Changes in Carbon, Nutrient, and Trace Metal Concentrations During the Transition from Freshwater to Marine Environments - A Case Study in Southwest Louisiana

Songjie He
Louisiana State University and Agricultural and Mechanical College

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CHANGES IN CARBON, NUTRIENT, AND TRACE METAL CONCENTRATIONS DURING THE TRANSITION FROM FRESHWATER TO MARINE ENVIRONMENTS - A CASE STUDY IN SOUTHWEST LOUISIANA

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 School of Renewable Natural Resources

by
Songjie He
B.S., Minzu University of China, 2009
M.S., Minzu University of China, 2013
May 2018
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ABSTRACT

Rivers carry terrestrial nutrients and other materials to estuaries, affecting biogeochemical cycles and ecosystems in coastal margins. This dissertation research incorporated five studies to investigate the dynamics of carbon, nutrients, and trace metals in four major coastal rivers in southwest Louisiana – the Sabine, Calcasieu, Mermentau, and Vermilion Rivers. The overarching goal of this research was to broaden the knowledge and understanding of biogeochemical processes in freshwater – saltwater mixing zones. These studies employed decade-long monitoring records of water chemistry, utilized monthly field measurements conducted over a two-year period, and used analysis of over 200 water samples for carbon, nitrogen, phosphorus, and trace metals. Results gained from the studies showed that land use effects were clearly reflected in the much higher TOC, NO$_3$+NO$_2$, TKN, and TP yields from the Mermentau and Vermilion Rivers draining more agriculture-intensive watersheds, when compared with those of the Sabine and Calcasieu Rivers. The high average pCO$_2$ value (2528 µatm) for the entire Calcasieu River reach suggests that an estuarine river functions as a CO$_2$ source in the atmosphere. The DIC concentrations and δ$^{13}$C$_{DIC}$ values increased rapidly with the increase of salinity. The DIC concentration appeared to be mostly controlled by conservative mixing. The δ$^{13}$C$_{DIC}$ values during the study period were either close to or below those values suggested by the conservative mixing model, implying that an estuarine river can fluctuate from a balanced system to a heterotrophic system seasonally. The DOC concentration decreased with decreasing distance to the northern Gulf of Mexico, but to a much smaller degree. The depleted δ$^{13}$C$_{DOC}$ values (-30.56‰ to -25.92‰) in the Calcasieu River suggest that the DOC discharged by this river was highly terrestrially derived. The DIP concentration versus salinity plots in the Calcasieu River suggest some sources were present throughout the Calcasieu Estuary. Such
mixing dynamic were probably caused by desorption of DIP from suspended solids and river bed sediments, urban inputs, as well as stronger calcium carbonate and phosphorus co-precipitation at the marine endmember. The total Sr concentration and the Sr/Ca ratio both increased significantly with increasing salinity. In contrast, salinity has no effect on Ba concentration.
CHAPTER 1. INTRODUCTION

Due to rapid population growth, urbanization, land use change, and intensive agriculture in many river basins worldwide, estuaries are the most heavily impacted aquatic systems on Earth (Kennish, 2002; Bianchi, 2007). Nutrient enrichment and chemical pollution caused by excessive land-based sources and sea level rise caused by climate change are two main stressors to estuarine rivers. Eutrophication due to nutrient enrichment has become the primary water quality issue in the world (Smith, 2003; Conley et al., 2009). A hypoxic zone with dissolved oxygen (DO) concentrations < 2 mg/L has been observed each summer since the mid-1980s off Louisiana’s coast in the northern Gulf of Mexico (NGOM) (Rabalais et al., 2007; Turner et al., 2008; Rabalais et al., 2010). A recent study (Obenour et al., 2013) also found that the thickness of the hypoxic zone has increased over the past 30 years. Eutrophication in estuarine and coastal waters of the United States often causes hypoxic and anoxic conditions and large-scale harmful algal blooms (Scavia and Bricker, 2006), leading to fish kill and lost food processing income (O’Connor and Whitall, 2007; Diaz and Rosenberg, 2011).

Over the past century, the global mean sea level has increased by nearly 200 mm (e.g. IPCC, 2007; Church and White, 2011) due to an increase in 20th century ocean heat content (Munk, 2002) and mass increase (Miller and Douglas, 2004). The rise rate was found to be accelerating in the past two decades, averaging 3.2 mm per year in a range between 2.8 and 3.6 mm (IPCC, 2013). As sea level rise continues, saltwater intrudes upstream inland, which can cause changes in water chemistry, especially salinity and pH, and changes in soil physical and chemical properties of estuarine river floodplains. Salinity and pH are two important factors affecting many chemical and biological processes in estuarine waters. Salinity and pH have been found to strongly affect mobility and flux rates of carbon, nutrients, and trace metals (e.g.,
Turner, 1996; Kaldy et al., 2005; Meng et al., 2015) when they are carried by rivers to various estuarine/coastal systems around the world.

My dissertation research aims to address the issues introduced above, specifically in southwest Louisiana, as the coastal region has been strongly affected by nutrient enrichment seawards and sea level rise and saltwater intrusion landwards. The overall goal of this research was to broaden the knowledge and understanding of biogeochemical processes of carbon, nutrient, and trace metals in freshwater – saltwater mixing zones. This research consists of five interrelated studies that investigate the dynamics of carbon, nutrients, and trace metals in four major coastal rivers in southwest Louisiana – the Sabine, Calcasieu, Mermentau, and Vermilion Rivers. These studies aim to test the following hypotheses: 1) The best management practices since the early 1990s have had positive effects in water quality; 2) The nutrient, carbon, and trace metal concentrations vary largely spatially and temporally in an estuarine river, and salinity is the main impact factor on nutrient, carbon, and trace metal dynamics in the freshwater – saltwater mixing zone.

The objectives of these studies are 1) to quantify fluxes of nutrients and carbon from four major coastal rivers in Louisiana to the NGOM; 2) to determine seasonal, interannual, and decadal trends of nutrient and carbon fluxes in these rivers; 3) to determine spatial and temporal variations of carbon, nutrients, and trace metals within an estuarine river; 4) to assess mixing dynamics across salinity gradients for carbon, nutrients, and trace metals in an estuarine river. To achieve these objectives, five interrelated studies were conducted, and this dissertation attempts to introduce them in five separate chapters. Following this Introduction, chapter 2 presents a study of the long-term inputs of total organic carbon and nutrients from four major coastal river basins to the summer hypoxic zone of the NGOM. Chapter 3 discusses the freshwater-saltwater
mixing effects on dissolved carbon and CO\textsubscript{2} outgassing of a coastal river entering the NGOM. Chapter 4 presents a study of dissolved carbon transport and transformation along an estuarine river with stable isotope analysis. Chapter 5 focuses on recent total and dissolved inorganic phosphorus transport from three coastal watersheds under varied agriculture intensities to the NGOM, and mixing dynamics in one of the coastal watersheds. Chapter 6 presents a study of dissolved Sr, Ba, and Ca concentrations and ratios along an estuarine river. Chapter 7 summarizes the major findings from the five studies. Chapters 2 through 6 are written as stand-alone manuscripts with their own introductions, methods, results, and discussion sections.

Chapter 2 was published as two journal papers in Marine Pollution Bulletin and Water, Air, & Soil Pollution. Chapter 3 was published in Estuaries and Coasts. Chapter 4 was published in Estuarine, Coastal and Shelf Science. Chapter 5 is currently under review in Water, Air, & Soil Pollution. Chapter 6 was published in Water.
CHAPTER 2. LONG-TERM HISTORIC CARBON AND NUTRIENTS

2.1 Introduction

A hypoxic zone with dissolved oxygen (DO) concentrations < 2 mg L\(^{-1}\) has been observed each summer since the mid-1980s off Louisiana’s coast in the northern Gulf of Mexico (NGOM; Rabalais et al., 2007; Turner et al., 2008; Rabalais et al., 2010). A recent study (Obenour et al., 2013) also found that the thickness of the hypoxic zone has increased over the past 30 years. The hypoxic area has large reaching effects, ecologically and economically, including massive fish kill and economic consequence from lost fisheries and food processing incomes (O’Connor and Whitall, 2007; Diaz and Rosenberg, 2011). Researchers have attributed this “dead zone” to the enrichment of nitrogen and phosphorus (Turner and Rabalais, 1991, 1994) as high annual inputs of the nutrients have been found from the Mississippi-Atchafalaya River System (MARS) (Goolsby et al., 2001; Turner et al., 2012; Xu, 2013).

As is the case in terrestrial ecosystems, nitrogen and phosphorus are key nutrients in water regulating aquatic plant productivity. These elements can limit rates of biological activities, individually or in combination, and the Redfield ratio (16 N: 1 P, Redfield, 1958) often serves as an index for nutrient limitation to aquatic ecosystems. Early research established that a low N:P supply ratio (< 29:1) would be favorable for the production of cyanobacteria blooms (Smith, 1983), because cyanobacteria are able to compete for nitrogen better than other
phytoplankton species when nitrogen is limited. In an undisturbed natural ecosystem, nitrogen is accumulated through nitrogen fixation from the atmosphere, while phosphorus input is through mineral weathering and dust deposition. Human activities (e.g., intensive agriculture, combustion of fossil fuels, and land use change) have largely altered sources and fluxes of nitrogen and phosphorus (Hill et al., 2011), causing changes in biological activities in aquatic systems around the world. As an indicator of phytoplankton growth, N:P ratio can be used to demonstrate the human alterations in biological activities in aquatic systems.

Nutrient availability, especially nitrogen, can be affected by organic carbon levels in water bodies (Newcomer et al., 2012; Xing et al., 2013). For instance, denitrification bed, which uses organic carbon as substrates, is a cost-effective technology for removing nitrate from point source discharge (Cameron et al., 2010). To manage nitrogen and phosphorus, it is important to manage the amount and availability of organic carbon. Therefore, riverine transport of organic carbon to the oceans plays a significant role in the global carbon, nitrogen, and phosphorus cycling. At the same time, the input of organic carbon to the oceans provides a crucial source of carbon to the food web of estuarine ecosystems.

As the largest river system in North America, MARS has been investigated intensively. Fluxes of nutrients and organic carbon from MARS to the NGOM have been estimated for the past several decades (e.g. Bianchi et al., 2007; Turner et al., 2007; Xu, 2006 and 2013). A high organic carbon input to NGOM has been quantified from the Mississippi River main stem (403.0 ×10⁴ t yr⁻¹, Bianchi et al., 2007) and from its tributary, the Atchafalaya River (113.9 ×10⁴ t yr⁻¹, Xu, 2013). A high NO₃+NO₂ nitrogen input to the NGOM has also been quantified from the Atchafalaya River (179 ×10³ t yr⁻¹, Xu, 2013), and from MARS (953 ×10³ t yr⁻¹, Goolsby et al., 2001). High levels of phosphorus fluxes were reported for the Mississippi River (136 ×10³ t yr⁻¹,
Goolsby et al., 1999) and the Atchafalaya River (41 × 10³ t yr⁻¹, Xu, 2013), providing critical information on the causes of the hypoxic dead zone in the NGOM. However, little is known about fluxes of nutrients and carbon from four major coastal rivers in southwest Louisiana that discharge a considerable amount of freshwater and sediment to NGOM (Rosen and Xu, 2011).

I hypothesize that 1) intensive agriculture will cause organic carbon, nitrogen, and phosphorus enrichment; 2) best management practices since the early 1990s have positive effects on water quality protection. The objectives of this study are to quantify the fluxes of total organic carbon (TOC), nitrogen, and phosphorus from the four major coastal rivers in southwest Louisiana to the NGOM, and to determine seasonal, interannual, and decadal trends of TOC, nitrogen, and phosphorus inputs in these rivers.

2.2 Methods

2.2.1 Study area

The four coastal rivers investigated in this study are the Sabine, Calcasieu, Mermentau, and Vermilion Rivers, all of which enter the NGOM in southwest Louisiana, USA (Figure 2.1). These rivers flow through the Chenier Plain comprising an area of approximately 5000 km² with a west-east coastline of about 200 km (Gammill, 2002), stretching geographically from approximately 29.5° N to 33.2° N and from 91.3° W to 94.0° W. The Sabine River has a drainage area of 25,267 km² with a total length of 893 km (Phillips, 2003) bordering Texas and Louisiana and draining into the Sabine Lake before the NGOM. The Calcasieu River is 322 km long with a drainage area of 9780 km² (Nichol et al., 1992), discharging into the Calcasieu Lake before the NGOM. The Mermentau River drains a land area of 16,997 km² with a length of 115 km (USACE, 2015), and discharges into the Grand Lake before reaching the NGOM. The
Vermilion River is 116 km long with a basin area of 4470 km$^2$ (USEPA Region 6, 2001; USACE, 2004), draining into the Vermilion Bay.

![Image of the geographical location of the rivers and sampling sites](image)

Figure 2.1. Geographical location of the Sabine, Calcasieu, Mermentau, and Vermilion Rivers entering the Northern Gulf of Mexico, and the locations of USGS river gauging stations and LDEQ water quality sampling sites.

During the past half century, these rivers were hydrologically altered to various degrees. These alterations may have had considerable effects on water quality and riverine nutrient transport. For instance, along the Sabine River, three major dams were constructed with the Toledo Bend Dam (above the river gauge and water quality stations used in this study) controlling outflow in the river’s middle-low reach. Along the Calcasieu River, two dams were constructed in its upper reach, and a saltwater barrier gate (below the river gauge and water quality stations used in this study) was constructed in its middle-low reach to prevent saltwater intrusion further upstream as well as to regulate freshwater outflow. The Mermentau and
Vermilion Rivers are two shorter rivers. Except for some navigational locks, no dams were constructed along the main channels of these two rivers. The Vermilion River is heavily human-modified with canals for agriculture irrigation. In addition to local runoff, this river also receives water from the Atchafalaya River (Rosen and Xu, 2011), a distributary that discharges approximate 25% of the Mississippi River’s flow, as well as the total flow of the Red River (Xu, 2013). This river diversion may have resulted in a relatively stable flow throughout the year as Rosen and Xu (2011) found little variation in seasonal discharge of the Vermilion River.

The climate of the study area is characterized by hot, humid summers and generally mild winters. Land use conditions are different among the four river basins. The Mermentau and Vermilion River Basins are much more dominated by agricultural land use (67% and 61%, respectively) when compared with the Sabine and Calcasieu River Basins (14% and 26%) (Baker 1999; LDEQ 2001 and 2002; Rosen and Xu, 2011). The latter two river basins have much higher forest-pasture land use (54% and 51%) than the first two do (7% and 22%). The difference in land use dominance may have profound effects on nutrient input from the river basins.

2.2.2 Data collection

To estimate total organic carbon, nitrogen, and phosphorus fluxes for each of the four coastal rivers, long-term (1980-2009) daily discharge at the lower Sabine, Calcasieu, Mermentau, and Vermilion Rivers were collected from the U.S. Geological Survey (USGS). The gauge stations were chosen based on their proximity to the mouth of the river for optimal drainage representation and minimal tidal influence. Specifically, the locations with their USGS gauge station numbers were Sabine River near Ruliff, TX (08030500), Calcasieu River near Kinder, LA (08015500), Mermentau River at Mermentau, LA (08012150), and Vermilion River at Perry, LA (07386980).
Long-term monthly water quality data were obtained from the Louisiana Department of Environmental Quality (LDEQ) for the following stations (station#:): Sabine River northeast of Orange, TX (LA110301_00), Calcasieu River near Kinder, LA (LA030103_00), Mermentau River at Mermentau, LA (LA050401_00), and Vermilion River at Perry (LA060802_00) (Figure 2.1). Table 2.1 summarized the station identification numbers and data coverage of the four rivers. Water quality data included monthly measurements on a series of chemical and physical parameters, of which concentrations of TOC, total Kjeldahl nitrogen (TKN, which is the sum of organic nitrogen and ammonia nitrogen), and nitrate plus nitrite nitrogen (NO$_2$+NO$_3$), and total phosphorus (TP) were used in this study. Details on field sampling and laboratory analysis methods can be found in LDEQ’s Quality Assurance Project Plan for the Ambient Water Quality Monitoring Network (LDEQ, 2013).

Table 2.1. River gauge and water quality sampling stations and their data coverage of the four studied rivers in southwest Louisiana entering the northern Gulf of Mexico (USGS = U.S. Geological Survey; LDEQ = Louisiana Department of Environmental Quality).

<table>
<thead>
<tr>
<th>River</th>
<th>Gauge station</th>
<th>Water quality station</th>
<th>Drainage area (km$^2$)</th>
<th>Data coverage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sabine</td>
<td>USGS 08030500</td>
<td>LA110301_00</td>
<td>25,267$^a$</td>
<td>1980-2009</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>24,162$^c$</td>
<td>1980-2006</td>
</tr>
<tr>
<td>Calcasieu</td>
<td>USGS 08015500</td>
<td>LA030103_00</td>
<td>9,780$^b$</td>
<td>1980-2009</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4,403$^c$</td>
<td>1980-2009$^i$</td>
</tr>
<tr>
<td>Mermentau</td>
<td>USGS 08012150</td>
<td>LA050401_00</td>
<td>16,997$^c$</td>
<td>1984-2009</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3,577$^g$</td>
<td>1980-2009</td>
</tr>
<tr>
<td>Vermilion</td>
<td>USGS 07386980</td>
<td>LA060802_00</td>
<td>4,470$^d$</td>
<td>1984-2009</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1,259$^b$</td>
<td>1980-2009$^i$</td>
</tr>
</tbody>
</table>


2.2.3 Data analysis

Riverine concentrations of TOC, TKN, and TP have been found to be closely and positively correlated with river discharge. In this study, a log-linear regression model using daily average discharge was developed to estimate daily fluxes of TOC, TKN, and TP. The regression,
i.e., rating curves for TOC, TKN and TP, can be described in a general equation as below (Xu, 2013):

\[
\ln(S_i(t)) = b_0 + b_1 \ln(Q_{day}(t)) + \varepsilon(t)
\]  

(1)

where \(Q_{day}(t)\) represents the daily discharge in liters, \(S_i(t)\) is the daily flux in grams, \(i\) is the type of element, and \(\varepsilon(t)\) is an error term assumed to be normally distributed.

To reduce possible long-term change effects, we developed three rating curves for each element for each of the four rivers to represent the three decades, the 1980s, 1990s, and 2000s. All the TOC, TKN, and TP rating curves obtained satisfactory fitting parameters with an \(R^2\) between 0.70 and 0.98 (Table 2.2). The regression analysis (i.e., Eq. (1)) was performed using SAS Statistical Software (SAS Institute Inc., Cary, NC). Figures 2.2 to 2.4 show the comparisons between measured and estimated TN and TP fluxes for the four rivers.

Riverine concentration of NO\(_3^+\)NO\(_2^+\) generally does not correlate with river discharge. Application of Eq. (1) for NO\(_3^+\)NO\(_2^+\) in this study yielded unsatisfactory fitness of the model parameters (all \(R^2\) values < 0.6). Therefore, monthly records of NO\(_3^+\)NO\(_2^+\) concentrations for the rivers were used as the average daily concentrations for calculation of daily fluxes in the corresponding months. Daily NO\(_3^+\)NO\(_2^+\) fluxes were calculated using the equation below:

\[
S_{day}(t) = \sum_{day=1}^{n} c_{day}(t) Q_{day}(t)
\]

(2)

where \(S_{day}(t)\) represents the daily flux in milligrams, \(c_{day}(t)\) is the daily concentration in mg/L, and \(Q_{day}(t)\) is the daily discharge in liters.

The daily fluxes of TOC, NO\(_3^+\)NO\(_2^+\), TKN, and TP were summed up over time to provide monthly, annual, and decadal fluxes for the period from 1980 to 2009. Carbon and nutrient yields
(mass per unit area per unit time) were calculated for each basin by dividing the fluxes by the basin drainage area at the gauge station. This normalized the fluxes so that comparisons could be made among basins of varying sizes.

Table 2.2. Parameter estimates ($b_0$ and $b_1$) used in Equation (1) for estimating daily fluxes of TOC, TKN, and TP and their regression coefficients ($R^2$) (RMSE = root of mean square error, n = sampling size).

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC Sabine</td>
<td>-5.5964</td>
<td>-4.2354</td>
<td>-5.9032</td>
<td>0.93</td>
<td>0.2838</td>
<td>102</td>
</tr>
<tr>
<td>TKN</td>
<td>-8.1904</td>
<td>-8.7432</td>
<td>-6.6080</td>
<td>0.86</td>
<td>0.4182</td>
<td>102</td>
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<tr>
<td>TP</td>
<td>-8.5179</td>
<td>-9.7448</td>
<td>-9.9049</td>
<td>0.70</td>
<td>0.6304</td>
<td>102</td>
</tr>
<tr>
<td>TOC Calcasieu</td>
<td>-13.6688</td>
<td>-12.2047</td>
<td>-13.4754</td>
<td>0.95</td>
<td>0.3724</td>
<td>104</td>
</tr>
<tr>
<td>TKN</td>
<td>-10.8997</td>
<td>-10.6468</td>
<td>-11.7462</td>
<td>0.85</td>
<td>0.5050</td>
<td>106</td>
</tr>
<tr>
<td>TP</td>
<td>-10.9748</td>
<td>-11.4356</td>
<td>-17.3719</td>
<td>0.78</td>
<td>0.5179</td>
<td>97</td>
</tr>
<tr>
<td>TOC Mermentau</td>
<td>-4.7943</td>
<td>-4.6687</td>
<td>-4.5345</td>
<td>0.96</td>
<td>0.2508</td>
<td>47</td>
</tr>
<tr>
<td>TKN</td>
<td>-7.0633</td>
<td>-7.2102</td>
<td>-6.9344</td>
<td>0.94</td>
<td>0.3889</td>
<td>43</td>
</tr>
<tr>
<td>TP</td>
<td>-8.6400</td>
<td>-8.6468</td>
<td>-9.4927</td>
<td>0.93</td>
<td>0.3505</td>
<td>49</td>
</tr>
<tr>
<td>TOC Vermilion</td>
<td>-5.5054</td>
<td>-4.5206</td>
<td>-4.2393</td>
<td>0.91</td>
<td>0.3513</td>
<td>51</td>
</tr>
<tr>
<td>TKN</td>
<td>-5.6897</td>
<td>-8.2345</td>
<td>-8.1083</td>
<td>0.89</td>
<td>0.3792</td>
<td>45</td>
</tr>
<tr>
<td>TP</td>
<td>-7.7825</td>
<td>-8.6491</td>
<td>-11.8128</td>
<td>0.85</td>
<td>0.4646</td>
<td>45</td>
</tr>
</tbody>
</table>
Two independent samples t-test was used to evaluate the significance of differences in TOC, \( \text{NO}_3+\text{NO}_2 \), TKN, and TP concentrations, fluxes, and yields among the four rivers over the past three decades. All statistical analyses were performed with the SAS Statistical Software package. All statistical tests and confidence intervals are reported at \( \alpha = 0.05 \) critical level.

Figure 2.2. The relationship between measured TOC flux and estimated TOC flux using regression equations (Eq. (1)) for the four studied rivers in southwest Louisiana entering the Northern Gulf of Mexico.

Carbon, nitrogen, and phosphorus ratio can provide important complementary information that is needed to understand the nutritional condition of the source waters to the Gulf of Mexico. In this study, we estimated carbon, nitrogen, phosphorus ratios in molar basis for the four studied rivers using TOC, total nitrogen (TN, the sum of \( \text{NO}_3+\text{NO}_2 \) and TKN), and total phosphorus (TP). All the ratios are molar ratios. We compared the long-term seasonal and interannual variations of the C:N, C:P, N:P ratios among these rivers.
Figure 2.3. The relationship between measured TKN flux and estimated TKN flux using regression equations (Eq. (1)) for the four studied rivers in southwest Louisiana entering the Northern Gulf of Mexico.

Figure 2.4. The relationship between measured TP flux and estimated TP flux using regression equations (Eq. (1)) for the four studied rivers in southwest Louisiana entering the Northern Gulf of Mexico.
2.3 Results

2.3.1 River hydrological conditions

During the 30 years from 1980 to 2009, the Sabine River, when compared to the other three rivers, showed the highest average daily discharge (mean ± std: 238 ± 257 m$^3$/s), ranging between 14 and 3058 m$^3$/s. The Vermilion River had the lowest average daily discharge (36 ± 36 m$^3$/s), ranging from 0 to 396 m$^3$/s. The daily discharges of the Calcasieu and Mermentau Rivers averaged 73 m$^3$/s (±129) and 88 m$^3$/s (±116), ranging from 5 to 2674 m$^3$/s and from 0 to 1624 m$^3$/s, respectively. Overall, the four rivers showed neither an increasing nor a decreasing trend in discharge during the past 30 years (Figure 2.5). In general, the Sabine, Calcasieu, and Mermentau Rivers all had higher discharges in the 1990s, while the Vermilion River showed a higher discharge in the 1980s (Table 2.3). Seasonally, the Sabine, Calcasieu, and Mermentau Rivers showed a higher discharge during the winter and spring months and a lower discharge during the summer and fall months, while the discharge in the Vermilion River was relatively constant over the seasons (Figure 2.5).

Figure 2.5. Long-term annual (a) and monthly (b) average discharge of the four studied rivers in southwest Louisiana entering the Northern Gulf of Mexico.
Table 2.3. Decadal means of discharge and concentrations of TOC, NO$_3$+NO$_2$, TKN, and TP for the four studied rivers in southwest Louisiana entering the northern Gulf of Mexico.

<table>
<thead>
<tr>
<th>River</th>
<th>Discharge ($m^3\cdot s^{-1}$)</th>
<th>TOC (mg L$^{-1}$)</th>
<th>NO$_3$+NO$_2$ (mg L$^{-1}$)</th>
<th>TKN (mg L$^{-1}$)</th>
<th>TP (mg L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sabine</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80s</td>
<td>223 ±277$^a$</td>
<td>7.7±2.2$^a$</td>
<td>0.08±0.05$^a$</td>
<td>0.76±0.47$^a$</td>
<td>0.07±0.07$^a$</td>
</tr>
<tr>
<td>90s</td>
<td>277 ±262$^a$</td>
<td>9.2±2.2$^a$</td>
<td>0.07±0.05$^a$</td>
<td>0.81±0.25$^a$</td>
<td>0.06±0.03$^a$</td>
</tr>
<tr>
<td>00s</td>
<td>214 ±231$^a$</td>
<td>8.5±1.9$^b$</td>
<td>0.09±0.02$^a$</td>
<td>0.61±0.18$^b$</td>
<td>0.08±0.02$^a$</td>
</tr>
<tr>
<td>$\bar{X}$</td>
<td>238 ±257$^A$</td>
<td>8.4±2.1$^A$</td>
<td>0.08±0.04$^A$</td>
<td>0.73±0.30$^A$</td>
<td>0.07±0.04$^A$</td>
</tr>
<tr>
<td>Calcasieu</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80s</td>
<td>81 ±181$^a$</td>
<td>7.0±3.5$^a$</td>
<td>0.09±0.05$^a$</td>
<td>0.70±0.42$^a$</td>
<td>0.08±0.04$^a$</td>
</tr>
<tr>
<td>90s</td>
<td>83 ±132$^a$</td>
<td>7.7±4.6$^b$</td>
<td>0.08±0.06$^a$</td>
<td>0.61±0.30$^a$</td>
<td>0.08±0.05$^a$</td>
</tr>
<tr>
<td>00s</td>
<td>56 ±73$^b$</td>
<td>5.2±2.6$^c$</td>
<td>0.11±0.08$^b$</td>
<td>0.64±0.43$^a$</td>
<td>0.09±0.05$^a$</td>
</tr>
<tr>
<td>$\bar{X}$</td>
<td>73±129$^B$</td>
<td>6.8±3.6$^B$</td>
<td>0.09±0.06$^B$</td>
<td>0.65±0.38$^B$</td>
<td>0.08±0.05$^B$</td>
</tr>
<tr>
<td>Mermentau</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80s</td>
<td>82±139$^a$</td>
<td>9.9±3.0$^a$</td>
<td>0.27±0.19$^a$</td>
<td>1.42±0.65$^a$</td>
<td>0.31±0.13$^a$</td>
</tr>
<tr>
<td>90s</td>
<td>98±9$^a$</td>
<td>10.0±2.7$^a$</td>
<td>0.25±0.19$^a$</td>
<td>1.27±0.71$^a$</td>
<td>0.25±0.12$^b$</td>
</tr>
<tr>
<td>00s</td>
<td>84±115$^a$</td>
<td>12.3±4.8$^b$</td>
<td>0.22±0.18$^a$</td>
<td>1.28±0.62$^a$</td>
<td>0.25±0.14$^b$</td>
</tr>
<tr>
<td>$\bar{X}$</td>
<td>88±116$^C$</td>
<td>10.7±3.5$^C$</td>
<td>0.24±0.19$^C$</td>
<td>1.32±0.66$^C$</td>
<td>0.27±0.13$^C$</td>
</tr>
<tr>
<td>Vermilion</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80s</td>
<td>43±42$^b$</td>
<td>9.2±3.3$^a$</td>
<td>0.50±0.33$^a$</td>
<td>1.51±0.69$^a$</td>
<td>0.52±0.19$^a$</td>
</tr>
<tr>
<td>90s</td>
<td>32±33$^a$</td>
<td>9.1±3.5$^a$</td>
<td>0.58±0.41$^a$</td>
<td>1.27±0.71$^b$</td>
<td>0.36±0.13$^b$</td>
</tr>
<tr>
<td>00s</td>
<td>33±32$^a$</td>
<td>9.2±3.8$^a$</td>
<td>0.57±0.37$^a$</td>
<td>1.07±0.40$^c$</td>
<td>0.34±0.12$^b$</td>
</tr>
<tr>
<td>$\bar{X}$</td>
<td>36±36$^D$</td>
<td>9.2±3.5$^b$</td>
<td>0.55±0.37$^D$</td>
<td>1.28±0.60$^C$</td>
<td>0.41±0.15$^D$</td>
</tr>
</tbody>
</table>

Values in *italics* denote standard deviations; Means followed by the same letter within a column are not significantly different at the 0.05 level; Capital letters are for mean value testing (also at the 0.05 significance level) between the four rivers.

2.3.2 TOC, NO$_3$+NO$_2$, TKN, and TP concentrations

From 1980 to 2009, the Mermentau and Vermilion Rivers showed a statistically significantly higher concentration of TOC (mean±std: 10.7±3.5 mg L$^{-1}$ and 9.2±3.5 mg L$^{-1}$, respectively) than the Sabine (8.4±2.1 mg L$^{-1}$) and Calcasieu (6.8±3.6 mg L$^{-1}$) Rivers (Table 2.3). All the four rivers showed a high annual variation in TOC concentration: from 5.1 to 11.5 mg L$^{-1}$ for the Sabine River, from 5.0 to 14.6 mg L$^{-1}$ for the Calcasieu River, from 5.9 to 15.4 mg L$^{-1}$ for the Mermentau River, and from 6.8 to 11.7 mg L$^{-1}$ for the Vermilion River (Figure 2.6). Seasonally, all four rivers showed higher TOC concentrations during the winter and spring months and lower TOC concentrations in summer and fall months (Figure 2.6). Annual average of TOC concentration varied largely (2 to 3 folds) in all four rivers during the past 30 years.

There appears to be an increasing trend of TOC in the Mermentau River since the mid-1990s (Figure 2.6).
Figure 2.6. Long-term annual and monthly means of TOC concentrations and fluxes of the four studied rivers in southwest Louisiana entering the Northern Gulf of Mexico.

From 1980 to 2009, the Mermentau and Vermilion Rivers, which drain intensive agricultural land areas, showed 3-6 times higher NO$_3$+NO$_2$ concentrations (mean ± std: 0.24 ± 0.19 mg L$^{-1}$ and 0.55 ± 0.37 mg L$^{-1}$, respectively) than the Sabine and Calcasieu Rivers (0.08 ± 0.04 mg L$^{-1}$ and 0.09 ± 0.06 mg L$^{-1}$), which drain forest/pasture-dominated land areas (Table 2.3). All four rivers showed a large annual variation in NO$_3$+NO$_2$ concentration: from 0.04 to 0.10 mg L$^{-1}$ in the Sabine River, from 0.07 to 0.24 mg L$^{-1}$ in the Calcasieu River, from 0.14 to 0.44 mg L$^{-1}$ in the Mermentau River, and from 0.35 to 0.89 mg L$^{-1}$ in the Vermilion River (Figure 2.7). No long-term change in NO$_3$+NO$_2$ concentration could be seen over the past 30 years. Seasonally, the Mermentau and Vermilion Rivers showed clearly higher NO$_3$+NO$_2$
concentrations during the late spring and early summer months, while the Sabine and Calcasieu Rivers had little variable NO$_3$+NO$_2$ concentrations (Figure 2.7).

![Figure 2.7](image)

**Figure 2.7.** Long-term annual and monthly means of NO$_3$+NO$_2$ concentrations and fluxes of the four studied rivers in southwest Louisiana entering the Northern Gulf of Mexico.

Similarly, the Mermentau and Vermilion Rivers had significantly higher TKN concentrations (1.32 ± 0.66 mg L$^{-1}$ and 1.28 ± 0.60 mg L$^{-1}$, respectively) when compared with the Sabine and Calcasieu Rivers (0.73 ± 0.30 mg L$^{-1}$ and 0.65 ± 0.38 mg L$^{-1}$) (Table 2.3). All four rivers showed a high annual variation in TKN concentration: from 0.52 to 1.49 mg L$^{-1}$ in the Sabine River, from 0.42 to 1.22 mg L$^{-1}$ in the Calcasieu River, from 0.99 to 1.97 mg L$^{-1}$ in the Mermentau River, and from 0.77 to 1.88 mg L$^{-1}$ in the Vermilion River (Figure 2.8). Over the past 30 years, a declining trend in TKN concentration was observed in the Mermentau and Vermilion Rivers. Seasonally, as with the NO$_3$+NO$_2$ concentration, the Mermentau and
Vermilion Rivers showed higher TKN concentrations during the spring and early summer months, while the TKN concentrations in the Sabine and Calcasieu Rivers remained more or less constant over the year (Figure 2.8).

The Mermentau and Vermilion Rivers also had significantly higher TP concentrations (0.27 ± 0.13 mg L\(^{-1}\) and 0.41 ± 0.15 mg L\(^{-1}\), respectively) when compared with the Sabine and Calcasieu Rivers (0.07 ± 0.04 mg L\(^{-1}\) and 0.08 ± 0.05 mg L\(^{-1}\)) (Table 2.3). Annual TP concentrations varied from 0.04 to 0.11 mg L\(^{-1}\) and 0.06 to 0.16 mg L\(^{-1}\) in the Sabine and Calcasieu Rivers, and from 0.16 to 0.41 mg L\(^{-1}\) and 0.23 to 0.67 mg L\(^{-1}\) in the Mermentau and Vermilion Rivers, respectively. A clear, declining trend in TP concentration over the past 30 years could be seen in the Mermentau and Vermilion Rivers (Figure 2.9).
Figure 2.9. Long-term annual and monthly means of TP concentrations and fluxes of the four studied rivers in southwest Louisiana entering the Northern Gulf of Mexico.

2.3.3 Decadal trends of carbon and nutrient fluxes

From 1980 to 2009, the four coastal rivers transported annually a total of 1.3×10^4 t organic carbon into the Northern Gulf of Mexico, nearly half of which were discharged by the Sabine River (Table 2.4). The annual TOC fluxes of the rivers varied largely (Figure 2.6): 1.7×10^4 - 11.1×10^4 t yr\(^{-1}\) from the Sabine River, 0.5×10^4 - 8.1×10^4 t yr\(^{-1}\) from the Calcasieu River, 1.1×10^4 - 4.2×10^4 t yr\(^{-1}\) from the Mermentau River, and 0.5×10^4 - 1.4×10^4 t yr\(^{-1}\) from the Vermilion River. The variation in annual TOC flux closely corresponded to the annual river discharge (Figures 2.5 and 2.10). The Sabine River showed the lowest TOC flux in the low-flow year of 1996 (1.7×10^4 t) and the highest flux in the high-flow year of 1991 (11.1×10^4 t).

