

# Water Resources Research

## RESEARCH ARTICLE

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### Special Section:

Coastal Hydrology and Oceanography

### Key Points:

- NDVI, a vegetation index, is a useful predictor of nitrate removal in delta environments
- Intermediate elevation areas are hot spots for nitrate removal on Wax Lake Delta
- Eastern channels receive and remove more nitrate from Wax Lake Delta

### Supporting Information:

- Supporting Information S1
- Figure S1
- Figure S2
- Figure S3
- Figure S4

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## Nitrate Removal Across Ecogeomorphic Zones in Wax Lake Delta, Louisiana (USA)

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**Abstract** Human activities have increased nitrate export from rivers, degrading coastal water quality. At deltaic river mouths, the flow of water through wetlands increases nitrate removal, and the spatial organization of removal rates influences coastal water quality. To understand the spatial distribution of nitrate removal in a river-dominated delta, we deployed 23 benthic chambers across ecogeomorphic zones with varying elevation, vegetation, and sediment properties in Wax Lake Delta (Louisiana, USA) in June 2018. Regression analyses indicate that normalized difference vegetation index is a useful predictor of summertime nitrate removal. Mass transfer velocity were approximately three times greater on a vegetated submerged levee (13 mm hr<sup>-1</sup>), where normalized difference vegetation index was greatest, compared to other locations (4.6 mm hr<sup>-1</sup>). Two methods were developed to upscale nitrate removal across the delta. The flooded-delta method integrates spatially explicit potential removal rates across submerged portions of the delta and suggests that intermediate elevations on the delta—including submerged levees—are responsible for 70% of potential nitrate removal despite covering only 33% of the flooded area. The channel network method treats the delta as a network of river channels and suggests that although secondary channels are more efficient than primary channels at removing received nitrate, primary channels collectively contribute more to overall removal because they convey more of the total nitrate load. The two upscaling methods predict similar rates of nitrate removal, equivalent to less than 4% of nitrate entering the delta. To protect coastal waters against high nitrate loads, management policies should aim to reduce upstream nutrient loads.

## 1. Introduction

Over the past century, humans have increased global nitrogen availability primarily through fertilizer use and energy production (Galloway et al., 2008). Excess nitrogen leaches from the landscape into shallow groundwater and surface waters, reducing water quality and stimulating the development of algal blooms that can reduce biodiversity and compromise fisheries. As a prime example, the Mississippi River delivers up to  $1.6 \times 10^6$  t of nitrogen to the Gulf of Mexico annually, leading to the development of one of the world's largest hypoxic zones (Alexander et al., 2008; Goolsby et al., 1999; Rabalais et al., 2002).

Coastal wetlands act as sinks for nitrate (Odum, 1988; Reddy & Gale, 1994; Seitzinger et al., 2006), and deltaic wetlands are ideally positioned to help buffer nutrient loads from rivers (Sawyer et al., 2015). Since deltas form at 40% of all coastal river mouths (Caldwell et al., 2019), they are important final filters of continental water before it is discharged into the ocean. Moreover, deltas are under threat from rising relative sea levels, climate change, and sediment starvation due to the construction of dams and reservoirs (Syvitski et al., 2009). In threatened deltas, river diversion projects are a proposed mechanism to reclaim coastal wetlands by building new land (Day et al., 2007; Foufoula-Georgiou et al., 2011; Paola et al., 2011; Twilley & Rivera-Monroy, 2009). River diversion projects can benefit from an improved understanding of nitrate retention in deltas and the biophysical factors that control it.

Nitrate may be removed through several mechanisms in deltaic wetlands, including denitrification, biological uptake, and dissimilatory nitrate reduction to ammonium (DNRA) (Saeed & Sun, 2012). Denitrification is a form of anaerobic respiration typically occurring in low oxygen environments and at anoxic microsites (Seitzinger et al., 2006). In the presence of sufficient organic matter, facultative bacteria reduce nitrate to



gaseous nitrogen, permanently removing nitrogen from the ecosystem. Plants and microbes take up ammonium and nitrate (biological uptake), converting the inorganic nitrogen to organic forms for use as building blocks for cells and tissues (Vymazal, 1995). However, plants eventually release much of this accumulated nitrogen back into the environment as detrital organic matter (Vymazal, 2007). DNRA involves the reduction of nitrite and nitrate to ammonium, but ammonium is converted back to nitrate by chemolithotrophs through nitrification in the presence of oxygen (Burgin & Hamilton, 2007; Reddy et al., 1984). Thus, both biological uptake and DNRA only temporarily remove nitrate from the aquatic ecosystem, while denitrification is a permanent sink (Burgin & Hamilton, 2007; Saunders & Kalff, 2001).

The efficiency of nitrate removal in wetlands generally depends on the residence time of flowing water and reaction rates (Baker & Vervier, 2004; Hernandez & Mitsch, 2007; Kjellin et al., 2007). For example, riparian wetlands can be highly efficient sinks of nitrate under low discharge rates (DeLaune et al., 2005; Forshay & Stanley, 2005). However, the efficiency of nitrate removal within deltaic wetlands, which can have a wide range of residence times and reaction rates, remains unclear. Within Wax Lake Delta, 23–54% of water that enters the channel network moves through the mostly inundated interiors of islands via overtopping of levees and flow through secondary channels and embayments (Hiatt & Passalacqua, 2015). Travel times through the islands are at least three times greater than those through the channels (Hiatt & Passalacqua, 2015), and residence times within islands further increase with hydraulic roughness associated with vegetation (Hiatt et al., 2018). Reaction rates also appear to be heterogeneous, as older islands with more mature soils have higher potential denitrification rates compared to younger islands (Henry & Twilley, 2014). Removal rates may further depend on biophysical parameters such as water depth—a control on sediment-water interactions (Alexander et al., 2000)—and vegetation density, a control on biotic uptake (Hill, 1986).

Given the dependence of nitrate removal on residence times and reaction rates and thus biophysical parameters such as water depth and vegetation density, nitrate removal should vary across ecogeomorphic zones with distinct hydrologic and biogeochemical characteristics such as delta levees, channels, and embayments (defined by Shaw et al., 2013, as the centers of islands that are continually flooded and open to the bay). To understand how nitrate removal varies across ecogeomorphic zones, we measured rates of nitrate removal with benthic chambers in an island of Wax Lake Delta, Louisiana, USA. We relate chamber measurements to environmental parameters associated with ecogeomorphic zones, such as water depth and vegetation cover, in order to upscale nitrate removal estimates to the whole delta. The first upscaling approach estimates spatially explicit potential nitrate removal rates across the submerged delta area but does not consider transport processes; while the second approach treats the delta as a network of channels and considers the integrated effect of transport and reactions along flow paths through the channel network but only implicitly includes removal in off-channel storage zones like levees and embayments. Despite the simplicity of these disparate upscaling approaches, both calculations suggest that removal represents a small portion of the total incoming nutrient load to Wax Lake Delta under typical summer conditions.

