

# Consequences of Mississippi River diversions on nutrient dynamics of coastal wetland soils and estuarine sediments: A review

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## ABSTRACT

Coastal Louisiana is dominated by the Mississippi River Deltaic Plain, which is composed of a series of overlapping and truncated sub-delta lobes that formed an extensive coastal wetland – open water shallow bay and low relief upland mosaic across the entire coastal zone (~25,000 km<sup>2</sup>). These coastal wetlands have been eroding at an alarming rate during the past century, coincident with major modifications to the deltaic landscape. One of these former modifications included extensive leveeing of the Mississippi River, essentially isolating the river from the coastal basins. One restoration technique involves re-connecting the previously isolated coastal basins to the river via diversions, which would once again allow the influx of freshwater, sediments and nutrients into the coastal basins. We review issues on potential impacts of nutrient loading from the river as a consequence of river diversions, focused on nitrogen (N) and phosphorus (P) dynamics including denitrification related to carbon dynamics. We also examined how water residence times in these shallow systems, compared to deeper, often seasonally stratified, coastal systems, are more likely to lead to greater N removal potential in the context of a large scale river diversion helping to reduce N transport to the coastal ocean.

## 1. Introduction

Energy flow in deltaic coastal wetlands and shallow submerged sediments with high freshwater input is dominated by microbial activity associated with the decomposition of organic matter and associated biogeochemical interactions as riverine constituents interact with the coastal system. The underlying anaerobiosis, or reducing condition, that develops in waterlogged and flooded wetland soils and submerged sediments is well documented (Reddy and Delaune, 2008). Here we discuss how wetland soil and submerged sediments can change in response to the addition of freshwater, nutrients and sediments from freshwater and sediment diversion flows with emphasis on the Mississippi River Deltaic Plain (MRDP).

Oxygen is the most efficient respiratory terminal electron acceptor in terms of energy return and aerobic organic matter decomposition dominates the decomposition and nutrient release pathways when O<sub>2</sub> is readily available (Reddy and Delaune, 2008). However, O<sub>2</sub> is consumed rapidly in flooded wetland soils and bay bottom sediments because the O<sub>2</sub> diffusion rate is 10,000 times slower in water than in air

(Greenwood, 1961). The soil microbial consortia are not limited to the use of O<sub>2</sub> as their terminal electron acceptor. Some facultative organisms can alternatively utilize nitrate (NO<sub>3</sub><sup>-</sup>), while others use manganic manganese (Mn<sup>4+</sup>), ferric iron (Fe<sup>3+</sup>), sulfate (SO<sub>4</sub><sup>2-</sup>) and acetate/carbon dioxide (CO<sub>2</sub>) as receptors for electrons. These chemical species are preferentially utilized by soil microbial consortia in the order listed because of the declining efficiency of energy return per unit of carbon oxidized (Reddy and Delaune, 2008).

There is substantial accumulation of organic carbon through time in flooded anaerobic systems because of the declining efficiency of terminal electron acceptors and lower concentrations of each acceptor in waterlogged soils, the high rate of supply of organic matter, and the refractory nature of most soil organic matter. The electron acceptors and their reduced products are referred to as redox couples. The measurable electrochemical environment as defined by the reduction-oxidation status (redox potential or *E<sub>h</sub>*) indicates the dominant redox couple and allows for a prediction of reduced and oxidized electron acceptors (Reddy and Delaune, 2008). All of the aforementioned factors lead to much slower soil organic matter decomposition under anaerobic

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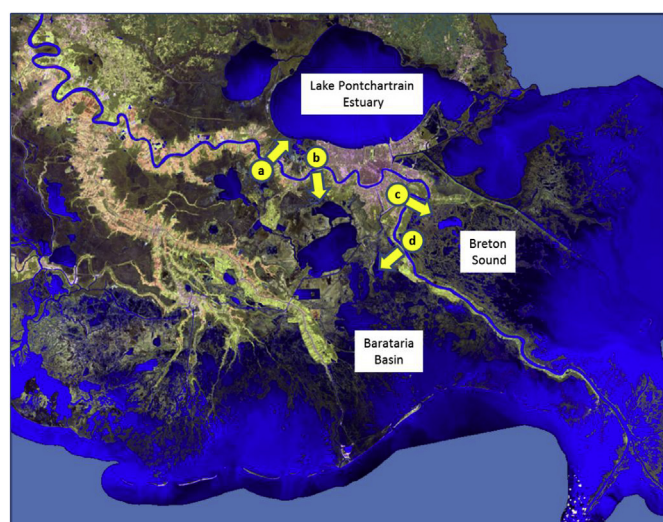
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**Fig. 1.** In the deltaic plain, the coastal basins are separated by current and abandoned river channels. a) Bonnet Carré Spillway b) Davis Pond Diversion, c) Breton Sound Diversion d) proposed Mid-Barataria Sediment Diversion.

than aerobic conditions (DeLaune and White, 2012).

