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From the River to the Gulf: An Investigation of Biogeochemical Cycling in Wetland Soils and Coastal Shelf Sediments

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FROM THE RIVER TO THE GULF:
AN INVESTIGATION OF BIOGEOCHEMICAL CYCLING
IN WETLAND SOILS AND COASTAL SHELF SEDIMENTS

A Thesis
Submitted to the Graduate Faculty of the
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ABSTRACT

Louisiana is home to 40% of the coastal wetlands in the lower 48 states, yet accounts for 80% of the coastal wetland loss in this region. This loss is attributed to decreased sediment supply, levee alteration, sea level rise, channelization, and subsidence. The levee system in Louisiana disconnected coastal wetlands from the main stem of the Mississippi River (MSR), reducing the amount of land-building sediment that reaches coastal wetlands. This disconnection also allows a greater percentage of river discharge, including agricultural contaminants and runoff, to flow into the northern Gulf of Mexico (NGOM).

The 2012 Coastal Master Plan proposed eight sediment diversions to combat coastal land loss within Barataria and Breton Basins. The Mid-Barataria Sediment Diversion (MBSD) is projected to divert up to 2,100 m$^3$ s$^{-1}$ of sediment-laden water into degraded areas of Barataria Basin. In Chapter 1, we aim to quantify the effects of incoming river water temperature from the MBSD on nitrate removal in marsh and bay sediments within Barataria Basin. Results show that influx of colder river water limited nitrate removal processes from 5-14°C, before increasing 2-fold in 20°C treatments. Findings from this study can inform restoration modelers of the net impact of the MBSD on Barataria Basin.

Nitrate removal properties of coastal wetlands are becoming increasingly important as hypoxia remains an issue for the NGOM. Excess N and P from the MSR has led to a seasonally present hypoxic area with <2 mg/L O$_2$ in bottom waters, approximating 26,000 km$^2$ in 2017. Under low oxygen conditions, sedimentary P can become an internal source to marine systems through iron reduction. Benthic P flux can potentially combine with excess N in the water column to support primary production and possibly prolong hypoxia. In Chapter 2, we aim to quantify the significance of P mobilization in the NGOM. Despite variations in seasons of
sediment collection, bottom water oxygen concentrations, and differences in P pool concentrations, there was no benthic P flux into the water column. This is the first study to report P speciation in NGOM sediments coupled with benthic P flux rates on a spatial and temporal scale.
CHAPTER 1. INTRODUCTION

1.1. Biogeochemical Importance of Wetlands

Wetland environments are extremely valuable to the terrestrial and aquatic systems that they lie between, and they are protected and preserved by several national and international policies. In 1972, Congress passed the Clean Water Act, which was the first legislation aimed at protecting waterways and wetlands across the United States. Wetlands provide shoreline and floodwater protection, food and shelter for wildlife and fisheries, carbon sequestration, and water quality enhancement through biogeochemical cycling. Wetlands are of such value because their unique soil and hydrological characteristics allow them to act as filters for contaminants that otherwise would pollute adjacent terrestrial and aquatic environments.

Because wetlands are inundated with water for some part of the year, anaerobic conditions typically develop near the surface of the soil. These unique environmental conditions are ideal for microbial organisms, allowing them to process nutrients and contaminants through the oxidation-reduction reactions of organic matter degradation. These processes can transform nutrients into bioavailable forms and remove contaminants or excess nutrients, such as those from the Mississippi River or from atmospheric deposition, from the system. The nitrate removal capacity of wetlands is growing exceedingly important as hypoxia and eutrophication become important issues for coastal Louisiana.

Wetlands are some of the most biologically productive ecosystems in the world. Many forms of biota are supported by wetlands, including numerous species of plants, mammals, birds, invertebrates, reptiles, amphibians, and fish. Humans are also supported by wetlands. The Louisiana Coastal Wetlands Conservation and Restoration Task Force estimated that Louisiana’s wetlands exceed $100 billion in ecosystem services and infrastructural developments. Out of
every 100 jobs in Louisiana, one is attributed to the fishing industry (Southwick and Associates, 2008), and approximately 16% of the national fisheries, shrimp, crab, crawfish, and oyster harvest comes from the Louisiana coast (USDOC 1996). However, Louisiana’s valuable wetlands are facing serious threat from coastal land loss – approximately an entire football field is lost every 100 minutes (USGS 2017).

1.2. Wetland Restoration

Coastal Louisiana was formed from a series of lobe-shaped sediment deposits from the Mississippi River, creating the Mississippi Deltaic Plain. Currently, the Mississippi River deposits sediment along the Louisiana coast via the Atchafalaya Basin and offshore along the continental slope at the Plaquemine-Balize delta. Humans have altered the natural process of the deltaic lobe system by constructing levees along the Mississippi River. In addition to the levee system, anthropogenic influences have limited sediment deposits by 50% from the input of locks and dams along the northern portions of the Mississippi River (Blum and Roberts, 2009). Across the globe, sea level is rising at an average rate of 3-4 mm/year (IPCC, 2014). However, sea level is rising at a rate of 10 mm/year on the Louisiana deltaic coast due to decreased sediment supply from upstream damming of the Mississippi River, hydrologic alteration from levees, channelization for marine transportation, and subsidence (DeLaune and White, 2012). Louisiana is home to 40% of the nation’s coastal wetlands, yet accounts for 80% of the nation’s coastal wetland loss (Williams et al. 1997). Figure 1.1 depicts recent land loss and gain since 1932 and projects future land loss up to 2050.

To combat coastal land loss, the Coastal Protection and Restoration Authority (CPRA) developed the first Coastal Master Plan in 2007 to quantify and report coastal restoration needs to the public. This plan is updated every 5 years to report restoration progress and future projects.
The 2012 Coastal Master Plan for Louisiana proposed eight sediment diversions to enhance and build coastline and wetlands within Barataria and Breton Basins which flank the Mississippi River Delta. Through heavy investment in coastal restoration projects like sediment diversions, federal and state entities aim to promote the rebuilding effort as freshwater and Mississippi River sediments are supplied to degraded areas. The Mid-Barataria Sediment Diversion (MBSD) is the first large sediment diversion project to take place in Louisiana. The MBSD is a $1.3 billion restoration project that is currently in the design and permitting phase. Once built, it will divert up to 2,100 cubic meters per second of sediment-laden water directly into Barataria Basin.

Figure 1.1. 100 years of wetland change in coastal Louisiana (USGS).

1.3. Nutrient Loading from the Mississippi River

The Mississippi River is the largest river in North America and the third largest in the world. Coastal Louisiana relies on the Mississippi River for trade, transportation, land-building sediment, and nutrient delivery to coastal wetlands and the Gulf of Mexico. Discharge from the Mississippi River is the major source of Nitrogen (N) and Phosphorus (P) to the Northern Gulf of Mexico (NGOM) coastal shelf system. These nutrients primarily stem from agricultural runoff,
as the Mississippi River drains approximately 41% of the conterminous United States, 58% of which is agricultural crop land (Figure 1.3). In the early 1900s, the Haber-Bosch process was invented, creating a cost-effective way to mass produce nitrogen fertilizers and sustain maximum crop yields. From this invention, the amount of bioavailable N has doubled through N fixation by microbial organisms (Vitousek, 1997). According to the EPA Report on Environment (ROE), the use of nitrogen fertilizers has nearly tripled since the 1960s to supply a growing population and sustain a shift to large-scale commercial farming (Figure 1.2).

In 2011, the average consumption of commercial fertilizers in the U.S. was 22 million tons (USDA, 2016), 7 million of which were applied within the Mississippi River Basin (Goolsby and Battaglin, 2000). In the spring of 2016, approximately 127,000 metric tons of N and 5,400 metric tons of P were discharged from the Mississippi River and Atchafalaya River Drainage Basins into the NGOM (USGS Toxic Substances Hydrology Program). This excess nutrient loading has led to record-high concentrations of nitrate in the Mississippi River, ultimately leading to coastal eutrophication and the Gulf of Mexico “Dead Zone.”

![Figure 1.2. Commercial fertilizer use in the U.S., 1960-2011, based on data from the USDA Economic Research Service. (EPA ROE, n.d.)](image-url)
Excess loading of phosphorus (P) and nitrogen (N) into aquatic systems leads to degradation of water quality and diminished important ecosystem services. In the NGOM, excess N and to a lesser extent, P, from the Mississippi River has led to a seasonally present hypoxic area with less than 2 mg/L O$_2$ in bottom waters, approximating 26,000 km$^2$ in 2017. In the previous year, the hypoxic zone measured 16,760 km$^2$, holding the 2017 measurement as the largest hypoxic zone on record in the NGOM (Figure 1.4).

As discussed above, excess P and N loading from the Mississippi River causes eutrophic conditions that ultimately restrict oxygen from entering the water column (Rabalais 2002). Increased nutrient uptake by phytoplankton and subsequently high rates of microbial respiration result in quick turnover rates of oxygen at the water's surface (Bianchi 2007). Continuous degradation of sinking dead phytoplankton and zooplankton fecal pellets further limits oxygen in bottom waters (Bianchi 2010). Oxygen depletion in bottom waters can severely disrupt benthic communities and has been shown to adversely affect several species of fish (Pavela et al, 1983).
1.5. Phosphorus Cycle

Phosphorus (P) availability is essential to all trophic levels as plants, animals, and microbes rely on this essential macronutrient to drive primary production. In a river-dominated system, the most abundant form of P is particulate organic matter, which is recycled by microbial processes into bioavailable, inorganic compounds. Following remineralization, P is primarily bioavailable as soluble reactive phosphate (HPO$_4^{2-}$) in marine environments and orthophosphate (H$_2$PO$_4^-$, HPO$_4^{2-}$, or PO$_4^{3-}$) in wetland environments (M.L. Delaney 1998; Reddy and Delaune, 2008). Major external sources of P to coastal shelf systems include riverine input, agricultural runoff, and atmospheric deposition from dust (Froelich 1982). External sources of P to wetland environments also include atmospheric deposition and agricultural runoff, with the addition of plant biomass P and litter fall (Reddy and Delaune, 2008).

