Decadal Changes of Soil Physiochemical Properties in A Freshwater Wetland After Hydrologic Reconnection

Alina Spera
Louisiana State University and Agricultural and Mechanical College

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DECADAL CHANGES OF SOIL PHYSIOCHEMICAL PROPERTIES IN A FRESHWATER WETLAND AFTER HYDROLOGIC RECONNECTION

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

Alina Spera
B.S., University of Miami, 2016
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# TABLE OF CONTENTS

ACKNOWLEDGEMENTS ........................................................................................................... ii

LIST OF TABLES ........................................................................................................................ v

LIST OF FIGURES.................................................................................................................... vi

ABSTRACT ................................................................................................................................... viii

CHAPTER 1. REVIEW OF LITERATURE .................................................................................... 1
  1.1. Coastal Wetlands of Louisiana ......................................................................................... 1
  1.2. Freshwater Diversion Controversy .................................................................................. 6
  1.3. Nitrogen Cycle ................................................................................................................ 11
  1.4. Phosphorus Cycle .......................................................................................................... 13
  1.5. Geostatistics .................................................................................................................. 15
  1.6. Davis Pond: Site Description and Previous Work ......................................................... 20
  1.7. Synopsis of Chapters .................................................................................................... 24

CHAPTER 2. IMPACTS OF INCREASED MINERAL SEDIMENTATION AND NUTRIENT ENRICHMENT ON WETLAND SOILS AS A RESULT OF FRESHWATER DIVERSION OPERATION ......................................................................................... 25
  2.1. Introduction.................................................................................................................... 25
  2.2. Materials and Methods ............................................................................................... 29
  2.3. Results and Discussion ............................................................................................... 38
  2.4. Conclusions .................................................................................................................. 58

CHAPTER 3. FRESHWATER RIVER DIVERSION DRIVING DISTRIBUTION OF INORGANIC AND ORGANIC PHOSPHORUS STOCKS IN WETLAND RECEIVING BASIN ................................................................................................................................. 64
  3.1. Introduction.................................................................................................................... 64
  3.2. Materials and Methods ............................................................................................... 67
  3.3. Results and Discussion ............................................................................................... 74
  3.4. Conclusions .................................................................................................................. 86

CHAPTER 4. SUMMARY AND CONCLUSIONS ......................................................................... 88

APPENDIX A. EXPERIMENTAL VARIOGRAMS ..................................................................... 91

APPENDIX B. VARIOGRAM MODEL FIT PARAMETERS AND MSDR .................................. 93

APPENDIX C. MIXTURE MODEL RESULTS ............................................................................. 94

APPENDIX D. MEASURED AND PREDICTED RAW DATA .................................................. 95

REFERENCES ............................................................................................................................ 96
LIST OF TABLES

Table 2.1. Mean soil variable values for 0-10 cm soil layer for measured sites .............38
Table 2.2. Mean soil variable values for 0-10 cm soil layer for predicted soil maps .........42
Table 2.3. Estimated area of diversion impacted for each sampling year ......................47
Table 2.4. Davis Pond Diversion discharge and nitrate concentration of the Mississippi River in the months leading up to sampling in 2007 and 2018 ..................................................50
Table 2.5. Total stock of carbon and nitrogen from 0-10 cm and 10-20 cm soil layer in each year ..............................................................................................................51
Table 2.6. Volumetric content and ratio of carbon and nitrogen from 0-10 cm soil layer from the river- impacted and non-impacted wetland areas in each year ....................52
Table 2.7. Results of principal components analysis .............................................................55
Table 2.8. Means of soil variables, PC1 and PC2 values by cluster number .................56
Table 3.1. Mean volumetric P content for each fraction at 140 measured sites and from predicted dataset presented with standard error .................................................................76
Table 3.2. Mean volumetric P content by year of each soil P fraction inside and outside of the diversion impact zone ................................................................................77
LIST OF FIGURES

Figure 1.1. Total land area in coastal Louisiana, 1930 to 2012 with 95% confidence band (blue lines)........................................................................................................................................2

Figure 1.2. Map of projects completed, ongoing and future outlined in CPRA Coastal Master Plan ..................................................................................................................................................4

Figure 1.3. Map of southeastern Louisiana indicating the two major freshwater diversions, Davis Pond and Caernarvon...................................................................................................................5

Figure 1.4. Major pathways for the nitrogen cycle in wetlands.......................................................10

Figure 1.5. Major pathways of the wetland Phosphorus cycle .........................................................13

Figure 1.6. Standard variogram with model parameter labels ............................................................18

Figure 1.7. Map of study area, Davis Pond freshwater diversion, and its location relative to Louisiana...........................................................................................................................................21

Figure 1.8. Drone images of Davis Pond Diversion in March 2018..................................................22

Figure 1.9. Results from 2012 study, interpolated maps for total carbon and bulk density in 2007 soils ..................................................................................................................................................23

Figure 2.1. Satellite images of Davis Pond Diversion ponding area ..................................................28

Figure 2.2. Map of Davis Pond Diversion and surrounding area.......................................................29

Figure 2.3. Vegetation and Habitat Type Map ...................................................................................42

Figure 2.4. Maps of mineral (ash) content in 0-10 cm soil layer in each sampling year .........44

Figure 2.5. Map of $^{15}$N (‰) in 0-10 cm soil layer from each year .............................................46

Figure 2.6. Denitrification Enzyme Activity in 0-10 cm soil layer from each sampling year ................................................................................................................................................49

Figure 2.7. Difference in volumetric carbon content in the 0-10 cm soil layer from 2007 to 2018 outside of the 95% confidence interval ..................................................................................................51

Figure 2.8. Carbon and nitrogen content, C:N and $^{15}$N by marsh or habitat type ..................54

Figure 2.9. Map of soils types based on cluster assignments for predicted sites from 2018 dataset ................................................................................................................................................58
Figure 3.1. Maps of predicted values for concentration of total inorganic phosphorus and total organic phosphorus in 2007 and 2018 .................................................................75

Figure 3.2. Map sediment influenced zone in 2007 and 2018 ..................................................77

Figure 3.3. Contribution of volumetric content of each soil P fraction by year in the diversion sediment influenced zone and the non-influenced zone .................................................78

Figure 3.4. Davis Pond map demonstrating where, between years, new soils has change in soil OP and IP outside the 95% confidence interval for change ........................................79

Figure 3.5. Soil N:P ratio values for each sampling year in the sediment influenced and non-influenced wetland areas ..................................................................................83

Figure 3.6. C:N and C:OP ratio values for each sampling year in the sediment influenced and non-influenced wetland areas ........................................................................84
ABSTRACT

Sediment, nutrient deprivation and salt water intrusion, among other factors, are driving widespread organic soil collapse and marsh loss in the Mississippi River Delta. Freshwater diversions were designed to reintroduce Mississippi River water and dissolved nutrients into the adjacent basins to manage salinity and slow land loss by maintaining marsh vegetation and nutrient cycling functions. These diversions are controversial by a few, suggesting that nutrient enrichment without a sediment subsidy can lead to further wetland loss in the receiving basins. In this study, a soil characterization is presented for the receiving marsh of the Davis Pond diversion in 2007, just as full-scale operation began, and again in 2018 after 11 years of diversion influence. Data for the top 10 cm of soil from 140 stations in both years were used in spatial analysis to create maps of soil properties. As a result of sedimentation from the diversion, there has been a significant increase of soil mineral content, and consequently soil bulk density. Elevated soil δ15N isotope values and increased inorganic phosphorus stocks suggest elevated rates of nutrient enrichment in the wetland, leading to increased mean organic matter and carbon content, especially in those immediate areas of diversion influence. Changes to biogeochemical cycling is apparent in altered soil nutrient ratios. Multivariate methods demonstrate the effectiveness of certain soil parameters for monitoring impacts of river diversions in wetlands. The δ15N isotope is an important indicator of river water-influenced soils, whereas mineral content and inorganic phosphorus can identify in which areas a river sediment subsidy was provided. Previous to this study, the long-term impacts of lower Mississippi River hydrologic restoration projects had yet to be statistically quantified due to little or no pre-sampling. The results of this study have implications for monitoring diversion impacts, providing guidance for continued use of freshwater diversions in Louisiana, and informing future management strategies in coastal areas around the world.
CHAPTER 1. REVIEW OF THE LITERATURE

1.1. Coastal Wetlands of Louisiana

1.1.1. Biogeochemical Importance of Wetlands

Wetland environments are an integral part of the natural landscape in the US and across the globe. While they exist at the interface of terrestrial and aquatic ecosystems, benefits from wetland services can be seen on a local and global scale. Wetlands can be diverse in terms of hydrology, vegetation and soil types, but the importance of wetlands lies in the conditions found ubiquitously that provide essential services to the environment and to humans. Flooded wetland soils tend to have low oxygen conditions providing habitat for anaerobic microbial communities which drive biogeochemical processes. Anaerobic microbial respiration reduces oxidized compounds and mineralizes organic matter, which can transform excess nutrients or contaminants, and remove them from the system. Wetlands can store, transform or transport many materials while providing flood protection, habitat for wildlife and fisheries, improving water quality and sequestering carbon.

The Louisiana Coastal Wetlands Conservation and Restoration Task Force estimated the economic value of ecosystem services of Louisiana wetlands is over $100 billion (Louisiana Coastal Wetland Functions and Values, 1997). That valuation not only depends on the capacity for them to store or remove nutrients and contaminants, it also includes several other important contributions like commercial fishing, recreation, carbon storage, transportation and storm surge protection. Wetlands provide important habitat and act as the base of trophic interactions within the coastal system. Recreational fishing of wetland-dependent species contributes $235 million annually to the state’s economy (Cowan et al., 1988), along with $21.7 billion in tourism and recreation in and around wetlands across the state. With more than 1.1 billion pounds harvested
each year, Louisiana provides more fishery landings that any other state in the contiguous US, and over 75% of commercially harvested fish and shellfish species in Louisiana are wetland dependent (LA Coast, 1997).

1.1.2. Coastal Land Loss and Restoration

Wetland loss along the Louisiana coastal zone is a major concern in the Mississippi River Delta (MRD). The current rate of land loss in Louisiana is a little over 75 km$^2$ per year, and since the 1930s the state has lost approximately 25% of its total wetland area (Figure 1.1) (Couvillion et al. 2017). The land of the MRD was formed as sequential delta lobes from natural sediment deposition by the Mississippi River. Historically, breaches of natural levees along the river provided materials like nutrients and sediments from the river, driving productivity of emergent vegetation and influencing organic and inorganic accretion (DeLaune et al., 2013). Many factors contribute to the widespread subsidence and erosion of marshes, like sea level rise (SLR), storms, and human alteration of the natural hydrological regime. By building levees that

![Figure 1.1. Total land area in coastal Louisiana, 1930 to 2012 with 95% confidence band (blue lines). Adapted from Couvillion et al., 2017.](image-url)
disconnect the river from riparian coastal basins, humans have caused widespread fresh water, nutrient and sediment deprivation.

The average rate of eustatic SLR is 3-4 mm year\(^{-1}\) (IPCC, 2014), however, when combined with local subsidence, the true rate of rising seas in coastal Louisiana is \(\sim 10\) mm year \(^{-1}\). As a result, inland wetlands are facing high rates of saltwater intrusion and flood stress. This damages vegetation root systems that prevent collapse of highly organic soils (Delaune & White, 2012). When inland marshes are continually disconnected from an external nutrient or sediment supply there is concern that they can no longer gain elevation at rates that match or exceed those of concomitant SLR and basin wide subsidence.

Coastal Louisiana is a nitrogen limited environment and excessive N loading from the river has led to eutrophication and hypoxic conditions in the coastal environment. One such impact is the so-called “Gulf of Mexico Dead Zone” where low bottom water oxygen conditions are caused by excessive algal blooms (Rabalais et al., 2002). It’s known that wetlands generally act as a nutrient sink for excess nitrogen either by assimilation by emergent vegetation or denitrification (Reddy and DeLaune, 2008). With the leveed river system and current wetland loss rates, nutrient trapping within the river system is limited and excess nutrients in the river do not have a chance to interact with wetland environments before moving directly to the Gulf of Mexico (Kroes et al., 2015).
The Coastal Protection and Restoration Authority (CPRA) developed the first iteration of the Coastal Master Plan in 2007 with a new plan released every 5 years (Figure 1.2). CPRA engages with stakeholders, scientific community and the public to outline the coastal restoration goals of the state and proposes projects that will address current and future issues on the Louisiana Coast. With more than 135 projects completed and 36,000 acres of land benefited since 2007, the Coastal Master Plan has been effective not only at establishing a need for restoration but implementing solutions that are updated with each release of a new plan. Some of the largest projects outlined in 2017 are large scale sediment diversions that will use the Mississippi River to supply sediment and freshwater to large areas of degraded wetland in Barataria and Breton Sound Basins (CPRA, 2012 & 2017). Although advances in modeling allow researchers to investigate large scale impacts of diversions, there are few examples of this.

Figure 1.2. Map of projects completed, ongoing and future outlined in CPRA Coastal Master Plan 2017. Adapted from CPRA 2017.
type of project elsewhere in the world that can be used to validate those models and improve their utility.

Before CPRA developed plans for the large sediment diversions, freshwater surface diversions, such as Caernarvon and Davis Pond, were built to reintroduce freshwater from the Mississippi River to maintain salinity gradients within Louisiana’s large coastal basins to preserve habitat for commercially important fisheries (Figure 1.3). Secondary goals of these projects were to help coastal marsh vegetation and enhance marsh accretion within the adjacent coastal wetlands. Freshwater diversions were designed to direct approximately 0.2% of the Mississippi River discharge, with very little inorganic sediment or other river material, into the receiving basins (Barras et al., 2003). Freshwater diversion discharge is determined by operational plans developed by CPRA, and discharge varies seasonally and annually based on measured salinities in Barataria Basin (Barras et al., 2003). In the years 2008-2018, average

![Map of southeastern Louisiana indicating the two major freshwater diversions, Davis Pond and Caernarvon. Adapted from the Advocate.](image-url)
annual discharge of the Davis Pond varied from 25.9 and 119.3 m$^3$s$^{-1}$ (USGS). Since the Caernarvon and Davis Pond diversions began full operation in 1998 and 2009, respectively, there have been conflicting reports of positive and negative impacts from sustained river input. As such, uncertainty associated with the outcomes of freshwater diversion projects, and potential issues related to the planned sediment diversions, are reported in the literature. These controversies will be described and reviewed in the following section.

1.2. Freshwater Diversion Controversy

1.2.1. Nutrient and Sediment Enrichment and Wetland Soils

The most contentious issue regarding the freshwater diversion controversy is the impact of incoming nutrients and sediments on marsh soil stability. The annual river NO$_3^-$ concentrations have doubled since the Upper Barataria Basin and Davis Pond marsh were hydrologically isolated by levees in 1904 (Goolsby et al., 2001; Evers et al., 1992). Increasing frequency of high energy storm events are a threat mainly to Louisiana low-salinity marshes (Day et al., 2007). High buoyancy (Howes et al., 2010) and supposed low soil strength as a result of fertilization (Turner et al., 2009) have been proposed as causes for conversion of marsh area to open water after Hurricanes Katrina and Rita.

Initial operation of freshwater diversions caused concerns that input of nutrients from river laden water or sediments will lead to eutrophication in wetland basins. According to several studies, nutrient addition provides substrate for microbial respiration and therefore increases decomposition rates. Nutrient enrichment will also contribute to a loss of belowground biomass due to biomass partitioning by the wetland vegetation. These mechanisms can lead to loss of stability and organic soil collapse (Darby and Turner, 2008a; Swarzenski et al. 2008; Wigand et al., 2009). Another concern for use of diversions as restoration tools in order to combat
subsidence is evidence that nutrient enriched marshes tend to have lower elevation gain rates or in some cases experience elevation loss once enriched (Turner et al., 2009; Langley, 2009). In contrast, many studies of sediment and nutrient enrichment report a neutral or even positive response of marsh soils (Morris et al. 2002; Langley et al. 2009; Graham and Mendelssohn 2014; Shaffer et al. 2015; Hillmann et al. 2018)

If marsh vegetation is nutrient-limited, fertilization encourages high productivity (Craft, 2007; Graham and Mendelssohn 2010; Shaffer et al. 2015), and accretion of organic material at the surface (Anisfield & Hill 2012). In addition, Anisfield and Hill (2011) reported that although fertilization increases CO$_2$ loss from *Spartina alterniflora* wetlands, common in Breton Sound and the Caernarvon freshwater diversion, there is no negative impact on belowground decomposition and C stocks. In fact, Valiela et al. (1976) observed an increase in below-ground production after fertilization of a *S. alterniflora* salt marsh. Nutrient addition impacts on *Sagittaria lancifolia*, and other species common to the Davis Pond receiving basin, are not as well studied. Evidence suggests, however, that intermediate and high loading of N resulted in increased productivity of *S. lancifolia* (Graham & Mendelssohn, 2010). Additionally, decomposition rates in *S. lancifolia* marshes are N limited and so enrichment may stimulate mineralization processes (Laursen, 2004). In bald cypress (*Taxodium distichum*) swamp ecosystems, which inhabit many of the higher elevation wetland areas in the Davis Pond, sediment and nutrient addition has shown to increase productivity, sediment accretion and flood tolerance (Day et al., 2012; Effler et al., 2006). Hydroperiod, however, also plays an important role in bald cypress response to nutrient addition such that trees limited by flood stress do not benefit from nutrient addition (Keim, et al. 2012, Nyman & Lindau, 2016). Although increased decomposition rates are common with marsh nutrient enrichment in many wetland types across
coastal Louisiana, an increase in plant productivity could offset soil organic matter loss leading to maintenance of C stocks and accretion rates (Holm et al., 2014; Graham and Mendelssohn, 2016).

Freshwater diversions are also efficient at delivering fine-grained sediments, a process that has been shown to be beneficial for wetland plants and encourages formation of soils which are more structurally stable (Morris et al. 2013). Deposited sediments can increase the elevation of wetlands, improve soil aeration and buffer vegetation from flood or salt stress, all of which lead to increased productivity and in turn contribute to organic accretion processes (Mendelssohn, 1981; Wilsey, 1992, Mendelssohn and Kuhn, 2003). Mineral sediments can also be a source of Mn and Fe that reduce toxicity of reduced hydrogen sulfides by precipitating sulfidic materials (Slocum et al. 2005). Floating marshes are a common feature of disconnected freshwater inland wetlands because lack of mineral sediments and an accumulation of methane gas leads to a buildup of highly organic soils. In floating marshes fresh methanotrophic conditions develop and produce gases which push root mats up to the water surface. If high mineral sediment loads can be deposited on sunken floating marshes they will have lower buoyancy and may cause the floating mats to sink, becoming open water areas. However, nutrient addition can increase productivity enough to produce organic matter that will stabilize mats (Sasser et al. 1995) and help promote conversion to rooted marsh (Izdepski et al. 2009).