Similarly, the lowest and highest TOC fluxes of the Calcasieu River fluctuated from 0.5×10^4 t in
2000 (dry year, low discharge) to $8.1 \times 10^4$ t in 1989 (wet year, high discharge), averaging $2.9 \times 10^4$ t per year. Relatively, TOC fluxes of the Mermentau and Vermilion Rivers showed much lower variation, fluctuating from $1.1 \times 10^4$ t in 1986 and 1987 to $4.2 \times 10^4$ t in 1985 and from $0.5 \times 10^4$ t in 1984 to $1.4 \times 10^4$ t in 1985, respectively (Figure 2.6).

![Figure 2.10](image)

Figure 2.10. Influence of the river discharge on TOC flux in the Sabine, Calcasieu, Mermentau, and Vermilion Rivers entering the Northern Gulf of Mexico.

No clear decadal trend of TOC flux was found from 1980 to 2009. The Sabine River discharged $5.4 \times 10^4$ t, $7.7 \times 10^4$ t, and $5.9 \times 10^4$ t TOC during the 1980s, 1990s, and 2000s, respectively, into the Gulf of Mexico. During the same three decades the Calcasieu, Mermentau, and Vermilion Rivers showed a much lower annual TOC fluxes: $3.6 \times 10^4$, $2.9 \times 10^4$ and $2.2 \times 10^4$ t TOC from the Calcasieu River, $2.7 \times 10^4$, $3.0 \times 10^4$ and $2.8 \times 10^4$ t TOC from the Mermentau River, and $1.3 \times 10^4$, $0.9 \times 10^4$ and $0.9 \times 10^4$ t TOC from the Vermilion River (Table 2.4).
Table 2.4. Annual average fluxes of TOC, NO$_3$+NO$_2$, TKN, and TP for the four studied rivers in southwest Louisiana entering the northern Gulf of Mexico.

<table>
<thead>
<tr>
<th>River</th>
<th>TOC ($\times 10^4$ t yr$^{-1}$)</th>
<th>NO$_3$+NO$_2$ (t yr$^{-1}$)</th>
<th>TKN (t yr$^{-1}$)</th>
<th>TP (t yr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sabine</td>
<td>80s 5.4±6.9$^a$</td>
<td>487±616$^a$</td>
<td>5043±659$^a$</td>
<td>358±410$^a$</td>
</tr>
<tr>
<td></td>
<td>90s 7.7±7.1$^b$</td>
<td>537±709$^b$</td>
<td>7064±714$^b$</td>
<td>494±466$^b$</td>
</tr>
<tr>
<td></td>
<td>00s 5.9±6.7$^a$</td>
<td>583±675$^b$</td>
<td>3859±398$^c$</td>
<td>507±558$^b$</td>
</tr>
<tr>
<td></td>
<td>$\bar{X}$ 6.3±6.9$^A$</td>
<td>536±667$^A$</td>
<td>5322±5908$^A$</td>
<td>453±478$^A$</td>
</tr>
<tr>
<td>Calcasieu</td>
<td>80s 3.6±15.2$^a$</td>
<td>209±514$^a$</td>
<td>2312±7316$^a$</td>
<td>196±486$^a$</td>
</tr>
<tr>
<td></td>
<td>90s 2.9±7.2$^b$</td>
<td>189±323$^b$</td>
<td>1759±3587$^b$</td>
<td>184±316$^a$</td>
</tr>
<tr>
<td></td>
<td>00s 2.2±7.7$^c$</td>
<td>179±220$^b$</td>
<td>2406±9176$^a$</td>
<td>192±438$^a$</td>
</tr>
<tr>
<td></td>
<td>$\bar{X}$ 2.9±10.0$^B$</td>
<td>192±352$^B$</td>
<td>2159±669$^B$</td>
<td>190±413$^B$</td>
</tr>
<tr>
<td>Mermentau</td>
<td>80s 3.0±2.8$^a$</td>
<td>722±788$^b$</td>
<td>3602±3470$^a$</td>
<td>757±726$^a$</td>
</tr>
<tr>
<td></td>
<td>90s 2.8±3.9$^a$</td>
<td>457±631$^a$</td>
<td>3105±4447$^a$</td>
<td>636±957$^b$</td>
</tr>
<tr>
<td></td>
<td>00s 2.9±7.7$^B$</td>
<td>189±323$^b$</td>
<td>1759±3587$^b$</td>
<td>184±316$^a$</td>
</tr>
<tr>
<td></td>
<td>$\bar{X}$ 2.8±3.8$^B$</td>
<td>556±692$^A$</td>
<td>3369±4621$^C$</td>
<td>736±1042$^C$</td>
</tr>
<tr>
<td>Vermilion</td>
<td>80s 1.3±1.3$^a$</td>
<td>514±467$^a$</td>
<td>1790±1662$^a$</td>
<td>623±610$^a$</td>
</tr>
<tr>
<td></td>
<td>90s 0.9±0.9$^b$</td>
<td>442±444$^b$</td>
<td>1211±1360$^b$</td>
<td>355±381$^b$</td>
</tr>
<tr>
<td></td>
<td>00s 0.9±0.8$^b$</td>
<td>458±386$^b$</td>
<td>1073±1116$^c$</td>
<td>385±466$^b$</td>
</tr>
<tr>
<td></td>
<td>$\bar{X}$ 1.0±1.0$^C$</td>
<td>471±432$^A$</td>
<td>1358±1379$^D$</td>
<td>454±486$^A$</td>
</tr>
</tbody>
</table>

Values in *italics* denote standard deviations; Means followed by the same letter within a column are not significantly different at the 0.05 level; Capital letters are for mean value testing (also at the 0.05 significance level) between the four rivers.

Over the past 30 years, the four coastal rivers transported annually a total of 1755 t NO$_3$+NO$_2$ nitrogen into the NGOM. The annual NO$_3$+NO$_2$ input in the rivers fluctuated largely: 174 – 1101 t yr$^{-1}$ in the Sabine River (mean ± std: 536 ± 667 t yr$^{-1}$), 103 – 399 t yr$^{-1}$ (192 ±352 t yr$^{-1}$) in the Calcasieu River, 170 – 1261 t yr$^{-1}$ (556 ± 692 t yr$^{-1}$) in the Mermentau River, and 134 – 730 (471 ± 432 t yr$^{-1}$) in the Vermilion River (Figure 2.7). The variation in annual NO$_3$+NO$_2$ input corresponded to both the annual river discharge (Figure 2.11) and the NO$_3$+NO$_2$ concentration. Despite considerably lower river discharges when compared with the Sabine and Calcasieu Rivers, the Mermentau and Vermilion Rivers showed high NO$_3$+NO$_2$ inputs. None of the four rivers exhibited a clear decadal trend of NO$_3$+NO$_2$ input from 1980 to 2009.
During the 30 years from 1980 to 2009, the four coastal rivers transported annually a total of 12208 t TKN into the NGOM, more than 40% of which was discharged by the Sabine River (mean ± std: 5322 ± 5908 t yr\(^{-1}\)). During the same three decades, the other three rivers showed much lower annual TKN fluxes: 2159 ± 6693 t yr\(^{-1}\) for the Calcasieu River, 3369 ± 4621 t yr\(^{-1}\) for the Mermentau River, 1358 ± 1379 t yr\(^{-1}\) for the Vermilion River (Table 2.4). The variation in annual TKN input closely corresponded to the annual river discharge (Figure 2.12). The Sabine River showed the lowest TKN input in the low-flow year of 1996 (1310 t) and the highest input in the high-flow year of 1991 (10459 t). Similarly, the lowest and highest TKN fluxes of the Calcasieu River fluctuated from 469 t in 2000 (dry year, low discharge) to 5110 t in 2004 (wet year, high discharge). Relatively, the TKN fluxes of the Mermentau and Vermilion Rivers
showed lower variation, fluctuating from 1453 t in 1987 to 5321 t in 1985 and from 721 t in 2005 to 2001 t in 1985, respectively (Figure 2.8). Overall, from 1980s to 2000s, the Vermilion River showed a decreasing trend of TKN input, while the other three rivers had no clear trends of TKN input (Table 2.4).

![Figure 2.12](image)

**Figure 2.12.** Influence of the river discharge on TKN flux in the four studied rivers in southwest Louisiana entering the Northern Gulf of Mexico.

During the same period, the four coastal rivers transported annually a total of 1833 t TP into the NGOM. The Mermentau River showed a much higher annual input of TP (mean ± std: 736 ± 1042 t yr⁻¹), when compared to those of the Sabine River (453 ± 478 t yr⁻¹), the Calcasieu River (190 ± 413 t yr⁻¹), and the Vermilion River (454 ± 486 t yr⁻¹). The variation in annual TP input corresponded to not only the annual river discharge (Figure 2.13), but also the TP
concentration. The Vermilion River showed a high TP input due to its high TP concentration, despite its considerably lower discharge. The annual TP fluxes of the four rivers varied largely (Figure 2.9): from 104 to 941 t yr\(^{-1}\) for the Sabine River, from 62 to 384 t yr\(^{-1}\) for the Calcasieu River, from 346 to 1282 t yr\(^{-1}\) for the Mermentau River, and from 239 to 699 t yr\(^{-1}\) for the Vermilion River. In the past 30 years, the Sabine River showed an increasing trend of TP input, the Calcasieu River showed no clear trend of TP input, and the Mermentau and Vermilion Rivers had declining trends of TP input. The reduction mainly occurred in the 1990s, and was maintained through the 2000s (Table 2.4).

Figure 2.13. Influence of the river discharge on TP flux in the four studied rivers in southwest Louisiana entering the Northern Gulf of Mexico.
2.3.4 Seasonal trends of nutrient fluxes

Seasonally, the Sabine, Calcasieu, and Mermentau Rivers showed an overall trend with higher TOC fluxes in the winter and spring and lower in the fall months (Figure 2.6), corresponding to the river discharge changes (Figure 2.5). Vermilion River showed more stable TOC flux compares to Sabine, Calcasieu, and Mermentau Rivers because discharge in Vermilion River is more stable. Mean monthly TOC flux for the Sabine River during the study period was 5200 t with the highest average flux in March (9100 t) and the lowest in October (2200 t). The Calcasieu River had a mean monthly TOC flux of 2400 t with February averaging the highest flux (4300 t) and August averaging the lowest flux (280 t). The Mermentau River averaged a monthly flux of 2300 t, with November having the highest average flux (3400 t) and August the lowest (950 t). The Vermilion River mean monthly flux was 780 t, February averaging the highest (1000 t) and August averaging the lowest (580 t). Comparably, the Sabine River showed much higher monthly flux than Calcasieu, Mermentau, and Vermilion Rivers because the Sabine River has the highest discharge when compared with other three rivers.

The Sabine, Calcasieu, and Mermentau Rivers showed an overall trend with higher NO$_3$+NO$_2$ fluxes in the winter and spring, and lower fluxes in the fall, while the Vermilion River showed higher NO$_3$+NO$_2$ fluxes during summer months (Figure 2.7), corresponding to the river discharge (Figure 2.5) and the NO$_3$+NO$_2$ concentration changes (Figure 2.7). The mean monthly NO$_3$+NO$_2$ input for the Sabine River during the study period was 42 t, with the highest input in April (72 t) and the lowest in September (14 t). The Calcasieu River had a mean monthly NO$_3$+NO$_2$ input of 16 t, with April averaging the highest input (30 t) and October averaging the lowest (4 t). The Mermentau River averaged a monthly input of 44 t, with May having the highest input (83 t) and August the lowest (12 t). The Vermilion River mean monthly input was
38 t, with June averaging the highest (55 t) and November averaging the lowest (28 t).

Comparably, the Sabine, Mermentau, and Vermilion Rivers showed much higher monthly fluxes than the Calcasieu River.

The Sabine, Calcasieu, and Mermentau Rivers showed an overall trend with higher TKN fluxes in the winter and spring, and lower fluxes in the fall months (Figure 2.8), corresponding to river discharge changes (Figure 2.8). The Vermilion River showed a more stable TKN input compared to the Sabine, Calcasieu, and Mermentau Rivers because discharge in the Vermilion River is more stable. The mean monthly TKN input for the Sabine River was the highest, 439 t, ranging from 173 t in October to 772 t in March. The Calcasieu River had a mean monthly TKN input of 178 t, ranging from 25 t in August to 322 t in February. The Mermentau River averaged a monthly TKN input of 273 t, ranging from 113 t in August to 406 t in November. The Vermilion River showed the lowest mean monthly TKN input of 105 t, ranging from 77 t in August to 139 t in February.

Seasonally, all four rivers showed an overall trend with higher TP fluxes in the winter and spring, and lower fluxes in the fall months (Figure 2.9), corresponding to river discharge (Figure 2.5) and the TP concentration changes (Figure 2.9). The mean monthly TP input for the Sabine River was 37 t, ranging from 17 t in October to 65 t in March. When compared with the other three rivers, the Calcasieu River had the lowest mean monthly TP input of 16 t, ranging from 3 t in August to 28 t in February. The Mermentau River averaged a monthly TP input of 59 t, ranging from 25 t in August to 91 t in November. The Vermilion River mean monthly TP input was 35 t, ranging from 25 t in August to 46 t in February.
2.3.5 C:N, C:P, and N:P ratios

Ratios of C:N and C:P of all the four rivers showed annual variation, but no clear interannual trend (Figure 2.14). The Sabine River had an annual average C:N ratio of 24, varying from 22 in 1986 to 30 in 2001. C:N ratio of the Calcasieu River fluctuated from 16 in 1981 to 31 in 1991, averaging 23. Relatively, annual average C:N ratio of the Mermentau and Vermilion Rivers showed less variation, fluctuation from 15 in 1989 and 1987 to 19 in 2009 and from 11 in 1999 to 15 in 2009, respectively. Annual means of C:P ratio (range) for the Sabine, Calcasieu, Mermentau, and Vermilion Rivers were 351 (285-417), 236 (148-349), 106 (85-124), and 63 (50-74), respectively.

There appears to be a seasonal pattern of C:N ratio in the Calcasieu, Mermentau, and Vermilion Rivers and a clear seasonal pattern of C:P ratio in the Calcasieu River (Figure 2.14). Mean monthly C:N ratio for the Sabine River during the study period was 24 with the highest average C:N ratio in July (25) and the lowest in April (23), fairly consistent. The Calcasieu River had a mean monthly C:N ratio of 23 with February averaging the highest (28) and September averaging the lowest (19). The Mermentau River averaged a monthly C:N ratio of 17, with September having the highest (18) and April the lowest (15). The Vermilion River mean monthly C:N ratio was 13, with February averaging the highest (14) and May averaging the lowest (11). Mean monthly C:P ratios (range) of the Sabine, Calcasieu, Mermentau, and Vermilion Rivers were 351 (342-358), 236 (175-303), 106 (104-108), and 63 (61-65), respectively, and there was little seasonal variation in the Sabine, Mermentau, and Vermilion Rivers. The Calcasieu River, however, showed a clear seasonal trend with high C:P ratios in the winter months decreasing towards summer months and then increasing over the fall months.
Figure 2.14. Long-term annually and monthly C:N, C:P, and N:P ratios of Sabine, Calcasieu, Mermentau, and Vermilion Rivers entering the Northern Gulf of Mexico.

Overall, the N:P ratios in the four rivers had little interannual change (Figure 2.14). Among the four rivers, the Sabine River had the highest average annual N:P ratio (15.3), varying from 10.0 in 2002 to 17.6 in 1998. The Calcasieu River had the second highest annual average N:P ratio (10.9) ranging from 8.9 in 2005 to 12.2 in 1984. The Mermentau and Vermilion Rivers
showed significantly lower N:P ratios (6.3 and 5.2, respectively), fluctuating from 5.1 in 1984 to 7.9 in 2005 in the Mermentau, and from 4.0 in 1984 to 6.4 in 1990 in the Vermilion.

Seasonally, these rivers displayed similar trends: higher N:P ratios during the winter and spring months, and lower N:P ratios during the summer and fall months. The long-term mean of monthly N:P ratios for the Sabine River was highest in April (16.7) and lowest in October (14.7). The Calcasieu River had the highest long-term mean of monthly N:P ratios in April (12.0) and the lowest in October (9.4). The Mermentau River had the highest monthly mean N:P ratio in April (7.1) and the lowest in August (5.7). The Vermilion River showed its highest monthly mean N:P ratio in May (5.9) and its lowest in February (4.5).

2.4 Discussion

During the past half century, all the four studied rivers were hydrologically altered to various degrees. The modification may have had considerable effects on water quality and riverine organic carbon transport. For instance, along the Sabine River, three major dams were constructed with the Toledo Bend Dam (above the gauge and water quality stations used in this study) controlling outflow in the river’s middle-low reach. Along the Calcasieu River two dams were constructed in its upper reach and a saltwater barrier gate (below the gauge and water quality stations used in this study) was constructed in its middle-low reach to prevent saltwater intrusion further upstream as well as to regulate freshwater outflow. The Mermentau and Vermilion Rivers are two shorter rivers and no dam was constructed along the river main channels except for some navigation locks. The Vermilion River is heavily human-modified with canals for agriculture irrigation. The river also receives water from the Atchafalaya River (Rosen and Xu, 2011), a distributary that discharges approximate 25% of the Mississippi River’s flow
and the total flow of the Red River (Xu, 2013). This river diversion may have resulted in the relatively stable flow and TOC fluxes during the year (Figures 2.5 and 2.6).

The carbon, nitrogen, and phosphorus fluxes from the four rivers studied are comparably higher than or within the same range of those found from other coastal rivers entering the NGOM in south Louisiana. For instance, Saksa and Xu (2006) reported that the average annual TOC fluxes from three coastal rivers in southeast Louisiana – the Amite, Tangipahoa, and Tickfaw Rivers – varied from 2404 t (Tickfaw) to 15,780 t (Amite). The average annual TN fluxes from three coastal rivers in southeast Louisiana – the Amite, Tangipahoa, and Tickfaw Rivers – were 2592, 1183, and 358 t. The average annual TP fluxes of the Amite, Tangipahoa, and Tickfaw Rivers were 468, 178, and 42 t (Saksa and Xu, 2006). On the other hand, the carbon and nutrient fluxes from the four rivers in this study are insignificant when compared with those from the Atchafalaya River (113.9×10^4 t yr^-1 TOC, 179.3×10^3 t yr^-1 NO_3^-+NO_2^-, 151.1×10^3 t yr^-1 TKN, and 41.3×10^3 t yr^-1 TP; Xu, 2013) and the Mississippi River (403.0×10^4 t yr^-1 TOC, Bianchi et al., 2007; 1824 ×10^3 t yr^-1 TN, 106.5×10^3 t yr^-1 TP; Turner and Rabalais, 1991) to the NGOM, demonstrating the important role of discharge on carbon and nutrient input in river systems. Although the small coastal river basins discharge comparably modest amounts of organic carbon nutrients, their annual and seasonal fluctuations in nutrient discharge could have important effects on estuaries and near-shore ecosystems.

When compared with other coastal rivers entering the NGOM, the four rivers in this study showed higher organic carbon and nutrient yields. For instance, yields in the Mermentau and Vermilion Rivers were greater than those of the Mississippi River (1.4 t km^-2 yr^-1 TOC; 483 kg km^-2 yr^-1 TN, and 45 kg km^-2 yr^-1 TP; Turner and Rabalais, 2004). Although discharges of the Mermentau and Vermilion Rivers were low, yields of TOC, NO_3^-+NO_2^-, TKN, and TP were much
higher from the Mermentau (7.8 t km\(^{-2}\) yr\(^{-1}\) TOC; 156 kg km\(^{-2}\) yr\(^{-1}\) NO\(_3\)+NO\(_2\), 942 kg km\(^{-2}\) yr\(^{-1}\) TKN, and 206 kg km\(^{-2}\) yr\(^{-1}\) TP) and the Vermilion (7.9, 374, 1078, and 360) than those of the Sabine River (2.6, 22, 220, and 19) and Calcasieu River (6.6, 44, 490, and 43) (Table 2.5).

Correll et al., 2001 studied discharges of organic carbon from eight contiguous small watersheds on the Atlantic Coastal Plain in Maryland for up to 24 years and found the highest TOC yields were from the cropland watersheds, even though the forested watersheds had much higher organic carbon content in their 1-cm top soil layer (4.3%) when compared with the cropland watersheds (0.87%). They attributed the higher TOC flux rate from the cropland to a higher surface erosion rate and a higher decomposition of organic matters while the forested land was normally covered by leaf litters. The agricultural control of TOC and nutrients yields was clearly reflected in the much higher TOC and nutrients yields from the Mermentau and Vermilion River Basins, when compared the Sabine and Calcasieu River Basins.

The two agriculture-intensive river basins – the Mermentau and Vermilion Rivers – also showed significantly higher carbon and nutrient yields than three similar agriculture-intensive river basins in east Louisiana: the Amite (4.8 t km\(^{-2}\) yr\(^{-1}\) TOC; 780 kg km\(^{-2}\) yr\(^{-1}\) TN, and 140 kg km\(^{-2}\) yr\(^{-1}\) TP; Saksa and Xu, 2006), Tangipahoa (2.8 t km\(^{-2}\) yr\(^{-1}\) TOC; 710 kg km\(^{-2}\) yr\(^{-1}\) TN, and 110 kg km\(^{-2}\) yr\(^{-1}\) TP; Saksa and Xu, 2006), and Tickfaw (3.8 t km\(^{-2}\) yr\(^{-1}\) TOC; 560 kg km\(^{-2}\) yr\(^{-1}\) TN, and 70 kg km\(^{-2}\) yr\(^{-1}\) TP; Saksa and Xu, 2006) Rivers. These results indicate that, in addition to intensive agriculture, the higher yields from the Mermentau and Vermilion River Basins may also have been a result of the higher population density and urban development in the two coastal river basins. Putting aside differences between borders of the natural drainage areas and administrative units, the Mermentau and Vermilion River Basins have higher populations than
the Amite, Tangipahoa, and Tickfaw River Basins, according to the Louisiana 2010 Census (Louisiana, 2010).

Table 2.5. Average yields of NO$_3$+NO$_2$, TKN, and TP from the four studied rivers in southwest Louisiana entering the northern Gulf of Mexico.

<table>
<thead>
<tr>
<th></th>
<th>TOC (t km$^{-2}$ yr$^{-1}$)</th>
<th>NO$_3$+NO$_2$ (kg km$^{-2}$ yr$^{-1}$)</th>
<th>TKN (kg km$^{-2}$ yr$^{-1}$)</th>
<th>TP (kg km$^{-2}$ yr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sabine</td>
<td>2.6±2.8$^a$</td>
<td>22±28$^a$</td>
<td>220±244$^a$</td>
<td>19±20$^a$</td>
</tr>
<tr>
<td>Calcasieu</td>
<td>6.6±22.8$^b$</td>
<td>44±80$^b$</td>
<td>490±1520$^b$</td>
<td>43±94$^b$</td>
</tr>
<tr>
<td>Mermentau</td>
<td>7.8±10.5$^c$</td>
<td>156±193$^c$</td>
<td>942±1292$^c$</td>
<td>206±291$^c$</td>
</tr>
<tr>
<td>Vermilion</td>
<td>7.9±7.9$^c$</td>
<td>374±343$^d$</td>
<td>1078±1095$^d$</td>
<td>360±386$^d$</td>
</tr>
</tbody>
</table>

Values in *italics* denote standard deviations; Means followed by the same letter within a column are not significantly different at the 0.05 level.

Human intervention within the natural landscape has altered stream and river water quality on the scale of the world’s largest river basins (e.g., Turner and Rabalais, 1991; Howarth et al., 1996; Jordan et al., 1997; Caraco and Cole, 1999). A key conclusion of the Goolsby et al. (1999) report concerned the source of nutrient loading delivered to the NGOM. They concluded that nonpoint sources contribute about 90% of the nitrogen and phosphorus discharging to the Gulf, and agricultural activities are the largest contributors of both nitrogen and phosphorus. It is difficult to identify precise cause-and-effect relationships between land use and nutrient fluxes (Turner et al., 2007). However, watersheds with intensive agriculture tend to have higher nutrient input into adjacent water bodies, when compared with other land uses (Alexander et al., 2006). Furthermore, the report (USEPA, 2008) identifies agriculture and urban development as major causes of excess nitrogen and phosphorus causing annual hypoxia in the NGOM. In the present study, the agricultural control of nitrogen and phosphorus fluxes was clearly reflected in the much higher nitrogen and phosphorus fluxes from the Mermentau and Vermilion River Basins, when compared the Sabine and Calcasieu River Basins.
In order to reduce nitrogen and phosphorus inputs to aquatic ecosystems, best management practices (BMPs) have been implemented in agriculture, forestry, road construction, and other land use practices in the state of Louisiana. For instance, in agriculture, Poudel et al. (2010) showed that surface run-off from a sugar cane field and pastureland with BMPs exhibited lower median values of nitrogen and phosphorus than the surface run-off from a sugar cane field and pastureland without BMPs. In 2000, the Louisiana Forestry Association, the Louisiana Department of Environmental Quality, and the Louisiana Department of Agriculture and Forestry developed a manual of recommended forestry BMPs for Louisiana (LDEQ, 2000), and the implementation of the forestry BMPs was reported to be high across various land ownerships (Xu and Rutherford, 2005). A study conducted in Louisiana by DaSilva et al. (2013) showed that timber harvest with BMPs can maintain DO in low-gradient and oxygen-depleted streams. In road construction, Bakr et al. (2012) showed that the use of compost/mulch was successful in significantly reducing TSS and turbidity in runoff from highway right-of-ways in Louisiana. The BMP adoption rates in the crawfish industry in southwestern Louisiana vary widely, depending upon the BMP, from 3% for streambank and shoreline protection to 79% for irrigation water management (Narayan and Gillespie, 2011). The Mermetau and Vermilion River Basins drain much of this area. Reduction of the TKN and TP concentrations in the Mermetau and Vermilion Rivers over the past two decades may indicate positive effects of the implementation of BMPs in agriculture and other land use activities.

Several studies (e.g., Dodds, 2003; Guilford and Hecky, 2000) have suggested that inorganic molar ratio of nitrogen and phosphorus should not be used to determine phytoplankton growth limitation in marine and fresh waters. Guilford and Hecky (2000) concluded that the TN:TP molar ratio was the most effective ratio to determine whether nitrogen or phosphorus...
limited phytoplankton growth. They found that a TN:TP molar ratio of less than 20:1 was indicative of a nitrogen-limiting system, while a TN:TP molar ratio of more than 50:1 was an indication of a phosphorus-limiting system. The TN:TP molar ratios in the four rivers studied in this paper were all less than 20:1, especially for the Mermentau and Vermilion Rivers, suggesting that nitrogen is the limited nutrient in these rivers. The TN:TP ratio in the Sabine and Calcasieu Rivers were very close to the Redfield ratio (16 N: 1 P, Redfield, 1958). Therefore, according to Justić et al. (1995), any nutrient can become limiting during different time periods, perhaps in response to small differences in nutrient supply ratios such as the seasonal changes exhibited in this study (see section 3.5). Changes in the N:P ratio can both increase blooms and change diatom species, because different species have different optimal N:P ratios for growth (Philips and Tanabe, 1989; Hodgkiss and Ho, 1997). The TN:TP ratios found in this study were within the optimal N:P ratio for the growth of many diatom species (Hodgkiss and Ho, 1997). This raises concern regarding blooms of many harmful species in the four rivers studied here, despite the lack of clear interannual trends of the TN:TP ratios in these rivers.

A number of studies (e.g. Koerner et al., 1997; Compton et al., 1998; Jussy et al., 2000) found that intensive agriculture and long-term fertilization can cause high soil N contents and low soil C:N ratios. A similar relation of soil C:P ratio with the intensity of agriculture was found (e.g. Frost et al., 2009; Vanni et al., 2011). The much lower C:N and C:P ratios in the Mermentau and Vermilion Rivers, when compared with those in the Sabine and Calcasieu Rivers (Figure 2.14), can be a reflection of the intensive agriculture and other anthropogenic activities within the two river basins. The agricultural effect on the quality of riverine carbon may be long lasting as the effect has been found in N cycling of previously cultivated soils abandoned 100 years later (Jug et al., 1999; Ritter et al., 2003).
Organic carbon in rivers can consist of particle organic carbon and dissolved organic carbon derived from terrestrial and phytoplankton sources. The proportions of the different sources have been found to be influenced by river discharge and suspended sediment (e.g., Benner and Opsahl, 2001; Bianchi et al., 2002 and 2004). River high flows are typically associated with high surface runoff, which can cause higher yield of organic and mineral particles due to surface erosion. Elser et al., 2000 found that terrestrial food webs are built on an extremely nutrient-poor autotroph base with C:P and C:N ratios higher than in lake particulate matter. The higher C:N ratios in the Calcasieu, Mermentau, and Vermilion Rivers and higher C:P ratios in the Calcasieu River in early spring months may indicate a higher terrestrial input of organic material, and the lower C:N and C:P ratios during the low-flow summertime may be a reflection of relative higher portion of phytoplankton sources.

This study fills a knowledge gap in the quantity and quality of organic carbon, nitrogen, and phosphorus discharged from four major coastal rivers entering a large summer hypoxic zone of the NGOM. This information is crucial, especially for riverine carbon and nutrient fluxes to large hypoxic open waters as carbon, nitrogen and phosphorus are important constituents of all life forms, whose structure, energetics, and functioning depend on the linkage of these elements with other major elements such as carbon, oxygen, hydrogen, and sulfur. A recent study (Aufdenkampe et al., 2011) concluded that only about 30% of carbon that entered from terrestrial ecosystems was delivered to the oceans. The mean residence time of nitrogen in any given pool can range from a few days to several hundred years (Reddy and Delaune, 2008). Global transport of phosphorus from rivers to the sea is about $21 \times 10^6$ t yr$^{-1}$ with approximately 10% of this being bioavailable to marine biota, while the remaining 90% associated with sediment particles is deposited (Schlesinger, 1997). It is not clear how much of the $13.0 \times 10^4$ t yr$^{-1}$ TOC, $1755$ t yr$^{-1}$ NO$_3$+NO$_2$
nitrogen, 12208 t yr\(^{-1}\) TKN, and 1833 t yr\(^{-1}\) TP fluxes from the four rivers are retained in the estuaries, will be actually delivered to the Gulf of Mexico, and ultimately be bioavailable to marine biota. Further studies on carbon and nutrient transport from near-shore to the deeper sea are needed to elucidate these questions.

2.5 Conclusions

This study investigated fluxes and variability of total organic carbon, nitrate and nitrite nitrogen, total Kjeldahl nitrogen, and total phosphorus from four major coastal rivers in Louisiana entering the coast of a large summer-hypoxic zone of the Northern Gulf of Mexico from 1980 to 2009. Over the past 30 years, the four coastal rivers – the Sabine, Calcasieu, Mermentau, and Vermilion Rivers – annually transported a total of 13.0\(\times 10^4\) t TOC, 1755 t \(\text{NO}_3^-+\text{NO}_2^-\) nitrogen, 12208 t TKN, and 1833 t TP into the NGOM. The variation in annual \(\text{NO}_3^-+\text{NO}_2^-\) and TP fluxes corresponded to not only the annual river discharge, but also to the \(\text{NO}_3^-+\text{NO}_2^-\) and TP concentrations. However, TOC and TKN inputs from the rivers mainly corresponded to the discharge due to a close, positive relation of TOC and TKN concentration with the river flow. Both monthly and annual means of TOC, \(\text{NO}_3^-+\text{NO}_2^-\), TKN, and TP concentrations were much higher in the Mermentau and Vermilion Rivers, which drain agriculture dominated land areas, than the Sabine and Calcasieu Rivers, which drain forest-pasture dominated land areas. Land use effects were clearly reflected in the much higher TOC, \(\text{NO}_3^-+\text{NO}_2^-\), TKN, and TP yields from the Mermentau River (7.8 t km\(^{-2}\) yr\(^{-1}\) TOC; 156 kg km\(^{-2}\) yr\(^{-1}\) \(\text{NO}_3^-+\text{NO}_2^-\), 942 kg km\(^{-2}\) yr\(^{-1}\) TKN, and 206 kg km\(^{-2}\) yr\(^{-1}\) TP) and Vermilion River (7.9, 374, 1078, and 360), when compared with those of the Sabine River (2.6, 22, 220, and 19) and Calcasieu River (6.6, 44, 490, and 43). Annual nutrient concentrations in all four rivers fluctuated largely over the past three decades, and there appear to be a clear increasing trend in TOC concentration.
in the Mermentau River since the mid-1990s and decreasing trends of the TKN and TP concentrations in the Mermentau and Vermilion Rivers since the 1990s. The two rivers draining agriculture intensive watersheds showed consistently lower C:N, C:P, TN:TP ratios, when compared with the two rivers draining forest-pasture dominated watersheds, further indicating the strong effect of agricultural practices in coastal river basins on the quantity and quality of nutrient input to estuaries.
CHAPTER 3. DISSOLVED CARBON FLUXES AND CO₂ OUTGASSING

3.1 Introduction

Rivers play an important role in the coupling of biogeochemical cycles between continents, atmosphere, and oceans (Meybeck, 1982 and 1993; Aufdenkampe et al., 2011; van Geldern et al., 2015). Riverine carbon concentrations and their variations can reflect terrestrial ecosystem changes. Accurate estimation of their mass export into oceans presents an important constraint on oceanic carbon budgets and cycling. The global riverine carbon flux has been estimated by various studies in a wide range from 0.38 to 2.6 Pg C yr⁻¹ for dissolved inorganic carbon (DIC) (e.g. Meybeck, 1982; Kempe et al., 1991; Lerman et al., 2007; Cai et al., 2008), and from 0.17 to 0.78 Pg C yr⁻¹ for dissolved organic carbon (DOC) (e.g., Meybeck, 1982; Mantoura and Woodward, 1983; Hedges and Keil, 1995; Ludwig et al., 1996; Aitkenhead and McDowell, 2000; Harrison et al., 2005; Cai et al., 2008; Dai et al., 2012). The large variation of riverine dissolved carbon fluxes can be related to several factors. First, most estimates are based on data from the world’s major large rivers with other rivers only occasionally included (Ludwig et al., 1996; Cauwet, 2002; Dai et al., 2012). Second, most riverine flux estimates are based on measurements tens to hundreds of kilometers upstream of the river mouth due to sampling constraints and limitations in determining water discharge in tidal reaches (Dai et al., 2012; Cai et al., 2016). Third, these estimates usually neglect the biogeochemical reactions within the estuaries (Dai et al., 2012). Furthermore, these estimates often do not consider the dynamic seasonal changes in DIC and DOC concentrations (Harrison et al., 2005; Dai et al., 2012).

