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Seasonal and Spatial Water Quality Changes in the Outflow Plume of the Atchafalaya River, Louisiana, USA

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ABSTRACT: The objective of this study was to examine the interaction between the Atchafalaya River and the Atchafalaya Delta estuarine complex. Measurements of suspended sediments, inorganic nutrients (NO_3^-, NH_4^+, PO_4^{3-}), chlorophyll *a* (chl *a*), and salinity were taken monthly from December 1996 to January 1998. These data were compiled by season, and the Atchafalaya River plume data were also analyzed using the Generalized Additive Model technique. There were significant decreases in NO_3^- concentrations during summer, fall, and winter as river water passed through the estuary, that were attributable to chemical and biological processes rather than dilution with ambient water. In some regions there were higher chl *a* concentrations during summer and fall compared to winter and spring, when river discharge and the introduction of inorganic nutrients were highest, suggesting biological processes were active during this study. The presence of NH_4^+, as a percentage of available dissolved inorganic nitrogen, increased with distance from the Atchafalaya River, indicative of remineralization processes and NO_3^- reduction. Mean PO_4^{3-} concentrations were often higher in the estuarine regions compared to the Atchafalaya River. During summer total suspended solid (TSS) concentrations increased with distance from the river mouth, suggesting a turbidity maximum. Highest chl *a* concentrations were found in the bayous and shallow water bodies of the Terrebonne marshes, as were the lowest TSS concentrations. The low chl *a* concentrations found in other areas of this study, despite high inorganic nutrient concentrations, suggest light limitation as the major control of phytoplankton growth. Salinity reached near seawater concentrations at the outer edge of the Atchafalaya River plume, but much lower salinities (< 10 psu) were observed at all other regions. The Atchafalaya Delta estuarine complex buffers the impact of the Atchafalaya River on the Louisiana coastal shelf zone, with a 41% to 47% decrease in Atchafalaya River NO_3^- concentrations before reaching Gulf waters.

Introduction

Eustatic sea-level rise stabilized near its present rate after the last glaciation between 5,000 to 7,000 years ago (Milliman and Emery 1968). Since that time, delta switching of the Mississippi River has created a series of overlapping deltaic lobes that presently form the Mississippi deltaic plain in coastal Louisiana (Scruton 1960). Delta switching occurs every 1,000 to 2,000 years, resulting in new loci for sedimentation and marsh development (Frazier 1967). The Atchafalaya River is the most recent diversion in the delta switching process with subaerial expression of the new Atchafalaya Delta occurring in 1972 (van Heerden and Roberts 1980).

The Atchafalaya River introduces large quantities of nutrients, sediments, and freshwater to a large coastal marsh and bay complex that includes the Terrebonne Marshes to the east, Fourleague Bay to the southeast, and Vermilion and Cote Blanche Bays to the west (Fig. 1). Increased flow in the Atchafalaya River during this century has had the effect of freshening surrounding marshes, in some cases converting brackish marsh to fresh marsh, as well as providing a source of mineral sediments and nutrients.

The purpose of this paper is to extend our understanding of the interaction between the Atchafalaya River and the Atchafalaya Delta marsh complex. There are at least three characteristics of riverine inputs that have large impacts on estuarine ecology: the magnitude of flow, nutrient concentration, and their seasonal variation (Nixon 1981). Our objectives are to examine these characteristics and their effect on the Atchafalaya Delta estuarine complex by mapping the distribution of sediments, inorganic nutrients, chlorophyll *a* (chl *a*), and salinity, and determining changes in these constituents in time and space. We hypothesized there would be strong non-conservative reduction of NO_3^-, PO_4^{3-}, and total suspended sediments during the flood season, and uptake of inorganic nutrients would be strongest in the marsh-dominated system (western Terrebonne), intermediate in the shallow open water (Vermilion and Cote Blanche

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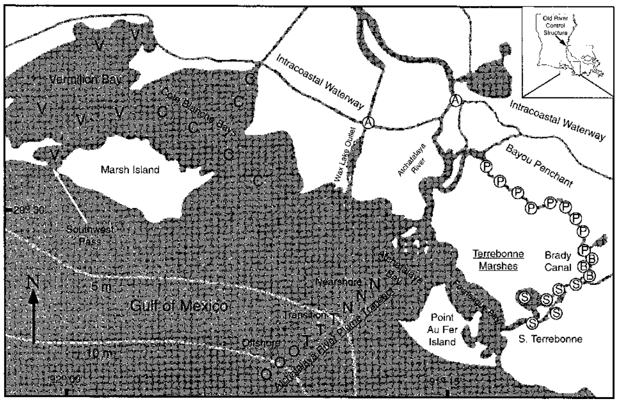

Fig. 1. Map of the Atchafalaya Delta estuarine complex. Letters refer to where water samples were taken in each region. The study area was divided into nine regions: Atchafalaya River (A), Nearshore (N), Transition (T), Offshore (O), Vermilion Bay (V), Cote Blanche Bays (C), Bayou Penchant (P), Brady Canal (B), and Southern Terrebonne (S).

Bays), and least in the offshore plume, and regeneration of NH_4^+ and PO_4^{3-} during the summer.

Study Area

The Atchafalaya River starts at the Old River control structure and flows 226 km before entering Atchafalaya Bay and the Gulf of Mexico. The control structure was constructed by the Corps of Engineers in 1963 to regulate Atchafalaya River flow and prevent the full capture of the Mississippi River by this shorter route. The Atchafalaya River and Wax Lake Outlet has a combined mean flow of 5,100 $m^3\ s^{-1}$ with a flood peak from December to June with a mean of about 11,000 $m^3\ s^{-1}$. During this study, there was a combined mean flow of 7,500 $m^3\ s^{-1}$ and a peak December to June flow of approximately 11,200 $m^3\ s^{-1}$ (Fig. 2). Depending on discharge, up to 70% of the flow is by way of the lower Atchafalaya River into eastern Atchafalaya Bay, and the remaining 30% is by way of the Wax Lake Outlet, a 21-km dredged canal to western Atchafalaya Bay. Atchafalaya Bay is a fluvially-dominated 545 km^2, shallow (< 2 m) basin characterized by low wave energy, low tidal range, weak littoral drift, and a low offshore slope.

The Vermilion-Cote Blanche Bay complex is characterized by shallow, highly turbid, vertically well-mixed waters (Fig. 1). Vermilion Bay covers 492 km^2 with direct connection to the Gulf of Mexico by way of Southwest Pass. In 1855, Southwest pass had a depth of 3.3 m, but currently its depth is over 53 m (Juneau 1975), suggesting increased communication with the Gulf of Mexico during the last century. West Cote Blanche Bay is approximately 360 km^2, and is connected to East Cote Blanche and Vermilion Bays by 10-km wide passes.

