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GASEOUS NITROGEN LOSSES FROM GULF COAST MARSHES

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ABSTRACT: The low evolution of N_2O and NH_3 from unamended brackish and salt marsh soils suggests a conservative internal nitrogen cycle exists in Louisiana's coastal marshes. The gaseous evolution of NH_3 and N_2O increased following the addition of $(\text{NH}_4)_2\text{SO}_4$. The maximum rates of NH_3 volatilization from the salt and brackish marshes were 5.7 and 3.2 $\text{mg N m}^{-2} \text{ d}^{-1}$, respectively. The corresponding total NH_3 volatilization was 34 and 15 mg N m^{-2} for the salt and brackish marshes. Volatilization from unamended cores amounted to 6.0 and 0.9 $\text{mg NH}_3\text{-N m}^{-2}$ from the salt and brackish marshes. Approximately 29 and 15 $\text{mg N}_2\text{O-N m}^{-2}$ was evolved from the brackish and salt marsh sediment amended with 1243 and 1469 $\text{mg NH}_4^+\text{-N m}^{-2}$. The N_2O evolution from the unamended cores was 0.4 and 2.2 mg N m^{-2} from the brackish and salt sediment.

Gaseous nitrogen emission to the atmosphere from coastal marshes is one aspect of nitrogen cycling which has not been quantified. Ammonia volatilization from marshes is generally assumed to be negligible, although data to support this hypothesis is inconclusive. Gaseous N emissions have been estimated by the indirect nitrogen balance approach (Buresh *et al.*, 1981). The N deficit is attributed to NH_3 volatilization and denitrification. However the reliability of the values obtained by difference are at best no better than the reliability of the other measurements, and all errors are accumulated in the difference value. Ammonia volatilization from the Massachusetts salt marsh was estimated from data obtained from North Carolina ponds (Valiela and Teal, 1979). The conclusion was that volatilization accounted for less than 0.1 percent of the total nitrogen loss from these marshes. In contrast, appreciable NH_3 losses has been reported for a freshwater pond fertilized with $\text{NH}_4^+\text{-N}$ (Bouldin *et al.*, 1974). The contrasting data indicates the need to quantify NH_3 volatilization. Ammonium is the predominant ionic species found in anoxic marsh and marine sediments and NH_3 volatilization can occur when alkaline

conditions are encountered. In addition, the volatilization of NH_3 is strongly affected by environmental conditions such as temperature, windspeed, and evaporation rate (Denmead *et al.*, 1974, 1976).

Likewise there is little quantitative information available on the magnitude of the N_2O emission from coastal wetlands. Nitrous oxide originates principally from the biological reduction of NO_3^- (denitrification) in the sub-surface anaerobic layers. Indirect procedures have been used to estimate the rate of denitrification and the methods used include the disappearance of $^{15}\text{NO}_3^-$ or the production of $^{15}\text{N}_2$ (Koike and Hattori, 1978). Interest in N_2O emission has been stimulated by the recent concern over depletion of stratospheric ozone by N_2O in the upper atmosphere originating from the earth's surface (Cast, 1976). The marine environment plays a major role in the global cycling of N_2O with sources identified in surface ocean waters and sinks in low oxygen environments. Similarly NH_3 has negative effects in atmospheric chemistry.

The aim of research reported in this paper is to quantify two (N_2O , NH_3) ecologically and environmentally important gaseous N emissions from a

Louisiana Gulf Coast brackish and salt water marsh. The total area of coastal marshes in Louisiana represents 41% of the total coastal marshes in the United States (Turner and Gosselink, 1975).

METHODS AND MATERIALS

The sediments used in this study were collected from typical brackish (*Spartina patens*) and salt (*Spartina alterniflora*) marshes found in Barataria Basin. This hydrological unit has been described in detail elsewhere (Day *et al.*, 1973; DeLaune *et al.*, 1981). Vertically intact core sections of the marsh, cross-sectional area 177 cm², were taken between the plant clumps and the top 15 cm section transferred to the plexiglass incubation apparatus. The cores were flooded and returned to the laboratory.

The incubation apparatus consisted of a plexiglass cylinder (177 cm²) 30 cm long attached to a base plate. The lower 15 cm of the cylinder was covered with aluminum foil. A washer shaped flange was attached to the upper end of the cylinder to facilitate the attachment of a flat cover. Provision was made in the cover for NH₃ free air to flush the system. The incoming air was scrubbed free of NH₃ by bubbling through 100 cm³ of 5 M H₂SO₄, followed by two 100 cm³ containers of distilled water. Ammonia in the exit air was trapped in two 30 cm³ volumes of 0.05 M H₂SO₄ connected in series. Provisions were made in the inlet and exit air stream for gas samples to be withdrawn for N₂O analysis (Smith *et al.*, 1981). The air inflow rate was controlled at 50 cm³ min⁻¹ with a needle valve.

The cores were incubated (at 26°C) for 14 days under 16 hours of light. Following the equilibration period, the floodwater was removed and 500 cm³ of water (depth = 3 cm) was added. The water was obtained from the open water body adjacent to the marsh at the time the

cores were collected and stored at 2°C until used. Ammonium in the form of (NH₄)₂SO₄ was added at the rates of 0, 1, and 22 or 26 mg N/column.

