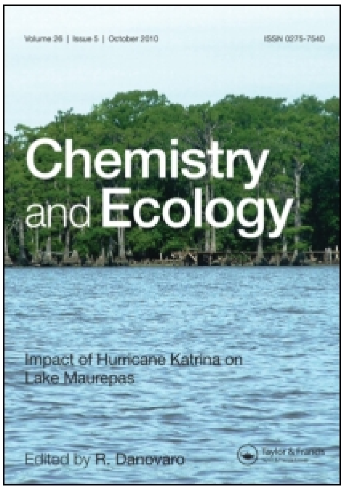

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Sediment nutrient flux in a coastal lake impacted by diverted Mississippi River water

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The internal nutrient load from bottom sediment to the water column of a Louisiana Barataria Basin lake (Lake Cataouatche) receiving diverted Mississippi River water was determined. Dissolved reactive phosphorus (DRP), ammonium (NH_4-N) and nitrate (NO_3-N) flux from sediment to water column were measured. The DRP flux averaged $-0.22\,mg\,m^{-2}\,d^{-1}$ under aerobic water column conditions, as compared with that $3.29\,mg\,m^{-2}\,d^{-1}$ under anaerobic conditions. The average NH_4-N released under anaerobic conditions ($1.42\,mg\,m^{-2}\,d^{-1}$) was significantly greater than rates under aerobic conditions ($-0.02\,mg\,m^{-2}\,d^{-1}$), indicating a strong relationship between nutrient flux and oxygen availability in the water column. The average NO_3-N flux was $2.13\,mg\,m^{-2}\,d^{-1}$ under aerobic conditions as compared with $-0.24\,mg\,m^{-2}\,d^{-1}$ under anaerobic conditions in the sediment–water column. When the water column maintained under anaerobic conditions was switched to aerobic conditions, the DRP, NH_4-N, and NO_3-N concentrations in overlying water decreased rapidly over a short period of time. The mean annual internal DRP and NH_4-N load from the sediment to the overlying water was estimated to be 69.26 and 29.9 tonnes (Mg) yr^{-1} respectively, which represents a significant portion of the total nutrient load to the Lake. Results demonstrate that the internal flux of nutrients from sediments can contribute a significant portion of the total nutrient load to the water column and should be considered in decisions on impact of nutrient in diverted Mississippi River on water quality of Barataria Basin.

Keywords: Dissolved reactive phosphorus (DRP); Total phosphorus (TP); Nitrogen; Total maximum daily load (TMDL); Internal nutrient load; Sediment flux

1. Introduction

Eutrophication of estuaries is the process of increased organic enrichment of estuary through increased nutrient input. Nitrogen and phosphorus are the two nutrients of concern in eutrophication of freshwater and coastal systems [1]. Phosphorus can limit or co-limit phytoplankton growth in estuaries and marine environment receiving a high nitrogen input [2]. In many coastal waters, nitrogen is the nutrient limiting primary production [3]. In lower portions of coastal estuaries, both nitrogen and phosphorus can limit phytoplankton growth [2]. External nutrient loading can not only result in an increase in the total nutrient content of the

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water column but also increase nutrient concentration into sediment column [4]. In Louisiana, Davis Pond diversion was constructed to divert Mississippi River water into the Barataria Basin estuary for coastal restoration or slowing wetland loss. The high load of nutrients in diverted Mississippi River water can potentially increase phytoplankton production leading to eutrophication. Following the reintroduction of river water, there were measured increases in nutrient loading and concentration [5, 6] in Lake Cataouatche with a parallel increase in concentration of chlorophyll A, suggesting a change in phytoplankton composition [7]. In addition to nutrient in diverted river water, sediment can also function as a source of P and N to the overlying water column. Quantification of the magnitude of nutrient flux, especially P and N, from sediment is of importance in assessing the relative internal to external loading of nutrients to ecosystem [8, 9]. Nutrient enrichment of estuarine waters and associated increase in productivity can result in accelerated accumulation of organic matter in sediment and an increase in nutrient flux from the sediment to the overlying water column [10]. Quantifying the nutrient source from sediment to the water column can be used in determining the contribution of internal sediment load to the overall lake nutrient budget. Nutrient transformation/flux at the sediment–water interface can be an important source of nutrient to the water column. Denitrification occurring mainly at the sediment–water interface in wetland is important because it represents a direct loss to the atmosphere [11]. Denitrification rate is controlled by nitrate concentration and diffusion of nitrate from the floodwater to the anaerobic sediment layer [6]. TMDL is used to determine the pollutant loading that a waterbody can assimilate without exceeding the water quality standard and to establish the load allocation for meeting the water-quality standard. TMDL is the sum of all point and non-point source load allocation, with a margin of safety and consideration for seasonal variation [12]. Both point and non-point source of nutrients are routinely used, but internal cycling and the water column must also be considered as a contribution to the nutrient load. The margin of safety is a percentage of the TMDL that accounts for the uncertainty associated with the model assumptions and data inadequacies. Quantifying TMDL is complex, requiring the development of individual water-quality models for each impaired water body, often requiring collection of significant data not available in the literature [13].

The overall objective of this study was to quantify sediment source (non-point) of nutrients to the water column in a Barataria Basin coastal lake (Lake Cataouatche) receiving diverted Mississippi River water. The specific objectives were: (1) to determine factors governing nutrient flux from sediment to the water column; (2) to estimate the annual internal or non-point source load of P and N from the sediment to the overlying water column; (3) to quantify the relationship between P and Fe release from the sediment; and (4) to determine the denitrification potential of the lake sediment.