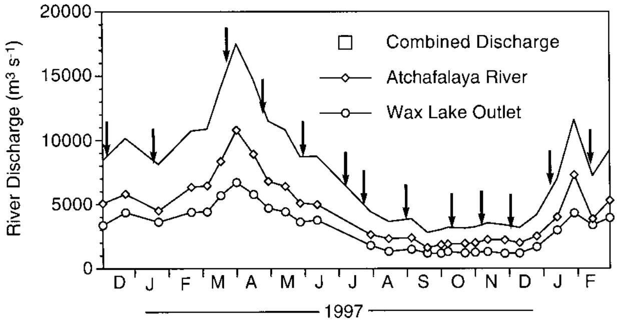

Fig. 2. Discharge through the Atchafalaya River and Wax Lake Outlet, as well as combined flow, during the study period. Arrows indicate when water sampling was carried out.

East Cote Blanche Bay is 333 km^2 and has free exchange of water with Atchafalaya Bay and the Gulf of Mexico. The Intracoastal Waterway cuts through the Atchafalaya River and Wax Lake Outlet, shunting river water westward to connections with the northern portions of Vermilion and West Cote Blanche Bays.

The western Terrebonne marsh complex receives Atchafalaya River water by way of a number of natural and artificial channels, with the largest being Bayou Penchant (Fig. 1). River water flows along Bayou Penchant, eventually reaching Brady Canal. Brady Canal is actively managed with weirs and other water control structures and is characterized by rapidly deteriorating, fragmented marsh. Brady Canal connects to a series of bayous in the southern Terrebonne marshes that eventually terminate at Fourleague Bay. Upper Fourleague Bay is connected to the Atchafalaya River by a 4 km wide pass, and the Lower Bay communicates with the Gulf of Mexico through a 180 m wide tidal channel. Upper and lower Fourleague Bay combined encompass approximately 95 km^2. More detailed description of this area are given by van Heerden and Roberts (1980), Madden et al. (1988), and Perez et al. (2000).

Materials and Methods

The Atchafalaya Delta estuarine complex was divided into three sampling areas: the Atchafalaya River plume, Vermilion-Cote Blanche Bays, and Terrebonne Marshes (Fig. 1). The Vermilion-Cote Blanche Bays and Terrebonne Marshes were sampled by boat. The Atchafalaya River plume was sampled by helicopter, with additional samples of Vermilion and Cote Blanche Bays also taken. An effort was made to sample the three areas over three consecutive days during 1997, but due to bad weather or boat failure, this goal was sometimes not met. There were 9 Vermilion-Cote Blanche Bay, 10 Terrebonne Marsh, and 13 helicopter transects. Ten to fifteen water samples were collected during each boat transect in the Terrebonne marsh complex, and 11 during the Vermilion-Cote Blanche boat transects (Fig. 1). Helicopter transects ran 70 km from the mouth of the Atchafalaya River, through Atchafalaya Bay, into the Gulf of Mexico (Fig. 1). Nine water samples were taken along this transect, and another 13 samples were taken in Vermilion and West Cote Blanche Bays at many of the same locations as the boat transects. Samples were collected by lowering a rope from a height of 15–20 m. The sampler was weighted which caused it to quickly sink below the surface and samples were collected from the first meter. The water samples were analyzed for total suspended solids (TSS), nutrients (NO_3^-, NH_4^+, and PO_4^{3-}), chl *a,* and salinity. All constituents were plotted with salinity to determine if changes in concentration were conservative and due to mixing of river and Gulf waters or non-conservative due to biological (e.g., assimilation or denitrification) or physical (e.g., flocculation) processes (Liss 1976).

WATER QUALITY

Water samples were collected in 500 ml acid-washed polyethylene bottles, stored on ice, and taken to the laboratory for processing. Within 24 h, 60 ml from each water sample were filtered through pre-rinsed 25 mm 0.45 μm Millipore filters. The filtered water samples, and filters, were frozen until analyzed for nutrients and chlorophyll, respectively. Within one week of sample collection, TSS was determined by filtering 100–200 ml of sample water through pre-rinsed, dried, and weighed 47 mm glass microfiber filters. Filters were then dried for 1 h at 105°C, weighed, dried for another hour, and reweighed for quality assurance (Greenberg et al. 1992). Salinity was also determined within a week of sample collection using an Atago S-10 hand held refractometer (accuracy = ± 2 psu). Within one month of sample collection, frozen water and filter samples were analyzed for inorganic nutrients and chl *a,* respectively. NO_3^--N and NO_2^--N were determined separately using the automated cadmium reduction method (detection limits: $0.05 < \text{mg N l}^{-1} < 10.0$) with an Alpkem autoanalyzer (Greenberg et al. 1992). NO_3^- was the predominate form (> 90%) of total oxidized nitrogen ($NO_3^- + NO_2^-$), and therefore $NO_3^- + NO_2^-$ was reported as NO_3^- in this study. NH_4^+-N was determined by the automated phenate method (detection limits: $0.02 < \text{mg N l}^{-1} < 2.0$), and PO_4^{3-} by the automated ascorbic acid reduction method (detection limits: $0.005 < \text{mg P l}^{-1} < 10.0$), again with an Alpkem autoanalyzer (Greenberg et al. 1992). The accuracy of the nutrient analysis was checked every 20 samples with a known standard, and the samples were redone if the quality control was off by 5%. Chl *a* was determined by a modified version of the technique suggested by Strickland and Parsons (1972). Chlorophyll pigments were extracted with a 40:60 ratio of dimethyl sulfoxide (DMSO):90% acetone as described by Burnison (1980). The extract was measured fluorometrically with a Turner Designs model 10-AU fluorometer (Greenberg et al. 1992).

The Atchafalaya River water quality data used in this study was recorded by the U.S. Geological Survey (USGS) as part of their ongoing monitoring program (USGS 1998). The USGS recorded NO_3^--N, NH_4^+-N, PO_4^{3-}-P, and TSS concentrations. Data from Melville, Morgan City, and Calumet, Louisiana, were combined into one data set to characterize water quality in Atchafalaya River before reaching the coastal zone. Total river discharge was calculated by combining river flows from the Wax Lake Outlet and Morgan City.

