Nitrate Flux into the Sediments of a Shallow Oligohaline Estuary during Large Flood Pulses of Mississippi River Water

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Lake Pontchartrain is a large, oligohaline estuary located in coastal Louisiana that receives episodic diversions of nitrogen-rich Mississippi River water via the Bonnet Carré Spillway to alleviate flood threats to the city of New Orleans. These events may be linked to expressions of eutrophication, and it is therefore important to investigate pathways of nitrate (NO_3^-) loss. Nitrate flux into the sediments of Lake Pontchartrain was investigated using two independent methods: (i) simulating high NO_3^- flood events under aerobic and anaerobic incubations in intact sediment cores collected during 2010 and (ii) in situ field measurements of the vertical profiles of dissolved inorganic nitrogen species at the sediment–water interface during the 2011 Bonnet Carré Spillway opening. Mean rates of NO_3^- flux into sediments based on mass transfer in intact cores collected in 2010 and in situ porewater measurements in 2011 were −17.4 and −1.4 mg NO_3–N m^{-2} d^{-1}, respectively, for water column NO_3^- concentrations observed in situ in 2011. During the laboratory incubations, there was no significant difference in NO_3^- flux between oxygen treatments. We estimate that NO_3^- flux into sediments accounted for up to 3.1% (309 Mg NO_3–N) of water column NO_3^- loss during the 2008 Bonnet Carré Spillway event. Sediment characteristics, field measurements, and results from the laboratory experiment suggest that denitrification is the primary pathway for NO_3^- reduction. Even though there is significant NO_3^- reduction occurring in Lake Pontchartrain sediments during Mississippi River diversion events, this pathway of NO_3^- loss from the water column plays a relatively minor role in the transformation of the very large amount of NO_3^- received during these times.

HUMAN ALTERATION of the global nitrogen (N) cycle due to agriculture and other activities has approximately doubled the rate of N input into the terrestrial N cycle and has greatly increased the transfer of N through rivers to coastal ecosystems (Vitousek et al., 1997). The result has been widespread coastal eutrophication, expressions of which can include harmful algal blooms and hypoxia (Smith and Schindler, 2009). These global trends are exemplified in the Mississippi River basin where a nearly threefold increase in the N load carried by the river has contributed to the expansion of the second largest zone of coastal hypoxia in the world on the adjacent Gulf of Mexico continental shelf (Goolsby and Battaglin, 2001; Rabalais et al., 2002).

In addition to coastal eutrophication and hypoxia in the Gulf of Mexico, Mississippi River flooding is of significant concern in coastal Louisiana. After the Great Flood of 1927, the Bonnet Carré Spillway was constructed by the U.S. Army Corps of Engineers to protect New Orleans, LA, from massive flooding (Barry, 1997). The spillway can divert approximately 17% (7.1 ML s^{-1} [250,000 ft^3 s^{-1}]) of the flood level Mississippi River capacity (42.5 ML s^{-1} [1,500,000 ft^3 s^{-1}]) along with significant nutrient and sediment loads through the Lake Pontchartrain estuary into the Gulf of Mexico on the eastern side of the Bird's Foot Delta (White et al., 2009).

During a 1-mo diversion event in 2008, approximately 8 km^3 of water containing approximately 10,000 Mg of NO_3–N was discharged into Lake Pontchartrain (White et al., 2009). The spillway was again opened in May 2011. Phytoplankton growth in Lake Pontchartrain is typically N limited, and there is concern that opening the Bonnet Carré Spillway can trigger eutrophic conditions (Turner et al., 2002; Turner et al., 2004; Bargu et al., 2011). During spillway openings, potential pathways of nitrate (NO_3^-) removal from the water column in Lake Pontchartrain include flux into sediments, assimilation by phytoplankton, and transport to the coastal ocean. Estimates of the magnitudes of these pathways are essential for determining the ecological consequences of pulses of N-rich Mississippi River water into Lake Pontchartrain.

The focus of this study is on NO_3^- flux into the sediments of Lake Pontchartrain. Potential major pathways of NO_3^- reduction after diffusion into the sediment include

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Abbreviations: DNRA, dissimilatory NO_3^- reduction to ammonia.

respiratory denitrification and dissimilatory NO_3^- reduction to ammonia (DNRA). These reduction pathways can alter NO_3^- concentration gradients between the water column and sediment porewater. Therefore, diffusive flux rates of NO_3^- into the sediment are limited by NO_3^- reduction in the sediment. Respiratory denitrification is a microbial-mediated process whereby facultative anaerobic bacteria in sediment use NO_3^- or nitrite (NO_2^-) as the terminal electron acceptor during the oxidation of organic carbon (microbial respiration), resulting in the production of gaseous end products, N_2O and N_2, which are lost to the atmosphere (Reddy and DeLaune, 2008). The rate of water column NO_3^- loss by respiratory denitrification in sediments has been shown to depend on the concentrations of NO_3^- and O_2 in the overlying water column. The latter determines (i) the thickness of the oxic zone in the sediment that water column NO_3^- must diffuse across to reach the denitrification zone and (ii) whether respiratory denitrification is driven by water column NO_3^- or sediment porewater NO_3^- produced by nitrification (Rysgaard et al., 1994). Critically, respiratory denitrification can reduce the amount of inorganic N available for primary production in the water column, thereby preventing algal blooms. Previous researchers have documented respiratory denitrification throughout coastal Louisiana (Rivera-Monroy et al., 2010). Dissimilatory NO_3^- reduction to ammonia is a process mediated by obligate anaerobic bacteria where NO_3^- is reduced to NH_4^+ by dissimilative NO_3^- reductase enzymes (Reddy and DeLaune, 2008). Dissimilatory NO_3^- reduction to ammonia requires high electron pressure (i.e., a high carbon to NO_3^- ratio), low redox potential, and/or high sulfate concentrations (Tiedje, 1988; Burgin and Hamilton, 2007; Reddy and DeLaune, 2008). An important difference between DNRA and respiratory denitrification is that the NH_4^+ produced by DNRA in sediments can be regenerated to the water column and contribute to eutrophication as NH_4^+ or as NO_3^- after nitrification (Burgin and Hamilton, 2007). There are NO_3^- reduction pathways in sediments other than DNRA and respiratory denitrification; however, these pathways typically result in the conversion of NO_3^- to N_2 gas (Burgin and Hamilton, 2007) and therefore are grouped here with respiratory denitrification and referred to collectively as *denitrification*.

