AMMONIA VOLATILIZATION FROM APPLIED SWINE EFFLUENT IN THE SOUTHERN GREAT PLAINS

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FOREWORD

This document is presented as four chapters. Each chapter is formatted as a stand-alone article following the formatting specifications of the journals; Journal of Environmental Quality, and Communication in Soil Science and Plant Analysis.

CHAPTER I

AMMONIA VOLATILIZATION FROM APPLIED SWINE EFFLUENT IN THE SOUTHERN GREAT PLAINS

ABSTRACT

The objectives of these experiments were to determine the extent of ammonia volatilization from swine effluent applied to a calcareous clay loam in the Southern Great Plains as effected by climatic conditions and plant cover. A micrometeorological mass balance technique employing passive flux samplers was used to measure the NH_3 fluxes exiting the plots. The amount of NH_3 volatilized from the applied swine effluent ranged from 9 to 48 percent of the ammoniacal nitrogen applied. Ammonia volatilization was highest when the temperature and wind speeds were high and relative humidity was low. Temperature seemed to have the greatest impact on the NH_3 volatilization. Rainfall events occurring during the experiments reduced volatilization. The extent of this reduction seemed to depend on the timing of the event. The presence of wheat and corn canopies significantly reduced NH_3 volatilization as compared to loses from fallow cropland. The presence of a winter wheat canopy reduced NH_3 volatilization by as much as 59% compared to fallow cropland. NH_3 volatilization from corn plots was 65% less than from fallow cropland. The decrease in NH_3 volatilization due to crop cover is attributed to the decreased wind speed above the soil as well as other changes in the microclimate. Experiments in this study also provide evidence that application timing can have an impact on the amount of NH_3 lost via volatilization. Late afternoon to evening applications of effluent may have the potential to decrease NH_3 volatilization.

INTRODUCTION

Between 1990 and 1999, the Panhandle of Oklahoma experienced a 120-fold increase in its swine population, from approximately 11,000 head in 1990 to almost 1.4 million head in 1999 (National Agricultural Statistics Service, 1999). In Texas county alone approximate 1.5 million swine were sold in 1997 (National Agricultural Statistics Service, 1997). This large swine production not only brings incredible revenue into the county, but also leaves behind millions of gallons of effluent that without proper management and disposal could pose a significant threat to the environment of the Southern Great Plains region.

Most of the approximate 1.7 billion liters of swine effluent produced in the Oklahoma Panhandle region each year (calculation estimate from Hamilton et al., 1997) is stored in outdoor earthen lagoons until it can be land applied to cropland as a fertilizer. Currently, it is common practice to assume that 50 % of the nitrogen present in the effluent is plant available during the first year of application (Zhang and Hamilton, 1998). This assumption is based on the amount of nitrogen mineralized during the growing season, but does not account for loss of nitrogen from applied effluent due to ammonia (NH_3) volatilization. A better understanding of the mechanisms that promote ammonia volatilization from cropland-applied swine effluent is needed in order to better estimate the impact of ammonia volatilization on agricultural nutrient budgets and nitrogen sensitive ecosystems. Because nitrogen is a chief input expense in most crop production systems, producers may have an economic incentive to employ management practices that minimize NH_3 volatilization. By accurately estimating the amount of gaseous nitrogen lost from land-applied swine effluent, crop producers would be able to better manage their nitrogen budgets, thereby maximizing crop yields while reducing input costs. Volatilization estimates would also enhance the understanding of the potential contribution of effluent-derived ammonia to atmospheric ammonia concentrations, as the deposition of the ammoniacal nitrogen in nitrogen sensitive environments can lead to changes in the species composition, eutrophication, and acidification of such environments (Schulze et al., 1989).

Volatilization of NH_3 has long been identified as a major pathway of nitrogen loss from land applied manure and effluent. In the 1930's Heck (1931), through indirect measurements, inferred NH_3 losses of 50 to 100 percent from solid and liquid manure, respectively. Recently, scientists have developed direct methods for measuring NH_3 volatilization in hopes of acquiring more precise volatilization data. Methods of direct measurement of nitrogenous gas movement between soil, plants and the atmosphere include: 1) Calculating gas movement in the soil profile using diffusion theory, 2) determining the total gas flux from the soil surface by using the NH_3 concentration near the soil surface in an enclosed environment, and 3) measuring the vertical flux of NH_3 above the surface using micrometeorological techniques (Denmead, 1983). Enclosure methods including miniature wind tunnels (Lockyer, 1984), microplot chambers (Hoff et al., 1981) and closed-dynamic chambers (Svensson, 1994) and micrometeorological methods including aerodynamic mass balance (Beauchamp et al., 1978), ZINST mass balance (Wilson et al., 1982; 1983), and passive flux mass balance (Schjoerring et al., 1992) are commonly used to measure ammonia volatilization from surface applied swine effluent. Because of the wide variety of sampling methods, comparing NH_3 volatilization data across multiple studies is difficult.

Ammonia volatilization from land applied swine effluent can be affected by a variety of soil, manure, and climactic conditions. Soil properties such as: cation exchange capacity, pH, pH buffer capacity, soil moisture, and calcium carbonate content (Freney et al., 1983) along with manure characteristics such as total ammoniacal nitrogen concentration, pH, alkalinity, buffering capacity, ionic strength and activity, dry matter content, fluidity, and viscosity (Svensson, 1994) can significantly affect the volatilization rates of ammonia from land applied effluents. Ammonia volatilization has also been correlated with wind speed and solar radiation (Brunke et al., 1988) and air temperature and humidity (Sommer et al., 1991). Typically environments with low relative humidity, high air temperatures, high wind speeds and high solar radiation experience large rates of ammonia volatilization from animal waste-derived nitrogen additions. The environment in the Southern Great Plains region, characterized by the aforementioned climactic conditions, has the potential for high ammonia volatilization rates. Regional wind speeds can reach up to 16 m s^{-1} and daytime relative humidity is often as low as 7 percent. These high wind speeds and low humidity coupled with the dramatic increase in the number of swine animals produced in the region has prompted increased interest in the management and utilization of swine effluent as a nutritive additive for crop growth. The objectives of these experiments were to determine the extent of ammonia volatilization from swine effluent applied to a calcareous clay loam and to evaluate the effects of weather conditions and plant cover on NH_3 volatilization rates.

METHODS AND MATERIALS

The experiments were conducted at the Oklahoma Panhandle Research and Extension Center located in Goodwell, OK on a Richfield clay loam with an average pH of

7.5. Experiments were conducted in May, July, and September 1998; July and December 1999; and March and July 2000 (Table 1). Swine effluent with an average pH of 7.8 was collected from a facultative anaerobic lagoon. For the 1998 experiments swine effluent was applied to three of four established fallow cropland plots (radius of 7.62 m) at a rate of 2.54 cm (4,680 L). The plot that did not receive effluent served as a background plot and was used to determine ambient atmospheric NH_3 levels. The 1999 and 2000 experiments compared volatilization rates from swine effluent applied to fallow and crop covered soils. Five circular plots, two fallow plots and two crop covered plots, with radii of 7.62 m were established with one plot serving as a background plot. Cover crops evaluated during the four experiments conducted in 1999 and 2000 were sorghum, wheat, and corn. Cumulative NH_3 volatilization measurements from the follow and cropped plots during experiments conducted in 1999 and 2000 were compared using a two treatment t-test. Again, applied swine effluent was collected from a nearby facultative anaerobic lagoon and applied to the treatment plots at a rate of 2.54 cm (4,680 L). All plots in the 1998, 1999, and 2000 experiments were spaced at least 100 m apart to minimize potential contamination between plots.

A micrometeorological mass balance method employing passive flux samplers (Schjoerring et al., 1992) was used to measure ammonia volatilization from the established plots. Passive flux samplers consisting of three glass tubes, two tubes 100 mm in length and one 23 mm (all with an internal diameter of 7 mm), were connected by silicon tubing with the shorter tube placed on one end. The tubes used in these experiments were obtained from Mikrolab Aarhus A/S, Axel Kiers Vej 34, DK-8270 Hoejbjerg, Denmark (Schjoerring et al., 1992). A stainless steel disk with a thickness of 0.05 mm and a centered hole of 1.0 mm was glued to the end of the 23 mm tube in order to reduce airflow through the sampler and maximize NH_3 absorption. The internal walls of the two 100 mm tubes were coated with oxalic acid to a length of 70 mm. Oxalic acid absorbed the ammonia traveling through the sampler and converted it to ammonium. The ammonium was then later extracted with 3 mL of deionized water and the extract was analyzed for NH_4^+-N using Lachat Method 12-107-06-1-B (Bloxham, 1993).

Passive flux samplers were placed on four masts positioned 90 degrees around the perimeter of each plot. Sample heights used in the three experiments conducted in 1998 were 15, 47, 109, and 184 cm above the soil surface. Because considerable horizontal NH_3 fluxes were measured at the top height during the first three experiments (Figure 1) the sampling heights used in the fallow plots of the later experiments were adjusted to 15, 61, 130, and 274 cm above the soil surface. Five heights were used for the cropped plots when the crop height exceeded 15 cm. The sample heights in the cropped plots (Figure 2) were selected based on crop heights in order to measure a representative horizontal NH_3 flux profile.

Effluent was applied by flood irrigation to each plot. Flood irrigation is not common practice in the southern Great Plains region, however it was used in this experiment to reduce sample contamination due to ammonia drift or overspray that would occur from sprinkler application. Ammonia sampling began immediately after the effluent applications and continued until ammonia volatilization was negligible. Meteorological data including wind speed, relative humidity, temperature, and solar radiation (Table 2) was obtained from the Oklahoma Mesonet weather station located at the Oklahoma Panhandle Research and Extension Center within1600 m of the treatment site.

Equations used to calculate the horizontal flux, horizontal net flux, vertical flux and cumulative NH_3 loss were developed by Schjoerring et al. (1992). The horizontal flux of ammonia (F_{hm}, μg NH_3-N m^{-2} s^{-1}) through the two tubes facing the same direction was calculated using the following equation:

$$F_{hm} = \frac{A_1 + A_2}{2 * \pi * r^2 * K * \Delta t}, \qquad [1]$$

Where:

A_1 and A_2 = NH_4^+-N (μg) captured in tubes facing the same direction at each height.

r = radius (m) of the hole in the samplers steel plate.

K =correction factor (0.77), which corrects for the reduction in wind velocity through the sampler due to the steel plate.

Δt = duration (s) of the sample period.

When wind speeds less than 10 m s^{-1}, the net horizontal flux of ammonia ($F_{(net\ h)}$, μg NH_3-N m^{-2} s^{-1}) at each height would be calculated using the following equation:

$$F_{(net\ h)} = \sum_{m=1}^{m=4} (F_{hm,s} - F_{hm,b}), \qquad [2]$$

where:

h = height (m) of the horizontal flux measurement,

m = mast at which the measurement was made,

$F_{hm,s}$ and $F_{hm,b}$ = horizontal fluxes (μg m^{-2} s^{-1}) measured from the tubes pointing into and away from the plot which received the effluent application, respectively.

However, Sommer et al. (1996) observed that NH_3 bypassed the sampling tubes when wind speeds were above 10 m s^{-1}. Wind speeds greater than 10 m s^{-1} are common in the research area; therefore the likelihood of the bypass occurring in the tubes was anticipated. To prevent underestimation of the horizontal flux by subtracting NH_3 adsorbed to the background tube, which potentially came from the plot, the fluxes of NH_3 measured in the exposed tubes were added to the fluxes of NH_3 measured in the background tubes. In order to account for the ambient NH_3, captured NH_3 in the background plot was subtracted from the treatment plot values. The revised equation for net horizontal flux that accounts for NH_3 blowby is as follows:

$$F_{(net\ h)} = \sum_{m=1}^{m=n} (F_{hm,s} + F_{hm,b}) - (F_{hm,sz} + F_{hm,bz})], \qquad [3]$$

Where:

h = height (m) of the horizontal flux measurement,

m = mast at which the measurement was made,

$F_{hm,s}$ and $F_{hm,b}$ = horizontal fluxes (μg m^{-2} s^{-1}) measured from the tubes pointing into and away from the plot which received the effluent application, respectively,

$F_{hm,sz}$ and $F_{hm,bz}$ = horizontal fluxes (μg m^{-2} s^{-1}) measured from the tubes pointing into and away from the background plot, respectively.

Assuming the rate of volatilization is uniform over the entire plot the vertical net-flux of NH_3 from the plot is calculated using the following equation:

$$F_v = \frac{1}{2x} \sum_{h=1}^{h=n} F_{(net\ h)} \Delta h, \qquad [4]$$

Where:

x = radius (m) of the plot,

h = height (m) of the horizontal flux measurement,

Δh = height (m) interval between the samplers.

The cumulative NH_3-N volatilization was calculated using the equation:

$$T_{Vol} = \sum_{t=1}^{t=n} F_{v,t} * \Delta t \,, \qquad [5]$$

Where:

t = Sample period,

$F_{v,t}$ = vertical flux ($\mu g\ m^{-2}\ s^{-1}$) measured during each sampling period,

Δt = time (s) duration of each sampling period.

RESULTS AND DISCUSSION

Data presented from experiments 1 through 3 was collected and reported by Zupancic (1999). It is included here in order to provide a more extensive data set that will allow for a more complete understanding of NH_3 volatilization in the Southern High Plains.

Ammonia Volatilization Patterns

Ammonia volatilization followed a diurnal pattern during the first two to three days of all the experiments (Figures 3 and 4). This diurnal pattern of higher NH_3 volatilization during the day than at night is similar to that described by Beauchamp et al. (1978), Pain et al. (1989), Harper et al. (1983), and Van Der Molen et al. (1990). Diurnal fluctuations in ammonia volatilization are due to decreased air temperature, solar radiation, and wind speed and an increase in relative humidity during the night time hours. These climatic conditions are less optimal for high rates of ammonia volatilization as they reduce the reaction rates involved in NH_3 transfer to the atmosphere (Reddy et al., 1979; Genermont and Celier, 1997).

Ammonia volatilization is usually the greatest during the first 8 to 12 hours after effluent application. Approximately 50 percent of the total NH_3 lost during experiments 1 through 4 was lost during the first sampling period (8-12 hours) from the fallow plots as well as from the sorghum plots in experiment 4 (Figures 5 and 6). This is consistent with Sommer et al. (1997) who found that on average 50 percent of the total NH_3 volatilized was lost within eight hours after the land application of swine slurry. Pain et al. (1989) found that as much as 85 percent of the total volatilization of NH_3 occurred within 12 hours of land application. Ammonia volatilization during the first sample period of the remaining three experiments accounted for a considerably smaller percentage of the total loss. Six and ten percent of the total NH_3 lost from effluent applied to the fallow and wheat plots respectively, was lost during the first 8 hours of experiment 5 (Figure 6). The explanation for the low loss during the first eight hours as compared to other experiments is that the flux of NH_3 from the plots in experiment 5 was low (because of low temperatures) throughout the experiment and did not significantly change with time. Therefore the percentage of NH_3 lost during any of the seven sample periods was a function of the length of the sample period.

During the first nine hours of experiment 6, 30 and 19 percent of the total cumulative NH_3 volatilized was lost from the fallow and wheat plots, respectively (Figure 6). This smaller percentage of the total cumulative NH_3 volatilization lost during the first sampling as compared to other experiments is attributed to the cool temperatures experienced during the experiment. The low temperatures suppressed volatilization to a greater degree during the first sampling period than in later sampling periods (Sommer et al., 1991). Because of the reduced loss during the first sampling, NH_4^+ remained at the surface and was allowed to volatilize later in the experiment were as in experiments 1 through 4 more NH_3 was quickly volatilized during the first sampling period.

During the first nine hours of experiment 7, 33 and 40 percent of the total cumulative NH_3 volatilized was lost from the fallow and corn plots, respectively (Figure 6). Ammonia volatilization may have been suppressed during this sampling period by a brief rainfall event, which occurred three hours after application. In the fallow plots of experiment 7 the volatilization rate during the third sample period accounted for a large portion (32 percent) of the total NH_3 lost. The high NH_3 volatilization rates during this period could be attributed to high initial soil moisture contents. The high soil moisture content measured prior to effluent application reduced the infiltration rate of the effluent thereby reducing the depth to which the ammoniacal nitrogen could move into the soil profile (Sommer, et al., 1997). Also, because of the low volatilization rates measured during the first and second sampling periods, a substantial amount of ammoniacal nitrogen was present at the soil surface during the third sampling period allowing increased volatilization. However, this phenomenon was not observed in the corn plots as the microclimate within the corn plots presumably moderated the effects of the daytime weather conditions on NH_3 volatilization.

Cumulative Ammonia Volatilization

Cumulative NH_3 lost via volatilization from the fallow treatments ranged from 17.5 to 129.5 kg ha^{-1}, which accounted for 23 and 48 percent of that applied respectively (Table 2). The average temperatures and wind speeds measured during experiments 2, 3, 4, and 7 are quite similar. Also, precipitation occurred during all of these experiment at differing times and magnitudes. Yet the cumulative NH_3 volatilization during experiment 2 accounts for only 23 percent of the applied ammoniacal nitrogen whereas NH_3 loss accounted for more than 30 percent in experiments 3, 4 and 7. The higher level of precipitation and subsequently higher average relative humidity (Appendix I) present during experiment 2 could explain this lower loss of NH_3. The low volatilization rates during this time could also be a result of the late starting time of the experiment (3:00 p.m. Central time). Because the experiment was initiated in the afternoon rather than in the morning as in the other experiments, conditions during the first 7.5 hours of experiment 2 were not as conducive to high volatilization rates as experiments started earlier in the day. The decrease in air temperature and solar radiation and the increase in relative humidity during the late afternoon and nighttime hours may have suppressed NH_3 volatilization during the crucial first 7 to 12 hours of the experiment (Sommer et al., 1997; Sommer et al., 1991; and Brunke et al., 1988). Application of effluent in the afternoon may have also allowed the effluent to infiltrate the soil overnight, thereby reducing the NH_3 lost via volatilization the next day. Decreased volatilization from late day applications were also observed by Moal et al. (1995). These results demonstrate the importance of application timing during diurnal cycle and suggest that applications during the late afternoon to evening hours may maximize NH_3 retention in the soil. The much colder temperatures present during experiments 5 and 6 explain the reduced percent loss due to the decrease in the reaction rates involved in the transfer of ammonia to the atmosphere (Genermont and Celier, 1997).

The presences of crop cover significantly decreased the cumulative NH_3 volatilization in three of the four experiments conducted in 1999 and 2000. In experiment 4 the sorghum did not significantly reduce the cumulative NH_3 volatilization. However, one would have expected the sorghum plots to have lower rates of ammonia volatilization due to vegetative-induced decreases in wind speeds across the plots. The lack of significance between the two treatments in this experiment is likely the result of wide variations in the amount of vegetative growth on the two sorghum plots, as ground cover on the sorghum plots ranged from 30 to 60 percent. The vertical NH_3 fluxes from the sorghum plots were 75.7 and 104.8 $\mu g\ NH_3\text{-}N\ m^{-2}\ s^{-1}$, for the plots containing 60 and 30 percent coverage, respectively (Figure 4) during the first sampling period. This suggests increased vegetative cover can decrease the amount of ammonia volatilization from applied effluent.

Cumulative NH_3 volatilization from the wheat plots in experiments 5 and 6 was significantly lower than the cumulative NH_3 volatilization from the fallow plots with p values of 0.0921 and 0.0843, respectively (Figure 6). The presence of wheat in these experiments reduced the loss of NH_3 by 59 and 47 percent respectively. The presence of corn in experiment 7 significantly ($p = 0.0835$) reduced cumulative volatilization by 66 percent. It is thought the decreased wind movement in the wheat plots due to plant coverage resulted in an increase in NH_3 partial pressure directly above the soil surface thereby suppressing ammonia volatilization (Sommer et al. 1997). According to literature on transfer models, vegetation increases the aerodynamic roughness length of the surface, which is inversely related to the rate of NH_3 transfer from the surface to the atmosphere (Van Der Molen et al., 1990).

This data shows that a significant amount of NH_3 can be lost during the first 5 to 7 days after swine effluent application. Considering the current cost of nitrogen as anhydrous ammonia, a nitrogen fertilizer commonly used in the Southern Great Plains, the volatilization rate measured in experiment 1 would have resulted in a monetary loss of approximately $58 per ha. The magnitude of the cumulative volatilization is dependent on multiple meteorological, soil and effluent parameters and can be reduced by the presence of crop cover.

Horizontal Flux Profiles

The horizontal NH_3 flux from the fallow plots in this study decreased with height (Figures 1 and 7 through 10). This was expected as the NH_3 concentration gradient should decrease above the volatilization surface (Wilson et al. 1982; Ferm and Svensson 1993). During the first sampling period of experiments 1 and 2, horizontal NH_3 fluxes of 524 and 263 $\mu g\ NH_3\text{-}N\ m^{-2}\ s^{-1}$ were measured at the 184 cm height, respectively (Figure 1). This suggests NH_3 may be escaping the plot above the 184 cm height, which would result in an underestimation of NH_3 volatilization from the plots. This high level of NH_3 leaving the plots at the 184 cm height could be caused by the concentration boundary layer (Incropea and Dewitt, 1990) extending above the sampling height. The extension of the boundary layer above this height can be attributed to the high NH_3 concentrations present at the surface, which force NH_3 further up into the atmosphere. The sampling heights were adjusted in experiments 4 through 7 to prevent NH_3 from leaving the plot above the top sampling height.

