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Ronald D. DeLaune
Louisiana State University

Charles W. Lindau
Louisiana State University

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NITRIFICATION AND NITRATE REDUCTION IN BOTTOM SEDIMENT OF LOUISIANA'S BARATARIAN BASIN

Many of the coastal drainage basins along the Louisiana Gulf Coast are rapidly becoming eutrophic as a result of increased nutrient loading. Nutrients from domestic wastes are becoming an increasing problem because of inadequate sewage treatment and increasing population growth. Agricultural runoff also results in large quantities of nutrients entering these basins via drainage canals.

An understanding of internal nutrient cycling is important in developing loading rates for Louisiana's coastal drainage basins. Emphasis must be placed on understanding the various nutrient cycles and related processes occurring within the water column and at the sediment-water interfaces of coastal bays, lakes, and channels. These processes have important effects on productivity and water quality in these systems.

Along the Louisiana Gulf Coast, nutrient exchange between sediment and overlying water, is an ecologically significant process occurring in shallow bays and lakes. Nitrification-denitrification reactions are important components of the N cycle in these shallow bays and lakes, contributing to the regulation of the trophic state of these waters. These processes are important in removing excess nitrogen from such systems. An important biological reaction occurring at the sediment-water interface is nitrification (Jenkins and Kemp 1984); a high rate of nitrification being essential for any appreciable denitrification. By producing NO_3^- , nitrification serves as an important substrate source for denitrifi-

cation (Jenkins and Kemp 1984). These two processes are contemporaneous and cannot take place in the same redox environment. Nitrification, an obligate aerobic reaction, can occur only in the water column and in the surface oxidized layer in bottom sediment (Patrick and Reddy 1976), whereas denitrification, which is an anaerobic reaction, occurs in anoxic sediments (Kemp *et al.* 1982).

Ammonium-nitrogen being discharged into coastal water bodies can also be nitrified, assimilated or absorbed by bottom sediment. Organic N can be mineralized to ammonium-nitrogen which can be nitrified if the ammonium diffuses into the surface oxidized sediment or water column. The nitrate formed can subsequently be denitrified if it diffuses down into the anaerobic sediment layer.

In this study we determine the rate of nitrification and nitrate reduction using an isotope dilution technique in sediment-water columns representing two lakes in Louisiana Barataria Basin.

MATERIALS AND METHODS

Sediment and water samples were collected from Lac Des Allemands and Little Lake, a freshwater and brackish lake in Barataria Basin (Fig. 1). Sediment samples were taken using a Peterson dredge. Surface water samples were collected in 20-L plastic bottles.

In the laboratory, the sediment was mixed and placed into large plexiglass columns (150-cm height by 14-cm i.d.). A sediment water-column consisting of a 30-cm layer of sediment with 100 cm of water was established in the column and pre-incubated at 25°C for 30 d in order to allow for equilibration and establishment of a thin surface-oxidized layer at the sediment-water interface.

After equilibration, ^{15}N -labeled NO_3^-

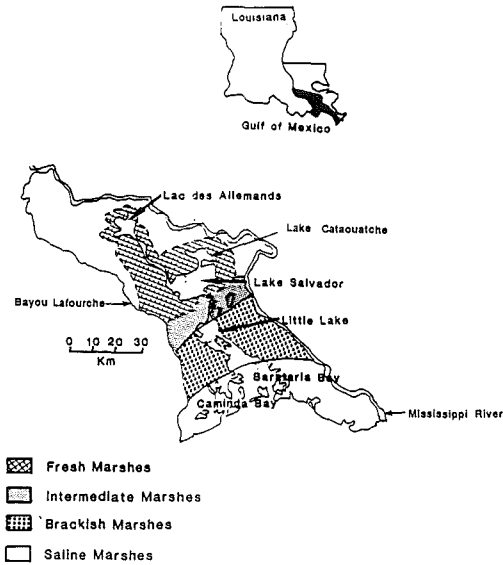


Figure 1. Location of Lac Des Allemands and Little Lake within Louisiana Barataria Basin.

was added to the microcosm to produce an initial concentration in the water column of approximately 2.00 mg N m^{-3} . The NO_3^- spike was approximately 3 times greater than ambient concentrations. The systems were incubated in the dark at 20°C for 142 d. At the times indicated, samples (200 cm^3) of the overlying water were filtered through $0.45\mu\text{m}$ filters, and the filtrates stored at 0°C prior to isotopic analysis. Concentrations of the dissolved inorganic $\text{NO}_2^- + \text{NO}_3^-$ were estimated by steam distillation procedures (Keeney and Nelson 1982). Ammonium was first extracted by an alkaline distillation into boric acid and the combined qualities of ^{15}N -labeled $\text{NO}_2^- + \text{NO}_3^-$ was separated by reduction to NH_4^+ with Devardas alloy distilled into boric acid. Nitrogen content in the distillates were determined by titration procedures. The distillates were acidified, concentrated to 1 ml, and stored in closed vials prior to isotope ratio analysis (Hauck 1982).