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Large rivers with substantial discharges play an important role in global carbon cycling (Cole et al., 2007; Butman and Raymond, 2011). Concentrations of DOC in rivers are often positively correlated with discharge (Schlesinger and Melack, 1981; Mulholland et al., 1990; Wehr et al., 1997; Benner and Opsahl, 2001; Guo et al., 2012), while DIC concentrations are usually negatively correlated to river discharge (Brunet et al., 2005; Cai et al., 2008; Guo et al., 2012; Cai et al., 2016), showing a hydrological control on dissolved carbon flux. However, this is not always the case. In recent years, several studies have found a disproportionately high contribution of lower-order rivers and streams to the carbon budget, especially CO₂ emission (Johnson et al., 2008; Humborg et al., 2009; Butman and Raymond, 2011; Raymond et al., 2013). While our understanding of coastal carbon budgets is gradually improving due to a growing body of reliable measurements and modeling efforts in river, estuarine, and coastal waters, large uncertainties still exist for modern carbon flux estimates of many rivers because most studies continue to focus on the world’s major rivers (Cai et al., 2008; Dai et al., 2012). As the largest river system to the Gulf of Mexico, the Mississippi-Atchafalaya River System (MARS) has been investigated intensively, including carbon and nutrient transport and transformation (Cai, 2003; Dubois et al., 2010; Shen et al., 2012; Xu, 2013; Tian et al., 2015). However, these studies mainly focused on carbon budgeting. The dynamics of carbon in the mixing zones, as well as these processes in other coastal rivers near the Northern Gulf of Mexico, have been largely overlooked despite their potentially active role in carbon cycling. The export of dissolved carbon from small coastal rivers around the NGOM could have a significant regional influence on the coastal carbon budget and ecosystem as a whole (Johnson et al., 2008; Humborg et al., 2009; Raymond et al., 2013).
Rivers are not passive pipes that simply transport carbon from terrestrial ecosystems to the oceans (Cole et al., 2007; van Geldern et al., 2015). The transformation between carbon species can impact nutrient and trace metal cycling, biological productivity, net ecosystem metabolism, and air-water CO$_2$ exchange (Cai and Wang, 1998; Borges and Abril, 2011; Fichot and Benner, 2014), making carbon dynamics in freshwater-saltwater mixing zones a primary challenge in understanding global carbon cycling. For instance, the fate of DOC released to rivers is controlled by its coupled photochemical and biological oxidation (Cory et al., 2014), and studies have shown that photochemical oxidation usually accounts for less than 10% of total oxidation (Fichot and Benner, 2014; Robert and Doty, 2015). However, this is not the case for some systems. For instance, the rate of photochemical consumption of DOC was approximately seven times greater than bacterial DOC utilization in Rio Negro surface waters (Amon and Benner, 1996). Cory et al. (2014) showed that photochemical oxidation accounts for 70-95% of the total DOC processed in the water column of arctic lakes and rivers. Recent studies have shown that in estuarine rivers, the lateral exchange of carbon with wetlands will also affect organic and inorganic carbon variability (Cai et al., 2016; Lambert et al., 2016; Abril et al., 2014; Borges et al., 2015). Chemical and biological transformations are not the only mechanisms controlling carbon dynamics. For instance, DOC can be removed by salinity-induced flocculation within a river (Benner and Opsahl, 2001; Fransner et al., 2016), and at the same time, a source of DOC can be due to desorption of organic matter from suspended sediments (Mannino and Harvery, 2001; Etcheber et al., 2007). For coastal rivers, the physical mixing between river freshwater and ocean saltwater can also play an important role in carbon dynamics due to the existence of turbidity maximum, the zone of elevated suspended particulate material resulting from turbulent resuspension of sediment and flocculation of particulate matter in an
This is particularly relevant for small estuarine rivers that have low freshwater discharges and are strongly affected by tides and saltwater intrusion.

Most inland waters are supersaturated with CO$_2$ and serve as sources of CO$_2$ in the atmosphere (Raymond et al., 2013; van Geldern et al., 2015). Carbon dioxide transfer from inland waters to the atmosphere is a component of the global carbon cycle (Raymond et al., 2013). Raymond et al. (2013) reported a global average of ~3100 µatm for pCO$_2$ of rivers and streams, and emphasized the disproportional large contribution to CO$_2$ outgassing from low-order rivers. The high contribution of CO$_2$ outgassing from small rivers is due to the high concentration of CO$_2$ within small rivers and the negative relationship between gas transfer velocity and stream order (Butman and Raymond, 2011). The important role of small rivers has also been highlighted by other studies on CO$_2$ outgassing from inland waters (e.g., Johnson et al., 2008; van Geldern et al., 2015). Quantification of CO$_2$ outgassing from small rivers is essential for a better understanding of the global carbon cycle.

In the recent past, the Louisiana Gulf coast has had one of the highest relative sea-level rises in the United States (Dixon et al., 2006; Ivins et al., 2007). Saltwater intrusion has been observed in many coastal rivers in the region, and the Calcasieu River is a prime example. The river flows 322 km through a low-lying Chenier Plain in Southwest Louisiana entering the Northern Gulf of Mexico (NGOM). In the late 1940s, the U.S. Congress authorized the U.S. Army Corps of Engineers to construct a deep-draft channel in the Calcasieu River from Lake Charles to the Gulf of Mexico (GOM). Millions of cubic meters of material were dredged from the river reach so that the waterway would be sufficiently deep so as to handle ocean-going vessels (USACE). Since the completion of this project in 1953, the Port of Lake Charles has
become one of the America’s largest ports (USACE, 2010). On the other hand, the channel deepening allowed saltwater intrusion from the Gulf, threatening the upper Calcasieu River, which provides water for agricultural irrigation. To prevent saltwater from traveling north further upstream, as well as to regulate freshwater outflow, a saltwater barrier dam was constructed upstream of Lake Charles in the 1960s (USACE). This saltwater intrusion problem makes the river estuary an ideal location to study dissolved carbon dynamics in a mixing zone across salinity gradients, as the aforementioned hydrological alterations may have had considerable effects on river carbon transport.

Many studies have been conducted on dissolved carbon for the Mississippi River (e.g. Cai, 2003; Bianchi et al., 2004; Raymond et al., 2008; Cai et al., 2008; Roberts and Doty, 2015), which has a high volume of freshwater discharge pushing into the far-shore open water. On the other hand, little is known about dissolved carbon dynamics in Louisiana’s small estuarine rivers such as the Calcasieu, which has low freshwater discharge and is strongly affected by tides and saltwater intrusion. This study aims to determine how DIC and DOC concentrations change along the Calcasieu River, to elucidate which processes most likely control carbon dynamics in this system. The primary goal of the study is to test the hypothesis that physical mixing of freshwater and saltwater in an estuary is the ultimate controlling factor on dissolved carbon dynamics. The specific objectives of this study were to (1) quantify the terrestrial fluxes of DIC and DOC into the Calcasieu River estuary and CO₂ outgassing to atmosphere from the Calcasieu River; (2) investigate temporal and spatial dynamics of DIC and DOC concentrations from the upstream to the downstream of the Calcasieu River, and (3) assess factors that influence the spatiotemporal dynamics of DIC and DOC concentrations and fluxes. Since the mineralization of organic carbon is closely tied to production of DIC, studying DIC and DOC concentrations and
yields together in this estuarine river can help improve both our understanding and estimation of carbon flux in freshwater-saltwater mixing zones. Our recent publication on the same river estuary (He and Xu 2017) assessed dissolved carbon sources and changes in the estuarine reach using DIC and DOC concentrations and their stable isotopes collected from May 2015 to February 2016. The present manuscript, with thirteen-month data collected from November 2013 to December 2014, complements the previous study by focusing on dissolved carbon mass fluxes, CO₂ outgassing, and carbon seasonal dynamics in this estuarine river.

3.2 Methods

3.2.1 Study area

This study was conducted along the Calcasieu River’s last 88-km reach to the NGOM (Figure 3.1a) in southwest Louisiana, the United States. Historically, this river reach experienced extensive saltwater intrusion; hence, a saltwater barrier dam (Figure 3.1a) was constructed at the upstream location in the 1960s. The climate of the study area is subtropical, characterized by long, hot, and humid summers and generally short, mild winters. During the sampling period from November 2013 to December 2014, the average monthly temperature ranged from 8.6 °C in January 2014 to 27.9 °C in August 2014, with an annual mean of 19.7 °C for 2014 (National Oceanic and Atmospheric Administration (NOAA) station: Lake Charles, LA - Station ID: 8767816). Land use in the northern part of the river drainage area (Calcasieu Parish) is primarily agricultural. More than 65% of the land is used as cultivated cropland, pastureland, and woodland, and the remaining acreage is urban, marshland, or swampland (USDA, 1988). The southern part of the river drainage area (Cameron Parish) is mostly covered by coastal marshland. These marshes are used mainly as habitats for wildlife, rangeland, and oil and gas fields (USDA, 1995).
Figure 3.1. (a) Geographic locations of the Calcasieu River estuary, six sampling sites, and the United States Geological Survey (USGS) discharge gauging station at Kinder in Louisiana (Station# 08015500) and the USGS tidal gauging at Cameron in Louisiana (Station# 08017118); This map was generated using ArcGIS10.2 (http://www.esri.com/software/arcgis/arcgis-for-desktop). (b) Discharge at Kinder and gage height at Cameron. River water sampling and in-situ measurements were conducted over a wide range of river discharge and tidal conditions from November 1, 2013 to December 31, 2014.
3.2.2 Water sampling and in-situ measurements

Six sampling sites were selected along the aforementioned 88-km reach of the Calcasieu River (Figure 3.1a). Sites 1 and 2 were located above the saltwater barrier dam and, therefore, water samples collected from the two sites were freshwater. All other sites downstream (i.e. sites 3, 4, 5, and 6) were saltwater affected to varied degrees, depending on river discharge and tidal mixing at the time of field sampling. Monthly field trips to the sites were made between November 2013 and December 2014. During each trip, composite water samples were collected at each site approximately 30-50 cm below the river surface. Note that site 3 was only sampled from August 2014 to December 2014. The samples were collected from piers reaching out about 8-15 m into the river channel with a grab sampler consisting of a 3.7-meter aluminum pole with a polyethylene bottle attached at the end of the pole. High Density Polyethylene (HDPE) bottles were used to store water samples, and all bottles were thoroughly acid-cleaned before use. All the water samples were stored in a cooler with wet ice during transportation, and refrigerated until chemical analysis.

These sampling trips were conducted over a wide range of river discharge and tidal conditions (Figure 3.1b). To record ambient water conditions, in-situ measurements were performed on water temperature, dissolved oxygen (DO) concentration, pH, and salinity with an YSI 556 multi-probe meter (YSI Inc., Yellow Springs, OH, USA).

3.2.3 Water sample analysis

Water samples were analyzed for concentrations of DIC and DOC at the Central Analytical Instruments Research Laboratory, Louisiana State University Agricultural Center using EPA Method 415.1. All samples were filtered by 0.45-µm syringe disk filters that were pre-cleaned with 20 mL of deionized water. The samples were analyzed for DIC and dissolved
total carbon (DTC) using a TOC-Vcsh Total Organic Carbon Analyzer (Shimadzu Corporation, Japan). The DOC concentrations were calculated as the difference between DTC and DIC. Field and lab blanks and carbon standard solutions (100 ppm, SCP Science) were used for quality control to ensure that the samples were not contaminated, and that all sample analyses were within control limits. Laboratory duplicate measurements of identical water samples typically yielded differences of less than 6.6%. The recovery rates of lab control samples were ranged from 91.0% to 103.5%.

3.2.4 pCO₂ calculation

In order to assess CO₂ outgassing from the Calcasieu River, monthly partial pressure of CO₂ in the surface water was estimated using the following equation developed by Cai and Wang (1998):

\[
pCO_2(\text{water}) = \frac{[CO_2]}{K_H} = \frac{c_{DIC}[H]^2}{((H)^2+(H)K_1+K_1K_2)K_H} \tag{1}
\]

where \( pCO_2(\text{water}) \) is the estimated pCO₂ in water in µatm, \( c_{DIC} \) is the DIC concentration in µM, \( \{H\} = 10^{-pH} \), and \( K_H \) is the solubility constant expressed in moles L⁻¹ atm⁻¹. Parameters \( K_1 \) and \( K_2 \) are the dissociation constants of carbon acid, which can be calculated by (Cai and Wang, 1998):

\[
logK_1 = -\frac{3404.71}{T} - 0.032786T + 14.8435 + 0.071692\left(\frac{200.1}{T} + 0.3220\right)S^{0.5} - 0.0021487\left(\frac{200.1}{T} + 0.3220\right)S \tag{2}
\]

\[
logK_2 = -\frac{2902.39}{T} - 0.02379T + 6.4980 + 0.3191\left(\frac{-129.24}{T} + 1.4381\right)S^{0.5} - 0.0198S \tag{3}
\]
where $T$ is the absolute temperature in Kelvin, and $S$ is the salinity.

The solubility constant can be calculated using Eq. (4) (Weiss, 1974):

$$\ln K_H = A_1 + A_2 \left( \frac{100}{T} \right) + A_3 \ln \left( \frac{T}{100} \right) + S[B_1 + B_2 \left( \frac{T}{100} \right) + B_3 \left( \frac{T}{100} \right)^2]$$

(4)

where $A_1 = -58.0931$, $A_2 = 90.5069$, $A_3 = 22.2940$, $B_1 = 0.027766$, $B_2 = -0.025888$, $B_3 = 0.0050578$, $T$ is the absolute temperature in Kelvin, and $S$ is the salinity.

With the estimated pCO$_2$ in surface water, CO$_2$ outgassing from water to the atmosphere ($F_{CO_2}$ in mmol m$^{-2}$ d$^{-1}$) can then be calculated by (Cai and Wang, 1998):

$$F_{CO_2} = K_T ([CO_2(\text{water})] - [CO_2(\text{air})]) = K_T K_H [pCO_2(\text{water}) - pCO_2(\text{air})]$$

(5)

where $pCO_2(\text{air})$ is the atmospheric CO$_2$ pressure set as 390 µatm (van Geldern et al., 2015) for this study period, and $K_T$ is the gas transfer velocity. Raymond et al. (2012) reported an average gas transfer velocity of 4.7 m d$^{-1}$ for small streams and rivers, while Raymond et al., 2013 reported a global average gas transfer velocity of 5.7 m d$^{-1}$ for streams and rivers. Ideally, one should correlate gas transfer velocities to local wind and physical mixing conditions (Cai et al., 1999). However, there were not enough data to develop a meaningful correlation between pCO$_2$ and wind. Considering the hydrological and environmental conditions of the Calcasieu River, we chose the 4.7 m d$^{-1}$ as the gas transfer velocity to calculate CO$_2$ fluxes in this study.

To calculate the amount of CO$_2$ outgassing for the study area (kg C yr$^{-1}$), water surface areas of the river (Table 3.1) was calculated using ArcGIS 10.2 by digitizing the water area on a satellite image downloaded from the United States Geological Survey Earth Explorer (https://earthexplorer.usgs.gov/). The satellite image was taken on December 16, 2013 by the American earth observation satellite Landsat 8. The mean $F_{CO_2}$ at each site was used to represent the CO$_2$ flux rate around that site. For instance, the mean $F_{CO_2}$ at site 1 was used to represent the
CO₂ flux rate at the upper half of the water surface area between sites 1 and 2, while the mean $F_{CO₂}$ at site 2 was used to represent the CO₂ flux rate at the lower half of the water surface area between sites 1 and 2 as well as the upper half of the water surface area between sites 2 and 3, and so on.

Table 3.1. Water surface area at different sections of the studied 88-km reach of the Calcasieu River. The areas were calculated using ArcGIS 10.2 by digitizing the water area on a satellite image downloaded from United States Geological Survey Earth Explorer (https://earthexplorer.usgs.gov/). The image was taken on December 16, 2013 by the American earth observation satellite Landsat 8.

<table>
<thead>
<tr>
<th>River Section</th>
<th>Area (km²)</th>
<th>CO₂ Outgassing (kg C yr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site 1 to Site 2</td>
<td>2.33</td>
<td>0.047×10⁸</td>
</tr>
<tr>
<td>Site 2 to Saltwater Barrier</td>
<td>1.49</td>
<td>0.032×10⁸</td>
</tr>
<tr>
<td>Saltwater Barrier to Site 3</td>
<td>1.49</td>
<td>0.030×10⁸</td>
</tr>
<tr>
<td>Site 3 to Site 4</td>
<td>4.66</td>
<td>0.11×10⁸</td>
</tr>
<tr>
<td>Site 4 to Site 5</td>
<td>57.49</td>
<td>1.19×10⁸</td>
</tr>
<tr>
<td>Site 5 to Site 6</td>
<td>201.87</td>
<td>1.71×10⁸</td>
</tr>
<tr>
<td>Site 6 to Gulf of Mexico</td>
<td>2.71</td>
<td>0.0048×10⁸</td>
</tr>
<tr>
<td>Total</td>
<td>272.05</td>
<td>3.12×10⁸</td>
</tr>
<tr>
<td>Lake Charles</td>
<td>4.27</td>
<td>0.098×10⁸</td>
</tr>
<tr>
<td>Calcasieu Lake</td>
<td>176.86</td>
<td>1.93×10⁸</td>
</tr>
<tr>
<td>West Cove</td>
<td>37.98</td>
<td>0.067×10⁸</td>
</tr>
</tbody>
</table>

3.2.5 Riverine carbon flux calculation and statistical analysis

To estimate dissolved carbon mass input from freshwater of the Calcasieu River into its mixing zone near the NGOM, daily discharge and gage records for the Calcasieu River were collected from the United States Geological Survey (USGS). The gage stations were chosen based on availability and their proximity to the sampling sites for optimal representation. Specifically, daily river discharge was collected at the Calcasieu River near Kinder, LA (USGS 08015500), and the daily river gage data was collected at the Calcasieu River near Cameron, LA (USGS 08017118) (Figure 3.1b).
The total carbon load of a river has been found to be essentially the product of the river’s discharge and carbon concentration (Goolsby et al., 2001; Xu, 2013). In this study, we estimated daily DOC fluxes of the Calcasieu River using a rating curve that can be described as the following log-linear regression model (Xu, 2013):

\[
\ln(S(t)) = b_0 + b_1 \ln(Q(t)) + \varepsilon(t)
\]

where \(Q(t)\) represents the discharge in \(m^3 \text{ s}^{-1}\), \(S(t)\) is the DOC flux in \(\text{mol} \text{ s}^{-1}\), and \(\varepsilon(t)\) is an error term assumed to be normally distributed. Application of the equation yielded satisfactory results (Table 3.2).

Table 3.2. Parameter estimates (\(b_0\) and \(b_1\)) used in Equation (6) and Equation (7) for estimating carbon mass loads and their regression coefficients (\(R^2\)) (SE=standard error, RMSE = root of mean square error, \(n = \) sample size). Discharge and concentrations of DIC and DOC at site 1 were used for the regressions.

<table>
<thead>
<tr>
<th></th>
<th>(b_0)±SE</th>
<th>(b_1)±SE</th>
<th>(R^2)</th>
<th>RMSE</th>
<th>(p) value</th>
<th>(n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIC(^a)</td>
<td>3.46±0.89</td>
<td>0.11±0.01</td>
<td>0.85</td>
<td>2.40</td>
<td>&lt;0.0001</td>
<td>13</td>
</tr>
<tr>
<td>DOC(^b)</td>
<td>-0.90±0.41</td>
<td>1.28±0.12</td>
<td>0.92</td>
<td>0.33</td>
<td>&lt;0.0001</td>
<td>13</td>
</tr>
</tbody>
</table>

\(^a\)Used Eq. (7);  
\(^b\)Used Eq. (6);

However, application of Eq. (6) for DIC in this study yielded unsatisfactory fitness of the model parameters (\(R^2\) value< 0.6). Therefore, a different regression model was used for DIC:

\[
S(t) = b_0 + b_1 Q(t) + \varepsilon(t)
\]

where \(Q(t)\) represents the discharge in \(m^3 \text{ s}^{-1}\), \(S(t)\) is the DIC flux in \(\text{mol} \text{ s}^{-1}\), and \(\varepsilon(t)\) is an error term assumed to be normally distributed (Table 3.2).

Carbon concentrations at site 1 were used to calculate daily carbon fluxes from the Calcasieu River freshwater. Because site 1 and the USGS discharge gage station at Kinder were about 40 km apart, we used an area-weighting to estimate the runoff from the land between the two locations. First, the drainage areas to Kinder and to site 1 were delineated using ArcSWAT
2012, an ArcGIS extension, and digital elevation model (DEM) data obtained from the USGS National Map (https://viewer.nationalmap.gov/basic/). Then, a discharge correction for site 1 was computed based on the ratio between the drainage area of site 1 and the drainage area of Kinder, similar to the method used by Wu and Xu (2007), as follows

\[
Q_{site\ 1} = Q_{Kinder} \cdot \frac{\text{drainage area at site 1}}{\text{drainage area at Kinder}}
\]  

(8)

This simple approach is based on the fact that the drainage area of site 1 has very similar climate, soil, and vegetation conditions to the drainage area for Kinder.

The calculated discharge for site 1 \(Q_{site\ 1}\) was then used to estimate daily carbon fluxes from the Calcasieu River freshwater. A comparison between measured dissolved carbon fluxes and estimated dissolved carbon fluxes are shown on Figure 3.2. Even though the relationships between discharge and dissolved carbon concentrations at site 1 were not clear (Figure 3.3), relationships between discharge and dissolved carbon fluxes at site 1 were significant (Figure 3.4). Carbon yield for the Calcasieu River basin (mass per unit area per unit time) was calculated by dividing the carbon flux by the basin drainage area at site 1. This normalizes carbon flux so that comparison in discussion with other river basins could be made.

A two-way analysis of variance (ANOVA) comparing water sample values was performed separately for each of DIC concentration, pCO\(_2\), DOC concentration, and DIC/DOC based on the sampling sites and months. Pearson correlation coefficients were calculated to analyze the relationships of DIC concentration, pCO\(_2\), DOC concentration, and DIC/DOC with environmental parameters, including salinity, pH, temperature, and DO concentration, as this coefficient measures the strength of a linear relationship between two parameters (Kim et al., 2015). While being a useful and straightforward way to investigate potential factors affecting
carbon concentrations, the Pearson correlation coefficient only considers one factor at a time, which can lead to large p values due to large numbers of variables. To explore potential factors affecting carbon concentrations, a backward stepwise linear regression was also performed between DIC concentration, pCO$_2$, DOC concentration, DIC/DOC, and environmental parameters. All statistical analyses were performed with the SAS Statistical Software package (SAS Institute Inc., Cary, NC).

![Graph](image)

**Figure 3.2.** Relationships of measured DIC and DOC fluxes with estimated DIC and DOC fluxes using Eq.6 for DOC and Eq.7 for DIC, for the Calcasieu River between November 2013 and December 2014.

![Graph](image)

**Figure 3.3.** Relationships of DIC and DOC concentrations with discharge at site 1 for the Calcasieu River between November 2013 and December 2014.
3.3 Results

3.3.1 Hydrology and ambient conditions

From November 2013 to December 2014, the Calcasieu River showed an average daily discharge of 32 m$^3$ s$^{-1}$ (std: ±27), ranging from 6 to 172 m$^3$ s$^{-1}$ (Figure 3.1b). The discharge during this sampling period was notably lower than the reported long-term average of 72 (±66 m$^3$ s$^{-1}$) from 1980 to 2009 (He and Xu, 2015). The river exhibited the same seasonal pattern during the study period as in the period from 1980 to 2009, with February having the highest average discharge (78 m$^3$ s$^{-1}$) and August the lowest (13 m$^3$ s$^{-1}$). The average daily gage height at Cameron ranged from -0.32 to 0.83 m, with an average of 0.28 m (±0.20). Seasonally, in contrast with the river discharge, the tidal stage at the river mouth was high in the fall months, with September having the highest monthly average (0.58 m), and low in the winter months, with March having the lowest monthly average (0.05 m), influencing salinity distribution along the 88-km river estuary.

Figure 3.4. Relationships of DIC and DOC fluxes with discharge at site 1 for the Calcasieu River between November 2013 and December 2014.
The ambient conditions at the six sampling sites varied largely (Table 3.3 and Figure 3.5). Salinity levels at site 6, the closest location to the Gulf of Mexico, ranged from 4.80 to 29.50, with an average of 19.71, which was more than 280 times higher than that of site 1, the most upstream location. The salinity levels increased with decreasing distance from the GOM (Table 3.3 and Figure 3.5a) and, as expected, pH was positively correlated to salinity (Table 3.4). However, pH had a larger variation than salinity did (Figure 3.5b), as seen at sites 1 and 2 where the salinity levels were both low, but the pH levels varied from 3.79 to 8.76. From November 2013 to March 2014, pH exhibited large variation, and stayed fairly stable after March 2014 (Figure 3.5b). The average DO concentrations at sites 5 and 6 were significantly higher than those of the other sites (Table 3.3). Being nearest to the GOM, sites 5 and 6 were strongly impacted by saltwater. The stronger tidal movement at these two sites may have aerated the water, as reflected by the higher DO levels at the sites. Due to the negative relationship between temperature and DO, the DO concentrations were higher during winter and spring months and lower during summer and fall months (Figure 3.5d).

Table 3.3. Means and standard deviations of environmental parameters at six sampling sites along the Calcasieu River between November 2013 and December 2014. Tukey-Kramer’s adjustment was used to group sampling sites when ANOVA shows significant differences among sites. Means with the same letter are not significantly different at the 0.05 level (Tukey groupings). Due to limited data, site 3 was excluded from the Tukey groupings.

<table>
<thead>
<tr>
<th>Site ID</th>
<th>River Kilometer</th>
<th>n</th>
<th>Salinity</th>
<th>pH</th>
<th>Temperature (°C)</th>
<th>DO (mg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site 1</td>
<td>87.9</td>
<td>13</td>
<td>0.04±0.02a</td>
<td>6.51±0.85</td>
<td>19.99±7.09</td>
<td>6.02±2.31a</td>
</tr>
<tr>
<td>Site 2</td>
<td>73.5</td>
<td>13</td>
<td>0.13±0.16a</td>
<td>6.33±0.81</td>
<td>20.03±7.80</td>
<td>5.35±2.42a</td>
</tr>
<tr>
<td>Site 3</td>
<td>62.6</td>
<td>4</td>
<td>2.93±1.63</td>
<td>6.68±0.35</td>
<td>24.18±6.57</td>
<td>4.00±1.57</td>
</tr>
<tr>
<td>Site 4</td>
<td>58.1</td>
<td>13</td>
<td>5.90±4.08b</td>
<td>6.54±0.96</td>
<td>20.41±7.81</td>
<td>5.65±2.56a</td>
</tr>
<tr>
<td>Site 5</td>
<td>27.0</td>
<td>13</td>
<td>16.09±4.09c</td>
<td>7.56±0.52</td>
<td>20.58±7.82</td>
<td>7.05±2.41ab</td>
</tr>
<tr>
<td>Site 6</td>
<td>4.5</td>
<td>13</td>
<td>23.24±2.70d</td>
<td>8.08±0.33</td>
<td>20.82±7.59</td>
<td>8.10±2.78b</td>
</tr>
<tr>
<td>Calcasieu</td>
<td>69</td>
<td></td>
<td>8.05±2.11</td>
<td>6.95±0.64</td>
<td>21.00±7.45</td>
<td>6.03±2.34</td>
</tr>
</tbody>
</table>
Figure 3.5. Temporal trends of salinity (a), pH (b), temperature (c), and DO concentration (d) at six sampling sites along the Calcasieu River between November 2013 and December 2014.

Table 3.4. Pearson correlation coefficients between carbon and environmental parameters in the Calcasieu River between November 2013 and December 2014. Only significant \((p<0.01)\) correlations are shown.

<table>
<thead>
<tr>
<th></th>
<th>DIC</th>
<th>pCO(_2)</th>
<th>DOC</th>
<th>DIC/DOC</th>
<th>Salinity</th>
<th>pH</th>
<th>Temperature</th>
<th>DO</th>
<th>Discharge</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIC</td>
<td>1.00</td>
<td>-0.32</td>
<td>-0.49</td>
<td>0.60</td>
<td>0.93</td>
<td>0.69</td>
<td>0.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pCO(_2)</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td>-0.43</td>
<td>-0.71</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>DOC</td>
<td>1.00</td>
<td>-0.49</td>
<td></td>
<td>-0.61</td>
<td>-0.62</td>
<td>-0.62</td>
<td>-0.52</td>
<td>0.42</td>
<td></td>
</tr>
<tr>
<td>DIC/DOC</td>
<td></td>
<td></td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Salinity</td>
<td></td>
<td></td>
<td></td>
<td>1.00</td>
<td>0.36</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>pH</td>
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<td></td>
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<td></td>
<td>1.00</td>
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<tr>
<td>Temperature</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.00</td>
<td>-0.84</td>
<td>-0.52</td>
</tr>
<tr>
<td>DO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.00</td>
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<td>0.49</td>
</tr>
<tr>
<td>Discharge</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.00</td>
</tr>
</tbody>
</table>
3.3.2 Spatiotemporal trend of DIC concentration

The DIC concentration showed considerable variation among the six sampling sites, with a clear, significantly increasing trend as the river travels to the NGOM (Table 3.5 and Figure 3.6a). The average DIC concentration at the river-mouth site (site 6) was 1.64 mM, which was about 6 times higher than that (0.24 mM) at the upstream site (site 1) (Table 3.5). There was also a large temporal variation in DIC concentration at each site: from 0.05 to 0.41 mM at site 1, from 0.12 to 0.45 mM at site 2, from 0.25 to 0.73 mM at site 3, from 0.21 to 1.21 mM at site 4, from 0.38 to 1.80 mM at site 5, and from 0.50 to 2.14 mM at site 6 (Figure 3.6a). The difference in monthly DIC concentration was statistically significant ($p=0.0137$, Table 3.6). Different sites showed distinct seasonal trends of DIC concentration (Figure 3.6d). For instance, sites 1 and 2 had the highest DIC concentration during summer months, while site 4 had the highest DIC concentration during fall months and sites 5 and 6 had the highest DIC concentration during winter months. In the interactive effect of sampling site and month, the DIC concentration showed no statistically significant differences ($p=0.2064$, Table 3.6).

Table 3.5. Means ± standard deviations of dissolved carbon concentrations, DIC/DOC ratio, and pCO$_2$ at six sampling sites along the Calcasieu River between November 2013 and December 2014. Tukey-Kramer’s adjustment was used to group sampling sites when ANOVA shows significant differences among sites. Means with the same letter are not significantly different at the 0.05 level (Tukey groupings). Due to limited data, site 3 was excluded from the Tukey groupings.

<table>
<thead>
<tr>
<th>Site ID</th>
<th>n</th>
<th>DIC (mM)</th>
<th>pCO$_2$ (µatm)</th>
<th>DOC (mM)</th>
<th>DIC/DOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site 1</td>
<td>13</td>
<td>0.24±0.10$^a$</td>
<td>2948±1944</td>
<td>1.13±0.41$^a$</td>
<td>0.26±0.19$^a$</td>
</tr>
<tr>
<td>Site 2</td>
<td>13</td>
<td>0.25±0.10$^a$</td>
<td>3201±2283</td>
<td>1.17±0.46$^a$</td>
<td>0.27±0.19$^a$</td>
</tr>
<tr>
<td>Site 3</td>
<td>4</td>
<td>0.45±0.23</td>
<td>3148±1114</td>
<td>0.99±0.45</td>
<td>0.53±0.33</td>
</tr>
<tr>
<td>Site 4</td>
<td>12$^*$</td>
<td>0.58±0.28$^b$</td>
<td>3682±2450</td>
<td>1.05±0.36$^a$</td>
<td>0.60±0.30$^b$</td>
</tr>
<tr>
<td>Site 5</td>
<td>13</td>
<td>1.29±0.38$^c$</td>
<td>2117±2588</td>
<td>0.75±0.28$^a$</td>
<td>1.87±0.74$^b$</td>
</tr>
<tr>
<td>Site 6</td>
<td>13</td>
<td>1.64±0.41$^d$</td>
<td>583±506</td>
<td>0.56±0.30$^b$</td>
<td>4.50±5.28$^c$</td>
</tr>
<tr>
<td>Calcasieu</td>
<td>68</td>
<td>0.74±0.25</td>
<td>2528±2237</td>
<td>0.94±0.38</td>
<td>1.34±1.17</td>
</tr>
</tbody>
</table>

$^*$One of the samples was destroyed during transportation
Figure 3.6. Spatiotemporal trends of DIC, DOC, and DIC/DOC at six sampling sites along the Calcasieu River from November 2013 to December 2014; River Kilometer: distance between the site and the river mouth. Distance between the Gulf of Mexico and sites 1 to 6 are 87.9, 73.5, 62.6, 58.1, 27.0, and 4.5 km, respectively; Spring represents the average concentration of March, April, and May 2014; Summer represents the average concentration of June, July, and August 2014; Fall represents the average concentration of November 2013, September 2014, and October 2014; Winter represents the average concentration of December 2013, January, February, and December 2014; Site 3 was only sampled from August 2014 to December 2014; Error bars represent standard errors of means; At least two measurements are needed to calculate standard error; The small inside-figure in (f) has the same axes as the larger figure, except that the y-axis has smaller range.
## Table 3.6: Results from two-way analyses of variance (ANOVAs) performed separately for DIC concentration, pCO$_2$, DOC concentration, and DIC/DOC ratio for main (site, month) and interactive effects (site $\times$ month) of sampling site and month. Num DF is the degrees of freedom of the numerator in the F distribution, and Den DF is the degrees of freedom of the denominator in the F distribution. A high F value and a low p value indicate significant main and interactive effects.

<table>
<thead>
<tr>
<th></th>
<th>Num DF</th>
<th>Den DF</th>
<th>F</th>
<th>p value</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIC</td>
<td>Site</td>
<td>5</td>
<td>4</td>
<td>200.4</td>
</tr>
<tr>
<td></td>
<td>Month</td>
<td>11</td>
<td>4</td>
<td>12.20</td>
</tr>
<tr>
<td></td>
<td>Site $\times$ Month</td>
<td>47</td>
<td>4</td>
<td>2.38</td>
</tr>
<tr>
<td>pCO$_2$</td>
<td>Site</td>
<td>5</td>
<td>4</td>
<td>1.34</td>
</tr>
<tr>
<td></td>
<td>Month</td>
<td>10</td>
<td>4</td>
<td>0.62</td>
</tr>
<tr>
<td></td>
<td>Site $\times$ Month</td>
<td>43</td>
<td>4</td>
<td>0.24</td>
</tr>
<tr>
<td>DOC</td>
<td>Site</td>
<td>5</td>
<td>4</td>
<td>12.25</td>
</tr>
<tr>
<td></td>
<td>Month</td>
<td>11</td>
<td>4</td>
<td>11.37</td>
</tr>
<tr>
<td></td>
<td>Site $\times$ Month</td>
<td>47</td>
<td>4</td>
<td>0.42</td>
</tr>
<tr>
<td>DIC/DOC</td>
<td>Site</td>
<td>5</td>
<td>4</td>
<td>60.17</td>
</tr>
<tr>
<td></td>
<td>Month</td>
<td>11</td>
<td>4</td>
<td>12.73</td>
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<tr>
<td></td>
<td>Site $\times$ Month</td>
<td>47</td>
<td>4</td>
<td>8.99</td>
</tr>
</tbody>
</table>

### 3.3.3 Spatiotemporal trends of DOC concentration and DIC/DOC

In general, the DOC concentration decreased with decreasing distance to the GOM (Table 3.5), and the spatial difference in DOC concentration was statistically significant ($p=0.0154$, Table 3.6). Temporally, the DOC concentration varied largely at all the sampling sites: from 0.48 to 1.91 mM at site 1, from 0.53 to 1.91 mM at site 2, from 0.58 to 1.61 mM at site 3, from 0.53 to 1.79 mM at site 4, from 0.43 to 1.26 mM at site 5, and from 0.10 to 1.02 mM at site 6. Seasonally, the DOC concentration had a large variation and there was a significant difference among sampling months ($p=0.0156$, Table 3.6). In general, all six sites had highest DOC concentration during winter months and lowest during summer (Figure 3.6). In the interactive effect of sampling site and month, the DOC concentration showed no significant differences ($p=0.9342$, Table 3.6).