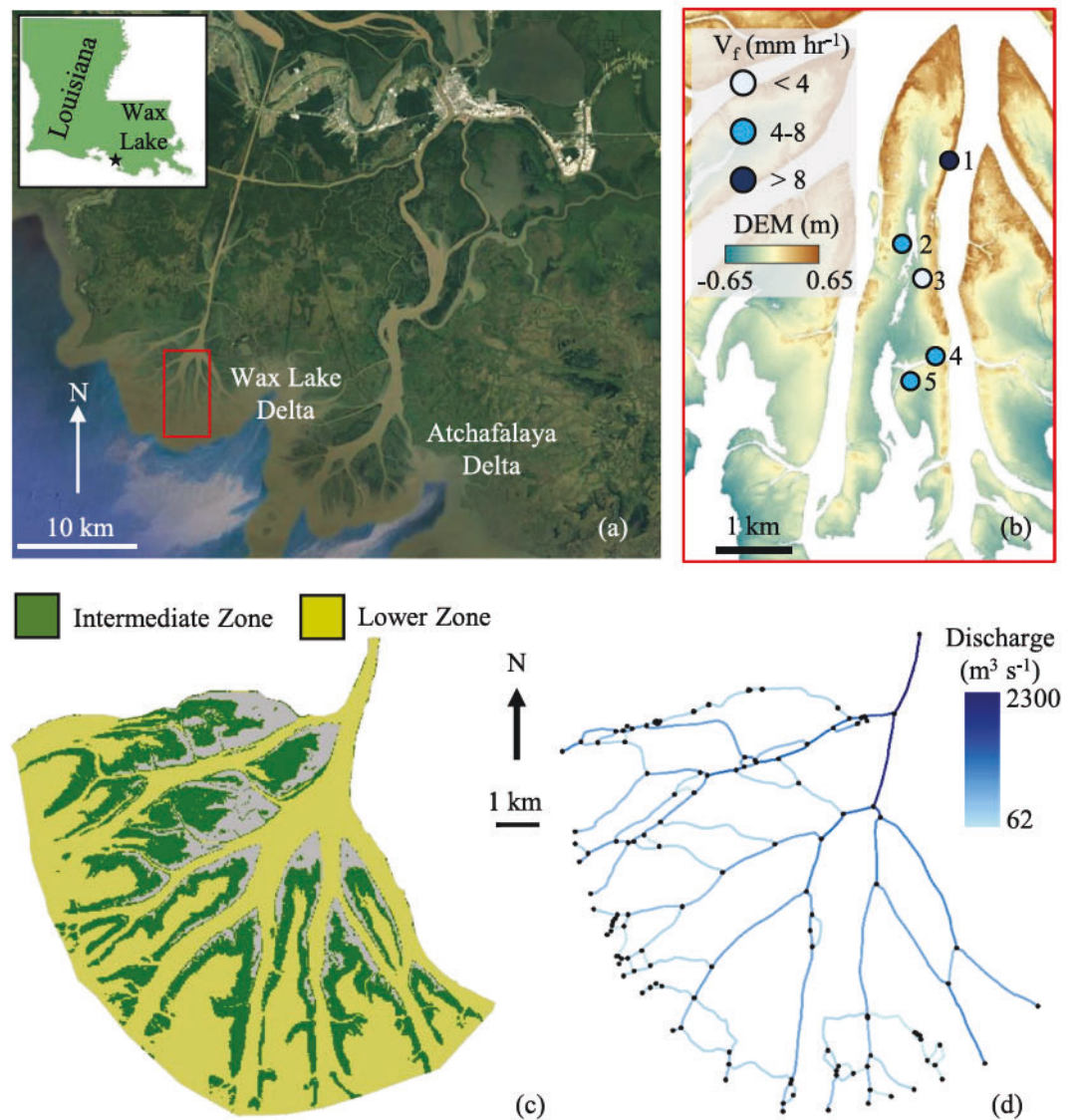
## 2. Methods

### 2.1. Study Site

Wax Lake Delta is an actively prograding river-dominated delta located in Atchafalaya Bay (Louisiana) and is characterized by a number of arrowhead-shaped islands surrounded by distributary channels (Figures 1a–1c). The delta developed after the dredging of an artificial channel in 1941 by the U.S. Army Corps of Engineers (Fisk, 1952) and became emergent in 1973 after record flooding. Elevation ranges from below 0 to ~0.75 m, referenced to the NAVD88 datum (Wagner et al., 2017). Given that mean sea level across the delta is 0.116 m and tidal range is 0.35 m (NAVD88) (Rosen & Xu, 2013), most of the delta is submerged. The median monthly discharge for 2018 was  $3,500 \text{ m}^3 \text{ s}^{-1}$  as measured at USGS Calumet, LA (Gage 07381590). Large river inputs result in low salinity conditions (<0.5 ppt) throughout the delta (O'Connor & Moffett, 2015; Shaw et al., 2013).

Wax Lake Delta can be divided into ecogeomorphic zones based on land surface elevation and vegetation species (Johnson et al., 1985; Olliver & Edmonds, 2017). The highest elevations (above 0.25 m and approximately 13% of the delta) include north-pointing island apexes and are dominated by colonies of *Salix nigra* (Black Willow) (Carle et al., 2014; Johnson et al., 1985; Paola et al., 2011). For this study, we exclude this





**Figure 1.** (a) Wax Lake Delta located just west of the Atchafalaya delta. (b) Sampling was done within five daily sites (1–5) spanning a range of elevations on Mike island. Within each main location, up to six benthic chambers were deployed and a mass removal rate ( $V_f$ ) calculated for each chamber. The colors of dots indicate average mass removal rate of nitrate for each of the five sample clusters. (c) Two ecogeomorphic zones were defined based on elevation. Subaerial sections (gray) are not included in the analysis. (d) The channel network was represented as a series of links and nodes and is color coded by median discharge from Wax Lake Outlet at Calumet, LA (USGS Gage 07381590) at the time of sampling (23–27 June 2018).

upper ecogeomorphic zone because it was generally subaerial throughout our field measurements, and nutrient removal rates in unsaturated soils cannot be estimated from our methods. Intermediate elevations (between  $-0.12$  and  $0.25$  m, referenced to the NAVD88 datum) include submerged or intertidal levees along channel edges. The intermediate ecogeomorphic zone hosts *Colocasia esculenta* (elephant ear) interspersed with other herbaceous vegetation, such as *Polygonum punctatum* (dotted smartweed). These herbaceous species can also organize in large monotypic stands near the lower centers of islands (Carle, 2013; Olliver & Edmonds, 2017). The lower ecogeomorphic zone (less than  $-0.12$  m) encompasses channels and embayments or the central and distal (southern) parts of islands. These areas are continuously flooded and characterized by open water or dominated by floating-leaved vegetation such as *Nelumbo lutea* (American lotus) (Carle, 2013; Johnson et al., 1985; Olliver & Edmonds, 2017).



All field measurements were made on Mike Island, located near the center of Wax Lake Delta (Figure 1b) with an elevation range from approximately 0.5 m at the apex (north end) to −0.4 m at the distal, southern end.

## 2.2. Field Measurements

Benthic chambers were used to measure nitrate removal rates on Mike Island at 28 total locations clustered within five submerged sites, numbered in a basinward direction from north to south (Figure 1b). Specifically, a group of five to six chambers was deployed at a single site each day during the 5-day field campaign between 23 and 27 June 2018 (only one site was visited each day due to accessibility factors). The deployed group of five to six chambers was removed from the site at the end of each field day and redeployed at a new site at the beginning of the next field day. The coordinates of the daily sites were randomly selected from a 30-m resolution grid overlain on the eastern half of the island, which was targeted to exploit the bilateral symmetry of the island (Johnson et al., 1985). We ensured coverage across intermediate and lower elevation platforms by dividing the eastern grid into a northern and southern quadrant and sampling from both. If the selected site for a given day was deemed inaccessible by airboat or unsafe due to water depth, a new location was randomly chosen. All chambers at a given site were spaced within approximately 30 m of the selected site's coordinates. Site 1 was located on a densely vegetated levee and was the northernmost, upstream site. Sites 2 and 3 were centrally located within the island's embayment and were heavily and sparsely vegetated, respectively. Sites 4 and 5 were the two southernmost, downstream sites and were located within the embayment. Site 5 was more densely vegetated than Site 4.