Ultimately it is difficult to describe the impact of one or two factors, like nutrients or sediments, in a complex system of diverse limitations and stresses. One must also consider that wetland plants, soils, and organic matter also exist in the context of changing climate and environmental influences.
1.2.2. *Carbon Cycle*

Wetlands account for 20-25% of global terrestrial C storage (DeLaune and White, 2012). Globally, freshwater tidal wetlands store, on average, 140 g-C m$^2$yr$^{-1}$ which is the upper range for average C storage in all wetland types reported by Mitra et al. (2005). Carbon storage is a result of coupled accumulation and loss of organic marsh soil. As such, erosion or conversion of vegetated marsh to open water areas releases organic matter into the oxygenated water column that is degraded and released as greenhouse gases into the atmosphere (Steinmuller, 2018). If the yearly wetland loss in Louisiana is greater than one percent of total wetland area, the carbon emissions released will equal the amount of carbon stored each year, assuming one-meter depth of erosion (DeLaune and White, 2012).

River diversions are a solution which could increase basin-wide C sequestration rates by up to 14% (Wang et al., 2017). Environmental parameters such as temperature, pH, sediment delivery and water table depth will be altered by diversion input, and each affect decomposition rates and C stability in wetlands. For example, flux of CO$_2$ from wetlands is higher in drained conditions rather than soils that are flooded (Nyman & DeLaune, 1991). Emission of methane gas, however, is higher during flooded conditions because methanogenesis is a strictly anaerobic process that occurs in highly reduced organic soils and flooding slows methane oxidation (Kayranli et al., 2009).

Vegetation type also affects organic carbon and long-term C storage. Freshening of coastal marshes changes vegetation biodiversity and species composition (Morris et al. 2013), which will have an impact on substrate quality. Factors such as C:N ratio and lignin:cellulose ratios alter decomposition rates by affecting the degradability of organic material. Humic substances are more recalcitrant so C storage or even sequestration can increase; however, if
organic matter is highly degradable it could stimulate decomposition and prime more recalcitrant organic matter to enter the mineralization process (Reddy & DeLaune, 2008).

Although freshwater coastal wetlands are not considered in global blue carbon estimates, these ecosystems contribute significantly to worldwide carbon storage. Thus, encouraging accretion of organic matter and long-term C storage in freshwater wetland soils should be among the prioritized goals of MRD restoration.

1.2.3. Freshwater Diversion in the Context of Louisiana Restoration Goals

Because they were planned and built before the implementation of the CPRA coastal master plan, legacy freshwater diversions have become somewhat of an artifact of past coastal restoration goals in Louisiana. Although they served as inspiration for the larger scale projects (i.e. Mid Barataria Sediment Diversion), freshwater diversions were not designed with current MRD restoration goals in mind and as a result do not optimize highly valued services like sediment delivery (Lopez, 2014; Snedden et al. 2007) or nutrient removal (DeLaune, 2005; Gardner & White, 2010, VanZomeren et al. 2013). Continuing research and informed management of freshwater diversions can ensure these projects are a successful, long-term investment in restoring Louisiana coastal basins. This also ensures they will be available to inform the design and management of future diversion projects.

1.3. Nitrogen Cycle

Nitrogen is frequently a limiting nutrient in coastal wetlands in Louisiana and around the world. Nitrogen is present in wetland environments in several organic and inorganic forms, with a range of oxidation states. Cycling of the different N forms serves as a driving force in the flow of energy through wetland environments (Figure 1.4). For example, denitrifying microbes can drive the mineralization, or breakdown, of organic materials even in reduced soil conditions, using
alternate electron receptors such as nitrate (NO₃⁻). Denitrification process can also remove inorganic NO₃⁻ from the wetland system, releasing it as dinitrogen gas (N₂) into the atmosphere. Fixation of N₂ from the atmosphere back into the system as inorganic ammonium (NH₄⁺) by a few specific bacterial species common in the roots of legumes closes the loop of natural N availability. There also is dynamic cycling of nitrogen species within wetlands that spans aerobic and anaerobic soil zones, including nitrification, the conversion of NH₄⁺ to NO₃⁻, and ammonification, the breakdown of organic N to NH₄⁺. Assimilation of inorganic N sources (NH₄⁺ or NO₃⁻) is also a requirement of vegetation growth. Except when salinity or flood stress are severe, N is a limiting nutrient and availability can drive plant growth rates (Nyman & Lindau, 2016) and community structure.

There are anthropogenic or natural sources of N, however biological N₂ fixation or deposition from the atmosphere is limited because the environment is at a natural equilibrium between N formation and use. Anthropogenic point sources of nitrogen like wastewater

![Figure 1.4](image_url). Major pathways for the nitrogen cycle in wetlands, including redox regions where various anaerobic and aerobic reactions take place. Made using Biorender.com.
discharge or industrial waste can alter this equilibrium, as well as non-point sources like urban or agricultural run-off. Inputs of nitrogen into a system such as these can be transformed, stored or transported from the system. Transformation during the N cycle processes mentioned above tend to either lead to storage of N, or to export from the system. Wetlands store nitrogen in plant or microbial biomass, soil organic matter or in exchangeable forms in porewater or the water column. Volatilization of NH$_4^+$, gaseous N$_2$ losses from denitrification and general outflow are all output processes by which nitrogen can leave a wetland system.

1.3.4. Denitrification

In wetlands, nitrate is used as an electron acceptor for metabolic activities when oxygen is unavailable and nitrate is available. Denitrification is the process by which nitrate is reduced by microbial groups called denitrifiers, for cellular respiration. Gaseous by products such as dinitrogen or nitrous oxide (NO$_2$) are produced. After oxygen is depleted, nitrogen is the most energetically favorable electron acceptor available in soils and so denitrification will only occur in anaerobic regions of the soil where nitrate also is available. The main source of nitrate in interior wetlands is formed during nitrification. Nitrification is an aerobic process which occurs in the oxygenated areas of the soil profile or water column, during which microorganisms oxidize ammonium in order to form nitrate. Wetland soils will have tight nitrification-denitrification coupling where nitrogen must cycle between an aerobic-anaerobic soil interface in order to be nitrified and then denitrified. And so, the presence of the aerobic-anaerobic soil interface is important in driving denitrification.

Nitrogen in excess can lead to numerous ecological impacts, including the degradation of coastal or aquatic environments (Diaz and Rosenberg, 2008). As a result nitrification-denitrification functions in wetlands are an essential nutrient buffer because it is one of the few
processes that will naturally remove excess inorganic nitrogen from the system. In the case of freshwater diversion wetlands, denitrification can remove up to 68% of added nitrate from the water column (DeLaune et al. 2009; Yu et al. 2008). Together with assimilation by emergent vegetation, nitrogen removal rates can exceed loading in these systems (VanZomeren et al. 2012). Although assimilation by plants may keep nitrogen in the wetland system, accumulation of organic matter will also lead to the burial of organic nitrogen in flooded conditions, essentially preventing it from contributing to eutrophication.

1.4. Phosphorus Cycle

The phosphorus (P) cycle (Figure 1.5) is complex and involves interactions between biotic and abiotic pools. Phosphorus can be limiting in some ecosystems because is an essential nutrient in the production of plant biomass. As a result, P availability can regulate primary productivity, impacting almost all trophic levels. P can exist in many different forms that vary in bioavailability, as such, P behavior is complex and varied (Wang et al., 2006). Riparian wetlands are an effective control on nutrient buffering between riverine and aquatic ecosystems. Wetlands

![Figure 1.5. Major pathways of the wetland Phosphorus cycle. Made using Biorender.com.](image-url)
act as P transformers or sinks by immobilizing inorganic P or producing organic P with varying bioavailability (Mitsch and Gosselink, 2000a).

External sources of P in aquatic systems are mainly from upland environments, including riverine inputs, agricultural runoff, as well as some contributions from atmospheric deposition (Reddy and DeLaune, 2008). In river dominated systems, most delivered P is in the form of particulate organic matter, which can be mineralized into more available inorganic compounds. Riverine sediments tend to have NaOH-P as the dominant inorganic P form, making up approximately 20 to 71% of total P pool (Reddy et al., 1995). This form represents the P that is bound to Fe and Al, a complex that is only desorbed under extended reduced or low pH conditions. Some stream sediments will have other major forms of inorganic P that are less biologically available, such as those bound to Calcium (Ca) and Magnesium (Mg) (Reddy and DeLaune, 2008).

A major sink for P is the accrual within wetland soils. In some cases, peat accumulation is the only long-term P storage function. P uptake by plants can account for 30-80% of total P removal in wetland systems (Reddy and DeBusk, 1987), this rate is limited by net productivity and concentration of P in the plant tissue (Reddy et al., 1995). However, after plant senescence the organic material begins to decompose and some P is quickly returned to the water column. Organic P-rich material that is not broken-down is incorporated as soil organic matter. P that is not particularly labile will enter into the soil detrital pool in association with humic material or in association with mineral additions to the soil, acting as a form of short-term storage. Stored P, either in organic matter or associated with metal-bound complexes, can also serve as an internal source to the wetland (Reddy and Delaune, 2008). Whether the wetland will store or release P depends on several physico-chemical factors (Reddy et al., 1995).
In a high flow system such as a diversion wetland, hydrological forces drive nutrient dynamics. This consideration is especially important for P because sedimentation of particulate inorganic and organic P from external sources will increase accumulation of the nutrient. Vegetation tends to create tortuous flow paths for incoming water and will act as an effective sediment sink by trapping particles or reducing water velocity, forcing particulates to drop out from the water column (Day et al., 2009). Although P particulates accumulate in soils through sedimentation processes, trapped P returns to surface and pore waters through resuspension or leaching (Reddy and DeLaune, 2008). Water flow can remove those soluble and particulate P that are now labile in a process called entrainment. In soils with high P loading, high flows can increase the gradient of diffusive forces and drive higher P flux from the soils into the water column (Reddy et al., 1999).

1.5. Geostatistics

1.5.1 Geostatistics in Soil Science

The previous sections outline how wetland biogeochemical processes and the distribution of other soil characteristics may control soil C, N and P. Regulators of these soil properties are inherently spatial, and all observations of such properties aim to characterize soils at specific location in space and time. As a result, spatial and temporal information must be considered in order to understand soil information in that context (Goovaerts, 1999). Geostatistical modeling is one way through which soil and wetland scientists have begun to explore the spatial and temporal relationships between soil characteristics in wetlands.

Many studies have investigated spatial relationships of wetland soil data and have applied geostatistical methodologies in diverse ways. Some past uses of geostatistics in wetlands include observing impacts and rates of riverine sedimentation (French et al., 1995), modelling how flood
pulse impacts wetland organic matter dynamics (Nogueira et al., 2002), mapping wetland vegetation (Arieira et al., 2011), and understanding the spatial variability of several soil properties (Kral et al., 2012) in addition to parameters such as soil type (Walder et al., 2007), and phosphorus (Grunwald et al., 2004). Geostatistical considerations are also useful in optimizing sampling design to create better soils maps while reducing effort and costs of analyses (Nogueira et al., 2002, Szatmari et al., 2015).

1.5.2. Introduction to Geostatistics

Geostatistics is the investigation of spatial relationships by statistical methods, and is commonly applied to a wide array of disciplines to model spatial relationships of variables of interest (Webster and McBratney, 1987; Webster and Oliver, 2007; Taylor et al. 2003). In many instances of soil characterization, averaging of bulk soil properties to describe an area is appropriate, but often expression of the variation over the expanse of the study site is preferred (Webster and McBratney, 1987). Geostatistics can evaluate the spatial dependence of soil characteristics by relying on the concept of continuity, which states that points in a system with more similar values tend to be in close geographical proximity. The purpose of geostatistical analysis is to capture that spatial correlation and represent those relationships in an analytical function (Olea, 2018).

1.5.3. The Variogram

Geostatistical analysis assumes there is some random function which determines the value of a variable of interest, Z, in a given region. In a finite set of locations, Z would be one realization of said function that constitutes the regionalized variable. Equation 1 is a linear model of describing Z at location x:
\[ Z(x) = m(x) + \epsilon(x) + \epsilon'(x) \]  
(Eq. 1)

Where \( m(x) \) is the structural component, a directional and causal influence. \( \epsilon(x) \) is the spatially autocorrelated component, which is also causal but is omni-directional and does not have a directional trend. Finally, \( \epsilon'(x) \) is stochastic, or random, spatially uncorrelated variation drawn from a normal distribution with mean zero that is due to random events or error in sampling or taking measurements.

In order to define the random process which governs \( Z(x) \), we must assume first order stationarity, as stated in Matheron’s intrinsic hypothesis, that certain attributes of the distribution of the function, such as the mean or variance of two points, are constant. In other words, the models of the spatially dependent variance are the same over the entire sampled area, regardless of absolute position. As a result, one can find covariance with only the lag distance (\( h \)) of points instead of their absolute positions within the region. Consequently, the variance of differences in spatial relation of two points could also be calculated under Matheron’s assumption of stationarity because it depends only on the lag distance, as well (Webster & Oliver, 2000). This value, called the semivariance (\( \gamma \)), can be used to describe spatial dependency or similarity of values of \( Z \) at certain lag vectors, \( h \). In a binned variogram, semivariance represents the average value of the difference in variable \( Z \) at two points at a given \( h \):

\[
\gamma(h) = \frac{1}{2} E \{ [z(x) - Z(x + h)]^2 \} 
\]  
(Eq. 2)
In the creation and analysis of a variogram, three main components are considered: the range, sill and nugget (Figure 1.6). The range represents the lag distance, or the distance between points, at which the semivariance stabilizes. At $h$ value represented by this range, values of the variable are no longer correlated. The sill is the semivariance value at which the variogram stabilizes and sill size demonstrates the contribution of variance, or the maximum variability between two points. Variograms normally have a modelled line through the experimental values with a non-zero intercept, implying a discontinuity in the function $Z(x)$ for semivariances at values of $h$ closer to zero. In applied examples the semivariance generally does not approach zero, this artifact is called the nugget effect and arises either from sampling error or variability at $h$ shorter than the sampling interval that cannot be properly represented.

Figure 1.6. Standard variogram with model parameter labels. Lag Distance is the distance between two points, semivariance reflects average difference in value of
1.5.4. Kriging and Spatial Auto Correlation

Variograms are used to summarize the spatial relationships in the data, but this information is only useful if we can approximate the theoretical continuous variogram that would represent the true values of $Z$ across the whole region. As such, a continuous function can be fit through the variogram estimates so that a value for semivariance ($\gamma$) can be estimated at any $h$ (Webster & Oliver, 2007). The fitted function is then used for ordinary kriging of each soil characteristic, whose estimator can be modeled as Equation 3:

$$Z_{OK}(B) = \left\{ \sum_{i=1}^{k} \lambda_i Z(x_i) \right\} \left( \sum_{i=1}^{k} \lambda_i = 1 \right) \quad (\text{Eq. 3})$$

Where $Z_{OK}$ is the estimate of geographic location $s_0$, $s_i$ is location of measurement $i$ and $\lambda_i$ is a weight used to minimize the mean square estimate error.

Spatial autocorrelation estimates the value of the studied variable area at unsampled locations $Z(x_o)$ using the autocovariance function fitted to the data. The variogram is integrated over grid cells, or area blocks, to create surfaces of spatial predictions. An advantage of ordinary kriging is that the variance associated the predictions can also be calculated. Mean-square-error variance is found with equation 4:

$$\sigma_B^2 = \sum_{i=1}^{k} \lambda_i \gamma(x_i, x_0) - \mu \quad (\text{Eq. 4})$$

Where $\mu$ is the variation in the $\sigma^2$ per unit of change or the within grid cell variance, is the average semivariance between site 0 and site $i$. $\lambda_i$ is weights used to minimize the mean square estimate error. The values obtained from this calculation underestimate the true kriging variance because of the error associated with estimation of the semi variogram, however, this error is not large enough to affect the overall usefulness of the technique (Webster and McBratney, 1987).

Maps produced from kriging can be used in many applications because they can describe variation of environmental parameters at various resolutions. Many parameters of interest for
environmental quality can efficiently be modeled with geostatistics, improving the quality of management. Another important use of variography is to optimize sampling density in the MRD in order to most accurately model impacts of restoration efforts while minimizing cost of analyses (Webster and Oliver, 2007).

1.6. Davis Pond: Site Description and Previous Work

1.6.1. Davis Pond Site Description

The Davis Pond freshwater diversion is a freshwater wetland located in Barataria Basin, Louisiana, USA (Figure 1.7, Figure 1.8). The diversion structure is positioned on the west bank of the Mississippi River, located roughly 19 km upstream and on the opposite bank of the city of New Orleans. At maximum flow the diversion structure can redirect up to 302 m$^3$s$^{-1}$ of water into a wetland with an approximate area of 37.6 km$^2$. Discharge is adjusted according to salinities in the receiving basin. Between 2008-2018, average discharge was approximately 58 m$^3$s$^{-1}$ with a median discharge of 36 m$^3$s$^{-1}$ (USGS, 2018). During that time the diversion had negligible average daily discharge 44 days each year, on average. The basin is surrounded by 19 miles of levees on the north, east and west side boundaries. The southeastern boundary of the ponding area is composed of a shallow rock weir cut with several outflows canals which allow flow into Lake Cataouatche and Lake Salvador further south. Construction by the U.S. Army Corps of engineers was completed in 2002. However, drainage issues from weir and levee construction lead to unexpected flooding in the residential areas surrounding the wetland during high stages in the ponding area (McAlpin et al. 2008). Construction on the levees and inflow canal prevented Davis Pond diversion from running at full capacity before 2009. Diversion influence reaches approximately 3,145 km$^2$ of wetland and estuary area within Barataria Basin. Initial costs to build the Davis Pond diversion were $106.8 million. The Army Corps of Engineers estimated the
total economic benefit of the Davis Pond Diversion for coastal Louisiana at $15.3 million per year, including $14.99 million from improvement of habitat for commercial fish and wildlife with additional benefit to recreation of $298,000 (USACE, 2000).

In 1885 the river breached the natural levee bordering the Davis Pond wetland and deposited a mineral sediment splay in the wetland surface. This event drove the current the morphological and vegetation regime in the basin, with higher elevation areas in the western part of the wetland dominated by a declining *Taxodium distichum* (Bald Cypress) forest (Kral et al., 2012). On the fringe of the cypress forests was mainly floating marsh with various sedge species (*Eliocharis* spp, *Spartina patens*) or *Sagittaria latifolia*. Other parts of the wetland are dominated by various freshwater marsh plants, mainly *Zizaniopsis miliacea* (Giant Cutgrass) surrounding the northern ponding areas and *Sagittaria lancifolia* and *S. latifolia* (Bull Tongue and Arrow weed) in the south. During the growing season there is floating vegetation, both invasive and native, in the shallow standing water and fringes of diversion canals throughout the wetland.