2. Material and methods

2.1 *Site description*

The Davis Pond Diversion located near Luling, Louisiana in St. Charles Parish on the west bank of the Mississippi River became operational in 2002. The freshwater diversion structure designed for coastal restoration is capable of delivering a maximum discharge of 300 $m^3\ s^{-1}$ through four 4.3 m × 4.3 m gated box culverts [14]. The diversion can potentially benefit 134 000 ha of marsh in Barataria Basin estuary, a 314 400 ha wetland complex hydrologically bound on the east by the Mississippi River levee and to the west by Bayou LaFourche. The diversion discharge water follows a course south through a 3400-m-long channel under the Highway 90 underpass and into a 3700 ha ponding area bound by constructed levees

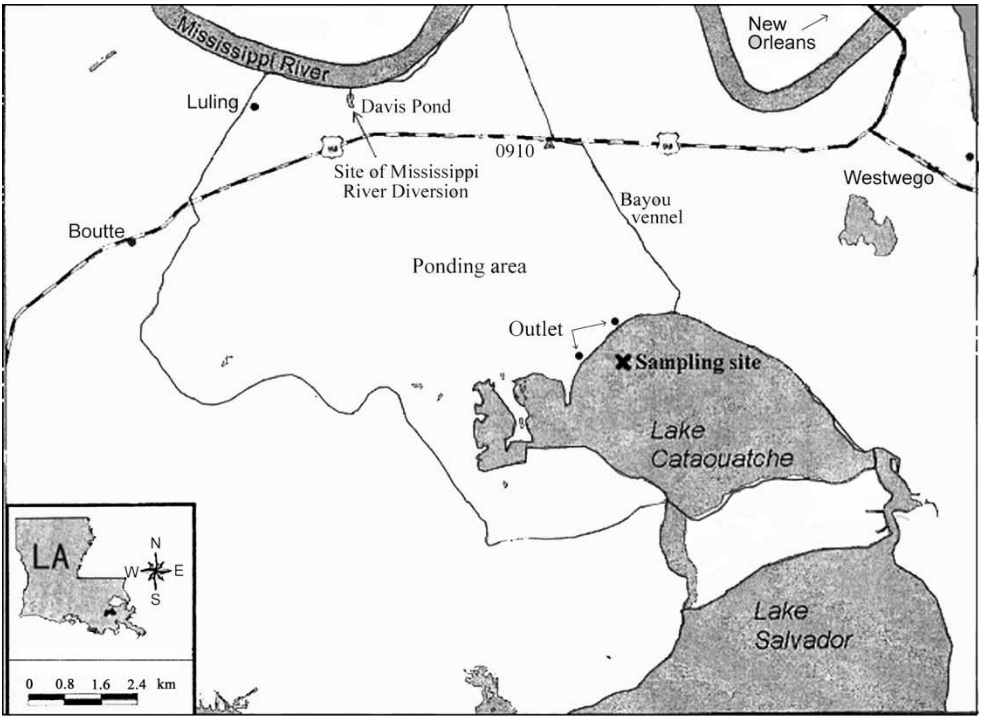

Figure 1. Map showing sampling location in Lake Cataouatche.

before entering Lake Cataouatche. Lake Cataouatche is a shallow (mean depth ~2 m) freshwater lake in the northern portion of the Barataria Basin estuary with a mean tidal range of 0.03 m, representing an area of 5767.2 ha (figure 1). Nutrient sources to the upper Basin are from local runoff and diverted Mississippi River water. Lake Cataouatche has open connections with Lake Salvador to the south, through which discharge water will reach the brackish and salt marshes in the lower reaches of Barataria Basin estuary and finally to the Gulf of Mexico. Sediment was collected on 30 March 2005 in Lake Cataouatche. Three submerged aquatic plants, named *Ceratophyllum demersum* L. (Ceratophyllaceae, Coontail or Hornwort), *Myriophyllum spicatum* L. (Haloragaceae, Eurasian watermilfoil), and *Cabomba caroliniana* Gray. (Nymphaeaceae, Fanwort), were found at the site where the sediment was collected.

Surface sediment (0–15 cm) samples were collected with a Peterson dredge from 10 locations over an approximately 2.0 ha area at the study site. The sediment was brought back to the laboratory and thoroughly mixed and composited. Subsamples of the surface sediment were measured into glass containers (8.0 cm i.d. and 6 cm in depth). Water collected from the Lake was placed above the sediment (10 cm) for establishment of sediment–water columns. Nutrient flux in the sediment/water column was measured following adequate time for equilibration.

2.2 *Sediment characterization*

A subsample of the mixed sediment sample was dried at 105 °C to a constant weight for determining moisture content. The following sediment physical and chemical parameters were measured: pH (1:1 soil:water ratio), extractable P, exchangeable Na, K, Mg, and Ca (NH_4OAc, pH 7.0), organic matter [15], total nitrogen, and carbon (Dumas dry combustion method using an FP-428 nitrogen analyser). Sediment texture was determined using the hydrometer method [16].

2.3 *Nutrient flux measurement*

Nutrient flux rates were determined by measuring changes in water-column concentrations in the sediment–water column over time [10]. Two sets of six parallel sediment–water columns were used to study the nutrient flux. One set was maintained under anaerobic and the other under aerobic water column conditions. Floodwater was replaced with filtered (no. 5 Whatman filter paper) site water to maintain a 10 cm water column (500 ml) in order to allow time for the system to reach equilibrium. The sediment–water column was equilibrated for 1 month prior to initiation of the experiment. Sediment was incubated for 2 months with water columns purged with either O_2-free N_2 (Ultra High Pure compressed) gas for the anaerobic treatment and air (Ultra High Pure compressed) for the aerobic treatment. The columns were covered with an opaque aluminium foil to exclude light and incubated in laboratory at temperature of 21 °C. Water samples were taken at designated intervals over a 34 d period (0, 2 h, 4 h, 8 h, 0.5 d, 1 d, 2 d, 5 d, 9 d, 14 d, 19 d, 24 d, 28 d, and 34 d). The samples were filtered through 0.45 μm syringe filters, and a drop of concentrated H_2SO_4 was added into the water samples to prevent any precipitation. The volume of water removed for each sampling from the cores (20 ml) was replaced with filtered lake water. The lake water used in the study contained 0.083 ± 0.004, 0.031 ± 0.001, 0.091 ± 0.005 mg l^{-1} DRP, NH_4-N, and NO_3-N, respectively.