No direct experimental measurements of water column NO_3^- loss in Lake Pontchartrain by flux into sediments have been reported. Previous researchers have based indirect estimates of denitrification in Lake Pontchartrain on water column measurements and mass balance (Turner et al., 2004) or used measured rates from other estuaries in models of Lake Pontchartrain (McCorquodale et al., 2009). Available measurements of bottom water dissolved O_2 in Lake Pontchartrain indicate aerobic conditions (dissolved O_2 >> 2 mg L^{-1}) in spring and summer during normal conditions and spillway diversion events (Brammer et al., 2007; White et al., 2009). It has been hypothesized that episodic events of hypoxia may go undetected (Brammer et al., 2007).

Several experimental and in situ methods exist for estimating NO_3^- flux into aquatic sediments (Cornwell et al., 1999). Previous researchers have noted that water column NO_3^- concentration is a key parameter for determining NO_3^- flux into sediments (e.g., Mengis et al., 1997; Birgand et al., 2007). Consequently, comparing results from studies using a wide range

of NO_3^- concentrations is problematic, especially in coastal Louisiana given that there is a paucity of NO_3^- reduction studies at NO_3^- concentration levels that typically enter these systems (Rivera-Monroy et al., 2010). Additionally, reporting a single rate fails to adequately describe the diffusion process in a manner that accounts for the impacts of variable water column NO_3^- concentrations, thereby limiting analyses across space and time, including modeling applications. The purpose of this study was to use a combination of techniques to estimate the potential for water column NO_3^- removal by flux into Lake Pontchartrain sediments and to determine the primary pathway of NO_3^- transformation in the sediments. An equation is developed for the rate of NO_3^- flux into sediments as a function water column NO_3^- concentration, increasing the applicability of results. The results herein are expected to aid the construction of ecosystem-level N budgets and models of Lake Pontchartrain during high-N loading disturbances from the Bonnet Carré Spillway. A simple model is developed for determining the maximum amount of water column NO_3^- loss likely accounted for by flux into sediments during the 2008 Bonnet Carré Spillway event.

Materials and Methods
Study Site

Lake Pontchartrain is a shallow (mean depth, 3.7 m), oligohaline estuary with a surface area of 1637 km^2 and a volume of approximately 6 km^3 located just north of New Orleans, LA (Turner et al., 2002). Fresh water containing NO_3^- enters the lake via several small rivers along the northern rim, from the south contained in pumped urban runoff from the New Orleans area, and from the southwest where Mississippi River water enters as seasonal leakage and as episodic large pulses through the Bonnet Carré Spillway. The Bonnet Carré Spillway is a managed flood-release valve used only when the lower Mississippi River flood stage threatens New Orleans and downstream communities (most recent openings occurred in 1997, 2008, and 2011) and is capable of diverting up to approximately 17% of the flood stage of the Mississippi River into Lake Pontchartrain.

Sediment Sampling and Characterization

Intact sediment cores 20 to 30 cm in length were collected from two stations in Lake Pontchartrain: one station proximal to the Bonnet Carré Spillway inflow (0.9 km from spillway inflow) and the other in the lake center (25.9 km from spillway inflow) (Fig. 1). Sand, silt, and clay contents, as well as sediment characteristics, were determined from 20- to 30-cm cores collected on 5 Mar. 2010 by driving a 7-cm-diameter piston-core sampler into the sediment. A single core from the peeper station (4.9 km from spillway inflow) was collected for grain size analysis. Cores were sectioned on return to the laboratory and stored at 4°C for analysis. Sediment core samples used for the NO_3^- diffusive flux experiment were collected on 23 and 30 Sept. 2010. At the spillway inflow and lake center stations, nine cores were collected: two cores for determining in situ sediment characteristics, four cores for aerobic laboratory incubations, and three cores for anaerobic laboratory incubations.

Particle size (sand, silt, and clay) was determined using Stoke's law and a hydrometer in a 1-L graduated cylinder containing water, 40 g dry soil, and 25 mL of a 200 g L^{-1} sodium
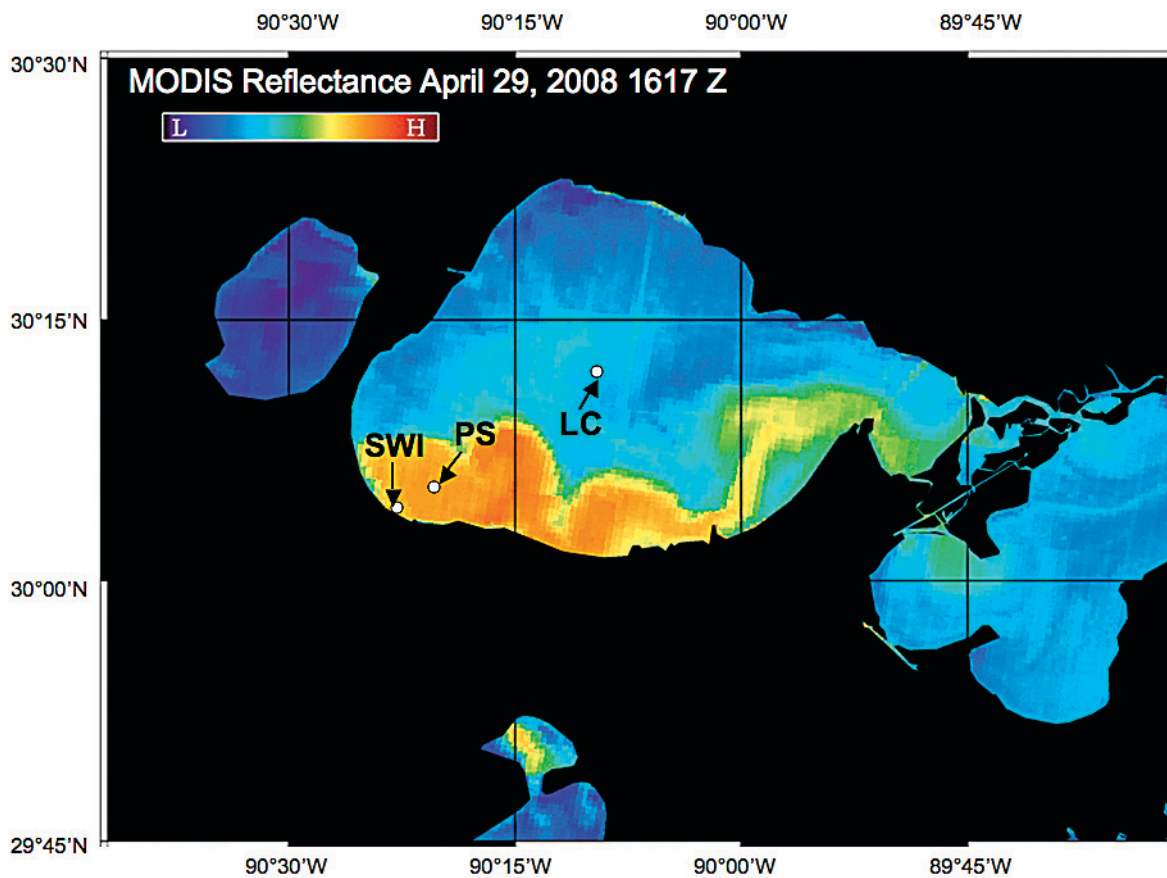
Fig. 1. Terra-1 MODIS band 1 (red) reflectance data obtained during the 2008 Bonnet Carré Spillway opening (White et al. 2009) with sampling stations (white circles) superimposed. Orange tones depict sediment-laden Mississippi River water (high red band reflectance values). Blue tones depict low red band reflectance, and land is colored black. LC, lake center; PS, peeper station; SWI, spillway inflow.