Internal sources of P in marine systems include organic matter degradation by microbial organisms and several storage mechanisms such as mineral formation with Iron, Aluminum, Calcium, and Magnesium (Ruttenberg, 1993). Under low oxygen conditions, sedimentary P can
act as an internal source to marine systems through the reduction of iron oxyhydroxides or the
dissolution of manganese oxides (McManus, 1997; Filippelli, 2008). Internal sources of P in
wetland environments are similar to those in marine environments, and can include
remineralization of organic P from peat accretion and storage mechanisms such as Iron,
Aluminum, and Calcium mineral formations (Reddy and Delaune, 2008).

In a P limited system, low P availability can limit primary production and potentially
reduce Carbon (C) sequestration in marine sediments. Alfred Redfield’s well-established
Redfield ratio showed the C:N:P ratio of particulate organic matter to be 106:16:1, holding N as
the limiting nutrient for primary production in marine environments. However, P limitation is
heavily overlooked, as P has been shown to limit primary production of phytoplankton across a
variety of coastal and open ocean environments in the presence of excess N loading, like that of
the NGOM (Fourquarean et al. 1992, Cotner et al. 1997). The approximate N:P ratios discharged
from the Mississippi River into the NGOM for May 2016 and August 2016 were 24:1 and 15:1,
respectively (USGS Toxic Substances Hydrology Program). Especially in spring months when
discharge is high, benthic flux of P can potentially combine with excess N in the water column to
support primary production and potentially prolong hypoxia. This can have further adverse
impacts on the marine ecosystem if the plume extends further out into the deep ocean where P is
highly limited.

Sedimentary phosphorus dynamics in the continental margin are highly complex as
oxygen concentration, carbon oxidation, oxygen penetration, and iron cycling can have varying
influences on benthic P flux into the water column (McManus, 1997). Although there is a large
body of evidence supporting benthic P flux in low oxygen environments (Ingall and Jahnke,
1994, 1996), low carbon oxidation could result in a negative P flux as iron oxyhydroxides form
near the sediment-water interface (McManus, 1997). Understanding the organismal need of various P pools is also crucial to conceptualizing nutrient limitation of these ecosystems and the potential impact of benthic P flux.

1.6. Nitrogen Cycle

Nitrogen (N) is also an essential macronutrient that plays a major role in regulating primary production in coastal marine environments. Inputs of Nitrogen (N) into aquatic systems includes atmospheric N\(_2\) fixation by microbial organisms, N sourced from agricultural runoff or wastewater, dry and wet deposition, and N from detrital sources such as plants and animals. Wetlands act as a reservoir for N and a buffering system, blocking excess N from entering marine environments. Wetlands can retain and store N through plant and microbial biomass, soil organic matter and pore water, and clay fixed NH\(_4\)-N. Outputs of N in wetland systems include ammonia volatilization, hydrologic outflow, gaseous losses through denitrification, and plant harvest (Reddy and Delaune, 2008). N dynamics are similar in wetland and marine coastal shelf environments. However, N can be limiting in wetlands that are not directly fed from a riverine system, and N cycling in marine environments can be limited by the disparity between the water column volume and amount of C available in marine sediments.

N cycling can be limited by C content in the soils and organic matter decomposition, as much of the N in organic matter and detritus is bonded to C. Through organic matter decomposition, organic N forms are converted to ammonia through Ammonification, or Nitrogen Mineralization. The released ammonia can be quickly utilized by nitrifying organisms to form nitrite (NO\(_2\)) and then nitrate (NO\(_3\)). This process is called Nitrification (Reddy and Delaune). Through microbial respiration of organic matter, NO\(_3\) is utilized as the terminal electron acceptor for C oxidation and is converted to nitrous oxide (N\(_2\)O) and eventually lost to the atmosphere as
nitrogen gas (N\textsubscript{2}). This process is called denitrification. Several environmental conditions are needed for denitrification to occur, including an anaerobic environment, vegetative growth to supply organic C, and the availability of denitrifying organisms such as Bacillus and Pseudomonas that contain the proper enzymes to perform this process (Firestone et al, 1980; Reddy and Delaune, 2008).

The following processes can occur within the N cycle in wetland environments (Figure 1.5):

1. Nitrogen Fixation: \( \text{N}_2 > \text{NH}_3 \)
2. Ammonification/N Mineralization: Organic N > NH\textsubscript{4}\textsuperscript{+}
3. Nitrification: NH\textsubscript{4}\textsuperscript{+} > NO\textsubscript{3}\textsuperscript{-}
4. Denitrification: NO\textsubscript{3}\textsuperscript{-} > NO\textsubscript{2}\textsuperscript{-} > NO > N\textsubscript{2}O > N\textsubscript{2}
5. Ammonia Volatilization: NH\textsubscript{4}\textsuperscript{+} > NH\textsubscript{3}
6. Anaerobic Ammonium Oxidation (Anamox): NH\textsubscript{4}\textsuperscript{+} > N\textsubscript{2}
7. Dissimilatory Nitrate Reduction to Ammonia (DNRA): NO\textsubscript{3}\textsuperscript{-} > NH\textsubscript{3}

**Figure 1.5.** The Nitrogen Cycle in Wetland Environments (Reddy and Delaune, 2008).
1.7. Synopsis of Chapters

Chapter 2 focuses on an investigation of denitrification in marsh soils and bay sediments that will be influenced by the Mid-Barataria Sediment Diversion. While the MBSD is projected to have a positive land-building effect, the influx of colder river water could negatively impact ecosystem services provided by the wetlands of Barataria Basin. In this controlled laboratory study, we aimed to quantify the effects of incoming river water temperature from the MBSD on the NO$_3^-$ reduction rate in marsh and bay sediments within Barataria Basin. This study was performed in part to support and enhance the basin-wide model created by the Water Institute of the Gulf. These models are used to study the overall environmental impact associated with the Mid-Barataria and Breton Sound diversions.

Chapter 3 evaluates the influence of the “Dead Zone” on biogeochemical cycling of P in NGOM coastal shelf sediments. A major goal of this study was to determine and quantify the significance of P mobilization and speciation under short-term hypoxic conditions in the NGOM. Under hypoxic conditions, P can be released from the sediment into the water column as Iron becomes reduced. This P release could potentially combine with excess N to support primary production, possibly prolonging the hypoxic season. Similarly, increased internal P supply from the coastal shelf could adversely affect the P-limited deep ocean, extending the current range of hypoxia. This study aims to eliminate some of these existing knowledge gaps and inform effective nutrient management strategies for NGOM hypoxia.
CHAPTER 2. IMPACT OF MISSISSIPPI RIVER DIVERSIONS ON DENITRIFICATION IN NEARBY MARSH AND BAY SEDIMENTS

2.1. Introduction

Across the globe, sea level is rising at an average of 3.4 mm per year (IPCC, 2014). However, sea level is rising at a rate of 10 mm/year on the Louisiana deltaic coast due to decreased sediment supply, hydrologic alteration from levees, channelization, and subsidence (DeLaune and White, 2012). Louisiana is home to 40% of the nation’s coastal wetlands, yet accounts for 80% of the nation’s coastal wetland loss (Williams et al. 1997). Louisiana’s fisheries, oil, and natural gas industries depend on the sustainability of the coastline and wetland ecosystem services. These ecosystem services include water quality improvement through microbial-mediated processes, such as denitrification. Through denitrification, denitrifying organisms convert fixed nitrogen (N) into N\textsubscript{2}O and atmospheric N\textsubscript{2} gas. The nitrate removal capacity of wetlands is becoming increasingly important as agricultural runoff has led to high concentrations of nitrate in the Mississippi River, ultimately leading to coastal eutrophication and the Gulf of Mexico Hypoxic Zone (Seo, 2008).

The 2012 Coastal Master Plan for Louisiana proposed eight sediment diversions to combat coastal land loss within Barataria and Breton Basins which flank the Mississippi River Delta. Through heavy investment in coastal restoration projects like sediment diversions, federal and state entities aim to promote the rebuilding effort as freshwater and Mississippi River (MSR) sediments are supplied to degraded areas. River control structures, channel aggradation, and overbank flow have reduced the sediment load, sand load, and water discharge rates in the MSR from Belle Chasse, Louisiana to the Head of Passes by 43%, 74%, and 44.8%, respectively (Allison et al 2012). Limited sediment availability near the Gulf of Mexico highlights the importance of capturing and diverting the MSR into adjacent basins like Barataria Basin.
The Mid-Barataria Sediment Diversion is a $1.3 billion restoration project that is currently in the design and permitting phase. Once built, it will divert up to 2,100 cubic meters per second of sediment-laden water directly into Barataria Basin. Aside from land-building potential, the diversion could also reduce saltwater intrusion and promote wetland vegetation growth in the receiving basin, which is typically a nitrogen-limited environment. This diversion could also increase the nitrate removal capacity of diversion-impacted wetlands, as increased vegetative growth provides a source of carbon that acts as an electron acceptor during denitrification (Seo et al, 2008; Kadlec and Alvord, 1989; Knight et al, 1993). Similarly, a study conducted in Barataria Bay in 2008 concluded that lowered salinity from a legacy diversion allowed for increased nitrate removal in Barataria Basin estuaries (Seo et al, 2008).