STATISTICAL ANALYSES

Two types of statistical analysis were carried out, each using as response variables NO_3^-, NH_4^+, PO_4^{3-}, TSS, chl *a,* and salinity concentrations. The first analysis divided the study a priori into 9 distinct regions, and grouped the sampling times into seasons, then investigated interactions between these two variables. Winter was designated as the months of January, February, and March; spring as April, May, and June; summer as July, August, and September; and fall as October, November, and December. The Atchafalaya River data were combined to form a single region. The Atchafalaya River plume transect was divided into three regions: Nearshore, Transition, and Offshore (Fig. 1). Vermilion Bay was designated as a region, and East and West Cote Blanche Bays were combined to form a single region. The Terrebonne marsh complex was divided into three regions: Bayou Penchant, Brady Canal, and Southern Terrebonne. The stations served as replicates within each region, that were further grouped into seasons. The following factorial model was used with crossed and nested effects: region, station (region), season, region × season, with station classified as a random effect. In this way, we simultaneously modeled a variety of regions, seasons, and their interactions. Least-squared means, along with 95% confidence intervals, were calculated for significant region × season interactions, and p values were used to test for differences between seasons and regions using SAS statistical software (SAS Institute Inc. 1999).

The second type of analysis focused on the Atchafalaya River plume transect data using the technique of generalized additive modeling (GAM;

Hastie and Tibshiriani 1990). Data from the Nearshore, Transition, and Offshore regions were used in this analysis. The GAM model fit the mean of a response variable (NO_3^-, NH_4^+, PO_4^{3-}, etc.) by a sum of smooth functions of the explanatory variable, in this case distance from the river mouth and time of sampling. The model used in this analyses was: $\log(\mu) = \alpha + f_1(\text{Distance}) + f_2(\text{Time})$; where α was the overall mean and f was the smooth function. The GAM technique is useful because the smooth functions provide useful approximation to the regression surface, upholding the richness of more traditional parametric regression approaches, but relaxing the linear (polynomial) structure of the additive effects. Continuous functional forms were estimated for the responses as both distance and time varied, allowing the visualization of the changes in data with distance, independent of time, and vice versa.

N:P MOLAR RATIOS

Dissolved inorganic nitrogen (N) and phosphorus (P) molar ratios were examined in relation to autotrophic production, as measured by chl *a* concentration. Nitrogen was defined as the sum of NO_3^- and NH_4^+, and phosphorus as PO_4^{3-}. These values were converted to their molar equivalents by dividing them by their respective atomic weights. The means and standard errors of these data were calculated after grouping them by the same season and region classifications described above.

NO_3^- LOADING RATE ANALYSIS

We used water flow distributions and nutrient concentrations to calculate nutrient and sediment loading and retention in the shallow Atchafalaya Delta estuarine complex. Most Atchafalaya River water flowed directly into Atchafalaya Bay and Offshore, but some water also flowed west into Vermilion and Cote Blanche Bays, and east into the Terrebonne marsh complex. Estimates of seasonal water flow patterns were derived from a TABS two dimensional, finite element hydrodynamic model developed by Joseph V. Letter at the Waterways Experiment Station, U.S. Corps of Engineers (Thomas and McAnally 1985). This model was developed as part of a lower Atchafalaya River evaluation study conducted by U.S. Corps of Engineers, New Orleans district. From model output, equations were developed to calculate flow into different parts of the Atchafalaya outfall area. The following three equations yield flow into the Vermilion/Cote Blanche bays, the western Terrebonne marshes, and Atchafalaya Bay and adjacent near-shore Gulf of Mexico.

$$Q_{\text{verm/cote bays}} = (0.01Q_{\text{atch}} + 2.14) + (0.033Q_{\text{atch}} + 67.714) - (0.002Q_{\text{atch}} + 1.279) \quad (1)$$

$$Q_{\text{terrebonne}} = (0.051Q_{\text{atch}} + 181.266) \quad (2)$$

$$Q_{\text{nearshore}} = (0.658Q_{\text{atch}} + 219.392) + (0.205Q_{\text{atch}} + 26.424) \quad (3)$$

The seasonal loading of NO_3^- to each of the three zones was calculated by multiplying seasonal water fluxes by mean seasonal concentrations of the constituents. This was then divided by the area of each region to calculate the seasonal loading rate. To obtain the area of Atchafalaya Bay and the offshore zone, we estimated the depth that stratification occurred. We did this because once stratification occurs and river water flows over deeper, saline Gulf water, it effectively eliminates the possibility of nitrate loss via denitrification in the anaerobic sediments. For the Atchafalaya Bay and near-shore region, the loading rate was calculated using the area shoreward of the 5 and 10 m depth contours. We used these depths based on consultations with scientists familiar with nearshore Gulf hydrography and by studying vertical profiles of salinity and temperature off the Atchafalaya mouth collected during Louisiana Stimulus for Excellence in Research (LaSER) cruises (Wisemand and Justic personal communication). The following estimates of area for each region were used: Atchafalaya Bay and Offshore area ($<$ 5 m 1,250 km^2; $<$ 10 m 2,560 km^2), Vermilion and Cote Blanche Bays (1,185 km^2), and Terrebonne marshes (975 km^2).

The removal efficiency (RE) of NO_3^- was calculated using Eq. 4,

$$RE = (\text{Mass}_{\text{in}} - \text{Mass}_{\text{outadj}})/\text{Mass}_{\text{in}} \quad (4)$$

where Mass_{in} is the concentration of the constituent in the Atchafalaya River, and $\text{Mass}_{\text{outadj}}$ is the concentration at the end member station. The end member station for the Vermilion/Cote Blanche Bays was located at Southwest Pass, for Terrebonne Marshes at the most southern Bayou Penchant region station, and for Nearshore at the fourth and seventh station of the Atchafalaya River plume transect which corresponds to the 5 and 10 m depth contours, respectively. Salinity mixing diagrams were used in cases where end member salinity concentrations were over 3 psu, as often occurred in the Atchafalaya River plume. The area between the conservative and nonconservative mixing lines was integrated to provide estimates of NO_3^- decreases not caused by simple mixing with Gulf waters. The use of mixing diagrams in this case assumes that there are only two significant end-members. The discharge of the Atchafalaya completely overwhelms any other freshwater source such as precipitation and inflow from smaller rivers. The regular and gradual increase in salinity in the Nearshore zone indicates that mixing of river water and Gulf water, not intrusions of other water masses, accounts for salinity patterns in the Nearshore area in front of the Atchafalaya River mouth.

Total percent removal was calculated using Eq. 5,

$$\text{Total \% Removal} = \text{RE} \times \% \ Q_{\text{atch}} \qquad (5)$$

where removal efficiency was multiplied by the percentage of Atchafalaya River water ($\% \ Q_{\text{atch}}$) that flowed into each area. The sum of the total percent removal for each region was used to estimate the efficiency of the inshore and unstratified nearshore coastal region in non-conservatively removing NO_3^- from the Atchafalaya River.