From upstream to downstream, the DIC concentration increased while the DOC concentration decreased. Consequently, the DIC/DOC ratio increased with the decreasing
distance to the GOM (Table 3.5). The spatiotemporal difference in DIC/DOC ratio was statistically significant ($p=0.0007$ and $p=0.0127$, Table 3.6). The average DIC/DOC ratio increased from 0.26 at site 1 to 4.50 at site 6. The DIC/DOC ratio varied largely at all sites: from 0.06 to 0.73 at site 1, from 0.07 to 0.68 at site 2, from 0.16 to 0.95 at site 3, from 0.12 to 1.16 at site 4, from 0.77 to 3.49 at site 5, and from 1.64 to 21.49 at site 6. Seasonally, the DIC/DOC ratio was the highest in summer months and lowest in winter months (Figure 3.6f).

3.3.4 pCO$_2$ and CO$_2$ outgassing

Throughout the sampling period, all six sites exhibited CO$_2$ supersaturation with respect to the atmospheric CO$_2$ pressure during most of the sampling trips (Figure 3.7a). The average pCO$_2$ values at site 1 through site 6 were 2948, 3201, 3148, 3682, 2117, and 583 µatm, respectively, with the first four sites having higher values than the last two downstream sites. However, the spatial difference in pCO$_2$ was not statistically significant ($p=0.3994$, Table 3.6). There was a large temporal variation in pCO$_2$ at each site: from 24 to 6350 µatm at site 1, from 617 to 8574 µatm at site 2, from 1516 to 3976 µatm at site 3, from 827 to 8822 µatm at site 4, from 134 to 9552 µatm at site 5, and from 102 to 1924 µatm at site 6 (Figure 3.7a). Seasonal trends of pCO$_2$ varied among different sites. For instance, for sites 1 through 3, pCO$_2$ was the highest during summer months, while for sites 4 through 6, pCO$_2$ was the highest during winter months (Figure 3.7b).

The spatiotemporal trend of the CO$_2$ outgassing flux ($F_{CO_2}$) was similar to that of pCO$_2$ (Figure 3.7). At sites 1 through 6, the average $F_{CO_2}$ ranged from 15 to 218 mol m$^{-2}$ yr$^{-1}$, with a mean of 140 mol m$^{-2}$ yr$^{-1}$ for the whole study area (Figure 3.7c). The carbon emission through CO$_2$ outgassing from the last 87.9 km of the river was estimated to be $3.12\times10^8$ kg C yr$^{-1}$, which includes the emissions from the three largest lakes in this area: Lake Charles ($0.098\times10^8$ kg C yr$^{-1}$...
1), Calcasieu Lake (1.93×10^8 kg C yr^{-1}), and West Cove (0.067×10^8 kg C yr^{-1}). When the three lakes are included, the portion of the river from site 1 to the Saltwater Barrier (freshwater) accounts for 1.40% of the total water surface area and 2.54% of the total CO\textsubscript{2} emission. When the three lakes are excluded, the portion of the river from site 1 to the Saltwater Barrier accounts for 7.22% of the water surface area and 7.69% of the CO\textsubscript{2} emission.

3.3.5 Riverine dissolved carbon flux and yield

For the sampling period from November 2013 to December 2014, the Calcasieu River discharged 0.25×10^9 mol DIC and 1.77×10^9 mol DOC from its freshwater into the estuary water (Figure 3.8), showing a DIC yield of 43×10^3 mol km\textsuperscript{-2} yr\textsuperscript{-1} and a DOC yield of 296×10^3 mol km\textsuperscript{-2} yr\textsuperscript{-1} from the drainage basin. As a whole, the annual total export of dissolved total carbon (DIC + DOC) from the river’s freshwater was 2.02×10^9 mol C yr\textsuperscript{-1}, or 339×10^3 mol C km\textsuperscript{-2} yr\textsuperscript{-1}. Seasonally, the Calcasieu River showed the highest monthly fluxes of DIC and DOC in February 2014 (Figure 3.8), corresponding to the river high flow conditions (Figure 3.1b). In that month, the river discharged 0.04×10^9 mol DIC and 0.44×10^9 mol DOC into the estuary, contributing 15% and 25% of the annual total DIC and DOC exports, respectively. The yields of DIC and DOC in the month were 6.49×10^3 and 73.44×10^3 mol km\textsuperscript{-2} month\textsuperscript{-1}, respectively. The DOC had much higher fluxes and yields than the DIC (Figure 3.8) due to the higher DOC concentration at freshwater site 1.

3.4. Discussion

3.4.1 Factors affecting DIC concentration in a mixing zone

This study shows that DIC concentration in an estuarine river increases rapidly from the upstream to downstream reaches despite a relatively low DIC input from the river’s freshwater.
DIC content in a river can be controlled by several biogeochemical processes, including soil emission, in-stream respiration, photosynthesis of phytoplankton, carbonate and silicate weathering, and gas exchange with the atmosphere (Aucour et al., 1999; Cai et al., 2008; Butman and Raymond, 2011; Raymond et al., 2013; van Geldern et al., 2015). Although it is difficult to identify individual contributions of these processes without further evidence, we can, based on the observed spatiotemporal trend of DIC and its relationships with several environmental parameters, make some very possible inferences. We suggest that conservative physical mixing between freshwater from the river and saltwater from the NGOM has been the main factor controlling the spatial trend of DIC concentration in the studied river, while other factors, such as respiration, photosynthesis, weathering, and CO$_2$ outgassing, have play a role in the seasonal trend, and partially influence the spatial trend as well.

To analyze these factors, we performed backward stepwise multiple linear regressions that included DIC concentration and environmental parameters (see Section 2.5). The results showed that the DIC concentration was only significantly correlated with salinity, which explained 87% of the variation in the DIC concentration (Table 3.7). When DIC concentrations were plotted against salinity (Figure 3.9), the mixing curve of DIC concentration across the salinity gradient in the Calcasieu River was linear, with only a few outliers. DIC concentrations in the world’s ocean waters were reported by Doi et al. (2015) to be ranging from 1900 to 2500 µmol kg$^{-1}$ (1.95-2.56 mM, when assuming a seawater density of 1.025 kg L$^{-1}$), while DIC concentrations in the GOM were found to be 1900-2320 µmol kg$^{-1}$ (1.95-2.38 mM) by Huang et al. (2015), Xue et al. (2015), and Hu et al. (2016). A conservative mixing line was drawn on Figure 3.9a between the river (0.24 mM; site 1) and marine end member. To simplify the situation, 2.20 mM was used as the DIC concentration for GOM. As illustrated in Figure 3.9a,
the mixing of DIC between Calcasieu river water and saltwater from the GOM appears to be conservative.

Figure 3.7. Calculated pCO$_2$ (a and b) and CO$_2$ outgassing flux (c and d) in the Calcasieu River between November 2013 and December 2014; River Kilometer: distance between the site and the river mouth. Distance between the Gulf of Mexico and sites 1 to 6 are 87.9, 73.5, 62.6, 58.1, 27.0, and 4.5 km, respectively; Spring represents the average value of March, April, and May 2014; Summer represents the average value of June, July, and August 2014; Fall represents the average value of November 2013, September 2014, and October 2014; Winter represents the average value of December 2013, January and December 2014; Site 3 was only sampled from August 2014 to December 2014; Error bars represent standard errors of means; At least two measurements are needed to calculate standard error.

Riverbed soils and in-stream respirations can produce CO$_2$, affecting DIC concentration in a waterbody. Aquatic photosynthesis consumes CO$_2$, causing a decrease in DIC concentration. The photosynthetic rate in a river is usually much lower than the respiration rate (Schurr and Ruchti, 1977). Therefore, photosynthesis cannot be considered here as a major sink of riverine DIC. If respiration is the main factor controlling DIC content in a river, then temperature should
be positively correlated with the DIC concentration because both soil emission and in-stream respiration are usually higher during summer months when water temperature is higher (Aucour et al., 1999; Brunet et al., 2005; Roberts and Doty, 2015). The DIC concentration in the Calcasieu River was not correlated with temperature (Table 3.4). The freshwater sites 1 and 2 had the highest DIC concentrations during summer months. For the other four sites, the DIC concentrations were high even though not the highest during summer months (Figure 3.6). From site 1 to site 6, the DIC concentration increased 583% (1.4 mM), while the DOC concentration decreased only 50% (0.57 mM) (calculated using Table 3.5). Therefore, it is reasonable to suggest that respiration plays a role in the temporal trend of the DIC concentration, but it is not the main factor controlling DIC content in the Calcasieu River.

![Graph](image)

Figure 3.8. Mass fluxes of DIC and DOC in the Calcasieu River between November 2013 and December 2014; Discharge and carbon concentrations at site 1 were used to calculate mass fluxes using the regression models; Fluxes of DIC and DOC during sampling dates were also calculated using discharge and the measured DIC and DOC concentrations at site 1 to show the model performance. The small inside figure has the same axes as the larger figure, except that the y-axis has smaller range.
Table 3.7. Relationships of DIC concentration, pCO₂, DOC concentration, DIC/DOC ratio with environment parameters including salinity (S), water temperature (T), dissolved oxygen concentration (DO), and river discharge (Q) at Kinder. A backward stepwise regression was used to perform the statistical analysis for 68 samples collected from six sites along the Calcasieu River during 13 sampling trips. Slope and intercept estimates are presented with standard error (±SE). Only statistically significant relationships are reported (p<0.05). Variables included in the model are significant at the 0.05 level.

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Environmental Parameters</th>
<th>Final Equation</th>
<th>$R^2$</th>
<th>F</th>
<th>$p$ value</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIC</td>
<td>Salinity</td>
<td>$DIC = 0.06(±0.003)S + 0.25(±0.04)$</td>
<td>0.87</td>
<td>406.4</td>
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</tr>
<tr>
<td>pCO₂</td>
<td>Salinity</td>
<td>5.12</td>
<td></td>
<td>51.42</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td></td>
<td>pH</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Discharge</td>
<td>$pCO₂ = 70(±31)S − 2472(±345)pH − 33(±15)Q + 20036(±2353)$</td>
<td>0.57</td>
<td>25.60</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>DOC</td>
<td>Salinity</td>
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<td>0.0053</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Temperature</td>
<td>64.83</td>
<td>&lt;0.0001</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>DO</td>
<td>15.66</td>
<td>0.0002</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Discharge</td>
<td>6.02</td>
<td>0.0172</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S+T+DO+Q</td>
<td>DOC = $−0.01(±0.004)S − 0.07(±0.008)T − 0.10(±0.02)DO − 0.005(±0.002)Q + 3.20(±0.31)$</td>
<td>0.76</td>
<td>44.93</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>DIC/DOC</td>
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</tr>
<tr>
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<td>0.0154</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>S+T</td>
<td>DIC/DOC=0.18(±0.03)S+0.10(±0.04)T−2.28(±0.95)</td>
<td>0.43</td>
<td>22.93</td>
<td>&lt;0.0001</td>
</tr>
</tbody>
</table>

Rock weathering, including carbonate and silicate weathering, is an important source of DIC in rivers. Weathering rate is correlated with rock composition, climate conditions including temperature and humidity, surface area, and so on (Amiotte Suchet et al., 2003; Brunet et al., 2005; Cai et al., 2008). A study conducted by Zhang et al. (2013) showed that the ocean sediment (shell-material) from the GOM was able to reach about 32 km (close to site 5 in this study) into the Calcasieu Ship Channel, and that the Gulf sediment was the dominate sediment source in the lower portion of the ship channel. Our previous study (He and Xu, 2016) found that total Ca concentration at site 6 was 60 times higher than that at site 1, suggesting that in the Calcasieu River estuary, the sites closer to the GOM (e.g. sites 5 and 6) should have more carbonates because of the proximity to the Gulf and, therefore, should have higher input of inorganic carbon. This may partially explain the significantly higher DIC concentrations at sites 5 and 6. Because higher temperature promotes weathering (Bodin et al., 2015; Li et al., 2016),
there is a likelihood that weathering rates of the riverbed shell materials could be higher during the warm summer months. However, the DIC concentration showed no significant correlation with temperature in our study (Table 3.4). Therefore, even though weathering of carbonate rocks could affect the DIC concentration in the Calcasieu River, we suspect it is not a main impact factor on the DIC concentration.

Figure 3.9. Relationships of DIC (a) and DOC (b) with salinity in the Calcasieu River between November 2013 and December 2014; The solid straight line in (a) represents the conservative mixing line drawn between the river and marine end members.
CO₂ exchange between the atmosphere and river surface water depends on the CO₂ partial pressure (pCO₂) in the river water column. Most rivers in the world serve as sources of CO₂ in the atmosphere because the river water pCO₂ is generally greater than the atmospheric pCO₂ (van Geldern et al., 2015). For instance, Raymond et al. (2013) reported a global average of ~3100 μatm for rivers and streams while the present pCO₂ in the atmospheric air is about 390 μatm. In the Calcasieu River, all sites showed higher pCO₂ than the atmospheric pCO₂ during most of the sampling trips, thus the river serves as a carbon source to the atmosphere (Figure 3.7). Previous studies have also shown that within a river, the pCO₂ value is usually higher at the source, and lower at the mouth (Johnson et al., 2008; van Geldern et al., 2015). It is the same case for this study. For the Calcasieu River, the pCO₂ value in the upstream was much higher than the atmospheric pCO₂ than the downstream sites, which means a higher CO₂ flux rates at the upstream sites. Therefore, the lower DIC concentration upstream might have been partly caused by the higher CO₂ outgassing rate into the atmosphere.

It should be noted that CO₂ flux calculations strongly depend on the selection of the value for the gas transfer velocity K_T (Raymond and Cole, 2001; Raymond et al., 2012; van Geldern et al., 2015). This gas transfer velocity is usually not precisely known, and accounts for most of the uncertainties in estimating CO₂ outgassing fluxes (Raymond and Cole, 2001; van Geldern et al., 2015). Therefore, CO₂ outgassing calculations performed in this study should be considered as approximations rather than precise values. Salinity, pH, discharge, and wind also impact CO₂ flux (Tables 3.4 and 3.7). For instance, wind data was collected at the Calcasieu Pass, which is close to site 6, to evaluate the impact of wind on pCO₂. The calculated values of pCO₂ at site 6 were highest on December 2013 and March 2014 (Figure 3.7), and these two days had the highest wind speed when compared with other sampling dates (Figure 3.10). However, it should
be noted that due to a lack of wind data, we were not able to conclude that wind speed impacts pCO₂ at other sites.

Figure 3.10. Wind roses from November 2013 to December 2014. Hourly wind data 10 m above sea level at Calcasieu Pass, LA (NOAA Tides and Currents station#: 8768094) were used. (1) Nov 2013 to Dec 2014: hourly wind data from November 1, 2013 to December 31, 2014; (2)-(14): hourly wind data during the 24 hours right before the sampling time at site 6.
3.4.2 Factors affecting DOC concentration in a mixing zone

The DOC concentration in the Calcasieu River showed a decreasing trend from the upstream to the downstream locations, indicating the influence of terrestrial- and/or riverine-derived organic matter in the estuary. Since the DIC concentration increase in the Calcasieu River is mainly caused by physical conservative mixing with the saltwater from the GOM, the DOC concentration decrease cannot be solely attributed to organic oxidation. Comparing with salinity, pH, DO concentration, and discharge, water temperature plays the most important role in regulating the DOC concentration (Tables 3.4 and 3.7). All the sites in the Calcasieu River had the highest DOC concentration during winter months and the lowest DOC concentration during summer months (Figure 3.6). The ratio of DIC to DOC in this study was highest in summer months and lowest in winter months (Figure 3.6). The mineralization rate of DOC is usually much higher during summer than during winter (Moran et al., 1999; Fichot and Benner, 2014). Therefore, the significant relationships between temperature and the DOC concentration and the DIC/DOC ratio suggest that decomposition of organic carbon during warm months is one important sink of DOC, even though it is not the main source of DIC in the Calcasieu River. However, it should be noted that the downstream decrease from site 1 to site 6 in DOC concentration was 0.57 mM, while the 1.4 mM increase of DIC from site 1 to site 6 was mainly from mixing with the GOM water. Therefore, there must be another sink of DOC within the river to explain this decrease in DOC concentration. Otherwise, we would expect the increase of DIC concentration to be more significant.

Unlike with the DIC concentration change, physical mixing of the river freshwater with saltwater from the NGOM should not be considered a main cause in regulating DOC concentration in the river. Even though the DOC concentration was correlated with salinity, the F
value from the backward stepwise regression for salinity was fairly small when compared with the F values for temperature and DO (Table 3.7). The DOC concentration difference for a certain salinity (e.g., lower salinity at sites 1 and 2) was also larger than the differences of average DOC concentrations among different salinities (Figure 3.9b). Here, we suspect an indirect effect of the physical mixing on DOC concentration decrease due to the change in sediment amount and type as explained below.

Several studies have found that the exchange of organic matter between river water and sediment plays an important role in controlling DOC concentration during the mixing of fresh and marine waters. For instance, DOC can be removed by salinity-induced flocculation within a river (Benner and Opsahl, 2001; Fransner et al., 2016), and, at the same time, desorption of organic matter from suspended sediments is a potential source of DOC (Mannino and Harvey, 2001; Shilla et al., 2011). Salinity-induced flocculation is a process known to take place in proximity to river mouths because of the aggregation of DOC. This aggregation is due to a change in ionic strength and an increase in divalent cations when freshwater mixes with seawater (Forsgren et al., 1996; Søndergaard et al., 2003; Fransner et al., 2016). Even though flocculation is widely recognized as a DOC removal mechanism in coastal rivers, it is usually not a major removal process (Mulholland, 1981; Forsgren et al., 1996; Powell et al., 1996; Søndergaard et al., 2003). For the Calcasieu River, salinity-induced flocculation could be one of the DOC sinks, though, in light of the above studies, we anticipate that it is not a significant one.

Many catchment variables, including slope, peat cover, and soil carbon content, can be relevant in controlling riverine DOC flux (Hope et al., 1994 and 1997). Aitkenhead et al. (1999) showed that the single most important determinant of the amount of DOC transported out of catchments in streams is the size of the soil carbon pool, and that percentage peat cover was as
good a predictor of stream water DOC concentration as catchment soil carbon pool. Therefore, the type and amount of sediment in the Calcasieu River can be very important in regulating the DOC concentration in this river. Sites 4, 5, and 6 in this study are located within the Calcasieu River deep draft channel. In order to maintain the depth of the channel, the United States Army Corps of Engineers dredges various portions of the channel ranging from twice a year to once every 5 to 8 years, with the exception of the Pass Channel, which is the portion of the Calcasieu River located between kilometer 0 and kilometer 8 (USACE, 2010). The Pass Channel requires no dredging because strong tidal currents passing through this narrow inlet prevent the settling and accumulation of sediments (USACE, 2010; Zhang et al., 2013). Based on the river kilometer and the dredge report (USACE, 2010), the site 4 area is dredged once every 5 to 8 years, and the site 5 area is dredged once every two years, and the site 6 area requires no dredging. Even though we do not have the specific dredging record, one thing we can be sure of is that the naturally accumulated organic rich sediment in this part of the river is kept minimal by maintenance of the shipping channel. Also, a previous study (Zhang et al., 2013) found that tides and currents are able to transport organically poor marine sediment from the NGOM up to 32 km (above site 5) into the Calcasieu shipping channel. Furthermore, Gulf (shell-) sediment was the most dominate sediment source in the lower portion of the shipping channel, which confirms the fact that there is little organically rich sediment in the very low reach of the Calcasieu River. Therefore, the lower DOC concentration in the downstream could be partially caused by the lower availability of organic matter in the sediment.

3.4.3 DOC and DIC fluxes from freshwater

The annual flux of dissolved organic carbon from the Calcasieu River found in this study is about 73% of the long-term annual average of total organic carbon reported by He and Xu.
When compared with the Mississippi and Atchafalaya Rivers, the largest river system entering the GOM, the Calcasieu River had comparable DIC concentrations and higher DOC concentrations (Bianchi et al., 2004; Cai et al., 2008; Dubois et al., 2010; Shen et al., 2012). The DIC and DOC fluxes from the Calcasieu River were small when compared with those from the Atchafalaya (0.79×10^{11} mol yr^{-1} DOC; Shen et al., 2012) and Mississippi Rivers (DIC: 15.7×10^{11} mol yr^{-1}; Shen et al., 2012; Tian et al., 2015; DOC: 1.45×10^{11} mol yr^{-1}; Shen et al., 2012), demonstrating the dominant role of discharge on carbon flux in river systems. However, the DIC and DOC yields from the Calcasieu River (DIC: 43×10^{3} mol km^{-2} yr^{-1}; DOC: 296×10^{3} mol km^{-2} yr^{-1}) were comparable with those from the Atchafalaya (DOC: 321×10^{3} mol km^{-2} yr^{-1}; Shen et al., 2012) and Mississippi Rivers (DIC: 487×10^{3} mol km^{-2} yr^{-1}; Tian et al., 2015; DOC: 45×10^{3} mol km^{-2} yr^{-1}; Shen et al., 2012). Although small coastal rivers discharge comparably modest amount of dissolved carbon, their annual and seasonal fluctuations in DIC and DOC discharges could have important effects on estuaries and near-shore ecosystems.

### 3.5 Conclusions

This study investigated changes in dissolved inorganic and organic carbon concentrations and pCO_{2} along the 88-km estuarine reach of the Calcasieu River, with salinity ranging from 0.02 to 29.5. From November 2013 to December 2014, the river discharged 0.25×10^{9} mol DIC and 1.77×10^{9} mol DOC from its freshwater into the estuary. The average pCO_{2} values at site 1 through site 6 were 2948, 3201, 3148, 3682, 2117, and 583 µatm, respectively, with a mean of 2528 µatm for the entire river reach, suggesting that the Calcasieu Estuary serves as a source of CO_{2} in the atmosphere. During the study year, 0.079 ×10^{8} kg carbon were emitted to the atmosphere in the freshwater river reach before the Saltwater Barrier. In contrast, a much larger amount of carbon (3.04 ×10^{8} kg) was emitted to the atmosphere in the freshwater-saltwater
mixing zone during the same period. The change in DIC concentration from the upstream to the downstream locations near the river mouth was large (583% increase), indicating the overwhelming role of physical mixing on DIC in a coastal area. The DOC concentration, on the other hand, showed a decreasing trend from the upstream to the downstream locations (50% decrease), suggesting the influence of organic matter oxidation, flocculation, and sediment composition, alone or in combination. Based on the findings, we conclude that riverine dissolved carbon undergoes a rapid change in freshwater-saltwater mixing zones, and that this change should be considered in carbon processing and budgeting in the world’s estuarine systems. This is especially relevant as global sea level continues to rise, pushing freshwater-saltwater mixing zones more and more inland.
CHAPTER 4. DISSOLVED CARBON STABLE ISOTOPE ANALYSIS

4.1 Introduction

The quantification of dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) sources and sinks in estuaries is challenging. It is often hindered by a number of complex and overlapping interactions between dissolved carbon sources and sinks and relatively short residence times of estuarine waters (Raymond and Bauer, 2001a; van Geldern et al., 2015). As a consequence, DIC and DOC concentrations and mixing curves alone often do not constrain potential sources and sinks in estuaries. For instance, both photosynthetic CO$_2$ fixation into organic matter and the degassing of dissolved CO$_2$ into the atmosphere decrease the DIC concentration, and a mixing curve of DIC will not indicate the exact process causing the lower DIC concentration. Also, apparent conservative behaviors of DIC or DOC can be caused by the existence of simultaneous sources and sinks that result in small net changes in bulk concentrations (Abril et al., 2002). Estuaries may remove terrestrial and riverine DIC and DOC and simultaneously add and export DIC and DOC, having a unique estuarine character that potentially has very different isotopic signatures, chemical characteristics, and biological lability (Raymond and Bauer, 2001a). Therefore, carbon isotopic composition has widely been used as an effective tool for distinguishing carbon originating from a variety of sources (Rau, 1978; Raymond and Bauer, 2001b; Wang et al., 2016). Riverine DIC and DOC concentrations largely depend on a river’s drainage basin and surrounding environment (Downing et al., 1993; Meybeck, 1982; Richey et al., 2002; Raymond et al., 2004).

Riverine DIC can originate from several biogeochemical processes, such as soil emission and in-stream respiration, carbonate and silicate weathering, and exchange with the atmosphere (Aucour et al., 1999; Bouillon et al., 2003; Cai et al., 2008; Butman and Raymond, 2011; Raymond et al., 2013; van Geldern et al., 2015). Along a river estuary, the relative importance of atmospheric CO\textsubscript{2} exchange, photosynthetic activity, organic matter decay, carbonate precipitation and dissolution, and carbon dioxide evasion on DIC concentration can be assessed more precisely by dissolved inorganic carbon stable isotope analyses because the $\delta^{13}$C\textsubscript{DIC} isotopic signature is of particular value in distinguishing and tracing sources, sinks, and transformations of carbon in the water column (Fry, 2002; van Geldern et al., 2015; Burt et al., 2016). Each DIC source has a different $\delta^{13}$C\textsubscript{DIC} isotopic signature as found in previous studies: -26 to -9‰ for soil organic matter (Schiff et al., 1990), -8 to -6‰ for atmospheric CO\textsubscript{2} (Cerling, 1991), and around 0‰ for carbonate rocks (Keith and Weber, 1964).

The $\delta^{13}$C\textsubscript{DIC} in mixing zones of coastal rivers is determined largely by the conservative mixing of river water and seawater (Aucour et al., 1999; Miyajima et al., 2009). However, non-conservative changes in $\delta^{13}$C\textsubscript{DIC} in mixing zones occur due to several natural processes including exchange with atmospheric CO\textsubscript{2} (Gray et al., 2011; van Geldern et al., 2015), photosynthesis and respiration (Hellings et al., 2001; Kaldy et al., 2005), and carbonate precipitation and dissolution (Barth et al., 2003; Kanduč et al., 2007). Air-water exchange with atmospheric CO\textsubscript{2} includes the dehydration and degassing of dissolved CO\textsubscript{2} into the atmosphere and the dissolution and hydration of atmospheric CO\textsubscript{2} to under-saturated water (Mook et al., 1974; Miyajima et al., 2009). The former process causes an increase in $\delta^{13}$C\textsubscript{DIC} in estuarine water, and the latter process causes either a decrease or increase in $\delta^{13}$C\textsubscript{DIC} in estuarine water depending on the $\delta^{13}$C\textsubscript{DIC} in the water (Cerling, 1991; Miyajima et al., 2009; van Geldern et al., 2015). Since massive dissolution
and hydration of atmospheric CO\textsubscript{2} to under-saturated water is known to occur only at pH > 9, this process can be excluded in most estuaries (Herczeg and Fairbanks, 1987; Miyajima et al., 2009). Respiration, usually dominant in aquatic systems, causes $\delta^{13}$C\textsubscript{DIC} to be negative, whereas photosynthesis drives it back toward less negative values (Wang and Veizer, 2000). Carbonate precipitation and dissolution both influence $\delta^{13}$C\textsubscript{DIC} in the water (Miyajima et al., 2009; van Geldern et al., 2015). However, most freshwater systems are typically under-saturated with respect to CaCO\textsubscript{3}, so the precipitation of CaCO\textsubscript{3} is a negligible process in many estuaries. Relative to the water exchange rate in many estuaries, the dissolution of carbonate minerals within a river channel is a slow process. Therefore, the effects of carbonate precipitation and dissolution on $\delta^{13}$C\textsubscript{DIC} are presumably restricted (Miyajima et al., 2009).

Dissolved organic carbon in estuaries can have two sources: allochthonous, i.e., DOC supplied by the erosion of soil organic matter, and autochthonous, i.e., DOC produced by photosynthesis in the river water (Brunet et al., 2005). The autochthonous fraction is generally more labile than the DOC coming from soil leaching (Raymond and Bauer, 2001a; Brunet et al., 2005). Labile organic carbon can be easily transformed into DIC by oxidation processes, which means that the sources of DOC will impact the sinks of DOC. Estuarine DOC has three main potential sinks: (1) it may be exported to adjacent coastal and continental shelf waters (Moran et al., 1991; Raymond and Bauer, 2000); (2) it may be oxidized directly to CO\textsubscript{2} through bacterial respiration (Moran et al., 1999) or photo-oxidation (Amon and Benner, 1996); or (3) it may undergo physicochemical transformations, e.g., flocculation to form less soluble colloids and particles (Benner and Opsahl, 2001; Fransner et al., 2016). Mixing curves of DOC alone often do not constrain potential sources and sinks of DOC in estuaries due to complex biogeochemical
processes in the mixing zone. Therefore, the stable carbon isotope ratio of dissolved organic
carbon ($\delta^{13}C_{DOC}$) can be a tracer of DOC sources.

The loading and characteristics of organic matter are key parameters to our understanding
of the autotrophic and heterotrophic balance in estuaries (Hopkinson and Vallino, 1995). Net
metabolism in estuaries is a significant term in the oceanic carbon budget (Smith and
Hollibaugh, 1993). $\delta^{13}C_{DIC}$ has been used to assess the net difference between production and
respiration, where the imbalance between production and respiration leads to deviations from
conservative behavior (Chanton and Lewis, 1999; Kaldy et al., 2005). The respiration rate in an
estuarine river is usually much higher than the photosynthetic rate (Schurr and Ruchti, 1977),
which means most estuaries are net heterotrophic (Smith and Hollibaugh, 1993). However,
studies have shown than estuaries oscillate between net metabolism states depending on the
sources of carbon, the reactivity of that material, and the residence time of the system (Coffin
and Cifuentes, 1999; Kaldy et al., 2005). Therefore, evaluating the net metabolism of an
estuarine river is very important to its coastal carbon budget and ecosystem.

The Mississippi-Atchafalaya River System, being the largest river system to the Gulf of
Mexico (GOM), has been the subject of intensive investigation, including carbon and nutrient
transport and transformation (e.g. Cai, 2003; Bianchi et al., 2004; Raymond et al., 2008; Cai et
al., 2008; Xu, 2013; Roberts and Doty, 2015). Despite their potentially active role in carbon
cycling, the dynamics of carbon in the mixing zones in other coastal rivers entering the Northern
Gulf of Mexico (NGOM) have been largely overlooked. The export of dissolved carbon from
these rivers could have a significant regional influence on the coastal carbon budget and
ecosystem (Johnson et al., 2008; Humborg et al., 2009; Raymond et al., 2013). This study aims
to determine how DIC and DOC concentrations and isotope signatures change along an estuarine
river in southwest Louisiana, USA - the Calcasieu River - to better understand which processes are most likely to control the carbon dynamics in this river – estuary – coast continuum. The specific objectives of this study were to (1) investigate temporal and spatial dynamics of DIC and DOC concentrations and isotope signatures from upstream to downstream of the Calcasieu River, (2) assess factors that influence the spatiotemporal dynamics of DIC and DOC concentrations and isotopes, and (3) evaluate the net metabolism of the Calcasieu Estuary using $\delta^{13}C_{\text{DIC}}$.

4.2 Methods

4.2.1 Study area

This study was focused on the Calcasieu River’s last 88-km reach to the NGOM (Figure 3.1a). The Calcasieu River flows 322 km through the low-lying Chenier Plain in Southwest Louisiana before entering the NGOM. In the late 1940s, the U.S. Army Corps of Engineers was authorized by the U.S. Congress to construct a deep-draft channel in the Calcasieu River from Lake Charles to the GOM. The channel deepening allowed saltwater intrusions from the Gulf, threatening the upper Calcasieu River, a source of water for agricultural irrigation. In the 1960s, a saltwater barrier dam was constructed upstream of Lake Charles (Louisiana Department of Wildlife and Fisheries, 2012; United States Army Corps of Engineers, website accessed on June 15, 2017), to prevent saltwater from traveling further upstream, as well as to regulate freshwater outflow.

The southwest coast of Louisiana including the Calcasieu Estuary is subject to a microtidal environment (tides $< 0.5$ m) where the semidiurnal mixed tide dominates (Spargo and Woolard, 2005). The climate of the study area is subtropical, characterized by long, hot, and
humid summers and generally short, mild winters. During the sampling period from May 2015 to February 2016, the average monthly temperature ranged from 11.1 °C in January 2016 to 28.4 °C in August 2015, with a mean of 21.7 °C for the ten-month study period (National Oceanic and Atmospheric Administration (NOAA) station: Calcasieu Pass, LA - Station ID: 8768094). The average monthly precipitation ranged from 35.4 mm in July 2015 to 261.2 mm in December 2015, with a monthly mean of 136.54 mm for the 10-month period (NOAA National Centers for Environmental Information site: latitude: 30.255˚N, longitude: 93.219˚W). Agriculture is the primary land use in the northern part of the Calcasieu River Basin (Calcasieu Parish). More than 65% of the land is used as cultivated cropland, pastureland, and woodland, and most of the remaining acreage is used as urban land, marshland, or swampland (United States Department of Agriculture National Resources Conservation Service, 1988). The southern part of the Calcasieu River Basin (Cameron Parish) is primarily coastal marshland, used mainly as rangeland, oil and gas fields, and habitats for wildlife (United States Department of Agriculture National Resources Conservation Service, 1995).

4.2.2. Field measurements

In May 25, 2015 (sunny), June 24, 2015 (cloudy with light rain), July 26, 2015 (sunny), November 29, 2015 (cloudy), and February 17, 2016 (sunny), five sampling events were conducted, taking place at six sampling sites selected along the 88-km reach of the Calcasieu River (Figure 3.1a). Sites 1 and 2 were located above the saltwater barrier dam and, therefore, water samples collected from the two sites were freshwater. All sampling sites below the barrier (i.e., sites 3, 4, 5, and 6) were saltwater affected to varied degrees, depending on river discharge and tidal mixing at the time of field sampling. During each trip, water temperature, dissolved
oxygen (DO) concentration, pH, and salinity were measured using an YSI 556 multi-probe meter (YSI Inc., Yellow Springs, OH, USA).

In addition, surface water samples were collected at each site approximately 30-50 cm below the water surface. The samples were collected from piers reaching out about 8-15 m into the river channel with a grab sampler. The sampler was a 12-foot aluminum pole with a polyethylene bottle attached at the end of the pole. High Density Polyethylene (HDPE) bottles (250 mL) were used to store water samples for DOC analysis. Samples to be analyzed for DIC were septum capped in 20 mL glass vials and immediately placed on ice, along with DOC samples. All bottles for DIC stable isotope analyses were filled without headspace, closed with butyl rubber/PTFE septa (placed with butyl rubber side towards the sample) and open-hole caps and sealed with Parafilm®. Two one-liter water samples were collected from each site for total suspended solids (TSS) analysis and chlorophyll a analysis. Samples for chlorophyll a analysis were covered with aluminum foil immediately after collecting. All bottles were thoroughly acid-cleaned and rinsed using river water before use. Duplicate samples were collected at one site per trip for quality control purposes. All the water samples were stored in a cooler with wet ice during transportation, and refrigerated until chemical analysis.

4.2.3. DOC, DIC and δ¹³C analysis

Prior to analysis, DOC samples were filtered using 0.25 μm nylon syringe filters (Environmental Express, Charleston, SC, USA) and frozen. Samples to be analyzed for DOC and DIC were shipped on ice to University of California Davis Stable Isotope Facility. The detailed information about DIC and DOC analysis can be found at their website (http://stableisotopefacility.ucdavis.edu). Briefly, for DIC and δ¹³C_{DIC} analysis, water samples (1-4 mL) were injected into helium-filled 12 mL septum capped vials (Exetainers, Labco, High...
Wycombe, UK) containing 1 mL 85% phosphoric acid, which forces the equilibrium between CO₂ and H₂CO₃ to gaseous CO₂. The evolved CO₂ was purged from vials through a double-needle sampler into a helium carrier stream (20 mL min⁻¹). The gas was sampled using a six-port rotary valve (Valco, Houston TX) with either a 100 µL, 50 µL, or 10 µL loop programmed to switch at the maximum CO₂ concentration in the helium carrier. The CO₂ was passed to the IRMS through a Poroplot Q GC column (25m × 0.32mm ID, 45°C, 2.5 mL min⁻¹). A reference CO₂ peak was used to calculate provisional delta values of the sample CO₂ peak. Final δ¹³CDIC values were obtained after adjusting the provisional values for changes in linearity and instrumental drift such that correct δ¹³C values for laboratory reference materials were obtained. At least two laboratory reference materials were analyzed with every 10 samples. Laboratory reference materials were lithium carbonate dissolved in degassed deionized water and deep seawater (both calibrated against NIST 8545). Final δ¹³C values were expressed relative to the ¹³C:¹²C ratio of the international standard VPDB (Vienna PeeDee Belemnite) as follows:

\[
\delta^{13}C = \left( \frac{R_s}{R_{VPDB}} - 1 \right) \times 1000‰
\]  

(1)

where \( R_s \) is the ¹³C:¹²C ratio of samples, and \( R_{VPDB} \) is the ¹³C:¹²C ratio of the VPDB sample. The method detection limit and long-term standard deviation for \( \delta^{13}C_{DIC} \) as CO₂ were approximately 150 nanomoles and 0.1‰.

