The effect on water quality of riverine input into coastal wetlands

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THE EFFECT ON WATER QUALITY OF RIVERINE INPUT INTO COASTAL WETLANDS

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Oceanography and Coastal Sciences

by

Robert R. Lane
B.S., SUNY College of environmental science & forestry, 1993
M.S., Louisiana State University and Agricultural and Mechanical College, 1998
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ABSTRACT

This dissertation focuses on impact on water quality of two freshwater diversions, the Bonnet Carre Spillway and the Caernarvon freshwater diversion, as well as the Atchafalaya River Estuarine Complex. As water passed through the Bonnet Carre Spillway, there were reductions in total suspended sediment concentrations of 82-83%, in nitrite+nitrate of 28-42%, in total nitrogen (TN) of 26-30%, and in total phosphorus (TP) of 50-59%. The Si:N ratio generally increased and the N:P ratio decreased from the river to the plume edge in Lake Pontchartrain. At the Caernarvon diversion, there were reductions in concentrations of dissolved inorganic Si, N, and P of up to 38%, 57% and 23%, respectively. The DSi:DIN ratio rose from 0.9 to 2.6 at the Gulf end member station, while the DIN:DIP ratio fell from 107 to 26. There were decreases in total suspended sediment, large changes in salinity correlated to diversion discharge, and decreased water temperatures associated with riverine discharge. Chlorophyll concentrations near the diversion were low due to light limitation, but increased after suspended sediments decreased below 80 mg L\(^{-1}\), then decreased Gulfward. In the Atchafalaya River estuarine complex, salinity fluctuated seasonally, with the lowest salinities occurring during high river discharge. There was a 41-47% decrease in NO\(_3^-\) concentrations and total suspended sediments decreased as river water flowed through the estuarine complex.

In summary, the following conclusions can be made from these studies of the effect on water quality of riverine input into coastal wetlands: (1) riverine input has a pronounced effect on salinity throughout a receiving basin. Whereas nutrients and
sediments are actively deposited and/or transformed as riverine derived water passes through an estuarine system, freshwater passes conservatively with no change, diluting higher salinity waters; (2) There is rapid and effective trapping of suspended sediments in estuarine systems due to decreased water velocity and sediment settling; (3) Nitrate concentrations are substantially reduced in the estuarine environment due to the processes of denitrification, assimilation and reduction; (4) dissolved inorganic molar Si:N ratios increase, and N:P ratios decrease as riverine water flows through an estuarine system.
CHAPTER 1
INTRODUCTION

BACKGROUND

During the last 5,000 years, sedimentation from the Mississippi River created a series of overlapping deltaic lobes that formed the present day Mississippi deltaic plain in coastal Louisiana (Roberts 1997). The Mississippi delta was intricately tied to the river through a series of semi-abandoned river distributaries that included Bayou Teche, Bayou LaFouche, Bayou Terra aux Boeufs, and Bayou la Loutre, as well as the relatively newly formed Atchafalaya River. These distributaries carried river water to remote regions of the deltaic plain during spring floods. In addition, seasonal overbank flooding and crevasses supplied massive quantities of river water to wetlands directly surrounding the Mississippi River (Hatton et al. 1983; Kesel 1988; Kesel 1989; Roberts 1997; Davis 2000; Day et al. 2000). Davis (2000) documented 16 crevasses that occurred along the river between 1750 and 1927. Seasonal floods of the Mississippi River supplied pulses of freshwater, suspended sediments, inorganic nutrients, and organic materials that stimulated primary and secondary production throughout the delta (Delaune et al. 1983; Hatton et al. 1983; Day et al. 1983). Increased plant production provided higher rates of food production for consumers, and increased organic soil formation. Pulsed freshwater input also maintained a salinity gradient that supported a high diversity of wetland and aquatic habitats for estuarine species (Day et al. 1997).

The construction of flood control protection levees and closure of minor distributary channels began soon after colonization of New Orleans by the French in 1719 (Boesch 1996; Colten 2000). By the early 1900’s most of coastal Louisiana had been hydrologically isolated from the Mississippi River by the completion of massive flood control levees (Kesel 1988; Kesel 1989; Mossa 1996). Since, there has been an enormous loss of coastal wetlands that has been linked to the lack of riverine input (Salinas et al.)
As a restoration effort, the State of Louisiana has developed a plan of freshwater diversions that will mimic flooding events of the Mississippi River (Chatry and Chew 1985).

When freshwater diversions were first planned over two decades ago, the primary goal was to control salinity in oyster producing regions along the coast (Chatry et al. 1983). More recently, as the effects of lack of nutrients and sediment input have become better understood, diversions have been increasingly viewed as a way of delivering these materials to coastal wetlands and estuaries (Crandall and Lindsey 1981; Day and Templet 1989; Boesch et al. 1994; Day et al. 1997; Lane et al. 1999). This dissertation focuses on impact on water quality of two of these freshwater diversions, the Bonnet Carre Spillway and the Caernarvon freshwater diversion. In addition, the impact of the Atchafalaya River on water quality in the Atchafalaya Bay estuarine complex is examined. The Atchafalaya River is semi-controlled, and is viewed here as a very large ‘natural’ river diversion.

There has been controversy about the effects of diverting Mississippi river water into coastal wetlands because of possible eutrophication, and associated phytoplankton blooms, as currently observed in Louisiana’s offshore waters (Turner and Rabalais 1991; Rabalais et al. 1994; Paerl et al. 1998) and other estuaries throughout the world (Cedarwall and Elmgren 1990; Justic et al. 1995; Rosenberg 1985; Cloern 2001). On death, bacterial decomposition of algal cells may deplete oxygen levels in the lower water column, leading to disruption of the benthic community and other deleterious affects (Paerl et al. 1998). The shallow depth and relatively strong mixing of Louisiana’s estuarine waters, however, contribute to a relatively complete and rapid coupling of
heterotrophic and autotrophic processes (Nixon 1981). This homogeneity of the water column prevents stratification, a major physical phenomena that is necessary for hypoxia formation.

Phytoplankton production in coastal systems is most 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 (Reddy and Patrick 1984; Howarth 1988). Phytoplankton can generally assimilate only inorganic nitrogen, which exists in two forms, nitrate (NO$_3^-$) and ammonium (NH$_4^+$). Other forms of nitrogen are generally not available for phytoplankton assimilation or growth. The inorganic nitrogen fraction in Mississippi River water is predominantly (>90%) in the form of nitrate.

Various studies have reported reduction of NO$_3^-$ in estuarine environments with much of the reduction due to denitrification (Khalid and Patrick 1988; Lindau and DeLaune 1991; Nowicki et al. 1997). Denitrification and the subsequent release of nitrogen to the atmosphere occurs 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. This process is carried out by denitrifying bacteria that use nitrate as an electron acceptor to oxidize organic matter anaerobically (Koike and Hattori 1978). Another transformation pathway of NO$_3^-$ is assimilation into particulate organic matter by phytoplankton and vascular plants. Burial is an important loss pathway of material in the Louisiana coastal zone due to subsidence. DeLaune et al. (1981), for example, studied wetlands in Barataria Bay, Louisiana, and found nitrogen was buried in the interior marsh
at a rate of 13.4 g-N m$^{-2}$yr$^{-1}$, and Smith et al. (1985) found nitrogen burial of up to 23.0 g-N m$^{-2}$yr$^{-1}$ in wetlands surrounding the Atchafalaya River delta.

The rate of nitrogen removal is dependent on the loading rate, the form of nitrogen (e.g., NO$_3^-$ vs. NH$_4^+$; Boustany et al. 1997), and residence time (Nixon et al. 1996; Dettmann 2001). Maximum efficiency of nitrogen removal occurs at low loading rates and when diverted water is spread over wetlands as much as possible, increasing the sediment/water interface and residence time (Richardson and Nichols 1985; Blahnik and Day 2000). There have been several studies of the relationship between the nutrient loading rate into wetlands and associated removal efficiency (Richardson and Nichols 1985; Boustany et al. 1997; Faulkner and Richardson 1989; Spieles and Mitsch 2000; Mitsch et al. 2001).

The most comprehensive studies of wetland nutrient removal efficiency have been of wetland wastewater treatment systems, where the predominant form of nitrogen is NH$_4^+$. Mississippi River water contains predominantly NO$_3^-$, which is much more reactive than NH$_4^+$. Boustany et al. (1997) observed that N removal efficiency was largely dependent on the NO$_3^-$:NH$_4^+$ ratio. When NO$_3^-$:NH$_4^+$ ratio was >1, averaged N removal efficiency ranged from 95-100%, but ratios that were <1 averaged efficiencies were as low as 57%. The Mississippi River has an average molar NO$_3^-$:NH$_4^+$ ratio of 18 with a range of 8-30 (Lane et al. 1999). Therefore, Mississippi River water entering wetlands should have much higher removal efficiency than wetland wastewater studies indicate.
STUDY AREAS

Only a few areas in the Louisiana coastal zone still receive direct input of Mississippi River water. These include the Atchafalaya delta region and several areas where river water is diverted into the coastal zone. I chose study sites in these areas.

Bonnet Carre Spillway

The Bonnet Carre Spillway was constructed in 1931 after the great flood of 1927 to protect New Orleans from flooding by the Mississippi River. The spillway has since been opened eight times during high water events, with the most recent opening occurring in 1997 (Sikora and Kjerfve 1985; Day et al. 1999). The spillway is located 25 km west of New Orleans, Louisiana (Fig. 1.1). The 3.4 km wide spillway is confined by two 8.6 km levees, and connects the Mississippi River to Lake Pontchartrain. The spillway is located in an area that was one of the many crevasses that breached the Mississippi River levee in the 1800s and introduced up to 4,000 m$^3$s$^{-1}$ of water into Lake Pontchartrain during spring floods (Davis 1993; Kesel 1989; Davis 2000). The present spillway is designed to divert up to 7,000 m$^3$s$^{-1}$ from the river during floods. Although the spillway was designed strictly for flood control, a freshwater diversion project proposes to use the spillway to divert fresh water regularly into Lake Pontchartrain to maintain optimum salinity levels in oyster producing areas in Lake Borgne.

Though increases in the catch of oysters, saltwater finfishes and penaeid shrimp have been attributed to previous openings of the Bonnet Carre Spillway (Viosca1938; Gunter 1953; Chew and Cali 1981), there has been controversy about the effects of diverting Mississippi River water into Lake Pontchartrain, a 1630 km$^2$ brackish-water lagoon. A major concern is possible eutrophication as currently observed in Louisiana’s
offshore waters (Turner and Rabalais 1991; Rabalais et al. 1994; Dortch et al. 1999) and other estuaries throughout the world (Justic et al. 1995; Rosenberg 1985). Another concern is that suspended sediments in the river water would flow into Lake Pontchartrain and not reach wetlands where they are needed to offset rising water levels. As a result of these concerns, a reanalysis of the Bonnet Carre diversion project was initiated to further evaluate the impacts of the diversion and potential alterations of the project. The reanalysis was carried out by an interdisciplinary team composed of state and federal agency scientists and managers, academic scientists, and members of environmental groups. It consisted of analyses of data on water quality in Lake Pontchartrain, fisheries, nutrient assimilative capacity of wetlands, the development of alternative diversion scenarios, and hydrodynamic modeling to determine the impacts of the different scenarios on salinity. As part of the reanalysis, an experimental diversion was carried out in April 1994 to monitor the effects of the discharge on Lake Pontchartrain and to quantify any changes in nutrient and sediment concentrations as water passed through the Bonnet Carre spillway, which is partially vegetated by forested wetlands, and thence into the lake. Chapter 2 of this dissertation reports on the findings from this experimental diversion.

Caernarvon Freshwater Diversion

The Caernarvon freshwater diversion structure is located on the east bank of the Mississippi River at river mile 81.5 (Fig. 1. 1), and consists of five 4.6 meter wide box culverts with vertical lift gates, with a capability of passing 226 m$^3$s$^{-1}$ of river water. The structure was completed in 1991 and freshwater discharge began in August of that year. The Breton Sound estuary lies between the Caernarvon diversion and Breton Sound Bay.
in the Gulf of Mexico, and comprises about 1100 km² of fresh and brackish wetlands and shallow water ponds, lakes and bays. Diverted water must travel about 30-40 km through two major routes dominated by wetlands before reaching open waters of Breton Sound, and an additional 50 km before reaching Gulf waters. There is considerable interaction between diverted river water and estuarine wetlands due to tides, northerly wind events, and storms.

Two separate studies are reported in this dissertation that were conducted in the Breton Sound estuary. Chapter 3 of this dissertation examines the spatial and temporal changes in suspended sediment, chlorophyll $a$, salinity and temperature over a two-year period. The purpose of this study was to extend our understanding of the effect of pulsed riverine input into coastal wetlands. Chapter 4 of this dissertation reports on changes in
nutrient concentrations and ratios of water flowing from the Caernarvon diversion through the Breton Sound Estuary. The purpose of this study is to determine if the differential reduction of inorganic nutrient species led to substantial changes in nutrient stoichiometric ratios as diverted river water passed through the estuary.

Atchafalaya River Estuarine Complex

The Atchafalaya River starts at the Old River control structure and flows 226 km before entering Atchafalaya Bay and the Gulf of Mexico. The Corps of Engineers constructed the control structure in 1963 to regulate Atchafalaya River flow and prevent the full capture of the Mississippi River by this shorter route. The Atchafalaya River has a 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$^{-1}$. The river introduces large quantities of nutrients, sediments and freshwater to the Atchafalaya Delta estuarine complex (see Perez et al. 2000), a large expanse of wetlands and shallow water bodies that river water must pass through before reaching offshore Gulf waters (Fig. 1.1). 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 the study reported in chapter 5 of this dissertation was to extend our understanding of nutrient dynamics in 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). My objectives were to examine these characteristics and their effect on the Atchafalaya Delta estuarine complex by mapping the distribution of
HYPOTHESES

A diversion of Mississippi River water into Lake Pontchartrain by way of the Bonnet Carre Spillway has been proposed as a restoration technique to help offset regional wetland loss. An experimental diversion of Mississippi River water into Lake Pontchartrain was carried out in April 1994 to monitor the fate of nutrients and sediments in the spillway and Lake Pontchartrain. I hypothesized there would be (1) substantial decreases in suspended sediments due to decreased water velocity and sediment settling; (2) low or moderate decreases in nutrient concentrations as water passed through the spillway; and (3) decreases in the N:P ratio and increases in the Si:N ratio as water passed through the spillway and entered Lake Pontchartrain. Results of this study are reported in chapter 2 of this dissertation.

Spatial and temporal changes in suspended sediment, chlorophyll a, salinity and temperature in the Breton Sound estuary were examined over a two-year period. Water quality in the estuary is greatly affected by the Caernarvon freshwater diversion. I hypothesized there would be (1) rapid reduction of suspended sediments concentrations with distance from the diversion structure due to decreased water velocity and sediment settling; (2) low chlorophyll a levels in areas of high suspended sediment near the Caernarvon structure, with rising chlorophyll levels immediately after suspended sediment concentrations decrease to low levels, and then decreased chlorophyll a levels Gulfward; and (3) a reduction in salinity and temperature throughout the estuary
associated with structure discharge. Results of this study are presented in chapter 3 of this dissertation.

I studied changes in nutrient concentrations and ratios in water flowing from the Caernarvon diversion through the Breton Sound Estuary. The use of coastal wetlands and shallow water bodies to process Mississippi River water before entering the Gulf of Mexico has been proposed as a partial solution to help reduce the size of the hypoxic zone, as well as restore and maintain rapidly eroding coastal wetlands (Coast 2050, 1998; Mitsch et al. 2001). I hypothesized that as diverted Mississippi River water passed through the Breton Sound estuary there would be (1) decreases in dissolved inorganic nitrogen (DIN) and silicate (DSi), with larger decreases in DIN than DSi; (2) small or no changes in dissolved inorganic phosphorus (DIP) concentrations; (3) decreases in the DIN:DIP ratio, and (4) increases in the DSi:DIN ratio. Chapter 4 of this dissertation reports on these changes in nutrient concentrations and ratios.

