favorable for authigenic glauconite (glauconyl/verdine facies: shallow marine, free access to sea water, and a sediment rich in constituent elements). Studies of the geologic record document the close association of glauconitization episodes and anoxic episodes in shelf settings (Bréhéret, 1991). Moreover, we believe compelling evidence exists for the role of anthropogenic input in enhancing the formation of hypoxia with

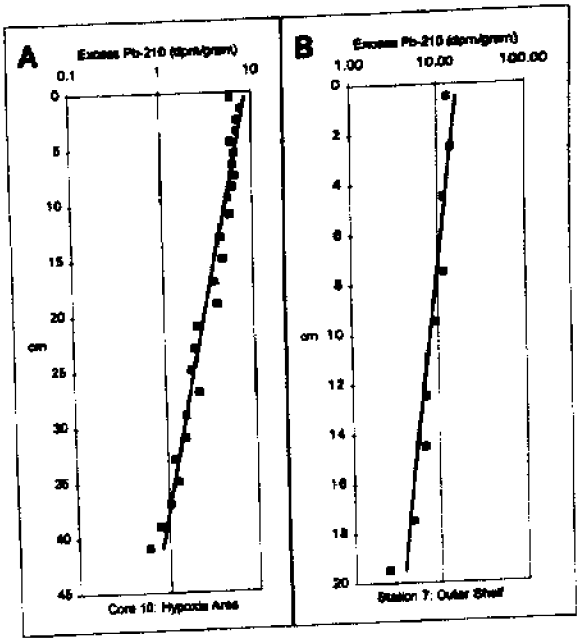

Fig. 9. Excess ^{210}Pb curves for: A. Core 10 from an area of chronic seasonal hypoxia, B. core at Station 7 on the outer shelf and not in an area of documented seasonal hypoxia.

concomitant formation of authigenic glauconite in Core 10. This is suggested by a transitional increase of ~2.3x in mean glauconite abundance after the late-1930's to early-1940's time horizon (Fig. 11A, arrow). Specifically, below the transition, average glauconite abundance accounts for ~5.8% of the coarse fraction while above this horizon it accounts for ~13.4%.

Our study of benthic foraminifera from Core 10 augments and confirms trends and interpretations based on glauconite data as will be shown next. Evaluation, using both light and electron microscopy, indicates that post-depositional processes have not altered the benthic foraminifera tests in Core 10. Therefore, detailed identification and trend analysis was feasible down to core base (~1900) for both total foraminifera abundance and species identification. Relative to the former, Fig. 10B contains a plot of foraminifera abundance and a linear trend analysis for these data. As with glauconite data, an upcore increase mimics the increasing coarse percent trend and is also antithetical to the lithogenic quartz trend (Fig. 10A). In addition, a total of 49 benthic foraminifera species were identified from seven levels in this core. Contrasting trends of upcore species composition variability emerged. One assemblage, Epistominella vitrea, Buliminella morgani, Brizalina lowmanii, Nonionella atlantica, Nonionella opima and Ammonia parkinsoniana lepida (referred to hereafter as

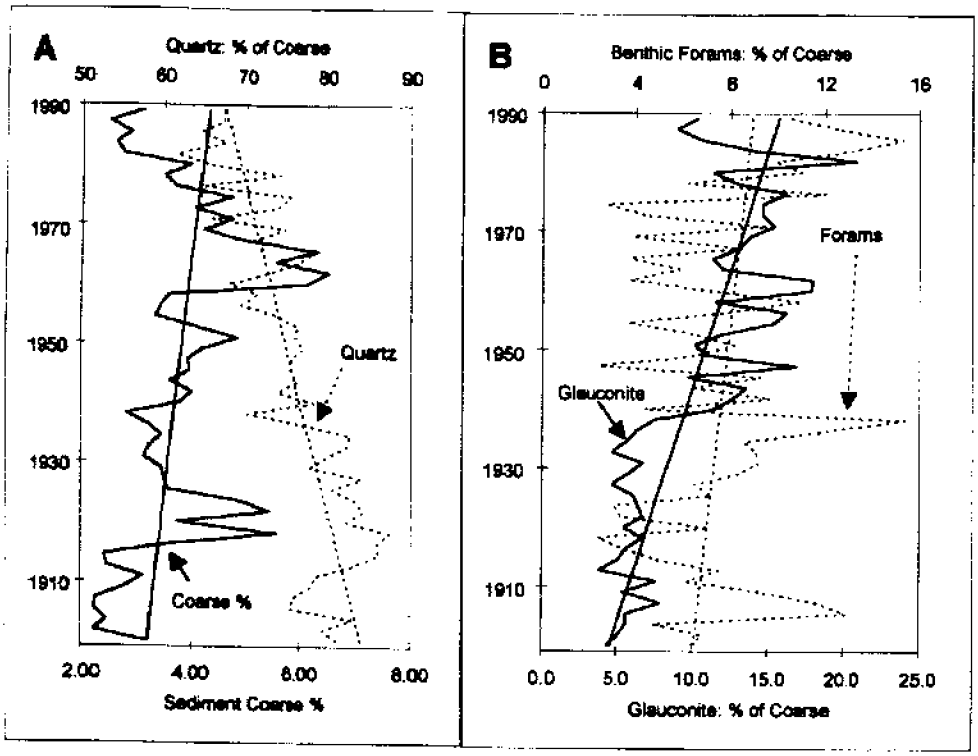

Fig. 10. Distribution and trends of sediment coarse (63m) fraction components in Core 10 showing: A. total coarse fraction (solid) and quartz (dashed), and B. glauconite (solid) and benthic foraminifera (dashed).

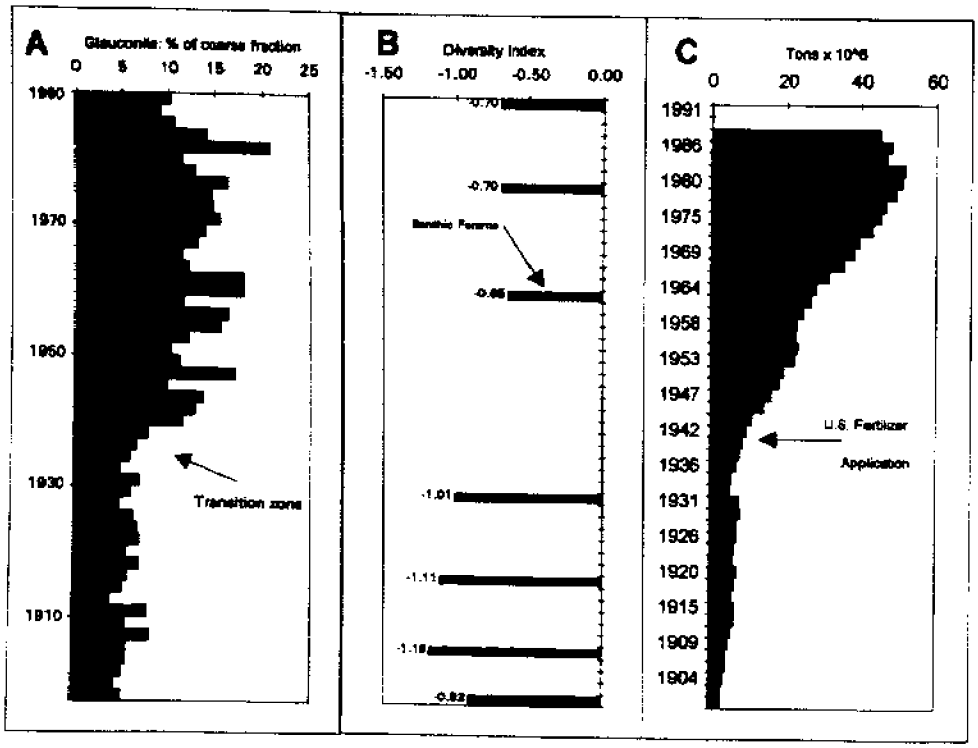

Fig. 11. A. Glauconite grain abundance, B. the Shannon-Wiener Diversity Index for benthic foraminifera for Core 10 compared to: C. the application of fertilizer in the United States for the years 1900-1990.

Group A), displayed an upcore increase in group abundance, as a percentage of total foraminifera species, from 52% at 42-43 cm (~1910) to 90% at 3-4 cm (mid-1980's). Group A was dominated by hypoxia-tolerant E. vitrea and B. morgani which changed from 22% and 27% (= 49%) at core bottom, to 15% and 58% (= 73%) at core top, respectively. In contrast to this, agglutinated, miliolid and hypoxia-intolerant hyaline foraminifera species (Group B) decrease upcore. Specific upcore decreases, as a percentage of total foraminifera population, are: 1) agglutinated - 17% at 42-43 cm (~1910) to 1.5% at 3-4 cm (mid-1980's), 2) miliolids - 9% at 42-43 cm to 1.1% at 3-4 cm, 3) hypoxia-intolerant hyaline - 17% at 42-43 cm to 7% at 3-4 cm.

The ostracodes are an additional benthic population of interest in Core 10. This group is known to be sensitive to variability in environmental parameters such as salinity, temperature, substrate, and availability of food supply (Athersuch et al., 1989). Preliminary results of our study of Core 10 indicate that diversity as well as population abundance of ostracodes decreases upcore (Alvarez-Zarikian et al., in prep.). These findings suggest that the ostracode population may be more sensitive than the foraminifera to the onset of hypoxia, and is an important potential indicator of historical low-oxygen conditions.

