SEASONAL TRANSPORT OF DISSOLVED INORGANIC CARBON AND TOTAL ALKALINITY ACROSS THE LOUISIANA SHELF

Michelle M. Anderson
Louisiana State University and Agricultural and Mechanical College

Follow this and additional works at: https://repository.lsu.edu/gradschool_theses

Part of the Biogeochemistry Commons, Climate Commons, Environmental Monitoring Commons, Fresh Water Studies Commons, Geochemistry Commons, Inorganic Chemistry Commons, Oceanography Commons, Other Environmental Sciences Commons, Other Oceanography and Atmospheric Sciences and Meteorology Commons, and the Radiochemistry Commons

Recommended Citation
https://repository.lsu.edu/gradschool_theses/5171

This Thesis is brought to you for free and open access by the Graduate School at LSU Scholarly Repository. It has been accepted for inclusion in LSU Master's Theses by an authorized graduate school editor of LSU Scholarly Repository. For more information, please contact gradetd@lsu.edu.
SEASONAL TRANSPORT OF DISSOLVED INORGANIC CARBON AND TOTAL ALKALINITY ACROSS THE LOUISIANA SHELF

A Thesis

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 Master of Science

in

The Department of Oceanography and Coastal Sciences

by

Michelle M Anderson
B.S., California Polytechnic State University, San Luis Obispo, 2018
August 2020
Acknowledgements

I would like to express my gratitude to all involved with the project.

This includes NASA EPSCoR, LA Board of Regents, my graduate advisor Dr. Kanchan Maiti, and committee members Dr. Zuo “George” Xue and Dr. Jennifer Brum.

A sincere thank you to all who assisted me with field sampling and allowed me to work with them over the period of this project, including: the captains and crews of the R/V Acadiana and the R/V Pelican, Dr. Nancy Rabalais and the NOAA funded NNRT Hypoxia Cruise of 2019, Bingqing Liu, Ivan Vargas, Le Zhang, Caitlin Neal, and Jill Broussard.

Thank you to all my lab mates who have assisted me over my time at LSU, including: Wokil Bam, Hannah Beck, Owen Clower, Byron Ebner, Jocelyn Forsman, Songjie He, and Laura Thompson.

Finally, thank you to all my friends and family, who have supported me through this process and made it incredibly fun.
# Table of Contents

Acknowledgements ........................................................................................................ ii  
List of Figures .................................................................................................................. v  
Abstract ........................................................................................................................... vi  

Chapter 1. Introduction ................................................................................................. 1  
  1.2. Research Goals and Objectives ........................................................................ 7  
  1.3. Thesis Organization ......................................................................................... 8  

Chapter 2. Seasonal Pattern in Alkalinity and DIC Distribution in Two Contrasting Sections of the Louisiana Shelf ................................................................. 9  
  2.1. Introduction ...................................................................................................... 9  
  2.2. Study Site, Sample Collection, and Cruises .................................................. 12  
  2.3. Methodology .................................................................................................. 14  
  2.4 Results ............................................................................................................... 17  
  2.5. Discussion ....................................................................................................... 21  
  2.6. Conclusion ...................................................................................................... 29  

Chapter 3. Seasonal Changes in Cross-shelf Transport of Dissolved Inorganic Carbon Across the Louisiana Shelf ................................................................. 31  
  3.1. Introduction ...................................................................................................... 31  
  3.2. Study Site ........................................................................................................ 33  
  3.3 Sample Collection and Cruises ......................................................................... 35  
  3.4. Methodology .................................................................................................. 36  
  3.5. Results ............................................................................................................. 38  
  3.6. Discussion ....................................................................................................... 49  
  3.7. Conclusion ...................................................................................................... 58  

Chapter 4. Conclusions ............................................................................................... 60
List of Figures

1.1. Predicted Land Change in Louisiana ................................................................. 3

2.1. Discharge Rates of the Mississippi River and Wax Lake Outlet ....................... 13

2.2. Map of Louisiana Coastal Shelf and Study Areas ............................................. 14

2.3. Salinity Distribution in the Wax Lake Delta Sector ......................................... 18

2.4. Salinity Distribution in the Barataria Bay Sector ............................................. 19

2.5. DIC Concentrations for WLD and BB ............................................................... 20

2.6. TAik Concentrations for WLD and BB ........................................................... 21

2.7. DIC:TAik as a function of salinity ................................................................. 25

2.8. $\Omega_A$ relationship with [TAik – DIC] ......................................................... 27

2.9. $\Omega_A$ against salinity ..................................................................................... 28

3.1. Discharge Rates of the Mississippi River and Wax Lake Outlet ....................... 35

3.2. Map of Louisiana Coastal Shelf and Study Areas ............................................. 36

3.3. Salinity Distribution in the Wax Lake Delta Sector ......................................... 40

3.4. Salinity Distribution in the Barataria Bay Sector ............................................. 41

3.5. Average DIC Concentrations for WLD and BB ............................................... 42

3.6. $^{224}$Ra Concentrations for WLD ................................................................. 43

3.7. $^{223}$Ra Concentrations for WLD ................................................................. 44
3.8. $^{224}\text{Ra}$ Concentrations for BB .............................................................. 45

3.9. $^{223}\text{Ra}$ Concentrations for BB .............................................................. 46

3.10. Seasonal Mixing Rates for WLD .............................................................. 48

3.11. Seasonal Mixing Rates for BB .............................................................. 48

3.12. Seasonal Residence Times for WLD ........................................................ 52

3.13. Seasonal Residence Times for BB ........................................................ 53

3.14. Seasonal DIC Transport for WLD ........................................................ 56

3.15. Seasonal DIC Transport for BB ........................................................ 56
Abstract

Rivers and wetlands are a major source of terrestrial derived carbon for coastal ocean margins. Unfortunately, Louisiana’s wetlands are threatened by ongoing high rates of erosion, deterioration, and unprecedented rates of river water discharge that changes seasonally, leading to a net loss of terrestrial carbon into the northern Gulf of Mexico (nGOM). There exists a current lack of understanding about the distribution of dissolved inorganic carbon (DIC) and total alkalinity (TAlk) within the shallowest regions of the Louisiana shelf. Even less is known about how the transport of DIC alters seasonally with changes in river outflow and shelf currents. Quantifying seasonal shifts in carbon transport is critical to comprehending coastal water quality, as dissolved constituents from these terrestrial fresh water sources can change the nGOM’s ability to buffer decreases in pH and aragonite saturation states (ΩA). This study investigated the DIC and TAlk dynamics in the shelf regions adjacent to the Wax Lake Delta (WLD) and Barataria Bay (BB), which represent contrasting areas of net land gain and net land loss along the Louisiana coast, respectively. DIC and TAlk samples were collected, in conjunction with short-lived radium isotopes $^{224}$Ra ($t_{1/2} = 3.66$ days) and $^{223}$Ra ($t_{1/2} = 11.43$ days) samples for the month of June and September in 2019, to quantify cross-shelf transportation processes. Our results suggest that the buffering capability of surface water on the Louisiana shelf during the summer months were weaker than what has been reported by previous studies. Net cross shelf transport of DIC was found to be higher for the WLD region compared to BB, highlighting the importance of freshwater discharge in exporting DIC across the shelf. Extrapolating our study for the entire Louisiana shelf indicates that $9.7 \times 10^{10}$ mol C d$^{-1}$ and $1.85 \times 10^{10}$ mol C d$^{-1}$ in the form of DIC was exported across the shallow region of the shelf (<40 m isobath) during high and
low river flow seasons. Predicted future changes in freshwater discharge are thus estimated to have a major impact on DIC transported into the interior nGOM and the Loop Current.
Chapter 1. Introduction

1.1. Background

Currently, up to 0.22 Gt of carbon is sequestered globally in coastal wetlands per year, while the ocean sequesters 2.5 Gt of carbon on an annual scale (Hopkinson et al., 2012; Friedlingstein et al, 2019). Numerous studies have endeavored to quantify carbon cycling within terrestrial and marine systems exclusively. However, few studies investigate the transformation and transport pathways of carbon at the land-ocean interface. This has resulted in a major gap in our current understanding of the global carbon budget. Thus, understanding carbon transport, storage, and transformation along this land-ocean continuum has become increasingly relevant when considering the implications of climate change and ocean acidification. Rivers are major conduits for the carbon exchange between terrestrial, atmospheric, and oceanic reservoirs, transporting approximately 1.0 Gt carbon annually from continental regions to open oceans (Suchet et al., 2003; Huang et al., 2012; Cai et al., 2015). However, large uncertainties exist due to the lack of seasonal and integrated measurements of major carbon species, i.e., dissolved inorganic carbon (DIC) and total alkalinity (TAlk), as they interact and contribute to global and regional carbon budgets.

Major deltaic systems are the main global pathway for the input of terrestrial derived carbon to the coastal ocean (Bianchi et al., 2004, 2007). Despite the importance of these systems in estimating a global carbon budget, there is still a lack of understanding about the interaction and temporal-spatial linkages between the highly productive wetlands of these river basins and the adjacent coastal waters (Bianchi et al., 2004, 2007; Hopkins et al., 2012). The need for comprehensive understanding of the transport of carbon to the coastal ocean is made even more
imperative, as global coastal wetlands are undergoing substantial alterations due to climatic and anthropogenic forcing.

Coastal wetlands have a great capacity to store carbon due to their high net primary productivity and overall slow soil organic matter decomposition rate (Hopkinson et al., 2012). It is estimated that global coastal wetland coverage could be reduced between 30-59% by the end of this current century, based on current sea-level rise and levels of human intervention (Spencer et al., 2016; Schuerch et al., 2018). Nowhere is this more apparent than the Mississippi River delta in the northern Gulf of Mexico (nGOM), accounting for 40% of the wetlands within the conterminous United States of America (USA) (Bianchi et al., 2011; Bi et al., 2019). The wetlands of coastal Louisiana are experiencing relative sea-level rise faster than most coastlines around the world (Kolker et al., 2011). Some areas of the Louisiana coast are subsiding twice as fast than the estimated eustatic sea level rise of 3 mm y$^{-1}$ to 4 mm y$^{-1}$ (Blum and Roberts, 2009; Stocker et al., 2013). This is a result of reduced sediment supply to the wetlands due to upstream dams and the extensive levee infrastructure along the Mississippi River (Blum and Roberts, 2009). The wetland loss in the state of Louisiana is directly associated, although not directly quantified, to the net export of carbon from coastal wetlands to adjacent coastal waters of the nGOM.

Two regions, nearly 150 km apart, represent the extreme land changes that can occur along the Louisiana coast. The Wax Lake Delta (WLD) region is one of the only areas of net wetland gain within Louisiana (Figure 1.1). WLD was recently formed, starting in 1972, as a result of dredging efforts that diverted water from the Atchafalaya River to the nGOM, moving sediment input through the man-made Wax Lake Outlet (Rosen and Xu, 2013). The delta is accreting land at a rate of 1 km$^2$ yr$^{-1}$, allowing for the establishment of marsh and forested wetlands across elevation gradients (Holm and Sasser, 2001; Allen et al., 2012). In contrast to WLD, Barataria
Bay (BB) has historically experienced significant wetland loss (Figure 1.1). The BB basin has an extensive estimated wetland loss of 23 km$^2$ yr$^{-1}$ (U.S. Geological Survey and Barras et al., 2006; Couvillion et al., 2011, 2017), exporting 1000 to 2050 g C·m$^{-2}$·yr$^{-1}$ of soil organic carbon out of the basin (Wang et al., 2017). Wetland loss in BB is predicted to continue and increase drastically, due to a coupling of increasing sea-level rise and decreased modern sediment loading to the deltaic plain (Barras et al., 2003; Blum and Roberts, 2009).