### 1.1. The context of the Mississippi River Deltaic Plain

The biogeochemistry of coastal wetlands and shallow open water ecosystems of the MRDP is strongly impacted by the size and morphology of the delta. The MRDP is one of the largest coastal ecosystems in the world, covering ~25,000 km<sup>2</sup> of shallow inshore open waters, wetlands and low relief uplands (Day et al., 2007, 2014; Day and Erdman, 2018). The delta was formed by a series of adjacent and overlapping delta lobes as “channel switching” occurred over millennial time frames, leading the river to take alternate pathways to the Gulf of Mexico distributing water, sediments, and nutrients over the broad deltaic plain (Roberts, 1997; Blum and Roberts, 2012). These antecedent river channels formed elevated distributary ridges due to sand deposition along the margins that separates or subdivides the sub-basins of the current deltaic plain (Fig. 1; Roberts, 1997).

The delta is characterized by a series of vegetation zones along a salinity gradient, with saline marshes at the coastline that grade to brackish and freshwater marshes and freshwater forested wetlands in interior parts of the delta. The distributary ridges and barrier islands form a skeletal framework that protected freshwater interior parts of the delta from direct marine influences. Prior to hydrologic modifications, river water entered the coastal zone via the main river channels, but also by crevasses, minor distributaries, and overtopping of natural river levees during high river flow events (Day et al., 2000).

The delta has been impacted by a variety of human activities such as levee construction and closure of distributaries, pervasive hydrological alterations due to oil industry activities, impoundments, and barrier island losses beginning in the 18th century, and greatly accelerating throughout the 20th century. Flood control levees built during the last two centuries separated the lower Mississippi River from most of the deltaic plain, preventing seasonal flooding and inputs of freshwater, nutrients, and sediments to the surrounding wetlands (Kesel, 1988, 1989; Mossa, 1996; Roberts, 1997; Day et al., 2000, 2007; Twilley and Rivera-Monroy, 2009; Twilley et al., 2016). Factors impacting delta hydrology include the proliferation of dredged canals and induced subsidence due to oil and gas extraction (Day et al., 2000; Morton and Barras, 2011; Chan and Zoback, 2007). The sum total of these aforementioned alterations have led to salt water intrusion, deterioration of the skeletal delta framework, and contributed to the loss of about 25% of the coastal wetland land area. A significant contributing factor to

**Table 1**

A hierarchy of forcing or pulsing events affecting the formation and sustainability of deltas (adapted from Day et al., 1997, 2007, 2016).

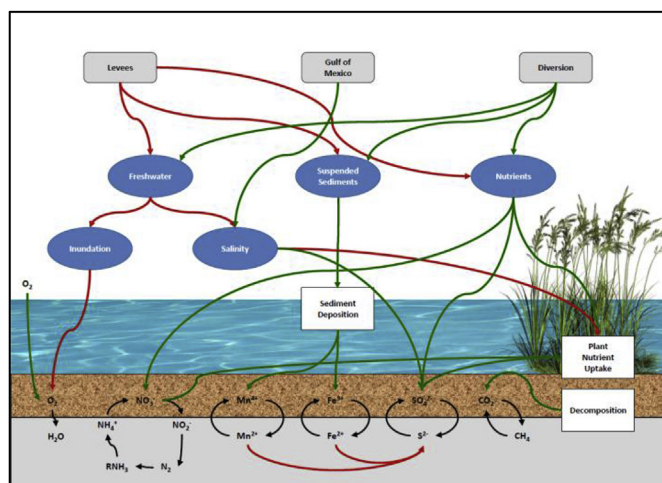
Event	Time Scale	Impact
Deltaic Lobes	100s to > 1000 years	Deltaic Lobe Development
Crevasses	10s–100 s years	Natural Levee development, Minor Lobe Development
Sea level rise	10 s years	Delta re-generation by flooding the estuarine flood plain.
Major River Floods	20–100 yrs.	Channel Switching
Major Storms	5–20 yrs.	Major Sediment Deposition
Average River Floods	Annual	Moderate Deposition
		Enhanced Production
		Enhanced Deposition
		Freshening (lower salinity)
		Nutrient Input
		Enhanced 1° and 2° Production
Normal Storm Events (Frontal Passages)	Weekly	Enhanced Deposition
		Organism Transport
		Net Sediment and Chemical Transport
Tides	Daily	Drainage/Marsh Production
		Low Net Transport

wetland loss is regional geologic subsidence (mean ~ 10 mm yr<sup>-1</sup>), primarily caused by compaction and consolidation of sediments, increasing rates of inundation by the sea. The river channel migration and switching delivered sediments and nutrients broadly across the coastal plain and were able to help compensate for most subsidence in the past. Once the river course was changed and stabilized, the abandoned delta lobes slowly eroded and the shoreline receded. Only in the active delta lobe, connected to and nourished by the river, is it possible to build and maintain substantial coastal land despite the coupled subsidence and global sea level rise.

The MRDP, and indeed all major deltas, is characterized by large scale spatial and temporal gradients. The functioning of deltas depends on regular and episodic, external and internal, inputs of energy and materials that produce benefits over different spatial and temporal scales (Odum et al., 1995; Day et al., 1997, 2007, 2016). These scales range from daily tides to longer term (100s–1000 years) development of new delta lobes (Table 1). Infrequent events, such as channel switching, crevasse formation, major river floods, and tropical cyclones largely control sediment delivery and impact coastal delta geomorphology (Roberts, 1997). More frequent events such as tidal inundation and frontal passages primarily alter salinity gradients and regulate biogeochemical and biological processes.