The Atchafalaya River is the primary source of nutrients and sediments to the Atchafalaya Delta estuarine complex, a large expanse of wetlands and shallow water bodies that river water must pass through before reaching offshore Gulf waters. I examined inorganic nutrient, sediment, chlorophyll $a$, and salinity concentrations over a large area of the estuarine complex. I hypothesized there would be (1) a reduction in salinity throughout the estuarine complex associated with river discharge (2) strong non-conservative reduction of NO$_3^-$ and total suspended sediments; and (3) regeneration of NH$_4^+$ and PO$_4^{3-}$ during the summer. Results of this study are presented in Chapter 5 of this dissertation.
LITERATURE CITED


CHAPTER 2
THE 1994 EXPERIMENTAL OPENING OF THE BONNET CARRE SPILLWAY TO DIVERT MISSISSIPPI RIVER WATER INTO LAKE PONTCHARTRAIN, LOUISIANA*

INTRODUCTION

Eustatic sea-level rise stabilized near its present level after the last glaciation between 5,000 to 7,000 years ago (Milliman and Emery 1968). Since that time, sedimentation from the Mississippi River created a series of overlapping deltaic lobes that presently form the Mississippi deltaic plain in coastal Louisiana (Roberts 1997). Deltaic lobes go through a cycle of active progradation followed by river abandonment and subsequent deterioration and eventually submergence due to the combined effects of shore-face erosion and coastal subsidence (Penland and Ramsey 1990; Roberts 1997). In addition to discharge at the mouth of the river, sediment and nutrients were delivered to wetlands adjacent to the Mississippi River during spring floods (Hatton et al. 1983; Kesel 1988, 1989; Kesel et al. 1992). These floods provided a source of nutrients, sediments, and fresh water to the surrounding ecosystem.

Since the early 1900’s most of coastal Louisiana has been hydrologically isolated from the river by the construction of flood control levees (Kesel 1988, 1989; Mossa 1996). These levees prevent seasonal flooding and consequently the introduction of fresh water and materials into nearby wetlands and water bodies. As a restoration effort, the

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State of Louisiana has developed a plan of freshwater diversions that will mimic flooding events of the Mississippi River (Chatry and Chew 1985). When freshwater diversions were first planned over two decades ago, the primary goal was to reduce salinity to enhance oyster production in surrounding regions (Chatry et al. 1983). But more recently, as the effects of lack of nutrients and sediment input have become better understood, diversions have been increasingly viewed as a way of delivering these materials to coastal wetlands and estuaries (Crandall and Lindsey 1981; Day and Templet 1989; Boesch et al. 1994; Day et al. 1997; Lane et al. 1999).

The subject of this study is a proposed diversion of Mississippi River water into Lake Pontchartrain by way of the Bonnet Carre Spillway. When initially planned, the major benefit of the diversion was to decrease salinity over productive commercial oyster beds in Lake Borgne (Fig. 2.1). Though increases in the catch of oysters, saltwater finfishes and penaeid shrimp have been attributed to previous openings of the spillway (Viosca 1938; Gunter 1953; Chew and Cali 1981), there has been controversy about the effects of diverting Mississippi River water into Lake Pontchartrain. A major concern is possible eutrophication as currently observed in Louisiana’s offshore waters (Turner and Rabalais 1991; Rabalais et al. 1994) and other estuaries throughout the world (Justic et al. 1995; Rosenberg 1985). Another concern is that suspended sediments in the river water would flow into Lake Pontchartrain and not reach wetlands where they are needed to offset rising water levels. As a result of these concerns, a reanalysis of the Bonnet Carre diversion project was initiated to further evaluate the impacts of the diversion and potential alterations of the project. The reanalysis was carried out by an interdisciplinary team composed of state and federal agency scientists and managers, academic scientists,
and members of environmental groups. The reanalysis consisted of analyses of data on water quality in Lake Pontchartrain, fisheries, nutrient assimilative capacity of wetlands, the development of alternative diversion scenarios, and hydrodynamic modeling to determine the impacts of the different scenarios on salinity. As part of the reanalysis, an experimental diversion was carried out in April 1994 to monitor the effects of the discharge on Lake Pontchartrain and to quantify any changes in nutrient and sediment concentrations as water passed through the Bonnet Carre spillway, which is partially vegetated by forested wetlands, and thence into the lake. This paper reports on the findings from this experimental diversion.

Fig. 2.1. Study area located in southeastern Louisiana. Inset graph indicates discharge from the Bonnet Carre Spillway during the experimental opening.
STUDY AREA

The Bonnet Carre Spillway is located 25 km west of New Orleans, Louisiana (Fig. 2.1). The 3.4 km wide spillway is confined by two 8.6 km levees, and connects the Mississippi River to Lake Pontchartrain. The Bonnet Carre Spillway has 1300 ha of forested wetlands, or nearly 50% of the total spillway area. A water flow regulation structure, consisting of 350 flood gates (each with twenty 20x30 cm creosote wooden timbers 3.1-3.6 m in length), is located at the Mississippi River inlet. The structure is opened and closed by removing or replacing the timbers one at a time. Thus, it can take a week or more to open or close the structure. The Spillway was constructed in 1931, after the great flood of 1927, to protect New Orleans from flooding by the Mississippi River, and has since been opened eight times during high water events (Sikora and Kjerfve 1985; Day et al. 1999), with flows ranging from 3100 to 9000 m$^3$s$^{-1}$. The spillway is located in an area that was one of the many crevasses that breached the Mississippi River levee in the 1800s and introduced up to 4,000 m$^3$s$^{-1}$ of water into Lake Pontchartrain (Davis 1993; Kesel 1989). The present spillway is designed to divert up to 7,000 m$^3$s$^{-1}$ from the river during floods. Although the spillway was designed strictly for flood control, the freshwater diversion project proposes to use the spillway to divert fresh water regularly into Lake Pontchartrain to maintain optimum salinity levels in oyster producing areas in Lake Borgne (Fig. 2.1).

Lake Pontchartrain is a 1630 km$^2$ brackish-water lagoon located directly north of New Orleans. It has been subjected to numerous anthropogenic changes, including eutrophication, increased salinities, and loss of wetlands, as the city of New Orleans expanded and numerous hydrologic modifications were made (Sikora and Kjerfve 1985).
Lake Pontchartrain is connected to Lake Borgne and the Gulf of Mexico by way of the Rigolets and Chef Menteur Pass. Lake depth ranges from 2 to 5 m, with an average depth of 3.3 m, and a volume of $1.66 \times 10^9$ m$^3$. Tides in the lake are diurnal with a mean range of 12 cm. Circulation in the lake is wind driven, with mean current speeds in the range of 10 to 20 cm s$^{-1}$ (Swenson 1981). The Tangipahoa and Tchefuncte rivers discharge to the lake directly from the north, and the Amite, Tickfaw, and Natalbany rivers flow into the lake by way of Lake Maurepas from the west. The rivers supply 5% of the tidal prism in the lake, with the remainder entering through the tidal passes (Swenson and Chuang 1983). Salinity in Lake Pontchartrain ranges from nearly fresh in the western side to 22 psu on the eastern side (Sikora and Kjerfve 1985).

**METHODS**

Mississippi River water entered Lake Pontchartrain by way of the Bonnet Carre spillway from April 20 to May 27, 1994. In April, water flow in the spillway was measured by the United States Geological Survey (USGS) using a USGS pygmy current meter and a Price AA Standard current meter (Buchanan and Somers 1969). In May, instantaneous discharge measurements were made using a Price AA Standard current meter attached to a 14 kg sounding weight.

Mississippi River water quality was obtained from the U. S. Geological Survey publicly accessible water-quality database (USGS 1994). Unfortunately, Mississippi River water quality data at the Bonnet Carre Spillway was not collected during this study. Water quality data was collected, however, at St. Francisville, Louisiana, located approximately 150 river miles (233 km) upriver from the spillway (Table 2.1). Since nutrient and sediment concentrations in the river would only increase as water flowed...
down river, we believe the St. Francisville data are useful in conservatively estimating river concentrations at the spillway. Data was collected on March 16 and June 30, and an average was used to estimate riverine nutrient and sediment concentrations during the experimental diversion. Decreases in nutrient concentration of water passing through the spillway were calculated using this average as initial concentration and nutrient concentration from the last spillway station (A5) as ending concentration (Fig. 2.2).

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<tr>
<td>30-June</td>
<td>1.3</td>
<td>0.02</td>
<td>0.30</td>
<td>1.62</td>
<td>0.14</td>
<td>133</td>
</tr>
<tr>
<td>Average</td>
<td>1.3</td>
<td>0.06</td>
<td>0.42</td>
<td>1.76</td>
<td>0.22</td>
<td>131</td>
</tr>
</tbody>
</table>

Suspended sediment samples were collected with a weighted-bottle sampler at five locations in the spillway (Fig. 2.2) on May 18 and 25. Water velocities at these locations were less than 0.5 m$^3$s$^{-1}$. Sediment was separated into sand and silt (<0.0625 mm) fractions as described by Guy (1969). Accretion along the center of the spillway was monitored at eight locations (Fig. 2.2) in the middle third of the spillway using the feldspar marker technique (Cahoon and Turner 1989). Feldspar was laid out 1 cm thick in 0.25 m$^2$ plots a week before the experimental diversion began and measured several weeks after it ended.

Samples were collected at five locations (Fig. 2.2) in the Bonnet Carre Spillway for water quality analysis on May 18 and 26. Depth-integrated water quality samples were taken from water less than 6 m deep with velocities less than 0.5 m s$^{-1}$ using an epoxy coated wire basket sampler containing 1 L glass bottles that had been baked at
Fig. 2.2. Locations of water quality samples taken during the experimental opening of the Bonnet Carre Spillway. Asterisks '*' indicate feldspar marker horizons.

350°C for 6 h and acid washed. Duplicate 1 L samples were taken 0.5 m below the water surface for chlorophyll a analysis. The water samples were cooled to 4°C for preservation and transported to the USGS analytical laboratory in Baton Rouge, Louisiana, for analysis. Nitrite+nitrate (NO\textsubscript{x}-N), ammonium (NH\textsubscript{4}\textsuperscript{+}), total phosphorus (TP), and silicate (SiO\textsubscript{2}) concentrations were determined using methods described by Fishman and Friedman (1989). Organic nitrogen (ON) concentrations were determined using methods described by Wershaw et al. (1987). Total nitrogen (TN) was calculated
by summing the values of the three nitrogen species analyzed for this study. Chlorophyll-a samples were analyzed according to the method described by Britton and Greeson (1988).

A series of physical and chemical properties were measured on May 18, 19, and 27, in Lake Pontchartrain at the mouth of the Bonnet Carre on either side of the freshwater plume entering the lake from the experimental release. The water column was stratified at the spillway mouth as the cold, dense river water flowed beneath the lake water. Mixing occurred once the water temperatures began to equilibrate several km into the lake, where the freshwater plume edge was evident. Measurements were taken at three depths (top, middle, and bottom) of specific conductance, pH, salinity, water temperature, and dissolved oxygen. These values are not included in this paper, but were used to determine the location of the leading edge of the plume where water quality samples reported in this paper were collected.

Statistical analyses were carried out to determine differences between the spillway and Lake Pontchartrain plume edge water quality constituents. May 18 spillway data (sites A1-A5, Fig. 2.2, Table 2.3) were compared to May 18 (sites B1-B3, Fig. 2.2, Table 2.3) and May 19 (sites C1-C5, Fig. 2.2, Table 2.3) plume edge data, and May 26 spillway data (sites A1-A5, Fig. 2.2, Table 2.3) were compared to May 27 plume edge data (sites D1-D3, Fig. 2.2, Table 2.3). Non-parametric analysis was carried out using the Wilcoxon Rank Sum test (Sall and Lehman 1996). An alpha probability level of <0.05 was used to define a significant difference.

In addition, a two-factor analysis of variance was carried out, with the two factors of interest being discharge and location, each having two levels. Discharge during the two
water quality sampling periods was 224 m$^3$sec$^{-1}$ (referred to as low flow) and 335 m$^3$sec$^{-1}$ (referred to as high flow) on May 18 and 26, respectively. The two levels of location were the stations within the Bonnet Carre Spillway, and those in Lake Pontchartrain. Least square means were calculated for significant discharge x location interaction, and a p-value of <0.05 was used to define a significant effect. In the case of significant interactions, discharge levels were compared within each location.

RESULTS

Spillway discharge on April 20, 1994, due to leakage through the spillway structure was 25 m$^3$s$^{-1}$ (Fig. 2.1). This leakage was a result of gaps between the wooden timbers that form the flood gates of the structure. Leakage peaked at 248 m$^3$s$^{-1}$ on May 11 as the Mississippi River stage crested. On May 15, leakage decreased to 207 m$^3$s$^{-1}$. As Mississippi River stage decreased, four bays of the spillway structure (80 timbers) were opened to maintain discharge through the spillway. Discharge on May 17, 18, 20, 23 was 248, 244, 238, and 283 m$^3$s$^{-1}$, respectively. The discharge increased to 396 m$^3$s$^{-1}$ by May 25, and the bays were closed on May 26-27. Discharge through the spillway was 0.3 m$^3$s$^{-1}$ on May 31. A total of 6.4 x 10$^8$ m$^3$ of Mississippi River water was discharged into Lake Pontchartrain during the experimental opening. Mississippi River flow from April 20 to May 31 ranged from 20,500 to 33,000 m$^3$s$^{-1}$. The mean annual discharge is about 18,000 m$^3$s$^{-1}$.

Mississippi River water quality at St. Francisville had very small ranges for the two dates sampled, with the same value for NO$_x$ (1.3 mg l$^{-1}$), and very similar values for TN (1.90-1.62 mg l$^{-1}$) and TSS (129-133 mg l$^{-1}$). Other variables had broader differences.
between dates, however, with \( NH_4^+ \) changing from 0.07 to 0.02 mg l\(^{-1}\), ON from 0.53 to 0.30 mg l\(^{-1}\), and TP from 0.30 to 0.14 mg l\(^{-1}\).

Total suspended sediment concentrations decreased 83-82%, from the river to the last spillway station (A5), on May 18 and 25, respectively (Table 2.2, Fig. 2.2). Both dates sampled had approximately the same silt concentrations, but the later date, which had 30% higher flow, had a sand component that was absent from the earlier date. This sand fraction dropped out of the water column by station A4, however, leaving water exiting the spillway on both dates to have approximately the same TSS concentrations (22-24 mg l\(^{-1}\)). In the middle third of the spillway there was 3.9±1.1 cm of accretion that accumulated during the experimental diversion.

Table 2.2. Suspended sediment concentrations in the Bonnet Carre Spillway on May 18 and 25, 1994\(^a\).

<table>
<thead>
<tr>
<th>Date</th>
<th>Site No.</th>
<th>Sand (mg l(^{-1}))</th>
<th>Silt (mg l(^{-1}))</th>
<th>TSS (mg l(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>18-May</td>
<td>A1</td>
<td>0</td>
<td>38</td>
<td>38</td>
</tr>
<tr>
<td>18-May</td>
<td>A2</td>
<td>0</td>
<td>36</td>
<td>36</td>
</tr>
<tr>
<td>18-May</td>
<td>A3</td>
<td>0</td>
<td>33</td>
<td>33</td>
</tr>
<tr>
<td>18-May</td>
<td>A4</td>
<td>0</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>18-May</td>
<td>A5</td>
<td>0</td>
<td>22</td>
<td>22</td>
</tr>
<tr>
<td>25-May</td>
<td>A1</td>
<td>28</td>
<td>34</td>
<td>62</td>
</tr>
<tr>
<td>25-May</td>
<td>A2</td>
<td>4</td>
<td>36</td>
<td>40</td>
</tr>
<tr>
<td>25-May</td>
<td>A3</td>
<td>2</td>
<td>28</td>
<td>30</td>
</tr>
<tr>
<td>25-May</td>
<td>A4</td>
<td>0</td>
<td>24</td>
<td>24</td>
</tr>
<tr>
<td>25-May</td>
<td>A5</td>
<td>0</td>
<td>24</td>
<td>24</td>
</tr>
</tbody>
</table>

\(^a\)The site numbers correspond to sites indicated in figure 2.2.

Nitrate concentrations decreased 28-42% as water passed through the spillway on May 26 and May 18, respectively (Table 2.3, sites indicated in Fig. 2.2). TN decreased 26-30%, and TP decreased 50-59%, on the two dates sampled, respectively. Ammonium and organic nitrogen concentrations did not show any consistent pattern. Chlorophyll \( a \)
levels varied between 1.3 and 3.5 mg l\(^{-1}\) in the spillway. Silicate concentrations fluctuated slightly, but remained relatively constant (5.3-5.8 ppm). Salinity in the spillway was reported as essentially fresh.

Table 2.3. Water quality data in the Bonnet Carre Spillway and Lake Pontchartrain\(^a\).