Figure 1.1. Predicted Land Change Over the Next 50 years with No Additional Action (modified from Coastal Protection and Restoration Authority of Louisiana, 2017)

WLD and BB represent two extremes of the ongoing changing to the Louisiana coast, in which both wetland/deltaic systems are in constant flux with the nGOM. Both regions produce freshwater plumes, providing an important source of dissolved inorganic carbon (i.e. DIC = $[\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{CO}_2]$) (Suchet and Ludwig, 2003; Cai et al., 2011) and TAlk to the nGOM (Yang et al., 2015). Aerobic respiration on the surface of wetlands result in the production of
DIC, but this produces no net increase in TAlk. However, anaerobic respiration, which is prevalent below the top few centimeters of wetland soils, generates both DIC and TAlk. As wetlands degrade, the lower depth of the soil profile is exposed, leading to an increase export of DIC and TAlk to the coastal ocean within the freshwater plume (Cai et al., 2000; Wang and Cai, 2004).

The relative contributions of DIC to TAlk from these wetland/deltaic systems is critical to Louisiana’s coastal water quality. Both the pH and the carbonate saturation state (Ω) of coastal waters are controlled by the ratio of DIC to TAlk. An increased input of DIC in relation to TAlk can alter the coastal waters’ ability to buffer decreases in pH, otherwise known as ocean acidification (Cai et al., 2011). In an ideal carbonate solution, the balance of these two properties is represented as such: TAlk – DIC = [CO$_3^{2-}$] – [CO$_2$] and pH is calculated as

$$pH = -\frac{1}{2} \log(K_1 K_2) - \frac{1}{2} \log \left( \frac{[CO_2]}{[CO_3^{2-}]} \right)$$

(1)

Where $K_1$ and $K_2$ are defined as dissociation constants of the carbonic acid. Therefore, when DIC concentrations approaches TAlk (i.e. [CO$_2$] = [CO$_3^{2-}$]), a small increase of [CO$_2$] results in a large decrease of the system’s pH, thereby weakening the buffering capacity of the water (Cai et al., 2011). This buffering system not only affects the overall chemistry of coastal waters, but also impacts biological processes like photosynthesis and calcification. Therefore, quantifying the influx balance of DIC to TAlk is essential when determining a freshwater plume’s impact on coastal pH.

The exchange of material between the eroding continental margin and ocean interior plays a major role in global biogeochemical cycles. However, material fluxes across shelf waters are difficult to quantify, as these systems are exceedingly complex due to small-scale temporal and
spatial variability. Commonly, freshwater plumes and their dissolved materials are traced by offshore negative salinity and/or positive silica anomalies (Chen et al., 2010). However, the salinity signal can be altered by evaporation and precipitation, and the silica signal is sensitive to biological uptake (Chen et al., 2010). To avoid some of these drawbacks, naturally occurring short-lived radium isotopes ($^{224}$Ra and $^{223}$Ra) have been successfully used to quantify fluxes of dissolved components transported across continental shelves (Moore and Krest, 2004; Windom et al., 2006; Li and Cai, 2011; Burt et al., 2013; Sippo et al., 2019).

There are four natural isotopes of radium produced from natural uranium and thorium decay. These include short-lived isotopes $^{224}$Ra, ($t_{1/2} = 3.66$ days), and $^{223}$Ra ($t_{1/2} = 11.4$ days) and long-lived isotopes $^{226}$Ra ($t_{1/2} = 1620$ years) and $^{228}$Ra ($t_{1/2} = 6.7$ years). These isotopes are introduced to seawater through contact with thorium-bearing sediments carried by fresh river water or deposited bottom sediments (Moore and Krest, 2004; Chen et al., 2010). Radium isotopes are strongly adsorbed on sediments in fresh river water and will desorb as they come into contact with the high ionic strength of coastal waters (Moore and Krest, 2004; Chen et al., 2010). Once introduced to near shore waters, the radium’s activity can only decrease by mixing with water with lower activity and by radioactive decay (Moore and Krest, 2004; Chen et al., 2010). Since the short-lived radium isotopes decay rapidly, their activities will quickly decrease with increasing distance from their freshwater source (Chen et al., 2010). By tracking the decay of these two short-lived radium isotopes, the time scale of transport of freshwater as it moves across the shelf and mixes with adjacent coastal waters can be constrained (Moore, 2000; Moore and Krest, 2004; Windom et al. 2006; Chen et al., 2010). In this sense, radium isotopes are akin to adding a tracer at the source of the freshwater plume and the distribution of these short-lived isotopes over the shelf can be expressed as a balance of diffusion and advection (Moore 2000):
\[
\frac{dA}{dt} = K_h \frac{\partial A}{\partial x^2} - \omega \frac{\partial A}{\partial x} - \lambda A
\]

(2)

where \(A\) is the concentration or activity, \(t\) is time, \(K_h\) is the eddy diffusion coefficient, \(x\) is the distance offshore, \(\omega\) is the advective velocity, and \(\lambda\) is the decay constant. Lateral effects are ignored in this one-dimensional approximation and assumes no additional input of the tracer beyond the nearshore. Assuming \(K_h\) and \(\omega\) are constant, the offshore distribution of a conservative tracer may be used to determine the relative importance of the signal offshore through dilution and advection. If the offshore signal is dominated by diffusion with constant \(K_h\), a plot of activity vs. distance will be a straight line between end members. If the offshore signal is dominated by advection, offshore advection will cause a positive curvature and onshore advection will cause a negative curvature to the activity vs. distance plot.

Assuming diffusion to be more dominant than advection, equation 2 can be rewritten as

\[
\frac{dA}{dt} = K_h \frac{\partial A}{\partial x^2} - \lambda A
\]

(3)

The solution to this equation is shown below under the following boundary conditions

\[A = A_i \text{ at } x = 0,\]

\[A \to 0 \text{ as } x \to \infty.\]

If \(K_h\) is constant and the system is in steady state,

\[A_x = A_0 \exp \left[ -x \sqrt{\frac{\lambda}{K_h}} \right]\]

(4)

Where \(A_x\) is the activity at distance \(x\) from the coast, \(A_0\) is the activity at distance 0 from the coast.
Thus, a linear plot of $\ln^{224}\text{Ra}$ or $\ln^{223}\text{Ra}$ as a function of distance from the coast can be used to estimate $K_h$ from the slope of the line as shown below

$$\ln A_x = \ln A_0 - x \frac{\lambda}{K_h}$$  \hspace{1cm} (5)

However, it must be kept in mind that several assumptions are required to apply this model: (1) the system is in steady state; (2) cross-shelf mixing is constant; (3) net cross-shelf advection is much lower compared to mixing; and (4) radium addition to the surface water occurs only in the near-shore zone (Moore, 2000).

Cross-shelf mixing rates determined through radium isotopes can be utilized in combination with dissolved parameters to determine the rate of transport of any dissolved constituent, such as nutrients, metals, and carbon species (Moore, 2000; Windom et al. 2006; Chen et al., 2010; Burt et al., 2013; Sippo et al., 2019). Due to the short half-lives of these radium isotopes, this approach is highly efficient at quantifying the changes in the transport of dissolved constituents around seasonal events over continental shelves. In this study, we evaluate the seasonal lateral transport of DIC from the WLD and BB regions, using $^{224}\text{Ra}$ ($t_{1/2} = 3.6$ days) and $^{223}\text{Ra}$ ($t_{1/2} = 11.43$ days).

### 1.2. Research Goals and Objectives

The major goals of this research are to understand the seasonal pattern in distribution of DIC and TAlk and estimate the cross-shelf transport of DIC from the WLD and BB regions of the Louisiana shelf. We hypothesize that (i) river discharge will have larger impact on seasonal distribution in DIC and TAlk, thereby affecting the calcium carbonate buffering capacity and (ii)
the outflow of Wax Lake outlet and Atchafalaya river into the shallow shelf will result in higher oceanward transport of DIC compared to the BB region and (iii) the magnitude of DIC transport will be higher in late spring (June) than in late summer (September), due to seasonal decrease in river discharge. To test this overarching hypothesis, we will carry out the following objectives:

1. Measure DIC, TAlk, and $^{224,223}$Ra distribution during late spring and early fall along offshore transects in WLD and BB region.

2. Utilize radium isotopes to determine cross-shelf mixing rates of freshwater across the Louisiana shelf.

3. Estimate transport and residence time of dissolved inorganic carbon exported from Wax Lake Delta and Barataria Bay across the shelf.

4. Compare variability in the rates of transport from Wax Lake Delta and Barataria Bay on a seasonal scale.

### 1.3. Thesis Organization

To meet the goals and objectives of this study, the thesis is organized into two main chapters. In chapter 2, I discuss the seasonal and spatial distribution of DIC and TAlk on the shelf and its impact on buffering capacity and calcium carbonate (aragonite) saturation states. In chapter 3, I focus on utilizing short-lived radium isotopes to determine mixing rates and residence time of shelf water. These rates are then utilized to determine lateral transport of DIC on a seasonal scale.
Chapter 2. Seasonal Pattern in Alkalinity and DIC Distribution in Two Contrasting Sections of the Louisiana Shelf.

2.1. Introduction

Continental shelves play a key role in the global exchange of carbon, despite making up only 7-10% of total ocean area (Muller-Karger and Robins, 2019). It is estimated that these ocean margins adsorb 0.25-0.36 Pg C yr\(^{-1}\) from the atmosphere (Chen and Borges, 2009), equivalent to 6-23% of the net annual open-ocean CO\(_2\) uptake (Takahashi et al., 2009), and contribute up to 30% of all global ocean primary production (Bauer et al., 2013). Unfortunately, the role continental shelves play in the global carbon cycle leaves these regions susceptible to climate changes, sea level rise, and ocean acidification (Cai et al., 2010; Feely et al., 2018). In order to discern how these shallow waters will respond to these environmental changes, we must first obtain a better understanding of how regional differences influences ocean margin carbon chemistry. An important site of carbon exchange for ocean margins is at the interface of rivers and wetlands with coastal shelf waters (Bianchi et al. 2004; Bianchi et al. 2007, Najjar et al., 2018). Rivers and associated coastal wetlands transport approximately 1.0 Gt carbon from continental regions to oceans annually, with dissolved inorganic carbon (DIC), expressed as the sum of all carbonates species: \([\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{CO}_2]\), representing about 41% of this transported carbon (Suchet et al., 2003; Cai et al., 2015). While the importance of rivers in modulating the transfer of carbon from the land to coastal areas has long been recognized (Smith and Hollibaugh, 1993), only recently have a few studies shown that various respiration processes in marsh sediments can also result in the increase of total alkalinity (TAlk), \(p\text{CO}_2\) and DIC concentrations in adjacent channel water (Cai et al., 2000; Wang and Cai, 2004), which is subsequently exported to coastal waters. Thus, in addition to parameters such as DIC and \(p\text{CO}_2\),
total alkalinity (TAlk) is one of the most frequently measured quantities in shelf carbon cycle studies.

The global input of DIC through river systems accounts for almost 40% of the total fluvial carbon entering the coastal ocean (Ludwig et al., 1996), whereas fluvial export of terrestrial alkalinity via riverine bicarbonate, produced from weathering, is the predominant source of oceanic alkalinity and a key regulator of the CaCO$_3$ saturation state in the ocean (Raymond and Cole, 2003). In the open ocean, alkalinity has been used to address a variety of geochemical questions, such as global ocean carbonate production and dissolution (Chung et al., 2003; Milliman and Droxler, 1996; Berelson et al., 2007). However, on a global scale, the rate of riverine alkalinity input does not match the rate of oceanic alkalinity removal via carbonate preservation, leading to an alkalinity imbalance (Chen, 2002; Berelson et al., 2007; Cai et al., 2010). Thus, it is imperative that we have a better understanding of ocean margin DIC and TAlk in terms of its distribution and transport to the open ocean. It is even more relevant to understand the fate and distribution of DIC and TAlk in a river dominated system like the Louisiana shelf, where the combination of high DIC and $p$CO$_2$ originating from natural and anthropogenic organic matter might result in calcium carbonate undersaturated river-influenced areas (Salisbury et al., 2008; Zhai et al., 2015; Cai et al., 2011).