There are strong horizontal gradients that traverse tens to hundreds of kilometers because of the large spatial extent of the delta complex. One of the most important regulators of biogeochemical and ecological processes is salinity (Fig. 2). There are large freshwater environments in the Mississippi delta that cover 1000s of square kilometers. Biogeochemical processes that dominate in freshwater, such as methane production, are often relatively unimportant in many saline coastal estuarine environments, due to the higher poised redox level associated with SO<sub>4</sub> reduction (Reddy and Delaune, 2008). In deltaic systems, the large spatial expanse produces a complex geometry of marsh and open water with high potential for frictional forces which can slow water flow, generally producing long residence time for freshwater. The diurnal, low tidal range in the Mississippi also contributes to longer residence times. Just as longer retention times generate increased nutrient removal in treatment wetlands (Wang et al., 2006; Hunter et al., 2018), this environment leads to high rates of nutrient retention in the delta.

The vertical dimension in the delta is of particular importance due to the high rate of subsidence (~10 mm yr<sup>-1</sup>) coupled with increasing



**Fig. 2.** Conceptual model of the biogeochemistry of emergent wetlands. Green lines indicate a positive response between model components, and red lines indicate a negative response, as discussed in the accompanying text. Figure adapted from Steyer et al. (2008). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

rates of eustatic sea level rise ( $\sim 3\text{--}4\text{ mm yr}^{-1}$  at the end of the 20th century). Therefore, burial and hence sequestration of C, N, P, and other elements can be very high compared to most non-deltaic, more stable coastal environments which are solely influenced by global eustatic sea-level rise (Boynton and Kemp, 2008; DeLaune et al., 2018).

### 1.2. How do river diversions impact deltaic ecosystems?

River diversions transport freshwater, nutrients and sediments into previously disconnected coastal basins which can alter the biogeochemistry of these wetlands and shallow open waters (Peyronnin et al., 2017) (Fig. 2). The increased hydraulic loading pushes isohalines towards the ocean, leading to a freshening up of the surface water and soils of the basin (Huang et al., 2011; Das et al., 2012). In addition, significant flows increase flooding frequency and duration of the coastal marshes, leading to increased preservation of the organic substrate (DeLaune and White, 2012). Sediments, which include sand, silt and clay particles carried by river water, are also discharged into the coastal basins during flood events. Deposition of inorganic material on the wetland surface plays a vital role in helping increase the elevation of the marsh in face of rising sea level and increases the bulk density of the marsh soils (Day et al., 2011; Kral et al., 2012; Roberts et al., 2015).

The sediment load of the Mississippi River is the major pool of phosphorus (P) to the coastal basins, as the river water column concentration is generally low ( $\sim 0.08\text{ mg P L}^{-1}$ ) in bioavailable dissolved reactive P (DRP) (Lane et al., 1999, 2002; White et al., 2009). The riverine sediment-bound P, which includes associations with Ca, Mg, Fe and Al, can substantially increase the total P of the receiving basin sediment. This influence was observed in the Lake Pontchartrain estuary where surface sediment TP concentrations doubled after a month-long flood release discharge from the Mississippi River via the Bonnet Carré Spillway, a flood control outlet on the Mississippi River (Roy et al., 2017). This increase is sediment TP, typically referred to as the internal load, can undergo a transformation shifting to bioavailable over time which can alter the nutrient stoichiometry of the estuary (Reddy et al., 2011). Once deposited, the sediment P load, primarily unreactive total P, is subjected to reducing conditions. Over several months, there is a slow release of this newly added sediment TP, as dissolved reactive P, leading to an increase in the water column concentrations (Roy et al., 2012). The increase in P availability over time is due to the reduction of the deposited insoluble ferric iron ( $\text{Fe}^{3+}$ ) to mobile soluble ferrous iron ( $\text{Fe}^{2+}$ ) under anaerobic conditions in

submerged sediments. This mechanism of Fe-bound P release from Mississippi River sediment has been documented in both coastal LA wetlands (Zhang et al., 2012) and along the LA coastal shelf (Adhikari et al., 2015; Ghaisas et al., 2019) as well as in many estuaries around the world (Boynton et al., 2018). A major concern for rapid release of bioavailable P from river-diverted sediments is the potential for development of algal blooms, in particular harmful cyanobacteria. Several species forming harmful algal blooms are capable of exploiting high P, low N conditions due to N-fixing capabilities, and can lead to a delayed expression of eutrophication as the P leaks from the sediment to the water column over time (Roy et al., 2016; Bargu et al., 2011, 2019).

