The Effect of Restoration on Nitrate Reduction and Biogeochemical Functioning in Louisiana Wetlands: Bottomland Hardwood Forests and Deltaic Sediments

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THE EFFECT OF RESTORATION ON NITRATE REDUCTION AND BIOGEOCHEMICAL FUNCTIONING IN LOUISIANA WETLANDS: BOTTOMLAND HARDWOOD FORESTS AND DELTAIC SEDIMENTS

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

Nia R. Hurst
B.S., DePaul University, 2014
August 2016
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ABSTRACT

Nitrogen loading in the Mississippi River from increased N fertilization of agricultural land helps to trigger an area of hypoxic water in the northern Gulf of Mexico (GOM) every summer. Louisiana wetlands can play a vital role in removing nitrate from river waters prior to discharge in the GOM. However, Louisiana’s wetlands have experienced significant losses in recent years. Efforts to restore wetlands include reconnecting floodplain wetlands to rivers and utilizing river diversions to re-introduce sediment to coastal wetlands. Increasing wetland connection to rivers can reduce water nitrate by expanding opportunities for nitrate reduction. I examined soil physicochemical properties, microbial characteristics, and nitrate reduction rates in a hydrologically restored bottomland hardwood forest adjacent to the Ouachita River in Louisiana. Nitrate reduction rates in the restored site were only 28% lower than those in a natural site (11.8 ± 3.4 vs 16.4 ± 8.1 mg N m$^{-2}$ day$^{-1}$) (P<0.1), removing approximately 48.1 metric tons of nitrate from the Ouachita River annually. Results suggest that restoring floodplain wetlands can be useful for enhancing nitrate reduction in river floodwaters, improving water quality while reducing the areal extent of hypoxia in the northern GOM.

I also investigated nitrate reduction in turbulent surface water conditions resulting from sediment diversions. There is a paucity of data on nitrate loss in areas of diversions where turbulent conditions impart significant shear stress on the sediment surface, suspending fine grained sediments. Sediment cores were collected from Wax Lake Delta in Louisiana and subjected to shear stresses using a flow-through erosional microcosm system for 24 hrs. Nitrate reduction rates were determined under high, medium, and zero shear stress conditions of 0.45, 0.2, and 0 Pa, respectively. Nitrate reduction rates under high, low, and zero shear stresses were 303 ± 65.6, 186 ± 55.1, and 18.7 ± 20.2 mg N m$^{-2}$ day$^{-1}$, respectively (P<0.001). Rates of nitrate
reduction increased significantly with an increase in shear stress, indicating that turbulent flow conditions from river diversions can significantly increase nitrate reduction rates. Results from this research can help inform modelers in predicting potential nutrient impacts of river diversions on coastal receiving basins.
CHAPTER 1: REVIEW OF LITERATURE

1.1 Nitrogen Eutrophication

The world’s population has increased from 1.6 to over 7 billion people since the beginning of the 20th century, primarily due to increased agriculture production driven by synthetic fertilizer input (UN, 2012). The area of land on earth remains fixed, while population continues to rise, requiring more intensive and rigorous use of existing agricultural land to satiate an ever growing demand for food (Hanson et al., 2008). Application of fertilizer has allowed for increased global population growth through increased crop production and it has been estimated that half of the world’s population today could not exist without nitrogen fertilization (Erisman et al., 2008). Nitrogen fertilizers are often heavily applied to croplands to increase plant production, since nitrogen tends to be a limiting factor of primary productivity in terrestrial ecosystems (Ribaudo, 2011). Despite these gains, nitrogen pollution of our aquatic systems has become pervasive around the globe and has led to detrimental impacts on ecosystem functioning and human health (Lovett et al., 2009; Townsend et al., 2003; Rabalais, 2002a; Townsend et al., 2003). Once excess nitrogen enters aquatic systems, it can cause an exponential increase in algal population, known as algal blooms, some of which may have harmful effects. The subsequent death and decomposition of the large mass of algal material can lead to hypoxic/anoxic waters. One such area of hypoxic water can be found off the coast of Louisiana during summer months from the stimulation of algal production by nitrate loading in the Mississippi River (Rabalais, 2002).

1.2 Lower Mississippi River Alluvial Valley

The Mississippi River is the longest river in North America, at 3701 km from its headwaters in Minnesota to its terminus into the Gulf of Mexico (Kammerer, 1990). The Lower Mississippi Alluvial Valley (LMAV) runs the course of the southern portion of the Mississippi
River, which begins in Cairo, Illinois and ends in the Gulf of Mexico. The Mississippi River’s drainage basin encompasses 4.76 million km² and covers approximately 41% of the contiguous U.S and parts of Canada (Figure 1.1). The river discharges water through two outlets into the Gulf of Mexico: offshore of Louisiana at the Belize/Bird Foot Delta and through the Atchafalaya basin.

![Watershed area of the Mississippi River (NOAA)](image)

The average discharge rate of the Mississippi River at Baton Rouge is 15,192 m³ s⁻¹ (536,500 ft³ s⁻¹) (USGS Water Data). The discharge of the river can peak at over 30,000 m³ s⁻¹ (1,000,000 ft³ s⁻¹) during spring flooding (Allison and Meselhe, 2012). On average, the Mississippi River discharges 580 km³ of freshwater in the Gulf of Mexico each year and, based on a 42-year average from 1963-2005, carries with it $150\times10^6$ ton yr⁻¹ of sediment, most of
which is in the form of silt (Milliman and Meade, 1983; Meade and Parker, 1985; Keown et al., 2008). A major portion of the drainage basin is located in central United States, where the majority of crop production and fertilizer application in the nation occurs. Approximately 58% of the land in the basin is in agricultural land use, with over 7 million metric tons of fertilizer applied in the region annually (Goolsby and Battaglin, 2000). This fertilizer input, in conjunction with the over 72 million people living within the watershed, can significantly affect the water quality of the Mississippi River.

One such effect on water quality is nutrient loading. The Mississippi River has seen a dramatic increase in nitrate load in recent years. Prior to 1972, the average yearly nitrogen export (60% of total in the form of nitrate) of the river averaged around 300,000 metric tons; since 1980 this average is now 1.5 million metric tons per year (Goolsby, 1997). This nitrate pulse to coastal waters triggers a hypoxic zone in the Gulf of Mexico each summer that, in recent years, has averaged approximately 14,200 km² (Figure 1.2) (Rabalais, 2002; NOAA, 2014; EPA, 2011). It is important to determine and increase the ways that nitrogen can be removed and prevented from entering aquatic systems, given the necessity of nitrogen for agriculture, but also the negative effects of its excess. One strategy by which nitrate can be removed is through the conversion of NO₃⁻ to N₂ through denitrification, a microbial process which returns nitrate (NO₃⁻) to the atmosphere as dinitrogen gas (N₂). This process only occurs in anaerobic environments, such as those found in wetland soils and aquatic sediments, and is a critical part of the global cycling of N in wetlands (Reddy and DeLaune, 2008).
Figure 1.2: 2015 Area of Hypoxia (<2 mg L\(^{-1}\) of Oxygen) in the Northern Gulf of Mexico (NOAA)

### 1.3 The Nitrogen Cycle

The cycling of nitrogen is an important biogeochemical process occurring in wetlands (Figure 1.3). Nitrogen can exist in several forms, both organic and inorganic, though only two forms, NO\(_3^-\) and NH\(_4^+\), are readily available for plant uptake. There are several processes involved in the N cycle that introduce N into wetlands, remove N via gaseous release, or retain N in the system (Table 1.1). N\(_2\) in the atmosphere can be fixed into the soil in a form available for plant uptake through a process known as Nitrogen Fixation. Mineralization/Ammonification, Assimilation, Nitrification, Dissimilatory Nitrate Reduction to Ammonia (DNRA) and Assimilatory Nitrate Reduction to Ammonia are processes of the nitrogen cycle that retain N within wetlands. Denitrification, Anaerobic Ammonium Oxidation (ANAMOX), and Ammonia Volatilization are processes that remove N through gaseous losses. Ammonia tends to be the dominate form of nitrogen in wetland soils since it is stable in anaerobic conditions (Reddy and DeLaune, 2008).
Figure 1.3: Schematic of nitrogen cycling in wetlands (Reddy and DeLaune, 2008)

Table 1.1: Phases of the Nitrogen cycling in wetlands and their processes

<table>
<thead>
<tr>
<th>Phase of Nitrogen Cycle</th>
<th>Definition</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen fixation</td>
<td>A process mediated by the enzymes of nitrogen fixing bacteria that reduces atmospheric N$_2$ to ammonia (NH$_3$) in soil. The primary method of reducing N$_2$ to ammonia prior to the Haber-Bosch process.</td>
<td>N$_2$ $\rightarrow$ NH$_3$</td>
</tr>
<tr>
<td>Mineralization/</td>
<td>The breakdown and conversion of organic N to ammonium (NH$_4^+$). It is the main process by which plants assimilate nitrogen.</td>
<td>Organic Nitrogen $\rightarrow$ NH$_4^+$</td>
</tr>
<tr>
<td>Ammonification</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ammonia Volatilization</td>
<td>The gaseous release of NH$_3$ by conversion of NH$_4^+$ in basic soil conditions.</td>
<td>NH$_4^+$ $\rightarrow$ NH$_3$(g)</td>
</tr>
</tbody>
</table>
Table 1.1 Continued

<table>
<thead>
<tr>
<th>Phase of Nitrogen Cycle</th>
<th>Definition</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anaerobic Ammonium Oxidation</td>
<td>The anaerobic oxidation of ammonium to dinitrogen gas.</td>
<td>$\text{NH}_4^+ \rightarrow \text{N}_2$</td>
</tr>
<tr>
<td>Nitrification</td>
<td>A biological aerobic process that oxidizes ammonium ($\text{NH}_4^+$) to nitrate ($\text{NO}_3^-$)</td>
<td>$\text{NH}_4^+ \rightarrow \text{NO}_2^- \rightarrow \text{NO}_3^-$</td>
</tr>
<tr>
<td>Denitrification</td>
<td>An anaerobic, microbial enzymatic facilitated process that either completely reduces nitrate ($\text{NO}_3^-$) to dinitrogen ($\text{N}_2$) or incompletely to nitrous oxide ($\text{N}_2\text{O}$).</td>
<td>$\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2$</td>
</tr>
<tr>
<td>Assimilatory Nitrate Reduction to Ammonia</td>
<td>The reduction of nitrate to ammonium where ammonium is incorporated into vegetation.</td>
<td>$\text{NO}_3^- \rightarrow \text{NH}_3 \rightarrow \text{Protein complexes}$</td>
</tr>
<tr>
<td>Dissimilatory Nitrate Reduction to Ammonia</td>
<td>The anaerobic reduction of nitrate to ammonium under anoxic conditions.</td>
<td>$\text{NO}_3^- \rightarrow \text{NH}_3$</td>
</tr>
</tbody>
</table>

1.3.1 Denitrification

Denitrification is the primary pathway by which nitrate is removed from a wetland via gaseous losses (Reddy and Delaune, 2008). Wetlands tend to be important facilitators of denitrification, primarily due to their high organic matter content and low soil redox potential (Reddy and DeLaune, 2008). Denitrifying bacteria are facultative anaerobes and preferentially use oxygen as an electron acceptor because it provides the greatest amount of energy. However, when oxygen levels are low (<0.2 g ml$^{-1}$) and soil Eh decreases to below +400 mV, denitrifiers will utilize nitrate as the terminal electron acceptor for respiration (Budford & Bremner, 1975). Nitrate is usually completely denitrified to N$_2$, though some may only be partially denitrified and...
released as N₂O. N₂O is a greenhouse gas that has 298 times the global warming potential of CO₂ (EPA, 2014). Incomplete denitrification tends to occur where diffusion rates are high and water levels are low, allowing N₂O to escape before being reduced to N₂ (Reddy and Delaune, 2008).

The ability of a wetland to denitrify exogenous nitrate is governed by several factors, including readily decomposable organic matter (carbon) with low C: N ratios, oxygen availability, soil saturation, and the size and activity of the denitrifying population (Table 1.2) (Hunter and Faulkner, 2001; Budford & Bremner, 1975; Reddy and Delaune, 2008).

Denitrification in wetlands is often highly variable, both spatially and temporally (Hamersley and Howes, 2005; Bastviken, 2006; Bruland et al., 2006; Wall et al., 2006). Rates of denitrification may be higher where nitrification and denitrification processes are coupled closely together and at aerobic/anaerobic interfaces, which supply a steady supply of NO₃⁻ for reduction to N₂ (Jenkins and Kemp, 1984; Reddy and Delaune, 2008; Hamersley and Howes, 2005; Bastviken, 2006). A common experimental method utilized to study nitrate reduction involves incubating soil cores to measure the rate of nitrate loss over time (Groffman, et al., 2006). To better understand methods of nitrate loss, the acetylene block method and measurement of NH₄⁺ mineralization can be used to measure loss via denitrification and DNRA, respectively.

Table 1.2: Factors influencing denitrification in wetlands

<table>
<thead>
<tr>
<th>Factor</th>
<th>Influence</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Organic Matter (Carbon)</strong></td>
<td>Provides energy for microbial growth and serves as an electron donor (carbon) for nitrate reduction. Organic matter decomposition consumes oxygen and helps to create anaerobic condition.</td>
</tr>
<tr>
<td><strong>Oxygen Availability</strong></td>
<td>Denitrification only occurs in areas where oxygen is depleted (&lt;0.2mg L⁻¹), allowing facultative anaerobes to use nitrate as a terminal electron acceptor.</td>
</tr>
</tbody>
</table>
Table 1.2 Continued

<table>
<thead>
<tr>
<th>Factor</th>
<th>Influence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil Saturation</td>
<td>Increased soil saturation, or the proportion of water filled pore spaces, helps to facilitate denitrification by reducing oxygen availability in soil pore spaces.</td>
</tr>
<tr>
<td>Size of Denitrifying Population</td>
<td>The size of the microbial pool in a wetland capable of performing denitrification helps to regulate the rate of denitrification.</td>
</tr>
</tbody>
</table>

1.4 Reducing Nitrate Delivery to the Gulf of Mexico

The Mississippi River/Gulf of Mexico Watershed Nutrient Task Force has established a goal to reduce the nitrate load of the Mississippi River by 20% by 2025 to reduce the areal extent of hypoxic water creation in the northern Gulf (Mississippi River/Gulf of Mexico Watershed Nutrient Task Force, 2015). A large reduction in nitrate loading will necessitate the cooperation of all states within the Mississippi River Alluvial Valley, but increasing the opportunities for nitrate removal can significantly help reduce the river’s nitrate concentration. The removal of nitrate from the Mississippi River and its tributaries can be facilitated by denitrification in both coastal and riparian wetlands since it is widely known that these wetlands are beneficial to reducing the nutrient loads of adjacent rivers (Reddy and DeLaune, 2008; Walbridge, 1993). Bottomland hardwood forests (BLH), the dominant floodplain wetland adjacent to the Mississippi River and its tributaries, and coastal marshes can play a crucial role in reducing the nitrate load from river waters prior to reaching the Gulf of Mexico. However, the construction of 2,700 km of levees along both sides of the lower Mississippi river has limited the area of floodplain interacting with river floodwaters by 90% since the 1700’s (USGS, 1998). Historically, the Mississippi River and its tributaries would overflow their banks during spring
flooding, creating the opportunity for sediment deposition and nutrient removal, particularly nitrate, within the floodplain and coastal areas. As a consequence of channelization, much of the Mississippi River is now funneled almost directly into the Gulf of Mexico instead of interacting with floodplain and coastal wetlands prior to discharge, transporting valuable marsh building sediment and nutrients out to the sea and helping to trigger hypoxia (Mitsch et al., 2001; Rabalais, 2002). Furthermore, both bottomland hardwoods and coastal wetlands in Louisiana have suffered significant spatial losses that also limit their opportunity to reduce nutrient delivery to the Gulf of Mexico.

