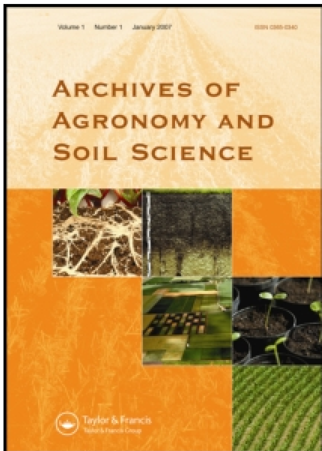

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Influence of salinity level on sediment denitrification in a Louisiana estuary receiving diverted Mississippi River water

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The Mississippi River water containing elevated nitrate is being diverted into Louisiana coastal estuaries to abate wetland deterioration attributed to lack of sediment and nutrients, rapid subsidence and accompanying salt water intrusion. In this study effect of salinity change on sediment denitrification at a Mississippi River freshwater diversion site (Davis Pond, Louisiana) was determined. Results show that the denitrification potential of the sediment was highest under fresh water condition (salinity close to 0‰). Addition of sea water immediately inhibited the denitrification activity of the sediment. Further analysis, by separate treatment of NaCl and K_2SO_4 addition, revealed that inhibition of the denitrification of the sediment by sea water was mainly caused by NaCl content in sea water. Denitrification activity of the sediment was not significantly affected by the sulfate content in sea water. Salinity increase seems a primary reason for the sediment denitrification rate decrease. A significant inverse relationship of denitrification rate and salinity was obtained [denitrification rate (mg N kg^{-1} day^{-1}) $= -0.20 \times$ salinity(‰) $+ 10.41$, $R^2 = 0.91$]. Under highest sea water condition (salinity = 36‰), denitrification rate of the sediment would be 30.8% of its original activity (salinity = 0‰).

Keywords: denitrification; salinity; nitrous oxide; wetland; sea level rise; Mississippi River; coast

Introduction

The Mississippi River accounts for approximately 90% of the freshwater input into the northern Gulf of Mexico (Mitsch et al. 2001). Extensive agricultural development and fertilizer use over the last century in the Mississippi River basin has substantially increased nutrient loadings into the rivers and northern Gulf of Mexico (Turner and Rabalais 1994). Large influx of nutrients from the Mississippi River discharge stimulates coastal eutrophication and development of bottom-water hypoxia (water $O_2 < 2$ mg l^{-1}) on the continental shelf of the northern Gulf of Mexico (Turner and Rabalais 1994; Rabalais et al. 1996). The Mississippi River levee built for flood control has prevented major course changes, allowing nutrients found in river water to enter the Gulf of Mexico without any buffering effect or processing by coastal wetlands. In addition, levee construction also prevents Louisiana coastal wetlands from receiving sufficient fluvial sediment to counteract rapid regional subsidence and seal level rise (Swanson and Thurlow 1973), providing nutrients for wetland vegetation growth and freshwater to prevent saltwater

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intrusion (Nyman et al. 1990; Turner 1997). Ultimately, this has caused Louisiana to experience a significant wetland loss.

Nitrogen, largely in form of nitrate (NO_3^-), is a major nutrient species in the Mississippi River. Wetlands are efficient in removing nitrate from waters through sediment denitrification and vegetation uptake (Kadlec and Alvord 1989; Johnson 1991; Knight et al. 1993). Denitrification is the most important mechanism of N removal by which fixed N in the biosphere, returns to the atmosphere (Firestone et al. 1980). Wetlands have two environmental characteristics that are favorable for denitrification to occur: (1) Sediments are generally anoxic (redox potential, Eh < 300 mV), a favorable condition for denitrification (Yu and Patrick 2003, 2004; Yu et al. 2007), and (2) vegetation growth provides a continuous source of carbon as an electron donor for denitrification process. It is estimated that several million hectares of wetland and riparian ecosystems are needed to sufficiently remove nitrogen for alleviating the hypoxic development in the Gulf of Mexico (Mitsch et al. 2001).