The chambers were constructed from translucent polyethylene barrels (88 cm tall, inner diameter of 51.4 cm) with the top and bottom barrel faces removed. The large volume of the chambers and openness to the atmosphere were chosen to minimize incubation or "bottle effects" (supporting information Figures S1 and S2). Closed or small benthic chambers can allow solutes and gases to accumulate or become depleted, leading to shifts away from natural water chemistry (e.g., O'Brien et al., 2012). Chambers were inserted ~12 cm below the sediment-water interface. The depth of water measured manually in the field within all chambers ranged between 0.31 and 0.53 m. Approximately 30 g of sodium chloride was added to each chamber as a conservative tracer to monitor potential evaporative losses or dilution due to water exchange across the bottom of the chamber. Salinity of all samples remained below 500 ppm. To ensure that changes in nitrate concentration would be detectable within one sampling day, nitrate concentrations were elevated above background by the addition of potassium nitrate (1.5 to 3 g of  $\text{KNO}_3^-$ ). Resulting nitrate concentrations within the chambers were approximately 1.4 to 4.8  $\text{mg N L}^{-1}$  greater at the start of the experiments compared to water outside the chambers (average concentration of 0.81  $\text{mg N L}^{-1}$ ). In order to test the effect of varying concentration on removal rate, two clusters consisting of three benthic chambers each (6 of 28 chambers) were installed less than 0.5 m apart at Site 3. Within each group, one chamber was selected as the control where nitrate concentration remained at the background value (0.89  $\text{mg N L}^{-1}$ ). In the other two chambers, concentrations were elevated approximately 5 and 10 times above background.

Basic water quality parameters were monitored with a Yellow Springs Instrument ProPlus multiparameter probe to verify that temperature, dissolved oxygen concentrations, and pH remained similar between the benthic chambers and surface water throughout our measuring period (Figure S2). Measurements in each chamber and outside the chambers were taken at the time of sample collection (Knights, 2020). In addition to measuring basic water quality parameters, samples were collected from inside and outside the chambers for laboratory analysis of nitrogen constituents and dissolved organic carbon (DOC). During sampling, chambers were gently stirred, and approximately 60 ml was withdrawn from the middle of the water column by syringe. The samples were filtered through 0.45- $\mu\text{m}$  Fisherbrand nylon syringe filter into an HDPE pre-rinsed bottle and immediately placed on ice. The sample volume represented, on average, ~0.72% of total water in the chamber and had a negligible effect on water levels or chemical mass budgets. Samples and Yellow Springs Instrument measurements were taken before the addition of NaCl and  $\text{KNO}_3$ , immediately after, and at selected time intervals (30–90 min) throughout the experiment.

At the end of each field day (within 12 hr of sample collection), all samples collected that day were subsampled and filtered through 0.2- $\mu\text{m}$  Fisherbrand nylon syringe filters into combusted glass amber vials for DOC analysis and optical analysis of dissolved organic matter pools. The subsample for DOC was immediately refrigerated, and the remaining sample was frozen in the original HDPE bottle for analysis of nitrate, chloride, and ammonium.



Nitrate and chloride were measured using ion chromatography (ICS-2100, Dionex), with detection limits of  $0.065 \text{ mg N L}^{-1}$  and  $0.27 \text{ mg L}^{-1}$ , respectively (Knights, 2020). Ammonium was measured using a Skalar flow-injection nutrient analyzer with a detection limit of  $0.027 \text{ mg N L}^{-1}$ . DOC was analyzed using high-temperature combustion with an OI Aurora 1,030 W Analytical Total Organic Carbon Analyzer (detection limit:  $0.08 \text{ mg L}^{-1}$ ). Three-dimensional fluorescence of optically active dissolved organic matter pools was analyzed using a Horiba Scientific Aqualog instrument. The fluorescence index of organic material was calculated using the slope of an emission curve at an excitation wavelength of 370 nm (Cory et al., 2010).

Sediment cores were collected from the benthic chambers upon the conclusion of sampling each day using a 3.6-cm-diameter polyvinyl chloride corer (depth of 5 cm). The percent of sediment lost on ignition (LOI) was determined by combustion at  $440^\circ\text{C}$  for 4 hr and used as a measure of organic matter content (Knights, 2020). Sand, silt, and clay ratios were determined by hydrometer analysis (Haverland et al., 1984).

### 2.3. Chamber Removal Rates

A first-order uptake rate constant ( $k$ ) was calculated for each benthic chamber from the slope of nitrate concentration (natural log) as a function of time (Figure S3) (Knights, 2020). All nitrate concentrations within each chamber were corrected for mixing with outside water based on changes in chloride concentration (Text S1).

Mass transfer velocity ( $V_f$ ) and areal uptake rate ( $U$ ) were calculated from  $k$  (Stream Solute Workshop, 1990):

$$V_f = h \times k, \quad (1)$$

$$U = V_f \times C, \quad (2)$$

where  $h$  is water depth in the chamber and  $C$  is normalized concentration.  $V_f (\text{L T}^{-1})$  is often used as a measure of removal efficiency relative to availability (Mulholland et al., 2008) and can be considered an average downward velocity for nitrate in the water column if removal is idealized to occur in the benthic layer.  $U (\text{M L}^{-2} \text{T}^{-1})$  represents the mass of nitrate removed within the water column per bed surface area per time. Because  $U$  depends linearly on concentration (Equation 2; Ensign & Doyle, 2006; Stream Solute Workshop, 1990) and the concentration in the chambers was artificially increased, we use  $V_f$  as the dependent variable in our regression analysis, similar to others (Ensign & Doyle, 2006; Wollheim et al., 2006, 2008). Some benthic chamber results (5 out of 28 installed) were excluded from further analysis due to complications during field sampling related to impending thunderstorms (four chambers) and a poor bottom seal connection resulting in substantial mixing of chamber water with surface water (one chamber).

### 2.4. Regression Analysis

Regression models were used to explore environmental controls on nitrate removal in order to upscale chamber measurements to the entire delta under observed summer conditions. The response variable ( $V_f$ ) was normalized to meet the requirements of statistical tests by applying a Box-Cox transformation (Box & Cox, 1964). Seven independent variables were considered in model development: bed elevation, water depth, daily change in water depth, ambient nitrate concentration, percent of sediment mass LOI, sediment grain size, and normalized difference vegetation index (NDVI). Water temperature, DOC concentrations, and fluorescence index did not vary between sites (i.e., coefficient variation—standard deviation/mean—was less than 0.1) and were not included in the regression analysis. Elevation was obtained from a 3-m DEM of Wax Lake Delta (OCM Partners, 2020, while water depth was measured in the field. Water surface elevation on the delta fluctuates with river discharge, tides, and wind (Hiatt & Passalacqua, 2015; Sendrowski & Passalacqua, 2017) and is independent of bed elevation on daily time scales; thus, water depth and bed elevation were included as two independent variables. NDVI was obtained from preprocessed Landsat surface reflectance data via USGS Earth Resources Observation and Science on-demand interface. NDVI measures the greenness in a pixel and is used as a proxy for biomass and vegetation health (Box et al., 1989; Gamon et al., 1995; Serrano et al., 2000). It is calculated as the surface reflectance ratio of near-infrared and red bands and ranges from  $-1.0$  to  $1.0$ . Water absorbs near-infrared light and produces a negative NDVI, while bare sediment reflects both near-infrared and red light resulting in a positive NDVI close to 0. On Wax Lake Delta, bare earth or minimally vegetated shallow water tends to result in NDVI between 0 and 0.2 (Olliver & Edmonds, 2017). Landsat imagery for NDVI calculations was acquired on 30 June 2018 (2 days after the final



day of benthic chamber sampling). Regression models were ranked by Akaike (1974) information criteria, and variables were selected using backward stepwise algorithms in R.