1.5 Bottomland Hardwood Forests

Bottomland hardwood forests are forested wetlands located within the riparian zones of large rivers and streams in the southeast and south central U.S., spanning an area from Texas to Florida and along the Atlantic coastline (Figure 1.4). They are the dominant wetland type along the LMAV (LDWF, 2005). These forests experience alternating wet and dry periods connected to river stage, whose duration, frequency, and extent greatly influence community composition (Haynes, 2004). Trees, which are predominantly deciduous, often include species of cypress, ash, gum, and oak. Bottomland hardwoods provide a plethora of ecosystem services and functions, including habitat for wildlife and aquatic species, aquifer replenishment, water quality improvement by nutrient retention and removal, sediment removal, flood protection, and carbon sequestration (Walbridge, 1993). Despite the positive value of these ecosystem services, almost 80% of the BLH’s in the LMAV have been destroyed, primarily due to harvesting for timber in the late 1800’s/early 1900’s and then subsequent clearance for agriculture (Llewellyn et al., 1995; MacDonald et al., 1979). Consequently, BLH cover in the LMAV has been reduced to 2.1
million hectares from the 9.7 million in existence prior to largescale European settlement due to land conversion, (MacDonald et al, 1979; King and Keeland, 1999).

![Map of Bottomland Hardwood Forests](image)

Figure 1.4: Distribution of Bottomland Hardwood Forests in the lower midwest and southeastern United States. (Putnam et al., 1960)

### 1.5.1 Potential of Bottomland Hardwood Restoration to Reduce Nutrient Loading

Many restoration efforts are underway to restore these BLHs to their former status, given the extensive loss of BLHs and their various ecosystem services in the Southeastern U.S. Hydrologic reconnection is imperative for BLH restoration and it is crucial to understand how these restorative activities influence biogeochemical functioning (Hunter et al., 2008; Forshay and Stanley, 2005; King and Keeland, 1999). Increasing the connection between rivers and their floodplains can have a significantly positive effect on denitrification potential within a site (Forshay and Stanley, 2005). In the Tensas River Basin in northeastern Louisiana, Hunter and Faulkner (2001) found that natural and restored BLHs could remove 8.2 and 5.7 g NO$_3^-$ kg$^{-1}$ soil yr$^{-1}$, respectively, with only a 30% difference in denitrification capacities between the sites.
Additionally, soils in BLHs of the Cache River in eastern Arkansas successfully removed 59-82% of nitrate received over 40 days (DeLaune et al., 1996). If given access to flood waters through hydrologic reconnection and restoration, bottomland hardwood forests located in the LMAV could play a crucial role in removing nitrate from surface waters. Evaluating the effectiveness of hydrologic restoration of BLHs in the LMAV can provide significant insight on their contribution to nutrient removal from the Mississippi river and its tributaries.

1.6 Coastal Wetlands in Louisiana

Similar to Bottomland Hardwood Forests, Louisiana’s coastal wetlands provide an abundance of ecosystem services, including water retention, flood prevention, nutrient transformation and removal, water quality improvement, carbon sequestration and storage, and buffering from storms and hurricanes, generating billions of dollars for Louisiana’s economy (LDNR, 1997; LDWF, 2006). In addition to anthropogenic services, wetlands supply habitat and food to native plant, wildlife, and aquatic species as well as ideal habitat for over-wintering waterfowl (Richardson, 1994). However, Louisiana’s coastal wetlands are experiencing a high rate of loss, despite persistent research outlining the benefits of these unique and vital areas (Figure 1.5). Louisiana’s coastal wetlands comprise 25% of all wetlands in the U.S. and 40% of coastal wetlands, but accounts for 80% of all wetland loss in the nation (Thorne et al., 2008). Between 1932 and 2010, Louisiana lost over 4800 km² (1883 mi²) of coastal land, most of which were comprised of wetlands (Couvillion et al., 2011). Rates of coastal land loss vary depending on the time period studied, but recent rates (1985-2010) of wetland loss have been observed at 43 km² yr⁻¹ (16.7 mi²) (Couvillion et al., 2011).

The degradation and land loss of coastal Louisiana are the result of several factors, both natural and anthropogenic. Natural causes range from subsidence and sea level rise, while
anthropogenic causes include reducing sediment delivery to the coast and oil and gas extraction. Salt water intrusion to freshwater and brackish marshes, facilitated by canal dredging, oil and gas extraction, storms, and rising sea levels, can create salinity stress on vegetation in freshwater and brackish marshes, resulting in marsh deterioration. Subsidence, the process by which land gradually settle, heavily influences land loss in Louisiana. The causes of subsidence are primarily due to natural compaction, dewatering, fluid withdrawal, and oil and gas extraction (Yuill et al., 2009). Subsidence rates as high as 35 mm per year have been observed in coastal LA (Boesch et al., 1983; CPRA, 2012). Wetland loss is exacerbated when the effects of subsidence are combined with eustatic sea level rise. Recent global sea level is, on average, 3.2 mm each year, but relative sea level rise is 10 mm per year in coastal Louisiana due to subsidence (Boesch et al., 1983; Morton et al., 2005; DeLaune and White, 2012; IPCC 2014). Consequently, relative sea level rates in Louisiana are among the highest in the world (Day et al., 2000; Gagliano et al., 1981).

Figure 1.5: Historic and future land loss/gain in coastal Louisiana (USGS, National Wetlands Research Center)
1.6.1 Loss of Sediment Delivery to Coastal Wetlands

Reduction in sediment delivery to coastal areas has reduced wetland accretion rates in the face of increasing sea level rise. The Mississippi River has undergone extensive channelization and damming over the last century and, while these activities have facilitated navigation and provided flood control, these measures have significantly reduced sediment and nutrient delivery to Louisiana’s coastal wetlands (Meade and Parker, 1985; Poore, 2006; Thorne et al., 2008; Blume and Roberts, 2012). Sediment discharge of the lower Mississippi has decreased significantly, with some estimates as high as 70% since the early 1900’s (Meade and Parker, 1985; Kesel, 1988; Keown et al., 1986; Thorne et al., 2008; Blume and Roberts 2012). Between 1963 and 1981, Keown et al. (1981) estimated that the average suspended sediment load of the lower Mississippi river decreased from 427*10^6 tons yr\(^{-1}\) to 251*10^6 tons yr\(^{-1}\). The greatest decline in suspended sediment load occurred during the 1950’s and 60’s, which is likely the result of an increase in dam construction during the same time (Kesel, 1988). Over 50,000 dams and reservoirs have been constructed along the Mississippi River’s drainage basin, trapping sediment and reducing the amount of sediment delivered to coastal Louisiana (Kesel, 1988; Graf, 1999; Syvitski and Milliman, 2012). Levees also substantially decrease erosion and sediment loss from floodplain areas, further reducing sediment delivery (Kesel, 1988; USGS, 1999).

Current rates of sediment delivery and marsh accretion in the coastal zone are not sufficient to keep pace with sea level rise, causing submergence and marsh loss (Baumann, Day Jr., and Miller, 1984; Blume and Roberts, 2012). Over 1750 mi\(^2\) (4500 km\(^2\)) of wetlands could be lost over the next 50 years if no preservation and/or restoration steps are taken to stall or reverse land loss (CPRA, 2012).
1.7 Sediment Diversions

Louisiana created a Coastal Master Plan in 2012 to provide plans and solutions to address the issue of coastal land loss. The 2012 Coastal Master plan was devised to offer sustainable solutions to reduce and eventually reverse wetland loss while ensuring the protection of coastal communities. Several sediment diversions along the lower Mississippi and Atchafalaya rivers have been proposed, along with several other projects, to help slow the rate of wetland loss in coastal Louisiana by transferring sediment from the river to sediment deprived coastal marshes (Figure 1.6). Of the diversions proposed, five would be considered large-scale sediment diversions, with the potential to operate at greater than 50,000 ft³ s⁻¹, and would use up to 50% of the river’s peak flow to channel water to coastal areas (CPRA, 2012). These diversions would reconnect the Mississippi River to coastal wetlands as it would naturally prior to hydrologic alteration and disconnection by river channelization. Increased reconnection between the river and coast would build land by mimicking natural delta lobe development and providing much needed sediment for marsh accretion (Dean et al., 2014; Day et al., 2000). These diversions can deliver a significant sediment supply to eroding and subsiding Louisiana coastal wetlands and aid in marsh land development. Sediment diversions can provide a dual benefit to coastal marshes, by delivering both sediment and nutrients to coastal areas. The delivery of fine and coarse sediment can provide a foundation for marsh development, while the introduction of nutrients can provide accretion via organic matter production by enhancing marsh productivity (Teal et al., 2012; Morris et al., 2014; DeLaune et al., 2016). Nutrient input would also help to maintain long-term vegetative growth, thus increasing marsh development and marsh ability to trap and retain incoming sediment (DeLaune et al., 1990; Morris, Nyman, and Shaffer, 2014).
Increasing sediment delivery to eroding marshes could enhance plant productivity, regeneration, and marsh development (DeLaune et al., 1990).

Figure 1.6: Planned freshwater and sediment diversions from the Mississippi and Atchafalaya river. (Schleifstein, 2014)

1.7.1 Review of Sediment Diversions

The effectiveness of sediment diversions to build land depends on several factors, including discharge rates of water, location near riverine source, and sediment load of the river (Lane, Day Jr., and Day, 2006). Previous studies have found that wetland sites located nearest sediment diversions and receiving the largest volume of river water tend to have higher rates of accretion and wetland elevation compared to other sites (Lane, Day Jr., and Day, 2006; Boustany, 2010). Areas closest to the diversions will receive more sediment input, specifically of coarser sands, while areas further away from the diversion will receive more fine-grained
sediment delivery (Dean et al., 2014). Percentage of sand to total sediment load in 11 current diversions in Louisiana ranged from 10% to 35% (Allison et al., 2012). The amount of sand delivered by sediment diversions is crucial, since newly formed wetlands need to develop a strong foundation of inorganics sediments before vegetation can take hold. Both muds and sands are necessary to aid coastal land growth, but heavy sands can provide a more stable basis for development. Heavy sands often settle out faster than finer material, thus requiring higher rates of discharge to transport sands to coastal areas. Larger diversions will allow for a higher sand to water ratio delivery to marsh sites. Diversions may only operate during high discharge times during spring flooding to maximize sediment delivery during short periods of time.

Table 1.3: Examples of current Freshwater and Sediment Diversions in Louisiana

<table>
<thead>
<tr>
<th>Diversion</th>
<th>Type</th>
<th>Opening Date</th>
<th>Maximum Capacity</th>
<th>Location and Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caenarvon</td>
<td>Freshwater</td>
<td>1991</td>
<td>8,000 ft³ s⁻¹</td>
<td>Located 15 miles downriver of New Orleans near Caenarvon, La. Designed to minimize saltwater intrusion in Breton Sound and enhance vegetation growth.</td>
</tr>
<tr>
<td>Davis Pond</td>
<td>Freshwater</td>
<td>2002</td>
<td>10,600 ft³ s⁻¹</td>
<td>Located 15 miles upstream of New Orleans. Designed to reduce saltwater intrusion in Barataria Basin.</td>
</tr>
<tr>
<td>West Bay</td>
<td>Sediment</td>
<td>2004</td>
<td>20,000 ft³ s⁻¹</td>
<td>Located 4.7 miles upstream of the Head of Passes. Designed to divert sediment and freshwater to West Bay to reduce subsidence.</td>
</tr>
</tbody>
</table>
Table 1.3 Continued

<table>
<thead>
<tr>
<th>Diversion</th>
<th>Type</th>
<th>Opening Date</th>
<th>Maximum Capacity</th>
<th>Location and Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bonnet Carré Spillway</td>
<td>Freshwater</td>
<td>1931 (Construction Completed)</td>
<td>250,000 ft³ s⁻¹ (7100 m³ s⁻¹)</td>
<td>Located upstream of New Orleans, La. The spillway was built after the Great Flood of 1927 to prevent flooding and diverts Mississippi water into Lake Ponchartrain. Only opens when the flood stage of the River is above 1.25 million ft³ s⁻¹.</td>
</tr>
</tbody>
</table>

Figure 1.7: Examples of current freshwater and sediment diversions in Louisiana. (Google Maps)
1.7.2 Uncertainty of Sediment Diversions

Although sediment diversions may seem a simple and viable solution to addressing Louisiana’s coastal loss, there are several concerns over the effects of implementation. In addition to delivering sediment, diversions will deliver significant amounts of nutrients (primarily N as NO₃) to receiving basins with potential for environmental impact. Concern has been raised that diverting nutrient-laden river water may further degrade water quality in receiving basins given the increased nitrogen loading of the Mississippi River over the last century. Nitrate delivery into the northern Gulf of Mexico can help to trigger algal blooms in coastal waters since nitrogen tends to be a limiting nutrient in aquatic ecosystems. During the summer when waters are stratified and experience very little mixing, the death and decomposition of algal blooms via respiration depletes water oxygen and creates an area of low oxygen/hypoxia (<2 mg L⁻¹) (Nixon, 1995). Considerable research has also focused on the negative impact nutrient addition could have on below ground biomass and soil strength in coastal wetlands, possibly increasing the erodibility of wetlands, though this argument is widely debated (Darby and Turner, 2008; Swarzenski, 2008; Turner, 2010; Teal et al., 2012; Morris et al., 2014).

1.7.3 Potential of Diversions to Reduce Nutrient Loading

Diverting Mississippi water may provide an opportunity for increased nutrient reduction prior to waters reaching the Northern Gulf of Mexico, despite concerns over increased nutrient loading to wetlands and coastal waters via diversions. Soils in newly formed deltas, which are also representative of the soils delivered to coastal areas by diversions, have a significant capacity for nitrate removal, especially those receiving nutrient rich surface waters which may help to increase denitrification rates (Heney and Twilley, 2014). While evaluating nitrate
removal aided by the Caenarvon diversion, VanZomeran, White, and DeLaune (2013) found that diversions can be useful in removing nitrate from floodwater prior to discharge in the Gulf if water interacts with a substrate high in carbon content and with the aid of vegetative uptake. DeLaune et al. (2005) observed that a 3700 ha ponded wetland receiving diverted water from the Mississippi by the Davis Pond diversion was able to process and remove almost all nitrate received from a flooding event, but only at lower discharge rates (35 m³ s⁻¹ vs >100 m³ s⁻¹). If diversions are able to enhance nitrate removal by delivering water to coastal land prone to nitrate reduction, they can be a viable addition to solutions addressing coastal eutrophication.