**Figure 1.7.** Map of study area, Davis Pond freshwater diversion, and its location relative to Louisiana. From Kral et al., 2012.
1.6.2. Previous Work

A baseline study by Kral et al. (2012) described plant and soil samples at the Davis Pond Diversion wetland in 2007 before full scale operations began in 2009. There is an ~11-year record of hydrologic restoration to this coastal, deltaic wetland. The work established a baseline of the following parameters: moisture content, bulk density (BD), total C (C), total N (N), total P (P), total inorganic P (IP), and percent organic matter (OM). This reflects the nutrient status and accretion processes of The Davis Pond marsh before freshwater, sediment and nutrient input occurred. From the spatial correlation analysis, Kral et al (2012) observed that g kg$^{-1}$ of N, C and OM percent by weight, in the 0- to 10-cm depth interval had similar spatial patterns and were closely inversely related to BD. The results (Figure 1.9) allowed them to infer the mechanism of accretion across the wetland. Contribution of mineral matter decreased with distance from the river where highly organic soils began to dominate. There was an absence of spatial autocorrelation in the 2007, 10-20 cm soil layer which was attributed to the lack of mobility in the wetland before the diversion began operation. Diversion driven influx of river materials and remobilization of materials within the wetland could be a driver for the trends observed in the 0-

**Figure 1.8.** Drone photos of Davis Pond diversion wetland in March 2018. Photos from Eddie Weeks, 2018.
10 cm layer; without this driver the lower soil layer lacked the same spatial continuity as the upper 0-10 cm.

Maps of kriged values showed high variability for total phosphorus that was controlled on a finer spatial scale than the resolution possible with the sampling density. Small patches of high P values were present contributing to the high nugget value for this parameter resulting in a high kriging variance. Cross-varioagrams presented by Kral et al. (2012) suggest that P was very loosely related to other soil parameters and total phosphorus may not accurately depict what is driving P distribution in this wetland. In 2007, P had a large nugget and the variogram’s fitted model was not able to distinguish values for P at small lag distances. Further separation of soil phosphorus into inorganic and organic fractions might help elucidate how P availability has changed with diversion influence as both forms of external P are likely contributing.

**Figure 1.9.** Results from 2012 study, interpolated maps for total carbon and bulk density in 2007 soils. (Kral et al., 2012).
1.7. Synopsis of Chapters

The presented work employed geostatistical analysis to observe variation of soil characteristics over varying spatial scales within a Mississippi River freshwater diversion receiving basin. As there has been little to no pre-sampling in other diversion-affected wetlands, this will be the first complete pre- and post-diversion impact study. The focus of Chapter 2 was to compare soil conditions in the wetland before and after 11 years of river water impact in order to determine how sedimentation and nutrient enrichment changed general soil characteristics and nutrient storage. We compared the spatial distribution of soil characteristics each year in order to identify any spatial patterns which aid in understanding significant drivers of soil character and storage of carbon and nitrogen. Our secondary aim was to investigate effective methods for identifying the impact of introduced river water in wetland soils, including geospatial considerations for sampling, the use of stable $^{15}$N isotopes and analysis of soil inorganic phosphorus fraction, which can be applied to other diversion wetland systems in the Mississippi River Basin.

Chapter 3 evaluates changes in soil phosphorus dynamics in the Davis Pond receiving basin during hydrologic reconnection to the Mississippi River. Phosphorus is a major limiting nutrient that drives plant or algal productivity, and can contribute to eutrophic conditions. The dominant source of soil P in Davis Pond has changed from autochthonous organic P to allochthonous inorganic P that enters with river materials. There is a high diversity in P forms within this wetland and the interactions of factors controlling P bioavailability and storage are equally as complex. The study outlined in Chapter 3 aims to observe how diversion impact will alter the spatial distribution of soil P fractions and how that will control P cycling within the wetland system.
2.1. Introduction

Marsh loss resulting from human alteration of landscape-level hydrology is a major concern in the Mississippi River Delta (DeLaune et al., 2013). Levees built along the Mississippi River disconnect coastal floodplains from the river, which has led to sediment and nutrient deprivation in much of Louisiana’s coastal wetlands. Saltwater intrusion as a result of disconnection, channelization, concomitant subsidence and sea level rise also threatens wetland plant communities whose root systems otherwise prevent collapse of the highly organic soils (DeLaune et al., 1994). The resultant open water increases flood and/or salt stress on plants and continues the marsh loss cycle (DeLaune and White, 2012). A major restoration goal for slowing freshwater wetland loss in Louisiana is to increase the rate of elevation gain so it can match the pace of relative sea level rise. Freshwater diversions are one restoration tool currently used in coastal Louisiana with the goal of reintroducing freshwater and sediments from the Mississippi River to maintain coastal marsh vegetation and deposit inorganic materials for enhanced marsh accretion.

Many studies identified organic matter accretion as the driver for elevation gain in organic-rich coastal Louisiana after river disconnection through levee construction in the early 20th century (Nyman et al. 2006; DeLaune et al., 2013; Turner, 2001). Organic matter accumulation is driven by plant productivity, and is negated by decomposition or oxidation of organic material (Nyman et al. 1994, Nyman et al. 2006; Morris and Bradley 1999; Sundareshwar et al. 2003; Caffrey et al. 2007). Accumulation of inorganic material in systems with high mineral sediment loads can lead to surface elevation gain in coastal marshes and reduction of flood stress for plants (Day et al. 2016). Deposition and accretion processes are
scale and location dependent, affected by interactions between river influence, location and the local plant community (Kral et al., 2012). Highly organic soils tend to have lower shear strength and are less resistant to physical stress such as storms (Turner et al., 2009). For example, after Hurricane Katrina there were reports of neutrally buoyant “marshballs” formed from uprooted marsh grass and root mats in freshwater portion of Breton Sound marshes. Additionally, there were many unvegetated areas at the marsh surface which appeared after Hurricane Katrina and Rita and are thought to be due to erosion during the storms (Howes et al. 2010).

Closely coupled with accumulation or loss of organic marsh soils is carbon storage. In fact, wetlands account for 20-25% of global terrestrial C storage (DeLaune and White, 2012). Marsh erosion releases organic matter which is degraded and produces greenhouse gases (Steinmuller, 2018). If yearly wetland loss in Louisiana is greater than one percent of total wetland area, the carbon emissions released will equal the amount of carbon stored each year assuming one-meter depth (DeLaune and White, 2012). Added sediments and nutrients from the diversion will stimulate plant productivity, may change marsh elevation, and can alter carbon accumulation rates in wetland soils. Modeling carbon stocks in the freshwater diversion wetlands will help form a consensus about the effect of river water input on organic matter accretion rates and carbon burial.

The annual Mississippi River NO$_3^-$ concentration has doubled since the Upper Barataria Basin was hydrologically isolated by levees in 1904 (Goolsby et al., 2000; Evers et al., 1992), leading to nutrient enrichment of coastal and estuarine areas that receive river water. The impact of nutrient enrichment and sedimentation on plant productivity is a topic of great concern in this region, and is widely debated. Added sediments positively impact productivity in wetland vegetation by increasing elevation and soil aeration and relieving plants from flood stress,
additionally, nutrients released from sediments can improve fertility (DeLaune et al. 2016). In some cases, increased nutrient concentrations also stimulated organic accretionary processes (Fox et al. 2012; Anisfeld & Hill, 2012) but in other cases had negative effects on belowground biomass and structural integrity of the soil matrix (Graham and Mendelssohn, 2014; Turner et al. 2009). In addition, eutrophic conditions can lead to changing species composition or reduction in biodiversity, which in turn will impact litter quality and organic matter mineralization rates.

Although increased decomposition is common after marsh nutrient enrichment, an increase in plant productivity could offset soil organic matter loss leading to maintenance of C stocks and accretion rates (Holm et al., 2014; Graham and Mendelssohn, 2016).

Since their opening in the 1990s and 2000s, freshwater river diversions like Davis Pond, the subject of this study, have been shrouded by controversy. Freshwater diversions were designed only to deliver freshwater and nutrients, so there is concern they cannot deliver sediments necessary to promote plant establishment or sustain plant growth (Kesel et al. 1992; Slocum et al. 2005; Stagg and Mendelssohn 2010, Day et al. 2013). Additionally, excess nutrients may increase wetland vulnerability to storms by producing eutrophic conditions with poor live root standing stocks and low soil strength (Turner et al., 2009). Kearny et al. (2011) reported that there has not been a significant increase in land area of the receiving basins of three other freshwater diversions within the MRD based on satellite images taken from 1984-2009. Kearny et al. (2011) did not include Davis Pond in the analysis and did not consider water level at the sites when measuring emergent land. Emergent wetland area in the Davis Pond ponding area has increased over the previous 20 years, as is evident in satellite images taken from the diversion site (Figure 2.1). Most reports about freshwater diversion impact lack significant presampling efforts, and there is little information on the original state of the sites before restoration.
efforts began. This study will be the first description of pre- and post-diversion conditions over an entire ponding area. With the use of reference data from 2007 we can more accurately measure the impact of the freshwater diversion and its effectiveness as a wetland restoration technique.

**Figure 2.1.** Satellite images of Davis Pond Diversion ponding area. Google earth V 6.2.2.6613 (February 2, 1998; January 24, 2018) Davis Pond, Louisiana 29 53’14 N, 90 17’32 W. USGS, Landsat.

A baseline soil characterization study by Kral et al. (2012) presented analysis of samples of the top 10 cm of soil at 142 sites within the Davis Pond Diversion ponding area taken during the summer of 2007 just as full-scale operations began. The data were used to create geospatial maps of soil characteristics in order to compare them at different spatial scales across the wetland. As the first detailed sampling performed in this diversion wetland, it included characterization of the organic matter content (OM), mineral content, total carbon (C), total nitrogen (N) and phosphorus content of the soils. The sampling design of that study was a template for the work presented in this report. Findings from the work of Kral et al. (2012) established a baseline of the initial conditions governing the wetland before substantial hydrological reconnection took place. Contribution of mineral matter decreased with distance.
from the river where highly organic soils dominated. It is likely that with full operation of the
diversion since 2007, the soils within Davis Pond transitioned away from a highly organic state
and currently reflect a riverine dominated system. In the years following initial sampling, the
wetland has accreted 0.59 to 1.03 cm yr\(^{-1}\) cm of new soil each year (DeLaune et al., 2013).
Resampling the top 20 cm, separated into 0-10 cm and 10-20 cm layers, in 2018 provides a look
at the status of those soils produced since 2007 and provides more context for the shifting soil
conditions.

2.2. Methods

2.2.1. Study Site

This study examined the Davis Pond Diversion, a freshwater wetland located in Barataria Basin,
Louisiana, USA, that receives water from the Mississippi River (Figure 2.2). The diversion
structure is approximately 19 km upstream and across the Mississippi River from New Orleans
and controls discharge into a 37.6 km\(^2\) wetland. The wetland receiving basin is surrounded by
levees on the northern, eastern and western side boundaries. The southern boundary of the

Figure 2.2. Map of Davis Pond Diversion and surrounding area
including the water body into which diversion water empties, Lake
Cataouache, and New Orleans which is located 19 km downstream of
the Mississippi River from Davis Pond. Adapted from: Gardner, 2008.
wetland is composed of a shallow rock weir through which several outflow canals have been cut that allow flow into Lake Cataouatche and Lake Salvador further south. At maximum flow the diversion structure can divert up to 302 m$^3$s$^{-1}$ of water. Discharge is adjusted according to salinities in the receiving basin. For the years 2009-2018, average discharge was approximately 58 m$^3$s$^{-1}$ with a median discharge of 36 m$^3$s$^{-1}$ (USGS, 2018). During that time the diversion had negligible mean daily discharge 44 days each year, on average. There is also a storm water pump that directs water over the northern levee which borders US 90 though this is negligible flow comparatively. The Davis Pond Freshwater diversion was finished in 2002 and operation began later that year. However, drainage issues caused flooding risk in communities surrounding the ponding area and the diversion was not run at full capacity until 2009, after appropriate alterations were made to the inflow channel and levees.

2.2.2. Sampling

The sampling scheme for this study was the same as used by Kral et al (2012) which was generated using spatial simulated annealing (VanGroenigen et al., 1999). The design was purposeful to ensure that the area was uniformly sampled and short- and long-range variability was accounted for when performing spatial statistical analysis. Push core samples of the top 20 cm of soil were collected at 142 stations in May through July 2007 and May through June 2018 and separated into two subsamples, 0- to 10 cm and 10- to 20 cm soil intervals, during extrusion in the field.

2.2.3. Soil Characteristics

Soils were analyzed for bulk density (BD), total carbon (C), total nitrogen (N), total phosphorus (P), total inorganic phosphorus (IP), total organic phosphorus (OP) and percent organic matter by mass loss on ignition was used to measure organic matter content (OM) and mineral content.
Wet samples were homogenized and sub-samples were dried at 70°C until at constant weight, then reweighed for soil moisture and bulk density calculations. Dried, ground subsamples were combusted at 550°C for 4 hours, the difference in pre- and post-burn weight indicated OM and mineral content. Total C and total N were measured with dried and ground samples using an Elemental Combustion System with a detection limit of 0.005 g kg\(^{-1}\) (Costech Analytical Technologies, Inc., Valencia, CA).

Total phosphorus was prepared by ignition and acid digested using the ascorbic acid automated colorimetric procedure (Method 365.1; USEPA, 1993). Dried samples (0.5 g) were analyzed for total P on a SEAL AQ2 Automated Discrete Analyzer (SEAL Analytical, West Sussex, England), using US EPA Method 353.2 (US EPA, 1983). Minimum detection for total P was 0.002 mg P l\(^{-1}\). Samples were extracted for total IP with the method outlined by Reddy et al. (1998). 0.5 g of dried sample was added into centrifuge tubes with 25 mL of 1M HCl and shaken for 3 hours on longitudinal shaker. Samples were then placed in a refrigerant centrifuge for 10 mins. The supernatant fluid was filtered through a 0.45-μm membrane filter. Filtrate was analyzed for SRP on a SEAL AQ2 Automated Discrete Analyzer (SEAL Analytical, West Sussex, England), using US EPA Method 353.2 (US EPA, 1983). Minimum detection for SRP was 0.002 mg P l\(^{-1}\). Total OP was the difference between total P and total IP.

Dried ground samples were used for \(^{15}\)N analysis and run on Delta Plus XP IRMS (Thermo Finnigan) with an Elemental Analyzer (Costech ECS 4010) in the Stable Isotope Ecology Laboratory at Louisiana State University, Baton Rouge, LA.

2.2.4. Denitrification Enzyme Activity

Denitrification enzyme activity (DEA) was measured with the incubation methods outlined by Tiedje (1982), with adaptations by White and Reddy (1999). Moist soil was added to glass serum
bottles, sealed with aluminum crimps and headspace was evacuated to -70 kPa. A slurry was achieved in the bottle with the addition of 8 mL of a solution containing 56 mg N L⁻¹ nitrate, 286 mg C L⁻¹ dextrose and 0.05g L⁻¹ Chloramphenicol, an enzyme inhibitor that would prevent synthesis of new enzymes. 10 mL of acetylene gas (C₂H₂) was also injected into the headspace of the sealed bottles which prevents N₂O from being reduced to N₂ gas. Headspace was sampled at thirty to sixty-minute intervals and gas samples were analyzed for N₂O on Shimadzu GC-8A ECD (Shimadzu Scientific Instruments, Columbia, MD), detection limit 0.0006 mg N₂O-N kg⁻¹ h⁻¹. Nitrous oxide production was calculated in an aqueous phase using the Bunsen adsorption coefficient 0.6133 (Tiedje, 1982) and plotted with time to realize a rate.

2.2.5. Vegetation Mapping

Habitat type was identified across the wetland with remote sensing in order to observe how soil parameters may vary over different vegetation or soil types. Mapping used ten-meter resolution Sentinel-2 satellite imagery from 18 October, 2018. We selected 140 training pixels, approximately twenty from each known habitat type, based on observations made in the field. Classifications include floating marsh, Zizaniopsis dominated marsh, emergent marsh, Sagittaria dominated marsh, forested wetland and open water. Satellite data acquired included four visible and near infrared wavebands that correspond to the blue (0.42–0.50µm), green (0.52–0.60µm), red (0.61–0.69µm) and near infrared (0.76–0.89µm) spectral channels. Vegetation index normalized difference vegetation index (NDVI) was also used in the classification. R package “randomForest” (Breiman & Cutler, 2018) was used to perform Random Forest machine learning in order to relate vegetation type to satellite data with the use of decision-like trees. Final random forest models consisted of 500 trees and from those trees a final prediction was made using a majority voting scheme. Results of the classifications were assessed with a random
forest cross-validation. Once habitat type was assigned to each site, ANOVAs were used to determine relationships in volumetric C and N content, C:N ratios and δ^{15}N values between each habitat type.

2.2.6. Statistical analysis

The methodological framework for observing and analyzing potential spatial patterns of river diversion influence in the Davis Pond wetland involved (1) analyzing univariate relationships of soil variables between years to identify how diversion operation will change soils over time; and (2) observe spatial variation within and between years by modelling each soil parameter through spatial auto-correlation to (3) performing a principal components analysis using predictions from variographic models to further understand how variables reflect influence on the soil from river-borne material; and (4) performing a cluster analysis to develop definitions of soil types which reflect extent of river diversion impact. Because geostatistical analysis provides an integrative method for modeling error, we were able to integrate uncertainty calculations into the analysis and identify spatial extent of areas which were significantly impacted by diversion derived materials.

2.2.6.1. Univariate Statistics

Paired t-tests were conducted to evaluate how soil characteristics changed at each site between sampling years. P values < 0.05 are considered significant.

2.2.6.2. Geostatistical Analysis

The purpose of performing a geostatistical analysis was to model distribution of each soil parameter using measured soil variables in each sampling year, 2007 and 2018. We were able to integrate the limited data collected from 140 sites within the system into an interpolated surface that represents continuous data for soils across the wetland. Additionally, the study is designed to
analyze pre- and post-diversion conditions so we also modeled a difference value, or the change in each soil parameter between years, identifying how conditions changed at each point continuously across the wetland. As a result, we expected to observe how the diversion is driving change within the system over space within each year and over time.

2.2.6.3. Variograms and Spatial Autocorrelation (Kriging)

Geostatistics is the investigation of spatial relationships by statistical means, and is commonly used in soil science. As with the approach outlined in Kral et al. (2012), here a geostatistical approach was used to describe the spatial variability in soil characteristics across the Davis Pond wetland. This analysis assumes that there is some random function that determines the value of a variable of interest, $Z$, in a given region. In a finite set of locations, $Z$ would be one realization of said function that constitutes the regionalized variable. Equation 1 is a linear model of describing $Z$ at location $x$:

$$Z(x) = m(x) + \epsilon(x) + \epsilon'(x)$$  \hspace{1cm} \text{(Eq. 1)}

Where $m(x)$ is the structural component, a directional and causal influence. $\epsilon(x)$ is the spatially autocorrelated component, which is also causal but is omni-directional and does not have a directional trend. Finally, $\epsilon'(x)$ is stochastic, or random, spatially uncorrelated variation drawn from a normal distribution with mean zero that is due to random events or error in sampling or taking measurements.