Horizontal NH_3 flux profiles measured from the sorghum and corn plots in experiments 4 and 7, respectively, were greatly affected by the standing crop. The flux profile from the sorghum plots (figure 7) showed that a majority of the NH_3 did not leave the plots near the surface as was typically seen in the fallow plots, but was allowed to diffuse upwards and move off the plot above the sorghum canopy. This diffusion upwards in the canopy was also observed in the corn plots in experiment 7 although to a greater degree (Figure 10). This phenomenon is a result of decreased wind speed at the surface due to crop cover. The decrease in wind speed in the canopy allowed NH_3 to diffuse up through the canopy into the air stream above the canopy where it was carried off the plot, creating the horizontal flux bulge near the top of the crop canopy.

The wheat plots in experiments 5 and 6 did not seem to affect the horizontal NH_3 flux profiles (Figures 8 and 9). If the wheat affected the horizontal NH_3 flux the effect was too small to be measured using the sampling heights used in this experiment. The wheat in both experiments was less than 10 cm tall and therefore could not effectively change the shape of the profile measured in this study.

The average horizontal flux of ambient NH_3 as measured throughout each experiment at each height by the passive flux samplers located in the background plot ranged from 23.4 to 107.0 $\mu g\ NH_3\text{-}N\ m^{-2}\ s^{-1}$ (Tables 3 and 4). This wide range may be due to temporal changes in the ambient NH_3 concentration in the atmosphere from experiment to experiment as well as differences in horizontal flux with height of measurement due to decreases in wind speed with decreasing height.

CONCLUSION

The experiments conducted in this study were used to: 1) determine the extent to which NH_3 volatilization would occur after the application of swine effluent to a calcareous clay loam in the Southern Great Plains and 2) evaluate the effects of weather conditions and plant cover on NH_3 volatilization rates. The amount of NH_3 volatilized from the applied swine effluent ranged from 9 to 48 percent of the ammoniacal nitrogen applied (Table 1). The greatest quantity of ammonia volatilized when air temperature and wind speeds were high and the relative humidity was low. These conditions, along with the occurrence of no rainfall and a high ammoniacal nitrogen application rate, allowed for a high level of NH_3 volatilization relative to other experiments. The lowest occurrence of NH_3 volatilization was observed for the wheat plots where there were low ammoniacal nitrogen concentrations and low air temperatures were measured. The presence of a ground cover further reduced NH_3 volatilization by slowing wind speeds at the soil surface.

Of the ground covers tested, corn was most effective in reducing NH_3 volatilization due to its considerable height and vegetative mass, which reduced wind speeds through the plot. The sorghum cover in Experiment 4 did not significantly reduce NH_3 volatilization from the plots, however it was shown that increasing the amount of sorghum ground cover from 30 to 60 percent seemed to reduce the amount of ammonia lost through volatilization.

Climatic conditions played an important role in determining the potential NH_3 volatilization from soil applied swine effluent in these experiments. At low temperatures, wind velocities and high relative humidity, NH_3 volatilization tended to be suppressed due to the decrease in the transfer rate of ammonia from the surface to the atmosphere. The data also suggests effluent application timing has an effect on NH_3 volatilization. When effluent is applied in the afternoon to evening hours, NH_3 volatilization may be reduced due to non-conducive climactic conditions during the crucial first 6 to 12 hours when volatilization is the greatest. Changes in the timing of effluent applications may provide producers a means to increase the retainment of effluent applied nitrogen for crop production.

There is significant monetary incentive for producers to retain the ammonium in the swine effluent. From the data collected in this study it was found that NH_3 volatilization could account for a monetary loss of as much as $58 per ha. This demonstrates the importance of managing effluent application to reduce NH_3 volatilization. In order to minimize losses producers should apply effluent at times at which wind speeds and temperatures are low. Also to reduce volatilization they can apply effluent to standing crops, which have been shown here to reduce volatilization. Further research is needed to directly measure the effects of application timing as well as the effects of crop density and height.

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Table 1: NH_4^+-N added to a calcareous clay loam via swine effluent and the amount NH_3-N volatilized during seven experiments conducted in 1998 through 2000.

Exp.	Starting date	Application time*	Sample Duration		NH_4^+-N Added	NH_3-N Volatilized	% of Applied Lost
			Hours		kg ha^{-1}	kg ha^{-1}	
1	5/28/98	0700	168	Fallow	271	129.6	48
2	7/28/98	1500	168	Fallow	221	50.9	23
3	9/12/98	1000	113	Fallow	236	76.8	33
4	7/28/99	1000	101	Fallow	198	63.7	32
				Sorghum	198	47.7	24
5	12/15/99	1100	144	Fallow	77	17.5	23
				Wheat	77	7.2	9
6	3/14/00	0900	144	Fallow	199	33	17
				Wheat	199	17.5	9
7	7/13/00	1000	144	Fallow	199	70.9	36
				Corn	199	24.4	12

* U. S. Central Standard Time

Table 2: Meteorological conditions during seven field experiments as measured by the Goodwell Mesonet weather station located at the Oklahoma Panhandle Research and Extension Center, Goodwell, OK.

Exp.	Temp.			Relative Humidity			Wind Speed			Rain	Soil Water*
	Min.	Avg.	Max	Min.	Avg.	Max.	Min.	Avg.	Max.		
	°C			%			m s^{-1}			cm	g g^{-1}
1	9	24	38	7	42	93	1	5.5	11.7	0	0.015
2	17	24	35	36	72	97	0.3	4.1	13	5.1	0.049
3	13	22	31	27	61	93	0.8	3.4	7.2	0.3	NA
4	18	28	39	18	50	95	1.1	5.5	16.3	0.6	0.047
5	-8	2	16	6	56	93	0	5.3	12.9	<0.1	0.133
6	-5	5	18	14	70	96	0.4	5.9	13	0.7	0.155
7	18	27	39	19	59	95	0.4	4.9	12.1	0.6	0.291

* Soil moisture measured at soil surface 0 to 2.54 cm.

NA = Not available

Table 3: The average horizontal NH_3 flux measured at each height throughout each experiment conducted in 1998.

Height	Exp. 1	Exp. 2	Exp. 3
cm	---------$\mu g\ NH_3\text{-}Nm^{-2}\ s^{-1}$--------		
184	87.92	80.27	45.68
109	73.60	76.10	46.97
47	92.07	62.92	58.39
15	71.76	44.59	53.65

Table 3: The average horizontal NH_3 flux measured at each height throughout each experiment conducted in 1999 and 2000.

Height	Exp. 4	Exp. 5	Exp. 6	Exp. 7
cm	-----------$\mu g\ NH_3\text{-}Nm^{-2}\ s^{-1}$----------			
274	66.76	56.11	93.95	107.01
213	NA	NA	NA	95.94
182	61.85	NA	NA	110.41
130	31.19	68.46	71.43	101.10
107	39.41	NA	NA	NA
61	27.64	53.58	77.33	83.65
15	23.36	43.58	55.16	73.82

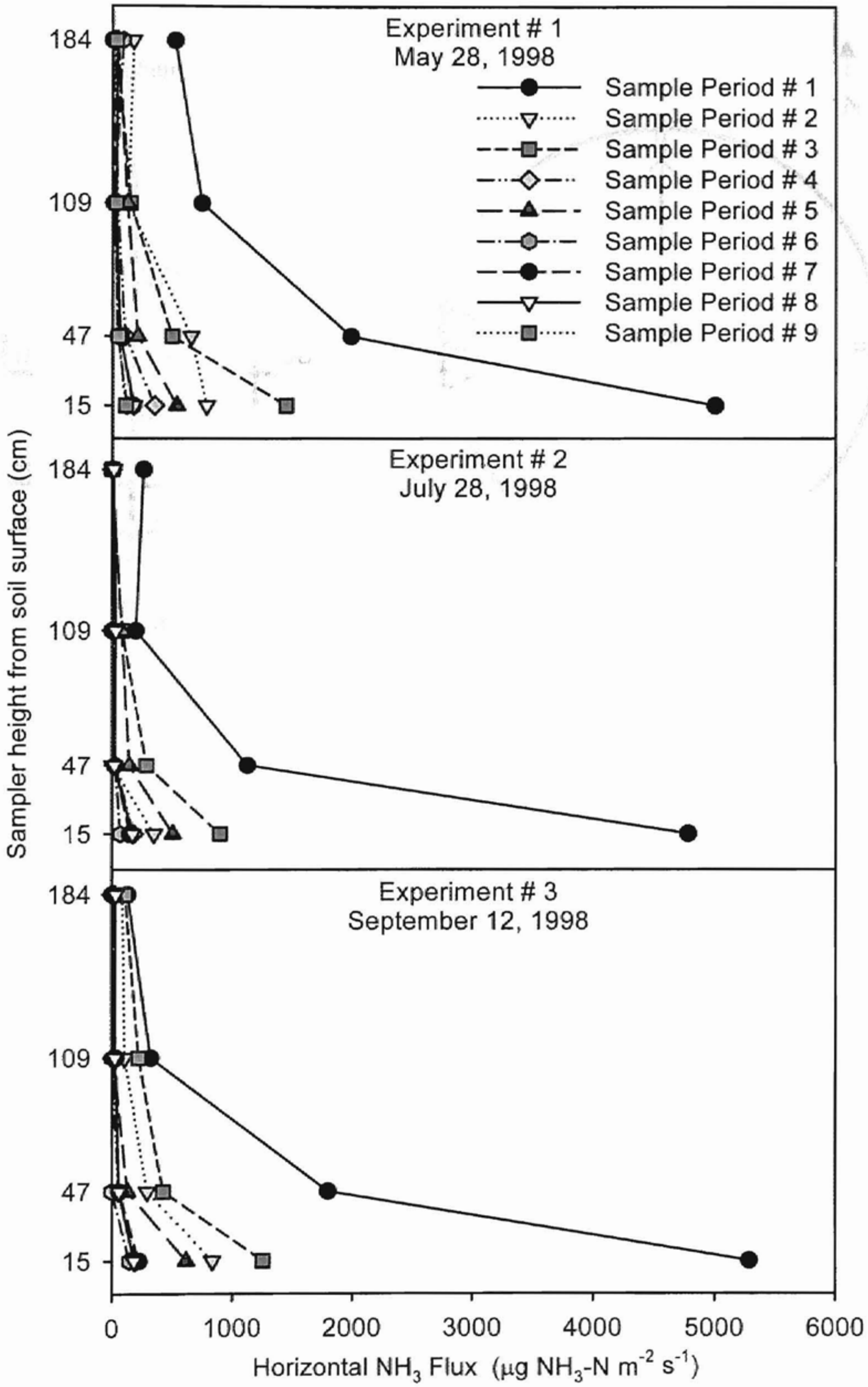

Figure 1: Average (n=3) horizontal NH_3 flux profiles measured after application of swine effluent for three experiments conducted during 1998.

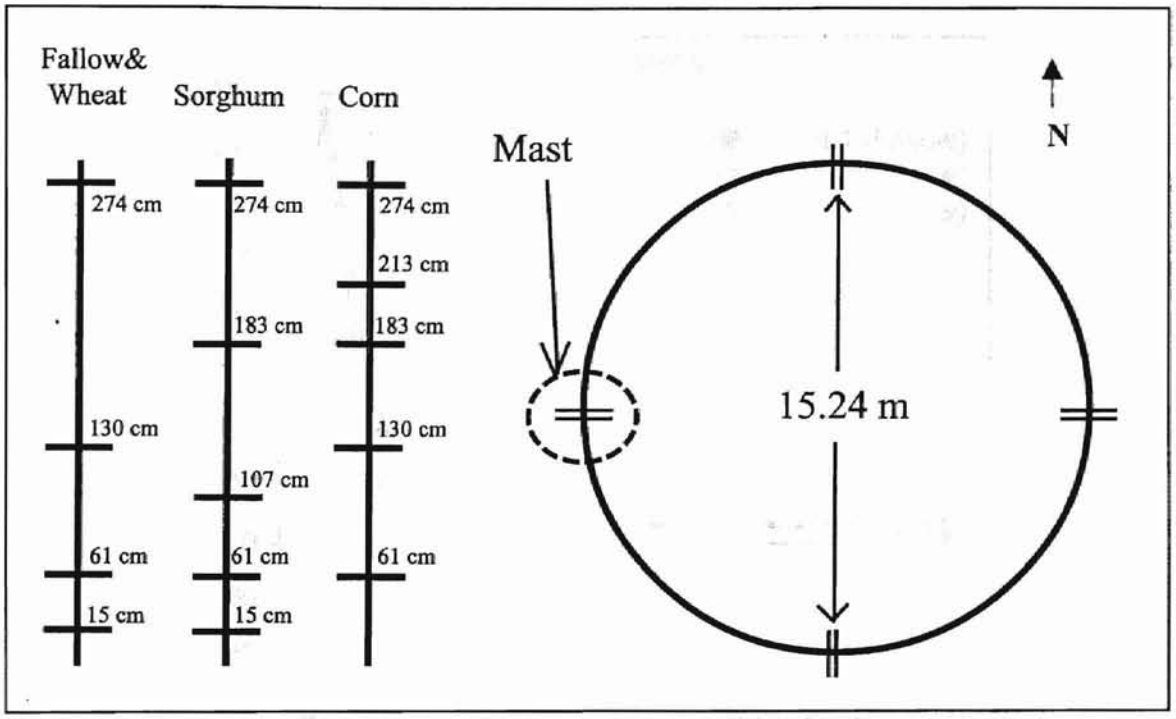

Figure 2: Sampler heights from soil surface and mast position in plots.

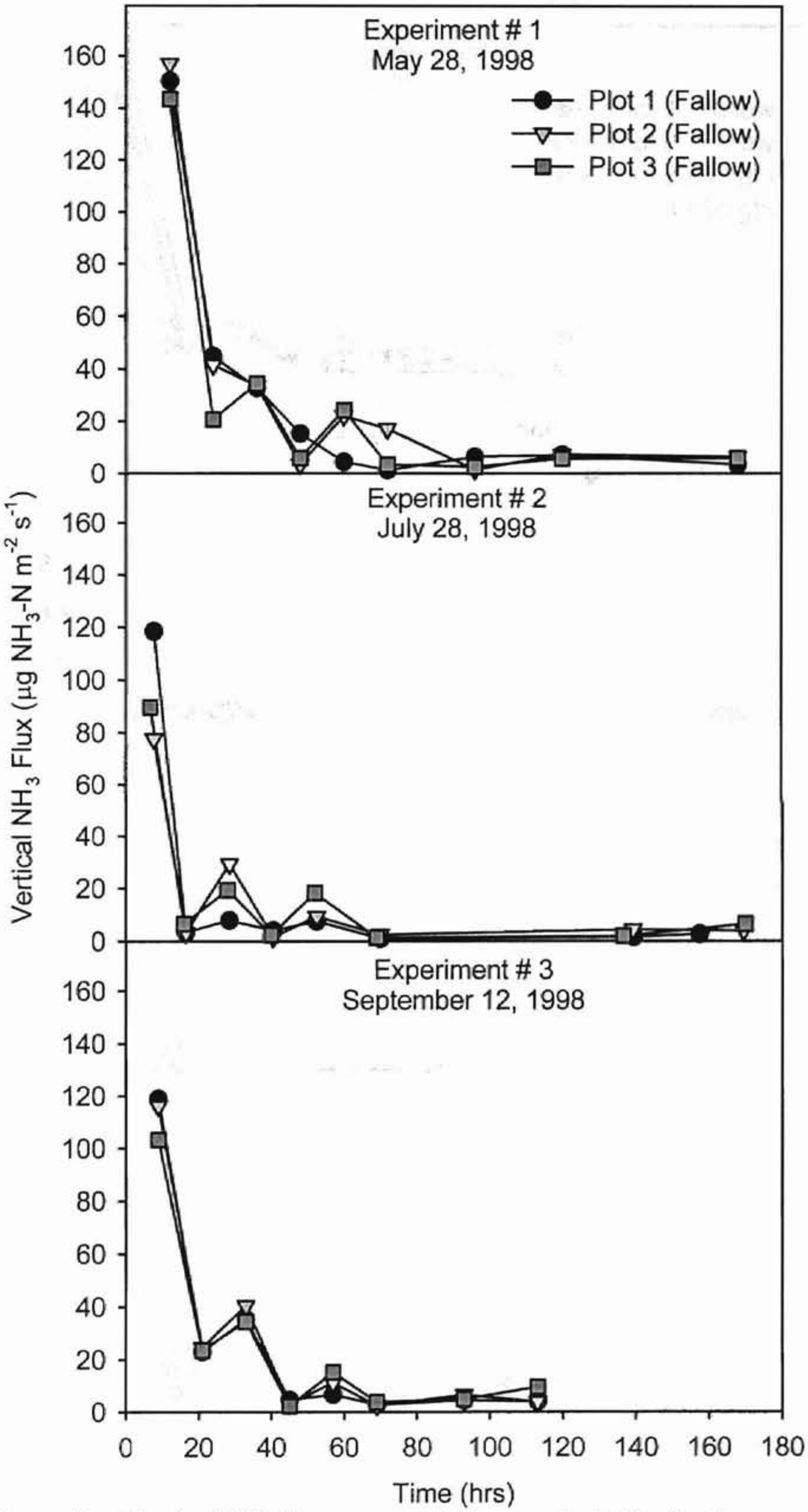

Figure 3: Vertical NH_3 flux measured from each plot in the three experiments conducted in 1998.

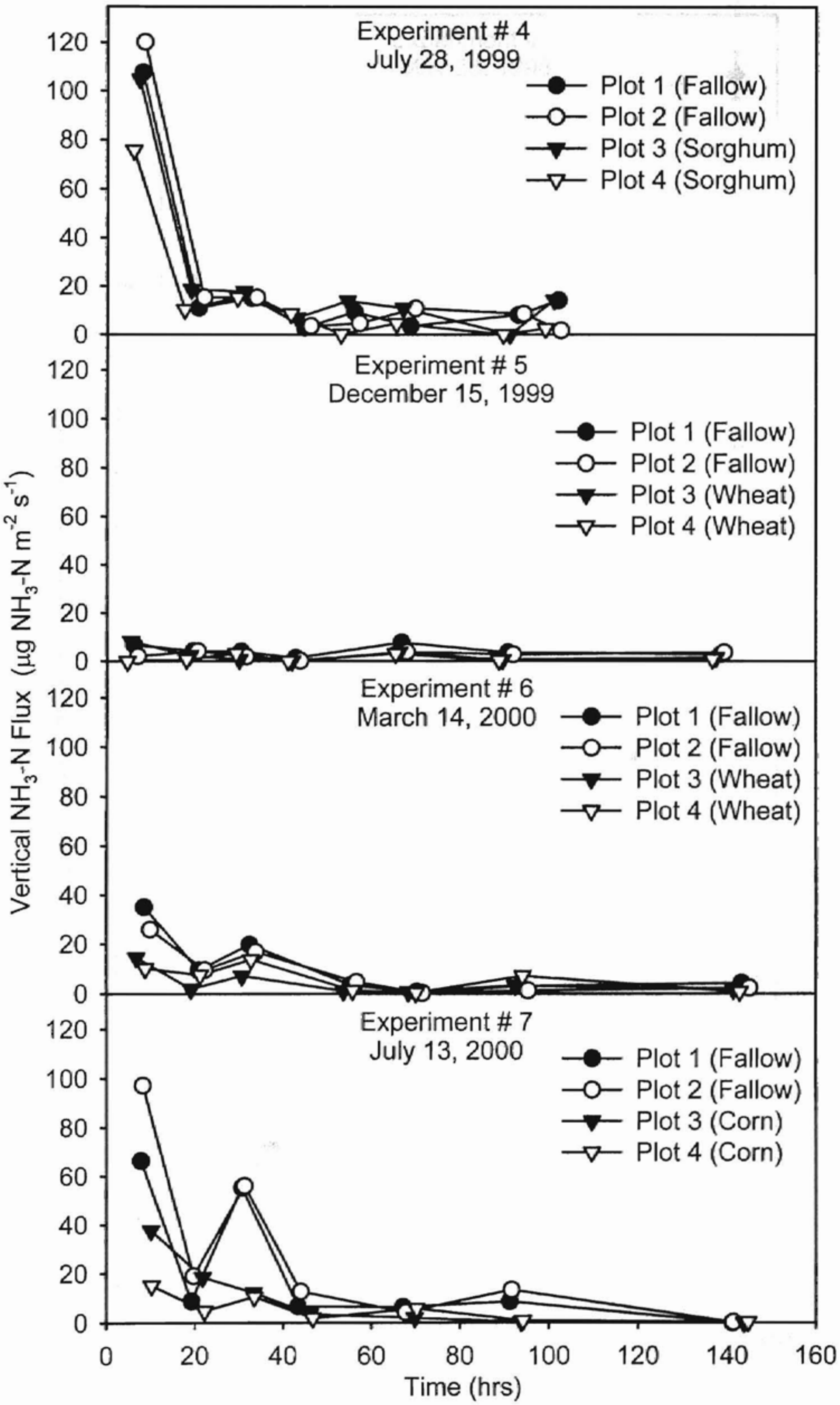

Figure 4: Vertical NH_3 flux measured from each plot in the 1999 and 2000 experiments.