hexametaphosphate solution (Day, 1956; Patrick, 1958). Gravimetric moisture content was determined by placing field-moist subsamples in a forced-air oven at 70°C until constant weight. Bulk density was calculated on a dry weight basis. Mass loss on ignition was measured on dried, ground subsamples by difference after combustion at 550°C for 4 h in a muffle furnace as a proxy for percent organic matter content (White and Reddy, 2000). Extractable NH_4–N and NO_3–N were determined by shaking triplicate subsamples with 25 mL of 2 mol L^{-1} KCl at a ratio of approximately 1:40 (g dry soil:extractant) for 1 h on a longitudinal shaker. Samples were centrifuged for 10 min at 5000 rpm and filtered through Whatman no. 42 filter paper. Extractable NH_4–N and NO_3–N were quantified colorimetrically using the SEAL AQ2 Automated Discrete Analyzer (SEAL Analytical), as were all dissolved inorganic N measurements made in this study. Student's t tests were used to determine significant differences in sediment properties at the α = 0.05 significance level, grouping all cores by station (n = 9 per station). Data normality for sediment properties was determined using the Kolmogorov–Smirnov test (α = 0.01) and log-transformed to fit a normal distribution when necessary.

Nitrate Diffusive Flux Laboratory Incubations

High NO_3^- loading events were simulated in intact sediment cores by draining the original water column, reflooding the cores with a 1:2 mix of filtered water collected at the spillway inflow and deionized water (salinity, 0.68 PSU), and then spiking the water columns (volume = 0.77 L) with a NO_3^- solution (KNO_3 and deionized water) to produce concentrations of 2 mg NO_3–N L^{-1}, the maximum observed in the Mississippi River (Lane and Day, 1999). Filtered field water was mixed with deionized water to produce fresher flood water while retaining dissolved biological and chemical characteristics of the field water. Cores were placed in a water bath to maintain consistent temperature (~20.9°C), and incubations were performed in the dark for the duration of the experiment. For the aerobic incubation, room air was bubbled continuously into the water columns to maintain aerobic conditions (dissolved O_2 = 4.1–5.4 mg L^{-1}). For anaerobic incubations, O_2–free N gas was bubbled into the water column continuously to purge O_2 (Roy et al. 2012). Anaerobic cores were sealed with rubber stoppers to prevent the entrance of O_2 (dissolved O_2 < 0.75 mg L^{-1}). Samples (5 mL) were collected every 1 to 2 d from the center of the water column, filtered through 0.45-μm membrane syringe filters, and analyzed for NO_3–N. Additional floodwater (<10 mL) was introduced approximately 2 h before sampling to maintain a 0.77-L water column. After 2 wk, the intact cores were emptied of floodwater, reflooded, and spiked with NO_3^-. Maximum NO_3–N loss rates were calculated from the steepest portion of individual core NO_3–N loss curves including a minimum of three data points (Malecki et al., 2004). Nonparametric Wilcoxon rank sum tests were performed to determine significant differences in flux rates at the α = 0.05 significance level.

To avoid the limitations associated with reporting a single rate and to increase the applicability of the study results, an equation was developed to estimate the rate of NO_3^- flux into the sediments as a function of water column NO_3^- concentration. For each of the eight combinations of station, O_2 condition, and experimental flood (e.g., spillway inflow, anaerobic incubations, flood 1), mean values of NO_3^- concentration (C, mg NO_3–N m^{-3}) were calculated at each time interval (note: 1 mg NO_3–N L^{-1} = 1000 mg NO_3–N m^{-3}). Using these mean values, an exponential trendline was fit to the data in the form of

$$C(t) = C(0)e^{(\rho/h)t} \qquad [1]$$

where ρ is the mass transfer coefficient (m d^{-1}), h is the water column depth (0.2 m), and t is the time of incubation (d). Equation [1] is based on the first-order nutrient retention process with respect to the time of travel in streams (Stream Solute Workshop, 1990), which is related to the mass transfer coefficient (ρ) by Birgand et al. (2007). Only data from the first approximately 7 d of each incubation were used to determine these trendlines due to the fact that, in most cases, NO_3^- concentrations approached 1 mg NO_3–N L^{-1} at t = 7 d, the minimum concentration to which this method should be applied according to Birgand et al. (2007). Correlation coefficients (r^2) for the exponential trendlines ranged from 0.96 to 1.00. The mass transfer coefficient (ρ) is the velocity at which a molecule moves from the water column into sediments as a result of biological demand or sorption processes (Peterson et al., 2001). The term conveniently describes the NO_3^-–removing affinity of sediments and associated microbial communities independent of water column NO_3^- concentration (Birgand et al., 2007). Using ρ/h in Eq. [1], ρ was determined for each of the eight data sets. The areal rate of change in NO_3^- concentration (R, mg NO_3–N m^{-2} d^{-1}) was then determined as a function of ρ and C:

$$R = \rho C \qquad [2]$$

as in previous studies (e.g., Peterson et al., 2001).