The significance of these population changes is evident when compared to the current surficial distributions of these same species, and their environmental settings. Considerable environmental insight has been gained from contemporary distributions of the foraminifera species in Groups A and B, obtained from the surface grab samples, which is relevant to Core 10. Detailed comparisons of areas of documented hypoxia and surficial distribution of foraminifera indicate that Group A species dominate the hypoxic-area populations. In contrast, members of Group B are either absent or form a very-minor component of hypoxia-area samples. The latter become more abundant in better oxygenated areas. In general, the foraminifera assemblage observed in the lower portion (>25 cm, early-1940's) of Core 10 resembles that from non-hypoxic area surface grab samples. In contrast, near core top, the assemblage is similar to that observed in surficial samples from hypoxic areas. In order to examine quantitatively the extent to which the benthic foraminifera population may have changed over time, the SWDI was calculated for each of the seven levels examined in Core 10. The results, shown here in Fig. 11B indicate that the diversity decreases from near -1.0 at core base (~1900) to -0.70 at the core top (~1991). The greatest change occurred between 1930 and 1960. It has been established in previous studies that variation in

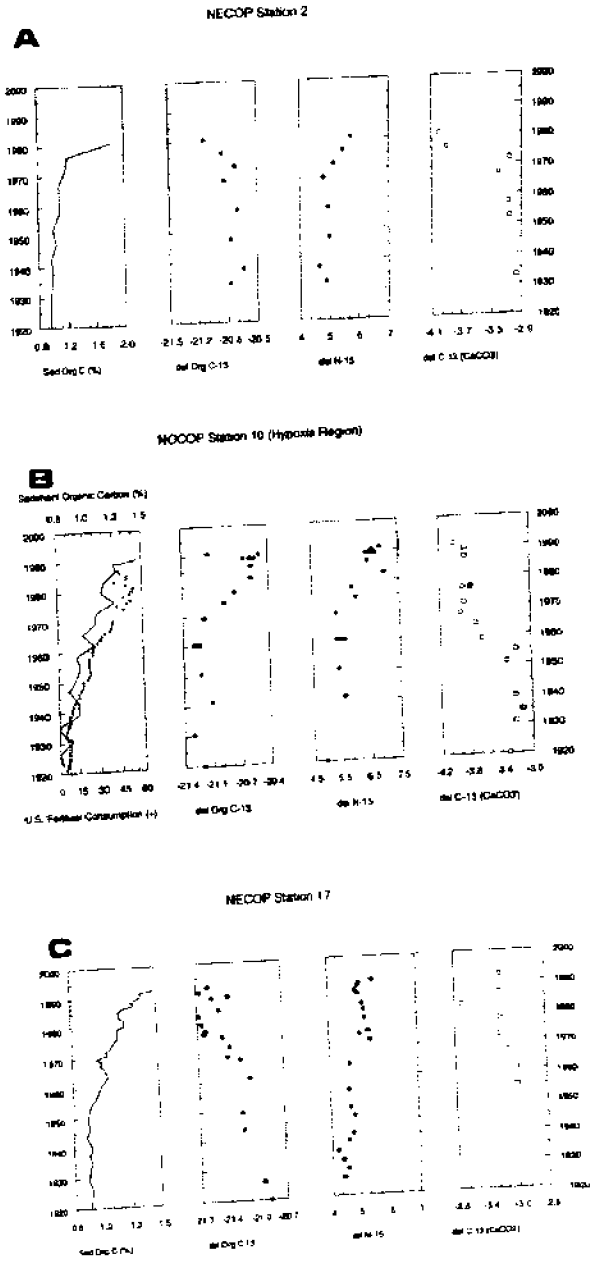

Fig. 12. Organic chemical data for: A. NECOP station 2, B. NECOP Core 10, and C. NECOP station 17.

population diversity can be used to measure the degree of perturbation by man (Patrick, 1983). Therefore, we believe that the water quality variability (i.e. hypoxia) plays a role in our observations. This was independently confirmed by in-depth observations of organic-carbon and nitrogen chemistry in Core 10 and

other cores within the study area which will be presented next.

Surface organic carbon concentrations (first panel, Figs. 12A-C) were greater than 1.3%, similar to previously reported values for the northern Gulf shelf (Shokes, 1976; Entzeroth, 1982) and throughout the record of this century until a relatively constant background level of approximately 0.8% is reached below a depth corresponding to approximately 1945.

The organic carbon isotope ratio data is shown in the second panel for each core (Figs. 12A-C). The surface intervals are isotopically light and may be contaminated or contain materials (such as labile, isotopically light lipids) that are rapidly remineralized near the sediment-water interface, and thus are not characteristic of the materials that are eventually consolidated. Below the first cm, the ^{13}C values from Core 10 are heavier (more marine) near the surface, then get lighter downcore to a relatively constant value below the early 1960s horizon. The overall downcore change in ^{13}C is small, less than 1‰, but real. Triplicates (split sediment samples) of three depths for Core 10 and two depths for station 2 provide an average standard deviation of 0.06 ‰. The decrease in ^{13}C at Core 10 (within the region of recurrent hypoxia) is larger than that of station 2. At this station the ^{13}C peaks at the 1930s level, although the overall profile is virtually constant. The profile for station 17 (Fig. 12C) appears to be an inverse of Core 10, a progressive increase in ^{13}C values downcore implying a decrease of terrestrial component downcore.

The nitrogen isotope records in all three cores (third panel, Figs. 12A-C) decrease downcore from heavier values to a relatively constant value below the mid 1960s. With this tracer, the decreases downcore were approximately the same, approximately 1.5‰. Del-^{15}N has been used with success in identifying sources of sedimentary (Coakley et al., 1992) and organic (van Dover et al., 1992) nitrogen. Del-^{15}N is also known to fractionate biologically (DeNiro and Epstein, 1981), becoming heavier as it moves into higher organisms.

The change in the ^{13}C of the sediment $CaCO_3$ is illustrated in the forth panel of Figs. 12A-C. Although there have been some species shifts in the foraminifera in the core from Core 10, Nelsen et al. (1994) report that Bulliminella morgani and Epistominella vitrea have been the predominant benthic foraminifera, averaging 42 and 23 % respectively of the total populations throughout its' length. Less than 5% of the biogenic carbonates could be attributed to pelagic foraminifera and virtually no non-biogenic carbonates were observed (Hood and Blackwelder, pers. comm.). Beginning around 1940, the ^{13}C of this carbonate material became lighter by approximately 0.6 ‰, with a similar change at station 2, but smaller at station 17. If primary production increased in the past century, we would expect to see lighter carbonate carbon as more isotopically light organic matter decomposed in the bottom waters and was incorporated into benthic foraminifera tests. The filled circles in the data for Core 10 are values for Bulliminella morgani sorted by Terri Hood.

Summary and Conclusions.

If benthic foraminifera population studies and glauconite abundance trends are viewed together, a coherent picture begins to emerge. These trends are temporally linked to known anthropogenic loading of fertilizer application (Fig. 11C) during this century (SAUS 1991-1975; Berry and Hargett, 1987). Thus, by inference they are linked to the resulting increases in nutrient flux down the Mississippi River (Bratkovich and Dinnel, 1992). Our working hypothesis is that the upcore increase in glauconite abundance, coupled with decreased benthic foraminifera species diversity, is related to anthropogenic forcing. Although benthic foraminifera were analyzed for only seven levels, a comparison of Fig. 11A vs. B indicates that the more diverse pre-1940's populations (mean SWDI = -1.06) coincides with low glauconite values. After the early-1940's, less diverse benthic foraminifera populations are reflected in a reduction in the SWDI (mean = -0.68). This upcore diversity decrease coincides with highly elevated glauconite abundance values. These transitions, at ~1940, temporally coincide with the inflection point for increase application of fertilizer in the United States. We propose that this relationship is the first evidence of linkage between the abundance of an authigenic phase (glauconite), biological species shifts, and an anthropogenic input factor.

Cores representing approximately 100 years of accumulation also have increasing concentrations of organic matter over this period, indicating increased accumulation of organic carbon, rapid early diagenesis, or a combination of these processes. Stable carbon isotopes and organic tracers show that virtually all of this increase is of marine origin. Evidence from three cores near the river mouth, two (stations 10 and 17) within the region of chronic seasonal hypoxia and one nearby but outside the hypoxic region (station 2) indicate that changes consistent with increased productivity began by approximately the mid-1950s when the inorganic carbon in benthic foraminifera rapidly became isotopically lighter at both stations. Beginning in the mid 1960s, the accumulation of organic matter, organic $d^{13}C$ and $d^{15}N$ all show large changes in a direction consistent with increased

productivity. This last period coincides with a doubling of the load of nutrients from the Mississippi River which leveled off in the mid-1980s. These data, in conjunction with the foraminifera and glauconite data, support the hypothesis that anthropogenic nutrient loading has had a significant impact on the Louisiana shelf.

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SEDIMENT METABOLISM AND HETEROTROPHIC BIOMASS ASSOCIATIED WITH THE MISSISSIPPI RIVER PLUME

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Abstract:

Sediment metabolic processes associated with the Mississippi River plume are altered from those in typical continental shelf sediments due to high sediment accumulation rates near the delta and intermittant seasonal low oxygen conditions. Measurements have been made of sediment oxygen demand, inorganic nutrient and DIC production, and organic nitrogen fluxes across the sediment water interface using *in situ* chambers. Sulfate reduction rates within the sediments have been estimated with ship-board incubations of $^{35}SO_4$ in sediment subsamples from cores at the same sites where *in situ* chambers were set. Direct counts of bacteria down the sediment column where the sulfate reduction measurements were made allowed the estimation of anaerobic respiration per unit biomass, both of which on average declined rapidly with depth. The largest biomass was found during hypoxic periods in the bacterial component rather than in the invertebrate component during normoxic conditions. The secondary production of sulfide oxidizers during hypoxic periods consumes large quantities of metabolic carbon dioxide generated within the sediments, thus "re-fixing" organic matter remineralized by anaerobic heterotrophs. Photosynthesis on the bottom and the dependence of oxygen demand on oxygen concentrations during stratified conditions could contribute to small diurnal variations in oxygen in the deep low-oxygen water and diminish the rate at which the deep water goes hypoxic.

Introduction

The Mississippi River system introduces large quantities of nitrate and fresh water on the the narrow continental shelf of Louisiana (Dinnel and Bratkovitch 1993). One effect of this is high primary production on the continental shelf (Redaljc et al., In press). Secondly, the hydrographic stratification results in the bottom water going hypoxic (Rabalais et al., 1991). The purpose of the present study has been to describe and contrast the effects of the high input of plant detritus versus debilitating low oxygens on the biomass of dominant functional groups of organisms along with important rates of processes on and in the sea floor.

Methods

In situ chambers were used to measure fluxes of metabolic compounds (sinks and products) across the sediment - water interface. These have been compared to sulfate reduction rates measured with $^{35}SO_4$-labelled incubations in sediments to depths of over a meter. The stations were located near the delta where accumulation is high (#1 and #4, Figure 1), and downstream in the plume where hypoxia is most prevalent (C and D Stations, Figure 1).