At the end of the 34 d period, the columns were then switched from either anaerobic to aerobic conditions or from aerobic to anaerobic conditions for a 9 d period. During the period, water samples were also collected and filtered, and water removed was replaced with filtered lake water as mentioned before. The water samples were kept frozen until analysis. The samples were autoanalysed for DRP, NH_4-N, and NO_3-N with Latchet Analysis (QuickChem, LACHAT Instrument, QuickChem® 8000, Automated Ion Analyzer, Zellweger Analytics, Inc.). Fe and total P solution concentrations were determined by inductively coupled plasma (ICP) spectrometry.

Flux calculations were based on the change in water-column concentrations of DRP, NH_4-N, and NO_3-N over time. These gradients were used to estimate the diffusive P and N fluxes. Average flux rates were calculated using the linear portion of the concentration vs. time curves for the DRP and NH_4-N under anaerobic and aerobic water column conditions [10]. Nitrification rates were calculated in the cores with anaerobic and aerobic conditions water columns using the linear portion of the NO_3-N concentration vs. time curves.

2.4 *Denitrification experiment*

The acetylene (C_2H_2) blockage technique [17] was used to measure the denitrification potential of the bottom sediment sample collected from the Lake. The experimental design was a randomized complete block with three levels of NO_3^- additions, and either N_2 gas only or N_2 plus C_2H_2 gas treatment. Ten grams of field moist sediment was placed into 45 ml glass vials (2.5 cm i.d.), with 5 ml of an amending solution containing 2, 20, or 40 μg NO_3-N ml^{-1}, and swirled for mixing. This resulted in an addition of either 1, 10, or 20 μg N g^{-1} wet sediment, respectively. The vials were purged with N_2 gas (UHP, 99.9998%) to remove O_2. Four replicates of each treatment were included. For half of the replicates, 10 ml of the headspace was replaced with acetylene (C_2H_2), resulting in a displacement of approximately 25% of the headspace [18]. The samples were then incubated in the dark at 21 ± 1 °C.

Periodically (0, 2, 5, 8, 22, 28, 44, 70, 96, 132, 168, and 196 h) the concentrations of N_2O in the headspace of the sample vials were measured. Nitrous oxide (N_2O) analysis was performed on a Shimadzu gc (GC-14A) equipped with a 10 m Ci 63Ni electron capture detector (ECD). A 1.8 m × 2 mm ID stainless steel column packed with Poropak Q (80–100 mesh) was also used in this GC. The injector, column (isothermal), and detector temperature were 65, 40, and 340 °C, respectively. The carrier gas (5%) methane in argon flow rate was 30 ml min^{-1}. Working standards consisted of N_2O diluted in N_2 gas (Alltech Assoc Calibration Gas).

The basic calculations to quantify the amount of N_2O evolved or produced by sediments involved multiplying the concentration of N_2O in the headspace of vial during a 24 h period and then divided by the weight (wet or dry) of sediments. For the denitrification rate in a shaken assay as in this experiment, it is necessary to account for N_2O dissolved in solution using Bunsen coefficients that predict the amount of gas dissolved in the liquid phase from the concentration in the gas phase [17]:

$$M = C_{\mathrm{g}} \times (V_{\mathrm{g}} + V_{\mathrm{l}} \times \beta),$$

where M = total amount of N_2O in the water plus gas phase, C_{g} = concentration of N_2O in the gas phase, V_{g} = volume of gas phase, V_{l} = volume of liquid phase, and β = Bunsen coefficient (0.632 at 20 °C).

The denitrification rate was defined as the total N_2O concentration in the water plus gas phases evolved from the 45 ml glass vials (2.5 cm i.d.) and was expressed as mg N m^{-2} d^{-1}.

2.5 *Statistical analysis*

The mean and standard deviation of sediment properties, and nutrient fluxes were calculated using Excel [19]. Additionally, linear regression analysis was used to determine nutrient flux rates over time and the relationship between Fe and P concentration [19]. One-way ANOVAs and multiple comparisons by Fisher's least significant difference (LSD) were used to determine significant differences ($p < 0.05$) in nutrient fluxes between different redox conditions [20].

3. Results and discussion

3.1 *Sediment characterization*

The sediment contained relative high levels of total phosphorus, organic matter, and total nitrogen (table 1). The organic matter content was 9.44%. The sediment had a pH of 6.53. Sediment contained 0.80% total nitrogen and 7.24% carbon. The total phosphorus content was 193 mg kg^{-1}. The sediment texture consisted of 50% sand, 38% silt, and 12% clay.

3.2 *Phosphorus flux*

Both DRP and TP concentrations released from the sediment to the water column under anaerobic conditions were significantly ($p < 0.01$) greater than the fluxes measured under aerobic conditions (figure 2). The DPR and TP concentrations in the water column continued to increase over time in the anaerobic water column treatment while remaining relatively low and stable over time for the aerobic treatment (figure 2). Following 34 days' incubation and when the treatments were switched from anaerobic to aerobic, the DRP concentration decreased, rapidly reaching low levels within a 9 d period (figure 2).

Table 1. Mean sediment characterization data.

Item	Content
Ca (mg kg^{-1})	3553 ± 101
Mg (mg kg^{-1})	1605 ± 46
Na (mg kg^{-1})	576 ± 8.2
K (mg kg^{-1})	387 ± 8.3
P (mg kg^{-1})	193 ± 9.4
Organic matter (%)	9.44 ± 0.31
Total N (%)	0.80 ± 0.01
Total C (%)	7.24 ± 0.23
pH	6.53 ± 0.01
Water (%)	81.5 ± 0.1
Sand (%)	50.3 ± 4.7
Clay (%)	11.6 ± 2.1
Silt (%)	38.1 ± 2.5

Note: Data are shown in average ± SD ($n = 3$).