While the Mid-Barataria Sediment Diversion is projected to have a positive land-building effect within the receiving basin, the higher water discharge rates and the influx of colder river water could negatively impact ecosystem services provided by the wetlands of Barataria Bay. Higher discharge rates of diverted river water could reduce the residence time of water in Barataria Bay, possibly muting denitrification. A 2006 study in the legacy Davis Pond diversion in northern Barataria Basin found that nitrate removal capacity was highest at a low water discharge rate and higher retention time (Yu et al, 2006). Similarly, since temperature regulates the diffusion of oxygen at the sediment-water interface, the depth of the sediment anoxic layer where denitrification occurs can be limited by colder, oxygen-rich water (Lindau, 2008; Rivera-Monroy, 2010). A $Q_{10}$ temperature coefficient for denitrification is not well established in the literature. This can be difficult to calculate, as the effect of temperature on microbial respiration and organic matter decomposition varies depending on the availability of electron acceptors and substrates and the intensity of anaerobic conditions (Reddy and DeLaune, 2008). A quantitative
impact of river water temperature on denitrification in diversion-impacted marshes is also lacking in the literature. A 2013 study modeled the denitrification capacity of various Louisiana ecosystems using rates reported in the literature from 1981-2011 to estimate nitrate removal under different restoration scenarios (Rivera-Monroy et al, 2013). While useful, this study highlights the need for a consensus on if wetland restoration will enhance or limit the denitrification capacity of wetlands. In this study, we aim to quantify the effects of incoming river water temperature from the Mid-Barataria Sediment Diversion on denitrification in marsh and bay sediments within the receiving basin, Barataria Bay. Marsh and bay cores were chosen to determine a relationship in nitrate reduction across different sediment types that will be impacted by the MBSD. VanZomeren 2012 found that, when marsh vegetation was removed, nitrate reduction occurred faster in bay sediment than marsh soils. We hypothesize that incoming river water temperature will result in slower denitrification processes in Barataria Bay, especially nearest to the inflow where temperatures fall below 10°C. This study was performed in part to inform the basin-wide model created by the Water Institute of the Gulf. These models are used to study the overall environmental impact associated with the Mid-Barataria and Breton Sound diversions.

2.2. Materials and Methods

2.2.1. Sampling Sites

Four triplicate sets of intact sediment cores were collected from one bay bottom site and one marsh site in Barataria Bay on June 12, 2018, resulting in 24 cores total. Sampling sites were located approximately 5.4 miles from the proposed inflow location of the Mid-Barataria Sediment Diversion project to ensure that the sampling site would not be impacted by the initial scour created from the diversion opening (Figure 2.1). The marsh site was located at latitude
29°33”57.2 N and longitude -89°59”37.3’S, and the bay site was located at latitude 29°33”30.64’N and longitude -89°59”48.41’S. Sites were selected based on water temperature predictive models created by the Water Institute of the Gulf (Baustian et al 2018). These models were created to show how the water temperature of various locations in Barataria Bay will change following the opening of the MBSD.
Figure 2.1. Map of sampling sites (marsh and bay) in relation to the proposed inflow location of the Mid-Barataria Sediment Diversion Project.
2.2.2. Experimental Design

Immediately following collection, sediment cores were covered with plastic to facilitate O\textsubscript{2} exchange and transported back to Louisiana State University. Upon arrival, overlying site water was drained from each sediment core, and filtered site water was added until reaching 15 cm depth. Six intact cores (3 marsh and 3 bay bottom) were placed in four separate water bath incubators that were set at 5, 8, 14, and 20°C. Incubation temperatures (5, 8, 14, and 20°C) were selected as the environmentally relevant temperatures proposed by the Water Institute of the Gulf models. Each incubator was located within a low-light environment to prevent algal growth that could potentially alter N reduction rates. All cores were left undisturbed for three days to allow for temperature equilibration. After equilibration, nitrate standard was added to each core to create a 15 cm water column with 2 mg/L NO\textsubscript{3}-N, which is the well-established springtime concentration used to represent the Mississippi River (USGS 2017). All 24 cores were continuously bubbled with O\textsubscript{2} throughout the duration of the experiment to ensure an aerobic water column.

Cores were incubated for 11 days. A 6 mL water sample was collected from each core on day 0, 1, 2, 4, 6, 8, 10, and 11 for a total of 8 time points. Deionized water was added when needed to account for evaporation, and water removed from sampling was replaced with 6 mL of site water. All water samples were filtered using a 0.45 μm syringe filter and immediately frozen until analysis. Temperature, dissolved oxygen (DO), pH, and salinity measurements were taken within each water column before and after incubation using a YSI 556 Multi-Probe meter to ensure stability during the experiment. Water bath temperatures were monitored 3 times per day until cores were extruded on day 11. Following incubation, all 24 cores were sectioned in 0-5 and 5-10 cm intervals and analyzed for soil physicochemical properties, extractable nutrients,
and denitrification potential.

2.2.3 Soil Physicochemical Properties

Samples were homogenized, dried, and ground to measure bulk density, moisture content, percent organic matter (%OM), Total Carbon (TC), Total Nitrogen (TN), and Total Phosphorus (TP). Moisture content and bulk density were measured after drying each sample at 70°C until reaching a constant weight. %OM and TP were determined after combustion of each sample at 550°C for 4 hours. TC and TN were measured using an Elemental Combustion System with a method detection limit of 0.005 g kg\(^{-1}\). Total Phosphorus (TP) was measured using the ashing method by Anderson, 1976, and analyzed on a SEAL AQ2 Automated Discrete Analyzer (SEAL Analytical, West Sussex, England).

Extractable \(\text{NH}_4^+\), SRP, and \(\text{NO}_3^-\) were measured through KCl extraction. Approximately five grams of all homogenized 0-5 cm and 5-10 cm sediment samples were placed in 40 mL centrifuge tubes and 20 mL of KCl was added. The tubes were shaken in a longitudinal shaker for 1 hour, centrifuged, and vacuum filtered through a 0.45 \(\mu\)m filter. Extraction samples were measured on a SEAL Analytical AQ2 Automated Discrete Analyzer.

2.2.4 Potential Denitrification Capacity

Denitrification potential was measured on the top 0-5 cm of sediment for two triplicate sets of marsh and bay cores, for a total of six samples. Each sample was homogenized and added to an aluminum crimped and \(\text{N}_2\)-purged glass serum bottle. \(\text{N}_2\)-purged site water, an acetylene inhibitor, and 2 mg \(\text{NO}_3^-\)-N L\(^{-1}\) were then added to the serum bottles (White and Reddy, 1999). This nitrate concentration represents levels found in Mississippi River water. Samples were incubated in the dark on a longitudinal shaker at room temperature. The headspace was sampled every 4-6 hours for \(\text{N}_2\text{O}\)-N and analyzed on a Shimadzu GC-8A ECD (Shimadzu Scientific...
Instruments, Columbia, MD). Concentrations of N₂O-N were plotted over incubation time to create a denitrification potential rate.

2.2.5. **Water column measurements**

All water samples were analyzed for NH₄⁺, NO₃⁻, and SRP using a SEAL Analytical AQ2 Automated Discrete Analyzer with method detection limits of 0.012, 0.014, and 0.005 mg L⁻¹, respectively. The rate of nitrate loss was measured in each water column to calculate areal N reduction rates. Nitrate reduction rates are expressed as mg N m⁻² day⁻¹.

2.2.6. **Q₁₀ Assessment**

Q₁₀ coefficients were calculated across all four temperature treatments (5, 8, 14, and 20°C) using the Arrhenius equation (Equation 2.2) (Reddy and DeLaune, 2008). This function is commonly used to evaluate a biogeochemical response to 10°C temperature change.

\[
Q_{10} = \left( \frac{R_2}{R_1} \right)^{\frac{10}{T_2-T_1}}
\]

**Equation 2.2.** The Q₁₀ function, or Arrhenius equation.

2.2.7. **Statistical Analysis**

A paired t-test was used to determine a relationship between bay and marsh cores from each separate temperature treatment. An ANOVA was used to determine a relationship between all marsh cores (5, 8, 14, and 20°C) and all bay cores (5, 8, 14, and 20°C). All P values less than 0.05 were considered significant.

2.3. **Results**

2.3.1. **Study Site Environmental Conditions**

At the marsh site, water temperature measured 27.8°C and salinity 4.4 PSU. Dissolved oxygen was at 63% saturation, or 4.83 mg O₂ L⁻¹, and pH measured 7.28. At the bay site, water
temperature measured 28.63°C and salinity 5.5 PSU. Dissolved oxygen measured 72.9% saturation, or 5.42 mg O₂ L⁻¹, and pH measured 7.19.