In Situ Porewater Nitrogen and Diffusion

The opening of the Bonnet Carré Spillway during the 2011 Mississippi River flood provided a unique opportunity to measure in situ dissolved inorganic N profiles at the sediment–water interface. The NO_3^- and NH_4^+ gradients across the sediment–water interface were examined at the peeper station (PS, 4.9 km from spillway inflow) shown in Fig. 1 using dialysis porewater samplers ("peepers"; Urban et al., 1997) deployed in duplicate on 4 June 2011. During deployment, the peepers were within the freshwater Mississippi River plume entering the lake via the Bonnet Carré Spillway (salinity, 0.17–0.18 PSU). Water depth was approximately 4 m, and surface water temperature ranged from 24.3 to 27.6°C. Peepers consisted of 50 cm × 10 cm × 2.5 cm lexan blocks that have 8 cm^3 chambers machined at 1-cm vertical intervals covered with membrane filter paper (0.45 μm pore size, Pall). Before deployment, chambers were filled with N_2–purged deionized water, after which peepers were placed in a N_2–purged water bath over night and then sealed within the anaerobic water bath during

transport to maintain anoxic conditions. Peepers were lowered into the sediment so that roughly half of the chambers were submerged in the sediment while the top chambers were within the water column and remained in place for 9 d. Upon retrieval, samples were collected using individual syringes and stored on ice during transport to the laboratory, where they were stored at 4°C until analysis for NO_3–N and NH_4–N. Surface water samples were also collected and analyzed for NO_3–N and NH_4–N.

Fickean diffusive flux of NO_3^- (F) across the sediment–water interface was estimated as

$$F = D_{eff} \frac{\Delta C}{\Delta z} \qquad [3]$$

where D_{eff} is the effective areal sediment diffusion coefficient (cm^2 d^{-1}) and $\Delta C/\Delta z$ is the concentration gradient of NO_3^- (Urban et al., 1997). The value used for $\Delta C/\Delta z$ was determined based on linear regression using points along the sharp decrease in NO_3^- observed at the sediment–water interface (Urban et al., 1997). Following Urban et al. (1997), D_{eff} was calculated as

$$D_{eff} = \phi^n D \qquad [4]$$

where ϕ is the porosity, n is a constant set here to equal 1 (Urban et al., 1997), and D is the molecular diffusion coefficient for NO_3^- in water (1.64 cm^2 d^{-1} at 25°C) (Li and Gregory, 1974). Porosity, measured as weight loss on drying sediments for 72 h at 70°C (Urban et al., 1997), was 0.39 for the peeper station. Therefore, D_{eff} = 0.64 cm^2 d^{-1}.

Model for Nitrate Flux to Sediments during the 2008 Bonnet Carré Spillway Event

To investigate the potential water column NO_3^- removal by flux into sediments during the 2008 Bonnet Carré Spillway opening (total NO_3–N load ≈ 10,000 Mg; mean NO_3–N concentration ≈ 1.4 mg L^{-1}) (White et al., 2009), a model was developed based on plume surface area and the aerial NO_3^- loss equation (R, Eq. [2]). A piecewise function was used to estimate the freshwater plume area for each day of the 2008 Bonnet Carré Spillway event and subsequent plume collapse period:

$$A(t) = (5.71 \times 10^7)t \quad (0 \le t \le 11; n = 3) \qquad [5]$$

$$A(t) = (-1.58 \times 10^7)t + (7.70 \times 10^8) \quad (11 < t < 48; n = 3)$$

$$A(t) = 0 \quad (t = 49)$$

where $A(t)$ is the plume area (m^2) and t is day (0–49) from 11 Apr. 2008 to 30 May 2008. Discrete data used to determine the function were obtained using satellite imagery (White et al., 2009). Results from Bargu et al. (2011) indicate that the NO_3–N associated wtih the freshwater plume was depleted by 30 May 2008. The following function was used to determine the total mass of NO_3–N in the plume removed by flux into sediments during the 2008 Bonnet Carré Spillway diversion event:

$$M_{sed} = \sum_{t=0}^{49} A(t)^* - R^* 10^{-9} \qquad [6]$$

where M_{sed} is the total mass of NO_3–N removed by flux to sediments (Mg) and R is the NO_3^- loss rate (mg NO_3–N m^{-2} d^{-1}) determined here using $C = 1400$ mg NO_3–N m^{-3} in Eq. [2].

Results and Discussion
Sediment Characterization

Sediments at the spillway inflow were predominantly composed of sand (31%) and clay (61%), whereas those in the lake center were composed mainly of silt (58%) and clay (34%). Peeper station sediments were within this range, made up primarily of 25% silt and 59% clay. The organic content of Lake Pontchartrain sediments ranged from approximately 3 to 9%. Spillway inflow sediments were characterized by significantly ($P < 0.05$) greater bulk density and significantly ($P < 0.05$) lower organic content than those from the lake center (Table 1). Extractable NO_3^- data confirm that water column NO_3^- diffusing into the sediment was reduced and did not accumulate in the porewater (Table 1). The greater extractable NH_4^+ values observed at all depths for experiment cores in comparison to field cores representing in situ conditions (Table 1) indicate that NH_4^+ produced by the mineralization of organic N was accumulating during the laboratory incubation. In comparison, under field conditions in Lake Pontchartrain where surface sediments are frequently resuspended by wind-waves (Flocks et al., 2009), disturbance of sediments likely limits the accumulation of porewater NH_4^+. The absence of porewater NO_3^- suggests that accumulating NH_4^+ was not oxidized to NO_3^- or was oxidized and the resulting NO_3^- immediately reduced. This lack of porewater NO_3^- indicates that the sediment depth to which water column NO_3^- had to diffuse to encounter anaerobic conditions that promote reduction was extremely small during the experiment regardless of the water column O_2 concentration.

Sediment Core Nitrate Flux Experiments

During the first flood of the intact incubation cores from the spillway inflow and lake center stations, water column NO_3^- concentrations decreased from approximately 2 mg NO_3–N L^{-1} to 0.64 to 1.06 mg NO_3–N L^{-1} over approximately 13 d (Fig. 2). Maximum NO_3^- loss rates were not significantly different between O_2 treatments for both stations or among stations (Table 2). For the second laboratory NO_3^- flood event, water column NO_3^- concentrations decreased from ~2 mg NO_3–N L^{-1} to 0.66 to 0.95 mg NO_3–N L^{-1} over approximately 15 d (Fig. 2b), and there was again no significant difference in NO_3–N flux rates between O_2 treatments for both stations or among stations (Table 2). Mean maximum NO_3–N flux rates ranged from −24.3 to −61.9 mg NO_3–N m^{-2} d^{-1}. The lack of a significant difference in flux rates for aerobic and anaerobic incubations suggests that (i) O_2 availability in the benthic waters of Lake Pontchartrain does not limit NO_3^- reduction and (ii) nitrification of sediment porewater ammonium was not a significant source of NO_3^- (Rysgaard et al., 1994).