## 2.5. Upscaling Calculations

To explore spatial patterns of reactivity across the delta, two independent but complementary approaches were used to upscale benthic chamber measurements of nitrate removal during summer conditions. The first method treats the delta like a static lake, that is, transport is not considered, and yields spatially distributed potential removal rates based on reaction potentials over all submerged regions of the delta. The second method treats the delta like a network of distributary channels, considers transport, and yields removal rates along each channel segment within the network.

For the method examining reaction potential based on static environmental conditions, we used a regression model to estimate  $V_f$  on a 30-m by 30-m resolution grid over the submerged portions of the delta. Subaerial regions were considered those with elevations above 0.25 m. This approach is coarse, as water levels vary over the delta due to wind. Total potential nitrate removal over the submerged delta ( $R$  [ $\text{M T}^{-1}$ ]) was estimated by summing the potential removal in each grid cell, assuming the median measured surface water nitrate concentration ( $C$  [ $\text{M L}^{-3}$ ]) of  $0.95 \text{ mg N L}^{-1}$  in each cell:

$$R = AC \sum_{i=1}^n V_{f,i} \quad (3)$$

where  $A$  ( $\text{L}^2$ ) is cell area ( $900 \text{ m}^2$ ) and  $V_{f,i}$  is the cell-specific mass transfer velocity from the regression model. It is important to note that  $C$  likely varies over the delta due to removal processes, but samples from this study and monitoring stations are too sparse to characterize the variability, so we used the mean from our surface water samples as a best estimate.

We used stream spiraling theory as a second approach to estimate nitrate loss along the network of channels in the delta (Ensign & Doyle, 2006; Mulholland et al., 1985; Newbold et al., 1981; Tank et al., 2006; Wollheim et al., 2006, 2008; Ye et al., 2017). Briefly, stream spiraling theory considers the integrated effect of water velocity and biochemical demand, typically envisioned to occur in the bed, on downstream nutrient transport and removal. Nitrate flux exported from each link,  $i$ , in the channel network was determined as

$$Q_{\text{down}}^i C_{\text{down}}^i = Q^i C^i \times \exp\left(\frac{-v_f}{H_L^i}\right) \quad (4)$$

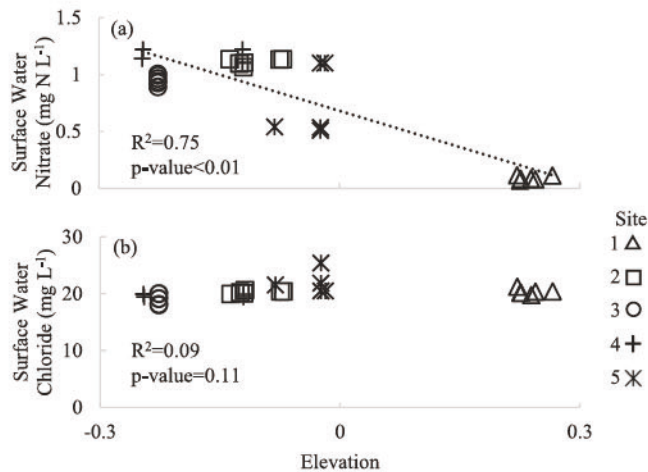
where  $Q_{\text{down}}^i$  ( $\text{L}^3 \text{ T}^{-1}$ ) and  $C_{\text{down}}^i$  ( $\text{M L}^{-3}$ ) are the discharge and solute concentration of the adjoining link(s) immediately downstream of link  $i$ , and  $Q^i$  and  $C^i$  are the discharge and concentration of the current link. The exponential term is the transfer efficiency or fraction of nitrate that remains in the water column after transport through link  $i$ .  $H_L^i$  represents the hydraulic load, defined as

$$H_L^i = \frac{Q^i}{w^i L^i} \quad (5)$$

where  $w^i$  and  $L^i$  are the width and length of the current link, respectively (Wollheim et al., 2006). At the inlet of Wax Lake Delta, we assumed an incoming nitrate concentration of  $0.95 \text{ mg N L}^{-1}$  and discharge of  $2,300 \text{ m}^3 \text{ s}^{-1}$  (median at USGS Gage 07381590 during the time of fieldwork). Unlike the flooded-delta upscaling approach, the channel network analysis does not require a specification of  $V_f$  in off-channel storage zones, which are considered to contribute implicitly to removal along channels in stream spiraling theory. Because it is unclear how to attribute  $V_f$  in channels and their adjacent off-channel storage zones to one link-scale value of  $V_f$ , we assumed all benthic chamber measurements were equally plausible representations of  $V_f$  along links and assigned a single mean  $V_f$  across all links. Though simplistic, this approach is similar to approaches by Wollheim et al. (2006) and Ensign and Doyle (2006). To quantify uncertainty, we repeated the calculation with minimum and maximum  $V_f$  values from our observations.

$H_L^i$  of each channel link was determined based on remotely sensed surface water observations and a simple flux partitioning scheme, after Tejedor et al. (2015). RivGraph, a Python package (Schwenk et al., 2020), was





**Figure 2.** (a) Surface water nitrate (precision: 0.8%) decreases with elevation on Mike Island compared to (b) chloride (precision: 2%) indicating preferential nitrate processes at higher elevation (levees).

used to vectorize the channel network from a georeferenced binary image obtained from a 3-m DEM (2012) of Wax Lake Delta (OCM Partners, 2020) delineating channels from land, resulting in a set of connected links and nodes. RivGraph uses the user-prescribed locations of inlet and outlet nodes, as well as morphologic features obtained from the masks (e.g., link orientation relative to neighboring links and the general downstream direction) to assign flow directions and compute widths of each link. A fractional discharge was computed for each link by assuming a unit discharge at the delta's apex and partitioning this discharge proportionally to the downstream channel widths at each bifurcation or trifurcation (e.g., Tejedor et al., 2017). Local discharge within each channel link was obtained by multiplying the fractional discharge by the observed mean daily discharge over the field sampling period at the delta apex ( $2,300 \text{ m}^3 \text{ s}^{-1}$  USGS Gage 07381590, Wax Lake Outlet at Calumet, LA).

