



The denitrification potential of eroding wetlands in Barataria Bay, LA, USA: Implications for river reconnection



Jessica Vaccare^a, Ehab Meselhe^b, John R. White^{a,*}

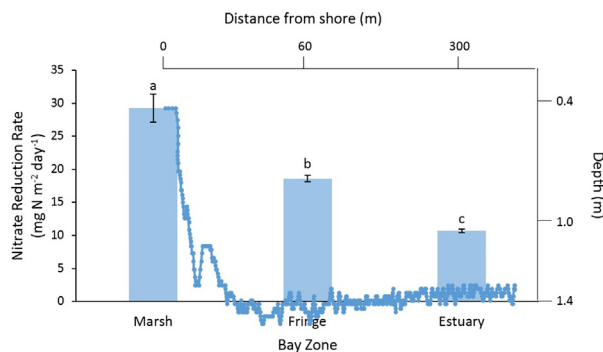
^a Department of Oceanography and Coastal Sciences, Louisiana State University, Baton Rouge, LA, United States

^b Department of River-Coastal Science and Engineering, Tulane University, New Orleans, LA, United States

HIGHLIGHTS

- NO₃ reduction rate of the submerged, eroded peat was within reported denitrification rates for a variety of brackish marshes
- the majority (~93%) of added NO₃ was converted to N₂O, indicating that denitrification was the major NO₃ reduction pathway
- the submerged, eroded marsh soils will most likely play a large role in nitrate reduction with river reconnection

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 30 April 2019

Received in revised form 25 May 2019

Accepted 31 May 2019

Available online 1 June 2019

Editor: Jay Gan

Keywords:

Denitrification
Sediment diversion
Erosion
Sea level rise

ABSTRACT

Expressions of eutrophication have led to increased stress on coastal ecosystems around the world. The nitrogen (N) removal potential of coastal wetland ecosystems is important due to increased loading of N to the coast. In Louisiana, there is rapid coastal wetland loss due primarily to the presence of river levees, which have isolated the coastal basins, and a high relative sea level rise. Ecosystem managers are planning to construct the Mid-Barataria sediment diversion which will reconnect the Mississippi River with Barataria Basin to build new wetlands and nourish existing marsh. The sediment diversion will deliver large amounts of nitrate into the surface waters of Barataria Bay. This research sought to quantify the nitrate removal potential of three bay zones; vegetated marsh, submerged peat fringe, and bay-bottom muddy estuarine sediment in intact soil cores incubated with a 2 mg L⁻¹ N-NO₃ water column. We noted: i) The areal nitrate reduction rates for the marsh, fringe, and estuary zones were 29.29 ± 3.28, 18.83 ± 1.31, and 10.83 ± 0.62 mg N m⁻² day⁻¹, respectively; ii) the majority (~93%) of NO₃ was converted to N₂O, indicating denitrification was the major NO₃ reduction pathway; iii) the submerged, eroded marsh soils (peat fringe zone) will play a large role in nitrate reduction due to increased contact time with the surface water. These findings can inform the predictive numerical models produced and utilized by ecosystem managers to better quantitatively understand how the coastal basin will respond to nutrient loading from river reconnection. In a broader context, the current relative sea level rise in coastal Louisiana is within the range of eustatic sea level rise that most stable coastlines will experience within the next 65–85 years. Therefore, these findings can serve as an example of potential future impacts to coastal wetland systems, globally, within the next century.

© 2019 Elsevier B.V. All rights reserved.

* Corresponding author at: 3239 Energy, Coast, and Environment Building, Department of Oceanography and Coastal Sciences, Louisiana State University, Baton Rouge, LA 70803, United States.

E-mail address: jrwhite@lsu.edu (J.R. White).

1. Introduction

Currently, coastal Louisiana is experiencing relative sea level rise at higher rates than most of the world's coastlines due to the combined effects of eustatic sea level rise at approximately 3 mm y^{-1} (DeLaune and White, 2012; Cazenave and Llovel, 2010) and regional coastal subsidence at an average of 10 mm y^{-1} (Morton et al., 2005). Therefore, the rates of relative sea level rise in coastal Louisiana today ($\sim 13 \text{ mm y}^{-1}$) puts this region within the predicted range of eustatic sea level rise for most stable coastlines in the next 65–85 years (Boesch et al., 1994; Church et al., 2013; DeLaune and White, 2012). This ultimately makes current coastal Louisiana an ideal proxy for studying the future effects of sea level rise and coastal processes on other wetland dominated coastlines.

Louisiana contains 40% of the coastal and estuarine wetlands in the lower 48 United States yet experiences approximately 80% of the Nation's total wetland loss (Williams et al., 1997). Coastal land loss in Louisiana is due to global eustatic sea level rise, land subsidence, anthropogenic factors, and shoreline erosion, often involving wetland peat collapse (Boesch et al., 1994; DeLaune and White, 2012). Between 1932 and 2016, coastal Louisiana has lost $\sim 4877 \text{ km}^2$ (1883 mi^2) of land, approximately 25% of what existed in 1932 (Couvillion et al., 2017).

Coastal wetlands are an important natural resource as they perform many valuable ecosystem services including providing habitat for commercially valuable species, buffering the coastline from storm surges, and improving water quality (CPRA, 2017). Through denitrification, and to a much smaller extent anammox, coastal wetlands are able to remove nitrate from the ecosystem by reducing it to nitrogen gas, driving loss to the atmosphere. The high rates of coastal wetland loss in Louisiana pose the question: How will the ecosystem service of water quality improvement in Louisiana's and the world's coastal wetlands change as sea level continues to rise?

The 2017 Louisiana's Comprehensive Master Plan for a Sustainable Coast by the Coastal Protection and Restoration Authority (CPRA) is a \$50 billion planned investment designed to build and maintain coastal wetlands, reduce flood risk to communities, and provide habitats to support fisheries and overall ecosystem health (CPRA, 2017) The Master

Plan includes multiple categories of projects including barrier island restoration, hydrologic restoration, marsh creation, ridge restoration, shoreline protection, structural/nonstructural protection, and sediment diversions (CPRA, 2017). A strategically important component of the plan is to implement the Mid-Barataria Sediment Diversion, which will restore the historical connection between the Mississippi River and Barataria Basin. The Mid-Barataria Sediment Diversion is an approximately \$1 billion restoration project that is designed to deliver sediment to the coastal basin in order to build and maintain land. The connection will be located near Myrtle Grove, LA and is currently in the design and permitting phases of its construction (Fig. 1; CPRA, 2017).

When the diversion is in operation, concomitant with the delivery of sediment and water, there will be a relatively high concentration of nitrate from the Mississippi River that enters the estuary. Coastal wetlands are a natural sink for nutrients and therefore have the potential to remove excess nitrate in the surface water through denitrification, anammox, and plant uptake before reaching the Gulf of Mexico; ultimately helping to alleviate coastal eutrophication and subsequent hypoxia (VanZomeran et al., 2013; Hurst et al., 2016).

The coastal wetlands in Barataria Bay have approximately 1 to 2 m of accreted carbon-rich peat soils which, due to the undercutting from small waves, slumps into the estuary causing substantial marsh edge erosion (DeLaune et al., 1994; Valentine and Mariotti, 2019). This loss of marsh poses a critical question: When the marsh is eroded and submerged, does the ecosystem still have the capacity for nitrate removal? Therefore, the objective of this study was to compare the nitrate removal capacities of the intact vegetated marsh, the submerged, carbon-rich fringe zone, and the muddy estuarine sediment.