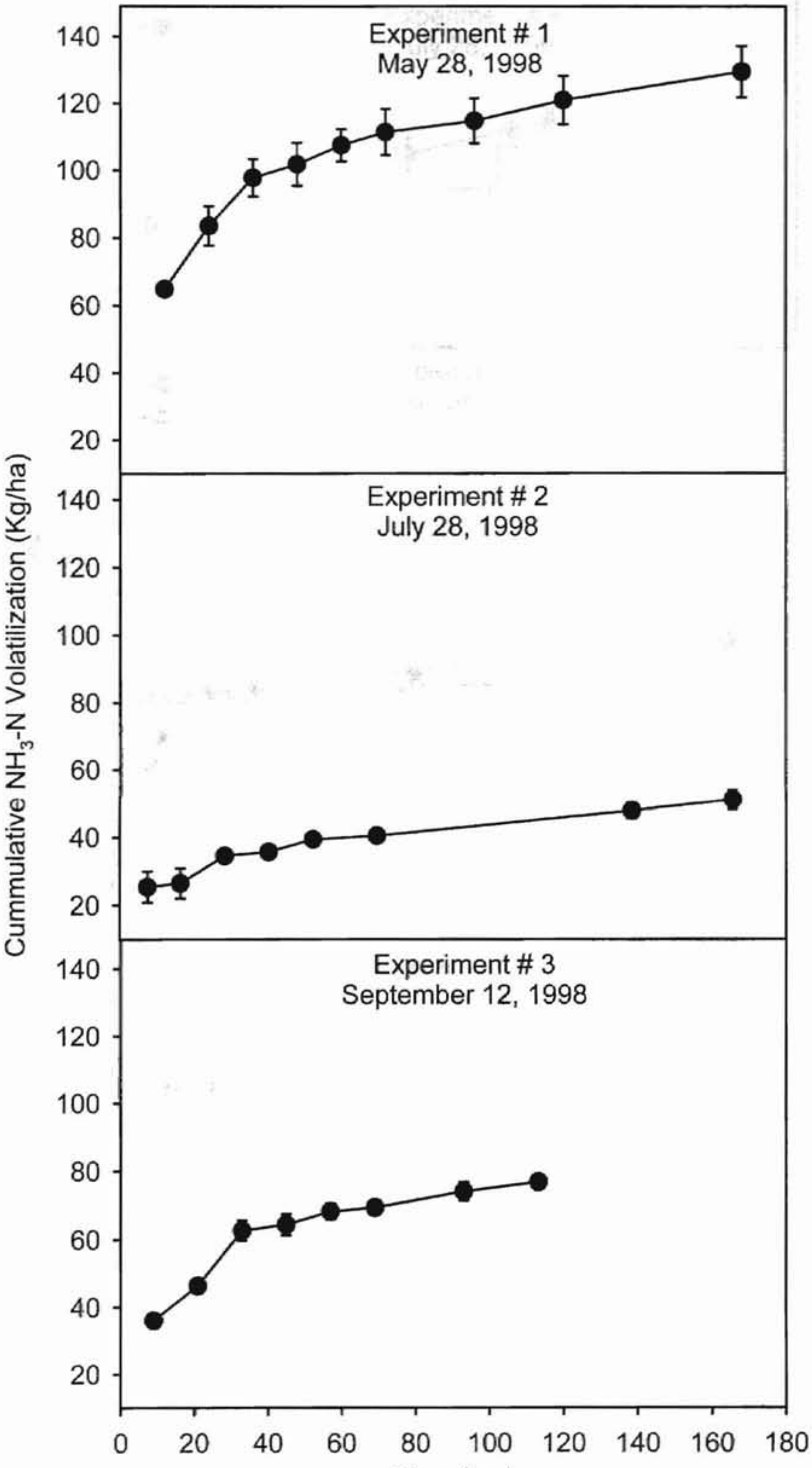

Figure 5: Average (n=3) and standard error of the cumulative NH_3 volatilized from applied swine effluent in the 1998 experiments.

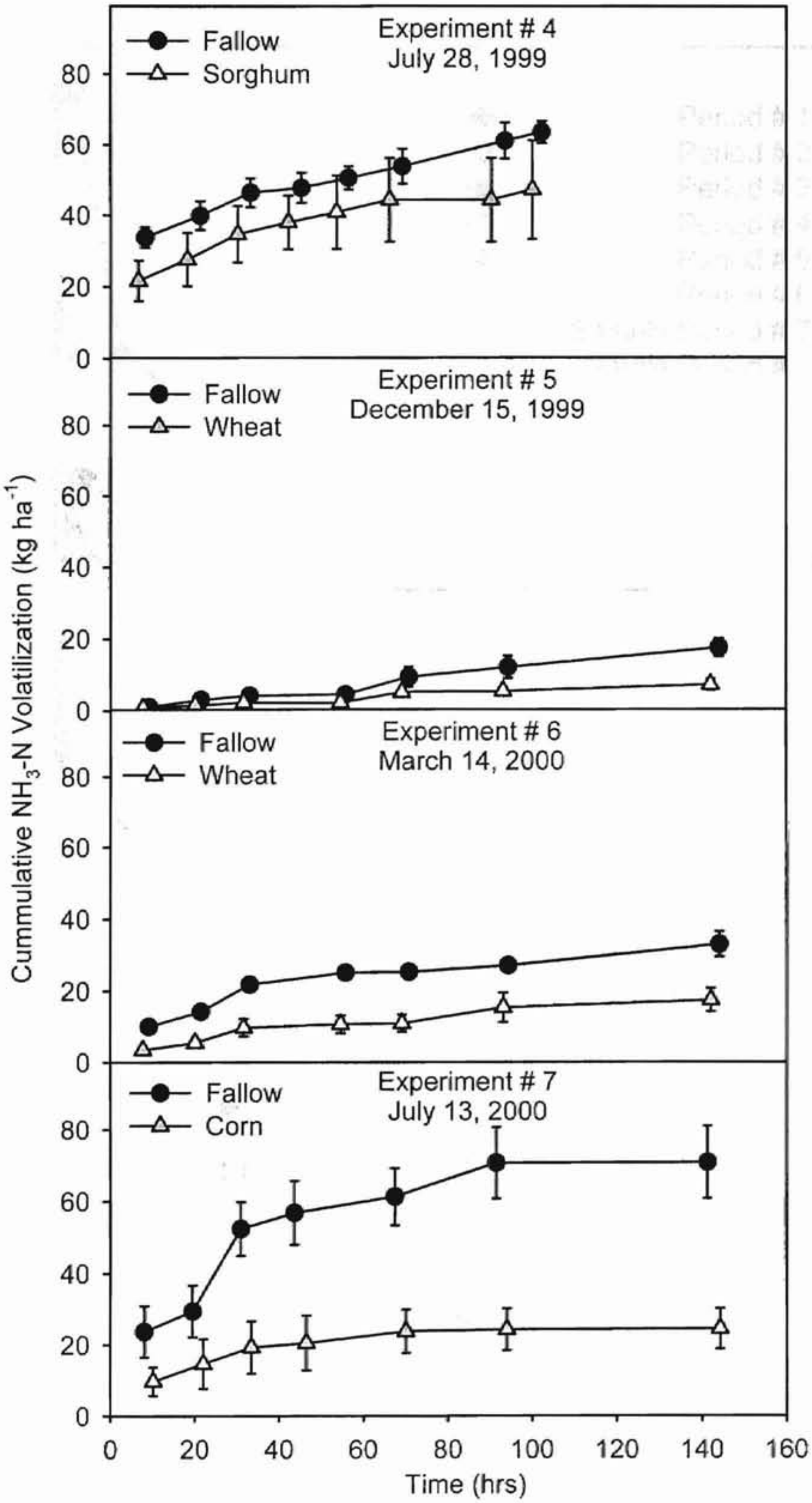

Figure 6: Average (n=2) and standard error of the cumulative NH_3 volatilized from applied swine effluent in the 1999 and 2000 experiments.

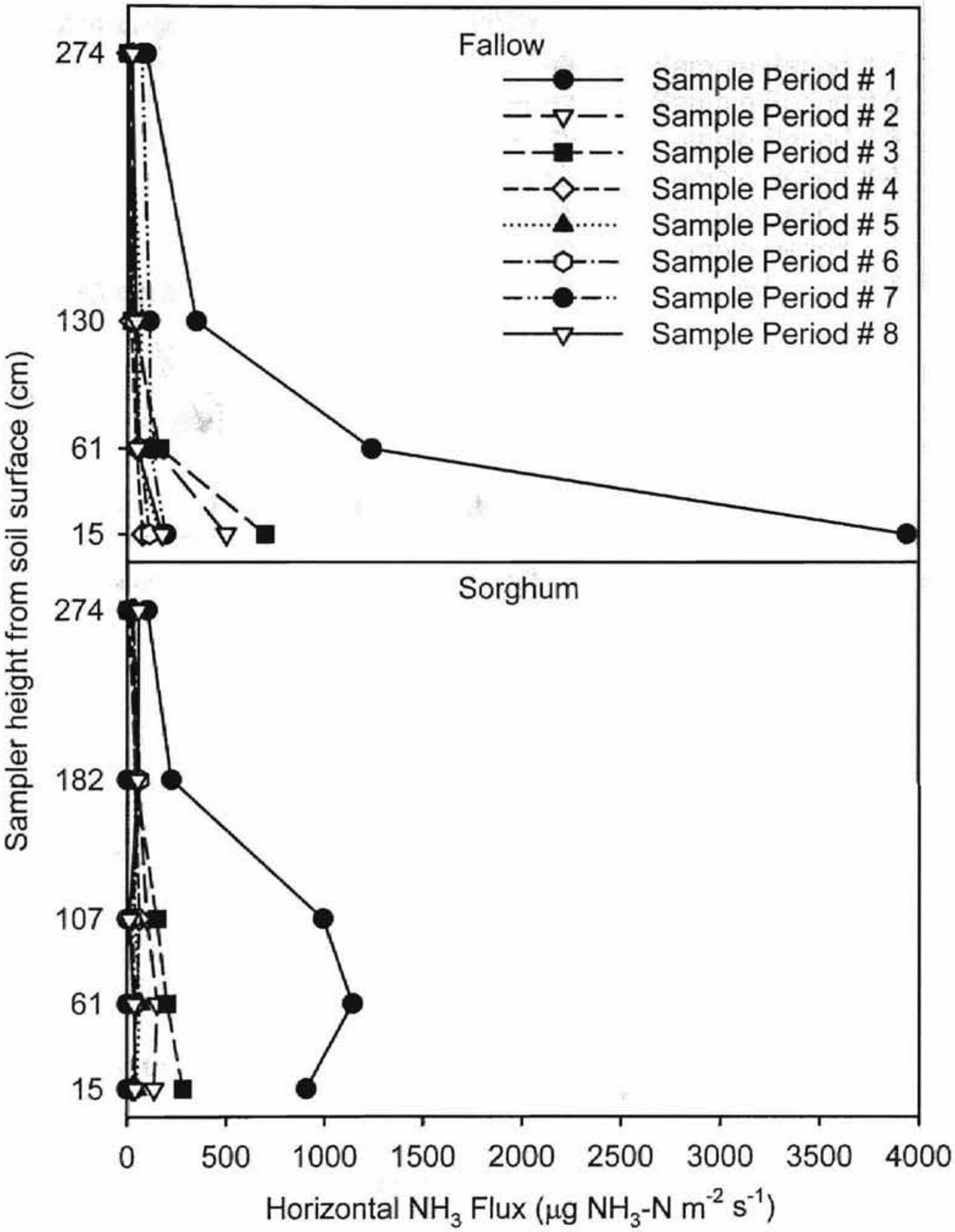

Figure 7: Average horizontal NH_3 flux profiles measured from two fallow plots and two plots of sorghum receiving swine effluent applications in July 1999.

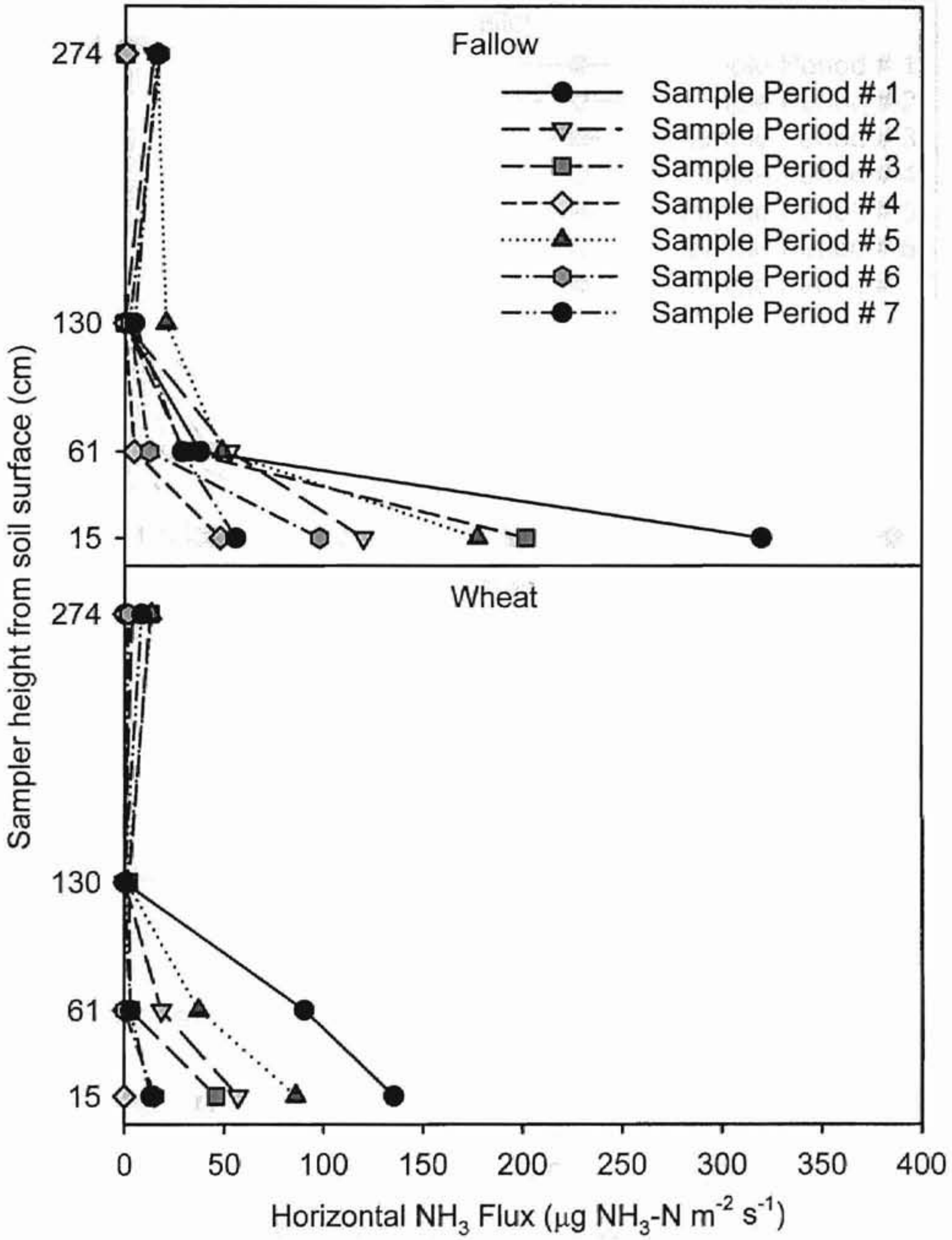

Figure 8: Average horizontal NH_3 flux profiles measured from two fallow plots and two plots of wheat receiving swine effluent applications in December 1999.

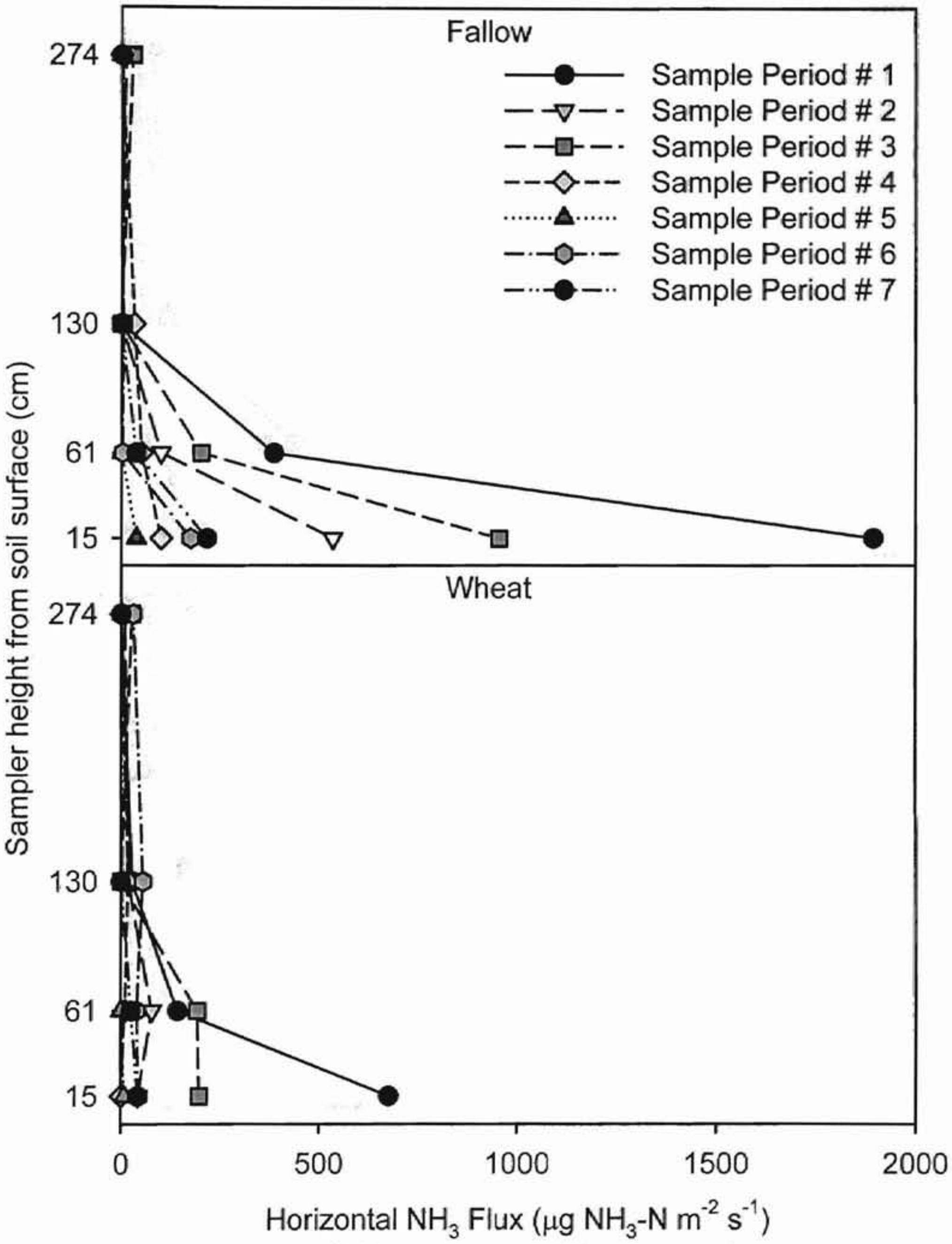

Figure 9: Average horizontal NH_3 flux profiles measured from two fallow plots and two plots of wheat receiving swine effluent applications in March 2000.

