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PHOSPHORUS VARIABILITY IN THE AREA OF INFLUENCE OF THE MID-BARATARIA SEDIMENT DIVERSION

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
Peter T. Mates
B.S. Louisiana State University, 2018
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ABSTRACT

Man-made levees along the lower Mississippi River prevent delivery of sediment from building and maintaining Louisiana's coastal wetlands. The Mid-Barataria sediment diversions is designed to reintroduce Mississippi River water, sediment, and nutrients into the sediment-starved Barataria Basin. Phosphorus (P) is an important macronutrient for regulating primary production in coastal marine ecosystems. Wetlands can serve as a sink or source for phosphorus to the overlying water column through various retention and release processes, dependent on concentration. Louisiana coastal systems can be phosphorus limited due to much higher concentrations of bioavailable Nitrogen in river water. The high soluble molar N:P ($>50:1$) ratio in the river water is offset by the high sediment total phosphorus load. The wetland soil P flux has the potential to decrease the N:P ratio of the surface water creating an optimum nutrient condition for increased algal bloom formation. We analyzed soil characteristics from 60 wetland stations in Barataria Basin, LA to include both vegetated marsh and open water stations. Total P and organic P was significantly higher by 11% in the marsh sites compared with the open water sites. Soil samples from twenty sites were analyzed for inorganic and organic P pools. Marsh sites had a higher organic P pool while open water sites had higher Iron (Fe) and Aluminum (Al) bound P. The Fe/Al bound pool is expected to release P months after the diversion operation has ceased increasing water column P concentrations. Both site types have relatively low equilibrium P concentrations indicating that the soil will take up P during sediment diversion operations. This research can help inform ecosystem modelers in accurately predicting diversion effects on the nutrient status of the coastal basin as well as serving as a wetland soil baseline condition prior to river reconnection for coastal restoration. Future research should explore changing P flux dynamics in the area of influence of the operating Mid-Barataria sediment diversion.

CHAPTER 1. REVIEW OF LITERATURE

1.1. Introduction

1.1.1. History of the Louisiana Deltaic Plain

The coastal plain of Louisiana is a direct result of the Mississippi River meandering and depositing sediment to build land over the past thousands of years. Since the last glacial maximum, 20,000 years ago, average sea level rise has been about 6 mm y^{-1} , including a range of rates of sea level rise that exceed 40 mm y^{-1} , roughly 13,000 years ago (Donoghue 2011). Global sea level rise at this peak magnitude began to slow about 8,000 years ago (Roberts 1997). This slowing rate was coincident of the appearance of the world's deltas as sediment supply exceeded the erosion and submergence rates (Coleman 1988; Figure 1.1).

Over time, active deltas become inactive as sediment deposition decreases the slope of the river channel, and the river shift towards more energetically favorable areas. Over the past 6,000 years, the Mississippi River has constructed 16 anastomosing delta lobes which are collectively expressed as the delta we see today (Frazier 1967; Figure 1.1). Louisiana's coastal wetlands have established a platform of Mississippi River sediment, accreting organic matter to keep pace with rising sea level.

Deltas are highly productive ecosystems because of the vast array of ecosystem services they provide. The state of Louisiana, situated at the mouth of the Mississippi River valley, has accessed these services for centuries leading to an economy of robust water borne transportation, economically important fisheries, and tapping of geologic deposits of oil and gas buried beneath the delta (Kolker et al., 2011; Mendelssohn et al., 2012). Due to levee construction, the Mississippi River no longer supplies the coastal wetlands with nutrients and sediment during

spring river floods. These sediment-laden flooding events are critical in helping the coastal wetlands keep pace with an ever-increasing sea level rise. Jankowski et al. (2017) showed that with rates of current sea level rise, (12 ± 8 mm per year), compared with Louisiana marsh vertical accretion rates, 65% of wetlands in the Mississippi Delta region (southeast Louisiana) may keep pace with rising sea levels.

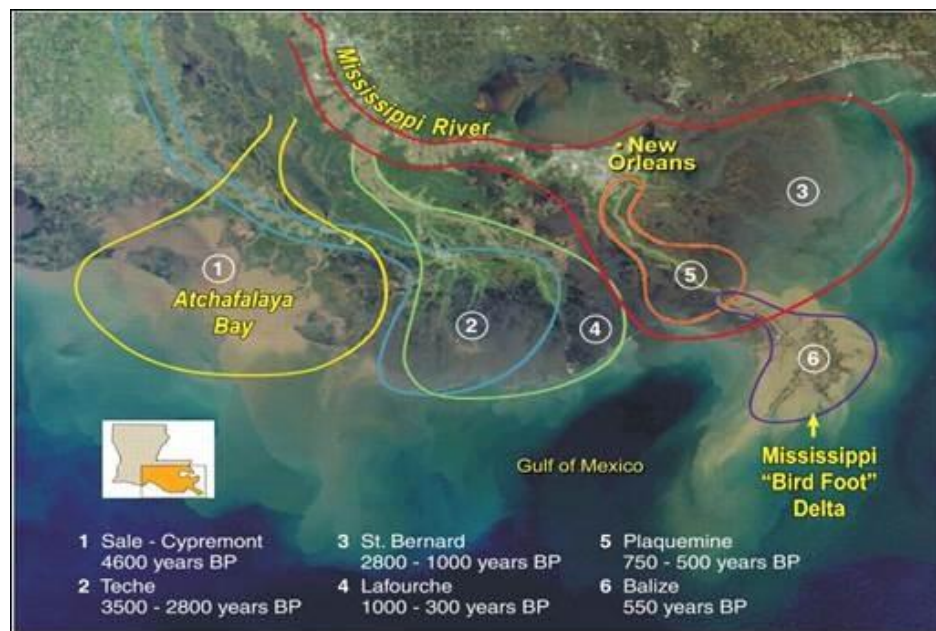


Figure 1.1. Louisiana delta lobe formation (Day et al., 2007 modified from Roberts 1997).

1.1.2. Flood Prevention

Individual levee construction projects were implemented over time to protect communities and agricultural lands from river floods. After the Great Flood of 1927, levees were improved to protect Louisiana's increasing population, and agricultural and industrial bases from flood impacts (Riekenberg et al., 2014). What was once a disconnected series of levees along the lower river was now a continuous levee system completely isolating the river from the coastal

basins. This act also prevented the natural tendency of the river to meander over time, which once-spread sediment deposition all across the coastal plain.

The levee system alone, however, was not enough to protect the delta region from extreme flood events that could overtop and erode the levees. Therefore, a series of flood release valves called spillways were built after the 1927 flood to provide a mechanism for removal of river water from the channel to prevent flooding of communities downriver.

The Bonnet Carré spillway (BCS) was constructed in 1931 to serve as a hydrologic release of flood waters to protect the city of New Orleans from flooding at high river stage. The BCS is a structure within the levee upstream from New Orleans that can be opened during flood stage. The water is diverted into the Lake Pontchartrain Estuary (LPE) and eventually flows into the Gulf of Mexico. Recently, the introduction of Mississippi River water via the Bonnet Carré Spillway has been the cause of environmental issues such as eutrophication which has led to the formation of harmful algal blooms in Lake Pontchartrain (Roy et al., 2012). Several other environmentally adverse effects have been directly correlated to the openings of the Bonnet Carré Spillway (Lane et al., 2001; Bargu et al., 2011; Roy et al., 2016).

1.1.3. How the Mississippi River Has Changed

The Mississippi River discharges an annual average of over $15,360 \text{ m}^3 \text{ sec}^{-1}$, with a maximum discharge of almost $60,000 \text{ m}^3/\text{sec}$ and an annual sediment discharge of $6.21 \times 10^{11} \text{ kg}$ (Roberts 1997). The river drains an area of $3,344,560 \text{ km}^2$ flowing into the Gulf of Mexico (Coleman 1988). Pre-1900, the Missouri-Mississippi River system was responsible for depositing roughly 400 million metric tons per year of sediment from the interior US to coastal Louisiana but has decreased to 145 million metric tons per year over the last two decades (Meade

and Moody 2010). This decrease in sediment load can be largely attributed to the incorporation of upstream dams that prevent downstream communities from flooding, but ultimately withhold sediment. Large increases in fertilizer runoff, from agricultural lands to the Mississippi River basin post World War II, have added significant nutrient concentration increases to river water (Turner and Rabalais 1991; Roy et al., 2013). Nitrate flux from the Mississippi River to the Gulf has tripled since the 1950's (Rabalais et al., 2002; Adhikari et al., 2015). The Mississippi River contains generally low soluble reactive phosphorus (SRP) values ($<0.05 \text{ mg L}^{-1}$) in its floodwaters (White et al., 2009), but can contribute a significant amount of phosphorus (P) from the suspended sediment load of the river (Zhang et al., 2012). Total phosphorus (TP) concentrations for Mississippi River sediments and fine particulates, carried in the total suspended sediment load, are 829 and 1,085 mg TP kg^{-1} (Sutula et al., 2004).

1.1.4. Coastal Land Loss

The isolation of the river for flood protection prevents the freshwater, nutrients, and sediment that once nourished the coastal wetlands from being deposited. In 1928, freshwater and marine biologist, Percy Viosca stated that Louisiana was “killing the goose that laid the golden egg”, referring to man-made levees restriction on natural sediment loads to wetlands and water ways (Viosca 1928). This statement was rather prophetic as Louisiana has lost roughly 5000 km^2 of coastal wetlands over the past century (Couvillion 2017). It has also been predicted that without action, Louisiana will lose another 4,548 km^2 of wetland and coastal area over the next 50 years (Barras et al., 2003; Barbier et al., 2013; Figure 1.2).

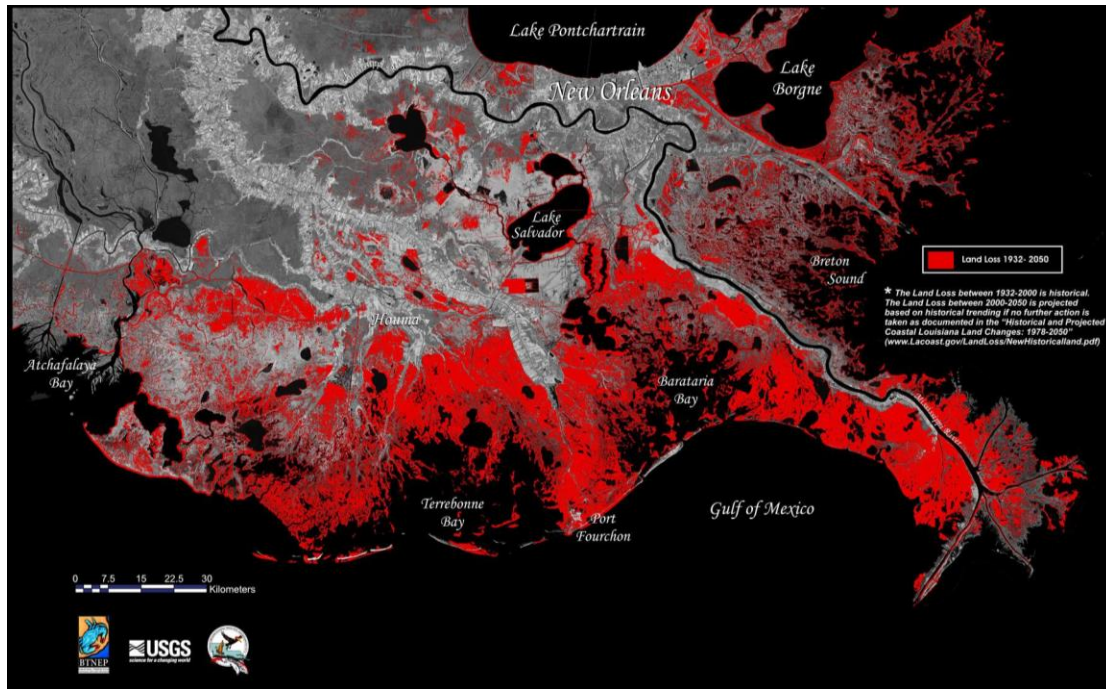


Figure 1.2. Predicted Louisiana wetland loss over the next 50 years without action (Barras et al., 2003).

Today Louisiana faces crucial wetland loss and serious impacts from subsidence and eustatic sea level rise (SLR) accounting for one of the highest coastal land loss rates in the world. While Louisiana's coast contains 40% of coastal wetlands in the contiguous US, this area represents 80% of coastal wetland loss (Couvillion 2017). The Barataria Basin (Figure 1.3) has been one of the most highly affected basins due to this river isolation and subsidence, accounting for one of the highest rates of coastal wetland erosion in the nation at approximately $\sim 41 \text{ km}^2 \text{ yr}^{-1}$ (Wood et al., 2017). On average the Barataria basin experiences 1.9 mm yr^{-1} SLR (Morton et. Al, 2009). Marsh edges within the Barataria basin have greater exposure to wind driven waves making these marshes vulnerable to coastal erosion with an average erosion rate of $1.41 \pm 0.22 \text{ m yr}^{-1}$ (Sapkota and White 2019). Currently the Davis Pond freshwater diversion is the only hydrologic input into the basin with a very low maximum flow of $302 \text{ m}^3 \text{ s}^{-1}$ compared to the

river flow (Spera et al., 2020). In a study by Bass et al. (1997), it was found that wetland loss rates correlated to the age



Figure 1.3. Map of Louisiana coastal basins (Coastal Protection and Restoration Authority 2017).

of the delta lobe in which they are located. Their conclusion was based on the concept that older delta lobes have solidified and compacted over time creating land masses that take longer periods of time to erode. The Barataria Basin is one of the youngest basins in Louisiana and shows the highest rates of wetland loss.

1.1.5. Wetland Functions and Values

Coastal wetlands serve as a bridge between terrestrial and aquatic environments, containing characteristics from both. Wetland functions and values include both aesthetic and significant economic value. Louisiana coastal wetlands provide a great abundance of services ranging from biological activity to structural investment that exceeds \$100 billion (Louisiana

Coastal Wetlands Conservation and Restoration Task Force 1993). Coastal wetlands provide ecosystem services benefitting wildlife habitat, fisheries, water quality, nutrient cycling, and can offer protective buffers from river floods and coastal storm surge (Nyman 2011; Barbier 2013; Costanza et al., 2014; Jankowski et al., 2017). Carbon storage is also a key function of wetlands for retaining large amounts of carbon in peat soils (Nyman 2011). Agriculture and agricultural management can play a large role in the use of wetlands and their natural ability to remove excess nutrients from agricultural and storm water runoff. Other benefits provided by wetlands are flood water storage, sediment control, source of water supply, timber production, and municipal waste processing (National Research council 1992; Barbier 1994; Brinson and Rheinhardt 1996; Nyman 2011).

Over the past century sea level has been rising at about 2 mm yr^{-1} . Louisiana faces some of the greatest rates of relative sea level rise in the world. Subsidence and compaction account for roughly 1 cm yr^{-1} SLR (Meckel et al., 2006), totaling an average $12 \pm 8 \text{ mm yr}^{-1}$ (Jankowski et al., 2017). Louisiana's coastal wetlands are built on deltaic sediments in alluvial valleys that subside at higher rates than delta plain areas outside the valley (Roberts 1997). This well-defined alluvial valley stretches southward 870 km before ending at the Gulf of Mexico (Coleman 1988). As well as factors induced by SLR causes for increased wetland loss such as dredging, conversion of wetlands for agricultural and industrial use and sediment detainment from upstream dams have been widely practiced.

1.1.6. Early Wetland Restoration Plans

In its best effort to restore Louisiana coastal wetlands the State of Louisiana has implemented river reconnections, known as river diversions, designed to allow Mississippi River sediments, nutrients, and an influx of freshwater to once again deposit into Louisiana's coastal

wetlands. The Davis Pond freshwater diversion and the Caernarvon freshwater diversion are some very early attempts at reconnecting the river with the isolated coastal basins. These diversions are both in effect today and used mainly to modify salinities in the outfall areas to enhance secondary productivity within the estuary (Lane et al., 2007; Das et al., 2012; Riekenberg et al., 2014). The Davis Pond diversion feeds into the Barataria Basin from the Northwest and from the years 2008-2018 Davis Pond has discharged 25.9 to 119.3 m³s⁻¹ (Spera 2019, USGS). The Caernarvon freshwater diversion feeds into the Breton sound estuary, on the opposite side of the Mississippi River, and can discharge water at a maximum rate of approximately 226 m³ s⁻¹ with an average of 54 m³s⁻¹ since 2001 (Riekenberg et al., 2014, USGS).

In a study by Spera et al. (2020) comparing wetland soils from diversion pre-opening in 2007 and post-opening in 2018, it was found that wetlands in the area of influence of the Davis Pond diversion showed more than two times higher mean total P values and almost nine times greater total inorganic P values than the non-diversion influenced soils. Although the Davis Pond diversion was not specifically designed to accumulate sediment into the affected wetland areas, it was found that spatial distribution of mineral density increased in the areas receiving diverted river water.

The next proposed river diversion to be built from the state of Louisiana is the Mid-Barataria sediment diversion. This sediment diversion is designed to restore sediment delivery to the sediment starved Barataria Basin and begin to rebuild its degrading coastal marshes. This diversion aims to revive the historical connection between the Mississippi River and the coastal marshes in Barataria Basin.

Freshwater diversions are designed to mimic hydrological conditions during the inactive stages of the delta lobe cycle with the main purpose of reducing salinity stress and promoting marsh vertical accretion in emergent wetlands via vegetative growth. Sediment diversions are designed to mimic the hydrological conditions during the active delta stage of the delta lobe cycle, promoting rapid mineral sedimentation in open water areas, creating emergent wetlands (Nyman 2014).

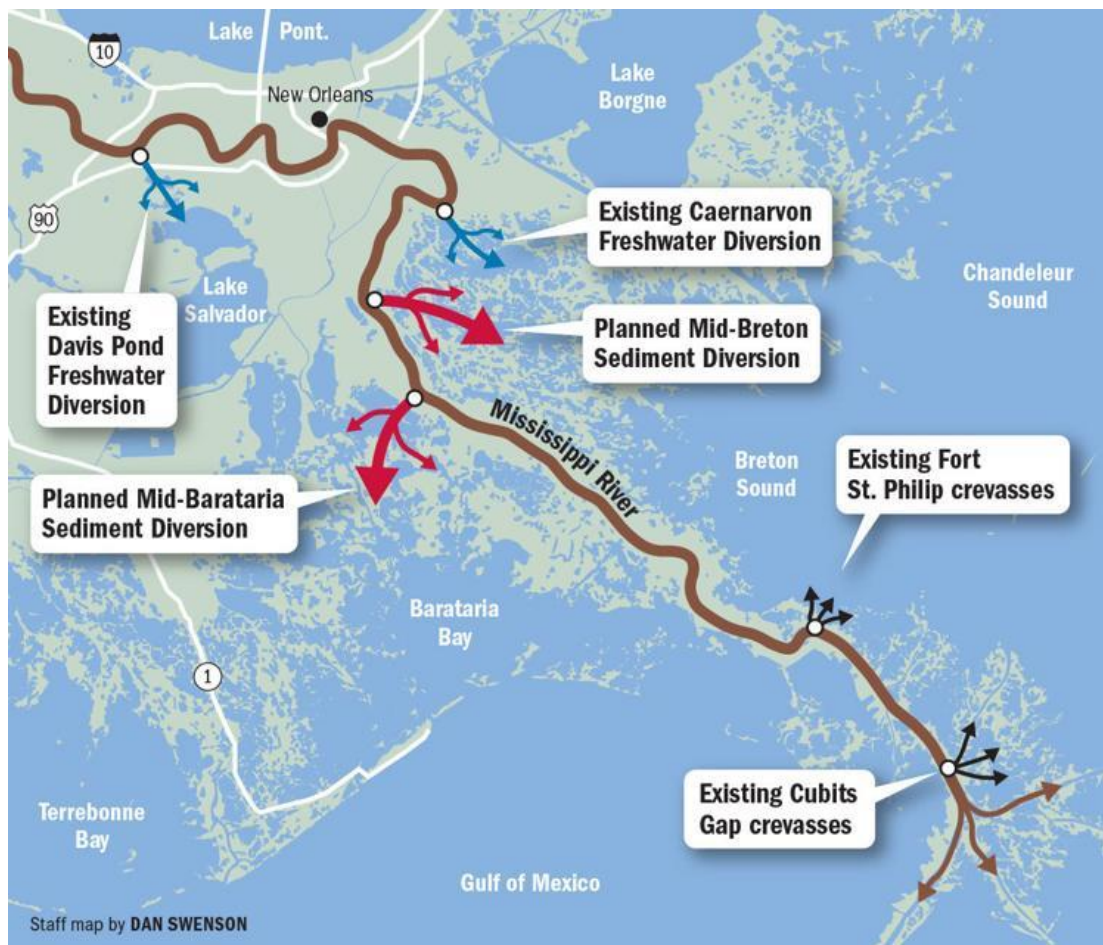


Figure 1.4. Map of current and planned Mississippi River diversions in lower Louisiana (Dan Swenson; Nola.com).

1.1.7. The Louisiana Coastal Master Plan

In response to hurricanes Katrina and Rita in 2005, the state of Louisiana has established a Coastal Master Plan. This plan is revisited every 6 years as a mean of adaptive management, focusing on things that are working and incorporating the latest science. The 2017 plan aims to restore Louisiana's degrading coastlines through a series of restoration projects including sediment diversions, marsh enhancement, hydrologic restoration, and marsh creation with the main goal of creating a sustainable coastal landscape in Louisiana into the next century (CPRA 2017). The first sediment diversion to be constructed is the Mid-Barataria sediment diversion (Figure 1.4). This diversion will be positioned along the river near mile marker 61 in Ironton, Louisiana. When opened at full capacity, the 2-mile-long structure will permit $2123.76 \text{ m}^3 \text{ s}^{-1}$, (75,000 cfs), of river water to flood into the Barataria Basin (CPRA 2017). The goal of a sediment diversion is different from the earlier diversion attempts in that the diversion will be opened when sediment transport in the river is at the highest to maximize sediment capture (Peyronnin et al., 2017).

1.1.8. Model of Sediment Diversion

An integrated biophysical model representing the ecosystem characteristics of a rapidly evolving deltaic landscape with the implementation of a sediment diversion was derived to help predict the expected ecosystem changes of major river diversions into the Barataria and Breton Basins (Baustian et al., 2018; Figure 1.5). The main objective for the sediment diversion is to build land and in order to build as much land as quickly as possible the diversion would remain open at all time. While this would build maximum land, adverse ecological effects to environmental aspects such as fish, wildlife, and vegetation could be negatively affected. It is inevitable that the entirety of the Barataria Basin will be affected, but it is necessary to take into

account the complex and uncertain interactions of the ecological and social landscapes in hand. The model takes into account Mississippi River hydrology and sediment loads with the possible geologic influence on the basin and land building. Other factors such as water quality, wetland health, fish and wildlife species, and socio-economics are taken into consideration with the outcomes of the model (Peyronnin et al., 2017).