The river nitrogen load is in stark contrast to the particle-associated P load. The major N load in the river is  $> 90\%$  in the bioavailable pool as  $\text{NO}_3^-$ . Therefore, river diversions can immediately stimulate denitrification in flooded, organic-rich wetland soils and bay sediments by providing the limiting substrate  $\text{NO}_3^-$ . Therefore, diversion of river water into coastal basins can potentially reduce the mass of bioavailable N reaching the coastal ocean (Gardner and White, 2010; Hurst et al., 2016; Lane et al., 1999, 2004). In addition, N retention and sequestration is increased through plant uptake of bioavailable N in the coastal marshes, eventually deposited as detrital material as macrophytes senesce and is preserved through reduced conditions in the soil (Esley-Quirk et al., 2019 this issue). Greater rates of land subsidence will support greater rates of C and N sequestration in the wetland soil as the organic matter is more quickly buried and becomes part of the anaerobic portion of the soil profile. Due to high concentrations, bioavailable N is the predominant nutrient concern in coastal LA leading to a relatively high molar N:P ratio of river water (Roy et al., 2013). However, as river water flows through coastal basins, nitrogen is rapidly reduced due to the non-conservative uptake of nitrate, resulting in decreases in the N:P ratio often to below the Redfield ratio (Lane et al., 1999, 2002, 2004, 2010; Day et al., 2009). Nitrogen is the primary nutrient driving the annual formation of hypoxic coastal waters and is therefore the focus of much of the research and policy in coastal LA (Rabalais et al., 2002). Only recently have researchers investigated the role of DRP release from coastal shelf sediments in potentially extending periods of hypoxia by providing a secondary source of P once the river DRP has been reduced during primary production (Adhikari et al., 2015; Ghaisas et al., 2019).

The Atchafalaya River discharges high levels of nitrogen and other nutrients to a large deltaic estuary along the central Louisiana coast (Bianchi and Allison, 2009). The dynamics of nutrient cycling in this river-influenced estuary can serve as model of how nutrients from major river diversions will be processed in Mississippi delta coastal system that extend out onto the shallow shelf compared to inshore systems that are shallow with extensive wetlands (Perez et al., 2000, 2003, 2010; Lane et al., 2010; Twilley et al., 2019 this issue). Four-league Bay is a  $95\text{-km}^2$  delta estuary bounded by a vast coastal wetland complex located  $\sim 10\text{ km}$  southeast of the mouth of the Atchafalaya River with a mean depth of  $\sim 1.5\text{ m}$ , with a well-mixed water column and a tidal range of about  $0.30\text{ m}$ . The advection of river water into these wetlands is driven by high water induced by Atchafalaya River discharge and by pre-frontal winds during frontal passages (Perez et al., 2000, 2003). A majority of the mean discharge of  $6400\text{ m}^3\text{ s}^{-1}$  from the Atchafalaya River discharges into Atchafalaya Bay, which is a  $150\text{-km}$ -wide shelf area with shallow water extending  $40\text{ km}$  offshore to shelf edge. The unbounded Atchafalaya Bay is a broad, shallow ( $< 2\text{--}3\text{ m}$ ) embayment coupled to a shallow and broad low-gradient shelf ( $10\text{-m}$  isobath is more than  $40\text{ km}$  offshore of the delta), which is exposed to episodically energetic storms (Allison et al., 2000). The river plume from the Atchafalaya extends out beyond the shelf edge during high flow, generating physical and biogeochemical impacts in the coastal and deep-water ocean mostly westward to the Texas shelf. This easily identifiable turbid water plume at high discharge defines the large delta estuary seaward boundary (Bianchi and Allison, 2009). The fate of nutrients from a river diversion in this region involves two sub-estuaries



with contrasting processes in the way that wetlands, benthic biogeochemical processes, and residence time influence nitrogen transport to the coastal ocean.

In the bounded Fourleague Bay estuary, denitrification reduces nitrogen in both estuarine and marsh sediments under anaerobic conditions, whereas wetlands have much less impact, due to limited contact with inflowing river water, in the open waters of Atchafalaya Bay. In addition, the lower concentration of  $\text{NO}_3$  in ebb waters from a marsh compared to higher concentrations when tidal waters flood a marsh are also indicative of denitrification and plant uptake. Denitrification is controlled by the availability of  $\text{NO}_3$  in water column in river-dominated estuaries and we estimated denitrification rates of  $40 \mu\text{mol m}^{-2} \text{hr}^{-1}$  in the Atchafalaya Bay unbounded estuary that extends to the shallow shelf (Roberts and Doty, 2015) compared to  $50\text{--}100 \mu\text{mol}$  in Fourleague Bay. Fourleague Bay has higher  $\text{NO}_3$  uptake rates by sediment exceeding  $200 \mu\text{mol m}^{-2} \text{hr}^{-1}$  when  $\text{NO}_3$  levels are over  $100 \mu\text{M}$  in water column (Teague et al., 1988; Twilley et al., 1999). However, actual rates of denitrification using acetylene blockage in sediment slurries from 5 bay and 5 marsh stations in Fourleague Bay ranged from  $17$  to  $14 \mu\text{mol m}^{-2} \text{hr}^{-1}$  for estuarine and marsh sediment, respectively (Smith and DeLaune, 1985; Smith et al., 1985;  $2.1 \text{ g N}_2\text{-N m}^{-2} \text{yr}^{-1}$  and  $1.7 \text{ g N}_2\text{-N m}^{-2} \text{yr}^{-1}$ , respectively). It has been estimated that approximately  $1.95 \times 105 \text{ kg N}$ , predominantly as  $\text{N}_2$ , is being returned to the atmosphere via denitrification. This mass is estimated to be equivalent to 50% of the riverine  $\text{NO}_3$  entering Fourleague Bay. These rates for denitrification are much lower than rates estimated from benthic flux studies, and lower than denitrification rates using estimates of  $\text{N}_2$  fluxes from sediments in coastal deltaic floodplains (Henry and Twilley, 2014). Thus, the direct conversion of  $\text{NO}_3$  to  $\text{N}_2$  may represent half of the major loading of inorganic nitrogen to these river-dominated estuaries.