All previous studies attempting to understand nitrate reduction as a result of sediment diversions have studied removal rates in marsh sediments and the floodplain areas of delta. For the purpose of this study, these areas are classified as “far-field” environments, where sediment and vegetation are well-developed and located further downstream of diversion sites. To date, no studies have attempted to quantify nitrate loss rates in the “near-field” area of diversions, where turbulent conditions impart significant shear stress on the sediment surface, suspending fine grained sediments. These areas are located close to diversion outfalls, in the immediate area of where crevasses are cut to allow for diverted river water. The turbulent environments created in these areas could allow for enhanced rates of nitrate reduction by providing ample opportunity for water column and sediment interaction, increasing microbial exposure to nitrate, and increasing rates of nitrification due to NH₄⁺ release. To better understand the spatial variability of nitrate reduction resulting from sediment diversions, it is critical to quantify nitrate removal in these near-field environments.
CHAPTER 2: AN EVALUATION OF NITRATE REDUCTION IN A HYDROLOGICALLY RESTORED BOTTOMLAND HARDWOOD FOREST IN NORTHERN LOUISIANA

2.1 Introduction

Nitrogen fertilizers are often heavily applied to croplands to increase plant production, since nitrogen tends to be a limiting factor of primary productivity in terrestrial ecosystems (Ribaudo, 2011). Application of fertilizer has allowed for increased global population growth through increased crop production and it has been estimated that half of the world’s population today could not exist without nitrogen fertilization (Erisman et al., 2008). Despite these gains, nitrogen pollution of our aquatic systems has become pervasive and has led to detrimental impacts on ecosystem functioning and human health (Lovett et al., 2009; Townsend et al., 2003; Rabalais, 2002a; Townsend et al., 2003). Once excess nitrogen enters aquatic systems, it can cause an exponential increase in algal populations, known as algal blooms, some of which may have harmful effects (Bargu et al., 2011). The subsequent death and decomposition of this large quantity of algal material can lead to hypoxic/anoxic waters, such as that created off the coast of Louisiana every summer as a result nitrate loading from the Mississippi River (Rabalais, 2002).

The Mississippi River has seen a dramatic increase in the nitrate load over time, primarily as a result of agricultural fertilization. Prior to 1972, the average yearly nitrogen export (60% in the form of nitrate) of the river averaged 300,000 metric tons; today, this average is closer to 1.5 million metric tons (Goolsby, 1997). The nitrate pulse from the river to coastal waters triggers a hypoxic event in the Gulf of Mexico each summer that, in recent years, has averaged approximately 14,200 km\(^2\) (Rabalais, 2002; NOAA, 2014, EPA, 2011). Areas of hypoxic waters in the Gulf can have detrimental impacts on important recreational and commercial fisheries by inducing stressful environments and threatening spawning and migration habitats (Diaz and
Rosenberg, 2008; Rabalais, Turner, and Wisemen, 2002). Wetlands are well adapted to removing nitrate from surface waters via denitrification (Reddy and DeLaune, 2008); consequently, any restoration plan which increases the Mississippi river’s access to wetlands can aid in reducing the river’s nitrate load delivery to coastal waters.

Bottomland Hardwood (BLH) forests located along the Mississippi River and its tributaries can play a crucial role in reducing nitrate delivery to the GOM (Lindau et al., 2008). BLHs are the dominant floodplain wetland type along the Lower Mississippi Alluvial Valley (LMAV) (LDWF, 2005). When rivers overflow their banks into BLHs during spring flooding, these floodplain wetlands can act as nutrient transformers. One especially prominent transformation is denitrification. Denitrification is an anaerobic, microbial enzymatic facilitated process that reduces $\text{NO}_3^-$ to $\text{N}_2$ and removes nitrate from the system via gaseous losses. When soil oxygen levels are low (< 0.2 g ml$^{-1}$) and when Eh decreases below +400 mV, facultative anaerobes will use $\text{NO}_3$ as the terminal electron acceptor for respiration. Denitrification is the primary pathway by which nitrate is removed from wetlands due to the high organic matter content and low soil redox potential commonly found in wetlands (Reddy and DeLaune, 2008).

Despite the positive impacts BLHs can have on nutrient removal, almost 80% of the BLH’s in the LMAV have been destroyed, primarily due to harvesting for timber and subsequent clearance for agriculture (Llewellyn et al., 1995; MacDonald et al. 1979). Consequently, BLH cover in the LMAV has been reduced to 2.1 million hectares from the 9.7 million in existence prior to large scale European settlement (MacDonald et al, 1979; King and Keeland, 1999).

Concomitant with the decline of forested wetland cover, a decrease in river-floodplain connectivity has also greatly hindered nitrate removal in the LMAV. The construction of 2,700 km of levees along both sides of the lower Mississippi River has limited the area of floodplain
interacting with river floodwaters by 90% since the 1700’s (USGS, 1998). Historically, the Mississippi River and its tributaries were able to freely overflow their banks during spring flooding, creating the opportunity for sediment deposition and nutrient removal, particularly nitrate, by their floodplain areas. Instead of interacting with its floodplain as it makes its way down the valley, much of the discharge of Mississippi River is delivered directly in to the Gulf of Mexico, transporting valuable marsh building sediment and nutrients out to the sea and helping trigger hypoxia (Mitsch et al., 2001; Rabalais, 2002).

Restoration of BLHs, including the reconnection of rivers in the LMAV to their natural floodplains, could help reduce the nitrate load of the Mississippi River prior to its discharge in to the GOM (Mitsch et al., 2001; Schramm et al., 2009; Mississippi River/Gulf of Mexico Watershed Nutrient Task Force, 2008). Forested wetlands soils are important denitrification sites, especially since these soils tend to have higher denitrification and nitrate removal rates than agricultural land (Ullah et al., 2005). Mollicy Farms, a 6,475 hectare BLH site in northern Louisiana, is the largest floodplain reconnection and bottomland hardwood reforestation project in the Mississippi River Basin (TNC, 2009). The restoration and hydrologic reconnection of Mollicy Farms has potential to positively influence N reduction in the LMAV. Though vegetation and hydrology in Mollicy Farms have been restored, restoration of biogeochemical functioning and the site’s ability to remove nitrate has yet to be quantified. It is therefore imperative to determine the nutrient removal capabilities of the site, given that the restoration goal of the Mollicy Farms is to restore site functionality. The objective of this study was to determine the nitrate reduction potential of hydrologically restored soils in Mollicy Farms compared to those of a natural control site and quantify their contribution to the removal of nitrate from river floodwater.
2.2. Site Descriptions

2.2.1 Mollicy Farms

Mollicy Farms (Figure 2.1; 2.3) is a 6,475 hectare BLH restoration site in Morehouse Parish, La., in the Upper Ouachita National Wildlife Refuge in Northern Louisiana. It is located on the east bank of the Ouachita River, a tributary of the Mississippi River, between River Miles 216.5 and 202.5. Mollicy Farms has an elevation ranging from 16.5 to 22 m above mean sea level (MSL), generally increasing away from the river. Originally a bottomland hardwood forest, Mollicy Farms was first cleared for row crop agricultural production (initially soybeans and eventually rice) in 1969. A 17-mile long and 30-mile high levee was built the same year to protect Mollicy Farms from flooding, disconnecting the site from the adjacent Ouachita River except for a single 2.4 m wide pipe that was inserted through the levee to pump water in and out of the site (TNC, 2011). In the early 1990s, The Nature Conservancy began to purchase the site in small segments and acquired most of it by 1997. Approximately 2,864 hectares (44%) of the Mollicy Unit was restored between 1998 and 2001 by planting more than 3 million bottomland hardwood trees, including bald cypress, willow oak, water tupelo, and green ash trees (TNC, 2011; Weber et al., 2012). Levees breaches were planned at five locations the site in 2009, but a heavy and unpredicted flood the same year naturally breached the levee in two places, stalling plans and negatively impacting 60% of the trees planted in previous years due to submergence stress (Weber et al., 2012). In 2010, the levee was breached in four additional places to further reconnect the site with the Ouachita River (Figure 2.2).

In addition to restoring vegetation in the site and breaching levees, the interior hydrology within Mollicy Farms has also undergone restoration. Interior hydrologic restoration in the Mollicy Unit has focused on reconnecting streams and bayous to their headwaters and
facilitating water movement in and out of the site to restore floodplain functionality. Although restoring the hydrology to pre-disturbance conditions is not possible, recreating networks of streams, bayous, embedded wetlands, and connection to the river allows a functional floodplain to be achieved. This has included removing culverts, dredging ditches and bayous, removing and breaching roads, and plugging in existing channels to direct water flow and retention in the site.

Figure 2.1: Map of Mollicy Farms (outlined in yellow) within Upper Ouachita National Wildlife Refuge (The Nature Conservancy)

2.2.2 Control Site

Directly across the Ouachita river, on the west bank, is a naturally occurring BLH that has never been leveed or farmed and serves as a reference site to Mollicy Farms (Figure 2.4). The control site has an elevation ranging from 18.6 to 24 m above MSL, generally increasing from away from the river, though approximately 80% of the site is 19.5 m above MSL.
Vegetation at this site is predominately composed of mature bottomland hardwood species, such as oak, tupelo, and ash trees.

Figure 2.2: Location of levee breaches (red) in Mollicy Farms (Google Earth, 2016)

Figure 2.3: Mollicy Farms

Figure 2.4: Control Site
2.3 Materials and Methods

2.3.1 Experimental Design

In both the restored and control sites, four stations were established in the areas likely to be flooded immediately after the Ouachita River exceeded its bankfull stage, which is 20 m (Figure 2.5). Intact sediment cores (7.5 cm diameter, to 20 cm depth) were collected during July 2015. Triplicate intact cores were collected at each station within the two sites for N reduction analysis, resulting in 12 cores collected from each site. Triplicate samples of the top 10 cm of soil were also collected at each station for physicochemical analysis using the push core method. Samples for soil physicochemical characteristics were extruded in the field, placed in Ziploc bags, set on ice, and transported back to the laboratory where they were stored at 4°C until analysis.

Figure 2.5: Sampling stations in Mollicy Farms and the Control Site (Google Earth, 2016)
Intact cores were brought to the Wetland and Aquatic Biogeochemistry Laboratory at Louisiana State University in Baton Rouge, La. the same day they were collected. Each core was drained of excess site water and wrapped in aluminum foil to the soil surface to minimize light penetration. Cores were given a 20 cm depth water column of 1 mg NO₃-N L⁻¹ solution (similar to the nitrate concentration of the Ouachita river) and incubated in a 20°C water bath (TNC, 2013). Cores were incubated in a low-light environment to prevent algal growth, which could influence areal N reduction rates. The water column of each core was bubbled with air for the duration of the incubation to ensure an aerobic water column, similar to field conditions (Figure 2.6). Water samples were collected from the water column of cores at the onset of the incubation and subsequently every other day for 2 weeks. The 7 ml water samples were filtered using a 0.45 µm syringe filter, acidified with H₂SO₄, and stored in a refrigerator at 4°C until analysis. Samples were measured for NO₃-N by colorimetric analysis using a SEAL AQ2 Automated Discrete Analyzer with a method detection limit of 0.014 mg N L⁻¹. Water sampled from cores was replaced with 1 mg L⁻¹ NO₃-N to maintain constant core water volume.

Figure 2.6: Core Incubation Setup
Dissolved Oxygen (DO), pH, and salinity measurements were taken twice a week using a YSI 556 Multi-Probe Meter to ensure stable water conditions. The temperature of core water column was recorded daily. Rates of areal N reduction were calculated by measuring the rate of nitrate loss in core water column over time.

2.3.2 Soil Physicochemical Properties: Moisture Content (MC), Bulk Density (BD), Total Carbon (TC), Total Nitrogen (TN), and Total Phosphorus (TP)

The top 10 cm of soils were homogenized and 50 g subsamples were dried at 70°C until constant weight. Moisture content was determined by weighing soil subsamples before and after being dried, which also allowed for the determination of soil dry weight. Bulk density was calculated using the moisture content, total wet weight, and soil core volume. Bulk density measurements were expressed in units of g cm⁻³. Dried soil was ground using a ball grinder and stored in scintillation vials. Total C and total N values were determined using a Costech 1040 CHNOS Elemental Combustion System (Valencia, Ca) with a method detection limit of 0.005 g C kg⁻¹ and 0.005 g N kg⁻¹, respectively. Total C and total N values were expressed in grams of C and N per kg of soil.

Total P was measured using the ashing-digestion method (Anderson, 1976). Five grams of dried soil sample were weighed in to 50 ml beakers and placed in a furnace (Barnstead Thermolyne 62700) at 550°C for 4 hours. Soil in each beaker was weighed after removal from the furnace to determine organic matter content by loss on ignition (LOI), where final soil weight is subtracted from initial soil weight. Twenty ml of 6M HCL was added to each sample and samples were then placed on a hot plate at 120°C until dry, removed, and returned to the hot plate for an additional hour. Samples were moistened with 2.25 ml of 6M HCL and returned to the hot plate and brought to near boiling. Samples were filtered through Whatman #41 filter
paper into 50 ml volumetric flasks, rinsing both the beaker and filter three times. Samples were brought to volume, shaken vigorously, and 20 ml of sample was placed in scintillation vials and stored at room temperature until analysis. Total P was measured by colorimetric analysis using a SEAL AQ2 Automated Discrete Analyzer (Seal Analytical Inc., Mequon, Wisconsin) with a method detection limit of 0.02 mg P L⁻¹. Total P was expressed in mg of Phosphorus per kg of dry soil.

2.3.3 Extractable NH₄⁺

Extractable NH₄⁺ was measured to determine bioavailable nitrogen (NH₄⁺) available in soil for plant uptake. Five grams of wet, thoroughly homogenized soil sample was placed in to 40 ml centrifuge tubes and 20 ml of 2M KCL was added to each sample. Tubes were shaken in a longitudinal shaker for 1 hour. Samples were placed in a Sorvall RC, 5C Plus centrifuge (Weaverville, NC) at 5000 g for 10 minutes. Samples were then passed through a 0.45 µm filter with vacuum filtration, acidified with H₂SO₄ to a pH of <2 for preservation, and refrigerated at 4°C until analysis. Samples were measured by colorimetric analysis using a SEAL AQ2 Automated Discrete Analyzer with a detection limit of 0.012 mg N L⁻¹. Extractable NH₄⁺ values were expressed in units of mg NH₄⁺ per kg of dry soil.

2.3.4 Potentially Mineralizable N (PMN)

Potentially Mineralizable N rates were determined to measure the net mineralization rates of NH₄⁺ in site soils. PMN rates were measured over 9 days, at days 3, 6, and 9. Day 0 extractable controls were determined in the same manner as extractable NH₄⁺ measurements. Ten grams of homogenized wet soil from each sample were placed in three 70 ml serum bottles and labeled with their respective days for incubation. In each day set there were four samples that contained triplicates to measure within sample variability. Each serum bottle was fitted with a
rubber septum and an aluminum seal crimp. Air in each serum bottle was evacuated using a vacuum pump and replaced with 99.99% pure nitrogen gas to create an anaerobic headspace. Pressure in bottles was equal to room pressure to inhibit air diffusion. Bottles were then injected with 10 ml of nitrogen purged deionized water and placed in a temperature controlled incubator (Jeio Tech Lab Companion IS-971R, Seoul, Korea) oscillating at 100 rpm at 40°C. Samples were incubated for their allotted days, removed from the incubator, and extracted with 30 ml of 2M KCL. Samples were shaken for an hour in a horizontal shaker, centrifuged at 5000 g for 10 minutes, and filtered through 0.45 µm filters with the aid of vacuum suction pump. Samples were placed into scintillation vial, acidified with H2SO4, and placed in a refrigerator at 4°C until analysis. Potentially Mineralizable N samples were measured using a SEAL AQ2 Automated Discrete Analyzer with a detection limit of 0.012 mg N L\(^{-1}\). Potentially Mineralizable N units were expressed in mg of NH4\(^+\) mineralized per kg of dry soil per day.