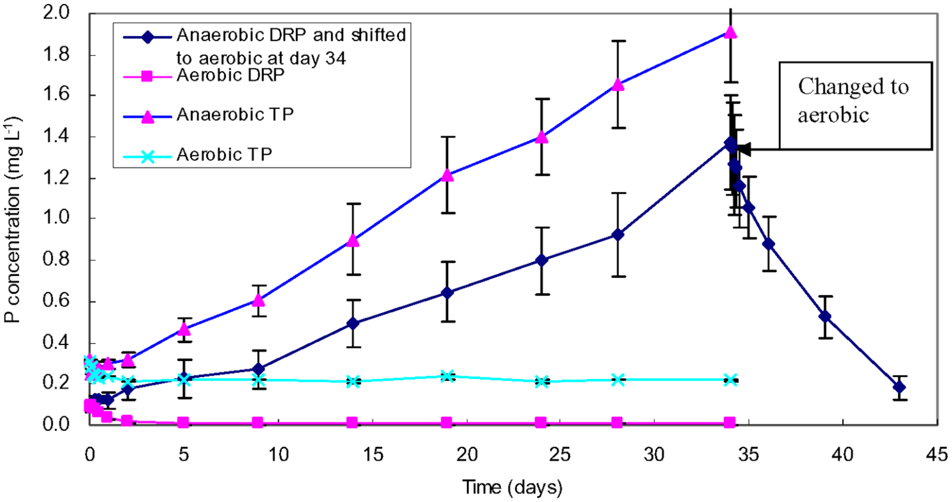

Figure 2. Changes in dissolved reactive phosphorus (DRP) and total phosphorus (TP) concentration for the water column under anaerobic conditions (after day 34 shifted to aerobic) and aerobic conditions from the sediment–water cores of Lake Cataouatche ($n = 6$).

When comparing DRP flux rates from this study (table 2) to similar flux studies conducted elsewhere (table 3), DRP flux rates under either anaerobic or aerobic conditions in the Lake Cataouatche were similar or slightly lower than flux rates reported in the literature [8–10]. Results suggest that it is important to maintain an adequate oxygen levels in Lake Cataouatche surface water, which could decrease should the increase in the external load from nutrients associated with diverted Mississippi River stimulate eutrophic conditions in the Lake. The measured nutrient flux from the sediment to the water column could increase productivity in the Lake. Maintaining the oxygen status of the Lake will result in less P release to the water column, thereby decreasing the internal sediment load.

3.3 *Relationship of Fe and P concentration*

Under anaerobic conditions, both DRP and TP concentration in the water column were highly correlated with Fe concentration (0.804 and 0.880, $p < 0.001$, respectively). Under aerobic

Table 2. DRP and TP fluxes from sediments to water column under different redox conditions.

		Flux (mg m^{-2} d^{-1})				
Redox condition	Nutrient	Initial (<1 d)	Minimum	Maximum	Average	r, of average curve (periods covered)
Anaerobic	DRP	2.18	−0.12	7.54	3.29	0.984^{***} (34 d)
	TP	1.00	−7.88	6.11	4.90	0.998^{***} (34 d)
Aerobic	DRP	−5.46	−5.46	0.004	−0.22	0.718^{**} (34 d)
	TP	−5.59	−5.59	0.51	−0.12	0.508 (34 d)
Anaerobic to aerobic	DRP	−23.98	−23.98	−8.62	−16.37	0.974^{***} (5 d)

Note: **significant at 1%; *** significant at 0.1%, respectively.

Table 3. DRP fluxes of this study and comparing with other studies.

			P flux (mg m^{-2} d^{-1})		
Study area	Sediment type	Redox	Minimum	Maximum	Reference
Lake Okeechobee, Usa	Littoral, Sand, mud	Oxic	−0.37	1.54	[8]
South Bay, Usa	Peat	Oxic	0.05	0.77	[8]
Swan–Canning Estuary, Australia	Coarse mud	Anoxic	2.00	53.0	[21]
		Oxic	0.50	5.40	
Everglades, USA	Peat	Anoxic	1.50	6.50	[9]
St. Johns River, USA	Mud	Anoxic	2.35	11.7	[10]
Lake Cataouatche, USA	Loam	Anoxic	−0.12	7.54	This study
		Oxic	−5.46	0.004	

conditions, there was either no significant relationship or a negative ($p < 0.05$) relationship between phosphorus and Fe concentration (figure 3). The P released to the water column under anaerobic conditions was likely attributed to sediment Fe reduction due to the lower redox conditions at the sediment–water interface under anaerobic conditions [22]. In a lake, P removal under oxic conditions is due to settling of detritus and plankton, in addition to adsorption by iron oxy-hydroxides. In this laboratory study, phosphorus removal under oxic conditions is usually attributed to its binding with ferric iron (Fe^{3+}), forming insoluble

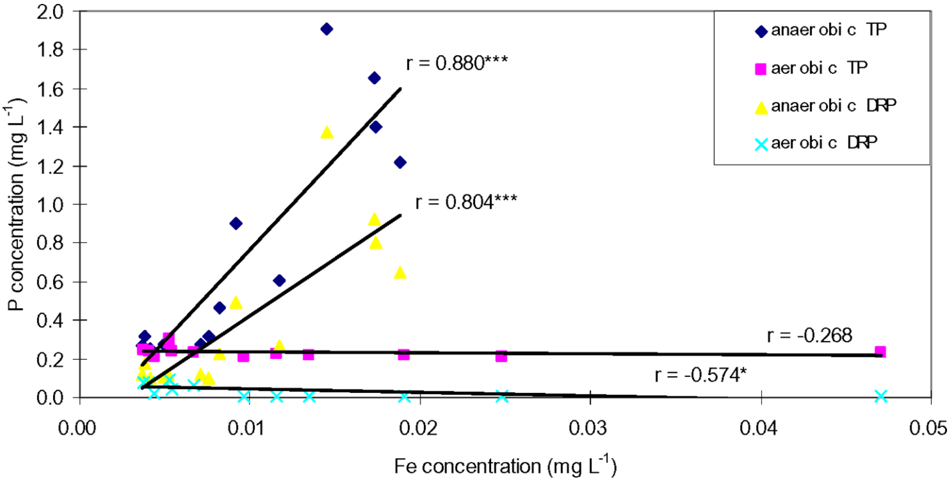

Figure 3. Correlation between Fe and P concentration in water column from sediment maintained under either anaerobic or aerobic conditions.

complexes [23]. The lines in figure 3 for the aerobic parts meant that there are no significant or relative lower significant relationships between TP and Fe, or between DPR and Fe concentration under aerobic conditions. In fact, Fe concentrations are lower than under anaerobic conditions which might be because the sediment was from the coastal freshwater lake with a high sulfide concentrations ($1400 \sim 1800\,\mathrm{mg\,kg^{-1}}$[24]). Many metals have multiple valence states, and the reduced forms that exist under low-oxygen conditions are more readily complexed with organic acids, taken into solid solution by authigenic sulfides, or precipitated as insoluble oxyhydroxides [25]. In coastal sediments or other areas with high concentrations of sulfides, the opposite trend (greater solubility under aerobic conditions) is observed for many metals [26].