The integrated biophysical model of the diversion was designed to represent the receiving estuarine basin processes by incorporating hydrodynamics, morphodynamics, vegetation dynamics, and nutrient dynamics (Baustian et al., 2018). This numerical model processes data sets to generate bathymetric and topographic predictions for the hydrodynamic and morphological components. Sediment dynamics in the Mississippi River differ from the receiving basins. In the river, fine grained sediments are well vertically mixed and are easily transported, whereas in the receiving basins, fine particles are most likely to deposit in low-energy areas, especially with the presence of vegetation (Baustian et al., 2018). Significant morphological impacts can be expected to occur in the areas closest to the outfall of the diversion. Research shows that locating the diversion intake in the vicinity of a known sand bar in the river is a guaranteed source of sediment, especially sand (Meselhe et al., 2012). Sand is considered a key factor in the formation of land growth. The presence of sand creates a stable substrate that once subaerial can establish vegetation and then accumulate finer sediment size classes such as silt and clay (Gaweesh and Meselhe 2016).

Operational strategies strive to maximize land building while sustaining minimal ecosystem disruption with the functioning of the diversion. Practices such as operating the diversion in the spring/summer for short periods of time, synchronized with high river stages, plan to capture the highest sediment loads during the rising limb of the flood peak while

minimizing ecosystem impacts (Peyronnin et al., 2017). The diversion is predicted to hydrologically impact the entirety of the basin and produce a smaller geomorphic impact of sand deposition closer to the mouth of the opening. The model shows an increase in vegetation, particularly invested in *S. alterniflora* at a site in the Barataria Basin, predicting an increase in biomass of 269 g C m⁻² (Baustian et al., 2018). Operation of the diversion will be gradually increased over the initial 5 to 10 years in order to facilitate the development of a distributary channel network, reduce flood risk potential to surrounding communities, limit erosion of adjacent marshes, and reduce stress to vegetation and wildlife species (Peyronnin et al., 2017).

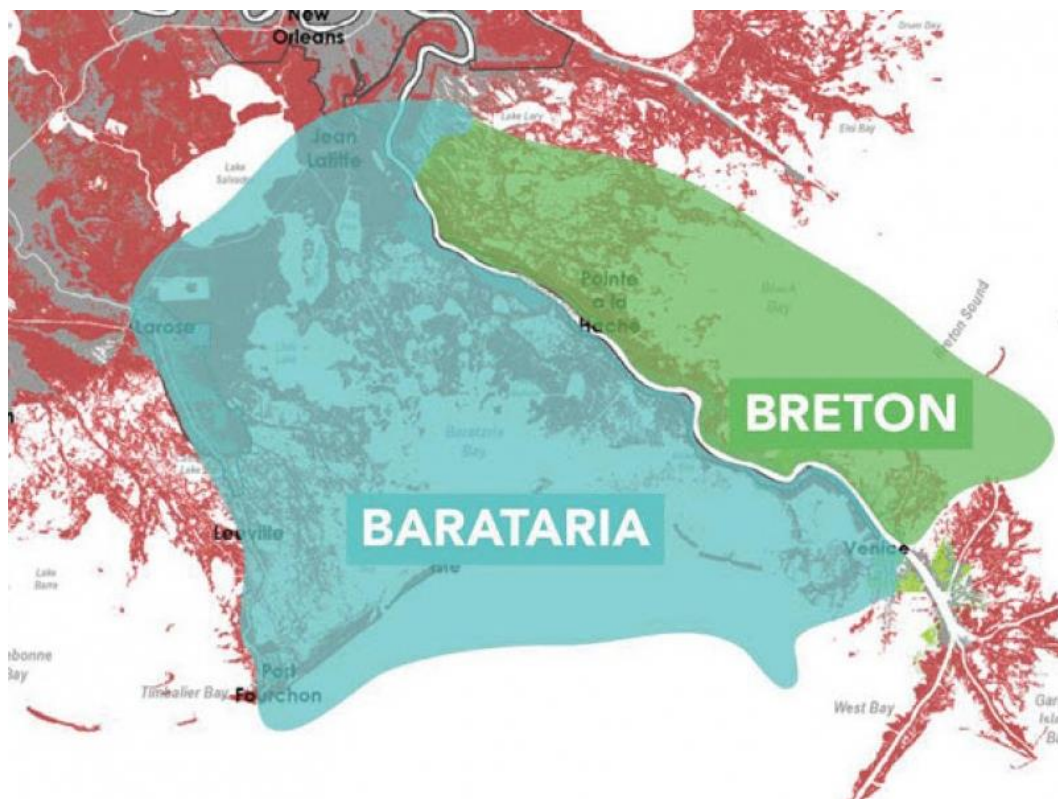


Figure 1.5: Predicted range of hydrologic influence of sediment diversions on Barataria and Breton Basins (Coastal Protection and Restoration Authority 2017).

1.1.9. Nutrient Dynamic Implications

The Mississippi River water contains elevated concentrations of bioavailable nitrogen (N) that can alter the basin's water quality. Coastal wetlands are an excellent environment for removal of bioavailable N, in particular NO_3 , from surface water through nitrate reduction (White et al., 2019). During this microbially mediated process, facultative anaerobic bacteria use nitrate, or NO_2 in the absence of O_2 , to breakdown organic material and produce gaseous N in the form of N_2O and N_2 (White and Reddy 1999). Denitrification is the dominant nitrate removal process in wetland environments (Patrick and Delaune, 1977). Less common, the process of anammox reduces ammonium and nitrate to nitrogen gas but essentially converts the N from the system to the atmosphere.

Excess N in the aquatic environment can create the potential for eutrophication and algal blooms. The Barataria Basin degrading coastal marsh edges have been shown to provide water quality improvement services through denitrification due to high microbial biomass, total carbon, anaerobic conditions and constant contact with the water column (Vaccare et al., 2019). Much attention and concern has been given to N loading from the Mississippi River in Louisiana's coastal wetland systems and the coastal ocean. However, in concert with N-enrichment, one also needs to consider P as it plays a critical role in productivity. Until recently, very little research has been conducted on P loading and the potential effects on Louisiana's coastal wetlands.

1.1.10. Phosphorus Forms

Phosphorus enters wetland systems in either particulate or dissolved form and can be classified into four forms: i) Soluble reactive P (SRP), ii) dissolved organic P (DOP), iii) particulate inorganic P (PIP), iv) particulate organic P (POP). SRP represents the most

bioavailable form of phosphorus that can be taken up by diatoms and other forms of algae. The other forms of P must undergo enzymatic processes to become bioavailable (Martin 2004). The Mississippi River has an average of $<0.05 \text{ mg L}^{-1}$ SRP, which is a generally low concentration in terms of nutrients required for primary productivity (White et al., 2009). Total reactive-P pools, encompassing SRP and sediment bound P, can both contribute to the reactive P-pool that can trigger algal bloom formation. Total P is comprised of total inorganic P and total organic P. While river water SRP concentration remains fairly low (Zhang et al., 2012), the suspended P load associated with Mississippi River sedimentary bound P can be substantial (Sutula et al., 2004). The total reactive P-pool resides primarily in 5 forms 1) Available- P_i (labile-P), 2) Alkali extractable organic-P, 3) Fe/Al- P_i , 4) Ca/Mg- P_i , and 5) Residual Organic P (White et al., 2004). The Mississippi River exports roughly $134 \times 10^6 \text{ kg yr}^{-1}$ of total reactive P, bioavailable to diatoms, to the Gulf of Mexico (Sutula et al., 2004).

Phosphorus is generally more available under anaerobic conditions than under aerobic conditions (Patrick and Delaune, 1977). P does not directly undergo redox transformations, but its availability to plants is directly related to anaerobic respiration of reduced cations, in particular iron. P binds to Fe^{3+} in the water column which is not dissolved. Once newly settled sediment has covered the settled Fe-P and becomes anaerobic, the Fe^{3+} reduces to Fe^{2+} releasing the P back into the water column, where it is bioavailable. Research shows that the Fe-bound P is representative of the largest fraction of P in Mississippi River suspended solids (Sutula et al., 2004). Fe and Al are the most abundant P associated metals in Mississippi River sediments and show direct correlations with mineral density that has been shown to be a direct effect of river diversions (Spera et al., 2020). Soil P remobilization can be directly linked with pulses of water

release, such as in the case of diversions, fluctuating the concentrations of O₂ in bottom waters and sediments (Upreti et al., 2019).

Sutula et al., (2004) found that as P-bound Mississippi River sediments travel further off of the coast of the Gulf of Mexico the majority Fe/Al-P bounds shift to Ca/Mg-P. Excess P and N are primary nutrients that cause eutrophication and can trigger algal blooms. SRP and DOP are both sources of P that can be released from the sediment to the water column through biogeochemical processes (Zhang et al., 2012). In a study reviewing soil impacts of the Davis Pond diversion, over a 10-year period, it was found that the soil P shifted from organic to dominantly inorganic P forms (Spera et al., 2020). Algal growth, in coastal estuaries, is heavily reliant on high bioavailable nitrogen loading from the Mississippi River, which has almost tripled since the middle of the century (Rabalais et al., 2002; Adhikari et al., 2015). N has shown to be a limiting nutrient for primary productivity in coastal Louisiana estuaries, but when its abundance is in such great presence, P switches to the limiting nutrient. Adhikari et al., (2015) found that in Louisiana continental shelf sediments, the Ca/Mg-P pool had the highest P concentrations which holds consistent with several other findings in the area (Sutula et al., 2004; Nguyen 2014).

1.1.11. Algal Blooms

The main purpose of the sediment diversion is to reintroduce river sediment into the starved coastal wetlands. However, substantial amounts of freshwater and nutrient inputs can also be expected to come with the river water that is particularly rich in dissolved N and P. This can have a great effect on algal bloom formations that can cause degradation in water quality (Bargu et al., 2011, Roy et al., 2016, Bargu et al., 2019). Fresh and brackish estuarine systems are ideal habitats for toxin producing cyanobacteria that have been observed to have a wide

effect on secondary consumers such as blue crabs and catfish in coastal Louisiana that are later harvested for human consumption (Garcia et al., 2010).

Algal bloom formation in coastal Louisiana shows a cyclic seasonal pattern directly affected by the release of Mississippi River water into surrounding estuaries and fluctuation in temperature (Bargu et al., 2011, Roy et al., 2016, Bargu et al., 2019). The winter season allows a large mixed layer with plenty of nutrients, but is limited by sunlight. The spring, with general high river levels, has abundant nutrients, sunlight, and a smaller mixed layer. The increasing photosynthetically active radiation present in the spring season together with nutrient enrichment, promotes spring algal blooms (Bargu et al., 2011). By the summer season, with increased sunlight and temperatures, decreased turbidity and reduced bioavailable nutrients, spring bloom collapses and potentially toxic cyanobacteria presence can be observed more frequently (Bargu et al. 2011, Roy et al. 2013, Riekenberg et al. 2015). Cyanobacteria blooms favor calm conditions, with high surface water temperatures to maximize bloom formation efficiency.

In a study analyzing the effects of the Bonnet Carré spillway's release into Lake Pontchartrain, it was found that diatoms and chlorophytes dominated the system during the opening. The diatoms and chlorophytes dominance shifted to toxic cyanobacteria following the closure of the spillway and the onset of more stable, warm, and nutrient limited water conditions (Bargu et al., 2011, Roy et al. 2013). *Dolichospermum* (formerly known as *Anabaena*) and *Microcystis* are the two most common cyanobacteria genera found along coastal Louisiana (Day et al., 1998; Bargu et al., 2011). Main differences between the two genera are driven by the availability of *N*. *Microcystis* depend on dissolved inorganic nitrogen (DIN) in the water column and are seen during the spring and early summer (Roy et al., 2016). N-fixing species of

cyanobacteria such as *Dolichospermum* (formerly known as *Anabaena*) are able to fix atmospheric N₂ when N from the water column has been depleted. N-fixing species favor low molar DIN:DIP ratios (<15), where non-N-fixing cyanobacteria species favor high N:P ratios (Paerl, 1988). This has been observed in the Bonnet Carré Spillway releasing Mississippi River water into Lake Pontchartrain estuary (Roy et al., 2012). The mechanisms of N limitation, potential P storage mechanisms, when water column SRP concentrations are low or have been depleted can be explained by 1) phytoplankton cell P storage, 2) internal P regeneration, 3) use of dissolved organic P (DOP) as a P source, and (4) P scavenging on cell surfaces (Ren et al., 2009).

1.2. Site Description

1.2.1. Barataria Bay

The sampling area is in the Barataria Basin, Louisiana, USA. Sampling locations were distributed in the predicted area of influence of the proposed Mid-Barataria sediment diversion (Figure 1.6; Appendix C). The Barataria Basin is an estuary bound between the Mississippi River on the east, the Gulf of Mexico on the south, the city of New Orleans on its north and Terrebonne Basin on its west, encompassing approximately 7100 km² in southeast Louisiana (Byrnes et al., 2019). The basin faces some of the greatest marsh edge erosion rates due to a combination of wind wave driven marsh edge erosion and isolation from the Mississippi River preventing wetland progradation (Sapkota and White 2019). There are no natural sources of riverine input into the basin (Ren et al., 2009), the Davis Pond diversion is the only hydrologic connection into the basin. Although there is a relatively small amount of riverine input from siphons at Naomi and West Pointe à la Hache that can periodically pump a maximum of 60 m³ s⁻¹ of Mississippi River water into the Barataria Basin (Inoue et al., 2008; Boustany 2010). The

basin has lost approximately 1172 km² of land from 1932 to 2016 (Couvillion et al., 2017).

When opened at full capacity the diversion can allow 2123.76 m³ sec⁻¹ (75,000 cfs) of river water to flood into the Barataria Basin (CPRA, 2017). *Spartina alterniflora* is the dominant vegetation and salinities range from 0.6 to 7.85 ppt in the sampling area.

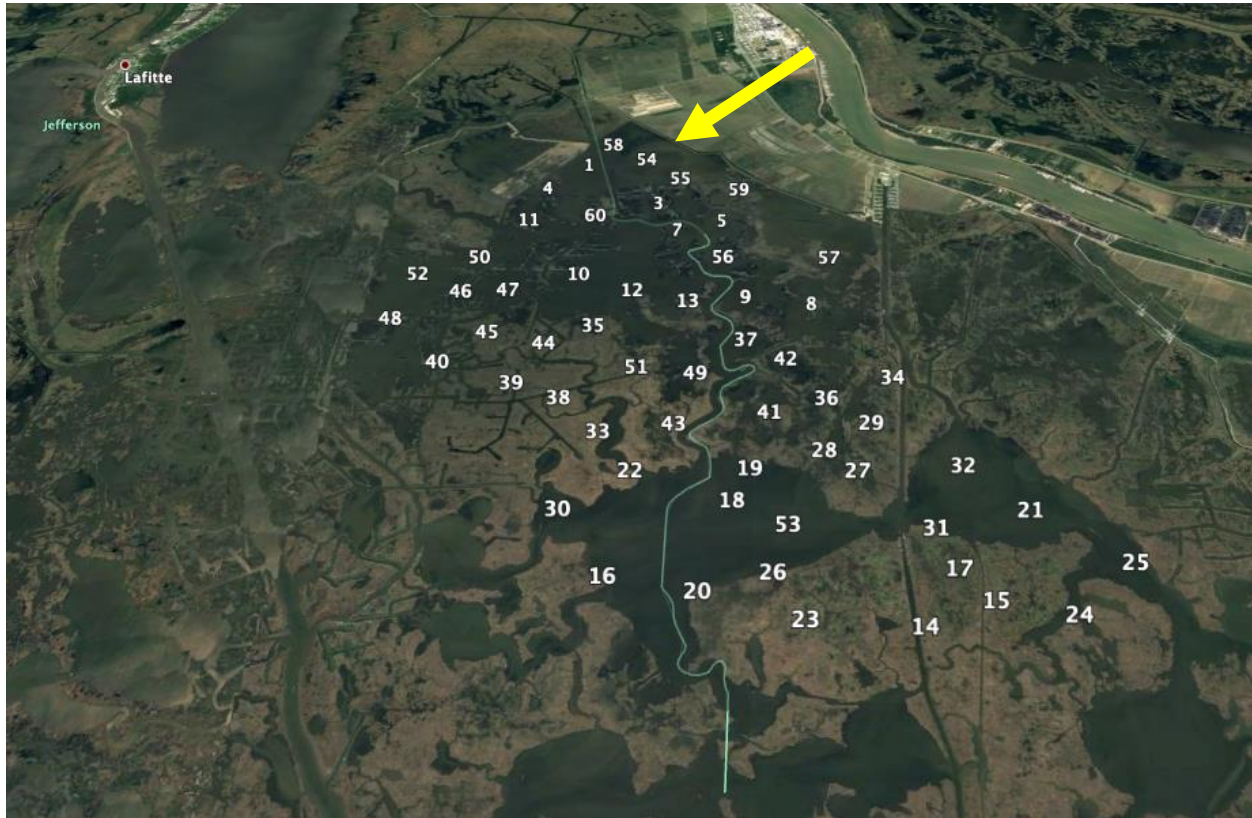


Figure 1.6. Map of study sites in area of geomorphological influence of proposed Mid-Barataria sediment diversion indicated by yellow arrow. (Source: Google Earth)

1.2.2. Mardi Gras Pass

The proposed Mid-Barataria sediment diversion will deposit Mississippi River sediments into the wetlands of the Barataria Basin. The samples we took characterized the present sediment in the area of influence of the sediment diversion in the Barataria Basin. In efforts to predict the

condition of the sediment that will be deposited into the wetlands, samples were collected from Mardi Gras Pass (MGP), an area comprised of Mississippi River deposits (Figure 1.7; Appendix C.1). Mardi Gras Pass is the end of the man-made levee along the Mississippi River that feeds into the wetlands in the Breton Sound. Mardi Gras Pass overtopped the Bohemia spillway in 2012 due to high water events on the Mississippi River (Henkel et al., 2018). The sampled Mardi Gras Pass site receives continual input from the Mississippi River, representative of the sediment that is to be deposited with the operation of the Mid-Barataria sediment diversion. The pass in

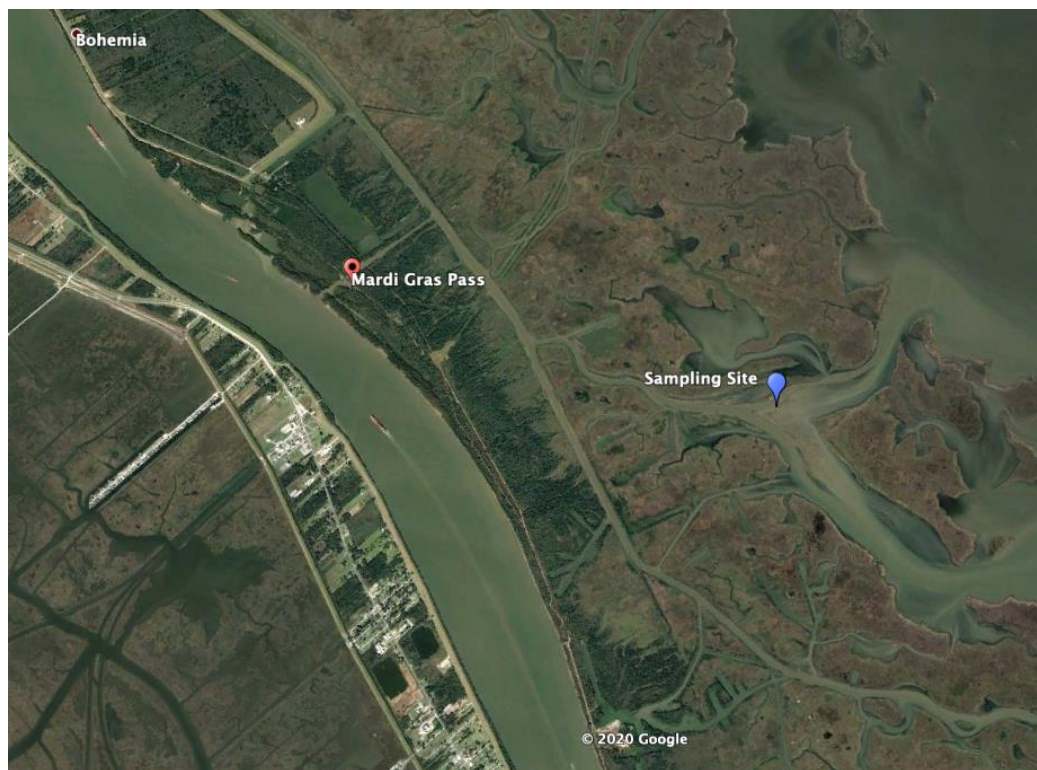


Figure 1.7. Map of Mardi Gras Pass and area sampled to represent recently deposited river sediment. (Source: Google Earth)

the river has expanded since its initial breach in 2012 funneling river water faster and remaining an effective sediment delivery system primarily along the banks of its channels (Henkel et al., 2018). Observed on site at the Mardi Gras Pass station, the deposition of river sediment is

quickly followed by the establishment of vegetation increasing marsh stability in the receiving basins. Twelve sediment cores were collected to run an equilibrium phosphorus concentration (EPC) experiment. This Mardi Gras Pass sediment provides characterization of the Mississippi River sediment that will be deposited onto the Barataria wetlands.

CHAPTER 2. SEDIMENT DIVERSION EFFECTS ON SOIL PHOSPHORUS FORMS

2.1. Introduction

Louisiana's coastal wetland loss rates are due in part to both increased sea level rise and subsidence in the coastal deltaic areas. The compaction of river sediments deposited in the late Holocene period in the alluvial valley have increased the rate of marsh degradation and overall wetland loss. Coastal wetlands produce both organic matter and trap inorganic sediments to maintain elevation at mean sea level. In order for coastal marsh elevation to be maintained, an adequate supply of nutrients is required for sustaining vegetative growth that provides the organic production, as well as a sediment subsidy from the river to provide inorganic material (Boustany 2010). Barataria Basin has one of the highest rates of coastal wetland erosion in the World at approximately $41 \text{ km}^2 \text{ yr}^{-1}$ (Wood et al., 2017). Studies have shown that coastal Louisiana marsh accretion rates are not sufficient to keep up with the combined increasing sea level and subsidence (Wood et al., 2017). The reason for this loss is primarily due to the disconnect of the Mississippi River from the coastal marshes through the construction of a continuous levee system designed to protect communities from flooding.