2. Materials and methods

2.1. Study area

The study area is in the northeastern portion of Barataria Basin which is an approximately 628,600 ha bay bordered by the Mississippi River and Bayou Lafourche (Nelson et al., 2002). The basin is shallow,

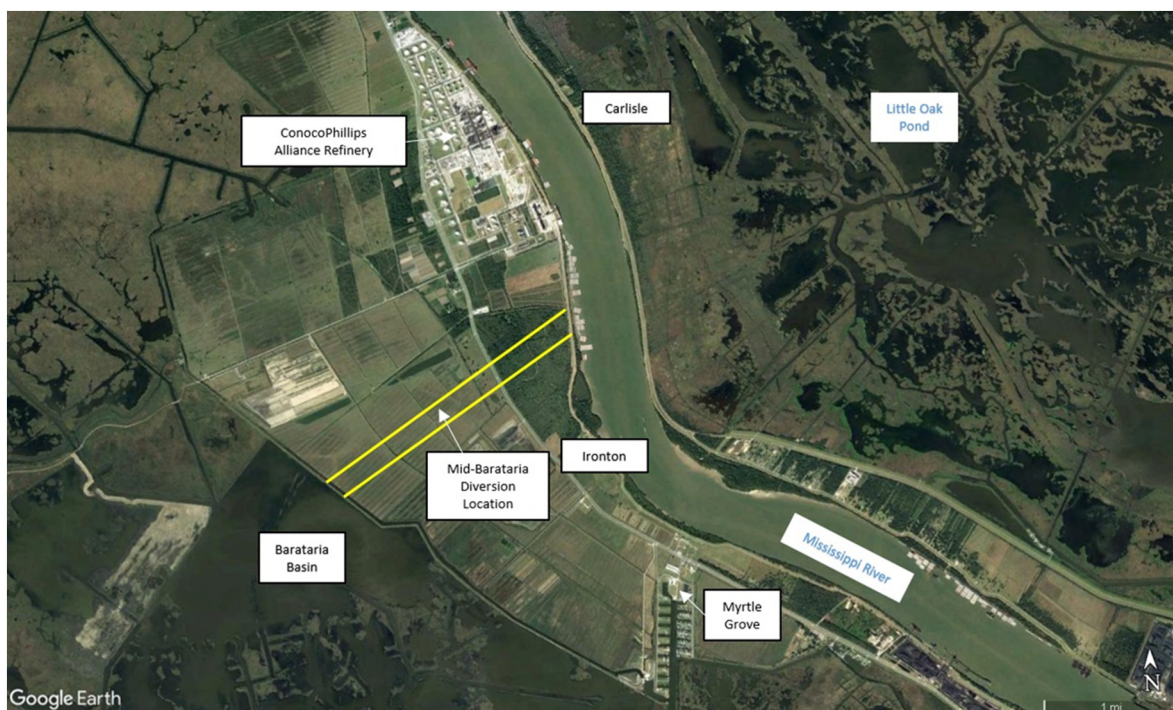


Fig. 1. The location of the proposed Mid-Barataria Sediment Diversion (adapted from CPRA, 2017; Google Earth).

turbid, and the water column is aerobic with an average depth of about 2 m (Happ et al., 1977; Conner and Day, 1987). Barataria Bay experiences a 30 cm diurnal lunar tide, but larger water level changes can be caused by wind (Happ et al., 1977). The salinity in Barataria Basin can range from 0 psu in the upper portion to 22 psu in the saltwater coastal marsh zone proximal to the inlets that connect to the Gulf of Mexico (Nelson et al., 2002). The study sites were all dominated primarily by *Spartina alterniflora*, had a mean surface water salinity of 10.7 psu, and have marsh edge erosion rates ranging from 67.16 to 324.85 cm yr⁻¹ (Sapkota and White, 2019).

2.2. Sampling design and methodology

Three marsh sites (islands) in Barataria Bay were sampled in May 2018. The water level at the USGS station 07380251 (Barataria Bay N of Grand Isle, LA) was approximately 1.5 ft. (0.46 m) and was approximately 1 cm below the marsh soil surface. Four, 20 cm intact, field-replicate cores were taken in the vegetated marsh (marsh), peat fringe (fringe), and muddy estuarine bay- bay bottom (estuary) along a shore-normal transect at each island (Fig. 2; Table 1). The intact cores were sealed with stoppers on the bottom and transported back to the Wetland and Aquatic Biogeochemistry Laboratory (WABL) at Louisiana State University (LSU).

2.3. Side-scan imagery and bathymetric scans

On September 17, 2018 a Humminbird Helix 9 Chirp Mega DI GPS G2N was used to determine the bathymetry and bottom roughness of the submerged bay area at the study sites. The water level at the USGS station 07380251 (Barataria Bay N of Grand Isle, LA) was approximately 1.5 ft. (0.46 m) and was approximately 1 cm below the marsh soil surface. The transducer was mounted to the stern of the boat to collect and record bathymetric and side scan data. The fathometer provided the

Table 1

Coordinates and distance from the marsh shoreline into the bay for each sampling site.

Yadav's island	Ben's island	WABL island
Marsh 29°26'48.25"N 89°54'21.23"W 3.0 m into the marsh	Marsh 29°26'36.25"N 89°53'59.48"W 4.6 m into the marsh	Marsh 29°26'29.61"N 89°54'5.00"W 2.8 m into the marsh
Fringe 29°26'48.01"N 89°54'23.72"W ~ 60 m	Fringe 29°26'35.56"N 89°53'57.88"W ~ 40 m	Fringe 29°26'27.64"N 89°54'3.78"W ~ 60 m
Estuary 29°26'48.34"N 89°54'33.08"W ~ 320 m	Estuary 29°26'36.06"N 89°53'55.32"W ~ 100 m	Estuary 29°26'21.37"N 89°53'56.40"W ~ 350 m

depth profile and the side scan showed bottom roughness which visually identified where the peat fringe area disappeared into the bay. The side scan transects that were collected were stitched together using the ReefMaster2 program.

2.4. Intact core incubation: nitrate reduction

Upon returning to the lab, carboys of site water were filtered through a 1 µm vacuum filtration system into Nalgene bottles and stored at 4 °C. The cores were drained of their initial site water and re-flooded with the filtered site water to a 20 cm water column. The cores were placed into a water bath to moderate the temperature and left to equilibrate and bubble with room air overnight. Each core was spiked to bring the water column to a concentration of 2 mg L⁻¹ NO₃-N to represent the approximate nitrate concentration of the Mississippi River during a spring flood event (Mitsch et al., 2005); according to the USGS station 07374000 (Mississippi River at Baton Rouge, LA) this was approximately the concentration of nitrate + nitrite in the Mississippi