<table>
<thead>
<tr>
<th>Date</th>
<th>Site No.</th>
<th>NO(_x) (mg l(^{-1}))</th>
<th>NH(_4^+) (mg l(^{-1}))</th>
<th>ON (mg l(^{-1}))</th>
<th>TN (mg l(^{-1}))</th>
<th>TP (mg l(^{-1}))</th>
<th>CHL a (ug l(^{-1}))</th>
<th>SiO(_2) (mg l(^{-1}))</th>
<th>Salinity (psu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18-May</td>
<td>A1</td>
<td>0.94</td>
<td>0.04</td>
<td>0.38</td>
<td>1.36</td>
<td>0.12</td>
<td>1.3</td>
<td>5.2</td>
<td>.</td>
</tr>
<tr>
<td>18-May</td>
<td>A2</td>
<td>0.93</td>
<td>0.06</td>
<td>0.41</td>
<td>1.40</td>
<td>0.11</td>
<td>1.6</td>
<td>5.4</td>
<td>.</td>
</tr>
<tr>
<td>18-May</td>
<td>A3</td>
<td>0.85</td>
<td>0.05</td>
<td>0.42</td>
<td>1.32</td>
<td>0.12</td>
<td>3.5</td>
<td>5.3</td>
<td>.</td>
</tr>
<tr>
<td>18-May</td>
<td>A4</td>
<td>0.88</td>
<td>0.05</td>
<td>0.35</td>
<td>1.28</td>
<td>0.11</td>
<td>1.7</td>
<td>5.3</td>
<td>.</td>
</tr>
<tr>
<td>18-May</td>
<td>A5</td>
<td>0.75</td>
<td>0.05</td>
<td>0.44</td>
<td>1.24</td>
<td>0.11</td>
<td>2.4</td>
<td>5.3</td>
<td>.</td>
</tr>
<tr>
<td>18-May</td>
<td>B1</td>
<td>0.14</td>
<td>0.04</td>
<td>0.50</td>
<td>0.68</td>
<td>0.06</td>
<td>10</td>
<td>3.1</td>
<td>0.4</td>
</tr>
<tr>
<td>18-May</td>
<td>B2</td>
<td>0.52</td>
<td>0.05</td>
<td>0.53</td>
<td>1.10</td>
<td>0.12</td>
<td>1.0</td>
<td>3.8</td>
<td>0.1</td>
</tr>
<tr>
<td>18-May</td>
<td>B3</td>
<td>0.10</td>
<td>0.03</td>
<td>0.55</td>
<td>0.68</td>
<td>0.07</td>
<td>11</td>
<td>2.8</td>
<td>0.2</td>
</tr>
<tr>
<td>19-May</td>
<td>C1</td>
<td>0.12</td>
<td>0.05</td>
<td>0.80</td>
<td>0.97</td>
<td>0.12</td>
<td>4.2</td>
<td>3.1</td>
<td>0.8</td>
</tr>
<tr>
<td>19-May</td>
<td>C2</td>
<td>0.39</td>
<td>0.05</td>
<td>0.72</td>
<td>1.16</td>
<td>0.15</td>
<td>8.7</td>
<td>3.8</td>
<td>0.0</td>
</tr>
<tr>
<td>19-May</td>
<td>C3</td>
<td>0.55</td>
<td>0.04</td>
<td>0.74</td>
<td>1.33</td>
<td>0.20</td>
<td>3.0</td>
<td>4.2</td>
<td>0.0</td>
</tr>
<tr>
<td>19-May</td>
<td>C4</td>
<td>0.40</td>
<td>0.04</td>
<td>0.61</td>
<td>1.05</td>
<td>0.11</td>
<td>6.3</td>
<td>3.9</td>
<td>0.1</td>
</tr>
<tr>
<td>19-May</td>
<td>C5</td>
<td>0.06</td>
<td>0.03</td>
<td>0.53</td>
<td>0.62</td>
<td>0.08</td>
<td>3.8</td>
<td>2.8</td>
<td>0.7</td>
</tr>
<tr>
<td>26-May</td>
<td>A1</td>
<td>1.00</td>
<td>0.06</td>
<td>0.28</td>
<td>1.34</td>
<td>0.11</td>
<td>3.0</td>
<td>5.5</td>
<td>0.2</td>
</tr>
<tr>
<td>26-May</td>
<td>A2</td>
<td>1.10</td>
<td>0.06</td>
<td>0.92</td>
<td>2.08</td>
<td>0.11</td>
<td>2.9</td>
<td>5.8</td>
<td>0.2</td>
</tr>
<tr>
<td>26-May</td>
<td>A3</td>
<td>1.00</td>
<td>0.05</td>
<td>0.43</td>
<td>1.48</td>
<td>0.10</td>
<td>2.9</td>
<td>5.5</td>
<td>.</td>
</tr>
<tr>
<td>26-May</td>
<td>A4</td>
<td>1.00</td>
<td>0.04</td>
<td>0.33</td>
<td>1.37</td>
<td>0.10</td>
<td>2.6</td>
<td>5.6</td>
<td>.</td>
</tr>
<tr>
<td>26-May</td>
<td>A5</td>
<td>0.93</td>
<td>0.04</td>
<td>0.34</td>
<td>1.31</td>
<td>0.09</td>
<td>2.6</td>
<td>5.8</td>
<td>.</td>
</tr>
<tr>
<td>27-May</td>
<td>D1</td>
<td>0.78</td>
<td>0.07</td>
<td>0.34</td>
<td>1.19</td>
<td>0.06</td>
<td>2.4</td>
<td>4.9</td>
<td>.</td>
</tr>
<tr>
<td>27-May</td>
<td>D2</td>
<td>0.80</td>
<td>0.06</td>
<td>0.39</td>
<td>1.25</td>
<td>0.07</td>
<td>2.7</td>
<td>4.8</td>
<td>.</td>
</tr>
<tr>
<td>27-May</td>
<td>D3</td>
<td>0.62</td>
<td>0.06</td>
<td>0.44</td>
<td>1.12</td>
<td>0.07</td>
<td>3.2</td>
<td>4.4</td>
<td>.</td>
</tr>
</tbody>
</table>

\(^a\)The site numbers correspond to sites indicated in figure 2.2.

Compared to the spillway, the freshwater plume edge in Lake Pontchartrain on May 18 had significantly lower NO\(_x\) concentrations (Table 2.4). There was no significant difference in ammonium concentrations, but ON levels were significantly higher at the plume edge. Total nitrogen concentrations, however, were significantly lower in the plume edge compared to the spillway. Total phosphorus levels were not significantly different between the spillway and plume edge. Chlorophyll a levels were several times
higher at two of the plume edge stations (10 and 11 mg l\(^{-1}\)), compared to the spillway, but overall were not statistically significant. Silicate concentrations were significantly lower at the plume edge than in the spillway. Salinity at the plume edge ranged from 0.1 to 0.4 psu. Compared to the Mississippi River (Table 2.1), the plume edge had an average of 81% lower NO\(_x\), 25% higher ON, 53% lower TN, and 62% lower TP on May 18.

May 19 plume edge data showed many of the same trends in nutrient concentration as May 18 (Table 2.4). There were significantly lower NO\(_x\) and silicate, higher ON and chlorophyll a, and no significant difference in NH\(_4^+\) or TP concentrations at the plume edge compared to the May 18 spillway data. TN concentrations, however were not significantly different. Salinity at the plume edge ranged from 0 to 0.8 psu. Compared to the Mississippi River (Table 2.1), the plume edge on May 19 had an average of 76% lower NO\(_x\), 61% higher ON, 42% lower TN, and 40% lower TP.

Table 2.4. Results of statistical analysis comparing water quality data collected at the freshwater plume edge in Lake Pontchartrain (LP) to data collected in the Bonnet Carre Spillway (BC).\(^a\)

<table>
<thead>
<tr>
<th></th>
<th>NO(_x)</th>
<th>NH(_4^+)</th>
<th>ON</th>
<th>TN</th>
<th>TP</th>
<th>CHL a</th>
<th>SiO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>5/18 LP vs 5/18 BC</td>
<td>↓</td>
<td>NS</td>
<td>↑</td>
<td>↓</td>
<td>NS</td>
<td>NS</td>
<td>↓</td>
</tr>
<tr>
<td>5/19 LP vs 5/18 BC</td>
<td>↓</td>
<td>NS</td>
<td>↑</td>
<td>NS</td>
<td>NS</td>
<td>↑</td>
<td>↓</td>
</tr>
<tr>
<td>5/27 LP vs 5/26 BC</td>
<td>↓</td>
<td>NS</td>
<td>NS</td>
<td>↓</td>
<td>NS</td>
<td>↓</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Higher (↑) or lower (↓) arrows indicate significant differences in constituent concentrations in LP compared to BC. 'NS' indicates no significant difference was detected.

May 27 data of the plume edge also had many of the same trends as the previous two sampling results (Table 2.4). Nitrate and silicate concentrations at the plume edge were significantly lower compared to the May 26 spillway data. No significant changes in ammonium or ON levels were found, but there were significantly lower TN and TP concentrations at the plume edge. Chlorophyll a levels at the plume edge were not
significantly different to spillway concentrations a day earlier. Compared to the Mississippi River (Table 2.1), the plume edge on May 27 had lower average concentrations of $NO_x$ (44%), ON (7%), TN (33%), and TP (70%).

The two factor analysis of variance failed to find a significant interaction between discharge and location for TN and TP. TN, however, had a significant ($p<0.005$) main effect for location, with mean concentrations decreasing from 1.42 ppm in the spillway to 1.07 ppm in Lake Pontchartrain. TP had a significant ($p<0.05$) main effect for flow, with mean concentrations being greater during low discharge.

There were significant discharge x location interactions for $NO_x$, $NH_4^+$,ON and Si. For $NO_x$, ON, Si, and CHL there was no significant difference between high and low flows at the Bonnet Carre Spillway (Fig. 2.3). At Lake Pontchartrain, however, $NO_x$ concentrations were significantly lower ($p<0.001$) at low flow compared to high flow; mean ON concentrations were significantly higher ($p=0.03$) at low flow compared to high flow; CHL concentrations were higher at low flow compared to high flow, but with only moderate significance ($p=0.088$); and Si concentrations were significantly lower ($p<0.001$) at low flow compared to high flow. The behavior of $NH_4^+$ was variable, with no significant change during low flow and significantly ($p<0.04$) lower concentrations in the lake during low flow compared to high flow.

**DISCUSSION**

Suspended sediments decreased by 82 to 83% as water passed through the spillway, presumably due to decreased velocity allowing settling of particles. This was especially evident on May 25 when a large sand component present at the first station rapidly dropped out of the water column and was deposited farther down the spillway,
as indicated by accretion in the middle third of the spillway and the absence of suspended sand in the lower third of the spillway. The sand component found at the first few stations in the spillway on May 25 was either derived directly from the river, which contains over 50% sand in its bed load (Mossa 1996), or was resuspended in the upper spillway due to increased discharge. Water entering Lake Pontchartrain had approximately the same suspended sediment concentration (22-24 mg l⁻¹) on both dates sampled. Lane et al. (1999) also showed rapid decreases in TSS at similar discharge rates and distances from the river at a freshwater diversion site at Caernarvon, down river from New Orleans.

![Figure 2.3. Results of the two-factor analysis of variance for NOₓ, ON and CHL. The factors of interest are location and flow. BC indicates concentrations in the Bonnet Carre Spillway and LP indicates concentrations in Lake Pontchartrain. Open circles represent Low Flow (224 m³sec⁻¹) and closed circles High Flow (335 m³sec⁻¹). Asterisks indicate significant differences (alpha<0.05), NS=non-significant.](image)

Nutrient concentrations generally decreased as river water passed through the spillway, with a 28-42% reduction in nitrate, 26-30% in TN, and 50-59% decrease in TP. In the spillway there are 1300 ha of forested wetlands, approximately 20% of which received continuous overland surface flow during the experimental diversion (personal observation by Lane). Forested wetlands have been shown to be effective sinks for
nutrients (Ewel and Odum 1979; Faulkner and Patrick 1989; Breaux and Day 1994; Boustany et al. 1997), and may be responsible for the decrease in nutrient concentration in the spillway, especially \( \text{NO}_x \). Phosphorus decreases may be due to the highly charged phosphate anion, \( \text{PO}_4^{3-} \), which is readily sorbed onto the surfaces of charged clay (and detrital organic) particles (Jitts 1959), some of which were undoubtedly deposited in the spillway. These results suggest that the spillway and surrounding wetlands can be used to decrease nutrient and sediment concentrations of diverted Mississippi River water before reaching Lake Pontchartrain, thus buffering the effect of the diversion on the lake.

Nitrate concentrations decreased considerably as river water flowed through the spillway and entered Lake Pontchartrain. There was increased reduction of nitrate concentration during low flow (Fig. 2.3), most likely do to decreased nutrient loading. Though it is uncertain if these decreases were due to dilution with ambient lake water, the low salinities at the water collection sites suggest that dilution was not a major factor. Background salinity for this region of Lake Pontchartrain is 2-3 psu (Day et al., 1999). The plume salinity data in this report averages 0.3 psu, indicating dilution could have contributed a maximum of 15% reduction, much lower than the nutrient reductions reported in this paper.

Nitrate concentrations rapidly decreased as river water flowed through the spillway and entered Lake Pontchartrain. Day et al. (1999) showed similar nitrate reductions during the 1997 opening of the Bonnet Carre spillway and Lane et al. (1999) reported rapid non-conservative nitrate decreases at the Caernarvon freshwater diversion site. Various studies have reported similar reduction of \( \text{NO}_x \) in estuarine environments with much of the reduction due to denitrification (Smith et al. 1982; Khalid and Patrick
reported that up to 50% of NO$_3^-$ introduced into the Patuxent River estuary was lost due to denitrification. Denitrification is carried out by denitrifying bacteria that use nitrate as an electron acceptor to oxidize organic matter anaerobically (Koike and Hattori 1978). Denitrification was most likely an important mechanism for the loss of nitrogen from the system, which had significantly lower total nitrogen concentrations at the freshwater plume edge on two of the three sampling dates.

Another transformation of NO$_x$ is assimilation into particulate organic matter (i.e. organic nitrogen and chlorophyll $a$) by phytoplankton. Vascular plants as well as algae incorporate NO$_x$ into cellular mass. This process may have accounted for the statistically significant increases in organic nitrogen levels found on May 18 and 19, and the significantly increased chlorophyll $a$ concentrations found on May 19 at the freshwater plume edge (Table 2.4, Fig. 2.3).

The introduction of fresh water in estuaries has been found to have broad effects on phytoplankton productivity. High primary productivity in estuaries receiving fresh water has been attributed to the introduction of nutrients (Nixon 1981), but production is also limited by light availability that is attenuated by high suspended sediment concentrations usually associated with fresh water inputs (Cole and Cloern 1984; Day et al. 1994). In river-dominated estuaries, environments with turbidity often exceeding 50 mg l$^{-1}$, light is attenuated rapidly in the water column and phytoplankton photosynthesis is confined to a shallow photic zone. For this reason, phytoplankton productivity is often higher at intermediate salinities in estuaries, where suspended sediment has dropped out of the water column yet high nutrient concentrations are still available (Cloern 1987).
The higher chlorophyll a concentrations at the plume edge compared to the spillway was probably due to this effect.

Our results show that there can be significant changes in nutrient ratios as water flows through wetlands and shallow waters. Findings from the literature indicate that these changes can have important impacts on phytoplankton growth. Officer and Ryther (1980) described two types of phytoplankton communities and their different effects on the estuarine ecosystem. The first is a phytoplankton community dominated by diatoms, which are the usual food for filter feeding fishes and zooplankton. The second is a non-diatom based community usually dominated by flagellates, which are poor foods for most grazers and may include noxious or toxic species (Smayda 1997). Diatoms require a dissolved inorganic Si:N molar ratio of about 1:1 (Redfield et al. 1963). A ratio lower than 1:1 (a silicon deficiency) may exacerbate eutrophication by reducing the potential for diatom growth in favor of noxious flagellates (Officer and Ryther 1980). Silicate concentrations where significantly lower at the freshwater plume edge than in the same water flowing through the Bonnet Carre Spillway, possibly due to incorporation by diatomic phytoplankton upon entering Lake Pontchartrain. The dissolved inorganic Si:N molar ratio of water in the spillway was 1.3, while at the freshwater plume edge the ratio ranged from 1.4 to 3.0 (Table 2.5). These Si:N ratios suggest that there was an adequate supply of silicon to support a diatom based phytoplankton community at the plume edge, and that nitrogen was being lost from the system faster than would be estimated from phytoplankton assimilation alone, based on the Redfield ratio.

Previous openings of the Bonnet Carre Spillway have resulted in increases in oysters, saltwater finfishes and penaeid shrimp in the surrounding coastal region (Viosca
A number of negative environmental impacts, however, have also been attributed to previous openings of the Bonnet Carre spillway. In 1997, the spillway was opened during the fifth largest flood of the century, and discharged up to 6800 m$^3$s$^{-1}$ into Lake Pontchartrain (Day et al. 1999). Following the closure of the spillway, however, there was an extensive blue-green algal bloom, predominantly *Anabaena circinalis* and *Microcystis aeruginosa* in Lake Pontchartrain from late May which persisted through July (Dortch et al. 1998; Porrier and King 1998). Fish kills attributed to the bloom were reported during June and July, during which time algal cell counts were as high as $10^{10}$ cells per L (Porrier and King 1998). On death, bacterial decomposition of excess algae cells may deplete oxygen levels in the lower water column, leading to disruption of the benthic community and mortality of commercial fish populations. Rabalais et al. (1994) have documented seasonal oxygen depletion in the riverine influenced continental shelf of Louisiana. These results suggest that regular additions of river water directly into the lake, especially at high levels, can have serious deleterious impacts.