Restoration plans for combatting coastal Louisiana land loss includes the implementation of sediment diversions outlined in the State Coastal Master Plan (CPRA, 2017). Sediment diversions will reintroduce river water, which will transport nutrients and sediment into the hydrologically isolated wetlands (Sapkota and White, 2019). These planned sediment diversions are much larger than the existing freshwater river diversions which provide a relatively small managed connection between the Mississippi River with Barataria Basin and Breton Sound. Both sediment and freshwater diversions overcome the hydrologic barriers of the river levees.

Freshwater diversions are designed to mimic hydrological conditions during the inactive stages of the delta lobe cycle with the main purpose of reducing salinity stress and promoting marsh vertical accretion in emergent wetlands via vegetative growth. Sediment diversions are designed to mimic the hydrological conditions during the active delta stage of the delta lobe cycle, promoting rapid mineral sedimentation in open water areas, creating emergent wetlands (Nyman 2014). The implementation of diversions has raised concerns due to the excess nutrients and the uncertainty of any adverse ecosystem effects that may be realized (Bargu et al., 2011; Bargu et al., 2019; Turner et al., 2019; White et al., 2019).

Freshwater river diversions divert surface waters at relatively low rates into the receiving basin. The Davis Pond diversion is a freshwater diversion designed to create a salinity gradient to improve ecosystem services and maintain marsh vegetation. The diversion, operating at 10,000 cfs maximum flow at high river stage, is a connection between the Mississippi River and northern Barataria Bay. Although the intention of the Davis Pond diversion was not to build land, fine grained mineral sediment accumulated into organic wetland soils. This was demonstrated in a study by Spera et al. (2020) which compared soil characteristics and chemistry from the Davis Pond freshwater diversion in 2007 and again in 2018. This study found that wetlands in the diversion flow path had an overall increase in mineral content, essentially doubling the bulk density (Spera et al., 2020). The Davis Pond diversion main purpose is to decrease salinity in the wetlands, but Spera (2019) found that 80 percent of the soils doubled in bulk density, a consequence of introduced fine-grained river sediment. The area of diversion influence of the Davis Pond diversion showed shifts from greater abundances of total organic P to total inorganic P over the 11-year period of diversion function. Greater abundances of total

inorganic P lead to increased plant uptake, which increases the overall storage of organic matter post diversion opening.

The Mid-Barataria sediment diversion is designed to transport up to $2123.76 \text{ m}^3 \text{ sec}^{-1}$ (75,000 cfs) of Mississippi River water (Meselhe et al., 2012), which will also include a significant suspended sediment load with the purpose of building coastal land and providing a sediment subsidy to the deteriorating coastal wetland. River sediment diversions are located to maximize transport of suspended and bedload sediments to the coastal basin. There has been an extensive modeling effort put forth by the State of Louisiana and the US Army Corp of Engineers to predict 50 years of sediment diversion operation to include land building, water quality, and ecosystem response (Peyronnin et al., 2017).

Phosphorus is an important ecosystem macronutrient that is dependent on the chemical form. Phosphorus can be present in the dissolved or particulate state in either organic or inorganic form. Metals such as Fe, Al, Ca, and Mg play an important role in P retention in soils. Fe-P relies on the presence or absence of oxygen to retain or release P into the water column. Ca/Mg-P is dictated by shifts in pH of the system. Dissolved inorganic P is the most bioavailable form of P for microbes and plant uptake in both the water column and soil porewater. Dissolved inorganic P is composed of the phosphate anion (PO_4^{3-}) protonated dependent upon pH. The fate of bioavailable P can sorb on to settling particulate matter, be taken up by primary producers, and sorb on to soil particles or form insoluble complexes which can transition to crystalline minerals over time (Martin 2004).

All sediment is not equal when it comes to P loading. For example, a study in the Atchafalaya River delta found that silt/clay particles, associated with suspended sediments, contained a higher percentage of Fe/Al-P, while sand size particles were dominant in the Ca-P

pool (Poach and Faulkner 2007). Both biotic and abiotic processes must be taken into consideration in order to evaluate P retention capacities of wetlands (Reddy et al., 1999).

The Lake Pontchartrain estuary can serve as a recent analog to a sediment diversion. The estuary receives up to 20% of the Mississippi River flood stage flow as a means to prevent flooding of downstream New Orleans and other communities only during those years when the river reaches flood stage, <1,000,000 cfs (Lane et al., 2001). Nguyen (2014) found a significant increase (27%) of total P after a one-month diversion of the river in the top 0-5 cm of the sediment suggesting a significant sediment bound load of P to the estuary. Roy et al., (2013) found that after an initial algal bloom stripped the surface of SRP, the water column SRP concentrations rebounded to $\sim 0.07 \text{ mg P L}^{-1}$ one month later, a consequence of the internal loading/release from the deposited river sediment under the exposure of anoxic conditions (Figure 2.1). This subsequent release of bioavailable P from the sediment at a time with little available N can create a situation favorable for nitrogen-fixing cyanobacteria blooms (Roy et al., 2016).

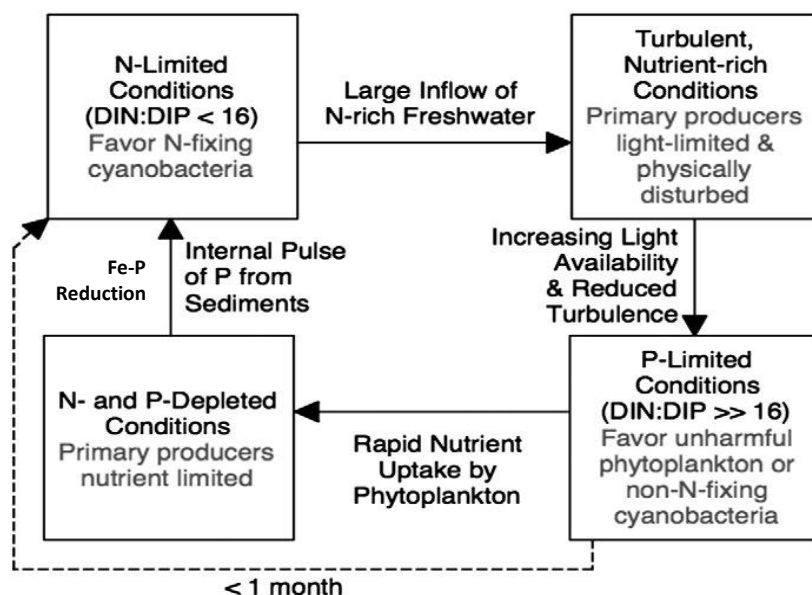


Figure 2.1. Estuarine biogeochemical dynamics during large inflows of nitrate-rich freshwater via Mississippi River diversions. Dotted line indicates that the system can move from P-

limitation to N-limitation in <1 month during warm periods (water temperature $\geq 25^{\circ}\text{C}$). (Modified from Roy et al., 2013).

Algal bloom formation is driven primarily by availability of nutrients and physical conditions of the water column. Nitrogen is generally the macro-limiting nutrient in coastal systems due to efficient recycling of P and loss of N to denitrification (Sylvan et al., 2006; Rabalais et al., 2002). However, P can be the limiting macronutrient in deltaic regions due to the high nitrate concentrations of the Mississippi River ($\sim 2 \text{ mg N L}^{-1}$) (Roy et al., 2013). Consequently, it was found that phytoplankton growth was limited by P in the summer coastal waters of Louisiana (Sylvan et al., 2006). This situation is due to the high N:P ratio that is seen in the Mississippi River ($\geq 50:1$) (Roy et al., 2013). A shifting species of algal bloom occurrence has been documented in the Lake Pontchartrain estuary as a consequence of Mississippi River water nutrient loading. During the diversion itself, there is low primary production because the river plume is highly turbid and well mixed, pushing the phytoplankton in and out of regions of light extinction slowing primary production. Additionally, the river water has been found to be 2°C colder in the early part of the year which will also slow production. Post closure, diatom and chlorophyte blooms were observed, which strips out bioavailable nutrients until the estuary reaches a N-P limitation at which time the bloom ceases (Bargu et al., 2011). Several months later, as P is released from the sediment, an N-fixing cyanobacteria bloom can potentially begin to form (Figure 2.1). These toxin producing blooms can contain microcystin, anatoxins, and saxitoxins, which can affect organisms when ingested as well as skin irritations (WHO, 1999). There has been little to no research quantifying the abundance of toxin producing bloom presence in the upper Barataria Basin.

These toxins have also been found to bioaccumulate throughout secondary feeders in coastal Louisiana such as in the tissues of blue crabs and catfish and among surface waters in upper Barataria Basin (Garcia et al., 2010). Vegetative cells of cyanobacteria can lay dormant cysts in estuarine sediments over long periods of time (Paerl 1988). The formation of thick-walled resting cells allows cyanobacteria to lay dormant, yet viable, under unfavorable conditions and become viable under more favorable conditions, such as an influx of nutrients that a sediment diversion would bring (Preece et al., 2017).

The goal of this study is to predict the changes in wetland and open water soil P forms as a consequence of the operation of the Mid-Barataria sediment diversion. The following objectives were met to achieve the study goals 1) determine a baseline P soil characterization for marsh and open water sites in the area of influence of the Mid- Barataria sediment diversion and to 2) compare the baseline conditions with sediment from an area already receiving Mississippi River sediment to predict changes with diversion operation. Open water areas of the Barataria Basin hold the potential consequence of hosting the formation of harmful algal blooms. Vegetated marsh areas of the Barataria Basin contain the potential to release nutrients into the water column under flooded conditions, such as when a diversion is in operation.

This research can be used by coastal managers and ecosystem modelers in predicting nutrient impacts of a sediment diversion on Barataria Bay and with the tailoring of diversion operation. The data from this baseline study can be used to compare to a future resampling effort in verifying changes to the P pool and P dynamics once the diversion has been in operation for an extended period of time. The sediments of the same sampling stations can be analyzed to detail changes to diversion influences on phosphorus availability. This study will compare the P data collected here with that from Lake Pontchartrain estuary collected immediately after a river

discharge, as a proxy for how the river diversion will influence Barataria Basin P dynamics. This is the first study to compare current P fractionation data in the area of influence of the Mid-Barataria sediment diversion with what can be expected post operation of the sediment diversion.

2.2. Materials and Methods

2.2.1. Study Area

The sampling area is in the Barataria Basin, Louisiana, USA. Sampling locations were randomly distributed in the predicted area of land building influence of the proposed Mid-Barataria sediment diversion (Figure 2.2). The Barataria Basin is an estuary bound between the Mississippi River on the east, the Gulf of Mexico on the south, the city of New Orleans on its north and Terrebonne Basin on its west, encompassing approximately 7100 km² in southeast Louisiana (Byrnes et. al, 2019). The basin faces some of the greatest marsh edge erosion rates due to a combination of wind wave driven marsh edge erosion and isolation from the Mississippi River preventing wetland progradation (Sapkota and White 2019). There are no natural sources of riverine input into the basin (Ren et. Al, 2009), the Davis Pond diversion is the only hydrologic connection into the basin. The basin has lost approximately 1172 km² of land from 1932 to 2016 (Couvillion et al. 2017). *Spartina alterniflora* is the dominant vegetation and salinities range from 0.6 to 7.85 in the sampling area.

The Mid-Barataria sediment diversion will be positioned along the river near mile marker 61 in Ironton, Louisiana. When opened at full capacity the 2-mile-long structure will permit 2,123 m³ s⁻¹, (75,000 cfs), of river water to flood into the Barataria Basin (CPRA 2017). The goal of a sediment diversion is inherently different from the surface water diversions, in that the

diversion will be opened when sediment transport in the river is at the highest (Peyronnin et al., 2017).

2.2.2. Sampling

Samples were collected from 24 open water stations and 36 marsh stations within the predicted influence land building of the sediment diversion (Appendix C.1). Stations were portioned out based on their relative spatial coverage. The total sampling area was divided into 3 sections, with each section, progressively further away from the diversion (Figure. These sites were chosen to best represent the marsh and open water sites in the desired area of study (Figure 2.2). Cores, at 0-10 cm, were collected with a 7 cm diameter coring tube and extruded in the field. Open water site cores were obtained with a piston core allowing sediment covered at significant water depths to be obtained while remaining the core intact. Sediment samples were extruded and homogenized in the field to express uniformity among the top 10 cm of sediment.

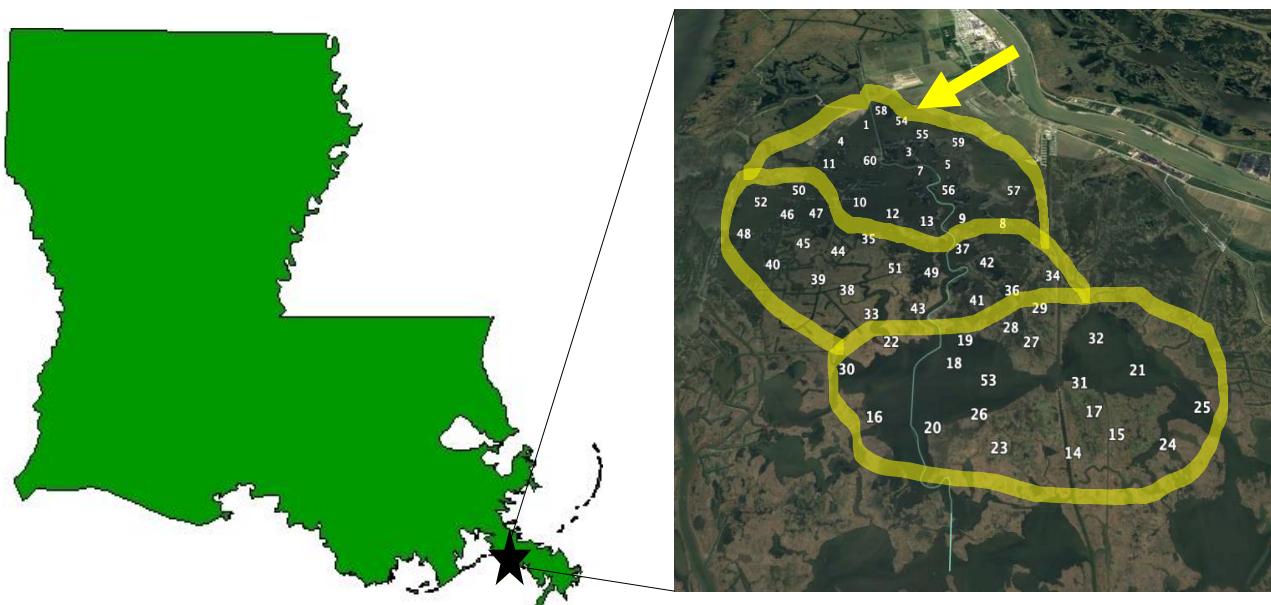


Figure 2.2. Map of 60 sample stations divided into 3 sections in the area of influence of planned Mid-Barataria sediment diversion. Yellow arrow indicates location of planned diversion. (Source: Google Earth).

Samples were stored on ice until returned to laboratory where they were stored at 4° C until processed.

2.2.3. Soil Characteristics

Wetland samples were analyzed for bulk density (BD), moisture content (MC), organic matter content (OM), total carbon (TC), total nitrogen (TN), total P (TP), inorganic P (IP) and organic P (OP). Wet samples were homogenized, and sub samples dried at 70° C until at constant weight, which were then reweighed for soil moisture and bulk density calculations. OM and mineral content were indicated by the difference in weight of pre- and post- burned subsamples that were dried, ground, and combusted at 550° C for 4 hours in muffle furnace. Total C and total N were analyzed by placing dried, ground sediment into tin capsules that were combusted at 1000° C by an Elemental Combustion System with a detection limit of 0.005 g kg⁻¹ (Costech Analytical Technologies, Inc., Valencia, CA). The combusted sample is mixed with helium to give a reading of respective CO₂ and N₂ evolved.

For our Total P determination, we dried, ground, weighed and placed the samples in the muffle furnace at 550°C for 4 hours. The subsequent ash was treated with 20 mL of 6 M HCl and placed on a hot plate to boil. This post burning process dissolves all the inorganic P contained within minerals remaining in the sediment sample (Nguyen 2014). Samples were then cooled and filtered through Whatman #41 filter paper and analyzed colorimetrically for P on a SEAL AQ300 Automated Discrete Analyzer (SEAL Analytical, West Sussex, England). For total inorganic P measurements dried, ground and weighed samples were extracted with 25 mL of a 1 M HCl solution and shaken for 3 hours on a longitudinal shaker. Samples were then placed in a refrigerant centrifuge for 10 minutes. The supernatant fluid was filtered through 0.45 µm membrane filter, Filtrate was analyzed for SRP on a SEAL AQ300 Automated Discrete Analyzer (SEAL Analytical,

West Sussex, England). Subtracting total inorganic P from total P provides an estimate of total organic P.

2.3. Phosphorus Fractionation

A detailed P fractionation scheme after Reddy et al. (1998) with modifications by White et al. (2004) was performed on a subset of sites in the basin (Figure 2.4). From the original 60 sampling sites, a subset of 20 sites were randomly chosen to represent marsh and open water sites in the area of diversion influence (Figure 2.3). Marsh coverage is more heavily dominant in the area so there were 13 marsh sites and 7 open water sites of the originally sampled 60 sites were chosen. Various pools of P bound sediment were identified through chemical extraction with salt, acid and base. Roughly 3 g of moist sediment sample, equivalent to ~0.5 g dry weight underwent extraction for P-fractionation. First, the readily available pool of P was extracted with a 1 M KCl solution. Samples were then continuously shaken for 2 hours followed by centrifugation and filtration through 0.45 μm filters to represent the water soluble plus exchangeable pools. While this pool is typically small, it is important because it represents the most bioavailable P pool that is loosely bound to sediment particles and available for direct uptake by algae and macrophytes.



Figure 2.3. Subset of 20 from 60 original stations that underwent P fractionation in the area of land building influence of the proposed Mid-Barataria sediment diversion. Waves indicate open water sites; Grass indicates marsh sites. (Source: Google Earth)

Next 0.1 M NaOH was added to the residual soil obtained from the KCl extraction to remove the P associated with humic and fulvic acids (association with organic P) as well as Fe/Al-P. Samples were continuously shaken for 17 hours and centrifugation time allowed the soil suspensions to equilibrate. The supernatant solution was filtered through a 0.45- μ m-membrane filter and the residual solution analyzed for SRP and total P. The SRP fraction represents the iron/aluminum-bound P. A subsample of NaOH-P was used to extract the P that is associated with organic P bound to alkali metals found in the sediment (Nguyen 2014). Briefly, a 5 ml of the aliquot, 1 ml of 11 M H_2SO_4 , and ~0.35 g of $\text{K}_2\text{S}_2\text{O}_8$ were added to a digestion tube and heated for 4 hours at 150°C to remove water from the sample. The temperature was then

increased to 380°C for 4 hours for complete digestion. After the digestion, samples were cooled to room temperature and diluted with 10 ml of deionized water, filtered through a 0.45 µm membrane filter and analyzed for DIP (USEPA, method 365.1, 1993). This pool is representative of the total P in the sample. By subtracting the Fe-bound P, from the total P-NaOH, the alkali extractable organic bound P is found.

The residual soil was next treated with 0.5 M HCl. The solution was continuously shaken for 24 hours, centrifuged and filtered through a 0.45-µm-membrane filter. The filtered solution was then analyzed for SRP. This fraction represents the Ca and Mg-bound P pool that is typically tied up as apatite.

$$\text{Residual P} = \text{TP} - (\text{KCl-P} + \text{NaOH-P} + \text{HCl-P})$$

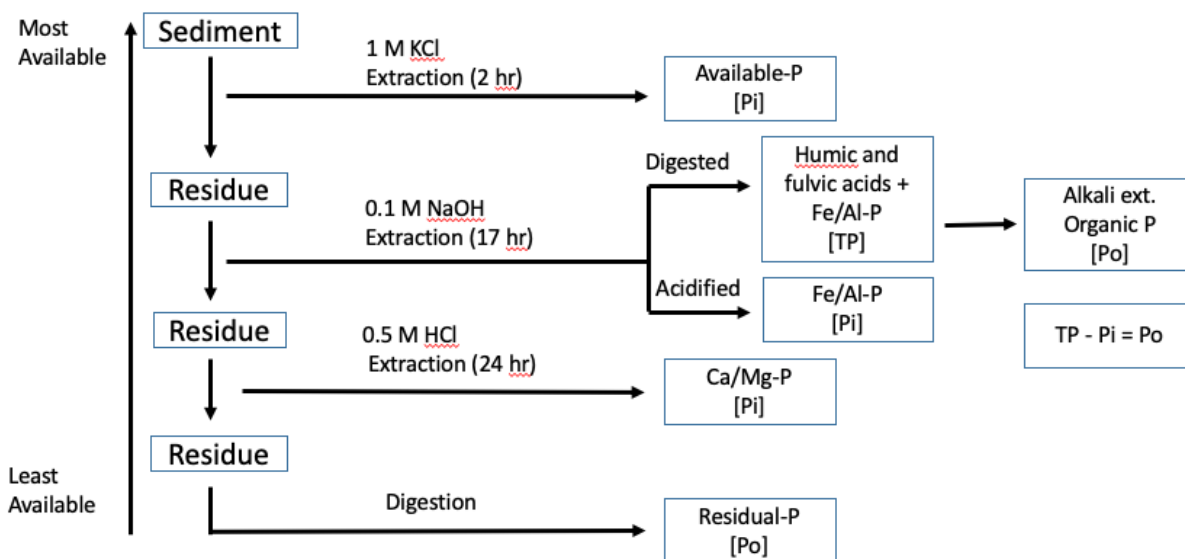


Figure 2.4. Sequential extraction scheme of inorganic and organic pools of Phosphorus modified from White et al., 2006). 1.0 M KCl-Pi representing labile P; 0.1 M NaOH-Pi representing Fe and Al bound P; 0.1 M NaOH- Po representing fulvic and humic bound P; 0.5 M HCl-Pi representing Ca and Mg bound P; Residual P representing refractory organic P.

2.4. Results and Discussion:

Barataria sediment characteristics are separated into marsh and open water soils (Table 2.1; Appendix A.1 and A.2). Mean bulk density (BD) values were $0.188 \pm 0.090 \text{ g cm}^{-3}$ for open water sites and $0.187 \pm 0.061 \text{ g cm}^{-3}$ for marsh sites. Loss of ignition, a proxy for organic matter, was $41\% \pm 19.1$ for open water sites and $41\% \pm 0.125$ for marsh sites. Total carbon for open water sites were 13.4 ± 4.2 weight % of the sample and 17.5 ± 5.48 weight % for marsh sites. Total N (Weight %) was $1.3 \pm 0.52\%$ of the sample for open water sites and $1.2 \pm 0.36\%$ for marsh sites. There were no significant differences between marsh and open water sites for any of the aforementioned soil characteristics (Table 2.1), which is not surprising given the open water sites were once intact marsh soil containing similar characteristics (Sapkota and White, 2019).