In order to define the random process which governs $Z(x)$, we must assume first order stationarity, as stated in Matheron’s intrinsic hypothesis, that certain attributes of the distribution of the function, such as the mean or variance of two points, are constant. In other words, the models of the spatially dependent variance are the same over the entire sampled area, regardless of absolute position. As a result, one can find covariance with only the lag distance ($h$) of points instead of
their absolute positions within the region. Consequently, the variance of differences in spatial relation of two points could also be calculated under Matheron’s assumption of stationarity because it depended only on the lag distance, as well (Webster & Oliver, 2000). This value, called the semivariance \( (\gamma) \), can be used to describe spatial dependency or similarity of values of \( Z \) at certain lag vectors, \( h \). In a binned variogram, semivariance represents the average value of the difference in variable \( Z \) at two points at a given \( h \):

\[
\gamma(h) = \frac{1}{2} E \{ [z(x)-Z(x+h)]^2 \} 
\]

(2)

Variograms are used to summarize the spatial relationships in the data, but a continuous function must be fit through the variogram estimates so that a value for \( \gamma(h) \) can be estimated at any \( h \) (Webster & Oliver, 2007) Classical Matheron’s method of moments variogram estimator was used for least squares fitting, weighted by the number of sites separated by vector \( h \). Exponential and spherical models are commonly used for variogram fitting in soils with a mixture of visual and statistical methods. Range for each variogram was identified as the lag distance at which the variogram stabilized, or where the semivariance stopped increasing and the behavior either remained the same or became erratic. Final model selection was based on minimization of weighted sum of squares then finalized at the discretion of the practitioner by determining which model appeared to represent the continuous trend of the true variogram.

We used fitted models to perform autocorrelation for each soil variable in both sampling years, as well as for the values of difference between variables in each year by subtracting 2007 raw data at each site from the 2018 data. Ordinary kriging was used to estimate the value of a variable at unsampled locations across the wetland by implementing parameters from the previously fitted model function. The variogram model is interpolated over grid cells, or area
blocks, to create maps of predicted values for the soil parameters. Final maps were produced in ArcMap.

We used the variance maps of the difference between years to find the 95% confidence interval around zero for change in each grid cell with equation:

\[ X \pm 1.96 \cdot \sqrt{\sigma^2} \]  

(Eq. 3)

A grid cell value within this confidence interval would signify no significant change; those outside were considered significant for our analysis.

Finally, mean squared deviation ratio (MSDR) was calculated from cross validation to measure accuracy of model. The value of MSDR should be close to 1. MSDR values are reported in Appendix B. Equation 3 was adapted from Webster and Oliver (2007):

\[ \text{MSDR} = \frac{1}{n} \sum_{i=1}^{n} \frac{|z(x_i) - \hat{z}(x_i)|^2}{\sigma_{KR}(x_i)} \]  

(Eq. 4)

Where \( n \) is the number of points in the dataset.

2.2.6.4. Soil Nutrient Stock Estimations

Soil nutrient stocks in the top soil layers in each year were estimated using the methodology outlined by Veronesi et al. (2014). First, soil carbon density, or volumetric carbon content, was calculated using spatially autocorrelated surfaces with the following:

\[ \text{C Density} = C_i \cdot \text{BD}_i \cdot d \]  

(Eq. 5)

Total carbon concentration (\( C_i \)) were normalized with Bulk Density (g cm\(^{-3}\)) and the depth of the soil layer (\( d = 10 \text{ cm} \)) to produce estimates of carbon density (t km\(^{-2}\)). Total C stock (t) across the sampled area was estimated by summing the mass of carbon in each prediction grid cell with equation 5:

\[ \text{C Stock} = \text{C Density} \cdot \text{Area} \]  

(Eq. 6)
Where “Area” is the area of a single prediction grid cell in m² and C Density is volumetric C content of each grid cell across the wetland.

2.2.5.5. Nutrient Stock Variation Estimation

After calculating nutrient stocks with the above process, we addressed error propagation in the C Density estimations by assessing uncertainty associated with each variable. Estimation of variance of the carbon stock in each predicted grid cell were computed with equation 6, adapted from Goidts et al. (2009) and Schrumpf et al. (2011):

\[
\text{Var} (\text{C Density}) = (\text{C Density})^2 \left( \frac{\sigma_C^2}{C^2} + \frac{\sigma_{BD}^2}{BD^2} + 2 \frac{\sigma_{C-BD}}{C \cdot BD} \right) 
\]

(Eq. 7)

Where Var (C Density) in each grid cell is the error associated with the density prediction in t km⁻². \(\sigma_C\) and \(\sigma_{BD}\) are the standard deviation of carbon concentration and bulk density and \(\sigma_{C-BD}\) is the covariance of C and BD.

The difference in variance (\text{var} (C density) 2018 – \text{var} (C Density) 2007) from each predicted grid cell were used to find the 95 percent confidence interval around zero of the change in carbon stocks (Eq. 3).

2.2.6.6. Multivariate (PCA and Cluster Analysis)

Multivariate statistical analysis allows interpretation of interactions between multiple soil variables in order to better understand how either in situ or outside influences can impact soil physio-chemical properties. Pearson’s correlation coefficients were considered to identify soil variables with close correlative relationships. We then used a principal components analysis (PCA) to narrow the large set of modeled soil characteristics into a smaller number of summary variables, called components. We expected that the component values for each site would reveal correlative relationships between different soil variables, and how they changed over space. This would aid in identifying which variables may have become associated with diversion influenced
soils between years. Additional insight could be gained from observing spatial patterns in component results because this would provide information on the spatial distribution of all soil parameters together (Ha et al., 2014), rather than earlier in the analysis where each had to be analyzed separately.

We looked to further categorize soils across the wetland by soil type with a K-means clustering analysis using modeled values from 7 soil parameters from 2018. Scree plots were used to identify the ideal number of clusters. K-means cluster analysis assigns a cluster number to each site based on a minimization of a site’s squared distance from an established cluster center. Once a cluster number is assigned, cluster means and spatial distribution of the clusters helped us further pinpoint how interactions of soil variables will result in various soil “types” that can be classified by degree of impact from river diversion materials.

2.3. Results and Discussion

2.3.1. Univariate Analysis

Raw data from 140 measured sites from 2007 and 2018 (Table 2.1) were compared to analyze change in soil characteristics over the past decade. Results from paired t-tests demonstrated that mean difference from each year was significant for bulk soil density, inorganic density (g cm\(^{-3}\)) and \(\delta^{15}\text{N}(\%o)\) \((p < 0.0001)\). Overall, mean bulk soil density of the top 10 cm of soil increased by two times and 80% of measured sites had an increase in mineral matter content between years.

Table 2.1. Mean soil variable values in 2007 and 2018 for 0-10 cm soil layer at 140 measured sites reported with standard error.

<table>
<thead>
<tr>
<th></th>
<th>Bulk Density (g/cm(^3))</th>
<th>Mineral Matter Density (g/cm(^3))</th>
<th>Organic Matter Density (g/cm(^3))</th>
<th>Carbon Density (g/m(^2))</th>
<th>Nitrogen Density (g/m(^2))</th>
<th>(\delta^{15}\text{N} (%o))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2007</td>
<td>0.12 ± 0.010</td>
<td>0.07 ± 0.004</td>
<td>0.049 ± 0.02</td>
<td>2415 ± 944</td>
<td>162 ± 50</td>
<td>2.09 ± 0.32</td>
</tr>
<tr>
<td>2018</td>
<td>0.21 ± 0.012</td>
<td>0.14 ± 0.005</td>
<td>0.047 ± 0.01</td>
<td>2254 ± 605</td>
<td>167 ± 57</td>
<td>4.35 ± 0.42</td>
</tr>
<tr>
<td>Paired t-test (p)</td>
<td>(p &lt; 0.0001)</td>
<td>(p &lt; 0.0001)</td>
<td>(p = 0.64)</td>
<td>(p = 0.38)</td>
<td>(p = 0.16)</td>
<td>(p &lt; 0.0001)</td>
</tr>
</tbody>
</table>
Nutrient enrichment from the diversion manifests in alteration of $\delta^{15}$N values present in the soils of the diversion wetland. There were no significant changes at each site in volumetric organic matter content (g cm$^{-3}$), C or N content (g m$^{-2}$), after 11 years of diversion influence. Phosphorus dynamics are discussed in great detail in Chapter 3, however, total IP and total OP results will be included in multivariate analysis in this study as they are important indicators of diversion impact.

2.3.2. Variography and Kriging

Semi variogram is a value that reflects the average difference in a variable between two points at a certain lag distance from each other. The semivariogram values for measured sites are plotted against increasing lag distance. Semivariogram plots (Appendix A) were used to visually match a variogram model through the semivariogram values. Models were then used to predict values for soil variables across the wetland based on their original measured spatial distribution. Parameter values taken from the models, like height of the curve or range of values, can be compared as indicators of how well the predicted values from kriging represent the measured soil variables.

The model parameters (Appendix B) for each variable in Davis Pond were similar between years, indicating that the forces driving spatial distribution of the soil characteristics were likely maintained between years. Ratio of nugget size relative to the sill, called the relative nugget, is a metric of strength of the variogram in capturing the variation in spatial trends in the dataset. Larger relative nugget effects could indicate the underlying processes controlling the parameter in question has relatively little spatial dependence. Relative nugget values of BD and total IP decreased, indicating the driver of BD and total IP distribution is stronger in 2018 and can be better represented by the variogram model. In 2018 the diversion is impacting larger areas of the wetland and has a stronger influence on spatial patterns of total IP and BD. Relative
nugget effect in total C and total N is stable between years. Range values, representative of the maximum distance that two points are spatially correlated, remained relatively stable for all soil parameters. The scale of the forces impacting distribution of soil characteristics seem to be the same regardless of intensity of diversion influence. Mean Square Deviation Ratio (MSDR) was used to validate kriging. Each model was cross-validated and MSDR for all variables was close to 1 and within the acceptable range, several of the change maps did not perform well and were not included in the analysis (Appendix B).

Denitrification Enzyme Activity (DEA) is a measure of the activity of extracellular enzymes produced by denitrifying microbes in the soils in response to inputs of available NO$_3^-$ (Gardner & White, 2010). There is a high variance associated with the spatial autocorrelation for DEA in both years and variograms cannot represent this variance well as there was a large nugget effect in both cases. It does not appear that there is a strong basin-scale spatial driver of DEA, however, the number of stations analyzed for this parameter was relatively low so it may be that the scale represented by the sampling density does not capture the variability of this parameter. Preliminary work showed that DEA and NO$_3^-$ concentration are tightly coupled in the flow path of the Davis Pond diversion at discharge of 72.18 m$^3$s$^{-1}$ (data not shown), which implies that the Davis Pond wetland is N limited and local water column N concentrations will drive DEA. This parameter fails to represent basin-scale nutrient loading from the diversion because NO$_3^-$ will change seasonally with discharge volume and nutrient concentrations in the river. DEA does not represent N loading on a large enough time scale or spatial scale to drive basin-wide patterns within the wetland (White and Reddy, 1999). Thus, the predicted DEA values from kriging will not be discussed further.
Datasets produced from models based on raw data for total C, N (g kg\(^{-1}\)), mineral and organic matter content by percent weight are reported in Appendix D. Representing those parameters by concentration and by weight obscures the effects of the diversion on Davis Pond soil character and so only density calculations of these soils parameters will be discussed in analysis.

2.3.3. Vegetation maps

Habitat type classifications were organized into six categories designated from field observations and satellite imagery (Figure 2.3). The model was able to distinguish between floating marsh, emergent marsh, forested area, *Sagittaria* dominated marsh, *Zizaniopsis* (giant cutgrass) dominated marsh and open water. For the analysis *Zizaniopsis* dominated and emergent marshes were combined because they had similar soil conditions. As noted from field observation, on the west side there are several ridges of bald cypress forests which reach eastward across the wetland and tend to direct flow from the diversion to the south east. There are other patches of forested areas throughout the wetland (i.e. *Salix nigra*), and many diversion channels are lined with small levees containing various tree and shrub species. Marsh areas between the forested wetland tend to be highly organic floating marsh which transition out of the forested area. Open water is limited to known diversion channels with some small ponding areas throughout the wetland. Emergent marsh areas that were not characterized by a dense *Sagittaria* monoculture tend to be patchy and distributed down the hypothesized diversion flow path. There was a similar trend in wetland dominated by *Zizaniopsis*, whose irregular presence was not noted before 2018 sampling. Much of the giant cutgrass was likely growing on new land built from diversion sedimentation. Around the eastern and southern edge of the wetland are large, unfragmented patches of dense *Sagittaria lancifolia*, a common wetland plant found in Louisiana freshwater
tidal marshes. Distribution of habitat types will control many aspects of diversion impact, including flooding and soil characteristics.

2.3.4 Spatial Distributions of Soil Variables

The following sections will discuss results from modeled variables which have undergone stock calculations with associated error propagation (Table 2.2).

Table 2.2. Mean soil variable values from predicted stock maps for 0-10 cm layer reported with standard error.

<table>
<thead>
<tr>
<th></th>
<th>Bulk Density (g/cm³)</th>
<th>Mineral Matter Density (g/cm³)</th>
<th>Organic Matter Density (g/cm³)</th>
<th>Carbon Density (g/m²)</th>
<th>Nitrogen Density (g/m²)</th>
<th>δ¹°⁵N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Predicted 2007</td>
<td>0.093 ± 0.038</td>
<td>0.060 ± 0.0002</td>
<td>0.059 ± 0.03</td>
<td>2933 ± 2.62</td>
<td>196.7 ± 0.02</td>
<td>1.89 ± 0.30</td>
</tr>
<tr>
<td>Predicted 2018</td>
<td>0.147 ± 0.065</td>
<td>0.120 ± 0.0003</td>
<td>0.062 ± 0.04</td>
<td>3046 ± 2.77</td>
<td>220.1 ± 0.12</td>
<td>4.04 ± 0.39</td>
</tr>
</tbody>
</table>
2.3.4.1. Sedimentation

Average predicted bulk density and mineral content increased significantly between sampling years. BD is higher in soils with more inorganic sediments, as mineral sediment is more dense than organic material. Areas with increased BD also have a larger mass of total soil material, a result of sediment settling out from diverted river water. Porosity fraction at measured sites in 2007 averaged at 0.96 ± 0.01, in 2018 that fraction is reduced significantly according to paired t-test ($p<<0.0001$) to 0.85 ± 0.01. As soils formed, any river sediment which was deposited onto the marsh surface could have settled into the pore space of the soils and was possibly buried as new soils formed, becoming part of a dense soil matrix.

Mineral content is a measure of inorganic material present in the soils, in this case, it is related to fine grained sediment delivery from the diversion. The spatial distribution of mineral content demonstrates that the theorized flow path of the wetland received the most inorganic material during diversion operation (Figure 2.4). Predicted mineral content (g cm$^{-3}$) values for 2007 were subtracted from 2018 and the 95% confidence interval value for change in mineral content was determined from mapping variance. A majority of areas within the wetland did not experience a significant change in volumetric mineral content, however these areas are theorized to be outside of the flow path of the wetland. A negligible area located in the northwestern corner experienced a significant loss in mineral content from 2007 to 2018. Presumably diversion flow
Figure 2.4. Maps of mineral (ash) content in 0-10 cm soil layer in each sampling year reported in percent by weight, maps are based on geostatistical modelling. Small maps represent associated variance values across the wetland for each prediction.

into this area is blocked by a dense forested wetland. In contrast, 12% of wetland area, mostly in the northern parts of the theorized flow path, experienced a significant increase in mineral content.

Freshwater diversions were not specifically designed to deliver sediment from the Mississippi River (Barras et al., 2003; Snedden et al., 2007). However, our results demonstrate that a majority of soils in the wetland have received, to varying degrees, inorganic sediments from the river water. The diversion flow path is likely driven by elevation and physical barriers within the wetland that direct water flow. Dense stands of *Sagittaria* in the east/south east and bald cypress forests along the western side of the wetland may slow the diversion water and sediments settle out quickly (Day et al. 2009), depositing them closer to the flow path and preventing interaction of sediments with the soils in the less hydrologically connected vegetated areas.

The northern areas of the wetland experienced direct impact from preliminary running of the diversion before the first sampling in 2007 and because they are in close proximity to the river they are affected by regular flooding of the Mississippi River. Initial sedimentation of in
diversion systems tends to occur near the inflow structure (Day et al., 2009, Kroes et al., 2015), when larger particles settle out and fill in basins closest to the river. Once those areas fill in with sediment, larger materials will begin to settle farther south due to increased flow. Consequently, a progressive bulge of settled sediments forms that is localized along the preferential flow path. At high diversion flows, the finest grained sediments remain suspended and can be seen in satellite images traveling down the length of the main channels of the wetland and even transported out of the wetland into downstream Lake Cataouache, potentially settling farther south in Barataria Basin.

2.3.4.2. Water and Nitrogen Impact

The Mississippi River has an average inorganic N concentration of 2 mg l$^{-1}$ and reported range of $\delta^{15}$N values between 3.4 and 6.4 ‰ (Battaglin et al. 2001). In unimpacted oligotrophic marshes, $\delta^{15}$N values are reported to be in the range 0.35-4 ‰ (Elliot and Brush, 2006; Sorrel et al. 2011). Enrichment outside of these ranges in the soil can occur due to emergent wetland plant uptake of $^{15}$N$_{NO3}$ from diversion water which alters the isotopic signature of organic plant material to be more similar to river N. Plant tissues are preserved in the soils after senescence along with the $^{15}$N signature. Analysis of $\delta^{15}$N in plant material has been previously used to track assimilation of Mississippi River nitrate into plant tissues. One study conducted in a similar freshwater diversion wetland in Breton Sound found that plant $\delta^{15}$N decreased with distance from the point of Mississippi River input (DeLaune et al., 2008).

Our study analyzed isotope fractionation of organic soil N in the place of fresh plant material to in order to visualize distinct spatial patterns of river-influenced soils. The 2007 $\delta^{15}$N map (figure 2.5 a) predicts that the maximum value, 4.33 ‰, is located in the northern end of the wetland, close to the levee and the diversion inflow channel. This is slightly above the expected...
range for non-river influenced marshes, and reflects minimal exposure to river nitrate. In 2018 (figure 2.5 b), the maximum $\delta^{15}$N values are almost doubled at 8.52 ‰. Mean value throughout the wetland in 2007 was 1.8‰, by 2018 mean enrichment was 4.03‰, an increase of 124%.

![Figure 2.5](image)

**Figure 2.5.** Map of $\delta^{15}$N (‰) in 0-10 cm soil layer from each year. Small maps represent associated variance across the wetland for each prediction.

The $^{15}$N concentration has a bimodal distribution, and we used a mixture model (Appendix C) to find that a value of 3‰ acts as a breaking point between the two populations. We therefore used that value as a threshold for identifying river-influenced areas. The area of influence has increased by 4 times between years; in 2018 approximately 75% of wetland soils have $^{15}$N greater than background levels (Table 2.3). Inorganic anthropogenic N loading seems to have increased and a majority of vegetated areas in the wetland assimilate that N into plant tissue and eventually into the soils. Elevated $^{15}$N soils exist at sites that are not directly located in the diversion flow path where a majority of sediment delivery has occurred. It is likely that $\text{NO}_3^-$ which is dissolved in diversion water can be spread more extensively because low flows would drop sediment out of suspension, but continue to distribute dissolved $\text{NO}_3^-$ ions. Therefore, $^{15}$N may be a stronger indicator of the spatial distribution of river water-influenced soils, but not necessarily soils where a river sediment subsidy is provided.
Using this observed water impact zone, a true N loading rate from diversion impact can be calculated. On days that it was operating in 2018, the Davis Pond diversion had average discharge of 45 m$^3$s$^{-1}$ (USGS site 295501090190400, 2018), and average annual NO$_3$ concentration of Mississippi River water was approximately 2 mg L$^{-1}$. So, the loading rate of nitrate on the river-influenced area is approximately 100.19 g N-NO$_3$ m$^{-2}$ yr$^{-1}$, or 1.63 mol N m$^{-2}$ yr$^{-1}$. Day et al. (2018) found that for a river diversion wetland with an area 10 times the size of Davis Pond has an average loading rate of 7.2 g N-NO$_3$ m$^{-2}$ yr$^{-1}$, but they were unable to delineate a true diversion influenced area over which that N was dispersed.