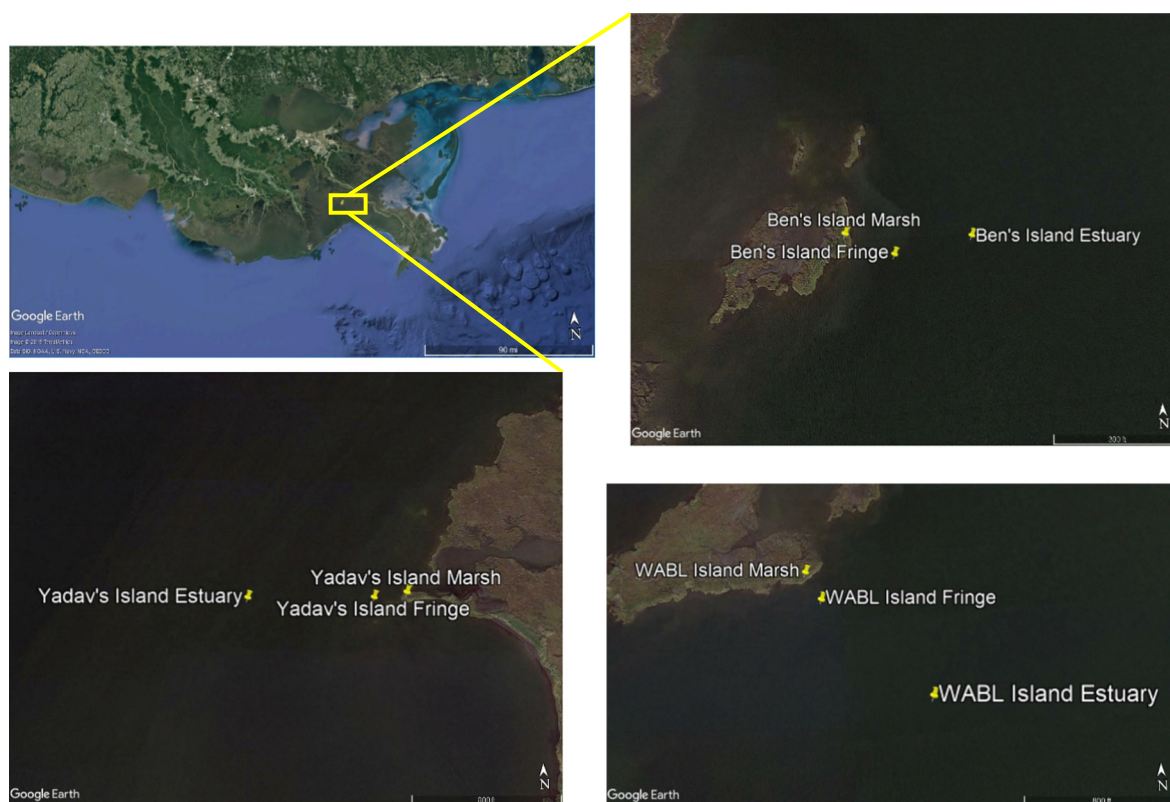


Fig. 2. Google Earth satellite images of Barataria Bay, LA with sampling sites. For each island, each sampling location/bay zone (marsh, fringe, and estuary) is represented by yellow pins.

River at the time of sampling. The cores were incubated for 11 days with an aerobic water column to match the water column conditions of the shallow bay (Conner and Day, 1987; Steinmuller et al., 2018). Water samples were taken over time, syringe filtered through a 0.45 µm membrane filter, acidified with concentrated H₂SO₄ to a pH < 2, and stored at 4 °C until analysis. DI water was added before sampling to account for evaporation losses and 6 mL of filtered site water replaced the 6 mL of sample taken after each time point to maintain a constant core water volume. The cores were incubated in the dark to prevent the growth of algae which could impact areal nitrate reduction rates. Temperature of the water bath was monitored over the incubation period and remained around 21 °C. Water samples were analyzed for nitrate (U.S. EPA Method 353.1) concentrations on a SEAL AQ2 Automated Discrete Analyzer with a detection limit of 0.016 mg N L⁻¹ (U.S. EPA, 1993).

After the 11-day incubation, the soil cores were extruded and sliced into 0–5 cm and 5–10 cm sections. While 20 cm of soil was collected and used in the intact core incubation, only the top 10 cm of soil were used for further analyses after Gardner and White (2010). The soil sections were placed into polyethylene sediment containers and stored at 4 °C until analysis of soil physicochemical properties, microbial biomass, and potential denitrification.

2.5. Soil properties

Soil samples were analyzed for moisture content, bulk density, total nitrogen, total carbon, percent organic matter, and total phosphorus. Gravimetric moisture content in the soil was determined by weighing soil subsamples before and after they dried to constant weight at 70 °C. Bulk density was calculated by dividing the dry weight of the total soil sample by the volume in the 5 cm core section. Total C and N values were determined on dried, ground subsamples of soil using a Costech 1040 CHNOS Elemental Combustion System with method detection limits of 0.07 g C kg⁻¹ and 0.005 g N kg⁻¹ (Costech Analytical Technologies, Inc. Valencia, California). Total phosphorus was determined using the ashing method after Andersen (1976). Dried and ground subsamples of approximately 0.3 g were placed into 50 mL glass beakers and placed into a muffle furnace at 550 °C for 4 h. Percent organic matter was measured by loss on ignition of the ashed samples by dividing the ashed weight by the pre-burn weight (Sparks, 1996). After being ashed, 20 mL of 6.0 M HCl was added to each beaker. The beakers were placed on a hot plate at 100–120 °C until dry and then the temperature was raised to ~370 °C for an additional hour. Samples were then saturated with 2.25 mL of 6.0 M HCl and placed back on the hot plate until near boiling. After cooling, samples were filtered through a Whatman #41 filter into 50 mL volumetric flasks and diluted to volume with deionized water. Samples were analyzed for total phosphorus (U.S. EPA Method 365.1) using a SEAL AQ2 Automated Discrete Analyzer (SEAL Analytical Inc., Mequon, Wisconsin) with a detection level 0.006 mg P L⁻¹ (U.S. EPA, 1993).

Extractable dissolved organic C (DOC) was determined on approximately 4 g of homogenized field moist soil sample placed into 40 mL centrifuge tubes. Twenty-five mL of 0.5 M K₂SO₄ was added to each centrifuge tube as an extractant. The centrifuge tubes shook on a longitudinal shaker at room temperature for an hour, were placed into a Sorvall RC, 5C Plus centrifuge (Newtown, Connecticut) for 10 min at 4000 g, and then subsequently filtered through a 0.45 µm membrane filter into 20 mL scintillation vials. Samples were acidified to a pH < 2 using 1 M HCl before being stored at 4 °C until analysis. The DOC concentrations were determined on a Shimadzu TOC-V CNS Analyzer (Kyoto, Japan).

Microbial Biomass C and N were determined using the chloroform-fumigation method after Brookes et al. (1985) with modifications by White and Reddy (2000). For each sample, approximately 4 g of field moist soil from the top 0–5 cm soil section was weighed out into a duplicate fumigate and duplicate non-fumigate centrifuge tubes. Non-fumigate samples were extracted with 25 mL of 0.5 M K₂SO₄ and represent the previously described extractable DOC. Fumigate samples were placed into a glass vacuum desiccator, fumigated with chloroform, vacuum sealed,

and incubated for 24 h. The samples were then extracted with 25 mL of 0.5 M K₂SO₄, put on a longitudinal shaker for an hour, centrifuged for 10 min at 4000g, and filtered through a 0.45 µm membrane filter into scintillation vials. Samples were acidified to a pH < 2 and refrigerated at 4 °C until analysis. Microbial biomass C and N were analyzed on a Shimadzu TOC-V CNS Analyzer. The difference in total dissolved C and N between the fumigate and non-fumigate paired samples represents the size of the microbial pool (Brookes et al., 1985; Vance et al., 1987).