Floodwater pH was measured with a combination glass electrode. Ammonium-N content of the trapping solution and the floodwater was determined colorimetrically following nesslerization. Initially the NH₃ traps were changed daily but the time interval was lengthened as the experiment proceeded. At all times the NH₃ in the second trap was not detectable. Ammonium content of the floodwater was determined on a 2 cm³ subsample withdrawn through the air inlet. A larger sample (10 cm³) was withdrawn for pH determination and returned when the measurement was completed.

Nitrous oxide was determined on a Varian 3700 gas chromatograph equipped with a ⁶³Ni electron capture detector operated at 380°C. Air samples were injected through a 0.5 cm³ sampling loop onto a Chromosorb 106 column (80/100 mesh, 250 cm L by 0.2 cm, I.D.) maintained at 40°C. The carrier gas was 5% CH₄, balance argon and the flow rate was maintained at 30 cm³ min⁻¹ (Smith *et al.*, 1981).

The emission of nitrous oxide was determined by monitoring the incoming and exit air stream. Air samples (10 cm³) were collected in all glass syringes sealed with Pharmaseal teflon 3-way stopcocks (Dowdell *et al.*, 1972). Nitrous oxide evolution was determined by integration of the differences between the incoming and exit N₂O temporal curves. The average N₂O concentration in the incoming air was 308±4 nM throughout all the experiments performed. All results reported are the average of the results obtained from two randomly selected cores.

RESULTS AND DISCUSSION

Ammonium added at the rate of 0, 57

and 1461 mg N m² to cores taken from the brackish marsh produced NH₄⁺ concentrations < 1, 3 and 85 mg N l⁻¹ in the surface water two hours after addition. These rates produces levels of 2, 10 and 115 mg N l⁻¹ in the surface water of the cores taken from the salt marsh. Ammonia volatilization losses from the sediment-water columns was dependent on the NH₄⁺ concentration in the surface water (Figure 1 and 2). Losses were greater in the cores receiving the higher addition of (NH₄)₂SO₄ with 15 mg NH₃-N m⁻² and 34 mg NH₃-N m⁻² being volatilized respectively from the brackish and salt marsh cores (Table 1). In contrast, cores that were not fertilized lost NH₃ at the rate of 0.9 mg N m⁻² and 6.0 mg N m⁻² from the salt and brackish marshes, respectively.

The NH₄⁺ concentration in the surface water of the columns receiving the highest NH₄⁺ addition decreased rapidly (Figures 3 and 4). The rate of decline in

Figure 1. Ammonia volatilization from brackish marsh soil cores.

Figure 2. Ammonia volatilization from salt marsh soil cores.

ammonical nitrogen was faster than that observed from flooded rice (Vlek and Craswell, 1979). Maxima rates of decrease were 15 and 20 mg N l⁻¹ d⁻¹, equivalent to 409 and 565 mg N m⁻² d⁻¹ from the salt and brackish marshes res-

Table 1. Ammonia and nitrous oxide evolution from *Spartina alterniflora* and a *Spartina patens* marshes following fertilization with (NH₄)₂SO₄.

NH ₄ ⁺ -N Application mg m ⁻²	NH ₃ -N Volatilized mg m ⁻²	N ₂ O-N Evolved mg m ⁻²
<i>S. alterniflora</i> — salt marsh		
0	6.0	2.2
57	12	2.2
1469	34	15
<i>S. patens</i> — brackish marsh		
0	0.9	0.4
57	2.8	0.6
1243	15	29

+Cores 177 cm² cross section area, incubated for 10 days.

Figure 3. Ammonium-N concentration in floodwater overlying brackish marsh soil cores.

pectively. The corresponding rate of NH_3 volatilization, from the salt and brackish marshes were 5.7 and 3.2 $\text{mg N m}^{-2} \text{d}^{-1}$ respectively, which was less than the observed NH_4^+ -N disappearance rate from the water column. Volatilization rates were also observed to decline as the NH_4^+ concentration of the floodwater declined. Major processes removing NH_4^+ -N from the water column other than volatilization would be microbial assimilation, nitrification, and adsorption into the sediment (Patrick and Reddy, 1976; Reddy and Graetz, 1981; Rosenfield, 1979).

Rates of NH_3 volatilization are directly related to NH_4^+ concentration and pH. In this study the pH of the surface water remained relatively close to values observed at field stations. The pH of the water increased from 7.2 to 7.6 during the incubation period for the unamended salt

marsh cores. However, the pH increase was lower in cores amended with $(\text{NH}_4)_2\text{SO}_4$, which was possibly due to acidity produced by NH_3 volatilization or nitrification. The pH of the brackish marsh cores also remained relatively constant ranging from 7.0-7.4 throughout the study. The pH observed is less than the pH reported for other systems where significant NH_3 volatilization has been shown to take place (Vlek and Stumpe, 1978; Vlek and Craswell, 1979).