3.4 *Ammonium flux*

Ammonium N release from the sediment to the water column under anaerobic condition were significantly ($p < 0.01$) greater than in treatments maintained under aerobic conditions. Under anaerobic conditions, NH_4-N was continuously released from the sediment, increasing water-column concentrations of NH_4-N over time (figure 4). The increase in NH_4-N under the anaerobic treatment was attributed to the lack of nitrification as a result of the absence of oxygen in the water. In contrast, under aerobic conditions, NH_4-N released from the sediment did not build up in the water column due to nitrification [10]. Once the nitrifying microbial population became established, NH_4-N concentrations dropped to less than $0.03\,\mathrm{mg\,L^{-1}}$ and remained low for the remainder of the incubation period (figure 4). Switching redox conditions of the sediment–water column from anaerobic to aerobic condition (after day 34) also resulted in a sharp decrease in NH_4-N (figure 4) which was attributed to nitrification.

When comparing flux rates from this study (table 4) to similar studies conducted elsewhere (table 5), the average NH_4-N flux rates under anaerobic condition in Lake Cataouatche were within the range of flux rates reported for sediment in Morlaix Bay, France (-10.7 to $21.0\,\mathrm{mg\,m^{-2}\,d^{-1}}$) [27] and intertidal sediment in Koningshafen, Germany (-41.5 to $493\,\mathrm{mg\,m^{-2}\,d^{-1}}$) [28], but lower than fluxes for the other sites reported in the literature.

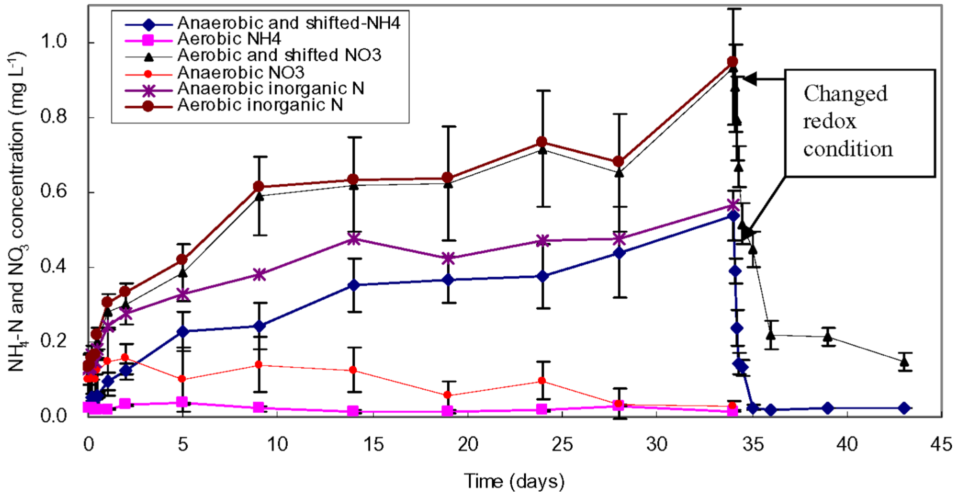

Figure 4. Changes in ammonium nitrate, and inorganic N concentration for the water column under different redox conditions from sediment cores of Lake Cataouatche ($n = 6$).

Table 4. NH_4-N and NO_3-N fluxes from sediments to water column under different redox conditions.

Item	Treatment	Flux ($mg\ m^{-2}\ d^{-1}$) Initial ($<$1 d)	Minimum	Maximum	Average	r, of average curve (periods covered)
NH_4–N	Anaerobic	6.28	0.19	13.36	1.42	0.969*** (34 d)
	Aerobic	−0.51	−0.51	1.07	−0.02	0.355 (34 d)
	Aerobic to anaerobic	−44.41	−44.41	−7.35	−20.53	0.755* (2 d)
NO_3–N	Anaerobic	4.74	−1.83	13.61	−0.24	0.749** (34 d)
	Aerobic	18.01	−1.61	18.01	2.13	0.938*** (34 d)
	Aerobic to anaerobic	−50.51	−84.02	−0.12	−13.29	0.797* (5 d)

Note: *significant at 5%; **significant at 1%; ***significant at 0.1%, respectively.

Table 5. Ranges of sediment–water NH_4-N fluxes reported in previous studies.

Study area	Sediment type	Redox	NH_4-N flux ($mg\ m^{-2}\ d^{-1}$) Minimum	Maximum	Reference
Koningshafen, Germany	Intertidal, sand, mud	Both	−41.5	493	[28]
Long Island Sound, USA	Sand, mud	Oxic	0.003	0.01	[29]
Morlaix Bay, France	Mud	Oxic	−10.7	21.0	[27]
St. Johns River, USA	Mud	Anoxic	2.14	28.5	[10]
Shannon estuary, Ireland	Intertidal, mud	Anoxic	17.3	130	[30]
Lake Cataouatche, USA	Loam	Anoxic	0.19	13.36	This study
		Oxic	−0.51	1.07	

3.5 *Nitrate flux*

The trend for changes in NO_3-N concentration in the water column among the treatments was opposite that for NH_4-N (figure 4). The nitrification rate under aerobic conditions was significantly greater than under anaerobic conditions ($p < 0.01$). Nitrification occurs both at the oxidized sediment–water interface and in the water column under aerobic conditions.

