Distribution of ammonium-N in the water-soil interface of a surface-flow constructed wetland for swine wastewater treatment

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Abstract Most livestock wastewaters treated in constructed wetlands are typically rich in ammonium N. The objective of this study was to evaluate the soil-water ammonium distribution and the diffusive flux through the soil-water interface. Wetland system 1 (WS1) was planted to rush and bulrushes, and wetland system 2 (WS2) was planted to bur-reed and cattails. Nitrogen was applied at a rate of 2.5 g m^{-2} d^{-1}. Interstitial soil water was sampled at 9, 24, 50, and 70 m from the inlet. In both wetlands, we found that NH_4^+ diffusion gradient and N losses were highest in the wetland system with lowest water depth. From other studies, we knew that shallower depths may have promoted a more effective interfacing of nitrifying and denitrifying environments. In turn, this N reduction in the water column may be the reason for steady NH_4^+-N upward diffusion fluxes. The assumed mechanism for N removal has been nitrification and denitrification but ammonia volatilization could also have occurred. Although diffusion may explain a significant portion of the material transport between the soil-water interface, the large differences in concentrations between outlet and inlet need further explanation.

Keywords Ammonia; diffusion; denitrification; hogs; surface-flow wetland; wastewater

Introduction

Confined swine production generates large amounts of wastewater that are typically treated and stored in anaerobic lagoons. Lagoon effluents are rich in ammonia/ammonium (NH_4^+/NH_3) nitrogen and customarily land applied for terminal treatment. However, over application of nitrogen can occur in operations when land is limiting. An alternative to land application of liquid manure is the use of constructed wetlands. It is believed that constructed wetlands can be part of a farm-wide waste management plan that could minimize the adverse environmental impact to water resources (Cronk, 1996; Szögi *et al.*, 2000). Hunt *et al.* (1999) report consistent removals in surface-flow wetlands of at least 80% of the added N with loading rates ranging from 0.3 to 2.5 g NH_4^+-N $m^{-2}d^{-1}$ (3 to 25 kg ha^{-1} d^{-1}). These authors also found that at the lower loading rates, plant and soil accumulation constituted a significant portion (~ 30%) of the total amount applied, but at the higher loading rates, microbial transformations were likely the more dominant treatment factors. Although these results were very encouraging, denitrification enzyme assays indicated that nitrate was the limiting factor. Moreover, the denitification values were not exceptionally high, which indicated that ammonia volatilization might have been significant. The objective of this study was to evaluate the soil-water ammonium nitrogen distribution along a constructed wetland system used for swine wastewater treatment and estimate ammonium flux across the soil-water interface that may be contributing to N gaseous losses.

Materials and methods

The study site was located in Duplin Co., NC. The study was performed in two wetland systems that consisted of parallel sets of two 4-m × 33.5-m cells connected in series with a

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total length, from inlet to outlet, of 82 m (Hunt *et al.*, 1999). Wetland system 1 (WS1) was planted to a mixture of rush (*Juncus effusus*) and bulrushes (*Scirpus americanus, Scirpus cyperinus* and *Scirpus validus*). Wetland system 2 (WS2) was planted to a mixture of burreed (*Sparganium americanum*) and cattails (*Typha latifolia and T. angustifolia*). Both wetlands were used to treat the effluent from an anaerobic lagoon that stored the wastewater generated by a confined hog production unit. Wastewater was applied during 1998 at a mean loading rate of 2.5 g NH_4^+-N m^{-2} d^{-1} (2.5 kg NH_4^+-N ha^{-1} d^{-1}) to both wetland systems. The hydraulic retention time was about 12 days. The loading rate was obtained by diluting anaerobic lagoon wastewater with fresh water. Wastewater characteristics were monitored on a weekly basis during the plant growth season (33 weeks), April–October 1998 (Table 1).

Eight Plexiglas soil pore water equilibrators were used to sample ammonia-N, and nitrate-N concentrations in interstitial soil water and the overlying water column. Each equilibrator had two parallel sets of 3 mL compartments spaced at 1 cm intervals, with a total of 23 compartments per set (Simon *et al.*, 1985). Once each compartment was filled with distilled-deionized water, both sides of the equilibrator were covered with a rectangular 0.2 μM Nucleopore polycarbonate membrane and sealed with a Plexiglas cover. The equilibrators were stored in plastic containers, also filled with distilled-deionized water, and bubbled with N_2 for 24 h. After the N_2 supply was disconnected, the plastic containers were covered with a lid and sealed. Then, the equilibrators were carried in containers to the field. The equilibrators were installed in WS1 and WS2 at 9, 24, 50, and 70 m from the wastewater inlet. The equilibrators were inserted in the soil leaving two sets of 8 compartments in the water column and allowed to equilibrate in the field for 14 days (July 24 to August 8, 1998). Water level in each wetland system was maintained at least 9 cm above the soil surface. Average daily water temperature varied from 23 to 26°C. Immediately after the equilibrators were taken out of the constructed wetland, the compartments were sampled with a syringe. Samples were placed in 4 mL plastic vials, acidified (1 μL of 50% H_2SO_4) to < pH 2 and transported with ice to the laboratory. Ammonium and nitrate plus nitrate (NO_{2+3}-N) were analyzed with a Technicon Auto Analyzer II using USEPA Methods 350.1, and 363.2 (USEPA, 1983).