The rate of production (nitrification) or reduction of NO_3^- was determined from the changes in concentration with

time and the isotopic ratio of the $\text{NO}_2^- + \text{NO}_3^-$ in the overlying water. If only nitrification and NO_3^- reduction are responsible for changes in the NO_3^- pool in the sediment-water columns, their rates can be calculated using the equations outlined by Koike and Hattori (1978), DeLaune and Smith (1987). Briefly the equations are:

$$N_2 - N_1 = Z - Y \quad [1]$$

$$N_2 X_2 - N_1 X_1 = Z X_a - Y X \quad [2]$$

where $Y = \text{NO}_3^-$ reduction; $Z =$ production of NO_3^- by nitrification; N and $X =$ the concentrations of NO_3^- and its ^{15}N content; respectively, and X and X_a are the average isotopic content of the NO_3^- and NH_4^+ between observations t_1 and t_2 , respectively. Natural ^{15}N abundance ($0.3663 \text{ atom } \% \text{ }^{15}\text{N}$) was assigned for X_a , because the amount of natural NH_4^+ present in the microcosm was large compared with that of ^{15}N - NH_4^+ produced by dissimilatory NO_3^- reduction to NH_4^+ .

RESULTS AND DISCUSSION

Concentration of inorganic ^{15}N labeled and nonlabeled $\text{NO}_2^- + \text{NO}_3^-$ in the water of the sediment-water columns decreased with incubation time in columns representing the two study sites (Figs. 2 and 3). The decrease in ^{15}N labeled and unlabeled (NO_2^- and NO_3^-)-N was linear. Correlation coefficients of decrease ranged between 0.92 to 0.98 and were highly significant ($P < 0.01$). The rates of unlabeled $\text{NO}_2^- + \text{NO}_3^-$ decreases were 7.3 and $9.7 \text{ mg N m}^{-3} \text{ d}^{-1}$, whereas ^{15}N labeled $\text{NO}_2^- + \text{NO}_3^-$ decreased at the rate of 1.7 and $2.5 \text{ mg }^{15}\text{N m}^{-3} \text{ d}^{-1}$ for columns 1 and 2 for the Lac Des Allemands sediment-water columns.

For Little Lake sediment water columns the rate of unlabeled $\text{NO}_2^- + \text{NO}_3^-$ decreases were 11.5 and $10.8 \text{ mg N m}^{-3} \text{ d}^{-1}$ whereas ^{15}N labeled $\text{NO}_2^- + \text{NO}_3^-$ decreased 3.9 and $4.0 \text{ mg }^{15}\text{N m}^{-3} \text{ d}^{-1}$ for

columns 1 and 2.

The slower rate of decrease in ^{15}N -labeled NO_3^- in the water columns from the two lakes show nitrate is being formed in the sediment-water columns.

Nitrification and nitrate reduction rates for sediment-water columns representing the two lakes are shown in Table 1. The mean rate of nitrification and nitrate reduction was $39.4 \mu\text{mol N m}^{-2} \text{h}^{-1}$ and $65.0 \mu\text{mol N m}^{-2} \text{h}^{-1}$ for the Lac Des Allemands sediment-water columns. The mean rate of nitrification and nitrate reduction was $45.7 \mu\text{mol N m}^{-2} \text{h}^{-1}$ and $74.2 \mu\text{mol N m}^{-2} \text{h}^{-1}$ for the Little Lake sediment-water columns.

Appreciable NO_3^- was being produced in the sediment-water columns representing each lake. The production rate was less than the NO_3^- reduction rate. Results presented show that nitrification were 60% and 62% of denitrification, respectively for Lac Des Allemand and Little Lake. The process limiting nitrification and denitrification in such a system is NH_4^+ diffusion from bottom sediment to the sediment-water interface where nitrification can occur (Patrick and Reddy 1976).

If the columns were incubated for

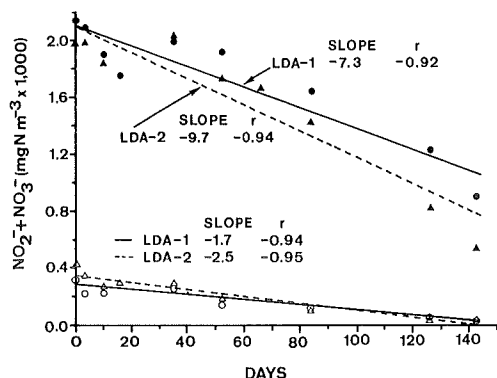


Figure 2. Nitrite + NO_3^- reduction in sediment-water microcosms Lac Des Allemands (LDA). Change with time in $(\text{NO}_2^- + \text{NO}_3^-)\text{-N}$ (●, ▲) and ^{15}N content $(\text{NO}_2^- + \text{NO}_3^-)\text{-N}$ [○, △] in two replicate microcosms LDA-1 and LDA-2, respectively.