Dissolved organic carbon and \( \delta^{13}C_{DOC} \) were analyzed using an O.I. Analytical Model 1030 TOC Analyzer (Xylem Analytics, College Station, TX) interfaced to a PDZ Europa 20-20 isotope ratio mass spectrometer (Sercon Ltd., Cheshire, UK) utilizing a GD-100 Gas Trap Interface (Graden Instruments). Samples were acidified and purged with helium off-line to remove all DIC. Depending on sample concentration, a 1 mL to 9 mL aliquot of sample was
transferred into a heated digestion vessel and reacted with sodium persulfate to convert DOC into a pulse of CO$_2$. The CO$_2$ was carried in a helium flow to the isotope ratio mass spectrometer where the $^{13}$C:$^{12}$C ratios were measured. During analysis, samples were interspersed with several replicates of at least three different laboratory reference materials. These reference materials have been previously calibrated against international reference materials, including: IAEA-600, USGS-40, USGS-41, and Elemental Microanalysis (EM) reference materials. A sample’s provisional isotope ratio was measured relative to a reference gas peak analyzed with each sample. These provisional values were finalized by correcting the values for the entire batch based on the known values of the included laboratory reference materials. Similarly, the final $\delta^{13}$C$_{DOC}$ values were expressed relative to the $^{13}$C:$^{12}$C ratio of the international standard VPDB as given in Equation 1. The analytical precision for $\delta^{13}$C$_{DOC}$ at DOC concentrations greater than 0.5 ppm was 0.4‰. The reported DOC and $\delta^{13}$C$_{DOC}$ here are averaged values because duplicated samples were analyzed in the lab.

Extraction and analysis of chlorophyll $a$ from the water samples were done at the Wetland Biogeochemistry Analytical Services, Louisiana State University Department of Oceanography and Coastal Sciences, using a Turner Designs TD-700 Fluorometer (Turner Designs, Sunnyvale, CA, USA) using EPA method 445. The TSS samples were filtered, whereby gravimetric analysis was used to determine TSS at the W. A. Callegari Environmental Center, Louisiana State University Agricultural Center. The method detection limits in our study for chlorophyll $a$ and TSS are 0.05 $\mu$g L$^{-1}$ and 4 mg L$^{-1}$, respectively.

4.2.4. Mixing analysis

Daily discharge and gage height for the Calcasieu River were collected from the U.S. Geological Survey (USGS). Gage stations were selected based on their proximity to the sampling
sites for optimal representation and on availability. Specifically, daily river discharge was
collected at the Calcasieu River near Kinder, LA (USGS 08015500), and the daily river gage
data was collected at the Calcasieu River near Cameron, LA (USGS 08017118) (Figure 3.1a).

Concentrations of DIC and DOC expected by the conservative-mixing model were
calculated using the following formula (Fry, 2002; Kaldy et al., 2005):

\[ C_{mix} = fC_r + (1 - f)C_m \]  \hspace{1cm} (2)

where \( C \) denotes concentration, the subscripts \( r \) and \( m \) indicate river and marine endmembers,
respectively, and \( f \) represents the fraction of freshwater in each sample calculated from salinity:

\[ f = (S_m - S)/(S_m - S_r) \]  \hspace{1cm} (3)

where \( S \) is the salinity at the sampling point and the subscripts are the same as Equation 1. \( S_m \)
and \( S_r \) are salinity at the marine and river endmembers. The \( \delta^{13}C_{DIC} \) and \( \delta^{13}C_{DOC} \) expected by the
conservative-mixing model were calculated as:

\[ \delta_{mix} = [fC_r\delta_r + (1 - f)C_m\delta_m]/C_{mix} \]  \hspace{1cm} (4)

Subscripts and terms are the same as before and \( C_{mix} \) is from Equation 2. Because of the
concentration-based weighting of endmember isotopic contributions, mixing diagrams for
isotopes usually show curvilinear mixing unless the endmember concentrations are equal, or
endmember isotope values are equal, which rarely happen (Fry, 2002). Site 1 in this study
generally had salinity around 0.03 (Table 4.1), which can be considered as freshwater
endmember. Site 6 was the closest site to the GOM and had the highest salinity so was used as
the marine endmember. While we believe the findings from our study can provide a plausible
indication of carbon gain and loss for the entire estuarine reach, we acknowledge that discussing
conservative mixing is difficult, given that there are only six sampling sites with marine endmember located in the mixing zone.

Table 4.1. Environmental conditions during the study period at six sampling sites along the Calcasieu River entering the Northern Gulf of Mexico in the southern United States.

<table>
<thead>
<tr>
<th>Site</th>
<th>Date</th>
<th>Time</th>
<th>Salinity</th>
<th>pH</th>
<th>Temperature (°C)</th>
<th>DO (mg L⁻¹)</th>
<th>TSS (mg L⁻¹)</th>
<th>Chlorophyll a (µg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site 1</td>
<td>5/25/2015</td>
<td>8:40</td>
<td>0.02</td>
<td>6.06</td>
<td>23.11</td>
<td>6.05</td>
<td>15</td>
<td>0.86</td>
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<tr>
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<td>8:50</td>
<td>0.02</td>
<td>6.43</td>
<td>28.87</td>
<td>4.07</td>
<td>13</td>
<td>3.13</td>
</tr>
<tr>
<td></td>
<td>7/19/2015</td>
<td>10:50</td>
<td>0.06</td>
<td>6.26</td>
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<td>3.47</td>
<td>15</td>
<td>2.28</td>
</tr>
<tr>
<td></td>
<td>11/29/2015</td>
<td>9:10</td>
<td>0.02</td>
<td>6.10</td>
<td>16.96</td>
<td>4.78</td>
<td>15</td>
<td>0.17</td>
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<tr>
<td></td>
<td>2/17/2016</td>
<td>11:15</td>
<td>0.03</td>
<td>5.81</td>
<td>15.00</td>
<td>7.70</td>
<td>21</td>
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<tr>
<td>Mean</td>
<td></td>
<td></td>
<td>0.02</td>
<td>6.39</td>
<td>23.14</td>
<td>5.59</td>
<td>16</td>
<td>3.67</td>
</tr>
<tr>
<td>Site 2</td>
<td>5/25/2015</td>
<td>9:20</td>
<td>0.02</td>
<td>5.71</td>
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<td>1.37</td>
</tr>
<tr>
<td></td>
<td>6/24/2015</td>
<td>9:50</td>
<td>0.03</td>
<td>6.10</td>
<td>28.83</td>
<td>2.63</td>
<td>13</td>
<td>2.28</td>
</tr>
<tr>
<td></td>
<td>7/19/2015</td>
<td>11:30</td>
<td>0.05</td>
<td>6.72</td>
<td>31.87</td>
<td>2.82</td>
<td>8</td>
<td>21.42</td>
</tr>
<tr>
<td></td>
<td>11/29/2015</td>
<td>12:15</td>
<td>0.03</td>
<td>5.89</td>
<td>17.29</td>
<td>5.28</td>
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<td>0.29</td>
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<td>0.03</td>
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<tr>
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<td>23.18</td>
<td>4.87</td>
<td>14</td>
<td>5.36</td>
</tr>
<tr>
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<td>0.03</td>
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<td>4.80</td>
<td>13</td>
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</tr>
<tr>
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4.2.5. Statistical analysis

Pearson Correlation Coefficients were calculated to analyze the relationships among DIC, DOC, δ¹³C_DIC, δ¹³C_DOC, and environmental parameters, including salinity, pH, temperature, DO
concentration, TSS, Chlorophyll $a$, river discharge, and river gage height (Table 4.2a). While being a useful way to investigate potential factors affecting carbon concentrations, the Pearson Correlation Coefficient only considers one factor at a time, which can lead to large $p$ values due to large numbers of modeling. Furthermore, our data is not normally distributed, which could be another limitation in using the Pearson Correlation Coefficient. To explore potential factors affecting carbon concentrations and isotopic values, backward stepwise linear regressions were also performed between DIC, DOC, $\delta^{13}$C$_{DIC}$, $\delta^{13}$C$_{DOC}$, and environmental parameters that had significant correlations with each of the corresponding carbon species (Table 4.2b).

### Table 4.2. Relationships between dissolved inorganic carbon concentration (DIC), dissolved organic carbon concentration (DOC), and their isotopic values ($\delta^{13}$C$_{DIC}$ and $\delta^{13}$C$_{DOC}$) and environmental parameters from all sampling sites: (a) Pearson Correlation Coefficients; only significant ($p<0.01$) correlations are shown. (b) backward stepwise linear regression; only statistically significant ($p<0.05$) relationships are reported. Variables left in the model are significant at the 0.05 level. Slope and intercept estimates are presented with standard errors (±SE). $S =$ Salinity; $T =$ Temperature; $Q =$ Discharge; $GH =$ Gage Height. The regression for $\delta^{13}$C$_{DOC}$ did not yield any statistically meaningful output.

#### (a)

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<td>$S + \text{pH}$</td>
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4.3 Results

4.3.1 Ambient conditions

From May 2015 to February 2016, the Calcasieu River showed an average daily discharge of 61 m$^3$ s$^{-1}$ (std: ±79), ranging from 4 (October 21, 2015) to 595 m$^3$ s$^{-1}$ (November 7, 2015) (Figure 4.1). The average discharge during this sampling period was comparable to the reported long-term average of 72 (±66 m$^3$ s$^{-1}$) from 1980 to 2009 (He and Xu, 2015). However, the river exhibited more pronounced seasonal patterns during the study period than in the period from 1980 to 2009, with November having the highest average discharge (200 m$^3$ s$^{-1}$) and September the lowest (6 m$^3$ s$^{-1}$), influencing salinity and pH distribution along the 88-km river estuary. For instance, the salinity and pH during the July 2015 sampling event were the highest for most sites due to the very low river discharge when compared with other sampling trips (Table 4.1). Although discharges during the five field trips did not catch the high flow events in May and November 2015, discharges during the five trips ranged from 9 (July 26, 2016) to 108 m$^3$ s$^{-1}$ (May 25, 2016) for the five field trips (Figure 4.1). Therefore, our sampling design represents low to median high flow in the Calcasieu River. The average daily gage height at Cameron ranged from -0.45 to 0.78 m, with an average of 0.36 m (±0.19). Seasonally, the tidal stage at the river mouth was high in the fall months, with November having the highest monthly average (0.53 m), and low in the winter months, with February having the lowest monthly average (0.02 m). Gage heights during sampling days were positively correlated with discharge (Table 4.2).

The ambient conditions at the six sampling sites varied largely (Table 4.1). Salinity levels at site 6, the closest location to the GOM, ranged from 9.48 to 21.92, with an average of 15.55. As expected, pH was positively correlated to salinity (Table 4.2). However, pH at sites 1
and 2 had a larger variation than salinity did. The average DO concentrations at sites 5 and 6 were higher than those of the other sites. Being nearest to the GOM, sites 5 and 6 were strongly impacted by saltwater. The stronger tidal movement at these two sites may have aerated the water, as reflected by the higher DO levels at the sites. Due to the negative relationship between temperature and DO, the DO concentration was higher during winter and spring months and lower during summer and fall months. Site 6 showed much larger variation of TSS than other sites. For most of the sites, the July 2015 samples showed the highest chlorophyll $a$ concentration and the November 2015 samples had the lowest.

![Figure 4.1. Discharge at Kinder, LA (USGS Station# 08015500) and tidal gage height at Cameron, LA (USGS Station# 08017118) during the study period. Red squares and triangles indicate the daily discharge and gage height during the five sampling trips.](image)

4.3.2 Longitudinal and seasonal trends of dissolved carbon concentrations

The DIC concentration showed considerable variation among the six sampling sites, with a clear increasing trend as the river travels downstream (Figure 4.2a). The average DIC concentration at the river-mouth site (site 6) was 1.31 mM, which was about 3 times of that (0.42 mM) at the upstream site (site 1) (Figure 4.2a). The DOC and DIC concentrations showed
opposite spatial trends, but to a smaller degree for the DOC concentration. In general, the DOC concentrations at the downstream sites 5 (0.73 mM) and 6 (0.62 mM) were lower than the other four sites (0.93 to 1.09 mM) (Figure 4.2b).

Figure 4.2. Dissolved inorganic (DIC) and organic carbon (DOC) concentrations and their isotopic values ($\delta^{13}$C$_{\text{DIC}}$ and $\delta^{13}$C$_{\text{DOC}}$) at six sampling sites along the Calcasieu River entering the Northern Gulf of Mexico in the southern United States. Distance between the Gulf of Mexico and sites 1 to 6 are 87.9, 73.5, 62.6, 58.1, 27.0, and 4.5 km, respectively.

There was a large temporal variation in DIC concentration at each site, with all sites reaching a maximum DIC concentration during July 2015 (Figure 4.2a), with a mean of 1.14 mM, and minimum in May 2015 and November 2015, with a mean value of 0.53 and 0.54 mM, respectively. Different sites showed distinct seasonal trends of DOC concentration. For instance, sites 1 to 3 had the highest DOC concentration during the May 2015 sampling trip, while sites 4,
5, 6 showed the highest DOC concentration during November 2015, June 2015, and July 2015, respectively. On average, DOC concentration in May 2015 was the highest (1.13 mM), and in February 2016 was the lowest (0.64 mM).

4.3.3 Longitudinal and seasonal dissolved carbon isotope trends

Similar to the DIC concentration, $\delta^{13}$C$_{DIC}$ showed a pronounced increasing trend with decreasing distance to the NGOM (Figure 4.2c). The average $\delta^{13}$C$_{DIC}$ increased from -20.83‰ to -6.34‰ from site 2 to site 6 (Figure 4.2c). There was no clear spatial trend of $\delta^{13}$C$_{DOC}$ (Figure 4.2d). The average $\delta^{13}$C$_{DOC}$ values of all six sites were within a small range (-28.67 to -28.41‰).

Temporally, $\delta^{13}$C$_{DIC}$ values varied largely at all the sampling sites: from -25.71 to -16.33‰ at site 1, from -24.55 to -15.83‰ at site 2, from -21.49 to -14.19‰ at site 3, from -19.49 to -12.15‰ at site 4, from -13.15 to -6.95‰ at site 5, and from -8.57 to -3.79‰ at site 6 (Figure 4.2c). In general, the river had the highest $\delta^{13}$C$_{DIC}$ values during July 2015, with a mean value of -11.75‰, and lowest in November 2015, with a mean of -18.25‰. The temporal variation of $\delta^{13}$C$_{DOC}$ was larger than the spatial variation of $\delta^{13}$C$_{DOC}$: from -29.48 to -27.03‰ at site 1, from -29.55 to -27.93‰ at site 2, from -29.33 to -27.78‰ at site 3, from -29.42 to -27.70‰ at site 4, from -30.54 to -27.34‰ at site 5, and from -30.56 to -25.92‰ at site 6 (Figure 4.2d). Mean $\delta^{13}$C$_{DOC}$ was the highest in February 2016 (27.76‰), and was the lowest in May 2015 (-29.81‰).

4.3.4 Relationships between dissolved carbon concentrations and isotopes

In general, DIC and DOC concentrations are negatively correlated (Table 4.2 and Figure 4.3a). However, the correlation between $\delta^{13}$C$_{DIC}$ and $\delta^{13}$C$_{DOC}$ was not statistically significant (Table 4.2). The $\delta^{13}$C$_{DIC}$ values become more positive as concentrations of DIC increase, and
become more negative as DOC concentration increases (Figures 4.3c and 4.3d). The δ^{13}C_{DOC} values did not show any statistically significant correlations with DIC and DOC concentrations (Table 4.2 and Figures 4.3e and 4.3f).

Figure 4.3. Relationships among dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), and their isotopic values (δ^{13}C_{DIC} and δ^{13}C_{DOC}) at six sampling sites along the Calcasieu River entering the Northern Gulf of Mexico in the southern United States.
4.4 Discussion

4.4.1 DIC concentration

This study shows that DIC concentration in the Calcasieu Estuary increased rapidly by 212% from the upstream to downstream reaches. Assessing estuarine DIC dynamics is difficult, since the biogeochemical processes that control DIC concentration in a river are spatially and temporally dynamic on a variety of scales (Raymond and Bauer, 2001a; van Geldern et al., 2015). Carbon concentrations versus salinity plots are frequently used to study estuarine carbon dynamics, where deviations from conservative mixing lines are taken to indicate sources or sinks of materials within a system (Kaldy et al., 2005). For the Calcasieu River, all field trips except the July 2015 trip (Figure 4.4) suggest that DIC concentration was mostly controlled by conservative mixing, or that the addition of DIC in the estuary was balanced by substantial DIC losses. The contribution of conservative mixing was calculated for samples with salinity at least 1 unit larger than the salinity of site 1 in the corresponding field trip (Table 4.3). The results showed that conservative mixing accounted for 66% to 147% of the DIC concentration change for the May 2015, June 2015, November 2015, and February 2016 trips, while for the July 2015 trip, only 33% to 47% of the DIC concentration change was due to conservative mixing (Table 4.3). Backward stepwise multiple linear regressions that included dissolved carbon concentrations and isotope values, as well as environmental parameters, quantified potential factors affecting dissolved carbon concentrations and isotope values. Multiple regression analysis for all sites together showed that the DIC concentration was significantly correlated with salinity, temperature, and discharge, which together explained 94% of the variances in the DIC concentration (Table 4.2b). The large contribution from conservative mixing is confirmed by the
high F value for salinity in the multiple regression analysis. However, temperature and discharge are also important parameters that can impact DIC concentration.

Figure 4.4. Relationships between dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), and their isotopic values ($\delta^{13}C_{DIC}$ and $\delta^{13}C_{DOC}$) and salinity in the Calcasieu River entering the Northern Gulf of Mexico in the southern United States. Solid circles represent actual measurements. Corresponding conservative mixing values are denoted by stars. Lines and curves represent conservative-mixing models (see Equations 2 and 4). Site 1 was used as the river endmember, and site 6 was used as the marine endmember.
Table 4.3. Contributions of conservative mixing in dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), and their isotopic values ($\delta^{13}$C$_{\text{DIC}}$ and $\delta^{13}$C$_{\text{DOC}}$). The calculation was only performed for samples with salinity at least 1 unit larger than the salinity of site 1 in the corresponding field trip (salinity difference $\geq$ 1). Sites 1 and 6 are not listed in the table because these two sites were used as the river and marine endmembers, which means that the contributions of conservative mixing will always be calculated as 100% at these sites (see Equations 2, 3 and 4).

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Photosynthesis by phytoplankton causes a decrease in DIC concentration through the consumption of CO$_2$. On the other hand, soil and in-stream respirations produce CO$_2$, which can increase DIC concentration in a waterbody. As both soil emission and in-stream respiration are usually higher during summer months when water temperature is higher (Aucour et al., 1999; Brunet et al., 2005; Roberts and Doty, 2015), therefore, temperature should be positively correlated with the DIC concentration if respiration is an important factor in controlling DIC content in the river. This is demonstrated in the Calcasieu River as temperature was positively correlated with DIC concentration (Table 4.2) and all sites had the highest DIC concentrations during the July 2015 field trip when the hottest temperatures occurred (Table 4.1).
Temperature induced respiration in July 2015 also explains the notable positive deviation of DIC concentration from the conservative line.

Among all five sampling trips, DIC concentration was most conservative during the November 2015 trip, and the least conservation during the July 2015 trip. As discussed, temperature explains a good part of this behavior. However, discharge and residence time as well as nutrients are also factors that need further clarification. In general, when discharge is high, residence time is short, which is not favorable for biological processes like respiration and photosynthesis. Daily discharge at Kinder during our July 2015 trip was only 9 m$^3$ s$^{-1}$. Consequently, the residence time was longer in July when compared with the other four trips, suggesting that biological processes were more active in July. On the other hand, daily discharge during the November 2015 trip was 71 m$^3$ s$^{-1}$, about 7 times higher than the July 2015 trip. Hence, the residence time was much shorter than the July trip, and biological processes such as respiration was not as active as they were in July. In addition, the November trip occurred immediately after a very high flow period, which partially explains why the DIC concentration was more conservative in November than in May 2015, despite the fact that the May trip had higher discharge (108 m$^3$ s$^{-1}$) than the November trip. Nutrient concentration provides another explanation for the difference between the DIC concentration behavior during May and November. Average nitrate+nitrite and phosphate concentrations for the May 2015 trip were 7.295 mg N L$^{-1}$ and 0.015 mg P L$^{-1}$, while for other trips, the average nitrate+nitrite concentrations ranged from 0.043 to 0.066 mg N L$^{-1}$, and the phosphate concentrations ranged from 0.007 to 0.016 mg P L$^{-1}$. The higher nutrient concentration in May is consistent with fertilizer application season (spring). High nutrient concentration promotes plant growth, which
in turn promotes photosynthesis and respiration, explaining why DIC concentration in May was less conservative than in November despite the fact that discharge in May was the highest.

4.4.2 DOC concentration

Riverine DOC can originate from autochthonous origin (phytoplankton production in the river itself) and from allochthonous origin (erosion of soil organic matter) (Brunet et al., 2005). The DOC concentrations in the upstream freshwater sites (sites 1, 2 and 3) showed a positive trend with increasing discharge (Figure 4.5), suggesting an allochthonous origin of the organic carbon. Downstream in the mixing zone, such a relationship did not exist, showing a declined role of terrestrial- and/or riverine-derived organic matter in the estuary. This spatial trend of DOC along the river estuary appeared to be less pronounced when compared with the temporal trend of DOC. For example, DOC concentration at site 1 varied from 0.44 to 1.46 mM while the average DOC concentration at the six sites varied from 0.62 to 1.09 mM. During May 2015, the DOC versus salinity plot suggests a sink was present throughout the Calcasieu Estuary since measured DOC concentrations were lower than predicted by mixing (Figure 4.4). On the other hand, the DOC versus salinity plots for other four trips suggest an autotrophic source was present throughout the Calcasieu Estuary since measured DOC concentrations were higher than those predicted by mixing (Figure 4.4). Like DIC, DOC concentration integrates both respiratory and photosynthetic processes that occur simultaneously (Kaldy et al., 2005). Therefore, when measured DOC concentration is lower than predicted, it means that photosynthetic processes are outrun by respiratory processes, sediment burial, or other processes that could lower the DOC concentration, and vice versa.
Figure 4.5. Relationships between dissolved inorganic carbon (DIC, a to f), dissolved organic carbon (DOC, g to l) concentrations and the freshwater inflow across the six sampling sites from the upstream to the downstream during the study period. The $p$ and $R^2$ values are shown in the figure.
Sunlight conditions at sampling time may have had some impact on DOC concentration along this river estuary. During the May 2015 trip on a sunny day, all water samples were collected between 8:40 am and 12:00 noon, in the order from the upstream site 1 to the downstream site 6. There was a clear increasing trend of chlorophyll a from the upstream to the downstream (Table 4.1), accompanied by lower DOC concentrations at sites 2 to 5 (Figure 4.4). Since the photosynthesis rate is usually higher from noon to early afternoon around 15:00 (Shikata et al., 2017), DOC accumulation was assumed to be the highest at site 6 (sampled at 12:00 noon). In addition, site 6 was used as the marine endmember. Therefore, sites 2 to 5 tend to have lower measured DOC concentration than predicted by mixing, which is possibly due to lower photosynthesis rates at these sites, and higher photosynthesis introduced DOC concentration at the marine endmember (site 6). During the June 2015 and November 2015 trips, however, the weather was cloudy and such a longitudinal trend of chlorophyll a did not exist (Table 4.1). During these two trips, chlorophyll a concentrations ranged from 0.17 to 3.79 µg L\(^{-1}\), much lower than those in the other three trips on sunny days, ranging from 0.86 to 29.16 µg L\(^{-1}\). The chlorophyll a variation indicates variable photosynthesis rates, which may have had some effect on DOC variation in our study.

In contrast with sites 2 through 4, during February 2016, site 5 had DOC concentration very close to the predicted concentration using the conservative mixing model (Figure 4.4). This is because we collected the water sample at site 5 around 7 pm after sunset, so the respiration process may have balanced out the produced DOC by photosynthesis. The can also be explained by the very high TSS concentration (96 mg L\(^{-1}\)) at site 5 during the February 2016 trip. Exchange of organic matter between river water and sediment plays an important role in controlling DOC concentration during the mixing of fresh and marine waters. For instance, DOC concentration in
river water can be increased by desorption of organic matter from suspended sediments (Mannino and Harvey, 2001; Shilla et al., 2011), and, at the same time, salinity-induced flocculation within a river is a potential sink of DOC (Benner and Opsahl, 2001; Fransner et al., 2016). Due to the aggregation of DOC, flocculation is a process known to take place in proximity to river mouths. This aggregation is due to a change in ionic strength and an increase in divalent cations when freshwater mixes with seawater (Forsgren et al., 1996; Søndergaard et al., 2003; Fransner et al., 2016). The higher TSS concentrations at site 5 during February 2016 promotes the precipitation of DOC, which makes it an important sink for the DOC in the Calcasieu River.

As a heavy industry area, there are other anthropogenic DOC sources around the Lake Charles area that could contribute to the riverine DOC level, such as wastewater treatment plants, paper plants, and chemical refineries. Since we do not have measurements from those potential sources, discussing their inputs to the Calcasieu Estuary is beyond the scope of this study. However, it is reasonable to consider this because many studies have shown that anthropogenic DOC sources are important factors controlling the organic carbon dynamics in an estuary (Abril et al., 2002; Kaldy et al., 2005; Raymond et al., 2008; Zhang et al., 2014). If this is the case for the Calcasieu Estuary, then the dynamics of carbon might be modified due to anthropogenic DOC input.

4.4.3 Isotope signatures of DIC

The $\delta^{13}\text{C}_{\text{DIC}}$ value at the surface of the ocean is relatively consistent, around $+1\%o$ (Racapé et al., 2010; Filipsson et al., 2016). Compared with ocean waters, riverine DIC is $^{13}\text{C}$-depleted due to the decomposition and respiration of terrestrial-derived and riverine derived organic matter (Kaldy et al., 2005; Miyajima et al., 2009). The $\delta^{13}\text{C}_{\text{DIC}}$ in an estuary can provide
important insight into the sources of available carbon (Chanton and Lewis, 1999; Kaldy et al., 2005). The relationship between salinity and $\delta^{13}\text{C}_{\text{DIC}}$ in estuaries is influenced by mixing of coastal and riverine inputs, the balance of production and respiration, gas exchange with the atmosphere, and the dissolution of carbonate (Finlay, 2003; Kaldy et al., 2005). Negative deviations from conservative behavior (i.e., $^{13}\text{C}$-depletion) often indicate net heterotrophy ($P/R<1$); positive deviations (i.e., $^{13}\text{C}$-enrichment) often suggest net autotrophy ($P/R>1$; Coffin and Cifuentes, 1999; Kaldy et al., 2005). It is important to note that when deviations of $\delta^{13}\text{C}_{\text{DIC}}$ from conservative behavior are used to determine the net metabolism of an estuary, the assumption is that photosynthetic and respiratory processes are the only or dominant processes in that estuary that could impact $\delta^{13}\text{C}_{\text{DIC}}$.

May, June, and November plots of $\delta^{13}\text{C}_{\text{DIC}}$ versus salinity appear to be mostly conservative, but with site 5 in June showing obvious positive deviation from conservative behavior (i.e., $^{13}\text{C}$-enrichment) (Figure 4.4). The contribution of conservative mixing was calculated for samples with salinity at least 1 unit larger than the salinity of site 1 in the corresponding field trip (Table 4.3). The results showed that conservative mixing accounts for 64% (site 5 in June 2015) to 99% of the DIC concentration change for May 2015, June 2015, and November 2015 trips (Table 4.3). There are multiple mechanisms that could potentially cause $\delta^{13}\text{C}_{\text{DIC}}$ to shift upward. For instance, air-water CO$_2$ exchange, photosynthesis, and carbonate dissolution generally increase $\delta^{13}\text{C}_{\text{DIC}}$, resulting in an upward deviation in $\delta^{13}\text{C}_{\text{DIC}}$ with respect to the conservative mixing curve (Miyajima et al., 2009). Zhang et al. (2013) showed that Gulf sediment was the most dominate sediment source in the lower portion of the Calcasieu Ship Channel, and that ocean sediment (shell-material) from the GOM could reach about 32 km (close
to site 5 in this study) into the Ship Channel. Therefore, carbonate dissolution could be a reason for the high δ\(^{13}\)C\(_{\text{DIC}}\) value at site 5 because of the carbonate-concentrated substratum.

For the July 2015 and February 2016 trips, the measured δ\(^{13}\)C\(_{\text{DIC}}\) were lower than the values expected by the conservative mixing model, even though the longitudinal change of DIC concentration in February 2016 was apparently conservative. Non-conservative changes in δ\(^{13}\)C\(_{\text{DIC}}\), in contrast to conservative changes in DIC concentration across estuarine transects, have also been reported in other estuaries. For instance, due to the \(^{13}\)C-depleted DIC inputs from riverside mangroves, δ\(^{13}\)C\(_{\text{DIC}}\) values from two Southeast Asian estuaries were generally lower than expected for the mixing of the river water and seawater, despite the fact that the longitudinal change of DIC concentration was conservative (Miyajima et al., 2009). The DIC concentrations at the East Siberian Sea of 160°E below the surface were mostly conservative, while the δ\(^{13}\)C\(_{\text{DIC}}\) from the same locations were in general much lower than expected for conservative mixing (Alling et al., 2012). Non-conservative downward deviation of δ\(^{13}\)C\(_{\text{DIC}}\) is usually ascribed to the addition of isotopically light respiratory CO\(_2\) to the DIC pool because respiratory DIC usually has similar δ\(^{13}\)C\(_{\text{DIC}}\) value to decomposing organic matter in river waters and sediments (-30 to -25‰; Miyajima et al., 2009). For July 2015, both photosynthesis and respiration were active within the Calcasieu Estuary because of the high water temperature. For both July 2015 and February 2016, the system was net heterotrophy (P/R<1) since measured δ\(^{13}\)C\(_{\text{DIC}}\) values were lower than the values expected by the conservative mixing model. As we discussed earlier, when deviations of δ\(^{13}\)C\(_{\text{DIC}}\) from conservative behavior is used to determine the net metabolism of an estuary, the assumption is that photosynthetic and respiratory processes are the only or the dominant processes in that estuary that could impact δ\(^{13}\)C\(_{\text{DIC}}\). However, for both July 2015 and February 2016, confidence in the results on the net metabolism of the Calcasieu River is justified
because, while there are other importance processes like CO$_2$ degassing that could increase $\delta^{13}C_{\text{DIC}}$ in an estuary, respiration is the dominant process that could decrease $\delta^{13}C_{\text{DIC}}$. Therefore, it is more reasonable to conclude an estuary is heterotrophy when $\delta^{13}C_{\text{DIC}}$ is below the conservative mixing line than to conclude an estuary is autotrophy when $\delta^{13}C_{\text{DIC}}$ is above the conservative mixing line.

Generally, the $\delta^{13}C_{\text{DIC}}$ value in the Calcasieu River decreases when the DOC concentration increases (Figure 4.3d), indicating that the riverine isotopic signature of DIC could be impacted by the DOC content in the river. This could happen in two situations. First, organic carbon oxidation in the river can contribute to a decrease in the riverine $\delta^{13}C_{\text{DIC}}$. Second, the contribution of drainage areas with significant soil organic matter can lead to a negative relationship between DOC concentration and $\delta^{13}C_{\text{DIC}}$. The DIC supplied by these organic-rich areas is largely produced by CO$_2$ released by the degradation of this soil organic carbon. Therefore, the riverine $\delta^{13}C_{\text{DIC}}$ coming from these areas could be in equilibrium with the isotope signature of the soil CO$_2$, which should be around -20‰ (vegetation of the Calcasieu River is mainly of C3 type) (Brunet et al., 2005). The very low DO concentration at sites 2 and 3 during the warmer June and July trips confirms that soil organic carbon degradation does happen in the Calcasieu River. Further measurements are needed to confirm which of the two processes is dominant.

4.4.4 Isotope signatures of DOC

The origins of natural riverine organic matter include terrestrial plant detritus and soils, exogenous offshore marine environments like continental and marine sedimentary rocks, and in-situ aquatic production (Meybeck, 1993; Raymond and Bauer, 2001c; Bauer et al., 2013). For different estuarine systems, these sources are proportionally different (Guo et al., 2015). Some
studies (Raymond and Hopkinson, 2003; Wang et al., 2004) have found that phytoplankton production was a dominant source to the estuarine organic carbon pool, while other studies have shown that terrestrial origin was the dominant source of organic carbon for most rivers (Meybeck, 1993; Raymond and Bauer, 2001c). The $\delta^{13}$C$_{DOC}$ values in the ocean are consistent, ranging from around $-22\permil$ to $-21\permil$, despite large geographic variations (Williams and Druffel, 1987; Druffell et al., 1992; Fry et al., 1998). When compared with the $\delta^{13}$C$_{DOC}$ values in the northern Gulf of Mexico ($-24\permil$ to $-20\permil$, Wang et al., 2004), the $\delta^{13}$C$_{DOC}$ values in the Calcasieu River were depleted ($-30.56\permil$ to $-25.92\permil$), which is consistent with the $\delta^{13}$C$_{DOC}$ values of terrestrially derived plant matter and/or old sediment sources as reported by Raymond and Bauer (2001c).

Even though $\delta^{13}$C$_{DOC}$ can provide information about the sources of organic material available for estuarine respiration, the interpretation of $\delta^{13}$C$_{DOC}$ measurements in rivers and estuaries can be challenging due to a small range of values and a significant degree of overlap in the isotopic signatures for the presumed major DOC sources (Raymond and Bauer, 2001a; Kaldy et al., 2005). For the Calcasieu River, the interpretation of $\delta^{13}$C$_{DOC}$ is made difficult due to the small range of the $\delta^{13}$C$_{DOC}$ values ($-30.56\permil$ to $-25.92\permil$). There were no clear mixing trends for $\delta^{13}$C$_{DOC}$ in the Calcasieu River except that the mixing was not conservative (Figure 4.4), and a multiple regression did not yield any statistically meaningful output, as expected due to the small range of the $\delta^{13}$C$_{DOC}$ values. Furthermore, the $\delta^{13}$C$_{DOC}$ values in the Calcasieu River were not correlated with DOC concentrations (Figure 4.3f), suggesting that the DOC discharged by the Calcasieu River were not derived from a single dominant terrestrial source and that the riverine DOC concentrations were not simply diluted by horizontal mixing with seawater (Figure 4.4). It is highly possible that local processes like photosynthesis and respiration play important roles in
controlling the distribution and cycling of DOC in the Calcasieu River estuary as discussed in section 4.2.