Extractable ammonium, soluble reactive phosphorus (SRP), and nitrate were determined by placing approximately 4 g of field moist soil into centrifuge tubes and adding 20 mL of 2 M KCl as an extractant. Samples were placed on a longitudinal shaker for an hour then centrifuged for 10 min at 4000g at 10 °C. Samples were vacuum filtered through a 0.45 µm membrane filter into scintillation vials, acidified to a pH < 2, and refrigerated at 4 °C until analysis. Samples were analyzed for nitrate, ammonium, and SRP on a SEAL AQ2 Automated Discrete Analyzer with detection limits of 0.016 mg N L⁻¹, 0.012 mg N L⁻¹, and 0.002 mg P L⁻¹, respectively.

2.6. Bottle incubation: potential denitrification

A bottle incubation using the acetylene block technique, adapted from Tiedje (1994) and White and Reddy (1999), was used to calculate the mass balance of added 2 mg L⁻¹ NO₃-N conversion to nitrogen gas through the denitrification pathway. A secondary goal of this incubation was to examine the difference in the percent recovery of nitrate as N₂O gas between ambient salinity water (10.7 psu) and freshwater. For each island, one 0–5 cm core section from the marsh, fringe, and estuary zones were randomly selected for the incubation. Approximately 4 g of field moist subsample was placed into duplicate glass serum bottles. One of the duplicates was treated with ambient salinity site water while the other was treated with deionized water (DI). The DI water treatment represents the denitrification potential of the soils/sediments under a river diversion operation. The soil was placed into glass serum bottles, capped with rubber septa and aluminum crimp caps, evacuated for 30 s at -75 kPa, and purged with 99.99% O₂-free N₂ gas for 5 min. Either 8 mL of N₂-purged site water or 8 mL of N₂-purged DI water was added to the designated bottles to create a slurry. Approximately 20% of the headspace was replaced with acetylene gas (C₂H₂). Eight mL of a 4 mg L⁻¹ NO₃-N solution made with either site water or DI water was added to each bottle at time zero. Bottles were shaken in the dark on a longitudinal shaker and gas samples were taken over the course of a week using insulin syringes and analyzed on a GC-8A equipped with an electron capture detector (Kyoto, Japan) with a detection limit of 0.006 mg N₂O-N kg⁻¹ h⁻¹ (White and Reddy, 2003). The incubation was considered complete when the graph of N₂O concentration over time levelled off, indicating that the substrate (nitrate) was completely reduced. The average maximum N₂O concentration was used to determine the amount of added nitrate that was converted to N₂O gas as percent recovery.

2.7. Data analysis

One-Way, single factor ANOVAs ($\alpha < 0.05$) were used to examine differences among rates and soil properties. Nitrate concentrations over time were plotted for the intact core incubation study and the slope of the linear regression line provided the nitrate reduction rate (Roy and White, 2012).

3. Results and discussion

3.1. Marsh erosion and submerged bay-bottom patterns across islands and bay zones

In Barataria Bay, the vegetated marshes erode due to waves undercutting the interwoven root-mat just below the surface of the marsh

(Valentine and Mariotti, 2019; Nyman et al., 1994). The undercutting of the once-anaerobic intact marsh soil results in the organic marsh soil slumping into the bay and being exposed to oxygenated bay water which markedly increases decomposition rates (Steinmuller et al., 2018). After the top of the marsh slumps into the bay, the remaining underlying soil layers become submerged, creating an area of sub-aqueous marsh. This submerged, peaty marsh area is also continuously eroded by wave action which contributes further to lateral marsh edge retreat. The rapid relative sea level rise creates accommodation space where incision rates tend to decrease towards the base of the submerged marsh. The lack of erosive forces at the base of the marsh allows suspended estuarine bay-mud to accumulate and settle on top of the peaty substrate and create some lateral continuity of marsh facies (Wilson and Allison, 2008; Haywood, 2018). This trend was also clearly evident in the observation of the fringe cores and in the side-scan surveys taken in the submerged portion of the three study sites in Barataria Bay (Figs. 3, 4, and 5). The side-scan imagery and bathymetry at WABL island (Figs. 4, 5, and 6) are provided as examples of the sediment surface trends, similar patterns were seen on the other two islands. While the side-scan imagery can delineate peaty areas (rough bay-bottom) undergoing erosion, it isn't possible to see how far the older, eroded marsh extends into the bay due to capping by estuarine mud (smooth bay-bottom). Therefore, investigation of the soil properties along a transect is needed to delineate the submerged eroded marsh capped by mud vs. estuarine bay-bottom mud (Table 2). Soil/sediment properties for each bay zone indicate that the marsh and the submerged fringe zones are statistically similar for mean organic matter content, MBC, C:N ratio (0–5 cm), and TP (0–5 cm); and the fringe has statistically higher values than the marsh zone for average moisture content, TC (0–5 cm), and extractable DOC, indicative of decomposition processes (Table 2).

3.2. Nitrate reduction

The average areal nitrate reduction rates across all three of the islands for the marsh, fringe and estuary zones were 29.29 ± 3.28 , 18.83 ± 1.31 , and $10.83 \pm 0.62 \text{ mg N m}^{-2} \text{ day}^{-1}$, respectively. Average areal nitrate reduction rates for the marsh, fringe, and estuary zones across all three of the islands demonstrated significant differences from one another with the highest average rate in the marsh zone (Fig. 7). The average estuarine mud denitrification rate was ~37% of the rate in the vegetated marsh while the average denitrification rate for the submerged peat fringe was ~64% of the rate in the vegetated marsh. A summary of published in situ and experimental denitrification rates for coastal Louisiana found a 2–3 times decrease in denitrification potential between vegetated marsh and benthic muddy sediment (Rivera-Monroy et al., 2013). This trend was also seen in another study which found a 4 times decrease in denitrification rates from the vegetated marsh to the subtidal sediment in the Chandeleur Islands in the Gulf of Mexico (Hinshaw et al., 2017). These past studies looked at the differences in denitrification rates between marsh soil and estuarine bay-bottom sediment and didn't include submerged eroded peat soils. The denitrification rates for the marsh and fringe areas were similar to denitrification rates from across coastal Louisiana for brackish and saline marshes (Rivera-Monroy et al., 2013; Levine et al., 2017; Hurst, 2016). Therefore, in this system we found that the loss of vegetated marsh through erosion and submergence leads to ~36% reduction in denitrification rate, but the resulting peat fringe zone is almost twice as effective at improving water quality through denitrification than the bay-bottom muddy estuarine sediment.

A likely explanation for the lower nitrate reduction rates in the fringe bay zone compared to the marsh bay zone is the differences in diffusion of nitrate into the sediment from the water column. A characteristic of the fringe cores is a thin layer of fine-grained mineral sediment that caps the older marsh peat layer. This fine-grained sediment layer may restrict the diffusion rate of nitrate into the deeper layers of



Fig. 3. Picture of a fringe core with a lighter mud layer on the top covering the darker, peat layer.

the soil, therefore slowing the overall nitrate reduction rate compared to the vegetated marsh.

3.3. Potential denitrification

An anaerobic bottle incubation was conducted to determine the mass balance for added nitrate conversion to nitrous oxide and to assess which nitrate reduction pathway is dominant in this system. The experiment was also conducted to assess the potential denitrification of the soils/sediments exposed to ambient site water salinity (10.7 psu) and freshwater salinity (DI water treatment) to represent conditions under a river diversion operation. The percent recovery of NO_3 converted to N_2O for the potential denitrification of the marsh, fringe, and estuary samples between the site water and DI treatments were not significantly different from one another. Therefore, the data for both treatments were combined. Since there was no significant difference in the percent recovery between the site water and DI treatments, this finding indicates that the resident microbial communities in the soil/sediment samples are acclimated to fluctuating salinities which is typical for estuarine systems. Therefore, significant changes in salinity, as a result of freshwater introduction from the Mid-Barataria sediment diversion, may not widely impact the denitrification capabilities of the soil/sediment in this area, in contrast to what has been seen in other studies (Marks et al., 2016).