There were significantly greater total P values in marsh vs. open water sites. Mean marsh site total P values, $677 \pm 183 \text{ mg P kg}^{-1}$, are subdivided into total inorganic P, $197 \pm 93 \text{ mg P kg}^{-1}$, and total organic P, $479 \pm 149 \text{ mg P kg}^{-1}$. Mean open water site total P values, $503 \pm 90 \text{ mg P kg}^{-1}$, are subdivided into total inorganic P, $209 \pm 96 \text{ mg P kg}^{-1}$, and total organic P $296 \pm 105 \text{ mg P kg}^{-1}$. For both marsh and open water sites, the distribution of total inorganic P vs. total organic P is skewed more heavily toward the organic P. Open water and marsh sites have comparable moisture content percentages of $83.5 \pm 6.8\%$ and $82.7 \pm 4.7\%$.

Table 2.1. Average sediment characterization for Barataria Bay open water and marsh sampling sites. (a and b indicate significant difference).

	Open Water	Marsh
Moisture Content (%)	83.5 ± 6.8	82.7 ± 4.7
Bulk Density (g cm ⁻³)	0.188 ± 0.090	0.187 ± 0.061
Loss of Ignition (%)	41 ± 0.191	41 ± 0.125
Total C (%)	13.4 ± 4.20	17.5 ± 5.48
Total N (%)	1.3 ± 0.52	1.2 ± 0.36
Total P (mg P/kg)	503 ^a ± 90	677 ^b ± 182
Total Inorganic P (mg P/kg)	209 ^a ± 96 (41 %)	197 ^b ± 93 (30%)
Total Organic P (mg P/ kg)	296 ^a ± 105 (59%)	479 ^b ± 149 (70%)

2.4.1. Phosphorus Fractionations

The P extracted with KCl represents the most bioavailable pool of P for algal uptake which is loosely bound to sediment particles and present in porewater. Barataria open water and marsh sites had an identical mean KCl P pool concentrations of $1.19 \pm 0.55 \text{ mg P kg}^{-1}$ and $1.19 \pm 0.58 \text{ mg P kg}^{-1}$. This represents approximately 0.26% of the open water sediments and 0.18% of the marsh sediment total P concentration in the Barataria Bay (Table 2.2; Appendix B.1 and B.2). This readily available KCl pool is typically the smallest pool of P indicating substantial particulate P bound to minerals and associated with organic matter.

Table 2.2. Average P concentrations and percent of total P from sequential P fractionation scheme. Pi represents the inorganic P pool and Po represents the organic P pool.

Phosphorus Pool	Open Water mg kg ⁻¹	Marsh mg kg ⁻¹	Open Water %	Marsh %
Readily Available [Pi]	1.19 ± 0.55	1.19 ± 0.58	0.3	0.2
Fe/Al bound [Pi]	77.9 ± 57.9	89.7 ± 31.2	16.8	13.8
Alkali Organic P [Po]	73.1 ± 24.1	188 ± 88.6	15.8	29.0
Ca/Mg bound [Pi]	102.5 ± 59.0	116 ± 67.9	22.2	17.9
Residue [Po]	208 ± 65.9	254 ± 78.2	44.9	39.1
Sum of Total P	462 ± 123	649 ± 130	100	100
Total P	474 ± 94.6	616 ± 118		

The residual P and alkali extractable P fractions represent the total organic P pool. The residual P pool is the most abundant P fraction for Barataria open water and marsh sites is associated with the most stable residual P pool, in which the breakdown of the pool is resistant to the fractionation scheme. The average residual P pool concentration for Barataria open water sites is 208 ± 65.9 mg P kg⁻¹ and average Barataria marsh site concentration is 254 ± 78.2 mg P kg⁻¹. Open water sites average ~45% and marsh sites average ~39% of the total P pools. Residual P pools breakdown over long periods of time and will eventually contribute to the alkali organic P pool. Barataria open water and marsh sites had a mean alkali extractable P concentration of 73.1 ± 24.1 and 188 ± 88.6 mg P kg⁻¹ representing 15.8 and 29% of the total P pools respectively.

Nguyen (2014) examined P forms in Lake Pontchartrain estuarine sediment, both pre and post operation of the Bonnet Carré spillway where the post operation sediment values represent fresh Mississippi River sediment deposited, while the pre-opening values represented changes to fraction pools over the three years since the last spillway operation in 2008. It was found that the residual pool in the top 0-5 cm sediment interval experienced ~100% increase from 145 ± 10.9

mg P kg⁻¹ to 289 ± 19.4 mg P kg⁻¹ after the diversion operation. This result suggests a significant pool distribution increase in the residual P pools for both Barataria open water and marsh sediments under influence of a river diversion (Figure 2.5). The residual P pool is unavailable for algal uptake in the water column during the short term due to the general makeup of complex organic compounds but can become available for biological uptake over longer time periods as these compounds degrade releasing P.

The Fe/Al bound P pool had mean open water concentration in Barataria Bay of 77.9 ± 57.9 mg P kg⁻¹ and 89.7 ± 31.2 mg P kg⁻¹ in marsh sites. These concentrations represent 16.8% and 13.8% respectively of their total P pools (Figure 2.6). This percentage would increase with the introduction of Fe/Al rich sediments from the Mississippi River. Nguyen (2014) found that in 2011 after a one-month operation of the Bonnet Carré spillway, the Fe/Al-P pools increased, 44% in the 0-5 cm interval and 21% in the 5-10 cm interval clearly demonstrating the influence of the river sediment on this pool. An increase in this pool demonstrates a higher propensity for sediment to release bioavailable P to the water column under anaerobic soil conditions (Ghaisis et al, 2019; Adhikari et al., 2015; Roy et al 2012). This is due to the low redox conditions in the soil and reduction of particulate Fe³⁺ to dissolved Fe²⁺, which releases attached P under these soil conditions (Reddy and Delaune, 2008).

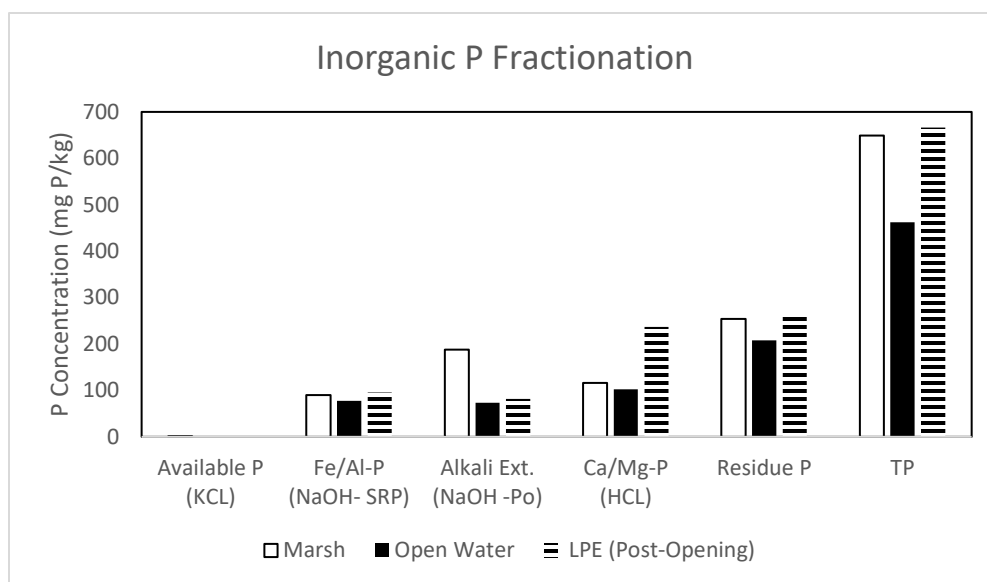


Figure 2.5. Mean P concentration (mg kg^{-1}) of Barataria open water and marsh sites compared with Nguyen (2014) Lake Pontchartrain Estuary pre BCS opening fractionation concentrations.

The Ca and Mg bound pool was, on average $102 \pm 59 \text{ mg P kg}^{-1}$ for open water sites and $116 \pm 67.9 \text{ mg P kg}^{-1}$ for marsh sites. This pool represented 22.2% and 17.9% respectively of the total P pools. Nguyen (2014) observed that in the fresh Mississippi River sediments deposited into Lake Pontchartrain, Ca/Mg-P pools decreased, -13% in the 0-5 cm interval and remained constant, 0% change, in the 5-10 cm interval. Due to the steady nature of Mississippi River chemical composition, this decrease in the Ca/Mg-P pool is caused by the introduction of fresh Mississippi River sediments. However, with the closure of the spillway the Ca/Mg-P pools gradually increase which can be attributed to high levels of Ca/Mg from marine influence.

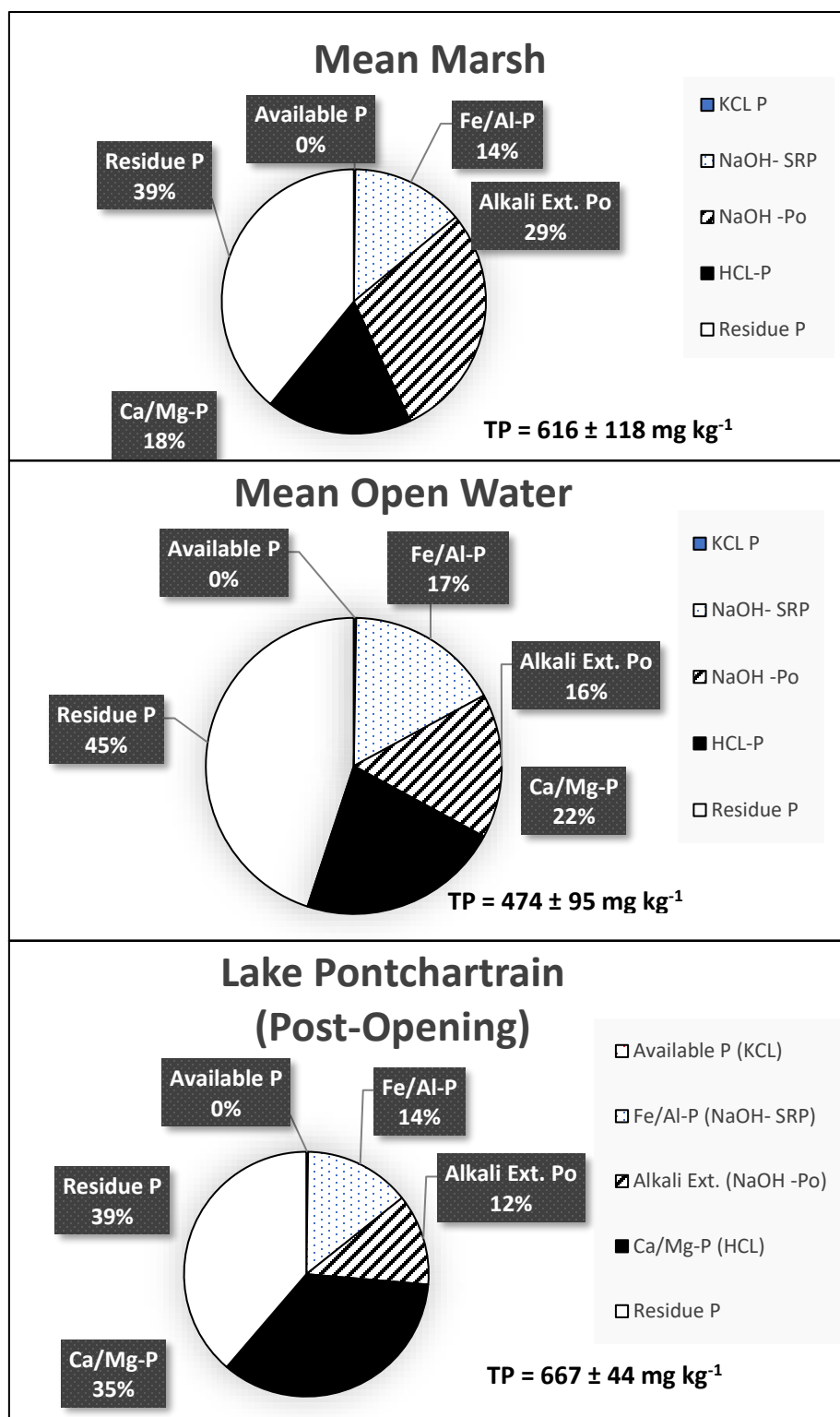


Figure 2.6. Mean P concentration (mg kg^{-1}) and percent of total P of Barataria open water and marsh P sites and Lake Pontchartrain estuary open water sites (Nguyen 2014) from sequential fractionation scheme.

2.4.2. Implications for Restoration

It is expected that the higher total P concentrations of the Mississippi River sediment will lead to a release of P once deposited in the receiving basins. The total P of freshly deposited Mississippi River sediment was found to be 677 ± 11.4 mg TP kg⁻¹ in the surface sediment of Lake Pontchartrain estuary. However, the total P of the sediment was 22.5% lower (525 ± 16.1 mg TP kg⁻¹) 3 years after deposition (Figure 2.7; Nguyen 2014). This phenomenon can also be observed on the Louisiana continental shelf as Mississippi River particulates have a total P of $1,085 \pm 78$ mg TP kg⁻¹ while the Gulf of Mexico shelf sediments showed a 40% decrease at 658 ± 176 mg TP kg⁻¹ (Adhikari et al., 2015; Table 2.3). The Mid-Barataria sediment diversion, during a month of operation at full capacity, is expected to deliver 900 Mt total P in fine particulates and 182 Mt in sand (Personal Communication). This influx of high sediment P is predicted to lead to a slow release of P from the deposited sediment each year.

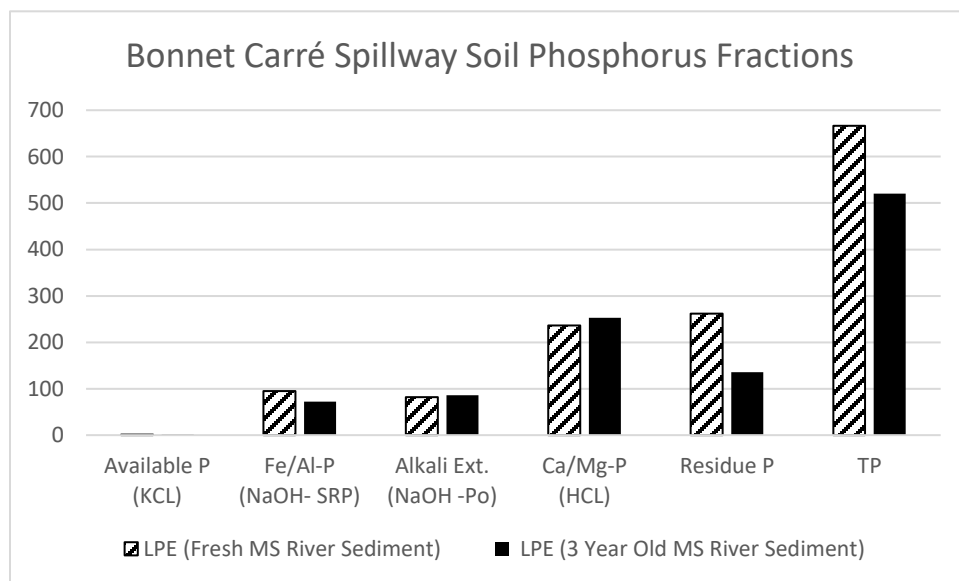


Figure 2.7. Graph of Bonnet Carrè spillway sediment P fractionation results from 2011 freshly deposited sediment and deposition of 2008 opening. (Nguyen 2014).

The primary P fraction or pool that is released from the sediment relatively quickly after deposition is the Fe/Al-bound P, the most dynamic of the substantial pools. This mobilization or release is due to the reduced conditions of wetland soil, as Iron, as Fe^{3+} is reduced to Fe^{2+} becoming soluble and releasing the attached phosphate. The Fe/Al bound P pool of the Bonnet Carré Spillway freshly deposited Mississippi River sediment was $93.2 \pm 5.92 \text{ mg P kg}^{-1}$ compared with river sediments from the 2008 BCS spillway opening, had a mean Fe/Al- bound pool of $64.5 \pm 8.6 \text{ mg P kg}^{-1}$ after three years, a loss of 30% over time (Nguyen, 2014). Even more dramatic, Louisiana continental shelf sediments contains just ~19% of the total P in the Fe/Al bound pool at $23.0 \pm 22.4 \text{ mg P kg}^{-1}$, a decrease of 76%. It has been observed that shelf sediment total P decreases by nearly 40% over time and distance from the discharge of Mississippi River, and that loss is directly attributed to the loss of the Fe-bound fraction (Sutula et al., 2004; Adhikari et al., 2015).

Table 2.3. P fractionation concentrations and percent of total P comparisons across Louisiana coast sediment types.

Major P Phase Digestion	TP	Org-P NaOH Po	Detr-P Residue Po	Labile-P KCl Pi	Fe-P NaOH Pi	Ca-P HCl Pi
Location	mg P kg ⁻¹	mg P kg ⁻¹	mg P kg ⁻¹	mg P kg ⁻¹	mg P kg ⁻¹	mg P kg ⁻¹
Mississippi River Particulates (Sutula et al., 2004)	1085	62	25	337	469	190
% of Total P		6	2	31	43	18
Mississippi River Sediments (Sutula et al., 2004)	829	136	87	108	339	160
% of Total P		16	10	13	41	19
Lake Pontchartrain (Nguyen 2014)	667	82	262	2	95	237
% of Total P		12	39	0	14	35
Barataria Marsh (This Study)	649	188	254	1	90	116
% of Total P		29	39	0	14	18
Barataria Open Water (This Study)	462	73	208	1	78	102
% of Total P		16	45	0	17	22
GOM Shelf (Adhikari et al., 2015)	658	20	77	4.2	23	524
% of Total P		3	13	1	4	79

Moreover, there is evidence that a portion of the total P can swap or switch to more stable pools. Nguyen (2014) found opposing shifts in the Fe/Al-bound pool and Ca/Mg-bound P pools with a decrease in the former and a concomitant increase in the latter pool over a three-year period (Fig 2.8). Adhikari et al, (2015) found that Fe/Al bound pool of Gulf of Mexico shelf sediments contained just $4.2 \pm 4.4\%$ of the total P pool, while the Ca/Mg fraction increased to $79 \pm 9.4\%$.

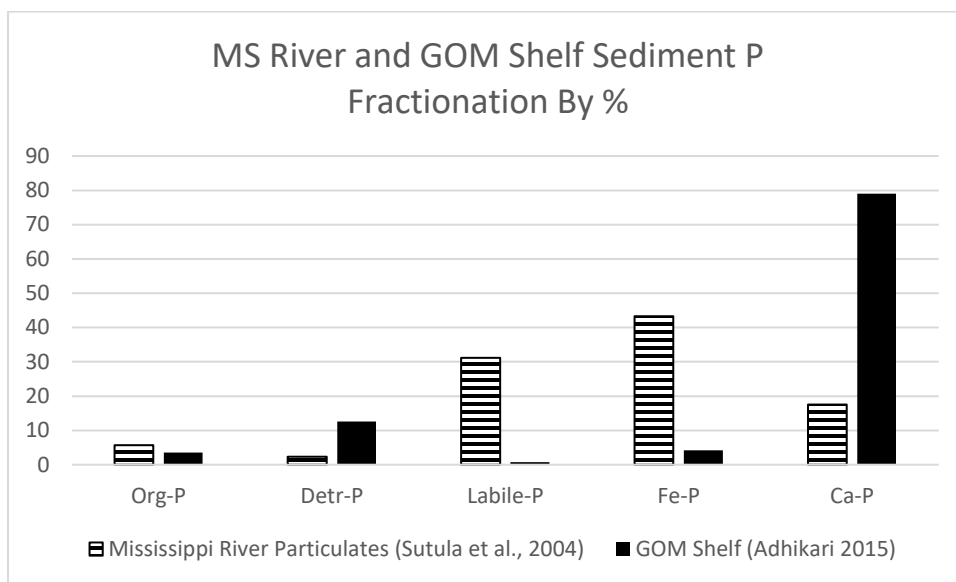


Figure 2.8. Graph comparing sediment P fractionation from MS River particulates (Sutula et al., 2004) and Gulf of Mexico shelf sediments (Adhikari et al., 2015).

These Louisiana continental shelf sediments under a marine influence had dominance of the Ca/Mg bound P pool. This artifact is likely due to the fact that ocean water contains elevated amounts of Ca/Mg, providing the needed cations to lock up the P. Ca and Mg are two of six major ions that comprise 99% of seawater salinity by weight and hence the stability of P under marine influence is highly correlated to Ca/Mg abundances.

The mean Barataria open water and marsh sediment Fe/Al-bound P represents 17 and 14% of the total P, respectively. One can expect that Barataria Bay surface soil to increase in Fe

and Al P with diversion operation due to the addition of the river sediment. Over time, little change can be expected in the Ca/Mg pool of the Barataria sediments due to lack of marine influence and hence lower Ca/Mg concentration in the fresh conditions of the northeastern region under influence of the sediment diversion. The operation of the sediment diversion will undoubtedly provide a lower salinity conditions for much of the year.

Mississippi River influence has shown switches in P pools in Lake Pontchartrain estuary (Nguyen 2014) and the Louisiana intercontinental shelf (Sutula et al., 2004; Adhikari et al., 2015) from the Fe/Al bound pool to the Ca/Mg bound pool. This P pool switch toward the Ca/Mg bound pool in the Barataria Bay sediments is unlikely due to the lack of marine influence and high organic matter content of its soils (Figure 2.9).