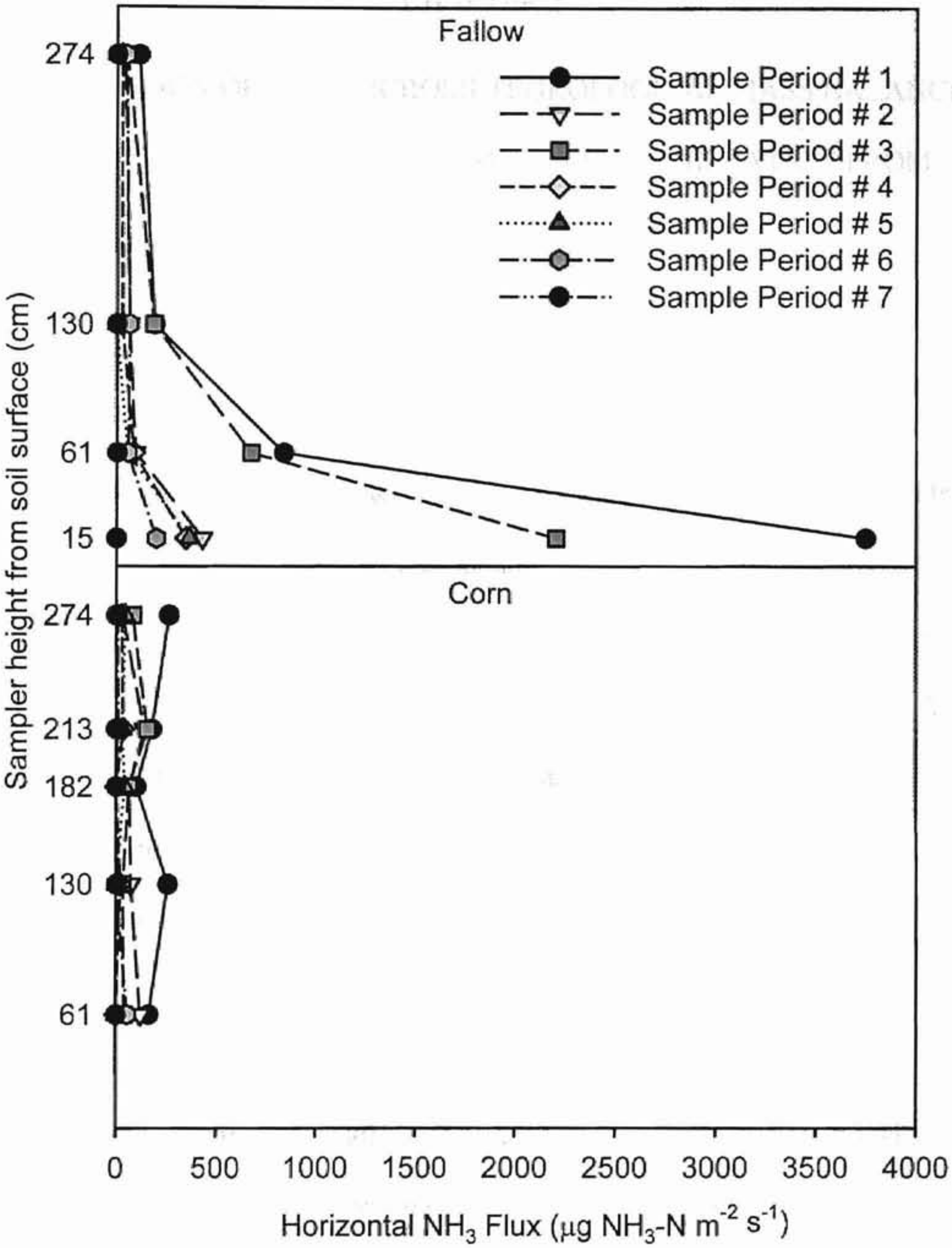

Figure 10: Average horizontal NH_3 flux profiles measured from two fallow plots and two plots of corn receiving swine effluent applications in July 1999.

CHAPTER 2

COMPARISION OF TWO MICROMETEOROLOGICAL MASS BALANCE METHODS TO DETERMINE AMMONIA VOLATILIZATION FROM SWINE EFFLUENT

ABSTRACT

The study objective was to compare the scientific and economic feasibility of two micrometeorological mass balance methods for measuring ammonia volatilization from applied swine effluent. An accurate and economical method of estimating NH_3 volatilization under field conditions is needed in order for agricultural producers to effectively and prudently use swine effluent as a nitrogen source for crop growth. The first method posts four masts on the perimeter of a circular plot (7.62 m radius) The second method replaces the four perimeter masts with one rotating mast fitted with a wind vane placed in the center of the plot. Experiments were carried out in December 1999, March 2000, and July 2000 on effluent applied and non-effluent applied plots located at the Oklahoma Panhandle Research and Extension Center, Goodwell, Oklahoma. Treated plots received a single application of 4,680 L (2.54 cm) of swine effluent. Immediately after effluent application NH_3 sampling began and continued for six days. A quadratic relationship was found between the two sampling methods for the net horizontal flux. A linear relationship existed between the vertical fluxes for the two methods. Using the perimeter mast measurements, cumulative NH_3 losses of 19.9, 36.4, and 55.5 kg NH_3-N ha^{-1} were calculated for the December, March and July experiments, respectively. Losses calculated using the center mast measurements were 13.9, 35.6, and 58.3 kg NH_3-N ha^{-1} in

December, March, and July, respectively. Because of the strong correlation between the two methods and the decreased cost of equipment and manpower associated with the center mast method, the center mast method is the more efficent method for determining ammonia volatilization from swine effluent application.

INTRODUCTION

Ammonia volatilization from cropland applied swine effluent can have a detrimental impact on the environment as deposition of atmospheric ammonia in nitrogen sensitive environments often results in eutrophication and acidification of surface waters (Schulze et al., 1989). In addition, ammonia volatilization significantly reduces the nutrient value of effluent (Zupancic, 1999). Therefore, an accurate estimate of volatized nitrogen loss under different environmental conditions is needed in order for agricultural producers to effectively and prudently use swine effluent as a nitrogen source for crop growth.

Denmead (1983) described three types of direct methods to determine nitrogenous gas movement between soil, plants and the atmosphere. These methods include: 1) calculating gas movement in the soil profile using diffusion theory, 2) enclosure methods which utilize the concentration of ammonia near the soil surface in the enclosure to determine the total gas flux from the soil surface, and 3) micrometeorological techniques to measure the vertical flux of NH_3 above the soil surface. Of these methods micrometeorological methods are preferred as they minimize the disturbance of environmental factors that effect NH_3 volatilization.

Early micrometeorological methods required expensive anemometers, flow meters and air pumps. Later, passive flux samplers (Leuning et al., 1985; Schjoerring et al., 1992) eliminated the need for complicated field equipment. Yet, passive flux samplers are not without problems. Samplers developed by Leuning et al. (1985) are expensive to construct (Wood et al., 2000). Samplers developed by Schjoerring et al. (1992) are more economical per unit, but the sampling method requires a large number of the sampling units and therefore, a large labor force to change and analyze the samples.

Wood et al. (2000) used a sampling system similar to that used by Schjøerring et al. (1992) but replaced the four perimeter masts with a single, center rotating mast with a wind fane to keep the samplers pointing into the wind. Wood et al. (2000) also used samplers constructed with one 200 mm glass tube instead of the two 100 mm tubes used by Schjoerring et al. (1992). Because the rotating mast is placed in the center of a circular plot the fetch is constant and equal to the radius of the plot, whereas the effective fetch length for the perimeter mast method is the diameter of the plot. After the initial investment, the rotating mast method is considerably less time consuming and more efficient to maintain than the perimeter mast method developed by Schjoerring et al. (1992). The improved efficiency is due to the decrease in the number of samplers used in the center mast method. Total sampling tubes required for the center mast method is one fourth of the number of tubes required by the perimeter mast method. Not only does this reduce the cost of tubes but also the time and expense associated with preparation and analysis of the tubes.

Because numerous environmental factors, such as wind speed, temperature, and relative humidity, effect ammonia volatilization, it is important to test new volatilization determination methods in various environments. The objective of this research is to compare NH_3 volatilization determination methods developed by Wood et al. (2000) and Schjoerring et al. (1992) at various times of the year in the semi-arid environment of the Southern Great Plains. Previously Wood et al. (2000) compared the use of glass tube passive flux samplers to passive flux samplers developed by Leuning et al. (1985). Both types of samplers were place on a rotating mast in the center of a circular plot in which there was an emission of NH_3 from the surface. Good correlation was found between the amount of NH_3 captured by each of the methods (Wood et al., 2000). The following study was conducted to determine if glass tube passive flux samplers mounted on a center rotating mast with a wind vane will measure NH_3 fluxes similar to those measured by a method developed by Schoerring et al. (1992) in which the glass tube passive flux samplers are mounted on four fix mast positioned on the perimeter of a circular plot

MATERIALS AND METHODS

Experiments were conducted on a Richfield clay loam ($pH \approx 7.5$) at the Oklahoma Panhandle Research and Extension Center, Goodwell, Oklahoma. Each experiment consisted of two fallow plots with a radius of 7.62 m in which one plot received 4,680 L of effluent (2.54 cm ha^{-1}) and the other received no effluent. The plot with no effluent was used to account for ambient NH_3 concentrations in the atmosphere. Four perimeter masts were positioned at 90-degree angles around the perimeter at the cardinal directions (N, S, E, W) and one rotating mast was placed in the center of each plot. It was assumed that any change in wind flow patterns caused by the masts would be negligible allowing for little or no disturbance of the horizontal flux profiles measured.

Passive flux samplers were constructed using two 100 mm tubes coated with oxalic acid, coupled with a 23 mm tube containing a solid steel disk with a 1 mm hole in the center. Two samplers were placed at 15, 61, 130, and 274 cm above the soil surface on both the perimeter and center masts in the treated and non-treated plots. Samplers were arranged on the perimeter mast so that the steel tip of one sampler pointed towards and the other away from the plot, as called for by the Schjoerring et al. (1992) method. On the center mast two samplers were placed so that the steel tip faced into the wind. The 200 mm tubes used by Wood et al. (2000) were not used in this study as they did not allow for estimation of blowby in the windward tube. Blowby, which is when NH_3 passes through the windward tube, may occur at wind speeds above 10 m s^{-1} (Sommer et al. 1996). Because wind speeds in the region can often exceed 10 m s^{-1}, complication with blowby needed to be considered.

Ammonia volatilization experiments were conducted in December 1999, March 2000, and July 2000. A single application of 4,680 L (2.54 cm) of effluent was applied at rates of 80, 199, and 215 kg NH_4^+-N ha^{-1} to the treatment plots in the December, March, and July experiments, respectively. The difference in NH_4^+-N application rates among the experiments is due to variable concentrations of NH_4^+ found in the effluent used. The weather conditions present during the three experiments are presented in table 1. As can be seen the methods were compared during a wide range of weather conditions.

After effluent application, NH_3 flux measurements were collected over a six day period. Samplers were changed approximately every 12 hours during the first two days, 24 hours during the next two days, and 48 hours the last two days. Adsorbed NH_4^+ was extracted from each 100 mm tube using 3 ml of deionized H_2O. Extractions were analyzed using Lachat Method 12-107-06-1-B (Lachat, 1993; Bloxham, 1993).

Equations used to calculate the horizontal flux, horizontal net flux, vertical flux, and cumulative NH_3 loss were modified from Schjoerring et al. (1992) and Wood et al. (2000) as described below. Horizontal flux (μg NH_3-N m^{-2} s^{-1}) was calculated for the center and perimeter mast methods at each height and mast using the equation:

$$F_h = \frac{A_1 + A_2}{2 * \pi * r^2 * K * \Delta t} \qquad [1]$$

Where:

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$$F_h = \frac{A_1 + A_2}{2 * \pi * r^2 * K * \Delta t} \qquad [1]$$

Where:

A_1 and A_2 = NH_4^+-N (μg) captured in tubes facing the same direction at each height.

r = radius (m) of the hole in the samplers steel plate.

K = correction factor (0.77), which corrects for the reduction in wind velocity through the sampler due to the steel plate.

Δt = duration (s) of the sample period.

Two equations were needed to calculate the vertical flux of NH_3 from the soil surface from the two methods. The vertical flux (μg NH_3-N m^{-2} s^{-1}), the amount of NH_3 leaving the soil surface per unit time, is calculated from the perimeter mast measurements using the equation;

$$F_v = \frac{1}{2x}\sum_{h=1}^{h=n}\sum_{m=1}^{m=n}[(F_{mh,s} + F_{mh,b}) - (F_{mh,sz} + F_{mh,bz})] * \Delta h \qquad [2]$$

Where:

x = radius (m) of the plot.

h = height (m) of the horizontal flux measurement.

m = mast at which the measurement was made.

$F_{mh,s}$ and $F_{mh,b}$ = horizontal fluxes (μg NH_3-N m^{-2} s^{-1}) measured from the tubes pointing into and away from the plot which received the effluent application, respectively.

$F_{mh,sz}$ and $F_{mh,bz}$ = horizontal fluxes (μg NH_3-N m^{-2} s^{-1}) measured from the tubes pointing into and away from the background plot, respectively.

Δh = height (m) interval between the samplers.

The vertical flux ($\mu g\ NH_3\text{-}N\ m^{-2}\ s^{-1}$) was calculated from the center mast measurements using the equation:

$$F_v = \frac{1}{x}\sum_{h=1}^{h=n}[(F_{h,s} + F_{h,b}) - (F_{h,sz} + F_{h,bz})] * \Delta h \qquad [3]$$

Where:

x = radius (m) of the plot.

h = height (m) if the horizontal flux measurement.

$F_{h,s}$ and $F_{h,b}$ = horizontal fluxes ($\mu g\ NH_3\text{-}N\ m^{-2}\ s^{-1}$) calculated from measurements from the windward and leeward tubes in the plot that received the effluent applications, respectively.

$F_{h,sz}$ and $F_{h,bz}$ = horizontal fluxes ($\mu g\ NH_3\text{-}N\ m^{-2}\ s^{-1}$) calculated from measurements from the windward and leeward tubes in the background plot, respectively.

Δh = height (m) interval between the samplers.

It should be noted that in equation [2] the diameter was used as the fetch length over which vertical NH_3 flux was measured, where as the radius was used in equation [3]. This is an important difference in the calculation of vertical NH_3 flux between the two methods. The center mast method only measures NH_3 volatilization from a fetch length equal to the radius of the plot where as the perimeter mast methods has an effective fetch length equal to the diameter of the plot (Schoerring et al., 1992).

The cumulative NH_3-N volatilization was calculated using the equation:

$$T_{Vol} = \sum_{t=1}^{t=n} F_{v,t} * \Delta t \qquad [4]$$

Where:

$F_{v,t}$ = vertical flux (μg NH_3-N m^{-2} s^{-1}) measured during each sampling period.

Δt = time duration (s) of each sampling period.

RESULTS AND DISCUSSION

A strong relationship exists between the horizontal flux measurements obtained from the perimeter and center mast methods (Figure 1). The overall relationship between the horizontal fluxes measured by the center and perimeter mast methods among experiments is quadratic with an $r^2 = 0.9777$ ($p < 0.001$). The relationships between the two methods within the experiments conducted in December 1999 and March 2000 are linear with $r^2 = 0.9336$ ($p < 0.001$) and 0.9777 ($p < 0.001$), respectively, and the relationship in July is quadratic with an $r^2 = 0.9965$ ($p < 0.001$). Using indicator variables to compare the regression trends among experiments, there was a significant difference between the linear and quadratic components for the March and July 2000 experiments ($p < 0.001$). The differences among the regression trends found in July and March 2000 result from differences in the shape of concentration boundary layers present in the two experiments and the resulting horizontal flux profiles (Figure 2). According to Wilson et al. (1982) wind speed and fetch length effect the height to which NH_3 will diffuse into the atmosphere before passing a vertical plane. Therefore differences in wind speed (Table 1) during the March and July 2000 experiments result in differences between the trend lines correlating the horizontal fluxes measured by the two methods in March and July 2000. Because the fetch length for the center mast method is equal to the radius of the plot, whereas the fetch length for the perimeter mast method is the diameter of the plot, horizontal fluxes calculated for the center mast method are lower than or equal to those measured by the perimeter method (Figure 2). The relationship between the horizontal fluxes measured by the two methods is not always linear because of the shape and concentration gradients of NH_3 within the concentration boundary layer above the plot. No significant differences were found when comparing the December 1999 experiment to the July or March 2000 experiment. This lack of significant difference between the regression trend found in December 1999 and those found in the following experiments is believed to be due to the narrow range of horizontal fluxes measured in December.

In the March and July 2000 experiments, comparisons of the vertical fluxes measured by the center vs. perimeter methods yielded slopes of 1.0074 ($r^2 = 0.9892$, $p < 0.0001$)) and 1.044 ($r^2 = 0.9589$, $p = 0.0006$), respectively. This indicates that the two methods are capable of producing similar results when NH_3 volatilization rates are relatively high. Although the vertical fluxes calculated from the center and perimeter mast methods correlated well ($r^2 = 0.8643$, $p = 0.0024$), the slope (slope = 0.4214) of the regression line suggests that the center mast measured a lower vertical NH_3 flux (Figure 3).

Vertical fluxes calculated from the two methods during all of the experiments are highly correlated (slope = 1.0645, $r^2 = 0.9681$, $p < 0.001$). Using indicator variables to compare the slopes among experiments no significant differences were found among the relationships between the vertical fluxes measured by the center and perimeter mast methods. This indicates the difference between the vertical fluxes measured by the center and perimeter mast methods in December are within the range of variability found in July and March. The low concentrations measured during the December 1999 experiment are believed to have caused the poor agreement between methods in this experiment. This suggests the center mast method as described in this paper is less sensitive at low volatilization rates. To improve the sensitivity of the method larger plots could be used to increase the surfaces from which NH_3 volatilizes or the samplers could be placed nearer the soil surface in order to collect NH_3 from within the concentration boundary layer. In addition, the sampling times for each sampling period could be increased. This would allow for the capture of more NH_4^+ in the samplers thereby reducing the need for low level NH_4^+ detection in the lab.

In December 1999 there were differences in NH_3 volatilized per sample period measured by the two methods (slope =0.5625, $r^2 = 0.9027$, $p = 0.0011$) (Figure 4). These differences indicate that at low concentrations the two methods do not measure similar NH_3 volatilization. Again this is because the center mast method is not sensitive at the low volatilization rates observed in December. At higher volatilization rates such as those in March and July 2000, the two methods yield very similar results with slopes of 0.9098 ($r^2 = 0.9098$, $p = 0.0002$) and 0.9591($r^2 = 0.8962$, $p = 0.0042$), respectively. The slopes associated with the three experiments were not found to be significantly different. This indicates that the differences between the NH_3 volatilized per sample period calculated form the center and perimeter mast methods in December are within the range of those differences found in proceeding experiments and that the differences found between methods in December are due to poor sensitivity at low concentrations. The NH_3 volatilized per sampling period measured by the two methods for all the experiments is highly correlated (slope = 0.9848, $r^2 = 0.9124$, $p< 0.001$) (Figure 4). Again this supports the idea that the two methods are capable of producing similar results, yet at low volatilization rates the effects of variability associated with sampling increases.

The total cumulative NH_3 volatilization calculated using the two methods were similar in the March and July 2000 experiments (Table 2). The center mast measured 35.6 and 58.5 kg NH_4^+-N ha^{-1} during the March and July 2000 experiments, respectively. While the perimeter mast method measured 36.4 and 55.5 kg NH_4^+-N ha^{-1} in March and July, respectively. The differences between the two methods are 2.2% in the March and 5.1 % in the July 2000 experiments. In the December 1999 experiment the two methods had less agreement. The center mast method measured 13.9 kg NH_4^+-N ha-^{1}, whereas the perimeter mast method measured 19.9 kg NH_4^+-N ha^{-1}, a difference of 30%. The difference between the amounts of total NH_3 volatilized calculated from the two methods in December again shows that the center method is less sensitive at low volatilization rates, yet from a practical aspect the 6 kg NH_4^+-N ha^{-1} difference between the cumulative volatilization measured by the two methods may have little significance.

The rates measured in December were two to three times smaller than those in July and March 2000. To increase the sensitivity of the methods at low volatilization rates the plot could be enlarged or the samplers could be placed closer to the ground. Enlarging the plot would increase the fetch length thereby increasing the horizontal fluxes passing through the tubes of both the center and perimeter masts. By placing the samplers closer to the soil surface they are more likely to be within the NH_3 concentration boundary layer above the soil surface. The sampling height used in the experiments describe in this paper were chosen to prevent NH_3 from leaving the plot above the top sampling height which would result in an underestimate of NH_3 loss. The results of these experiments show the importance of choosing appropriate plot sizes and sample heights when using the center mast methods. At high volatilization rates the center and perimeter mast methods produce similar result whereas at low volatilization rates such as those in the December experiment the sensitivity of the center mast method is lessened.

The use of the center mast method reduces the number of samplers needed by 75 percent. The perimeter mast method requires 448 samplers per plot at a cost of 560 USD, whereas the center mast requires only 112 samplers at a cost of 140 USD per plot (Table 3). Not only does the center mast method reduce the sampler cost, but also reduces the labor needed to prepare, analyze, and handle the tubes by 75 percent. These differences in labor and sampler needs dramatically decrease the cost of conducting multiple experiments needed for a better understanding of ammonia volatilization in various climatic regions.

It has been shown that the center mast method, developed by Wood et al. (2000) has the capability of producing results similar to those of the more proven method developed by Schjoerring et al. (1992). The use of the center mast method is a more economical method for determining NH_3 volatilization from soil applied swine effluent under field conditions. When NH_3 volatilization rates are high the center mast method as described in this paper could be used as a more economical method to determine ammonia loss in the field. With modifications of the method it has the potential to be a legitimate replacement for the perimeter mast method at low volatilization rates as well.

CONCLUSION

The center mast method has the capability of producing similar results to those of the more proven perimeter mast method. The vertical fluxes and cumulative NH_3 volatilization measured by the two methods are very similar in March and July 2000. Yet, in December 1999 the perimeter method measured larger fluxes and total cumulative NH_3 volatilization. Improvement could be made to the center mast method in order to increase its sensitivity at low volatilization rates such as those found in December. The plot size and/or the sample time durations could be increased. Also, the sampling height could be placed closer to the soil surface.

The center mast method is a considerably more efficient method to measure ammonia volatilization from surface applied swine effluent. The sampler costs as well as the labor costs associated with the center mast method are 25 percent of those associated with the perimeter mast method. The decrease in labor and equipment will more easily allow for experiments with multiple treatments and replications, which will allow for a better understanding of factors effecting ammonia volatilization.