The northern Gulf of Mexico (nGOM) is unique among continental shelves in North America, as it is largely influenced by riverine discharge and its proximity to wetlands undergoing unprecedented rates of degradation (U.S. Geological Survey and Barras et al., 2006; Couvillion et al., 2011, 2017; Wang et al., 2017). While most of the GOM’s surface water $p$CO$_2$ concentration changes are controlled by seasonal temperatures, carbon dynamics in the nGOM are largely controlled by the Mississippi-Atchafalaya River System, which discharges high-DIC,
high-TAlk water into the Louisiana shelf (Cai 2003; Lohrenz et al., 2013; Wang et al., 2013; Yang et al., 2015). In addition to influencing the concentrations of $p$CO$_2$ in surface water, the introduction of DIC and TAlk to shelf water can have a substantial influence on coastal ocean acidification dynamics and water quality. The pH and the calcium carbonate (aragonite) saturation state ($\Omega_A$) of coastal water is controlled by the ratio of DIC to TAlk. As a result, when DIC concentrations approach TAlk (i.e. $[CO_2] = [CO_3^{2-}]$), a small increase of $[CO_2]$ results in a large decrease of the system’s pH, thereby weakening the buffering capacity of the water. This buffering system not only affects the overall chemistry of coastal waters, but also impacts biological processes like photosynthesis and calcification. Despite the importance of these systems, there is still a lack of understanding about the interaction and temporal-spatial linkages between highly productive wetlands and adjacent coastal waters (Bianchi et al. 2004, 2007; Cai et al., 2010; Hopkins et al., 2012; Wang et al., 2013). Prior work on the Louisiana shelf has focused on defining general carbon dynamics and fluxes of $p$CO$_2$ (Wang et al., 2013; Huang et al., 2015; Yang et al., 2015; Gomez et al., 2020). However, few observational studies have assessed DIC and TAlk temporal variability within nearshore waters (< 20 m water depth), as it pertains to seasonal changes in river discharge.

In this study, we evaluate the seasonal patterns of DIC and TAlk over two contrasting regions of the Louisiana shelf, in terms of river input. The Wax Lake Delta (WLD) is one of the few regions in Louisiana undergoing sediment accretion, due to large inputs of mineral sediment through the Wax Lake Outlet (Rosen and Xu, 2013). The Wax Lake Outlet is an artificial channel that diverts 30% of Atchafalaya river flow (AR) before directly entering the nGOM (Rosen and Xu, 2013). In contrast to the WLD, the Barataria Bay (BB) region has historically high land loss rates, due to the lack of mineral sediment input, preventing the land from keeping
up with sea level rise and land subsidence (Barras et al., 2003; Blum and Roberts, 2009). This region has no river discharging directly into coastal waters. Instead, freshwater diffuses through the BB and then passes through several barrier island inlets before entering the nGOM. We thus hypothesize that river discharge will have larger impact on seasonal distribution in DIC and TAlk, thereby affecting the carbonate buffering capacity.

2.2. Study Site, Sample Collection, and Cruises

WLD and BB represent two extremes of the ongoing changes to the Louisiana coast. Both regions produce freshwater plumes, providing an important source of DIC and TAlk to shelf waters (Suchet and Ludwig, 2003; Cai et. al, 2011), Yet, despite the importance of these coastal ecosystems, there is still a lack of understanding about the temporal and spatial linkages between coastal wetlands and adjacent shelf water, in terms of DIC and TAlk concentrations. One major temporal shift in southeast Louisiana is the seasonal decrease of river discharge. In 2019, the river discharge was high, averaging $125 \times 10^4$ ft$^3$ s$^{-1}$ and $25 \times 10^4$ ft$^3$ s$^{-1}$ for the Mississippi River (MSR) and Wax Lake Outlet during late spring/early summer months, as a result of freshwater input from snowmelt in northern USA (Figure 2.1). However, by early September the freshwater discharge is reduced to $45 \times 10^4$ ft$^3$ s$^{-1}$ and $10 \times 10^4$ ft$^3$ s$^{-1}$ for the MSR and Wax Lake Outlet, respectively (Figure 2.1). Thus, our seasonal sampling during June and September of 2019, shown in boxes in Figure 2.1, can provide a better understanding of how such drastic decreases in freshwater can alter the DIC and TAlk concentrations in coastal shelf waters.
Field sampling was conducted adjacent to WLD and BB regions on the *R/V* Acadiana during June 2019 and September 2019 to coincide with seasonal high and low river discharges of the MSR, AR, and Wax Lake Outlet (Figure 2.2). The samples were collected along 2 cross shelf transects for both the WLD and BB regions (Figure 2.2). Surface water sampling was collected from 1 m below the surface at 9 km intervals for WLD transects and 5 km intervals for BB transects, until a salinity of ~30 was reached in June 2019. Bottom water sampling was conducted at every other station along each transect. These stations were repeated in September 2019 (Figure 2.2). The WLD sector extended 84 km offshore and the BB sector extended 57 km offshore, reaching a water depth of at least 35 m. Water samples were also collected from the Wax Lake channel and inside the Barataria Bay as representative endmembers for each transect.
2.3. Methodology

Sample collection and analysis

For DIC samples, water was passed through a 0.45 mm glass fiber syringe filter and collected into 12 mL Labco septa vials (https://www.labco.co.uk/), thoroughly flushed with extensive overflow (> 12 mL), and spiked with a 10 µL Hg solution. DIC samples were stored at 5°C and measured back in the laboratory, using the standard protocol for the semi-automated system Apollo SciTech Dissolved Inorganic Carbon Analyzer. The instrument was calibrated using certified reference materials (CRM batch 180; Dickson, 2010).

For TAlk samples, water was passed through a 0.45 mm glass fiber syringe filter and collected into 40 mL glass scintillation vials, thoroughly flushed with extensive overflow (> 20 mL), and spiked with a 10 µL Hg solution. TAlk samples were stored at 5°C and measured back in the laboratory, using the standard protocol for the semi-automated system Apollo SciTech AS-ALK2.
Total Alkalinity Titrator. The instrument was calibrated using certified reference materials (CRM batch 180 and batch 187; Dickson, 2010).

Calculation of aragonite saturation state

The increase in DIC concentrations relative to TAlk weakens the buffering capacity of seawater; causing a susceptibility to eventual ocean acidification. As DIC:TAlk increases, a hydrogen ion (H\(^+\)) and bicarbonate (HCO\(_3^-\)) are produced and carbonate ion (CO\(_3^{2-}\)) concentrations in the water decreases via a series of chemical reactions:

\[
\text{CO}_2(aq) + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \tag{1}
\]

\[
\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-; \tag{2a}
\]

where

\[
K_{1}^* = [\text{H}^+] [\text{HCO}_3^-]/([\text{CO}_2(aq)] + [\text{H}_2\text{CO}_3]) \tag{2b}
\]

\[
\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}; \tag{3a}
\]

where

\[
K_{2}^* = [\text{H}^+] [\text{CO}_3^{2-}]/[\text{HCO}_3^-] \tag{3b}
\]

\[
\text{Ca}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CaCO}_3; \tag{4a}
\]

where

\[
K_{\text{sp}} = [\text{Ca}^{2+}] [\text{CO}_3^{2-}] \tag{4b}
\]
As dissolved CO$_2$ increases in the surface water, it reacts with H$_2$O to form carbonic acid (Eq. 1). The carbonic acid can quickly dissociate into a hydrogen ion and a bicarbonate ion (Eq. 2a), with K$_1$ as the dissociation constant for (Eq. 2b). The bicarbonate ion can dissociate into another hydrogen ion and carbonate ion (Eq. 3a), with the K$_2$ being the dissociation constant for (Eq. 3b). Calcium (Ca$^{2+}$) and CO$_3^{2-}$ can combine to form the calcium carbonate (CaCO$_3$) mineral aragonite (Eq. 4a), with K$_{sp}$ being the stoichiometric solubility product at saturation for calcium carbonate (Eq. 4b). The net result of this additional CO$_2$ leads to an overall increase in hydrogen ion and bicarbonate and a decrease in carbonate. This can be detrimental to many calcifying marine organisms, as they require the precipitation of CaCO$_3$ for their survival. The aragonite saturation state ($\Omega_A$) is one measure of the thermodynamic favorability for the precipitation of CaCO$_3$. It is an important parameter in understanding water quality, as the in-situ saturation state (solubility ratio) for aragonite ($\Omega_A$) is given by

$$\Omega_A = [\text{CO}_3^{2-}] [\text{Ca}^{2+}] / K_{sp}$$  (5)

Where [CO$_3^{2-}$] is the carbonate ion concentration, [Ca$^{2+}$] is the calcium ion concentration, and K$_{sp}$ is the temperature and pressure-dependent stoichiometric solubility product of aragonite. At $\Omega_A = 1$, aragonite is in equilibrium with the surrounding water. At $\Omega_A > 1$, the precipitation or preservation of carbonate minerals is thermodynamically favored. At $\Omega_A < 1$, dissolution of aragonite is favored (Mucci, 1993). For the present study, calculations of aragonite saturation state (Eq. 5) were made using measurements of TAlk, DIC, temperature, pressure, salinity, and the CO2SYS.XLS (Lewis et al., 1998; Pierrot and Wallace, 2006), by selecting $K_1$ and $K_2$ carbonic acid dissociation constants of Millero (2010), and $K_{SO_4}$ as determined by Dickson (1990).
2.4. Results

To assess the spatial distribution of the DIC and TAlk, four shore-perpendicular transects were sampled from the coastline to 84 km and 57 km offshore of the Wax Lake Delta and Barataria Bay region in June 2019, including shallow regions of the shelf not often studied due to vessel limitations. To provide temporal information, these transects were resampled once more in September. This intensive sampling effort required 14 days and produced over 120 sets of samples from surface and endmember locations.

Wind and salinity distribution:

In WLD transects, during June 2019, average wind direction was from the east and average wind speed was 4.7 m/s (National Data Buoy Center). Surface salinity ($S$) increased from 2 to 30 with distance from shore. Average surface temperature was 28.3 °C. There was a strong vertical stratification at around 5 m depth, separating the upper mixed layer and bottom water (Figure 2.3). During September 2019, average wind direction was from the south, average speed was 3.93 m/s (National Data Buoy Center), average temperature was 30.0°C, and surface $S$ increased from 4 to 29 with distance from shore and showed vertical stratification at around 8 m depth (Figure 2.3). The prominent surface freshwater lens observed in June 2019 was less pronounced by September 2019, due to reduced freshwater input in the shelf.
Figure 2.3. Salinity distribution along the Wax Lake Delta sector in June 2019 (top) and September 2019 (bottom).

For the BB transects, during June 2019, average wind direction was from south southwest, with an averaged wind speed of 2.4 m/s (National Data Buoy Center). Average temperature was 29.0°C. The surface $S$ increased from 13 to 27 with distance offshore. There was a strong vertical stratification at around 5 to 7 m depth, separating the upper mixed layer and bottom water (Figure 2.4). In September 2019, the $S$ was significantly different from June 2019 (T-test, $P < 0.05$), with a much higher overall $S$ being observed, varying from 23 to 30. A vertical stratification at around 7 to 10 m depth was still present (Figure 2.4). The average wind direction was from the southeast and average wind speed was 2.54 m/s (National Data Buoy Center) and average temperature was 29.9°C.
Figure 2.4. Salinity distribution along the Barataria Bay sector in June 2019 (top) and September 2019 (bottom).