Table 2.5. Stoichiometric nutrient ratios in the Bonnet Carre Spillway and the freshwater plume edge during the experimental opening.

<table>
<thead>
<tr>
<th>Date - Location</th>
<th>Discharge (m$^3$s$^{-1}$)</th>
<th>Si:N:P</th>
<th>Si:N</th>
</tr>
</thead>
<tbody>
<tr>
<td>18 May - Bonnet Carre</td>
<td>240</td>
<td>24:18:1</td>
<td>1.3:1</td>
</tr>
<tr>
<td>18 May - Plume Edge</td>
<td>240</td>
<td>21:7:1</td>
<td>3.0:1</td>
</tr>
<tr>
<td>19 May - Plume Edge</td>
<td>245</td>
<td>15:6:1</td>
<td>2.5:1</td>
</tr>
<tr>
<td>26 May - Bonnet Carre</td>
<td>160</td>
<td>29:23:1</td>
<td>1.3:1</td>
</tr>
<tr>
<td>27 May - Plume Edge</td>
<td>150</td>
<td>37:27:1</td>
<td>1.4:1</td>
</tr>
</tbody>
</table>

An ecological model developed by Caddy (1993) may help in our understanding of the effects of various discharges of Mississippi River water into Lake Pontchartrain.
Caddy (1993) proposed a model for the effect of increasing nutrient inputs on various
trophic levels in large semi-enclosed, stratified water bodies. Additions of nutrients
initially increases overall production for all trophic levels, with peak rates occurring when
the water body is slightly eutrophic. As the system becomes more eutrophic the benthic
community declines rapidly in response to bottom water anoxia. This trend is followed
by other trophic levels and leads to eventual system collapse.

Diversions of Mississippi River water into Lake Pontchartrain can be managed to
provide optimal fisheries production and wetland restoration without causing detrimental
effects such as eutrophication, harmful algal blooms, and hypoxia. Our results, along with
other studies in coastal Louisiana, indicate that diversions through wetlands and smaller
shallow water bodies can result in substantial nutrient reductions and changes in nutrient
ratios (Lane et al. 1999; Day et al. 1994; Madden 1992). We recommend that all
diversions of Mississippi River water into Louisiana’s coastal wetlands be ‘buffered’ by
wetland overland flow before reaching larger lakes and bays where conditions for hypoxic
events may be present. At the Bonnet Carre site, we suggest that further studies be
carried out to determine the feasibility of using the wetlands surrounding the Bonnet
Carre Spillway to process Mississippi River water before reaching Lake Pontchartrain.
Diversions via the spillway allow river water to flow directly into the lake often
bypassing some wetlands in the spillway. Diversions into wetlands upstream or
downstream of the spillway would allow a much more efficient uptake of nutrients and
sediments. In addition, additional studies need to be conducted of the ecological response
of Lake Pontchartrain to various diversion flow regimes and quantities.
LITERATURE CITED


Nixon, S. W. 1981. Freshwater inputs and estuarine productivity. Proceedings of the National Symposium on Freshwater Inflow to Estuaries, Slidell, LA.


CHAPTER 3
THE EFFECTS OF RIVERINE DISCHARGE ON CHLOROPHYLL \(a\), SUSPENDED SEDIMENT, SALINITY AND TEMPERATURE IN THE BRETON SOUND ESTUARY, LOUISIANA

INTRODUCTION

Overbank flooding and crevasses of the Mississippi River was a major geological process in the formation and maintenance of the Mississippi delta (Hatton et al. 1983; Kesel 1988; Kesel 1989; Roberts 1997; Davis 2000; Day et al. 2000). Each year the river flood supplied a pulse of freshwater, suspended sediments, inorganic nutrients, and organic materials that stimulated primary and secondary production. This increased plant production provided higher rates of food production for consumers, and increased organic soil formation. Pulsed freshwater input also maintained a salinity gradient that supported a high diversity of wetland and aquatic habitats for estuarine species (Day et al. 1997).

The construction of flood control protection levees and closure of minor distributary channels began soon after colonization of New Orleans by the French in 1719 (Boesch 1996; Colten 2000). Since the early 1900’s most of coastal Louisiana has been hydrologically isolated from the Mississippi River by the completion of massive flood control levees that completely halted overbank flooding (Kesel 1988; Kesel 1989; Mossa 1996). During the 20\textsuperscript{th} century there was a massive loss of coastal wetlands, with approximately 73 km\(^2\) being lost each year by the 1960’s, which has been linked to the lack of riverine input (Salinas et al. 1986; Boesch 1994; Coast 2050, 1998; Day et al. 2000). As a consequence of this lack of river flooding, resuspended sediment from bay bottoms and eroded marsh edge have replaced fluvial sources of inorganic sediments in many regions of coastal Louisiana (Hatton et al. 1983; Baumann et al. 1984; Reed 1988).
There is a strong consensus in the scientific and management community that the long-term survival of Louisiana’s coastal wetlands must depend on the reintroduction of river flow into the interdistributary basins to stem salinity intrusion and supply nutrients and sediments for wetland aggradation and progradation (Templet and Meyer-Arendt 1988; Kesel 1989; Boesch 1996; Day et al. 1997; Gosselink 2001).

As a restoration effort, the State of Louisiana has developed a plan for freshwater diversions that will mimic flooding events of the Mississippi River (Chatry and Chew 1985; Coast 2050, 1998). This study focuses on the second largest diversion structure in operation in Louisiana, located at Caernarvon, and the effect of diverted river water on several key water quality parameters in Breton Sound estuary, a large expanse of coastal wetlands between the diversion structure and the Gulf of Mexico (Fig. 3.1). This region is greatly affected by the Caernarvon diversion structure that allows up to 226 m$^3$ sec$^{-1}$ of Mississippi River water to enter the estuary (Lane et al. 1999). We carried out twenty-seven water quality transects in the major waterways of Breton Sound between September 7, 2000, and August 28, 2002. We deployed a flow-through system to continuously measure fluorescence, turbidity, salinity, and temperature. Fluorescence and turbidity were statistically compared and calibrated to discrete samples of chlorophyll $a$ and TSS, respectively, taken at 18 locations along each transect.

The work presented in this paper is based on a larger interdisciplinary PULSES project studying the effects of the Caernarvon diversion on the Breton Sound estuary. The purpose of this paper is to extend our understanding of the effect of pulsed riverine input into coastal wetlands. Our objectives are to examine this effect by measuring the spatial and temporal distribution of sediments, chlorophyll $a$, salinity and temperature in
Figure 3.1. Site map with water quality monitoring sites in the Breton Sound estuary (1-19). Gray shaded areas indicate upland habitats, white areas wetlands, and black areas open water.
the Breton Sound estuary. We hypothesized there would be (1) rapid reduction of suspended sediments concentrations with distance from the diversion structure; (2) low chlorophyll $a$ levels in areas of high suspended sediment, with rapidly rising chlorophyll levels immediately after suspended sediment concentrations decrease to low levels; (3) an overwhelming negative effect on salinity and temperature throughout the estuary associated with structure discharge.

**STUDY AREA**

The Caernarvon freshwater diversion structure is located on the east bank of the Mississippi River at river mile 81.5 (Fig. 3.1), and consists of five 4.6 meter wide box culverts with vertical lift gates, with a capability of passing 226 m$^3$s$^{-1}$ of river water. The structure was completed in 1991 and freshwater discharge began in August of that year. The Breton Sound estuary lies between the Caernarvon diversion and Breton Sound Bay in the Gulf of Mexico, and comprises about 1100 km$^2$ of fresh and brackish wetlands and shallow water ponds, lakes and bays. Diverted water must travel about 30-40 km through two major routes dominated by wetlands before reaching open waters of Breton Sound, and an additional 50 km before reaching Gulf waters. The two major routes are via (1) Lake Leary and Bayou Terra aux Boeufs (BTAB) to the east, which carries approximately 2/3 of the flow, and (2) Manuel's Canal and River aux Chene (RAC) to the west of Big Mar, which carries the remaining 1/3 of flow (Lane et al. 1999). There is considerable interaction between diverted river water and estuarine wetlands due to tides, northerly wind events and storms. Levees prevent Mississippi River water from entering most of Breton Sound estuary. However, river water can flow directly into Breton Sound
Bay below the point where levees end on the eastern bank of the river, and may impact water quality in the outer bays of the estuary (see Fig. 3.1).

METHODS

Structure Discharge

Discharge from the structure was calculated from a rating curve developed by the Louisiana Department of Natural Resources (Chuck Villarubia, personal communication). Discharge from the structure was also measured episodically by the USGS using an acoustic doppler velocimeter deployed in the discharge channel located between the Caernarvon structure and Big Mar. The instrument collected hourly velocity and water height measurements. Water heights were then converted to volume using a stage-to-discharge relationship calibrated several weeks earlier using an acoustic doppler current profiler. Regression analysis found a linear relationship between the two methods ($R^2=0.98$, $p<0.01$), and the resulting equation was used to back calculate the flows determined using the doppler velocimeter, which was thought to be a more accurate estimate of flow than the head differential equation (Gregg Snedden, personal communication).

Flow-through System

The flow-through system consists of a 1.5 cm diameter pipe, mounted on the transom of a small boat that scoops surface water at planing speed, routes the water into a bubble trap, where a submersible pump moves water past the environmental sensors, and eventually flushes out where it can be either sampled or discarded en route (Lorenzen 1966; Madden and Day 1992). All continuous measurements were taken using a YSI-6600 probe modified for flow-through measurement (www.ysi.com). The probe
measured turbidity, fluorescence, salinity, and temperature every 5 seconds. The average speed of the boat was 50 km hr$^{-1}$, providing a reading approximately every 70 meters. Prior to each transect the YSI-6600 probe was calibrated for turbidity and conductivity using known standards, and the time synchronized with an onboard digital time device. The flow-through system was run through the two main routes between the Caernarvon diversion and the Gulf of Mexico: the Eastern Route (Lake Leary/Bayou Terra aux Bouefs (BTAB)), and the Western Route (Manuel’s Canal/River aux Chene (RAC)) (Fig. 3.1). Each route had a spur into the basin interior; with the BTAB route including a side trip into Little Lake, and the RAC route including a side trip into Grand Lake. Along each transect discrete samples were taken at 18 locations, and the time these samples were taken was recorded (Fig. 3.1). The total transect was completed in 4-6 hours, covering approximately 210 km, providing an essentially synoptic survey of the estuary.

Discrete Sample Analysis

Discrete samples were taken from water exiting the flow-through system and immediately stored at 4°C for preservation. Total suspended sediment were determined by filtering 100-200 ml of sample water through pre-rinsed, dried and weighed 47 mm 0.45 um Whatman GF/F glass fiber filters. Filters were then dried for 1 hr at 105°C, weighed, dried for another 15 minutes, and reweighed for quality assurance (Standard Methods 1992). Chlorophyll $a$ was determined using a modified version of Strickland and Parsons (1972) technique. Pigments were extracted with a 40:60 ratio of dimethyl sulfoxide (DMSO):90% acetone (Burnison, 1980). The extract was measured with a Turner Designs model 10-AU fluorometer.
Statistical Analysis

Temperature and salinity data were taken directly from the YSI-6600 Sonde instrument, while turbidity and fluorescence were converted to TSS and chlorophyll $a$, respectively, using linear regression. Simple linear regression analysis was carried out for each transect using turbidity and fluorescence as independent variables and TSS and chlorophyll $a$ as dependent variables. JMP statistical software (Sall and Lehman 1996) was used to test for significant difference between the slope of the regression and the mean (alpha < 0.05), provide R-square correlation coefficients, and the regression equations that were used to calculate TSS and chlorophyll $a$ values from turbidity and fluorescence data, respectively, from the flow-through system.

In addition, an analysis of variance was carried out on the discrete water samples, with the factors of interest being structure discharge, season, route and distance from the diversion structure. Discharge was smoothed using a two-week running average, and divided into three categories: Low Flow (0-19 m³ sec⁻¹), Medium Flow (20-59 m³ sec⁻¹), and High Flow(60-100 m³ sec⁻¹). Seasons were designated according to solar solstice and equinox designations. The routes were the Eastern Route (Lake Leary/Bayou Terra aux Bouefs (BTAB)), and the Western Route (Manuel’s Canal/River aux Chene (RAC)). Distance was divided into three categories: D1 (1-8 km), D2 (9-18 km), and D3 (19-40 km). Data were available for all treatment combinations, but the number of replications was unbalanced. Least square means were calculated for significant interactions and main effects. Statements about interaction plots reflect an experimentwise Type 1 error rate (falsely finding significance) controlled at the 5% level, using Bonferroni adjustment.
RESULTS

Discharge from the Caernarvon structure ranged from 0 to 213 m$^3$ sec$^{-1}$ (Fig. 3.2). Most of the discharge in 2000 occurred between March and September, with flows peaking at 139 m$^3$sec$^{-1}$ on March 14, ramping down to an almost constant discharge of 37 m$^3$sec$^{-1}$ for the rest of March, and rapidly rising to a constant of 68 m$^3$sec$^{-1}$ in June that persisted for the rest of the Summer. There was no water discharged during several months in Fall 2000, when this study started, but starting in late November, three moderate sized ($\approx$100 m$^3$sec$^{-1}$) pulses were released, followed by a large ($\approx$ 200 m$^3$sec$^{-1}$) in the Spring of 2001. Discharge decreased and remained relatively constant ($\approx$40 m$^3$sec$^{-1}$) during Summer and Fall, with short interruptions of no flow. Discharge increased again in December 2001, and continued to increase, with short interruptions in flow, peaking in February 9, 2002, at 166 m$^3$sec$^{-1}$. Discharge decreased and peaked again on March 15 at 181 m$^3$sec$^{-1}$. Flow decreased to a constant rate of $\approx$20 m$^3$sec$^{-1}$, rising briefly to $\approx$37 m$^3$sec$^{-1}$, and then falling to zero for the remainder of the study.

![Figure 3.2. Mississippi River discharge through the Caernarvon diversion structure. Arrows indicate when water quality data were taken.](image)

Simple linear regression analysis found significant correlations between turbidity/TSS and fluorescence/chlorophyll $a$ for all transects. R-square coefficients of correlation ranged from 0.96 to 0.45, with the lowest correlations occurring between turbidity and
The data were separated into the two main routes, East (BTAB) and West (RAC), and graphed (a complete set of figures can be found in Appendix C).

The diversion affected salinity throughout the estuary along both routes, with the scale of the effect dependent on discharge volume (Fig. 3.3). For example, on November 10, 2000, after several months of zero discharge, salinities along the BTAB route were elevated, with a salinity of 14 at station 8 (Fig. 3.4). Several months later, at the start of the third moderate sized (=100 m$^3$sec$^{-1}$) pulse on January 25, 2001, salinities were lower, with 3 psu salinity at station 8. There also appears to be a temporal lag between discharge and effect on salinity in the lower estuary. For example, there was a two-week lag from the onset high discharge (211 m$^3$sec$^{-1}$) on March 9, 2001, and the apparent effect on salinity at the end member stations on March 22 (Fig. 3.5). The analysis of variance results indicate a significant route x distance class interaction (p<0.001). Further analysis of this interaction indicates increased salinities along the Eastern route compared to the Western route at distance class D3 (Fig. 3.6), with no significant differences found at distance classes D1 and D2. The analysis of variance also found a significant three-factor interaction for discharge x season x distance (p=0.04). A major contributor to this interaction was increased salinity at D3 during Fall and Winter at Low discharge when compared to High discharge (Figure B1, Appendix B).

Temperature of incoming Mississippi River water ranged from 6-32°C, as measured at the diversion structure (station 1). River water temperature was always cooler than estuarine waters, but generally equilibrated to the rest of the estuary within several kilometers (Fig. 3.7). During large structure discharges there were several times when cooler water from the diversion propagated through the entire estuary. The most
Figure 3.3a. Caernarvon structure discharge (top panel), and spatial (y-axis) and temporal (x-axis) changes in salinity (bottom panel) along the Eastern route.