<table>
<thead>
<tr>
<th>Year</th>
<th>River Influenced Area (km$^2$)</th>
<th>Non-River Influenced Area (km$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2007</td>
<td>7.16</td>
<td>30.50</td>
</tr>
<tr>
<td>2018</td>
<td>28.33</td>
<td>9.33</td>
</tr>
</tbody>
</table>

The fate of those added nutrients can be theorized based on past studies of nitrogen removal in diversion impacted wetland areas. In Davis Pond diversion at a discharge of 35 m$^3$s$^{-1}$, DeLaune et al. (2005) and Yu et al. (2006) estimated that N removal rates were at 23 g N m$^{-2}$ yr$^{-1}$, driven primarily by denitrification at a rate of 14.7 g N m$^{-2}$ yr$^{-1}$. Further research at the Caernarvon diversion system found that the remaining 36% of nitrate removal outside of denitrification is due to macrophyte uptake and assimilation (Van Zomeren et al. 2012). N assimilation removes the nutrient from the water column, which improves water quality and contributes to productivity that will maintain organic accretion in the soils. Unlike denitrification, which removes N from system, N assimilation drives C sequestration while keeping N inside the system in the form of organic soil N. Our $^{15}$N data confirm that a significant proportion of added nitrate is kept within soil OM, which either contributes further to
productivity or could be stored long term during burial of organic material (Reddy & DeLaune, 2008; Graham & Mendelssohn, 2014).

Measuring the rate of denitrification is another method of determining nutrient loading impacts in Davis Pond. Denitrification Enzyme Activity (DEA) reflects the concentration of denitrifying enzymes produced and their activity, which is closely related to the concentration of available nitrate. As such, DEA can be used as an integrative indicator of NO$_3^-$ loading to a wetland area (Gardner & White, 2010). Similarly, a significant correlation exists between spatial distribution of denitrification and NO$_3^-$ loading and between distribution of DEA and NO$_3^-$ (White and Reddy, 1999). Sampling density for DEA in 2007 and 2018 (n=88, n=25 respectively) were too low for spatial interpolation and the patterns of DEA spatial distribution were not translatable to the scale of Davis Pond due to poor spatial autocorrelation. However, trends in measured DEA rates between years (Figure 2.6) are informative in looking at NO$_3^-$ loading which occurred in the weeks and months leading up to sampling.

High N loading at sites will result in higher DEA, and on average the DEA rates increased between years from 0.389 ± 0.006 to 1.29 ± 0.028 mg N$_2$O-N kg$^{-1}$h$^{-1}$. Maximum rates from 2007 have also doubled (2.09 to 4.04 mg N$_2$O-N kg$^{-1}$h$^{-1}$). Soils analyzed for DEA in 2007 were collected from May until July at an average discharge of 47.97 m$^3$s$^{-1}$, and during that time 80% of the overall observed denitrification in the marsh occurred in an area of the marsh that was proximal to the diversion inflow and equal to 7.15 km$^2$ (Gardner, 2008). In 2018 all but 8 sites were sampled during the months of May and June 2018 when average discharge was 28.83 m$^3$s$^{-1}$. However, N loading in the several months leading up to sampling will have a larger impact on DEA rates than conditions while soils are collected (DeLaune et al. 2005).
monthly diversion discharge was greater in February and March of 2018 than those same months in the first sampling year, however, total mass of NO$_3^-$ delivered to the wetland was much greater between March and May in 2007 due to high discharge (Table 2.4). Timing of N loading plays an important role in determining denitrification rates within Davis Pond. The spatial trend observed in 2007 was no longer present in 2018. The area of wetland influenced by NO$_3^-$ loading has reached greater distances from the inflow after a decade of river influence, which is reflected in the distribution of high DEA rates across the entire wetland area in 2018.

2.3.4.3. Carbon and Nitrogen Content

There were strong correlative relationships between predicted values of total C, total N, OM, and BD ($p<0.0001$) in surface layers (0-10 cm) in 2018 and 2007. A strong positive correlation ($p<0.0001$) exists between volumetric OM, C and N content, highlighting the influence of
organically accreted soils in the distribution of carbon and nitrogen in the wetland. OM and N have a weaker but positive relationship with BD likely due to the positive impact of diversion materials on organic matter production. Measured sites with high OM also tended to have higher soil moisture \( (r=0.78, p<0.001) \), the inverse is true for BD at measured sites \( (r=-0.99, p<0.0001) \).

Average volumetric C content represents the mass of C found in the top 10 cm of soil per unit area (Table 2.2). When analyzed at only sampled sites, there was no significant change in OM content, however, modeled results better represent trends in the top 10 cm of soil across the entire wetland and show an increase in organic material. Between sampling years, C content by volume averaged across the wetland increased significantly. Total C stock in the top 10 cm of soil is the sum of total C mass in each grid cell of kriged maps. We found that C stock increased by 4,259 MT in between 2007 and 2018, which equates approximately to an additional 1,121 g m\(^{-2}\) across the entire wetland (Table 2.5). Variance could not account for the difference in average volumetric C content between years (Table 2.2), indicating that full scale diversion

<table>
<thead>
<tr>
<th>Date</th>
<th>Discharge (m(^3) s(^{-1}))</th>
<th>NO(_3^-) Concentration (mg l(^{-1}))</th>
<th>Date</th>
<th>Discharge (m(^3) s(^{-1}))</th>
<th>NO(_3^-) Concentration (mg l(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jan-07</td>
<td>39.21</td>
<td>1.48</td>
<td>Jan-18</td>
<td>34.15</td>
<td>1.13</td>
</tr>
<tr>
<td>Feb-07</td>
<td>38.87</td>
<td>1.53</td>
<td>Feb-18</td>
<td>55.25</td>
<td>1.33</td>
</tr>
<tr>
<td>Mar-07</td>
<td>75.82</td>
<td>1.48</td>
<td>Mar-18</td>
<td>121.77</td>
<td>1.03</td>
</tr>
<tr>
<td>Apr-07</td>
<td>89.97</td>
<td>2.27</td>
<td>Apr-18</td>
<td>39.00</td>
<td>1.19</td>
</tr>
<tr>
<td>May-07</td>
<td>61.86</td>
<td>2.87</td>
<td>May-18</td>
<td>26.18</td>
<td>1.49</td>
</tr>
<tr>
<td>Jun-07</td>
<td>37.51</td>
<td>2.17</td>
<td>Jun-18</td>
<td>29.46</td>
<td>1.59</td>
</tr>
<tr>
<td>Jul-07</td>
<td>44.53</td>
<td>1.14</td>
<td>Jul-18</td>
<td>33.80</td>
<td>2.57</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Total Discharge (m(^3))</th>
<th>Total NO(_3^-) (MT)</th>
<th>Total Discharge (m(^3))</th>
<th>Total NO(_3^-) (MT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cumulative 1,017,513,792</td>
<td>1,952</td>
<td>889,375,680</td>
<td>1,196</td>
</tr>
</tbody>
</table>

Table 2.4. Diversion discharge and average nitrate concentration in the months leading up to sampling in 2007 and 2018. Cumulative diversion discharge and total N loaded are also shown for those same months.
influence has maintained average OM content over time and allowed for increased rates of C production on a decadal timescale.

**Table 2.5.** Total stock of carbon and nitrogen from 0-10 cm soil layer in each year, and 10-20 cm soil layer from 2018, reported with standard error.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Total C stock (MT)</th>
<th>Total N stock (MT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2007 0-10 cm</td>
<td>110,431</td>
<td>7,405</td>
</tr>
<tr>
<td>2018 0-10 cm</td>
<td>114,690</td>
<td>8,288</td>
</tr>
<tr>
<td>2018 10-20 cm</td>
<td>142,108.9</td>
<td>12,315.46</td>
</tr>
</tbody>
</table>

We mapped the values of the difference in volumetric C content between years which are outside of the 95% confidence interval around zero in order to visualize the spatial distribution of significant change in C stocks between years (Figure 2.7). There was no clear spatial pattern related to the diversion flow path that indicates river influence is the major driver of changing volumetric C content between sampling years. There are soils within and outside of the water influenced zone that have significantly higher volumetric C content than soils formed before diversion impact (dark blue). There are also regions with significant loss of volumetric C

![Figure 2.7](image.png)

**Figure 2.7.** Difference in volumetric carbon content in the 0-10 cm soil layer from 2007 to 2018, white areas are Δ vol. C content values within the 95% confidence interval. Light and dark blue are areas of significant negative and positive Δ vol. C content, respectively, outside of this range.
content, mainly in the connected zone (Figure 2.7), but it was not exclusive to those connected regions. Some highly organic soils with continued riverine disconnection also have lower volumetric C content and show evidence of decreased C accumulation rates. Mean soil volumetric C content increased in soils after diversion input in both the disconnected and river-influenced areas (Table 2.6). Diversion operation has likely increased flooding throughout the entire wetland (Barras, 2003) and we speculate that redox state of the soils may be reduced.

**Table 2.6.** Volumetric content and ratio of carbon and nitrogen from 0-10 cm soil layer from the river-impacted and non-impacted wetland areas in each year, reported with standard error.

<table>
<thead>
<tr>
<th>Year</th>
<th>Vol Carbon Content (g/m²)</th>
<th>Vol Nitrogen Content (g/m²)</th>
<th>Vol C : N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Connected</td>
<td>Disconnected</td>
<td>Connected</td>
</tr>
<tr>
<td>2007</td>
<td>2590 ± 2.4</td>
<td>3013 ± 2.4</td>
<td>179.0 ± 0.09</td>
</tr>
<tr>
<td>2018</td>
<td>2993 ± 2.7</td>
<td>3206 ± 3.3</td>
<td>221.5 ± 0.14</td>
</tr>
</tbody>
</table>

Slower decomposition of organic material accumulated in the soils may have led to increased preservation of carbon. Additionally, the gain in C content in the river-influenced region almost two times higher than the disconnected region where there is less flooding and nutrient enrichment. Due to the lack of clear spatial trends related to diversion flow path (Figure 2.7), we argue there are other environmental factors that more strongly control C storage across the receiving basin than just input of river water or sediments.

Volumetric N content (Table 2.2, Table 2.5, Table 2.6) followed the patterns seen in volumetric C content distribution, however, the increase in mean volumetric N content in the water influenced area was 21%, whereas C increased by 14% between years. Furthermore, average volumetric C content : volumetric N content ratio decreased from 14.93 to 13.86. Differences between river-influenced and non-influenced soils are also apparent (Table 2.6), with lower ratios in diversion influenced areas. Generally, N concentration in plant tissues reflects N concentration in the wetland water column and soils (Reddy and DeLaune, 2008).
Therefore, vegetation in areas receiving high concentrations of river N are incorporating more N. The excess N is transformed into soil material upon plant senescence and increases soil volumetric N content over time, drawing down C:N ratios in areas receiving water input from the diversion.

2.3.4.4 Soil Parameters by Wetland Type

Discussion of the numerous controls on wetland vegetation distribution is beyond the scope of this study, however, dominant plant type can influence aspects of diversion impact. It is important to recognize that the Davis Pond diversion receiving basin is a mosaic of different wetland and vegetation types and this will impact how wetland areas respond to diversion influence. Therefore, habitat type classifications were used to compare soils across the wetland (Figure 2.8). According to an ANOVA analysis, all classes had different mean C and N content, except for emergent marsh, floating marsh and open water areas, which had the lowest. *Sagittaria* marshes have the highest mean volumetric C content, likely due to naturally large belowground tuber and rhizome stock (Martin & Shaffer, 2005), followed by forested wetland areas. Although statistically, open water and some marsh areas have less C content than other habitat types, the difference is small and the contribution of these areas to carbon storage should be investigated further.
In 2018, C:N ratios and $\delta^{15}N$ enrichment also varied by wetland type (Figure 2.8).

Variation in soil $\delta^{15}N$ can indicate either a difference in $^{15}N$ fractionation processes between plant types, the connectivity of certain marsh types to diversion influence, or the effect of nutrient availability on the outcome of plant competition. Low C:N ratios could indicate river water influence is driving accumulation of organic N in the soils. ANOVA results demonstrated that floating, forested and Sagittaria marshes are the least river-influenced areas due to the significantly lower value of $\delta^{15}N$ enrichment in those soils ($p < 0.0001$) and higher C:N values ($p < 0.0001$). Emergent marsh and open water areas have the highest $^{15}N$ enrichment and have lower C:N ratios. Those areas entail most of the hypothesized flow path, and represent regions of

Figure 2.9. Carbon and nitrogen content, C:N ratio and $\delta^{15}N$ by marsh or habitat type. Dark bars are means.
the wetland with the most diversion influence. Although open water areas do not have emergent vegetation, production by SAV and algae in the water column is a mechanism by which organic matter containing elevated $\delta^{15}N$ is incorporated into the soils. In fact, these plant types incorporate $^{15}N$-NO$_3^-$ from the water column more efficiently through their leaves than emergent vegetation (Cole et al., 2004). The *Sagittaria* marsh also has reduced C:N conditions but likely does not receive diversion materials as this area has the lowest $\delta^{15}N$ fractionation. Dense vegetation reduces flow velocity and prevents inner areas of these stands from more directly receiving diversion water.

2.3.5. Multivariate Approach

Principal Components Analysis (PCA) was carried out using predicted values of 7 soil parameters from 2018. The first two components (PC1 and PC2) accounted for 89.5% of the total variance in the 2018 data. The remaining five components have eigenvalues less than one and explain little of the variability in each year and will not be discussed further in the analysis. Loading values for PC1 and PC2 reflect the amount of variability within each parameter that is explained by the components (Table 2.7). Sign indicates negative or positive correlation between the measured variable with the calculated component. PCA identified soil parameters of interest which would aid in discerning diversion impact.

PC1 accounts for approximately 51% of the total variability in the dataset, and represents if a soil is dominated by organic material. PC1 is positively loaded with OM, C and N and organic phosphorus content and had a negative loading with BD, mineral content and $\delta^{15}N$. PC1 values were assigned to each site and they reflect the degree to which sites are dominated by non-river influenced organic soils (positive) and river-influenced soils (negative). The second component in 2018, PC2, accounts for 39% of variation in the dataset and is closely associated
with the intensity of inorganic phosphorus (IP), mineral content and $^{15}$N impact in the soils. IP content reflects the source of inorganic phosphorus, in this case, associated with inorganic sediments in the diversion water. There is a positive loading with total IP and $^{15}$N, so soils with positive PC2 values have high water and sediment impact from the diversion. There is also a weaker but positive loading to C, N and OM content, highlighting that areas receiving river impact are also storing large amounts of organic material. PC2 has heavy negative loading associated with total OP and less significant correlation with BD. Assigned PC2 values are a reflection of non-river influenced organic soils (negative) and river-influenced soils (positive).

Table 2.7. Results of principal components analysis on 7 variables describing soils of Davis Pond wetland. Loading coefficients listed describe how strongly each soil characteristics associated with each principal component (PC1 and PC2). Bolded loading values denotes significant association.

<table>
<thead>
<tr>
<th>Loading</th>
<th>PC1</th>
<th>PC2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mineral Density</td>
<td>-0.25</td>
<td>0.95</td>
</tr>
<tr>
<td>Organic Density</td>
<td>0.87</td>
<td>0.47</td>
</tr>
<tr>
<td>Carbon Content</td>
<td>0.94</td>
<td>0.31</td>
</tr>
<tr>
<td>Nitrogen Content</td>
<td>0.85</td>
<td>0.47</td>
</tr>
<tr>
<td>Inorganic P Content</td>
<td>-0.45</td>
<td>0.82</td>
</tr>
<tr>
<td>Organic P Content</td>
<td>0.86</td>
<td>-0.22</td>
</tr>
<tr>
<td>$^{15}$N</td>
<td>-0.42</td>
<td>0.73</td>
</tr>
</tbody>
</table>

K means clustering was performed for the same 7 soil characteristic variables. Scree plots indicated that the ideal number of clusters (K) was equal to three. Cluster means for each variable clarify which soil characteristics are most important during categorization (Table 2.8). Mean PC1 values for clusters produced with 2018 data decrease by cluster number. Cluster 1 (C1) has highest, indicating this cluster has more organic soils (high C, N and OM content), and
could represent the areas that receive no diversion impacts. Cluster 3 (C3), however has the lowest PC1 values and more inorganic soils (high total IP and BD) with more diversion influence \((^{15}N)\), indicating this may be parts of the wetland which receive sediments and water from the diversion. And spatially, the extent of those clusters correlates to the extent of river-influenced and non-influenced regions (Figure 2.9). Cluster 2 (C2) mean values of each variable were

### Table 2.8. Means of soil variables, PC1 and PC2 values by cluster number.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>OM 18</th>
<th>TC 18</th>
<th>TN 18</th>
<th>BD 18</th>
<th>TIP 18</th>
<th>TOP 18</th>
<th>N15 18</th>
<th>Vol. C 18</th>
<th>PC1</th>
<th>PC2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>59.28</td>
<td>304.23</td>
<td>20.36</td>
<td>0.10</td>
<td>208.40</td>
<td>630.72</td>
<td>2.76</td>
<td>31.83</td>
<td>1.35</td>
<td>-0.14</td>
</tr>
<tr>
<td>2</td>
<td>36.63</td>
<td>181.46</td>
<td>13.24</td>
<td>0.18</td>
<td>333.57</td>
<td>467.90</td>
<td>4.36</td>
<td>27.34</td>
<td>-0.31</td>
<td>0.90</td>
</tr>
<tr>
<td>3</td>
<td>20.18</td>
<td>91.84</td>
<td>7.09</td>
<td>0.31</td>
<td>591.80</td>
<td>299.18</td>
<td>5.56</td>
<td>31.03</td>
<td>-1.40</td>
<td>-0.75</td>
</tr>
</tbody>
</table>

between the two other clusters for all variables except C content, where this region had slightly lower values. C2 seems to represent soils present in areas of the wetland with high river water influence (elevated \(^{15}N\)), and intermediate sediment input (low BD, IP), which could lead to lower OM content over time.