DIC distribution:

In June 2019, the surface DIC concentrations in the WLD sector ranged between 1765 µmol·kg⁻¹ and 2290 µmol·kg⁻¹, with mean concentration of 1979 ± 103 µmol·kg⁻¹. In September 2019, the DIC concentrations ranged between 1721 µmol·kg⁻¹ and 2153 µmol·kg⁻¹, with a mean concentration of 1924 ± 90 µmol·kg⁻¹. There was no significant trend with distance offshore (Figure 2.5). The corresponding DIC endmember measured at WLD channel were 1946±40 µmol·kg⁻¹ and 2586±22 µmol·kg⁻¹ for June and September.

In the BB sector, DIC concentrations ranged between 1926 µmol·kg⁻¹ and 2279 µmol·kg⁻¹, with a mean concentration of 2043 ± 72 µmol·kg⁻¹ in June 2019. While in September 2019, the DIC
ranged from 1851 µmol·kg⁻¹ to 2390 µmol·kg⁻¹, with a mean concentration of 2047 ± 132 µmol·kg⁻¹ (Figure 2.5). Similar to WLD, there was no significant trend with season or distance offshore.

Figure 2.5. DIC distribution as a function of salinity in the WLD and BB sectors.

**TALK distribution:**

In June 2019, the TALK concentration within the WLD sector ranged between 1215 µmol·kg⁻¹ and 2358 µmol·kg⁻¹, with a mean concentration of 1969 ± 338 µmol·kg⁻¹. The TALK concentrations in September 2019 ranged between 1482 µmol·kg⁻¹ and 2436 µmol·kg⁻¹, with a mean concentration of 2074 ± 217 µmol·kg⁻¹. In both seasons, the WLD sector showed significant increases of TALK concentrations with distance offshore (Figure 2.6). The corresponding TALK in the Wax Lake channel were measured to be ~1750 µmol·kg⁻¹ and ~2090 µmol·kg⁻¹ in June and September respectively.
The BB sector in June 2019 had TA\text{lk} concentrations that ranged between 1651 µmol·kg$^{-1}$ and 2603 µmol·kg$^{-1}$, with a mean concentration of 2196 ± 209 µmol·kg$^{-1}$. By September 2019, the TA\text{lk} concentrations in the BB sector between 1880 µmol·kg$^{-1}$ and 2265 µmol·kg$^{-1}$, with a mean concentration of 2174 ± 123 µmol·kg$^{-1}$. Similar to observations in the WLD region, TA\text{lk} concentrations increased with distance offshore in the BB sector (Figure 2.6).

![Figure 2.6. TA\text{lk} distribution as a function of salinity in the WLD and BB sectors.](image)

### 2.5. Discussion

The surface DIC concentrations measured during our sampling are similar to what has been previously reported from the region, which ranged between 1860 µmol·kg$^{-1}$ and 2050 µmol·kg$^{-1}$ (Guo et al., 2012; Wang et al., 2013). The shelf DIC distribution indicates non-conservative behavior for both WLD and BB. The DIC distribution is indicative of significant biological control. Biogeochemical processes, such as photosynthesis, respiration, and air–sea CO$_2$ exchange can impact DIC. In the shallow shelf region, high concentrations of riverine nutrients
stimulate intensive biological production throughout the water column, leading to the uptake of DIC and acts as the most important control on DIC distribution within the region. The biological uptake in this region is reported to be one of the highest in the world, ranging between 160-250 mmol m$^{-2}$ d$^{-1}$ (Cai, 2003a).

The observed TAlk concentrations in this study are lower than what has been previously reported for the region, which ranged between 2325 µmol·kg$^{-1}$ and 2447 µmol·kg$^{-1}$ (Cai et al., 2010; Wang et al., 2013). We observed few alkalinity values at salinity less than 7.5, which are lowest reported from the shelf region. There are two possible reasons for our lower values (i) Previous studies were not focused on the inner shelf and TAlk were reported for $S > 24$ (Wang et al., 2013) and $S > 20$, with the exception of one point (Cai et al., 2010) and (ii) The TAlk concentration in the Wax Lake channel are measured to be $\sim$1750 µmol·kg$^{-1}$ and $\sim$2090 µmol·kg$^{-1}$ in June and September, which are lower than the previously reported values for AR and MSR of 1960 µmol·kg$^{-1}$ and 2375 µmol·kg$^{-1}$, respectively, from June – August in 2007 (Cai et al., 2010). This result is unlike a previous study (Guo et al., 2012) which suggested a difference of 30 µmol/kg between DIC and TAlk for river endmembers, whereas this study found the Wax Lake channel endmember showed much larger differences between the two carbonate parameters.

Seawater alkalinity is largely affected by environmental factors, including precipitation, evaporation, water mass mixing, carbonate dissolution, lateral transport, and to a lesser effect, primary production and remineralization (Brewer et al., 1975; Millero and Roche, 1998). Nonetheless, alkalinity is often treated as a conservative variable in seawater chemistry. Previous studies from the Mississippi river plume region also reported quasi-conservative behavior of alkalinity for mid to low salinity regions of the Louisiana shelf (Guo et al., 2012). However, for
our current study, TALK distribution at low salinity (S<15) did not follow conservative mixing on the inner Louisiana shelf (Figure 2.6). This is more pronounced for the BB section compared to the WLD section, possibly due to greater influence of the MSR plume in the BB region. Interestingly, we also observe alkalinity values lower than those measured in the Wax Lake Outlet channel for our June WLD transects. Previous studies have reported a low alkalinity signal of up to 100 µmol·kg$^{-1}$ below the conservative mixing line in mid-salinity waters and attributed it to either a third endmember, biological carbonate production, or fluctuation in river alkalinity (Cai, 2003; Cai et al., 2010; Guo et al., 2012). We think the low alkalinity values observed nearshore are probably a result of sudden changes in concentration of river alkalinity, which can change significantly with discharge, or a result of precipitation. The WLD endmember samples and shelf samples were collected a few days apart, which can play a role in this apparent alkalinity removal. Depending on whether river discharge was increasing or decreasing, the river end-member alkalinity value could be decreasing or increasing, as earlier studies have shown that alkalinity could change significantly with river discharge in the MSR (Cai, 2003) and other middle latitude large rivers (Cai et al., 2008).

Regional and temporal differences in carbonate chemistry

The ratio of DIC to TALK concentrations can indicate the relative abundance of carbonate species (e.g., CO$_2$ and CO$_3^{2-}$) in coastal water. For specific salinity and temperature ranges, the ratio of DIC:TALK can be closely correlated with carbonate system parameters, such as $\Omega_A$ and pH (Xue and Cai, 2020). As such, DIC:TALK has been widely utilized in studies of coastal carbonate chemistry (e.g., Wang et al., 2013; Mol et al., 2018). The DIC:TALK ratio provides similar information to that of TALK - DIC i.e. $\sim[\text{CO}_3^{2-}] – [\text{CO}_2^*] +$ other alkalinity, where CO$_2^*$ is the
sum of dissolved CO$_2$ and carbonic acid (Broecker et al., 1979; Broecker and Peng, 1982)). Therefore, differences in DIC:TA$k$ ratios can imply a difference in buffer intensity. When the DIC:TA$k$ ratio approaches 1, that is $[\text{CO}_2] \approx [\text{CO}_3^{2-}]$, a small increase of $[\text{CO}_2]$ results in a large decrease of the system’s pH, thereby weakening the buffering capacity of the water. Consequently, changes in DIC:TA$k$ serve to directly alter the sensitivity of coastal water pH and $\Omega_A$.

The WLD and BB sectors during both the late spring (June 2019) and late summer (September 2019) showed DIC:TA$k$ gradients that generally decreased with distance offshore ($n = 71$, Figure 2.7). In June 2019, the average DIC:TA$k$ ratio in the WLD sector was 0.99 ± 0.17 and in the BB sector was 0.94 ± 0.44. By September 2019, the average DIC:TA$k$ ratios of the contrasting study regions slightly decreased, with the WLD sector having a ratio of 0.94 ± 0.09 and the BB sector having a ratio of 0.93 ± 0.077. During both seasons, both sectors approached a near constant ratio of DIC:TA$k$ ~ 0.91 at $S > 20$. However, in June 2019, at $S < 20$, the WLD sector had consistently higher values of DIC:TA$k$ than the BB sector. This indicates that this region of the WLD sector in June had a weaker buffering ability compared to that of the BB sector in the same season. By September, the DIC:TA$k$ across all $S$ in the WLD sector was relatively well buffered.
Figure 2.7. DIC:TAlk as a function of salinity for both the June 2019 and September 2019 sampling periods within both the WLD and BB sectors.

The increase in buffer ability between June and September observed in the surface waters of the WLD sector is likely influenced by the observed decrease in seasonal river discharge during this study’s timeframe (Figure 3.1). The WLD sector receives direct river discharge from the Wax Lake Outlet and AR, whereas the BB has limited freshwater inflow from the MSR and less freshwater input to the Louisiana shelf (Huang et al., 2015; Bi et al., 2019). Since DIC and TAlk concentrations are relatively independent of temperature, their relative abundances are directly associated with fluxes between reservoirs, with river end members playing a major role (Wang et al., 2013). The MSR and AR characteristically have high values of DIC, are highly supersaturated in $p\text{CO}_2$, and generally have much larger $p\text{CO}_2$ values than adjacent bays (Huang et al., 2015; DelDuco and Xu, 2019). In addition, seasonal export of riverine DIC in both the AR and MSR have historically been highest in summer months (Huang et al., 2015; Tian et al., 2015; DelDuco and Xu, 2019). These factors could explain the higher DIC:TAlk concentrations
observed in the WLD sector during June, which was subject to high seasonal river discharge during our study.

Previous work on the Louisiana shelf has reported notably lower values of DIC:TAlk. A previous study by Wang et al. (2013) reported surface DIC:TAlk values up to 0.85 for July 2007 near our BB sector and also estimated an average DIC:TAlk value of 0.85 for the entire nGOM shelf in the same year. The values of DIC:TAlk reported in our study in both June and September 2019 are significantly larger than these values. This could indicate that coastal Louisiana’s buffering ability to decreases in pH has been weakening since 2007. Unfortunately, it is difficult to accurately assess seasonal and regional values between studies for this carbonate system parameter alone, as the DIC:TAlk values reported by Wang et al. (2013) are the only ones expressively reported within the last decade for this region. This becomes even more difficult when considering studies that extrapolate the buffering capacity of surface water to the shallowest regions of the shelf, as they often estimate DIC concentrations in river endmembers to be either equal to or 30 µmol·kg⁻¹ higher than TAlk concentrations when observed freshwater DIC data is not available (Guo et al., 2012; Wang et al., 2013). However, it has been estimated that the MSR-AR system’s export of carbon to the Louisiana shelf has significantly increased from 1.51 x 10^{12} mol C yr⁻¹ during 1904-1910 to 1.70 x10^{12} mol C yr⁻¹ during 2004-2010 (Xue et al., 2016), and is recently estimated to export up to ~2.0 x 10^{12} mol C yr⁻¹ in DIC alone (Tian et al., 2015; DelDuco and Xu, 2019). This indicates river discharge is an important contributor to increases of DIC:TAlk to coastal waters on the Louisiana shelf. In the future, more studies assessing DIC:TAlk should be conducted, as relative concentrations of DIC to TAlk can provide key insights to deciphering the underlying mechanisms of ocean acidification over extended time periods (Xue and Cai, 2020).
Regional and temporal differences in aragonite saturation state

Concentrations of DIC and TAlk, for given temperatures and salinities, can be used to estimate the $\Omega_A$ of coastal waters. Seawater $\Omega_A$ is chiefly defined by $[\text{CO}_3^{2-}]$, and as a result, seawater [TAlk – DIC] presents a linear relationship with $\Omega_A$ (Broecker and Peng, 1982; Xue and Cai, 2020). However, there are limitations to using DIC and TAlk to estimate $\Omega_A$ at low values of [TAlk - DIC] and salinity (Xue and Cai, 2020). At [TAlk – DIC] $\leq$ 50 $\mu$mol·kg$^{-1}$ and $S < 20$, $[\text{CO}_3^{2-}]$ is very low and not sensitive to changes of [TAlk - DIC], causing $\Omega_A$ to deviate upward from its linear relationship with [TAlk – DIC] (Figure 2.8, n= 71). Therefore, samples with [TAlk – DIC] $\leq$ 50 $\mu$mol·kg$^{-1}$ were removed from $\Omega_A$ analysis and samples collected at $S > 20$ will be focused on for this section (Figure 2.9, n = 46 within the dashed area).