Figure 3.3b. Caernarvon structure discharge (top panel), and spatial (y-axis) and temporal (x-axis) changes salinity (bottom panel) along the Western route.
obvious of these events occurred on January 8 and February 7, 2002, when discharge was 117 and 149 m$^3$ sec$^{-1}$, respectively. Water entering the estuary on these dates had temperatures of 6.3 and 9.7 °C, respectively, and water throughout the estuary on both dates never rose above 10.2 °C. It is interesting to note, however, that on January 22, 2002, when structure discharge was 0, estuarine temperatures rose to 15-16 °C, presumably due to lack of cold water input (Fig. 3.7). For temperature, the analysis of variance found a moderately significant discharge x season x distance interaction (p=0.06). With the exception of Summer, there was consistent hierarchical ordering of discharge levels over all three distance classes (Figure B2, Appendix B). During
Figure 3.6. Route x Distance Class interaction for salinity. Asterisk indicates a significant difference between Eastern and Western routes. Type 1 error rate = 0.02 after Bonferroni adjustment to control experiment wise error rate due to multiple comparisons (0.05 divided by 3 comparisons).

Summer, Medium and Low discharge levels had significantly higher (p<0.001) temperature than High discharge at distance classes D2 and D3.

Total suspended sediment of Mississippi River water entering the structure ranged from 40 to 252 mg L\(^{-1}\), with an average of 118 mg L\(^{-1}\). The lowest concentrations occurred during late summer/early fall, and the highest concentrations during winter and spring (Fig. 3.8). Sediment derived from the diversion appeared to reach \(\approx 10\text{-}15\) km into the estuary during the spring pulses of 2001 and 2002 (Fig. 3.8). Total suspended sediment concentrations decreased with distance from the Caernarvon structure, but often displayed a turbidity maximum in Lake Leary (stations 4, 19, & 5) during winter (e.g. Fig. 3.9). There were also highly elevated and fluctuating TSS concentrations at the southern end of the estuary of the eastern route during many transects during winter and spring (e.g. Figs. 3.8a and 3.9), most likely due to storm and/or high wind events. For TSS, the analysis of variance found a significant discharge x season x route interaction (p=0.02). A major contributor to this three-factor interaction was non-significant.
differences between East and West routes during all seasons except Fall, when there was significantly higher TSS concentrations along the Eastern Route at High discharge (Fig. B3, Appendix B). There was also a significant flow x season x distance class interaction (p=0.04), with a major contributor to this interaction being increased TSS concentrations at distance classes D1 and D3 during Fall and at High discharge. The high concentrations, however, were found not to be significant in part because of the Bonferroni adjustment (alpha<0.001) to control experiment wise error rate due to multiple comparisons (Fig. B4, Appendix B).

Figure 3.9. Flow-through data of total suspended sediment concentrations along the Bayou Terra Aux Boeufs route on February 16 and 23, 2001. Individual data points indicate discrete sample concentrations. Arrows in subplot indicate discharge for respective dates

Chlorophyll \(a\) levels generally peaked during late summer and fall, and were lower during and shortly after large pulses of diverted river water (Fig. 3.10). The highest concentrations occurred during the summer, peaking at 38 ppb in 2001 and >60 ppb in 2002. There were also high chlorophyll concentrations during the fall of 2000 and early winter of 2001, with peak concentrations ranging from 40-56 ppb. Incoming Mississippi River water chlorophyll \(a\) levels were always near zero. Concentrations increased with distance from the diversion structure and were negatively correlated to

Chlorophyll \(a\) levels generally peaked during late summer and fall, and were lower during and shortly after large pulses of diverted river water (Fig. 3.10). The highest concentrations occurred during the summer, peaking at 38 ppb in 2001 and >60 ppb in 2002. There were also high chlorophyll concentrations during the fall of 2000 and early winter of 2001, with peak concentrations ranging from 40-56 ppb. Incoming Mississippi River water chlorophyll \(a\) levels were always near zero. Concentrations increased with distance from the diversion structure and were negatively correlated to
Figure 3.8a. Caernarvon structure discharge (top panel), and spatial (y-axis) and temporal (x-axis) changes in TSS concentration (bottom panel) along the Eastern route.

Figure 3.8b. Caernarvon structure discharge (top panel), and spatial (y-axis) and temporal (x-axis) changes in TSS concentration (bottom panel) along the Western route.
TSS, with chlorophyll levels increasing after TSS levels dropped below 80 mg L\(^{-1}\) (e.g. Fig. 3.11).

Chlorophyll concentrations generally peaked at mid-estuary and decreased Gulfward, with consistently higher levels in River aux Chene and Grand Lake (e.g. Fig. 3.11). The analysis of variance found a significant main effect for distance class (p<0.0001), with the D2 distance class having higher chlorophyll \(a\) concentrations than either D1 or D2 (Fig. 3.12). There was also a moderately significant discharge x season interaction (p=0.06), with the highest chlorophyll \(a\) concentrations occurring at Low Flow during Summer and Fall (Fig. 3.12).

DISCUSSION

The riverine supply of inorganic nutrients to estuaries makes them areas of potentially high primary production, but light attenuation by suspended sediments confines the photic zone to a small fraction of the water column, causing light limitation to be the major control of phytoplankton growth (Joint and Pomroy 1981; Cloern 1987; Cloern 2001). In this study, chlorophyll \(a\) concentrations were inversely related to suspended sediment concentration, even though inorganic nitrogen concentrations were highest in regions of high riverine input (personal communication, Emily Hyfield). This effect was especially evident along Manuel's Canal and River aux Chene (Fig. 3.11).

During periods of high riverine discharge, phytoplankton concentrations were suppressed until suspended sediment concentrations declined, directly after which phytoplankton levels increased. Cloern (1987) observed in San Francisco Bay that suspended sediment concentrations above 50 mg L\(^{-1}\) often attenuate light enough to limit phytoplankton photosynthesis. Data from this study suggests sediment concentrations
Figure 3.10a. Caernarvon structure discharge (top panel), and spatial (y-axis) and temporal (x-axis) changes in chlorophyll \( a \) concentration (bottom panel) along the Eastern route.

Figure 3.10b. Caernarvon structure discharge (top panel), and spatial (y-axis) and temporal (x-axis) changes in chlorophyll \( a \) concentration (bottom panel) along the Western route.
above 80 mg L\(^{-1}\) inhibited phytoplankton growth. This difference is most likely due to the shallow nature of the Breton Sound estuary, compared to the relatively deep San Francisco Bay, which decreases the amount of time a particular phytoplankton cell spends in the dark as water circulates vertically. It appears that this mixing depth is especially important in turbid systems, as the time spent in the dark, relative to the light, may be the most important regulating factor of phytoplankton growth (Grobbelaar 1985; Cloern 1987; Randall and Day 1987; Alpine and Cloern 1988).

Chlorophyll \(a\) levels were generally higher during summer and fall, especially during low flow, though discharge through the Caernarvon structure was highest during winter and spring, and was the principle source of ‘new’ nutrients to the system. Such decoupling between riverine input and peak phytoplankton productivity has been observed in many estuaries (Nixon 1981; Boynton et al. 1982; Bennet et al. 1986; Fisher et al. 1988). Kemp and Boynton (1984) presented a conceptual model for understanding this phenomena based on observations from the Patuxent River estuary. During high river discharge, some dissolved nutrients are converted into particulate forms, via sorption and assimilation, and deposited on the estuarine bottom. As temperatures rise, these nutrients are regenerated by benthic metabolism, releasing dissolved nutrients back into the euphotic zone where they support phytoplankton production. Madden et al. (1988) observed this process in the Atchafalaya Bay system in south-central Louisiana. Riverine input is highly seasonal, and the estuary receives most of its sediment input and high loadings of nutrients during spring, but high turbidity and colder temperatures limit phytoplankton productivity during this time. During the period of low flow in summer and fall, when there is clearer water, riverborne and regenerated nutrients are maximally
exploited by phytoplankton. These studies suggest that some nutrients introduced to the Breton Sound estuary during spring pulses may be retained in the estuary and later released to support phytoplankton production during warmer summer months.

Figure 3.11. Flow-through data of total suspended sediment and chlorophyll \( a \) concentrations along the River Aux Chene route on March 9, 15 and 22, 2001. Individual data points indicate discrete sample concentrations. Arrows in subplot indicate discharge for respective dates.

Breton Sound estuary has a seasonal signal of chlorophyll blooms during the summer and fall, with a chlorophyll maximum in mid-estuary reaching \( \geq 60 \) ppb (Fig. 3.10). Seasonal blooms of such magnitude have been reported in other estuaries (Cloern 1996; Fichez et al. 1992). Rapid production and deposition of organic matter during algal blooms influences the depth of the oxic-anoxic interface within sediments, causing
dramatic changes in sediment chemistry, nutrient release, and rates of oxygen consumption (Cloern 2001). The shallow depth and relatively strong mixing of the Breton Sound estuary due to storms and tidal mixing contribute to a relatively complete and rapid coupling of heterotrophic and autotrophic processes (Nixon 1981). This homogeneity of the water column prevents stratification and associated hypoxia from forming. Summer algal blooms trigger a complex suite of responses at different trophic levels, including stimulation of bacterial productivity, growth of microzooplankton, and reproduction and growth of zooplankton, mollusks, worms, crustations and other consumer animals (Cloern 1996).

Figure 3.12. Distance main effect (left) and Discharge x Season interaction for chlorophyll $a$. Asterisks indicate a significant difference for points above and below. Type 1 error rate = 0.02 left, = 0.004 right, after Bonferroni adjustment to control experiment wise error rate due to multiple comparisons (0.05 divided by 3 comparisons left, 0.05 divided by 12 comparisons right).

The use of the flow-through system revealed detailed sediment and chlorophyll $a$ dynamics that were not captured by the discrete sampling. Certainly the turbidity maximum in Lake Leary and the fluctuating levels at the outer reaches of the estuary
would have been missed, or at least suspect (Fig. 3.9). Turbidity maximums usually develop in the oligohaline region of an estuary where salt and freshwater mix, causing the flocculation of freshwater-derived material as ionic strength increases towards the sea (Sholkovitz 1976; Zabawa 1978; Fisher et al. 1988). Flocculation was probably not the cause of the observed turbidity maximum in this study, however, since Lake Leary is in the freshwater zone. It is more likely that high winds during frontal passages led to resuspension of sediments. The deposition of material from higher discharges earlier in the year that settled in the lake may have been the ultimate source of these sediments. Booth et al. (2000) calculated that winds of 4 m s\(^{-1}\) resuspended approximately 50\% of bottom sediments in Barataria Bay, and that winds of this magnitude occurred for 80\% of the time during the late fall, winter, and early spring. Perez et al. (2000) found highly fluctuating suspended sediment levels in a riverine influenced tidal channel associated with resuspension of bay bottom sediments during storm events. The highly erratic TSS measurements recorded during this study in the outer reaches of the estuary were also most likely the result of wind induced resuspension.

There was a large temporal and spatial variation in water temperature (Fig. 3.7), which likely affected a broad array of physiological and geochemical estuarine processes. Water temperature effects denitrification and nitrification rates (Bachand and Horne 2000; Nowicki et al. 1997), with temperatures below 15°C having a much more drastic effect compared to temperatures between 15-35°C (Reddy and Patrick 1984). Temperature also affects benthic decomposition of organic matter and regeneration of nutrients, with the rate of these processes rapidly accelerating with temperature (Kemp and Boynton 1984, Day et al. 1989; Cowan and Boyton 1996). The temperature of
Mississippi River water was always less than ambient estuarine water, possibly having a major role in decreasing the metabolism of the Breton Sound estuary, especially during periods of prolonged flow, such as the winter of 2002 (Fig. 3.7).

There were statistically significant increased salinities along the Eastern route compared to the Western route. This is counterintuitive because the Eastern route has more freshwater shunted to it than the Western route, and should thus have lower salinities. One probable explanation for this observation is the effect of the Mississippi River. Water from the Mississippi River may back into Breton Sound and stack up against the eastern river levee, greatly effecting salinities along the Western route, while generally bypassing the Eastern route. More study of the dynamics of the Mississippi River in this regard is necessary.

The Caernarvon diversion structure had a significant effect on salinity throughout most of the Breton Sound estuary. Lane et al. (1999) reached this same conclusion in an analysis of a seven year data set from the Breton Sound estuary. The original goal of the Caernarvon diversion was to establish optimal salinity conditions for oyster production (Chatry et al. 1983, Chatry and Chew 1985), but in addition, the Caernarvon diversion can also be managed to prevent saltwater intrusion during storms and drought. Freshwater pulses can be used to form a buffer against saltwater intrusion, while simultaneously allowing the coastal system to remain open to the movement of fishery species and important energetic pulses originating from the sea in the form of tides and storms (Day et al. 1997). Freshwater diversions are a much more holistic management method compared to other coastal salinity management techniques currently being
implemented, such as the use of levees, weirs and flap gates (Cowan et al. 1988; Boyer 1997).

CONCLUSIONS

This study revealed a very dynamic behavior of suspended sediments and chlorophyll \( a \), and their interactions. As documented in other studies, chlorophyll \( a \) was greatly limited by suspended sediment during high discharge due to light attenuation, and was most likely supported during periods of low discharge by benthically regenerated nutrients. The estuary efficiently trapped sediments and did not lead to persistent algal bloom. Salinity throughout the Breton Sound estuary was greatly influenced by the diversion structure, suggesting that saltwater intrusion events may be controlled with proper management of structure discharge. Continuous sampling of environmental data had merits over discrete sampling in being able to gather such data over a very short period of time, thus providing a detailed synoptic view of the system at work. This study demonstrated that the use of a flow-through system greatly enhanced the resolution of data compared to discrete sampling, allowing scientist and managers alike to better understand and visualize critical processes in the estuarine system.

LITERATURE CITED


Sources of Unpublished Materials:

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CHAPTER 4

CHANGES IN STOICHIOMETRIC Si, N AND P RATIOS OF MISSISSIPPI RIVER WATER DIVERTED THROUGH COASTAL WETLANDS TO THE GULF OF MEXICO

INTRODUCTION

Historically, many rivers had dissolved inorganic silicon (DSi) concentrations well in excess of dissolved inorganic nitrogen (DIN) or dissolved inorganic phosphorus (DIP), thus contributing to N or P deficiency in river plumes and adjacent coastal waters (Turner and Rabalais 1991; Conley et al. 1993; Humborg et al. 1997; Humborg et al. 2000). However, due to decreasing DSi concentrations and increasing DIN and DIP levels during the 20th century, the proportions of nutrients have changed in many of the world’s large rivers (Justic et al. 1995a). Using the atomic Si:N:P ratio of 16:16:1 (Redfield 1958) as a criterion for balanced nutrient composition, one can distinguish between phosphorus deficient rivers (e.g., Changjiang, Huanghe, Mackenzie, Yukon), nitrogen deficient rivers (e.g., Amazon and Zaire), silicon deficient rivers (e.g., Rhine and Seine), and those where the dissolved Si:N:P ratio approaches the Redfield ratio (e.g., Po and Mississippi) (Justic et al. 1995b).

In the Mississippi River there have been significant increases in DIN and DIP and decreases in DSi concentrations during the last 50 years, with DIN and DIP concentrations more than doubling and DSi concentrations decreasing by half (Rabalais et al. 1996). As a result, the dissolved DSi:DIN ratios in the lower Mississippi River have changed from about 4:1 to 1:1 (Rabalais et al. 1996). There has been a concurrent increase in the incidence of phytoplankton blooms and bottom water hypoxia in the coastal waters of the northern Gulf of Mexico, presumably in response to increased
riverine DIN and DIP inputs, and more balanced nutrient ratios (Turner and Rabalais 1991; Justic et al. 1995b; Rabalais et al. 1996). The northern Gulf of Mexico is presently the site of the largest (>20,000 km²) and the most severe coastal hypoxic zone in the western Atlantic Ocean region (Rabalais and Turner 2001). It is widely believed that decreasing DSi:DIN ratios in rivers exacerbate the eutrophication process in the adjacent coastal waters, primarily by reducing the potential for diatom growth in favor of noxious non-siliceous forms such as dinoflagellates (Officer & Ryther 1980; Cloern 2001).

Diatoms are generally heavily grazed upon and rarely are a nuisance. Heavily silicified diatoms, however, may be responsible for large vertical fluxes of carbon to bottom sediments in the Gulf of Mexico during spring, resulting in the formation of the hypoxic zone during the summer (Dortch et al. 2001; Turner 2001).

The high DIN concentrations in the Mississippi River are a result of two factors. First, there was a dramatic increase in agricultural fertilizer use in the second half of the 20th century (Turner and Rabalais 1991; Rabalais et al. 1996). Second, wetland and riparian ecosystems in the Mississippi basin have been greatly reduced and drainage efficiency of agricultural lands has been greatly increased (Mitsch et al. 2001). The lower Mississippi and its major tributaries are largely isolated from flood plain ecosystems by levees. This is especially so in the Mississippi delta where the river is confined by levees almost to the mouth. This isolation of the river from the delta is one of the most important factors contributing to the high rate of wetland loss in the Mississippi delta (Day et al. 2000). To counter coastal wetland loss caused by lack of river input, the State of Louisiana and the Federal Government have developed a comprehensive management plan that includes diversions of river water back into coastal
wetlands (Coast 2050 1998). One of the largest diversions is located on the east bank of the Mississippi River about 20 km south of New Orleans at Caernarvon, Louisiana.