### 3. Results

#### 3.1. Surface Water Chemistry

Surface water nitrate concentrations varied between 0.07 and  $1.2 \text{ mg N L}^{-1}$  across all chamber locations on Mike Island (mean and median of 0.81 and  $0.95 \text{ mg N L}^{-1}$ , respectively). The concentration was lowest ( $<0.1 \text{ mg N L}^{-1}$ ) on the densely vegetated submerged levee of Site 1 (located most upstream). Concentration was highest ( $>1.0 \text{ mg N L}^{-1}$ ) within the centrally located embayment of Sites 2 and 4. Surface water chloride concentrations did not vary as widely as nitrate across the island (mean of  $20 \text{ mg L}^{-1}$  range of  $18\text{--}22 \text{ mg L}^{-1}$ ). Thus, nitrate to chloride ratios were smallest (0.019) at Site 1 and greatest (0.26) at Site 4, suggesting substantial nitrate removal occurred at Site 1 (Figure 2).

DOC concentration in surface water averaged  $5.1 \text{ mg L}^{-1}$  (range from 4.6 to  $5.7 \text{ mg L}^{-1}$ ) across all sites. Fluorescence index ranged from 1.58 to 1.63, indicating a relatively consistent mixture of organic matter sources. For comparison, values  $>1.8$  indicate microbial sources, while values  $<1.4$  indicate terrestrial sources (McKnight et al., 2001).

#### 3.2. Vegetation

NDVI across benthic chamber locations ranged from 0.39 at Site 5 (located most downstream within the lower ecogeomorphic zone) to 0.82 at Site 1 (most upstream site, in the intermediate ecogeomorphic zone). Greater NDVI along submerged levees of the intermediate ecogeomorphic zone corresponded to observed dense stands of healthy vegetation. *C. esculenta* (elephant ear) and algal mats were exclusively found in the intermediate ecogeomorphic zone (Site 1). Submerged vegetation such as *Heteranthera dubia* (water star grass) and emergent vegetation like *Sagittaria platyphylla* were found at all sites except Site 3 (in an open, less vegetated region of the lower ecogeomorphic zone). Floating-leafed vegetation, primarily *N. lutea* (American lotus), was found at all sites.

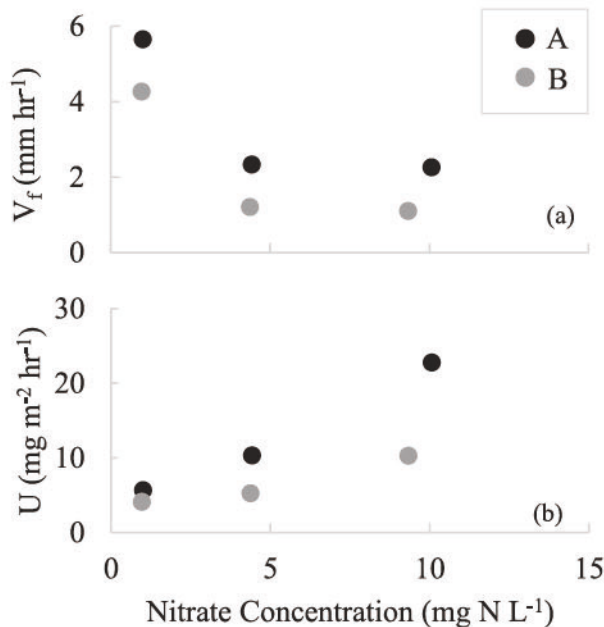
#### 3.3. Sediment Properties

Percent of mass LOI averaged  $2.1\% \pm 2.7\%$  across sites. Sediments were silt- and sand-rich with silt content (grain size between 4 and 62.5 microns) ranging from 33% to 79% and sand content (grain size greater than 62.5 microns) ranging from 2% to 60%. Clay content ranged from 0% to 25%. Site 5 (the most downstream) had the greatest sand content (60%) and lowest average LOI (0.74%), while Site 1 (a more proximal and densely vegetated site) had the greatest average LOI (4.8%).

#### 3.4. Nitrate Removal

Nitrate removal, reported as a mass transfer velocity ( $V_f$ ), ranged from 1.1 to  $19 \text{ mm hr}^{-1}$  within individual chambers (Figure 1). The average  $V_f$  across chambers at each site was smallest within the unvegetated lower ecogeographic zone of Site 3 ( $2.8 \text{ mm hr}^{-1}$ ) and greatest within the densely vegetated intermediate ecogeomorphic zone of Site 1 ( $13 \text{ mm hr}^{-1}$ ). The high mass transfer velocity at Site 1 (2.8 times greater than the

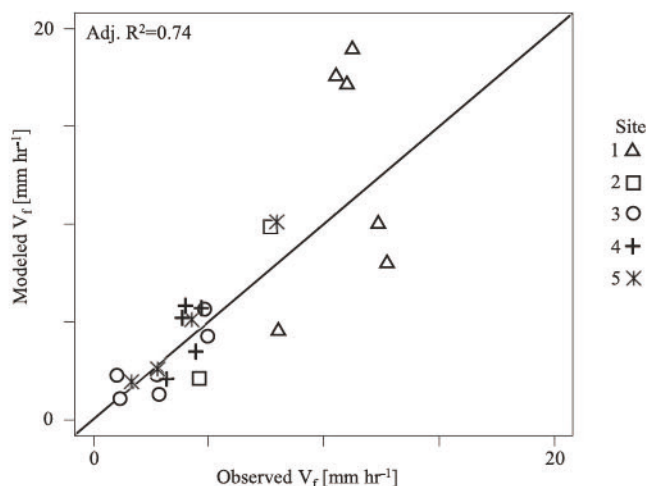




**Figure 3.** The effects of increasing concentration on (a) mass transfer velocity ( $V_f$ ) and (b) aerial uptake ( $U$ ) on Mike Island. Two clusters (A and B) of three closely spaced chambers were spiked with various amounts of nitrate. Each cluster had three chambers with starting concentrations of  $\sim 1\times$ ,  $5\times$ , and  $10\times$  natural surface water. The centers of the two clusters were located approximately 3 m apart from one another at Site 1, and we assume chambers within each cluster had similar reactivities such that only the initial nitrate concentrations differed. The cause of variability between Clusters A and B is uncertain but could be due to heterogeneity in bed surface organic matter that may control for nitrate removal.

nitrate concentration (0.07 to 1.2 mg N L<sup>-1</sup>) results in a relatively small 18% decrease in nitrate mass transfer velocity (i.e., calculated  $V_f$  from 9.2 to 7.5 mm hr<sup>-1</sup>).

Using the regression model and the median surface water nitrate concentration of 0.95 mg N L<sup>-1</sup>, we estimate  $V_f$  to vary from 0.25 to 18 across all submerged regions (intermediate and lower zones) (Figure 5a). Integrated across the submerged delta, the potential nitrate removal rate is 230 kg hr<sup>-1</sup> and ranges from 16–383 kg hr<sup>-1</sup> under scenarios of low (0.05 mg N L<sup>-1</sup>) and high (1.5 mg N L<sup>-1</sup>) nitrate concentrations typically observed in the lower Atchafalaya River (BryantMason et al., 2013; Joung et al., 2019; Lane et al., 2002) and spanning the range of surface water nitrate concentration observed in the field. Assuming a discharge of 2,300 m<sup>3</sup> s<sup>-1</sup>, this represents a removal of 3.4% of the incoming nitrate load (range of 4.0% to 3.1% under low to high concentration scenarios). The greatest potential removal rates are generally located in areas with the greatest amounts of vegetation, on higher northern islands of the western half of the delta and the levees of lower islands (Figure 5a). The intermediate elevation ecogeomorphic zone is responsible for 70% of the estimated potential nitrate removal though it only represents 33% of the analyzed inundated area (Table 1). This suggests that inundated delta islands, particularly those with dense vegetation, act as hot spots for biogeochemical processing.