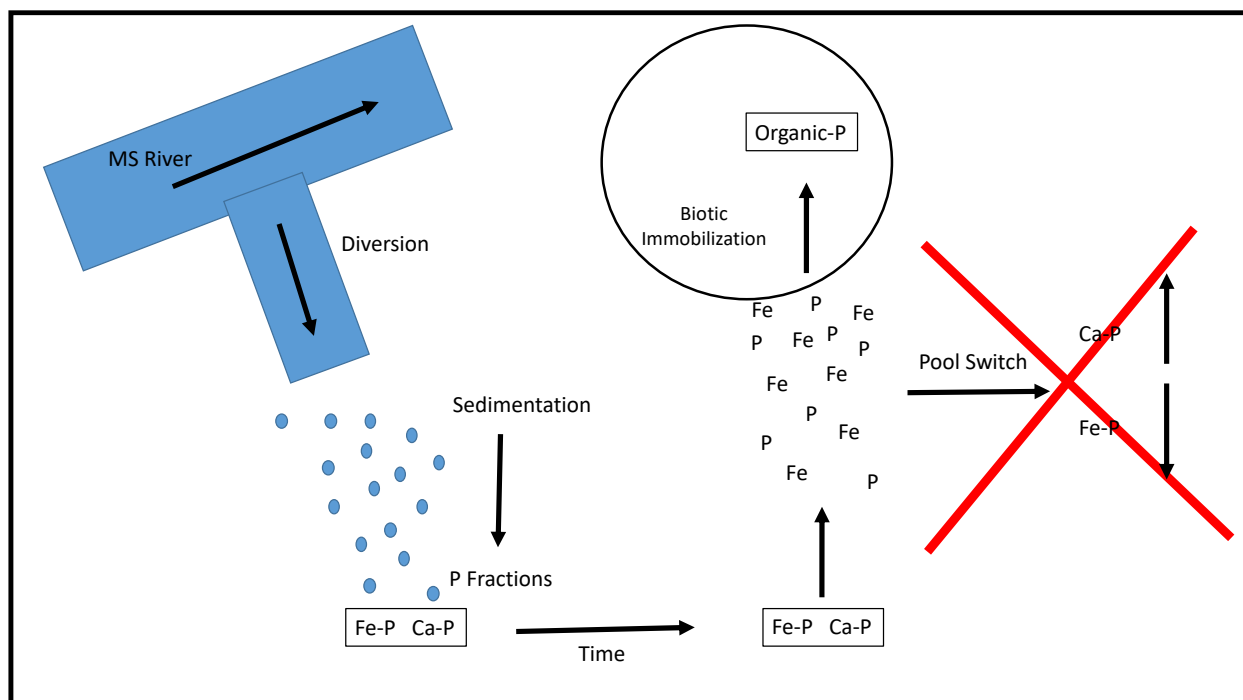


Figure 2.9. Diagram of fate of sedimentary P from Mississippi River to wetlands via sediment diversion. Red 'X' denotes that the shift from Fe-P to Ca-P is unlikely in the Barataria Bay sediments.

The diversion will deliver primarily mineral river sediment over top of the present day Barataria highly organic soil. This reduced, highly organic soil will likely mobilize the Fe/Al-bound pools more quickly because of the lower redox potential (Reddy and Delaune, 2008). In addition, organic soils produce weak organic acids through slow decomposition, which can potentially mobilize the Ca/Mg bound fraction, as seen in the Florida Everglades wetland system (Reddy et al., 1998). Therefore, the soil and water chemistry of the receiving basin is not particularly advantageous for the long-term storage of this river sediment P in the Ca/Mg pool. With the decreased chance of pool switching for the Fe/Al bound pool, its likely fate is to directly contribute to biotic immobilization, transferring to the organic P pool and becoming available for biological uptake (Figure 2.9).

Table 2.4. Correlation between Barataria sediment characteristics and available P fractions. For n=20, r=0.444 is significant at, p<0.05. Significant correlations in bold.

	BD	LOI	MC	Total P	NaOH -Po	Residue P	KCL P	NaOH- SRP
LOI	-0.801							
MC	-0.986	0.814						
Total P	-0.341	0.303	0.351					
NaOH -Po	-0.579	0.507	0.550	0.761				
Residue P	-0.804	0.793	0.796	0.665	0.796			
KCL P	-0.721	0.606	0.777	0.323	0.356	0.579		
NaOH- SRP	0.247	-0.268	-0.271	0.359	0.093	0.040	-0.224	
HCL-P	0.703	-0.565	-0.672	-0.256	-0.552	-0.489	-0.413	0.353

However, the solubilized P in the vegetated basin does have the opportunity to be taken up by primary producers and converted to organic P. The open water areas would favor phytoplankton uptake whilst much of the P in the vegetated areas would be incorporated into macrophyte organic matter. Therefore, the concern over algal blooms, and in particular, harmful algal blooms rests in the fragmented open water landscape of the northern basin. The influx of P to the system from a sediment diversion has the potential to spur the formation of algal blooms

when the diversion has been turned off and calm and warm conditions are created. In order for a toxic cyanobacteria bloom to form, *Microsytis* spp. and/or *Dolichospermum* (formerly known as *Anabaena*) must be present in the Barataria Bay either already or brought in from the Mississippi River diversion. Due to the excess amounts of N brought from the river and the present organic matter in the Barataria vegetative marshes, it is likely that *Microsytis* spp. will dominate over *Dolichospermum* (formerly known as *Anabaena*) which fixes its N from the atmosphere. It is unknown at this time if these algal species are generally present in open water areas and research looking for cyst forms would be instructive.

2.5. Conclusions

Barataria Bay sites are comprised of organic soils that will increase in mineral content over time from the operation of the Mid-Barataria sediment diversion. Most open water sites are degraded marsh sites and yield comparable results to the adjacent marsh sediment characteristics. Barataria open water and marsh sites hold the majority of total P in the residual pool, which is not immediately bioavailable, but can become available with the breakdown of organics over time through slow microbial enzymatic activity. This creates the potential for delayed P release to the water column in the weeks and months following the closure of river diversions into the Barataria Basin and can lead to potential algal bloom formations.

Lake Pontchartrain estuary sediments observed a 32.5% increase in Fe/Al-bound P pools with the operation of the Bonnet Carré spillway, which consequently has a direct relationship to the release of bioavailable P to the water column. Baseline Barataria sediment conditions show that in the marsh and open water the Fe/Al-bound P pools represent 14 and 17% which are expected to show the greatest increase among pools upon exposure to Mississippi River

sediments as Fe^{3+} reduces to Fe^{2+} releasing the attached P to the water column. Although, this pool has been observed to shift its majority to the Ca/Mg-bound pool, (Sutula et al., 2004; Nguyen 2014; Adhikari et al., 2015) the fate of the Ca/Mg-bound pools in the Barataria Bay is uncertain due to the high organic matter content in the present marshes. The organic soils, different from Lake Pontchartrain estuary soil characteristics, release organic acids that mobilize the Ca/Mg-bound pool preventing the retention of P over long time periods.

Total P values have shown to decrease by nearly 50% from the Mississippi River fine particulate concentrations, $1085 \text{ mg P kg}^{-1}$, to the Gulf of Mexico shelf sediments, 557 mg P kg^{-1} (Sutula et al., 2004). Roughly 500 mg P kg^{-1} is being taken up by ecosystem services in the journey from the Mississippi River to the drainage basin in the Gulf of Mexico.

There are no current studies on the P pool fractionations of sediment in the area of influence of the Mid-Barataria sediment diversion, and this fractionation is the first to be done in the area of influence of a Mississippi River diversion into the Barataria Basin. This sediment characterization of the future impacted area serves as a baseline for future water quality management and river control protocol. Further research characterizing the abundances of cyanobacteria, such as *Microcystis* spp., lying dormant in Barataria sediments would be useful in the determination of potential harmful algal blooms from the introduction of the Mississippi River via the Mid-Barataria sediment diversion.

CHAPTER 3. EQUILIBRIUM PHOSPHORUS CONCENTRATION

3.1. Introduction

Phosphorus is an essential macronutrient for biological productivity within all ecosystems. The phosphorus cycle is a dynamic interchange between biotic and abiotic pools. Typically, terrestrial P loads are intercepted by wetlands with some flow through to the adjacent aquatic systems. Land use changes, degradation and increased rates of wetland loss, and changes in regional hydrology have all contributed to decreased capacity of wetlands to intercept P on a watershed scale, leading to a direct input of P loads to aquatic environments (Reddy and Delaune, 2008). Excess P, in concert with N, can trigger algal blooms and other expressions of eutrophication, such as hypoxia, and therefore, landscape scale management of P is essential for decreasing eutrophic events in coastal systems.

The proposed Mid-Barataria sediment diversion is designed to help reconnect sediment-starved coastal wetlands with the sediment-rich Mississippi River to help mitigate and offset increased marsh edge erosion and degradation (CPRA, 2017). This reconnection of the Mississippi River to coastal wetlands will not only bring sediment but also bioavailable and particulate nutrients. The Mid-Barataria sediment diversion is designed to provide sediment to wetlands on a basin wide scale. Diverting the river water into these coastal marshes and associated with shallow water ways will promote accretion rates of sediment, leading to increased vegetative growth and marsh stability (Hatton et al., 1983; Delaune et al., 2003; Roy et al., 2017). Little spatially explicit research has been done to quantify nutrient levels in the vegetative marsh and open water areas of Barataria Bay that will be directly affected by this sediment diversion. The Louisiana Coastwide Reference Monitoring System (CRMS) provides constant data of coastal nutrient dynamics on a small scale, which does not necessarily

encapsulate the full effects of a localized sediment diversion. There are 3 CRMS sites in the area of morphological influence of the Mid-Barataria sediment diversion. Phosphorus forms, in particular dynamics, has been understudied in the receiving basin of the proposed diversion.

The Mississippi River exports $134 \times 10^6 \text{ kg yr}^{-1}$ of total reactive P, or bioavailable P, to the Gulf of Mexico (Sutula et al., 2004). The Mississippi River levels of SRP are generally low, ($<0.10 \text{ mg P L}^{-1}$), although significant amounts of total P can be contained in the suspended sediment (Zhang et al., 2012). Coastal waters as well as estuarine systems can shift N-limited systems to P-limitation upon the influx of high DIN from the Mississippi River. When the N rich river water enters the basin, there is a diffusive flux gradient of P between the sediment and the water column. If the concentration of P in the sediment porewaters is lower than the concentration of the water column, then SRP will diffuse into the sediments. However, if the sediment porewaters contain higher concentrations of SRP than the surface waters, then there will be a release of P from the sediment into the water column. The fate of bioavailable P in the open water regions is generally immobilization by phytoplankton while the macrophytes in the marsh edges can assimilate P in the vegetated marsh. When primary producers deplete the water column of SRP, the release rates of SRP from the sediment to the water column will increase as a result of dis-equilibrium.

Estuarine sediments, based on their physico-chemical characteristics, can act as a sink or source for P the overlying water column (Pant and Reddy 2001). SRP and DOP can potentially be released from the sediment to the overlying water column (Zhang et al., 2012). The sedimentary P cycle is dependent on the immobilization of organic P, the burial of particulate inorganic P, and the interaction of phosphate with metal oxides in the sediment (Roy et al., 2012). These three pathways are the primary modes for P-retention in the sediment. Phosphorus

forms can be characterized in order to determine the extent to which mechanism may be dominant in a system. There are a number of chemical fractionation schemes developed to separate out the various pools of P present in wetland soils, a common one developed by Reddy et al. (1998) has been frequently used. Phosphorus forms are separated into one of the following five groups: i) labile P_i loosely adsorbed; ii) P_i associated with Fe and Al; iii) P_i associated with Ca and Mg; iv) alkali-extractable organic P (fulvic and humic bound P); and v) residual organic P. Changes in the sediment redox conditions dictated by the presence of oxygen in the overlying water column can lead to the benthic regeneration of metal oxides and associated phosphate (Roy et al., 2012) whereas changes in pH can lead to the release of Ca-Mg bound P.

The Equilibrium Phosphorus Concentration (EPC) is the concentration of P in solution that is in equilibrium with P both in the porewater and sorbed onto the solid phase, essentially the concentration at which net P retained and released from the sediment to the water column is equivalent. Practically, if the water column concentration of SRP is above the EPC of the sediment, then SRP will be sorbed to the sediment. If the concentrations in the water column are lower than the sediment EPC, then SRP will be released into the water column (Figure 3.1). The EPC is dependent on the size of the internal sediment P, forms of P in the system and the water column P.

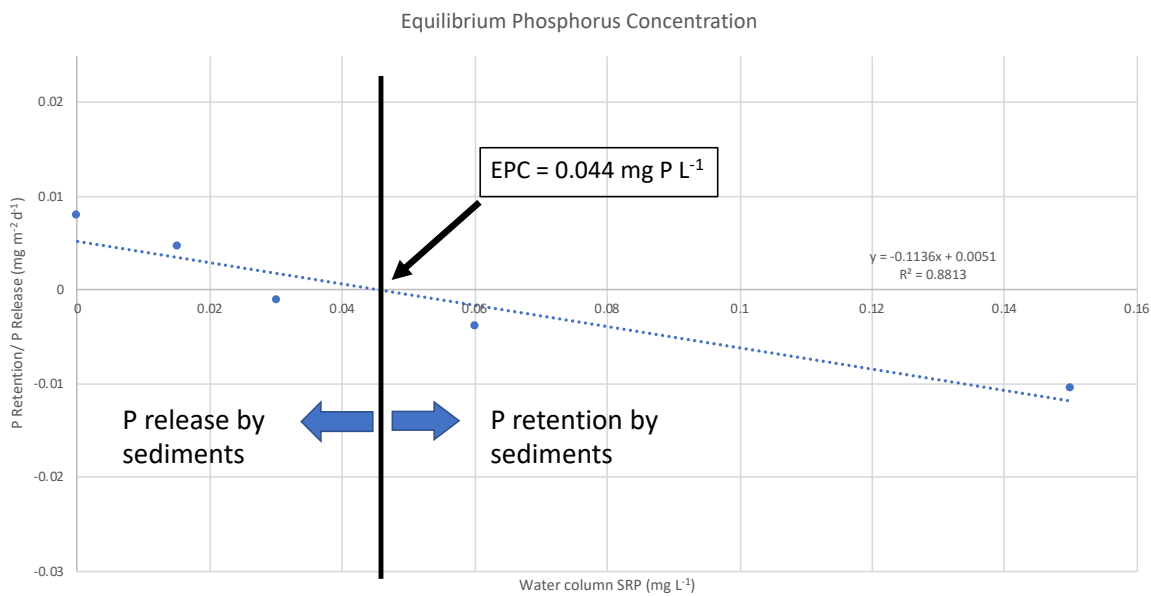


Figure 3.1. Example graph of equilibrium phosphorus concentration of 0.044 mg P L⁻¹.

The EPC can be a useful tool for water quality managers in determining P flux and historical loading of P to a system. Many Total Maximum Daily Load (TMDL) programs are focused on reducing water column concentrations of nutrients. The internal load or sediment P pool can be substantial. Spending time and money in reducing the watershed loading of nutrients to an aquatic system can be a futile effort, for example any reduction of phosphorus below the EPC will cause nutrients to leak out the sediment, preventing any further reductions. Therefore, the EPC is the concentration below in which it is difficult to restore because the sediment is continually releasing the internal load of P (Martin, 2004).

For example, the internal sediment load of P for the Saint Johns River estuary, FL was 25% of the total P load (Malecki et al., 2004). It was estimated that ~30-44% of the annual SRP load to the Lake Pontchartrain estuary originated from the diffusive flux of SRP from the sediment (Roy et al., 2012). Consequently, any attempts in reductions in surface water concentrations of P in large systems will need to come from reducing the external loads from the

watershed since removal of the internal load is prohibitively expensive as it involves the removal and disposal of a substantial amount of sediment.

Therefore, the overall goal of this study was to predict the direction and magnitude of flux of SRP when the Mississippi River is reconnected to Barataria Bay through the sediment diversion. Additionally, it was sought to predict how this dynamic would change with the deposition of Mississippi River sediment onto the organic soils of the bay. Specific objectives include 1) determination of the equilibrium flux rate of P between the sediment and water column for vegetated and open water sites under a range of water column P concentration and 2) comparisons of current organic soils EPC with the EPC of sediments currently deposited by the Mississippi River. The hypothesis for this study is that the reconnection of the Mississippi River to Barataria Basin via a sediment diversion will initially trigger a flux of SRP from the water column into the sediments. However, post closure of the diversion it can be expected that SRP will flux out of the sediment once water column concentrations decrease up to the EPC concentration.

3.2. Materials and Methods

3.2.1. Study Site

Barataria Basin is an estuary bound between the Mississippi River channel on the north and east, the Gulf of Mexico on the south, and a former distributary of the Mississippi River on the west, making the border between this basin and the Terrebonne Basin to the west. Barataria Basin encompasses approximately 7100 km² in southeast Louisiana (Byrnes et. al, 2019). The basin faces some of the greatest marsh edge erosion rates due to a combination of wind wave driven marsh edge erosion and isolation from the Mississippi River preventing wetland progradation (Valentine and Mariotti 2019; Sapkota and White 2019). There are no natural

sources of riverine input into the basin (Ren et al., 2009). A managed connection to the north called the Davis Pond diversion is the only freshwater hydrologic connection into the basin (Spera et al, 2020). The basin has lost approximately 1172 km² of land from 1932 to 2016, the vast majority being vegetated wetland (Couvillion et al., 2017).

The overall study area is the northeastern portion of the vegetated areas of Barataria Basin, Louisiana, USA proximal to proposed Mid-Barataria Basin sediment diversion (Figure 3.2). The diversion will be positioned along the river levee near mile marker 61 in Ironton, Louisiana. When opened at full capacity the 2-mile-long structure can allow 75,000 cfs of river water to flood into the Barataria Basin (CPRA, 2017). *Spartina alterniflora* is the dominant vegetation and surface water salinities range from 0.6 to 7.85 in the sampling area.

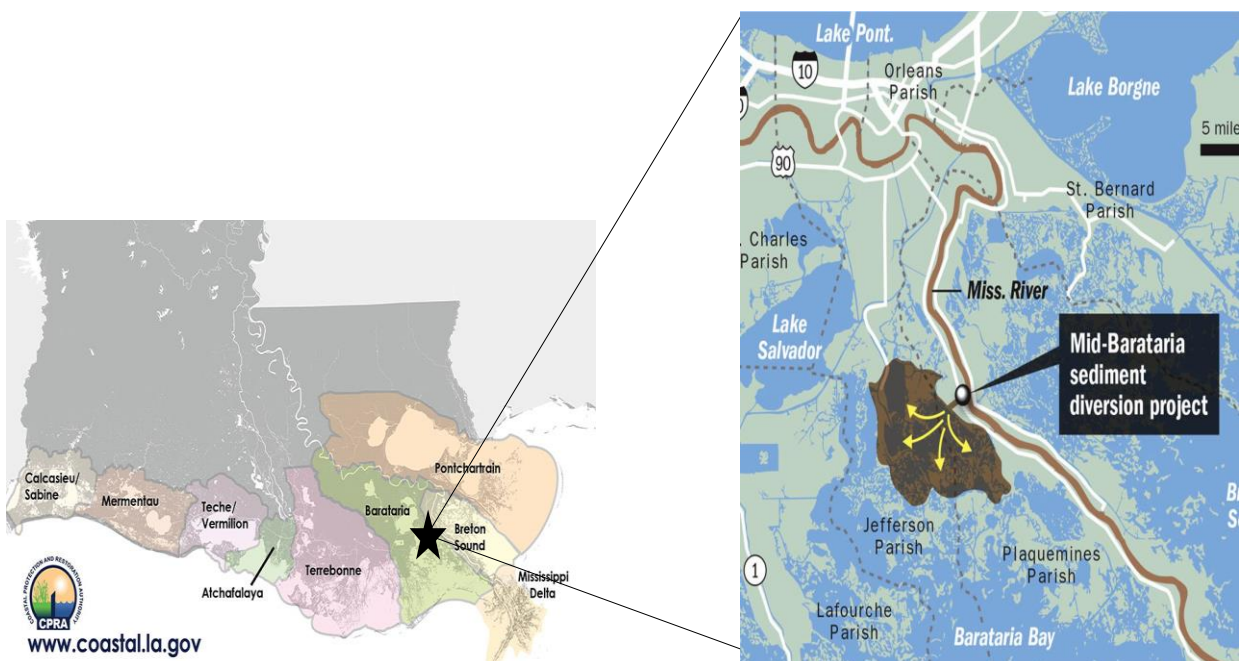


Figure 3.2. Map of area of influence of the Mid-Barataria Sediment Diversion along the Mississippi River at mile marker 61. (Source: The Advocate 2018)

3.2.2. Mardi Gras Pass

Mardi Gras Pass (Appendix C.1) is a natural connection between the Mississippi River and Breton Sound at river mile marker 43.7 and was formed when the river overtopped the Bohemia spillway in 2012 due to high water events on the Mississippi (Henkel et al., 2018). The pass through the river levee has expanded since its initial breach in 2012, funneling river water and remaining an effective sediment delivery system to the adjacent wetlands, forming new land over time (Figure 3.3; Henkel et al., 2018). The deposition of river sediment has been followed by the establishment of emergent vegetation increasing marsh stability in the receiving basin. This site was chosen to allow a predicative estimate of changes to Barataria Basin P that can be expected from the reconnection of the river (Figure 3.3).

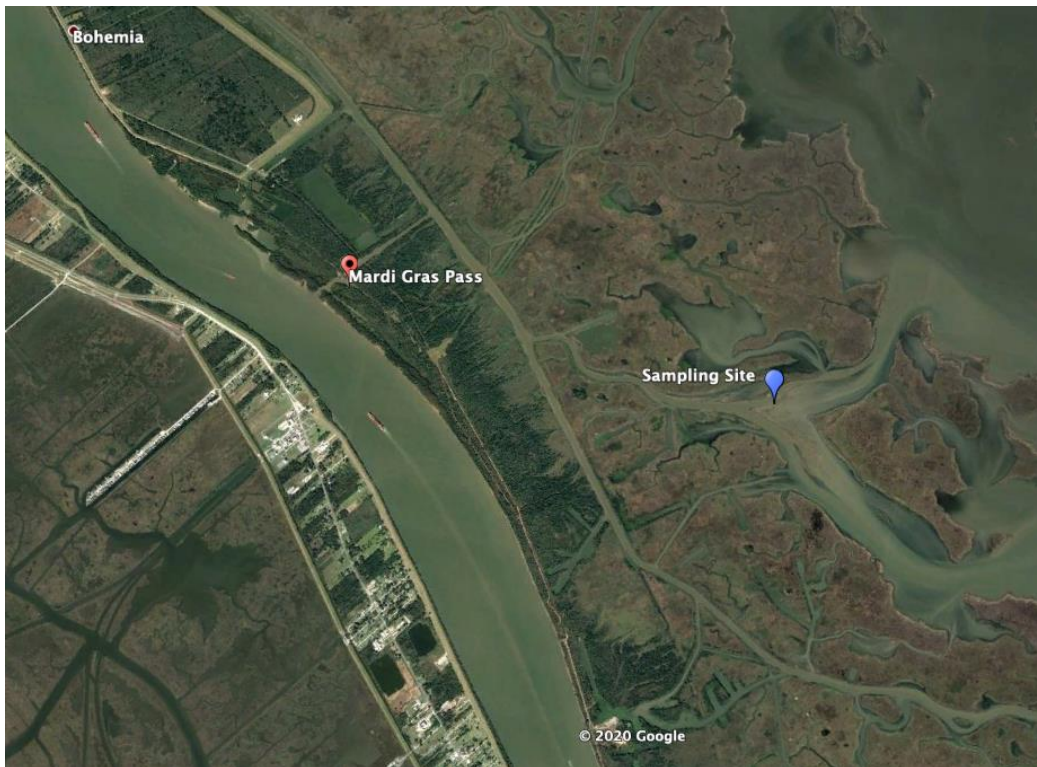


Figure 3.3. Map of natural breach in river levee at mile marker 43.7, Mardi Gras Pass and site sampled to represent river deposition. (Source: Google Earth)

3.2.3. Sampling

Six sites were selected to include 3 marsh sites and 3 open water sites (Figure 3.4; Appendix C). Five replicate intact cores were taken from the 6 sites for a total of 30 cores. In addition, five replicate cores were also taken in the newly accreted mudbank area created by Mardi Gras Pass to represent recently deposited riverine sediment (Figure 3.3).