Mass transfer coefficients (ρ) ranged from −0.009 to −0.023 m d^{-1} (Table 2). Using the mean value of ρ determined here for all incubations (aerobic mean = anaerobic mean = 0.015 m d^{-1}), the rate of NO_3^- diffusion into the sediment (R, mg NO_3–N m^{-2} d^{-1}) can be modeled as a function of water column NO_3^- concentration (C, mg NO_3–N m^{-3}) by

$$R = -0.015 \times C \qquad [7]$$

Birgand et al. (2007) suggest this methodology based on ρ should be applied when a clear concentration gradient in NO_3^- exists at the sediment–water interface and when NO_3–N concentrations are >1 mg L^{-1}. Both conditions were met here.

Table 1. Select physiochemical properties of sediments in Lake Pontchartrain in field conditions and after intact core water column nitrate loss experiments using aerobic and anaerobic incubations.

Station	Interval	Treatment	Bulk density	Organic matter	Extractable NO_3^-	Extractable NH_4^+
	cm		g cm^{-3}	%	——— mg N kg^{-1} ———	
Spillway inflow	0–5	field	0.88 ± 0.03†	3.43 ± 0.71	0.79 ± 0.16	0.63 ± 0.27
		aerobic	1.10 ± 0.04	2.99 ± 0.12	1.13 ± 0.07	7.34 ± 0.80
		anaerobic	0.98 ± 0.14	3.24 ± 0.45	0.97 ± 0.02	12.4 ± 2.1
	5–10	field	0.95 ± 0.18	4.14 ± 0.31	1.20 ± 0.39	1.06 ± 0.09
		aerobic	1.12 ± 0.04	2.81 ± 0.27	0.72 ± 0.01	17.7 ± 1.4
		anaerobic	0.91 ± 0.13	5.31 ± 2.17	0.43 ± 0.10	27.7 ± 5.9
	10–15	field	0.92 ± 0.04	2.90 ± 0.97	1.28 ± 0.71	13.8 ± 2.7
		aerobic	1.16 ± 0.05	2.80 ± 0.25	0.83 ± 0.06	20.3 ± 2.0
		anaerobic	1.11 ± 0.06	3.47 ± 0.81	0.66 ± 0.12	25.3 ± 4.9
Lake center	0–5	field	0.30 ± 0.01	9.12 ± 1.35	1.61 ± 0.23	0.00 ± 0.00
		aerobic	0.33 ± 0.02	7.99 ± 0.22	1.36 ± 0.04	32.2 ± 1.2
		anaerobic	0.33 ± 0.02	7.47 ± 0.24	1.16 ± 0.04	50.1 ± 11.1
	5–10	field	0.46 ± 0.03	8.11 ± 1.22	2.13 ± 1.13	17.0 ± 2.5
		aerobic	0.40 ± 0.02	7.43 ± 0.22	1.38 ± 0.34	78.8 ± 5.1
		anaerobic	0.43 ± 0.03	5.94 ± 0.38	0.55 ± 0.16	76.4 ± 3.6
	10–15	field	0.41 ± 0.02	7.79 ± 0.23	0.86 ± 0.05	38.5 ± 7.1
		aerobic	0.40 ± 0.02	8.49 ± 0.30	1.13 ± 0.06	94.3 ± 7.4
		anaerobic	0.46 ± 0.04	7.68 ± 0.32	0.50 ± 0.05	94.0 ± 7.1

† Data are mean values ($n = 2$ for field characterization cores; $n = 4$ for aerobic cores; $n = 3$ for anaerobic cores) ± 1 SE.
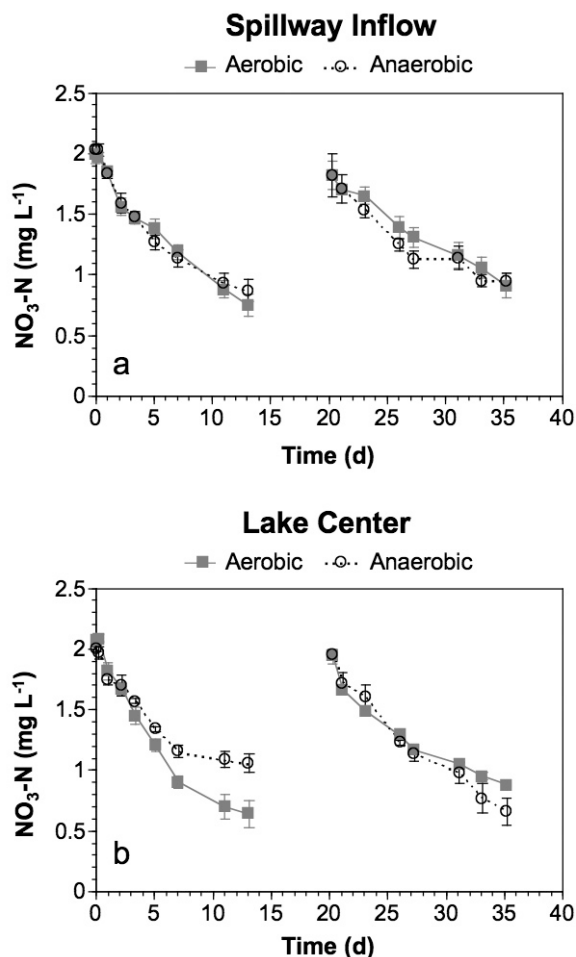
Spillway Inflow

Lake Center

Fig. 2. Changes in mean NO$_3$–N concentrations (±1 SE) of the water column under aerobic (*n* = 4) and anaerobic (*n* = 3) laboratory incubations for intact sediment cores from the Bonnet Carré Spillway inflow (a) and the lake center (b) stations in Lake Pontchartrain.

Porewater Nitrogen Profiles and Diffusion

Sharp negative gradients in NO$_3^-$ concentration occurred at the sediment–water interface for both peeper replicates in Lake Pontchartrain during the 2011 spillway opening (Fig. 3a). The greatest concentrations existed 2 to 7 cm above the sediment surface. The mean concentration of these data points (1.16 mg NO$_3$–N L^{-1}) was approximately equal to the surface water NO$_3^-$ concentration of 1.13 mg NO$_3$–N L^{-1}, suggesting little vertical variation in NO$_3^-$ in the water column, as seen by White et al.

(2009), until approximately 3 cm above the sediment surface. Below this point there was a negative gradient through the sediment until negligible concentrations of NO$_3$–N were found 3 cm below the sediment surface. Replicate concentration gradients $\Delta C/\Delta z$ between ±3 cm were 0.21 ($r^2 = 0.95$) and 0.22 ($r^2 = 0.86$). Mean Fickean diffusive flux, F, of NO$_3^-$ (± 1 SE) was −1.38 ± 0.02 mg NO$_3$–N m^{-2} d^{-1} (Table 2). In contrast to the NO$_3^-$ profiles, NH$_4^+$ concentrations were negligible from 2 to 7 cm above the sediment surface and increased linearly with depth at the sediment–water interface and within the sediments (Fig. 3b).