**Figure 4.** Scatter plots of predicted and observed  $V_f$ .

other sites) was also reflected by the lowest surface water nitrate concentration at that site (average of 0.089 mg N L<sup>-1</sup> compared to 0.99 mg N L<sup>-1</sup> at all other sites).

Within the two clusters of closely spaced benthic chambers,  $U$  increased almost linearly with initial nitrate concentration (Figure 3).  $V_f$  appears to follow an exponential relationship with nitrate concentration as reported elsewhere (Covino et al., 2010); however, this relationship is not definitive with only three points (Figure 3).  $V_f$  was greatest (5.7 and 4.3 mm hr<sup>-1</sup>) in the unspiked chambers (initial concentration  $\sim 1$  mg L<sup>-1</sup>).

### 3.5. Regression and Areal Upscaling

Based on the stepwise algorithm, the regression model (Figure 4) included measures of vegetation and nitrate concentration:

$$V_f = \exp(0.035 + 3.37NDVI - 0.17NO_3), \quad (6)$$

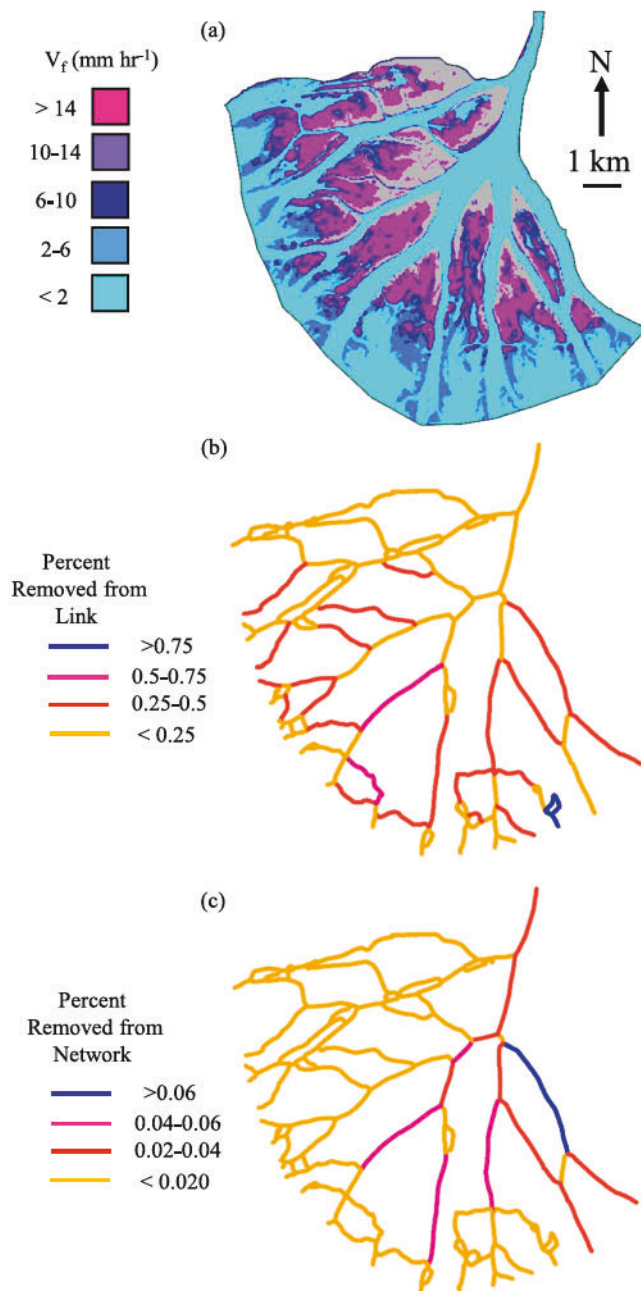
where  $NDVI$  is normalized difference vegetation index (unitless) and  $NO_3$  is nitrate concentration (in this case, spiked concentration inside chambers) (mg N L<sup>-1</sup>). This model explains 72% of the variability in nitrate mass transfer velocity measured during the experiments. Solving Equation 6 under mean observed conditions at the chamber locations ( $NDVI$  of 0.65 and  $NO_3$  of 0.81 mg N L<sup>-1</sup>) results in an expected  $V_f$  of 8.1 mm hr<sup>-1</sup>. Note that this calculation uses the mean observed surface water nitrate concentration to estimate  $V_f$  under natural conditions, as can be expected to occur outside the chambers rather than manipulated conditions inside the chambers. Holding nitrate concentration constant, as  $NDVI$  increases from the minimum (0.39) to the maximum (0.82) observed across chamber locations ( $\sim 110\%$  increase), the calculated  $V_f$  responds by  $\sim 326\%$  (3.4 to 14 mm hr<sup>-1</sup>). In contrast, an approximate 17-fold increase in surface water

nitrate concentration (0.07 to 1.2 mg N L<sup>-1</sup>) results in a relatively small 18% decrease in nitrate mass transfer velocity (i.e., calculated  $V_f$  from 9.2 to 7.5 mm hr<sup>-1</sup>). Using the regression model and the median surface water nitrate concentration of 0.95 mg N L<sup>-1</sup>, we estimate  $V_f$  to vary from 0.25 to 18 across all submerged regions (intermediate and lower zones) (Figure 5a). Integrated across the submerged delta, the potential nitrate removal rate is 230 kg hr<sup>-1</sup> and ranges from 16–383 kg hr<sup>-1</sup> under scenarios of low (0.05 mg N L<sup>-1</sup>) and high (1.5 mg N L<sup>-1</sup>) nitrate concentrations typically observed in the lower Atchafalaya River (BryantMason et al., 2013; Joung et al., 2019; Lane et al., 2002) and spanning the range of surface water nitrate concentration observed in the field. Assuming a discharge of 2,300 m<sup>3</sup> s<sup>-1</sup>, this represents a removal of 3.4% of the incoming nitrate load (range of 4.0% to 3.1% under low to high concentration scenarios). The greatest potential removal rates are generally located in areas with the greatest amounts of vegetation, on higher northern islands of the western half of the delta and the levees of lower islands (Figure 5a). The intermediate elevation ecogeomorphic zone is responsible for 70% of the estimated potential nitrate removal though it only represents 33% of the analyzed inundated area (Table 1). This suggests that inundated delta islands, particularly those with dense vegetation, act as hot spots for biogeochemical processing.

### 3.6. Channel Network Analysis

Channel network calculations based on the median observed  $V_f$  (5.1 mm hr<sup>-1</sup>) in the field (Equation 4) show that each channel link removes only a small percentage ( $<0.1\%$ ) of the total nitrate entering the





**Figure 5.** (a) Removal rate calculated using submerged-delta approach. (b, c) Removal rate calculated using nutrient spiraling approach as a percentage of (b) amount of nitrate entering each link and (c) amount of nitrate entering the delta at the apex.

delta (Figure 5c). The maximum removal efficiency in an individual link is 1.9% with most links removing  $< 1\%$  of the nitrate they receive (Figure 5b). The estimated removal rate for the collective network is  $79 \text{ kg hr}^{-1}$  and ranges from 18 to  $275 \text{ kg hr}^{-1}$  under scenarios of minimum to maximum  $V_f$  observed in chambers. This represents 1.0% of the incoming nitrate load (range of 0.2% to 3.5% for minimum to maximum  $V_f$ ), which agrees well with the aerial method of upscaling potential removal across the submerged delta. Channel network analysis further indicates that secondary channels and more distal portions of the delta are generally more efficient at processing nitrate (Figure 5b); however, these secondary channels and distal bifurcations individually receive small portions of the nitrate load (Figure 1d). Because the eastern half of Wax Lake Delta receives a greater portion of the discharge and nutrient load than the western portion, it contributes more to total removal (Figure 5c).