The rate of NH_3 volatilization is severely restricted by limiting the movement of air above the water (Vlek and Stumpe, 1978) which often occurs in laboratory studies. Ammonia volatilization may potentially be underestimated in this study because the air exchange rate was less than the rate required to be representative of an open system (Vlek and Stumpe, 1978; Kissel *et al.*, 1977).

Figure 4. Ammonium -N concentration in floodwater overlying salt marsh soil cores.

However, volatilization from $(\text{NH}_4)_2\text{SO}_4$ could be anticipated to be low due to the lack of alkalinity produced when dissolved (Vlek and Craswell, 1979; Mikkelsen *et al.*, 1978) and the acidity produced when the NH_4^+ is nitrified.

Nitrous emissions from both marsh sediment cores were small. The N_2O concentrations were less than $0.4 \mu\text{g l}^{-1}$ from the cores receiving 0 and 57 mg m^{-2} added NH_4^+ -N (Figures 5 and 6). However the sediment cores receiving the highest of NH_4^+ -N evolved considerably more N_2O . There was an initial lag of several days before maximum N_2O concentrations were measured. These maximum rates continued for approximately 6-8 days before decreasing, which corresponded with the decrease in NH_4^+ concentration in the overlying water. Approximately 29 $\text{mg N}_2\text{O-N m}^{-2}$ and 15 $\text{mg N}_2\text{O-N m}^{-2}$ was evolved from

Figure 5. Nitrous oxide emission from brackish marsh soil cores receiving added NH_4^+ -N.

Figure 6. Nitrous oxide emission from salt marsh soil cores receiving added NH_4^+ -N.

the brackish and salt marsh sediment, respectively. The treatments which were not amended with NH_4^+ evolved 0.4 and 2.2 $\text{mg N}_2\text{O-N m}^{-2}$ from the brackish and salt marsh sediment respectively, over the 10 day sampling period (Table 1).

Ammonium is the predominant form of inorganic N present in flooded marsh sediment. Ammonium is stable under anaerobic conditions but in the presence of both aerobic and anaerobic zones NH_4^+ -N can be lost as gaseous N via nitrification and subsequently denitrification (Koike and Hottori, 1978; Patrick and Reddy, 1976). Nitrification can occur in the oxidized surface soil layer, the oxidized rhizosphere of plants and in the water column of sediment-water systems, whereas denitrification occurs within the anoxic zone of the sediment. Although the potential for denitrification can be high in anaerobic marsh soils, the level of in situ denitrification is dependent

upon the availability of NO_3^- . The reported nitrate levels ($<1.0 \pm 0.8 \mu\text{g N g}^{-1}$ dry soil) were low in the marshes from which the cores were taken (Ho, 1971). The low N_2O emission observed in this study also indicates that there is relatively small amounts of $\text{N}_2\text{-N}$ being lost from the nitrification-denitrification process. Seitzinger *et al.* (1981) reported a ratio of 250:1 for N_2 to N_2O being evolved from coastal sediment. Others have reported ratios of 200:1 (Terry and Tate, 1980). Using the ratio reported by Seitzinger *et al.* (1981), we estimate relatively small amounts of N_2 ($<7.3 \text{ g N}_2\text{-N m}^{-2}$) being evolved from the brackish and salt marsh sediment. The N_2 estimation is based on the assumption that N_2O is principally evolved from biological denitrification and no allowance is made from the N_2O evolution during nitrification (Bremner and Blackmer, 1978; Freney *et al.*, 1979). Thus the N_2 evolution may be slightly overestimated.

Loss of nitrogen via NH_3 volatilization was also low in these marshes. This can be explained by the low values of NH_4^+ (Ho, 1971) and the near neutral pH (7.0-7.6) of the flood water covering these marshes. It has been shown that the presence of plants also reduces nitrogen losses from flooded systems (Buresh *et al.*, 1981). Actively growing wetland plants compete with nitrifiers and denitrifiers for available soil N and assimilate most of the NH_4^+ in the N-limited marsh sediment before it can be lost by NH_3 volatilization and nitrification-denitrification reactions.

CONCLUSION

The results shown in this study indicate that under natural conditions the gaseous N losses from salt and brackish marshes of the Louisiana Gulf Coast are minimal. These findings support other work conducted in these marshes.

Louisiana's coastal zone is rapidly subsiding (Swanson and Thurlow, 1973) however the marshes are rapidly accreting in order to remain intertidal. Accretion in these marshes has been quantified using ^{137}Cs dating (DeLaune and Patrick, 1978). Approximately 0.8 cm of organic matter and nutrient-enriched mineral sediment accumulates yearly thus the resulting peat accumulation is a vast sink for organic nitrogen (DeLaune *et al.*, 1981). Major nitrogen inputs of these marshes are sedimentation and nitrogen fixation (DeLaune *et al.*, 1981; Casselman *et al.*, 1981). These reported relationships between nitrogen inputs and the nitrogen sinks suggests a relative conservative internal cycling of nitrogen must exist which supports the low gaseous-N emission found in this study. Appreciable losses of gaseous N would only be expected when the marshes receive an extraneous source of nitrogen such as sewage and/or wastewater.

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