There has been research that has shown some of this  $\text{NO}_3$  may be reduced to  $\text{NH}_4$  by dissimilatory nitrate reduction. The  $^{15}\text{N}$  recovery measurements in Barataria salt marsh soils showed that up to 52% of nitrate “losses” may actually be retained within the system (Smith et al., 1982). Some of this ammonium becomes assimilated into organic matter that is then deposited or buried in marsh soils, and thus still represents nitrogen loss from sediment exchange. The annual sediment accumulation of N buried in estuarine and marsh sediments is also considered a nitrogen sink, considering this nitrogen is not transported downstream to Gulf shelf ecosystems. Nitrogen accumulation ranged from  $6.0$  to  $23 \text{ g N m}^{-2} \text{yr}^{-1}$  on the marsh and  $6.1\text{--}11.2 \text{ g N m}^{-2} \text{yr}^{-1}$  in Fourleague Bay. These rates are equivalent to  $50\text{--}90 \mu\text{mol m}^{-2} \text{hr}^{-1}$  of nitrogen losses, and are similar to ranges for  $\text{NO}_3$  described above for Fourleague Bay (Smith et al., 1985). Particulate organic nitrogen accumulation in the bay bottom due to sedimentation was estimated to be  $7.9 \times 10^5 \text{ kg N per yr}$ ; an amount equivalent to 60% of the inorganic N entering this estuary. Thus, the sum of direct denitrification of  $\text{NO}_3$  in the water column and nitrogen burial in sediments equals the loading of inorganic nitrogen from Atchafalaya River to the bounded sub-estuary, Fourleague Bay. It is important to note that while these processes may account for the inorganic loading from major river diversion to the gulf waters, there are still sources from organic nitrogen loading, mineralization of organic N and nitrogen fixation that could be contributing to the nitrogen budget.

### 1.3. Nitrogen export from estuarine systems vs residence time

Several studies have reported that freshwater residence time is a good predictor of the percentage of total nitrogen exported to the coastal ocean. Nixon et al. (1996) and Dettmann (2001) reported on a number of coastal systems and found that the percentage of annual-scale TN inputs that were exported was inversely related to the log of the water residence time (Fig. 3, black circles). The coastal systems analyzed by Nixon et al. (1996) and Dettmann (2001) are generally characterized as relatively deep, seasonally or annually stratified, mid

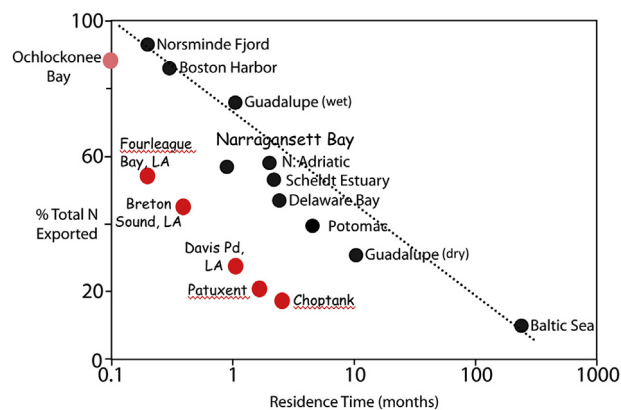


Fig. 3. Percent of total N inputs that are exported from different estuarine systems versus freshwater residence time. The black circles are from Nixon et al., (1996) and Dettmann (2001). Red circles are from more recent analyses by Lane et al., (2004), Boynton et al. 2008, Perez et al., (2010), and unpublished data from D. Justic (LSU) and T. Fisher and J. Cormwell (Univ MD Center for Environmental Science). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

to north temperate by location with small expanses or virtually no wetlands, with one exception (Ocklocknee Bay), compared to shallow, open water areas with large areas of emergent vegetation such as those in the Mississippi delta. More recent analyses, which included systems that are generally shallower, less likely to stratify, warmer and with large expanses of wetlands relative to open water (Fig. 3) suggest these systems do not fit the trend for systems characterized by Nixon et al. (1996) and Dettmann (2001), but rather remove considerably more N for a given water residence time.