Comparison of Methods

Inserting the water column NO$_3^-$ concentration observed in the field during the in situ porewater measurements (1160 mg NO$_3$–N m^{-3}) into Eq. [7] yields a rate of NO$_3^-$ flux into sediments, R, of −17.4 mg NO$_3$–N m^{-2} d^{-1}, more than 10-fold greater than the rate determined based on Fickean diffusion (−1.38 mg NO$_3$–N m^{-2} d^{-1}; Table 2). Previous researchers have reported similar discrepancies in results for these two methods (Urban et al., 1997; Mengis et al., 1997). There are limitations to both approaches, including (i) the difficulty of recreating boundary layer conditions in laboratory incubations (Mengis et al., 1997), (ii) uncertainty associated with the molecular diffusion coefficient D in Eq. [4], and (iii) the inadequate spatial resolution of porewater profiles needed to observe rapid mineralization processes that can occur at the sediment surface (Urban et al., 1997). NO$_3^-$ flux rates in Lake Pontchartrain calculated here based on peeper data likely underestimate actual flux rates due to a low diffusion coefficient and insufficient vertical resolution, thus yielding a lower limit estimate, as concluded previously by Mengis et al. (1997) for peeper measurements of NO$_3^-$ flux into sediments.

Comparison of Nitrate Loss Rates with Other Systems

Rates of water column NO$_3^-$ loss in Lake Pontchartrain found here for high NO$_3^-$ loading events (−1.4 to −61.9 mg NO$_3$–N m^{-2} d^{-1}; Table 2) fall within the range reported for other estuarine environments (Herbert, 1999). Gardner and White (2010) report a mean NO$_3^-$ loss rate of −137 mg NO$_3$–N m^{-2} d^{-1} for the Davis Pond marsh, an emergent vegetated ecosystem that receives diverted Mississippi River water, based on intact soil cores with 2 mg NO$_3$–N L^{-1} floodwater. Linear regression of results from Gardner and White (2010) for several floodwater NO$_3^-$ concentrations indicate that the mass transfer coefficient

Table 2. Nitrate flux rates from the water column to sediments, as well as mass transfer coefficients, in intact sediment cores from Lake Pontchartrain under aerobic (*n* = 4) and anaerobic (*n* = 3) laboratory incubations for two high-nitrate flood cycles. No significant differences at the α = 0.05 significance level were found between aerobic and anaerobic incubations for either station during both floods.

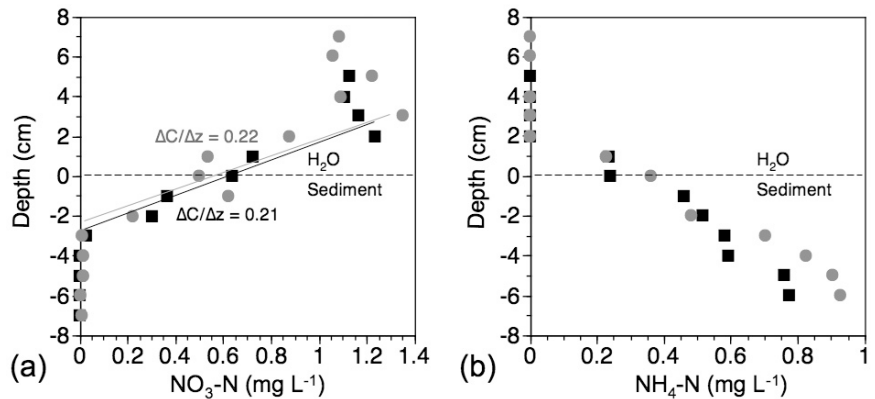| Flood	Site	Aerobic core incubation		Anaerobic core incubation		In situ porewater measurements
		Max NO$_3$–N flux rate	Mass transfer coefficient ρ	Max NO$_3$–N flux rate	Mass transfer coefficient ρ	Fickean NO$_3$–N flux rate
		mg NO$_3$–N m^{-2} d^{-1}	m d^{-1}	mg NO$_3$–N m^{-2} d^{-1}	m d^{-1}	mg NO$_3$–N m^{-2} d^{-1}
1	spillway inflow	−46.6 ± 4.5†	−0.015	−53.0 ± 9.5	−0.017	
	lake center	−61.9 ± 12.1	−0.023	−52.9 ± 14.0	−0.015	
2	spillway inflow	−26.4 ± 4.5	−0.009	−24.3 ± 7.1	−0.013	
	lake center	−33.1 ± 6.0	−0.013	−35.7 ± 8.6	−0.015	
	peeper station					−1.38 ± 0.02

† Values are means ± 1 SE.

(ρ) for Davis Pond Marsh is equal to -0.075 m d^{-1}. Comparison with results from this study (overall mean $\rho = -0.015$ m d^{-1}) illustrates that macrophyte-dominated marsh ecosystems receiving diverted Mississippi River water can potentially reduce NO$_3^-$ concentrations at a rate ~5 times greater than Lake Pontchartrain sediments. There are two major factors in these differences. Organic matter content in Lake Pontchartrain sediments (~3–9%) is substantially lower than in the soils of Davis Pond marsh, with values of approximately 24 to 63% organic matter by weight, typical of coastal Louisiana wetlands (DeLaune and White, 2012). Therefore, carbon availability may help explain the much lower rates of NO$_3^-$ flux into Lake Pontchartrain sediments due to a reduced microbial demand for NO$_3^-$ as the terminal electron acceptor (White and Reddy, 2001). In addition, convective flow through the plant, known as the transpiration stream, increases the flux of surface water constituents down into the wetland soil (Sorrell and Brix, 2003), which can significantly increase NO$_3^-$ loss from the water column in vegetated systems.

Fig. 3. Vertical distribution of nitrate (a) and ammonium (b) concentrations in the overlying water column and sediment porewater at the peeper station within the freshwater plume during the 2011 Bonnet Carré Spillway opening. The horizontal dashed line represents the sediment–water interface. Linear regression lines are shown for data at depths between −3 cm and +3 cm used to determine the concentration gradient ($\Delta C/\Delta z$) for Eq. 3 of NO$_3$–N concentration (*C*) with depth (*z*).