Four soil cores were taken along each wetland system at about 9, 24, 50, and 70 m from the wastewater inlet. The soil cores were sectioned in the field at four depths at 5 cm increments. A 3 cm layer of muck was underlain by loamy sand (86% sand, 10% silt and 4% clay) in both wetland systems. Samples were transported with ice to the laboratory and pH was measured in wet samples. Air-dried samples were digested using Kjeldahl N digestion and analyzed for total nitrogen (TKN) following the procedure described by Gallaher *et al.* (1976).

The NH_4^+-N profiles were used to calculate steady-state diffusive flux according to Fick's law (Berner, 1980):

$$J_i = -\phi D_i \theta^{-2} \, dc/dz$$

Table 1 Characteristics of the swine wastewater Duplin Co., NC (April–October 1998)

Parameter	Unit	Mean	Sample number	Standard Error
Total N	mg L^{-1}	249	33	18
Ammonium-N	mg L^{-1}	225	33	19
Nitrate-N	mg L^{-1}	3	33	1
pH		8.2	33	0.1

where J_i is the flux of the dissolved species i per unit area and time; ϕ is the porosity of the soil; D_i is the difussion coeficient of species i; θ is the tortuosity factor, and dc/dz is the concentration gradient with depth. The concentration gradient was estimated by linear regression between –4 to +4 cm depth. The porosity was assumed to be close to 1 since soil bulk density was very low (0.10 g cm^{-3}). A diffusion coefficient of 19.8×10^{-6} cm^2 s^{-1} at 25°C was used for NH_4^+, according to Li and Gregory (1974). Analysis of variance (proc ANOVA), regression (proc REG), means and standard errors (proc MEANS) were determined using SAS software (SAS Institute, 1988).

Results and discussion

The NH_4^+-N pore water profiles peaked just below the sediment-water interface (0–5 cm) and decreased with depth at all sites in both WS1 and WS2 (Figures 1 and 2). These NH_4-N peak levels in the 0 to 5 cm layer were likely related to the simultaneous supply of N from plant uptake, soil adsorption, microbial assimilation and mineralization of sediment organic matter, and none of these supplies would have acted as the ultimate source of N. These profiles are consistent with the distribution of total soil N with depth (Table 2).

In flooded soils, conditions exist under which both nitrification and denitrification can proceed at the same time and NH_4^+-N levels are greatly influenced by the presence of aerobic and anaerobic soil layers (Reddy and Patrick, 1984). Reducing soil conditions found at 20 mm depth in WS1 and WS2 were consistently below 100 mV. This indicated that nitrification was likely limited and that denitrification was predominant. This limitation was previously tested by denitrification enzyme assay in order to ascertain that nitrate was the most limiting factor for denitrification in the two-wetland systems (Hunt *et al.*, 1999). Analysis of the soil pore water showed no traces of NO_{2+3}–N, indicating that anaerobic conditions and limited nitrification and denitrification were prevalent in the wetland soils. Under these conditions, solution chemistry (pH and alkalinity) and environmental conditions (temperature and wind) could promote N losses via ammonia volatilization (Vlek and Stumpe, 1978).

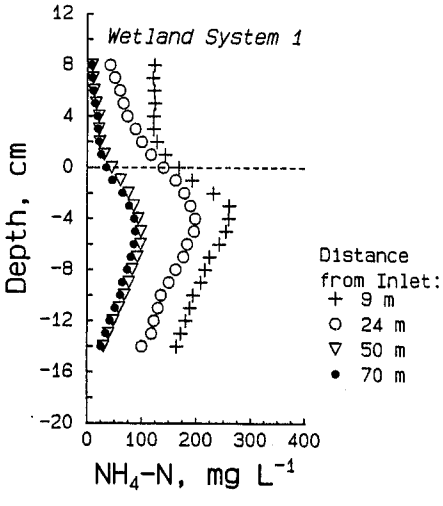

Figure 1 Mean (n = 2) surface water and soil pore water profiles of ammonia with depth (1-cm intervals) in Wetland System 1 (rush-bulrush plants) at four distances from the inlet

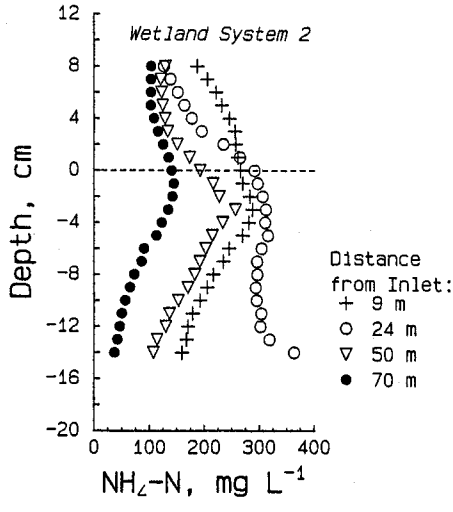

Figure 2 Mean (n = 2) surface water and soil pore water profiles of ammonia with depth (1-cm intervals) in Wetland System 2 (cattail-bur reed plants) at four distances from the inlet