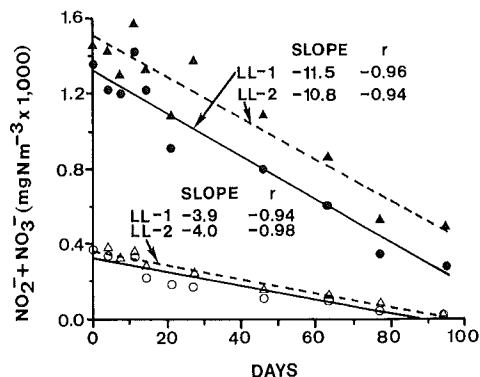


Figure 3. Nitrite + NO_3^- reduction in sediment-water microcosms Little Lake (LL). Change with time in $(\text{NO}_2^- + \text{NO}_3^-)\text{-N}$ (●, ▲) and ^{15}N content $(\text{NO}_2^- + \text{NO}_3^-)\text{-N}$ [○, △] in two replicate microcosms LL-1 and LL-2, respectively.

longer periods of time nitrification would likely equal denitrification. Such would be the case for water bodies not receiving input of inorganic nitrogen forms into the water column since the only NO_3^- which could be denitrified is that produced within the system.

The measured rates of NO_3^- reduction and NO_3^- production for the Lac Des Allemands and Little Lake sediment-water columns were similar to published values reported for other estuarine systems where denitrification was found to be a major sink for fixed nitrogen com-

Table 1. Rate of nitrification and nitrate reduction in Lac Des Allemands and Little Lake sediment-water columns.

	$\text{NO}_2^- + \text{NO}_3^-$ Production	$\text{NO}_2^- + \text{NO}_3^-$ Reduction
	$\mu\text{mol N m}^{-2} \text{h}^{-1}$	
(0-142d)		
*LDA-1	39.8	64.0
LDA-2	38.9	66.1
Average	39.4	65.0
(0-95d)		
**LL-1	42.2	71.5
LL-2	49.2	76.9
Average	45.7	74.2

*LDA - Lac Des Allemands.

**LL - Little Lake.

pounds. Denitrification rates were measured directly (N_2 production) by Seitzinger et al. (1984) from incubated subtidal coastal bay sediments and fluxes ranged from 10-115 $\mu\text{mol N m}^{-2} \text{h}^{-1}$. In later work, Seitzinger and Nixon (1985) showed that denitrification rates increased as inorganic nitrogen loading increased in bay sediment microcosms. Denitrification rates in the control microcosms were about 300 $\mu\text{mol N m}^{-2} \text{h}^{-1}$ and increased to 880 in microcosms receiving 65 times the control nutrient input (Seitzinger and Nixon 1985). Jenkins and Kemp (1984) report a coupling between nitrification and denitrification and rates of 77-240 $\mu\text{mol N m}^{-2} \text{h}^{-1}$. DeLaune and Smith (1987) reported nitrification rates averaging 90 $\mu\text{mol N m}^{-2} \text{h}^{-1}$ and nitrate reduction of 134 $\mu\text{mol N m}^{-2} \text{h}^{-1}$ in sediment-water columns of a coastal Louisiana drainage basin measured by the nitrate-15 dilution technique. Reddy and Reddy (1987) showed that in NO_3^- -enriched systems, floodwater nitrate removal rates ranged from about 140 to 210 $\mu\text{mol N m}^{-2} \text{h}^{-1}$ by monitoring changed in the added $^{15}\text{NO}_3^-$.

Nutrient and trophic state of water bodies in upper Barataria Basin are governed by agricultural and domestic nitrogen inputs, but as shown by this study nitrification-denitrification processes occurring in the sediment water-columns can act to remove appreciable quantities of nitrogen entering the Basin. These reactions serve an important role in preventing further water quality deterioration of the region. Nitrate reduction apparently can remove nitrogen at rates on the order of 70 $\mu\text{mol N m}^{-2} \text{h}^{-1}$. There is also significant benthic regeneration of inorganic nitrogen in Barataria Basin bottom sediment. Appreciable inorganic NH_4^+ nitrogen is formed from mineralization of organic nitrogen in the sediment. Nitrification

and subsequent denitrification of ammonium nitrogen diffusing from sediment into oxidized surface layers of sediment or into the water column in these water bodies is an important mechanism for removal of benthic regenerated nitrogen.

ACKNOWLEDGMENTS

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Ronald D. DeLaune and Charles W. Lindau, Center for Wetland Resources/Nuclear Science Center, Louisiana State University, Baton Rouge, LA 70803.