### 2.3.2. Soil Physicochemical Properties

Moisture content was significantly higher (p<0.001) at 85.4 ± 0.02% in marsh soils compared with 73.8 ± 0.02% in bay sediments. Bulk density was significantly higher (p<0.001) in bay sediments than in marsh soils and averaged 0.33 ± 0.04 g cm⁻³ and 0.17 ± 0.02 g cm⁻³, respectively. Percent organic matter (%OM) was significantly higher (p<0.001) in marsh soils than bay sediments and averaged 50.44 ± 8.12% and 19.60 ± 5.64%, respectively. Total C, Total N, and Total P were significantly higher in marsh soils than bay sediments (p<0.001). There was no significant difference in Total C, Total N, or Total P across temperature regimes or between surficial (0-5 cm) and subsurface (5-10 cm) sediments (Table 2.1).

Extractable NH₄⁺ was significantly different between marsh and bay cores (p=0.0003) and between surficial (0-5cm) and subsurface (5-10cm) sediments (p=0.0009). Extractable NH₄⁺ was not significantly different between temperature treatments in marsh soils or bay sediments. On average, surficial sediments measured 38.69 ± 11.57 mg NH₄-N kg⁻¹ in marsh soils and 47.19 ± 13.25 mg NH₄-N kg⁻¹ in bay sediments, and subsurface sediments measured 45.31 ± 23.36 mg NH₄-N kg⁻¹ in marsh soils and 94.69 ± 23.78 mg NH₄-N kg⁻¹ in bay sediments. Extractable NO₃⁻ was significantly different between marsh and bay surficial sediments (p<0.0001), but not significant between temperature treatments. On average, surficial (0-5 cm) marsh soil measured 3.78 ± 1.24 mg NO₃-N kg⁻¹, and surficial bay sediments measured 1.68 ± 0.44 mg NO₃-N kg⁻¹.
Table 2.1. Average Total C, Total N, and Total P in marsh soils and bay sediments (g kg\(^{-1}\))

<table>
<thead>
<tr>
<th>Soil Property</th>
<th>Marsh Soils</th>
<th>Bay Sediments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Carbon</td>
<td>247.91 ± 42.98</td>
<td>99.26 ± 32.07</td>
</tr>
<tr>
<td>Total Nitrogen</td>
<td>14.73 ± 2.47</td>
<td>6.25 ± 1.95</td>
</tr>
<tr>
<td>Total Phosphorus</td>
<td>0.59 ± 0.06</td>
<td>0.51 ± 0.04</td>
</tr>
</tbody>
</table>

2.3.3. Soil Property Relationships

In marsh soils, Total C was positively correlated with TN (0.77), %OM (0.90), and moisture content (0.45). In bay sediments, Total C was positively correlated with TN (0.95), %OM (0.78), moisture content (0.71), and extractable NH\(_4\) (0.56) and negatively correlated with bulk density (-0.40). (Tables 2.2-2.3).

Table 2.2. Correlation coefficients for soil physicochemical properties in marsh soils. Bolded values indicate significance at p < 0.01.

<table>
<thead>
<tr>
<th></th>
<th>TP (g/kg)</th>
<th>TN (g/kg)</th>
<th>TC (g/kg)</th>
<th>%OM</th>
<th>Moisture content %</th>
<th>Bulk density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP (g/kg)</td>
<td>0.33</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TN (g/kg)</td>
<td></td>
<td>-0.06</td>
<td>0.77</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TC (g/kg)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>%OM</td>
<td>0.07</td>
<td>0.64</td>
<td>0.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moisture content %</td>
<td>0.18</td>
<td>0.49</td>
<td>0.45</td>
<td>0.52</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bulk density (g/cm³)</td>
<td>0.05</td>
<td>-0.09</td>
<td>-0.27</td>
<td>-0.39</td>
<td>-0.64</td>
<td></td>
</tr>
<tr>
<td>Extractable NH(_4) (g/kg)</td>
<td>0.11</td>
<td>0.13</td>
<td>0.06</td>
<td>-0.06</td>
<td>-0.2</td>
<td>0.37</td>
</tr>
</tbody>
</table>

Table 2.3. Correlation coefficients for soil physicochemical properties in bay sediments. Bolded values indicate significance at p < 0.01.

<table>
<thead>
<tr>
<th></th>
<th>TP (g/kg)</th>
<th>TN (g/kg)</th>
<th>TC (g/kg)</th>
<th>%OM</th>
<th>Moisture content %</th>
<th>Bulk density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP (g/kg)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TN (g/kg)</td>
<td>0.29</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TC (g/kg)</td>
<td>0.28</td>
<td></td>
<td>0.95</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>%OM</td>
<td>0.13</td>
<td>0.72</td>
<td>0.78</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moisture content %</td>
<td>0.16</td>
<td>0.72</td>
<td>0.71</td>
<td>0.31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bulk density (g/cm³)</td>
<td>0.1</td>
<td>-0.44</td>
<td>-0.4</td>
<td>-0.26</td>
<td>-0.62</td>
<td>-0.29</td>
</tr>
</tbody>
</table>
2.3.3. *Nitrate Reduction*

Nitrate reduction rates in marsh vs. bay cores within 5, 8, and 14°C temperature treatments were not significantly different (p=0.6). Nitrate reduction rates for 20°C bay sediments were excluded from statistical analysis due to interference from hard clams. A negative flux rate indicates NO$_3^-$ flux into the soil. From 5-20°C, nitrate reduction rates in marsh soils increased 3.6x, from -14.14 mg N m$^{-2}$ day$^{-1}$ (5°C marsh) to -50.59 mg N m$^{-2}$ day$^{-1}$ (20°C marsh) (Table 2.4, Figures 2.3-2.5). Nitrate reduction rates in marsh soils alone are significantly different among temperature treatment groups (p<0.001), and nitrate reduction rates in bay sediments are not significantly different (p=0.59) among treatments. In marsh soils, nitrate reduction rates were not significantly different from 4 to 8°C (p=0.47) or from 8 to 14°C (p=0.13) but were significantly different from 14 to 20°C (p=0.002) and between 5 and 20°C treatments (p=0.0003).

**Table 2.4.** Nitrate reduction rates across temperature treatments expressed as mg N m$^{-2}$ day$^{-1}$.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Replicate 1 (mg N m$^{-2}$ day$^{-1}$)</th>
<th>Replicate 2 (mg N m$^{-2}$ day$^{-1}$)</th>
<th>Replicate 3 (mg N m$^{-2}$ day$^{-1}$)</th>
<th>Average Rate ± Standard Deviation (mg N m$^{-2}$ day$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5°C Marsh</td>
<td>-15.30</td>
<td>-10.99</td>
<td>-16.12</td>
<td>-14.14 ± 2.25</td>
</tr>
<tr>
<td>5°C Bay</td>
<td>-19.60</td>
<td>-14.22</td>
<td>-14.74</td>
<td>-16.19 ± 2.42</td>
</tr>
<tr>
<td>8°C Marsh</td>
<td>-16.80</td>
<td>-14.10</td>
<td>-15.76</td>
<td>-15.55 ± 1.11</td>
</tr>
<tr>
<td>8°C Bay</td>
<td>-24.18</td>
<td>-17.49</td>
<td>-13.88</td>
<td>-18.52 ± 4.27</td>
</tr>
<tr>
<td>14°C Marsh</td>
<td>-15.61</td>
<td>-25.80</td>
<td>-23.20</td>
<td>-21.54 ± 4.32</td>
</tr>
<tr>
<td>14°C Bay</td>
<td>-15.78</td>
<td>-20.33</td>
<td>-23.05</td>
<td>-19.72 ± 3.00</td>
</tr>
<tr>
<td>20°C Marsh</td>
<td>-45.34</td>
<td>-54.64</td>
<td>-51.78</td>
<td>-50.59 ± 3.89</td>
</tr>
</tbody>
</table>
Figure 2.3. Average nitrate reduction rates at 5, 8, 14, and 20°C, expressed as mg NO$_3^-$ m$^{-2}$ day$^{-1}$.
Figure 2.4. Differences in nitrate reduction rates in marsh soils across all four temperature treatments, expressed as mg NO$_3^-$ m$^{-2}$ day$^{-1}$.
2.3.4. Ammonification Rate

In marsh soil temperature treatments, ammonification rate increased with increasing temperature (p=0.017) (Table 2.5). Ammonification rates in bay sediments were not quantifiable because of
the influence of hard clams (*Rangia cuneata*) that likely degraded and released excess ammonia during the incubation period.

**Table 2.5. Average ammonification rates in marsh soils, expressed as mg N m$^{-2}$ day$^{-1}$.**

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Replicate 1 (mg N m$^{-2}$ day$^{-1}$)</th>
<th>Replicate 2 (mg N m$^{-2}$ day$^{-1}$)</th>
<th>Replicate 3 (mg N m$^{-2}$ day$^{-1}$)</th>
<th>Average Rate ± Standard Deviation (mg N m$^{-2}$ day$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5°C</td>
<td>7.35</td>
<td>13.13</td>
<td>5.67</td>
<td>8.71 ± 3.19</td>
</tr>
<tr>
<td>8°C</td>
<td>13.97</td>
<td>6.73</td>
<td>14.82</td>
<td>11.84 ± 3.63</td>
</tr>
<tr>
<td>14°C</td>
<td>11.86</td>
<td>33.11</td>
<td>29.49</td>
<td>24.82 ± 9.28</td>
</tr>
<tr>
<td>20°C</td>
<td>49.65</td>
<td>66.90</td>
<td>25.61</td>
<td>47.39 ± 16.93</td>
</tr>
</tbody>
</table>

**2.3.5. Potential Denitrification Capacity**

N$_2$O production results indicate that 58-77% and 67-72% of added nitrate was converted to N$_2$O in marsh and bay sediments, respectively. Potential denitrification capacity of marsh soils was significantly greater than that of bay sediments (p=0.001) (Table 2.6). Production of N$_2$O per hour was significantly higher in marsh soils than bay sediments (p<0.001). On average, marsh soils produced 1.01± 0.04 mg N$_2$O-N kg$^{-1}$ hr$^{-1}$ and bay sediments produced 0.53 ± 0.07 N$_2$O-N kg$^{-1}$ hr$^{-1}$.