Switching of redox conditions from aerobic to anaerobic resulted in a rapid decrease in NO_3-N concentration (figure 4) due to denitrification. The initial and average flux rates of NO_3-N under aerobic conditions were also higher than under anaerobic conditions (table 4). The NO_3-N concentration under anaerobic conditions initially increased ($<$1 d), then decreased at a lower rate over time.

3.6 *Denitrification rate*

The denitrification study showed a large potential for denitrification of any nitrate entering the sediment column. Differences in the amount and rate of N_2O accumulation were observed for the different NO_3-N additions. The higher the NO_3-N addition rate, the higher the N_2O produced, which reflected a higher denitrification potential. The production of N_2O resulting from C_2H_2 blockage was threefold greater than with treatments without C_2H_2. N_2O production peaked during the first day incubation, and then declined rapidly. C_2H_2 inhibition was adequate for estimating denitrification over the first 28 h, after which the rate of N_2O production decreased. The incubation time was somewhat shorter than reported in a previous study [18], which used a higher level of NO_3-N (40 ppm). Emission of N_2O from the control treatment was very low for all sampling periods. N_2O emission from the sediment–water columns increased in all treatments receiving added nitrate (figures 5 and 6).

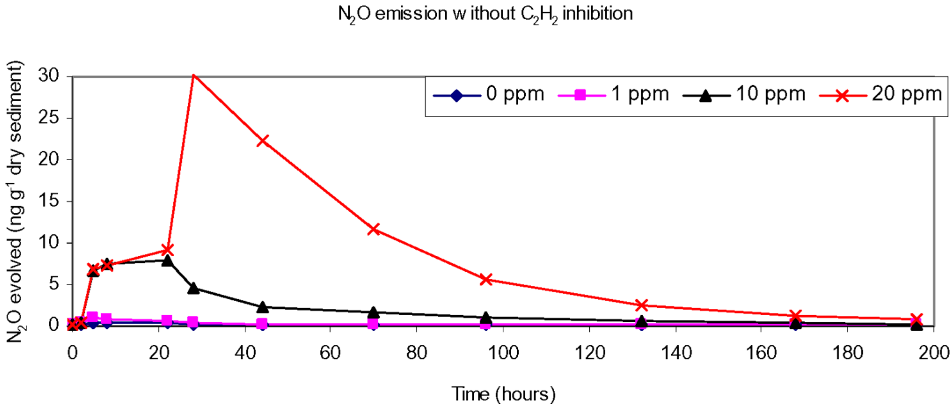

Figure 5. Accumulation of N_2O (without C_2H_2 treatment) in different concentrations added during denitrification in sediment samples from Lake Cataouatche.

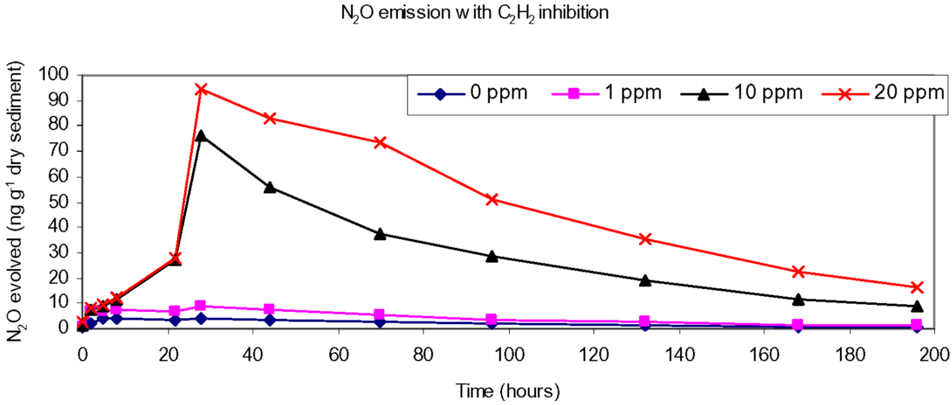

Figure 6. Accumulation of N_2O (with C_2H_2 treatment) in different NO_3-N concentrations added during denitrification in sediment samples from Lake Cataouatche.

Rates of denitrification in the control treatment (no nitrate added) were low, remaining relatively stable through the experiment, averaging 0.41 and 3.31 mg N m^{-2} d^{-1} without and with C_2H_2 inhibition, respectively. The denitrification rate in the control treatment without C_2H_2 blockage was higher than that reported in a previous study of 0.3 mg NO_3-N m^{-2} [31]. Over an 8 d period, significantly higher denitrification rates were measured for treatments receiving added NO_3^- as compared with control. Rates decreased with time after 1 d, indicating denitrification or immobilization of the added nitrate. With C_2H_2 inhibition, the average denitrification rates were 6.69, 46.35, 81.23 mg N m^{-2} d^{-1} for the 1, 10, and 20 μg NO_3-N g^{-1} wet sediment, respectively. When 10 μg NO_3-N g^{-1} soil was added, the potential denitrification rate of 11.78–104.54 mg N m^{-2} d^{-1} was lower than that of 60–920 mg N m^{-2} d^{-1} reported in a previous study [18] but similar to the range (57–87 mg N m^{-2} d^{-1}) reported by DeLaune and Jugsujinda [31] in another Louisiana water-body (table 6).

3.7 *Estimated annual internal sediment loads for Lake Cataouatche*

The estimate of the annual sediment contribution of P and N to the water column of Lake Cataouatche was calculated using the mean aerobic and anaerobic DRP and NH_4-N flux

Table 6. Denitrification rates in gas phase and in the liquid phase without C_2H_2 and with C_2H_2 inhibition from Lake Cataouatche sediment under control, 1, 10, and 20 μg g^{-1} wet sediment NO_3-N solution addition (during 8 d periods).