Results

REGION × SEASON INTERACTION

There were significant region × season interactions for all variables, except NH_4^+ and PO_4^{3-}. There were significant seasonal trends ($p < 0.001$) of high winter and low spring NH_4^+ concentrations (Fig. 3). The high winter concentrations were due to unusually high NH_4^+ levels in early 1997.

The Atchafalaya River plume regions had decreased NO_3^- concentrations with distance from the river mouth, regardless of season, and had significantly lower ($p < 0.02$) NO_3^- concentrations than the Atchafalaya River during summer, fall, and winter (Fig. 3). The Transition and Offshore regions were not significantly different from each other, but had significantly lower ($p < 0.001$) NO_3^- concentrations than the Nearshore region during spring, summer, and fall. During summer, fall, and winter, Vermilion and Cote Blanche Bay regions had significantly lower ($p < 0.001$) NO_3^- concentrations than the Atchafalaya River, with Vermilion Bay having significantly lower ($p < 0.01$) concentrations than Cote Blanche. There were no significant differences in NO_3^- concentrations between the Terrebonne marsh regions, but collectively these regions had significantly lower ($p < 0.001$) NO_3^- compared to the Atchafalaya River for all seasons. Bayou Penchant had higher NO_3^- concentrations than either Brady Canal or Southern Terrebonne, which were not different from each other.

The Nearshore ($p < 0.03$) and Cote Blanche ($p < 0.001$) regions had significantly higher PO_4^{3-} concentrations during summer and fall compared to spring (Fig. 3). During fall, the Cote Blanche Bay and Bayou Penchant regions had significantly higher ($p < 0.01$) PO_4^{3-} concentrations than the Atchafalaya River. Both Bayou Penchant and Brady Canal regions had significantly higher ($p < 0.01$) winter PO_4^{3-} levels compared to spring.

The Atchafalaya River plume regions had significantly lower ($p < 0.002$) TSS concentrations compared to the Atchafalaya River during winter and spring (Fig. 4). The Nearshore and Transition Zone regions had higher ($p < 0.03$) TSS concentrations during fall compared to summer, with the Nearshore region also having higher ($p < 0.02$) fall TSS when compared to winter. During winter, Vermilion and Cote Blanche Bay regions had significantly lower ($p < 0.001$) TSS concentrations compared to the Atchafalaya River. Bayou Penchant and Brady Canal regions had lower ($p < 0.01$) TSS concentrations than the Atchafalaya River during all seasons except fall. During winter, Southern Terrebonne regions had significantly higher ($p < 0.01$) TSS concentrations than Bayou Penchant.

Chl *a* concentrations were higher ($p < 0.001$) in the Transition zone compared to the Nearshore and Offshore regions during summer (Fig. 4). Vermilion ($p < 0.01$) and Cote Blanche Bay ($p < 0.03$) regions had higher summer chl *a* concentrations compared to winter and spring, but the regions themselves were not significantly different from each other during any season. During spring and summer, Bayou Penchant had significantly higher ($p < 0.04$) chl *a* concentrations than any other region, and generally the Terrebonne marsh regions had higher chl *a* levels than any other region in this study.

The Atchafalaya River plume regions had increasing salinity with distance from the river mouth, with the Offshore region having the highest salinity for most seasons (Fig. 4). The Nearshore region had significantly lower ($p < 0.001$) salinity than the Transition or Offshore regions during all seasons. Salinities in Vermilion and Cote Blanche Bay regions were not significantly different from each other during any season, but had significantly higher ($p < 0.001$) salinities during fall compared to other seasons. Salinity concentrations were low (< 5 psu) and generally not significantly different between the Terrebonne marsh regions except during fall, when there was a significant increase ($p < 0.01$) in salinity at the Brady Canal and Southern Terrebonne regions.

N:P MOLAR RATIOS

The Atchafalaya River N:P ratio fluctuated between 25:1 and 53:1 throughout the year (Fig. 3). This indicates that there was excess nitrogen in relation to phosphorus compared to the Redfield ratio of 16:1 for optimal phytoplankton growth (Redfield 1958). The N:P ratio at the Atchafalaya Plume regions remained higher than 16:1 during the win-