Both PCA and cluster analysis were useful for revealing patterns in the data that were not intuitive. One such conclusion is the positive relationship between river influence and OM accumulation in specific areas of the wetland. Additionally, these analyses can identify which soil variables are most important in driving soil type. Measuring total IP and \(^{15}N\) will give different information than just BD and looking at these variables in future monitoring may lead to a better understanding of restored wetland soil status by considering information beyond routinely measured soil characteristics.
2.4. Conclusions

2.4.1. Sedimentation

There are numerous benefits from increased sedimentation in reducing vulnerability of Mississippi River Delta freshwater wetlands to impacts from sea level rise and subsidence (Morris et al. 2013; Graham and Mendelssohn, 2013; Slocum et al. 2005), especially when that sediment is accompanied by increased OM accumulation. Soils which receive sediment will have increased BD (Poormahdi et al. 2018) and as a result will be less buoyant and less susceptible to erosion from wind waves (Sapkota et al. in review) or storms (Howes et al., 2010). With a 58% increase in average BD and two times higher mineral content since full operation of the diversion began, net contribution of inorganic materials is more pronounced, especially near the inflow and down the central flow path of the diversion in 2018. Satellite imagery also demonstrates that
significant land building has occurred throughout the diversion influence area. Sediment subsidies can increase elevation and stimulate plant growth by improving growing conditions in the soil. In addition, regular inorganic sediment supply relieves flooding stress and introduces new substrate into which vegetation can grow, increasing productivity in the system (Graham and Mendelssohn 2016; Mendelssohn and Kuhn, 2003).

A short-term field study which simulated Davis Pond sediment loading saw little or no vegetation response (Carpenter et al. 2007) and monitoring of other freshwater diversions have not demonstrated clear benefits to land building or marsh sustainability (Kearney et al. 2007). However, this study presents a more robust sampling of long-term soil conditions in a diversion ponding area that, unlike other systems, has not experienced significant impacts from major weather disturbances such as hurricanes. We suggest that in terms of soil stability and converting open water to vegetated marsh, there is an overall positive impact from fine-grained sediment delivery in the Davis Pond wetland.

2.4.3. Marsh Fertilization

With increasing eutrophic conditions reported in estuarine habitats across the world, there is concern that loading of excess nutrients from the Mississippi River into Barataria Basin wetlands could pose a threat to wetland ecosystem functions. $^{15}$N stable isotope analysis was used to observe that the area which received elevated river nutrients within Davis Pond increased by four times between sampling years. Marsh fertilization studies have used N application rates in the range between 1.8 - 30 mol N m$^{-2}$ yr$^{-1}$, much larger than those presently estimated in Davis Pond (1.63 mol N m$^{-2}$ yr$^{-1}$) or Caernarvon (0.12 mol N m$^{-2}$ yr$^{-1}$) diversion wetlands. Results from past work have widely varying conclusions about the impacts of marsh nutrient enrichment. Some found that increased fertilization of freshwater or tidal marshes can potentially lead to increased
soil OM decomposition (Wigand et al. 2009; Anisfeld & Hill 2012) less soil strength or increasing buoyancy (Turner et al. 2009), and decreased belowground biomass (Darby and Turner, 2008 a & b; Langley et al. 2009). However, many more argue that the introduction of nutrient enrichment either has no discernible impact on belowground mechanisms in marsh and forested wetland systems (Langley et al. 2009; Anisfeld & Hill 2012; Graham and Mendelssohn 2014, Day et al. 2018, Hillman et al. 2018) or can have a positive effect by increasing productivity and biomass (Morris et al. 2002; Shaffer et al. 2015; Hillmann et al. 2018).

In the present study, there was a positive correlation of nutrient enrichment due to river impact ($^{15}$N and IP content) and high organic content soils (C, N and OM content). River impact likely stimulated vegetation productivity and in turn increased OM content in soils because diversion sediment and water are a significant source of bioavailable nutrients and provide good growing conditions. Additionally, N content in river influenced surface soils in 2018 was 21% higher than 2007, compared to 14% increase in C content. During the 10+ years of diversion influence plants have incorporated a significant proportion of river-borne NO$_3^-$ for growth and eventually stored the nutrient within the system as soil organic matter. We also observed significant denitrification rates which would remove inorganic N from the wetland system, preventing transport to the Gulf of Mexico. Based on monthly average discharge and river NO$_3^-$, in 2018 the Davis Pond diversion diverted over 1,800 MT of NO$_3^-$ from the Mississippi River nitrate load into Barataria Basin. This equates to just 1.6% of the total nitrate delivered to the Gulf of Mexico each year.

Although marshes experiencing eutrophic conditions commonly demonstrate a loss in belowground standing crop, Graham and Mendelssohn (2016) propose that fertilization does not necessarily lead to soil collapse if certain mechanisms are present, like sedimentation, to offer
new resources for plant growth. Davis Pond diversion discharge delivers the necessary sediment subsidy to maintain organic accretionary processes in the marsh soils in spite of potential losses to soil OM due to nutrient enrichment. Indeed, Davis Pond river-influenced soils maintain C content and accumulation rates over time, with no apparent negative impacts from introduced nutrients.

2.4.2. Carbon Storage

Wetlands account for 20-25% of global terrestrial C storage (DeLaune & White, 2012) and when river diversions are used to revive hydrologically isolated and highly organic wetlands in the Mississippi River basin, C sequestration rates could increase by up to 14% (Wang et al., 2017). Diversions create better growth conditions for wetland vegetation and in turn allow for higher rates of organic matter accumulation. Organic material is an important structural component of soils that also prevents C from returning to the atmosphere in the form of greenhouse gases. Highly organic soils outside of the diversion flow path tended to be less dense with higher porosity. During diversion operation, fine-grained river sediments were deposited within the flow path and as soils formed, pore spaces were filled in, leading to an increase in mean BD over time and lower soil moisture, a proxy for pore space in flooded soils. However, the transition to riverine impacted soils also led to an increase in average density of C, N and mass of OM in soils formed during diversion operation. Furthermore, total mass of C and N in the surface soil layer that formed during the last decade is higher than the surface layer from 2007.

Even with diversion influence, Davis Pond soils are producing the same density of organic material and storage rates in river-influenced areas are higher than those that experience no direct diversion impact. There are several potential drivers for this trend. First, open water areas have filled in with deposited sediments, providing new vegetated areas for soil formation.
which can contribute to C stocks, and this is evident from satellite imagery. Elevated nutrient concentrations associated with diversion water and sediments along with improved soil conditions from mineral sediment addition could also stimulate high C accumulation rates. Additionally, diversion operation raised the water level throughout the wetland (Barras, 2003) slowing decomposition rates due to lower redox conditions (Reddy & DeLaune, 2008). Many projections are presented in the literature regarding decreased carbon stocks and soil strength due to nutrient and sediment addition in systems with a number of confounding factors. Those outcomes do not seem to be supported by this research at a large scale in the Davis Pond diversion.

2.4.4. Management Implications

Although models of sediment diversion impacts outlined in the Coastal Master Plan can relay useful information about the effects of diversions on coastal wetlands, there are few real-life analogs for diversion projects of that scale. Performance of large surface water diversions are a useful tool in evaluating how wetlands that are far afield from large sediment diversion inflows will be impacted. Coarse, sandy sediments will settle out closer to the inflow of sediment diversions, but nutrients and fine-grained river sediments may travel far distances into the vegetated receiving basins. Because it is not designed to deliver sandy sediments, conditions in the Davis Pond diversion can represent those far afield areas well.

One conclusion made from analysis of the Davis Pond diversion demonstrated that there is a lack of connectivity between some wetland areas and the diversion derived sediment supply, limiting the restorative capacity of diversion operation. Plant type, distribution of habitat class and morphological characteristics of the receiving basin control which areas experience diversion impact. Managers for future diversion projects across Louisiana must implement
solutions that will to spread diversion materials across the entire basin despite potential obstructions. We also show that $^{15}$N, in conjunction with total IP, might be useful indicators for monitoring of diversion impacts in coastal Louisiana wetlands in addition to traditional physiochemical characteristics. Analysis of the flow path of other diversions such as Caernarvon has proved difficult in the past, but geostatistical analysis of soil conditions may help identify the area of impact of diversion water through Breton Sound and monitor the impact of that long-term project. Additionally, on the condition that critical soil characterization baselines are established, these soil variables can be important for monitoring effects from large scale sediment diversions once they are operational.

The Davis Pond Diversion provides a more controlled study subject to analyze decadal impacts of freshwater surface diversions in coastal Louisiana wetlands. Because of little to no history of hurricane impacts, less negative scrutiny from the public and in the literature, and in depth pre- and post-diversion sampling Davis Pond may more accurately represent the future of restoration on the Louisiana coast than other previously sampled sites. The work presented here indicates that there are many benefits to not only continuing operation of freshwater diversions, but also to timely implementation of large-scale sediment diversions in Southeast Louisiana.
3.1. Introduction

Most wetlands serve as a natural buffer situated between terrestrial and aquatic ecosystems. These systems act as a transformer or sink for nutrients because various biotic and abiotic processes remove nitrogen (N) and phosphorus (P) from the water column and improve water quality. Riparian wetland basins are especially important for water quality because they exist at the intersection of anthropogenic influenced rivers and natural estuarine systems. The Davis Pond diversion wetland, located at the head of Barataria Basin, is a restored wetland that has received diverted Mississippi River Water since 2003 (McAlpin et al. 2008). Resource managers reconnected the Davis Pond diversion wetland with the Mississippi River in order to reverse increasing salinity gradients, driven by sea level rise, which threaten important fisheries and wetland vegetation in Barataria Basin. When the diversion is operating, an average of 45 m$^3$s$^{-1}$ water is siphoned from the Mississippi River through a diversion channel and is emptied into a 38 km$^2$ freshwater wetland which connects to Barataria Basin at the southern end. The diversion was designed to deliver freshwater and nutrients to the wetland and to the basin in order to maintain nutrient cycling and vegetation functions, however, the design did not intend to deliver other materials such as inorganic sediment (Barras et al. 2003, Snedden et al. 2007).

Concentrations of nutrients such as N and P have nearly doubled in the Mississippi River since the early 20th century (Goolsby et al., 2000; Evers et al., 1992), and many critics of freshwater diversions argue that river reconnection would encourage eutrophication in the receiving basins and reduce wetland resilience (Darby and Turner, 2008a). Evidence suggests, however, that application of fine-grained inorganic sediments increases the density of the soils (Anisfeld & Hill, 2012). Higher density soils may be more stable in contrast with low density
soils which are more susceptible to erosion (Howes et al. 2010, Sapkota et al. In Review). There is uncertainty surrounding how influx of riverine sediments that are also laden with nutrients will alter the biogeochemical processes within the system. Although in many cases wetlands serve as a means to remove or store nutrients, under certain conditions soils can release nutrients contributing further to primary productivity. Eutrophication is an increasingly common end result of nutrient pollution which can reduce the quality of ecosystem functions provided by wetland habitats (Zedler & Kercher 2005).

Phosphorus is the most important nutrients in controlling productivity in some wetlands, especially in systems with low mineral input. Abundance of P in relation to C and N is a main determinant in the net primary production of any aquatic system. Total P is commonly measured in wetland monitoring studies, and as such, understanding the availability of P contributes to interpreting overall health and functioning of a wetland system. As a wetland of the Mississippi River deltaic system, Davis Pond has P inputs associated with both riverine sediment and highly organic soil material (Reddy and DeLaune 2008). During the last decade, the Davis Pond wetland transitioned from a hydrologically disconnected state, with highly organic soils throughout, to a riparian-influenced system. Newly accreted soils have much more inorganic material and therefore greater amounts of inorganic P, and behavior differs between inorganic and organic P variants.

Organic P (OP) is phosphorus that has been taken up by either microbes or plants and incorporated into organic matter (OM). Up to 80% of bioavailable P removal can be performed by plants depending on the productivity of the system (Reddy et al. 1995; Reddy et al., 1998). Organic P is found in the form of ester-linkages, an important molecule in the formation of fatty-acids. Ester groups can be mineralized via phosphatase extracellular enzymes produced by
microbes when there is a demand for P. Mineralization, or breakdown, of OM produces bioavailable P and there are several factors which play a role in governing soil OP release rates including soil OM levels or decomposition rates or redox state (Reddy and DeLaune, 2008). For example, P associated with soil humic material can be stored on a long time-scale in non-P limited environments when decomposition is slowed by a lack of oxygen or soil organic matter is not particularly labile.

Inorganic P (IP) in a river system is present either in the form of dissolved phosphate (PO$_4^{3-}$) in river water or ortho-phosphate molecules that are associated with various elements in the inorganic sediment such as iron (Fe), aluminum (Al), calcium (Ca) and magnesium (Mg). In most conditions, dissolved IP is quickly utilized for growth by microbes and plants or complexes with particulates in the soil (Reddy et al., 1995). Metal-associated P can lead to mineral formation which is relatively stable in most soil conditions, and in some cases is considered a long-term storage mechanism (Malecki-Brown, et al., 2007). Soil physio-chemical properties like pH and redox condition, however, can cause IP to desorb and increase availability in the pore water or the water column. Desorbed IP is highly mobile but labile IP is taken up quickly for biological productivity if the environment is P limited (Reddy et al., 1995).

Soil P has diverse speciation which causes variability in the mobility and bioavailability between soil P types (Adams et al. 2018). It is difficult to predict P bioavailability without understanding the forms of soil OP and IP. Although total P is commonly measured for monitoring projects in Louisiana coastal wetlands, and other places globally, this soil characteristic does not represent the contribution from each P fraction and does not adequately predict the availability within the soils. The discharge of Mississippi River water into the Davis
Pond freshwater diversion has likely influenced the distribution of both P forms and this study aims to identify temporal variation in P.

A baseline study by Kral et al. (2012) collected samples of the top 20 cm of soil within the Davis Pond Diversion wetland shortly before full scale operations began in 2007. The data were used to create geospatial comparisons of several soil characteristics from across the wetland including total P. Predicted values for initial conditions across the wetland showed high variability in total P between sites that were relatively close to one another. Analysis did not demonstrate a strong spatial component driving the distribution of total P in 2007, likely due to the low volume operation of the diversion up to that point. Cross-variograms presented by the baseline study also suggest that total P distribution was not correlated to any other soil parameter. Separation of soil P into inorganic and organic fractions should help elucidate how the spatial drivers of the different forms of P are controlling P availability. In the 10 years following the first sampling, the wetland has accreted approximately one cm of new soil each year (DeLaune et al. 2013). A resampling effort was conducted in 2018 as part of this research to document the ~11-year record of hydrologic restoration to this coastal, deltaic wetland. We hypothesize that the relative contribution of Fe and Al- bound P from Mississippi River sediment to Davis Pond wetland soil OP stocks has increased over time.

3.2. Materials and Methods

3.2.1. Study Site

The Davis Pond Diversion discharges into a fresh water ponding area located in Barataria Basin, Louisiana, USA. The diversion structure is approximately 19 km upstream the Mississippi River and on the opposite bank from the city of New Orleans. At maximum flow, the diversion delivers up to 300 m$^3$ s$^{-1}$ of water into the 37.6 km$^2$ ponding area. Since 2007, average diversion
discharge was 58 m$^3$s$^{-1}$. The ponding area is surrounded by levees on the northern, western and eastern sides and the southeastern boundary of the wetland is composed of a rock weir that is cut with several outflow canals, draining water into Lake Cataouatche and Lake Salvador further south. The Davis Pond Freshwater diversion was built in 2002, however, water flow issues prevented running the diversion at full capacity before 2009 when modifications to the flow path were completed.

### 3.2.2. Sampling

The sampling scheme for this study was generated using spatial simulated annealing (SSA) (VanGroenigen et al., 1999). The plan was designed to ensure that the area is uniformly sampled and short-range variability is accounted for when performing variographic analysis. Push core samples of the top 20 cm of soil were collected at 142 stations in May through July 2007 and May through June 2018 and separated into two subsamples, 1- to 10 cm and 10- to 20 cm soil intervals, during extraction in the field.

### 3.2.3. Analysis of Soil Characteristics

Soils were analyzed for moisture content, bulk density (BD), total phosphorus (TP), total inorganic phosphorus (TIP), total organic phosphorus (TOP), mineral (ash) content and percent organic matter (OM) by combustion. Field moist samples were homogenized and sub-samples were weighed to dry at 70°C until at constant weight, then reweighed for soil moisture and bulk density calculations. Dried ground samples were combusted at 550°C for 4 hours and final weight was subtracted from initial weight for loss on ignition or OM content. Total phosphorus and metals were found with HCl acid digestion. Samples were analyzed for TP on a SEAL AQ2 Automated Discrete Analyzer (SEAL Analytical, West Sussex, England), using US EPA ascorbic acid automated colorimetric procedure Method 353.2 (US EPA, 1983). Minimum
detection for SRP was 0.002 mg P l\(^{-1}\). Metals (Fe, Al, Ca, and Mg) were analyzed with inductively coupled plasma atomic emission spectroscopy.

Samples were extracted for total IP with the method outlined by Reddy et al. (1998). Dried ground samples were added to a centrifuge tubes with 25 mL of 1M HCl to 0.5 g of dry soil and shaken for 3 hours on longitudinal shaker. Shaking period was followed by 10-minute centrifugation and the supernatant fluid was filtered through a 0.45-µm membrane filter (Reddy 1998; Reddy and DeLaune, 2008). Filtrate was analyzed for SRP on a SEAL AQ2 Automated Discrete Analyzer (SEAL Analytical, West Sussex, England), using US EPA Method 353.2 (US EPA, 1983). Minimum detection for SRP was 0.008 mg P l\(^{-1}\). Total organic P was determined by the difference (TP-TIP).

3.2.4. Statistical Analysis

Similar to the methodological framework for thesis Chapter 2, this study aimed to use geostatistical means to identify spatial and temporal patterns in the distribution of soil phosphorus fractions in the Davis Pond wetland. The work flow consisted of (1) univariate analysis of between year trends in measured site P data; (2) observing patterns in spatial distribution of soil P fractions across the wetland and over time by modeling soil variables through spatial auto-correlation; (3) creating a new dataset from modeled data in order to make univariate and multivariate comparisons between years and between distinct areas of the wetland.

3.2.4.1. Univariate Analysis

Paired t-tests were conducted in order to evaluate how soil characteristics changed at each site between sampling years. \(P\) values < 0.05 are considered significant.
3.2.4.2. Geostatistical Analysis

The purpose of performing a geostatistical analysis was to model distribution of each soil parameter using measured soil variables in each sampling year, 2007 and 2018. Additionally, the study is designed to analyze pre- and post-diversion conditions so we also modeled a difference value, or the change in each soil parameter between years, identifying how conditions changed at each point continuously across the wetland. As a result, we expected to observe how the diversion is driving change within the system over space within each year and over time.

3.2.4.3. Variograms and Spatial Autocorrelation (Kriging)

Geostatistics is the investigation of spatial relationships by statistical means, and is commonly used in soil science. As with the approach outlined in Kral et al. (2012), here a geostatistical approach was used to describe the spatial variability in soil characteristics across the Davis Pond wetland. This analysis assumes that there is some random function that determines the value of a variable of interest, \( Z \), in a given region. In a finite set of locations, \( Z \) would be one realization of said function that constitutes the regionalized variable. Equation 1 is a linear model of describing \( Z \) at location \( x \):

\[
Z(x) = m(x) + \epsilon(x) + \epsilon'(x)
\]

(Eq. 1)

Where \( m(x) \) is the structural component with a directional and causal influence. \( \epsilon(x) \) is the spatially autocorrelated component, which is also causal but is omni-directional and does not have a directional trend. Finally, \( \epsilon'(x) \) is stochastic, or random, spatially uncorrelated variation drawn from a normal distribution with mean zero that is due to random events or error in sampling or taking measurements.