Intact sediment cores were collected by pushcore, with diameter of 7 cm, to capture 25 cm of soil at the vegetated Barataria Bay sites. A piston corer was used to obtain the open water stations sediments in Barataria. Cores were sealed and brought back to the laboratory.

Immediately upon arrival, the existing water column was removed with a peristaltic pump and replaced with deionized water through a drip system into each core to ensure minimal surface disturbance. Each water depth was maintained daily at 17 cm above the sediment surface.

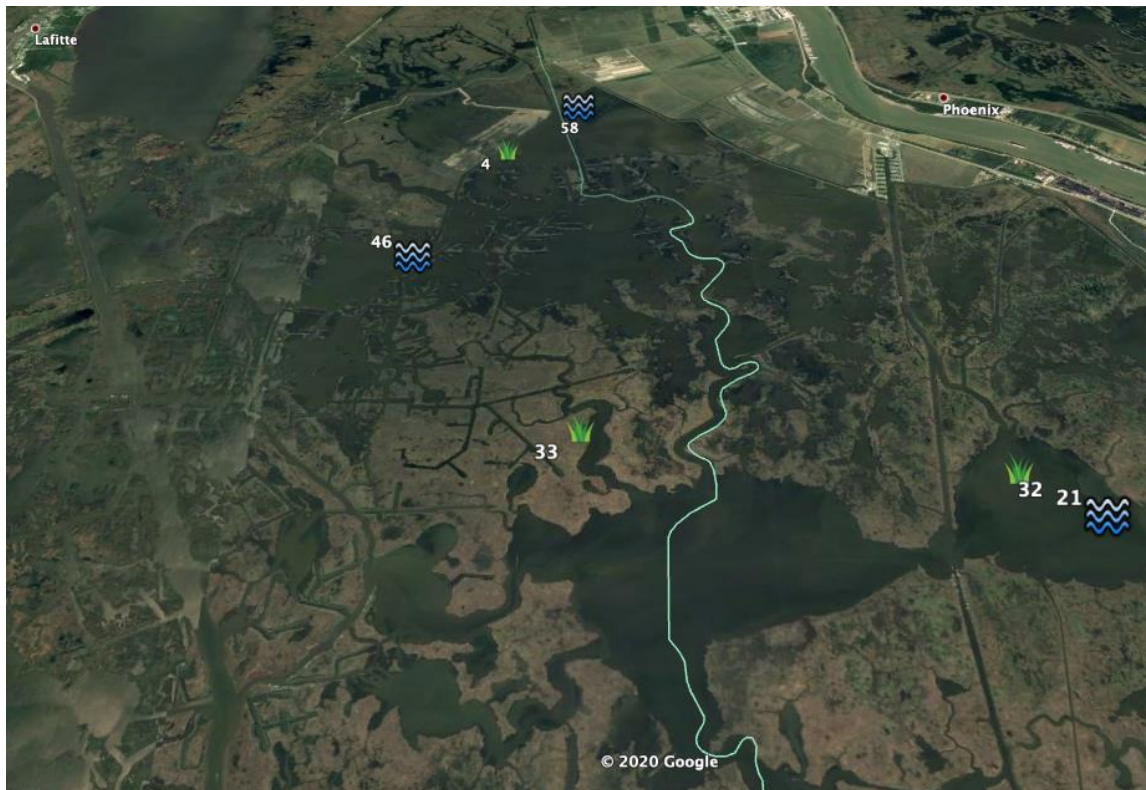


Figure 3.4. Map of sampling sites for equilibrium phosphorus concentration experiment in the area of influence of the Mid-Barataria Sediment Diversion. Open water sites are depicted with

the blue waves icon and marsh sites are depicted with the green vegetation icon. (Source: Google Earth)

3.2.4. Laboratory Analysis

Each of the 5 replicate cores from each site was spiked with SRP to produce water column P concentrations of 0, 15, 30, 60, 150 $\mu\text{g L}^{-1}$ at the onset of the incubation. The cores were maintained in the dark and in a water bath held at 20°C, to prevent photosynthetic activity, and the water column of each core was aerated with aquarium pumps to maintain aerobic conditions in the water column. Surface water was sampled over a 14-day period by sampling 7 ml and replacing the withdrawn volume with deionized water to maintain a consistent water column depth throughout the experiment. The withdrawn water samples were filtered through a 0.45- μm membrane filter, acidified to a pH <2 and stored at 4° C. Samples were analyzed for SRP colorimetrically by an AQ300 Automated Discrete Analyzer (SEAL Analytical, West Sussex, England), using US EPA method 353.2 (US EPA, 1983). Changes in concentration due to the reflood water was accounted for in the mass flux calculation.

3.2.5. Data Analyses

For each of the incubations, water column concentrations were converted to mg P m^{-2} on the y axis with time plotted on the x-axis. A linear best fit line was produced, and the slope represents the flux rate ($\text{mg m}^{-2} \text{d}^{-1}$). A positive rate indicates SRP flux out of the sediment while a negative slope indicates P flux into the sediment. Equilibrium phosphorus concentrations were calculated by plotting SRP flux rate ($\text{mg m}^{-2} \text{d}^{-1}$) along the y-axis against the initial water column SRP concentration (mg P L^{-1}) along the x axis (Figure 3.1). The EPC is that concentration where the regression line crosses the x-axis. Microsoft excel was used to perform regression analyses and correlations.

3.3. Results and Discussion

3.3.1. Soil Characterization

The three open water sites had soil bulk density values of 0.24, 0.085, and 0.118 g cm⁻³ comprising a mean bulk density of 0.148 ± 0.08 g cm⁻³. The three marsh sites had bulk densities of 0.193, 0.346, and 0.289 g cm⁻³ comprising a mean bulk density of 0.276 ± 0.08 g cm⁻³. Mardi Gras Pass sediment had an average bulk density of 1.22 ± 0.09 . The average loss on ignition (LOI), a proxy for organic matter, for the three open water sites was $48.6 \pm 24.8\%$. Average LOI for the three marsh sites was $32.7 \pm 18.1\%$. The average LOI for the Mardi Gras Pass site was significantly lower at 1.3 ± 1.0 (Table 3.1).

Of the three site types, the marsh had the greatest total P of 662 ± 260 mg TP kg⁻¹ that is divided between a total inorganic P value of 276 ± 72.5 mg TP kg⁻¹ and a total organic P value of 387 ± 274 mg TP kg⁻¹. The open water sites had a total P of 519 ± 90.6 mg TP kg⁻¹ comprised of total inorganic P value of 218 ± 170 mg TP kg⁻¹ and total organic P value of 301 ± 138 mg TP kg⁻¹. The Mardi Gras Pass site had a mean total P value of 459 ± 63.6 comprised of a total inorganic P value of 442.0 ± 36.7 mg TP kg⁻¹ and a total organic P value of 17.0 ± 32.0 mg TP kg⁻¹.

Table 3.1. Sediment characteristics of Barataria open water and marsh soils and Mardi Gras Pass soil.

Site	Bulk Density g cm ⁻³	LOI weight %	TP mg kg ⁻¹	TIP mg kg ⁻¹	TOP mg kg ⁻¹
Barataria Open Water	0.148 ± 0.08	48.6 ± 24.8	519 ± 90.6	218 ± 170.3	301 ± 138
Barataria Marsh	0.276 ± 0.08	32.7 ± 18.1	662 ± 260	276 ± 72.5	387 ± 274
Mardi Gras Pass	1.22 ± 0.09	1.3 ± 1.0	459 ± 63.6	442 ± 36.7	17 ± 32

3.3.2. No P Addition

Water column SRP concentrations: All experimental control cores showed increases in SRP concentration from day 1 to day 14 during incubation. The three open water sites controls started with water column SRP concentrations of 0.02, 0.009, and 0.01 mg P L⁻¹. Over time, there was a mean increase in SRP of 533.7 %. All open water sites showed increases in water column concentration over the 14-day sampling period with a mean final concentration of 0.087 ± 0.07 mg P L⁻¹. The three marsh sites controls started with water column SRP concentrations of 0.033, 0.047, and 0.016 mg P L⁻¹. On average, the three sites increase to 0.294 mg P L⁻¹, an average increase of 1149.3%. Mardi Gras Pass control core started with an initial water column SRP concentration of 0.015 mg P L⁻¹ and remained constant in day 2 of sampling. The water column concentration increased on day 7 to 0.058 ± 0.02 mg P L⁻¹, and to 0.088 ± 0.02 mg P L⁻¹ on day 14 representing a percent change increase of 487% (Table 3.2).

Phosphorus flux rates: The three open water sites had SRP flux rates of 1.85, 1.001, and 0.189 mg m⁻² d⁻¹ over the 14-day sampling period. The mean SRP flux rate for open water sites is 1.014 ± 0.83 mg m⁻² d⁻¹. This denotes a release of P from the sediment to the water column with no addition of P. The three marsh sites had SRP flux rates of 4.75, 3.83, and 5.20 mg m⁻² d⁻¹ over the sampling period. The mean SRP flux rate for marsh sites is 4.59 ± 0.69 mg m⁻² d⁻¹ which is significantly (P value < 0.005) higher than the open water sites. This indicates that on average, there is a 4.6 times larger flux rate from marsh soils to water column than from the open water sites. The one Mardi Gras Pass sediment site had an SRP flux rate of 1.006 mg m⁻² d⁻¹.

Table 3.2. Percent change in water column SRP (mg L^{-1}) under no P additions, for Barataria open water and marsh sites and Mardi Gras Pass marsh site on days 1, 2, 7, and 14. A negative (-) percent (%) change indicates a decrease in SRP concentration while a positive (+) percent change indicates an increase in SRP concentrations.

Site Type	Site #	Initial SRP (mg L^{-1})		SRP (mg L^{-1})			Percent Change (%)		
			2 d	7 d	14 d		2 d	7 d	14 d
Open Water	21	0.02	0.032 ± 0.05	0.095 ± 0.05	0.161 ± 0.06		60	197	69
Open Water	46	0.009	0.016 ± 0.10	0.021 ± 0.16	0.086 ± 0.17		78	31	310
Open Water	58	0.01	0.012 ± 0.12	0.017 ± 0.08	0.014 ± 0.04		20	42	-18
Marsh	4	0.033	0.048 ± 0.06	0.196 ± 0.09	0.147 ± 0.11		45	308	-25
Marsh	32	0.047	0.042 ± 0.17	0.061 ± 0.34	0.328 ± 0.33		-11	45	438
Marsh	33	0.016	0.034 ± 0.03	0.108 ± 0.06	0.408 ± 0.27		113	218	278
Mardi Gras Pass	MGP	0.015	0.015 ± 0.06	0.058 ± 0.02	0.088 ± 0.02		0	287	52

Table 3.3. Correlations of sediment characterizations $n=7$, $p<0.05$ at $r=0.754$. Significant correlations are in bold.

	BD	LOI	MC	Total P	Total Po
LOI	-0.905				
MC	-0.998	0.891			
Total P	-0.001	0.074	-0.061		
Total Po	-0.448	0.570	0.386	0.808	
Total Pi	0.735	-0.821	-0.731	0.246	-0.373

3.3.2. 15 $\mu\text{g P L}^{-1}$ Addition

Water column SRP concentrations: All open water site SRP concentrations showed a general increase over the 14-day incubation period. The three open water sites had initial SRP concentrations of 0.011, 0.010, and 0.011 mg P L^{-1} . Over time there was a mean increase in SRP of 1419%. The three marsh sites had initial SRP concentrations of 0.067, 0.303, and 0.106 mg P L^{-1} . Over the first 7 days there was a mean increase in SRP of 138%. Marsh site 33 showed a decrease in SRP concentration from day 1 to day 14 of -43%. The Mardi Gras Pass site showed a general increase through the 14-day incubation period with an initial SRP concentration of 0.01

mg P L⁻¹ and an overall percent change of 510% by day 14 increasing to 0.061 ± 0.02 mg P L⁻¹ (Table 3.4).

Table 3.4. Percent change in water column SRP (mg L⁻¹) under 15 ug P L⁻¹ additions, for Barataria open water and marsh sites and Mardi Gras Pass marsh site on days 1, 2, 7, and 14. A negative (-) percent (%) change indicates a decrease in SRP concentration while a positive (+) percent change indicates an increase in SRP.

Site Type	Site #	Initial SRP (mg L ⁻¹)		SRP (mg L ⁻¹)		Percent Change (%)		
		2 d	7 d	14 d	2 d	7 d	14 d	
Open Water	21	0.011	0.021	0.03	0.053	91	43	77
Open Water	46	0.01	0.179	0.368	0.373	1690	106	1
Open Water	58	0.011	0.019	0.028	0.038	73	47	36
Marsh	4	0.067	0.139	0.228	0.07	107	64	-69
Marsh	32	0.303	0.436	0.818	0.408	44	88	-50
Marsh	33	0.106	0.093	0.109	0.06	-12	17	-45
Mardi Gras Pass	MGP	0.01	0.021	0.047	0.061	110	124	30

Phosphorus flux rates: All cores showed general trends of increasing positive flux over the sampling period. The three open water sites had SRP flux rates of 0.505, 2.58, and 0.425 mg m⁻² d⁻¹. The mean SRP flux rate for open water sites is 1.17 ± 1.22 mg m⁻² d⁻¹. The three marsh sites had SRP flux rates of 4.068, 0.629, and 0.233 mg m⁻² d⁻¹. The marsh sites had a mean SRP flux rate of 1.64 ± 2.11 mg m⁻² d⁻¹. The Mardi Gras Pass site had a mean SRP flux rate of 0.643 mg m⁻² d⁻¹.

3.3.3. 30 ug P L⁻¹ Addition

Water column SRP concentrations: Cores with 30 ug L⁻¹ P addition showed a general increase in concentration over time. The three open water sites had initial SRP concentrations of 0.022, 0.012, and 0.012 mg P L⁻¹. All open water sites showed increasing percent changes, 114, 208, and 233% respectively by day 2 of sampling. This increase represented a mean percent change increase of 185% on day 2 and a mean percent change of 16% over the 14-day incubation

period. Site 46 showed a decrease in SRP water column concentration over time and sites 21 and 58 showed an increase in percent over time. The three marsh sites had initial SRP concentrations of 0.091, 0.014 and 0.031 mg P L⁻¹. All marsh sites showed water column SRP concentration increases over the time period. The increase is represented by a mean percent increases of 2616% over the sampling period. The Mardi Gras Pass site had an initial concentration of 0.012 mg P L⁻¹. Each sampling period showed concentration increases from the initial concentration for a maximum percent change of 192% percent from day 1 to day 2 increasing from 0.012 to 0.035 ± 0.06 mg P L⁻¹, then remaining in close proximity at days 7 and 14 at 0.027 ± 0.02 and 0.026 ± 0.02 mg P L⁻¹, showing a decrease over the 14-day incubation period (Table 3.5).

Table 3.5. Percent change in water column SRP (mg L⁻¹) under 30 ug P L⁻¹ additions, for Barataria open water and marsh sites and Mardi Gras Pass marsh site on days 1, 2, 7, and 14. A negative (-) percent (%) change indicates a decrease in SRP concentration while a positive (+) percent change indicates an increase in SRP.

Site Type	Site #	Initial SRP (mg L ⁻¹)	SRP (mg L ⁻¹)			Percent Change (%)		
			2 d	7 d	14 d	2 d	7 d	14 d
Open Water	21	0.022	0.047	0.038	0.025	114	-19	-34
Open Water	46	0.012	0.037	0.01	0.011	208	-73	10
Open Water	58	0.012	0.04	0.035	0.017	233	-13	-51
Marsh	4	0.091	0.119	0.18	0.297	31	51	65
Marsh	32	0.014	0.039	0.043	0.829	179	10	1828
Marsh	33	0.031	0.057	0.158	0.589	84	177	273
Mardi Gras Pass	MGP	0.012	0.035	0.027	0.026	192	-23	-4

Phosphorus flux rates: Open water sites showed a general negative flux rate suggesting retention of P in the sediments. Marsh and Mardi Gras Pass sites showed a general trend of increasing SRP flux rates with the addition of 30 ug P L⁻¹ to the water column. The three open water sites had SRP flux rates of -0.312, -0.343, and -0.333 mg m⁻² d⁻¹. The mean SRP flux rate for open water sites is -0.329 ± 0.015 mg m⁻² d⁻¹. The three marsh sites had significantly different SRP flux rates of 2.606, 0.601, and 3.55 mg m⁻² d⁻¹ with a p-value of 0.041. The mean SRP flux

rate for marsh sites is $2.25 \pm 1.504 \text{ mg m}^{-2} \text{ d}^{-1}$. Mardi Gras Pass created marsh site had a SRP flux rate of $0.200 \text{ mg m}^{-2} \text{ d}^{-1}$.

3.3.4. 60 ug P L⁻¹ Addition

Water column SRP concentrations: Open water and marsh cores with 60 ug P L⁻¹ addition showed general decreases in water column SRP concentration over time. Mardi Gras Pass sediment showed steady increase. The three open water sites had initial concentrations of 0.09, 0.128, and 0.123 mg P L⁻¹. This is represented by a mean percent change of -40.7% over the 14-day period. All open water samples showed decreases in water column concentration over the time period with site 21 being the only station to have an increased concentration on day 14 that was $0.12 \pm 0.06 \text{ mg P L}^{-1}$. The three marsh sites had initial concentrations of 0.085, 0.114, and 0.106 mg P L⁻¹. All marsh sites showed decreases in water column concentration representing a mean percent change of -71.3%. Mardi Gras Pass had an initial water column SRP concentration of 0.011 mg P L⁻¹. Over time Mardi Gras Pass has a percent change of 327% with a $0.047 \pm 0.02 \text{ mg P L}^{-1}$ on day 14. Mardi Gras Pass is the only soil type that showed steady increase throughout the time period at 60 ug P L⁻¹ addition (Table 3.6).

Table 3.6. Percent change in water column SRP (mg L⁻¹) under 60 ug P L⁻¹ additions, for Barataria open water and marsh sites and Mardi Gras Pass marsh site on days 1, 2, 7, and 14. A negative (-) percent (%) change indicates a decrease in SRP concentration while a positive (+) percent change indicates an increase in SRP.

Site Type	Site #	Initial SRP (mg L ⁻¹)		SRP (mg L ⁻¹)		Percent Change (%)		
		2 d	7 d	14 d	2 d	7 d	14 d	
Open Water	21	0.09	0.062	0.039	0.12	-31	-37	208
Open Water	46	0.128	0.165	0.048	0.019	29	-71	-60
Open Water	58	0.123	0.113	0.087	0.037	-8	-23	-57
Marsh	4	0.085	0.064	0.054	0.04	-25	-16	-26
Marsh	32	0.114	0.093	0.053	0.033	-18	-43	-38
Marsh	33	0.106	0.078	0.021	0.011	-26	-73	-48
Mardi Gras Pass	MGP	0.011	0.057	0.049	0.047	418	-14	-4

Phosphorus flux rates: The addition of 60 ug P L^{-1} most closely resembles the SRP concentration of the Mississippi River water that will be diverted over these Barataria sediments (White et al., 2009; Zhang et al., 2012). The general trend of P flux across all cores was a decrease in flux rate indicating retention of P to the sediments from the water column. The three open water sites had P flux rates of -1.23 , -1.41 , and $-1.097 \text{ mg m}^{-2} \text{ d}^{-1}$. The mean SRP flux rate for open water sites at 60 ug P L^{-1} addition is $-1.25 \pm 0.15 \text{ mg m}^{-2} \text{ d}^{-1}$. The three marsh sites had SRP flux rates of -0.582 , -1.609 , and $-2.26 \text{ mg m}^{-2} \text{ d}^{-1}$. The mean SRP flux rate for marsh sites at 60 ug P L^{-1} addition is $-1.48 \pm 0.84 \text{ mg m}^{-2} \text{ d}^{-1}$. The Mardi Gras Pass site had a SRP flux rate under approximate river SRP concentrations of $-0.136 \text{ mg m}^{-2} \text{ d}^{-1}$, which is an order of magnitude lower than the Barataria Bay sites. This result is likely due to the fact that this site continually receives Mississippi River water year-round and many of the sorption sites are already occupied.

3.3.5. 150 ug P L^{-1} Addition

Water column SRP concentrations: All cores showed general decrease in water column SRP concentration over time. The three open water sites had initial water column SRP concentrations of 0.231 , 0.260 , and $0.414 \text{ mg P L}^{-1}$. All open water sites showed percent change decreases from day 1 to day 2 and 7. Sites 21 and 58 had percent change decreases of -32 and -75% by day 14 representing concentrations of 0.158 ± 0.06 and $0.102 \pm 0.04 \text{ mg P L}^{-1}$. There was a mean percent change of -30% over the sampling period. The three marsh sites had initial concentrations of 0.238 , 0.285 , and $0.233 \text{ mg P L}^{-1}$. All marsh sites showed general decreases in water column concentration with the addition of 150 ug P L^{-1} to the water column. Marsh sites showed mean percent change decrease of -90.7% by day 14. The Mardi Gras Pass location had an initial concentration of $0.021 \text{ mg P L}^{-1}$ and showed a percent change increase of 710% on day

2 then a decrease of percent change of 271% on day 7 and finally percent change decrease to 76% change by day 14. Mardi Gras Pass was the only soil to have initial increase in concentration over the first time period but showed decreases in concentration over time (Table 3.7).

Table 3.7. Percent change in water column SRP (mg L^{-1}) under 150 ug P L^{-1} additions, for Barataria open water and marsh sites and Mardi Gras Pass marsh site on days 1, 2, 7, and 14. A negative (-) percent (%) change indicates a decrease in SRP concentration while a positive (+) percent change indicates an increase in SRP.