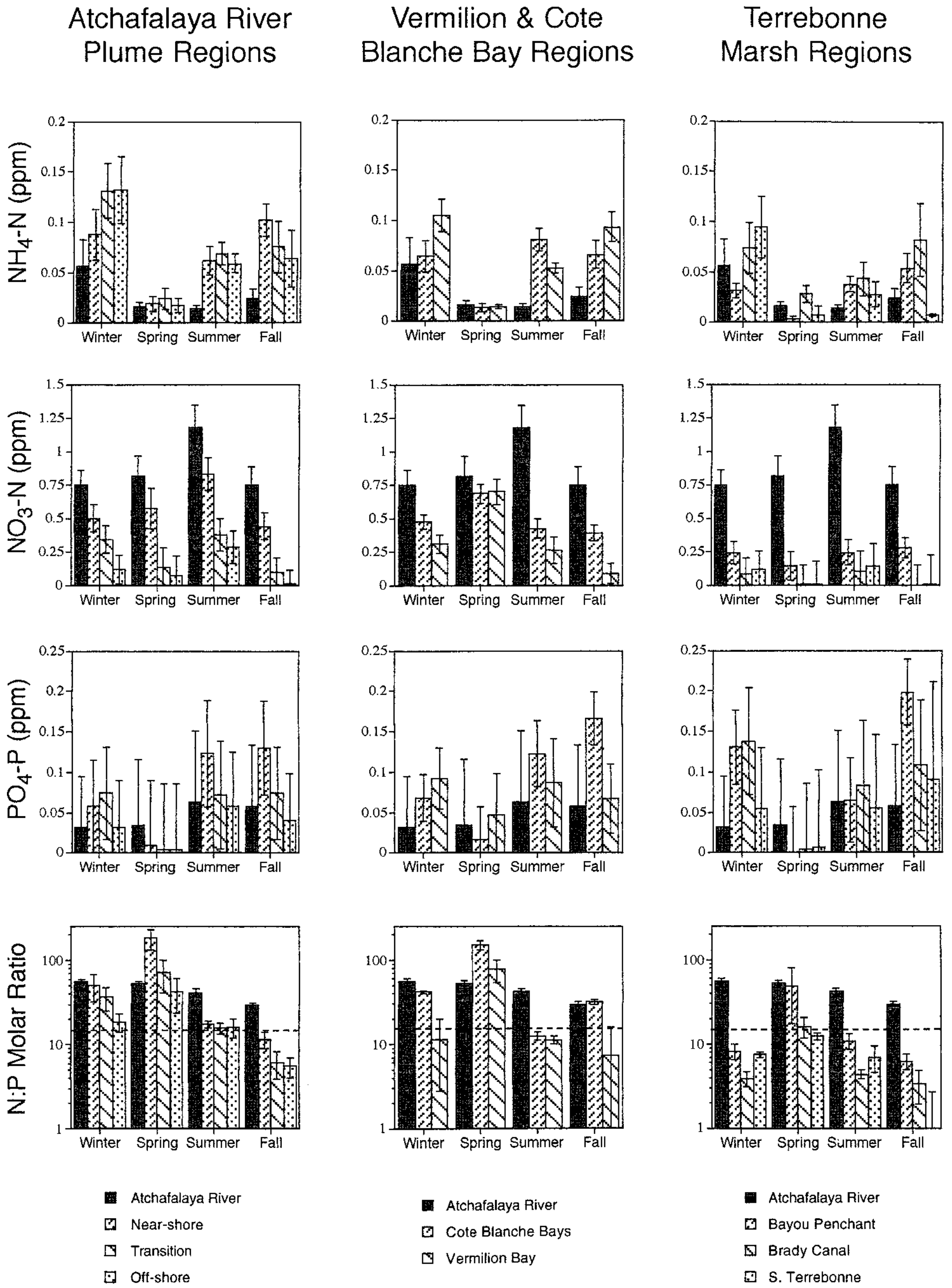

Fig. 3. Results of seasonal analysis for NH_4^+ (error bars are ± SE), NO_3^-, and PO_4^{3-} (error bars are 95% confidence intervals of the mean). Results of the N:P molar ratio analysis. The dashed lines represent the Redfield N:P ratio of 16:1, and error bars are 1 ± SE.

ter and spring, but decreased to near the Redfield ratio during the summer and was less than 16:1 during the fall. The Cote Blanche region remained high in nitrogen during all seasons except summer, when the ratio fell to 12:1, while the Vermilion Bay region was nitrogen limited during all seasons except spring. The N:P ratio was less than 16:1 in the Terrebonne marsh regions during all seasons except spring, when the Bayou Penchant region ratio was 48:1 and the Brady Canal region was 16:1.

Generalized Additive Model

The smooth function of the GAM model indicated that, independent of time, NO_3^-, NH_4^+, and PO_4^{3-} concentrations decreased with distance from

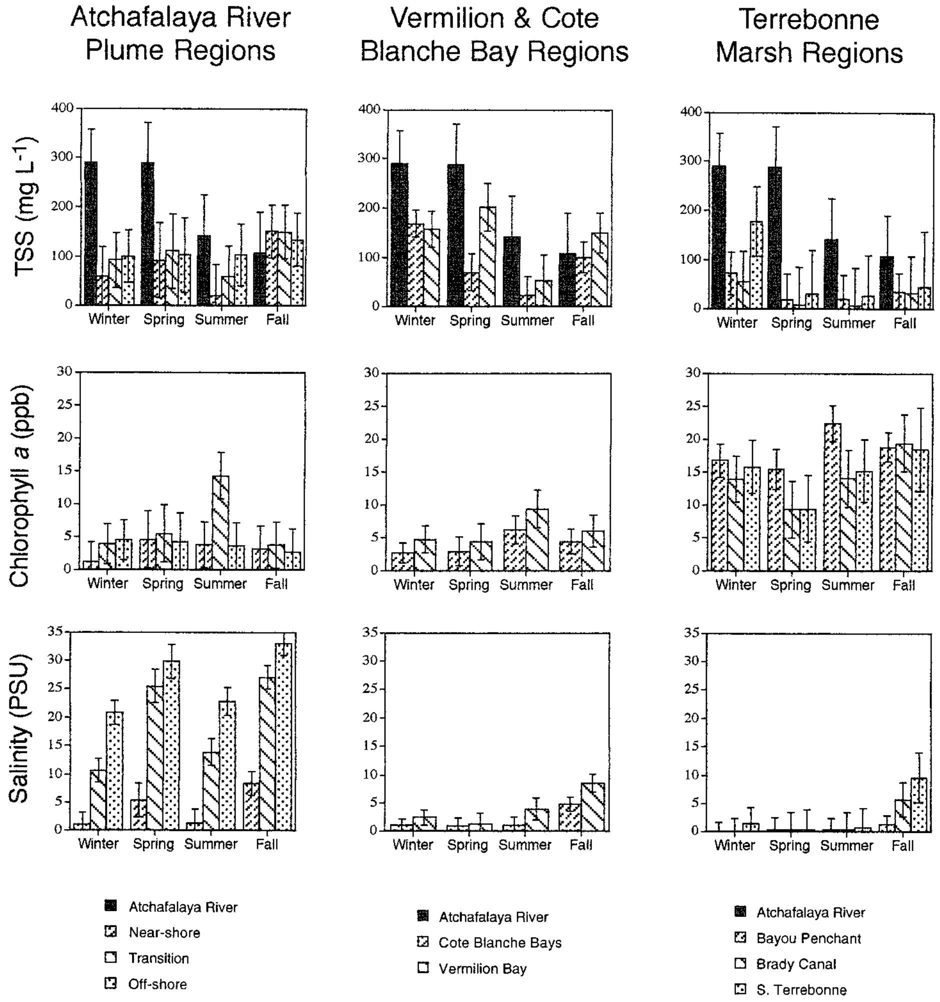

Fig. 4. Results of seasonal analysis for TSS, chlorophyll *a*, and salinity. Error bars are 95% confidence intervals of the mean.

Atchafalaya Bay as river water flowed into the Gulf of Mexico (Fig. 5). TSS tended to increase with distance from the Bay. The linearity of these results, on a log scale, were highly significant, indicating a steady rate of change for these constituents with distance. Chl *a*, however, exhibited non-linear behavior and peaked at approximately 35 km from Atchafalaya Bay. Salinity concentrations were also non-linear, and rose with distance from the Bay at a higher rate for the first 30 to 40 km compared for the rest of the 70 km transect.

Independent of distance, the smooth function of the GAM model indicated NO_3^- concentrations were moderate from January to May, then rose during the summer months, dropped off during the fall, and rose again during the winter of 1998 (Fig. 6). Peak NH_4^+ concentrations occurred in December 1996 and February 1997, then dropped to lowest levels in May, and rose again in late August. Lowest PO_4^{3-} levels occurred in April, and peak concentrations occurred in July and maintained high concentration for the rest of the year. TSS concentrations peaked during spring 1997 and winter 1998, and were lowest during the summer months. Lowest chl *a* concentrations were recorded on January 1997, but maintained higher concentrations for the rest of the year. Lowest salinities occurred January through March of 1997, and peak levels were during fall.