The use of coastal wetlands and shallow water bodies to process Mississippi River water before entering the Gulf of Mexico has been proposed as a partial solution to help reduce the size of the hypoxic zone, as well as restore and maintain rapidly eroding coastal wetlands (Coast 2050 1998; Mitsch et al. 2001). Studies have shown that when water flows through wetland dominated watersheds, there is a reduction in nutrient concentrations, especially in the concentration of nitrate (Boustany et al. 1997; Fisher et al. 1988; Lane et al. 1999; 2002, Nixon et al. 1996; Kadlec and Knight 1996, Mitsch et al. 2001; Richardson and Nichols 1985; Spieles and Mitsch 2000). Lane et al. (2002), for example, estimated that 41 to 47% of Atchafalaya River NO$_3^-$ was non-conservatively lost from the water column in the Atchafalaya Delta estuarine complex before reaching stratified Gulf waters. Similar reductions in nitrogen have been reported to occur in many estuaries (Smith et al. 1983; Jenkins and Kemp 1984; Lane et al. 1999) and wetland wastewater treatment systems (Richardson and Nichols 1985; Boustany et al. 1997; Zhang et al. 2000).

The work presented in this paper is based on a large interdisciplinary project called PULSES studying the effects of the Caernarvon diversion on the Breton Sound estuary. We report on changes in nutrient concentrations and ratios in water flowing from the Caernarvon diversion through the Breton Sound Estuary. We hypothesized that the diversion would lead to an overall decrease in DIN concentrations, and an increase in DSi:DIN ratios.
STUDY AREA

The Caernarvon freshwater diversion structure is located on the east bank of the Mississippi River south of New Orleans at river mile 81.5 (Fig. 4.1), and consists of five 4.6 meter wide box culverts with vertical lift gates, with a capability of passing 226 m³ s⁻¹ of river water. The structure was completed in 1991 and freshwater discharge began in August of that year. The Breton Sound estuary lies between the Caernarvon diversion structure and Breton Sound Bay, and comprises approximately 1100 km² of fresh and brackish wetlands and shallow water ponds, lakes and bays. Lane et al. (1999) found that salinity was significantly lowered in the Breton Sound estuary due to operation of the Caernarvon structure, with salinity in the upper half of the estuary generally lower than 5 PSU throughout the year. Diverted water must travel about 30-40 km through two major routes dominated by wetlands before reaching the open waters of Breton Sound, and an additional 50 km before reaching open Gulf waters. The two major routes are via (1) Lake Leary and Bayou Terra aux Boeufs (BTAB) to the east, which carries approximately 2/3 of the flow, and (2) Manuel's Canal and River aux Chene (RAC) to the west of Big Mar, which carries about 1/3 of flow (Lane et al. 1999). Levees prevent Mississippi River water from entering into the upper Breton Sound estuary. However, river water can flow directly into the bay below the point where levees end on the eastern bank of the river (Fig. 4.1), and may impact water quality in that area.

METHODS

During spring of 2001, an experimental large pulse of river water with a peak flow of 226 m³ s⁻¹ was released through the Caernarvon structure for 16 days (Fig. 4.2). Sampling was carried out during weekly transects from March 9 to March 30, 2001.
Discrete water samples were taken at 19 locations in the Breton Sound estuary (Fig. 4.1). They were collected in 1L acid-washed polyethylene bottles, immediately stored on ice, and taken to the laboratory for processing. Within 24 hours, 60 ml from each water sample were filtered through pre-rinsed 25 mm 0.45 um Whatman GF/F glass fiber filters into acid-washed bottles and frozen until nutrient analysis. Salinity was determined using an Atago © S-10 hand held refractometer (accuracy: ±2 PSU). Nitrate plus nitrite (NO₃+NO₂) was determined using the automated cadmium reduction method with an Alpkem © autoanalyzer (Greenberg et al. 1985). Ammonium (NH₄-N) was determined by the automated phenate method, phosphate (PO₄-P) by the automated ascorbic acid reduction method, and silicon (SiO₄-Si) by the automated molybdate reagent/oxilic acid method, all with an Alpkem © autoanalyzer (Greenberg et al. 1985). Total nitrogen (TN) and total phosphorus (TP) were determined by methods described by Valderrama (1981). The accuracy of the nutrient analysis was checked every 20 samples with a known standard, and the samples were redone if the accuracy was off by 5%.

**Water Budget Analysis**

A water budget analysis was carried out to illustrate the importance freshwater input from the Caerarvon diversion. Preliminary analysis of the results indicated that most chemical reactions occurred in the upper half of the estuary, making a water budget for this region essential. As part of another study, the volume of all lakes, bayous, canals and marsh ponds in the upper 441 km² of Breton Sound estuary was calculated (Erick Swenson, personal communication). The region was delineated by Bayou Terra aux Boeufs and the Mississippi River levee (see stippled area in Fig. 4.1). The water volume of this region, determined from aerial photos and field checked depth estimates, was
calculated to be 212 million cubic meters at mean tide (Erick Swenson, personal communication).

Figure 4.1. Map of the study area showing the location of the Caernarvon diversion structure and water quality monitoring sites in the Breton Sound estuary. Arrows along the lower Mississippi River show where the flood control levee ends and water can flow from the river to the estuary during high river stages. The stippled area indicates the upper 441 km$^2$ of Breton Sound estuary, shaded areas are uplands protected by flood control levees.
Analysis of Nutrient Reduction Efficiency

The nutrient reduction efficiency for TN, TP, DIN, DIP and DSi was calculated using equation (4.1),

\[
\text{Nutrient Reduction (\%) = \left( \frac{\text{Mass}_{\text{in}} - \text{Mass}_{\text{out}}}{\text{Mass}_{\text{in}}} \right) \times 100}
\] (4.1)

where Mass_{\text{in}} is the concentration of the constituent in incoming river water at the Caernarvon diversion, and Mass_{\text{out}} is the concentration at the end member station(s).

Since water passes through two major routes, Bayou Terra aux Boeufs (BTAB) and River aux Chene (RAC), nutrient reduction efficiency was calculated separately for each route and weighted, depending on the percentage of flow in each route, then summed (equation 4.2). Five pairs of stations along the two main flow routes were chosen in order to characterize the nutrient reduction efficiency: stations 5 and 13; 6 and 14; 8 and 15; 10 and 17; and 11 and 18. The stations on each route were selected because of direct hydrologic connection to each other, and paired because their similarity in distance from the diversion structure.

Equation (4.1) was modified to account for the different flow in the two pathways as shown in equation (4.2),

\[
\text{Total Nutrient Reduction (\%) = (0.66 \times \text{NR}_{\text{stBTAB}} + 0.34 \times \text{NR}_{\text{stRAC}}) \times 100}
\] (4.2)

where the percentage of diverted Mississippi River water through each route (66\% and 34\% for the BTAB and RAC routes, respectively) was multiplied by the reduction efficiency of the respective station. The sum of the total percent reduction for each route was used to estimate the percent reduction from station 1 to the respective end member.
Analysis of the salinity results discussed below imply that water from the diversion had a residence time of about 2 weeks before reaching the outermost stations. For this reason, the loading rate analysis used averages of March 9 and 15 concentrations at station 1 as initial concentrations ($\text{Mass}_{\text{in}}$), and the concentrations at the various pairs of end member stations on March 22 as ending concentrations ($\text{Mass}_{\text{out}}$). To account for dilution with Gulf waters, as evident from salinity at the last two pair of stations (10-17, and 11-18, Fig. 4.4), equations 4.1 and 4.2 were modified and to equations 4.3 and 4.4. These equations compensate for the effects of dilution by dividing salinity on March 22 by salinity on March 9, when the outermost stations were not affected by the diversion, and subtracting the resulting fraction from 1. Similarly, equation 4.5 was used to compensate for dilution in the end member concentration by adding 1 to the fraction obtained above and then multiplying the sum by the respective station concentration. Equations 4.3-4.5 were used to calculate nutrient reduction efficiencies and stoichiometric ratios for the last two pair of stations.
Nutrient Reduction (%) = \{((\text{Mass}_{\text{in mar9}} - \text{Mass}_{\text{out mar22}}) / \text{Mass}_{\text{in mar9}}) * (1 - \text{sal}_{\text{mar22}} / \text{sal}_{\text{mar9}})\} * 100 \quad (4.3)

Total Nutrient Reduction (%) = \{(0.66*\text{NR}_{\text{sBTAB}}*(1 - \text{sal}_{\text{mar22}} / \text{sal}_{\text{mar9}})) + (0.34*\text{NR}_{\text{sRAC}}*(1 - \text{sal}_{\text{mar22}} / \text{sal}_{\text{mar9}}))\} * 100 \quad (4.4)

Undiluted Conc. = \text{Conc}_{\text{endlmemb}}*(1 + \text{sal}_{\text{mar22}} / \text{sal}_{\text{mar9}}) \quad (4.5)

Stoichiometric Nutrient Ratios Analysis

Stoichiometric nutrient ratios were determined using molar concentrations of DSi, DIN and DIP. Stoichiometric ratios for the last two pair of stations were determined from concentration ratios after accounting for dilution by using equation (4.5).

Statistical Analyses

A simple linear model was used to test for linearity of the various constituents with distance. The two routes, BTAB and RAC, were tested separately in full and reduced models. The full model tested separate slopes and intercepts for each route, while the reduced model used a common slope and intercept for both routes. The full model was used only when the reduced model was found to be non-significant using Sum of Squares and Mean Square Error terms (alpha<0.05).

Statistical analyses of nutrient concentrations and ratios were carried out to determine changes in water quality at the diversion structure compared to the stations located within the estuary. The mean of incoming river water for the first two dates (March 9 and 15) was compared to the mean of each paired set of samples taken on March 22 using Dunnett’s procedure, with incoming river water designated as the control. The mean of all estuarine stations combined was also compared to the mean of incoming river water using Student’s t-test. Nutrient concentrations used for both the
Dunnett’s procedure and Student’s t-test were modified to account for dilution by using equation 4.5.

RESULTS

The spring 2001 pulse from the Caernarvon diversion began on March 6 with discharge rapidly rising from near zero to 212 m$^3$ s$^{-1}$ within 48 hours. Discharge on the water quality sampling dates was 211 m$^3$ sec$^{-1}$ on March 9, 212 m$^3$ s$^{-1}$ on March 15, 56 m$^3$ s$^{-1}$ on March 22, and 12 m$^3$ s$^{-1}$ on March 30 (Fig. 4.2). A total of 269 million cubic meters of river water were introduced during the pulse, compared to the 212 million cubic meters calculated as the volume of the upper 441 km$^2$ of the estuary at mean tide (Erick Swenson, personal communication), indicating a water replacement time of 12.6 days. If the 269 million cubic meters were spread uniformly, it would cover the upper 441 km$^2$ of the estuary with 61 cm of water, or the entire 1100 km$^2$ of the estuary with 25 cm. This compares to the 6 cm of rainfall that occurred during the same period (measured at the Class A weather station at the New Orleans International Airport).

Winds tended to circulate clockwise in a series of cold fronts with an approximate period of one week during January, February and March, and decreasing thereafter (Fig. 4.3). These shifts in wind, combined with the diversion, led to water level variations that often overwhelmed tidal influences and flooded the surrounding marsh surface for most of the two week pulse. Up to 40 cm of water was measured on the marsh surface in the region between Big Mar and Grand Lake (Gregg Snedden, personal communication). Perez et al. (2000) found extremely high TSS concentrations in Fourleague Bay, Louisiana, associated with cold fronts passages, and hypothesized that erratic water level fluctuations associated with winter storms are a major mechanism for the transport of
sediments to surrounding marshes. There were two frontal passages during the 2001 spring pulse, passing through the system on March 7 and 21 (Fig. 4.3).

Figure 4.3. Wind speed data taken from New Orleans International Airport. Arrows indicate water quality sampling dates.

Salinity ranged from 0 psu at the diversion to 17 psu at the end member stations (Fig. 4.4). The most pronounced decrease in salinity occurred on March 22, two weeks after the onset of the large pulse (March 9). For example, salinities at stations 10 and 17, over 25 km away from the diversion, decreased from 11 and 4 psu on March 15, to 2 and 1 psu on March 22, respectively. This rapid decrease in salinity at the two end member stations, followed by just as rapid increase in salinities after the pulse ended (Fig. 4.4, March 30), indicates that the Caernarvon diversion had an overwhelming influence on salinity, and that diverted waters completely displaced ambient water in the estuary. This corroborates the results of the water volume calculations that indicated a total inflow from the diversion of 269 million cubic meters compared to the total volume of the upper 441 km² of the estuary of 212 million cubic meters.

There were rapid, non-conservative reductions in TN, TP, DIN, and DSi in the first 20 km of the study area with little change further into the estuary (Figs. 4.5 and 4.6). However, DIP was released in the first 20 km and then decreased (Fig. 4.6).

Concentrations at station 1 (river water) of TN, TP, DIN, DIP and DSi were 137-140, 5.0-5.1, 104-153, 1.1-1.3 and 114-121 µM, respectively, and 36-122, 1.8-3.2, 19 119, 0.5-1.8 and 44-110 µM, respectively, at the end member stations (Table 4.1). There were
observed decreases in concentration of up to 44% in TN, 62% in TP, 57% in DIN, 23% in DIP and 38% in DSi (Fig. 4.6).

![Figure 4.4](image-url)

Figure 4.4. Salinity versus distance from the Caernarvon diversion structure. Numbers refer to the water quality monitoring stations shown in Figure 4.1. Distance was determined as a straight-line from the structure to the respective sampling stations.

Simple linear regression analysis failed to reject the reduced model, and found a linear response with distance, with a common slope and intercept for both routes, for DIN and TN. DIN and TN concentrations were found to be decreasing with distance from the diversion structure at a rate of 3.1 (p<0.0001) and 2.0 (p<0.003) µM L⁻¹ km⁻¹, respectively. There was also a linear response with distance, with a common slope and
Figure 4.5. Changes in observed concentrations versus distance from the Caernarvon diversion of total nitrogen (TN) and total phosphorus (TP). Distance was determined as a straight-line from the structure to the respective sampling stations. * indicate statistically significant differences between the paired stations and Mississippi River water (alpha = 0.05).

Figure 4.6. Changes in observed concentrations versus distance from the Caernarvon diversion of dissolved inorganic silicon (DSi), nitrogen (DIN) and phosphorus (DIP). Distance was determined as a straight-line from the structure to the respective sampling stations. * indicate statistically significant differences between the paired stations and Mississippi River water (alpha = 0.05).

Figure 4.7. Changes in observed molar ratios with distance from the Caernarvon diversion of DSi:DIN, and DIN:DIP ratios. Horizontal dashed lines indicate the Redfield ratio. Distance was determined as a straight-line from the structure to the respective sampling stations. * indicate statistically significant differences between the paired stations and Mississippi River water (alpha = 0.05).
intercept for both routes, for the DIN:DIP ratio. Incoming river water and the last paired stations had an average DIN:DIP ratio of 107 and 26, respectively (Fig. 4.7). The DIN:DIP ratio was found to be decreasing with distance at a rate of 2.1 uM L\(^{-1}\) km\(^{-1}\) (p<0.0002). The reduced model was rejected for the DSi:DIN ratio, but there was a significant linear response with distance using the full model (p=0.007). The different slopes for the DSi:DIN ratio, which can be interpreted as rates of change for the two routes, was found to be 0.08 uM L\(^{-1}\) km\(^{-1}\) and 0.03 uM L\(^{-1}\) km\(^{-1}\) along the BTAB and RAC routes, respectively (p<0.0028).

Dunnett’s procedure indicated significant difference between river water quality and the last three pairs of stations for TN and DIN, all pairs for TP, and the last pair of stations for DSi (indicated by stars on Figs. 4.5, 4.6 and 4.7; alpha = 0.05). Dunnett’s procedure did not discern a significant difference for DSi:DIN, but a significant difference was detected in DIN:DIP ratios of incoming river water and the means of the last two pairs of stations.

Student’s t-test indicated significant differences in nutrient concentrations of incoming river water and of the mean of the estuarine stations for TN (p<0.0005), TP (p<0.005), DSi (p<0.048), and DIN (p<0.043). Student’s t-test did not discern a significant difference for DSi:DIN, but did find a significant differences in DIN:DIP ratios of incoming river water and the mean of the estuarine stations.