		NO_3-N concentration (μg g^{-1} wet sediment) added			
Treatment	Incubation time	0	1	10	20
Without C_2H_2 inhibition	Days	mg N m^{-2} d^{-1}			
	1	0.42	0.72	8.17	48.25
	2	0.41	0.48	4.09	35.57
	3	0.41	0.41	3.14	18.54
	4	0.41	0.41	1.71	8.91
	5.5	0.41	0.41	0.97	3.93
	7	0.41	0.41	0.58	1.94
	8	0.41	0.41	0.41	1.22
	Average	0.41	0.47	2.72	16.91
With C_2H_2 inhibition	1	6.92	13.92	104.54	143.26
	2	5.52	10.98	76.73	125.31
	3	3.91	7.88	51.24	111.32
	4	2.85	5.49	38.76	77.04
	5.5	1.89	3.97	25.87	53.18
	7	1.21	2.57	15.56	33.85
	8	0.89	1.99	11.78	24.62
	Average	3.31	6.69	46.35	81.23

rates [10] and the reported 5767 ha surface area of Lake Cataouatche [32]. Under completely anaerobic conditions, 69.3 Mg of DRP would be released per year; meanwhile, under completely aerobic conditions, 4.6 Mg of DRP would be assimilated from the water column into sediment. Under aerobic sediment–water column conditions, Fe^{3+} was available to bind P; however, under anaerobic conditions, this reaction no longer occurred, thus allowing significantly more P to be released from the sediment into the water column. Under anaerobic conditions, 29.9 Mg of NH_4-N would be released from sediment to water column per year (table 7). Since the lake is highly eutrophic, anoxic or anaerobic conditions would likely exist in the summer months when there are low amounts of oxygen in the surface water for much of the lake.

Based on the TMDL for dissolved oxygen and nutrients in Lake Cataouatche, the TMDL were as follows: total for NH_4-N 409 kg d^{-1}, for NO_3-N plus NO_2-N 124 kg d^{-1}, and for P 62 kg d^{-1} [32], respectively. The estimated internal sediment nutrient load shown in this study for anaerobic conditions in surface water would represent 15.4% and 305% of the inorganic N and P external loading, respectively.

During high discharge or pulsing events, a significant amount of nitrate in the diverted Mississippi river water passes through the ponded wetland into Lake Cataouatche. The amount of nitrate-N in water entering the lake at typical discharge rate of 100 m^3 s^{-1} is of the order of 660 mg N m^3 s^{-1}, an amount equivalent to 5.7 Mg of NO_3-N per day [5, 6], so the internal load of nitrogen estimated from this study made up only approximately 1.44% of the total NO_3-N

Table 7. External and internal loads of nutrients and TMDLs for Lake Cataouatche (Mg yr^{-1}).

Item	Organic N	NH_4-N	$NO_2 + NO_3$-N	Phosphorus	Reference
Point source wasteload allocation	7.46	14.51	36.20	18.10	[32]
Non-point source load allocation	390.03	104.94	0.01	0.06	[32]
TMDL	496.87	149.81	45.27	22.70	[32]
Anaerobic condition	–	29.89	–	69.26	This study
Aerobic condition	–	–	–	−4.63	This study

external loading at maximum discharge events. However, when there is a low discharge or when no diverted water enters the Lake, the internal sediment load would represent a significantly greater percentage of the total load. The release of nutrient, however, is governed by the oxygen status of the water column. If added nutrient associated with diverted river water stimulates algae blooms and the Lake became euthrophic creating low oxygen conditions, the nutrient flux from the sediment would be impacted. As shown by this study, if oxygen became depleted at the sediment–water interface, a greater amount of ammonium N and phosphorus would be released from the sediment to the water column.

4. Summary and conclusions

Results have shown that P and N fluxes are governed by the redox status of the water column. The DRP and NH_4-N fluxes from the sediment to the overlying water column determined under anaerobic conditions were very high and significantly greater than flux rate under aerobic conditions. When the water column was switched from anaerobic to aerobic conditions, the DRP and NH_4-N concentrations in overlying water decreased rapidly over a short period of time (1–9 d), indicating the strong relationship between nutrient fluxes and oxygen availability in the water column. Both DRP and TP had a very strong correlation with Fe concentration in overlying water under anaerobic conditions and different from that under aerobic conditions. Using the C_2H_2 inhibition technique, the average denitrification rates measured were approximately threefold greater than without C_2H_2 inhibition treatments. Maximum rates were measured at day 1 for all the treatments. Rates then decreased with time, indicating denitrification or immobilization of the added nitrate. The mean annual internal DRP and NH_4-N load from the sediment to the overlying water can represent a significant portion of the total P and N load to the lake. Results clearly show that when determining TMDL or developing water-quality models for the Lake associated with determining the impact of nutrient-enriched Mississippi River water on the water quality of the Barataria Basin estuary, internal non-point sediment nutrients source and the oxygen status of water column must also be taken into consideration. In addition, managing the external nutrient loads or point sources associated with river diversion inputs is critical to maintaining water quality in the Lake. These are likely a synergistic relation between the two sources. For example, nutrient in diverted water could increase algae growth, which in turn would impact water quality lowering dissolved oxygen levels and, as shown by this study, would increase the benthic nutrient flux to the water column, which in turn could further impact water quality. Additional flux studies may be needed in the future after the diversion has been in operation for an extended period of time, and the system has reached equilibration. However, any in-depth analysis of Lake Cataouatche TMDL must consider both nutrient inputs from river diversion and sediment nutrient flux to the water column, which is regulated by the oxygen status of the water column.

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References

[1] D.M. Anderson, P.M. Glibert, J.M. Burkholder. Harmful algal blooms and eutrophication: nutrient sources, composition, and consequences. *Estuaries*, **25**, 704–726 (2002).

[2] M.M. Fisher, E.R. Peele, J.W. Ammerman, L.W. Harding. Nutrient limitation of phytoplankton in Chesapeake Bay. *Mar. Ecol. Prog. Ser.*, **82**, 51–63 (1992).

[3] P.M. Glibert. Primary productivity and pelagic nitrogen cycling. In *Nitrogen Cycling in Coastal Marine Environments*, T.H. Blackburn, J. Sorensen (Eds), Wiley, Chichester, UK, pp. 102–109 (1988).

[4] K.R. Reddy, Y. Wang, W.F. Debusk, M.M. Fisher, S. Newman. Forms of soil phosphorus in selected hydrologic units of the Florida Everglades. *Soil Sci. Soc. Am. J.*, **62**, 1134–1147 (1998).