NO_3^- LOADING RATE ANALYSIS

The Nearshore area received approximately 90% of the flow of the Atchafalaya River. This area, that was delineated as the area directly south and including Atchafalaya Bay with a depth of less than 5 or 10 m, had a NO_3^- loading rate of 136 and 66 g m^{-2} yr^{-1}, respectively (Table 1). The NO_3^- removal efficiency was 40% and 47%, respectively, that accounted for 36% and 42% of the total NO_3^- carried by the river, respectively. Approximately

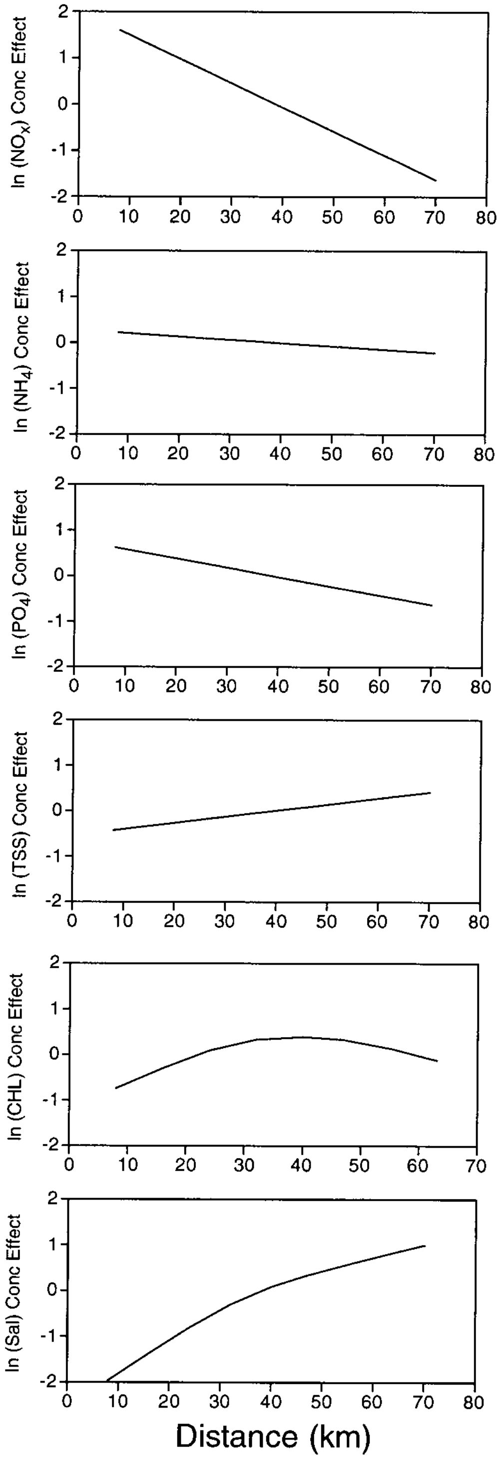

Fig. 5. Results of the GAM statistical model. The smooth function displayed above represents the behavior of the constituent, independent of time, along the 70 km transect from the southern boundary of Atchafalaya Bay out into the Gulf of Mexico.

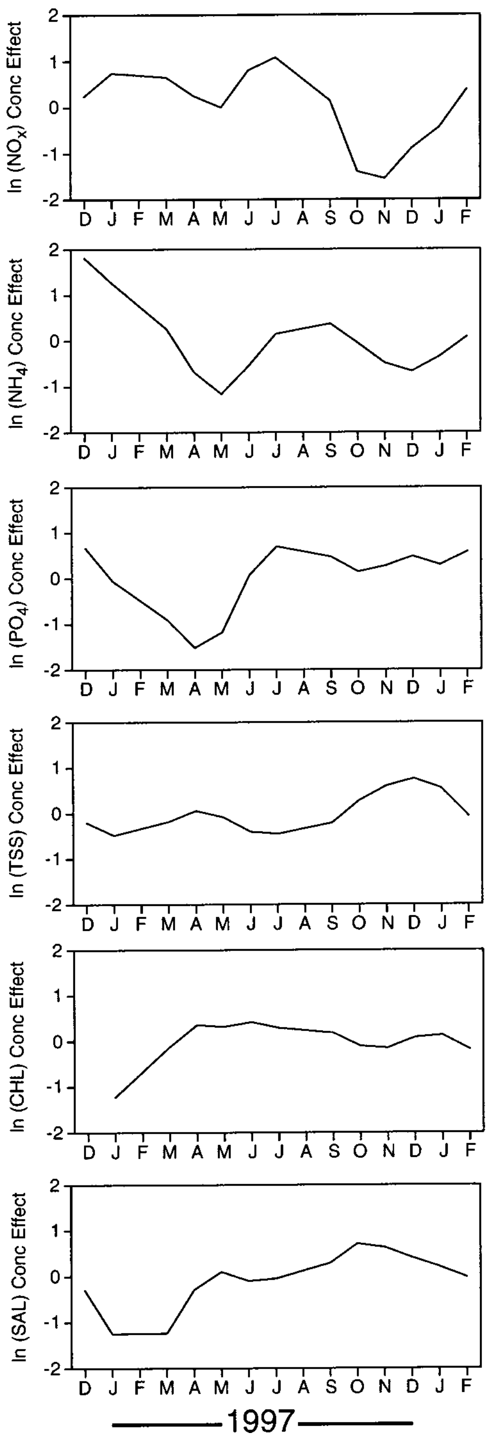

Fig. 6. Results of the GAM statistical model. The smooth function displayed above represents the behavior of the constituent through time, independent of distance, along the Atchafalaya River plume transect.

TABLE 1. Results of the NO_3^- loading rate analysis in the areas west (Vermilion/Cote Blanche Bays), east (Terrebonne Marshes), and directly in the path of (Near Shore) the Atchafalaya River at 5 and 10 m depth contours. Regional %NO_3^- removal refers to the amount of nitrate removed from river water flowing into the specific area mentioned. For the inshore areas, the figures are the same for the 5 and 10 m scenarios because the depth of the inshore area is less than 5 m. Total percent removal is an estimate of the efficiency of the coastal region in removing NO_3^- from the Atchafalaya River.