4.5 Conclusions

This study investigated spatial and temporal trends of dissolved inorganic carbon and dissolved organic carbon concentrations and their $^{13}$C isotopic signatures along an 88-km estuarine river entering the Northern Gulf of Mexico in the southern United States. The DIC concentrations and $\delta^{13}$C$_{DIC}$ values increased rapidly in the salinity range from 0.02 to 21.92 measured during the study period. The DIC concentration appeared to be mostly controlled by conservative mixing except when photosynthesis and respiration were active due to high water temperature and long residence time caused by low river freshwater inflow. The $\delta^{13}$C$_{DIC}$ values during the study period were either close to or below those values suggested by the conservative mixing model, implying that an estuarine river can fluctuate from a balanced system to a heterotrophic system seasonally. The DOC concentration decreased with decreasing distance to the NGOM, but to a much smaller degree. The depleted $\delta^{13}$C$_{DOC}$ values (-30.56‰ to -25.92‰) in the Calcasieu River suggest that the DOC discharged by this river was highly terrestrially derived. However, in this relatively small isotopic range, $\delta^{13}$C$_{DOC}$ alone has limitations in unambiguously indicating the dominant source of DOC in a river-ocean continuum.
CHAPTER 5. PHOSPHORUS FLUXES AND MIXING DYNAMICS

5.1 Introduction

Excess nitrogen and phosphorus loads in rivers have been considered the main cause for eutrophication and harmful algal blooms of world’s coastal and lake waters (Carpenter et al., 1998; Smith, 2003; Conley et al., 2009) because these two elements strongly affect biological activity in aquatic environments. Over the past few decades, a conceptual model of nitrogen versus phosphorus limitation for terrestrial ecosystems has emerged based on the difference between abiotic nitrogen and abiotic phosphorus inputs. Abiotic phosphorus inputs decline over time because phosphorus weathers out of rocks, whereas abiotic nitrogen inputs do not change much as soil develops because they come primarily from the atmosphere. Such declining phosphorus inputs during pedogenesis has been termed by Walker and Syers (1976) as a “terminal steady state” of phosphorus deficiency. This depletion-driven phosphorus model has been recently tested by two long-term studies (Boyle et al., 2013; Izquierdo et al., 2013) and its validity has been generally confirmed for the dynamic nitrogen versus phosphorus limitation in terrestrial ecosystems. It is interesting to know if pedogenic dynamics of phosphorus is also reflected in river waters that drain watersheds with differently dominated land uses. Such information can be useful for predicting long-term riverine phosphorus transport from large drainage areas to their receiving basins.

Results from a previous study (He and Xu, 2015) on nutrient inputs from four coastal rivers in southwest Louisiana found that two of the four rivers that drained pasture and forest dominated lands showed increasing or no clear trend of total phosphorus (TP) over a period of 30 years from 1980 to 2009, while the other two rivers that drained intensive agricultural lands had
a declining trend of TP input. A significant reduction occurred in the 1990s and stayed through the 2000s and, therefore, has been attributed to the implementation of agricultural best management practices (BMPs) whose implementation began in the early 1990s. There is a growing interest in the research community as well as with policy makers to review if such decadal trends of riverine phosphorus fluxes in these rivers have maintained in the past decade. Such information will provide insights into long-term BMP effectiveness as well as the pedogenic dynamics of phosphorus, which can help develop science-based nutrient management plans to protect coastal water quality.

The near-shore coastal waters of Louisiana in the northern Gulf of Mexico (NGOM) have experienced severe oxygen depletion each summer since the mid-1980s (Rabalais et al., 2007, 2010; Turner et al., 2008). Nutrient enrichment, including phosphorus enrichment, is considered one of the major causes for the summer hypoxic conditions in the NGOM (Turner and Rabalais, 1994; Turner et al., 2012). As the largest river system in North America, the Mississippi-Atchafalaya River System (MARS) has been investigated intensively. Fluxes of nutrients from the MARS to the NGOM have been estimated for the past several decades (e.g., Goolsby et al., 2001; Turner et al., 2007; Xu, 2013). Due to its large discharge volume and power, the MARS has strong off-shore effects on water quality and nutrient availability. In contrast, the coastal rivers of southwest Louisiana entering the NGOM may have strong seasonal effects on near-shore water quality and nutrient availability in the region’s estuaries. While many studies have focused on nutrient input from MARS, little is known about the transport and transformation of phosphorus from the major coastal rivers of southwest Louisiana, which discharge a considerable amount of freshwater and sediment to the NGOM (Rosen and Xu, 2011).
Phosphorus transport and transformation in an estuary can depend on phosphorus speciation (Bianchi, 2007). Total phosphorus can be divided into dissolved and particulate organic phosphorus (DOP and POP) and dissolved and particulate inorganic phosphorus (DIP and PIP) pools. The DIP fraction is composed of phosphate (PO$_4^{3-}$), phosphoric acid (HPO$_4^{2-}$), orthophosphate (H$_2$PO$_4^-$), and triprotic phosphoric acid (H$_3$PO$_4$). The relative abundance of these species will vary with pH in aquatic systems, making H$_2$PO$_4^-$ and HPO$_4^{2-}$ the more common species in freshwater and seawater, respectively (Bianchi, 2007). An important consideration in phosphorus dynamics is the within-stream transformation between various phosphorus forms. Depending on the initial concentration, the equilibrium phosphorus concentrations of the suspended sediments, as well as the composition of streambed sediments and stream bank material, adsorption-desorption interaction between soluble and particulate phosphorus adsorbed on sediments can increase or decrease the soluble phosphorus concentration (Sharpley and Menzel, 1987; Hooda et al., 1997; Sonoda and Yeakley, 2007). Rivers draining watersheds with differing land uses may have important impacts on phosphorus speciation due to the differences in phosphorus sources.

This study aimed to revisit phosphorus transport in three previously studied estuarine rivers in southwest Louisiana over the recent decade. One river drains a pasture/forest-dominated watershed and two rivers drain intensive agricultural lands. The study included the following specific objectives: 1) determining recent total and dissolved inorganic phosphorus (DIP) fluxes from rivers with different land use types entering to one of the world’s largest hypoxic zone; 2) investigating spatial and temporal variations of TP and DIP in an estuarine river; 3) assessing mixing dynamics across salinity gradients for TP and DIP in an estuary with steep salinity gradients.
5.2 Methods

5.2.1 Calcasieu, Mermentau, and Vermilion Rivers

The three coastal rivers investigated in this study are the Calcasieu, Mermentau, and Vermilion Rivers, all of which enter the NGOM in southwest Louisiana, USA (Figure 5.1). The Calcasieu River flows 322 kilometers through a low-lying Chenier Plain in Southwest Louisiana, USA, before entering the northern Gulf of Mexico. This study has focused on the river’s last 88-km reach (Figure 5.1) that has a clear salinity gradient and tidal water influence. In the late 1940s, the U.S. Army Corps of Engineers was authorized by the U.S. Congress to construct a deep-draft channel in the Calcasieu River from Lake Charles to the Gulf of Mexico (GOM). The channel deepening allowed saltwater intrusion from the Gulf, threatening the upper Calcasieu River, a source of water for agricultural irrigation. In the 1960s, a saltwater barrier dam was constructed upstream of Lake Charles (LDWF, 2012; USACE), to prevent saltwater from traveling further upstream, as well as to regulate freshwater outflow. The Mermentau and Vermilion Rivers are two shorter rivers. The Mermentau River drains a land area of 16,997 km\(^2\) with a length of 115 km (USACE, 2015), and discharges into the Grand Lake before reaching the NGOM. The Vermilion River is 116 km long with a basin area of 4470 km\(^2\) (USEPA Region 6, 2001; Rosen and Xu, 2011), draining into the Vermilion Bay. Except for some navigational locks, no dams were constructed along the main channels of these two rivers. The Vermilion River is heavily human-modified with canals for agriculture irrigation.
Figure 5.1. Geographic location of the Calcasieu, Mermentau, and Vermilion Rivers entering the Northern Gulf of Mexico, and the locations of eight sampling sites and USGS discharge gauging sites. The Vermilion and Mermentau River Basins are agriculture-intensive (i.e. 67% and 61% agricultural land use), while the Calcasieu River Basin is much less agriculture-intensive (i.e. 26%).

The climate of the study area is subtropical, characterized by long, hot, and humid summers and generally short, mild winters. During the sampling period from April 2014 to February 2016, the average monthly temperature ranged from 9.6 °C in January 2015 to 28.5 °C in August 2014, with a mean of 20.9 °C for the twenty-three-month study period (National Oceanic and Atmospheric Administration (NOAA) station: Calcasieu Pass, LA - Station ID:

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Land use conditions are different among the three river basins. The Mermentau and Vermilion River Basins are much more dominated by agricultural land uses (67% and 61%, respectively) when compared with the Calcasieu River Basin (26%) (Baker, 1999; LDEQ, 2001 and 2002; Rosen and Xu, 2011). The difference in land use dominance may have profound effects on nutrient input from the river basins.

5.2.2 Field measurements and laboratory analysis

From April 2014 to February 2016, seventeen sampling events were conducted, taking place at eight sampling sites: sites 1 to 6 along an 88-km reach of the Calcasieu River from freshwater to saltwater, site 7 near the mouth the Mermentau River, and site 8 near the mouth of Vermilion River (Figure 5.1). Among the seventeen sampling events, four of them had both sediment and water samples collected from the Calcasieu River, which were July 2014, December 2014, March 2015, and August 2015. Note that site 3 was only sampled from August 2014 to February 2016, and sites 7 and 8 were only sampled from April 2014 to July 2015. Sites 1 and 2 were located above the saltwater barrier dam; therefore, water samples collected from the two sites were freshwater. All sampling sites below the barrier (i.e. sites 3, 4, 5, and 6) were saltwater affected to varied degrees, depending on river discharge and tidal mixing at the time of field sampling. During each trip, water temperature, dissolved oxygen (DO) concentration, pH, and salinity were measured using an YSI 556 multi-probe meter (YSI Inc., Yellow Springs, OH, USA). Fluorescence was measured with an AquaFluor® handheld fluorometer (Turner Designs, CA, USA) and was reported as arbitrary fluorescence units (AFUs). Turbidity was measured with a Turbidimeter (Hach, Loveland, Colorado, United States).

In addition, surface water samples were collected at each site approximately 30-50 cm below the water surface. The samples were collected from piers reaching out about 8-15 m into
the river channel with a grab sampler. The sampler consists of a 3.7 m aluminum pole with a polyethylene bottle attached at the end of the pole. High Density Polyethylene (HDPE) bottles (250 mL and 1000 mL) were used to store water samples for TP, DIP and total suspended solids (TSS) analysis. All bottles were thoroughly acid-cleaned and rinsed using river water before use. Duplicate samples were collected at one site per trip for quality control purposes. Surface sediment samples from the riverbed surface were collected using a sediment sampler (AMS Inc., American Falls, ID, USA) at the six sites on the Calcasieu River. Sediment samples were collected at three locations at each site and then combined to represent that site. All water and sediment samples were stored in a cooler with wet ice during transportation, and refrigerated until chemical analysis.

Water samples were analyzed for TP at the W. A. Callegari Environmental Center, Louisiana State University Agricultural Center. The analyses were done with a LaChat Flow Injection Analyzer, QuikChem 8500, Series II (Hach, Loveland, Colorado, United States) using EPA Methods 365.3. Concentrations of DIP were measured using a segmented flow auto-analyzer (Flow Solution IV, O.I Analytical, College Station Texas, United States) at the Louisiana State University School of the Coast and Environment Wetland Biogeochemistry Analytical Services. Additional water samples were filtered for TSS determination with gravimetric method at the W. A. Callegari Environmental Center, Louisiana State University Agricultural Center. Field and lab blanks were used for quality control to ensure that the samples were not contaminated, and that all sample analyses were within control limits. Duplicate analyses of water samples typically yielded an error less than 6%. The recovery rates of lab control samples for TP were from 84% to 108%. The method detection limits for TP, DIP, and TSS were 0.01, 0.000279, and 4 mg L\(^{-1}\), respectively. In addition to the data collected for this
study, dissolved organic carbon (DOC) (data available in He and Xu, 2017a and 2017b) and total silicon (Si) concentrations in water samples collected during the same study period were processed, and results are included here where applicable. Sediment samples were digested and analyzed for TP, calcium (Ca), zinc (Zn) and manganese (Mn) using method EPA 200.7. All the analysis was done at the W. A. Callegari Environmental Center, Louisiana State University Agricultural Center using inductively coupled plasma-atomic emission spectroscopy. The detailed sample analysis for total silicon (Si) in water samples as well as TP and cations in sediment samples was the same as the method used in He and Xu (2016).

5.2.3 Riverine phosphorus flux calculation

To estimate TP and DIP mass input from freshwater of the Calcasieu, Mermentau, and Vermilion Rivers into their mixing zones near the NGOM, daily discharge records for the three rivers were collected from the United States Geological Survey (USGS). The gauge stations were chosen based on availability and their proximity to the sampling sites for optimal representation. Specifically, the locations with their USGS gauge station numbers were Calcasieu River near Kinder, LA (USGS 08015500), Mermentau River at Mermentau, LA (USGS 08012150), and Vermilion River at Perry, LA (USGS 07386980).

Fluxes of TP and DIP are the product of the river’s discharge and concentrations of TP and DIP; therefore, there often exists a close relationship between nutrient fluxes and discharge. In this study, we estimated freshwater daily nutrient fluxes of the three rivers using a rating curve that can be described as the following log-linear regression model (Xu, 2013):

\[
\ln(S(t)) = b_0 + b_1 \ln(Q(t)) + \epsilon(t)
\]  

(1)
where $Q(t)$ represents the discharge in m$^3$ s$^{-1}$, $S(t)$ is the nutrient flux in g s$^{-1}$, and $\varepsilon(t)$ is an error term assumed to be normally distributed. Application of the equation yielded satisfactory results for both TP and DIP (Table 5.1).

Table 5.1. Parameter estimates ($b_0$ and $b_1$) used in Equation 1 for estimating TP and DIP fluxes and their regression coefficients ($R^2$) for the Calcasieu, Mermentau, and Vermilion Rivers using data from this study and Louisiana Department of Environmental Quality (LDEQ). SE=standard error, RMSE = root of mean square error, n = sample size.

<table>
<thead>
<tr>
<th>Data Source</th>
<th>River</th>
<th>$b_0$$\pm$SE</th>
<th>$b_1$$\pm$SE</th>
<th>$R^2$</th>
<th>RMSE</th>
<th>p Value</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>This Study</td>
<td>Calcasieu (Site 1)</td>
<td>TP -3.12±0.61</td>
<td>1.20±0.15</td>
<td>0.80</td>
<td>0.62</td>
<td>&lt;0.0001</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DIP -3.61±0.40</td>
<td>0.89±0.10</td>
<td>0.83</td>
<td>0.41</td>
<td>&lt;0.0001</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>Mermentau</td>
<td>TP -1.64±0.39</td>
<td>1.04±0.11</td>
<td>0.91</td>
<td>0.43</td>
<td>&lt;0.0001</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DIP -2.16±0.35</td>
<td>0.94±0.10</td>
<td>0.91</td>
<td>0.38</td>
<td>&lt;0.0001</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>Vermilion</td>
<td>TP -2.06±0.53</td>
<td>1.35±0.16</td>
<td>0.90</td>
<td>0.19</td>
<td>&lt;0.0001</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DIP -3.00±1.00</td>
<td>1.46±0.31</td>
<td>0.74</td>
<td>0.36</td>
<td>0.0014</td>
<td>10</td>
</tr>
<tr>
<td>LDEQ (2010 - 2017)</td>
<td>Calcasieu (Kinder)</td>
<td>TP -1.71±0.56</td>
<td>0.93±0.15</td>
<td>0.76</td>
<td>0.55</td>
<td>&lt;0.0001</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>Mermentau</td>
<td>TP -1.51±0.12</td>
<td>1.00±0.03</td>
<td>0.95</td>
<td>0.39</td>
<td>&lt;0.0001</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>Vermilion</td>
<td>TP -1.77±0.21</td>
<td>1.20±0.06</td>
<td>0.84</td>
<td>0.31</td>
<td>&lt;0.0001</td>
<td>78</td>
</tr>
</tbody>
</table>

In the previous report on TP fluxes of the Calcasieu River for 1990-2009, He and Xu (2015) used water quality measurements conducted at Kinder, about 40 km upstream from site 1 in this study, by the Louisiana Department of Environmental Quality (LDEQ). To compare the change in TP flux for this river from 2010 to 2017, we compiled water quality data from 2010 to 2017 from LDEQ. Only for this comparison, Kinder was used to represent the Calcasieu River, and TP concentration data from LDEQ were used. For all other comparisons, site 1 was used to represent the Calcasieu River, and all TP and DIP concentrations were from this study, as described below.

Since DIP concentration is not available from LDEQ, to calculate the contribution of DIP flux to TP flux, TP and DIP concentrations from this study were used to calculate TP and DIP fluxes during the study period. Here, concentrations of TP and DIP at site 1 were used to
calculate daily TP and DIP fluxes from the Calcasieu River freshwater. Because site 1 and the USGS discharge gage station at Kinder were about 40 km apart, we used an area weighting to estimate the runoff from the land between the two locations. Detailed calculation is available at He and Xu (2017). All discharge for the Calcasieu River presented in this study were the calculated discharge at site 1. Phosphorus concentrations and river discharges at sites 7 and 8 were used to calculate daily TP and DIP fluxes from the Mermentau and Vermilion Rivers. Because the fluxes calculated in the study will be considered as freshwater phosphorus loading to the studied estuaries, all negative discharges were excluded in flux calculations. A comparison between measured phosphorus fluxes and estimated phosphorus fluxes are shown in Figure 5.2. Nutrient yield for the three rivers (mass per unit area per unit time) were calculated by dividing the nutrient flux by the basin drainage areas at the gauge stations. This normalized nutrient flux so that comparison between river basins could be made.

5.2.4 Mixing analysis

Mixing analysis was performed for TP and DIP in the Calcasieu River. Concentrations of TP and DIP expected by the conservative-mixing model were calculated using the following formula (Fry, 2002; Kaldy et al., 2005):

\[ C_{mix} = f C_r + (1 - f) C_m \]  \hspace{1cm} (2)

where \( C \) denotes concentration, the subscripts \( r \) and \( m \) indicate river and marine endmembers, respectively, and \( f \) represents the fraction of freshwater in each sample calculated from salinity:

\[ f = (S_m - S)/(S_m - S_r) \]  \hspace{1cm} (3)

where \( S \) is the salinity at the sampling point and the subscripts are the same as Equation 2. \( S_m \) and \( S_r \) are salinity at the marine and river endmembers. Site 1 in this study generally has a
salinity around 0.03 (Table 5.2), which can be considered as freshwater. Therefore, site 1 is considered as the river endmember. As the closest site to the GOM, site 6 had the highest salinity among all sites. To simplify the situation, site 6 was used as the marine endmember.

![Graphs showing relationships between measured and estimated fluxes for different sites](image)

Figure 5.2. Relationship between measured TP and DIP fluxes and estimated TP and DIP fluxes using regression equations (Equation 1) for the Calcasieu (Site 1), Mermentau, and Vermilion Rivers from April 2014 to February 2016.

5.2.5 Statistical analysis

A two-way analysis of variance (ANOVA) comparing water sample values was performed separately for TP concentration, DIP concentration, DIP:TP, DOC:TP, DOC:DIP, Si:TP, Si:DIP, as well as environmental parameters, including salinity, pH, water temperature, DO concentration, TSS, fluorescence, and turbidity based on the sampling sites. Tukey-Kramer’s adjustment was used to group sampling sites when ANOVA shows significant differences among sites. For the Calcasieu River, Pearson Correlation Coefficients were calculated to analyze the
relationships among TP, DIP, and environmental parameters, including salinity, pH, water temperature, DO concentration, TSS, fluorescence, turbidity, river discharge, and river gage height as this coefficient measures the strength of a linear relationship between two parameters (Kim et al., 2015). While being a useful and straightforward way to investigate potential factors affecting nutrient concentrations, the Pearson Correlation Coefficient only considers one factor at a time, which can lead to large p values due to large numbers of modeling. To explore potential factors affecting nutrient concentrations, backward stepwise linear regressions were also performed between TP, DIP, and environmental parameters that had significant correlations with TP and DIP. Correlation analysis between TP concentration and concentrations of calcium (Ca), zinc (Zn) and manganese (Mn) were also performed in sediment samples collected in the Calcasieu River. All statistical analyses were performed with the SAS Statistical Software package (SAS Institute Inc., Cary, NC).

Table 5.2. Environmental conditions during the study period at six sampling sites along the Calcasieu River entering the Northern Gulf of Mexico in the southern United States. Tukey-Kramer’s adjustment was used to group sampling sites when ANOVA shows significant differences among sites. Means with the same letter are not significantly different at the 0.05 level (Tukey groupings).

<table>
<thead>
<tr>
<th>River</th>
<th>Site</th>
<th>Temperature (°C)</th>
<th>Salinity</th>
<th>pH</th>
<th>DO (mg L⁻¹)</th>
<th>TSS (mg L⁻¹)</th>
<th>Fluorescence (RFU)</th>
<th>Turbidity (NTU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcasie</td>
<td>1</td>
<td>21.75±6.83</td>
<td>0.03±0.01</td>
<td>6.18±0.50</td>
<td>5.50±2.27abc</td>
<td>18±7a</td>
<td>43.49±16.35abc</td>
<td>40±23a</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>22.17±6.78</td>
<td>0.07±0.10</td>
<td>6.14±0.59</td>
<td>4.88±2.54abc</td>
<td>18±13a</td>
<td>39.26±11.63abc</td>
<td>33±15a</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>21.28±7.04</td>
<td>1.78±1.87</td>
<td>6.40±0.47abc</td>
<td>5.11±2.96abc</td>
<td>20±16a</td>
<td>31.79±8.38a</td>
<td>24±12a</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>22.57±6.81</td>
<td>3.54±3.04</td>
<td>6.69±0.46abc</td>
<td>5.22±2.21abc</td>
<td>14±7a</td>
<td>34.97±10.63a</td>
<td>23±14a</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>23.43±6.49</td>
<td>11.91±6.22</td>
<td>7.54±0.48abc</td>
<td>6.51±2.68abc</td>
<td>42±26ab</td>
<td>32.78±17.28a</td>
<td>27±27a</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>23.45±6.49</td>
<td>19.05±6.46</td>
<td>8.11±0.43d</td>
<td>7.43±2.44abc</td>
<td>74±43c</td>
<td>41.95±19.65abc</td>
<td>41±32a</td>
</tr>
<tr>
<td>Mermentau</td>
<td>7</td>
<td>23.26±6.66</td>
<td>0.09±0.04</td>
<td>7.56±0.55c</td>
<td>4.13±2.59c</td>
<td>21±8a</td>
<td>81.80±36.80c</td>
<td>73±48b</td>
</tr>
<tr>
<td>Vermilion</td>
<td>8</td>
<td>23.84±6.58</td>
<td>0.09±0.03</td>
<td>7.01±0.38c</td>
<td>3.89±2.36c</td>
<td>57±47bc</td>
<td>59.53±23.55b</td>
<td>72±42b</td>
</tr>
</tbody>
</table>
5.3 Results

5.3.1 Hydrology and ambient conditions

From April 2014 to February 2016, the Calcasieu River showed an average daily discharge of 73 m$^3$ s$^{-1}$ (std: ±91), ranging from 6 to 809 m$^3$ s$^{-1}$ (Figure 5.3), with November 2015 having the highest average discharge (271 m$^3$ s$^{-1}$) and September 2015 the lowest (8 m$^3$ s$^{-1}$). The large seasonal variation of discharge during the sampling period had clear impacts on salinity and pH along the estuarine river. For instance, the salinity and pH during the April 2015 sampling event were the lowest for most sites due to the high discharge when compared with other sampling trips (Figures 5.3a and 5.4a). The Mermentau and Vermilion Rivers showed a similar seasonal trend in river discharge (Figure 5.3a) but with a much lower average daily discharge than the Calcasieu river, at 53 (±83) m$^3$ s$^{-1}$ and 40 (±33) m$^3$ s$^{-1}$, respectively.

The ambient conditions at the six sampling sites along the Calcasieu River varied largely (Table 5.2 and Figure 5.4). Salinity levels at site 6, the closest location to the Gulf of Mexico, ranged from 4.80 to 29.50, with an average of 19.05, which was more than 700 times higher than that of site 1, the most upstream location. The salinity levels increased with decreasing distance from the GOM (Table 5.2 and Figure 5.4a) and, as expected, pH was positively correlated to salinity (Table 5.3). However, pH at sites 1 and 2 had a larger variation than salinity did (Figure 5.4). The average dissolved oxygen and total suspended solids concentrations at sites 5 and 6 were much higher than those of the other sites (Table 5.2 and Figure 5.4). Being nearest to the GOM, sites 5 and 6 were strongly impacted by saltwater. The stronger tidal movement at these two sites may have aerated the water, as reflected by the higher DO levels at the sites. Due to the negative relationship between temperature and DO (Table 5.3), the DO concentrations were higher during winter and spring months and lower during summer and fall months (Figure 5.4).
When compared with the Calcasieu River, the Mermentau and Vermilion Rivers clearly had lower DO concentrations, but higher fluorescence and turbidity (Table 5.2).

Figure 5.3. Daily (a-c) and monthly (d-f) discharge and mass fluxes of TP and DIP in the Calcasieu (Site 1), Mermentau, and Vermilion Rivers from April 2014 to February 2016; discharge data at sites 1, 7, and 8 were used to represent the three rivers; Discharge at site 1 was calculated using discharge data at Kinder (USGS 08015500). Discharges at sites 7 and 8 were downloaded from USGS gage stations (USGS 08012150 and USGS 07386980); dashed lines in (a) mark the sampling dates; phosphorus concentrations and discharges at sites 1, 7, and 8 were used to calculate mass fluxes for the Calcasieu, Mermentau, and Vermilion Rivers, respectively; missing data for the Mermentau and Vermilion Rivers are due to availability of phosphorus concentration and discharge data.

5.3.2 Freshwater phosphorus concentrations, fluxes and yields

Both total phosphorus and dissolved inorganic phosphorus concentrations showed the same trend among the three rivers: Vermilion > Mermentau > Calcasieu (Table 5.4 and Figure
The average total phosphorus concentrations at Calcasieu (site 1), Mermentau, and Vermilion were 0.11, 0.26, and 0.40 mg L\(^{-1}\), and the average dissolved inorganic phosphorus concentrations were 0.020, 0.11, and 0.22 mg L\(^{-1}\), respectively. DIP concentration accounted for 24% (site 1) to 34% (site 6) of the TP concentration in the Calcasieu River, but made a much higher proportion in the Mermentau River (42%) and Vermilion River (54%) (Table 5.4). Molars ratios of DOC:TP, DOC:DIP, Fe:TP, and Fe:DIP in the three rivers showed opposite trends: Calcasieu > Mermentau > Vermilion (Table 5.4 and Figure 5.5).

Figure 5.4. Temporal trends of salinity (a), water temperature (b), DO concentration (b), pH (c), TSS (d), fluorescence (e), and turbidity (f) at six sampling sites along the Calcasieu River from April 2014 to February 2016.
Table 5.3. Pearson Correlation Coefficients between phosphorus and environmental factors in the Calcasieu River entering the Northern Gulf of Mexico in the southern United States. Only significant (p<0.01) correlations are shown.

<table>
<thead>
<tr>
<th></th>
<th>TP</th>
<th>DIP</th>
<th>Salinity</th>
<th>pH</th>
<th>Temperature</th>
<th>DO</th>
<th>TSS</th>
<th>Discharge</th>
<th>Gage Height</th>
<th>Fluorescence</th>
<th>Turbidity</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>DIP</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>Temperature</td>
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<td>0.48</td>
<td>1.00</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>DO</td>
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<td>0.30</td>
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<tr>
<td>TSS</td>
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<td>Discharge</td>
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<tr>
<td>Gage Height</td>
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<td>0.36</td>
<td>0.36</td>
<td>0.36</td>
<td>1.00</td>
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</tr>
<tr>
<td>Fluorescence</td>
<td>0.64</td>
<td>0.46</td>
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<td>0.46</td>
<td>1.00</td>
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</tr>
<tr>
<td>Turbidity</td>
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<td>0.54</td>
<td>1.00</td>
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</tr>
</tbody>
</table>

Table 5.4. TP and DIP concentrations and ratios as well as DOC and silicon to phosphorus ratios at six sampling sites along the Calcasieu, Mermentau, and Vermilion Rivers entering the Northern Gulf of Mexico in the southern United States. Tukey-Kramer’s adjustment was used to group sampling sites when ANOVA shows significant differences among sites. Means with the same letter are not significantly different at the 0.05 level (Tukey groupings).

<table>
<thead>
<tr>
<th>River</th>
<th>Site</th>
<th>TP (mg L⁻¹)</th>
<th>DIP (mg L⁻¹)</th>
<th>DIP:TP</th>
<th>DOC:TP</th>
<th>DOC:DIP</th>
<th>Si:TP</th>
<th>Si:DIP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcasieu</td>
<td>Site 1</td>
<td>0.11±0.058a</td>
<td>0.020±0.0082a</td>
<td>0.24±0.18a</td>
<td>382±288</td>
<td>1680±1146</td>
<td>100±83</td>
<td>450±240a</td>
</tr>
<tr>
<td></td>
<td>Site 2</td>
<td>0.10±0.052a</td>
<td>0.023±0.014a</td>
<td>0.27±0.19a</td>
<td>414±318</td>
<td>1609±1006</td>
<td>98±60</td>
<td>430±210a</td>
</tr>
<tr>
<td></td>
<td>Site 3</td>
<td>0.10±0.052a</td>
<td>0.034±0.022a</td>
<td>0.32±0.25ab</td>
<td>408±313</td>
<td>1275±943ab</td>
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<td>280±250ab</td>
</tr>
<tr>
<td></td>
<td>Site 4</td>
<td>0.11±0.053b</td>
<td>0.038±0.023a</td>
<td>0.32±0.25ab</td>
<td>379±280</td>
<td>1160±811ab</td>
<td>73±45</td>
<td>240±190bc</td>
</tr>
<tr>
<td></td>
<td>Site 5</td>
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<td>0.047±0.022a</td>
<td>0.34±0.18ab</td>
<td>426±654</td>
<td>479±345bc</td>
<td>71±62</td>
<td>140±100bc</td>
</tr>
<tr>
<td></td>
<td>Site 6</td>
<td>0.11±0.070a</td>
<td>0.036±0.014a</td>
<td>0.34±0.26ab</td>
<td>293±549</td>
<td>447±248bc</td>
<td>83±74</td>
<td>190±110bc</td>
</tr>
<tr>
<td>Mermentau</td>
<td>Site 7</td>
<td>0.26±0.12b</td>
<td>0.11±0.045b</td>
<td>0.42±0.15ab</td>
<td>174±180</td>
<td>299±122bc</td>
<td>61±50</td>
<td>130±85bc</td>
</tr>
<tr>
<td>Vermilion</td>
<td>Site 8</td>
<td>0.40±0.080c</td>
<td>0.22±0.086c</td>
<td>0.54±0.16bc</td>
<td>61±23</td>
<td>110±43c</td>
<td>34±21</td>
<td>70±52c</td>
</tr>
</tbody>
</table>

For this study period, the Calcasieu River discharged 273 t of TP each year from its freshwater into coastal waters, of which 38 tons were DIP. When normalized to the drainage basin area, the fluxes represent an annual TP yield of 46 kg km⁻² year⁻¹, and an annual DIP yield of 6 kg km⁻² year⁻¹. The Mermentau and Vermilion Rivers discharged distinctively more TP and DIP into their estuaries than the Calcasieu River did. For the Mermentau River, the average annual fluxes of TP and DIP were 663 and 185 t year⁻¹, respectively. The Vermilion River had similar TP flux (693 t year⁻¹) to the Mermentau River, but more DIP flux (550 t year⁻¹). When normalized to the drainage basin area, the differences in phosphorus yield between the Calcasieu
and the two agricultural intensive rivers (the Mermentau and Vermilion) were even more apparent. The TP and DIP yields of the Mermentau River were 238 and 67 kg km\(^{-2}\) year\(^{-1}\), while the TP and DIP yields of the Vermilion River were 425 and 337 kg km\(^{-2}\) year\(^{-1}\), respectively.

Figure 5.5. Concentrations of TP and DIP in the Calcasieu, Mermentau, and Vermilion Rivers from April 2014 to February 2016; The Mermentau and Vermilion Rivers were only sampled from April 2014 to July 2015; Data for the Calcasieu, Mermentau, and Vermilion Rivers in (a) are data for sites 1, 7, and 8.
Seasonally, freshwater of the Calcasieu River showed the highest mean monthly fluxes of TP and DIP in November 2015, and the lowest in September 2015, corresponding to the river discharge regime (Figure 5.3). In November 2015, the Calcasieu River discharged 101 t TP and 7 t DIP into its estuary, contributing 20% and 15% of their average total annual exports, respectively. The Mermentau and Vermilion Rivers had a similar seasonal trend in TP and DIP fluxes. However, due to the data availability, the highest monthly phosphorus fluxes in the Mermentau and Vermilion Rivers were in April 2015 and June 2014, respectively (Figure 5.3).

5.3.3 Comparison between TP loading during 1990-2009 and 2010-2017

When compared with the total phosphorus exports for 1990-2009 from the Calcasieu and Mermentau Rivers (0.51 t day\(^{-1}\) and 1.87 t day\(^{-1}\); He and Xu, 2015), the recent average daily TP fluxes of these two rivers were only slightly lower (i.e., 0.48 t day\(^{-1}\) and 1.78 t day\(^{-1}\), respectively) (Table 5.5). For the Calcasieu River, the insignificant change in TP flux could be affected by both a significant decrease in river discharge and a significant increase in TP concentration in the past eight years. The insignificant change in TP flux from the Mermentau River reflected the insignificant change in both river discharge and TP concentration. The Vermilion River had statistically significant increase in river discharge from 1990-2009 period to 2010-2017 period, while the increase in TP concentration was not statistically significant (Table 5.5), resulting in a moderate but statistically significant increase in daily TP fluxes.

5.3.4 Phosphorus concentration change in a mixing zone

From the freshwater site to the saltwater sites along the 88-km Calcasieu River reach, no clear longitudinal trend in total phosphorus was found. The average TP concentration for the six sites ranged from 0.10 to 0.11 mg L\(^{-1}\) (Table 5.4 and Figure 5.5). Generally, the two upstream
fresh water sites (sites 1 and 2) had lower dissolved inorganic phosphorus concentrations than the four downstream sites, with site 5 having the highest DIP concentrations for more than half of the sampling trips (Table 5.4 and Figure 5.5). There was a large temporal variation in TP and DIP concentrations at all six sites in the Calcasieu River. Both TP and DIP concentrations were in general lower in winter months, and higher in summer and fall months (Figure 5.5). This trend was confirmed by the positive relationship between temperature and concentrations of TP and DIP (Table 5.3).

Table 5.5. Comparison between total phosphorus loading from 1990 to 2009 and from 2010 to 2017. Means followed by the same letter within a column for the same river are not significantly different at the 0.05 level, and vice versa. Only non-negative discharge data were used to calculate phosphorus flux and perform statistical analysis here. Data for 1990-2009 are from He and Xu (2015). TP concentration data used are all from LDEQ to keep the data source consistency. The sampling size used to calculate mean TP concentration for the Calcasieu, Mermentau, and Vermilion Rivers during 2010-2017 are 14, 53, and 78, respectively.