**Table 2.6. Denitrification potential capacity in triplicate marsh and bay cores over a 45-hour period, expressed as mg N$_2$O-N kg$^{-1}$hr$^{-1}$.**

<table>
<thead>
<tr>
<th>Core ID</th>
<th>Marsh Soil (mg N$_2$O-N kg$^{-1}$hr$^{-1}$)</th>
<th>Bay Sediment (mg N$_2$O-N kg$^{-1}$hr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Replicate 1</td>
<td>1.07</td>
<td>0.52</td>
</tr>
<tr>
<td>Replicate 2</td>
<td>0.99</td>
<td>0.61</td>
</tr>
<tr>
<td>Replicate 3</td>
<td>0.97</td>
<td>0.45</td>
</tr>
<tr>
<td>Average ± Standard Deviation</td>
<td>1.01 ± 0.04</td>
<td>0.53 ± 0.07</td>
</tr>
</tbody>
</table>
2.3.6. $Q_{10}$ Assessment

$Q_{10}$ results indicate that denitrification capacity increases with increasing temperature. $Q_{10}$ results were slightly linear from 5-14°C, as progression from 5-8°C, and 8-14°C in marsh soils resulted in $Q_{10}$ values of 1.28 and 1.72, and 1.57 and 1.11 in bay sediments, respectively. Differences in denitrification rates from 14 and 20°C in marsh soils resulted in a $Q_{10}$ value of 4.15, indicating that denitrification occurs 4 times faster over ten degrees within this temperature range. Values for 20°C bay sediments were not quantifiable because of interference from hard clams, discussed further in Section 2.4.

2.4. Discussion

It is well known in the literature that microbial processes are generally limited by colder temperatures. However, this can prove difficult to quantify in wetland environments, as the effect of temperature on microbial respiration and organic matter decomposition varies depending on the availability of electron acceptors and substrates and the intensity of anaerobic conditions (Reddy and DeLaune, 2008). A major goal of this study was to determine a quantitative impact of river water temperature on denitrification in diversion-impacted marshes. Based on nitrate reduction results from core incubations, we can conclude that denitrification in marsh soils and bay sediments were highly limited by the onset of colder river water. Denitrification was limited from 5-14°C before increasing 2x at 20°C. $Q_{10}$ results indicate that, if nitrate removal rates from 14°C and 20°C treatments were extrapolated over a ten-degree temperature change, denitrification would increase 4x. Therefore, it is likely that the cold river water temperatures will limit denitrification rates in areas proximal to the diversion inflow. This low removal rate will favor transport of nitrate further into Barataria bay where eutrophic conditions will be expressed. Similar eutrophic events have been observed in Lake Pontchartrain following
openings of the Bonnet Carré Spillway (Bargu et al 2011; Roy et al, 2013).

Similarly, ammonification rates increased with increasing temperature (p=0.017). This also represents a limitation to denitrification, as more NH$_4^+$ was available for nitrification at higher temperatures in marsh soils. Nitrate reduction rates in bay sediments at 20°C and ammonification rates in bay sediments were excluded from analysis because of excess NH$_4^+$ produced as *Rangia cuneata* degraded in the sediment. There was no visible pathway of denitrification in bay sediments at 20°C because of the excess NH$_4^+$ and subsequent increase of NO$_3^-$ through nitrification. *R. cuneata* mortality is significantly impacted by abiotic conditions in the water column. Findings from Cain 1973 indicate that *R. cuneata* mortality increased in low salinity – high temperature conditions, and survival was greatest in high temperature – high salinity conditions. Intact cores incubated at 20°C likely presented an environmental stressor to *R. cuneata* as salinity measured approximately 5.5 PSU.

Denitrification potential was significantly higher in marsh soils (p=0.001), and approximately 70 ± 0.002% of added nitrate was converted to N$_2$O in marsh and bay sediments, indicating that denitrification was the major pathway of nitrate removal in these sediments. Total C, TN, TP, extractable NH$_4^+$, and extractable NO$_3^-$ were significantly higher in marsh soils than bay sediments. Temperature treatments did not affect soil physicochemical properties, as all properties were not significantly different between temperatures. The C:N ratio was 16.8 in marsh soils and 15.8 in bay sediments, indicating that ammonification was greater than immobilization and microbial needs were adequately met. This C:N ratio is generally high for bay sediments, indicating that collected sediments were likely eroded from nearby marsh soils. Bay sediments had relatively high Total C and %OM, which makes them important reservoirs for supporting denitrification in Barataria Bay.
This is the first study the author is aware of that quantifies the impact of cold-water influx on intact marsh soil and bay sediment cores in this region. A previous core study evaluated nitrate reduction at 25°C in Wilkinson Bay, located 6 miles south from the current study site (Levine 2017). In this study, nitrate reduction rates were measured at -19.1 mg NO₃⁻ m⁻² d⁻¹. Nitrate reduction rates reported in this area are expectedly lower than results of this study due to the higher salinity conditions in Wilkinson Bay. A similar study evaluated nitrate reduction at room temperature in conjunction with shear stress treatments on soils collected from Wax Lake Delta (Hurst 2018). In treatments with no shear stress, nitrate reduction rates measured -27.1 mg NO₃⁻ m⁻² d⁻¹. These studies are useful in determining nitrate reduction rates and how they vary across the region. Because of this variation, a larger spatial study on the impact of colder river water on denitrification in diversion-impacted marshes would be valuable to predictive coastal restoration modelers.

Springtime represents an optimal time for opening the MBSD since the Mississippi River typically discharges the most freshwater and sediments during springtime flood peaks. From February to April of 2018, the average Mississippi River water temperature measured 11°C at Station 07374000 in Baton Rouge, LA (USGS 2016). Temperature in Barataria Bay north of Grand Isle (Station 07380251) and south of Lafite (Station 292859090004000) averaged 20.6°C and 20.9°C, respectively, for the same time period (USGS 2016). Opening the MBSD when temperatures are moderately warm during spring months will reduce the limitations on nitrate removal and the possibility of eutrophic conditions further out into the Basin. However, opening the MBSD during colder spring months would likely supply valuable sediment and nutrients to dormant estuaries that can better utilize these nutrients once the growing season begins (Peyronnin et al 2017). In turn, increasing vegetation growth would provide more available C to
support denitrification. Opening the MBSD in March could possibly balance the need for warmer Mississippi River water temperatures, maximum sediment load, and nutrient delivery prior to the growing season.

2.5. Conclusion

The purpose of this study was to provide a quantitative impact on denitrification in the receiving basin of the Mid-Barataria Sediment Diversion project. While the Mid-Barataria Sediment Diversion is projected to have a positive land-building effect within the receiving basin, this study shows that the influx of colder river water will likely negatively impact nitrate removal processes provided by the wetlands of Barataria Bay. Findings from this study can inform the basin-wide predictive diversion impact models produced by the Water Institute of the Gulf and the U.S. Army Corps of Engineers to better inform coastal managers of the net impact of the MBSD and its inflow path on the wetlands of Barataria Bay.
CHAPTER 3. SPATIAL AND TEMPORAL VARIABILITY IN SEDIMENT P DISTRIBUTION AND SPECIATION IN COASTAL LOUISIANA: IMPLICATIONS FOR HYPOXIA

3.1. Introduction

Phosphorus (P) availability is essential to all trophic levels as plants, animals, and microbes rely on this essential macronutrient to drive primary production. In a river-dominated system, the most abundant form of P is particulate organic matter, which is recycled by microbial processes into bioavailable, inorganic compounds. Following remineralization, P is primarily bioavailable as soluble reactive phosphate ($\text{HPO}_4^{2-}$) in marine environments (M.L. Delaney 1998). Major external sources of P to coastal shelf systems include riverine input, agricultural runoff, and atmospheric deposition (Froelich 1982). Riverine input is the major source of N and P to the NGOM shelf system. Approximately 127,000 metric tons of N and 5,400 metric tons of P were discharged from the Mississippi River and Atchafalaya River Drainage Basins into the NGOM in May 2016, and 77,500 metric tons of N and 5,220 metric tons of P in August 2016 (USGS Toxic Substances Hydrology Program). This nutrient loading primarily comes from agricultural runoff that drains into the Mississippi River. Internal sources of P in marine systems include organic matter degradation by microbial organisms and several storage mechanisms such as mineral formation with Iron, Aluminum, Calcium, and Magnesium (Ruttenberg, 1993). Under low oxygen conditions, sedimentary P can act as an internal source to marine systems through the reduction of iron oxyhydroxides or the dissolution of manganese oxides (McManus, 1997; Filippelli, 2008).