Site Type	Site #	Initial SRP (mg L^{-1})	SRP (mg L^{-1})			Percent Change (%)		
			2 d	7 d	14 d	2 d	7 d	14 d
Open Water	21	0.231	0.156	0.138	0.158	-32	-12	14
Open Water	46	0.26	0.246	0.229	0.303	-5	-7	32
Open Water	58	0.414	0.304	0.219	0.102	-27	-28	-53
Marsh	4	0.238	0.189	0.02	0.029	-21	-89	45
Marsh	32	0.285	0.256	0.071	0.031	-10	-72	-56
Marsh	33	0.233	0.124	0.014	0.011	-47	-89	-21
Mardi Gras Pass	MGP	0.021	0.17	0.078	0.037	710	-54	-53

Phosphorus flux rates: With the addition of 150 ug P L^{-1} the general trend of negative P flux rate was consistent across all cores. The three open water sites had P flux rates of -1.98, -0.78, and $-3.61 \text{ mg m}^{-2} \text{ d}^{-1}$. The mean SRP flux rate for open water sites is $-2.13 \pm 1.42 \text{ mg m}^{-2} \text{ d}^{-1}$. The three marsh sites had significantly greater SRP flux rates into the sediments of -6.038, -6.14, and $-5.41 \text{ mg m}^{-2} \text{ d}^{-1}$ with a p-value of 0.012. The mean SRP flux rate for marsh sites is $-5.86 \pm 0.39 \text{ mg m}^{-2} \text{ d}^{-1}$. The Mardi Gras Pass site had a SRP flux rate of $-1.83 \text{ mg m}^{-2} \text{ d}^{-1}$.

3.3.7. Equilibrium Phosphorus Concentration

The equilibrium phosphorus concentration tells us whether estuarine and wetland sediments are releasing or retaining P based on specific water column SRP concentrations. The SRP flux rates were determined under five water column concentrations (0, 15, 30, 60, 150 ug P

L⁻¹). Sediments function as a source of P at water column concentrations less than the EPC and as a sink of P at water column concentrations greater than the EPC.

Water column SRP concentrations increased in control cores representing P release from the sediment to the water column and generally decreased at high P additions (60 and 150 ug P L⁻¹), suggesting P sorption by the sediments for the open water and marsh sites (Table 3.8).

Table 3.8. Barataria open water and marsh and Mardi Gras Pass equilibrium phosphorus concentration averages and for each site.

Site Type	Site	EPC (mg P L ⁻¹)
Open Water	21	0.024
Open Water	46	0.007
Open Water	58	0.017
Open Water	Mean	0.016 ± 0.008
Marsh	4	0.055
Marsh	32	0.036
Marsh	33	0.026
Marsh	Mean	0.039 ± 0.015
Mardi Gras Pass	MGP	0.057

By calculating the equilibrium phosphorus concentrations of both open water and marsh sites and Mardi Gras Pass an environmental prediction can be made on the area of influence of the Mid-Barataria sediment diversion. Sutula et al. (2004) reported Mississippi River SRP values in April 1999 at 0.056 mg P L⁻¹ and in November 1999 at 0.099 mg P L⁻¹.

Marsh sites 4, 32, and 33 had EPC values of 0.055, 0.036, and 0.026 mg P L⁻¹ respectively (Table 3.8; Figure 3.5). Marsh site 4 holds an EPC value closest to Mississippi River conditions yielding the potential possibility of slower P uptake from the water column to the sediment post exposure to Mississippi River water from the diversion. The lower concentrations

of marsh sites 32 and 33 show to have the ability to sequester P more so than site 4 upon the exposure of Mississippi River SRP.

Open water sites 21, 46, and 58 had EPC values of 0.024, 0.007, and 0.017 mg P L⁻¹ respectively (Table 3.8; Figure 3.6). This finding demonstrates that the open water sites are unlikely to release P when the Mississippi River water (concentration ~ 0.70 mg P L⁻¹) is introduced into the basin. Additionally, there are numerous sorption sites available to take P out of the water column during the pulsed operation of the sediment diversion. The water column concentrations would need to be very low post closure of the sediment diversion for there to be significant flux out of the soil. This condition would not be conducive for algal bloom formation.

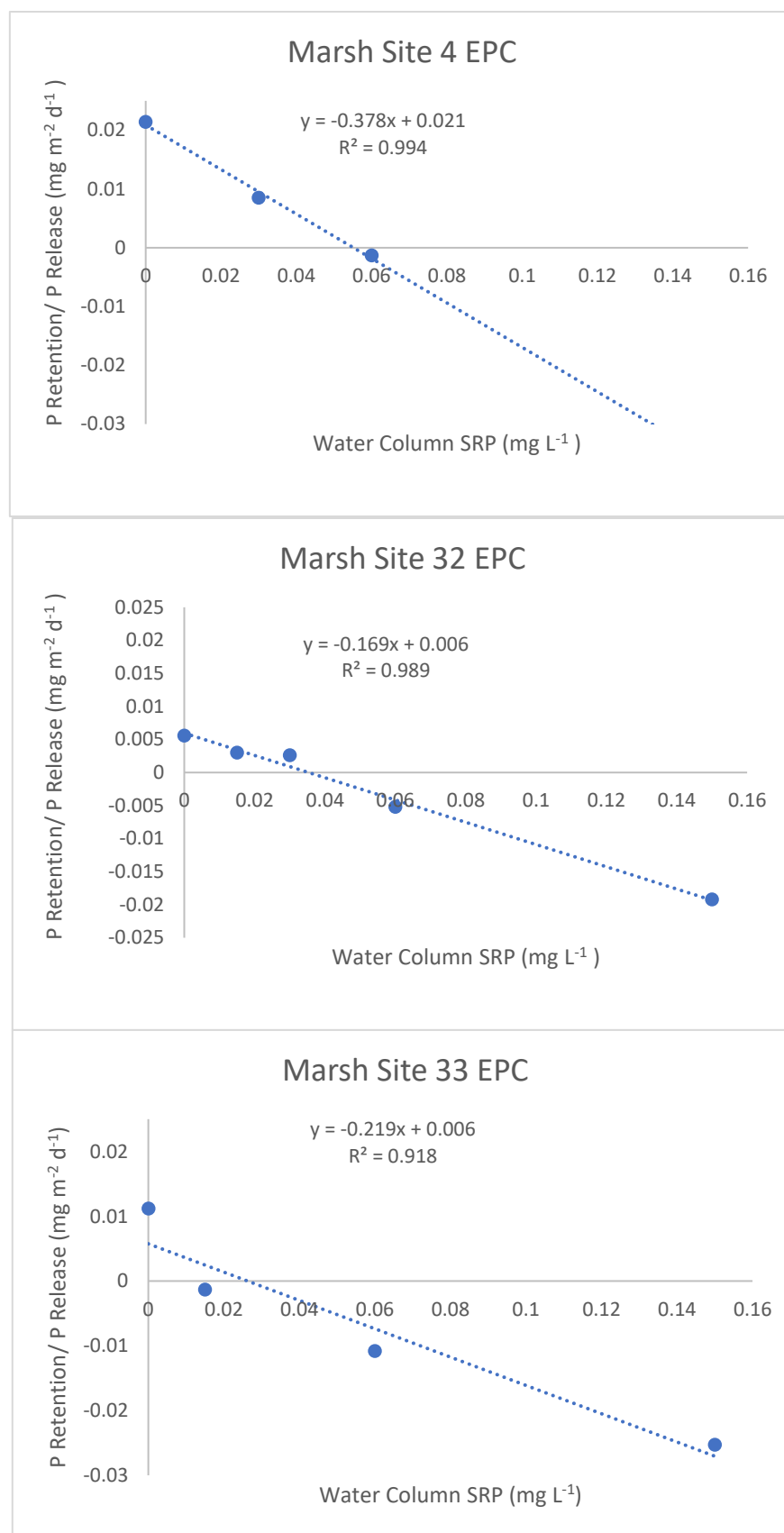


Figure 3.5. Graphs of 3 Barataria marsh site equilibrium phosphorus concentrations.

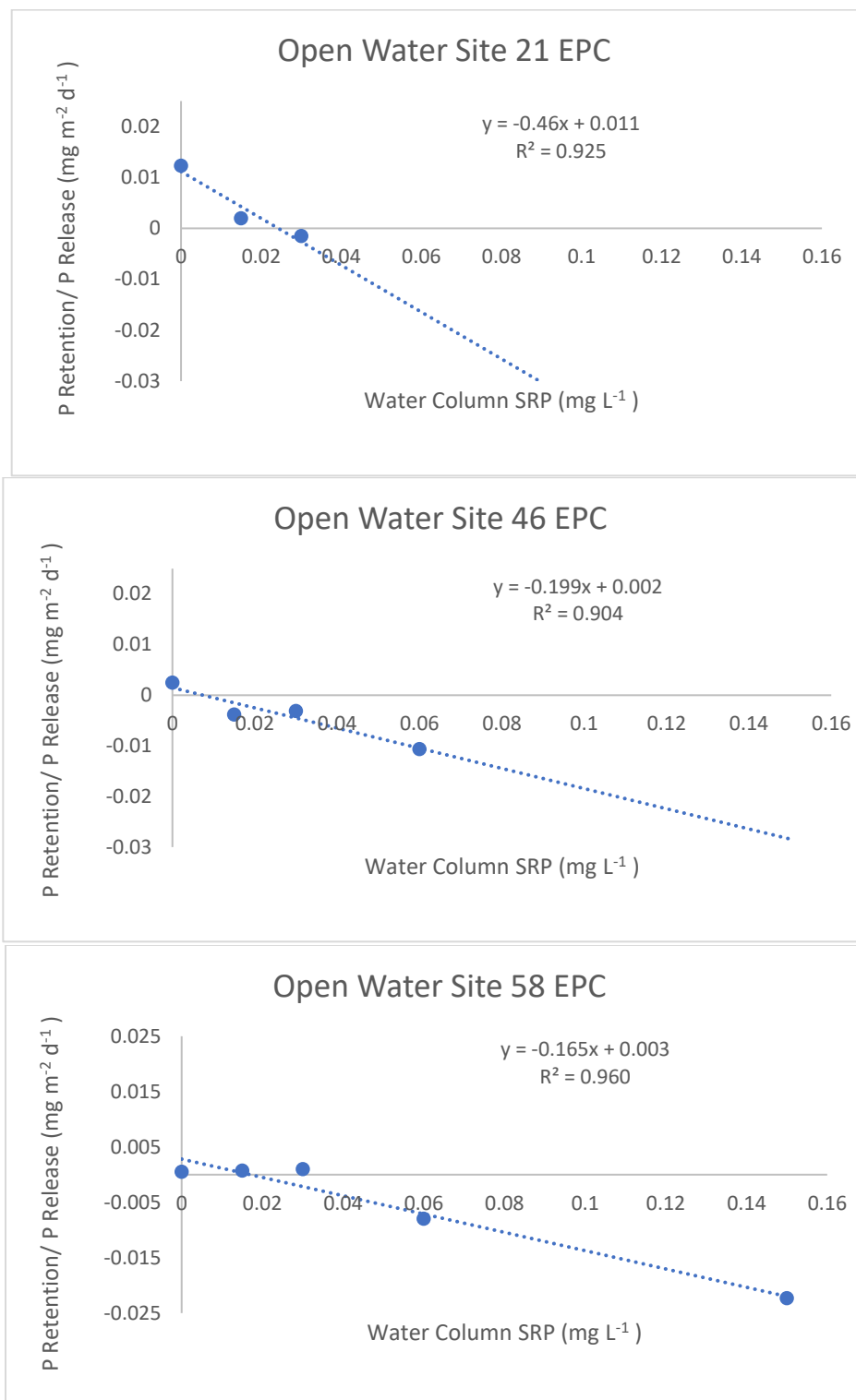


Figure 3.6. Graphs of Barataria open water site equilibrium phosphorus concentrations.

Mardi Gras Pass, which has been continually exposed to Mississippi River conditions for nearly 10 years, holds the highest EPC of 0.057 mg P L⁻¹, which is the closest to Mississippi River water column SRP concentrations. This result suggests that the sediment exchange sites are nearly full with little room for additional sorption because the EPC is close to the Mississippi River SRP concentration (Figure 3.7).

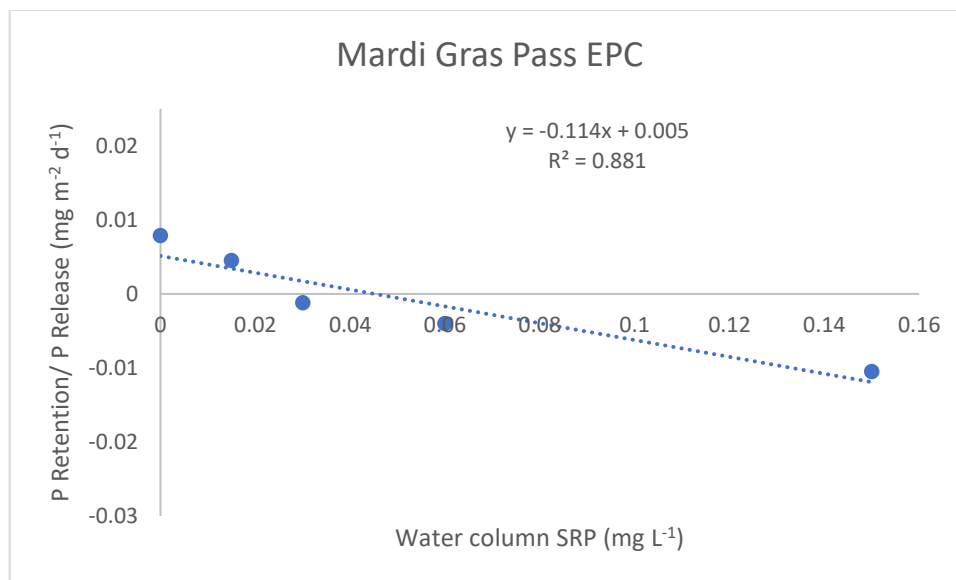


Figure 3.7. Graph of Mardi Gras Pass site equilibrium phosphorus concentration.

3.4. Diversion Impacts on Barataria Bay

The Mid-Barataria sediment diversion, during a month of operation at full capacity, is expected to deliver an estimated approximate 385 Mt of SRP at river concentration 70 ug P L⁻¹, which will be immediately available for biologic uptake. In this study, the control cores with no added P spike represent the current baseline conditions of the Barataria marsh and

open water environments that would be influenced by the Mid-Barataria sediment diversion. The cores spiked with 60 ug P L^{-1} best represent the SRP concentration of Mississippi River water that would come in with the diversion though the river SRP concentrations have been found to be in the $70\text{-}80 \text{ ug P L}^{-1}$ range. The Mardi Gras Pass site is an example of an environment that continually receives river sediment SRP year-round which is also the sediment that will be deposited over the organic wetland soil currently in the Barataria Basin. Based on the flux rates from the control and 60 ug P L^{-1} spiked cores we can expect an initial retention of P to the sediment in Barataria Bay, followed by a release back into the water column until the EPC is met.

Barataria marsh control cores showed positive flux rates from the sediment to the water column. The addition of 60 ug P L^{-1} spike altered the direction of flux in all Barataria marsh cores, changing the mean control core SRP flux rate from $4.6 \pm 0.696 \text{ mg m}^{-2} \text{ d}^{-1}$ to $-1.48 \pm 0.844 \text{ mg m}^{-2} \text{ d}^{-1}$ (Figure 3.8). This alteration of flux rate suggests that with the opening of the Mid-Barataria sediment diversion into the Barataria Bay marsh sites SRP will initially be retained by the sediments until the mean marsh EPC of 0.039 ± 0.015 is met.

Table 3.9. Mean SRP flux rates across all control and spike cores ($\text{mg m}^{-2} \text{ d}^{-1}$). 0 ug L^{-1} represents current wetland conditions. 60 ug L^{-1} best represents SRP levels of Mississippi River.

Site Type	0 ug L^{-1}	15 ug L^{-1}	30 ug L^{-1}	60 ug L^{-1}	150 ug L^{-1}
Barataria Marsh	4.59 ± 0.69	1.64 ± 2.1	2.25 ± 1.5	-1.48 ± 0.84	-5.86 ± 0.39
Barataria Open Water	1.01 ± 0.83	1.17 ± 1.22	-0.329 ± 0.02	-1.24 ± 0.15	-2.13 ± 1.42
Mardi Gras Pass	1.006	0.643	0.2	-0.136	-1.83

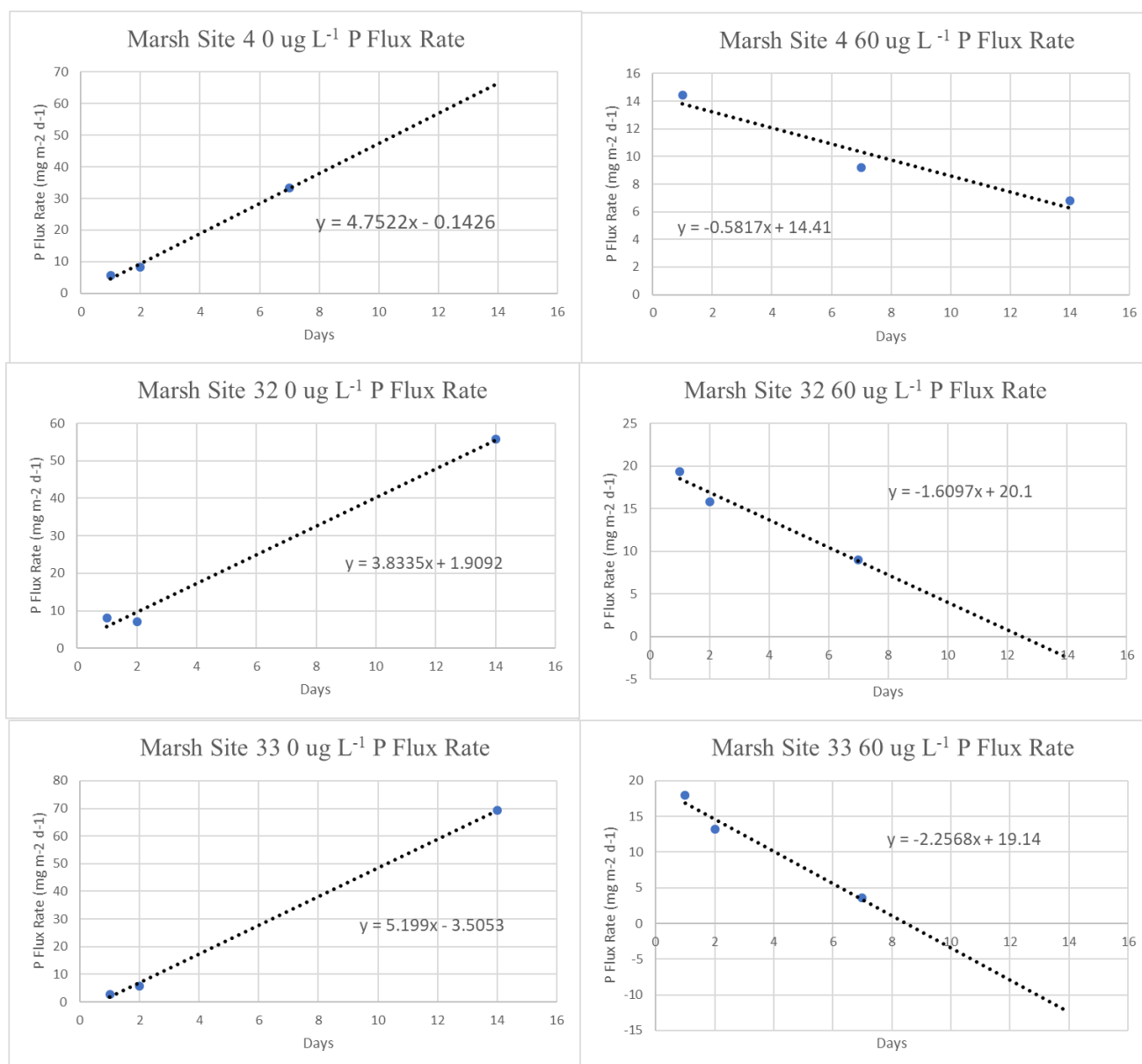


Figure 3.8. Graphs comparing marsh control flux rates to 60 ug L⁻¹, concentration most closely resembling Mississippi river SRP concentrations.

Barataria open water site control cores had positive flux rates from the sediment to the water column. The addition of 60 ug P L⁻¹ spike reversed the direction of the flux in all Barataria open water cores, leading to a change in mean control core SRP flux rate from 1.014 ± 0.832 mg m⁻² d⁻¹ out of soil to -1.25 ± 0.155 mg m⁻² d⁻¹ into the soil (Figure 3.9). This change in direction of flux suggests that with the opening of the Mid-Barataria sediment diversion into the Barataria Bay open water sites, SRP will initially be retained by the sediments until water column

concentrations drop below $0.016 \text{ ug P L}^{-1}$ at which point a release of SRP will begin until the EPC is met. Over time, the EPC can be expected to increase as more and more river sediment is added to Barataria Bay, moving closer toward the higher EPC of river sediment.