## 4. Discussion

### 4.1. Environmental Controls on Nitrate Removal

In this deltaic wetland, we show that mass transfer velocity ( $V_f$ ) is most sensitive to the presence and density of vegetation, as measured by NDVI (Equation 6). Nitrate retention and removal increased fourfold between zones of high and low NDVI. Therefore, nitrate removal via plant uptake is likely an important pathway on the delta. Assimilation into plant and algae biomass has previously been demonstrated to be an important nutrient removal pathway in wetlands (Saeed & Sun, 2012; Vymazal, 2011). Nitrate removal by plant uptake can range from minimal to up to about 60% of total removal (Kadlec, 1997; Matheson et al., 2002), with plant uptake removing between 4% and 11% of nitrogen in constructed wetlands (Lin et al., 2002; Matheson et al., 2002). In lake and estuarine sediments, up to 60% of nitrate removal is associated with plant uptake (Rysgaard et al., 1993). If plant assimilation is responsible for similarly high rates here, most of the nitrate removed could be released via mineralization during winter senescence, limiting the long-term impact of removal from the delta.

Locations with high NDVI not only reflect increased chances for plant uptake but may also reflect indirect effects of dense vegetation on other nitrate removal pathways. Detrital material in areas of high NDVI likely contributes to the organic carbon stock in soils (Vymazal et al., 1999; Weisner et al., 1994), which supplies organic carbon for denitrification, a permanent nitrate removal process. The positive relationship between NDVI and LOI ( $p$  value = 0.0021, Figure S4) suggests that regions of the delta with greater NDVI are more effective at trapping organic matter (Baker & Vervier, 2004; Inwood et al., 2007). Areas of the delta with greater NDVI may also have older, more developed soils due to the strongly coupled processes of sedimentation and vegetation succession in a prograding delta (Ma et al., 2018), and denitrification rates have been

shown to increase in older soils (Henry & Twilley, 2014). Topography is yet another variable that coevolves with vegetation (Johnson et al., 1985; Ma et al., 2018) and influences soil saturation, oxidation-reduction potential, and denitrification potential. We do see a positive relationship between NDVI and elevation ( $R^2 = 0.61$ ,  $p$  value =  $1.2 \times 10^{-5}$ ; Figure S4) but cannot separate the many potential mechanisms that link these variables with net nitrate removal here. Nitrate processing depends on many biogeochemical processes that cannot be measured directly from remote sensing products, and disentangling these processes is an important area for continued research in delta wetlands.



**Table 1**  
Summary of Input Parameters and Results for Two Methods of Estimating Nitrate Removal in Wax Lake Delta

Method	Region	Area of delta (%)	Discharge in ( $\text{m}^3 \text{s}^{-1}$ )	Conc. in ( $\text{mg N L}^{-1}$ )	$V_f$ ( $\text{mm hr}^{-1}$ )	Removed (%)
Submerged delta	Intermediate zone	33.3	2,300	0.05–1.5	0–19 <sup>a</sup>	2.1–2.7
Submerged delta	Lower zone	66.7	2,300	0.05–1.5	0–18 <sup>a</sup>	1–1.3
Network	Channels and immobile storage zones	—	2,300	0.95	1.1–19	0.2–3.5

Note. No channel area is used in the network calculation.

<sup>a</sup>Potential removal rates, as transport is not considered in the calculation.

By examining only one island, we acknowledge that our measurements come from a limited window of soil ages, organic matter contents, and soil reduction potential. NDVI across the submerged delta ranges from  $-0.39$  to  $0.92$ , and NDVI from our sites covers only 33% of that range ( $0.39$  to  $0.82$ ). By applying a regression model across the entire delta, we are extrapolating our measurements to a wider range of NDVI. We also note that our regression model is not well constrained in the channels, which are areas of low NDVI, where water was too deep for safe benthic chamber deployment. However, our measured range of  $V_f$  ( $1.1$  to  $19 \text{ mm hr}^{-1}$ ) is comparable to nitrate removal in other wetlands from similar climates (Table 2).

The observed relationship linking greenness with nitrate removal is most representative of summertime conditions. The regression model may also perform well in other seasons, though year-round field studies would be needed to test this. In winter months, browning vegetation results in lower NDVI values across the entire delta. This would coincide with reduced nitrate removal via plant assimilation. Denitrification also decreases with colder temperatures (Bachand & Horne, 1999; Bremner & Shaw, 1958), and lower NDVI during winter months would coincide with decreasing temperatures and denitrification. Although we expect less removal during winter months, our observations are not capable of testing this.

The concentration dependence of nitrate removal rates, both in terms of uptake rate ( $U$ ) and efficiency ( $V_f$ ) (Figure 3), suggests that removal mechanisms are not saturated with respect to nitrate. Other studies examining nutrient removal in river networks have also reported a negative correlation between  $V_f$  and nitrate concentration but a positive relationship between aerial uptake rate ( $U$ ) and concentration (Dodds et al., 2002; Mulholland et al., 2008). The inclusion of nitrate concentration as a significant variable in the regression model makes it challenging to apply over distributed areas, as spatially explicit nitrate concentration data are not available. We compensate for this by calculating removal under conditions of high and low nitrate inflow typically observed on the delta (BryantMason et al., 2013; Joung et al., 2019; Lane et al., 2002). It is important to note that nitrate mass transfer velocity is far less sensitive to nitrate concentration as compared to greenness.

We observe a negligible effect of water depth on the mass transfer velocity (Figure S4). The lack of a strong relationship may be due to the relatively small range in water depths captured by our chambers ( $0.31$  to  $0.53 \text{ m}$ ). Studies in rivers have shown that as water depth increases, the fraction of surface water interacting with a unit area of bed and its reactive biofilms decreases, leading to an inverse relationship between water depth and  $V_f$  (Böhlke et al., 2009; Ensign & Doyle, 2006; Wollheim et al., 2006). For example, relationships

**Table 2**  
Removal Rate in This Study Is Comparable to Other Coastal Wetlands

Source	Environment	Method	$V_f$ ( $\text{mm hr}^{-1}$ )	$U$ ( $\text{mg m}^{-2} \text{hr}^{-1}$ )
This study	Wax Lake Delta	Open chamber <sup>a</sup>	1.1–19	7.2–450
Henry and Twilley (2014)	Wax Lake Delta	Sediment core incubation <sup>b</sup>	0–1.01	0–3.9
Scott et al. (2008)	Freshwater wetland	Sediment core incubation <sup>b</sup>	21.8–45	3.3–17
Rysgaard et al. (1996)	Coastal lagoon	Sediment core incubation <sup>b</sup>	0–150	0–3.8
Yu et al. (2006)	Coastal Louisiana	Benthic chamber <sup>a</sup>	0–4.9	0–56
Childs et al. (2002)	Coastal Louisiana	Acetylene inhibition <sup>b</sup>	0.40–1.1	2.5–6.7
DeLaune et al. (2005)	Coastal Louisiana	Acetylene inhibition <sup>b</sup>	4.5–15	2.8–9.2
Lindau et al. (2008)	Coastal Louisiana	Acetylene inhibition <sup>b</sup>	0.002–2.9	0.01–18

<sup>a</sup>Total removal. <sup>b</sup>Denitrification.



between  $V_f$  and depth of inland rivers were demonstrated over ranges from 0.1 to >10 m (Alexander et al., 2000; Böhlke et al., 2009). It is also possible that aquatic vegetation provides critical surfaces for biofilms (Arango et al., 2007), rendering sediment-water interactions less important in controlling the overall denitrification rate in deltas than in rivers.