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Table 1: Weather conditions present during the three experiments used to compare the center and perimeter mast methods.

Exp.	Temp.			Relative Humidity			Wind Speed			Rain
	Min.	Avg.	Max	Min.	Avg.	Max.	Min.	Avg.	Max.	
	--------°C --------			------- % -------			------m s^{-1}------			cm
Dec. 99	-8.5	2.3	16.1	6	54	93	0	5.3	12.9	<0.025
Mar. 00	-5	4.7	18.3	14	70	96	0.4	5.9	13	0.65
July 00	17.8	26.8	39.4	19	58.9	95	0.4	4.9	12.1	0.6

Table 2: Cumulative NH_3 volatilization.

	Cumulative NH_3-N Vol.	
Experiment	Perimeter	Center
	-------kg ha^{-1}-------	
Dec. 1999	19.9	13.9
Mar. 2000	36.4	35.6
July 2000	55.5	58.5

Table 3: Cost of samplers needed for the perimeter and center mast methods.

		Perimeter		Center	
	Cost per unit	# per Plot*	Cost per Plot	# per Plot	Cost per Plot
	U.S. Dollars		U.S. Dollars		U.S. Dollars
23 mm Tips	3.50	32	112.00	8	28.00
100 mm Tubes	1.00	448	448.00	112	112.00

* Assuming seven sample periods

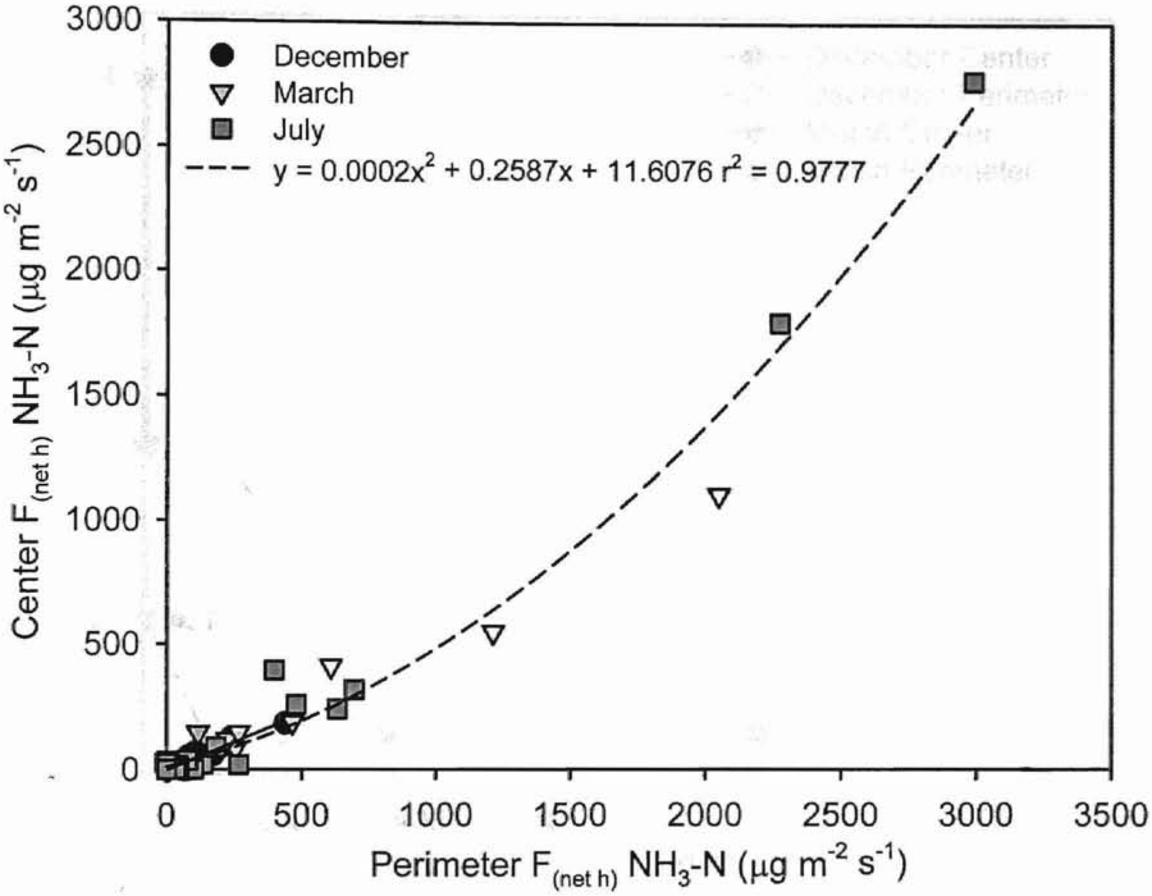

Figure 1: Net horizontal NH_3 flux measured during each sampling period and at each height above the plot by the center and perimeter mast methods from swine effluent applied to a calcareous soil at three application periods.

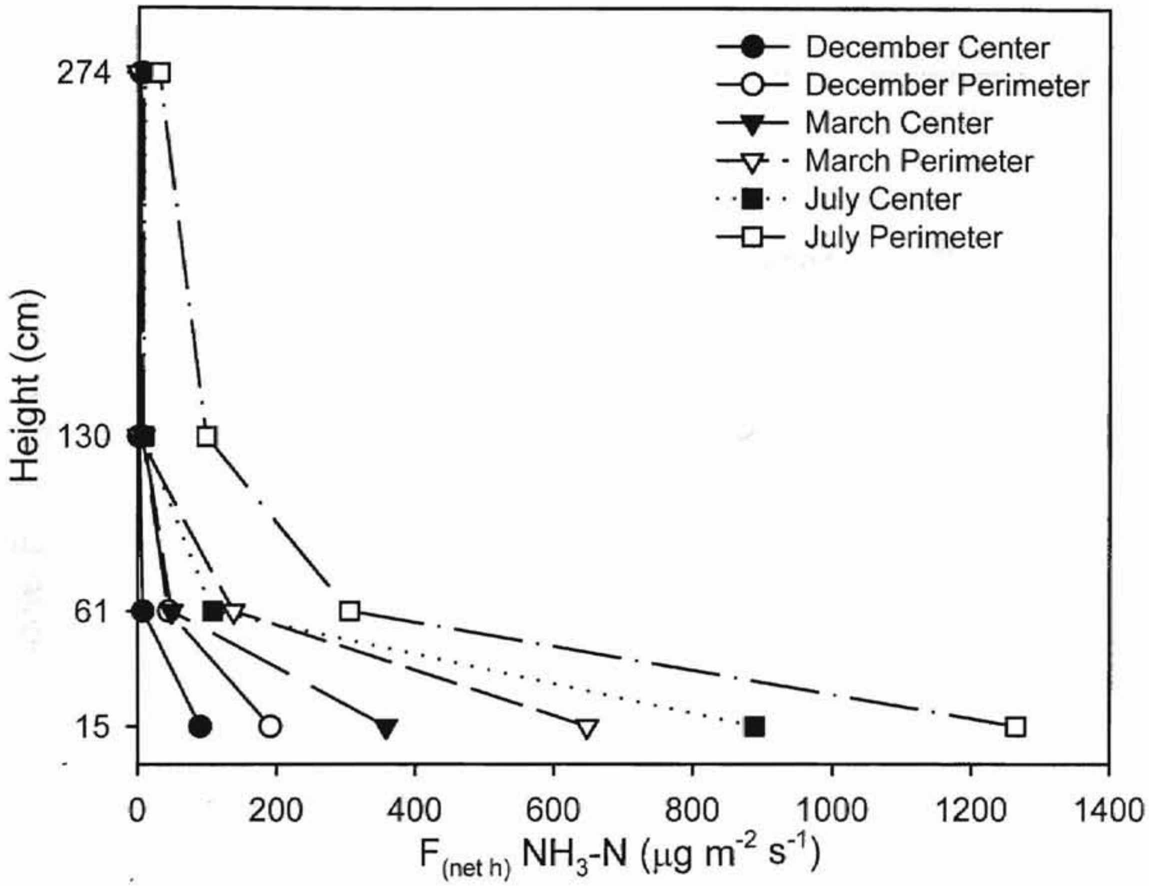

Figure 2: Profiles of the average net horizontal NH_3 flux measured throughout three experiments by the center and perimeter mast methods from swine effluent applied to a calcareous soil.

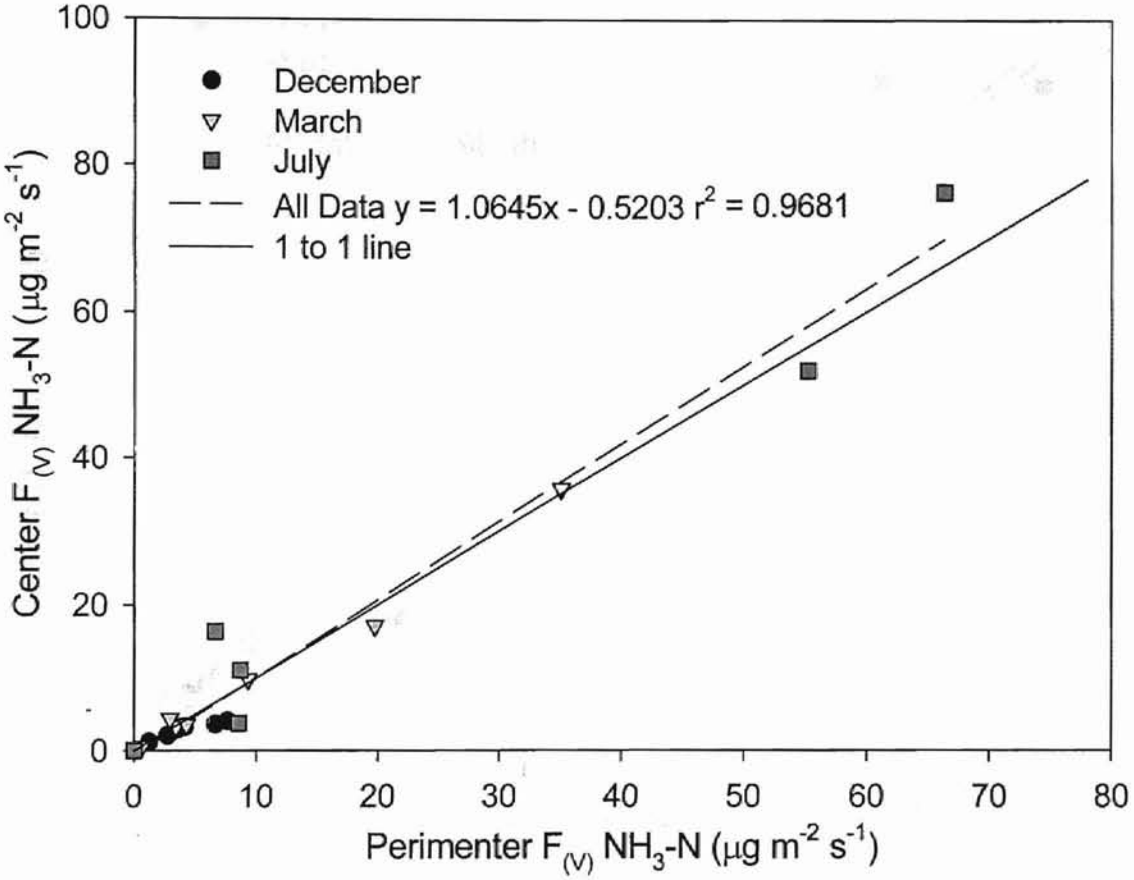

Figure 3: Vertical NH_3 flux measured during each sampling period by the center and perimeter mast methods at three application periods.

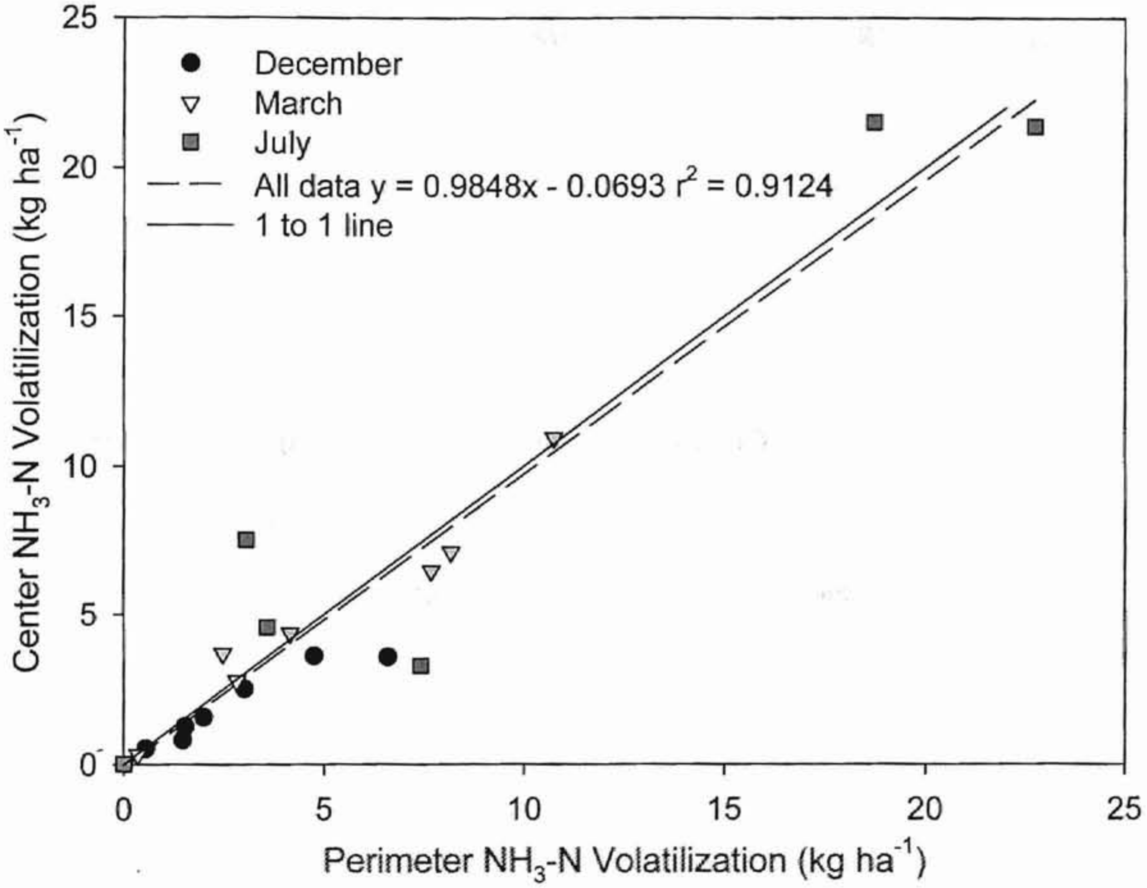

Figure 4: NH_3 volatilization from land applied swine effluent measured during each sampling period of three application periods.

CHAPTER 3

FEASIBILITY OF ACIDIFING SWINE EFFLUENT TO REDUCE NH_3 VOLAILIZATION

ABSTRACT

The objective of this study was to evaluate the feasibility of swine effluent acidification to reduce NH_3 volatilization. To determine the amount of acid needed to reduce the pH of swine effluent to 5, eight rates of 0.5 *N* sulfuric acid (0.0, 0.025, 0.0375, 0.05, 0.0625, 0.075, 0.0875, and 0.1 moles of $H^+ L^{-1}$) were added to 10 mL subsamples of five different lagoon samples. Effluent inorganic component information was input into the Menteqa2 Geochemical Assessment Model for Environmental Systems: (Version 4.0) to estimate equilibrium pH and to allow for a better understanding of chemical speciation after acid addition. The minimum amount of acid needed to reduce the pH of any effluent to below 5.0 was 0.05 moles of $H^+ L^{-1}$ effluent. This acid treatment initially reduced the pH to below 5.0 but after 15 minutes the effluent pH had increased to above 7.0 due to the buffering capacity of the effluent. Effluent used in this study had an average NH_4^+-N content of 426 mg L^{-1}. Using this effluent it would require approximately 235,000 L effluent ha^{-1} to provide 100 kg NH_4^+-N ha^{-1}. In order to acidify this quantity of effluent at a rate of 0.5 moles $H^+ L^{-1}$ effluent, 326 L of 36 *N* sulfuric acid would be required per hectare. This volume of acid would not maintain effluent pH at 5.0, the level previously suggested to significantly reduce NH_3 volatilization. The equilibrium mechanisms, which determine the pH of effluent after acidification are controlled by the kinetics of the system, therefore effluent can not treated as a simple H_2O system.

INTROUCTION

A significant amount of the nitrogen present in swine effluent can be lost to ammonia volatilization after land application (Beauchamp et al., 1982; Zupancic, 1999). Previous work on calcareous soils found that a swine effluent application of 221 kg NH_4^+-N ha^{-1} resulted in 83 kg NH_4^+-N ha^{-1} loss due to volatilization (Zupancic, 1999). At the current cost of nitrogen fertilizer, this translates into a 42.00 USD ha^{-1} nitrogen loss. Not only is there a direct fertilizer and monetary loss, but the volatilization of ammonia from applied animal waste also contributes to the nutrient loading of oligotrophic ecosystems through deposition of effluent derived atmospheric nitrogen. This deposition can result in eutrophication of ecosystems and changes in plant and animal species distribution (Schulze et al., 1989).

Ammonia volatilization can dramatically be reduced if effluent is injected into the soil (Svensson, 1994; Hoff et al., 1981), unfortunately injection application of effluent in the Oklahoma Panhandle where 60 percent (National, 1999) of Oklahoma's swine are produced is not a viable option due to large equipment and human resource costs. In this region effluent application via the center pivot irrigation systems is the most common mode of application. This form of application lends itself to the use of effluent amendments that could be added to the effluent prior to application.

Al-Kanani et al. (1992) evaluated several amendments (sphagnum peat moss, sulfuric acid, phosphoric acid, monocalcium phosphate monohydrate, elemental S, and calcium carbonate) as to their ability to reduce ammonia volatilization from fresh hog manure. They concluded that compounds that reduce the pH of the manure solution significantly reduced ammonia volatilization. When the pH of the manure solution was reduced to 6.0 with phosphoric acid, ammonia volatilization was reduced to 10% the volatilization at pH 6.8. At pH 4.0, volatilization was reduced further to 0.001% of the volatilization at pH 6.8. The effecacy of the compounds tested to acidify and decrease ammonia volatilization from the manure solution varied significantly. Phosphoric acid was found to be most effective in reducing volatilization while sulfuric acid was least effective at the same pH value. Nitric acid added at a concentration of 10 *M* to cattle slurry at a rate of 1.4% by volume reduced ammonia volatilization by greater than 75 percent after application to the soil (Stevens et al., 1992). Pain et al., (1990) added 2 *M* sulfuric acid in a range from 30 to 85 mL L^{-1} of cattle slurry in order to reduce the pH to 5.5. This treatment resulted in 30 to 60 percent less NH_3 volatilized from the slurry after application. The average application used in this experiment was 79.25 m^3 of slurry ha^{-1}. Using the low acid addition of 30 mL 2 *M* H_2SO_4 L^{-1} of slurry this application rate would require 264.2 L of 36 *N* sulfuric acid per hectare to reduce the pH to 5.5.

The objective of our study is to evaluate the feasibility of swine effluent acidification to reduce NH_3 volatilization and to evaluate the equilibrium pH of effluent after acid addition with an equilibrium model. Preliminary work suggested that additions of acid to effluent did not simply reduce and stabilize effluent pH, but instead reduced the pH momentarily after which the pH would increase. Previous research has shown that acidification of animal waste is effective in dramatically reducing NH_3 volatilization. However, at the acidification rates suggested large amounts of acid would be needed to acidify the amount of animal waste commonly applied to cropland in production systems. Because little research has focused on the quantity of acid needed to acidify anaerobicly treated swine effluent this study will focus on the amount of acid needed to sufficiently acidify swine effluent and maintain the pH at levels below 5. Evaluation of the effluent inorganic content using the Minteqeqa2 Geochemical Assessment Model for Environmental Systems: Version 4.0 allows for the estimations of equilibrium pH after addition of acid to the system. It will also allow for future analysis of inorganic speciation that may explain differences in NH_3 volatilization found by previous research (Al-Kanani et al., 1992) due to different acids used to acidify animal waste. For this study Minteqa2 will only be used to estimate the equilibrium pH of the effluent.

METHODS AND MATERIALS

Effluent was collected from a lagoon located on a sow breeding farm in southeastern Oklahoma (Effluent 1), two lagoons located on swine finisher farms in the Oklahoma Panhandle (Effluent 2 and 3) and two lagoons located on swine nursery farms in the Oklahoma Panhandle (Effluent 4 and 5) . The amount of acid needed to reduce the pH to below 5, for an extended period of time was determined by adding a one time application of 0.0, 0.5, 0.75, 1.0, 1.25, 1.75, and 2.0 mL of 0.5 N sulfuric acid to 10 mL effluent subsamples. Prior to acid addition and throughout the test period the 10 mL samples were stirred to mix the acid into the effluent. The treatments were replicated three times and effluent pH was measured directly after acid addition and every fifteen minutes for 135 minutes. Treatment effects were analyzed as a completely randomized design with repeated measures using the mixed procedure.