As a coastal restoration effort to counteract the extensive wetland loss due to lack of sediment and nutrients, rapid subsidence and accompanying salt water intrusion, Louisiana State developed a plan of diverting part of the Mississippi River water into coastal basins and estuaries to mimic annual flood events. The Caernarvon freshwater diversion facility (N 29°49.37′, W 89°55.30′) was constructed in 1991, and the Davis Pond facility (N 29°51.35′, W 90°14.40′) became operational in 2002. Field measurement of denitrification using labeled ^{15}N nitrate was conducted in a freshwater marsh at the Davis Pond facility (Yu et al. 2006), which diverts water into the Barataria Basin Estuary. This was the first on site denitrification measurement in wetland near this diversion site. Results of the study concluded that nitrate removal efficiency was largely determined by the water discharge rate. Low water discharge rate will have higher nitrate removal efficiency, but it raises a question if such low water discharge rate can sufficiently prevent sea water intrusion. In this region of Louisiana, relative sea level has been rising approximately 1 cm year^{-1} due to regional subsidence and eustatic global sea level rise (Penland and Ramsey 1990). Determination of denitrification potential of the sediment and evaluation of its potential impact by sea water intrusion is greatly needed for the long-term management of the Mississippi River Diversion Facility, which was the objective of this study.

Materials and methods

Sampling location and sediment characteristics

Surface sediment (0–15 cm) was collected in September 2006 from Lake Cataouatche (N 29°51.35′, W90°14.40′), a shallow lake (about 2 m depth) in the northern portion of Barataria Basin (Figure 1). The Davis Pond Mississippi River Freshwater Diversion Facility site (Louisiana, USA) discharges freshwater and nutrients into the estuaries through the Lake Cataouatche. The maximum diversion capacity of the facility is up to 302 m^3 s^{-1} (Addison 1999). A ponded freshwater marsh is bounded by constructed levees through which diverted water enters the Lake Cataouatche, then Lake Salvador and ultimately to lower portion of Barataria Bay estuary before entering into the Gulf of Mexico. Major sediment characteristics (especially redox active Fe, Mn and S content) were analyzed, and the results are shown in Table 1. Additional information on the study site and sediment characteristics can be found in a recent publication (Miao et al. 2006).

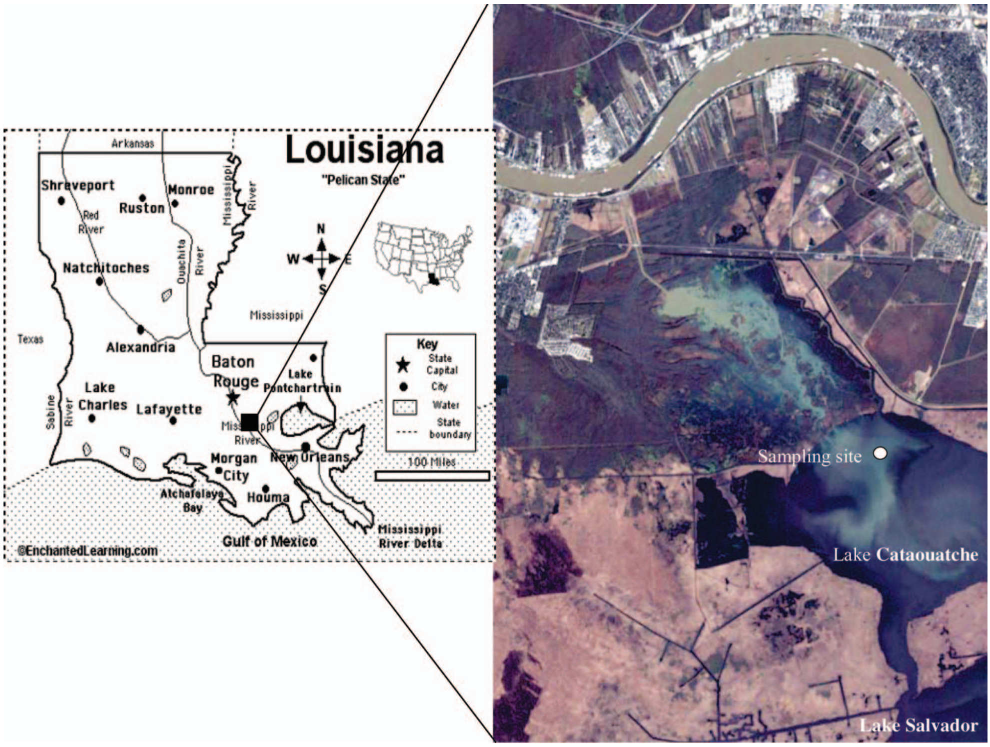

Figure 1. Sampling location and satellite image of the Davis Pond Freshwater Diversion Facility, Louisiana, USA.