![Graph showing the relationship between $[\text{TAlk - DIC}]$ and $\Omega_A$ for all samples measured during the study period. Quasi-linear relationship of $[\text{TAlk - DIC}]$ with $\Omega_A$ shown by gray dashed lines.](image)

Figure 2.8. $\Omega_A$ relationship with [TAlk – DIC] shown for all samples measured during the study period. Quasi-linear relationship of [TAlk – DIC] with $\Omega_A$ shown by gray dashed lines.
Figure 2.9. $\Omega_A$ against salinity for both the June 2019 and September 2019 sampling periods within both the WLD and BB sectors. Usable values for analysis are circled by the dashed lines.

All surface water samples on the Louisiana shelf during both study periods were supersaturated with respect to aragonite ($\Omega_A$). In June 2019, $\Omega_A$ in the WLD sector averaged $3.03 \pm 1.18$ ($n = 11$) and the BB sector had an average $\Omega_A$ of $3.94 \pm 1.80$ ($n = 9$). By September 2019, the WLD sector had almost no change in average $\Omega_A$ ($3.05 \pm 1.27$, $n = 13$), while the average $\Omega_A$ in the BB sector had significantly decreased ($2.97 \pm 0.96$, $n = 13$). No general trend was observed with increasing $S$ in either study area during both seasons, with the majority of $\Omega_A$ values ranging from 1 to 5 (Figure 2.9). The range of temperature in surface water was very small during the entirety of all cruises (~ 28 °C to 30 °C), suggesting that differences in regional $\Omega_A$ were primarily driven by relative concentrations of TAlk and DIC.

The range of values of $\Omega_A$ reported in our study are lower than those reported by Guo et al. (2013) for mid salinity water for the summer months of 2004 to 2006, which ranged between 3 to 8. This study also reported that aragonite saturation states were ~ 1 only within the lowest
salinity regions of the shelf near the Mississippi River mouth (Guo et al., 2012). Average values of \( \Omega_A \) reported in our study are lower than those reported by Wang et al. (2013) for the summer of 2007, which ranged between 4 to 5. This is not surprising given the observed differences in DIC:TAIk between the two studies, as previously mentioned. Gomez et al. (2020) reported average \( \Omega_A \) values of \( \geq 4.2 \) in the surface water of the inner Louisiana shelf during the summer, based on observations and model estimates for the years 2005-2014. Gomez et al. (2020) estimated these values \( \Omega_A \) to be some of the highest in the nGOM, linking these values to high biological uptake and high rates of MSR-AR discharge onto the shelf. It is estimated that \( \Omega_A \) will significantly decrease in the future, as CO\(_2\) emissions continue to build up in our atmosphere (Feely et al., 2017). Feely et al. (2017) estimates that the nGOM will experience \( \Omega_A \) values as low as 2.19 by the year 2100, corresponding to projected atmospheric \( pCO_2 \) concentrations. However, the overprint of changing river discharge on top of atmospheric \( pCO_2 \) concentrations can provide an exacerbated impact to \( \Omega_A \) states within the shallow shelf region in the future.

2.6. Conclusion

This study shows that significant freshwater discharges can influence the spatial and temporal variation in DIC and \( \Omega_A \) in shallow coastal systems, thereby influencing the dynamics of DIC and TAIk along the land-ocean continuum. The Louisiana shelf tends to have slightly higher DIC:TAIk during the period of peak river discharge, when the freshwater extended farthest on the shelf, and then gradually decreases by Fall, corresponding with reduced freshwater discharge. Such changes are more dramatic in the region with the highest river influence from the Wax Lake and Atchafalaya Deltas, where the DIC:TAIk ratio decreased from 0.99 to a 0.94 between
the seasons. This indicates that increased river discharge has the capability to significantly weaken the coastal oceans’ ability to buffer decreases in pH. In general, the surface water was supersaturated with respect to $\Omega_A$ for both seasons. However, the $\Omega_A$ values estimated in this study are lower than previous studies in the same region within the past two decades, indicating that the buffering strength on the Louisiana inner shelf is highly modulated by river input. Thus, future studies of coastal ocean acidification need to look at long-term trends, not only in context of atmospheric $p$CO2 and temperature changes, but also incorporating the effect of river discharge and associated eutrophication which are expected to change dramatically over next few decades.

3.1. Introduction

Deltaic systems are a major pathway for the input of terrestrial derived carbon to the coastal ocean (Bianchi et al. 2004; Bianchi et al. 2007). Globally, rivers and associated coastal wetlands transport approximately 1.0 Gt carbon from continental regions to oceans annually (Suchet et al., 2003; Cai et al., 2015). Dissolved inorganic carbon (DIC), which is the sum of all carbonate species dissolved in water (DIC = [HCO$_3^-$] + [CO$_3^{2-}$] + [CO$_2$]) represents about 41% of this transported carbon (Suchet et al., 2003; Cai et al., 2015). Despite the importance of these systems, there is still a lack of understanding about the interaction and temporal-spatial linkages between highly productive wetlands and the adjacent coastal waters in terms of a carbon budget (Bianchi et al. 2004, 2007; Hopkins et al., 2012). The need for a comprehensive understanding of the transport of carbon to the coastal ocean is made even more imperative, as global coastal wetlands are undergoing substantial alterations due to climatic and anthropogenic forcing.

It is estimated that global coastal wetland coverage could be reduced between 30-59% by the end of this current century, based on current sea-level rise and levels of human intervention (Spencer et al., 2016; Schuerch et al., 2018). Nowhere is this more apparent than the Mississippi River delta in the northern Gulf of Mexico (nGOM). This is the largest deltaic system in the region, accounting for 40% of the wetlands within the conterminous United States of America (USA) (Bianchi et al., 2011; Bi et al., 2019). Currently, coastal Louisiana is experiencing relative sea-level rise at rates faster than most coastlines around the world (Kolker et. al, 2011). While eustatic sea level rise is estimated to range between 3 mm y$^{-1}$ to 4 mm y$^{-1}$ (Stocker et al., 2013), some areas of the Louisiana coast are subsiding at 6 mm y$^{-1}$ to 8 mm y$^{-1}$ as a result of reduced
sediment supply to the wetlands associated with upstream dams and the extensive levee infrastructure along the Mississippi River (Blum and Roberts, 2009).

The high rates of erosion and deterioration results in the rapid loss of 26 – 30 km$^2$ of wetlands per year from this region, thereby generating a net loss of carbon, which would otherwise be stored in the wetlands (U.S. Geological Survey and Barras, 2006; Couvillion et al., 2011, 2017). While the wetland loss in this region is well documented, the associated carbon being transported into and across the continental shelf is not well constrained.

The exchange of material between the eroding continental margin and ocean interior plays a major role in global biogeochemical cycles. However, material fluxes across shelf waters are difficult to quantify, as these systems are exceedingly complex due to small-scale temporal and spatial variability. Commonly, freshwater plumes and their dissolved materials are traced by offshore negative salinity and/or positive silica anomalies (Chen et al., 2010). However, the salinity signal can be altered by evaporation and precipitation, and the silica signal is sensitive to biological uptake (Chen et al., 2010). To avoid some of these drawbacks, naturally occurring short-lived radium isotopes ($^{224}$Ra and $^{223}$Ra) have been successfully utilized to quantify fluxes of dissolved components transported across continental shelves (Moore and Krest, 2004; Windom et al., 2006; Li et al., 2011; Burt et al., 2013; Sippo et al., 2019).

In this study, we evaluate the lateral transport of DIC using $^{224}$Ra ($t_{1/2} = 3.6$ days) and $^{223}$Ra ($t_{1/2} = 11.43$ days) across two sections of the Louisiana shelf with contrasting rates of land loss and organic matter:mineral content. The Wax Lake Delta (WLD) is one of the few regions in Louisiana undergoing sediment accretion, due to large inputs of mineral sediment through the Wax Lake Outlet, an artificial channel off the Atchafalaya river (AR) (Rosen and Xu, 2013). The outlet was built by the U.S. Army Corps of Engineers in 1941 to protect Morgan City, Louisiana
during high flood stages by diverting 30% of the AR flow to the nGOM (Second New Orleans District, U.S. Army Corps of Engineers, 1938; Rosen and Xu, 2013). In contrast to WLD, the Barataria Bay (BB) region has historically high land loss rates, due to the lack of mineral sediment input, preventing the land from keeping up with sea level rise and subsidence (Barras et al., 2003; Blum and Roberts, 2009). We thus hypothesize that (i) larger freshwater outflow into the shallow shelf of the WLD region will result in larger oceanward transport of DIC compared to BB region and (ii) the magnitude of DIC transport will be higher in late spring (June) than in late summer (September), due to seasonal decrease in river discharge.

3.2. Study Site

The Wax Lake Delta (WLD) region represents an area of net wetland gain in Louisiana (Figure 3.1). WLD was recently formed as a result of dredging efforts that diverted water from AR to the nGOM, moving sediment input through the man-made Wax Lake Outlet (Rosen and Xu, 2013). Formation of WLD began in 1972, with accelerated growth occurring after large scale floods during the years of 1973 to 1975 (Rosen and Xu, 2013). Since these events, the delta has been growing naturally, with minimal active management (Allen et al., 2012). The delta’s current extension is 65 km², accreting land at a rate of 1 km² yr⁻¹ (Allen et al., 2012). This growth rate has allowed for the establishment of marsh and forested wetland vegetation across elevation gradients (Holm and Sasser, 2001). The WLD is less than 14 km from the mouth of the AR, both of which discharge into the Atchafalaya Bay before entering the nGOM.

In contrast to WLD, the Barataria Bay (BB) has historically experienced significant wetland loss. The Barataria Basin occupies more than 6000 km² of wetlands and bodies of water (FitzGerald et
The basin is bordered by the abandoned Bayou Lafourche distributary to the west, the mainstem of the active Mississippi River (MSR) to the east, and a series of barrier islands to the south, separating the estuary from the nGOM (FitzGerald et al., 2004). The basin is currently experiencing extensive loss of wetlands, with an estimated loss of 23 km² yr⁻¹ (U.S. Geological Survey and Barras et al., 2006; Couvillion et al., 2011, 2017) and a loss of soil organic carbon of 1000 to 2050 g C·m⁻²·yr⁻¹ (Wang et al., 2017). Subsidence and wetland loss in Barataria Bay are predicted to continue and increase drastically, due to a coupling of increasing sea-level rise and decreased modern sediment loading to the deltaic plain (Barras et al., 2003; Blum and Roberts, 2009).