In order to define the random process which governs \( Z(x) \), we must assume first order stationarity. As stated in Matheron’s intrinsic hypothesis, we assume that certain attributes of the
distribution of the function, such as the mean or variance of two points, are constant. In other words, the models of the spatially dependent variance are the same over the entire sampled area, regardless of absolute position. As a result, one can find covariance with only the lag distance \((h)\) of points instead of their absolute positions within the region. Consequently, the variance of differences in spatial relation of two points could also be calculated under Matheron’s assumption of stationarity because it depended only on the lag distance, as well (Webster & Oliver, 2000). This value, called the semivariance \((\gamma)\), can be used to describe spatial dependency or similarity of values of \(Z\) at certain lag vectors, \(h\). In a binned variogram, semivariance represents the average value of the difference in variable \(Z\) at two points at a given \(h\):

\[
\gamma(h) = \frac{1}{2} E \{[z(x) - Z(x + h)]^2} \tag{Eq. 2}
\]

Variograms are used to summarize the spatial relationships in the data, but a continuous function must be fit through the variogram estimates so that a value for \(\gamma(h)\) can be estimated at any \(h\) (Webster & Oliver, 2007). Classical Matheron’s method of moments variogram estimator was used for least squares fitting, weighted by the number of sites separated by vector \(h\). Exponential and spherical models are commonly used for variogram fitting in soils with a mixture of visual and statistical methods. Range for each variogram was identified as the lag distance at which the variogram stabilized, or where the semivariance stopped increasing and the behavior either remained the same or became erratic. Final model selection was based on minimization of weighted sum of squares then finalized at the discretion of the practitioner by determining which model appeared to represent the continuous trend of the true variogram.

We used the fitted models to perform autocorrelation for each soil variable in both sampling years, as well as for the values of difference between variables in each year by subtracting 2007 raw data at each site from the 2018 data. Ordinary kriging was used to estimate
the value of a variable at unsampled locations across the wetland by implementing parameters
from the previously fitted model function. The variogram model is interpolated over grid cells, or
area blocks, to create maps of predicted values for the soil parameters. Final maps were produced
in ArcMap.

We used the variance maps of the difference between years to find the 95% confidence
interval around zero for change in each grid cell with equation:

\[ \bar{X} \pm 1.96 \cdot \sqrt{\sigma^2} \]  \hspace{1cm} \text{(Eq. 3)}

A grid cell value within this confidence interval would signify no significant change; those outside were considered significant for our analysis.

Finally, mean squared deviation ratio (MSDR) was calculated from cross validation to
measure accuracy of model. The value of MSDR should be close to 1. Equation 3 was adapted
from Webster and Oliver (2007):

\[ \text{MSDR} = \frac{1}{n} \sum_{i=1}^{n} \frac{[z(x_i) - \bar{z}(x_i)]^2}{\sigma_{KR}(x_i)} \]  \hspace{1cm} \text{(Eq. 4)}

Where \( n \) is the number of points in the dataset.

3.2.4.4. Soil Nutrient Stock Estimations

Soil nutrient stocks in the top soil layers from each sampling year were estimated using the
methodology outlined by Veronesi et al. (2014). Soil total P (TP), total inorganic (TIP) and total
organic (TOP) volumetric content, g P m\(^{-2}\), was calculated using spatially autocorrelated surfaces
with the following equations:

\[ \text{TP Density} = TP_i \cdot BD_i \cdot d \]  \hspace{1cm} \text{(Eq. 5)}

\[ \text{TIP Density} = TIP_i \cdot BD_i \cdot AC_i \cdot d \]  \hspace{1cm} \text{(Eq. 6)}

Total inorganic phosphorus concentrations (IPi) were normalized with bulk density (g
cm\(^{-3}\)) of the proportion of total soil that was computed as inorganic material. In this case, percent
mineral content by weight of the soils was used. The depth of the soil layer \( (d = 10 \text{ cm}) \) was used to produce estimates of P density \( (\text{g P m}^{-2}) \). We replicated the IP method in order to perform OP density calculation but percent by weight organic matter was used as a proxy for density of organic material.

3.2.4.5. Nutrient Stock Variation Estimation

Error propagation in the TP, TOP and TIP fractions volumetric content estimations was addressed by assessing uncertainty associated with each variable. Estimation of variance of the TIP density in each predicted grid cell were computed with the following equations, adapted from Goidts et al. (2009) and Schrumpf et al. (2011):

\[
\text{Var (TP Density)} = (\text{TP Density})^2 \left( \frac{\sigma_{TP}^2}{\text{TP}^2} + \frac{\sigma_{BD}^2}{\text{BD}^2} + 2 \frac{\sigma_{TP-BD}}{\text{TP} \cdot \text{BD}} \right) \tag{Eq. 7}
\]

\[
\text{Var (TIP Density)} = (\text{TIP Density})^2 \left( \frac{\sigma_{TIP}^2}{\text{TIP}^2} + \frac{\sigma_{BD}^2}{\text{BD}^2} + \frac{\sigma_{AC}^2}{\text{AC}^2} + 2 \frac{\sigma_{TIP-BD}}{\text{TIP} \cdot \text{BD}} + 2 \frac{\sigma_{AC-BD}}{\text{AC} \cdot \text{BD}} + 2 \frac{\sigma_{TIP-AC}}{\text{TIP} \cdot \text{AC}} \right) \tag{Eq. 8}
\]

Where \( \text{Var (TP Density)} \) in each grid cell is the error associated with the density prediction in \( \text{g m}^{-2} \). \( \sigma_{TP} \), \( \sigma_{TIP} \), \( \sigma_{AC} \) and \( \sigma_{BD} \) are the standard deviation of TP, TIP concentration, inorganic material and bulk density. Covariance (\( \sigma \)) of TP, TIP, AC and BD were calculated from the raw dataset.

3.2.4.1. Univariate and Multivariate Analysis with Predicted Data

Once surfaces with predictions from kriging were produced, we were able to manipulate the soil parameters in order make comparisons between years and between areas of the wetland.

Standard errors calculated from variance maps of kriged predictions for each parameter allow us to assess the significance of changes in soil parameters between years and between different wetland areas. For multivariate comparisons, Pearson’s correlation coefficients were calculated.
to better understand interactions between the different parameters and how those interactions may be driving P availability in the wetland. P < 0.05 was considered significant.

3.3. Results and Discussion

3.3.1. Variography and Kriging

Relative nugget is the ratio between two parameters of the variogram model, the nugget and sill, and it represents how well the model describes the variance within the variable, especially at small lag distances. We first created variograms based on the measured concentrations (mg P kg\(^{-1}\) soil) of total P, total organic P (OP) and total inorganic P (IP) and compared the parameters to analyze the connectedness of P within this wetland system over time (variograms presented in Appendix A). In the first year of the study, 2007, the relative nugget value of the variograms for total P, and to a lesser extent total OP, are large because the semivariance, or average difference between two points at a certain lag distance, does not approach zero. In this case, our models do not accurately describe variability between points that are close to each other, such that any small-scale variability is missed. A large nugget effect arises either from sampling error or if the distance intervals between sampled points are not small enough to model the variable at the appropriately sized scale. Variogram parameters are presented in Appendix B.

In either case, the model does not represent total P particularly well. This result suggests that unlike the other soil characteristics, there is a weaker spatial driver in 2007 for total P and total OP distribution. Before the diversion reconnected the wetland to the river, the soil P and organic P pool was likely determined by smaller scale or local influences which created pockets of high and low concentration throughout. In short, before prolonged diversion operation, there were no basin-scale impacts on the nutrient that are interpretable by this method.
In 2018, the P and OP variogram models had relative nugget values that are both much lower, and are closer in value to other soils characteristics which are well represented by variogram models. In addition to the delivery of allochthonous materials, higher connectivity with the river diversion flow can also move internally sourced P material. Increased riverine input has led to a stronger spatial component in total P and total OP distribution, which creates a model that better represents the variability across lag distances leading to a more accurate map of these nutrients within the wetland.

Kriged maps and modeled data for concentration of total OP and IP (mg P kg⁻¹) demonstrate clear spatial and temporal trends in the distribution of the nutrient as a result of diversion influence (Figure 3.1, table in Appendix D), however, volumetric content of these

Figure 3.1. Maps of predicted values for concentration of total inorganic phosphorous and total organic phosphorous in 2007 and 2018 in mg P / kg soil. Variance maps are also presented.
parameters (g P m$^{-2}$) will be discussed in much greater detail in the following sections as the normalized data better represent the drivers of distribution in the Davis Pond.

3.3.2. *Change in Total P, OP and IP Over Time*

Results from paired t-tests indicate that differences in P pools (g P m$^{-2}$) between years of total P, total OP and total IP were significant ($p<0.0001$) at 140 measured sites. Total volumetric P content is greater in 2018, and with a shift from 10.2 g m$^{-2}$ to 15.2 g m$^{-2}$ (Table 3.1). There were significant gains in total volumetric IP and a decrease in total volumetric OP, it is clear that transport of IP from the diversion is the major driver for total $\Delta$ of P mass in the wetland soils. Predicted dataset reflected those same trends (Table 3.1). In 2007, 85% of modeled sites had OP as the dominant P fraction. By 2018, that area decreased to 56%. Distribution of dominant IP sites closely follows the pattern of the sediment deposition zone for each time period.

3.3.3. *River Influenced vs Non-Influenced Wetland Regions*

Over time as inorganic sediment was deposited onto the soils, bulk soil density increased, especially in the diversion influenced regions (Chapter 2). Soils with high mineral content have a higher mass of material and on average have more P per unit volume of bulk soil than non-river influenced soils. We compared P stocks between areas of the wetland where deposition of

**Table 3.1.** Mean volumetric P content for each fraction at 140 measured sites and from predicted dataset presented with standard error. Results from paired t-tests are for data from measured sites.

<table>
<thead>
<tr>
<th></th>
<th>Phosphorus Content (g/m$^2$)</th>
<th>Inorganic Phosphorus Content (g/m$^2$)</th>
<th>Organic Phosphorus Content (g/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured 2007</td>
<td>10.2 ± 3.2</td>
<td>3.28 ± 0.002</td>
<td>3.03 ± 0.27</td>
</tr>
<tr>
<td>Measured 2018</td>
<td>15.3 ± 3.2</td>
<td>7.43 ± 0.04</td>
<td>2.30 ± 0.35</td>
</tr>
<tr>
<td>Paired t-test $p$</td>
<td>$p &lt; 0.0001$</td>
<td>$p &lt; 0.0001$</td>
<td>$p &lt; 0.0001$</td>
</tr>
<tr>
<td>Predicted 2007</td>
<td>10.5 ± 0.12</td>
<td>2.2 ± 0.19</td>
<td>3.7 ± 0.05</td>
</tr>
<tr>
<td>Predicted 2018</td>
<td>15.1 ± 0.20</td>
<td>5.3 ± 0.35</td>
<td>3.0 ± 0.05</td>
</tr>
</tbody>
</table>
inorganic material occurred versus those where it did not (Table 3.2), demonstrating how P dynamics differ between areas influenced by the diversion and wetlands where no effective river reconnection occurs. In order to discriminate between these areas, we fitted a mixture model to the mineral content dataset. Estimates of mixture distribution parameters would identify the breaking point between the bimodal distributions in this dataset, dividing the sites into two groups with significantly different sediment enrichment (Appendix C). Mineral content 65% by weight was used as a threshold value between sediment influenced and non-influenced soil.

Table 3.2. Mean volumetric P content by year of each soil P fraction inside and outside of the diversion influenced zone.

<table>
<thead>
<tr>
<th>Volumetric Content</th>
<th>Year</th>
<th>Connected</th>
<th>Disconnected</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total P (g P m⁻²)</td>
<td>2007</td>
<td>10.98 ± 0.92</td>
<td>6.21 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>2018</td>
<td>8.67 ± 0.54</td>
<td>7.16 ± 0.02</td>
</tr>
<tr>
<td>Inorganic P (g P m⁻²)</td>
<td>2007</td>
<td>11.03 ± 0.9</td>
<td>0.91 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>2018</td>
<td>10.83 ± 0.6</td>
<td>1.64 ± 0.03</td>
</tr>
<tr>
<td>Organic P (g P m⁻²)</td>
<td>2007</td>
<td>2.32 ± 0.8</td>
<td>3.95 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>2018</td>
<td>2.08 ± 0.3</td>
<td>3.66 ± 0.1</td>
</tr>
</tbody>
</table>

Figure 3.2. Map of sediment influenced zone from 2007 (blue) and 2018 (orange) defined by mixture model from mineral content dataset.
populations. In 2007 the influenced area is 4.8 km$^2$, in 2018 that area is 15.1 km$^2$ (Figure 3.2). Using this distinction, we tracked changing P stocks between years.

Due to different densities of inorganic and organic soils, influenced regions have more than two times higher mean total volumetric P content than non-influenced regions in both sampling years (Table 3.2, Figure 3.3). Average P content of influenced soils did not change significantly between years for any fraction, but soils which formed outside of the sedimentation zone are accumulating a higher mass of P over time.

**Figure 3.3.** Contribution of volumetric content of each soil P fraction by year in the diversion sediment influenced zone and the non-influenced zone.
3.3.3.2. *Organic Phosphorus*

We observed significant trends in volumetric OP content between years, however, there was no distinct pattern in how those changes were distributed spatially (Figure 3.4 b). Average OP decreased significantly between years in the non-river influenced areas which indicates that without input of diversion sediments or water there is overall a slower rate of organic P accumulation. Within the sediment influenced area there are some sites with significant OP loss (Figure 3.4 b), but on average, volumetric OP content did not change significantly in this region. In contrast to the non-influenced areas, organic P was generally preserved within the flow path during the transition from organic to inorganic dominated soils. In fact, several diversion related impacts could have led to stable OP content rates in the new surface soil layer. Inside the sphere of diversion influence, there is likely increased flooding, reduced rates of decomposition, and a higher potential for organic material preservation. Deposited inorganic material from diversion pulses may also act as a physical mechanism for burial of OM and create conditions conducive to OP production. Additionally, wetland plant productivity will be higher due to increased concentration and density of nutrients associated with diversion impact. River sediments deliver iron-bound IP upon deposition and under flooded conditions iron will become reduced and dissolved IP is released into the pore water (Zhang et al., 2012). Organic matter accumulation is higher in the diversion influenced zone (Chapter 2), and it is likely that bioavailable P released from the sediments contributed to production of organic material which is reflected in stable OP stocks.

3.3.3.2. *Inorganic Phosphorus*
IP stocks are almost nine times larger in the influenced soils in both years (Table 3.2, Figure 3.3), and that is driven by the delivery of river sourced P. Between years, all sites that experience a significant increase in IP content are located within the area of significant sedimentation (Figure 3.4a). Sediment deposited onto the surface of the marsh was buried over time as the wetland continued to accumulate organic and inorganic materials. As a result, mineral-associated P is buried in the soils and average inorganic volumetric P content increased slightly, but not significantly, over time within the flow path. Diversion sedimentation occurs closest to the inflow and there is decreased sediment deposition with distance from the river (Day et al., 2009). However, if over time enough sediment is captured to infill open water areas, the velocity of river diversion flow in the wetland can increase driving the area of sedimentation to extend farther down the flow path. Increased water flow could also entrain labile IP, removing it from the soils, and distributing it across the water influenced zone. Soils with delivery of inorganic material from the river may reach a certain threshold of sedimentation at which more will not

![Figure 3.4. Davis Pond map, black area demarcates where between years new soils had (a) an increase in volumetric IP content or (b) a decrease in volumetric OP content that was outside the 95% confidence interval for change in each variable. Red shaded area is diversion sediment impact zone (mineral content > 65%).](image-url)
settle, limiting the maximum amount of IP that can be deposited in association with sediment. Small concentrations of dissolved PO$_4^{3-}$ is a source of IP in diversion water that will also interact with influenced soils by attaching onto a limited number of sorption sites on the soil mineral particles (Reddy et al. 1995). In the long-term, soils in the flow path have experienced high sedimentation rates so maximum density of IP could have been met in many areas because more sediment cannot be deposited and adsorption sites are occupied.

The non-influenced regions do not have significant change in mineral content, however, on average they experienced a significant increase, approximately 0.73 g P m$^{-2}$, in TIP density. In the non-influenced regions there are two significant sources of IP. First, labile dissolved IP in diversion water can reach areas within the wetland that sediment cannot. Additionally, IP is produced from the declining stocks of OM in areas that are outside the sediment impact zone but are flooded with diversion water. These areas have significant loss of OP (Figure 3.4 b), and mineralization releases bioavailable dissolved IP. If labile IP in soil pore water is not used by microbes or plants for productivity, it will quickly be stored in the soils in complexes formed with organic or inorganic materials.

3.3.4. Multivariate Analysis

In 2007, organic P is the more dominant form in the soil, including that which is stored in microbial biomass and degrading plant material. In both sampling years, total volumetric P content and IP are strongly positively correlated ($p<0.001$), and there is a similarly strong but negative interaction between OP and total P density ($p<0.001$). These results again highlight the large contribution of inorganic P associated with the river to total soil P stock as a result of diversion operation.
Another interest of this study was to observe how inputs of P into the system influence other biogeochemical interactions within the soil. The N:P ratio of plant tissue is typically used to determine N or P dynamics, where ratios greater than 16 indicate P limitation, and values less than 14 are associated with N limited environments (Koerselman & Meulman, 1996). Other interpretations of soil N:P ratios associate larger values with wetlands that are less connected to riverine materials. These areas receive less sedimentation and have stagnant water conditions. Internal nutrient cycling is lower because of limited P input and slow rates of OM mineralization. Wetland areas that are generally better connected and receive high sediment and nutrient loads are generally more productive, and as a result they tend to have lower N:P values (Lockaby, 1999). The volumetric N content: volumetric P content ratio could be a useful metric to describe how nutrient dynamics have changed within the diversion influenced area.

Delivery of N and P from the diversion is changing soil nutrient ratios (Figure 3.5), and that metric reflects alterations to productivity of plants and microbes after diversion influence. In 2007, approximately 14% of the wetland area had volumetric N content: volumetric P content values that were less than 14, contained exclusively within the diversion influenced zone. Outside of that small area, sites had N:P above 16, the theorized threshold, and represent environments with more P limitation, slower mineralization and lower production. In 2018, the area of the wetland with N:P ratio less than 15 increased to 32%, and this area extends down the central flow path of the diversion. As previously discussed, delivery of inorganic sediments from the diversion is driving P distribution in a large part of the wetland. Although there is a high concentration of dissolved inorganic N associated with the diversion that has incorporated into the soil, the increase in density of P is large and has the potential to alter nutrient ratios across the
wetland. Moreover, diversion influence is changing other aspects of wetland functions like productivity and nutrient cycling. Other work demonstrated that diversion influenced is significantly increasing volumetric N content due to increased productivity (see Chapter 2). It could be that introduction of P is also stimulating plant and microbe activity, changing nutrient storage and availability in the wetland as a result.

![Figure 3.5](image)

**Figure 3.5.** Soil N:P ratio values for each sampling year in the influenced and non-influenced wetland areas. Bold bars are means and orange line denotes threshold N:P value 16.