Table 1. Major characteristics of the sediment used for this study.

	OM	Total Fe	Total Mn		Particle size (%)		
pH	%			Total S (mg kg^{-1})	Sand	Silt	Clay
5.8	5.67	3.9	0.07	17.8	27.8	54.4	17.8

OM: Organic matter. According to particle size analysis, the sediment texture is silt loam (United States Department of Agriculture).

Laboratory procedures

Denitrification potential of sediment was measured using the acetylene (C_2H_2) inhibition technique (Tiedje 1982) in sediment-water slurries. Sediment-water slurry was established by weighting 30 g sediment (wet weight, water content 80.6%) into a 155 ml glass vial with 60 ml deionized (DI) water or solution. Four treatments were applied for this study: (1) Control (60 ml DI water); (2) sodium chloride (NaCl) with three levels: I (20 ml NaCl solution + 40 ml DI water), II (40 ml NaCl solution + 20 ml D.I. water), and III (60 ml NaCl solution); (3) potassium sulfate (K_2SO_4) with three levels: I (20 ml K_2SO_4 solution + 40 ml DI water), II (40 ml K_2SO_4 solution + 20 ml DI water), and III (60 ml K_2SO_4 solution); (4) sea water with three levels: I (20 ml sea water solution + 40 ml

DI water), II (40 ml sea water solution + 20 ml DI water), and III (60 ml sea water solution).

The treatments with NaCl and K_2SO_4 were designed to identify the contribution from different components of sea water on sediment denitrification activity. Artificial sea water was made by dissolving Instant Ocean sea salt (Aquarium Systems, Mentor, Ohio, USA) into DI water (salinity 36.9‰). The sea salt is commercially available and free of nitrate and phosphate. The NaCl and K_2SO_4 solutions were made with salinity 30.7‰ (Cl^- 18.5‰) and 4.6‰ (SO_4^{2-} 2.5‰), respectively, close to the average ocean concentration of Cl^- (19.3‰) and SO_4^{2-} (2.7‰).

In total, 30 sediment slurries were established with three replicates for each treatment and each treatment level. To provide N source for denitrification, 1 ml KNO_3 solution (42.8 mM) was added to each vial with final concentration of 103.0 μg N g^{-1} dry sediment in the slurry. The vials were flushed with pure nitrogen for a minute to remove the air in headspace of the vials, and then immediately sealed with a rubber stopper. The headspace volume was estimated to be 75 ml, assuming particle density of the sediment was 2.54 g cm^{-3}. Pure C_2H_2 was injected replacing 10 ml of the headspace volume of each vial to inhibit reduction of N_2O to N_2 in denitrification process. The vials were incubated at room temperature (20°C) for two days. Gas samples were collected from headspace of the vials three times during this period of incubation for analysis of N_2O concentration. After taking the last gas samples, the vials were uncovered. Redox potential (Eh) and pH were measured immediately for each sediment slurry.

Sample analysis

Total organic matter (O.M.) was measured colorimetrically after oxidising with $K_2Cr_2O_7$ and concentrated sulfuric acid. Total Fe, Mn and S concentrations in the sediment were analyzed by inductively coupled plasma (ICP) after digestion. Particle-size distribution of the sediment was obtained by a hydrometer method (Patrick 1958). Redox potential in each sediment slurry was measured by two replicate platinum (Pt) working electrodes with a calomel reference electrode. A portable pH meter was used to measure the pH in each sediment slurry at end of the incubation. Nitrous oxide concentration was analyzed using a Tremetrics 9001 gas chromatograph (GC) with an electron capture detector (ECD), and calibrated with a certified N_2O standard (Scott Specialty Gases, Inc. Plumsteadville, PA, USA). Detail information on the GC specifications and operation conditions can be found in a recent publication (Yu et al. 2006). All gas analyses were subject to conventional quality control with a standard spike in every three samples. A sub-sample of the mixed sediment was dried at 105°C to a constant weight for determining moisture content. All data were presented by dry weight of the sediment.