WLD and BB thus represent two extremes of the ongoing changes to the Louisiana coast, in which both wetland/deltaic systems are in constant flux with the nGOM. Both regions produce freshwater plumes, providing an important source of DIC to shelf waters as they mix (Suchet and Ludwig, 2003; Cai et al., 2011). Yet, despite the importance of these coastal ecosystems, there is still a lack of understanding about the temporal and spatial linkages between the coastal wetlands, adjacent shelf waters, and their carbon transport through mixing. One major temporal shift in southeast Louisiana is the seasonal decrease of river discharge. In 2019, the river discharge was high (125x10⁴ ft³ s⁻¹ and 25x10⁴ ft³ s⁻¹ for the MSR and Wax Lake Outlet) during late spring and early summer as a result of freshwater input from snowmelt in northern USA (Figure 3.1). However, by early September the freshwater discharge is reduced to 45x10⁴ ft³ s⁻¹ and 10x10⁴ ft³ s⁻¹ for the MSR and Wax Lake Outlet, respectively. Thus, our seasonal sampling during June and September of 2019, shown in boxes in Figure 3.1, can provide a better understanding of how such drastic decreases in freshwater can alter the DIC transport in coastal shelf waters.
3.3. Sample Collection Stations and Cruises

Field sampling was conducted on the R/V Acadiana during June 2019 and September 2019 to account for seasonal high and low river discharges of the MSR, AR, and Wax Lake Outlet (Figure 3.2). The samples were collected along 2 cross shelf transects for both the WLD and BB regions, referred to as West and East (Figure 3.2). Surface water sampling was collected from 1 m below the surface at 9 km intervals for WLD transects and 5 km intervals for BB transects, until a salinity of ~30 was reached in June 2019. Bottom water sampling was conducted at every other station along each transect. These stations were repeated in September 2019 (Figure 3.2). The WLD sector extended 84 km offshore and the BB sector extended 57 km offshore, to reach a water depth of at least 35 m.

Figure 3.1. Discharge rates for the Mississippi River and Wax Lake Outlet for 2019 in cubic feet per second. The vertical rectangles indicate when sampling for this project occurred (modified from the U.S. Geological Survey, 2016).
3.4. Methodology

Sample collection and analysis

Radium water samples were collected in cubitainers by filtering 60 L water through a 1.0 μm cartridge filter. The filtered water sample was immediately drained through a column containing 20 g of manganese oxide coated fibers (Mn-fiber) at a rate of < 1 L/min to quantitatively collect radium as described by Moore (1976). In the laboratory, each Mn-fiber sample was rinsed with radium free water with a pH of 7, partially dried in the open air or by a stream of dry air and then measured for $^{224}$Ra and $^{223}$Ra using a delayed-coincidence system as described by Moore and Arnold (1996).

For DIC samples, water was passed through a 0.45 mm glass fiber syringe filter and collected into 12 mL Labco septa vials (https://www.labco.co.uk/), thoroughly flushed with extensive overflow (> 12 mL), and spiked with a 10 μL Hg solution. DIC samples were stored at 5°C and
measured back in the laboratory, using the standard protocol for the semi-automated system Apollo SciTech Dissolved Inorganic Carbon Analyzer. The instrument was calibrated using certified reference materials (CRM batch 180; Dickson, 2010).

Calculation of mixing coefficients

Radium isotopes have been used by a number of previous studies to measure coastal mixing rates across continental shelves, including: the South Atlantic Bight, southern Brazil, the South China Sea, the Scotian shelf, and the Gulf of Carpentaria (Moore, 2000; Windom et al. 2006; Chen et al., 2010; Burt et al., 2013; Sippo et al., 2019). There are four natural isotopes of radium produced from natural uranium and thorium decay. This work utilizes $^{224}$Ra and $^{223}$Ra, which have short half-lives of 3.66 days and 11.4 days, respectively. These isotopes are introduced to seawater through contact with thorium-bearing sediments carried by fresh river water or deposited bottom sediments (Moore and Krest, 2004; Chen et al., 2010). Radium isotopes are strongly adsorbed on sediments in fresh river water and will desorb as they come into contact with the high ionic strength of coastal waters (Moore and Krest, 2004; Chen et al., 2010). Once introduced to near shore waters, the radium’s activity can only decrease by mixing with water with lower activity and by radioactive decay (Moore and Krest, 2004; Chen et al., 2010). Since the short-lived radium isotopes decay rapidly, their activities will quickly decrease with increasing distance from their fresh water source (Chen et al., 2010). By tracking the decay of these two short-lived radium isotopes, the time scale of transport of freshwater as it moves across the shelf and mixes with adjacent coastal waters can be constrained (Moore, 2000; Moore and Krest, 2004; Windom et al., 2006; Chen et al., 2010). The distribution of these short-lived
isotopes over the shelf can be modeled and cross-shelf mixing rates determined using the following equation (Moore, 2000).

\[ \ln A_x = \ln A_0 - x(\lambda/K_h)^{1/2} \]  

(1)

where \( A_x \) is the measured activity at distance \( x \) from shore, \( A_0 \) is the activity at the shoreline, \( K_h \) is the mixing coefficient, and \( \lambda \) is the decay constant. Several assumptions are required to apply this model: (1) radium addition to the surface water occurs only in the near-shore zone; (2) net cross shelf advection is negligible compared to mixing; (3) cross shelf mixing is constant; (4) the system is in steady state (Moore, 2000). In this study we utilize short-lived \(^{224}\text{Ra}\) and \(^{223}\text{Ra}\), as their concentration in the open ocean can be assumed to be negligible. To further verify these assumptions, offshore sampling was carried out during both seasons, approximately 65 km offshore of the East BB transect, where the average \(^{224}\text{Ra}\) and \(^{223}\text{Ra}\) activities were much lower than the activities along the transect. Bottom sediments can be an important source of Ra to the overlying water column. However, during both the study periods, strong water column stratification was observed based on salinity (referred to in the next section), suggesting negligible input from sediments. The surface Ra activities were also found to be different from their near bottom activities, further indicating that the water column was not well mixed (supplementary data).

3.5. Results

To assess the spatial distribution of radium isotopes and DIC, four shore-perpendicular transects were sampled from the coastline to 84 and 57 km offshore of the Wax Lake Delta and Barataria
Bay region. To provide temporal information, these transects were resampled once more. This intensive sampling effort required 14 days and produced over 120 radium samples.

**Wind and salinity distribution:**

In WLD transects, during June 2019, average wind direction was from the east and average wind speed was 4.7 m/s (National Data Buoy Center). Surface salinity ($S$) increased from 2 to 30 with distance from shore. There was a strong vertical stratification at around 5 m depth, separating the upper mixed layer and bottom water (Figure 3.3). During September 2019, average wind direction was from the south, average speed was 3.93 m/s (National Data Buoy Center), and surface $S$ increased from 4 to 29 with distance from shore and showed vertical stratification at around 8 m depth (Figure 3.3). The prominent surface freshwater lens observed in June 2019 was less pronounced by September 2019, due to reduced freshwater input in the shelf.

For the BB transects, during June 2019, average wind direction was from south southwest, with an average wind speed of 2.4 m/s (National Data Buoy Center). The surface $S$ increased from 13 to 27 with distance offshore. There was a strong vertical stratification at around 5 to 7 m depth, separating the upper mixed layer and bottom water (Figure 3.4). In September 2019, the $S$ was significantly different from June 2019 (T-test, $P < 0.05$), with a much higher $S$ being observed, varying from 23 to 30. A vertical stratification at around 7 to 10 m depth was still present (Figure 3.4). The average wind direction was from the southeast and average wind speed was 2.54 m/s (National Data Buoy Center).
Figure 3.3. Salinity distribution along the Wax Lake Delta sector in June 2019 (top) and September 2019 (bottom).
Figure 3.4. Salinity distribution along the Barataria Bay sector in June 2019 (top) and September 2019 (bottom).

**DIC distribution:**

In June 2019, the surface DIC concentration in both the WLD transects ranged between 1765 µmol·kg\(^{-1}\) and 2290 µmol·kg\(^{-1}\), with a mean concentration of 1979 ± 103 µmol·kg\(^{-1}\). In September 2019, the DIC concentrations ranged between 1721 µmol·kg\(^{-1}\) and 2153 µmol·kg\(^{-1}\), with a mean concentration of 1924 ± 90 µmol·kg\(^{-1}\). There was no significant trend with distance offshore (Figure 3.5).

For both BB transects, DIC concentrations ranged between 1926 µmol·kg\(^{-1}\) and 2279 µmol·kg\(^{-1}\), with a mean concentration of 2043 ± 72 µmol·kg\(^{-1}\) in June 2019. While in September 2019, the
DIC ranged from 1851 µmol·kg⁻¹ to 2390 µmol·kg⁻¹, with a mean concentration of 2047 ± 132 µmol·kg⁻¹ (Figure 3.5). Similar to WLD, there was no significant trend with season or distance offshore.

Figure 3.5. Average DIC concentration for salinity ranges of 0-10, 10-20 and >20 in the WLD and BB sector.

$^{224}$Ra and $^{223}$Ra distribution:

In June 2019, the distribution of $^{224}$Ra and $^{223}$Ra ranged from 68 to 4 dpm 100 L⁻¹ and 9 to 0.9 dpm 100 L⁻¹ (Figures 3.6, 3.7). By September 2019, the activities of both $^{224}$Ra and $^{223}$Ra in the WLD transects were determined to be significantly different from the activities in June 2019 (T-test, P < 0.05), as the distribution of $^{224}$Ra and $^{223}$Ra now ranged from 19 to 0.05 dpm 100 L⁻¹ and 2 to 0.05 dpm 100 L⁻¹ (Figures 3.6, 3.7). Thus, between June 2019 and September 2019, the distribution range and mean activity of $^{224}$Ra decreased by 45 dpm 100 L⁻¹, while the distribution range of $^{223}$Ra decreased by 6 dpm 100 L⁻¹. During both seasons, the WLD transects experienced a decrease of $^{224}$Ra and $^{223}$Ra activities with distance offshore.
Figure 3.6. Variation in cross-shelf $^{224}$Ra activity for the Wax Lake Delta (WLD) transects between June 2019 (upper panels) and September 2019 (lower panels), used to determine mixing rates.
Figure 3.7. Variation in cross-shelf concentration of $^{223}$Ra isotopes for the Wax Lake Delta (WLD) transects between June 2019 (upper panels) and September 2019 (lower panels), used to determine mixing rates.

The distribution of $^{224}$Ra and $^{223}$Ra activities in the BB transects decreased offshore in both seasons. In June 2019, the distribution of $^{224}$Ra and $^{223}$Ra ranged from 54 to 2 dpm 100 L$^{-1}$ and 7 to 1 dpm 100 L$^{-1}$, (Figures 3.8, 3.9). In September 2019, the distribution of $^{224}$Ra and $^{223}$Ra ranged from 11 to 0.4 dpm 100 L$^{-1}$ and 1 to 0.09 dpm 100 L$^{-1}$ (Figures 3.8, 3.9). Overall, the distribution range of $^{224}$Ra decreased by 41 dpm 100 L$^{-1}$ while that of $^{223}$Ra decreased by 5 dpm 100 L$^{-1}$ respectively, representing a significant difference in the distribution between the two seasons (T-test, P < 0.05).
Figure 3.8. Variation in cross-shelf $^{224}$Ra isotopic activity for the Barataria Bay (BB) transects between June 2019 (upper panels) and September 2019 (lower panels), used to determine mixing rates.
Figure 3.9. Variation in cross-shelf concentration of $^{223}\text{Ra}$ isotopes for the Barataria Bay (BB) transects between June 2019 (upper panels) and September 2019 (lower panels), used to determine mixing rates.