Results

Although concentrations of organic carbon are not high in the area (ca. 1.0 to 1.8%) (Trefrey et al., this volume), carbon burial is rapid due to accumulation of riverborne lithogenic suspended matter adjacent to the Mississippi delta (Twilley et al., this volume). The invertebrate biomass was low, but the bacterial biomass was high and cells were active to relatively great depths in these sediments (Figure 2). Downstream in the plume, biomass of the bacteria was extremely high (Figure 2) during hypoxic periods. If this biomass represents growth from the preceding spring, a period of about 90 days, then daily production would amount to ca. 200 to 300 mg C $m^{-2}d^{-1}$, a healthy proportion of daily delivery of carbon to the sediments (Cruz-Kaegi et al. In revision). During this period a fairly large fraction of the carbon is fixed into bacterial cells, according to these estimates, in relation to sulfate reduction or oxygen demand, the two dominant mechanisms for remineralizing organic matter. On the order of 10^8 cells are responsible for the reduction of ca. one nM SO_4 $cc^{-1}d^{-1}$ (Figure 2).

Integration of sulfate reduction in the deeper cores amounted to ca. 0.6 mM $m^{-2}h^{-1}$, std. dev.=0.03, whereas oxygen demand in the same spots was only 0.69 mM $m^{-2}h^{-1}$, std. dev.=0.27. DIC flux averaged 1.14 mM $m^{-2}h^{-1}$(std. dev.=0.27) in the same locations, however, suggesting that a combination of sulfate reduction and oxygen demand were responsible for the remineralization of organic matter. An average of 110 mM NH_4 $m^{-2}h^{-1}$ was regenerated into the bottom water, but it can be estimated indirectly from the sum of the nitrogen fluxes that 70 mM NO_3 $m^{-2}h^{-1}$ was consumed by denitrification. A comparison of these fluxes suggests that utilization of all the dominant terminal

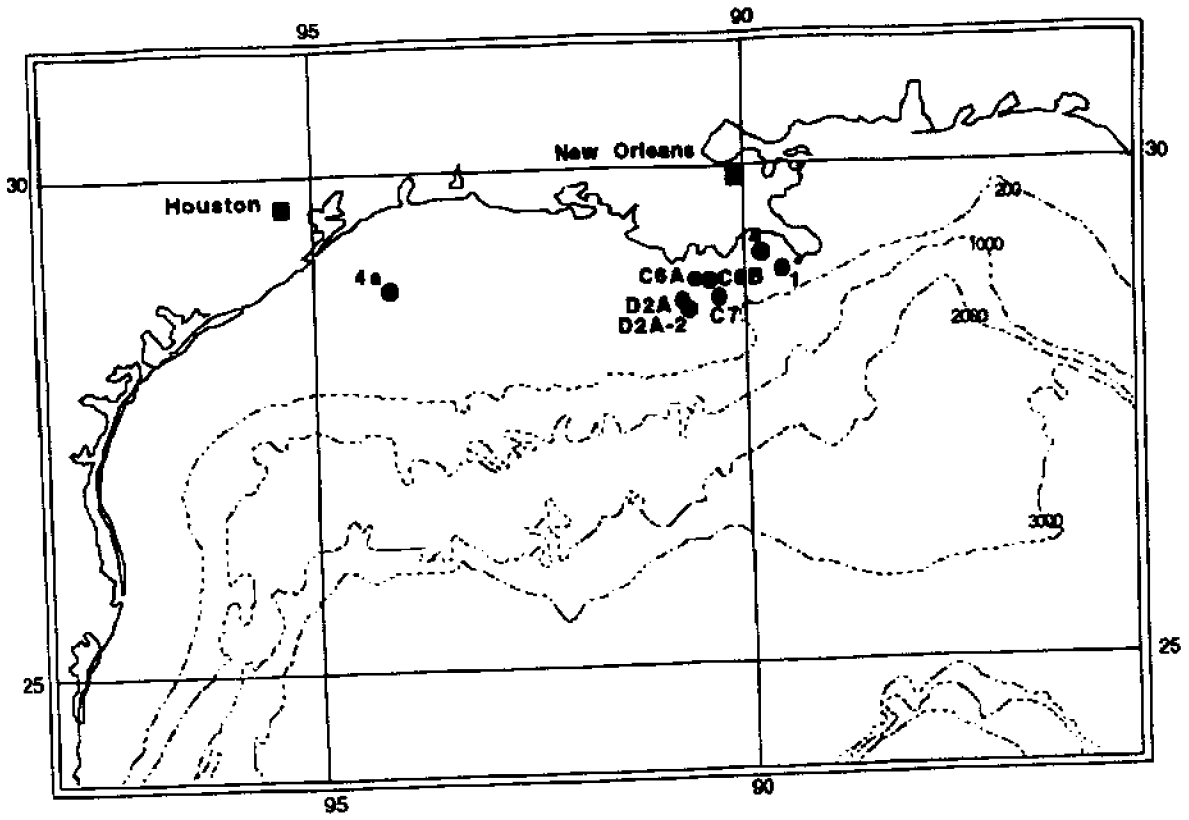

Fig. 1. Locations of GOMEX core samples from which biomass of bacteria, meiofauna and macrofauna have been assessed (in Cruz-Kaegi, Rowe and Harper In revision). Core incubations of $^{35}SO_4$ and *In situ* chamber flux data were taken at Sta. 1, 4, C6B and D2A.

electron acceptors matches the production of metabolic by-products fairly well.

During periods of stratification, bottom water light transmission increased, and primary production occurred directly on the sea floor. An average rate of ca. 93 mg O_2 $m^{-2}d^{-1}$ (std.dev.$_{(n-1)}$=34.8) was estimated by comparing oxygen demand in clear and opaque *in situ* chambers (Dortch et al. In press).

Discussion

The ecosystem adjacent to the Mississippi effluent is modified in ways which force the rates of processes and the biota in the sediments to be different from typical continental shelves. While sediment photosynthesis has been observed with our chambers, this rate was relatively small compared to surface water column nutrient-enhanced productivity. However, bottom and near-bottom photosynthesis may be enough to prevent hypoxic conditions from turning anoxic, which would in turn allow toxic sulfide to penetrate the water column.

Biomass of bacteria during hypoxic conditions reached high levels. These can be heterotrophic

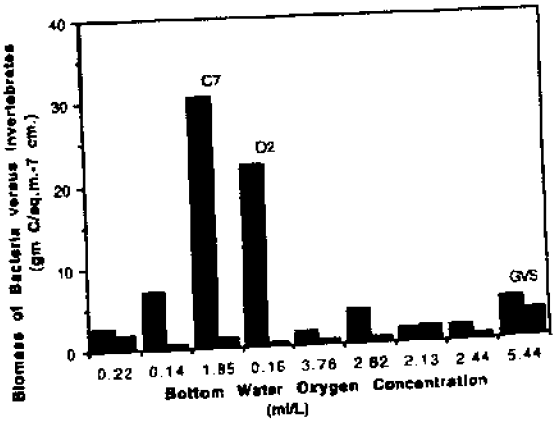

Fig. 2. Distribution of bacteria and invertebrate biomass at hypoxic area stations at various levels of bottom water oxygen. C7 was in a mat of Beggiatoa sp. sulfide oxidizing bacteria, whereas D2 was in black reducing mud without a surficial mat(from Cruz-Kaegi et al., In revision). GVS was taken at similar water depths, but far to the west of the other samples (see Figure 1).

Station	Macrofauna (ind m^{-2} - 15 cm depth)	Meiofauna (x10^5 ind m^{-2} integr. to 8 cm depth)	Bacteria (x 10^9 cells cm^{-3} in top 8 cm depth)	Bacteria (x 10^{14} cells m^{-2} integr. to 8 cm depth)
LOUISIANA SHELF				
Hypoxic season				
C6A (n = 1)	1830	8.7	0.51	0.36
C6B (n = 1)	549	3.8	1.6	1.13
C7 (n = 1)	8673	3.0	6.9	4.9
D2A (n = 1)	315.6	0.8	5.04	3.53
Mean Abundance	1092 (770)	4.08 (3.3)	3.5 (3)	2.48(2.1)
Normal oxygen				
1	904 (769)(n = 4)	0.73(2)(n = 2)	0.38	0.26
4	185.5(93)(n = 3)	2.5(1.9)(n = 3)	0.95	0.67
C6B-2	3644 (n = 1)	1.6(0.6)(n = 3)	0.39	0.27
D2A-2	711 (n = 1)	0.22(.09)(n = 3)	0.42	0.29
Mean Abundance	1361 (1532)	1.3 (0.9)	0.54(0.28)	0.37 (0.20)
GALVESTON SHELF				
4A (n = 2)	3424 (2828)	7.30 (3.50)	1.11(0.31)	0.78(0.22)

Table 1. Abundance of macrofauna, meiofauna and bacteria at two areas of the Texas-Louisiana Shelf (from Cruz Kaegi et al. In revision). Values in parentheses are standard deviations.

Station	Macrofauna (g C m^{-2})	Meiofauna (g C m^{-2})	Bacteria (g C m^{-2} -8 cm depth)	Total Biomass (g C m^{-2})
LOUISIANA SHELF				
Hypoxic Events				
C6A (n = 1)	0.68	1.1	2.7	4.45
C6B (n = 1)	0.16	0.43	7.1	7.71
C7 (n = 1)	0.56	0.76	30.5	31.8
D2 (n = 1)	0.11	0.21	22.2	22.5
Mean Biomass	0.38 (0.29)	0.66(0.34)	15.6 (12.9)	16.7 (12.9)
Normal Oxygen				
1	23 (.62)(n = 4)	.37(.08)(n = 2)	1.67	2.3
4	01(.007)(n = 3)	.55(.51)(n = 2)	4.18	4.7
C6B-2	1.24(0.7) (n = 3)	.55(0.3)(n = 2)	1.72	3.5
D2A-2	0.49 (n = 1)	.07(.03)(n = 2)	1.85	2.4
Mean Biomass	0.49(0.54)	0.38(0.23)	2.36(1.22)	2.81(0.99)
GALVESTON SHELF				
4A (n = 2)	1.820(0.6)	1.530(0.14)	4.89(1.9)	8.24(2.64)

Table 2. Macrofaunal, meiofaunal, and bacterial biomass at two areas of the Texas Louisiana Shelf (from Cruz Kaegi et al. In revision). Values in parentheses are standard deviations.

anaerobes (sulfate reducers, D2 in Figure 2), but the highest biomass encountered was in the sulfide oxidizers (C7 in Figure 2), thus suggesting that considerable carbon can be stored in living forms for transient periods of days to months, even though this is derived from carbon dioxide rather than organic matter. We have no information on how this living carbon might be transferred to other components of the ecosystem, both living and detrital. We do not know if these populations are top down or bottom up controlled, but the few invertebrates which colonize these sediments (mostly small polychaetes and meiofauna) during periods when oxygen concentrations allow it, do not necessarily appear to be species which selectively prey on bacteria.