	NO_3^- Loading ($g\ m^{-2}\ yr^{-1}$)		Regional % NO_3^- Removal		Total % NO_3^- Removal	
	5 m	10 m	5 m	10 m	5 m	10 m
Verm/Cote bays	8	8	45%	45%	2%	2%
Near shore	136	66	40%	47%	36%	42%
Terrebonne	5	5	90%	90%	3%	3%
				Total Removal:	41%	47%

4% of Atchafalaya River water flowed into Vermilion and Cote Blanche Bays, providing a NO_3^- loading rate of 8 $g\ m^{-2}\ yr^{-1}$. The Vermilion and Cote Blanche Bays had a NO_3^- removal efficiency of 45%, but this efficiency accounted for only 2% of the total NO_3^- carried by the river. The Terrebonne marsh complex received approximately 3% of the Atchafalaya River volume, and had a NO_3^- loading rate of 5 $g\ m^{-2}\ yr^{-1}$. The Terrebonne area had the highest removal efficiency with 90% of NO_3^- being assimilated. This high removal efficiency accounted for only 3% of the total NO_3^- carried by the river. These calculations indicate that 41% to 47% of NO_3^- is non-conservatively removed from Atchafalaya River water by coastal processes, most of which occurred in the lower Atchafalaya Basin and Nearshore regions.

Discussion

All regions in this study tended to have lower NO_3^- concentrations than the Atchafalaya River during winter, summer, and fall. These lower concentrations were either due to dilution with Gulf water, chemical transformation, denitrification, biological uptake processes, or burial. If decreasing NO_3^- concentrations were caused by simple mixing with salt water then there would be a linear correlation between NO_3^- concentration and salinity, which is not the case (Fig. 7). Dilution with rainwater was unlikely to have caused substantial NO_3^- decreases because of the high volume of Atchafalaya discharge, high evaporation rates, as well as high NO_3^- concentrations in rainwater (Paerl 1997). Chemical reduction of NO_3^- to NH_4^+ has been found to occur rapidly in the estuarine environment (Smith et al. 1982) with as much as 50% of NO_3^- applied to marine sediments being reduced to NH_4^+ (Sorenson 1978). Denitrification of NO_3^-, and the subsequent release of nitrogen to the atmosphere, has been found to occur at high rates (Smith et al. 1983; Khalid and Patrick 1988; Lindau and DeLaune 1991; Nowicki et al. 1997). Jenkins and Kemp (1984) reported that up to 50% of NO_3^- introduced into the Patuxent River estuary underwent denitrification. Significantly higher chl *a* concentrations in the Terrebonne marsh regions, as well as 35 km from the river mouth, indicates assimilation of NO_3^- into particulate organic matter by autotrophic photosynthetic organisms also occurred at high rates. During spring, the Nearshore, Cote Blanche, and Vermilion Bay regions did not have significantly different NO_3^- concentrations than the Atchafalaya River, most likely because high riverine flow did not provide enough residence time for biological processes to occur.

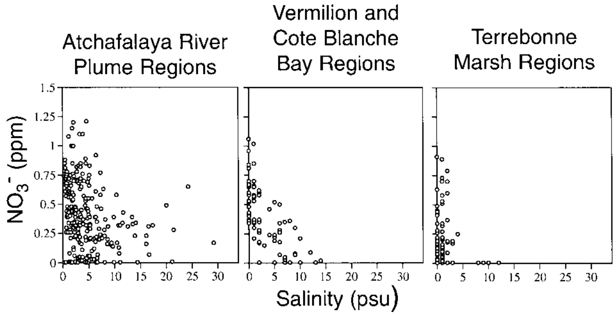

Fig. 7. Salinity mixing diagrams for the Atchafalaya River Plume, Vermilion and Cote Blanche Bays, and Terrebonne Marsh regions.

The Atchafalaya Delta estuarine complex has the effect of buffering the impact of the Atchafalaya River, and the introduction of NO_3^-, on the Louisiana coastal shelf zone. This zone is currently experiencing summer hypoxia due to direct introduction of nutrient laden water from the Mississippi River without benefit of processing by a shallow water marsh ecosystem (Turner and Rabalais 1994). The area of low oxygen bottom waters is now widespread during the summer and has been linked to fish kills and other deleterious effects (Turner and Rabalais 1991). Coastal wetlands and shallow waters have been found to be effective sinks for nutrients and sediments (Lane et al. 1999). Based on the results of this study, we estimate that 41% to 47% of Atchafalaya River NO_3^- was either transformed or lost before reaching stratified Gulf waters. Similar reductions in nitrogen have been reported to occur in wetland wastewater treatment systems (Nichols 1983; Breaux and Day 1994), as well as in other areas where Mississippi River water flows into shallow inshore areas (Lane et al. 1999; Perez 2000). The use of coastal wetlands and shallow water bodies to process Mississippi River water before entering the Gulf of Mexico has been proposed to help reduce the hypoxic zone, as well as restore and maintain rapidly eroding coastal marshes (Boesch et al. 1994; Mitsch et al. 2001). We believe that our results indicate a significant reduction of NO_3^- in Atchafalaya River water before it reaches the stratified Gulf of Mexico, although this is the first estimate of NO_3^- reduction, and more careful study is needed before definitive budgets can be constructed.

The Atchafalaya River was the primary source of NO_3^- to the Atchafalaya Delta estuarine complex, as evident from higher NO_3^- concentrations in the river compared to the estuarine regions. Mean NH_4^+ concentrations were generally higher in the estuarine regions compared to the Atchafalaya River. This was most likely caused by the regeneration of NH_4^+ by the decomposition of organic matter (Kemp and Boynton 1984), as well as reduction of NO_3^- to NH_4^+ (Sorenson 1978). Bacteria and fungi decompose organic material to obtain energy and in the process release nutrients in dissolved organic form (Day et al. 1989). Numerous studies have shown the net mobilization of NH_4^+ by benthic sediments (Koike and Hattori 1978; Callender and Hammond 1982; Teague et al. 1988). The relatively shallow water depths, rapid settling rates, and rapid bacterial utilization result in fairly short residence times for organic material in estuarine waters (Moran and Hodson 1989). Much of the regeneration of nutrients probably takes place on or in the bottom sediments, which is where NH_4^+ regeneration is highest (Blackburn 1979). Dugdale and Goering (1967) defined nitrogen available to phytoplankton to be in either new or regenerated form. They defined NO_3^- as new nitrogen derived from autochthonous sources, such as riverine, whereas NH_4^+ was defined as regenerated nitrogen resulting from remineralization within the benthos or the water column. Using this definition, in the Atchafalaya Delta estuarine complex it appeared that regenerated nitrogen composed a large portion of the available dissolved inorganic nitrogen to autotrophic organisms, especially during fall (Table 2). There were increasing $\%NH_4^+$ with distance from the Atchafalaya River; $\%NH_4^+$ increased as water flowed from the river mouth to the Offshore region, from the Cote Blanche region to the Vermilion Bay region, except during spring, and from the Bayou Penchant region to Brady Canal. The Terrebonne marsh regions generally had the highest $\%NH_4^+$, with the Brady Canal region having the largest $\%NH_4^+$ of any region. These results suggest a very high rate of remineralization of nitrogen, and indicate the importance of regenerated NH_4^+ as a source of dissolved inorganic nitrogen to autotrophic organisms in these regions.