The average percent recovery of NO_3 converted to N_2O for the potential denitrification of the marsh, fringe, and estuary samples was 91.2 ± 7.51 , 100 ± 6.01 , and $88.5 \pm 1.08\%$, respectively. There was no significant difference in average percent recovery across all three islands between the marsh, fringe, and estuary areas which results in an average percent recovery of 93% across all bay zones, indicating a consistency across bay zones in the basin. This result demonstrates that the vast majority of the nitrate added to the samples passed through the denitrification pathway, similar to what was found in another coastal basin, Breton

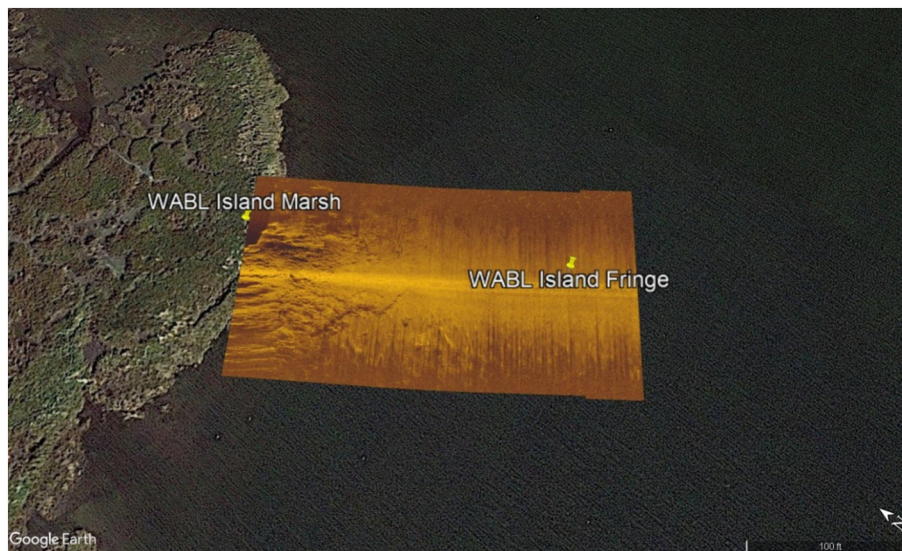


Fig. 4. A clip of the side-scan transect off of WABL Island that shows visible peat fringe up against the marsh and then the bottom of the bay becomes smoother (Google Earth).

Sound (VanZomerem et al., 2012). Additionally, Upreti (2019) recently demonstrated that anammox and DNRA were not significant contributors to nitrate reduction in LA coastal systems by isotope pairing and ^{15}N diffusion.

3.4. Management implications

An Integrated Biophysical Model was developed by the Coastal Protection and Restoration Authority and The Water Institute of the Gulf which models changes in water level, nutrient concentrations, vegetation growth, and hydrodynamics, etc. to predict how Barataria Bay will change over time and in relation to the planned Mississippi River sediment diversions (Baustian et al., 2018; Meselhe et al., 2015). Using the model, water level output was extracted at three existing monitoring station locations (CRMS 0224, USGS Barataria Waterway S of Lafitte, LA, and USGS Barataria Bay N of Grand Isle, LA), in close proximity to the current study sites (Fig. 8). The output predicts that the current study sites, located 26 km from the Mid-Barataria sediment diversion outfall, will likely not be subject to a substantial change in water level when the sediment diversion is operational (with 5000 CFS baseflow, open trigger point

when the Mississippi River is at 450,000 CFS, and max diverted discharge equal to 75,000 CFS when the Mississippi River reaches 1 M CFS) at model year 2040 (Sadid et al., 2019). The current study sites are close enough to the diversion to receive nutrients and sediment, but when the diversion is open, the water level in the marshes will most likely be more influenced by sea level rise, tides, climate, and subsidence rather than the opening of the river diversion. However, there are sites closer to the outfall of the diversion that will experience elevated water levels as well as nutrient and sediment loading. Barataria Bay experiences asymmetrical marsh edge erosion due a variety of factors including the amount of wave overshooting, wave undercutting, variation in marsh strength, and marsh orientation in the bay (Valentine and Mariotti, 2019). Based on erosion rates from this area (Sapkota and White, 2019) and aerial imagery for all three of the study sites (Google Earth historical imagery), unless the Mid-Barataria Sediment diversion is able to build land and slow marsh loss in this area, by 2070, all of the study islands will have eroded away; leaving behind submerged peat soil.

Based on a recent study, vegetated marshes in close proximity to the study sites, are only submerged 31%–46% of the time (Valentine and Mariotti, 2019). This inundation data, in conjunction with the fact that

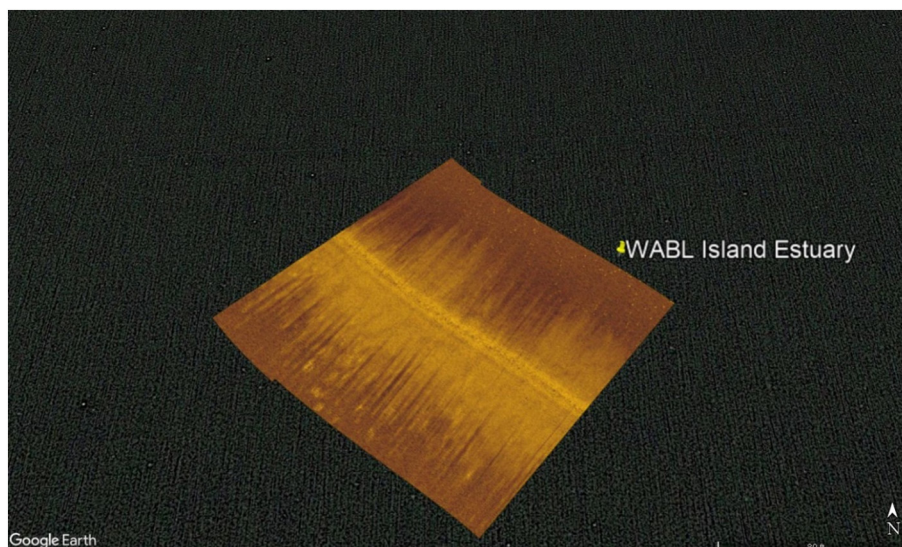


Fig. 5. A clip of the side-scan transect off of WABL Island that shows a smooth bay bottom where the WABL Estuary cores were taken (Google Earth).