Effluent dry matter contents were determined by drying 20 mL aliquots of effluent at 105 °C 15 hours and reweighing. A subsample of each effluent sample was filtered through a 0.45 μm filter to remove the solid portion the effluent. Total effluent Mg, Ca, Na, K, and B concentrations were determined for a filtered (0.45 mm) subsample using inductively coupled plasma atomic absorption analysis. The filtered subsample was also analyzed for NH_4, and PO_4 using flow injection analysis and CO_3, HCO_3 through acid titration. The inorganic composition of the effluent reported in table 1 was analyzed using the Menteqa2 Geochemical Assessment Model for Environmental Systems: Version 4.0 to predict the equilibrium pH of the filtered effluent after acid addition. This analysis gives an estimate of the effluent pH at equilibrium which may not have been reach during the 135 minutes the effluent-acid mixture was tested for changes in pH.

RESULTS AND DISCUSSION

Acid additions had a significant effect on pH of all the effluent samples at each pH measurement interval ($p < 0.05$). Similar changes in pH with treatment and time were observed among effluents 1, 2, and 3 (Figures 1, 2, and 3) whereas effluents 4 and 5 (Figures 4 and 5) were more buffered relative to changes in pH. There was an interaction between acid treatment and time when looking at all effluent samples ($p < 0.05$), therefore the effect of treatment was evaluated at each measurement time and the effect of time was evaluated for each acid treatment. Acid additions to samples 1, 2, and 3 equal to or greater than 0.0625 moles of $H^+ L^{-1}$ effluent resulted in an initial pH drop to below 3.0 with no significant increase in pH over time (Table 2). Acid additions of 0.025, 0.0375, and 0.05 moles $H^+ L^{-1}$ effluent resulted in an initial drop in pH followed by a significant (Table 2) increase in pH over time due to the buffering capacity of the effluent and the time needed for the system to reach equilibrium. Previous research has not addressed the buffering capacity of effluent and the subsequent increase in pH after the initial drop following acid addition. This subsequent increase in pH is due to slow reaction rate of the buffering mechanisms present in the effluent.

Upon the addition of sulfuric acid, the pH drop due to an increase in the hydrogen concentration in the effluent. With time, the inorganic and organic constituents of the effluent react with the hydrogen to buffer the system and increase the pH. The carbonates and bicarbonates react with the hydrogen to produce carbonic acid Eq. [1] and Eq. [2]. Carbonic acid then reacts to form dissolved carbon dioxide and water Eq. [3]. The dissolved carbon dioxide is then transferred to the atmosphere.

$$CO_3^{2-} + H^+ \Leftrightarrow HCO_3^-, \qquad [1]$$

$$HCO_3^- + H^+ \Leftrightarrow H2CO_3^o, \qquad [2]$$

$$H_2CO_3^o \Leftrightarrow H_2O + CO_2, \qquad [3]$$

These reactions are not spontaneous, thus the hydrogen concentration in the solution is high immediately following acid addition. As the carbonate and bicarbonate react with hydrogen, the solution pH increases until equilibrium is reached. The increase in pH of the unacidified effluent samples can be explained using equations 1 through 3. Biological activity in the lagoon elevates the carbon dioxide concentration in the effluent, which forces equations 1, 2, and 3 to the left, thereby increasing the hydrogen concentration and decreasing the pH of the effluent. Stirring the effluent releases carbon dioxide, which results in an increase in effluent pH.

The similarities between the responses of effluent 1 (collected in southeastern Oklahoma) and effluents 2 and 3 (collected in the Oklahoma panhandle) to the addition of acid suggest the buffering capacity of effluent is not affected by regional environmental factors such as water quality or soil type, which could affect the carbonate and bicarbonate content. The buffering capacity of swine effluent must be affected more by manure loading rate or other management practices that affect the dissolved carbonate and bicarbonate content and suspended solid content of the effluent.

The acid treatments significantly decreased the pH of effluent 4 over all time intervals and the pH significantly increased with time within treatments of 0.025, 0.0375, 0.05, 0.0625, and 0.075 moles $H^+ L^{-1}$ effluent (Table 2). The high LSD (Figure 4) calculated for Effluent 4 seems be due to the 0.0875 moles $H^+ L^{-1}$ effluent treatment falling near the buffer breakthrough curve (Figure 4). Small errors in acid addition or effluent measurement, produce large differences in pH from one replication to the next. The addition of 0.0625 moles $H^+ L^{-1}$ effluent was initially successful in reducing the pH of effluent 4 to below 5, although the pH increased to above 5 after fifteen minutes and continued rising throughout the experiment (Figure 4).

For effluent 5 the acid treatments again significantly reduced the pH of effluent over all time intervals and pH significantly increase with time within all treatments except the 0.1 moles $H^+ L^{-1}$ effluent treatment (Table 2). The highest acid treatment was the only treatment capable of reducing the pH below 5, although the pH was maintained below 5 (Figure 5).

The inorganic contents of the filtered effluent are shown in Table 1. These parameters were entered into Menteqa2 along with the appropriate sulfuric acid additions to predict the equilibrium pH after the addition of acid. The differences between the predicted and measured pH curves (Figures 1 to 5) may be due to the buffering capacity of the solid matter filtered from the effluent prior to chemical analysis which would contain organic and inorganic particulates, which may buffer against changes in pH. Slow kinetics associated with the transformation of carbonates to carbon dioxide and its release to the atmosphere (Eqn [1], [2], and [3]) may have increased the deviation between the predicted and final measured pH because equilibrium was not reached.

The minimum acid treatment capable of reducing the pH below 5.0 was 0.05 moles H^+ L^{-1} effluent. This was achieved on effluent 3 however it did not persist after the initial pH reading which increased to near pH 6 after 15 minutes.

Effluent used in this study had an average NH_4^+-N content of 426 mg L^{-1}, therefore, approximately 235,000 L effluent ha^{-1} would be needed to provide 100 kg NH_4^+-N ha^{-1}. In order to acidify this amount of effluent to pH 5.0 using an acid rate of 0.05 moles H^+ L^{-1} effluent, 326 L per hectare of 36 *N* sulfuric acid would be required. The lowest acid treatment of 0.025 moles H^+ L^{-1} effluent, which at best reduced the effluent pH to below 7 for 30 minutes, would require 136 L of 36 *N* sulfuric acid per hectare.

The approximate cost of industrial sulfuric acid, not including transportation and application costs, is approximately 44 USD per metric ton (Gena, A. 1999). At this price, the cost of acidifying 235,000 L, the amount of effluent used in this study needed to supply 100 kg NH_4^+-N ha^{-1}, at the 0.05 moles H^+ L^{-1} rate would be approximately 21 USD. At the current price of anhydrous ammonia the 100 kg NH_4^+-N ha^{-1} found in this volume of effluent on average has a monetary value of approximately 50 USD. Therefore, on a material cost basis it may be economical to acidify the effluent in order to preserve the nitrogen content of the effluent. Yet, from a practical stand point the volume of acid needed would be costly to transport, as well as hazardous to producers using the concentrated acid. The acid would also be corrosive to irrigation equipment. The reaction of the sulfuric acid with the carbonate and bicarbonate in the effluent would evolve carbon dioxide, which could adversely affect the irrigation process. Further economic analysis on the cost associated with these aspect of effluent acidification is needed in order to determine if it acidification is truly economically feasible.

CONCLUSIONS

To reduce the pH of effluent found in Oklahoma to below 5.0 a significant amount of acid must be added. The minimum treatment capable of reducing the pH to 5.0 was 0.05 moles $H^+ L^{-1}$ effluent, yet this treatment was not sufficient to maintain the pH below 5.0.

This study not only revealed the capacity to which swine effluent can resist changes in pH but that the equilibrium mechanisms in place are controlled by the kinetics of the system. Initially, acidification can reduce the pH of the effluent but as reactions take place the pH will increase with time to an equilibrium pH. This buffering capacity is due in large part to the carbonate and bicarbonate content of the effluent but may also be attributed in part to the buffering capacity of the suspended solids in the effluent.

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Table 1: Inorganic content and dry matter content of swine effluent samples.

Effluent #	Na	Ca	Mg	K	Cl	SO_4	CO_3	HCO_3	B	NH_4-N	PO_4-P	DM %
	mg L^{-1}											
1	419	26	15	879	386	90	259	2401	2.56	307	57	0.44
2	232	19	22	727	376	58	696	1459	1.57	400	10	0.27
3	194	14	20	625	266	54	538	1327	1.48	336	9	0.22
4	228	33	46	808	388	55	142	2425	1.86	356	13	0.46
5	346	63	5	1058	418	221	0	4795	2.47	937	30	0.61

Table 2: Significance of pH change for each effluent analyzed as a function of time, within each sulfuric acid treatment.

Effluent #	Treatment (moles H^+ L^{-1} effluent)							
	0	0.025	0.0375	0.05	0.0625	0.075	0.0875	0.1
1	NS	*	*	*	NS	NS	NS	NS
2	*	*	*	*	NS	NS	NS	NS
3	*	*	*	*	NS	NS	NS	NS
4	NS	*	*	*	*	*	NS	NS
5	*	*	*	*	*	*	*	NS

* = Significant at the p = 0.05 level

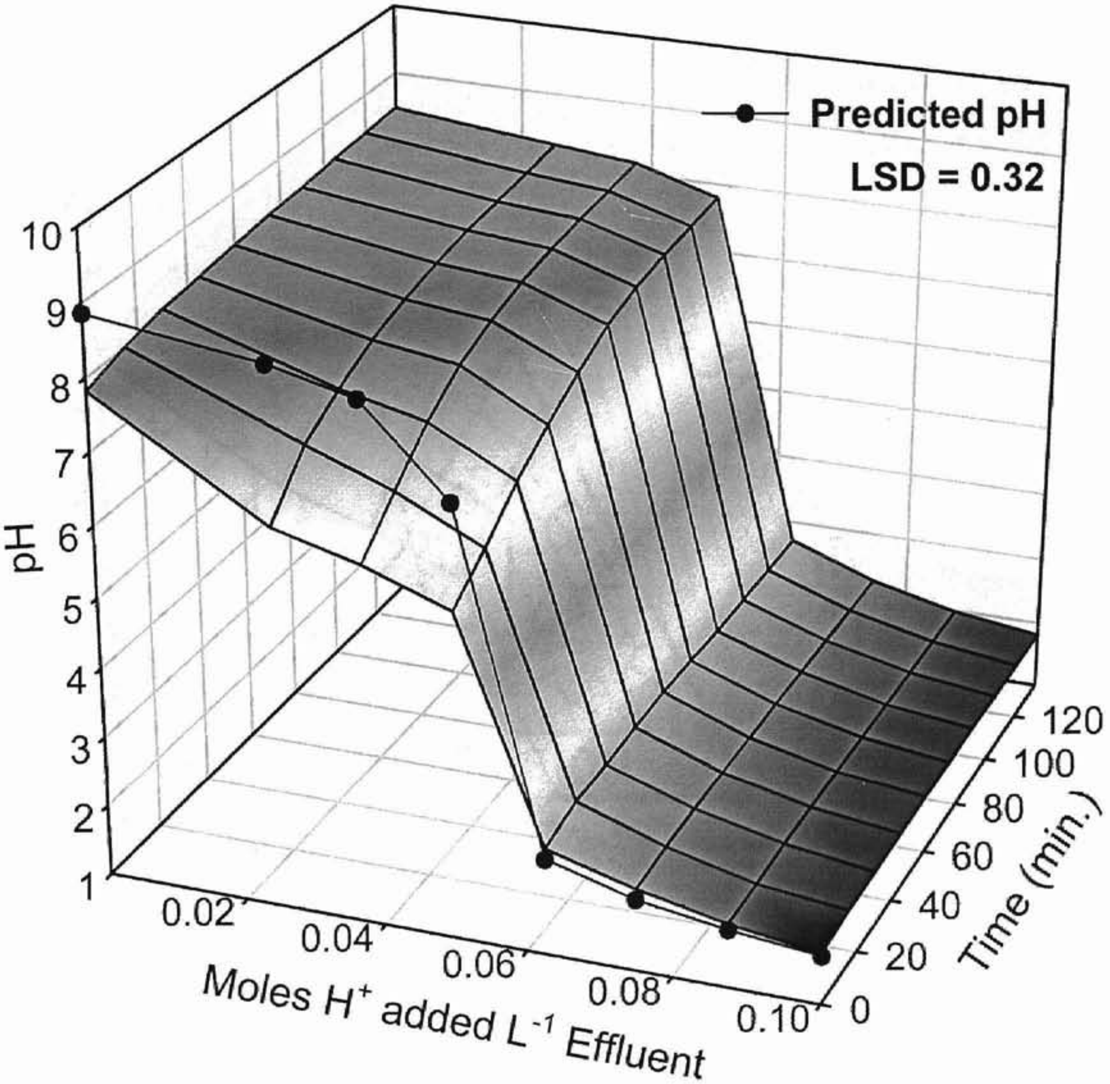

Figure 1: Predicted and measured effects of sulfuric acid addition and time on the pH of swine effluent 1.

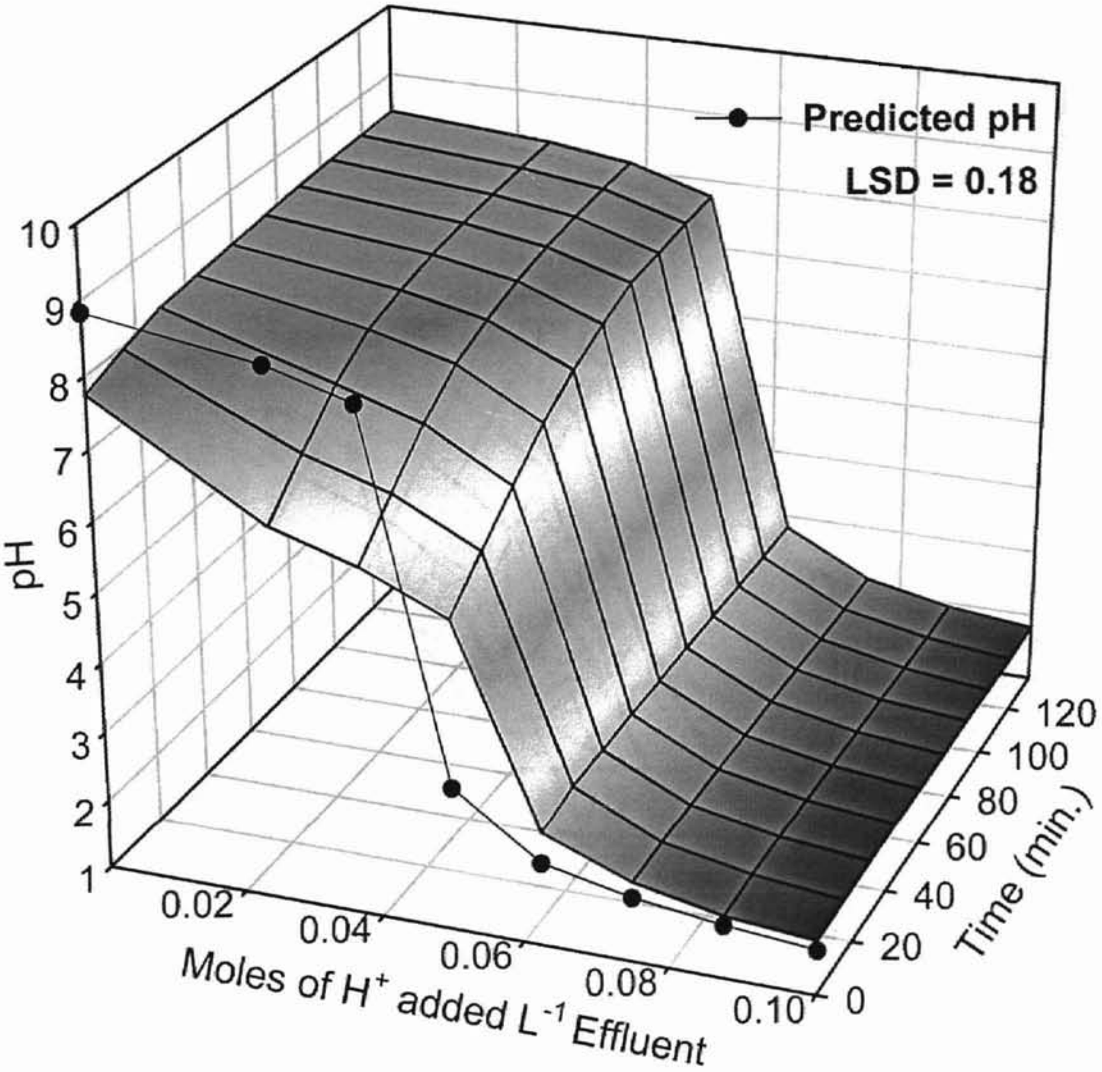

Figure 2: Predicted and measured effects of sulfuric acid addition and time on the pH of swine effluent 2.

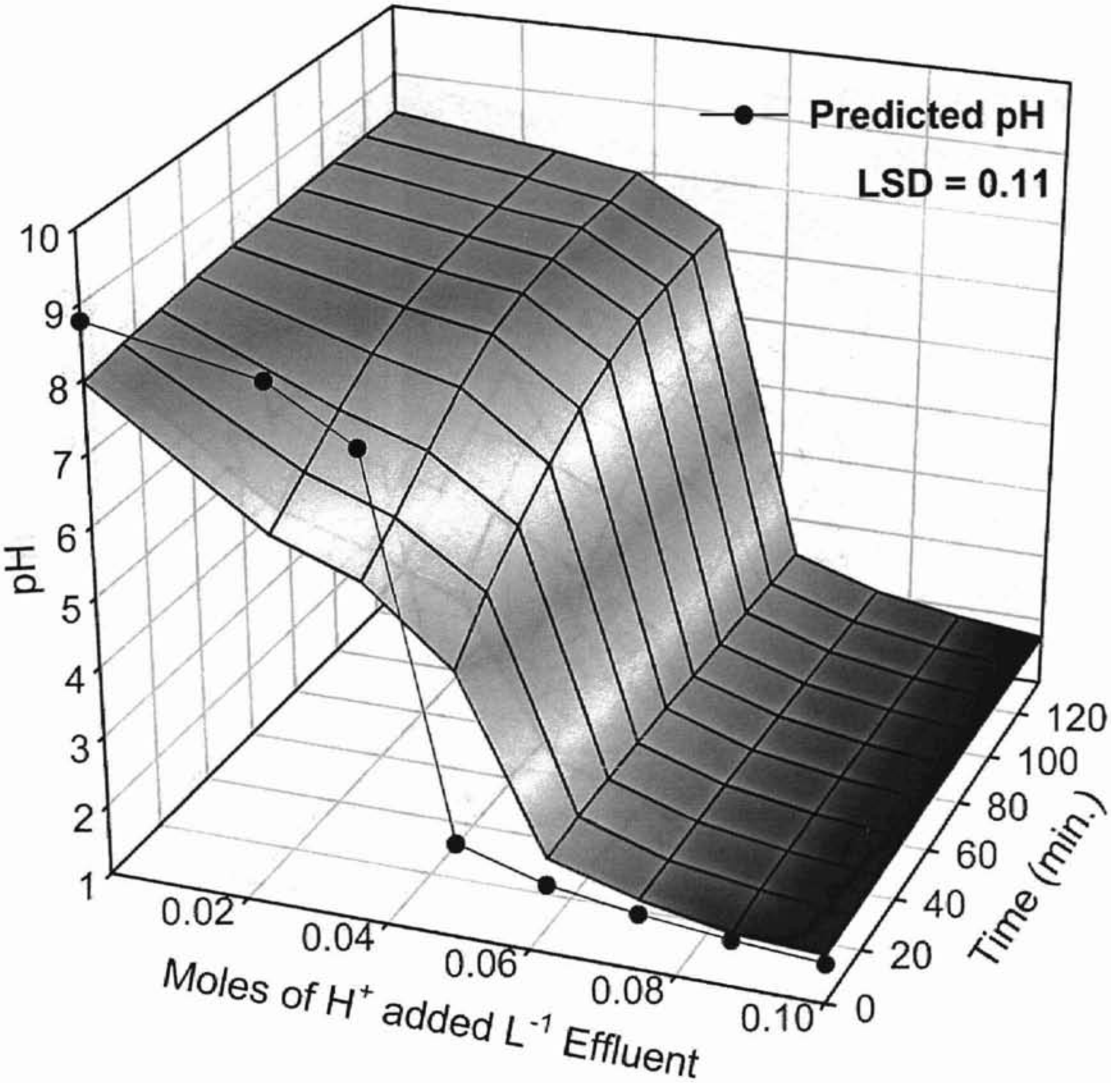

Figure 3: Predicted and measured effects of sulfuric acid addition and time on the pH of swine effluent 3.