<table>
<thead>
<tr>
<th>River</th>
<th>Year</th>
<th>Discharge (m³ s⁻¹)</th>
<th>TP concentration (mg L⁻¹)</th>
<th>TP Flux (t day⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcasieu (Kinder)</td>
<td>1990-2009</td>
<td>72±126⁠^a⁠</td>
<td>0.079±0.050⁠^a⁠</td>
<td>0.51±1.05⁠^a⁠</td>
</tr>
<tr>
<td></td>
<td>2010-2017</td>
<td>43±90⁠^b⁠</td>
<td>0.16±0.11⁠^b⁠</td>
<td>0.48±0.88⁠^a⁠</td>
</tr>
<tr>
<td></td>
<td>1990-2009</td>
<td>86±105⁠^a⁠</td>
<td>0.25±0.13⁠^a⁠</td>
<td>1.87±2.41⁠^a⁠</td>
</tr>
<tr>
<td>Mermentau</td>
<td>2010-2017</td>
<td>91±134⁠^a⁠</td>
<td>0.24±0.090⁠^a⁠</td>
<td>1.78±2.62⁠^a⁠</td>
</tr>
<tr>
<td></td>
<td>1990-2009</td>
<td>32±32⁠^a⁠</td>
<td>0.35±0.12⁠^a⁠</td>
<td>1.02±1.18⁠^a⁠</td>
</tr>
<tr>
<td>Vermilion</td>
<td>2010-2017</td>
<td>41±37⁠^b⁠</td>
<td>0.36±0.13⁠^a⁠</td>
<td>1.34±1.58⁠^b⁠</td>
</tr>
</tbody>
</table>

5.4 Discussion

5.4.1 Flow and rainfall effects on phosphorus fluxes

This study found that the Vermilion River, draining agriculture intensive land, had an increased total phosphorus export from the 1990-2009 period to 2010-2017 period. However, the increase should not be attributed to land use effects because the river discharge increased during the past eight years while the TP concentration in the river was relatively unchanged (Table 5.5). The Vermilion River receives partial flow from the Atchafalaya River through river diversion (Rosen and Xu, 2011) and it is not clear whether the discharge increase was caused by an
increased diversion from the Atchafalaya River or an increased rainfall within the drainage area. In any case, the findings indicate the important role of river discharge in TP export.

From 1990-2009 to 2010-2017, the variation of river discharge in the Calcasieu River was mainly caused by precipitation change. For instance, daily precipitation from a NOAA weather station (station number: USC00166938 Oberlin fire tower, LA US) which is about 16 km upstream of Kinder can explain 71% variance of the river discharge at Kinder during 1990-2017 (Figure 5.6). Other studies have demonstrated that climate condition such as precipitation has critical impact on riverine phosphorus export. Chen et al. (2015) showed that in the six catchments of the Yongan River watershed in eastern China will have an 8-18% increase from 2000-2010 in riverine TP flux by 2030 due to a 4% increase in precipitation with no changes in anthropogenic phosphorus inputs and land use condition. As future climate change drives an increase in hydrologic variability, the predictability of the response of nutrient flux such as TP flux to discharge may be important in understanding ecosystem responses to climatic change.

Figure 5.6. The relationship between discharge at Kinder (United States Geological Survey (USGS) station number: 08015500) and precipitation at Oberlin (National Oceanic and Atmospheric Administration (NOAA) station number: USC00166938). Each dot in the figure represent a pair of mean discharge and precipitation during a certain year from 1990 to 2017.
River discharge impacts TP flux not only because TP flux is the product of the river’s discharge and TP concentration in river water, but also because discharge influences TP concentration. In the Calcasieu and Mermentau Rivers, low discharges were not always accompanied by high TP concentrations, but high TP concentrations were usually accompanied by low discharges, suggesting the dilution effect of river discharge. For example, in the Calcasieu River, all samples with TP concentrations > 0.18 mg L\(^{-1}\) were collected when discharges were below 50 m\(^3\)s\(^{-1}\) (Figure 5.7). In the Mermentau River, all samples with TP concentrations > 0.30 mg L\(^{-1}\) were all collected when discharges were below 105 m\(^3\)s\(^{-1}\). The Vermilion River did not exhibit such trend, and we believe this is caused by the high nutrient availability in the Vermilion drainage basin due to the agriculture intensive land use conditions. In this river, discharge could have a dilution effect as well as have the ability to bring in more nutrients into the river surface water due to soil erosion.

5.4.2 Land use effects on phosphorus fluxes

The TP and DIP fluxes and yields from the Mermentau and Vermilion Rivers were clearly higher than those from the Calcasieu River, further confirming the strong effect of land uses on phosphorus input to estuaries in coastal river basins. Phosphorus in surface waters arises from various sources, including drainage from agricultural soils, domestic, farm, and industrial effluents, groundwater discharge, and atmospheric deposition (Ryding et al., 1990; Hooda et al., 1997; Alexander et al., 2008). Numerous studies have demonstrated the strong effect of agricultural practices in coastal river basins on the quantity and quality of nutrient input to estuaries (Groppo et al., 2015; He and Xu, 2015). The concentration of phosphorus in drainage water from agricultural land is a complex function of soil characteristic, land use, and management practices (Hooda et al., 1997; Shen et al., 2013). Due to the non-existence of
gaseous phase and phosphorus adsorption on oxides and clay mineral, phosphorus is less mobile in the soil-plant-atmosphere system than nitrogen (Groppo et al., 2015). One consequence of this lower phosphorus mobility throughout the soil profile is that when phosphorus fertilizers are applied, they tend to increase soil phosphorus concentration on the surface, which makes phosphorus more available by loss through soil erosion and surface runoff (Messiga et al., 2013; Groppo et al., 2015). The high availability of phosphorus by loss explains the strong impact of agriculture on river water TP and DIP concentrations and fluxes.

Land uses not only change the quantity of phosphorus loadings to estuarine rivers, but also change the forms and availability of phosphorus. The higher DIP contribution in rivers draining agricultural-intensive watersheds maybe due to the soluble phosphorus fertilizer used in these river basins. The Mermentau and Vermilion Rivers also had lower DOC:TP, DOC:DIP, Si:TP, and Si:DIP ratios than the Calcasieu River. The differences in those ratios can influence primary production and the composition of plankton communities, individually or in combination (Hodgkiss and Ho, 1997; Leong et al., 2014).

5.4.3 Phosphorus in fresh-saltwater mixing

In this study, we found no clear mixing dynamics of total phosphorus (Figure 5.8). The average TP concentrations at the six sites from upstream to downstream were fairly consistent. The mixing dynamics of DIP concentration versus salinity plots suggest a source was present throughout the Calcasieu Estuary since measured DIP concentration was usually higher than those predicted by conservative mixing (Figure 5.9), and this source is not related to seasonal change. The ultimate source of biologically available DIP is the weathering of continental rocks. However, only about 5% to 10% of the phosphorus eroded from continental rocks is thought to be carried to the oceans in dissolved form, and the rest is presumably carried as inert phosphorus
in fluvial detrital grains (Froelich, 1988; Meng et al., 2015). Therefore, the forms of phosphorus have important impact on phosphorus transport and transformation dynamics in a river system.

Figure 5.7. The relationship between discharge and TP concentration for the Calcasieu, Mermentau, and Vermilion Rivers from 2010 to 2017 using discharge data from USGS and TP concentration data from Louisiana Department of Environmental Quality (LDEQ).
Figure 5.8. Relationships between TP and salinity in the Calcasieu River entering the Northern Gulf of Mexico in the southern United States. Hollow circles represent actual measurements. Corresponding conservative mixing values are denoted by stars. Lines represent conservative-mixing models (see Equations 2 and 3). Site 1 was used as the river endmember, and site 6 was used as the marine endmember.

Figure 5.9. Relationships between DIP and salinity in the Calcasieu River entering the Northern Gulf of Mexico in the southern United States. Hollow circles represent actual measurements. Corresponding conservative mixing values are denoted by stars. Lines represent conservative-mixing models (see Equations 2 and 3). Site 1 was used as the river endmember, and site 6 was used as the marine endmember.
The interaction between water and sediment has important impacts on phosphorus concentration in water. In solution, DIP reacts quickly with a wide variety of surfaces, being taken up by and released from particles through a complex series of sorption reactions (Froelich, 1988; Van Raaphorst and Kloosterhuis, 1994). For instance, desorption of DIP from aluminum and iron oxides is an important source for DIP in estuarine waters, while adsorption of DIP on sediments is an important sink for some estuaries. Hobbie et al. (1975) reported that 60% of the DIP entering the Pamlico River estuary (USA) was scavenged by particulates and stored in sediments, while Evans et al. (2004) showed that sediment plays an important role in supplying phosphorus to the river channel. In both freshwater and estuarine systems, concentrations of DIP have been strongly linked with the suspended sediment load. In fact, a stable or “equilibrium” concentration range of DIP, between 0.5 µM (0.015 mg L\(^{-1}\)) and 2 µM (0.062 mg L\(^{-1}\)), has been reported for several estuarine systems (Pomeroy et al., 1965; Froelich, 1988), including the Calcasieu Estuary in this study. These stable DIP concentrations are believed to be controlled by a “buffering” of DIP through the adsorption and desorption onto metal oxide surfaces (Fox, 1989; Conley et al., 1995).

The release of phosphorus from estuarine sediment is a common and important process that varies spatially and temporally (Bianchi, 2007). Metal oxyhydroxide adsorption of phosphorus in sediment is an important control upon phosphorus mobility, while the re-suspension of phosphorus-rich particle from the river bed, combined with high pH and low oxygen concentrations, can cause desorption of particulate phosphorus into the water column via hydroxyl group exchange mechanisms (Evans and Johnes, 2004). Concentration of DIP in bottom water in the Baltic Sea was correlated with an area of the bottom covered by hypoxic water, and also shown to be negatively correlated with oxygen concentration, indicating the
release of DIP from sediments (Conley et al., 2002). Increases in pH can enhance the release of adsorbed P that is hydrated to Fe and Al oxides, through ligand exchange mechanisms involving competition between OH\(^{-}\) and PO\(_4^{3-}\) (Fox, 1989; Bianchi, 2007). In the Calcasieu River, desorption from suspended solids and sediments may be one of the sources of DIP in the estuary. The negative relationship between DO and DIP as well as the positive relationship between pH and DIP (Tables 5.3 and 5.6) can partially explain this. Further, correlation analysis showed significant relationships between TP and total Mn (Table S1; n=25, R\(^2\)=0.50, p<0.01), and total zinc (n=25, R\(^2\)=0.92; p<0.01) in sediment samples (Table 5.7) collected from the Calcasieu River. With that, however, release of P from estuarine sediment may not the only source of DIP in the Calcasieu River.

Table 5.6. Relationships between phosphorus concentrations and environment parameters from all six sampling sites in the Calcasieu River using backward stepwise linear regression. Slope and intercept estimates are presented with standard errors (±SE). Only statistically significant relationships are reported (p<0.05). Variables left in the model are significant at the 0.05 level. T=temperature; Turb=turbidity; DO=dissolved oxygen concentration; GH=gage height.

<table>
<thead>
<tr>
<th>Nutrient</th>
<th>Environmental Parameters</th>
<th>Final Equation</th>
<th>r(^2)</th>
<th>F</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP</td>
<td>Temperature</td>
<td>TP = −0.02(±0.02) + 0.004(±0.0006)T + 0.002(±0.0002)Turb</td>
<td>0.50</td>
<td>46.41</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td></td>
<td>Turbidity</td>
<td></td>
<td>33.63</td>
<td>68.71</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td></td>
<td>T+Turb</td>
<td></td>
<td>68.71</td>
<td>&lt;0.0001</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td>DIP = −0.06(±0.02) + 0.01(±0.002)pH − 0.005(±0.0009)DO + 0.05(±0.01)GH</td>
<td>0.47</td>
<td>22.06</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>DO</td>
<td></td>
<td></td>
<td>40.17</td>
<td>&lt;0.0001</td>
<td></td>
</tr>
<tr>
<td>Gage Height</td>
<td></td>
<td></td>
<td>24.87</td>
<td>&lt;0.0001</td>
<td></td>
</tr>
<tr>
<td>pH+DO+ GH</td>
<td></td>
<td></td>
<td>24.80</td>
<td>&lt;0.0001</td>
<td></td>
</tr>
</tbody>
</table>

As a heavy industry area, there are other anthropogenic DIP sources around the study area that could contribute to the riverine DIP level, such as wastewater treatment plants, paper plants, and chemical refineries. Since we do not have measurements from those potential sources, discussing their inputs to the Calcasieu Estuary is beyond the scope of this study. However, it is reasonable to consider this because many studies have shown that anthropogenic
DIP sources are important factors controlling the phosphorus dynamics in an estuary (Young et al., 1999; Sonoda and Yeakley, 2007). If this is the case for the Calcasieu Estuary, then the dynamics of phosphorus might have been modified due to anthropogenic phosphorus input.

Table 5.7. Concentration of TP, Ca, Mn, and Zn in sediment samples collected at the Calcasieu River.

<table>
<thead>
<tr>
<th>Site</th>
<th>Date</th>
<th>TP</th>
<th>Ca</th>
<th>Mn</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>mg L⁻¹</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Site 1</td>
<td>7/16/2014</td>
<td>84</td>
<td>2201</td>
<td>91</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>12/2/2014</td>
<td>140</td>
<td>18143</td>
<td>96</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>3/22/2015</td>
<td>244</td>
<td>2164</td>
<td>174</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>8/20/2015</td>
<td>88</td>
<td>1990</td>
<td>166</td>
<td>18</td>
</tr>
<tr>
<td>Site 2</td>
<td>7/16/2014</td>
<td>47</td>
<td>14229</td>
<td>60</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>12/2/2014</td>
<td>35</td>
<td>1521</td>
<td>133</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>3/22/2015</td>
<td>23</td>
<td>1724</td>
<td>61</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>8/20/2015</td>
<td>28</td>
<td>1920</td>
<td>63</td>
<td>45</td>
</tr>
<tr>
<td>Site 3</td>
<td>12/2/2014</td>
<td>443</td>
<td>121021</td>
<td>248</td>
<td>103</td>
</tr>
<tr>
<td></td>
<td>3/22/2015</td>
<td>121</td>
<td>7005</td>
<td>110</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>8/20/2015</td>
<td>64</td>
<td>18723</td>
<td>93</td>
<td>14</td>
</tr>
<tr>
<td>Site 4</td>
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<td>1226</td>
<td>31</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>12/2/2014</td>
<td>71</td>
<td>1172</td>
<td>53</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>3/22/2015</td>
<td>80</td>
<td>986</td>
<td>38</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>8/20/2015</td>
<td>48</td>
<td>806</td>
<td>65</td>
<td>13</td>
</tr>
<tr>
<td>Site 5</td>
<td>7/16/2014</td>
<td>1366</td>
<td>138547</td>
<td>488</td>
<td>196</td>
</tr>
<tr>
<td></td>
<td>12/2/2014</td>
<td>233</td>
<td>10380</td>
<td>166</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>3/22/2015</td>
<td>270</td>
<td>41157</td>
<td>201</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>8/20/2015</td>
<td>104</td>
<td>1818</td>
<td>128</td>
<td>26</td>
</tr>
<tr>
<td>Site 6</td>
<td>7/16/2014</td>
<td>385</td>
<td>22017</td>
<td>440</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td>12/2/2014</td>
<td>332</td>
<td>16627</td>
<td>642</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>3/22/2015</td>
<td>429</td>
<td>28450</td>
<td>481</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td>8/20/2015</td>
<td>474</td>
<td>10734</td>
<td>350</td>
<td>58</td>
</tr>
</tbody>
</table>

Calcium carbonate and phosphorus co-precipitation, as reported in other river systems (Evans et al., 2004; Evans and Johnes, 2004), could be another mechanism controlling the phosphorus dynamics in the Calcasieu River. Concentrations of TP and calcium in sediment samples collected from the Calcasieu River were statistically correlated (sample size n=23, \( R^2=0.68, p<0.01 \)). Furthermore, sites 5 and 6 had higher correlations (n=8, \( R^2=0.89, p<0.01 \)) than sites 1 to 4 did (n=15, \( R^2=0.73, p<0.01 \)), suggesting that calcium carbonate and phosphorus co-
precipitation was a more significant mechanism that could decrease phosphorus concentration at sites 5 and 6 when compared with the four upstream sites. Therefore, the observed mixing dynamics for DIP could be caused by using site 6 as the marine endmember.

As discussed above, riverine transport of phosphorus is controlled by a number of physical, chemical, and biotic mechanisms which are in turn dependent upon interactions between the water column and riverbed. The release and uptake of phosphorus by both suspended and bed sediments provide a critical control on in-stream phosphorus transport. Phosphorus transport and transformation dynamics in rivers can only be fully understood when considering both the water and sediment phases (Evans and Johnes, 2004). While we are confident that the discussions here are well supported by our results, a more detailed sampling design focusing on suspended sediment, river bed sediment, and water column interactions will provide us with a deeper understanding on the dynamics of phosphorus in our studied river systems.

5.5 Conclusions

This study investigated total phosphorus and dissolved inorganic phosphorus loadings from three coastal rivers that drain watersheds under varied agriculture intensities (i.e. 67%, 61%, and 26%) into the northern Gulf of Mexico, one of the world’s largest summer hypoxic zones. The study also examined the TP and DIP changes along an 88-km reach from freshwater to saltwater to discern mixing effects on phosphorus dynamics. The TP fluxes from one of the rivers (Vermilion River) draining an agriculture-intensive watershed increased from 1990-2009 period to 2010-2017 period, while no significant change was found in the other two rivers. River discharge variability caused by precipitation change, and probably river diversion as well, was the main reason for such TP flux trend. The two rivers draining more agriculture-intensive
watersheds (67% and 61%) showed consistently higher TP and DIP concentrations and fluxes than the one that drains a pasture-forest dominated area, confirming the strong effect of land uses on phosphorus input to estuaries in coastal river basins. The DIP concentration versus salinity plots in the Calcasieu River suggest some sources were present throughout the Calcasieu Estuary since measured DIP concentrations were usually higher than those predicted by conservative mixing. Such mixing dynamic were probably caused by desorption of DIP from suspended solids and river bed sediments, urban inputs, as well as stronger calcium carbonate and phosphorus co-precipitation at the marine endmember. To fully understand the phosphorus transport and transformation dynamics in rivers, a more detailed sampling design focusing on suspended sediment, river bed sediment, and water column interactions is necessary.
CHAPTER 6. STRONTIUM AND BARIUM MIXING DYNAMICS

6.1 Introduction

Estuarine systems face a variety of threats ranging from regional anthropogenic factors, such as river basin land use change (Birch et al., 2015; Dorado et al., 2015), riverine nutrient enrichment (Scavia et al., 2003; Ferreira et al., 2015), and coastal industrial pollution (Pinto et al., 2015), to global stressors such as climate change and sea level rise (Geselbracht et al., 2015; Wang et al., 2015). This is especially true for lowland estuarine rivers where any rise in sea level can have a far-reaching impact on the community. Over the past century, the global mean sea level has increased by nearly 200 mm (IPCC, 2007; Church and White, 2011) due to an increase in 20th century ocean heat content (Munk, 2002) and mass increase (Miller and Douglas, 2004). The rise rate was found to be accelerating in the past two decades, averaging 3.2 mm per year in a range between 2.8 and 3.6 mm (IPCC, 2013).

As sea level rise continues, saltwater intrudes upstream inland, which can cause changes in water chemistry, especially salinity and pH. Salinity and pH are two important factors affecting many chemical and biological processes in estuarine waters. One of the processes is the adsorption–desorption of trace metals in estuarine mixing zones. Salinity and pH have been found to strongly affect mobility and flux rates of trace metals (Turner, 1996) when they are carried by rivers to various estuarine/coastal systems around the world; for instance, in the Galveston Bay estuary in Texas (Wen et al., 1999), the San Francisco Bay Estuary in California (Sanudo-Wilhelmy et al., 1996), the Changjiang Estuary in China (Edmond et al., 1985; Zhang et al.)

The chapter, previously published as ‘He, S., Xu, Y.J., 2017. Spatiotemporal distributions of Sr and Ba along an estuarine river with a large salinity gradient to the Gulf of Mexico. Water, 8(8), 323’, is reprinted here by permission under the Creative Commons Attribution License.
al., 2008), the Bang Pakong Estuary in Thailand (Windom et al., 1989), the Scheldt Estuary in the Netherlands (Zwolsman et al., 1999), and the Conwy Estuary in North Wales (Zhou et al., 2003). The ongoing saltwater intrusion in the world’s estuaries may shift metal mobilization and precipitation landwards, the occurrence and effects of which are not well investigated. Such knowledge can be useful for future coastal resource management especially in low-lying, flat areas such as southern Louisiana where the estuaries extend 30 to 70 km inland.

The fate of trace metals in estuaries has been a great concern for aquatic life systems. Studies reported that high levels of strontium (Sr) and barium (Ba) concentrations could be toxic for marine embryos (abnormal shell calcification and embryo morphology) (Spangenberg and Cherr, 1996), benthic biota (Lira et al., 2011), and photosynthetic microorganisms (Polonini et al., 2014). For instance, Spangenberg and Cherr (1996) showed that adverse effects on mussel embryos occurred when Ba concentration was between 200 and 900 μg/L. In addition to their natural occurrence, the level of trace metals in waterways could be elevated from petrochemical industry (Fiedler et al., 2009). Offshore oil and gas drilling use two primary types of drilling fluids: water-based fluids and non-aqueous drilling fluids. Both of these fluids contain Ba as a major component (Melton et al., 2010; OGP). Lira et al., (2011) concluded that oil and gas drilling activities may potentially have important implications for meiobenthos through the toxicity of Ba. Southern Louisiana is a national center of the USA oil and petrochemical industry, and many processing plants are located along the estuaries. It is unknown if there is any elevated level of Ba in the estuarine waters in this region.

Determining movements and migrations of aquatic animals between environments is important, especially for the understanding of the life history characteristics of these animals. In complicated environments, such as estuaries, the movements and migrations of animals are
affected by multiple factors (Elsdon and Gillanders, 2005). Instead of using conventional tags, many animals have natural tags that can be used to answer ecological questions regarding their life histories. For instance, the elements present within otoliths (earbones) of fish are ideally suited to be used as natural tags, because elements, such as Sr and Ba, can be incorporated into their calcium carbonate matrix (CaCO$_3$) through either substitution (e.g., BaCO$_3$ or SrCO$_3$) or binding within the lattice matrix (Nielson and Christoffersen, 1982; Elsdon and Gillanders, 2003). Studies have shown that the ambient Sr/Ca and Ba/Ca ratios and environmental conditions, including salinity, influence the Sr/Ca and Ba/Ca ratios in fish otoliths and scales (Bath et al., 2000; Wells et al., 2000). For instance, fish with otolith Ba/Ca ≤ 5 μmol/mol were classified as resident in salt water, and those with ≥6 μmol/mol as resident in fresh water (Elsdon and Gillanders, 2005). Therefore, Sr/Ca and Ba/Ca ratios have been used as proxies across salinity gradients to detect aquatic animal (such as fish) movements.

Louisiana’s coast of the northern Gulf of Mexico experienced rapid land subsidence and land loss in the past century (Britsch and Dunbar, 1993; Törnqvist et al., 2008; Morton and Bernier, 2010). As a result, the Louisiana Gulf coast has had one of the highest relative sea-level rises in the United States (Dixon et al., 2006; Ivins et al., 2007). Saltwater intrusion has been observed in many coastal rivers in the region, and the Calcasieu River is a prime example. This river flows through the Chenier Plain comprising an area of approximately 5000 km$^2$ with a west-east coastline of about 200 km (LDNR), stretching geographically from approximately 29.5°N to 33.2°N and from 91.3°W to 94.0°W. The Calcasieu River is 322 km long with a drainage area of 9780 km$^2$ (Nichol et al., 1992), discharging into the Calcasieu Lake before the northern Gulf of Mexico. During the past half century, this river was hydrologically altered. For instance, along the Calcasieu River, two dams were constructed in its upper reach, and prior to
the 1960s, a deep draft channel in the Calcasieu River from the Gulf of Mexico to Lake Charles allowed saltwater from the Gulf to migrate further inland. Saltwater, which kills many types of vegetation, began to destroy some of the sensitive wetlands of the Calcasieu River Basin. To solve the saltwater intrusion problem, the Calcasieu River Saltwater Barrier was constructed in the 1960s to prevent saltwater from traveling north further upstream as well as to regulate freshwater outflow (LDWF; USACE). In addition to saltwater intrusion, the lower Calcasieu River is a heavy shipping channel for petrochemical industry concentrated on the river banks. These two problems make the river estuary an ideal location to study the Sr and Ba dynamics across salinity gradients, as the aforementioned hydrological alterations may have had considerable effects on water quality and riverine metal transport.

Studies have been conducted on trace metals for the Mississippi River (Xu, 2007; Shiller, 1997; Joung and Shiller, 2014), which has a high volume of freshwater discharge pushing into the far-shore open water. On the other hand, little is known about trace metal dynamics in Louisiana’s small estuarine rivers like the Calcasieu that has low freshwater discharge and is strongly affected by tides and saltwater intrusion. Due to its highest rate of relative sea-level rise among all regions in the United States, the study of saltwater impacts on metal dynamics in southern Louisiana can provide information that will have global implications. The ultimate goal of this study is to investigate the impacts of saltwater intrusion on trace metal distribution. Specifically, this study is to quantify spatial and temporal variations of Sr, Ca, Ba, Sr/Ca, and Ba/Ca in the Calcasieu River and to assess mixing dynamics across salinity gradients for these same constituents.
6.2 Materials and Methods

6.2.1 Study Area

The study area is the lower reach of the Calcasieu River that enters the northern Gulf of Mexico in southwest Louisiana, USA (Figure 3.1a). Six sampling sites were selected along the 88-km reach and they are all within the Calcasieu Parish (north) and the Cameron Parish (south). In the study area, the main soil types (>65%) are: Arat mucky silt loam (AR), Bancker muck (BA), Creole mucky clay (CR), Clovelly muck (CO), Crowley-Vidrine (Cr), Guyton-Messer silt loams (Gy), Gentilly muck (GC), Kinder-Gist complex (Kd), Mowata-Vidrine complex (Mt), Edgerly loam (Mr), Scatlake mucky clay (SC), and Udifluvents (UA) (USDA, 2014).

6.2.2 Data Collection

Long-term daily discharge (available since September 1922) and gage height (available since October 1997) data of the Calcasieu River was collected from the US Geological Survey (USGS). The gage stations were chosen based on their data availability and proximity to the sampling sites for optimal representation. Specifically, daily discharge was collected at the Calcasieu River near Kinder, LA (USGS 08015500), and the daily gage height was collected at the Calcasieu River near Cameron, LA (USGS 08017118) (Figure 3.1a).

6.2.3 Water Sample Collection

From May 2013 to August 2015, monthly field trips (except June 2013, October 2013 and November 2014) were made to conduct in-situ measurements and collect water samples at six sampling sites along the Calcasieu River (Figure 3.1a). Note that site 3 was only sampled from August 2014 to August 2015. The saltwater barrier is located approximately two km downstream of site 2, below which all sampling sites are affected by saltwater. During each trip,
field measurements on water temperature, dissolved oxygen (DO) concentration, pH, and salinity were conducted using an YSI 556 multi-probe meter (YSI Inc., Yellow Springs, OH, USA). In addition, a 250 mL water sample was collected from each site for elemental analysis. The samples were acidified to pH < 2 at the time of collection in the field without filtration. A one-liter water sample was collected from each site for total suspended solids (TSS) analysis. High Density Polyethylene (HDPE) bottles were used to collect water samples, and all the bottles were thoroughly acid-cleaned before use. All the water samples were taken approximately 30–50 cm below the surface. The samples were collected from piers reaching out about 8–15 m into the river channel with a grab sampler consisting of a 12-ft aluminum pole with a polyethylene bottle attached at the end of the pole. On each trip, samples were collected in duplicate at one of the sites; however, subsequent analyses indicated typically less than 5% differences in all constituents. As a result, duplicates data were removed from the data analysis. All the water samples were stored in a cooler with wet ice during transportation, and refrigerated until analysis. All efforts were made to avoid any possible contamination in the field, during transportation, and in Laboratory. Table 6.1 shows the sampling sites’ information.

Table 6.1. Geographical locations of six sampling sites along the Calcasieu River and their distance to the northern Gulf of Mexico.

<table>
<thead>
<tr>
<th>Site ID</th>
<th>Latitude</th>
<th>Longitude</th>
<th>River Distance from Gulf (km)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site 1</td>
<td>30.297</td>
<td>-93.118</td>
<td>87.9</td>
</tr>
<tr>
<td>Site 2</td>
<td>30.299</td>
<td>-93.188</td>
<td>73.5</td>
</tr>
<tr>
<td>Site 3</td>
<td>30.253</td>
<td>-93.245</td>
<td>62.6</td>
</tr>
<tr>
<td>Site 4</td>
<td>30.219</td>
<td>-93.250</td>
<td>58.1</td>
</tr>
<tr>
<td>Site 5</td>
<td>30.006</td>
<td>-93.334</td>
<td>27.0</td>
</tr>
<tr>
<td>Site 6</td>
<td>29.805</td>
<td>-93.349</td>
<td>4.5</td>
</tr>
</tbody>
</table>

6.2.4 Water Sample Analysis

Water samples were analyzed for total recoverable concentrations of all elements and total suspended solids at the W. A. Callegari Environmental Center, Louisiana State University
Agricultural Center using EPA Method 200.7. Briefly, water samples were digested using metals-grade concentrated HCl and HNO₃. Yttrium was added to the water samples as an internal standard. Element concentrations above the calibration curve were diluted by factors of 10, 20, 50, 100, or 1000 to bring them into the calibration curve. Finally, the analyses were conducted using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Varian Vista MP-X, Palo Alto, CA, USA). The one-liter water samples collected from each site were filtered, whereby gravimetric analysis was used to determine TSS. Field and Laboratory blanks, and Independent/Continuing Calibration Verification/Blanks were used for quality control to insure that the samples were not contaminated, and that all sample analyses were within control limits. Laboratory duplicate measurements of a same water sample typically yielded a difference of less than 5%. The method detection limits in our study for Sr, Ca, Ba, and TSS are 0.0088 µmol/L, 0.50 µmol/L, 0.14 µmol/L, and 4 mg/L, respectively.

6.2.5 Statistical Analyses

Multivariate analysis of variance (MANOVA) was performed for all element concentration/ratio for main and interactive effects of sampling site and month on differences in concentrations/ratios. Two-way analyses of variance (ANOVAs) comparing water sample values were calculated separately for each of the five measured element concentrations and ratios according to sampling site and month of collection. Pearson correlations were compared between element concentrations and ratios and environmental parameters, including salinity, pH, temperature, dissolved oxygen (DO), and TSS, to investigate potential relationships. All statistical analyses were performed with the SAS Statistical Software package. All statistical tests and confidence intervals are reported at $\alpha = 0.01$ critical level.
6.3 Results

6.3.1 Hydrology and Ambient Conditions

From 1 May 2013 to 31 August 2015, the Calcasieu River showed an average daily discharge of 39 m$^3$/s (standard deviation (std): ±46), ranging from 5 to 259 m$^3$/s. The discharge during the sampling period was notably lower than the long-term average from 1980 to 2009 (72 ± 66 m$^3$/s) (He and Xu, 2015). Seasonally, the Calcasieu River showed higher discharge during the winter and spring months and lower discharge during the summer and fall months in the period from 1980 to 2009 (He and Xu, 2015). During the sampling period, the river exhibited the same seasonal pattern as in the period from 1980 to 2009, with April having the highest average discharge (103 m$^3$/s) and August the lowest (9 m$^3$/s). During the 25 field sampling days from 1 May 2013 to 31 August 2015, the discharges ranged from 5 to 259 m$^3$/s with an average of 44 m$^3$/s (std: ±59) (Figure 6.1).

Figure 6.1. Discharge at Kinder, LA (USGS Station# 08015500) and tidal gage height at Cameron, LA (USGS Station# 08017118).

The Calcasieu River near its mouth at Cameron showed a long-term (October 1997–August 2015) average daily gage height (or tidal stage) of 0.31 m (±0.18), ranging from −0.48 to
2.31 m. Over the past eight years, the tidal stage showed a clear increasing trend (Figure 6.2a). During the two-year sampling period, the average daily gage height at Cameron ranged from −0.32 to 1.53 m, with an average of 0.34 m (±0.19). Seasonally, in contrast with the river discharge, the tidal stage at the river mouth was high in the fall months, with September having the highest monthly average (0.48 m), and low in the winter months, with January having the lowest (0.18 m). During the sampling period, the monthly average gage heights at the Calcasieu River near Cameron were similar to the historical monthly average gage heights, and the seasonal trend of gage height was similar to the historical trend, with larger variance (Figure 6.2b). During the 25 field trip days from May 2013 to August 2015, the average daily gage height at the Calcasieu River near Cameron ranged from −0.03 to 0.63 m, averaging 0.31 (std: ±0.18). The average daily gage heights at the Calcasieu River near Cameron were well represented by the average daily gage heights during the 25 field trip days (Figure 6.1).

The ambient conditions at the six sampling sites varied largely (Table 6.2). Salinities at site 6 ranged from 4.80 to 29.50, with an average of 19.91, which is more than 280 times higher than the average salinity at site 1. Salinity increased with the decrease of distance from the Gulf of Mexico. Overall, pH, DO concentration, and water temperature showed similar trends to salinity. During the 25 sampling trips, the average pH at all the sampling sites ranged from 6.08 at site 2 to 8.18 at site 6, while the average DO concentration ranged from 4.64 mg/L at site 3 to 7.77 mg/L at site 6. The average water temperature at site 3 was higher than other sites, which is attributed to a different sampling schedule for site 3. TSS concentrations varied from site 1 to site 6 and, overall, showed relatively low levels (mostly <20 mg·L⁻¹) in the four upstream sites (Table 6.2, Figure 6.3e). All six sites had higher salinity during summer and fall months (Figure 6.3a). From March to November, pH exhibited an increasing trend (Figure 6.3b). 

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June, July, and August had higher water temperatures, while December, January, and February had lower (Figure 6.3c). The dissolved oxygen (DO) concentration had the opposite trend from water temperature (Figure 6.3d). Correlation analysis showed that temperature and DO concentration were negatively highly correlated (Table 6.3). Sites 5 and 6 had higher TSS variation seasonally, but there was no clear trend (Figure 6.3e).

Figure 6.2. Seasonal trend of tidal gage height at Cameron, LA (USGS Station# 08017118): (a) monthly trend from 1997 to 2015, (b) averaged monthly trend.
Table 6.2. Means and standard deviations of water quality parameters at six sampling sites along the Calcasieu River during May 2013 and August 2015.