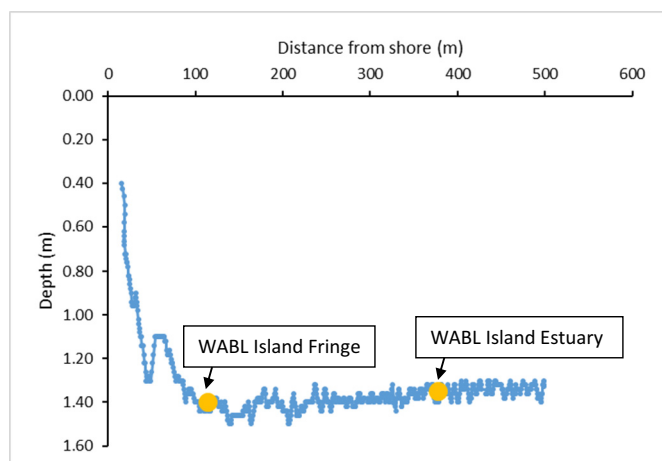


Fig. 6. Bathymetry off of WABL Island along the same transect as the side-scan.

operation of the river diversion will not likely contribute added periods of inundation to most of the vegetated marshes near the study sites, indicates that despite having the highest rates of denitrification, the vegetated marshes will have limited contact with the large influx of nitrate that comes in with the Mississippi River water. Comparatively, both the eroded marsh fringe and muddy estuarine bay zones are submerged 100% of the time and have continuous contact with the water, providing constant opportunity for reduction of the nitrate from the river diversion (Hurst et al., 2019). To assess this difference in contact, we multiplied the denitrification rates by the % of time submerged, to provide a measure of the relative contribution of each area to potential nitrate removal through denitrification. Despite having a denitrification rate that is 64% of the vegetated marsh, the eroded marsh, submerged fringe soil can provide up to 1.7 times more denitrification because it is flooded 100% of the time. The estuarine mud sediment which has a denitrification rate that is only 37% of the vegetated marsh, can provide 97% of the denitrification of the vegetated marsh since the marsh is flooded a mean of 38% of the time while the estuarine mud is in constant contact with the water column.

Therefore, it not only important to parse out the relative contributions of different soil types for denitrification, but it is also important to consider contact time. While coastal Louisiana is losing coastal marshes at very accelerated rates, the capacity for water quality improvement through microbial reduction of nitrate has increased in the basin due to erosion and submergence. The nitrate reduction capacity of this submerged fringe zone can be used in ecosystem modeling efforts to predict how Barataria Bay will process the influx of nitrate

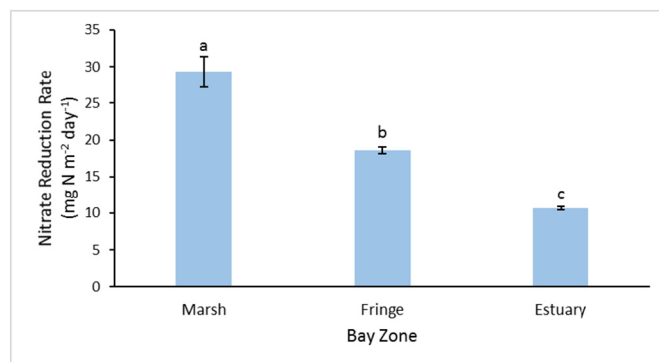


Fig. 7. Average nitrate reduction rates for the intact core experiment across all of the islands with standard error bars. Marsh $n = 12$, Fringe $n = 11$, and Estuary $n = 11$.

that enters during operation of the Mid-Barataria Sediment Diversion and how the submerged fringe zone can help mitigate potential expressions of eutrophication over time.

4. Conclusions

This study examined the denitrification potential of three different bay zones (vegetated marsh, submerged peat fringe, and estuarine bay-bottom mud) in Barataria Bay, LA to determine the water quality improvement function of these soils with the introduction of freshwater from the Mid-Barataria Sediment Diversion. Even as the vegetated coastal wetlands erode, the coastal marsh ecosystem can still provide the ecosystem service of water quality improvements because the submerged fringe zone is capable of substantial denitrification due to high microbial biomass, total carbon, and constant contact with the water column. The submerged peat fringe zone will have a larger impact than the vegetated marsh on the nitrate reduction potential of Barataria Bay as the high erosion of the vegetated marshes in this area continues. These findings can inform the predictive numerical models that are developed and utilized to more accurately predict how Barataria Basin will respond to river nitrate loading; and the findings can serve as a template for the possible impacts of future SLR and marsh erosion on other wetland dominated coastlines.

Acknowledgements

This work was partially funded under a collaborative National Science Foundation, USA Chemical Oceanography Grant (#1636052). Jessica Vaccare was funded by a Department of Oceanography and Coastal Sciences Graduate Assistantship at Louisiana State University.

Table 2

Average soil/sediment physicochemical properties with standard error across all of the islands for both sampling depths. Letters denote significant difference within each depth section. The letter 'a' denotes a significantly higher value with decreasing value for subsequent letters.

	0–5 cm soil interval			5–10 cm soil interval		
	Marsh	Fringe	Estuary	Marsh	Fringe	Estuary
Moisture content (%)	74.0 ± 2.0 ^b	82.0 ± 2.0 ^a	59.0 ± 3.0 ^c	75.0 ± 2.0 ^b	83.0 ± 2.0 ^a	60.0 ± 1.0 ^c
BD (g cm ⁻³)	0.32 ± 0.02 ^b	0.21 ± 0.02 ^c	0.56 ± 0.06 ^a	0.29 ± 0.03 ^b	0.20 ± 0.03 ^c	0.54 ± 0.02 ^a
OM (%)	25.6 ± 3.24 ^a	31.0 ± 2.74 ^a	8.54 ± 0.72 ^b	33.3 ± 3.35 ^a	41.0 ± 5.34 ^a	9.98 ± 0.35 ^b
TP (mg kg ⁻¹)	557 ± 25.96 ^a	507 ± 22.2 ^{ab}	471 ± 5.81 ^b	538 ± 39.1 ^a	408 ± 10.6 ^b	462 ± 12.5 ^a
TC (g kg ⁻¹)	116 ± 15.5 ^b	161 ± 15.3 ^a	36.3 ± 3.21 ^c	155 ± 19.03 ^a	190 ± 25.3 ^a	40.5 ± 1.87 ^b
TN (g kg ⁻¹)	5.97 ± 0.78 ^b	9.04 ± 0.85 ^a	2.46 ± 0.23 ^c	7.67 ± 0.94 ^a	11.4 ± 1.53 ^a	2.69 ± 0.13 ^b
C:N	19.3 ± 0.4 ^a	18.0 ± 0.67 ^a	14.9 ± 0.35 ^b	20.1 ± 0.35 ^a	16.9 ± 0.6 ^b	15.1 ± 0.37 ^c
Ext. NH ₄ (mg kg ⁻¹)	13.6 ± 1.56 ^a	7.71 ± 0.42 ^b	25.3 ± 8.84 ^{ab}	6.00 ± 1.93 ^b	23.6 ± 3.38 ^a	46.7 ± 11.8 ^a
Ext. PO ₄ (mg kg ⁻¹)	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
MBC (g kg ⁻¹)	3.83 ± 0.63 ^a	4.58 ± 0.57 ^a	1.88 ± 0.29 ^b			
MBN (mg kg ⁻¹)	3.30 ± 0.76 ^a	0.94 ± 0.44 ^b	0.59 ± 0.10 ^b			
Ext. DOC (mg kg ⁻¹)	168 ± 17.1 ^b	283 ± 18.6 ^a	91.1 ± 4.53 ^c			

BD = Bulk Density, MBC = Microbial Biomass Carbon, MBN = Microbial Biomass Nitrogen, Ext. = Extractable, b.d = Below Detection.