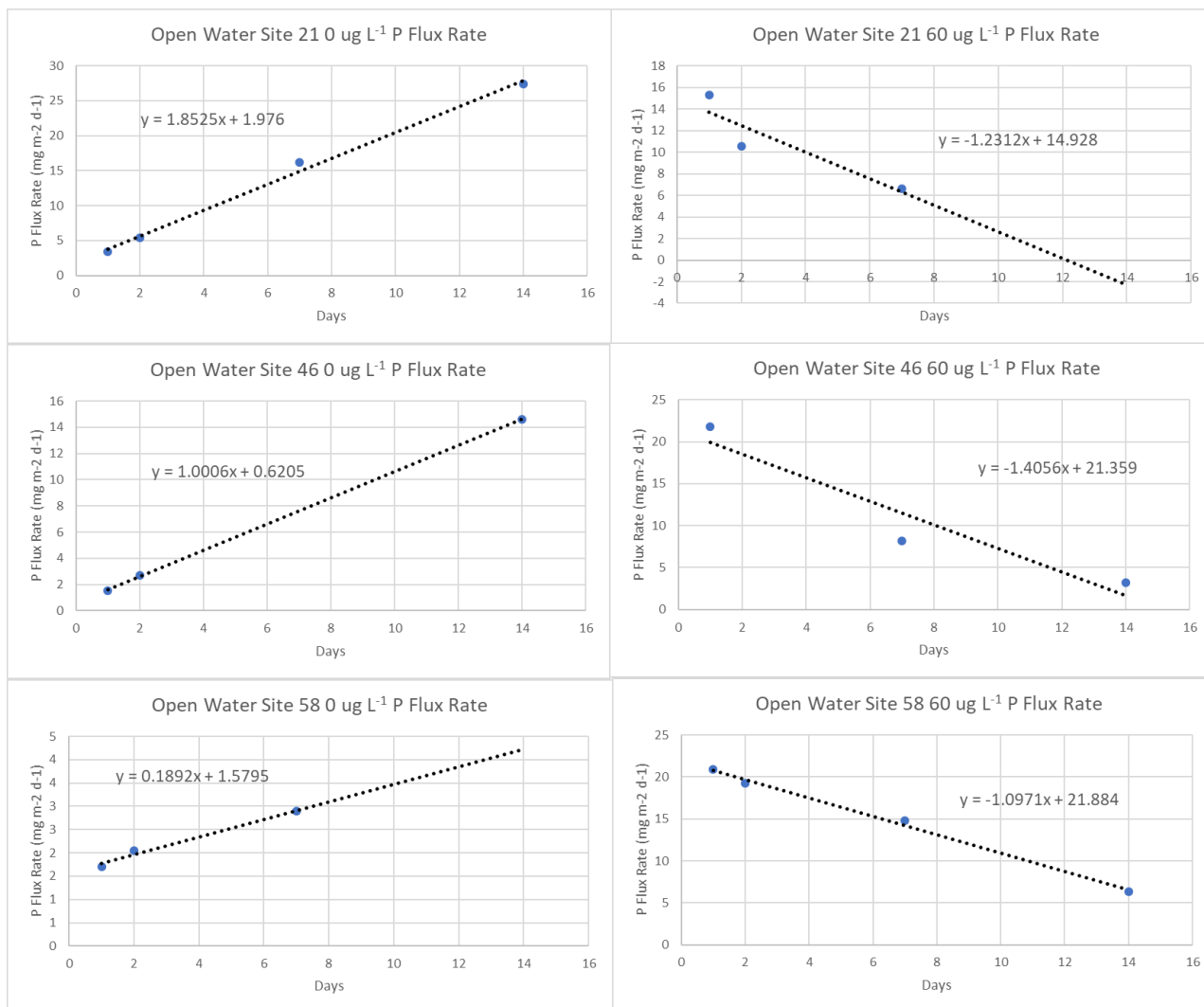


Figure 3.9. Graphs comparing open water site control flux rates to 60 ug L^{-1} spike addition, the concentration most closely resembling the concentration of the Mississippi River.

Mardi Gras Pass is created from sediment that have been recently deposited from the Mississippi River. This sediment represents the sediment that the Mid-Barataria sediment diversion will deposit on to the organic soils of Barataria Bay. Mardi Gras Pass control core had

a SRP flux rate of $1.0057 \text{ mg m}^{-2} \text{ d}^{-1}$. With the addition of a 60 ug P L^{-1} spike, the P flux rate changed direction to $-0.136 \text{ mg m}^{-2} \text{ d}^{-1}$ into the sediment (Figure 3.10).

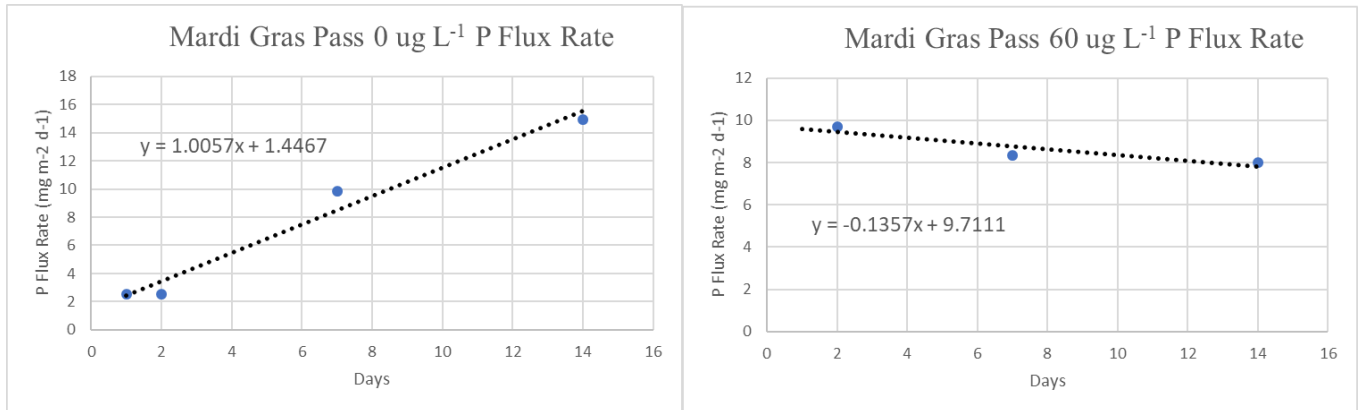


Figure 3.10. Graph comparing Mardi Gras Pass control flux rates to 60 ug L^{-1} spike addition, most closely resembling the concentration of the Mississippi River.

Table 3.10. Correlation between both open water and marsh site flux rates with total P fractionation pools. $n=7$, $r > 0.754$, and $P < 0.05$. Significant values are in bold.

	Flux Rate $\text{mg m}^{-2} \text{ d}^{-1}$	TP mg P kg^{-1}	NaOH Po mg P kg^{-1}	Residue Po mg P kg^{-1}	KCl Pi mg P kg^{-1}	NaOH Pi mg P kg^{-1}
TP	0.798					
NaOH Po	0.825	0.885				
Residue Po	0.482	0.856	0.823			
KCl Pi	-0.679	-0.352	-0.382	-0.123		
NaOH Pi	0.273	0.318	0.263	0.235	-0.631	
HCl Pi	0.189	-0.015	-0.208	-0.331	-0.659	0.714

3.5. Conclusions

The distribution of total organic P in Barataria open water and marsh sediments contains 59 and 70% of the total P. Mardi Gras Pass sediments are heavily dominated in the total inorganic P portion representing 97% of the total P breakdown. With the introduction of the Mississippi River it is expected that Barataria sediments will shift the majority portion total P to the total inorganic P form from the organic P form. As seen from Mardi Gras Pass sediments, Barataria sediments will likely be covered with a mineral layer (Figure 3.11).

Water column SRP concentrations for control cores with no added P showed general increases in SRP concentration over the 14-day incubation period. Barataria open water and marsh sites had EPC values of 0.016 and 0.042 mg P L⁻¹, indicating sorptive potential under the influence of Mississippi River water SRP levels (~0.07 mg P L⁻¹). Mardi Gras Pass site has a greater EPC value, 0.057 mg P L⁻¹, than the Barataria sites indicating an increase in EPC with operation of the river diversion over time. Barataria sediment EPC are currently below the reported Mississippi River SRP concentrations, indicating that upon exposure to Mississippi River SRP levels, SRP flux in Barataria sediments are expected to flux into the sediment. With the increased operation of the Mid-Barataria sediment diversion, the EPC and total P of Barataria sediments is forecasted to increase with each deposition event from the diversion. This increases the implication of available P release from the sediment to the water column for potential harmful algal bloom uptake.

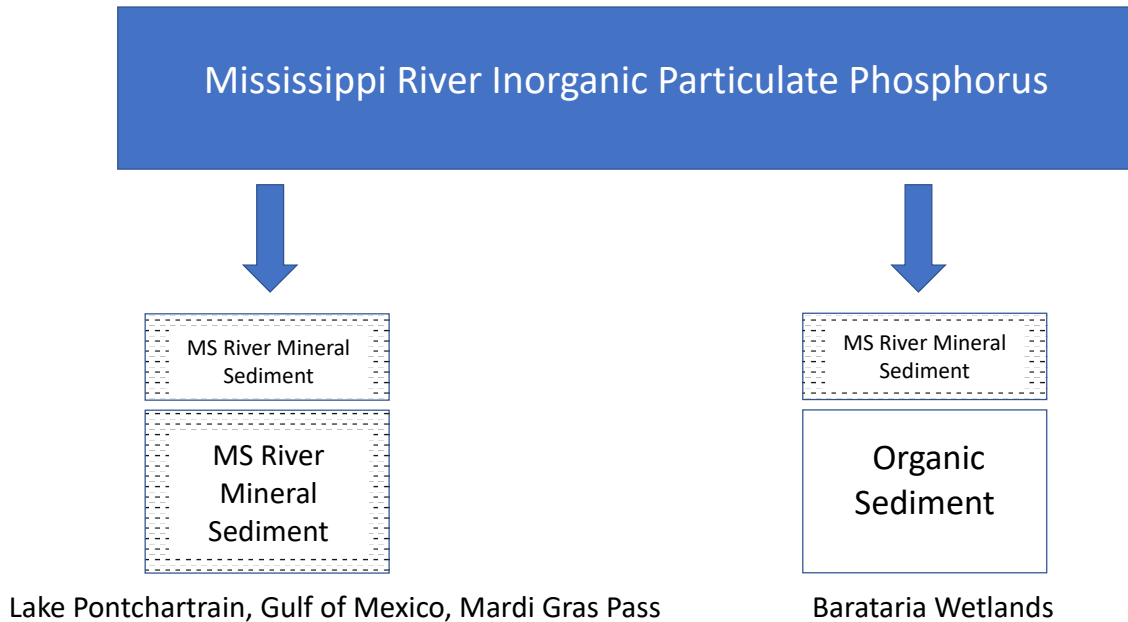


Figure 3.11. Diagram of Mississippi River inorganic phosphorus being deposited into several inorganic river influenced wetland areas of Louisiana compared to Mississippi River inorganic phosphorus being deposited onto Barataria organic sediment.

Mardi Gras Pass sediments are exposed to Mississippi River flows year-round leading to minimal sorptive P capacity of the deposited sediments. The Mid-Barataria sediment diversion will be operated only at high flood stages, giving Mississippi River sediments deposited into Barataria Basin time to settle and for P to be released from the sediments to the water column. This time between diversion operations will allow Barataria sediments greater time for sorptive P exchange from the sediments to the water column.

3.5.1. Implications For Restoration: Future Research Needed

This research has amassed baseline wetland and estuarine soil characteristics for the area of land build influence of the Mid-Barataria sediment diversion. In order to use this research to its maximum potential there are select areas of research that need further investigation.

Harmful algal blooms are a potential primary negative implication of Mississippi River sediment diversions. Further research on algal species composition and abundance in the area of diversion influence is needed in order to successfully predict and fully understand the magnitude of this river reconnection implication. Characterization of the phosphorus fractionation changes in Mississippi River sediments that have already been diverted into riparian wetlands, such as Mardi Gras Pass sediments, can yield more realistic predictions as to the distribution of available phosphorus pools post operation of the diversion.

There are several real-world environmental factors that have not been taken into consideration while the baseline soil characteristics of the area of influence have been investigated. It is known that Mississippi River sediment that is rich in mineral inorganic phosphorus however the fate of this material once deposited on top of a highly organic soil is unknown and there are no current analogs. Disturbances such as hurricanes, tidal forces and cold fronts are among many physical agitations that can potentially alter the phosphorus retention dynamics of the basin. A better understanding of the relationship between the turbidity of the water column under such circumstances and the phosphorus dynamics can better help coastal managers better predict potential expressions of eutrophication such as algal blooms. In addition, understanding the P dynamics and phytoplankton preferences in a shifting salinity regime is also something not well documented for the coastal basin.

Ultimately, this research serves as a first step or baseline sediment characteristics for the predicted most dynamic region of Barataria Basin before the planned Mid-Barataria sediment diversion is operated, that is the area where the majority of the land building will take place. The spatial scope of this research should be expanded pre diversion to better understand the baseline sediment conditions in more distal open water regions and marsh areas so that a post diversion

characterization will provide direct evidence of the extent of sedimentation and nutrient impacts throughout the entire coastal basin. This data can be used to calibrate existing models for Barataria Basin as well as fine tune future modelling efforts for additional planned sediment diversions.

APPENDIX A. BARATARIA SEDIMENT CHARACTERISTICS

A.1. Barataria Open Water Soil Characteristics From 0-10 cm Interval.

Open Water Sample ID	Bulk Density g cm ⁻³	LOI %	MC %	TP mg P kg ⁻¹	TIP mg P kg ⁻¹	TOP mg P kg ⁻¹
2	0.120	46.2	0.888	538.2	185.1	353.1
5	0.102	51.5	0.902	642.3	154.0	488.3
6	0.188	44.7	0.835	521.0	131.9	389.1
7	0.167	42.3	0.850	495.5	110.1	385.4
11	0.164	36.8	0.852	475.2	225.5	249.7
12	0.084	76.4	0.916	400.6	89.0	311.6
13	0.168	36.3	0.837	705.8	328.5	377.4
16	0.276	35.5	0.763	350.0	195.0	155.0
18	0.332	16.7	0.723	460.0	305.8	154.2
19	0.314	19.1	0.736	507.2	295.9	211.3
21	0.240	24.7	0.796	557.5	407.8	149.7
28	0.194	31.3	0.826	573.1	362.2	210.8
30	0.309	19.2	0.730	498.3	293.9	204.4
31	0.134	37.3	0.861	541.5	126.2	415.2
37	0.171	31.8	0.827	540.2	225.8	314.4
46	0.085	74.1	0.918	415.4	79.4	336.0
47	0.067	81.3	0.933	360.3	46.6	313.8
48	0.256	18.7	0.765	484.5	311.8	172.7
49	0.107	70.1	0.894	412.1	128.1	284.0
50	0.125	48.1	0.881	570.1	266.0	304.1
52	0.196	36.7	0.826	438.5	165.8	272.7
53	0.403	17.0	0.702	417.4	282.5	134.9
54	0.117	52.6	0.889	628.6	124.0	504.6
58	0.118	47.0	0.888	583.9	165.3	418.6

A.2. Barataria Marsh Site Sediment Characteristics in Top 0-10 cm Interval.

Marsh Sample ID	Bulk Density g cm ⁻³	LOI %	MC %	TP mg P kg ⁻¹	TIP mg P kg ⁻¹	TOP mg P kg ⁻¹
1	0.168	45.4	84.4	634.8	118.4	516.4
3	0.152	46.3	86.0	490.7	118.9	371.8
4	0.193	52.5	81.8	961.0	262.9	698.1
8	0.145	46.2	86.3	690.9	161.5	529.4
9	0.160	57.7	85.0	895.3	186.9	708.3
10	0.144	70.3	85.4	594.5	132.0	462.5
14A	0.230	29.6	80.0	561.5	151.4	410.1
14B	0.249	27.2	77.7	531.9	192.9	338.9
14C	0.186	35.0	81.9	607.8	146.7	461.1
15	0.151	42.5	85.4	559.8	117.7	442.1
17A	0.136	51.0	87.3	675.5	116.0	559.5
17B	0.174	42.0	83.9	648.1	145.9	502.2
17C	0.180	37.5	83.3	535.2	131.6	403.5
20	0.179	42.3	81.8	550.7	136.8	413.9
22	0.138	62.7	85.1	622.9	140.2	482.7
23	0.156	48.0	85.7	973.0	273.2	699.9
24	0.240	22.5	78.1	546.8	280.3	266.5
25	0.310	21.5	74.2	448.4	274.9	173.5
26	0.145	53.7	85.7	621.1	101.6	519.5
27	0.194	34.6	81.6	740.8	192.3	548.5
29	0.273	25.6	76.4	547.6	234.3	313.3
32A	0.366	17.6	71.3	476.0	318.5	157.5
32B	0.346	16.9	70.8	537.0	353.5	183.6
32C	0.315	18.0	73.7	527.2	313.6	213.6
33	0.289	28.6	75.2	489.1	210.1	279.0
34	0.086	51.7	91.5	757.2	106.2	651.0
35	0.130	49.1	88.1	692.7	175.1	517.6
36	0.167	38.9	85.0	668.2	188.8	479.4
38	0.286	24.4	75.7	483.4	189.8	293.6
39	0.187	32.4	81.8	551.4	125.6	425.7
40	0.182	37.8	82.4	919.9	300.7	619.3
41	0.208	38.8	80.8	611.2	126.4	484.8
42	0.188	39.4	82.1	778.4	230.6	547.8
43	0.242	28.3	78.2	547.3	233.1	314.3
44	0.182	31.3	82.0	590.4	162.2	428.2
45	0.091	53.2	91.6	746.8	139.2	607.6
51A	0.227	30.5	78.3	768.0	407.3	360.7
51B	0.158	44.2	84.3	784.8	176.4	608.5
51C	0.198	36.3	80.8	960.8	283.6	677.2
55	0.162	34.6	85.2	592.6	151.9	440.8
56	0.130	47.8	87.8	595.2	110.9	484.3
57A	0.155	59.2	83.2	1360.9	558.5	802.4
57B	0.159	59.3	83.6	1187.9	380.8	807.1
57C	0.173	53.6	83.2	1288.4	465.4	823.0
59	0.211	36.8	80.3	693.9	158.4	535.5
60	0.136	45.1	87.3	886.7	199.8	686.9

APPENDIX B. BARATARIA PHOSPHORUS FRACTIONATION DATA

B.1 Barataria Open Water Site Fractionation Data.

Site Type	ID	KCL P mg P kg ⁻¹	NaOH- SRP mg P kg ⁻¹	NaOH -Po mg P kg ⁻¹	HCL-P mg P kg ⁻¹	Residue P mg P kg ⁻¹	Sum TP mg P kg ⁻¹	TP sample mg P kg ⁻¹
Open Water	37	1.00	90.2	84.1	85.3	220.1	480.8	540.2
Open Water	58	1.64	67.5	103.5	38.1	276.3	487.0	583.9
Open Water	46	2.58	23.3	52.7	17.4	164.9	260.8	415.4
Open Water	48	0.73	170.6	61.6	179.0	155.4	567.3	484.5
Open Water	49	1.89	36.6	76.9	147.5	261.9	524.9	412.1
Open Water	16	0.68	24.5	39.5	62.3	125.0	252.0	350.0
Open Water	21	0.90	299.7	117.4	217.9	221.5	857.4	557.5

B.2 Barataria Marsh Site Fractionation Data.

Site Type	ID	KCL P mg P kg ⁻¹	NaOH- SRP mg P kg ⁻¹	NaOH -Po mg P kg ⁻¹	HCL-P mg P kg ⁻¹	Residue P mg P kg ⁻¹	Sum TP mg P kg ⁻¹	TP sample mg P kg ⁻¹
Marsh	4	1.06	160.7	331.3	84.1	344.0	921.3	961.0
Marsh	8	1.31	54.2	230.8	49.9	275.2	611.5	690.9
Marsh	55	1.28	92.5	213.3	97.1	269.8	674.0	592.6
Marsh	56	1.40	118.8	210.4	88.4	273.0	692.0	595.2
Marsh	33	0.75	90.5	161.3	91.8	177.0	521.3	489.1
Marsh	34	3.10	70.5	253.7	50.3	341.9	719.4	757.2
Marsh	43	0.93	87.9	122.3	102.6	155.0	468.8	547.3
Marsh	44	1.07	63.9	266.9	99.1	252.6	683.5	590.4
Marsh	44R	1.09	48.8	230.2	88.9	231.1	600.1	590.4
Marsh	20	0.97	45.7	135.2	82.9	244.3	509.1	550.7
Marsh	22	1.29	99.8	258.9	63.8	366.5	790.3	622.9
Marsh	24	0.81	117.0	79.8	205.4	221.2	624.3	546.8
Marsh	26	1.15	90.7	251.2	125.0	370.5	838.4	621.1
Marsh	32	1.01	120.9	33.2	235.0	134.4	524.5	476.0
Marsh	32R	0.57	83.2	41.4	277.0	150.7	552.8	604.7

APPENDIX C. BARATARIA SAMPLING SITE COORDINATES

C.1 Marsh Site Coordinates for Barataria Bay. All latitude coordinates are N and all longitude coordinates are W.

Sample ID	Latitude	Longitude
1	29.61711	89.96435
3	29.62742	-89.9932
4	29.63149	-90.0152
8	29.60241	-89.9663
9	29.60051	89.97849
10	29.61028	90.00735
14	29.54037	-89.9521
15	29.54709	-89.9418
17	29.54986	-89.9467
20	29.54679	-89.9813
22	29.56852	-89.9946
23	29.5433	89.97057
24	29.545	-89.9305
25	29.55307	-89.9211
26	29.55008	-89.9732
27	29.56852	-89.9601
29	29.57494	-89.9596
32	29.56949	-89.9439
33	29.57576	-90.0002
34	29.58285	-89.9553
35	29.59748	-90.0032
36	29.58226	-89.9643
38	29.58233	-90.0052
39	29.58532	-90.0132
40	29.58964	-90.0279
41	29.57949	-89.9734
42	29.58963	89.9715
43	29.57725	-89.9885
44	29.5936	-90.011
45	29.59606	-90.0208
51	29.5886	-89.9952
55	29.63548	-90.0055
56	29.59055	-89.9808
57	29.60564	-89.9786
59	29.60564	-89.9786
60	29.59496	-89.9994
MGP	29.5254	89.68543

C.2 Open Water Site Coordinates for Barataria Bay. All latitude coordinates are N. All longitude coordinates are W.

Sample ID	Lattitude	Longitude
2	29.638	-90.0082
5	29.62278	-89.9823
6	29.61502	-89.9628
7	29.62039	-89.9904
11	29.62293	-90.0176
12	29.60554	-89.9973
13	29.60308	-89.9875
16	29.55083	-89.997
18	29.56329	-89.979
19	29.56658	-89.9784
21	29.56165	-89.9348
28	29.57225	-89.963
30	29.5618	-90.0048
31	29.55635	-89.9473
37	29.59442	-89.9775
46	29.60524	-90.0269
47	29.60562	-90.0188
48	29.59905	-90.0377
49	29.58733	-89.9855
50	29.61345	-90.0271
52	29.60938	-90.0352
53	29.56107	-89.9645
54	29.63548	-90.0055
58	29.60564	-89.9786

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VITA

Peter Mates grew up in Evanston, Illinois with his parents Chris and Mindy Mates, brother Brian Mates and sister Julia Mates. He played Baseball at Evanston Township High School as well as participating in the school jazz band. Peter spent the majority of his free time outside playing sports and bordered by the coasts of Lake Michigan.

Peter studied Coastal and Environmental Science at Louisiana State University's School of the Coast and Environment and minored in Disaster Science Management. He worked as a lab assistant to Dr. John R. White in the Wetland and Aquatic Biogeochemistry Laboratory (WABL) and eventually went on to pursue his masters degree in the same lab. As an undergraduate laboratory assistant Peter assisted in the processing and analysis of CRMS and SWAMP samples for nutrient analysis. He plans to graduate with his masters of science degree in Oceanography and Coastal Sciences this August 2020.

Peter continued his work under Dr. John R. White in the WABL researching the preliminary estuarine and wetland soil characteristics related to sediment diversions. His master's research has strengthened Peter's interest in understanding nutrient dynamics in coastal systems. Peter hopes to continue his work in the coastal environmental field in the New Orleans area working on the implementations and effects of sediment diversions.