DISCUSSION

The results of this study show significant reductions in nutrient concentrations and changes in stoichiometric nutrient ratios occurred as diverted river water passed through the Breton Sound estuary (Figs. 4.5 & 4.6). This nutrient uptake may not be a
permanent loss pathway, however, if regeneration of nutrients occurs during the summer season as water temperature rise (Kemp and Boynton 1984). It is likely, however, that a major mechanism for the loss of nitrate is through denitrification, which is a permanent sink for nitrogen. Other studies in Louisiana and elsewhere have shown high rates of denitrification when river water with high nitrate concentrations flows into estuaries (Bachand and Horne 2000; Boynton et al. 1995; Brock 2001; Jenkins and Kemp 1984; Nixon et al. 1996; Smith et al. 1985).

Table 4.1. Concentrations of dissolved inorganic silicon (DSi), total nitrogen (TN), dissolved inorganic nitrogen (DIN), total phosphorus (TP), dissolved inorganic phosphorus (DIP) and salinity of incoming river water (Station 1, averaged data from March 9 & 15) and estuarine water quality stations along Bayou Terra aux Boeufs (BTAB) and River aux Chene (RAC; see Fig. 4.1).

<table>
<thead>
<tr>
<th>Station</th>
<th>Distance (km)</th>
<th>DSi (µM)</th>
<th>TN (µM)</th>
<th>DIN (µM)</th>
<th>TP (µM)</th>
<th>DIP (µM)</th>
<th>Salinity (PSU)</th>
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There were high fluxes of nitrate into the sediments and high rates of denitrification during the same period that we measured decreases in DIN (R. Twilley, personal communication). The subsurface anaerobic layer in the sediment supports the
reduction of NO$_3^-$ to N$_2$ and N$_2$O, which are released to the atmosphere (Reddy and Patrick 1984). This is a very important pathway for the loss of nitrogen from this system because approximately 95% of the DIN in diverted river water is in the form of nitrate. The alternate flooding and draining of the marsh soil surface resulting from fluctuating water levels due to tides and frontal passages ensure that diverted water has substantial contact with the marsh. Rates of denitrification are greater under conditions of fluctuating redox potential (flooding and draining cycles) than those where the redox is continuously high or continuously low, and is an important mechanism for the oxidation of ammonia to nitrate and subsequent denitrification (Smith et al. 1983).

Other potential pathways for nitrogen loss include vascular plant and phytoplankton uptake, burial, and reduction to ammonia (Reddy and Patrick 1984). Burial is an important loss pathway of material in the Louisiana coastal zone due to subsidence. DeLaune et al. (1981), for example, studied wetlands in Barataria Bay, Louisiana, and found nitrogen was buried in the interior marsh at a rate of 13.4 g-N m$^{-2}$ yr$^{-1}$, and Smith et al. (1985) found nitrogen burial of up to 23.0 g-N m$^{-2}$ yr$^{-1}$ in wetlands surrounding the Atchafalaya River delta.

In contrast to DIN, DIP is usually buffered in estuarine systems, being taken up when concentrations are high and released when they are low (Patrick and Khalid 1974). There is also rapid reduction of phosphorus during flocculation of Fe, Mn, Al, organic carbon and humic substances as salinity increases from 0 to 15-20 psu (Sholkovitz 1976). Phosphorus is also readily adsorbed onto the surface of sediments and lost from the water column as sediments are deposited on bay bottoms and surrounding marshes (Jitts 1959). Other major mechanisms for removal of phosphorus from the water column are plant
uptake, microbial incorporation and soil fixation (Patrick 1992). The fixation of phosphorus is more extensive and less reversible under alternating flooding-draining than under either continuously flooded or continuously moist soil conditions (Patrick 1992). Alternate flooding and drying increases the amount of phosphorus in the ferric phosphate and reluctant-soluble occluded fractions at the expense of the soluble and aluminum phosphate fractions (Patrick 1992).

Like phosphorus, silica is readily adsorbed onto the surface of sediments and lost from the water column as sediments are deposited (Mayer and Gloss 1980). Another major mechanism of loss for dissolved silicon is assimilation into diatom tests and eventual sinking (Day et al. 1989). Regeneration of Si is slow relative to both N and P. Regeneration of biogenic silica is primarily a chemical phenomenon whereas the regeneration of N and P are biologically mediated by grazers and bacteria (Conley et al. 1993). During this study there was most likely some DSi decreases due to diatom uptake, with little or no benthic regeneration due to low Spring temperatures, and most uptake was probably from adsorption onto sediments that were deposited in the estuary.

Most scientists agree that significant decreases in the Mississippi River nutrient concentrations would diminish the severity of the eutrophication in the northern Gulf of Mexico (Rabalais et al. 1996). Consistent with the hypothesis proposed by Officer and Ryther (1980), an increase in the DSi:DIN ratio would likely reduce the potential for harmful algal blooms (HAB). Nevertheless, while it is probable that the increasing DSi:DIN ratios would decrease the potential for non-diatom algal blooms, it is also possible that the increasing stoichiometric Si availability would increase the proportion of heavily silicified diatoms in the coastal phytoplankton assemblages (Dortch et al. 2001).
It is generally believed that heavily silicified diatoms are largely responsible for vertical carbon flux during spring and, consequently, for the formation of hypoxia on the Louisiana shelf (Dortch et al. 2001; Turner 2001). Most of harmful algal species are non-diatoms. Out of 24 potential HAB species that were identified in the Louisiana coastal waters (Dortch et al., 1999), four are diatoms (Pseudo-nitzschia sp.). Pseudo-nitzschia is considered to be a lightly-silicified diatom, whose increasing abundance over time is thought to reflect not only the increasing overall nutrient concentrations, but also the decreasing DSi:DIN ratios (Parsons and Dortch 2002). Assuming that the overall nutrient loading would remain unchanged, an increase in the riverine DSi:DIN ratios would probably cause a decrease in the abundance of Pseudo-nitzschia, but also an increase in the abundance of heavily silicified diatoms. This result would likely increase vertical carbon flux and exacerbate hypoxia in river-dominated coastal waters of the northern Gulf of Mexico. Thus, the most favorable management outcome for any freshwater diversion, as far as the coastal eutrophication problems are concerned, would be to reduce riverine N and P concentrations, while keeping the nutrient DSi:DIN ratio at or around 1:1. While this had not been entirely achieved in the described PULSES experiment, the study strongly suggests that freshwater diversions have a potential to significantly reduce the overall nitrogen loading and alter the stoichiometric ratios at which dissolved nutrients are delivered to the coastal ocean.

Boesch (1996) suggested that diversions of river water within the Mississippi delta may decrease the nitrogen load reaching hypoxic zone offshore, but may lead to hypoxic zones in inshore areas where none presently exists. Nutrient enrichment of coastal waters is known to cause enhanced production of organic material, leading to
subsequent decomposition and oxygen depletion near the bottom (Cloern 2001). During two years of intensive study in the Breton Sound estuary, however, hypoxia was not observed. Because water column stratification is an important factor affecting the development of bottom water hypoxia, it is unlikely that hypoxia will develop in a shallow and well-mixed Breton Sound estuary. This is consistent with the findings of Madden et al. (1988) and Day et al. (1992) for Fourleague Bay that is affected by the discharge of the Atchafalaya River. Chlorophyll levels during the diversions experiments were elevated only in the region surrounding Grand Lake (Fig. 4.1), and preliminary analysis of the phytoplankton community structure, both during high diversion events and later in the summer, showed a diverse community dominated by diatoms, without the strong occurrence of potentially harmful algal species (I. Ciugulea, personal communication).

CONCLUSIONS

This study indicates that the Breton Sound estuary acted as a sink for dissolved silicon and nitrogen, but at different rates, changing the stoichiometric nutrient ratio of water passing through the estuary. The DSi:DIN ratio rose from 0.9 at the Caernarvon diversion to 2.6 at the marsh end member stations, while the DIN:DIP ratio fell from 107 to 26 at the same stations. This study strongly suggests that freshwater diversions have a potential to significantly reduce the overall nitrogen loading and alter the stoichiometric ratios at which dissolved nutrients are delivered to the coastal ocean.

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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 1000 to 2000 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. 5.1). 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

* This manuscript, with minor changes, was published in a peer reviewed scientific journal and may be located through the following citation: Lane, R. R., J. W. Day, B. Marx, E. Reyes and G. P. Kemp. 2002. Seasonal and spatial water quality changes in the outfall plume of the Atchafalaya River, Louisiana, USA. Estuaries. 25: 30-42. Reprinted, with minor revisions, by permission of the Journal of the Estuarine Research Federation.
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, 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 Bays), and least in the offshore plume, with 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. 5.2). 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% 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. 5.1). 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 meters, but currently its depth is over 53 meters (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. 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.

Fig. 5.2. 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.

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. 5.1). 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 km². More detailed description of this area are given by van Heerden and Roberts (1980), Madden et al. (1988), and Perez et al. (2000).

METHODS

The Atchafalaya Delta estuarine complex was divided into three sampling areas: the Atchafalaya River plume, Vermilion-Cote Blanche Bays, and Terrebonne Marshes (Fig. 5.1). 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 nine Vermilion-Cote Blanche Bay, ten Terrebonne Marsh, and thirteen helicopter transects. Ten to fifteen water samples were collected during each boat transect in the Terrebonne marsh complex, and eleven during the Vermilion-Cote Blanche boat transects (Fig. 5.1). Helicopter transects ran 70 km from the mouth of the Atchafalaya River, through Atchafalaya Bay, into the Gulf of Mexico (Fig. 5.1). 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 top meter of water. The water samples were analyzed for total suspended solids (TSS), nutrients (NO₃⁻, NH₄⁺, and PO₄³⁻), chlorophyll a (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 hours, 60 ml from each water sample were filtered through pre-rinsed 25 mm 0.45 um 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 hr 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 with a 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 with the automated cadmium reduction method (detection limits: 0.05<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<mg N l$^{-1}$<2.0), and PO$_4^{3-}$ by the automated ascorbic acid reduction method (detection limits: 0.005<mg P l$^{-1}$<10.0), again with a 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%. Chlorophyll 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 with 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 nine 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. 5.1). 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 x 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 x season interactions, and p-values were used to test for differences between seasons and regions with SAS statistical software (SAS Institute Inc. 1999).

The second type of analysis focused on the Atchafalaya River plume transect data, with 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 (µ) of a response variable (NO₃⁻, NH₄⁺, PO₄³⁻ 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 \( \alpha \) was the overall mean and the f's were smooth functions. 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 NO₃⁻ and NH₄⁺, and phosphorus as PO₄³⁻. 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.

NO₃⁻ 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.

\[
Q_{\text{verm/cote bays}} = (0.01Q_{\text{atch}}+2.14)+(0.033Q_{\text{atch}}+67.714)
- (0.002Q_{\text{atch}}+1.279) \quad (5.1)
\]

\[
Q_{\text{terrebonne}} = (0.051Q_{\text{atch}}+181.266) \quad (5.2)
\]

\[
Q_{\text{near-shore}} = (0.658Q_{\text{atch}}+219.392)+(0.205Q_{\text{atch}}+26.424) \quad (5.3)
\]
The seasonal loading of NO₃⁻ 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 5m and 10m 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 (personal communication, William J. Wiseman and Dubravko Justic, Louisiana State University). The following estimates of area for each region were used: Atchafalaya Bay and Offshore area (<5m 1250 km²; <10m 2560 km²); Vermilion and Cote Blanche Bays (1185 km²); and Terrebonne marshes (975 km²).

The removal efficiency (RE) of NO₃⁻ was calculated using equation (5.4),

\[
RE = \frac{\text{Mass}_{\text{in}} - \text{Mass}_{\text{outadj}}}{\text{Mass}_{\text{in}}} \quad (5.4)
\]

where Mass_{\text{in}} is the concentration of the constituent in the Atchafalaya River, and 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 m 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 $\text{NO}_3^-$ 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 near-shore zone indicates that mixing of river water and Gulf water, not intrusions of other water masses, accounts for salinity patterns in the near-shore area in front of the Atchafalaya River mouth.

Total percent removal was calculated with equation (5.5),

$$\text{Total \% \ Removal} = \text{RE} \times \% Q_{\text{atch}} \quad (5.5)$$

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 near-shore coastal region in non-conservatively removing $\text{NO}_3^-$ from the Atchafalaya River.

RESULTS

Region*Seasonal Analysis

There were significant region by season interactions for all variables, except $\text{NH}_4^+$ and $\text{PO}_4^{3-}$. There were, however, significant seasonal trends ($p<0.001$) of high winter and low spring $\text{NH}_4^+$ concentrations (Fig. 5.3). The high winter concentrations were due to unusually high $\text{NH}_4^+$ 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. 5.3). 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 (Fig. 5.3). 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 (Fig. 5.3). Generally, 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. 5.3). During fall, the Cote Blanche Bay and Bayou Penchant regions had significantly higher (p<0.01) PO$_4^{3-}$ concentrations than the Atchafalaya River (Fig. 5.3). 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. 5.4). The Nearshore and Transition Zone regions had higher (p<0.03) TSS concentrations
Fig. 5.3. Results of seasonal analysis for NH$_4$\(^+\) (error bars are 1±s.e.), 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 ±1s.e.
during fall compared to summer, with the Nearshore region also having higher (p<0.02) fall TSS when compared to winter (Fig. 5.4). During winter, Vermilion and Cote Blanche Bay regions had significantly lower (p<0.001) TSS concentrations compared to the Atchafalaya River (Fig. 5.4). Bayou Panchant and Brady Canal regions had lower (p<0.01) TSS concentrations than the Atchafalaya River during all seasons except fall (Fig. 5.4). During winter, Southern Terrebonne regions had significantly higher (p<0.01) TSS concentrations than Bayou Panchant.

Chlorophyll a concentrations were higher (p<0.001) in the Transition zone compared to the Nearshore and Offshore regions during summer (Fig. 5.4). 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 (Fig. 5.4). During spring and summer, Bayou Panchant 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 (Fig. 5.4).

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. 5.4). 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 (Fig. 5.4). 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 (Fig. 5.4).

Fig. 5.4. Results of seasonal analysis for TSS, chlorophyll a, and salinity. Error bars are 95% confidence intervals of the mean.

N:P Molar Ratios

The Atchafalaya River N:P ratio fluctuated between 25:1 and 53:1 throughout the year (Fig. 5.3). 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 winter and spring, but decreased to near the Redfield ratio during the summer, and was less than 16:1 during the fall (Fig. 5.3). 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 (Fig. 5.3). The N:P ratio was less than 16:1 in the Terrebonne marsh regions during all seasons except spring, when the Bayou Panchent region ratio was 48:1 and the Brady Canal region was 16:1. (Fig. 5.3).

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 Atchafalaya Bay as river water flowed into the Gulf of Mexico (Fig. 5.5). Total suspended sediments tended to increase with distance from the Bay (Fig. 5.5). The linearity of these results, on a log scale, were highly significant, indicating a steady rate of change for these constituents with distance. Chlorophyll a, however, exhibited non-linear behavior and peaked at approximately 35 km from Atchafalaya Bay (Fig. 5.5). 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 (Fig. 5.5).

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. 5.6). Peak NH$_4^+$ concentrations occurred in December 1996 and February 1997, and then dropped to lowest levels in May, and rose again in late August (Fig. 5.6). Lowest
phosphate levels occurred in April, and peak concentrations occurred in July and maintained high concentration for the rest of the year (Fig. 5.6). TSS concentrations peaked during spring 1997 and winter 1998, and were lowest during the summer months (Fig. 5.6). Lowest chl a concentrations were recorded on January 1997, but maintained higher concentrations for the rest of the year (Fig. 5.6). Lowest salinities occurred January through March of 1997, and peak levels were during fall (Fig. 5.6).

Fig. 5.5. 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.
NO$_3^-$ Loading Rate Analysis

The near shore area received approximately 90% of the flow of the Atchafalaya River. This area, which was delineated as the area directly south and including Atchafalaya Bay with a depth of less than 5 m or 10 m, had a NO$_3^-$ loading rate of 136 and 66 g m$^{-2}$ yr$^{-1}$, respectively (Table 5.1). The NO$_3^-$ removal efficiency was 40% and 47%, respectively, which accounted for 36% and 42% of the total NO$_3^-$ carried by the river, respectively. Approximately 4% of Atchafalaya River water flowed into Vermilion and Cote Blanche Bays, providing a NO$_3^-$ loading rate of 8 g m$^{-2}$ yr$^{-1}$ (Table 5.1). 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$^{-1}$ (Table 5.1). The Terrebonne area had the highest removal efficiency with 90% of NO$_3^-$ being assimilated. This high removal efficiency, however, accounted for only 3% of the total NO$_3^-$ carried by the river. Overall, 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 near-shore 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. 5.7). Dilution with rainwater was unlikely to have caused substantial $\text{NO}_3^-$ decreases because of the high volume of Atchafalaya discharge, high evaporation rates, as well as high $\text{NO}_3^-$ concentrations in rainwater (Paerl 1997). Chemical reduction of $\text{NO}_3^-$ to $\text{NH}_4^+$ has been found to occur rapidly in the estuarine environment (Smith et al. 1982), with as much as 50% of $\text{NO}_3^-$ applied to marine sediments being reduced to $\text{NH}_4^+$ (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.