### 2.3.5 Microbial Biomass N (MBN)

Microbial Biomass N was measured to quantify the size of the microbial pool present in site soils. MBN was determined using the chloroform-fumigation extraction method which compares the organic N content of fumigated and non-fumigated subsamples of the same sample (Vance et al., 1987). Five grams of homogenized wet soil sample from each site were placed in 40 ml centrifuge tubes. Non-fumigated samples were extracted with 20 ml of 0.5M K\(_2\)SO\(_4\), shaken, and centrifuged at 5000 g for 10 minutes. Samples were filtered through a 0.45µm filter, acidified with HCL, and placed in the refrigerator at 4°C until analysis was completed. Fumigated samples were fumigated in a vacuum sealed desiccator, which contained 50 ml of chloroform, for 24 hours. After fumigation, samples were extracted with 20 ml of 0.5M K\(_2\)SO\(_4\), shaken on a longitudinal shaker for 30 minutes, and centrifuged. Samples were filtered through a
0.45µm membrane filter, acidified with HCL and refrigerated at 4°C until analysis. MBN was determined by the difference of TN between fumigate and non-fumigate results. Microbial Biomass N was analyzed using a Shimadzu-TOC-V CNS Analyzer and expressed in mg of N per kg of dry soil.

2.3.6 Beta-glucosidase Fluorometric Enzyme Assay

β-glucosidase enzyme activity was determined to measure the rate of organic matter, specifically carbon, decomposition by measuring extracellular enzymes release from microbes. Samples were evaluated for enzyme activity within 72 hours of field sampling. The 4-Methylumbelliferone (MUF), which can indicate fluorescence, was used as a standard to measure fluorescence throughout the experiment. The fluorescence of 4-Methylumbelliferyl β-D-glucopyranoside, a substrate that fluoresces when β-glucosidase enzymes cleave from microbes, was measured to determine the rate of enzyme activity. This experiment was conducted in low-light conditions due to the extreme light sensitivity of the substrates and standards used to measure enzyme emission. A standard curve of MUF was ran prior to the experiment in addition to a quench curve for soils in each site. Compared to the standard curve, soil samples may hide fluorescence, add fluorescence, or have no effect upon fluorescence. A quench curve accounts for the effect soil color may have on the standard curve by running a standard curve using only soil.

To prepare samples for the fluorometric enzyme assay, 1 gram of wet soil from samples were added to 99 ml of DI water in 160 ml serum bottles and placed in a longitudinal shaker for an hour for homogenization. Samples were pipetted into 96-well microplates using an 8 channel automated pipette. Each sample had eight replicates for the duration of the experiment and final activity values were averaged. One hundred µL of a 0.05 M solution of 4-Methylumbelliferyl β-
D-glucopyranoside substrate was transferred into 96-well microplate trays containing soil sample. Trays were analyzed on a Bio Tek FLx800 Microplate Fluorometer (Winooski, VT) for fluorescence immediately after substrate injection for a Time 0 reading. Subsequent readings of fluorescence were taken every 2 hours for 24 hours to obtain a linear rate of substrate hydrolysis. Enzyme activities were calculated as nmols of MUF (fluorescence) released per gram of dry soil weight per hour (nmol MUF gdw\(^{-1}\) h\(^{-1}\)).

2.3.7 Statistical Analysis

Data for nitrate reduction rates between the control and restored sites were statistically analyzed using a student t-test (n=12, \(\alpha < 0.10\)). Soil properties of moisture content, bulk density, TC, TN, TP, MBN, PMN, extractable NH\(_4\)\(^+\), potential denitrification, and enzyme activity for each site was also compared using a student t-test (n=12, \(\alpha < 0.10\)). The level of significance was set at 0.10 to account for normal variability within natural systems and to avoid Type II errors. All determined P values less than 0.10 were considered to be significant. Data are presented as an average of all samples (n=12). Relationships between variables were determined using correlation analysis.

2.4 Results

2.4.1 Soil Physicochemical Properties

Moisture content in the upper 10 cm of soil in Mollicy Farms was significantly lower than those in the control site (38.8 ± 2.70% vs 48.7 ± 10.3%) respectively, with P=0.004. Bulk density in the soils of Mollicy Farm was significantly higher than those in the control site (0.94 ± 0.10 g cm\(^{-3}\) vs. 0.64 g ± 0.17 cm\(^{-3}\), respectively) with a P value of 0.01.

Total C in Mollicy Farms was determined to be 14.2 ± 3.95 mg kg\(^{-1}\), while total carbon was significantly higher in the control site with 38.6 ± 16.6 mg kg\(^{-1}\) (P<0.001). Similarly, N was
1.22 ± 0.42 mg kg\(^{-1}\) in Mollicy Farms and 2.69 ± 1.15 mg kg\(^{-1}\) in the control site, with significantly lower values in Mollicy Farms (\(P < 0.001\)). Total P in Mollicy Farms (395 ± 41.2 mg kg\(^{-1}\)) was also significantly lower than that in the control site (524 ± 130 mg kg\(^{-1}\)) with a \(P\) value of 0.01. Extractable NH\(_4\)\(^+\) concentration was found to be significantly higher in Mollicy Farms than the control (47.9 ± 12.9 mg kg\(^{-1}\) vs. 13.9 ± 3.49 mg kg\(^{-1}\), respectively) with a \(P\) value < 0.001.

### 2.4.2 Microbial Properties

Potentially Mineralizable rates of NH\(_4\)\(^+\) in Mollicy Farms were significantly lower (3.89 ± 0.68 mg m\(^{-2}\) day\(^{-1}\)) than those in the control (8.92 ± 2.96 mg m\(^{-2}\) day\(^{-1}\)) and had a \(P\)-value of <0.001. Microbial biomass N was significantly lower in Mollicy Farms (5.93 ± 5.69 mg kg\(^{-1}\)) than the control site (33.4 ± 21.6 mg kg\(^{-1}\)) with a \(P\) value of <0.001 (Figure 2.7). The rate of β-glucosidase activity was 116 ± 32.6 nmol MUF gdw\(^{-1}\) h\(^{-1}\) in Mollicy Farms, which was significantly lower than the rate of 328 ± 152 nmol MUF g\(^{-1}\) h\(^{-1}\) in the control site (\(P < 0.001\)) (Figure 2.8).

### 2.4.3 Areal NO\(_3\)-N Reduction Rates

NO\(_3\)-N reduction rates were significantly lower in Mollicy Farms than in the control site with a \(P\)-value of 0.08 (Figure 2.10). The average NO\(_3\)-N reduction rate in Mollicy Farms was 11.8 ± 3.37 mg N m\(^{-2}\) d\(^{-1}\), while the average reduction rate in the control site was 16.4 ± 8.10 mg N m\(^{-2}\) d\(^{-1}\).
**Figure 2.7:** Mean microbial biomass nitrogen (MBN) values for Mollicy Farms and the control site (n=12), ± 1 standard deviation.

**Figure 2.8:** β-glucosidase activity for Mollicy Farms and the control site (n=12), ± 1 standard deviation.
Figure 2.9: Examples of nitrate loss in core water columns during the experiment. (A) Change in nitrate concentration in core water column over time. (B) Change in total nitrate per square meter over time. Nitrate reduction rates were determined using the slope of the linear trend line.

Figure 2.10: Mean NO$_3$-N reduction in Mollicy Farms and the control site (n=12), ±1 standard deviation.
2.4.4 Soil Property Relationships

Total C was positively correlated with moisture content, TN, TP, extractable \( \text{NH}_4^+ \) and \( \beta \)-glucosidase activity \((r=0.69, 0.98, 0.68, 0.62, \text{ and } 0.75, \text{ respectively})\) in the restored Mollicy Farms site (Table 2.1). Total N was positively correlated with moisture content, extractable \( \text{NH}_4^+ \), and \( \beta \)-glucosidase activity \((r=0.63-0.71)\). Extractable \( \text{NH}_4^+ \) was also positively correlated with TP \((r=0.71)\) and moisture content \((r=0.62)\) and negatively correlated with bulk density \((r=-0.58)\) in Mollicy Farms.

In the control site, TC had positive correlations with moisture content, TN, TP, PMN, MBN, \( \beta \)-glucosidase activity, and \( \text{NO}_3^- \) reduction \((r=0.91, 0.99, 0.89, 0.96, 0.88, 0.83, \text{ and } 0.66, \text{ respectively})\) and was negatively correlated with bulk density \((r=-0.89)\) (Table 2.2). Total N had positive correlations with moisture content, TP, PMN, MBN, \( \beta \)-glucosidase activity \((r=0.81)\), and \( \text{NO}_3^- \) reduction \((r=0.65)\) and was negatively correlated with bulk density \((r=-0.91)\). Total P was well correlated to moisture content, PMN, MBN, and \( \beta \)-glucosidase activity \((r=0.79, 0.78, 0.89, \text{ and } 0.65, \text{ respectively})\) and negatively correlated with bulk density \((r=-0.78)\).

Potentially mineralizable nitrogen was negatively correlated with bulk density \((r=-0.95)\). Microbial biomass N was also positively correlated with PMN \((r=0.78)\), \( \beta \)-glucosidase activity \((r=0.67)\) and \( \text{NO}_3^- \) reduction \((r=0.71)\) and displayed a negative correlation with bulk density \((r=-0.69)\). \( \beta \)-glucosidase activity was positively correlated with moisture content \((r=0.81)\) in addition to TC, TN, TP, PMN, and MBN and was negatively correlated with bulk density \((r=-0.82)\).
### Table 2.1: Correlation coefficients for soil characteristics and parameters in Mollicy Farms. Bold indicates significance at P <0.05 (n=12, at P=0.05, r=0.58).

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<th>TP</th>
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<td>0.46</td>
<td>-0.44</td>
<td>0.68</td>
<td>0.62</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PMN</td>
<td>0.24</td>
<td>0.10</td>
<td>0.40</td>
<td>0.49</td>
<td>-0.14</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>0.37</td>
<td>-0.58</td>
<td>0.62</td>
<td>0.63</td>
<td>0.71</td>
<td>0.11</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MBN</td>
<td>0.02</td>
<td>0.26</td>
<td>0.43</td>
<td>0.48</td>
<td>-0.06</td>
<td>0.23</td>
<td>0.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\beta$-glucosidase</td>
<td>0.58</td>
<td>-0.44</td>
<td>0.75</td>
<td>0.71</td>
<td>0.52</td>
<td>0.46</td>
<td>0.41</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>NO$_3^-$ flux</td>
<td>0.51</td>
<td>0.08</td>
<td>-0.08</td>
<td>-0.11</td>
<td>-0.13</td>
<td>0.29</td>
<td>0.02</td>
<td>-0.12</td>
<td>-0.10</td>
</tr>
</tbody>
</table>

### Table 2.2: Correlation coefficients for soil characteristics and parameters in the Control Site. Bold indicates significance at P <0.05 (n=12, at P=0.05, r=0.58).

<table>
<thead>
<tr>
<th></th>
<th>MC</th>
<th>BD</th>
<th>TC</th>
<th>TN</th>
<th>TP</th>
<th>PMN</th>
<th>NH$_4^+$</th>
<th>MBN</th>
<th>$\beta$-glucosidase</th>
</tr>
</thead>
<tbody>
<tr>
<td>BD</td>
<td>-0.94</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TC</td>
<td>0.91</td>
<td>-0.89</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TN</td>
<td>0.91</td>
<td>-0.91</td>
<td>0.99</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TP</td>
<td>0.79</td>
<td>-0.78</td>
<td>0.89</td>
<td>0.91</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PMN</td>
<td>0.96</td>
<td>-0.95</td>
<td>0.96</td>
<td>0.95</td>
<td>0.78</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>-0.33</td>
<td>0.45</td>
<td>-0.51</td>
<td>-0.48</td>
<td>-0.17</td>
<td>0.55</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MBN</td>
<td>0.71</td>
<td>-0.69</td>
<td>0.88</td>
<td>0.90</td>
<td>0.89</td>
<td>0.78</td>
<td>-0.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\beta$-glucosidase</td>
<td>0.81</td>
<td>-0.82</td>
<td>0.83</td>
<td>0.81</td>
<td>0.65</td>
<td>0.87</td>
<td>-0.53</td>
<td>0.67</td>
<td></td>
</tr>
<tr>
<td>NO$_3^-$ flux</td>
<td>0.65</td>
<td>-0.55</td>
<td>0.66</td>
<td>0.65</td>
<td>0.54</td>
<td>0.67</td>
<td>-0.29</td>
<td>0.71</td>
<td>0.49</td>
</tr>
</tbody>
</table>
Table 2.3: Summary of soil characterizations and percent restoration recovery. Data are presented as mean values ± standard deviation and n=12 for each treatment. * Indicates a significant difference between sites.

<table>
<thead>
<tr>
<th>Soil Parameter</th>
<th>Mollicy Farms</th>
<th>Control Site</th>
<th>P-Value</th>
<th>Percent Restoration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture Content (%)</td>
<td>38.8 ± 2.7</td>
<td>48.7 ± 10.3</td>
<td>0.004*</td>
<td>79.7</td>
</tr>
<tr>
<td>Bulk Density (g cm⁻³)</td>
<td>0.94 ± 0.03</td>
<td>0.65 ± 0.17</td>
<td>0.01*</td>
<td>144.6</td>
</tr>
<tr>
<td>Total Carbon (g kg⁻¹)</td>
<td>14.2 ± 3.95</td>
<td>38.6 ± 16.6</td>
<td>&lt;0.001*</td>
<td>46.3</td>
</tr>
<tr>
<td>Total Nitrogen (g kg⁻¹)</td>
<td>1.22 ± 0.42</td>
<td>2.69 ± 1.16</td>
<td>&lt;0.001*</td>
<td>44.4</td>
</tr>
<tr>
<td>Total Phosphorus (mg kg⁻¹)</td>
<td>395 ± 41.2</td>
<td>524 ± 130.1</td>
<td>0.01*</td>
<td>75.5</td>
</tr>
<tr>
<td>Extractable NH₄⁺ (mg kg⁻¹)</td>
<td>47.9 ± 12.9</td>
<td>13.9 ± 3.49</td>
<td>&lt;0.001*</td>
<td>344.5</td>
</tr>
<tr>
<td>Potentially Mineralizable Nitrogen (mg kg⁻¹ day⁻¹)</td>
<td>3.90 ± 0.68</td>
<td>8.90 ± 3.0</td>
<td>&lt;0.001*</td>
<td>43.8</td>
</tr>
<tr>
<td>Microbial Biomass N (g kg⁻¹)</td>
<td>5.90 ± 5.70</td>
<td>33.4 ± 21.6</td>
<td>&lt;0.001*</td>
<td>17.7</td>
</tr>
<tr>
<td>Beta-glucosidase Activity (nmol gdw⁻¹ h⁻¹)</td>
<td>116 ± 32.6</td>
<td>328 ± 152</td>
<td>&lt;0.001*</td>
<td>35.1</td>
</tr>
<tr>
<td>Areal NO₃-N Reduction (mg N m⁻² day⁻¹)</td>
<td>11.8 ± 3.37</td>
<td>16.4 ± 8.10</td>
<td>0.08*</td>
<td>71.9</td>
</tr>
</tbody>
</table>
2.5 Discussion

It has been well observed that the restoration of biogeochemical functioning in restored wetlands may take significantly longer to return to pre-disturbance conditions than other wetland characteristics, such as hydrology and vegetation, and can be both spatially and temporally variable (Orr et al., 2007; Theriot et al., 2011; Ballantine et al., 2012). Theriot et al. (2013) found that denitrification was significantly decreased in a restored riparian wetland of the Mississippi River after 2 years of hydrologic reconnection. In his study, there were significant differences among almost all measured physicochemical soil characteristics, demonstrating the time lag between hydrologic restoration and biogeochemical functioning. It is important to determine the restoration trajectory for critical wetland functions over time.