The log–linear distribution of $^{224}\text{Ra}$ and $^{223}\text{Ra}$ activities across all transects suggests cross-shelf mixing plays an important role in offshore transport of $^{224}\text{Ra}$ and $^{223}\text{Ra}$, with minimal impact from benthic fluxes (Moore et al., 2000; Sippo et al., 2019). Sediment core incubations carried out in this region between 2016-2019 showed benthic diffusive fluxes of $^{224}\text{Ra}$ and $^{223}\text{Ra}$ represent less than 6% of the water column’s radium inventories (Bam et al., 2016, unpublished data).
3.6. Discussion

The $^{224}\text{Ra}$ and $^{223}\text{Ra}$ activities found in this study ranged from 68 to 0.05 dpm 100 L$^{-1}$ and 11 to 0.05 dpm 100 L$^{-1}$. These values in this region are similar to those reported by Moore and Krest (2003), where $^{224}\text{Ra}$ and $^{223}\text{Ra}$ activities varied between 43.5 to -0.3 dpm 100 L$^{-1}$ and 3.78 to 0.04 dpm 100 L$^{-1}$ during sampling in 1994 for the same region. The mixing rates along each transect of the WLD and BB sectors were determined using the pattern of the radium distributions with distance (Figures 2.6 - 2.9), all of which showed significant linear correlation (p-value <0.005). There is a large variability in mixing rates for transects within the same sector, which we attribute to spatial heterogeneity and differences in physical processes within each region. The mixing rates calculated independently from the $^{224}\text{Ra}$ and $^{223}\text{Ra}$ distribution show similar rates along most transects and the differences in rates derived from each isotope is probably due to the differences in their half-lives of 3.66 days and 11.4 days, respectively (Moore 2000).

Radium derived mixing rates

Mixing rates ($K_h$) were estimated from the distribution of $^{224}\text{Ra}$ and $^{223}\text{Ra}$ activities with distance from shore using (Eq. 1) for each of the eight transects (Figures 3.10, 3.11). For the rest of the discussion, we report the average value of the west and east transects for the WLD and BB sectors to represent the average mixing rates within these regions (Table 3.1). In June 2019, the WLD had an average mixing rate of $3236 \pm 1829$ m$^2$s$^{-1}$ and $2658 \pm 2524$ m$^2$s$^{-1}$ for $^{224}\text{Ra}$ and $^{223}\text{Ra}$, respectively, while the BB transects had average mixing rates of $1125 \pm 710$ m$^2$s$^{-1}$ and $1181 \pm 793$ m$^2$s$^{-1}$ for $^{224}\text{Ra}$ and $^{223}\text{Ra}$, respectively (Figures 3.10, 3.11). In September 2019, the WLD transects had average mixing rates of $467 \pm 6$ m$^2$s$^{-1}$ and $613 \pm 509$ m$^2$s$^{-1}$ for $^{224}\text{Ra}$ and $^{223}\text{Ra}$, respectively (Figure 3.10) and the BB transects had average mixing rates of $634 \pm 334$ m$^2$
$s^{-1}$ and $626 \pm 260 \, m^2 \, s^{-1}$ for $^{224}\text{Ra}$ and $^{223}\text{Ra}$ (Figure 3.11). The WLD region experienced up to 18 times decrease in average mixing rates between June 2019 and September 2019, while the BB transects experienced up to 2 times decrease in average mixing rates (Table 3.1).

Figure 3.10. Mixing rates shown WLD for June 2019 and September 2019, as calculated with $^{224}\text{Ra}$ and $^{223}\text{Ra}$, respectively.

Figure 3.11. Mixing rates shown BB for June 2019 and September 2019, as calculated with $^{224}\text{Ra}$ and $^{223}\text{Ra}$, respectively.
The decrease in mixing rates between June and September can be attributed to the observed decrease in seasonal river discharge during this timeframe (Figure 3.1). While both the WLD and BB regions experienced a decrease in mixing rates as freshwater discharge decreased, this does not explain the difference between the two sectors within the same season. The differences in average $K_h$ estimates for WLD and BB during each season could be due to the fact that the Wax Lake Outlet and AR discharge directly into the shallow shelf region of the WLD sector, whereas Barataria Bay has limited freshwater inflow and a much steeper shelf slope (Bi et al., 2019). As the river water pools on the shallow shelf in the Wax Lake and Atchafalaya region, instabilities along the plume edge can then result in turbulent flow and a net offshore transport of the plume water (Thyng and Hetland, 2018). Previous studies of seasonal freshwater transport on the Louisiana shelf, using hydrodynamic models and lagrangian trajectory models, thus concluded that high river discharge into the Atchafalaya Bay can lead to greater offshore transport, similar to our current observation (Zhang et al., 2012; Thyng and Hetland, 2018).
Most studies of freshwater mixing over the Louisiana shelf have dealt with freshwater plume pathways and thickness, in context of seasonal hypoxia and indicate that maximum offshore transport of the freshwater plumes in the mid Louisiana shelf occur in mid-summer, depending on whether wind conditions are upwelling favorable (Zhang et al., 2012; Thyng and Hetland, 2018). Offshore transport is favored when the average wind direction is toward the southwest, while average wind oriented to the northwest is not associated with transport across the shelf (Zhang et al., 2012; Thyng and Hetland, 2018). During the majority of our study periods, the average wind directions were not upwelling favorable (National Data Buoy Center). However, offshore transport did occur, suggesting that the transport is strongly driven by freshwater discharge during our study periods. A few studies have published horizontal mixing rates for the mid Louisiana shelf. Brokaw et al. (2019) utilized satellite sea surface salinity and altimetric sea surface height to quantify low salinity transport by the Loop Current System in the nGOM and estimated that average August offshore transport in the BB region to reach around 800 m$^2$ s$^{-1}$. Ohlmann and Niiler (2005) used lagrangian observations to characterize circulation over the nGOM shelf and estimated that the region near the WLD had a mixing rate of 640 m$^2$ s$^{-1}$ between October 1993 and October 1994. Shelf water mixing rates ($K_h$) are influenced by a wide variety of environmental factors which generate water turbulence and therefore, can be highly variable (Inman et al., 1971; Sippo et al., 2019). Given such wide variability in mixing rates as a function of freshwater discharge, currents, and prevailing wind strength and direction, these reported values can be considered similar to the mixing rates estimated in this current study. The only possible exception is the WLD west transect in June, where we report the highest rates for the region, which could be related to rivers being in flood stage during our sampling period (Figure 3.1).
There are no prior estimates of radium based mixing rates reported from our study region and estimates from other coastal regions are found to vary widely. Colbert and Hammond (2007) reported eddy diffusive mixing rates as low as 1.4 m$^2$ s$^{-1}$ off a beach in southern California, USA. Sippo et al. (2019) reported a rate of 104 m$^2$ s$^{-1}$ in the Gulf of Carpentaria, Australia. Windom et al. (2016) estimated a rate of 338 m$^2$ s$^{-1}$ off a beach in south Brazil, while values in the Southern Drake Passage have been found to be as high as 64,000 m$^2$ s$^{-1}$ (Dulaiova et al., 2009). Temporal variability can also induce large shifts in mixing rates. Tides within the Delaware bay, USA have been reported to swing mixing rates from 40 m$^2$ s$^{-1}$ to 600 m$^2$ s$^{-1}$ (Sanders and Gavin, 2001). The rates reported in this study are within the rates estimated by radium isotopes reported in literature. The seasonal shifts in $K_h$ estimates in this study suggest variability in river discharge and other factors, such as wind, play an important role in controlling mixing rates on the Louisiana shelf, which would explain the large changes observed during this study period (Li and Cai, 2011).

*Shelf residence time*

To quantify the DIC transport across the shelf, a measure of residence time of the shelf water with respect to mixing is required. Residence time of water on the shelf is defined as the time required to remove the water from $1/e$ of the length of the shelf as shown below

$$L = (2K_h t)^{1/2} \quad (2)$$

Where $L$ is length of the shelf (WLD = 84 km; BB= 57 km), $K_h$ is the mixing rate, and $t$ is the residence time.
The average residence time of water in June 2019 in the WLD sector was 15 ± 8 days and 28 ± 27 days for $^{224}$Ra and $^{223}$Ra, respectively, and in the BB sector was 21 ± 13 days for $^{224}$Ra and 21 ± 13 for $^{223}$Ra, respectively (Figures 3.12, 3.13). However, by September 2019, the average residence time of the WLD sector increased to 88 ± 1 days and 102 ± 84 days for $^{224}$Ra and $^{223}$Ra, respectively, while that of BB sector increased to 35 ± 19 days and 55 ± 45 days for $^{224}$Ra and $^{223}$Ra, respectively (Figures 3.12, 3.13, Table 3.1). Moore and Krest (2004) calculated the $^{223}$Ra/$^{224}$Ra age of the water mass with an $S$ of 30 in the BB region to be between 8-21 days in May, which is similar to our current estimates.

![Figure 3.12. Residence time of the water in the WLD transects for June 2019 and September 2019 as calculated by their respective mixing rates.](image)

Previous studies from this region have utilized two different approaches to estimating timescales of freshwater on the Louisiana shelf. One approach is to estimate residence time or a transit time of freshwater. The second approach is to estimate the filling and flushing rate of freshwater on the shelf (Etter et al., 2004; Zhang et al., 2012). However, filling and flushing rates are not
analogous to residence time estimates. Residence time is defined as the average time for water to escape the reservoir of the shelf, where flushing time is defined as the time required for freshwater discharge to equal the amount of freshwater originally present on the shelf (Sheldon and Alber, 2002). Therefore, we will only compare residence time estimates from our study to other studies which have used a residence/transit time approach in the Louisiana shelf. Wiseman et. al (1997) utilized averaged time-series data from 10 years of survey cruises in late July/early August on the Louisiana shelf and estimated a 15-day lag of freshwater to a station located halfway between the WLD and BB sectors. Brokaw et al. (2019) estimated a $K_h$ value of 800 m$^2$ s$^{-1}$ in BB sector during August for 2013-2018. If we apply this $K_h$ value to our BB study area parameters (Eq. 2), it yields a residence time of 24 days, which is similar to our current estimates of 15 to 28 days for late spring and early summer. Similarly, using the estimated $K_h$ value of 640 m$^2$ s$^{-1}$ in the WLD sector, reported for October 1993 near that region (Ohlman and Niiler, 2005), results in a residence time of 64 days, which is similar to our September estimates of 88 to 101 days (Table 3.1).
Transport of Dissolved Inorganic Carbon

The surface DIC concentrations measured during our sampling are similar to what has been previously reported from the region, which ranged between 1860 µmol·kg$^{-1}$ and 2050 µmol·kg$^{-1}$ (Wang et al., 2013). The shelf DIC distribution indicates non-conservative behavior for both WLD and BB. The DIC distribution is indicative of significant biological control. Biogeochemical processes, such as photosynthesis, respiration, and air–sea CO$_2$ exchange can impact DIC. In the shallow shelf region, high concentrations of riverine nutrients stimulate intensive biological production throughout the water column, leading to the uptake of DIC and acts as the most important control on DIC distribution within the region. The biological uptake in this region is reported to be one of the highest in the world, ranging between 160-250 mmol m$^{-2}$ d$^{-1}$ (Cai, 2003a). Boundary current entrainment of shelf water DIC can also occur during summer, when Loop Current eddies approach and interact with the shelf processes, but it mostly occurs along the shelf break, further south of our study region (Wang et al., 2013).

The lateral transport of DIC within each study sector can be calculated from the total DIC inventory in the water column and the corresponding radium derived residence time (Table 3.1). The DIC inventory was calculated from the average DIC concentration in the water column within each sector and the volume of water for each study sector based on our study area boundaries (Figure 3.2) and the local bathometry at a 10 m resolution. The water volume for each sector is estimated to be 45.57 x10$^9$ m$^3$ in the WLD sector and 40.02 x10$^9$ m$^3$ in the BB sector. In June 2019, the average DIC transport from the WLD sector was estimated to be 7 ± 4 x10$^9$ mol d$^{-1}$ and 6 ± 7 x10$^9$ mol d$^{-1}$ for $^{224}$Ra and $^{223}$Ra, respectively (Figure 3.14). The corresponding DIC transport from the BB sector was estimated to be 5 ± 3 x10$^9$ mol d$^{-1}$ and 6 ± 4
x10⁹ mol d⁻¹ for ⁰²²⁴Ra and ⁰²²³Ra, respectively (Figure 3.15). Since transport is inversely related to residence time, the DIC transport of both sectors decreased with seasonal river decrease. In September 2019, the average DIC transport of the WLD transects was 1 ± 0 x10⁹ mol d⁻¹ and 2 ± 1 x10⁹ mol d⁻¹ for ⁰²²⁴Ra and ⁰²²³Ra, respectively, and the average DIC transport for the BB transects was 3 ± 1 x10⁹ mol d⁻¹ and 2 ± 1 x10⁹ mol d⁻¹ for ⁰²²⁴Ra and ⁰²²³Ra, respectively (Figures 3.14, 3.15). These estimates show that the WLD sector experienced a 4 to 7 times decrease in average DIC transport between June 2019 and September 2019. Whereas, the BB sector only experienced a 2 to 3 times decrease in average DIC transport between June 2019 and September 2019. This further highlights the importance of direct freshwater discharge from the AR into the bay.