The Atchafalaya Delta estuarine complex had 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 between 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. However, this is the first estimate of
nitrate reduction, and more careful study is needed before definitive budgets can be
constructed.

![Graph showing salinity mixing diagrams for the Atchafalaya River Plume, Vermilion and Cote Blanche Bays, and Terrebonne Marsh regions.](image)

Fig. 5.7. Salinity mixing diagrams for the Atchafalaya River Plume, Vermilion and Cote Blanche Bays, and Terrebonne Marsh regions.

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. Conversely, 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
Table 5.1. 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 5m and 10m 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 m 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.

<table>
<thead>
<tr>
<th></th>
<th>NO$_3^-$ Loading (g m$^{-2}$ yr$^{-1}$)</th>
<th>Regional % NO$_3^-$ Removal</th>
<th>Total % NO$_3^-$ Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5m</td>
<td>10m</td>
<td>5m</td>
</tr>
<tr>
<td>Verm/Cote Bays</td>
<td>8</td>
<td>8</td>
<td>45%</td>
</tr>
<tr>
<td>Near Shore</td>
<td>136</td>
<td>66</td>
<td>40%</td>
</tr>
<tr>
<td>Terrebonne</td>
<td>5</td>
<td>5</td>
<td>90%</td>
</tr>
<tr>
<td>Total Removal:</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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). Therefore, 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 the Atchafalaya River, whereas NH$_4^+$ was defined as regenerated nitrogen resulting from remineralization within the benthos or the water column. With this definition, it appeared that regenerated nitrogen composed a large portion of the available dissolved inorganic nitrogen to autotrophic organisms, especially during fall in the Atchafalaya Delta (Table 5.2). There was
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.

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, thus maintaining moderate ambient concentrations (Jitts 1959; Patrick and Khalid 1974). Also, cyclic aerobic and anaerobic conditions in the top several centimeters of the wetland soil effect the sorption and release of PO$_4^{3-}$, with PO$_4^{3-}$ being released during anaerobic conditions (Patrick and DeLaune 1977), possibly exacerbating 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 TP behaved similarly in Fourleague Bay, Louisiana, with little change in concentration throughout the year.
Table 5.2. The percentage of dissolved inorganic nitrogen as NH$_4^+$.

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

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. 5.3). The response of phytoplankton, as measured by chlorophyll 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, spatial and temporal changes in biomass) are largely controlled by light availability, and in many estuaries the spatial distribution of phytoplankton biomass...
production has an inverse relationship with the distribution 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. Regionally, 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 and Day (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 and sea water (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 Rhone delta, France.

CONCLUSIONS

The Atchafalaya River was the primary source for nutrients and sediments to the Atchafalaya Delta estuarine complex. There were significant non-conservative 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 chlorophyll $a$ 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 chlorophyll $a$ 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.

LITERATURE CITED


Sources of Unpublished Materials:

Justic, D. personal communication. Louisiana State University, Baton Rouge, Louisiana 70803 USA

121
Wiseman, W. personal communication. Louisiana State University, Baton Rouge, Louisiana 70803 USA
CHAPTER 6
CONCLUSIONS

I utilized three regions in the Louisiana coastal zone to test several hypotheses regarding the effect on water quality of diverting Mississippi River water into coastal wetlands: the Atchafalaya delta region, the Bonnet Carre Spillway and the Caernarvon diversion. These study areas differed greatly in the magnitude of riverine input and the size of the receiving basin. There was an order of magnitude difference in riverine input between the Atchafalaya delta, with flow ranging from 2,800 to 17,500 m$^3$ sec$^{-1}$, and the Caernarvon diversion and the Bonnet Carre Spillway, which had maximum flows of 212 and 386 m$^3$ sec$^{-1}$, respectively. There were two orders of magnitude difference in the size of the receiving basins, with the Atchafalaya delta region and the Caernarvon diversion having 3400 and 1100 km$^2$, respectively, while the Bonnet Carre Spillway only had 26 km$^2$.

Despite fundamental differences in the magnitude of riverine input and the size of receiving basins, water quality in the three regions behaved very similarly to the introduction of river water. There was rapid deposition of suspended sediments in all regions due to decreased water velocity and sediment settling. This occurred even in the Bonnet Carre Spillway, which had a very small area for deposition to occur, but where up to 80% of introduced sediments were retained (Chapter 2). Nutrient concentrations, especially nitrate, were non-conservatively reduced as riverine water passed through wetlands. Up to 47% of nitrate was removed at the Atchafalaya delta region, 57% at the Caernarvon diversion, and 42% at the Bonnet Carre Spillway. Associated with decreasing nutrient concentrations, there were also changes in nutrient stoichiometric
ratios. There were decreasing DIN:DIP ratios with distance from the riverine source at all three regions of this study, and increasing DSi:DIN ratios were found at the Caernarvon diversion (DSi was not measured at the regions). Salinity was also found to be greatly influenced by riverine discharge. For example, at the Caernarvon diversion salinity was decreased from 5-10 psu to 0 throughout most of the estuary with just two-weeks of riverine discharge (Chapter 4). These similarities in the response of water quality to riverine input can be summarized as follows: there were (1) rapidly decreasing suspended sediment concentrations with distance from the riverine source; (2) decreasing nutrient concentrations with distance from the riverine source; (3) decreasing DIN:DIP and increasing DSi:DIN ratios with distance from the riverine source; and (4) substantial decreases in salinity throughout the receiving basins. Listed below are the hypotheses and major results for each of the individual studies included in this dissertation.

At the Bonnet Carre Spillway I hypothesized there would be (1) substantial decreases in suspended sediments due to decreased water velocity and sediment settling; (2) low or moderate decreases in nutrient concentrations as water passed through the spillway; and (3) decreases in the DIN:DIP ratio and increases in the DSi:DIN ratio as water passed through the spillway and entered Lake Pontchartrain. Approximately 6.4 x 10^8 m^3 of Mississippi River water was diverted into Lake Pontchartrain over 42 days. As water passed through the Bonnet Carre Spillway, there were reductions in total suspended sediment concentrations of 82-83%, in nitrite+nitrate of 28-42%, in total nitrogen (TN) of 26-30%, and in total phosphorus (TP) of 50-59%. The DSi:DIN ratio generally increased and the N:P ratio decreased from the river to the plume edge in Lake Pontchartrain. These results agree with the hypotheses given above, with exception of higher than
expected reduction in nutrient concentrations, probably due to our conservative estimate of the area impacted wetlands.

Chapter 3 of this dissertation focused on the spatial and temporal changes in suspended sediment, chlorophyll a, salinity and temperature in the Breton Sound estuary over a two-year period. I hypothesized there would be (1) rapid reduction of suspended sediments concentrations with distance from the diversion structure due to decreased water velocity and sediment settling; (2) low chlorophyll a levels in areas of high suspended sediment near the Caernarvon structure, with rising chlorophyll levels immediately after suspended sediment concentrations decrease to low levels, and then decreased chlorophyll a levels Gulfward; and (3) a reduction in salinity and temperature throughout the estuary associated with structure discharge. Twenty-seven transects were carried out in the estuary from September 2000 through August 2002. Total suspended sediment generally decreased with distance from the Caernarvon structure (≈150 down to ≈30 mg L⁻¹), reaching 10-30 km into the estuary, but often displayed a turbidity maximum in the upper estuary near the diversion during Winter, and there were widely fluctuating TSS levels at the outer reaches of the estuary associated with storm events. Chlorophyll concentrations near the diversion were low due to light limitation, but increased after suspended sediments decreased below 80 μg L⁻¹. Chlorophyll levels often peaked at mid-estuary (≈45 μg L⁻¹), and gradually decreased to low levels in Breton Sound (≈5 μg L⁻¹). Temperature of incoming Mississippi River water ranged from 6-32°C and generally equilibrated to the rest of the estuary within 10 km from the diversion, but there were several times when cooler water from the diversion propagated through the entire estuary. The diversion affected salinity throughout the estuary, with
the scale of the effect dependent on discharge volume. These results support the hypotheses for this study.

I studied changes in nutrient concentrations and ratios in water flowing from the Caernarvon diversion through the Breton Sound Estuary during a several week period when a large ‘pulse’ of water was released from the structure. I hypothesized that as water passed through the estuary there would be (1) decreases in dissolved inorganic nitrogen (DIN) and silicate (DSi), with larger decreases in DIN than DSi; (2) small or no changes in dissolved inorganic phosphorus (DIP) concentrations; (3) decreases in the DIN:DIP ratio, and (4) increases in the DSi:DIN ratio. River water was discharged through a diversion structure at Caernarvon as a two-week pulse that peaked at 220 m$^3$s$^{-1}$. There were reductions in concentrations of dissolved inorganic Si, N, and P of up to 38%, 57% and 23%, respectively, as water flowed through the estuary. The DSi:DIN ratio rose from 0.9 at the Caernarvon diversion to 2.6 at the Gulf end member station, while the DIN:DIP ratio fell from 107 to 26. These results strongly agree with the hypotheses of this study, with exception of the relatively large decrease in DIP concentrations.

I examined inorganic nutrient, sediment, chlorophyll a, and salinity concentrations over a large area of the Atchafalaya River estuarine complex. I hypothesized there would be (1) a reduction in salinity throughout the estuarine complex associated with river discharge (2) strong non-conservative reduction of NO$_3^-$ and total suspended sediments; and (3) regeneration of NH$_4^+$ and PO$_4^{3-}$ during the summer. 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. Salinity in the estuarine complex fluctuated seasonally, with the lowest salinities occurring during high river discharge.
There was a 41-47% decrease in NO$_3^-$ concentrations and as Atchafalaya River water passed through the estuarine complex. Total suspended sediments decreased as river water flowed through the estuarine complex, but displayed a turbidity maximum in offshore waters during summer. 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 or bay. With exception of a turbidity maximum in Atchafalaya Bay, these results strongly agree with the hypotheses of this study.

In summary, the following conclusions can be made from these studies of the effect on water quality of riverine input into coastal wetlands:

- Riverine input has a pronounced effect on salinity throughout a receiving basin with significant reductions in all three study areas. Nutrients and sediments are actively deposited and/or transformed as riverine derived water passes through these estuarine systems, whereas salinity acts conservatively. This is an important conclusion because much of the Mississippi delta is degrading in part from saltwater intrusion, which may be alleviated with modest freshwater introduction.

- There is rapid and effective trapping of suspended sediments in estuarine systems due to decreased water velocity and sediment settling. The turbidity maximums found during the Caernarvon and Atchafalaya River studies are not exceptions to this conclusion because (1) the Caernarvon turbidity maximums were most likely due to resuspension of previously
deposited materials; and (2) the Atchafalaya River turbidity maximums occurred several km offshore, and were preceded by a large reductions in TSS concentration.

- Nitrate concentrations are rapidly reduced in the estuarine environment due to processes such as denitrification, assimilation and reduction. This is an especially important finding because (1) most nitrogen in river water is in the form of nitrate; and (2) excessive nitrate inputs by rivers has been linked to eutrophication in many coastal areas around the world.

- Dissolved inorganic molar DSi:DIN ratios increase, and N:P ratios decrease as riverine water flows through an estuarine system. This is a very important conclusion because over the last century there have been considerable increases in the DIN:DIP ratios and decreases in the DSi:DIN ratios of the lower Mississippi River. It is widely believed that changes in the stoichiometric ratios in rivers exacerbate the eutrophication process in the adjacent coastal waters, primarily by reducing the potential for diatom growth in favor of noxious non-siliceous forms such as dinoflagellates. The use of coastal wetlands and shallow water bodies to process Mississippi River water before entering the Gulf of Mexico has been proposed as a partial solution to help reduce the size of the hypoxic zone, as well as restore and maintain rapidly eroding coastal wetlands.
APPENDIX A

LETTERS OF PERMISSION

2 April 2002

Robert A. Lane
Coastal Ecology Institute
Louisiana State University
Oyster House IA
Via email: violencia@hotmail.com

Dear Robert A. Lane,

Regarding the above referenced publication. In Vol 17, 2004, pp 411-423, Lane et al; 'The IEP experiment: a cautionary tale of the...

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Jennifer Jones
Rights Assistant
Global Rights Department

Elsevier Science
On March 20, 2002, Robert Lane wrote:

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I intend to use the paper recently published in Ecological Engineering under the following citation for inclusion in my PhD dissertation. Please inform me of any specific forms or permission I need in order to do this.

Sincerely,

Robert R. Lane
Research Associate
Coastal Ecology Institute
Louisiana State University

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Stephen T. Reitheld

KSF/WK Program, Journal of the KSR Research Federation
Dr. Stephen T. Reitheld
KSR Research Federation
Department of Biology, University of Mississippi
300 University Blvd., University, MS 36777 USA
Phone: 662-915-5302, Fax: 662-915-5301
Email: ksfwk@emiss.com
Website: http://www.emiss.com

On Mon, 4 Mar 2002, Robert Lane wrote:

> Mr. Whit,
> 
> I intend to use mKRF 2002. "Seasonal and annual water quality changes in the
>_optical areas of the rhododendron zone dominated by S. reticulatum". Could I
> _Hebb, Shalmanin, To learn any special terms or permission that I need in
> order to do this?
> 
> Sincerely,
> 
> Robert R. Lane
> Research Associate
> USDA Forest Service
> Central Ecology Institute
> Louisiana State University
> 
> 
> Join the world's largest e-mail service with MSN Hotmail.
> http://www.hotmail.com
>
APPENDIX B

SELECTED RESULTS OF STATISTICAL ANALYSIS USED IN CHAPTER 3

Figure B1. Discharge x season x distance interaction for salinity. Asterisk indicates a significant difference between discharge levels. Type 1 error rate = 0.001 after Bonferroni adjustment to control experiment wise error rate due to multiple comparisons (0.05 divided by 36 comparisons).
Figure B2. Discharge x season x distance interaction for temperature. Asterisks indicate significant differences, with asterisks above the line indicating significant differences for all three points, and asterisks between lines indicating significant differences for points above and below. Type 1 error rate = 0.001 after Bonferroni adjustment to control experiment wise error rate due to multiple comparisons (0.05 divided by 36 comparisons).
Figure B3. Discharge x season x distance interaction for total suspended sediments (TSS). Asterisks indicate significant differences, with asterisks above the line indicating significant differences for all three points, and asterisks between lines indicating significant differences for points above and below (N.S.=non-significant). Type 1 error rate = 0.004 after Bonferroni adjustment to control experiment wise error rate due to multiple comparisons (0.05 divided by 12 comparisons).
Figure B4. Discharge x season x distance interaction for total suspended sediments (TSS). Type 1 error rate = 0.001 after Bonferroni adjustment to control experiment wise error rate due to multiple comparisons (0.05 divided by 36 comparisons). N.S.=non-significant.
APPENDIX C:

FLOW-THROUGH DATA USED IN CHAPTER 3
VITA

Robert R. Lane was born on June 24, 1970, in Kingston, New York. He spent his childhood living in the Catskill State Park in the Esopus River valley. He began his undergraduate work as an architecture major at Dutchess Community College in September 1988, but changed his major the following semester to environmental science. He received an Associate in Science from Ulster Community College in May 1991, and a Bachelor of Science from the SUNY College of environmental science & forestry (SUNY-ESF) in May 1993. During his last semester at SUNY-ESF, Mr. Lane had the opportunity to take a course in Ecosystem Ecology taught by Dr. Charlie Hall. After a class mid-semester, Dr. Hall gave Mr. Lane the phone number of Dr. John W. Day as a possible job source. Approximately six months later, Mr. Lane began a campaign of weekly telephone calls to Dr. Day in an attempt to convince the professor to hire him on a project. After three months, Dr. Day relented and offered Mr. Lane a three-month temporary position. Mr. Lane immediately accepted the position and drove from upstate New York to arrive in Baton Rouge, Louisiana, on January 4, 1994. After successfully completing the three-month study, he was continued as a full time research associate, working on several projects with Dr. Day, including the Bonnet Carre Spillway study included in this dissertation. Mr. Lane began taking courses offered free of charge by Louisiana State University (LSU) to employees. He received a Master of Science from LSU in May 1998. He currently works on numerous wetlands related projects in Louisiana for both LSU and a private consulting firm, Comite Resources. His research interests include wetland ecology and restoration, nutrient cycling, nutrient use
efficiency, wetland wastewater treatment, eustatic sea-level rise, marsh elevation and edge erosion, and the effects of humans on ecosystem function and sustainability.