Data analysis

Nitrous oxide production rate was determined by linear regression of the three measurements of gas concentration increase with time. Redox potential was reported to the standard H_2 electrode by adding 247 mV (the correction factor for calomel reference electrode at 20°C) to the recorded instrument reading. Statistical analysis was conducted using SAS software version 9.1 (SAS Institute Inc. Cary, NC, USA). It represents statistically significant different when the difference of the means among different treatments exceeds the least significant difference (LSD). The significance level was chosen at $\alpha = 0.05$.

Results and discussion

Nitrous oxide measurement

Biological denitrification is considered as the only source of N_2O production in this anaerobic incubation experiment. Denitrification rate of the sediment can be determined by N_2O production rate during the incubation with inhibition of N_2O reduction to N_2 by C_2H_2.

Nitrous oxide concentrations in the vials generally showed a linear increase with time during the 2-day incubation. Nitrous oxide production rates were calculated according to linear regression of N_2O concentration increase with time, and the results are shown in Figure 2. The control treatment showed the highest denitrification rate in the sediment. Addition of sea water into the sediment slurries caused denitrification rate decrease. Among the three levels of sea water addition, denitrification rates were in an order of level I > level II > level III. The difference in denitrification rate of the sediment was not statistically significant ($P > 0.05$) between the control and sea water level I treatment. In sea water addition treatments, probably mainly due to limited number of replication, only denitrification rates between level I and level III showed a significant difference (LSD = 2.76). Denitrification rate of the sediment in NaCl addition treatments showed the same tendency as in sea water addition treatments (Figure 2). Denitrification rates decreased as NaCl concentration increased in the sediment slurries, and there was a significant difference between level I and level III (LSD = 2.48). Addition of K_2SO_4 showed no significant impact on denitrification rate of the sediment compared to the control treatment ($p > 0.5$). No significant variations ($p > 0.05$) in denitrification rate were found among the three levels of K_2SO_4 addition treatments (LSD = 4.45).

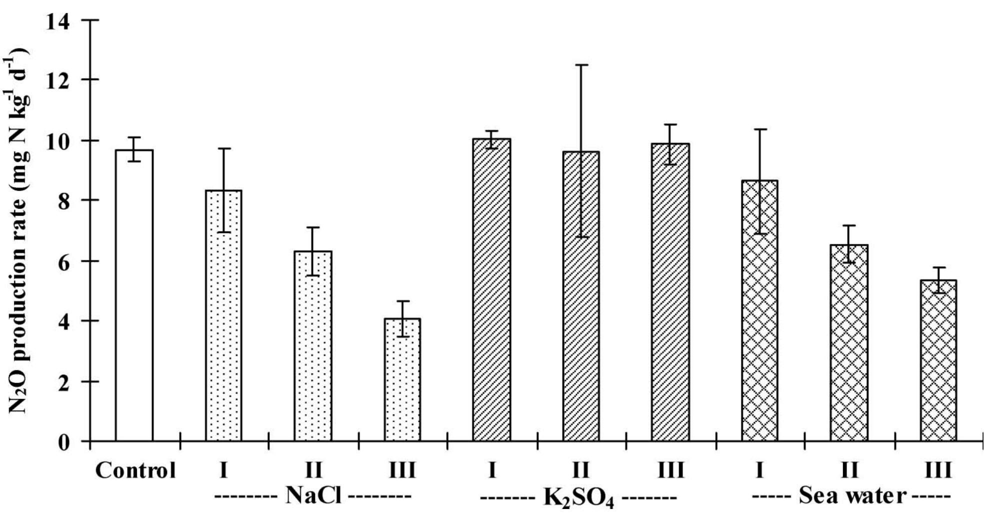

Figure 2. Nitrous oxide production rate in sediment slurries using acetylene inhibition technique. Note: Level I: 20 ml solution + 40 ml DI water; Level II: 40 ml solution + 20 ml DI water; Level III: 60 ml solution.