The net DIC transport for both the WLD and BB sectors was greater during the period of high river discharge in late spring (June 2019) than during the low river discharge in late summer (September 2019). There is no significant difference in total DIC transport between the WLD sector and the BB sector in either season, varying between 5 x10⁹ mol d⁻¹ to 7 x10⁹ mol d⁻¹ for June and 1 x10⁹ mol d⁻¹ to 3 x10⁹ mol d⁻¹ in September (T-test, P>0.05). However, we acknowledge that this is not a fair comparison because volumetrically, the BB sector is approximately 88% that of the WLD sector. Thus, DIC transport per unit volume for each of the sectors can provide more comparable data. WLD transport decreased from 142 ± 87 mmol m⁻³ d⁻¹ to 26 ± 15 mmol m⁻³ d⁻¹, while BB transport decreased from 127 ± 68 mmol m⁻³ d⁻¹ to 62 ± 33 mmol m⁻³ d⁻¹ in between June and September. To put this in perspective, the DIC contribution by the Loop Current in the nGOM is estimated to be 3.5 mmol m⁻³ d⁻¹ (Wang et al., 2013). The higher lateral export estimated at our study boundary of 40 m isobath, with respect to that transported by the Loop Current, indicates large biological uptake before the water mass leaving
Figure 3.14. Cross shelf transport of DIC rates for WLD in June 2019 and September 2019, as calculated with $^{224}$Ra and $^{223}$Ra, respectively.

Figure 3.15. Cross shelf transport of DIC rates for BB in June 2019 and September 2019, as calculated with $^{224}$Ra and $^{223}$Ra, respectively.

The shallow shelf gets entrenched. The Loop Current interacts directly with nearby shelves (Morey et al. 2003; Walker et al., 2005), suggesting that much of the DIC is ultimately supplied from the surrounding shelf, with the Louisiana shelf playing a dominant role. An observational study conducted by Wang et al. (2013) suggests there is a carbon export in the form of DIC of $\sim 3.30 \times 10^{12}$ mol C yr$^{-1}$ (or $\sim 9.04 \times 10^{9}$ mol C d$^{-1}$) from all the shelves within the GOM to Loop Current waters. Based on our calculations, the Louisiana shelf maybe a major contributor to DIC
exported to offshore waters. If we extrapolate our DIC flux estimates for the entire shelf up to the 40 m isobath, assuming the region between our WLD and BB sectors to behave similar to the BB sector, it translates to $9.7 \times 10^{10} \pm 1.2 \times 10^8$ mol C d$^{-1}$ transported across the shelf in June 2019 and $1.8 \times 10^{10} \pm 1.6 \times 10^9$ mol C d$^{-1}$ transported across the shelf in September 2019. However, this estimate for the entire shelf may not be accurate, given our focus on only two sections within the Louisiana shelf. Yet, these estimates can still provide some first order idea of DIC transport within the shallowest sections (< 20 m water depth) of the shelf, which is often understudied in most regional studies, e.g. GOMEC carried out sampling at and beyond the 20 m isobath in this region (Wang et al., 2013). Moreover, this estimate will be highly variable, not only between seasons, but also from year to year, as the river discharge is shown to play an important role in this transport.

A few studies have quantified the fluvial input of DIC into the Louisiana shelf by the Mississippi–Atchafalaya river system. Cai et al. (2003a) estimated the total DIC delivered from the Mississippi–Atchafalaya river system to the Louisiana shelf to be $1.8 \times 10^{12}$ mol C yr$^{-1}$. More recent estimates indicate the net transport of carbon in the form of DIC to coastal waters from the MSR and AR to be $1.57 \times 10^{12}$ mol C yr$^{-1}$ (Tian et al., 2015) and $4.46 \times 10^{11}$ mol C yr$^{-1}$ (DelDuco and Xue, 2019), respectively. It is difficult to make a direct comparison of these estimates of DIC river input with our current cross-shelf transport estimates. In 2019, the MSR stayed above flood stage for an unprecedented 226 days and had an annual discharge larger than the 10-year average (U.S. Geological Survey 2016; US Department of Commerce and NOAA, 2019). For example, the average discharge rates during our study period were $31.5 \times 10^3$ m$^3$ s$^{-1}$ and $10.5 \times 10^3$ m$^3$ s$^{-1}$ in June and September, while the previously mentioned study (Cai 2003a) which estimated fluvial DIC input from the MSR, experienced MSR discharge rates of $15.9 \times$
10^3 m^3 s^{-1} and 5.9 \times 10^3 m^3 s^{-1} for the same months. The difference in river discharge rates between the Cai et al. (2003a) study and our study is by a factor of three. Nevertheless, if we translate the estimated annual river input of DIC to the shelf by Cai et al. (2003a) to its average daily value, it comes to 5 \times 10^9 mol C d^{-1} entering the Louisiana shelf, which is lower by a factor of two to three than our current seasonal daily estimates of DIC transport across the shelf. The fluvial DIC input into the shelf during our study periods was likely higher than our estimated shelf transport rates, due to the uptake of DIC throughout the shelf region as a result of biological productivity and CO_2 outgassing (Xue et al., 2016).

3.7. Conclusions

Current rates of fluvial input of DIC into the coastal ocean are relatively well studied in the nGOM and, globally, rivers are estimated to contribute 0.38 to 2.6 Pg of DIC to world oceans (Lerman et al., 2007; Meybeck, 1982). However, estimates of DIC transport across shallow shelves in the nGOM and other river dominated shelves throughout the globe is sparse. DIC transport across the SE Taiwan Strait is reported to be 1.42 \times 10^{11} mol C d^{-1} (Huang et al., 2018), whereas DIC transport across the entire East China Sea is estimated to be 0.20 \times 10^{11} mol C d^{-1} (Tsunogai et al., 1997). Additionally, DIC transport across the entire South Atlantic Bight is estimated to be 0.59 \times 10^9 mol C d^{-1} (Cai et al, 2003b), suggesting the importance of DIC transport and its relation to shelf bathymetry and other environmental factors. The present study indicates that approximately 9.7 \times 10^{10} mol C d^{-1} and 1.85 \times 10^{10} mol C d^{-1} in the form of DIC is exported across the Louisiana shelf (up to 40 m isobath) during high and low river flow rates. However, more comprehensive seasonal studies need to be carried out to provide a better understanding of annual scale DIC transport. Lateral transport of DIC across the Louisiana shelf
is currently not well quantified (Coble et al., 2010) and current predictions suggest that
Mississippi-Atchafalaya river discharge to coastal waters may increase by up to 59.8% by 2090
(Tao et al., 2014), which would impact the lateral export of both DIC and nutrients to the ocean
interior dramatically in the future.
Chapter 4. Conclusion

Overall, this study investigates seasonal patterns in the distribution of DIC and TAlk and estimates the cross-shelf transport of DIC over the Louisiana shelf. These forms of inorganic carbon play a major role in shelf water quality and global carbon cycles. Concentrations of DIC compared to TAlk regulate the ability of seawater to buffer decreases in pH, leaving the shelf environment vulnerable to the effects of ocean acidification. Additionally, DIC can be transported from terrestrial systems over the continental shelves, contributing to carbon inputs to the open ocean. Thus, it is imperative that we form a better understanding of ocean margin DIC and TAlk distributions and how DIC transport rates vary on regional and seasonal scales. The goals of this study were to quantify changes in DIC and TAlk distribution and the transport of DIC in two contrasting regions of the Louisiana shelf, in terms of river influence during seasons of peak and low river discharge.

This study shows that the DIC and TAlk distributions on the Louisiana shelf between the months of June and September in 2019 were highly influenced by changes in river discharge, with additional influences from biological production. The Louisiana shelf tended to be highest in DIC:TAlk during the period of peak river discharge, when the freshwater extended farthest on the shelf. By September, a period of low river discharge, the concentration DIC:TAlk slightly decreased, with the most drastic decrease occurring in the region closest to the Wax Lake and Atchafalaya Deltas. All surface water on the Louisiana shelf during high and low river discharge seasons were supersaturated with respect to aragonite ($\Omega_A$), averaging ~3.00, though no general trend was observed between study areas or study periods. However, our reported values for DIC:TAlk were larger and our reported $\Omega_A$ values were lower than previous studies in the same region within the past two decades, indicating that the buffering strength of surface water on the
Louisiana shelf may be weakening over decadal time scales, causing the nGOM to be more susceptible to ocean acidification effects.

The DIC transport per unit volume was larger in the region of the shelf exposed to the outflow of the Wax Lake Outlet and Atchafalaya River compared to the region adjacent to Barataria Bay during peak river discharge. Interestingly, the opposite was true by September, a period of low river discharge. This present study estimates that approximately $9.7 \times 10^{10}$ mol C d$^{-1}$ and $1.85 \times 10^{10}$ mol C d$^{-1}$ in the form of DIC was exported across the Louisiana shelf (up to 40 m isobath) during high and low river flow periods. Based on our estimates, the Louisiana shelf maybe a major contributor to DIC exported to offshore waters.

This study provides a better understanding of carbon dynamics across the Louisiana shelf. This research contributes critical information for future studies attempting to understand long term effects on shelf water quality, as it pertains to ocean acidification. Additionally, this study helps to constrain the gaps in quantifying carbon fluxes to the open ocean in the northern Gulf of Mexico.
Works Cited


Coastal Protection and Restoration Authority of Louisiana. 2017. Louisiana’s Comprehensive Master Plan for a Sustainable Coast. Coastal Protection and Restoration Authority of Louisiana. Baton Rouge, LA.


Dickson, A.G. (1990) Standard potential of the reaction: AgCl(s) + 1/2H2(g) = Ag(s) + HCl(aq), and the standard acidity constant of the ion HSO4- in synthetic seawater from 273.15 to 318.15 K. *J. Chem. Thermodyn., 22*(1990),113-127


Stocker, T. F., Qin, D., Plattner, G. K., Tignor, M., Allen, S. K., Boschung, J., ... & Midgley, P. M. (2013). *Climate change 2013: The physical science basis. Contribution of working group I to the fifth assessment report of the intergovernmental panel on climate change*, 1535.


Second New Orleans District, U.S. Army Corps of Engineers, 1938

Second New Orleans District, U.S. Army Corps of Engineers Wax Lake Outlet, Constructed by the Corps of Engineers, U.S. Army (1938) (14 pp. and appendices)


National Data Buoy Center (1971). Meteorological and oceanographic data collected from the National Data Buoy Center Coastal-Marine Automated Network (C-MAN) and moored (weather) buoys. [Station GISL1 - 8761724 - Grand Isle, LA] NOAA National Centers


VITA

Michelle Marie Anderson, born in Concord, California, worked as an intern at the Guadalupe - Nipomo Dunes Center in Guadalupe, California before receiving her bachelor’s degree in Environmental Earth Science, concentrating in Geology, with a minor in Anthropology/Geography from California Polytechnic State University, San Luis Obispo. Upon completion of her master’s degree, she will enter the workforce as an environmental scientist in the field of coastal and ocean sciences.