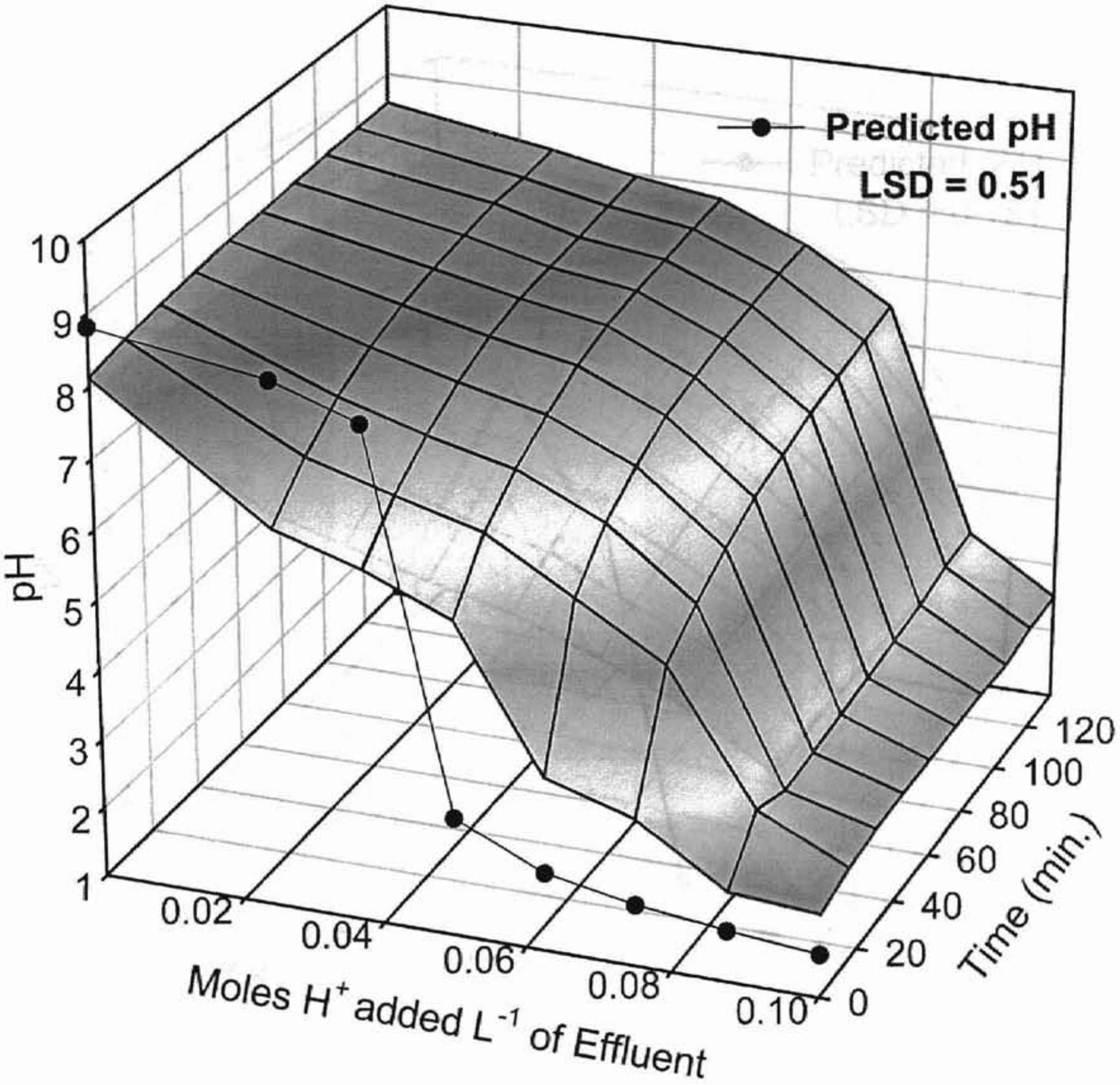

Figure 4: Predicted and measured effects of sulfuric acid addition and time on the pH of swine effluent 4.

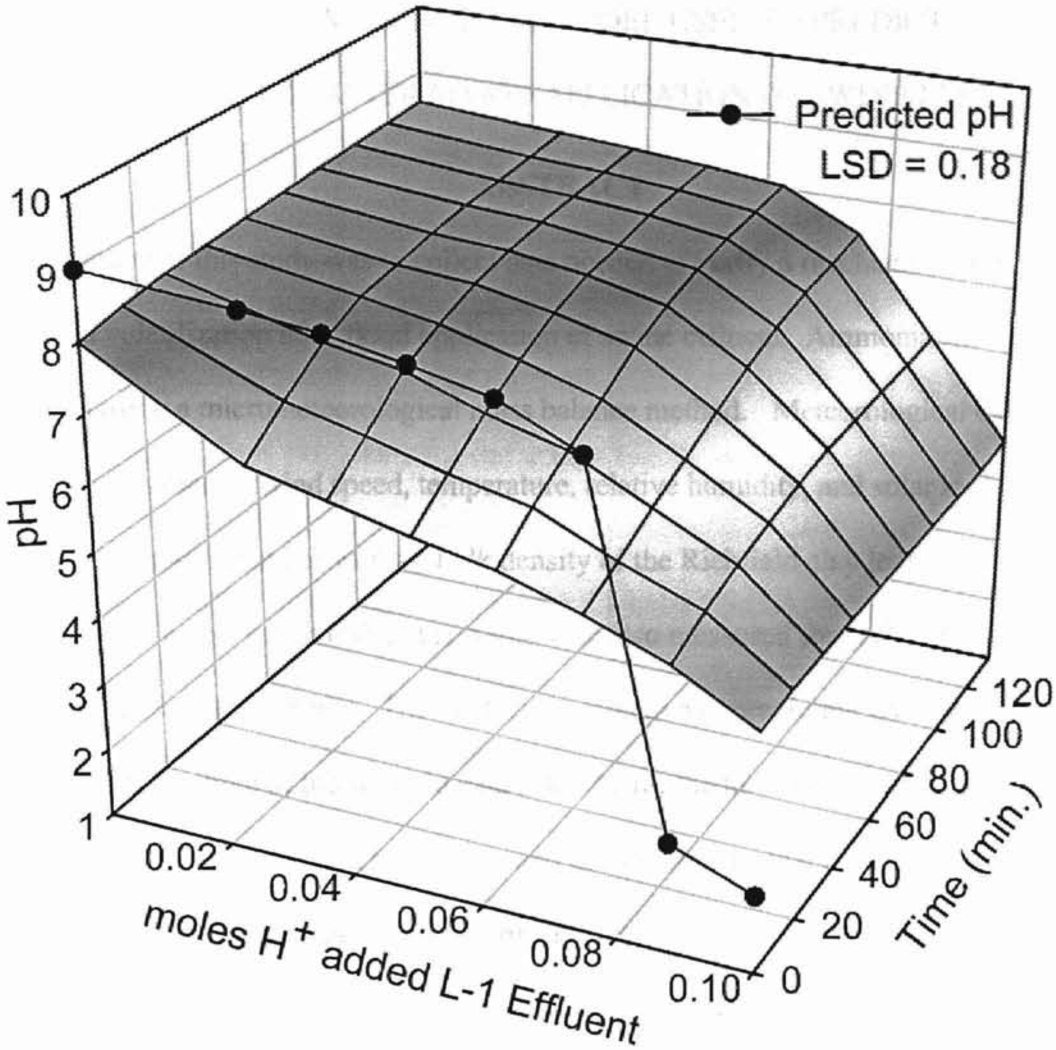

Figure 5: Predicted and measured effects of sulfuric acid addition and time on the pH of swine effluent 5.

CHAPTER 4

VERIFICATION OF A MECHANISTIC MODEL USED TO PREDICT AMMONIA VOLATILIZATION AFTER FLOOD APPLICATION OF SWINE EFFLUENT

ABSTRACT

The objective of this study was to collect data needed to verify a mechanistic model of ammonia volatilization after flood application of swine effluent. Ammonia flux data was collected using a micrometeorological mass balance method. Meteorological data collected consisted of wind speed, temperature, relative humidity, and solar radiation. The particle size distribution, as well as, bulk density of the Richfield clay loam was determined. The pH of the effluent and soil were also measured for each experiment as input parameters of the model. The model was effective in predicting the cumulative NH_3 volatilization for three of the six field data sets. As for the three data sets for which the model predictions did not match the measured data, it appears that the largest deviation between the predicted and measured volatilization occurred during the first sampling period of the experiments. This may be due to the non-uniform distribution of the ponded surface within the plot after application. The effect of this non-uniform distribution of the liquid surface may have been more dramatic for the three field data sets the model did not match because meteorological conditions or effluent pH measurements favored dramatic volatilization rates during ponding. Sensitivity analysis of the model will provide a better idea of those parameters that dramatically affect the predicted volatilization rates. Currently the model is a valuable tool that can be used to evaluate the measurements taken in the field and improve our understanding of ammonia volatilization from soil applied swine effluent.

INTRODUCTION

The field conditions present during the NH_3 volatilization studies greatly affect the results of ammonia volatilization experiments. Soil properties that affect ammonia volatilization include the cation exchange capacity, the pH, the pH buffer capacity, soil moisture, and the calcium carbonate content of the soil (Freney, 1983). Svensson (1994) stated that the manure characteristics affecting NH_3 volatilization can be divided into chemical and physical properties. The chemical properties include the total ammoniacal nitrogen concentration, pH, alkalinity, buffering capacity, and ionic strength and activity. The physical properties of manure affecting volatilization include dry matter content, fluidity, and viscosity. As for the environmental factors affecting NH_3 volatilization, Brunke et al. (1988) found NH_3 volatilization rate to be consistently correlated with wind speed and solar radiation. Also, temperature and air humidity can affect the rate of ammonia volatilization (Sommer et al., 1991).

Because many of these factors are interrelated it is difficult to determine what controls NH_3 volatilization in the field. Most often, controlled lab experiments are used to determine the affects of only a few of the factors affecting NH_3 volatilization. Attempting to determine the effect of environmental, soil, or effluent factors often results in poor correlation (Sommer et al., 1997; Brunke et al., 1988). Because of the multitude of factors and complexity of their interactions a model of the processes involved in NH_3 volatilization after the application of swine effluent is needed. Not only does a model assist in understanding the processes involved in ammonia volatilizaion, but if it can be verified by experiments conducted in the field it will be helpful in predicting nitrogen loss prior to or following applications. A number of attempts have been made to model ammonia volatilization from soil systems. Earlier models dealt with NH_3 volatilization from applied urea (Singh Nye, 1986). This model is a mechanistic model that describes the changes in soil pH, the transformations of urea, and ammoniacal nitrogen throughout the soil column and the processes involved in NH_3 volatilization. Recently similar models have been developed to simulate volatilization from soil-manure systems. Van Der Molen et al. (1990) derived a model of ammonia volatilization from land applied cattle slurry. This model described the movement and transformations of ammonia in the soil. It also accounts for climatic factors that affect volatilization. The drawback to the model is that it assumes instantaneous infiltration of the slurry after application. Genermont and Cellier (1997) developed another mechanistic model composed of six sub models which describe: 1) physical and chemical equilibia in the soil 2) aqueous and gaseous ammoniacal N transfers through the soil 3) gaseous ammonia transfer from the soil to the atmosphere 4) water transfer in the soil 5) heat transfer in the soil and 6) energy budget water and heat transfer between the soil and the atmosphere. Although the model described by Genermont and Cellier (1997) sufficiently predicted cumulative NH_3 loss it did not adequately describe the effects of water infiltration and soil drying. This caused it to underestimate ammonia volatilization during the first few days of the simulation and to over estimate volatilization during later time periods. During calibration of the model they found it necessary to use a constant pH value and also had to adjust the system pH up from 7.5 to 7.8 in order for the model estimations to fit the measured volatilization. A model developed by Hengnirun et al. (1999) uses three influencing factors to describe the volatilization rate from the soil surface. They include the influence of the cation exchange capacity of the soil, wind speed and temperature. This model does not account for movement or transformation of ammoniacal nitrogen within the soil profile it only deals with the transfer of NH_3 from the soil surface to the atmosphere.

An ideal model would be one that incorporates the previously mentioned soil and manure characteristics as well as the meteorological factors that affect the volatilization of ammonia from soil applied swine effluent. The model would need to accurately show the change observed in the field, such as diurnal fluctuation caused by fluctuations in net radiation and different volatilization rate distributions caused by differences in soil moisture from one site to the next. This may be possible through the modification of the previously mentioned mechanistic models. A working model that describes the movement of water, the transformation and movement of ammoniacal nitrogen and the processes of ammonia volatilization has been developed by Wu et al. (2001) from the principles similar to those described by Singh and Nye (1986). Principles described in the papers by Van Der Molen et al. (1990), Genermont and Cellier (1997), and Hengnirun et al. (1999) were also used to account for effluent and environmental characteristics.

Field verification of the model was needed in order to determine the models ability to predicted NH_3 volatilization in field conditions. The objective of this study was to collect data needed to test the mechanistic model developed by Wu et al. (2001).

METHODS AND MATERIALS

Soils Data

Equilibrium adsorption isotherm for ammonium adsorption to the Richfield clay loam was determined with a method similar to that used by Singh and Nye (1984). Eight solutions with concentrations of ammonium ranging from 0.005 to 0.12 M NH_4Cl in 0.1 M

$CaCl_2$ were prepared. Solution was added at 10 mL per 1 g of soil in a centrifuge tube and shaken for one hour. They were then centrifuge and the supernate was analyzed for NH_4^+-N concentration using Lachat Method 12-107-06-1-B (Bloxham, 1993). This isotherm was replicated three times from a composite sample of the Richfield clay loam.

Bulk density of the Richfield clay loam measured in July 2000 using a 7.62 cm core to a depth of 15.24 cm. The cores (n=3) taken were then dried at 105° C for 15 hours and weighed. Particle size distribution was determined on three samples of the Richfield clay loam using the pipet method described by Gee and Bauder (1986). Soil moisture content was measured prior to the experiments conducted in March 2000 and July 2000 to a depth of 50 cm at 10 cm increments using 4.5 cm cores. These cores were sectioned and weighed and then dried at 105° C and reweighed. Composite soil samples consisting of 15 cores were taken to a depth of 15.24 cm from each plot for determining soil pH. Soil pH was determined using a 2:1 water:soil ratio.

Effluent Data

Effluent pH was also measured in the field as well as in the lab. The effluent infiltration rate was estimated visually by noting the time at which the effluent was no longer ponding on the soil surface. Effluent ammonium concentrations were measured on effluent samples, which were acidified directly after sampling with 5 *N* sulfuric acid to a pH less than 4. The acidified sample was then filtered and analyzed for NH_4^+-N using Lachat Method 12-107-06-1-B (Bloxham, 1993).

Meteorological Data

Meteorological data including wind speed, temperature, relative humidity, solar radiation, and precipitation was obtained from the Oklahoma Mesonet weather station located within a 1.6 km of all NH_3 volatilization plots used in this study at the Oklahoma Panhandle Research and Extension Center, Goodwell, Oklahoma.

Ammonia Volatilization Data

Cumulative NH_3 volatilization from surface applied swine effluent was measured as described in chapter 1. A clear understanding of what is measured by the micrometeorological mass balance method is needed in order to insure that the model is estimating ammonia volatilization from the same physical surface, in the same way that the method measures ammonia volatilization.

The micrometeorological mass balance method described in chapter 1 measures the average vertical NH_3 flux leaving the surface of the plot. Through horizontal flux measurements this average vertical NH_3 flux can be estimated if we assume the rate of NH_3 volatilization is uniform over the entire plot. The vertical flux is derived from the horizontal flux measured at each height above the plot as restated from Schjøerring et al., (1992) below.

To begin the velocity of air traveling through the hole of the stainless steel disc can be expressed as;

$$V_{hole} = \frac{A_1 + A_2}{2 * \pi * r^2 * [NH_3] * \Delta t}, \qquad [1]$$

V_{hole} = the air velocity (m s^{-1}) through the hole of the stainless steel disc

A_1 and A_2 = NH_4^+-N (μg) captured in tubes facing the same direction at each height.

r = radius (m) of the hole in the samplers steel plate.

$[NH_3]$ = the concentration of NH_3 (μg m^{-3}) in the air.

Δt = duration (s) of the sample period.

V_{hole} is proportional to the ambient wind velocity (U) and the angle (α) between the wind direction and longitudinal axis of the sampler (Figure 1). Independent of the size of α Schjøerring et al., (1992) found a good correlation between the air velocity within the sampler (V_{hole}) and the air velocity outside the sampler (U). The equation; $V_{hole} = 0.77 (\cos \alpha * U) - 0.08$ gives the relationship between V_{hole} and cos α*U, the units for these two values are m s^{-1} given that they are both velocities. Because the y intercept goes to zero, it is dropped from the equation. Substituting for V_{hole} the following equation is derived;

$$\frac{A_1 + A_2}{2 * \pi * r^2 * [NH_3] * \Delta t} = 0.77 * \cos\alpha * U, \qquad [2]$$

Rearrange this equation;

$$\frac{A_1 + A_2}{2 * \pi * r^2 * 0.77 * \Delta t} \approx \cos\alpha * U * [NH_3], \qquad [3]$$

This equation is significant because $\cos \alpha * U * [NH_3]$ is the average air velocity through the sampler times the concentration of NH_3 in the air. This is the flux of NH_3 moving through the sampler, which is a component of the horizontal flux of NH_3 at a point in space. If α is zero then $\cos \alpha * U * [NH_3]$ is equal to $U * [NH_3]$ which would be the total horizontal flux of NH_3 at that point in space, again if α is not zero it is only a portion of the horizontal flux at that point.

The fetch length is the length of area from which the vertical flux of NH_3 is measured. Again, this method assumes that the amount of NH_3 emitted is proportional to the fetch length. This means that the volatilization rate is assumed to be constant throughout the fetch length, which requires NH_3 emission is uniform over the entire plot. With a circular plot the fetch lengths measured by the two sets of samplers positioned 90° for one another on the perimeter of the plot are equal to $2r \cos \alpha$ and $2r \sin \alpha$ (Figure 2), therefore two sets of samplers receive air that has passed a stretch of the plot that is $2r \cos \alpha + 2r \sin \alpha$ in length. Thus the fetch length can vary between 2r and 2.83r when α varies between 0 degrees and 45 degrees. Yet, the horizontal flux is also proportional to the cosine of the angle between the wind direction and the longitudinal axis of the samplers the effective fetch will be the sum of the products $2r \cos^2\alpha$ and $2r^* \sin \alpha * \cos(90-\alpha)$ which is equal to 2r.

In a simple example if the wind is blowing at an angle oriented 45 degrees from a set of samplers the samplers will measure 0.707*times the flux of NH_3 past that point ($\cos \alpha * U * [NH_3]$). This flux comes from an area of the plot with a fetch length equal to 0.707*2r ($\cos \alpha * 2r$). If the fetch length is multiplied by the proportion of the horizontal flux measured at that point, then $0.5 * r^2 *$ the flux of NH_3 passing that point ($\cos^2 \alpha * 2r * U * [NH_3]$). Now consider two sets of samplers measuring the same height at positions oriented 90° from one another on the perimeter of the plot. In this case there are two measurements of flux equal to 0.5 * r2* the flux of NH_3 passing the two points. If it is assumed that the NH_3 is emitted at a rate proportional to the fetch length and that the rate of emission is the same throughout the plot, the fluxes measured at both points can be added together and should be proportional to horizontal flux that would be measured had a measurement been taken at a point were the angle between the longitudinal axis of the samplers and the wind direction had been zero.

Given the above estimations the sum of horizontal fluxes measured at each height are integrated and multiplied by the change in height between the samplers and then summed. This is the average horizontal flux of NH_3 moving through a plane, which in the method used is 274 cm tall and 1mm wide (the diameter of the sample orifice in the stainless steel disk). Because it is assumed the flux is independent of the wind direction this average horizontal flux can be used to calculate the vertical flux through the equation;

$$F_v = \frac{1}{x}\sum_{h=1}^{h=n} F_{(net\ h)}\Delta h\,, \qquad [4]$$

where,

x = the fetch (diameter of the plot (m)).

$F_{(\mathrm{net\ h})}$ = the net horizontal flux (μg NH_3-N m^{-2} s^{-1}).

Δh = change in height (m) between samplers.

RESULTS AND DISCUSSION

Soils Data

The adsorption isotherm of NH_4^+ is shown in figure 1 and fit the Freudlich equation Eq. [5] as well as a linear model Eq. [6] as follows:

$$A_S=3.3A_L^{0.8023} \qquad [5]$$

$$A_S=1.388A_L \qquad [6]$$

Where A_S is the NH_4^+-N adsorbed to the soil (μmoles g^{-1} soil) and A_L is the NH_4^+-N in the solution at equilibrium (μmoles L^{-1}).

The particle size distribution of the Richfield clay loam as measured in July 2000 is shown in table 1. The bulk density of the Richfield clay loam measured before application in July 2000 was 1.34 g cm^{-3}. The soil moisture present during the March 2000 and July 2000 experiments to a depth of 50 cm is shown in table 2. Soil pH measured during the July 1999; and March, and July 2000 experiments are shown in table 3. The average soil pH measured for the experiments conducted in May, July, and September 1998 was 8.1 (Zupancic, 1999)

Effluent Data

Effluent pH measured for the experiments conducted in July 1999; and March and July 2000 are shown in Table 3. The average pH for effluent used in the May, July, and September 1998 experiments was 7.4 (Zupancic, 1999). The ponding time for March 2000 was approximately 3 hours and for July 2000 it was 10 hours. There were no estimates for ponding time for the experiments conducted in 1998 or for the experiment conducted in July 1999. Ammonium concentrations found in effluent used in the July 1999; and March, and July 2000 experiments are shown in Table 3. The ammonium concentrations found in effluent used in the May, July and September 1998 experiments were 1070, 876, and 930 mg NH_4^+-N L^{-1}, respectively (Zupancic, 1999).