Primary Pathway of Nitrate Reduction in Lake Pontchartrain Sediments

Whether the dominant pathway of NO$_3^-$ reduction in sediments is DNRA or denitrification can be determined based on the availability of carbon, NO$_3^-$, and sulfate (Burgin and Hamilton, 2007). Previous research suggests that DNRA is favored in NO$_3^-$–limited environments rich in available carbon, whereas denitrification is favored under carbon-limited conditions with ample NO$_3^-$ (Tiedje, 1988). During Mississippi River diversion events, Lake Pontchartrain sediments are exposed to NO$_3$–N concentrations >1 mg L^{-1} at the sediment–water interface. Given this high availability of NO$_3^-$ combined with the low organic content of Lake Pontchartrain sediments (~3–9%; Table 1), it is very unlikely that DNRA is the favored pathway. Furthermore, if DNRA were the dominant pathway of NO$_3^-$ reduction in the intact core experiment, the resulting NH$_4^+$ would have reentered the water column and would have been nitrified to NO$_3^-$ in the aerobic incubations, reducing the rate of water column NO$_3^-$ loss in comparison to anaerobic incubations where nitrification would be inhibited. The equivalent rates of NO$_3^-$ loss in aerobic and anaerobic incubations (Table 2) indicate that this was not occurring. Finally, during Bonnet Carré Spillway openings, the oligohaline Lake Pontchartrain estuary becomes fresh (salinity ≤0.18 PSU) in the region affected by the Mississippi River plume (White et al., 2009), thereby decreasing the availability of sulfide that can promote chemolithoautotrophic DNRA, as observed in high-salinity systems (e.g., An and Gardner, 2002). It is therefore concluded here that denitrification is the likely dominant pathway of NO$_3^-$ reduction in Lake Pontchartrain sediments when subjected to flood pulses of Mississippi River water. This denitrification appears to be driven primarily by water column NO$_3^-$ concentration but may be limited by carbon availability. Given available carbon, the denitrifier population would be expected to increase and become more active after continuous exposure to high NO$_3^-$ concentrations. The absence of an increase in NO$_3^-$ flux rates from flood event 1 to flood event 2 (Table 2) therefore suggests potential carbon limitation of denitrification in Lake Pontchartrain sediments (White and Reddy, 1999).

Nitrate Removal by Flux to Sediments during the 2008 Bonnet Carré Spillway Event

Using Eq. [7] with C = 1400 mg NO$_3$–N m^{-3} (the 2008 Bonnet Carré Spillway plume concentration observed by White et al. [2009]), the rate of NO$_3^-$ flux to Lake Pontchartrain sediments, R, is equal to -21.0 mg NO$_3$–N m^{-2} d^{-1}. Inserting this value in Eq. [6], it is estimated that NO$_3^-$ flux to sediments accounted for a maximum of approximately 3.1% (309 Mg NO$_3$–N) of water column NO$_3^-$ loss during the entire 2008 Bonnet Carré Spillway diversion event, including the period when the spillway was open and the plume-collapse period after its closure (total NO$_3$–N load = 10,000 Mg). These results suggest that a significant magnitude of NO$_3^-$ is denitrified in Lake Pontchartrain sediments during Bonnet Carré Spillway openings and that denitrification is an important process in the estuary's N cycle. However, as suggested by Turner et al. (2004), based on indirect measurements, the impact of denitrification appears to be relatively minimal during large pulses of inorganic N to Lake Pontchartrain associated with Mississippi River flood diversions due to the immense loading rate (e.g., 10,000 Mg NO$_3$–N over 1 mo in 2008). There may also be longer pathways to N removal by denitrification in the system after these large pulses, beginning with the decomposition of phytoplankton, followed by mineralization and coupled nitrification–denitrification processes in the sediments (White and Reddy, 2003).

Acknowledgments

References

An, S., and W.S. Gardner. 2002. Dissimilatory nitrate reduction to ammonia (DNRA) as a nitrogen link, versus denitrification as a sink in a shallow estuary (Laguna Madre/Baffin Bay, Texas). Mar. Ecol. Prog. Ser. 237:41–50. doi:10.3354/meps237041

Bargu, S., J.R. White, C. Li, J. Czubakowski, and R.W. Fulweiler. 2011. Effects of freshwater input on nutrient loading, phytoplankton biomass, and cyanotoxin production in an oligohaline estuarine lake. Hydrobiologia 661:377–389. doi:10.1007/s10750-010-0545-8

Barry, J.M. 1997. Rising tide: The Great Mississippi Flood of 1927 and how it changed America. Simon & Shuster, New York.

Birgand, F., R.W. Skaggs, G.M. Chescheir, and J.W. Gilliam. 2007. Nitrogen removal in streams of agricultural catchments: A literature review. Crit. Rev. Environ. Sci. Technol. 37:381–487. doi:10.1080/10643380600966426

Brammer, A.J., Z.R. del Rey, E.A. Spalding, and M.A. Poirrier. 2007. Effects of the 1997 Bonnet Carre Spillway opening on infaunal macroinvertebrates in Lake Pontchartrain, Louisiana. J. Coast. Res. 23:1292–1303. doi:10.2112/05-0571.1

Burgin, A.J., and S.K. Hamilton. 2007. Have we overemphasized the role of denitrification in aquatic ecosystems? A review of nitrate removal pathways. Front. Ecol. Environ 5:89–96. doi:10.1890/1540-9295(2007)5[89:HWOTRO]2.0.CO;2

Cornwell, J.C., W.M. Kemp, and T.M. Kana. 1999. Denitrification in coastal ecosystems: Methods, environmental controls, and ecosystem level controls, a review. Aquat. Ecol. 33:41–54. doi:10.1023/A:1009921414151

Day, P.R. 1956. Report of the committee on physical analyses (1954–1955). Soil Sci. Soc. Am. Proc. 20:167–169. doi:10.2136/sssaj1956.03615995002000020007x

DeLaune, R.D., and J.R. White. 2012. Will coastal wetlands continue to sequester carbon in response to an increase in global sea level? A case study of the rapidly subsiding Mississippi river deltaic plain. Clim. Change 110:297–314. doi:10.1007/s10584-011-0089-6

Flocks, J., J. Kindinger, M. Marot, and C. Holmes. 2009. Sediment characterization and dynamics in Lake Pontchartrain, Louisiana. J. Coast. Res. 54:113–126. doi:10.2112/SI54-011.1

Gardner, L.M., and J.R. White. 2010. Denitrification enzyme activity as an indicator of nitrate movement through a diversion wetland. Soil Sci. Soc. Am. J. 74:1037–1047. doi:10.2136/sssaj2008.0354

Goolsby, D.A., and W.A. Battaglin. 2001. Long-term changes in concentrations and flux of nitrogen in the Mississippi River Basin, USA. Hydrol. Processes 15:1209–1226. doi:10.1002/hyp.210

Herbert, R.A. 1999. Nitrogen cycling in coastal marine ecosystems. FEMS Microbiol. Rev. 23:563–590. doi:10.1111/j.1574-6976.1999.tb00414.x

Lane, R.R., and J.W. Day. 1999. Water quality analysis of a freshwater diversion at Caernarvon, Louisiana. Estuaries Coasts 22:327–336. doi:10.2307/1352988

Li, Y.H., and S. Gregory. 1974. Diffusion of ions in sea water and in deep-sea sediments. Geochim. Cosmochim. Acta 88:703–714.