<table>
<thead>
<tr>
<th>Site ID</th>
<th>n</th>
<th>Salinity</th>
<th>pH</th>
<th>Temperature (°C)</th>
<th>DO (mg/L)</th>
<th>TSS (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site 1</td>
<td>25</td>
<td>0.07 ± 0.18</td>
<td>6.30 ± 0.96</td>
<td>21.61 ± 7.09</td>
<td>5.40 ± 2.52</td>
<td>16.36 ± 7.66</td>
</tr>
<tr>
<td>Site 2</td>
<td>25</td>
<td>0.40 ± 1.24</td>
<td>6.08 ± 1.06</td>
<td>21.90 ± 7.45</td>
<td>4.78 ± 2.64</td>
<td>14.28 ± 13.71</td>
</tr>
<tr>
<td>Site 3</td>
<td>13</td>
<td>3.05 ± 5.29</td>
<td>6.45 ± 0.64</td>
<td>23.01 ± 6.97</td>
<td>4.64 ± 2.91</td>
<td>16.48 ± 18.43</td>
</tr>
<tr>
<td>Site 4</td>
<td>25</td>
<td>5.89 ± 5.67</td>
<td>6.59 ± 0.92</td>
<td>22.17 ± 7.53</td>
<td>5.20 ± 2.69</td>
<td>12.37 ± 7.97</td>
</tr>
<tr>
<td>Site 5</td>
<td>24</td>
<td>14.15 ± 6.67</td>
<td>7.51 ± 0.57</td>
<td>22.55 ± 7.67</td>
<td>6.75 ± 2.70</td>
<td>28.53 ± 23.63</td>
</tr>
<tr>
<td>Site 6</td>
<td>25</td>
<td>19.91 ± 5.73</td>
<td>8.18 ± 0.64</td>
<td>22.89 ± 7.31</td>
<td>7.77 ± 2.56</td>
<td>54.79 ± 33.78</td>
</tr>
</tbody>
</table>

Figure 6.3. Seasonal trends of salinity (a); pH (b); temperature (c); dissolved oxygen (DO) (d); and total suspended solids (TSS) (e) at six sampling sites along the Calcasieu River. Data in this figure are means of the different years.
6.3.2 Strontium, Ca Concentrations and Sr/Ca Ratio

During the sampling period, the Sr concentration showed a considerable variation among sampling sites, with sites closer to the Gulf having much higher concentrations (Table 6.4). The average Sr concentration at site 6 was 46.21 µmol/L, about 130 times higher than that at the stream site 1 (0.35 µmol/L). The spatial difference in Sr concentration was statistically significant (both $p < 0.01$, Tables 6.5 and 6.6). Seasonally, there was also a large variation in Sr concentration at each site: from not detected (n.d.) to 1.71 µmol/L at site 1, from n.d. to 7.19 µmol/L at site 2, from 0.23 to 18.26 µmol/L at site 3, from 0.34 to 35.61 µmol/L at site 4, from 1.60 to 63.00 µmol/L at site 5, and from 10.61 to 74.18 µmol/L at site 6. In general, all six sites had higher Sr concentrations during the summer and fall months (Figure 6.4a), and the difference in monthly Sr concentration was statistically significant (both $p < 0.01$, Tables 6.5 and 6.6). In the interactive effect of sampling site and month, the Sr concentration showed no significant differences (both $p > 0.01$, Tables 6.5 and 6.6).

Table 6.3. Pearson correlation between dissolved Sr, Ba, Ca and environmental factors in the Calcasieu River. Significant ($p < 0.01$) correlations using Pearson Correlation Coefficients are indicated in bold.

<table>
<thead>
<tr>
<th>Heading</th>
<th>Salinity</th>
<th>pH</th>
<th>Temperature</th>
<th>DO</th>
<th>TSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr</td>
<td>0.98</td>
<td>0.67</td>
<td>0.05</td>
<td>0.29</td>
<td>0.42</td>
</tr>
<tr>
<td>Ca</td>
<td>0.83</td>
<td>0.53</td>
<td>0.02</td>
<td>0.25</td>
<td>0.47</td>
</tr>
<tr>
<td>Sr/Ca</td>
<td>0.58</td>
<td>0.48</td>
<td>0.03</td>
<td>0.16</td>
<td>0.23</td>
</tr>
<tr>
<td>Ba</td>
<td>−0.05</td>
<td>0.02</td>
<td>0.33</td>
<td>−0.42</td>
<td>−0.17</td>
</tr>
<tr>
<td>Ba/Ca</td>
<td>−0.69</td>
<td>−0.63</td>
<td>−0.12</td>
<td>−0.17</td>
<td>−0.24</td>
</tr>
<tr>
<td>Salinity</td>
<td>1.00</td>
<td>0.70</td>
<td>0.07</td>
<td>0.27</td>
<td>0.37</td>
</tr>
<tr>
<td>pH</td>
<td>1.00</td>
<td>0.34</td>
<td>0.04</td>
<td>0.04</td>
<td>0.26</td>
</tr>
<tr>
<td>Temperature</td>
<td>1.00</td>
<td>−0.79</td>
<td>−0.02</td>
<td>1.00</td>
<td>0.15</td>
</tr>
<tr>
<td>DO</td>
<td>1.00</td>
<td>0.15</td>
<td>1.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TSS</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 6.4. Means and standard deviations of element concentrations and ratios in water samples from six sampling sites along the Calcasieu River.

<table>
<thead>
<tr>
<th>Site ID</th>
<th>Sr   (µmol/L)</th>
<th>Ca    (mmol/L)</th>
<th>Sr/Ca (mmol/mol)</th>
<th>Ba (µmol/L)</th>
<th>Ba/Ca (mmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site 1</td>
<td>0.35 ± 0.31</td>
<td>0.13 ± 0.17</td>
<td>2.89 ± 0.80</td>
<td>0.46 ± 0.11</td>
<td>4.82 ± 1.75</td>
</tr>
<tr>
<td>Site 2</td>
<td>0.77 ± 1.42</td>
<td>0.23 ± 0.53</td>
<td>3.49 ± 1.51</td>
<td>0.42 ± 0.09</td>
<td>3.94 ± 1.74</td>
</tr>
<tr>
<td>Site 3</td>
<td>5.13 ± 5.72</td>
<td>0.68 ± 0.67</td>
<td>6.06 ± 1.93</td>
<td>0.41 ± 0.11</td>
<td>2.10 ± 1.93</td>
</tr>
<tr>
<td>Site 4</td>
<td>9.91 ± 9.58</td>
<td>1.10 ± 1.24</td>
<td>8.11 ± 3.38</td>
<td>0.43 ± 0.11</td>
<td>1.22 ± 1.41</td>
</tr>
<tr>
<td>Site 5</td>
<td>30.85 ± 15.24</td>
<td>4.66 ± 4.56</td>
<td>8.67 ± 6.01</td>
<td>0.47 ± 0.09</td>
<td>0.30 ± 0.49</td>
</tr>
<tr>
<td>Site 6</td>
<td>46.21 ± 14.94</td>
<td>8.19 ± 9.89</td>
<td>8.41 ± 5.07</td>
<td>0.36 ± 0.07</td>
<td>0.09 ± 0.10</td>
</tr>
</tbody>
</table>

Table 6.5. Results from factorial multivariate analysis of variance (MANOVA, Wilks’ Lambda) performed for all element concentrations/ratios for main (site and month) and interactive (site × month) effects of sampling site and month on differences in concentrations/ratios. A high F value and a low p value indicate significant main and interactive effects. Non-significant interactive effect is required to interpret main effects.

<table>
<thead>
<tr>
<th>Value</th>
<th>Num DF</th>
<th>Den DF</th>
<th>F</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site</td>
<td>0.02</td>
<td>25</td>
<td>153.81</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>Month</td>
<td>0.08</td>
<td>55</td>
<td>193.37</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>Site × Month</td>
<td>0.05</td>
<td>240</td>
<td>209.57</td>
<td>0.73</td>
</tr>
</tbody>
</table>

The Ca concentration was significantly different among sampling sites (both p < 0.01, Tables 6.5 and 6.6), with sites closer to the Gulf having much higher concentrations (Table 6.4). The average Ca concentration at site 6 was 8.19 mmol/L, about 60 times higher than site 1 (0.13 mmol/L). The Ca concentration varied largely at all the sampling sites: from 0.06 to 0.92 mmol/L at site 1, from 0.07 to 2.64 mmol/L at site 2, from 0.07 to 2.07 mmol/L at site 3, from 0.08 to 5.51 mmol/L at site 4, from 0.24 to 18.25 mmol/L at site 5, and from 1.22 to 45.76 mmol/L at site 6. Seasonally, the Ca concentration had a large variation, with August having the highest concentration of all six sites except site 6 (Figure 6.4b). Furthermore, there was no statistically significant difference among sampling months (p > 0.01, Table 6.6). In the interactive effect of sampling site and month, the Ca concentration showed no significant differences (both p > 0.01, Tables 6.5 and 6.6).
Figure 6.4. Seasonal trends of Sr concentration (a); Ca concentration (b); Sr/Ca ratio (c); Ba concentration (d); and Ba/Ca ratio (e) at six sampling sites along the Calcasieu River. Data in this figure are means of the different years.

The Sr/Ca ratio increased with the decrease of distance to the Gulf and the spatial difference in the Sr/Ca ratio was statistically significant (both $p < 0.01$, Tables 6.5 and 6.6). The average Sr/Ca ratio at site 6 (8.41 mmol/mol) was about three times the average Sr/Ca ratio at site 1 (2.89 mmol/mol). Seasonally, the Sr/Ca ratio varied largely at all sampling sites: from 0 to
4.14 mmol/mol at site 1, from 0 to 6.48 mmol/mol at site 2, from 2.46 to 8.82 mmol/mol at site 3, from 4.32 to 20.83 mmol/mol at site 4, from 2.92 to 34.16 mmol/mol at site 5, and from 1.23 to 28.53 mmol/mol at site 6. There was no clear seasonal trend of the Sr/Ca ratio at sites 1 and 2, while the other four sites had large variations, with July having the highest Sr/Ca ratio for sites 4, 5, and 6 (Figure 6.4c). There was no statistically significant difference among sampling months ($p > 0.01$, Table 6.6).

Table 6.6. Results from two-way analyses of variance (ANOVAs) performed separately for each element concentration/ratio for main (site and month) and interactive (site × month) effects of sampling site and month on differences in concentrations/ratios. A high $F$ value and a low $p$ value indicate significant main and interactive effects. Significant main effects in MANOVA (Table 6.5) and non-significant interactive effects in both MANOVA (Table 6.5) and ANOVAs (this table) are required to interpret main effects in this table.

<table>
<thead>
<tr>
<th></th>
<th>Num DF</th>
<th>Den DF</th>
<th>$F$</th>
<th>$p$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sr</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Site</td>
<td>5</td>
<td>54</td>
<td>76.40</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>Month</td>
<td>11</td>
<td>54</td>
<td>3.14</td>
<td>0.0024</td>
</tr>
<tr>
<td>Site × Month</td>
<td>54</td>
<td>54</td>
<td>0.60</td>
<td>0.9701</td>
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6.3.3 Barium Concentration and Ba/Ca Ratio

Overall, spatial variation in Ba concentration was small among the six sites, from 0.36 µmol/L at site 6 to 0.47 µmol/L at site 5. However, there was significant difference in Ba concentration among sampling sites (both $p < 0.01$, Tables 6.5 and 6.6). Temporal variation of Ba concentration was larger (from one to three fold), but relatively smaller when compared with
the spatial variation of Sr and Ca concentrations (Table 6.4 and Figure 6.4d). There was significant difference of Ba concentration among sampling months (both $p < 0.01$, Tables 6.5 and 6.6), with winter months having lower Ba concentrations (Figure 6.4d). There was no statistically significant difference in the interactive effect of sampling site and month (both $p > 0.01$, Tables 6.5 and 6.6).

Unlike the Sr/Ca ratio, the Ba/Ca ratio decreased with decreasing distance to the Gulf of Mexico, and the spatial difference in the Ba/Ca ratio was statistically significant (both $p < 0.01$, Tables 6.5 and 6.6). The average Ba/Ca ratio at site 1 (4.82 mmol/mol) was about 54 times the average ratio at site 6 (0.09 mmol/mol). Temporally, the Ba/Ca ratio varied largely at all sampling sites: from 0.55 to 9.21 mmol/mol at site 1, from 0.16 to 7.24 mmol/mol at site 2, from 0.11 to 5.96 mmol/mol at site 3, from 0.09 to 5.68 mmol/mol at site 4, from 0.02 to 2.15 mmol/mol at site 5, and from 0.01 to 0.36 mmol/mol at site 6. Seasonally, the Ba/Ca ratio had large variation and there was significant difference among sampling months (both $p < 0.01$, Tables 6.5 and 6.6). In general, all six sites had higher Ba/Ca ratios during spring and fall months (Figure 6.4e). The Ba/Ca ratio was no significantly different in the interactive effect of sampling site and month (both $p > 0.01$, Tables 6.5 and 6.6).

6.3.4 Relationships between Concentrations and Ratios of Sr, Ba, and Ca and Environmental Parameters

The Sr and Ca concentrations were positively correlated to salinity, pH, DO, and TSS, while no clear correlation of these concentrations with water temperature was found (Table 6.3). The Sr/Ca ratio was positively correlated to salinity and pH, but not correlated to temperature, DO, and TSS (Table 6.3). In contrast with other element concentrations and ratios, the Ba concentration was positively correlated to temperature and negatively correlated to DO, while no
correlation was found between Ba concentration and salinity, pH, and TSS (Table 6.3). The Ba/Ca ratio was negatively correlated to salinity and pH, but not correlated to temperature, DO, and TSS (Table 6.3).

6.4 Discussion

Dissolved Sr loads in the world’s river waters have been reported by Gaillardet et al., (2003) to have the largest variation when compared with other trace metals. These loads ranged from a few ng/L to nearly 100 µg/L, with an average of 60 µg/L. On the other hand, dissolved Ba loads in the world’s river waters are among the least variable, ranging between 10 and nearly 100 µg/L with an average of 23 µg/L (Gaillardet et al., 2003). Similar to Sr, dissolved Ca concentrations in freshwaters can be highly variable, potentially reaching very low levels, e.g., <1–20 mg/L (Hem, 1985; Hamer et al., 2015). In this study, a very similar trend was found: Sr and Ca loads in river water samples collected above the saltwater barrier (freshwater) varied largely (0.35–0.77 µmol/L or 31–67 µg/L for Sr, and 0.13–0.23 mmol/L or 5.21–9.22 mg/L for Ca), both spatially and temporally, while Ba loads showed little change (0.42–0.46 µmol/L or 58–63 µg/L) in the same samples. The variations of element concentrations will in turn result in variations of element ratios. Variations of element concentrations and ratios include spatial and temporal variations. Spatial and temporal variations are discussed separately below.

6.4.1 Spatial Variation

The Sr and Ca concentrations in marine waters are significantly higher than in freshwaters due to different geological compositions of marine and fresh water systems (Brown and Severin, 2009; Walther and Nims, 2015). Brown and Severin reported average marine water Sr and Ca concentrations of 7.64 ± 0.53 mg/kg (87.19 ± 6.05 µmol/L) and 405.87 ± 27.49 mg/kg
(10.13 ± 0.68 mmol/L), respectively (Brown and Severin, 2009). The Sr and Ca concentrations in the Calcasieu River were lower than the average marine water Sr and Ca concentrations (Table 6.4). However, the Sr/Ca ratio in our study was fairly close to the average marine Sr/Ca ratio (8.61 mmol/mol, range: 8.17 to 8.87), and was much higher than the median river water Sr/Ca ratio (2.39 mmol/mol, range: 0.27 to 19.18) (Brown and Severin, 2009) (Table 6.4). According to Brown and Severin (2009), the Sr/Ca ratio varied across a wider range in river environments than in marine environments, with less than 3% of the 786 rivers reviewed having median Sr/Ca levels that exceeded minimum marine levels. In the Calcasieu River, two (sites 5 and 6) out of six sampling sites had Sr/Ca ratios that exceeded the minimum marine levels.

The Ba concentrations found in the Calcasieu River were higher than those found in the majority of surface and municipal water supplies in the USA (≤0.03 mg/L or ≤0.22 µmol/L) (Moffett et al., 2007). New and expanded industrial Ba uses are studied in Kravchenko et al. 2014 (Kravchenko et al., 2014). For instance, BaSO₄ is commonly used as a contrast agent in medical imaging studies (X-ray). Because of its high molecular weight, approximately 94% of barite mined today is used as a wetting agent or component of drilling mud for oil and gas drilling (USGS). In this study, however, there is no evidence suggesting any effect from the surrounding petrochemical industry on the concentration level of Ba. Sites 1 and 2, which are located above the saltwater barrier and petrochemical plants, showed a similar or even slightly higher level of Ba concentration than the other sites that are close to the chemical plants and the Gulf (Table 6.4). Previous studies found that dissolved Ba in natural waters is largely determined by the geological composition of the streambed and weathering processes (Gaillardet et al., 2003). For instance, Ba is often rich in the geographic areas characterized by volcanic terrains, specifically alkaline-rich volcanic products or detrital (sedimentary) volcanic by-products (e.g.,
black shales) (Chakrabarti et al., 2009; Cuoco et al., 2013). The levels of Ba concentration found in this study may indicate the role of geological origin of Ba.

Ba is usually elevated in fresh waters and then exhibits an oligohaline maximum, and shows generally conservative mixing afterwards for the remainder of the salinity range (Walther and Nims, 2015; Shaw et al., 1998). However, the mixing curves of Ba can be different from this pattern; for example, sampling season could play an important role in Ba distribution (Stecher and Kogut, 1999; Nozaki et al., 2001). For the Calcasieu River, opening and closing of the Saltwater Barrier can affect the quantity of freshwater flow, which may alter the mixing dynamics of Ba in this system. The level of Ba concentration in this study was not related with salinity or pH. However, because of a close positive relation of Ca concentration with salinity, there was a strong negative relation between Ba/Ca ratio and salinity (Table 6.3). In their study on trace metals in coastal waters along the Texas coast, Walther and Nims (2015) reported a wide range of the Ba/Ca ratio, 62 to 973 μmol/mol, similar to the Ba/Ca ratios found in our study at the two sites closest to the Gulf of Mexico (sites 5 and 6). The fact that higher Ba/Ca ratios were found at other sites upstream suggests that freshwater discharge plays an important role in this elemental ratio. This finding may further suggest that large river systems with high freshwater flows will not be chemically affected by sea level rise as much as small coastal rivers with low freshwater flow will.

Strontium has been the most widely used trace metal to study aquatic animal movements between freshwater and marine habitats (Secor and Rooker, 2000), and most studies of fish migration with otolith chemistry have used the Sr/Ca ratio. Recent studies have found that the Ba/Ca ratio may also be a sensitive indicator of freshwater residency (Elsdon and Gillanders, 2005; Milton and Chenery, 2001; Martin and Thorrold, 2005). However, not all constituents are
equally effective as proxies. For instance, Walther and Nims (2015) concluded that, in Texas systems, the capacity to detect animal movements across salinity gradients using the Sr/Ca ratio as a proxy will be more difficult compared to other systems, while using the Ba/Ca ratio as a proxy would be highly useful for tracking animal movements. In the Calcasieu River, the large spatial variations of the Sr/Ca and Ba/Ca ratios and the clear relationships between these ratios and salinity indicate that both would be very useful as proxies for tracking animal movement.

6.4.2 Temporal Variation

Understanding the causes of seasonal element concentrations and ratios in a coastal river can be complicated by interrelationships among potential control factors (Shiller, 1997). Shiller (1997) showed that changes in suspended particulate matter, pH, and discharge appear unable to account for the observed element seasonal variability, but redox processes remained as the likely candidate for causing the most significant element seasonal variability (Shiller, 1997). In our study, as mentioned above, pH had an increasing trend from March to November. However, no element concentration or ratio showed the same trend. Therefore, pH itself was unable to explain the seasonal variability of element concentrations and ratios even though pH was significantly correlated to all the studied element concentrations and ratios except the Ba concentration.

Linear or nearly linear mixing of Sr and Ca across salinity gradients has been reported in estuaries worldwide (Xu, 2007; Walther and Nims, 2015; Andersson et al., 1992; Surge and Lohmann, 2002; Wang et al., 2009). In our study, mixing curves of both the Ca and Sr concentrations across the salinity gradient in the Calcasieu River were linear (Figure 6.5). The Sr concentration was highly correlated to salinity, which may have also been the driving factor for the seasonal variability of the Sr concentration. The seasonal trend of salinity was basically the same as the seasonal trend of the Sr concentration (Figures 6.3a and 6.4a). Salinity may not be
the driving factor for the seasonal variability of the Ca concentration, as well as the variability of the Sr/Ca and Ba/Ca ratios because of differences in seasonal trends (Figures 6.3a and 6.4b–e). Therefore, for the Ca concentration and the Sr/Ca, Ba/Ca ratios, salinity was the essential reason for seasonal variability in the elemental concentrations, in the interactions with other environmental factors including pH, DO and TSS.

Figure 6.5. Mixing curves of Sr concentration (a); Ca concentration (b); Sr/Ca ratio (c); Ba concentration (d); and Ba/Ca ratio (e) across salinity gradient along the Calcasieu River.
In natural aquatic systems, the concentration of Ba depends on the mineral matrix of aquifer lithologies (e.g., sulfates, carbonates, granodiorite, and shale) as well as the physicochemical conditions (e.g., pH, temperature, and redox state) of the groundwater (Kravchenko et al., 2014). In general, Ba solubility increases with decreasing pH (USEPA, 1985). However, this was not the case in our study. The lack of or weak relationship between Ba concentration and environmental factors strongly indicate the role of geological origin of Ba.

Based on an examination of variability in mean trace element concentrations in the Mississippi River, Shiller (1997) suggested that hydrologic factors may be important in determining trace element variability. This is, however, not the case in our data analysis. The reason for the lack of a relationship between discharge variability and element concentration and ratio variability might be due to the fact that the discharge records for the Calcasieu River come from a gauge station that is much further upstream than all the sampling sites. Future studies with nearby discharge measurements can be used to test the impact of discharge on variations of element concentrations and ratios, and also to calculate freshwater loadings of Sr and Ba to the Gulf of Mexico.

Due to the mixing of freshwater and saltwater, estuaries are extremely dynamic and complex environments. Sea level rise, which causes saltwater intrusion, will change the mixing point of freshwater and saltwater, which in turn, may have a significant impact on biology. Due to its historic saltwater intrusion problem and the existence of the Calcasieu Saltwater Barrier, studies of metal dynamics in the Calcasieu River could have relevant implications for other similar systems worldwide. Current estimates of riverine metal fluxes are based entirely on measurements of dissolved metal concentrations, and neglect the impact of riverine particulate dissolution in seawater (Jones et al., 2014). However, the riverine particulate dissolution in
seawater could have considerable influence on the overall metal chemistry. For instance, the weathering of riverine particulate material upon arrival in coastal areas makes a significant contribution to the overall Sr chemistry of seawater over geological timescales (Jones et al., 2014; Odum, 1951). Further studies of dissolved and particulate interaction are needed to better understand metal dynamics in the Calcasieu River.

6.5 Conclusions

This study investigated strontium, barium, and calcium concentrations and their ratios in an 88-km long estuarine reach with a salinity range from 0.02 to 29.50 over two years. It is the first assessment on the spatial and temporal variations of these metals in an estuary for such a large salinity range and long period of time. The study found considerable spatiotemporal variation in the element concentrations and their ratios. Salinity strongly affects spatiotemporal distributions of Sr and Ca concentrations and their elemental ratios. Results showed that the total Sr concentration and the Sr/Ca ratio both increased significantly with increasing salinity. Total suspended solids concentration also plays a role in the element distribution. In contrast, salinity has no effect on Ba concentration, which appears mainly geochemically controlled. All elemental concentrations and ratios had considerable seasonal variations, with significant differences among sampling months for the Sr, Ba concentrations and the Ba/Ca ratio ($p < 0.01$). These results indicate that concentrations of Sr and Ca in the world’s estuaries will very likely increase in the future as sea level rise continues, and that the extent of these increases will depend on the extent of saltwater intrusion. For low-gradient estuarine rivers with low freshwater discharge, such as the Calcasieu River in southwest Louisiana, USA, water chemistry upstream would experience substantial Sr and Ca enrichment, which could affect aquatic environments and biological communities.
CHAPTER 7. SUMMARY AND CONCLUSIONS

This dissertation research investigated the dynamics of carbon, nutrients, and trace metals in four major coastal rivers in southwest Louisiana, namely, the Sabine, Calcasieu, Mermentau, and Vermilion Rivers. The overarching goal of this research was to broaden the knowledge and understanding of biogeochemical processes in freshwater – saltwater mixing zones. The research consists of several studies that aimed to 1) quantify fluxes of nutrients and carbon from four major coastal rivers in Louisiana to the northern Gulf of Mexico; 2) determine seasonal, interannual, and decadal trends of nutrient and carbon fluxes in these rivers; 3) determine spatial and temporal variations of carbon, nutrients, and trace metals within an estuarine river; 4) assess mixing dynamics across salinity gradients for carbon, nutrients, and trace metals in an estuarine river.

Objectives 1 and 2 were accomplished by examining the fluxes and variability of total organic carbon, nitrate and nitrite nitrogen, total Kjeldahl nitrogen, and total phosphorus from four major coastal rivers in Louisiana entering the coast of a large summer-hypoxic zone of the Northern Gulf of Mexico from 1980 to 2009. Objectives 3 and 4 were accomplished by investigating changes in dissolved inorganic and organic carbon concentrations, isotopes, and pCO₂, TP, and DIP concentrations, as well as strontium, barium, and calcium concentrations and their ratios along the 88-km estuarine reach of the Calcasieu River, with salinity ranging from 0.02 to 29.5. Major findings from the research are summarized below.

1) From 1980 to 2009, the four coastal rivers – the Sabine, Calcasieu, Mermentau, and Vermilion Rivers – annually transported a total of 13.0×10⁴ t TOC, 1755 t NO₃+NO₂ nitrogen, 12208 t TKN, and 1833 t TP into the NGOM. The variation in annual NO₃+NO₂ and TP fluxes corresponded to not only the annual river discharge, but also to the NO₃+NO₂ and TP
concentrations. However, TOC and TKN inputs from the rivers mainly corresponded to the discharge due to a close, positive relation of TOC and TKN concentration with the river flow. Both monthly and annual means of TOC, NO$_3$+NO$_2$, TKN, and TP concentrations were much higher in the Mermentau and Vermilion Rivers, which drain agriculture dominated land areas, than the Sabine and Calcasieu Rivers, which drain forest-pasture dominated land areas. Land use effects were clearly reflected in the much higher TOC, NO$_3$+NO$_2$, TKN, and TP yields from the Mermentau River (7.8 t km$^{-2}$ yr$^{-1}$ TOC; 156 kg km$^{-2}$ yr$^{-1}$ NO$_3$+NO$_2$, 942 kg km$^{-2}$ yr$^{-1}$ TKN, and 206 kg km$^{-2}$ yr$^{-1}$ TP) and Vermilion River (7.9, 374, 1078, and 360), when compared with those of the Sabine River (2.6, 22, 220, and 19) and Calcasieu River (6.6, 44, 490, and 43). Annual nutrient concentrations in all four rivers fluctuated largely over the past three decades, and there appear to be a clear increasing trend in TOC concentration in the Mermentau River since the mid-1990s and decreasing trends of the TKN and TP concentrations in the Mermentau and Vermilion Rivers since the 1990s. The two rivers draining agriculture intensive watersheds showed consistently lower C:N, C:P, TN:TP ratios, when compared with the two rivers draining forest-pasture dominated watersheds, further indicating the strong effect of agricultural practices in coastal river basins on the quantity and quality of nutrient input to estuaries.

2) From November 2013 to December 2014, the Calcasieu River discharged 0.25×10$^9$ mol DIC and 1.77×10$^9$ mol DOC from its freshwater into the estuary. The average pCO$_2$ values at site 1 through site 6 were 2948, 3201, 3148, 3682, 2117, and 583 µatm, respectively, with a mean of 2528 µatm for the entire river reach, suggesting that the Calcasieu Estuary serves as a source of CO$_2$ in the atmosphere. During the study year, 0.079 ×10$^8$ kg carbon were emitted to the atmosphere in the freshwater river reach before the saltwater barrier. In contrast, a much larger amount of carbon (3.04 ×10$^8$ kg) was emitted to the atmosphere in the freshwater-
saltwater mixing zone during the same period. The change in DIC concentration from the upstream to the downstream locations near the river mouth was large (583% increase), indicating the overwhelming role of physical mixing on DIC in a coastal area. The DOC concentration, on the other hand, showed a decreasing trend from the upstream to the downstream locations (50% decrease), suggesting the influence of organic matter oxidation, flocculation, and sediment composition, alone or in combination. Based on the findings, we conclude that riverine dissolved carbon undergoes a rapid change in freshwater-saltwater mixing zones, and that this change should be considered in carbon processing and budgeting in the world’s estuarine systems. This is especially relevant as global sea level continues to rise, pushing freshwater-saltwater mixing zones more and more inland.

3) The DIC concentrations and $\delta^{13}$C$_{DIC}$ values increased rapidly in the salinity range from 0.02 to 21.92 measured from May 2016 to February 2016. The DIC concentration appeared to be mostly controlled by conservative mixing except when photosynthesis and respiration were active due to high water temperature and long residence time caused by low river freshwater inflow. The $\delta^{13}$C$_{DIC}$ values during the study period were either close to or below those values suggested by the conservative mixing model, implying that an estuarine river can fluctuate from a balanced system to a heterotrophic system seasonally. The DOC concentration decreased with decreasing distance to the NGOM, but to a much smaller degree. The depleted $\delta^{13}$C$_{DOC}$ values (-30.56‰ to -25.92‰) in the Calcasieu River suggest that the DOC discharged by this river was highly terrestrially derived. However, in this relatively small isotopic range, $\delta^{13}$C$_{DOC}$ alone has limitations in unambiguously indicating the dominant source of DOC in a river-ocean continuum.
4) The TP fluxes from one of the rivers (Vermilion River) draining an agriculture-intensive watershed increased from 1990-2009 period to 2010-2017 period, while no significant change was found in the other two rivers. River discharge variability caused by precipitation change, and probably river diversion as well, was the main reason for such TP flux trend. The two rivers draining more agriculture-intensive watersheds (67% and 61%) showed consistently higher TP and DIP concentrations and fluxes than the one that drains a pasture-forest dominated area, confirming the strong effect of land uses on phosphorus input to estuaries in coastal river basins. The DIP concentration versus salinity plots in the Calcasieu River suggest some sources were present throughout the Calcasieu Estuary since measured DIP concentrations were usually higher than those predicted by conservative mixing. Such mixing dynamic were probably caused by desorption of DIP from suspended solids and river bed sediments, urban inputs, as well as stronger calcium carbonate and phosphorus co-precipitation at the marine endmember. To fully understand the phosphorus transport and transformation dynamics in rivers, a more detailed sampling design focusing on suspended sediment, river bed sediment, and water column interactions is necessary.

5) The study found considerable spatiotemporal variation in the element concentrations and their ratios. Salinity strongly affects spatiotemporal distributions of Sr and Ca concentrations and their elemental ratios. Results showed that the total Sr concentration and the Sr/Ca ratio both increased significantly with increasing salinity. Total suspended solids concentration also plays a role in the element distribution. In contrast, salinity has no effect on Ba concentration, which appears mainly geochemically controlled. All elemental concentrations and ratios had considerable seasonal variations, with significant differences among sampling months for the Sr, Ba concentrations and the Ba/Ca ratio ($p < 0.01$). These results indicate that concentrations of Sr
and Ca in the world’s estuaries will very likely increase in the future as sea level rise continues, and that the extent of these increases will depend on the extent of saltwater intrusion. For low-gradient estuarine rivers with low freshwater discharge, such as the Calcasieu River in southwest Louisiana, USA, water chemistry upstream would experience substantial Sr and Ca enrichment, which could affect aquatic environments and biological communities.

It should be noted that, due to finite resources, there are limitations in this dissertation research that merit future consideration. First, certain calculations in this study are subject to data availability. For example, CO$_2$ flux calculations strongly depend on the selection of the value for the gas transfer velocity, but this velocity, which accounts for most uncertainties in estimating CO$_2$ outgassing fluxes, is usually not precisely known. Therefore, CO$_2$ outgassing calculations performed in this study should be considered as approximations rather than precise values. Second, the sampling technique could have strong impact on some of the studied elements, especially on phosphorus dynamics since most phosphorus in rivers is transported in particulate form. Third, total concentrations were used to study trace metal dynamics in an estuarine, where dissolved and particulate concentrations should be used instead. Last, all temporal trends demonstrated in this study neglected diel variations, which could be large enough to affect some of the relevant findings. To fully understand the transport and transformation dynamics of carbon, nutrients, and trace metals in an estuarine river, a more comprehensive study design is necessary. Using newly developed and accurate instruments could allow us to acquire more precise estimates in CO$_2$ outgassing. A more detailed sampling design focusing on suspended sediment, river bed sediment, and water column interactions is necessary to understand phosphorus and trace metal dynamics. A concentrated sampling design with multiple samples
being collected within one day across all seasons and covering the salinity gradient will improve our understanding in the diel variations of carbon, nutrients, and trace metals.
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APPENDIX. PERMISSION TO REPRINT CHAPTERS

A.1 Permissions to reprint chapter 2

Three decadal inputs of total organic carbon from four major coastal river basins to the summer hypoxic zone of the Northern Gulf of Mexico

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Abstract
This study investigated long-term (1980–2009) yields and variability of total organic carbon (TOC) from four major coastal rivers in Louisiana entering the Northern Gulf of Mexico where a large-area summer hypoxic zone has been occurring since the middle 1980s. Two of these rivers drain agriculture-intensive (>40%) watersheds, while the other two rivers drain forest-pasture dominated (>50%) watersheds. The study found that these rivers discharged a total of 13.0 × 10^6 t TOC annually, fluctuating from 5.9 × 10^5 to 22.8 × 10^6 t. Seasonally, the rivers showed high TOC yield during the winter and early spring months, corresponding to the seasonal trend of river discharge. While river hydrology controlled TOC yields, land use has played an important role in fluxes, seasonal variations, and characteristics of TDC. The findings fill in a critical information gap of quantity and quality of organic carbon transport from coastal watersheds to one of the world’s largest summer hypoxic zones.

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Three Decadal Inputs of Nitrogen and Phosphorus from Four Major Coastal Rivers to the Summer Hypoxic Zone of the Northern Gulf of Mexico

Songjie He • Y. Jun Xu

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A.2 Permissions to reprint chapter 3

Freshwater-Saltwater Mixing Effects on Dissolved Carbon and CO₂ Outgassing of a Coastal River Entering the Northern Gulf of Mexico

Songjie He¹ · Y. Jun Xu¹

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Assessing dissolved carbon transport and transformation along an estuarine river with stable isotope analyses

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ABSTRACT
Estuaries play an important role in the dynamics of dissolved carbon from rivers to coastal oceans. However, our knowledge of dissolved carbon transport and transformation in mixing zones of the world’s coastal rivers is still limited. This study aims to determine how dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) concentrations and stable isotopes (δ¹³CDOC and δ¹³CDIC) change...
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Spatiotemporal Distributions of Sr and Ba along an Estuarine River with a Large Salinity Gradient to the Gulf of Mexico

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Abstract

Strontium and barium to calcium ratios are often used as proxies for tracking animal movement across salinity gradients. Many estuarine rivers face saltwater intrusion due to sea level rise, potentially causing changes in mobility and distribution of these metals upstream. From May 2013 to August 2015, monthly water samples were collected and in-situ measurements were performed at six sites along an estuary strongly affected by saltwater intrusion, the Calcasieu River, with salinity ranging from 0.02 to 29.50 Parts Per Thousand (ppt). Results showed that the total Sr concentration and the Sr/Ca ratio both increased significantly with increasing salinity. The average Sr concentration at the site closest to the Gulf of Mexico (Site 6) was 46.21 μmol/L, about 130 times higher than that of the site furthest upstream (Site 1, 0.35). The average Sr/Ca ratio at Site 6 (8.41 mmol/mol) was about three times the average Sr/Ca ratio at Site 1 (2.89). However, the spatial variation in total Ba concentration was marginal, varying from 0.36 to 0.47 μmol/L. The average Ba/Ca ratio at Site 1 (4.82 mmol/mol) was about 54 times the ratio at Site 6 (0.09), showing a negative relation between the Ba/Ca ratio and salinity. All elemental concentrations and ratios had considerable seasonal variations, with significant differences among sampling months for the Sr and Ba concentrations and the Ba/Ca ratio (p < 0.01). The results suggest that for low-gradient estuarine rivers such as the Calcasieu River, water chemistry upstream would experience substantial Sr and Ca enrichment, potentially affecting aquatic environments and biological communities.

Keywords: strontium; barium; estuary; Calcasieu River; Gulf of Mexico

Figures

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VITA

Songjie He was born in October 1986 and grew up in Yunnan province, south China. She received her Bachelor’s and Master’s degree from Minzu University of China in 2009 and 2013, respectively. She relocated to Baton Rouge in May 2013 to pursue a Ph.D. degree with the School of Renewable Natural Resources at Louisiana State University. Upon receiving her Ph.D. degree, she looks forward to applying her water quality and biogeochemistry expertise to current water issues in coastal areas.