Measurement of Eh and pH at end of the incubation

Redox potential quantitatively indicates soil/sediment reducing intensity. Denitrification initiates under moderately reducing conditions (Eh < 400 mV at pH $= 7$), and denitrification rate increases with Eh decreases (Firestone et al. 1980; Masscheleyn et al. 1993). Without inhibition of N_2O reduction to N_2 by C_2H_2, maximum N_2O production is normally found approximately at Eh $= 250$ mV (Yu and Patrick 2003, 2004). When Eh < 250 mV, reducing condition is intense enough favoring a complete reduction of nitrate to nitrogen gas (N_2). In this study, Eh in the sediment slurries was between 255 and 283 mV for all the treatments (Table 2), a typical Eh range for denitrification to take place. Simple linear regression showed no significant relation between denitrification rate and observed Eh in the sediment slurries ($R^2 = 0.03$, $p > 0.05$, $n = 10$).

Microorganisms involved in denitrification favor near neutral pH conditions. The pH in K_2SO_4 treatments was significantly higher than other treatments (LSD $= 0.30$). However, there was no significant difference in pH among the three levels of each treatment (Table 2). Higher pH in K_2SO_4 treatments might partially contribute to the higher denitrification rates than the sea water and NaCl treatments (Table 2 and Figure 2). Simple linear regression showed no significant relation between denitrification rate and observed pH in the sediment slurries ($R^2 = 0.14$, $p > 0.05$, $n = 10$).

Potential impact of sea water intrusion on denitrification

Sea water is of a complex nature, and different components may have different effect on microbial reactions. Louisiana's Barataria Basin estuary where this study was conducted commonly experiences salt water intrusion. Denitrification potential of the sediment in the estuary is an important factor to consider for management of nitrogen entering the estuary from both within the Basin and nitrogen found in the diverted Mississippi River water. The results showed that addition of sea water immediately inhibited the denitrification activity of the sediment. Further analysis by separate treatment of NaCl and K_2SO_4 addition revealed that inhibition of the sediment denitrification activity by sea water was mainly caused by its NaCl content (Figure 2).

Table 2. Measurement of pH, Eh, and calculated salinity in sediment slurries at end of the experiment.

Treatment	Level	Eh (mV)	pH	Salinity (‰)
Control		263 ± 6	5.8 ± 0.1	0.0
NaCl	I	283 ± 8	5.9 ± 0.1	8.0
	II	275 ± 4	6.1 ± 0.1	16.1
	III	267 ± 2	6.2 ± 0.1	24.1
K_2SO_4	I	256 ± 1	6.7 ± 0.1	1.2
	II	256 ± 1	6.6 ± 0.0	2.4
	III	267 ± 2	6.6 ± 0.0	3.6
Sea water	I	267 ± 6	6.1 ± 0.1	9.7
	II	270 ± 4	6.1 ± 0.0	19.3
	III	255 ± 3	6.1 ± 0.0	29.0

Level I: 20 ml solution + 40 ml DI water; Level II: 40 ml solution + 20 ml DI water; Level III: 60 ml solution. Data represent mean ± SD ($n = 3$). Water salinity in the Lake Cataouatche where the sediment was sampled for this study was less than 1‰. The salinity data for NaCl, K_2SO_4, and sea water treatment were calculated according to solution and DI water ratio, taking the original sediment salinity as 0‰.

Salinities in the sediment slurries for each treatment were calculated and summarized in Table 2. Denitrification rate tended to decrease with salinity increase in the sediment slurries when comparing the results of Figure 2 and Table 2. Liner regression showed a significant linkage between denitrification rate and salinity [denitrification rate (mg N kg^{-1} day^{-1}) $= -0.20 \times$ salinity (‰) $+ 10.41$, $R^2 = 0.91$, $p < 0.001$, $n = 10$]. This simple linear regression suggests that 91% of the denitrification rate decrease in different treatments can be explained by the salinity increase (Figure 3). According to this linear regression, denitrification rate of the sediment under complete sea water condition (salinity = 36‰) would be 30.8% of its original activity (salinity = 0‰). Half of the original denitrification rate would be achieved if salinity increased to 26.0‰. Salinity may provide a general physiological stress on biological reactions, such as microbial nitrification and denitrification (Rysgaard et al. 1999), and even higher plant growth (Ahmad and Jhon 2005; Sharma et al. 2005). However, halo-tolerant denitrifier communities may evolve under high salinity conditions (Magalhaes et al. 2005). Thus, long-term effect of salinity on denitrification rate of the sediment deserves careful evaluation.