In the NGOM, excess nutrient loading has led to a seasonally present hypoxic area, which is defined as having less than 2 mg/L $\text{O}_2$ in bottom waters. In 2017, this area was approximately 26,000 km$^2$, roughly the size of New Jersey (EPA, 2017). Although recent studies have identified
other potential drivers for NGOM hypoxia (Green et al. 2006, Bianchi 2010), eutrophication is most relevant to this study. Excess P and N loading from the Mississippi River causes eutrophic conditions that ultimately restrict oxygen from entering the water column (Rabalais 2002). Increased nutrient uptake by phytoplankton and subsequently high rates of microbial respiration result in quick turnover rates of oxygen at the water's surface (Bianchi 2007). Continuous degradation of sinking dead phytoplankton and zooplankton fecal pellets further limits oxygen in bottom waters (Bianchi 2010). Oxygen depletion in bottom waters can severely disrupt benthic communities and has been shown to adversely affect and displace several species of fish (Pavela et al, 1983). As mentioned previously, oxygen depletion in NGOM bottom waters could potentially create a positive feedback mechanism by which sediment P can be released into the water column as iron becomes reduced (Adhikari, 2015; McManus, 1997; Ingall and Jahnke, 1994). This efflux of sediment P can potentially support primary production in surface waters in late summer months when the Mississippi River discharge is relatively low (Roy et al, 2012).

Sediment P mobilization and bioavailability depends on speciation, i.e. exchangeable or loosely sorbed P, Fe-P, Authigenic-P, Detrital-P, and Organic-P. Quantifying the proportions of the different pools of P is crucial in understanding benthic P flux and the fate of buried sediment P and its impact on coastal shelf and deep ocean ecosystems. Sedimentary phosphorus dynamics in the continental margin are highly complex as oxygen concentration, carbon oxidation, oxygen penetration, and iron cycling can have varying influences on benthic P flux into the water column (McManus, 1997). Although there is a large body of evidence supporting benthic P flux in low oxygen environments (Ingall and Jahnke, 1994, 1996), low carbon oxidation could result in a negative P flux as iron oxyhydroxides form near the sediment-water interface (McManus, 1997). Understanding the organismal need of various P pools is also crucial to conceptualizing
nutrient limitation of these ecosystems and the potential impact of benthic P flux. Nutrient pools that are quickly exhausted are more necessary for primary production than nutrient pools with low turnover rates (Benitez-Nelson 2000). Therefore, measuring only the standing stock of a nutrient does not provide enough information relative to nutrient limitation. This study aims to quantify the various P pools to accurately determine the potential significance of P mobilization under short-term hypoxic conditions.

In a P limited system, low P availability can limit primary production and potentially reduce Carbon (C) sequestration in marine sediments. Alfred Redfield’s well established Redfield ratio showed the C:N:P ratio of particulate organic matter to be 106:16:1, holding N as the limiting nutrient for primary production in oceanic environments. However, P limitation is heavily overlooked, as P has been shown to limit primary production of phytoplankton across a variety of coastal and open ocean environments in the presence of excess N loading (Fourquarean et al. 1992, Cotner et al. 1997). The approximate N:P ratios discharged from the Mississippi River into the NGOM for May 2016 and August 2016 were 24:1 and 15:1, respectively (USGS Toxic Substances Hydrology Program). Especially in spring months when discharge is high, benthic flux of P can potentially combine with excess N in the water column to support primary production and potentially prolong hypoxia. This can have further adverse impacts on the marine ecosystem if the plume extends further out into the deep ocean where P is highly limited.

Several recent studies have aimed to quantify benthic P flux within of variety of locations and environmental conditions. Sudheesh 2017 found indirect evidence for P release using C:N:P analysis from sediment cores collected in near-anoxic and hypoxic conditions in the Arabian Sea shelf. Wang 2016 also found evidence for P release using the diffusive gradients in thin films (DGT) technique and 14-day near-anoxic and oxic box incubations from sediment collected in
Hongeng Reservoir. Although these studies provide useful information relative to P mobilization, analysis of how short-term hypoxic events affect P flux in river-dominated marine systems are lacking in the literature. A recent study in Barnegat Bay, New Jersey (Paudel et al., 2017), found negligible benthic P flux under 24-hr aerobic and anaerobic incubations of intact cores, but did not incubate under hypoxic conditions. While previous studies from this region have reported P-flux rates under anoxic conditions (Adhikari 2015), none have reported P speciation in these sediments coupled with benthic P flux rates and how they vary spatially and temporally with different intensities of bottom hypoxia. This current research addresses some of these existing knowledge gaps.

3.2. Materials and Methods

3.2.1. Sample collection

Sediment cores were collected from four coastal Louisiana shelf stations with increasing distance from the Mississippi River mouth on the R/V Pelican during May 2017 and August 2016, representing periods of high and low river flow regime, as well as pre and post hypoxic conditions, respectively, as bottom water oxygen data shows an increase in O$_2$ concentrations at all stations from May to August, as the breakdown of stratification typically occurs as Fall approaches. Stations were chosen by variation in salinity and are mapped according to the distance and collection year. For example, A16 represents the station closest to the river mouth in August 2016, and D17 represents the station furthest from the river mouth in May 2017 (Figure 3.1). Sediment cores were collected using a low wake MC-800 multi-corer system which usually preserves the sediment-water interface. Sediment cores were sliced at 1-centimeter intervals, weighed, homogenized, and dried. Dried sediment samples were ground and sieved through a 125-micron filter and stored in airtight containers.
3.2.2. Phosphorus fractionation

Sediment samples were sequentially extracted for various sediment bound P pools using the well-established SEDEX methodology (Ruttenberg 1992; Ruttenberg 2009). P pools extracted are operationally defined as loosely bound P, Iron bound P, Authigenic Ca/Mg bound P, Detrital P, and Organic P. Exchangeable or loosely bound P is the most reactive form, therefore it is “loosely sorbed onto sediment,” and was extracted with MgCl$_2$ that resulted in the formation of MgPO$_4$. Iron bound P was extracted through the addition of CDB, or citrate dithionite bicarbonate solution, that acts as a reducing agent of ferric iron and results in chelation by citrate. Authigenic P and Detrital P were extracted through acid dissolution by the addition of Na-acetate.
and HCl, respectively. Lastly, Organic P was extracted through dry oxidation at 550 C and HCl extraction of ashed sediment (Ruttenberg 1992; Ruttenberg 2009). An indirect measurement of TP was determined by summing all 5 pools of P (Loosely bound P, Detrital-P, Fe-P, Authigenic P, and Organic P). All P samples were analyzed using a SEAL Analytical Discrete Analyzer (SEAL Analytical Inc., Mequon, Wisconsin).

3.2.3. Intact core incubation

The NGOM can be characterized by several short-term hypoxic-to-oxic events, as mixing from storms and wind can disrupt stratification in summer months, allowing oxygen to penetrate into bottom waters. Intact sediment cores were collected from each station for short-term hypoxia incubation analysis. Immediately following sediment core recovery from each station on the R/V Pelican, triplicate incubation cores were sealed using PVC end caps to conduct a short-term incubation experiment to understand sediment oxygen consumption and benthic P flux during the transition from oxic to hypoxic conditions. The incubation processes were carried out in the laboratory onboard the R/V Pelican within one hour of sample collection. Overlying water was carefully siphoned out and replaced with filtered bottom water collected at the site. Filtered water was continuously mixed using a peristaltic pump. All cores were placed in a water bath matched to field temperature and monitored until reaching temperature equilibration. Every three hours, a 20 mL sample was collected for O2 and nutrient concentrations. Cores were incubated until dissolved oxygen concentrations dropped by approximately 90%. Incubation timing ranged from 12-42 hours. The benthic P flux rate was determined by dividing the P concentration in each timed sample over the total time of incubation.
3.3. Results

3.3.1. Phosphorus fractionation

For May (pre-hypoxia) sediments, SEDEX analysis indicates Organic P represents 56-66% of Sum-Total P; Loosely bound or exchangeable represents <2-12%, Detrital P represents 4-14%, Authigenic P represents 19-28%, and Fe-P represents <1-3% of Sum-Total P. August (post-hypoxia) sediments had variable proportions of P pools, as Organic P represents 39-56% of Sum-Total P; Loosely bound or exchangeable represents 6-25%; Detrital P represents <1-4%; Authigenic P represents 23-48%; and Fe-P <1-9% of Sum-Total P. Despite variability within P pools, post-hypoxia (August) sediments had significantly higher concentrations of Iron bound P at stations A, C, and D (+4-10% of Total P; p=0.02) and significantly lower concentrations of Detrital P (3-10% of Total P; p=0.008) and Organic P (10-20% of Total P; p=0.006) at all stations than pre-hypoxia (May) sediments.

Loosely bound P was significantly higher in May and August sediments at stations A and B than at stations C and D. Since Detrital and Organic P pools are not susceptible changes in dissolved oxygen, higher concentrations in May (pre-hypoxia) reflect increased nutrient and particulate flux from the Mississippi River. Iron bound P was significantly higher (+4-10%; p=0.02) in August sediments at stations A, C, and D than May sediments. Station B is also called “C6,” and is well known in NGOM hypoxia studies as having consistently low bottom water oxygen concentrations. Iron bound P results for this station are further discussed in Section 4. (Tables 3.1-3.2 and Figures 3.2-3.3) contain the P fractionation results for August 2016 and May 2017 sediments.
Table 3.1. May 2017: Relative phosphorus fraction concentrations and Sum Total P (mg P kg $^{-1}$), analyzed as an average of the top 5 cm.