Nitrogen retention in estuarine and wetland systems is also generally inversely related to hydraulic and nutrient loading rate with uptake related to the factors discussed above (Kadlec and Knight, 1996; Mitsch et al., 2001). For Breton Sound (Fig. 1), which receives river water through the Caernarvon diversion, 88–97% of  $\text{NO}_3$  was non-conservatively removed from the water column at loading rates less than  $13 \text{ g N m}^{-2} \text{yr}^{-1}$  with lower percent reduction at higher loadings (Lane et al., 1999, 2004). Lower retention rates have been reported for the Hudson River (15% retention; Lampman et al., 1999) and for the Ems estuary (17% retained; Van Beusekom and de Jonge, 1998). Smith et al. (1985) reported that approximately 50% of the  $\text{NO}_3$  entering Fourleague Bay was lost via denitrification, a higher percentage than reported for the Potomac (13%), Chesapeake (25%), Patuxent (31%; Boynton et al., 1995), and Ems (19%; Van Beusekom and de Jonge, 1998), but lower than the Choptank (79%; Boynton et al., 1995). Boynton et al. (1995) suggested that high removal of nitrogen inputs via denitrification was a function of the percentage of TN entering an estuary as  $\text{NO}_3$ . At low TN loading rates,  $\text{NO}_3$  and organic matter may limit denitrification with rates increasing with additional TN loading until hypoxia or anoxia hinders nitrification and thus an indirect source of nitrate, especially during warmer periods of the year (Boynton et al., 1995). This line of reasoning indicates that stratification limits N retention via inhibition of indirect denitrification in those cases where stratification promotes hypoxic conditions. Lane et al. (2002) reported that 41%–47% of Atchafalaya River  $\text{NO}_3$  was either transformed or lost before reaching stratified Gulf waters. Inherent in this comparison of systems is the difference in water volume to wetland soil and sediment surface area. Surface waters of the deeper coastal systems that stratify in the warmer parts of the year with less wetland area (black circles, Fig. 3) have limited contact with the estuarine sediment compared with the shallower systems. Beyond the aforementioned differences, there are several studies which have documented that the wetland soil denitrification rates are substantially greater than those of estuarine

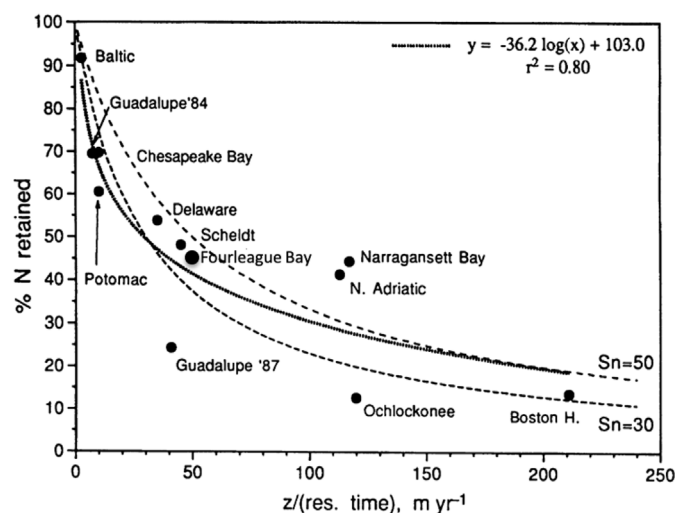


Fig. 4. The percent of total nitrogen input from land and atmosphere that is retained (buried and denitrified) as a function of the ratio of mean depth ( $z$ , m) to fresh water residence time in the system. Years are used rather than months in the x-axis units. The broken lines were calculated using the model of Kelly et al. (1987).

sediment. For example, Marks et al. (2016) found that denitrification potential was on average 4.7 times high in both salt and fresh marsh soils compared to the lower C, subaqueous sediment. This difference was attributed to the lower available carbon in the sediments and demonstrates the importance of the presence of wetland plants in N removal through denitrification (Marks et al., 2016).

When the % N exported is plotted against the ratio of mean depth to fresh water residence time, the impact of depth becomes clear for the data set of Nixon et al. and Dettman (Fig. 4). When depth divided by residence time is plotted for Fourleague Bay, it falls on the Nixon-Dettman relationship. This result shows the importance of depth in affecting N retention.

In summary, a number of factors can ultimately influence nutrient retention. There are several differences between the estuaries studied by Nixon et al. (1996) and Dettmann (2001) compared with Louisiana and shallow systems in the Chesapeake Bay region that help explain the difference in nutrient retention. Louisiana systems are microtidal and along with the Choptank, are shallow, warm temperate to subtropical, and rarely stratified (Choptank) or seasonally stratified (Patuxent) systems surrounded by extensive fresh, brackish, and saline marshes. In Louisiana systems, there is a high rate of organic matter burial due to the high subsidence. Due to these factors, nitrogen sinks such as denitrification, burial, and marsh plant uptake can remove more nitrogen than in systems not having these important characteristics (DeLaune et al., 1981; Smith and DeLaune, 1985; Smith et al., 1985; Penland and Ramsey, 1990). High rates of relative sea level rise (subsidence plus eustatic sea-level rise) in the Mississippi Delta of about  $1.3 \text{ cm yr}^{-1}$  (Penland and Ramsey, 1990) drives the high rates of nitrogen burial (e.g.,  $21 \text{ g N m}^{-2} \text{ yr}^{-1}$  accumulation in Barataria Bay marshes; DeLaune et al., 1981).

There is also a consistent time-dependence of N removal through organic matter accretion. DeLaune et al. (2018) note that over multi-decadal time scales (50 yr), organic matter accretion rates in Wax Lake Delta marsh soil averaged  $1.43 \text{ cm yr}^{-1}$ . However, that same location has a longer term accretion rate of  $0.12 \text{ cm yr}^{-1}$  over millennial ( $\sim 3000$  yrs) time scales. It is conceivable to have such variability in a deltaic setting due to channel switching/delta lobe switching which would dramatically change depositional environments dependent upon proximity to the active meandering river channel. However, DeLaune et al. (2018) noted that this disparity between short and long term accretion rates is consistently found in other more stable, non-deltaic

coastal settings (Bridgman and Richardson, 2003; Parkinson et al., 1994; Hussein et al., 2004) raising questions as to the permanence of carbon and nitrogen removal in coastal wetland systems over millennial time scales.