We also observed no relationship between change in water depth over the sampling day and mass transfer velocity, though changes in water depth could correspond with hydrologic connectivity, solute supply, or changes in soil oxic or anoxic conditions. Furthermore, chambers that were deployed during the rising tide could have received an influx of oxygen in surrounding pore waters that might have inhibited denitrification and vice versa during falling tide (Ensign et al., 2008). However, sampling roughly occurred over the same time period every day, which overlapped with falling tides. Furthermore, the change in water depth across each site was similar, as expected in this microtidal system. Thus, water depth held little explanatory power on mass transfer velocity.

#### 4.2. Delta-Scale Removal

Our calculations suggest the delta has a limited capacity to remove nitrate under typical summertime flow conditions (removal corresponds to 3.1% to 4.0% of the load based on the submerged-delta analysis and 0.2% to 3.5% based on channel network analysis). Estimates from the disparate upscaling approaches agree well with each other, lending confidence to the result. Our estimates reflect summertime removal conditions when primary production is greatest. Although removal rates are less clear in other seasons, the delta is unlikely to process nitrate at a higher rate during winter months when nitrate input into the delta and primary productivity are low. We expect that our estimated removal of up to ~4% therefore reflects upper annual limits.

Our two methods of upscaling reveal unique aspects of heterogeneity in nitrate removal across the delta. The submerged-delta results suggest that islands are more biogeochemically reactive than channels, and the regions with the greatest potential nitrate removal rates are the intermediate elevation ecogeomorphic zones ubiquitous on the northwestern islands but also common on the northern halves and subaqueous levees of southern islands (Figure 5a and Table 1). Because this method does not consider solute flow paths or nitrate supply, actual removal rates could be lower in regions that are hydrologically disconnected from channels and thus receive a low nitrate flux. This interpretation is consistent with Hiatt et al. (2018), who used particle tracking models to show that islands (both intermediate and lower ecogeomorphic zones) contribute to roughly half of all nitrate removal and that hydrologic exchange between islands and channels is an important control on nitrate fate. In comparison, the nutrient spiraling calculation shows that the eastern branches of the delta tend to be more effective at contributing to overall removal in the network (Figure 5c). If we integrate this result with the submerged delta patterns, the implication is that biogeochemical hot spots are likely to be the submerged but vegetated portions of the intermediate geomorphic platform along the eastern, more active channels of the delta because these zones have both high biogeochemical demand (potential reactivity) and are likely to receive a greater supply of nutrients from the most active channels. The western portion of the delta that is more inactive consists of smaller islands at greater elevation, and while these islands may be more biogeochemically reactive (Figure 5a), they receive a lower nutrient load through a network of short channels with low contact times (Figure 5b) and therefore can contribute less to overall removal (Figure 5c). This implies that, if other deltas behave similarly to Wax Lake Delta, older but hydrologically disconnected portions of deltas may play a relatively small role in nutrient removal, even if those areas have high potential removal rates. Greater resolution and understanding of the interactions between reaction kinetics and transport will require the use of reactive transport models of increasing complexity.

#### 4.3. Response to Environmental Changes

The future nitrate buffering capacity of the delta will depend on climatic and anthropogenic changes. For instance, if nitrate load increases due to upstream land use or climatic changes, the delta will remove a smaller portion of the load, based on the observed negative relationship between nitrate concentration and mass transfer velocity (Figure 3a). Conversely, if the nitrate load decreases due to improvements in management and policy, the delta will become even more effective at reducing the incoming load. However, these trends are based on field observations from a single summertime season and flow condition. Temperature is also



known to influence the mass transfer velocity in rivers (Donner et al., 2002; Seitzinger, 1988) and will increase with a changing climate. Furthermore, climate change will bring more extreme storm and flood events (Herring et al., 2014; IPCC, 2013) that will erode portions of the delta and drive changes in vegetation (Carle et al., 2015), one of the strongest predictors of mass transfer velocity in our models. Storms may have a long-term negative impact on the buffering capacity of the delta by eroding wetlands. However, the subaerial regions of delta islands would be most resilient as they are stabilized by more established vegetation communities (Braskerud, 2001; Day et al., 2011; Nardin & Edmonds, 2014), and these are some of the most effective sites of nutrient removal. If the intermediate elevation embayments remain protected by levees (Figure 5a), their removal function may remain intact too. Flooding may further increase nitrate removal on the delta as accretion associated with floods may expand wetland area available for nutrient buffering (Allen et al., 2012; Wagner et al., 2017).

During flood events, partially enclosed embayments could function as activated control points, as an increase in hydrologic connectivity could deliver more nitrate to areas of greater biogeochemical processing (Bernhardt et al., 2017). However, even if the removal rate temporarily increases across inundated areas during a flood, the removal efficiency may decrease if the nitrate load drastically increases. In other words, embayments may never receive enough water to disproportionately affect overall nutrient fluxes through the delta and therefore may never fit the definition of “control points” conceptualized by Bernhardt et al. (2017). In order to quantify changes in nitrate retention over rising and falling water levels, transient reactive transport models are needed.

## 5. Conclusion

Nitrate removal rates vary across ecogeomorphic zones on Wax Lake Delta, and the best predictor of nitrate mass transfer velocity during summertime is NDVI, a proxy for vegetation photosynthetic activity and greenness that is widely available. Our upscaling calculations suggest that potential hot spots of nitrate removal are located in intermediate-elevation ecogeomorphic zones where NDVI tends to be highest during the summer. Thus, older islands in the northwest region of Wax Lake Delta and the northern perimeters of younger southeastern islands, where NDVI values are greatest, have the potential to contribute the most to nitrate removal. However, an alternative nutrient spiraling calculation shows that the supply of nitrate across the channel network limits actual removal rates. Because the eastern portion of the channel network receives more water and nutrients, densely vegetated levees on the eastern half of the delta may contribute more to nitrate removal, as they are more hydrologically connected and have the potential to be biogeochemically “hot.” Estimates of nutrient removal and flow to coastal waters are essential for management practices and policy guidance. Importantly, estimates from this study using two different approaches both show that the capacity of Wax Lake Delta to remove nitrate from its receiving waters is limited to less than 4%. This research helps understand the biophysical factors that control heterogeneity in nutrient removal rates in deltas. Future work incorporating numerical simulations of variable flow (riverine, tidal, and wind-driven) coupled with spatially heterogeneous mass transfer velocities will improve estimates of nitrate fate in dynamic delta systems.

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## Data Availability Statement

Data sets are available in Hydroshare Repository (<https://www.hydroshare.org/resource/13841cb93b504bfc8f3e20f403cd2eda/>) under the Creative Commons Attribution CC and referenced as Knights (2020) in the manuscript. Data sets will be permanently published upon acceptance.

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