In most ecosystems, oxygen demand is a good indicator of total heterotrophic metabolism in sediments. In these sediments however oxygen did not account for total metabolism principally because low oxygen concentrations inhibit oxic respiration. In these cases, DIC flux measurements have proven to be useful as a measure of net reactions, but we must assume that both chemolithotrophic and heterotrophic reactions are going on simultaneously at different redox potentials over a narrow depth range, as well as in and out of "biological features" in the surficial sediments.

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HYPOXIA ON THE LOUISIANA SHELF AND SYSTEM RESPONSES TO NUTRIENT CHANGES IN THE MISSISSIPPI RIVER: A BRIEF SYNOPSIS

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Abstract

The distribution and characteristics of bottom water hypoxia was documented on the Louisiana shelf for 1985-1993. The influences of the Mississippi River were especially evident during the late spring and summer flooding of 1993. The temporal and spatial linkages between freshwater inflow (and subsequent nutrient flux) and net surface water productivity and bottom water oxygen deficiency are clear. These relationships led us to examine long-term changes in Mississippi River nutrient concentrations and flux, nutrient structure on the adjacent continental shelf, and responses of components of the ecosystem to long-term changes. Significant increases in Mississippi River nutrient concentrations and loadings of nitrate and phosphorus and decreases in silicate have occurred this century, and accelerated since 1950. Consequently, major alterations have occurred in the probable limitation of specific nutrients, nutrient ratios, and overall stoichiometric nutrient balance in the adjacent continental shelf system. Consequences of shifts in nutrient balances in the system are manifested in changes in silicate-based phytoplankton response and trophic structure, phytoplankton community structure, sediment carbon accumulation, and indicators of bottom water oxygen stress.

Introduction

Oxygen-depleted bottom waters are seasonally dominant features of the Louisiana continental shelf adjacent to the deltas of the Mississippi and Atchafalaya Rivers (Rabalais et al., 1991; 1992a; in press). The areal extent of bottom-water hypoxia (≤ 2 mg l^{-1} dissolved oxygen) in mid-summer may cover up to 9,500 km2, with spatial configuration varying interannually. More frequent sampling along a transect on the southeastern shelf, and continuous time series data off Terrebonne Bay, document hypoxic bottom waters as early as February and as late as October, with widespread, persistent and severe hypoxia/anoxia from mid-May to mid-September. Spatial and temporal variability in the distribution of hypoxia exists and is, at least partially, related to the amplitude and phasing of the Mississippi River discharge and, consequently, to nutrient flux to the coastal waters and subsequent flux of carbon from surface waters to the lower water column and seabed. Physical features of the system, e.g., large-scale circulation patterns, strong and persistent density stratification, and destratification due to wind-mixing events from local winds, tropical storm activity and thermal fronts, also control the dynamics of hypoxia. The influence of the Mississippi outflow was especially dramatic during the late spring and summer of 1993 when sustained freshwater inputs and nutrient flux occurred when flows are usually lowest (Rabalais et al., 1994). In the first part of this paper, we present conditions of hypoxic environments in 1993 compared to long-term averages.

Seasonal dynamics of net productivity in the northern Gulf of Mexico are coherent with the dynamics of freshwater discharge (Justic' et al., 1993). The surface layer in the Gulf shows an oxygen surplus during February-July; the maximum occurs during April and May and coincides with the maximum flow of the Mississippi River. The bottom layer, on the contrary, exhibits an oxygen deficit throughout the year, but reaches its highest value in July which is also the period when surface-to-bottom density differences are greatest. Cross correlation analysis shows that the correlation between Mississippi River flow and surface oxygen surplus peaks at a time-lag of one month and that highest correlation for bottom oxygen deficit is for a time-lag of two months (Justic' et al., 1993). These findings suggest that the oxygen surplus in the surface layer depends on nutrients coming from the river rather than on nutrients that have been regenerated in the water column or from the sediments. An oxygen surplus also means that there is an excess of organic matter derived from primary production which can be redistributed within the system, some of which will eventually reach the lower water column and sediments. The

development of summer hypoxia is associated with the decay of organic matter accumulated during spring phytoplankton blooms. These findings demonstrate a close coupling between riverborne nutrients, net productivity and hypoxia, as well as the implications that anthropogenic nutrient loads can alter a coastal marine ecosystem.

The close linkages between freshwater inflow (and subsequent nutrient flux) and net surface water production and bottom water oxygen deficiency led us to document long-term trends in nutrient structure (riverine and continental shelf), and the responses of various components of the ecosystem to these changes. These results are presented in the latter sections of this paper.

Methods

Data for hypoxia distributions and related water column features were drawn from mid-summer shelfwide cruises for 1985-1992, and similar monthly data for Station C6A, C6B, or C6 on the southeastern Louisiana shelf. Standard water column profile data were obtained from a Hydrolab Surveyor II, Hydrolab Surveyor 3, or a SeaBird CTD system. All dissolved oxygen probes were calibrated and quality controlled with Winkler titrations; conductivity was calibrated by discrete measurements on an AutoSal salinometer. Chlorophyll a concentrations were determined fluorometrically (Parsons et al., 1984).

While the influence of the Mississippi and Atchafalaya Rivers is far-ranging, we have limited our discussion of long-term effects discussion to the area influenced by the immediate and extended plumes of the current birdsfoot delta, in the Mississippi River bight west to about 90°30'W (the entrance to Terrebonne Bay). We refer to our completed research and data syntheses and comparisons to data in the literature (Rabalais et al., submitted).

Results and Discussion

Characteristics of hypoxia (1993 vs. long-term averages) Above normal freshwater inflow and nutrient flux from the Mississippi and Atchafalaya Rivers from late spring well into mid-summer, when flows are usually lowest, were clearly related in time and space to hypoxic water formation and maintenance on the Louisiana-Texas shelf in 1993. Monthly monitoring cruises along transect C and the deployment of the instrument mooring at station C6B occurred in March through November 1993. These data were compared to monthly data collections in 1985-1986 and 1989-1992. At the site of the instrument mooring, hypoxia occurred for much of the record (Fig. 1) in April and from late May through mid-June. Heavy winds and seas, resulting from the tropical depression which crossed the Gulf of Campeche and came to shore on the south Texas coast, reaerated the water column in late June. Hypoxia was re-established in early July at station C6B, and hypoxic/anoxic conditions prevailed through early October. Subsequently, a series of frontal passages with high winds and seas, thermal cooling of the surface waters, and subsequent breakdown in the strength of water column stratification, lead to the dissipation of hypoxia. Surface water salinities were much lower at station C6B in 1993 compared to previous years, (Fig. 2) as a result of sustained freshwater inputs of the Mississippi and Atchafalaya Rivers. Nitrate concentrations in surface waters are normally elevated in spring (1985-1992), but continued at higher than normal levels through summer 1993. Similarly, silicate and phosphate concentrations were also higher than normal in summer 1993. Surface water chlorophyll a concentrations are also elevated normally in spring, but continued at much greater values through October 1993 (Fig. 2). Bottom water dissolved oxygen follows an annual decline through the spring with lowest average values in June-August (Fig. 2). During 1993, bottom water dissolved oxygen values were similar, until the peak in flooding in August and September, when extensive areas remained anoxic for extended periods (Figs. 1 and 2).

On a shelfwide scale, surface water signatures of less saline, nutrient-rich, and high chlorophyll a biomass waters paralleled the sustained and high freshwater outflow of the flooded Mississippi River. Persistent westerly and southwesterly winds for much of July through mid-August retained large volumes of this fresh water on the Louisiana shelf and upper Texas coast. Results from three cruises in July 1993 that mapped bottom water oxygen deficiency indicated that the hypoxic water mass extending onto the upper Texas coast in early to mid-July was pushed back onto the Louisiana shelf in late July. The size of the area mapped during the July 24-29 NECOP Hypoxia Monitoring cruise was approximately twice as large as the average area mapped in previous mid-summer cruises (1985-1992) (Rabalais et al., 1994). Salinities between 15 and 25 ppt covered much of the southeastern shelf surface waters, where values averaged 25 to 30 ppt, and surface water salinities for additional areas of the shelf were lower than the long-term mid-summer average (Fig. 3). During late July 1993, surface water nutrient concentrations were especially elevated on the southeastern shelf (Rabalais et al., 1994), along with chlorophyll a biomass (Fig. 3). Lower than long-term average bottom water dissolved oxygen values were found over most of the Louisiana inner shelf along the 20-m isobath (Fig. 3), which