McCorquodale, J.A., R.J. Roblin, I.Y. Georgiou, and K.A. Haralampides. 2009. Salinity, nutrient, and sediment dynamics in the Pontchartrain estuary. J. Coast. Res. 54:71–87. doi:10.2112/SI54-000.1

Malecki, L.M., J.R. White, and K.R. Reddy. 2004. Nitrogen and phosphorus flux rates from sediment in the lower St. Johns River estuary. J. Environ. Qual. 33:1545–1555. doi:10.2134/jeq2004.1545

Mengis, M., R. Gächter, and B. Wehrli. 1997. Nitrogen elimination in two deep eutrophic lakes. Limnol. Oceanogr. 42:1530–1543. doi:10.4319/lo.1997.42.7.1530

Patrick, W.H. 1958. Modification of method of soil particle analysis. Soil Sci. Soc. Am. Proc. 22:366–367. doi:10.2136/sssaj1958.03615995002200040027x

Peterson, B.J., W.M. Wollheim, P.J. Mulholland, J.R. Webster, J.L. Meyer, J.L. Tank, E. Marti, W.B. Bowden, H.M. Valett, A.E. Hersey, W.H. McDowell, W.K. Dodds, S.K. Hamilton, S. Gregory, and D.D. Morrall. 2001. Control of nitrogen export from watersheds by headwater streams. Science 292:86–90. doi:10.1126/science.1056874

Rabalais, N.N., R.E. Turner, and W.J. Wiseman. 2002. Gulf of Mexico hypoxia, a.k.a. "The Dead Zone." Annu. Rev. Ecol. Syst. 33:235–263. doi:10.1146/annurev.ecolsys.33.010802.150513

Reddy, K.R., and R.D. DeLaune. 2008. Biogeochemistry of wetlands: Science and applications. CRC Press, Taylor & Francis Group, Boca Raton, FL.

Rivera-Monroy, V.H., P. Lenaker, R.R. Twilley, R.D. Delaune, C.W. Lindau, W. Nuttle, E. Habib, R.W. Fulweiler, and E. Castañeda-Moya. 2010. Denitrification in coastal Louisiana: A spatial assessment and research needs. J. Sea Res. 63:157–172. doi:10.1016/j.seares.2009.12.004

Roy, E.D., N.T. Nguyen, S. Bargu, and J.R. White. 2012. Internal loading of phosphorus from sediments of Lake Pontchartrain (Louisiana, USA) with implications for eutrophication. Hydrobiologia 684:69–82.

Rysgaard, S., N. Risgaard-Peterson, N.P. Sloth, K. Jensen, and L.P. Nielsen. 1994. Oxygen regulation of nitrification and denitrification in sediments. Limnol. Oceanogr. 39:1643–1652. doi:10.4319/lo.1994.39.7.1643

Smith, V.H., and D.W. Schindler. 2009. Eutrophication science: Where do we go from here? Trends Ecol. Evol. 24:201–207. doi:10.1016/j.tree.2008.11.009

Sorrell, B.K., and H. Brix. 2003. Effects of water vapor pressure deficit and stomatal conductance on photosynthesis, internal pressurization and convective flow in three emergent wetland plants. Plant Soil 253:71–79. doi:10.1023/A:1024517510541

Workshop, S.S. 1990. Concepts and methods for assessing solute dynamics in stream ecosystems. J. North Am. Benthol. Soc. 9:95–119. doi:10.2307/1467445

Tiedje, J.M. 1988. Ecology of denitrification and dissimilatory nitrate reduction to ammonia. In: A.J.B. Zehnder, editor, Biology of anaerobic microorganisms. John Wiley & Sons, New York. p. 197–244.

Turner, R.E., Q. Dortch, D. Justic, and E.M. Swenson. 2002. Nitrogen loading into an urban estuary: Lake Pontchartrain (Louisiana, U.S.A.). Hydrobiologia 487:137–152. doi:10.1023/A:1022994210268

Turner, R.E., Q. Dortch, and N.N. Rabalais. 2004. Inorganic nitrogen transformations at high loading rates in an oligohaline estuary. Biogeochemistry 68:411–422. doi:10.1023/B:BIOG.0000031039.56794.29

Urban, N.R., C. Dinkel, and B. Wehrli. 1997. Solute transfer across the sediment surface of a eutrophic lake: I. Porewater profiles from dialysis samples. Aquat. Sci. 59:1–25. doi:10.1007/BF02522546

Vitousek, P.M., J.D. Aber, R.W. Howarth, G.E. Likens, P.A. Matson, D.W. Schindler, W.H. Schlesinger, and D.G. Tilman. 1997. Human alteration of the global nitrogen cycle: Sources and consequences. Ecol. Appl. 7:737–750.

White, J.R., R.W. Fulweiler, C.Y. Li, S. Bargu, N.D. Walker, R.R. Twilley, and S.E. Green. 2009. Mississippi River flood of 2008: Observations of a large freshwater diversion on physical, chemical, and biological characteristics of a shallow estuarine lake. Environ. Sci. Technol. 43:5599–5604. doi:10.1021/es900318t

White, J.R., and K.R. Reddy. 1999. The influence of nitrate and phosphorus loading on denitrifying enzyme activity in Everglades wetland soils. Soil Sci. Soc. Am. J. 63:1945–1954. doi:10.2136/sssaj1999.6361945x

White, J.R., and K.R. Reddy. 2000. Influence of phosphorus loading on organic nitrogen mineralization of Everglades soils. Soil Sci. Soc. Am. J. 64:1525–1534. doi:10.2136/sssaj2000.6441525x

White, J.R., and K.R. Reddy. 2001. Influence of selected inroganic electron acceptors on organic nitrogen mineralization in Everglades soils. Soil Sci. Soc. Am. J. 65:941–948. doi:10.2136/sssaj2001.653941x

White, J.R., and K.R. Reddy. 2003. Potential nitrification and denitrification rates in a phosphorus-impacted subtropical peatland. J. Environ. Qual. 32:2436–2443. doi:10.2134/jeq2003.2436