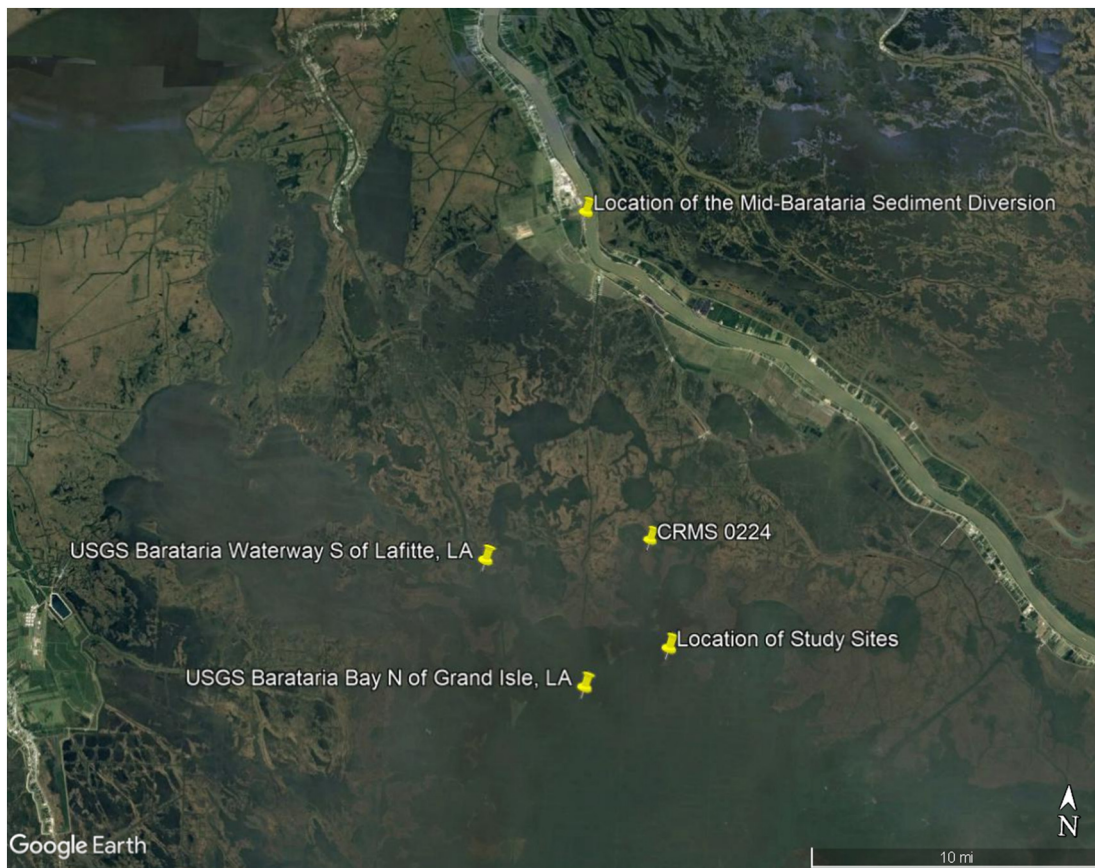


Fig. 8. Locations of the water level monitoring sites relative to the study sites and the location of the proposed Mid-Barataria Sediment Diversion in Barataria Bay, LA (Google Earth).

We also acknowledge Eddie Weeks, Michael P. Hayes, and Benjamin J. Haywood for extensive help with fieldwork, and Thomas Blanchard for laboratory assistance.

References

- Andersen, J., 1976. An ignition method for determination of total phosphorus in lake sediments. *Water Res.* 10 (4), 329–331. [https://doi.org/10.1016/0043-1354\(76\)90175-5](https://doi.org/10.1016/0043-1354(76)90175-5).
- Baustian, M., Meselhe, E., Jung, H., Sadid, K., Duke-Sylvester, S., Visser, J., et al., 2018. Development of an Integrated Biophysical Model to represent morphological and ecological processes in a changing deltaic and coastal ecosystem. *Environ. Model. Softw.* 109, 402–419. <https://doi.org/10.1016/j.envsoft.2018.05.019>.
- Boesch, D., Josselyn, M., Mehta, A., Morris, J., Nuttle, W., Simenstad, C., Swift, D., 1994. Scientific assessment of coastal wetland loss, restoration and management in Louisiana. *J. Coast. Res.* 20 Retrieved from. https://www.jstor.org/stable/25735693?seq=1#metadata_info_tab_contents.
- Brookes, P., Landman, A., Pruden, G., Jenkinson, D., 1985. Chloroform fumigation and the release of soil nitrogen: a rapid direct extraction method to measure microbial biomass nitrogen in soil. *Soil Biol. Biochem.* 17 (6), 837–842. [https://doi.org/10.1016/0038-0717\(85\)90144-0](https://doi.org/10.1016/0038-0717(85)90144-0).
- Cazenave, A., Llovel, W., 2010. Contemporary sea level rise. *Annu. Rev. Mar. Sci.* 2 (1), 145–173. <https://doi.org/10.1146/annurev-marine-120308-081105>.
- Church, J., Clark, P., Cazenave, A., Gregory, J., Jevrejeva, S., Levermann, A., et al., 2013. Climate change 2013: the physical science basis. Contribution of working group I: sea level change. Retrieved from. Cambridge University Press <http://dris.nio.org/drs/handle/2264/4605>.
- Coastal Protection and Restoration Authority of Louisiana (CPRA), 2017. Louisiana's comprehensive master plan for a sustainable coast. Retrieved from. http://coastal.la.gov/wp-content/uploads/2017/04/2017-Coastal-Master-Plan_Web-Book_CFinal-with-Effective-Date-06092017.pdf.
- Conner, W., Day, J., 1987. The Ecology of Barataria Basin, Louisiana: An Estuarine Profile. U.S. Fish and Wildlife Service Retrieved from. https://tigerprints.clemson.edu/cgi/viewcontent.cgi?article=1024&context=ag_pubs.
- Couvillion, B., Beck, H., Schoolmaster, D., Fischer, M., 2017. Land area change in coastal Louisiana (1932 to 2016). Retrieved from. U.S. Geological Survey https://pubs.usgs.gov/sim/3381/sim3381_pamphlet.pdf.
- DeLaune, R., Nyman, J., Patrick Jr., W., 1994. Peat collapse, ponding and wetland loss in a rapidly submerging coastal marsh. *J. Coast. Res.* 10 (4).
- DeLaune, R., White, J., 2012. Will coastal wetlands continue to sequester carbon in response to an increase in global sea level?: a case study of the rapidly subsiding Mississippi river deltaic plain. *Clim. Chang.* 110 (1–2), 297–314. <https://doi.org/10.1007/s10584-011-0089-6>.
- Gardner, L., White, J., 2010. Denitrification enzyme activity as an indicator of nitrate movement through a diversion wetland. *Soil Sci. Soc. Am. J.* 74 (3), 1037. <https://doi.org/10.2136/sssaj2008.0354>.
- Happ, G., Gosselink, J., Day, J., 1977. The seasonal distribution of organic carbon in a Louisiana estuary. *Estuar. Coast. Mar. Sci.* 5 (6), 695–705. [https://doi.org/10.1016/0302-3524\(77\)90042-1](https://doi.org/10.1016/0302-3524(77)90042-1).
- Haywood, B., 2018. Molecular Level Interactions and Transformations of Natural Organic Matter Within the Environment. Doctoral Dissertation. Louisiana State University, Louisiana, USA.
- Hinshaw, S., Tatariw, C., Flournoy, N., Kleinhuisen, A., Taylor, C., Sobecky, P., Mortazavi, B., 2017. Vegetation loss decreases salt marsh denitrification capacity: implications for marsh erosion. *Environ. Sci. Technol.* 51 (15), 8245–8253. <https://doi.org/10.1021/acs.est.7b00618>.
- Hurst, N., 2016. The Effect of Restoration on Nitrate Reduction and Biogeochemical Functioning in Louisiana Wetlands: Bottomland Hardwood Forests and Deltaic Sediments. Master's Thesis. Louisiana State University, Louisiana, USA.
- Hurst, N., White, J., Baustian, J., 2016. Nitrate reduction in a hydrologically restored bottomland hardwood forest in the Mississippi River watershed, northern Louisiana. *Soil Sci. Soc. Am. J.* 80 (6), 1698. <https://doi.org/10.2136/sssaj2016.08.0250>.
- Hurst, N.R., White, J.R., Xu, K., Ren, M., 2019. Nitrate reduction rates in sediments experiencing turbulent flow conditions. *Ecol. Eng.* 128, 33–38. <https://doi.org/10.1016/j.ecoleng.2018.12.027>.
- Levine, B., White, J., DeLaune, R., 2017. Impacts of the long-term presence of buried crude oil on salt marsh soil denitrification in Barataria Bay, Louisiana. *Ecol. Eng.* 99, 454–461. <https://doi.org/10.1016/j.ecoleng.2016.11.017>.
- Marks, B., Chambers, L., White, J., 2016. Effect of fluctuating salinity on potential denitrification in coastal wetland soil and sediments. *Soil Sci. Soc. Am. J.* 80 (2), 516. <https://doi.org/10.2136/sssaj2015.07.0265>.
- Basin wide model development for the Louisiana coastal area Mississippi River hydrodynamic and delta management study. In: Meselhe, E., Baustian, M.M., Allison, M. (Eds.), The Water Institute of the Gulf Funded by the Coastal Protection and Restoration Authority under Task Order 27.1, Baton Rouge, LA.
- Mitsch, W., Day, J., Zhang, L., Lane, R., 2005. Nitrate-nitrogen retention in wetlands in the Mississippi river basin. *Ecol. Eng.* 24 (4), 267–278. <https://doi.org/10.1016/j.ecoleng.2005.02.005>.
- Morton, R., Bernier, J., Barras, J., Ferina, N., 2005. Historical Subsidence and Wetland Loss in the Mississippi Delta Plain. *Gulf Coast Association of Geological Societies Transactions* vol. 55 Retrieved from. <http://www.bergan-et-al.com/Downloads/MortEtal.pdf>.