Nitrate reduction in Mollicy Farms was greater than 70% of nitrate reduction in the control site. However, other soil and microbial parameters did not exhibit similar restoration trajectories during the same time period. Total C (46.3% of values in the control site), total N (44.4%), PMN (43.8%), MBN (17.7%), and β-glucosidase (35.1%) values were considerably lessened in the restored site compared to the control site. The discrepancy between restoration levels of different characteristics highlights that not all functions follow the same restoration trajectory. While some factors may rebound quickly, others will take a longer time to recover.

While PMN rates were significantly lower in Mollicy Farms (44% of that in the control site), extractable NH$_4^+$ was significantly higher (345% of that in the control site). The dramatic increase in extractable NH$_4^+$ in Mollicy Farms compared to the control site is likely due to several reasons. Extractable NH$_4^+$ is a field condition variable, which means that values observed are likely the result of site conditions. Although not measured, observed soil temperatures in Mollicy were greater than those in the control site, likely due to lack of shading by limited
vegetation. Increased soil temperatures can allow for enhanced microbial activity, thus increasing the production of ammonia. Vegetation cover is also much less abundant in Mollicy Farms than in the control site, which would limit rates of NH$_4^+$ uptake. Having a large pool of extractable NH$_4^+$ would limit PMN rates since an abundant amount of NH$_4^+$ is already available, a result that may have been observed in Mollicy given the low rates of PMN measured relative to the control site. PMN rates in Mollicy may also be lower due to lower organic matter content.

The availability of nutrients on an areal (square meter) basis was determined to account for the influence of bulk density when measuring available nutrients (Table 2.4). With the inclusion of bulk density, the differences in nutrient values between the sites, while still significantly different, are lessened and percent restoration in Mollicy Farms increased. As expected, most values were significantly lower in Mollicy Farms than in the control site, with the exception of extractable NH$_4^+$, which was significantly higher in Mollicy Farms. However, when evaluating nutrients per square meter in each site, total P was also significantly higher in Mollicy Farms compared to the control site. A higher total P in Mollicy Farms is likely due to the presence of inorganic phosphorus associated with mineral sediment in the site, which has a higher bulk density than the control site. Although total P may be greater in Mollicy due to inorganic P, organic phosphorus is likely greater in the control site due to a higher organic matter content. Further analysis is necessary to confirm the differences and abundance in inorganic and organic phosphorus between the two sites. As carbon continues to accumulate in Mollicy Farms, bulk density is expected to decrease and available nutrients per square meter will have to be recalculated.
Table 2.4: Summary of soil characterization and percent restoration recovery per square meter. Data are presented as mean values ± standard deviation and n=12 for each treatment. * Indicates a significant difference between sites.

<table>
<thead>
<tr>
<th>Soil Parameter</th>
<th>Mollicity Farms</th>
<th>Control Site</th>
<th>P-Value</th>
<th>Percent Restoration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Total Carbon</strong> (kg m(^{-2}))</td>
<td>1.33 ± 0.34</td>
<td>2.26 ± 0.39</td>
<td>&lt;0.001*</td>
<td>58.8</td>
</tr>
<tr>
<td><strong>Total Nitrogen</strong> (kg m(^{-2}))</td>
<td>0.11 ± 0.04</td>
<td>0.16 ± 0.03</td>
<td>0.004*</td>
<td>68.8</td>
</tr>
<tr>
<td><strong>Total Phosphorus</strong> (kg m(^{-2}))</td>
<td>37.0 ± 4.41</td>
<td>32.0 ± 5.80</td>
<td>0.03*</td>
<td>115.6</td>
</tr>
<tr>
<td><strong>Extractable NH(_4)</strong> (g m(^{-2}))</td>
<td>4.45 ± 1.03</td>
<td>0.92 ± 0.38</td>
<td>&lt;0.001*</td>
<td>483.7</td>
</tr>
<tr>
<td><strong>Potentially Mineralizable Nitrogen</strong> (mg m(^{-2}) d(^{-1}))</td>
<td>366 ± 75.9</td>
<td>532 ± 48.5</td>
<td>&lt;0.001*</td>
<td>68.7</td>
</tr>
<tr>
<td><strong>Microbial Biomass N</strong> (kg m(^{-2}))</td>
<td>0.62 ± 0.52</td>
<td>1.93 ± 0.84</td>
<td>&lt;0.001*</td>
<td>32.1</td>
</tr>
<tr>
<td><strong>Beta-glucosidase Activity</strong> (mmol m(^{-2}) h(^{-1}))</td>
<td>10.8 ± 2.68</td>
<td>19.3 ± 6.13</td>
<td>&lt;0.001*</td>
<td>56.0</td>
</tr>
</tbody>
</table>

Areal nitrate reduction rates in Mollicity Farms ranged from 9.25 to 16.3 mg N m\(^{-2}\) day\(^{-1}\) with an average of 11.8 ± 3.37 mg N m\(^{-2}\) d\(^{-1}\). Reduction rates in the control site ranged from 4.83 to 28.6 mg N m\(^{-2}\) day\(^{-1}\) with an average of 16.4 ± 8. mg N m\(^{-2}\) d\(^{-1}\). Comparatively, nitrate reduction rates in soils of BLHs of the Cache River in Arkansas ranged from 7.5 to 11.5 mg m\(^{-2}\) d\(^{-1}\), similar to the rates observed in this study (DeLaune et al., 1993). While nitrate reduction rates in Mollicity Farms were significantly lower than those in the control site, there was only a
28% difference in reduction between the sites. These results suggest that hydrologic restoration has improved nitrate reduction ability within Mollicy Farms soils, despite Mollicy having significantly lower TC, MBN, and β-glucosidase values, the latter two of which are important microbial properties. In Mollicy Farms, NO$_3^-$ flux is not well correlated to any soil or microbial parameter measured, likely due to the legacy effects of 20+ years of farming in site soils. Orr et al. (2007) observed similar results in a restored floodplain wetland in the Midwest and credited the lack of correlation to a lack in nitrate delivery to the floodplain, but this is not the case for Mollicy, which is well supplied with river nitrate. Drury et al. (1997) found that sites exposed to fertilizer over a 35-year period had higher rates of microbial activity than those not experiencing fertilizer treatments. Though not measured, the pool of denitrifying microbes in Mollicy Farms may be highly active, possibly as a result of increased soil temperatures and prior continuous fertilizer application, which could account for increased nitrate reduction rates that are not well correlated to other soil parameters.

Carbon is a major driving factor influencing biogeochemical functioning in wetlands. Consequently, restoration activities that increase carbon abundance and accumulation are crucial for restoring microbial regulators of wetland functions. Though site dependent, studies have found that soil organic accumulation has a significant effect on the microbial denitrifying community and denitrification potential, making organic matter content in restored sites a good proxy for denitrifying potential (Roley et al., 2012; Reddy and DeLaune, 2008). It is likely that the eventual return of total C to pre-disturbance values such as those in the control site, would allow for greater rates of nitrate reduction in Mollicy Farms. An increase in total C would also increase microbial biomass and β-glucosidase activity, given how well these factors are correlated with total C in the control site.
Elevation in Mollicy is much lower than elevation in the control site, assumed to be due to the oxidation of carbon resulting from decades of farming. Elevation in Mollicy ranges from 16.5 to 22 m above sea level, compared to the control site which is predominately 19.5 m in elevation, ranging between 18.6 and 24 m. Decreased elevation in Mollicy may allow floodwater to interact with the site sooner, have access to a larger area of the floodplain, and provide a longer residence time for water compared to the control site. Consequently, Mollicy Farms may have the potential to have a greater total removal of N than the control site, despite having significantly lower nitrate reduction rates. Future studies should further evaluate this theory since a larger areal interaction between river water and the floodplain in Mollicy Farms may significantly increase total N removal rates in Mollicy compared to the control site.

Though Mollicy Farms has not fully returned to pre-disturbance conditions in terms of biogeochemical functioning, some functions, such as nitrate reduction, have exhibited a positive effect on water quality. Using the average nitrate reduction rate in Mollicy Farms soils (11.8 mg N m\(^{-2}\) d\(^{-1}\)), the 5-year average of annual flooding days in the site (105 days), and the area of the site that is likely to flood when the Ouachita river reaches bankfull stage (60%; 3874 hectares), annual nitrate removal by Mollicy Farms can be roughly estimated. Based on data in this study, Mollicy Farms soils can remove approximately 34.3-61.7 metric tons of nitrate, an average of 48.1 metric tons, from the Ouachita River every year. Additionally, the same flooding area and flooding duration in the natural site can yield a removal of 33.8-99.7 metric tons of nitrate, an average of 66.7 metric tons, from the Ouachita River every year. Results from this study lend support to restoration plans attempting to use hydrologic floodplain restoration as a strategy to remove nitrate from river floodwaters. While the restoration and hydrologic reconnection of Mollicy Farms alone will not significantly reduce nitrate loading in the Mississippi River or
nitrate delivery to the northern Gulf of Mexico, it can serve as an example for future floodplain restoration projects which, in combination, may significantly reduce nitrogen loading.

2.6 Conclusion

Reintroducing the Mississippi River and its tributaries to their historical floodplain can provide several ecosystem benefits, including nutrient removal. It is critical to maximize nitrate removal from the Mississippi River, given the negative impact nitrate loading can have on receiving basins, particularly hypoxic water development in the Gulf of Mexico. The restoration and reconnection of floodplain wetlands in the LMAV can provide critical nitrate reduction from river floodwaters. Mollicy Farms is the site of one such restoration project and it is currently the largest bottomland hardwood reforestation and floodplain reconnection project in the Mississippi River basin and one of the largest in the United States. There was only a 28% difference in nitrate reduction rates between Mollicy Farms and a control site after 6 years of hydrologic restoration. Results from the restoration of Mollicy Farms indicate that restoring floodplain wetlands and reconnecting them back to their adjacent rivers can increase nitrate reduction and aid in the reduction of nutrient delivery to the Gulf of Mexico.
CHAPTER 3: NITRATE REDUCTION RATES IN TURBULENT-FLOW CONDITIONS: REDUCING NITROGEN REMOVAL UNCERTAINTY FOR OPERATION OF MISSISSIPPI RIVER SEDIMENT DIVERSSIONS

3.1 Introduction

Louisiana’s coastal wetlands are being lost at an alarming rate. Between 1932 and 2010, Louisiana lost over 4800 km$^2$ (1883 mi$^2$) of coastal land, most of which were comprised of wetlands (Couvillion et al., 2011). Rates of coastal land loss vary depending on time period and study location, but between 1985 and 2010, Louisiana’s wetlands were loss at an average rate of 43 km$^2$ yr$^{-1}$ (16.7 mi$^2$) (Couvillion et al., 2011). Despite having only 25% of all wetlands in the U.S, Louisiana experiences 80% of total wetland loss in the country (Thorne et al., 2008). Land loss in coastal Louisiana is the result of a combination of factors, both natural and anthropogenic, and range from subsidence and sea level rise to declines in sediment delivery and oil and gas extraction (Boesch et al., 1994; Day et al., 2000; Turner 2007). However, relative sea level rise and lack of sediment replenishment to wetlands are two of the main driving forces behind wetland loss in Louisiana (Boesch et al., 1994; Blume and Roberts 2012).

Subsidence, the process by which land gradually settles or sinks, is a major factor controlling land loss in Louisiana. Subsidence rates as high as 35mm per year have been observed in coastal LA, with a long-term average of 2mm yr$^{-1}$ (CPRA, 2012; Morton et al., 2005). When the effects of subsidence are combined with eustatic sea level rise, impact on wetland loss is exacerbated. While recent global sea level rise is, on average, 3.2 mm each year, relative sea level rise can average 10 mm per year in coastal Louisiana due to the compounded effect of subsidence (Boesch et al., 1983; Morton et al., 2005; IPCC 2014; DeLaune and White, 2012). Consequently, relative sea level rates in Louisiana are among the highest in the world (Day et al., 2000; Gagliano, Meyer-Arendt, and Wicker 1981).
In natural coastal settings, subsiding wetlands can accrete via both organic accumulation and mineral sediment input. However, sediment delivery to Louisiana’s coastal wetlands has been severely limited in the last 100 years. The Mississippi river has undergone extensive channelization and damming over the last century and while these measures have facilitated navigation and provided flood control, they have also significantly reduced sediment and nutrient delivery to Louisiana’s coastal wetlands (Meade and Parker, 1985; Poore, 2006; Thorne et al., 2008; Blume and Roberts, 2012). Sediment discharge of the lower Mississippi has decreased significantly, with some estimates as high as 70% over the last 100 years (Meade and Parker, 1985; Kesel, 1988; Keown et al., 1986; Thorne et al., 2008; Blume and Roberts, 2012). Between 1963 and 1981, Keown et al. (1981) estimated that the average suspended sediment load of the lower Mississippi river decreased from $427 \times 10^6$ tons yr$^{-1}$ to $251 \times 10^6$ tons yr$^{-1}$. The construction of over 50,000 dams and reservoirs along the Mississippi River’s drainage basin traps sediment and helps to reduce the amount that is delivered to coastal Louisiana (Kesel, 1988; Graf, 1999; Syvitski and Milliman, 2012). The addition of 2,700 km of levees along both sides of the lower Mississippi river has also reduced floodplain-floodwater interaction by 90%, decreasing erosion and sediment loss from floodplain areas, further reducing sediment discharge (Kesel, 1988; USGS, 1998). Current rates of sediment delivery and marsh accretion in the coastal zone are not sufficient to maintain pace with sea level rise (Baumann, Day Jr., and Miller, 1984; Blume and Roberts 2012). If no preservation and/or restoration steps are taken to stall or reverse land loss, over 1750 mi$^2$ (4500 km$^2$) of wetlands could be lost over the next 50 years (CPRA, 2012).

To combat coastal land loss, Louisiana created a Coastal Master Plan designed to offer sustainable solutions to reduce and eventually reverse wetland loss, while ensuring the protection of coastal communities. Along with several other projects, sediment diversions along the lower
Mississippi and Atchafalaya rivers have been proposed to help slow the rate of wetland loss in Louisiana by delivering sediment from the rivers to coastal areas. These diversions will reconnect the Mississippi River to coastal wetlands as it would naturally prior to hydrologic alteration and disconnection by river channelization. Increased reconnection between the river and coast would build land by mimicking natural delta lobe development and providing much needed sediment for marsh accretion (Dean et al., 2014; Day et al., 2000). The delivery of fine and coarse sediment can provide a foundation for marsh development, while the introduction of nutrients can provide accretion via organic matter production by enhancing marsh productivity (Teal et al., 2012). Nutrient input would also help to maintain long-term vegetative growth, increasing marsh development and marsh ability to retain incoming sediment (DeLaune et al., 1990; Morris, Nyman, and Shaffer, 2014).

Sediment diversions may seem a simple and viable solution to addressing Louisiana’s coastal loss, but implementation raises several concerns. Although diversions will deliver significant amounts of material to sediment deprived coastal areas, they will also deliver significant amounts of nutrients (primarily N as NO$_3^-$) to receiving basins with potential for environmental impact. Given the increased nitrogen loading of the Mississippi River, there is concern that diverting nutrient-laden river water may further degrade water quality in receiving basins. Since nitrogen tends to be a limiting nutrient in aquatic ecosystems, one such negative impact could be an areal increase in algal blooms. When coastal waters are stratified and experience very little mixing during the summer months, the death and decomposition of algal blooms via respiration can deplete water of oxygen, resulting in areas of hypoxia, where oxygen concentration is less than 2 mg L$^{-1}$ (Nixon, 1995).
Despite concerns over increased nutrient loading to wetlands and coastal waters via diversions, diverting river water may provide an opportunity for increased nutrient reduction prior to waters reaching the Northern Gulf of Mexico (Lane et al., 1999; Lane et al., 2002; DeLaune and Jugsujinda, 2003). Soils in newly formed deltas, which are representative of the soils delivered to coastal areas by diversions, have a significant capacity for nitrate removal, especially those receiving nutrient rich surface waters (Henry and Twilley, 2014). Previous studies have observed that diversions can be useful in removing nitrate from floodwater if water interacts with a developed marsh prior to discharge (VanZomeren, White, and DeLaune, 2013; Mitsch et al., 2001). DeLaune et al. (2005), observed that a 3700 ha ponded wetland receiving diverted water from the Mississippi by a freshwater diversion was able to process and remove almost all nitrate received from a flooding event, further demonstrating the nitrate removal capacity of receiving basins.