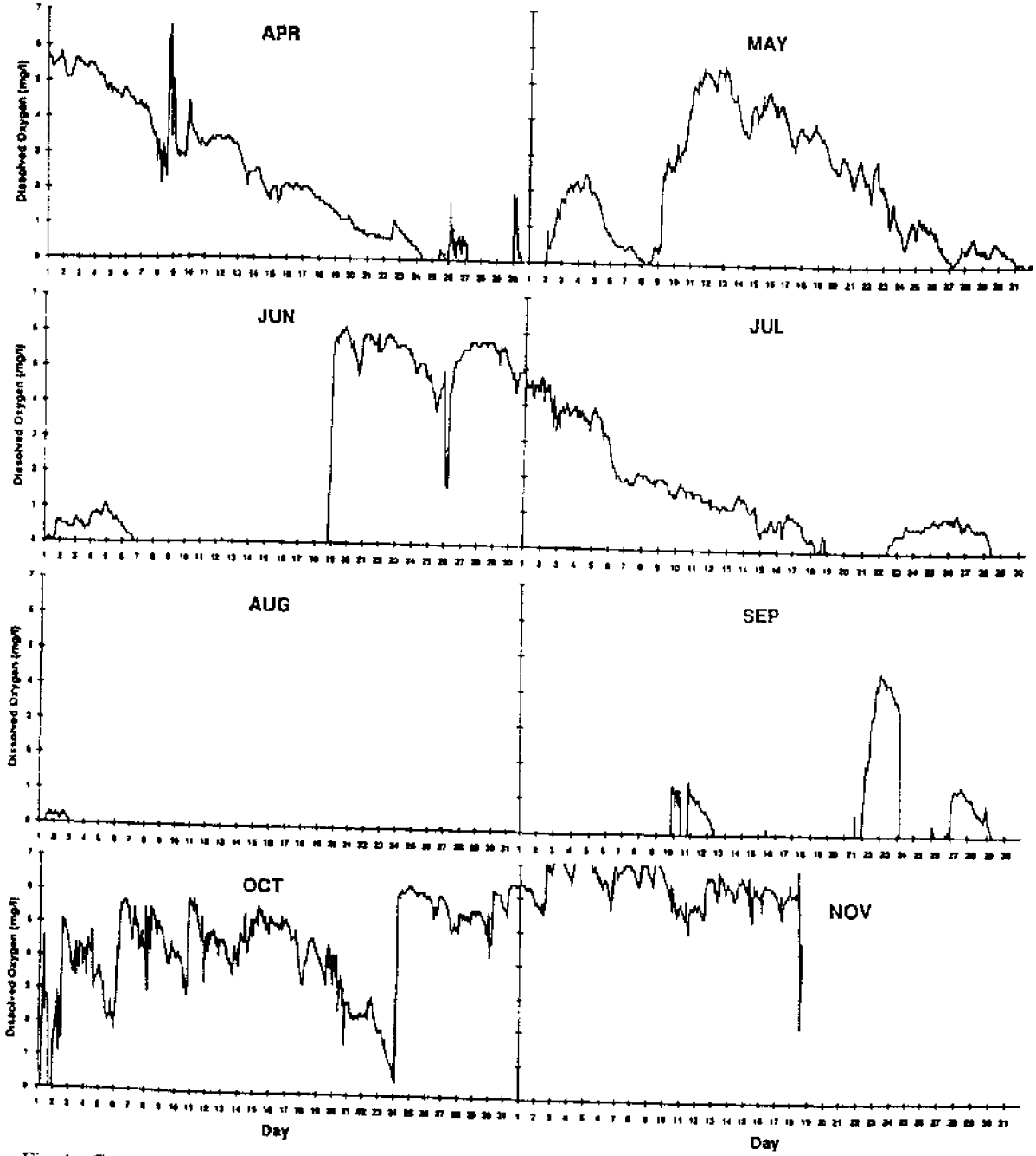

Fig. 1. Continuous recording of 1993 bottom water dissolved oxygen concentration at station C6B.

reflected an integration of surface water characteristics over the preceding 3-4 weeks.

Water quality changes in the lower Mississippi River Water quality data for the lower Mississippi River, previously elaborated by Turner and Rabalais (1991), indicate that the mean annual concentration of nitrate was approximately the same in 1905-1906 and 1933-1934 as in the 1950s, but it doubled in the last 35 years. The mean annual concentration of silicate was approximately the same in 1905-1906 as in the early

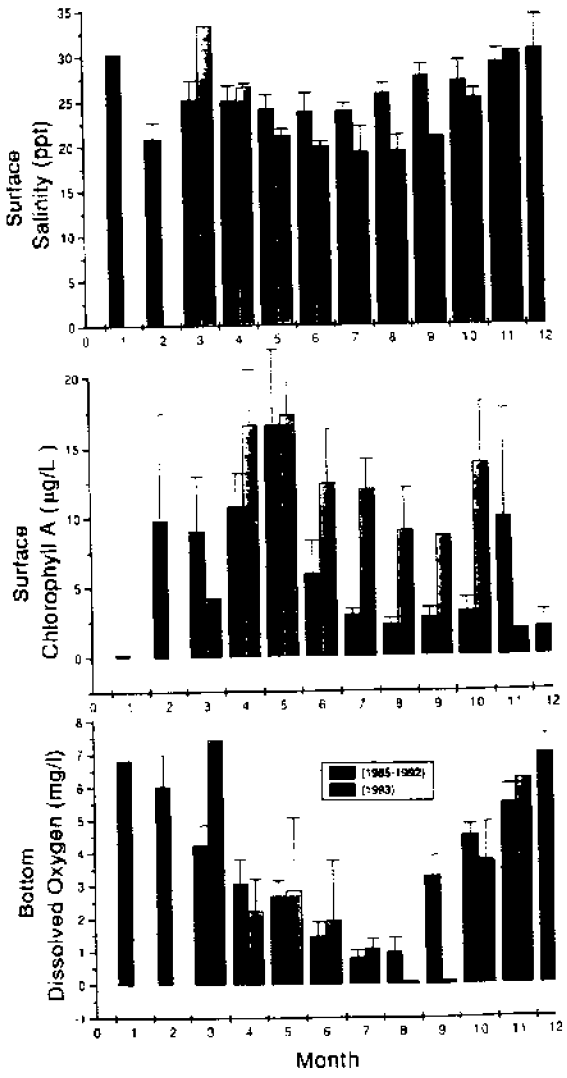

Fig. 2. Comparison of 1985-1992 monthly averages at station C6, C6A or C6B (preferentially selected order) to 1993 monthly average at station C6B for surface water salinity (upper panel), surface water chlorophyll a (middle panel), and bottom water dissolved oxygen (bottom panel).

1950s, then it declined by 50%. The concentration of silicate increased from 1985 to 1988, whereas the concentration of nitrate decreased slightly in that period. Although the concentration of total phosphorus appears to have increased since 1972, variations between years are large. The silicate-nitrate ratios have changed as the concentrations varied (Turner and Rabalais, 1991; in press). The silicate: nitrate atomic ratio was approximately 4:1 at the beginning of this century, dropped to 3:1 in 1950, and then rose to approximately 4.5:1 during the next ten years, before plummeting to 1:1 in the 1980s. There has been a modest rise in the recent three to five years, as a result of the simultaneous increase of silicate and decrease of nitrate concentrations.

The proportions of dissolved Si, N and P in the lower Mississippi River have changed historically in a way that now closely approximate the Redfield ratio (Si:N:P = 16:16:1) (Justic' et al., in press a,b; submitted). We compared the data for two periods: 1960-1962 and 1981-1987. By applying the Redfield ratio as a criterion for stoichiometric nutrient balance, one can distinguish between probable P-deficient, N-deficient, and Si-deficient rivers, and those having a well balanced nutrient structure. The nutrient ratios for the Mississippi River (1981-1987 data base) show an almost perfect coincidence with the Redfield ratio (Justic' et al., in press a,b; submitted). The proportions of Si, N and P have changed over time in such a way that they now suggest a balanced nutrient structure.

The seasonal patterns in nitrate and silicate concentration have also changed during this century (Turner and Rabalais, 1991; in press). There was no pronounced peak in nitrate concentration earlier this century, whereas there was a spring peak from 1975 to 1985, presumably related to seasonal agricultural activities (i.e., fertilizer application) timed with long-term peak river flow. A seasonal summer-fall maximum in silicate concentration, in contrast, is no longer evident. Consequently the seasonal signal of silica:nitrogen atomic ratio has also changed. The seasonal shifts in nutrient concentrations and ratios becomes increasingly relevant in light of the close temporal coupling of river flow to surface water net productivity and subsequent bottom water oxygen deficiency (Justic' et al., 1993).

Nutrient structure of adjacent continental shelf

We analyzed extensive nutrient data sets from the northern Gulf of Mexico to demonstrate that coastal nutrient structure may reflect long-term changes in the proportions of dissolved Si, N and P in riverine loads (Justic' et al., in press a,b; submitted). Comparison of the reconstructed data with the available historical nutrient data (Thomas & Simmons 1960, Turner and Rabalais in press) showed a reasonable agreement. Comparison of measured and reconstructed nutrient data revealed long-term changes in proportions of nutrients in the surface waters (Justic' et al., in press a,b; submitted). The reconstructed nutrient ratios for 1960, on average, scattered further from the center of the grid than the recent data. By applying the Redfield ratio as a criterion for balanced nutrient structure, it appeared that P and N deficiency decreased while Si deficiency increased. Equally important, recent nutrient ratios

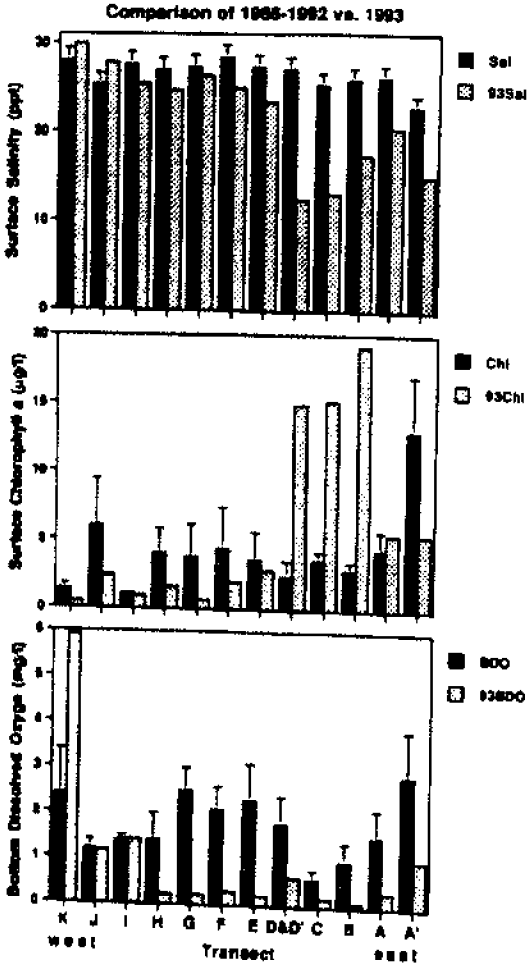

Fig. 3. Comparison of mean values for mid-summer cruises in 1985-1992 at 20-m isobath stations for surface water salinity (upper panel), surface water chlorophyll a (middle panel), and bottom water dissolved oxygen (bottom panel).

scattered very close to the Redfield ratio, suggesting an almost perfectly balanced nutrient structure.

Because stoichiometric limitation indicates only whether limitation is likely, probable limitation (Dortch and Whitledge, 1992) was also assessed by comparing the ambient nutrient concentrations with the ks for nutrient uptake and, in the case of Si, a threshold value for uptake. Plots of relative frequencies (Justic' et al., in press a) showed that dissolved N concentrations in the surface layer of the northern Gulf of Mexico during the period 1985-1992 were lower than 1 μM in about 13% of the cases. Reactive P was below 0.1 μM in 17% of the cases, while reactive Si concentrations lower than 2 μM occurred in 25% of the cases.

Changes in phytoplankton species composition

The changes in riverine and coastal nutrient concentrations and ratios over time suggests that there should be observable changes in phytoplankton species composition. Published reports of phytoplankton species composition for 1955-1957 (Simmons and Thomas, 1962) and 1972-1973 (Fucik, 1974; Ward et al., 1979) were compared with recently obtained data (1990-1993) (Dortch et al., 1992,;unpubl. data) (Rabalais et al., submitted). The qualitative comparison indicated the following:

(1) Demonstrable changes have occurred in the diatom and non-diatom species composition from the 1950s and 1970s to present. Some heavily silicified diatom species are either not observed at all in recent samples or are much less dominant.