### 3.3.4.1. Organic phosphorus

Percent OM by weight and OP concentration are positively correlated ($r = 0.87, p<0.001$) in 2007 demonstrating that in situ organic matter is the source of stored organic P. Autochthonous P, or that which is available internally following the breakdown of organic matter, is the dominant P pool on a concentration basis in both years, and volumetric basis only in 2007. Without
hydrologic reconnection to highly organic freshwater wetlands, internal OP could be a major source of bioavailable P, as it seems to be in Davis Pond in the 2018 non-influenced zone.

Although carbon (C) and N are highly correlated with OM content (r=0.98, r=0.97, respectively, p<0.001), there are weak relationships between OP and either of these nutrients (r=0.17, r=0.19, respectively, p<0.5). However, positive correlation between C:N and C:OP ratios in the soils are very strong (r= 0.96 and r = 0.70, respectively, p<0.0001). This dynamic is likely driven by the separation of soil OM based on density, into a light fraction, or particulate organic plant and animal material, and heavy fractions, small OM particles bound to mineral material. Primarily, the distinction between light fractions (LF) and heavy fractions (HF) describes a difference in decomposability of the OM based on molecular weight and chemical make-up (Gregorich and Ellert, 1993). The light fraction, or particulate organic matter, is enriched with C and tends to be highly degradable, while heavy forms of organic matter with higher molecular weight are less available for mineralization by microorganisms (Gregorich and Ellert, 1993, Kögel-Knabner et al.2008).

**Figure 3.6.** C:N and C:OP organic ratio values for each sampling year in the sediment influenced and non-influenced wetland areas. Bold bars are means.
The heavy and light fractions have different potentials for physical and chemical interactions with inorganic sediment and there is preferential adsorption of organic matter that is N- and P-rich to the inorganic material. As a result, the sedimentation influenced soils where there is more of the heavy OM fraction has higher proportions of OP and N compared to C, resulting in reduced C:N and C:OP values in those zones between years (Figure 3.6). In well drained and wetland soils the heavy OM is typically considered the more stable soil OM pool (Tan et al. 2007; Kögel-Knabner et al. 2008, Jinbo et al., 2007). Heavy fractions of OM are more resistant to microbial decomposition which prevents mineralization of N and P. As a result, OP in the sediment influenced zone is not easily degraded, preserving the P in its organic form and increasing OP storage in river diversion-influenced regions.

Pre-diversion, P associated with humic organic material in the soil was an important storage mechanism. Although in many cases OP can be stored on a long time-scale, high OM loss rates call the stability of organic P in the non-influenced zones, and it’s potential for long term burial, into question. After a decade of diversion influence, OP is no longer the driver of P distribution in Davis Pond and does not seem to be a stable storage mechanism.

3.3.4.2. Inorganic Phosphorus

In 2018, the presence of inorganic P is equally positively correlated to mineral content and bulk density of the soil. These relationships confirm that allochthonous sources of P are mainly in the inorganic particulate form and that P is likely bound up with inorganic sediments from the river. Soil IP content is also highly correlated to elevated soil δ^{15}N values in both years (r=0.61, r=0.64, respectively, p<0.001) linking the two as indicators of diversion influence. Soils exposed to diverted Mississippi River materials were simultaneously flooded with high concentrations of dissolved nitrate in the water column and large amounts of IP associated with Fe or Al in the
sediments. Organic matter that was formed from wetland plants using river borne nitrate will have a markedly larger $^{15}$N fractionation value, so soil $\delta^{15}$N can be used as an indicator for increased nutrient delivery from river diversions.

Large stocks of IP are associated with iron or aluminum and are added to soils upon deposition of river sediments. We found that iron and aluminum content are both positively correlated with bulk soil density in these soils ($R=0.4$, $p=0.01$; $R=0.34$, $p=0.03$ respectively), so it is likely that IP is stored within those metals within inorganic river sediments. However, changing physio-chemical conditions or a strong concentration gradient can force this metal-bound IP back into porewater where it can be taken up by vegetation and contribute to primary production. In fact, Zhang et al. (2012) observed that under extended reduced conditions, dissolved bioavailable IP and OP were released from Mississippi River sediments into the water column. In Davis Pond, IP content in the sediment-influenced soils does not change over time despite continued diversion influence. We also see that there is an increase in OP production in this region, alluding to the existence of reduced conditions in the soils that cause iron-bound P to be released from the river deposits. As a result, IP stocks in the soils do not increase over time and nutrients released from sediments contribute to OP accretion. Seasonal changes to diversion operation lead to varying flooding conditions in the wetland throughout the year, driving cycling of P between its organic and inorganic forms. Under dry conditions there is increased microbial mineralization of OM and a net release of IP, but IP bound to oxidized iron is stable. However, if flooded conditions are reintroduced, organic P becomes stable due to slowed decomposition, but large amounts of labile IP could be released from metal complexes.

3.4. Conclusions
Highly productive soils with strong riverine influence could be both a source and sink for bioavailable P. The main driver for this distinction in diversion wetlands is how external and internal P interact with environmental controls at small and basin-wide scales. After a decade of diversion-influenced sedimentation and water introduction, there is a large stock of inorganic P in the wetland soils, mainly in association with inorganic sediments. Nutrient cycling and availability are changing as a result of diversion influence, as is evident in changing nutrient ratios across the wetland. Although IP enters the soils in association with river sediments, during prolonged flooded conditions metal-bound IP can be released into porewater and contribute to primary productivity in the river influenced regions.

Production of TOP within and out of the diversion influenced area is an important opportunity for P burial. Influenced regions had stable rates of OP accumulation rate after 11 years of diversion influence, highlighting the importance of reconnecting coastal freshwater wetlands to river influence in order to maintain organic accretion. Stability of organic material is instrumental in accumulating C, N and P thus removing excess amounts from system. If stored in wetland soils they can no longer contribute to eutrophication or in the case of carbon, increased atmospheric greenhouse gas concentrations. However, with continued isolation from river influence, soils formed in the non-influenced regions store less OM, and therefore organic P, over time and can release it in the form bioavailable IP back into the system. If the overall loss of volumetric organic P content in non-influenced areas of the Davis Pond diversion is an indicator, we can estimate that wetland areas which remain disconnected from riverine influence may also lose the ability to store significant amounts of organic material over time.

The data presented imply that measuring total P concentration alone will not provide the necessary information to determine which pools of P are controlling distribution of the nutrient
in diversion wetland soils. P dynamics in deltaic systems are difficult to track because there are
countless complex interactions between the P forms and environmental conditions which drive P
cycling. By identifying the forms and potential behavior of P in this system we can begin to
understand how the Davis Pond diversion, and other restoration efforts throughout the
Mississippi River Delta Basin, will influence the distribution and availability of this important
nutrient over time.
CHAPTER 4. SUMMARY AND CONCLUSIONS

Wetlands which exist at the interface of human impacted waterways and natural coastal terrain are important providers of ecosystem services including removal of excess nutrients, providing carbon storage and habitat for fisheries and wildlife. Human alteration of the landscape has led to wide spread wetland loss in southeast Louisiana, with a current annual loss rate of over 75 km². According to the Economics and Policy Research Group at LSU, in the next 50 years without restoration efforts, coastal land loss is estimated to cost the state of Louisiana $11.2 billion in losses to the economy. The future of the coast depends on timely implementation of restoration projects by the state at varying scales. One such project is large scale sediment diversion which aims to transport mineral sediment into Louisiana coastal wetlands which can build land in open water area, restoring vegetated wetland areas. Projects from past restoration efforts, like the Wax Lake Delta or other freshwater diversions, provide a small number of real-life analogs for sediment diversions and can give some insight of how best to implement restoration of the Louisiana coast.

The primary purpose of freshwater diversion projects such as Caernarvon or Davis Pond was to control salinity in their respective coastal basins so as to combat salt intrusion and protect the freshwater habitat for commercially important fisheries. There is concern that freshwater diversions are unable to provide the needed sediment subsidy to help maintain organic accretion throughout the coastal basins and their fate into the future in uncertain. Additionally, input of Mississippi River water with elevated nutrient concentrations, like nitrogen and phosphorus, is associated with eutrophic conditions and has been implicated in a loss of marsh soil integrity. As more and larger diversion are planned, there is also interest in identifying soil parameters which could identify the spatial distribution of diversion water impact within receiving basins.
Davis Pond is a 37 km² wetland which has received full diversion water impact for over a decade and provides an opportunity to investigate the wetland’s transition from hydrologic isolation to its current reconnected state. In that time the wetland received negligible discharge (< 1.5 m³·s⁻¹) during an average of 20 days each year. The study presented in Chapter 2 aims to investigate the spatial distribution of water and sedimentation that is transported into the ponding area and how those materials are altering soil character and nutrient storage in the soils. We used soil characterization data from 140 sites in the wetland from 2007 before full diversion operation began and in 2018 after 11 years of diversion impact. The study was designed to sample at varying lag distances so soil variable distribution could be studied at several spatial scales. Geostatistical analysis produced predictions of soil parameters for 10 m grid blocks across the wetland, which were compared temporally between years and spatially between river water-impacted and non-impacted zones in the wetland.

We mapped soil δN¹⁵, bulk density, density of mineral and organic matter, and volumetric content of C and N. Soil δN¹⁵ is a representation of the amount of river nitrate assimilated by vegetation representing elevated isotope fractionation in the Mississippi River. Plant material enriched with ¹⁵N isotope is incorporated into the soil after plant senescence and can be measured in soil organic matter. With this metric we can track the spatial extent of soils over which diversion water interacted during operation. Between 2007 and 2018 the area of wetland which was impacted by diversion water increased by 75%. After identifying the water impact zone, change between years in soil bulk density and mineral content was used to find that an area of 26.9 km² experienced statistically significant sedimentation.

Finally, we investigated the spatial distribution of the soil nutrient stocks on a volumetric basis. The mass of C and N and density of organic matter increased significantly when averaged
across the entire wetland. In fact, the soils formed within the diversion flow path between 2007 and 2018 accumulated carbon at a rate 2 times greater than soils formed outside of the diversion influenced zone during that same time period. Increased flooding enhanced organic matter preservation and input of river materials likely improved plant growth conditions so there was a greater contribution to the soil organic matter pool. There was also evidence of increased inorganic N assimilation by wetland vegetation from diversion water. Soil N content increased by a greater proportion than C, drawing down the C:N ratio, especially in river-impacted areas of the wetland. Plant tissues are enriched with river N, and after senescence that plant material is incorporated into the soil, resulting in N rich soil organic matter. Vegetation is providing another inorganic N removal mechanism in addition to microbial processes. Wetlands receiving diverted Mississippi River water and fine-grained sediments have an external source of inorganic phosphorus, an important nutrient that can contribute to eutrophication. In Chapter 3, we aim to investigate how a changed dominant soil P source in Davis Pond would alter P storage or availability. An input of sediment-associated inorganic material drove large increases to the P stock across the diversion influenced and uninfluenced zones. After inorganic P (IP) is deposited into flooded soils in association with sediments, reduced conditions lead to a release of P from now reduced iron complexes. Soil porewater has high concentrations of dissolved IP which is taken up by vegetation and eventually drives accumulation of organic matter. Coastal managers may want to further investigate the dynamics of a nutrient pool dominated by inorganic P and the long-term stability of P stored in these systems.

With thorough spatial analysis which incorporated non-traditional soil parameters, we successfully modeled changes in soil character and nutrient composition due to diversion impact in the Davis Pond receiving basin. Results can be used to better understand potential impacts
from sediment diversions on areas far afield from the outflow that will receive only river water and fine-grained sediments. Overall, we identified several positive impacts of the diversion on wetland soils. P bioavailability is relatively stable as inorganic metal-bound P that left the soils seems to be held up as organic P in well-preserved organic matter. Soils affected by the diversion have increased stocks of organic N and maintained C storage over time. They have also become denser and therefore more stable with the incorporation of inorganic sediments. The work presented here indicates that many restoration goals in Southeast Louisiana can be met with river diversions if certain conditions are present and management practices are well informed.
APPENDIX A. EXPERIMENTAL VARIOGRAMS

A.1. Experimental autovariograms (dots) and fitted variogram models (lines) of soil properties in the 0-10 cm soil depth in 2007 and 2018; (a) bulk density, (b) loss on ignition or organic matter content (c) total nitrogen, (d) total carbon, (e) total phosphorus, (f) total inorganic phosphorus, (g) total organic phosphorus.
A.2. Experimental autovariograms (dots) and fitted variogram models (lines) of change in soil properties in the 0-10 cm soil depth between 2007 and 2018; (a) bulk density, (b) loss on ignition or organic matter content (c) total nitrogen, (d) total carbon, (e) total phosphorus, (f) total inorganic phosphorus, (g) total organic phosphorus.
APPENDIX B. VARIOGRAM MODEL FIT PARAMETERS AND MSDR

Table B.1. Variogram models used for kriging of soil properties at 0-10 cm soil layer from (a) 2007, (b) 2018 and (c) difference between years. Includes mean square deviation ratio (MSDR).

(a) | Variable | Nugget | Sill | Range | Model Type | Nugget:Sill | MSDR |
--- | --- | --- | --- | --- | --- | --- | --- |
| BD 07 | 0.023 | 0.053 | 2460 | exponential | 0.4467 | 1.00 |
| LOI 07 | 117 | 551 | 3429 | exponential | 0.2124 | 1.01 |
| TC 07 | 4504 | 16768 | 4399 | exponential | 0.2686 | 0.97 |
| TN 07 | 21 | 65 | 4187 | exponential | 0.3283 | 0.97 |
| TP 07 | 38770 | 27431 | 1753 | spherical | 1.4134 | 0.90 |
| TIP 07 | 8123 | 35657 | 1682 | spherical | 0.2278 | 0.74 |
| TOP 07 | 27557 | 38410 | 1943 | spherical | 0.7174 | 1.02 |
| ^15N 07 | 1.88 | 7.48 | 1198 | exponential | 0.25 | 0.96 |

(b) | Variable | Nugget | Sill | Range | Model Type | Nugget:Sill | MSDR |
--- | --- | --- | --- | --- | --- | --- | --- |
| BD 18 | 0.008 | 0.022 | 2047 | exponential | 0.3381 | 1.00 |
| LOI 18 | 164 | 555 | 4032 | exponential | 0.2962 | 1.07 |
| TC 18 | 4308 | 16480 | 4077 | spherical | 0.2614 | 1.08 |
| TN 18 | 23 | 71 | 4258 | spherical | 0.3303 | 1.02 |
| TP 18 | 11527 | 34635 | 994 | spherical | 0.3328 | 1.28 |
| TIP 18 | 6845 | 86780 | 1998 | exponential | 0.0789 | 0.97 |
| TOP 18 | 11814 | 55391 | 1878 | exponential | 0.2133 | 1.00 |
| ^15N 18 | 3.24 | 7.85 | 3342 | exponential | 0.41 | 0.99 |

(c) | Variable | Nugget | Sill | Range | Model Type | Nugget:Sill | MSDR |
--- | --- | --- | --- | --- | --- | --- | --- |
| ΔBD | 0.001 | 0.014 | 445 | exponential | 0.07 | 1.70 |
| ΔLOI | 59 | 477 | 553 | exponential | 0.12 | 1.33 |
| ΔTC | 5809 | 11810 | 1241 | exponential | 0.49 | 1.22 |
| ΔTN | 16 | 56 | 990 | exponential | 0.29 | 1.29 |
| ΔTP | 50968 | 33340 | 1173 | exponential | 1.53 | 1.39 |
| ΔTIP | 14003 | 819 | spherical | 1.80 |
| ΔTOP | 41480 | 34592 | 2422 | spherical | 1.20 | 1.19 |
APPENDIX C. MIXTURE MODEL RESULTS

Figure C.1. Mixture model results for $\delta^{15}$N (top) and mineral content (bottom). Threshold value was estimated from point of overlap of populations.
APPENDIX D. MEASURED AND PREDICTED RAW DATA

Table D.1. Raw measured and predicted data from Chapter 2 kriging dataset presented by concentration (g C/N kg\(^{-1}\) soil) or percent by mass with standard errors.

<table>
<thead>
<tr>
<th></th>
<th>Organic Matter (%)</th>
<th>Total Carbon (g/kg)</th>
<th>Total Nitrogen (g/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured 2007</td>
<td>58.35 ± 2.12</td>
<td>291.45 ± 11.22</td>
<td>19.49 ± 0.73</td>
</tr>
<tr>
<td>Measured 2018</td>
<td>38.59 ± 2.19</td>
<td>192.05 ± 11.64</td>
<td>13.55 ± 0.77</td>
</tr>
<tr>
<td>Predicted 2007</td>
<td>59.94 ± 0.031</td>
<td>302.47 ± 0.16</td>
<td>20.05 ± 0.010</td>
</tr>
<tr>
<td>Predicted 2018</td>
<td>41.57 ± 0.027</td>
<td>208.09 ± 0.15</td>
<td>14.56 ± 0.009</td>
</tr>
</tbody>
</table>

Table D.2. Raw measured and predicted data from Chapter 3 kriging dataset presented by concentration (mg P kg\(^{-1}\) soil) with standard errors.

<table>
<thead>
<tr>
<th></th>
<th>Phosphorous (mg/kg)</th>
<th>Inorganic Phosphorous (mg/kg)</th>
<th>Organic Phosphorous (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured 2007</td>
<td>10.2 ± 3.2</td>
<td>3.28 ± 0.002</td>
<td>3.03 ± 0.27</td>
</tr>
<tr>
<td>Measured 2018</td>
<td>15.3 ± 3.2</td>
<td>7.43 ± 0.04</td>
<td>2.30 ± 0.35</td>
</tr>
<tr>
<td>Predicted 2007</td>
<td>936 ± 3.69</td>
<td>291 ± 2.29</td>
<td>630 ± 3.33</td>
</tr>
<tr>
<td>Predicted 2018</td>
<td>848 ± 2.83</td>
<td>375 ± 3.79</td>
<td>490 ± 3.16</td>
</tr>
</tbody>
</table>
REFERENCES


Coastal Protection and Restoration authority of Louisiana.(2017). Louisians’s Comprehensive Master Plan for a Sustainable Coast. Coastal Protection and Restoration Authority of Louisiana, LA


VITA

Alina Spera spent her childhood in Westfield, New Jersey with her parents, Joann and Vincent Spera and her sister, Nicole Spera. She was a competitive athlete of many different sports, including field hockey and rugby, and helped produce award-winning theater productions at Westfield High School. Alina studied Marine Science and Biology as a double major at the University of Miami’s Rosenstiel School of Marine and Atmospheric Science. After completion of her B.S., Alina’s interest in marine science developed into a love for coastal research and restoration as she spent a year working in coastal ecology environmental education.

Alina accepted a research assistantship to attend Louisiana State University in Baton Rouge Louisiana with Dr. John White in the Wetland and Aquatic Biogeochemistry Lab. Her master’s research has strengthened Alina’s interest in understanding nutrient dynamics in coastal systems. Alina has accepted an assistantship with the Ecology and Evolutionary Biology Department at the University of Texas El Paso and plans to pursue her Doctor of Philosophy with Dr. Vanessa Lougheed starting in the fall of 2019.