[5] C. Johnson. Capacity of freshwater marsh to process nutrient in diverted Mississippi River water. Master thesis, Louisiana State University. Baton Rouge, LA (2004).

[6] R.D. DeLaune, A. Jugsujinda, J.L. West, C.B. Johnson, M. Kongchum. A screening of the capacity of Louisiana freshwater wetlands to process nitrate in diverted Mississippi River water. *Ecol. Eng.*, **25**, 315–321 (2005).

[7] N. Atilla, N.N. Rabalais, Q.F. Dorth, W.A. Mendenhall, A.E. Thessen, R.E. Turner. Phytoplankton communities in the Barataria estuary (Louisiana reflect gradients of nutrients and salinity, paper presented at the Conference of Abstract in Estuarine Research Federation, Norfolk, VA, 16–20 October (2005).

[8] P.A. Moore, K.R. Reddy, M.M. Fisher. Phosphorus flux between sediment and overlying water in Lake Okeechobee, Florida: Spatial and temporal variations. *J. Environ. Qual.*, **27**, 1428–1439 (1998).

[9] M.M. Fisher, K.R. Reddy. Temporal variability in dissolved inorganic nitrogen fluxes at the sediment–water interface and related annual budget on a continental shelf (NW Mediterranean). *Oceanol. Acta*, **24**, 85–97 (2001).

[10] M.L. Malecki, J.R. White, K.R. Reddy. Nitrogen and phosphorus flux rates from sediment in the lower St. Johns River estuary. *J. Environ. Qual.*, **33**,1545–1555 (2004).

[11] R. Knowles. *Denitrification. Microb. Rev*., **46**, 43–70 (1982).

[12] B.T. Neilson, S.C. Chapra. Integration of water quality monitoring and modeling for TMDL development. *Water Resour. Impact*., **5**, 9–11 (2003).

[13] L.S. Bazel. TMDLs: law and reality. *Water Environ. Technol.*, **10**,88 (1998).

[14] J. Addison. 'Davis Pond freshwater structure', US Army Corps of Engineers. Available online at: http://www.mvn.usace.army.mil/pao/dpond/davispond.htm.internet (1999) (accessed 10 August 2006).

[15] M.L. Jackson. *Soil Chemical Analysis*, Prentice-Hall, Englewood Cliffs, NJ (1958).

[16] W.H. Patrick, Jr. Modification of method of particle size analysis. *Soil Sci. Soc. Am. Proc*., **22**, 366–367 (1958).

[17] J.M. Tiedje. Denitrification. In *Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties*, 2nd ed., A.L.Pages, R.H. Miller, D.R. Keeney (Eds), pp. 1011–1026, American Society of Agronomy, Soil Science Society of America, Madison, WI (1982).

[18] P.M.Gale, I. Devai, K.R. Reddy, D.A. Graetz. Denitrification potential of soils from constructed and natural wetlands. *Ecol. Eng*., **2**, 119–130 (1993).

[19] Microsoft. *Microsoft Excel for Windows*. Microsoft, Redmond, WA (2000).

[20] Minitab. *Minitab Statistical Software*. Version 13.32. Minitab, State College, PA (2000).

[21] P.S. Lavery, C.E. Oldhan, M. Ghisalberti. The use of Fick's first law for predicting porewater nutrient fluxes under diffusive conditions. *Hydrol. Proc.*, **15**, 2435–2451 (2001).

[22] C.H. Mortimer. Chemical exchanges between sediments and water in the Great Lakes—Speculations on probable regulatory mechanisms. *Limnol. Oceanogr*., **16**, 387–404 (1971).

[23] J.B. Upchurch, J.K. Edzwald, C.R. O'Melia. Phosphates in Sediments of Pamlico Estuary. *Environ. Sci. Technol.*, **8**, 56–58.

[24] S.Y. Miao, R.D. DeLaune, A. Jugsujinda. Influence of sediment redox conditions on release/solubility of metals and nutrients in a Louisiana Mississippi River deltaic plain freshwater lake. *Sci. Total Environ.*, **371**, 334–343 (2006).

[25] T.J. Algeo, J.B. Maynard. Trace-element behavior and redox facies in core shales of Upper Pennsylvanian Kansas-type cyclothems. *Chem. Geol.*, **206**, 289–318 (2004).

[26] J.H. Pardu, W.H. Patrick Jr. Changes in metal speciation following alternation of sediment redox status. In *Metal contaminated aquatic sediments*. A.E. Herbert (ed.) pp. 169–185 (1995).

[27] Y. Lerat, P. Lasserre, P. Le Corre. Seasonal changes in pore water concentrations of nutrients and their diffusive fluxes at the sediment–water surface. *J. Exp. Mar. Biol. Ecol*., **135,** 135–160 (1990).

[28] R.M. Asmus, M.H. Jenson, K.M. Jenson, E. Kristensen, H. Asmus, A. Willie. The role of water movement and spatial scaling for measurement of dissolved inorganic nitrogen fluxes in intertidal sediments. *Estuar. Coast. Shelf Sci*., **46**, 221–232 (1998).

[29] R.C. Aller, L.K. Benninger. Spatial and temporal patterns of dissolved ammonium, Manganese, and silica fluxes from the bottom sediments of Long Island Sound, U.S.A. *J. Mar. Res.*, **39**, 295–314 (1981).

[30] M.T. Brennan, J.G. Wilson. Nutrient exchange between the sediment and the overlying water on the intertidal mudflats of the Shannon estuary. *Arch. Hydrobiol. Suppl.*, **75**, 423–450 (1993).

[31] R.D. DeLaune, A. Jugsujinda. Denitrification potential in a Louisiana wetland receiving diverted Mississippi River water. *Chem. Ecol*., **19**, 411–418 (2003).

[32] FTN Associates Ltd. Lake Cataouatche TMDLs for dissolved oxygen and nutrients. Available at http://www.epa.gov/region6/water/ecopro/latmdl/2005tmdls/lakecataoutchedoandnutrients.pdf (2005) (accessed 10 August, 2006).