(2) Similarly, more lightly silicified diatoms, especially at higher salinities, are documented for the 1970s and present, but not for 1955-1957.

(3) Methodological differences precluded conclusions about changes in non-diatoms, but the phytoplankton at C6A and C6B in 1990-1993 were often numerically dominated by small flagellates and cyanobacteria. Also, several species with importance to human health are now present but were either absent before or have increased in dominance.

Silicate-based phytoplankton community response Bien (1958) first documented the dilution and non-conservative uptake of silicate in the Mississippi River plume by sampling from the river mouth seaward in 1953 and 1955. A notable characteristic of the mixing diagram is that the concentration of silicate often falls below the conservative mixing line, thus indicating uptake. Uptake can be statistically modeled as a deviation from this mixing line, which we did for 31 adequately sampled data sets (Turner and Rabalais in press). We found that the concentration of silicate at the 20 ppt mixing point declined in the last several decades during the winter-spring (Jan-Apr) and summer months (Jun-Aug); however, there was no discernible change during the fall-winter months (Oct-Dec). We normalized for the effects of varying concentrations in the riverine end-member (e.g., Loder and Reichard, 1981) and compared the estimated net silicate uptake at 30 ppt as a function of silicate riverine end-member concentration. Non-conservative uptake of silicate was indicated in all data collections. The net uptake (at 30 ppt) above dilution ranged from 1 to 19% of the intercept concentration, and the data groups for before and after 1979 are remarkably similar. Further, the net silicate uptake appears to be even higher after 1979, than before 1979. In other words, although silicate concentrations have declined in the past few decades, the net uptake has stayed the same, or even increased.

Biologically bound silica and carbon accumulation We documented that surficial sediments, directly downstream and beneath the surface riverine/estuarine dilution plume, reflected the in situ primary production and subsequent transport of organics from surface to bottom waters within the Mississippi River bight (Rabalais et al., 1992b; Turner and Rabalais, 1994). We further quantified the silica in the skeletal remains of diatoms sequestered as biologically bound silica (BSi) in dated sediment cores from the same region (Turner and Rabalais, 1994). The general pattern that emerged was an equilibrium accumulation of BSi from 1800 to 1900, then a slow rise, followed by a more dramatic rise in the past two decades. The pattern in %BSi changes parallels the documented increases in nitrogen loading in the lower Mississippi River over the same period that the silicate concentrations have been decreasing. If the assumption is made that the BSi:C ratio at the time of deposition remained constant this century, then the increased BSi deposition represents a significant change in carbon deposition rates (up to 43% higher in cores dated after 1980 than those dated between 1900 to 1960). We concluded from our analyses (Turner and Rabalais, 1994) that the organic flux of diatoms from surface to bottom waters beneath the Mississippi River plume increased this century. These changes were coincidental with changes in riverine nitrogen loadings and resulted in higher organic sedimentation in bottom water layers.

Consequences of hypoxic bottom water formation and severity We used dominance trends of benthic foraminifera to determine their use as indicators of reduced oxygen levels and/or carbon-enriched sediments (Sen Gupta et al., 1981; Sen Gupta and Machain-Castillo, 1993). Some downcore shifts in species abundances at Station G27 in the Mississippi River bight (where mid-summer hypoxia frequency was 50-75% during 1985-1993, Rabalais et al., submitted) were interpreted as foraminiferal responses to increasing oxygen stress (Sen Gupta et al., 1993, 1994). In the context of modern hypoxia, species distribution in dated sediment cores revealed stratigraphic trends in the Ammonia parkinsoniana/Elphidium spp. ratio that indicate an overall increase in oxygen stress (in intensity or duration) in the last 100 years (Rabalais et al., submitted; Sen Gupta et al., in prep.). In particular, the stress seems especially severe since the 1950s. Thus, there are indications that oxygen deficiency stress increased as nutrient loads and carbon flux to the seabed increased.

Summary of Long-Term Trends

Mississippi River nutrient concentrations and loadings to the adjacent continental shelf have changed dramatically this century, with an acceleration of these changes since the 1950s. The concentrations of dissolved N and P doubled and Si decreased by 50%, the dissolved Si:N ratio dropped from 4:1 to 1:1, and seasonal trends have changed. The resulting nutrient structure in the receiving Gulf waters shifted towards stoichiometric nutrient ratios that are more balanced than previously. N and P are indicated to be now less limiting to phytoplankton growth, while some increase in Si limitation is probable. In spite of a probable decrease in Si availability, the overall system response appears to be increased productivity, as evidenced by (1) equal or greater net silicate-based phytoplankton community uptake of silica, and (2) accumulation of biologically bound silica in sediments. The increased %BSi in Mississippi River bight sediments that parallels increased N loading to the system is direct evidence for the effects of eutrophication on the shelf adjacent to the Mississippi River. Individual phytoplankton species composition shifts (heavily silicified diatoms---> lightly-silicified diatoms; diatom ---> non diatom) would indicate some population-level responses to reduced Si supplies and/or changes in nutrient ratios. Finally, an analysis of benthic foraminifera indicates an increase in oxygen deficiency stress this century, especially since the 1950s. Increased bottom-water hypoxia could result from increased organic loading to the seabed and/or shifts in material flux (quantity and quality) to the lower water column.

Acknowledgments

Data were collected during programs funded by NOAA Ocean Assessments Division, Louisiana Board of Regents LaSER award 86-LUM(1)-083-13 and LEQSF award (1987-90)-RD-A-15, Louisiana Sea Grant College Program, NOAA National Undersea Research Center, Louisiana State University, Louisiana Universities Marine Consortium, and the NOAA Nutrient Enhanced Coastal Ocean Productivity NECOP program grant no. NA90AA-D-SG691, awards no. MAR31, MAR24, MAR92-07 and MAR92-02. Funding for this synthesis and manuscript preparation was provided by the NOAA NECOP study.

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SYNOPTIC INVESTIGATIONS OF BENTHIC-PELAGIC COUPLING WITHIN THE LOUISIANA SHELF ECOSYSTEM

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Introduction

One of the major objectives of the Nutrient Enhanced Coastal Ocean Productivity (NECOP) Program is to understand the fate of nutrients and organic matter in the Mississippi River Plume and adjacent continental shelf. It is hypothesized that the anthropogenic nutrient enrichment has significantly modified the in situ production of biomass leading to altered oxygen dynamics in this region, and as a result has impacted regional fisheries and, potentially, the global carbon cycle. The rate and efficiency of material cycling through both benthic and water-column communities are central to the ultimate fate of inorganic nutrients and organic matter within the MAR region, and land-margin ecosystems in general. Of particular importance to understanding ecosystem response to nutrient enhancement is an understanding of those processes directly concerned with the input, remineralization, and loss of nutrients. The coupling of these processes is central to understanding the linkages of nutrient enrichment to the development of hypoxia in this region of the Louisiana shelf ecosystem. Previous studies of deposition suggest that the proximal region of the Mississippi River plume is a zone of extreme input of allochthonous particulate material to the seabed. Much of this material appears to be remineralized or transported out of the region. An important focus of this report is to determine the relative contributions of deposition, regeneration and redistribution, and burial to the fate of sediments and nutrients in the Louisiana shelf ecosystem.

Methodologies

Deposition and Burial. - This study utilized naturally occurring (^{234}Th and ^{210}Pb) radionuclides to determine rates of deposition and sedimentation. These radionuclides are very particle-reactive (i.e., rapidly sorbed onto particle surfaces) and have proven to be very useful as particle tracers (Broecker et al., 1973; Santschi et al., 1980). Because of natural radioactive decay, these radionuclides are particularly useful in examining rates of sedimentary processes at two time scales based on their halflives. ^{234}Th (24 day half-life) is used to examine processes that occur on a time scale of days to months (e.g., sediment deposition related to flood and storm events), while ^{210}Pb (22 year half-life) is used to examine processes that integrate over a period of 10 to 100 years (e.g., sediment accumulation during the past century).

Box core samples were collected from 42 stations in Mississippi River plume region. Additional cores were collected from selected stations within this grid after high and low discharge periods for measurements of ^{234}Th. Large diameter (16.5 cm) subcores were taken from box cores at each sampling station. Each core was carefully extruded and simultaneously subsectioned at precise 0.5- 1.0 cm intervals. Yield tracers (^{232}U/^{238}Th, ^{208}Po) were added to the dried core samples, then leached with a combination HNO_3, HCl and $HClO_4$ solution. Thorium and uranium are isolated and purified via ion exchange methods, plated onto stainless steel planchets and counted on a low-background beta detection system (McKee et al. 1986). ^{210}Po is spontaneously deposited onto silver planchets and ^{210}Pb is measured via the polonium method (Nittrouer et al. 1919). The deposition and accumulation (burial) of carbon, nitrogen and phosphorus in bottom sediments was calculated from the following equation (Hatton et al. 1983): A = Cd x R x D x 104 (g m^{-2} yr^{-1}); where A is the rate of nutrient deposition or burial, Cd is the dry mass nutrient concentration, D is bulk density, and R is the sedimentation rate (determined by ^{234}Th or ^{210}Pb).