There are frequent cold fronts that cause high resuspension of bay bottom sediments and large changes in water levels that lead to inundation of the marsh surface with high TSS levels and high deposition rates on the wetland surface in coastal Louisiana during the winter and spring seasons (Perez et al., 2003; Roberts et al., 2015). This tight coupling among water column, shallow benthic sediments and adjacent marshes combined with warmer temperatures enhances nitrogen retention/removal. These conditions are also characteristic of the Choptank and Patuxent, especially in the oligohaline and tidal freshwater regions, which contain extensive wetlands, where tidal water contact with wetland soil denitrifiers and wetland macrophytes is a regular occurrence (Boynton et al. 2008; Greene, 2005).

The seasonally variable TN export in the MRDP reflects greater variability in water residence times compared to the systems analyzed by Nixon et al. (1996) and Dettmann (2001). Systems impacted by river flow have variable residence times linked to seasonality of the river floods. For example, the TN export from Fourleague Bay, Louisiana ranged from less than 5% at high residence times (104 days) to greater than 80% at low residence times (3–7 days), that latter which occurred during cooler temperatures and high freshwater flow conditions (Perez et al., 2010). Nitrate uptake values exceeded 60% of inputs when temperatures were above  $20^\circ\text{C}$  (Perez et al., 2010). Madden et al. (1988) reported mean residence times of approximately 7 days during the spring discharge of the Atchafalaya River and 65 days during low flow discharge in summer and fall months. Reported residence times of other estuaries vary widely and include  $> 300$  days for Corpus Christi and Aransas Bays in Texas (Solis and Powell, 1999); 20 days for the Ems estuary (Netherlands, van Beusekom & de Jonge, 1998); and 7 days for Sabine Lake, Louisiana; 40 days for Galveston Bay, Texas; and 77 days for Matagorda Bay, Texas (Armstrong, 1982). Martin and Reddy (1997) noted in a modeling study that the limiting factor for nitrate removal in wetlands was the diffusion of  $\text{NO}_3$  from the water column to the soil. Consequently, increasing the residence time of the water dramatically increases N removal through denitrification.

#### 1.4. Effect of nitrate loading on wetland soils

The microbial reduction of nitrate in wetland soil is considered a valuable ecosystem service, such that a large number of constructed and natural wetlands are used to reduce bioavailable N pollution from wastewater discharges (Reddy and DeLaune, 2008). Conditions that are optimum for denitrification include 1) reduced soil conditions, since facultative denitrifiers would preferentially use oxygen for respiration, if available, 2) availability of low molecular weight DOC compounds, as an energy source, 3) availability of nitrate as an alternate respiratory substrate, and 4) the presence of microbial groups capable of denitrification. There appears to be a near ubiquitous presence of soil denitrifiers in soils and therefore the presence of functional microbial populations appears to almost never be the limiting factor for denitrification to proceed. High environmental nitrate concentrations in surface water are still relatively low, measured in parts per million, when compared to the soil carbon which is expressed in per cent or parts hundred. Consequently, the greater the water residence time in the basin, the greater the denitrification potential as soil bioavailable carbon is rarely limiting in these flooded systems. Denitrification activity, driven by coupled nitrification – denitrification processes, is generally low in comparison to nutrient loading from external sources (White and Reddy, 1999, 2003).

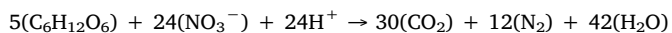
High nitrate uptake rates have been reported in areas of the Mississippi delta receiving river water. DeLaune et al. (2005) reported that nitrate in Mississippi River inflows into the vegetated Davis Pond diversion (Fig. 1) was removed at a rate of  $23 \text{ g N m}^{-2} \text{ yr}^{-1}$  which

includes N removal through plant uptake and denitrification. A  $^{15}\text{N}$  labeled field study at the same location estimated a denitrification rate of  $14.7 \text{ g N m}^{-2} \text{ yr}^{-1}$  through measurement of gaseous  $\text{N}_2$  production (Yu et al., 2006). Therefore, a total removal of  $23 \text{ g N m}^{-2} \text{ yr}^{-1}$  was primarily driven by the denitrification rate of  $14.7 \text{ g N m}^{-2} \text{ yr}^{-1}$ , which represents 63.9% of the loss of N. The remaining 36.1% reduction of N was concluded to be through assimilation by macrophytes. This relative rate of nitrate removal by macrophytes and denitrification was corroborated in a greenhouse study conducted by VanZomeren et al. (2012) for Breton Sound, under influence of river water flows from the Caernarvon diversion (Fig. 1). They reported that 36% of the added  $^{15}\text{N}$ -labeled  $\text{NO}_3^-$  was present primarily in the aboveground and belowground macrophyte compartments, while the vast majority of added N, an almost identical 64% in comparison to the DeLaune et al. (2005) study, was removed through gaseous loss. In another study, while the exact pathways of N loss are not identified, there is strong non-conservative uptake of  $\text{NO}_3^-$  in Breton Sound and in areas impacted by Atchafalaya River discharge (Lane et al., 1999, 2002, 2004; Perez et al., 2003, 2010).