<table>
<thead>
<tr>
<th>P Fraction</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loosely bound P</td>
<td>31.5 ± 13.1</td>
<td>30.6 ± 8.0</td>
<td>5.2 ± 2.6</td>
<td>8.8 ± 9.0</td>
</tr>
<tr>
<td>Iron bound P</td>
<td>0.3 ± 0.3</td>
<td>6.6 ± 5.0</td>
<td>0.5 ± 0.3</td>
<td>0.9 ± 0.5</td>
</tr>
<tr>
<td>Authigenic P</td>
<td>53.5 ± 5.7</td>
<td>63.3 ± 8.3</td>
<td>58.8 ± 11.0</td>
<td>39.8 ± 17.4</td>
</tr>
<tr>
<td>Detrital P</td>
<td>12.0 ± 3.4</td>
<td>13.8 ± 4.5</td>
<td>29.4 ± 3.3</td>
<td>22.0 ± 5.2</td>
</tr>
<tr>
<td>Organic P</td>
<td>190 ± 8.6</td>
<td>146.5 ± 14.5</td>
<td>118.3 ± 5.6</td>
<td>134.9 ± 4.4</td>
</tr>
<tr>
<td>Sum Total P</td>
<td>287.9 ± 11.3</td>
<td>260.8 ± 22.9</td>
<td>212.3 ± 13.1</td>
<td>206.5 ± 27.6</td>
</tr>
</tbody>
</table>

Table 3.2. August 2016: Relative phosphorus fraction concentrations and Sum Total P (mg P kg $^{-1}$), analyzed as an average of the top 5 cm.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loosely bound P</td>
<td>35.7 ± 15.1</td>
<td>25.1 ± 1.4</td>
<td>11.9 ± 3.6</td>
<td>8.8 ± 6.3</td>
</tr>
<tr>
<td>Iron bound P</td>
<td>5.5 ± 4.3</td>
<td>0.7 ± 0.7</td>
<td>12.0 ± 5.8</td>
<td>14.4 ± 3.6</td>
</tr>
<tr>
<td>Authigenic P</td>
<td>33.0 ± 5.6</td>
<td>112.9 ± 19.6</td>
<td>42.5 ± 3.6</td>
<td>45.9 ± 6.8</td>
</tr>
<tr>
<td>Detrital P</td>
<td>0.5 ± 1.3</td>
<td>4.8 ± 2.6</td>
<td>5.3 ± 2.9</td>
<td>1.3 ± 1.0</td>
</tr>
<tr>
<td>Organic P</td>
<td>68.8 ± 18.8</td>
<td>92.1 ± 10.0</td>
<td>58.8 ± 5.3</td>
<td>88.0 ± 38.2</td>
</tr>
<tr>
<td>Sum Total P</td>
<td>143.7 ± 29.4</td>
<td>235.6 ± 29.5</td>
<td>130.5 ± 12.9</td>
<td>158.4 ± 37.7</td>
</tr>
</tbody>
</table>
Figure 3.2. Temporal Variations in P-pool concentrations from stations A-D in May and August.
Figure 3.3. Phosphorus fractions from May (pre-hypoxia) and August (post-hypoxia) sediments, represented as % of Sum Total P.
3.3.2. Phosphorus flux

Results show that, irrespective of variations in P pool concentrations, seasons, or bottom water oxygen concentrations, there is no benthic P flux into the water column under short-term hypoxic conditions. Results also indicate no net flux when dissolved oxygen concentrations reach near anoxic conditions. The laboratory incubation experiment represents the upper limit of P flux compared to environmental conditions, as intact core collection reduces oxygen input from physical mixing compared to in-situ conditions. Figure 3 shows benthic P flux from stations A-D in May 2017 and August 2016 (Figure 3.4).
Figure 3.4. Benthic P Flux from Stations A-D in May 2017 and August 2016.
3.4. Discussion

3.4.1. Station Characteristics

Sampling stations were chosen based on distance from the Mississippi River mouth and corresponding salinity regimes. Salinity ranges for stations A-D are as follows: A (16 PSU), B (30 PSU), C (36 PSU), and D (33 PSU). Porewater oxygen concentrations were measured using a Unisense microprofiler that was deployed onto surficial sediments for up to 24 hours. Bottom water oxygen concentrations were lowest at Station B, at 1.56 mg/L O$_2$ in May and 1.35 mg/L in August. However, a separate shelf wide cruise from August 22-23, 2016, showed dissolved oxygen concentrations at Station B (“C6”) to be completely anoxic at 0 mg/L O$_2$. Dissolved oxygen concentrations were significantly higher at stations A, C, and D in post-hypoxic (August) waters than in May waters. Surface water temperatures at stations A-D ranged from 22-24 C in May, and from 29-30 C in August. Station characteristics for May and August are shown in Tables 3.3-3.4.

Table 3.3. Station Characteristics in May 2017.

<table>
<thead>
<tr>
<th>Station</th>
<th>Salinity (PSU)</th>
<th>Bottom water Oxygen (mg L$^{-1}$)</th>
<th>Bottom water dissolved N (µM-N)</th>
<th>Bottom water dissolved P (µM-P)</th>
<th>Oxygen penetration depth</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>16</td>
<td>3.08</td>
<td>3.72</td>
<td>1.35</td>
<td>4.90 mm</td>
</tr>
<tr>
<td>B</td>
<td>30</td>
<td>1.56</td>
<td>7.41</td>
<td>1.25</td>
<td>3.40 mm</td>
</tr>
<tr>
<td>C</td>
<td>36</td>
<td>2.70</td>
<td>2.59</td>
<td>0.92</td>
<td>5.90 mm</td>
</tr>
<tr>
<td>D</td>
<td>33</td>
<td>3.55</td>
<td>1.49</td>
<td>0.93</td>
<td>&lt; 1 cm</td>
</tr>
</tbody>
</table>
Table 3.4. Station Characteristics in August 2016.

<table>
<thead>
<tr>
<th>Station</th>
<th>Salinity (PSU)</th>
<th>Bottom water Oxygen (mg L⁻¹)</th>
<th>Bottom water dissolved N (μM-N)</th>
<th>Bottom water dissolved P (μM-P)</th>
<th>Oxygen penetration depth</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>16</td>
<td>3.41</td>
<td>0.98</td>
<td>0.73</td>
<td>5.90 mm</td>
</tr>
<tr>
<td>B</td>
<td>30</td>
<td>1.35</td>
<td>0.54</td>
<td>1.95</td>
<td>6.90 mm</td>
</tr>
<tr>
<td>C</td>
<td>36</td>
<td>4.95</td>
<td>0.55</td>
<td>0.80</td>
<td>&lt; 1 cm</td>
</tr>
<tr>
<td>D</td>
<td>33</td>
<td>4.65</td>
<td>0.30</td>
<td>0.17</td>
<td>&lt; 1 cm</td>
</tr>
</tbody>
</table>

There were no significant differences in P within the top 0-5 cm of each core, likely due to mixing and bioturbation. Presence of excess $^{234}$Th ($t_{1/2} = 24.1$ d) in the upper 3-5 cm of all cores indicates recent deposition in past ~5-6 months or mixing (Maiti et al., 2010). Previous study in this region indicate sedimentation rates of 0.70 -0.44 cm yr⁻¹ (Adhikari et al., 2016) suggesting mixing/bioturbation is the dominant process for the presence of excess $^{234}$Th.

3.4.2. Statistical Analysis

Since there were no significant differences in P fraction concentrations within the top 5 cm of each core, statistics were carried out using the average concentration of each P pool of the top 5 centimeters. We used a two-tailed t test to determine the possibility of a temporal relationship between May and August sediments. A comparison of the standard deviation of each average concentration was used to determine the possibility of a spatial relationship between stations A-D, as only one core was collected at each site.

3.4.3. Temporal Variability of P

Sum-Total P was significantly higher (110-200%; p=0.050) in May (pre-hypoxia) sediments than August (post-hypoxia) sediments. Organic P (P=0.006) and Detrital P (P=0.008) were significantly higher in concentration and in % of Total P by 10-20% and 3-10%, respectively, in
May sediments than in August sediments, likely due to higher influx of sediments, organic matter and nutrients from the Mississippi River. In August 2016, the mean discharge from the Mississippi River was 438,387 CFS (cubic feet per second). In May 2017, the mean discharge from was 1,014,000 CFS, representing over twice the river flow and likely twice the amount of N as shown in Section 1. Discharge data was taken from the USGS Station 07295100 at Tarbert Landing, Mississippi. The presence of larger algal blooms in spring months than summer months could also explain the higher concentrations of Organic P in May sediments as the Organic P pool is found to be composed of dead phytoplankton and zooplankton (Bargu 2016; Ruttenberg 1992). Similarly, excess detritus and particulate matter flowing in from the Mississippi River could explain the higher concentrations of Detrital P in May versus August sediments. Iron bound P concentrations were significantly higher (+4-10% of Total P; p=0.02) in post-hypoxic sediments at stations A, C, and D. Since the bottom water at Station B (“C6”) was completely anoxic in the late July (gulfhypoxia.net), Fe-P was likely released into the water column. This could explain the lower concentrations of sedimentary Fe-P at Station B in August. Although we expected Fe-P to be higher in post-hypoxia (August) sediments, porewater oxygen analysis shows only a 3-millimeter O₂ penetration in pre-hypoxia (May) sediments. Similarly, bottom water oxygen concentrations were significantly higher at stations A, C, and D in post-hypoxic (August) waters than in May waters. Since changes in Iron bound P are driven by oxidation-reduction reactions, we can determine a direct relationship between high oxygen concentrations and high levels of sedimentary Iron bound P. Statistical analysis showed no correlation between Loosely bound P and Authigenic P concentrations in pre and post hypoxic conditions.