Benthic Regeneration - A benthic flow through microcosm system (Miller-Way and Twilley 1991) was used to quantify ambient flux of nutrients across the sediment-water interface. The flow through system consists of three basic components: 1) intact sediment cores of 30 cm height and 15 cm diameter collected from box cores, 2) supply reservoirs of filtered (0.2 Am) ambient water collected from depth using the ship's CTD system, and 3) the peristaltic pump which supplies each core with ambient water at precisely controlled flow rates. A homogeneous water column is achieved using miniature stir plates which drive an internally mounted Nalgene stir bar. Cores are incubated in the dark onboard ship at ambient conditions. A minimum of three successive time determinations of process rates was made on triplicate cores. Flux rates were calculated using influent (I) and effluent (E) concentrations by the

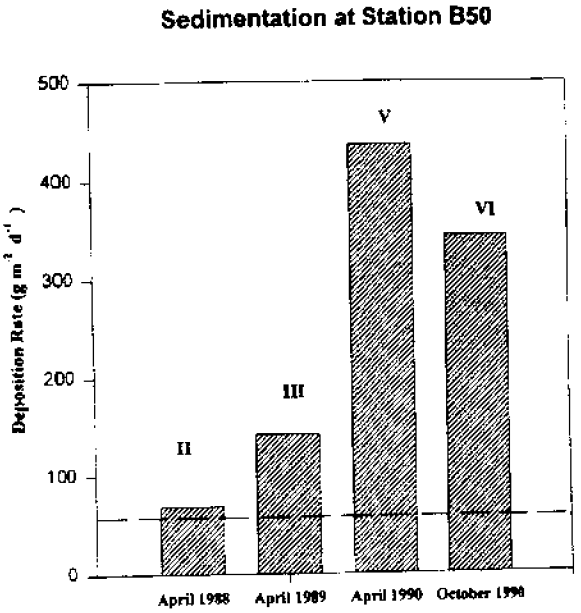

Fig. 1. Interannual estimates of sediment deposition at station B50 on the Louisiana shelf based on ^{234}Th (roman numerals indicate LaSER cruise), and the 100-yr average accumulation rate for this station based on ^{210}Pb (dashed line).

following equation: (I-E) V / A = Flux ; where V is the flow rate and A is the surface area of the core. At the cessation of each run, sediment samples were analyzed for total carbon, nitrogen and phosphorus. Total carbon and nitrogen was determined using a LECO Elemental Analyzer, while total phosphorus was determined by dissolving ashed samples with HCl and assaying for PO_4 concentrations.

Results and Discussion

The plume region of river-dominated land margin ecosystems are sites of high sedimentation of allochthonous carbon, nitrogen and phosphorus. However, nutrient retention may vary within the plume region, particularly during high flow, depending on differences in depth and circulation. A common observation in river-dominated environments is that most of the sediment discharge is initially deposited near the river mouth; sedimentation rates decrease with increasing distance from the river (DeMaster et al. 1985; Nittrouer et al. 1987). Deposition rates calculated from samples collected in April of three consecutive years range from 69 to 436 gdw m^{-2} d^{-1} near the mouth (station B50) of southwest pass (Fig. 1). This interannual variation reflects differences in cumulative discharge during the 3-4 months prior to sampling. Rates of deposition for similar discharge periods were generally less at downfield stations. During the low flow period, river discharge decreases by about 85%, resulting in reduced riverine input to the shelf

Deposition rates (100-day time scale) within the plume region of the Mississippi River (Fig. 1) are 5-10 times greater than the sediment accumulation rates (100-year time scale) determined using ^{210}Pb. The contrast in fate of materials deposited to the seabed based on relative rates of deposition and burial indicate that a substantial portion of these materials may be redistributed. Redistribution may occur from the shelf to shelf slope, or to more distal parts of the dispersal system along the shelf. Redistribution of materials delivered during high river flow leads to a more uniform distribution of particulates throughout the dispersal system.

Seasonal deposition of allochthonous organic matter during spring provides the predominant mechanism for sustaining peak rates of benthic regeneration in the plume region of the shelf During April, ammonium regeneration in the plume region (station B50 and C50) may exceed 500 umol m^{-2} h^{-1}, compared to fluxes of less than 200 umol m^{-2} h^{-1} during low river discharge in September and October. Further downfield (stations D50 and E50), ammonium regeneration is generally less than 200 umol m^{-2} h^{-1}. Seasonal differences in benthic regeneration are most evident nearest the mouth of the Mississippi River, while rates are more constant both temporally and spatially in more distant regions. The link between sediment deposition and benthic nutrient regeneration is clearly demonstrated in results of silicate flux at near and far - field stations on the Louisiana shelf (Fig. 2). Fluxes of silicate across the sediment-water interface to

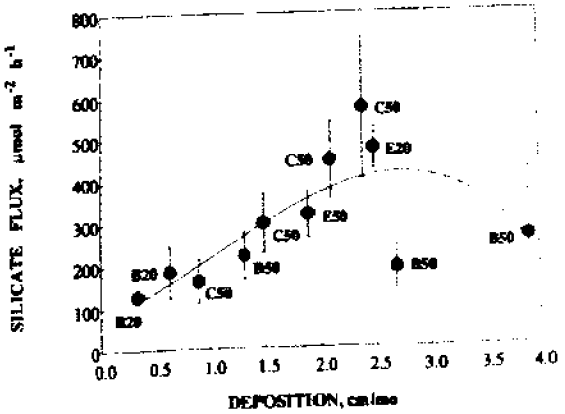

Fig. 2. Benthic fluxes of silicate to the water column relative to sediment deposition rates (based on ^{234}Th) for different stations and cruises on the Louisiana shelf.

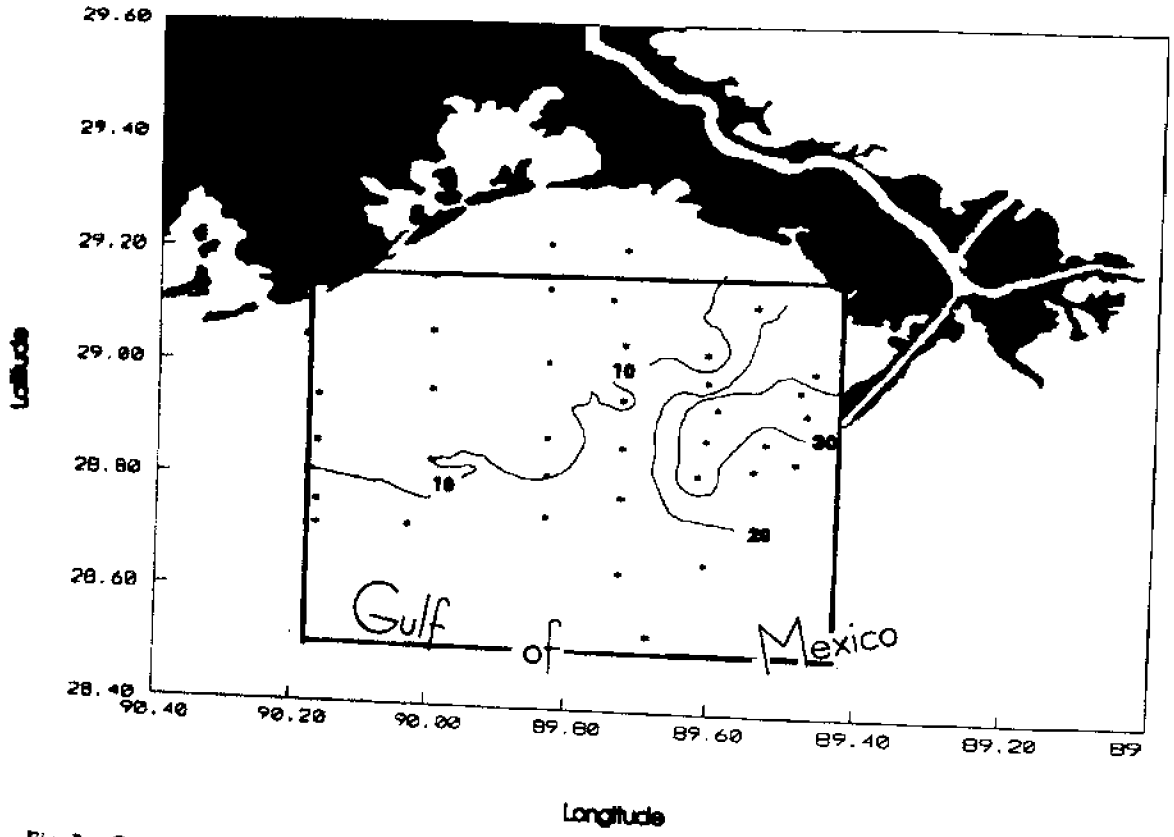

Fig. 3. Contours of nitrogen burial rates for a 5416 km^2 region of the Louisiana shelf (denoted by rectangle) based on 42-station survey of ^{210}Pb estimates of sediment burial and average nitrogen concentration in top 15 cm. of sediment.

the water column increase linearly with deposition rates from 0.3 to 2.5 cm /mo, reaching maximum silicate flux rates of 550 umol $m^{-2} h^{-1}$. Above a deposition rate of 2.5 cm/mo silicate flux was lower at less than half the maximum rates. However, this may be a station effect; there was a strong regression between deposition and silicate regeneration for station C50, but silicate fluxes at B50 were similar regardless of the sediment deposition rate (Fig. 2). Thus, the response of benthic fluxes to temporal variation of particulate input may vary spatially in the Louisiana shelf.

Coastal and shelf sediments may be considered large reservoirs of deposited nutrients that are not regenerated to the water column. The relative magnitude of burial is controlled by the quantity and quality of particulate material supplied to bottom sediments (Zeitzschel 1980; Klump and Martens 1983). Annual rates of nitrogen accumulation in the plume region of the Louisiana bight range from 0. 16 to 57 gN $m^2 y^{-1}$ (Fig. 3). Rates are highest along the 50m depth contour near the mouth of southwest pass of the Mississippi River. The maximum rate of nitrogen burial is 465 umol $m^2 h^{-1}$; equivalent to higher estimates of ammonium regeneration in this region of the shelf (Fig. 3). The mass balances of sediment, carbon, and nitrogen in a 17,500 km^2 region of the Louisiana bight (Fig. 3) are estimated by comparing riverine inputs with area-weighted accumulation rates of these materials in the shelf sea bed (Fig. 4). The annual sediment discharge estimate for the Mississippi River is averaged over the last 100 years taking into account the effects of reservoirs constructed in the Mississippi River watershed (pre and post 1963 annual estimates) and considering 30% of the river discharges through southwest pass (Malcolm and Durum 1976). Riverine inputs of carbon and nitrogen are calculated based on 1.6% and 0.23%

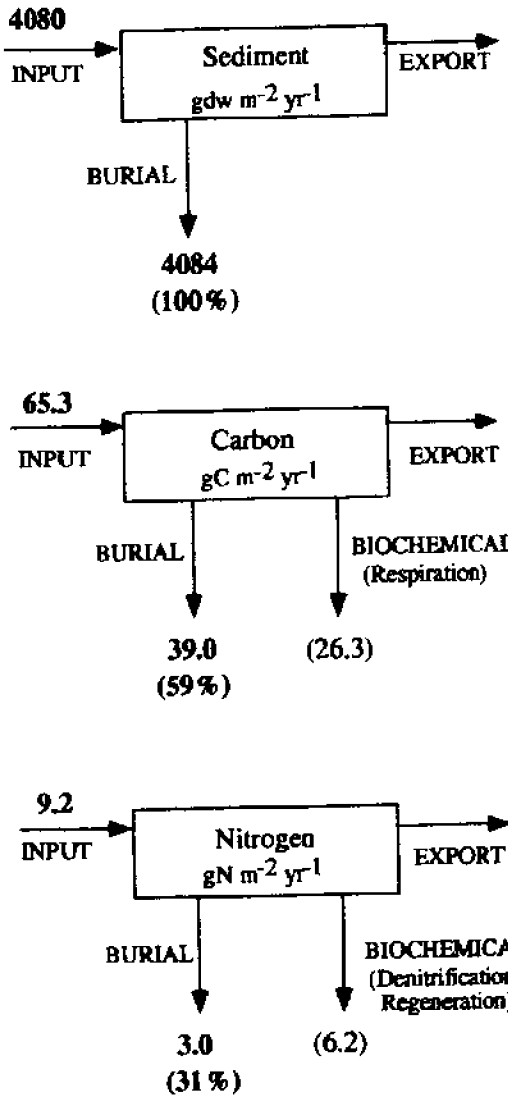

Fig. 4. Mass balance estimates of sediment, carbon and nitrogen in a 5416 km^2 region of the Mississippi River plume based on riverine inputs of particulate material and burial (100 yr time scale).