There have been concerns that denitrification has the potential for weakening or destabilizing the marsh soils. These concerns center on the fact that denitrification is coupled to the oxidation of organic matter (Deegan et al., 2012; Bodker et al., 2015).

Consider first the issue of denitrification affecting wetland soil carbon stocks. The process of nitrate reduction is highly unlikely to affect the stability of the high concentrations of high molecular weight solid organic matter comprising much of the coastal marsh soils. Heterotrophic microbes produce and expel extracellular enzymes capable of slowly breaking down more complex organic matter into small molecular weight compounds useable by the microbial pool (Wright and Reddy, 2007). However, not all carbon compounds are the same. Dodla et al. (2012) found that simple C compounds like polysaccharides increased denitrification rates while more stable compounds, like phenolic compounds, negatively affected denitrification rates. Organic C compounds that support denitrification include glucose, methanol, ethanol and acetate among others (Soares and Abeliovich, 1988; Korom, 1992). Consequently, microbial respiration is more likely driven by the available DOC in the surface and porewaters than *de novo* DOC production through the decay continuum (Reddy and DeLaune, 2008).

Increasing nitrate loading can potentially stimulate extracellular enzyme production capable of catabolism of carbon-containing compounds. But the organic carbon content of most peaty wetland soils is higher than 20% (parts per hundred) and the concentrations of nitrate is generally in the single digits  $\text{mg N L}^{-1}$  (ppm), thus denitrification cannot lead to significant soil organic matter decomposition. This is indicated by a stoichiometric analysis based on the following equation (after Reddy and DeLaune, 2008).



Some 30 mol of carbon are utilized for every 24 mol of N, which reduces to a molar ratio of 5 C: 4 N. Considering the soil has > 200,000 ppm total carbon, 4 ppm  $\text{NO}_3\text{-N}$  consumes 5 ppm C or 0.0025% of the soil total C. Given the microbial consortia are using only the small molecular weight DOC, the vast majority of the carbon in the soil, the “structural” carbon, is not at risk from this process. Day et al. (2018) reviewed three case studies where  $\text{NO}_3^-$  was added to coastal systems including a wetland assimilation system, a freshwater diversion in Louisiana, and a nutrient addition experiment in New England. They concluded that denitrification could oxidize a few percent of soil organic matter in Louisiana and only in the New England case with comparable organic matter content soil, where loading rates were very high, could denitrification potentially cause significant soil organic matter decomposition. This finding was further supported by the

observation that the organic matter along the creek banks, which had significant contact with the high concentrations of creek nitrate, was the more vulnerable C pool that likely played a role in causing bank collapse.

## 2. Conclusions

River deltas are highly dynamic systems shaped by river hydrology and ocean tidal and wave forcing. As sea level continues to rise, the stability of the world's deltas is at risk. River systems worldwide are currently enriched with nutrients derived from agricultural activities, atmospheric deposition, stormwater runoff and wastewater inputs. The state of Louisiana is embarking on large scale coastal system restoration using a variety of techniques that vary in spatial and temporal scale, cost and impact. Reconnection of the Mississippi River to the coastal basins via diversions is one restoration technique with the potential to impact large regions of the coastal basins. However, diversion of river water containing land building sediment, also directs significant nutrient loads, in particular nitrate, into estuarine and coastal bay waters. This paper examined the pertinent literature from coastal systems to examine the potential response of the shallow coastal basins of Louisiana to diversions of nutrients from the Mississippi River. The concern over nutrient loading from the Mississippi River is focused on N, primarily nitrate, due to the rapid uptake of  $\text{NO}_3^-$ , the decrease in the N:P ratio, and the immediately availability of N upon discharge into the coastal basins. Nitrate removal in coastal wetlands has been shown to be reduced by two major pathways; uptake and denitrification  $\sim 1/3$  taken up by macrophytes and subsequently incorporated into the peat soil and  $\sim 2/3$  denitrified and lost to the atmosphere. The denitrification process utilizes such a limited fraction of a very large C pool, that it is highly unlikely to affect the wetland soil C stocks or stability. The warmer and shallower coastal basins of the Mississippi River delta with large expanses of surrounding wetlands have comparatively larger N removal potential under similar water residence times compared with the more northern, cooler, deeper and more stratified estuarine systems with less important wetland interfaces. A major P pool, with low initial bioavailability, is located in the sediments of the river. However, once P is deposited in coastal system soils, anaerobic soil/sediment conditions lead to Fe reduction, slowly releasing dissolved reactive P over longer periods of time compared with N dynamics. Delta formation, stability and ecology is driven by delivery of freshwater, sediments and nutrients. The restoration of coastal deltaic Louisiana is therefore reliant upon re-initiating the river connections to the coastal bays and wetlands to help combat and slow some of the greatest coastal land loss rates in the world with the additional opportunity of reducing some of the bioavailable N load currently reaching the coastal ocean.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ecss.2019.04.027>.

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