The Coastal Protection and Restoration Authority (CPRA) and The Water Institute of the Gulf (TWIG) have identified the necessity of reducing the uncertainty surrounding the fate of nutrients delivered by sediment diversions and understanding the capacity of receiving basins to remove nutrients in order to better understand the impact of diversions (Yuill et al., 2014). Additionally, CPRA and TWIG are interested in nutrient removal rates occurring during times of diversion operation (peak diversion discharge) and during average flow conditions. Studies highlighting the potential of diversions to enhance nitrate reduction have only been conducted in marsh sediments and the floodplain areas of deltas. For the purpose of this study, these areas are classified as “far-field” environments, where soils and vegetation are well-developed. To date, no studies have attempted to quantify nitrate loss rates in the “near-field” area of diversions, where turbulent conditions impart significant shear stress on the sediment surface, suspending
fine grained sediments. These areas are located close to diversion outfalls, in the immediate area of where crevasses are cut to allow for diverted river water, and have short water residence times. This turbulent environment could induce enhanced rates of nitrate reduction by providing ample opportunity for water column and sediment interaction and increasing microbial exposure to nitrate. The effect of turbulent, resuspension conditions on nutrient removal will be experimentally determined by applying various shear stress forces (0.45, 0.2, and 0 Pa) to deltaic sediment. The objective of this study is to determine the fate of nitrate in turbulent surface water conditions in the near-field area of sediment diversions, which can help in predicting and better understanding potential nutrient impacts of river diversions on coastal receiving basins.

### 3.2 Site Description

Wax Lake Delta (WLD) is a 12,000 acre actively growing delta in the Atchafalaya Bay, located on the south central coast of Louisiana (29.5910° N, 91.4200° W) (Figure 3.1). WLD is situated downstream of the Wax Lake Outlet, a man-made channel created by the US Army Corps of Engineers in 1941. The 22 km outlet was dredged through Six Mile Lake to minimize the risk of flooding to Morgan City, located approximately 20 km downstream of the Atchafalaya. The outlet was designed to divert water from the lower Atchafalaya River, a distributary of the Mississippi River that receives 30% of the Mississippi’s discharge, through Atchafalaya Bay and into the Gulf of Mexico. WLD receives over 45% of the Atchafalaya’s water and sediment discharge and approximately 10% of the Mississippi River’s flow (Allen et al., 2011).

Over a 21-year average from 1989-2010, 81.3 km$^3$ of water was discharged through the outlet yearly, carrying with it an average of 19.2 MT of sediment per year, which is majorly composed of sand (Rosen and Xu, 2013). Sediment diverted through the Wax Lake Outlet into
the Atchafalaya Bay began to build land in 1973 and WLD has been prograding since, one of the only areas in Louisiana’s coast with a net growth of land. The outlet at Wax Lake has created approximately 1 km$^2$ (250 acres) of land per year during the period between 1983 and 2010 (Allen et al., 2011). Although yearly variable, WLD has an approximate net land gain of 1.2 km$^2$ yr$^{-1}$ (Rosen and Xu, 2013; Allen et al., 2012). Soils in WLD have a capacity to significantly reduce nitrate, despite its relative lack of carbon content, due to high nitrate input from the Mississippi river that helps to trigger increased denitrification potential (Henry and Twilley, 2014). Deltaic development at the Wax Lake outlet is similar to that of a natural delta development, both structural and nutrient wise, and is expected to follow a natural delta lobe cycle (Henry and Twilley, 2014). Sediment delivery to the delta is similar to the sediment that will be delivered to coastal areas by sediment diversions. Discharge rates into the delta average 2600 m$^3$ s$^{-1}$ and are highest during spring flooding (USGS Water Data).

![Figure 3.1](image)

**Figure 3.1:** The growth of Wax Lake Delta from 1984 to 2014. Adapted from NASA

### 3.3 Materials and Methods

#### 3.3.1 Experimental Design

In December 2015, sediment cores were collected in three sites within the mudflats of Wax Lake Delta (Figure 3.2). At each site, triplicate intact sediment cores were collected using
the push-core method for each shear stress evaluation, ranging from high to zero: three for 0.45 Pa (high), three for 0.2 Pa (medium), and three for 0 Pa (zero), resulting in nine cores collected at each site. For the zero shear stress treatments, sediment core samples were collected using 20 cm depth, 7 cm diameter cores. For the medium and high shear treatments, 10 cm depth, 10 cm diameter cores were collected. The variation in core sizes between treatments is due to size requirements of the microcosm erosional system used to apply the medium and high shear stresses. Care was taken to minimize disturbance of the sediment surface during the collection of cores. The headspace of cores was filled with site water and cores were tightly capped to prevent sediment disturbance during transit.

At each site, an additional 3 cores were collected (10 cm depth, 7 cm diameter) for soil physicochemical analysis. Cores were transported back to the laboratory, extruded, and separated in to 0-5 cm and 5-10 cm sections for analysis. Core sections were stored in polyethylene plastic containers and placed in a refrigerator at 4°C until analysis.

Figure 3.2: Sampling locations in Wax Lake Delta (Google Earth, 2016)
**Gust Erosion Microcosm System (GEMS)**

A dual-core, flow through Gust Erosion Microcosm System (GEMS) was used to mimic shear stress conditions on surface riverbed sediment resulting from the hydraulic loading of sediment diversions (Figure 3.3 and 3.4). The GEMS manipulates shear stress by using a computer to control the rate of spinning erosional heads inserted on the water column above sediment cores. A NO$_3$-N solution with an initial concentration of 2 mg L$^{-1}$, which mimics the average NO$_3$ concentration of the Mississippi River during spring flooding, was circulated throughout the system for 24 hours (Murphy et al., 2013). The inflow and outflow tubes of each core were placed in the same water container so that the same volume of water was continuously circulated throughout the cores for the duration of the experiment. Air was bubbled into the water holding containers during the experiment to ensure constant aerobic conditions in the water column of the cores. Water flowing out of each core was measured for turbidity continuously throughout the experiment using a turbidimeter, expressed in nephelometric turbidity units (NTU). Three cores from each site were evaluated for each shear stress application: high stress (0.45 Pa), a level that can be generated by turbulent currents or a cold front, medium stress (0.2 Pa), and no stress (0.0 Pa), which did not require the use of the GEMS. Shear stress forces were chosen based on a prior study analyzing the erodibility of northern Gulf of Mexico surface sediments (Xu et al., 2014a; Mickey et al., 2014). Using three levels of shear stress allows for the determination of the spatial variability of nitrate reduction resulting from sediment diversions, as the force of water on the sediment surface is likely to decrease with distance from the diversion outfall. All shear stress treatments were applied within two weeks of sample collection to minimize the effect of compaction. Rates of areal N reduction were calculated by measuring the rate of NO$_3$-N loss in water column over time.
Figure 3.3: Dual-Core Gust Erosion Microcosm System (GEMS). GEMS is comprised of a laptop, a power control box, two turbidimeters, a pump controller, two pumps, and two core erosional heads. Note that source water and exit water for each core are the same.

Figure 3.4: Schematic of the Gust Erosion Microcosm System (GEMS). Adapted from Lo, Bentley, and Xu (2014).
Medium and High Shear Stress Treatments

Medium and high shear stress cores were treated using a Gust Erosion Microcosm System (Figure 3.3). Medium shear core treatments were subjected to 0.2 Pa of bed shear stress, while high shear treatments were subjected to 0.45 Pa. Shear stresses were applied continuously to the cores for 24 hours while a 2 mg L⁻¹ NO₃⁻ solution recirculated through the cores. Six ml of water were collected from the outflow valve of each core every 2 hours over the 24-hour period. Sample volume was replaced with 6 ml of 2 mg L⁻¹ solution to maintain constant water volume. Samples were immediately filtered through a 0.45µm syringe filter, acidified to a pH of <2 with H₂SO₄, and refrigerated at 4°C until analysis.
**Zero Shear Stress Treatments**

Three cores from each site were incubated in a water bath at 20°C for 8 days with zero shear stress treatment. Cores without any applied shear stress were used to measure background nitrate reduction that would occur when diversions are not flowing. Cores were incubated in a dark environment to prevent algal growth, which would create an overestimation of areal nitrate reduction rates. Site water was siphoned from each core and replaced with a 20 cm water column of 2 mg NO$_3$-N L$^{-1}$ solution. Air was bubbled in the water column of cores throughout the experiment to ensure aerobic conditions, indicative of those found in the field. Although shear stress forces were not applied to these cores, the bubbling of air in core water columns provided mixing of the water column, preventing concentration gradients. Six ml of water were taken from each core every two days and replaced with 6 ml of nitrate stock solution (2 mg L$^{-1}$ NO$_3^-$) to maintain constant core water volume. Samples were filtered through a 0.45 µm syringe filter, acidified to a pH of <2 with H$_2$SO$_4$ and refrigerated at 4°C until analysis.

**Post Sediment Resuspension N Reduction (post-GEMS)**

After the 24-hour resuspension period, cores using the GEMS were removed and allowed to incubate in a 20°C water bath for 7 days. The water column of cores was sampled daily. Cores were incubated after stress application to measure the effects of resuspension on nitrate reduction after erosion and turbulence ceased, which is indicative of nitrate reduction that may occur after spring floods/diversion operation cease.

<table>
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<th>Shear Stress (Pa)</th>
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<th>Duration of Shear Stress Application (Hours)</th>
<th>Duration of Static Core Incubation (Days)</th>
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</table>
Water Quality Monitoring

Dissolved Oxygen (DO), pH, and conductivity of core water columns were recorded twice a week using a YSI 556 Multi-Probe Meter, while temperature was measured daily to ensure stable water conditions throughout the experiment.

3.3.2 Soil Physicochemical Properties

*Moisture Content (MC), Bulk Density (BD), Total Carbon (TC), Total Nitrogen (TN), and Total Phosphorus (TP)*

Soils were extruded from intact, undisturbed cores and separated in to 0-5 and 5-10 cm sections. Each section was homogenized and 50 g subsamples were placed in a drying oven until constant weight. Moisture content was determined by using the wet and dry weights of each sample. Bulk density was determined using the dry weight of soil in 0-5 and 5-10 cm soil intervals and soil core volume. Bulk density was expressed in units of g cm$^{-3}$. Dried soil was ground using a ball mill grinder and stored in scintillation vials. Total C and total N values were determined using a Costech 1040 CHNOS Elemental Combustion System (Valencia, Ca) with method detection limits of 0.005 g C kg$^{-1}$ and 0.005 g N kg$^{-1}$, respectively. Total C and total N values were expressed as grams of C and N per kg of dry soil.

Total P was measured using the ashing-digestion method (Anderson, 1976). Five grams of dried soil sample was weighed in to a 50 ml beaker and placed in a muffle furnace (Barnstead Thermolyne 62700) at 550°C for 4 hours. Twenty ml of 6M HCL was added to each sample and beakers were placed on a hot plate at 120°C until dry, removed, and returned to the hot plate for an additional hour on high. Samples were then moistened with 2.25 ml of 6M HCL and returned to the hot plate to near boiling. Samples were filtered through Whatman #41 filter paper into 50 ml volumetric flasks. Flasks were brought to volume, shaken vigorously, and 20 ml of sample
were placed in scintillation vials and stored at room temperature until analysis. Total P was measured by colorimetric analysis using a SEAL AQ2 Automated Discrete Analyzer (Seal Analytical Inc., Mequon, Wisconsin) with a method detection limit of 0.05 mg P L$^{-1}$ and expressed in units of mg of phosphorus per kg of dry soil.

3.3.3 Extractable NH$_4^+$ and NO$_3^-$

Extractable NH$_4^+$ was measured at all sites and soil sections to quantify the amount of bioavailable N (NH$_4^+$) available in soil for plant uptake. Extractable NO$_3^-$ was measured from the top 0-5 cm of soils treated with high and medium shear stresses to quantify the amount nitrate that may have fluxed into the sediment during the experiment. Five g of wet, homogenized soil sample were placed in 40 ml centrifuge tubes and 20 ml of 2M KCL were added to each sample. Samples were shaken on a longitudinal shaker for 1 hour and then centrifuged in a Sorvall RC, 5C Plus (Weaverville, NC) centrifuge at 5000 g for 10 minutes. Samples were then filtered through 0.45 µm membrane filters, acidified with H$_2$SO$_4$ for preservation, and refrigerated at 4°C until analysis. Inorganic N was determined by colorimetric analysis using a SEAL AQ2 Automated Discrete Analyzer with a method detection limit of 0.012 mg N L$^{-1}$ and 0.05 N mg L$^{-1}$ for NH$_4^+$ and NO$_3^-$, respectively. Extractable NH$_4^+$ and NO$_3^-$ measurements were expressed in units of mg N per kg of dry soil.

3.3.4 Grain Size Analysis and Turbidity

Soil sections of 0-1 and 1-2 cm from the surface of cores that were not subjected to shear stress treatments were sliced and analyzed for grain size analysis. Only the top 2 cm of sediment was analyzed because sediment erosion and deposition in the cores during the GEMS experiment were limited to the top 2 cm of sediment. Samples were homogenized, added to 50 ml centrifuge vials, and wet-oxidized using 30% hydrogen peroxide for 12 hours to remove all organic matter.
Vials were then placed in a centrifuge at 1500 g for 4 minutes. Any remaining hydrogen peroxide was removed and 5 ml of deionized water was added to each vial. Samples in vials were homogenized using an Analog Vortex Mixer and a subsample was analyzed using a Beckman Coulter particle size analyzer (Model LS 13 320). More details of grain size analysis can be seen in Xu et al. (2014b).

3.3.5 Statistical Analysis

The effect of shear stress treatments on nitrate reduction rates in the sediments was statistically analyzed using a one-way Analysis of Variance (ANOVA) test. A Tukey-Kramer post-hoc test was subsequently used when the ANOVA determined a significant difference between treatments (n=9, α < 0.05). An ANOVA was also used to analyze differences in soil properties between sites, including TC, TN, TP, grain size, extractable NO₃⁻ and NH₄⁺, and potential denitrification (n=9, α < 0.05). All determined P values less than 0.05 were considered to be significant. All values are reported as the mean of all samples ± 1 standard deviation for each site or for each treatment, depending upon measurement. Correlation analysis was used to determine relationships between variables.

3.4 Results

3.4.1 Soil Physicochemical Properties

Moisture content was not significantly different in the top 5 cm of sediment at the three sites, with means of 47.3 ± 4.71%, 57.2 ± 6.57%, and 41.8 ± 3.28% in sites 1, 2, and 3, respectively (P=0.06) (Table 3.4). In the 5-10 cm of soil, site 2 (35.4 ± 3.35%) had significantly higher moisture content values than site 1 (28.3 ± 0.75%), while site 3 was not significantly different from either site (31.2 ± 1.16%) (P=0.04) (Table 3.5). Moisture content was significantly
higher in the 0-5 cm soil layer (48.8 ± 8.13%) than in the 5-10 cm soil layer (31.7 ± 3.58%) due to less consolidation in the surface layer of newly deposited sediment (P < 0.001).