Ammonium-N levels decreased in the interstitial soil-surface water along WS1 and WS2. Ammonium-N levels were greatest at the closest distance from the inlet (9 m) for both WS1 and WS2 (Figures 1 and 2). Concurrently, the lowest NH_4^+-N concentrations were observed at the farthest distance from the inlet (70 m) for both wetland systems. In the surface water, NH_4^+-N levels were lower in WS1 than WS2 at all sampling sites. WS1 had a 7-fold reduction in average NH_4^+-N levels (130 versus 18 mg L^{-1}) in the overlying water column between 9 and 70 m from the inlet, while WS2 had only a 2 fold reduction (237 versus 115 mg L^{-1}). The pH in surface water, from the inlet to the outlet, ranged from 7.3 to 8.2 in WS1, and from 7.4 to 7.9 units in WS2. Similar pH values were found in soils of both wetland systems (Table 3). Within these pH ranges at 25°C, the estimated amount of free NH_3 (gas) present in the wastewater is 5 to 7% of the total soluble N according to Anthonissen *et al.* (1976). Similar percentage losses of NH_3 were measured in the field by Hunt *et al.* (2000). Although a larger proportion of NH_3 could have been lost due to rising water temperature, wind speed and water turbulence, ammonia volatilization could not explain the higher N losses in WS1.

In both wetland systems, distinct gradients in the pore water NH_4^+-N profiles were found at the soil-water interface (Table 4). The diffusion flux was not calculated for WS2 sites 24 and 70 m from the inlet because NH_4^+-N was almost at equilibrium at the soil-water interface. All positive fluxes indicated that NH_4^+-N moved from the water-soil interface upward. Diffusive fluxes were higher in the WS1 than the WS2 system except at the 50 m site where the flux in WS2 was almost two orders of magnitude higher than in WS1. These NH_4^+-N flux differences between WS1 and WS2 could be explained by the fluctuation of water levels. During the 14 days of the experiment, WS2 had much higher (> 15 cm) water levels than WS1 (9 to 10 cm). This may have promoted a more effective interfacing of nitrifying and denitrifying environments in WS1. Hunt *et al.* (2000) found that denitrification potential was highest in the shallower portion of the wetland. In turn, this N loss could have increased the NH_4^+-N diffusion gradient. At the highest diffusion gradient in Table 4, NH_4^+ would diffuse at a 0.35 g m^{-2} d^{-1} rate from the water-soil interface into the surface

Table 2 Mean total soil nitrogen concentrations ($n = 4$) in Wetland Systems 1 and 2

Soil Depth cm	Wetland System 1 g N kg^{-1}	Wetland System 2
0–5	0.45	0.63
5–10	0.36	0.42
10–15	0.32	0.39
15–20	0.29	0.37
$LSD_{0.05}$*	0.08	0.12

* Least significant difference ($P > 0.05$)

Table 3 Mean soil pH in WS1 and WS2. Means are average values at four soil depths

Distance from Inlet m	Wetland System 1	Wetland System 2
9	8.2	7.7
24	7.6	7.6
50	7.3	7.4
70	7.2	7.3
$LSD_{0.05}$*	0.6	0.2

Least significant difference ($P > 0.05$)

Table 4 Ammonium flux at the soil-water interface based in concentration gradients. NS indicates gradient had non-significant regression line ($P > 0.05$)

Distance from Inlet m	Wetland System	Gradient dc/dz	R^2	Diffusive Flux mg m^{-2} d^{-1}
9	1	−20.4	0.94	+349
	2	−4.8	0.92	+ 83
24	1	−16.7	0.99	+287
	2	−8.9	NS	NS
50	1	−10.2	0.95	+175
	2	−16.4	0.94	+280
70	1	−9.1	0.92	+155
	2	−2.6	NS	NS

water column. This diffusion rate is about 14% of the 2.5 NH_4^+g m^{-2} d^{-1} application rate. Although diffusion may explain a significant portion of the material transport between the soil-water interface, it alone cannot explain the large differences in concentrations between outlet and inlet.

Conclusions

We found that NH_4^+ diffusion gradient and N losses were highest in the wetland system with lowest water depth. From other studies, we knew that shallower depths may have promoted a more effective interfacing of nitrifying and denitrifying environments. In turn, this N reduction in the water column may be the reason for steady NH_4^+ upward diffusion fluxes. The assumed mechanism for N removal has been nitrification denitrification, but ammonia volatilization could have occurred. However, solution chemistry and environmental conditions did not support the assumption that major gaseous losses occurred due to ammonia volatilization. Diffusion explained a significant portion of the material transport between the soil-water interface. However, large differences in concentrations between outlet and inlet still need to be explained by other mechanisms.

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