3.4.4. Spatial Variation in Sediment P

Stations A-D were not significantly different from one another with respect to each of the P
pools, except loosely bound P was significantly higher at stations A and B than at stations C and D in both May and August sediments. Overall, there was no trend with P concentrations and distance from the Mississippi River mouth. This inconsistency could be a result of normal mixing due to storms and other weather events.

3.4.5. Benthic P Flux

A major goal of this study was to determine if there is any significant mobilization of P under short-term hypoxic conditions. As previously discussed, internal sourcing of P could adversely affect the NGOM and potentially prolong and increase the range of hypoxia. Results show that, irrespective of variations in P pool concentrations, seasons, or bottom water oxygen concentrations, there is no benthic P flux into the water column under short-term oxic-to-hypoxic conditions. This could be related to a number of factors, including the availability of Iron bound-P, P uptake by microbial organisms, possibly low rates of carbon oxidation, and oxygen penetration depth. Although May sediments were characterized by low oxygen conditions and limited oxygen penetration, low carbon oxidation could account for the lack of benthic P flux. Fractionation results show increased Fe-P in higher, but still hypoxic, oxygen conditions. This coincides with the possible formation of an iron oxyhydroxide layer near the sediment-water interface as discussed in McMacnus et al, 1997. We hypothesize that, only under prolonged near-anoxic or anoxic conditions coupled with high rates of carbon oxidation, will benthic P flux become significant in NGOM sediments.

3.5. Conclusion

The goal of this study was to determine the significance of P mobilization and speciation under short-term hypoxic conditions. Despite significant quantitative differences in P pools between May and August, there was no net flux of benthic P into the water column. This is the first study...
to report P speciation in NGOM sediments coupled with benthic P flux rates and how they vary spatially and temporally with different intensities of bottom water hypoxia. Supplemental information is needed to explain the possible factors contributing to the lack of P mobilization under hypoxic conditions, including carbon oxidation rates and the formation of iron complexes in these sediments.
CHAPTER 4. SUMMARY AND CONCLUSIONS

Human-induced impacts to the environment have altered Louisiana’s ecosystem at a variety of scales. Upstream damming of the Mississippi River combined with the construction of the levee system have significantly decreased the amount of land-building sediment that reaches the Louisiana coastline. Channelization for transportation, subsidence, and global sea level rise have further compounded wetland loss, placing these vital ecosystems and the Louisiana economy at risk. Wetlands provide shoreline and floodwater protection, food and shelter for wildlife and fisheries, carbon sequestration, and water quality enhancement through biogeochemical cycling. Wetlands are of such value because their unique soil and hydrological characteristics allow them to act as filters for contaminants that otherwise would pollute adjacent terrestrial and aquatic environments.

Because wetlands are inundated with water for some part of the year, anaerobic conditions typically develop near the surface of the soil. These unique environmental conditions are ideal for microbial organisms, allowing them to process nutrients and contaminants through the oxidation-reduction reactions of organic matter degradation. These processes can transform nutrients into bioavailable forms and remove contaminants or excess nutrients, such as those from the Mississippi River or from atmospheric deposition, from the system. The water quality and nutrient cycling properties of wetlands are becoming increasingly important as agricultural runoff has led to record-high concentrations of nitrate in the Mississippi River, ultimately leading to coastal eutrophication and the Gulf of Mexico “Dead Zone.”

The 2012 Coastal Master Plan for Louisiana proposed eight sediment diversions to combat coastal land loss within Barataria and Breton Basins which flank the Mississippi River Delta. Through heavy investment in coastal restoration projects like sediment diversions, federal
and state entities aim to promote the rebuilding effort as freshwater and Mississippi River sediments are supplied to degraded areas. The Mid-Barataria Sediment Diversion is a $1.3 billion restoration project that is currently in the design and permitting phase. Once built, it will divert up to 2,100 cubic meters per second of sediment-laden water directly into Barataria Basin. While the Mid-Barataria Sediment Diversion is projected to have a positive land-building effect within the receiving basin, the higher water discharge rates and the influx of colder river water could negatively impact ecosystem services provided by the wetlands of Barataria Bay.

In the study presented in Chapter 2, we aimed to quantify the effects of incoming river water temperature from the Mid-Barataria Sediment Diversion on denitrification in marsh and bay sediments within the receiving basin, Barataria Bay. To determine this effect, intact cores were collected from one marsh and one bay site within Barataria Bay. Cores were incubated in four distinct temperature treatments to determine a rate of nitrate reduction and then analyzed for various soil physicochemical properties. While the Mid-Barataria Sediment Diversion is projected to have a positive land-building effect within the receiving basin, results from this study show that the influx of colder river water limited nitrate removal processes from 5-14°C, before increasing 2-fold in 20°C treatments. $Q_{10}$ results indicate that, if nitrate removal rates from 14°C and 20°C treatments were extrapolated over a ten-degree temperature change, denitrification would increase 4x. Nitrate that is not recycled in diversion-impacted marshes will likely extend further into the bay and could possibly trigger algal growth and stimulate eutrophication. Findings from this study can inform the basin-wide predictive diversion impact models produced by the Water Institute of the Gulf and the U.S. Army Corps of Engineers to better inform coastal managers of the net impact of the MBSD and its inflow path on the wetlands of Barataria Bay.
The current state of the levee system in coastal Louisiana has disconnected coastal wetlands from the main stem of the Mississippi River, allowing a greater percentage of river discharge to enter the northern Gulf of Mexico. Because of this, excess N and P from the Mississippi River has led to a seasonally present hypoxic area with less than 2 mg/L O$_2$ in bottom waters, approximating 26,000 km$^2$ in 2017. This nutrient loading primarily comes from agricultural runoff that drains into the Mississippi River. Since 1960, the concentration of nitrate in the MSR has tripled due to the invention of cheap fertilizers and the need to feed a growing population. As the nutrient cycling properties of wetlands continue to diminish with coastal wetland loss, the NGOM is at greater risk for eutrophication and hypoxia.

The goal of the study presented in Chapter 3 was to determine the significance of P mobilization and speciation under short-term hypoxic conditions. Under low oxygen conditions such as those in the bottom waters of the NGOM, sedimentary P can act as an internal source to marine systems through the reduction of iron oxyhydroxides or the dissolution of manganese oxides. Especially in spring months when river discharge is high, benthic flux of P can potentially combine with excess N in the water column to support primary production and potentially prolong hypoxia. This can have further adverse impacts on the marine ecosystem if the plume extends further out into the deep ocean where P is highly limited.

To determine the significance of benthic P flux, intact cores and core slices were collected from four sites in the NGOM with increasing distance from the Mississippi River in May and August. Sediment cores were analyzed for oxygen consumption, organic matter degradation, porewater oxygen, and P pool concentrations. Despite variations in seasons, bottom water oxygen concentrations, and significant differences in P pool concentrations, there was no net flux of benthic P into the water column. This is the first study to report P speciation in
NGOM sediments coupled with benthic P flux rates and how they vary spatially and temporally with different intensities of bottom water hypoxia. Supplemental information is needed to explain the possible factors contributing to the lack of P mobilization under hypoxic conditions, including carbon oxidation rates and the formation of iron complexes in these sediments.
REFERENCES


EPA (Environmental Protection Agency), 2004. Evaluation of the Role of Nitrogen and Phosphorus in Causing or Contributing to Hypoxia in the Northern Gulf. U.S. Environmental Protection Agency Region 4, Atlanta, Georgia.


Wang, J., Chen, J., Ding, J., Guo, J., Christopher, D., Dai, Z., Haiquan, Y., 2016. Effects of seasonal hypoxia on the release of phosphorus from sediments in deep-water ecosystem:
A case study in Hongfeng Reservoir, Southwest China. *Environmental Pollution.* 219, 858-65.

“Water quality loading to the Gulf of Mexico through 2016.” *National Real-Time Water Quality*;
United States Geological Survey Toxic Substances Hydrology Program,
nrtwq.usgs.gov/mississippi_loads/#/GULF.


VITA

Katie Bowes grew up in New Orleans and Gretna, Louisiana, with her parents, Patrick and Julie Bowes and her brother and sister, Celeste and Cory Bowes. Katie’s hobbies mostly included volleyball, art, attending festivals, and serving on student council at her high school. Katie always had an admiration for animals, and her high school Biology class is what first peaked her interest in science.

Katie studied Natural Resource Ecology and Management at LSU from 2013-2016 and served as President of The Wildlife Society and on the Leadership Committee of the Ducks Unlimited LSU Student Chapter. During the course of her undergraduate career, she discovered her love for wetland wildlife while doing field work and lab analyses for the Coastal Ecology Lab under Dr. Megan LaPeyre. Upon graduation, Katie completed a fellowship with the United States Fish and Wildlife Service in Alaska before returning to Baton Rouge to work for an environmental consulting firm.

In January 2017, Katie decided to enroll in Master’s coursework at LSU to improve her knowledge of wetland science and expand her job opportunities. That spring, Katie met Dr. John White while taking his Wetland Biogeochemistry course. He and Dr. Kanchan Maiti soon offered her an assistantship, and the rest, as they say, is history! Katie is extremely grateful for the opportunity to continue her education and is honored to work to rebuild the Louisiana coastline that she has always called home.