Bulk density in the 0-5 cm soil sections in sites 1, 2, and 3 were 0.62 ± 0.14, 0.45 ± 0.11, and 0.79 ± 0.11 g cm⁻³, respectively, and there were no significant differences among the three sites (P=0.08). In the 5-10 cm soil interval, bulk density was significantly higher in site 1 than in site 2 (1.24 ± 0.10 vs. 0.99 ± 0.07 g cm⁻³) (P=0.04). Site 3 was not significantly different from the other sites, with 1.15 ± 0.04 g cm⁻³. Similar to moisture content, bulk density was significantly lower in the 0-5 cm section compared to the 5-10 cm section (0.62 ± 0.18 g cm⁻³ vs. 1.13 ± 0.13 g cm⁻³, respectively) with a P value <0.001.

Loss on ignition was determined to be 1.93 ± 0.54% in site 1, 3.36 ± 0.95% in site 2, and 1.70 ± 0.68% in site 3 and there was no significant difference between the sites (P=0.13). Loss on ignition in the subsurface soil intervals were also not significantly different, with values of 1.30 ± 0.44%, 1.80 ± 0.23%, and 1.68 ± 0.22% in sites 1, 2, and 3, respectively (P=0.32). There was no significant difference in LOI measurements between the surface and subsurface soil intervals (2.34 ± 1.04% vs. 1.59 ± 0.38%) (P=0.07).

The total C values in the top 5 cm of each site were 10.1 ± 1.70, 14.06 ± 3.93, and 8.17 ± 0.92 g kg⁻¹, respectively, and there was no significant difference between the sites (P=0.14). Total C in the 5-10 cm soil interval were also not significantly different (P=0.14), with 5.47 ± 1.56, 8.10 ± 1.33, and 5.79 ± 0.55 g kg⁻¹ in sites 1, 2 and 3, respectively. Total C in the upper soil sections (10.76 ± 3.52 g kg⁻¹) was significantly higher than total C in the lower soil sections (6.45 ± 1.70 g kg⁻¹) with a P value of 0.007.

Similar to total C, no significant differences in total N were observed among the sites for the surface or subsurface soil intervals. For the 0-5 cm soil layer, an average of 0.87 ± 0.10, 1.30
± 0.34, and 0.78 ± 0.06 g kg\(^{-1}\) was found in each respective site (P=0.09). In the 5-10 cm soil layer, values were below detection (b.d.), 0.55 ± 0.39, and 0.21 ± 0.31 g kg\(^{-1}\) in respective sites (P=0.23). Total N values decreased significantly with increasing depth, with 0.98 ± 0.33 g kg\(^{-1}\) in the 0-5 cm soil layer and 0.26 ± 0.39 g kg\(^{-1}\) in the 5-10 cm soil layer (P<0.001).

Total P among the sites were not significantly different. In surface soils, TP was determined to be 566 ± 44.1 g kg\(^{-1}\) in site 1, 714 ± 174 g kg\(^{-1}\) in site 2, and 544 ± 36.7 g kg\(^{-1}\) in site 3 (P=0.29). In subsurface soils, TP was 439 ± 77.6, 480 ± 44.7, and 425 ± 43.7 g kg\(^{-1}\) in sites 1, 2, and 3, respectively (P=0.63). Total P decreased significantly with depth, with 608 ± 130 g kg\(^{-1}\) in the upper profile and 448 ± 62.1 g kg\(^{-1}\) in the lower profile (P=0.006).

Extractable NH\(_4\)\(^+\) in the surface sediment were not significantly different between sites, with 7.33 ± 1.50, 12.6 ± 3.11, 6.52 ± 0.82 mg kg\(^{-1}\) in sites 1, 2, and 3, respectively (P=0.05). Values in the subsurface sediment were also not significantly different, with 0.61 ± 0.57, 4.99 ± 3.43, and 1.51 ± 0.48 mg kg\(^{-1}\) in sites 1, 2, and 3 respectively (P=0.15). Extractable NH\(_4\)\(^+\) was significantly higher in the 0-5 cm soil profile compared to the 5-10 cm soil profile (8.82 ± 3.38 g kg\(^{-1}\) vs 2.37 ± 2.77 g kg\(^{-1}\)) with a P value <0.001.

Extractable NO\(_3\)\(^-\) from sediment treated with high and medium shear stresses were 0.08 ± 0.13 mg N kg\(^{-1}\) and 0.24 ± 0.22 mg N kg\(^{-1}\), respectively. There were no significant differences between the two shear stress treatments (P=0.10).

### 3.4.2 Grain Size Analysis, Turbidity, and Total Suspended Solids

Grain size of the sediment exhibited a bimodal distribution (Figure 3.6). In all three sites, the dominant sediment particle type was silt (4–8 Phi; 4-63 μm). Sand makes up the second largest percentage and clay the smallest. There were no observable significant differences in sediment distribution between the 0-1 and 1-2 cm sediment sections. Turbidity results reveal
sediment erosion was higher in cores with high shear stress conditions than those experiencing medium conditions of stress (Figure 3.7). Consequently, total suspended solids (TSS) were significantly greater in cores with a high shear stress than those with a medium shear stress (2.03 ± 0.50 vs. 1.08 ± 0.24 mg L⁻¹) (P<0.001). However, TSS results can only be used to gain insight on relative, not absolute, differences between the two stress treatments, since not all suspended solids within sediment cores were able to be sampled.

### 3.4.3 Areal NO₃-N reduction rates

Areal NO₃-N reduction rates were determined during the 24-hour period of each shear stress application as well as during the seven following days, with no shear stress (Figure 3.8; 3.9). Nitrate reduction rates in high shear stress (0.45 Pa) cores was significantly higher than all other treatments, with an average reduction rate of 303 ± 65.6 mg N m⁻² day⁻¹ (P<0.001) (Figure 3.10). Reductions in cores experiencing medium shear stress treatments (0.2 Pa) were 186 ± 55.1 mg N m⁻² d⁻¹ and were significantly lower than high shear cores, but higher than static cores that weren’t subjected to any shear stress. Sediment cores receiving no shear stress reduced 18.7 ± 20.2 mg N m⁻² day⁻¹ of NO₃-N during the first day of receiving nitrate. The large standard deviation of nitrate reduction in cores that did not receive shear stress is likely due to the occurrence of nitrification, or nitrate production, in several cores.

On average, rates of nitrate reduction after shear stress treatment ceased (post-GEMS) were significantly lower than those observed under shear stress conditions (Figure 3.11). During the seven days after cores were removed from GEMS, nitrate reduction in cores that previously received high and medium shear stress treatments was 5.00 ± 2.36 and 21.1 ± 10.8 mg N m⁻² day⁻¹, respectively. The long term nitrate removal of cores that received no initial shear stress application was 27.1 ± 7.08 mg N m⁻² day⁻¹.
3.4.4 Soil Property Relationships

In the 0-5 cm soil sections, total C was positively correlated with MC (r=0.97), LOI (r=0.89), TN (r=0.98), TP (r=0.97), and extractable NH$_4^+$ (r=0.82) and negatively correlated with bulk density (r=-0.88) (Table 3.2). Total N was well correlated with MC (r=0.95), LOI (r=0.91), TP (r=0.97), and extractable NH$_4^+$ (r=0.87). Total P was positively correlated with MC (r=0.91), LOI (r=0.86), and extractable NH$_4^+$ (r=0.81), while being negatively correlated to BD (r=-0.79). Extractable NH$_4^+$ was positively correlated with MC (r=0.75) and LOI (r=0.79). Long term nitrate reduction rates in cores treated with a medium shear stress were positively correlated with MC (r=0.72) and negatively correlated with bulk density (r=-0.68).

In the 5-10 cm soil sections, total C was positively correlated to MC, TN, TP, and extractable NH$_4^+$ (r= 0.87, 0.73, 0.82, 0.80, respectively) (Table 3.3). Total N was positively correlated with MC (r=0.90) and negatively correlated to BD (r=- 0.71). Extractable NH$_4^+$ was well correlated with MC (r=0.87).
Figure 3.6: Laser grain size distributions in 0-1 and 1-2 cm soil sections for each site. (Xiaoyu Sha, 2016)
Figure 3.7: An example of rotational rates in RPM (rotations per minute) and turbidity in NTU (nephelometric turbidity units) over 24 hours for cores experiencing high (0.45) and medium (0.20) shear stress forces. (Xiaoyu Sha, 2016)
Figure 3.8: Examples of change in nitrate concentration in core water columns in the first 24 hours of nitrate addition and the following 7 days for each shear stress. (A1-A2) High Shear Stress (0.45 Pa). (B1-B2) Medium Shear Stress (0.2 Pa). (C1-C2): Zero Shear Stress (0 Pa).
Figure 3.9: Examples of nitrate reduction rates in the first 24 hours of nitrate addition and following 7 days for each shear stress. Rates of nitrate reduction was determined using the slope of the linear trend line of nitrate loss over time. (A1-A2) High Shear Stress (0.45 Pa). (B1-B2) Medium Shear Stress (0.2 Pa). (C1-C2) Zero Shear Stress (0 Pa)
Figure 3.10: Short term NO$_3$-N reduction. Values for high and medium shear stress treatments were determined during a 24-hour application on the GEMS. Values for the zero shear stress treatment were determined during the first 24 hours of nitrate addition.

Figure 3.11: Long term NO$_3$-N reduction. Values for high and medium shear stress treatments were determined after cores were removed from the GEMS and sampled over 7 days. Values for zero shear stress cores were determined over the first 8 days of incubation.
Table 3.2: Correlation coefficients for soil characteristics and parameters in 0-5 cm soil sections. Bold indicates significance at \( P < 0.05 \) (n=9, at \( P=0.05, r=0.67 \)).

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Table 3.3: Correlation coefficients for soil characteristics and parameters in 5-10 cm soil sections. Bold indicates significance at \( P < 0.05 \) (n=9, at \( P=0.05, r=0.67 \)).

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<td>-0.17</td>
<td>-0.45</td>
<td><strong>0.82</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH4</td>
<td><strong>0.87</strong></td>
<td><strong>-0.69</strong></td>
<td>-0.01</td>
<td><strong>0.80</strong></td>
<td><strong>0.66</strong></td>
<td>0.53</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HS</td>
<td><strong>0.70</strong></td>
<td><strong>-0.72</strong></td>
<td>0.58</td>
<td>0.59</td>
<td>0.56</td>
<td>0.18</td>
<td>0.56</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MS</td>
<td>-0.24</td>
<td>0.32</td>
<td>-0.42</td>
<td>0.18</td>
<td>-0.27</td>
<td>0.33</td>
<td>0.00</td>
<td>-0.14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LS</td>
<td>-0.15</td>
<td>0.13</td>
<td>0.09</td>
<td>-0.11</td>
<td>0.03</td>
<td>-0.30</td>
<td>-0.24</td>
<td>0.10</td>
<td>0.36</td>
<td></td>
</tr>
<tr>
<td>HS Post</td>
<td>-0.05</td>
<td>0.30</td>
<td>-0.10</td>
<td>0.06</td>
<td>0.05</td>
<td>-0.12</td>
<td>0.01</td>
<td>-0.06</td>
<td>0.50</td>
<td>0.73</td>
</tr>
<tr>
<td>MS Post</td>
<td>0.38</td>
<td>-0.48</td>
<td>-0.28</td>
<td>0.54</td>
<td>0.22</td>
<td>0.56</td>
<td>0.58</td>
<td>0.28</td>
<td>0.41</td>
<td>-0.20</td>
</tr>
<tr>
<td>LS Post</td>
<td>-0.08</td>
<td>-0.10</td>
<td>0.27</td>
<td>0.02</td>
<td>-0.25</td>
<td>-0.10</td>
<td>0.10</td>
<td>0.42</td>
<td>0.50</td>
<td>0.60</td>
</tr>
</tbody>
</table>
Table 3.4: Sediment characteristics in the upper 0-5 cm profile of soil. Values are presented as a mean (n=3) and ± 1 standard deviation.

<table>
<thead>
<tr>
<th>Soil Parameter</th>
<th>Site 1</th>
<th>Site 2</th>
<th>Site 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil Depth (cm)</td>
<td>0-5</td>
<td>0-5</td>
<td>0-5</td>
</tr>
<tr>
<td>Moisture Content</td>
<td>47.3 ± 4.71</td>
<td>57.2 ± 6.57</td>
<td>41.8 ± 3.28</td>
</tr>
<tr>
<td>Bulk Density (g cm(^{-3}))</td>
<td>0.62 ± 0.14</td>
<td>0.45 ± 0.10</td>
<td>0.79 ± 0.11</td>
</tr>
<tr>
<td>Loss on Ignition</td>
<td>1.93 ± 0.54</td>
<td>3.36 ± 0.95</td>
<td>1.70 ± 0.68</td>
</tr>
<tr>
<td>Total Carbon (g kg(^{-1}))</td>
<td>10.1 ± 1.70</td>
<td>14.1 ± 3.93</td>
<td>8.17 ± 0.92</td>
</tr>
<tr>
<td>Total Nitrogen (g kg(^{-1}))</td>
<td>0.87 ± 0.10</td>
<td>1.30 ± 0.34</td>
<td>0.78 ± 0.06</td>
</tr>
<tr>
<td>Total Phosphorus (g kg(^{-1}))</td>
<td>566 ± 44.08</td>
<td>714 ± 174.23</td>
<td>543 ± 36.7</td>
</tr>
<tr>
<td>Extractable NH(_4^+) (mg kg(^{-1}))</td>
<td>7.33 ± 1.5</td>
<td>12.6 ± 3.11</td>
<td>6.52 ± 0.82</td>
</tr>
</tbody>
</table>
Table 3.5: Sediment characteristics in the 5-10 cm profile of soil. Values are presented as a mean (n=3) and ± 1 standard deviation. Different letters indicate significant difference between values at P < 0.05.