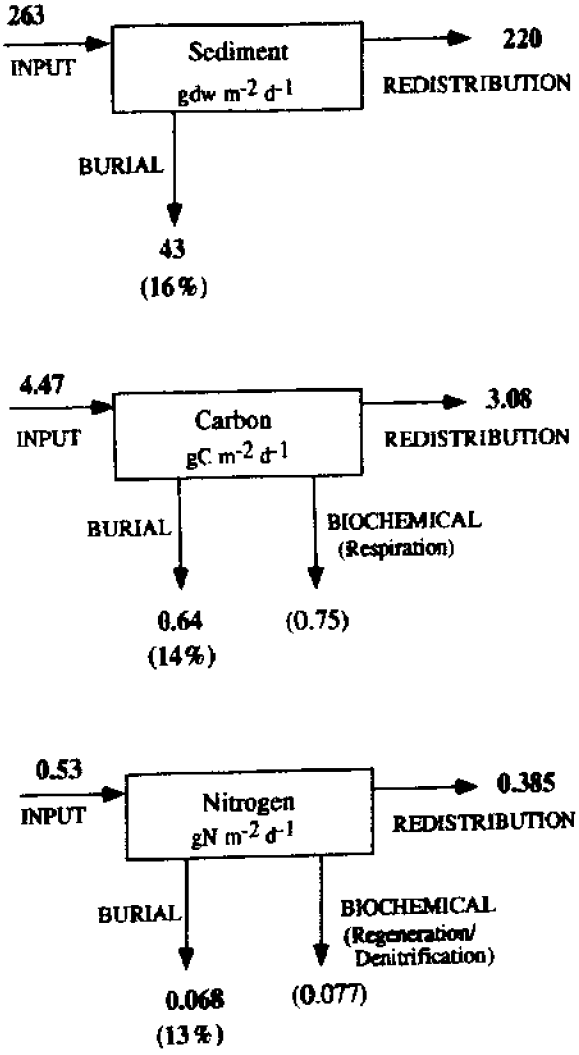

Fig. 5. Mass balance estimates of sediment, carbon and nitrogen during high river flow at station C50 based on inputs (^{234}Th), burial (^{210}Pb), and biochemical reactions in the sediment (flux studies). Redistribution is based on sediment excess between input and accumulation, and particulate concentration in surface sediments of 1.4% carbon and 0.175% nitrogen

content of sediment load, respectively (Trefry et al. 1991). The annual input of sediment, carbon, and nitrogen (7.14×10^{13}, 0.114×10^{13}, and $0.0\ 16 \times 10^{13}$ g yr^{-1}, respectively) were divided by study area (Fig. 3) to determine loading in units of g m^2 yr^{-1} (Fig. 4). All the sediment input from the river can be accounted for by the accumulation of sediment in the study area of the Louisiana shelf (Fig. 4); indicating that while there may be areas of excess deposition followed by redistribution, most of the sediment remains in this region of the shelf This has important implications to the mass balance estimates of carbon and nitrogen (Fig. 4); the deficit between input and accumulation is associated with biochemical processes rather than export Burial of carbon is 59% of riverine input of particulates, while nitrogen accumulation accounts for only 31 % of riverine input The deficit in carbon indicates that the contribution of the particulate carbon to respiration of this study area is 26.3 gC m^2 yr^{-1}, or 0.072 gC m^2 d^{-1}; other sources of respiration in the system are from DOC inputs and *in situ* production. This preliminary mass

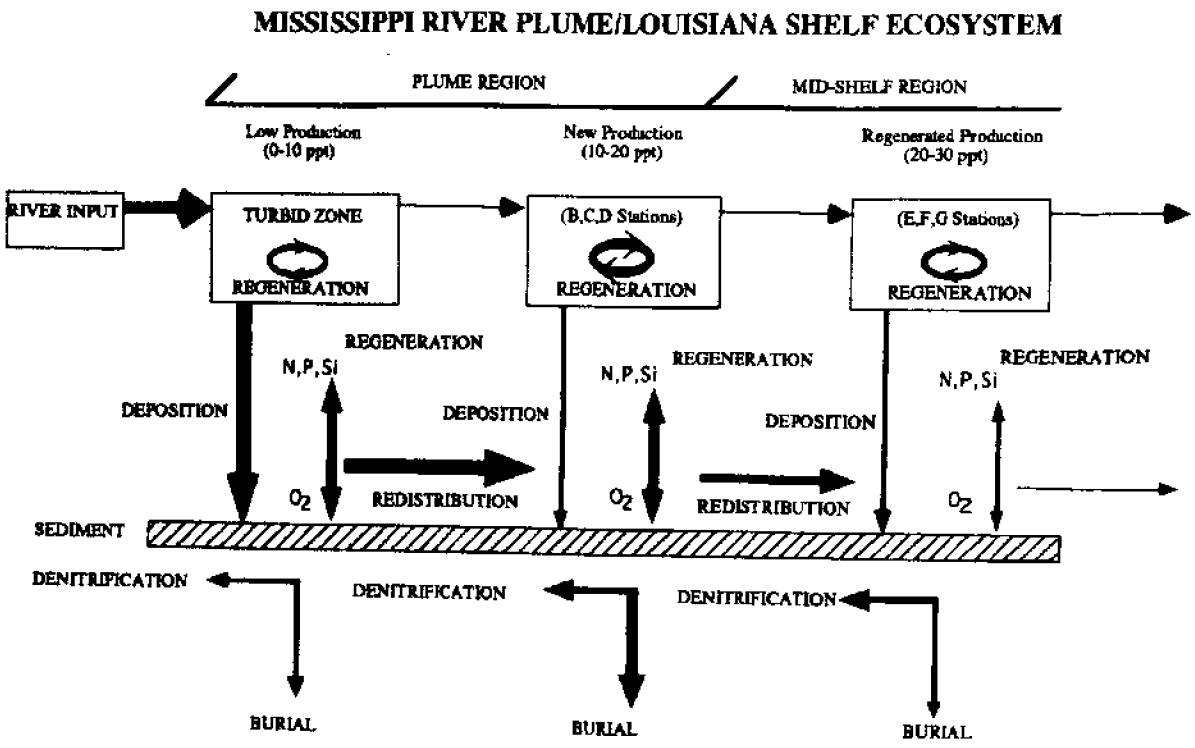

Fig. 6. Conceptual model of the fate of organic matter in the plume and mid-shelf region of the Louisiana shelf ecosystem.

balance of sediment, carbon and nitrogen, give insights into the metabolism of this region of the Louisiana shelf. Even though terrigenous organic matter is not as biologically reactive as its marine counterpart, the recycling of a small portion of the annual discharge of the Mississippi River (4×10^{12} gC; Malcolm and Durum 1976) may have a major impact on coastal ocean productivity.

Comparison of seasonal inputs of materials to the sediment (based on Th-234) relative to burial (based on Pb-210) indicate the seasonal nature of benthic-pelagic coupling (Fig.5). Sediment input (I) to station C50, about 15 km from the mouth of southwest pass at a water depth of 50m, was about 263 gdw m^2 d^{-1} during high river flow. However, only 43 gdw m^2 d^{-1} (or 16% of input) is buried (B) at this station. The remainder is redistributed (R) to other locations on the shelf. The redistribution of carbon and nitrogen was also estimated for C50 using the value for sediment redistribution together with surface sediment concentrations of carbon and nitrogen (Fig. 5). The biochemical fate (BC) of carbon and nitrogen can be estimated by the following: BC = I - (B + R). For carbon, 14% of the input is buried and majority is redistributed: the balance is 0.75 gC m^2 d^{-1}, which is similar to direct measures of respiration at this station. Nitrogen burial is only 13% of seasonally high input and a huge percent is redistributed (Fig. 5). The balance of nitrogen at C50 during April, 0.077 gN m^2 d^{-1}, is similar to direct estimates of ammonium regeneration of 0.067 gN m^2 d^{-1} (200 umol m^2 h^{-1}). During high river flow, only a small portion of materials deposited in near-field locations to southwest pass are stored or biochemically processed; a majority of material is transported to other locations on the shelf

Conceptual Model of Shelf Processes

The interrelationships among rates of material cycling through both benthic and water-column communities play an important role in the ultimate fate of inorganic nutrients and organic matter within land margin ecosystems (Fig. 6). The coupling of benthic and pelagic processes contributes to elevated rates of primary productivity in land margin ecosystems by recycling nutrients in the coastal zone. High concentrations of suspended sediments and nutrients introduced from the river are quickly deposited to the seabed in the near proximal zone of the plume region. Autotrophic production in this zone is limited by turbidity and remineralization in the water column is minor compared to the loading of organic nutrients. This zone is represented by high deposition rates to the

seabed, particularly from March to July, but dependent on the timing of maximum river discharge. Estimates of burial range from 1-2 cm/yr, compared to deposition rates of 1-4 cm/month. This difference suggests that a large percentage of this allochthonous material, both sediment and nutrients, is redistributed to other areas of the shelf The contribution of new production to vertical carbon flux is thought to be one of the major links to occurrence of hypoxia. In most seasons the location of the productivity and chlorophyll maximum is much closer to the river than to the hypoxic zone. Thus, the link between hypoxia and production may be indirect; we suggest that hypoxia results from the high rates of production and deposition during high flow periods (spring) over a large area and the subsequent redistribution of material to the hypoxic zone. This indirect link may explain the association of severe hypoxia with years of higher river discharge.

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