TABLE 2. The percentage of dissolved inorganic nitrogen as NH_4^+.

Region	Winter	Spring	Summer	Fall
Atchafalaya River	6%	2%	1%	3%
Nearshore	13%	4%	0%	29%
Transition	32%	25%	9%	59%
Offshore	54%	30%	17%	62%
Cote Blanche	18%	2%	13%	21%
Vermilion	19%	2%	24%	56%
B. Penchant	19%	48%	22%	36%
Brady Canal	42%	74%	30%	78%
S. Terrebonne	49%	56%	16%	58%

Like NH_4^+, mean PO_4^{3-} concentrations were often higher in the estuarine regions compared to the Atchafalaya River, suggesting benthic remineralization to be a major source of PO_4^{3-} to the water column. Estuarine sediments have been found to be net sources of PO_4^{3-} with flux rates highly correlated with temperature (Nixon et al. 1980), but cases of estuaries acting as net sinks for PO_4^{3-} have also been reported (Callender and Hammond 1982; Froelich 1988). These contradictory findings may be because PO_4^{3-} is readily sorbed by clay and detrital organic particles at high concentrations, while at lower concentrations PO_4^{3-} is released into the water, maintaining moderate ambient concentrations (Jitts 1959; Patrick and Khalid 1974). Cyclic aerobic and anaerobic conditions in the top several centimeters of the wetland soil affect the sorption and release of PO_4^{3-} with PO_4^{3-} being released during anaerobic conditions (Patrick and DeLaune 1977), possibly exasperating hypoxic events. Sharp et al. (1982) found these sorption-desorption processes provide a buffering mechanism for phosphorus in the Delaware estuary. Madden et al. (1988) showed that total phosphorous behaved similarly in Fourleague Bay, Louisiana, with little change in concentration throughout the year.

Coastal estuarine systems are more likely to be nitrogen limited relative to phosphorus due to denitrification, the preferential sedimentation of nitrogen in zooplankton fecal pellets, and the more rapid recycling of phosphorus (Nixon et al. 1980; Howarth 1988). This assertion is supported by the low N:P ratios in regions far removed from the Atchafalaya River, such as Vermilion Bay and the Terrebonne Marsh regions (Fig. 3). The response of phytoplankton, as measured by chl *a* concentration, to these changing nutrient ratios are not clearly seen. This is probably due to phytoplankton productivity in the highly turbid waters of the Atchafalaya Delta estuarine complex being limited by light, rather than nutrient, availability.

Primary productivity in nutrient-rich waters is a function of phytoplankton biomass and light availability (Cole and Cloern 1984). In river-dominated estuaries, environments with turbidity often exceeding 50 mg l^{-1} as were most regions in this study, light is attenuated rapidly in the water column and phytoplankton photosynthesis is confined to a shallow photic zone. As a consequence, phytoplankton dynamics (including productivity and spatial and temporal changes in biomass) are largely controlled by light availability, and in many estuaries the spatial distribution of phytoplankton production has an inverse relationship with the distribution of suspended sediments (Cloern 1987). Both Randall and Day (1987) and Madden and Day (1992) have shown that phytoplankton productivity in Fourleague Bay is primarily controlled by light with the highest productivity occurring at intermediate salinities when both light and nutrients are available. The Terrebonne Marsh regions generally had the lowest TSS and the highest chl *a* concentrations in this study. The higher chl *a* concentrations in the Vermilion and Cote Blanche Bay regions during summer also coincided with low TSS concentrations, as it did in the Transition region. Madden (1992) also showed that turbidity decreased and chlorophyll increased with distance into the marshes surrounding Fourleague Bay. The low chl *a* concentrations found in other regions of this study, despite high inorganic nutrient concentrations, also support light limitation as the major control of phytoplankton growth. Light limitation of phytoplankton, as well as the lack of stratified waters, makes hypoxic events in the Atchafalaya Delta estuarine complex unlikely.

The Atchafalaya River was the primary source of sediments in this study. There was also likely additional TSS formed by flocculation of dissolved organic and inorganic matter during the mixing of river water and seawater (Sholkovitz 1976) with subsequent deposition or export to Gulf waters. These sorption, flocculation, and precipitation processes may be partially responsible for the increased TSS concentrations at the Offshore region compared to the Nearshore and Transition regions during winter and summer. Such turbidity maximums have been reported for other rivers such as the Amazon, where suspended sediment concentrations a few meters from the bottom were as high as 500 mg l^{-1} (Gibbs 1976). Uncles and Stephens (1993) found the turbidity maximum in the Tamar estuary to be associated with the freshwater-saltwater interface, where there was considerable resuspension of near-bed sediment by relatively strong currents.

In coastal Louisiana, strong southerly winds prior to winter frontal passage play a key role in raising water levels and distributing available sediments into the marsh interior (Reed 1989). In this study, fall and winter seasons tended to have the higher TSS concentrations, possibly due to the resuspension of sediments during storm fronts. Stern et al. (1991) found the highest sediment retention in marshes surrounding Fourleague Bay to be during the winter and early spring. The same pattern of seasonal deposition was also found in Barataria Basin, Louisiana (Baumann et al. 1984; Madden et al. 1988). Though a sporadic and variable process, storm fronts are an important factor in delivering sediments and maintaining marsh elevation in the face of relative sea level rise (Reed 1989). Day et al. (1995) discussed similar pulsing events as a dominate force in the formation and maintenance of the Rhône delta, France.

Conclusions

The Atchafalaya River was the primary source for nutrients and sediments to the Atchafalaya Delta estuarine complex. There were significant nonconservative decreases in NO_3^- concentrations as river water entered the estuarine environment, most likely through the processes of denitrification, transformation, and biological assimilation. The Atchafalaya River plume had increasing turbidity with distance during some seasons and greatest chl *a* concentrations 35 km offshore. The Vermilion and Cote Blanche Bays were river dominated throughout most of the year, with high suspended sediment concentrations and low chl *a* levels. The Terrebonne marshes, however, exhibited high biological activity with large decreases in nitrate concentration and high levels of phytoplankton biomass. The overall effect of the Atchafalaya Delta estuarine complex was to buffer the impact of the Atchafalaya River on the Gulf of Mexico, possibly decreasing the potential severity of the hypoxic zone.

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