Multiple regression analysis using all three variables (salinity, pH, and Eh) showed negligible improvement in denitrification rate prediction ($R^2 = 0.92$, $n = 10$). Denitrification activity of the sediment was not significantly affected by the sulfate content in the sea water and K_2SO_4 addition treatments. The amount of sulfate in sea water (and the K_2SO_4 addition treatments) only contributed to a small fraction of the salinity (Table 2). Potential impacts of sulfate on microbial reactions (i.e. denitrification) mainly comes from S^{2-} ion following sulfate reduction, which requires a strictly reducing conditions, e.g. Eh < -100 mV (Connell and Patrick 1968). In this study, because of the presence of nitrate in all treatments, redox status in the sediment slurries remained at moderately reducing conditions with Eh > 250 mV, which was too high to initiate sulfate reduction.

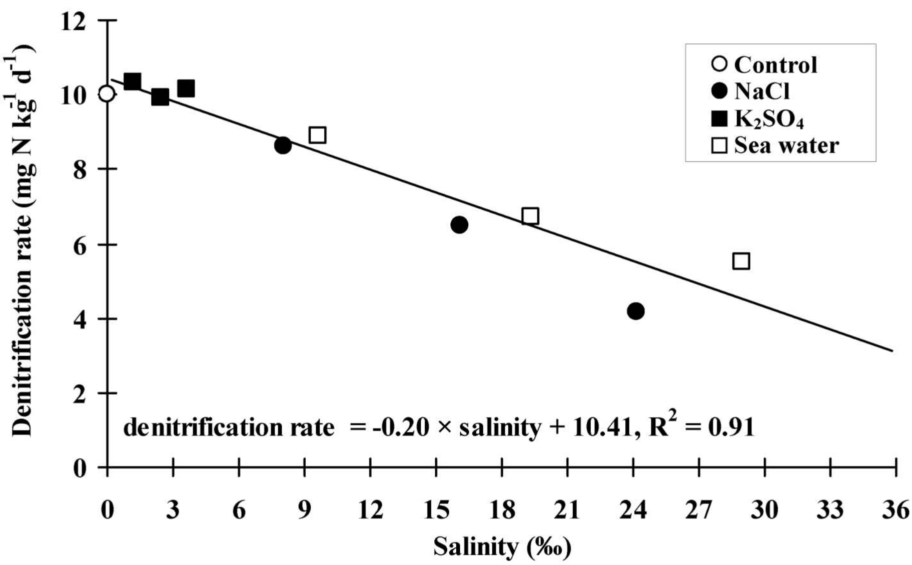

Figure 3. Relationship between denitrification rate and salinity in sediment slurries. Means of denitrification rate of each treatment and level were used.

Conclusions

This laboratory study shows that the sediment denitrification activity was strongest under fresh water condition, but could be significantly inhibited by salinity increase. Over 90% of the variations in denitrification rate of the sediment could be explained by the salinity difference. Under highest sea water condition (salinity = 36‰), denitrification rate of the sediment would be 30.8% of its original activity (salinity = 0‰). Diverting the Mississippi River water into northern Barataria Basin will restrict salt water intrusion into the study area. Discharge rate of the facility is a critical management practice to consider in both preventing sea water intrusion and nitrate removal efficiency in the diverted Mississippi River water (Yu et al. 2006). In addition, lowering salinity by receiving the diverted Mississippi River water should increase nitrate removal capacity in the Barataria basin estuaries. Results should also be applicable to lowering of salinity associated with Mississippi River discharge to offshore area currently experiencing hypoxia condition due to nutrient loadings.

Acknowledgements

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