<table>
<thead>
<tr>
<th>Soil Parameter</th>
<th>Site 1</th>
<th>Site 2</th>
<th>Site 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil Depth (cm)</td>
<td>5-10</td>
<td>5-10</td>
<td>5-10</td>
</tr>
<tr>
<td>Moisture Content (%</td>
<td>28.3 ± 0.75^a</td>
<td>35.4 ± 3.35^b</td>
<td>31.2 ± 1.16^ab</td>
</tr>
<tr>
<td>Bulk Density (g cm(^{-3}))</td>
<td>1.24 ± 0.10^a</td>
<td>0.99 ± 0.07^b</td>
<td>1.15 ± 0.04^ab</td>
</tr>
<tr>
<td>Loss on Ignition (%)</td>
<td>1.30 ± 0.44</td>
<td>1.80 ± 0.23</td>
<td>1.68 ± 0.22</td>
</tr>
<tr>
<td>Total Carbon (g kg(^{-1}))</td>
<td>5.47 ± 1.56</td>
<td>8.10 ± 1.33</td>
<td>5.79 ± 0.55</td>
</tr>
<tr>
<td>Total Nitrogen (g kg(^{-1}))</td>
<td>0.00</td>
<td>0.55 ± 0.39</td>
<td>0.22 ± 0.31</td>
</tr>
<tr>
<td>Total Phosphorus (g kg(^{-1}))</td>
<td>439 ± 77.56</td>
<td>480 ± 44.74</td>
<td>425 ± 43.72</td>
</tr>
<tr>
<td>Extractable NH(_4^+) (mg kg(^{-1}))</td>
<td>0.61 ± 0.57</td>
<td>4.99 ± 3.43</td>
<td>1.51 ± 0.48</td>
</tr>
</tbody>
</table>
Table 3.6: Results for experimental variables for each shear stress treatment (n=9). Different letters indicate significant difference between values at P < 0.05

<table>
<thead>
<tr>
<th>Experimental Variable</th>
<th>High Shear Treatment</th>
<th>Medium Shear Treatment</th>
<th>No Shear Treatment</th>
<th>P-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Extractable NO$_3^-$ (mg kg$^{-1}$)</strong></td>
<td>0.076 ± 0.13</td>
<td>0.238 ± 0.22</td>
<td>ND</td>
<td>0.10</td>
</tr>
<tr>
<td>Total Suspended Solids (mg L$^{-1}$)</td>
<td>2.03 ± 0.50$^a$</td>
<td>1.08 ± 0.24$^b$</td>
<td>ND</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Areal NO$_3^-$N Reduction: Short-Term (mg N m$^{-2}$ day$^{-1}$)</td>
<td>303 ± 65.6$^a$</td>
<td>186 ± 55.1$^a$</td>
<td>18.7 ± 20.2$^c$</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Areal NO$_3^-$N Reduction: Long-Term (mg N m$^{-2}$ day$^{-1}$)</td>
<td>5.00 ± 2.36$^a$</td>
<td>21.1 ± 10.8$^b$</td>
<td>27.1 ± 7.08$^b$</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

3.5 Discussion

There is a lack of data on nitrate reduction rates in turbulent environments where sediment is eroded and deposited. The resuspension of sediment can provide increased opportunities for denitrifying microbes to interact with nitrate-laden water, since nitrate diffusion into sediment can limit rates of reduction (Reddy, Patrick, and Phillips, 1978; Nielsen et al., 1990; Reddy and DeLaune, 2008). Resuspension can also facilitate increased rates of nitrification due to the release of NH$_4^+$ during sediment suspension, allowing for more nitrate to become available for reduction (Morris et al., 1985; Austin and Lee, 1973; Wang et al., 1998; Xia et al., 2009).
Impact of Sediment Resuspension on Nitrate Reduction Rates

Nitrate reduction rates in sediment cores experiencing high shear stress conditions were 39% higher than rates in cores experiencing medium shear stress conditions and 94% higher than those not receiving any shear treatment. Additionally, cores with medium stress application had nitrate reduction rates that were 90% higher than those without any shear stress application. Enhanced nitrate reduction in cores with resuspended sediment is likely the result of two main causes, one of which is an increase in reduction rates due to higher levels of microbe-nitrate interaction. There was no difference in bulk density or grain size between any of the sites and, although accurate erosional depth could not be determined from TSS results, both TSS and turbidity increased with shear stress; consequently, erosion of surface sediment must also increase with shear stress. Greater depths of erosion can mobilize the top layer of sediment, where obligate, aerobic microbes dominate, and allow nitrate to more easily access the underlying layer by advection, where facultative aerobes can perform denitrification (Reddy and DeLaune, 2008). Whereas diffusion can limit nitrate flux into sediment, erosion allows for nitrate to directly encounter the nitrate reducing layer of sediment via advection. In addition to erosion allowing greater contact between denitrifiers and microbes, denitrifiers can be attached to suspended particles in core water, further providing increased interaction between denitrifying microbes and nitrate in water.

Another possible cause of higher nitrate reduction rates observed in cores with resuspended sediment may be due to increased rates of nitrification resulting from NH$_4^+$ release from sediment. When sediment is resuspended in an aerobic water column, such as that in the cores studied here, NH$_4^+$ that is released can be nitrified, creating more nitrate to be available for reduction (Austin and Lee, 1973; Wang et al., 1998; Xia et al., 2009). It is hypothesized that an
increase in core water nitrate from nitrification is partially responsible for increased rates of nitrate reduction observed in cores experiencing shear stress. If this is true, then nitrate reduction rates are greater than those actually observed. Future studies should measure and consider the enhancement of nitrification brought on by resuspension when attempting to understanding nutrient dynamics resulting from sediment diversions.

**Nitrate Reduction Rates After Shear Stress Application (post-GEMS)**

Without the shear stress application provided by the GEMS, post-GEMS rates of nitrate reduction were similar, except those first treated with a high shear stress, which demonstrated significantly lower rates of reduction (Figure 3.10, Table 3.6). Lower long-term rates of nitrate reduction in cores initially experiencing high rates of reduction during the GEMS experiment may be due to nitrate depletion in core water. Fick’s law (Equation 3.1) describes diffusion of a substance as being proportional to the substance’s concentration and length of the diffusion gradient. As concentration of a substance decreases, so does diffusion. Cores with highest rates of nitrate reduction in the first 24 hours ended that time period with a lower concentration of nitrate than all other cores (Figure 3.12). This suggests that decreased nitrate diffusion in to the sediment due to significantly lower concentrations of nitrate may be a reason why reduction rates were much lower after 24 hours of sediment resuspension. During post-GEMS observations, diffusion is controlled solely by Fick’s law. In an actual delta, this problem would be eliminated by a constant input of nitrate from diverted water.

**Equation 3.1: Fick’s First Law of Diffusion**

\[ J = -D \frac{dc}{dz} \]

where \( J \) is diffusion flux, \( D \) is the diffusion constant, and \( \frac{dc}{dz} \) is the concentration gradient per unit length
Figure 3.12: Beginning and end concentrations of nitrate over 24 hours for each shear stress condition. End concentration of nitrate decreased with increases of shear stress force.

It is likely that most nitrate was removed from the system as gaseous loss by denitrification, given that nitrate remaining in the sediment was minimal, as demonstrated by extractable NO$_3^-$ data. There were no significant differences in total C and N or extractable NH$_4^+$ and NO$_3^-$ in surface sediments, which strongly suggests that observed differences in nitrate reduction were solely due to differences in shear stress application. While nitrate reduction rates are significantly higher in turbulent areas, areas where little shear stress is applied (i.e. well-developed marshes far away from the diversion outfall) will have the added benefit of vegetative uptake, which can significantly increase rates of nitrate removal from diverted water and should be taken in to account when modeling nutrient removal from diversions (VanZomeran, White, and DeLaune, 2013).

In Barataria Basin, which receives water from the Davis Pond diversion, Gardner and White (2010) found nitrate reduction rates that averaged 137 ± 24 mg N m$^{-2}$ d$^{-1}$, which is higher than the rates observed in static cores, but lower than those observed during resuspension. Total
C in the Barataria Basin soils studied by Gardner and White (2010) was much greater than the total C found in the deltaic sediments in this study, and likely heavily influenced rates of denitrification. In the Breton Sound estuary, which receives diverted water from the Caenarvon diversion, VanZomeren et al. (2013) measured nitrate reduction rates in marsh soils and bayou sediments with rates of $7.2 \pm 0.9$ and $9.5 \pm 1.5$ mg N m$^{-2}$ d$^{-1}$, respectively, which are lower than most rates observed in this study. The wide ranges of nitrate reduction rates observed highlight the spatial variability of nitrate reduction. The variability in reduction also emphasizes the significant effect resuspension and erosion can have on nitrate removal, given that reduction rates in sediments experiencing erosional stress were among the highest observed.

The methods used in this study are not only useful for determining rates of nitrate reduction in turbulent areas of diversion, but also for any flowing system where sediment is resuspended and in energetic conditions experienced during the passage of hurricanes and storms. If studies in flowing systems have quantified nitrate reduction rates using methods that do not mimic field conditions and account for the effect of sediment resuspension, calculated rates of reduction are likely to be much lower than actual values in the field. Future studies attempting to measure nitrate reduction rates in flowing systems should incorporate the impact of sediment resuspension; otherwise, values of nitrate reduction may be grossly underestimated.

Results from this research can help inform modelers and natural resource managers to predict potential nutrient impacts of river diversions on coastal receiving basins. Spatial and temporal variability in nutrient removal is necessary to better model the effects of sediment diversions and the fate of nutrients delivered. Assuming that the shear stress applied by the force of diverted water decreases with distance from the outfall and that nitrate reduction declines as shear stress decreases (as suggested by this study), these results imply that nitrate reduction rates
are likely to decrease with distance from the diversion as well. Results from this study suggest that sediment resuspension resulting from sediment diversions can significantly increase nitrate reduction. Results also suggest that shear stress applied by diverted water will successfully mobilize fine-grained sediments to coastal areas. Using solely a static rate of nitrate reduction will not appropriately approximate the nitrate removal capacities of receiving basins. This study demonstrates that nitrate reduction rates and total N removal will be variable depending upon the level of shear stress applied by diverted water (i.e. discharge rates, velocity, and distance from diversion outfall), whether diversions are open or closed, and the areal size of turbulent environments.

3.6 Conclusion

Sediment diversions have been planned to provide increased sediment input to subsiding coastal wetlands to slow and eventually reverse coastal land loss in Louisiana, providing a sustainable long-term solution to wetland loss. These diversions would deliver sediment, nutrients, and freshwater to struggling coastal marshes, but may also help trigger algal blooms and subsequent areas of hypoxia by delivering nitrate-laden water. There is a paucity of data on nitrate removal in the near-field area of diversions, where sediment is resuspended and turbidity is increased due to shear stress from the diversion outfall. This study measured rates of nitrate reduction resulting from sediment resuspension caused by diverted river water. Shear stress forces were applied to deltaic sediments using a Gust Erosion Microcosm System (GEMS), mimicking the turbulent environments created by sediment diversions. Nitrate reduction rates were 39-94% higher in sediments that received shear stress application compared to those that did not. The results from this study demonstrate the important role sediment resuspension plays in significantly reducing nitrate from diverted river water and emphasizes the spatial variability
of reduction as a gradient from diversion outfall to receiving basin. Modelers and resource managers should incorporate nitrate reduction in the near-field environment of diversions to better understand the fate of nutrients delivered by sediment diversions in Louisiana.
Chapter 4: Summary and Conclusions

The application of nitrogen fertilizer is necessary to sustain and support a growing world population. However, the increased usage of N fertilizers can put a significant strain on aquatic ecosystems. Consequently, N eutrophication has become pervasive around the globe and has become a particular problem in the coastal waters of Louisiana. A large portion of the Mississippi River’s drainage basin is located in central U.S., where almost 60% of the land is used for agriculture. Excess nitrate from these agricultural areas can run off to the Mississippi River, resulting in higher N concentrations of the River. When these nitrate-laden waters reach the northern Gulf of Mexico, they provide nutrients for algae, resulting in large populations of algal growth, known as algal blooms. In the summer months when coastal waters are stratified, the death and subsequent decomposition of large masses of algal material can result in an area of hypoxia. Areas of hypoxia, or low oxygen, can be detrimental to aquatic populations and threaten commercial fisheries.

Increasing opportunities for nitrate removal from the Mississippi River can help to reduce hypoxia in the northern Gulf of Mexico. Wetlands, both riparian and coastal, are well adapted at removing nitrate from river surface waters, primarily via denitrification. However, the intensive channelization and levee construction of the lower Mississippi River heavily restricts river water interaction with riparian and coastal wetlands. Consequently, nitrate removal by wetlands is limited. Fortunately, restoration practices in Louisiana include reintroducing the Mississippi River to its natural floodplain, including both riparian and coastal wetlands. The study presented here examined the effects of restorative practices on enhancing nitrate reduction from river floodwaters.

Nitrate reduction was first evaluated in a hydrologically restored bottomland hardwood forest in northern Louisiana. This particular bottomland hardwood was converted to agricultural
land and is adjacent to the Ouachita River, a tributary of the Mississippi river. The site was disconnected from the Ouachita River at the onset of farming in 1969 and reconnected in 2009. Soil cores were collected from the restored site and a nearby control site to evaluate nitrate reduction rates, which were compared between the two areas. Cores were flooded with a 20 cm water column of a 1 mg N L\(^{-1}\) nitrate solution. Samples were collected from the water column every other day for 2 weeks to measure nitrate loss over time. Potentially mineralizable N rates, extractable NH\(_4^+\), Beta-glucosidase activity, and microbial biomass N were also measured to compare biogeochemical functioning between the sites. All soil properties were significantly different between the restored and control sites, with the restored site usually having significantly lower measurements, with the exception of extractable NH\(_4^+\) and bulk density. However, nitrate reduction rates were only 28% lower in the restored site compared to the control site. Nitrate reduction was strongly related to total C, which suggests that as carbon increases in the restored site, so will nitrate reduction. Results suggest that the hydrologic reconnection of the bottomland hardwood site for the past 6 years has positively influenced water quality due to its contribution to nitrate reduction. The continued hydrologic restoration of bottomland hardwood Forests should further increase opportunities for nitrate reduction.

Nitrate reduction rates resulting from Mississippi River sediment diversions were also evaluated. Sediment diversions in Louisiana are designed to reintroduce water from the Mississippi River to coastal wetlands, similar to the interaction that occurred prior to hydrologic alteration. Large-scale sediment diversions will deliver freshwater and sediment to coastal areas, aiding marsh accretion and helping to slow or reverse coastal land loss. However, sediment diversions will also deliver nutrients, particularly nitrate, to receiving basins with potential for environmental impact. The fate of nitrate delivered by sediment diversions is not well understood.
and clarification is necessary to better understand the impact of diversion operation on receiving basins.

This study investigated nitrate reduction rates in the near-field area of sediment diversions, where the force of diverted water resuspends sediment and creates a turbulent environment. A Gust Erosion Microcosm System was used to mimic the shear stress applied by flowing diverted water. Sediment cores were collected from mudflats in Wax Lake Delta, a growing deltaic environment in Louisiana that receives sediment input similar to what is expected by sediment diversions. Three levels of shear stress were applied to sediment cores: high (0.45 Pa), medium (0.2 Pa), and zero (0 Pa), which were used to evaluate the spatial variability of nitrate reduction, given that shear stress is likely to decrease with distance from the diversion outfall. A 2 mg L$^{-1}$ nitrate solution was circulated throughout the cores while shear stress was applied to the sediment surface for 24 hours. Water samples were collected every 2 hours during the 24 hours.

Nitrate reduction rates were 39-94% higher in cores that received shear stress than those that received no shear stress. The erosion of sediment in cores experiencing shear stress likely allowed for a great interaction between denitrifying microbes and nitrate in the water column, thus increasing rates of nitrate reduction. Nitrate reduction decreased with decreasing shear stress, which implies that nitrate reduction is also likely to decrease with distance from the diversion outfall. Results from this study indicate that sediment resuspension can significantly increase rates of nitrate reduction. When attempting to model the fate of nitrate delivered by sediment diversions, higher nitrate reduction rates in the near-field areas of diversions must be incorporated.
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VITA
Nia R. Hurst grew up in New Orleans, La. with her parents and younger brother. Nia attended DePaul University in Chicago, IL where she graduated with a B.S. degree in Environmental Science and a minor in Community Service. Despite growing up in coastal Louisiana, Nia didn’t fully discover her love of wetlands until she began working on her undergraduate thesis on carbon storage in Great Lakes coastal wetlands with her research advisor, Dr. Beth Lawrence. Nia completed a Research Experience for Undergraduates (REU) at the University of Michigan’s Biological station the summer before her senior year and knew immediately that she wanted to pursue a Master’s degree in wetland sciences. After graduating from DePaul University in 2014, Nia accepted a fellowship offer at Louisiana State University in Baton Rouge, La. with Dr. John White to continue her wetland studies in wetland biogeochemistry.