- Nelson, S., Sorrano, P., Qi, J., 2002. Land-cover change in upper Barataria Basin estuary, Louisiana, 1972–1992: increases in wetland area. *Environ. Manag.* 29 (5), 716–727. <https://doi.org/10.1007/s00267-001-0060-9>.
- Nyman, J., Carlross, M., DeLaune, R., Patrick, W., 1994. Erosion rather than plant dieback as the mechanism of marsh loss in an estuarine marsh. *Earth Surf. Process. Landf.* 19 (1), 69–84. <https://doi.org/10.1002/esp.3290190106>.
- Rivera-Monroy, V., Branoff, B., Meselhe, E., McCorquodale, A., Dortch, M., Steyer, G., et al., 2013. Landscape-level estimation of nitrogen removal in coastal Louisiana wetlands: potential sinks under different restoration scenarios. *J. Coast. Res.* 67, 75–87. https://doi.org/10.2112/si_67_6.
- Roy, E., White, J., 2012. Nitrate flux into the sediments of a shallow Oligohaline estuary during large flood pulses of Mississippi River water. *J. Environ. Qual.* 41 (5), 1549. <https://doi.org/10.2134/jeq2011.0420>.
- Sadid, K., Messina, F., Jung, H., Meselhe, E., Duke-Sylvester, S., Baustian, M., 2019. Morphologic and ecologic analysis of a proposed network of sediment diversions in the Mississippi River delta estuaries. *Earth Surf. Process. Landf. Special Issue. RCEM Symposium*. (in review).
- Sapkota, Y., White, J., 2019. Marsh edge erosion and associated carbon dynamics in coastal Louisiana: a proxy for future wetland-dominated coastlines world-wide. *Estuar. Coast. Shelf Sci.* (in review).
- Sparks, D. (Ed.), 1996. *Methods of Soil Analysis. Part 3. Chemical Methods. Book Ser vol. 5. SSSA, Madison*.
- Steinmuller, H., Dittmer, K., White, J., Chambers, L., 2018. Understanding the fate of soil organic matter in submerging coastal wetland soils: a microcosm approach. *Geoderma* <https://doi.org/10.1016/j.geoderma.2018.08.020>.
- Tiedje, J.M., 1994. In: Weaver, R.W., et al. (Eds.), *Denitrifiers. Methods of Soil Analysis, Part 2 Wisconsin*. Soil Science Society of America, Madison, pp. 245–268.
- U.S. EPA, 1993. *Methods for Determination of Inorganic Substances in Environmental Samples. EPA/600/R-93/100* (Washington D.C).
- Upreti, K., 2019. *Evaluating Seasonal Nutrient Fluxes in Emerging and Eroding Wetlands of the Louisiana Delta Plain*. Doctoral Dissertation. Louisiana State University, Louisiana, USA.
- Valentine, K., Mariotti, G., 2019. Wind-driven water level fluctuations drive marsh edge erosion variability in microtidal coastal bays. *Cont. Shelf Res.* 176, 76–89. <https://doi.org/10.1016/j.csr.2019.03.002>.
- Vance, E., Brookes, P., Jenkinson, D., 1987. An extraction method for measuring soil microbial biomass C. *Soil Biol. Biochem.* 19 (6), 703–707. [https://doi.org/10.1016/0038-0717\(87\)90052-6](https://doi.org/10.1016/0038-0717(87)90052-6).
- VanZomerem, C., White, J., DeLaune, R., 2012. Fate of nitrate in vegetated brackish coastal marsh. *Soil Sci. Soc. Am. J.* 76 (5), 1919. <https://doi.org/10.2136/sssaj2011.0385>.
- VanZomerem, C., White, J., DeLaune, R., 2013. Ammonification and denitrification rates in coastal Louisiana bayou sediment and marsh soil: implications for Mississippi river diversion management. *Ecol. Eng.* 54, 77–81. <https://doi.org/10.1016/j.ecoleng.2013.01.029>.
- White, J., Reddy, K., 1999. Influence of nitrate and phosphorus loading on denitrifying enzyme activity in everglades wetland soils. *Soil Sci. Soc. Am. J.* 63 (6), 1945. <https://doi.org/10.2136/sssaj1999.6361945x>.
- White, J., Reddy, K., 2000. Influence of phosphorus loading on organic nitrogen mineralization of everglades soils. *Soil Sci. Soc. Am. J.* 64 (4), 1525. <https://doi.org/10.2136/sssaj2000.6441525x>.
- White, J., Reddy, K., 2003. Nitrification and denitrification rates of everglades wetland soils along a phosphorus-impacted gradient. *J. Environ. Qual.* 32 (6), 2436. <https://doi.org/10.2134/jeq2003.2436>.
- Williams, S., Stone, G., Burrus, A., 1997. A perspective on the Louisiana wetland loss and coastal erosion problem. *J. Coast. Res.* 13 (3).
- Wilson, C., Allison, M., 2008. An equilibrium profile model for retreating marsh shorelines in Southeast Louisiana. *Estuar. Coast. Shelf Sci.* 80 (4), 483–494. <https://doi.org/10.1016/j.ecss.2008.09.004>.