Meteorological Data

Meteorological data as measured by the Oklahoma Mesonet weather station located on the Panhandle Research and Extension Center is shown in Appendix I.

Ammonia Volatilization Data

Predicted and measured cumulative NH_3 volatilization for experiments conducted in May, July, and Sept. 1998; July 1999, and March and July 2000 are shown in figures 4 through 9. As can be seen agreement was found between the measured and predicted volatilization in experiments conducted in May and Sept. 1998 and March 2000. Yet, the model did not sufficiently simulate the measured cumulative NH_3 volatilization during the experiments conducted in July 1998, 1999, or 2000 (Figures 5, 7, and 9). The model seemed to over estimate the volatilization rate during the first 4 hours of these experiments. Despite this over estimation after the first hours of the experiments the model seems to simulate the patterns observed in the measured data. For the July 1999 and 2000 experiments the model predicted a vertical NH_3 flux during the first sample period which was approximately 135 $\mu g\ NH_3\text{-}N\ m^{-2}\ s^{-1}$ greater than that measured in the field where as the predicted minus the measured losses were between -10 and 12 $\mu g\ NH_3\text{-}N\ m^{-2}\ s^{-1}$ for the remaining sample periods of the two experiments (Figures 7 and 9). This suggests that the difference between the measured and predicted volatilization rates in these two experiments is due in large part to an under estimation of NH_3 volatilization by the method used to measured NH_3 volatilization during the first sample period or an error in the prediction of NH_3 volatilization during the initial hours of the experiments. Predicted vertical NH_3 fluxes deviated from measured fluxes during each sampling period of the May and September 1998 and the March 2000 experiments by 30 and negative 20 $\mu g\ NH_3\text{-}N\ m^{-2}\ s^{-1}$ (Figures 4, 6, and 8). Although there were differences between the predicted and measured vertical NH_3 fluxes during these experiment the predicted was not consistently higher than the measured or vice versa, therefore they tended to correspond well overall. For the July

1998 experiment the model consistently overestimated NH_3 volatilization throughout the time period (Figure 5).

The model over estimation of NH_3 volatilization during the initial hours following application as compared to the measured estimates could be caused by a non-uniform rate of volatilization across the plot. This non-uniform rate of volatilization could be caused by the distribution of the liquid surface within the plot. Because the plots were not graded to a flat surface, there was most often a slope to the plots. This slope allowed the effluent to pond in specific areas of the plots instead of in a uniform pond covering the entire plot. The model estimates the rate of volatilization with the assumption that the rate of volatilization is uniform over the entire plot. In order for this assumption to be valid the pond of effluent must also be uniform, which is most often not the case.

The errors associated with the non-uniform ponding may be compounded by other factors that alter the model predictions. These factors include meteorological parameters such as relative humidity, temperature, wind speed, and solar radiation, as well as soil and effluent pH measurements. During the experiments conducted in July of 1998, 1999 and 2000 these factors may have been such as to maximize the error associated with the non-uniform ponding of the effluent, thereby causing a gross overestimate of NH_3 volatilization. Sensitivity analysis of the model will yield information on the parameters to which the model is most sensitive. Currently, it is know that the model is quite sensitive to small changes in the pH of the effluent. This is due to the reaction;

$$NH_4^+ \Leftrightarrow NH_3^o + H^+, \qquad [7]$$

From which we derive;

$$K = \frac{(NH_3^o)(H^+)}{(NH_4^+)}, \qquad [8]$$

Which when solved for NH_3^o gives;

$$(NH_3^o) = \frac{K*(NH_4^+)}{(H^+)}, \qquad [9]$$

The Log K for this reaction is negative 9.28 (Lindsay, 1979), therefore with each half-unit increase in pH the NH_3 activity in solution doubles and with every full unit increase in pH the NH_3^o activity increases by ten fold. This sensitivity to pH requires soil and effluent pH measurements be very accurate and that no change in the pH of the effluent occur during ponding due to reactions with the soil or atmosphere. It also requires that the addition of effluent not affect the soil pH.

Another possible explanation for the deviation between the predicted and measured volatilization rates during the first few hours of the July 1998, 1999 and 2000 experiments is that the micrometeorological method used to measure NH_3 volatilization during these experiments underestimated NH_3 volatilization. Data from chapter 2 comparing the micrometeorological method used to an alternative method however shows that the two methods produced similar results during the March 2000 and July 2000 experiments. This is evidence that the method used to collect all the data is a consistent method of measuring NH_3 volatilization as compared to the center mast method (chapter 2). Because the model did a good job of predicting NH_3 volatilization in March 2000 and not in July 2000 the data from chapter 2 suggest that there is another explanation for the low measured values as compared to the predicted values in July 2000.

CONCLUSIONS

The mechanistic model developed predicted volatilization rates very similar to those measured in three of the six field experiments conducted in 1998, 1999 and 2000. The model predicted the patterns of NH_3 volatilization in two of the three remaining experiments even though it did not predict the magnitude the cumulative NH_3 volatilization. This difference in the magnitude of NH_3 loss predicted verses that measured may be due to non-uniform ponding of effluent that occurred at the beginning of all of the experiments. At this point the model seems to predict patterns of NH_3 volatilization from surface applied swine effluent in the field. Although, improvements in the field experiments are needed to better evaluate the model. One improvement would be to provide a uniform liquid surface at the onset of the field experiment or to minimize the liquid surface there by taking it out of the model. The former would provide a comparison of the sub model that predicts NH_3 transfer from a liquid surface whereas the latter would provide a comparison of the sub model that predicts NH_3 transfer within the soil and from the soil surface.

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Table 1: Particle size distribution for the Richfield clay loam from the Oklahoma Panhandle Research and Extension Center, Goodwell, OK, used for applicaton of swine effluent.

	Particle Size (µm)								
	<2	2-5	5-20	20-50	50-100	100-250	250-500	500-1000	>1000
% of Soil	32.7	3.9	9.8	33.4	9.3	6.3	3.8	0.9	0.2

Table 1: Moisture content profiles measured prior to application during the March and July 2000 experiments.

	March 2000	July 2000
Depth	Moisture Content	Moisture Content
cm	$g\ g^{-1}$	$g\ g^{-1}$
0-10	0.13	0.20
10-20	0.21	0.17
20-30	0.19	0.19
30-40	0.20	0.18
40-50	0.20	0.17

Table 3: Soil and effluent pH, and NH_4 concentrations in effluent used for experiments conducted in July 1999, and March and July 2000.

	Soil pH	Effluent pH	Effluent NH_4^+-N
			mg L^{-1}
July 1999	7.2	7.95	779
March 2000	7.26	8.25	782
July 2000	7.59	7.86	841

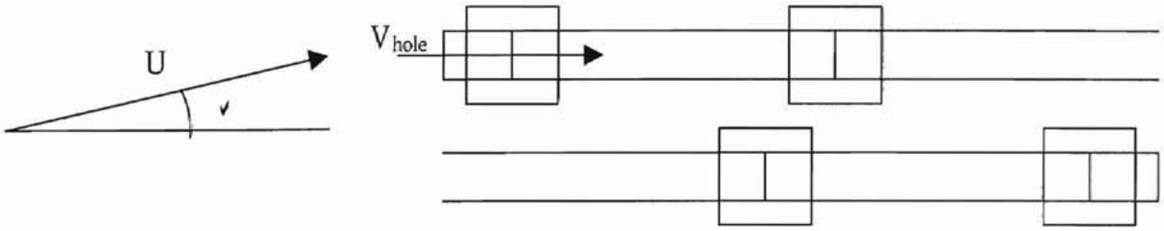


Figure 1: The air velocity traveling through the sampler is proportional to the ambient wind velocity and the angle α between the wind direction and the longitudinal axis of the samplers.

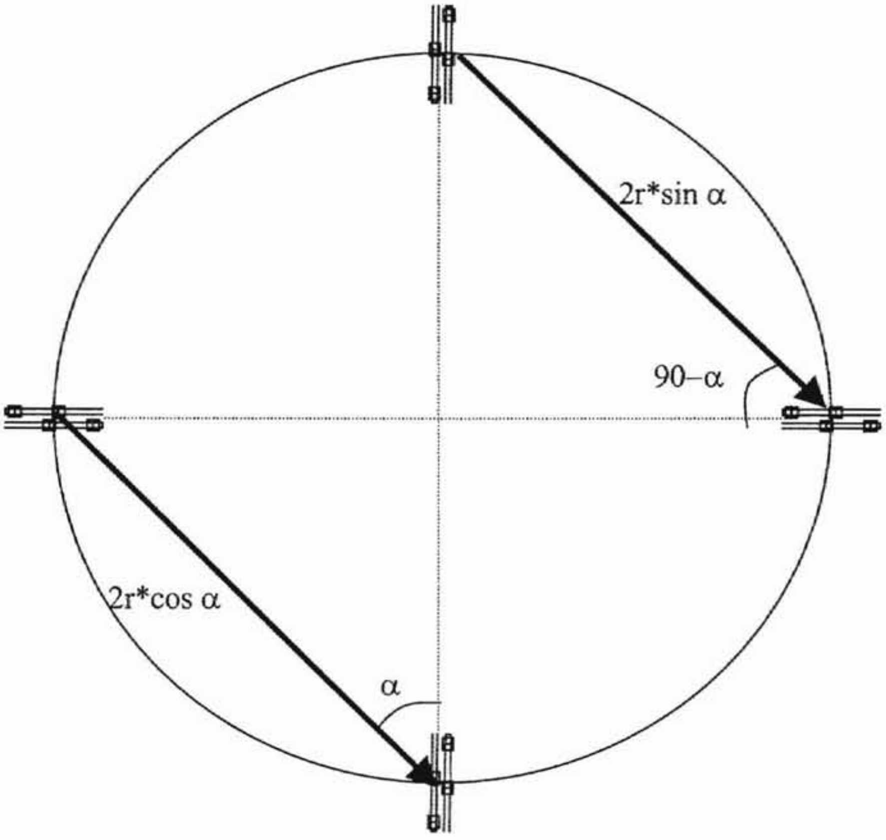


Figure 2: Graphical representation of the fetch lengths measured by the passive flux samplers.

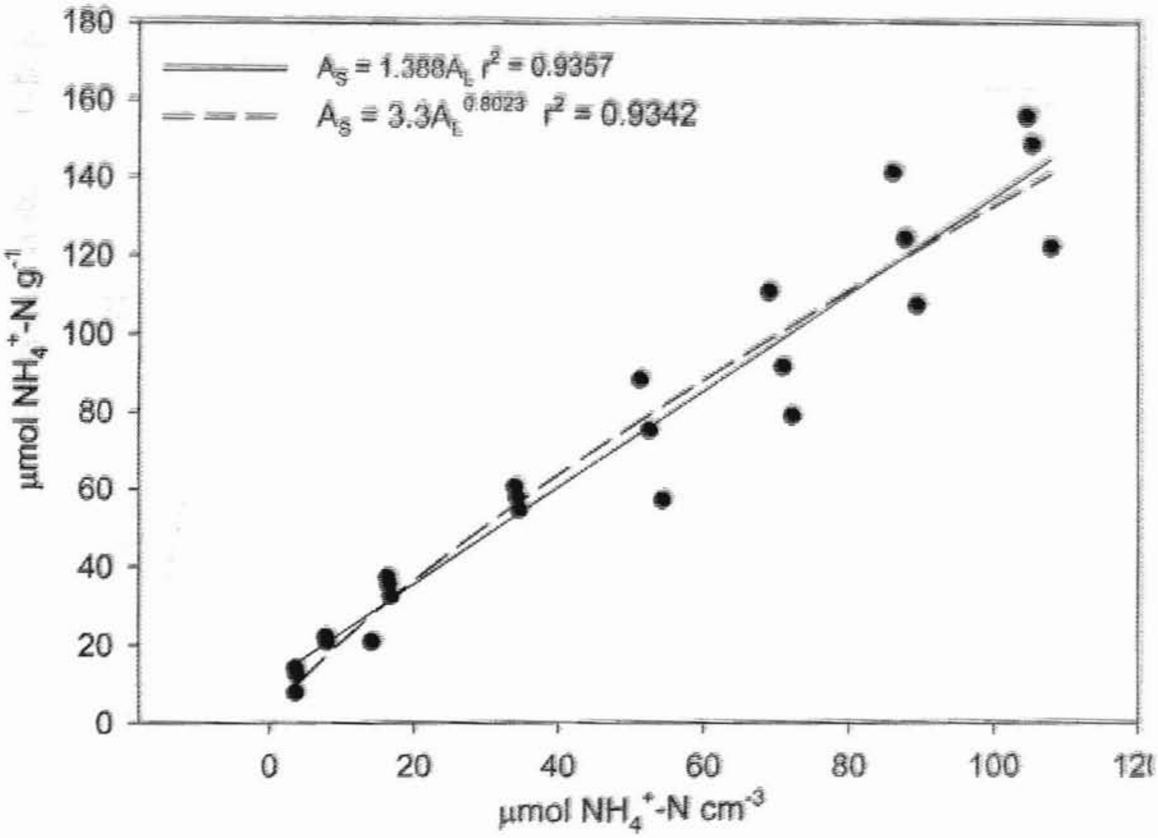


Figure 3: NH_4^+-N adsorption isotherm for the Richfield clay loam.

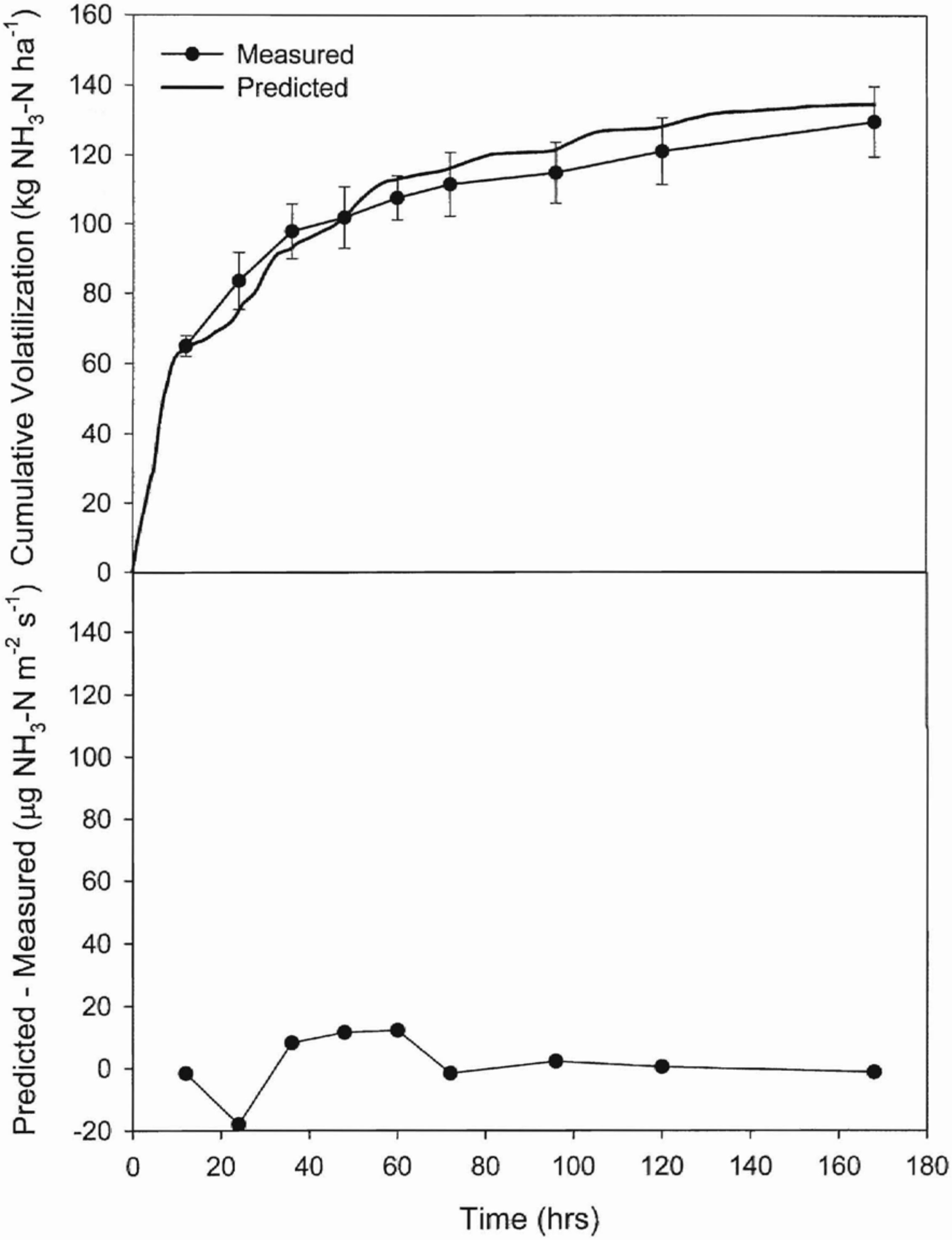


Figure 4: Predicted and measured cumulative NH_3 volatilization and the difference between the vertical NH_3 flux predicted and measured per sampling period in May 1998.

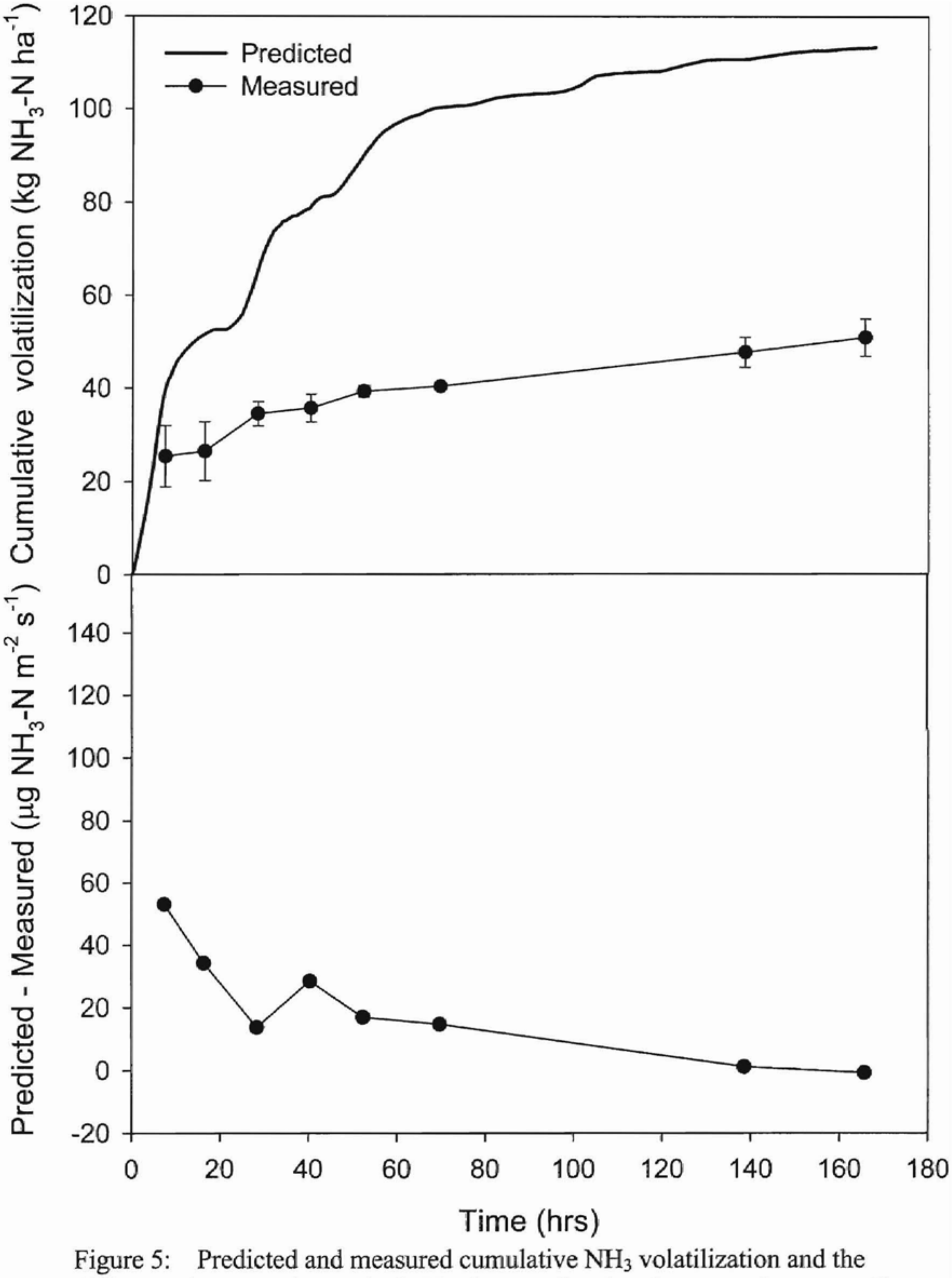


Figure 5: Predicted and measured cumulative NH$_3$ volatilization and the difference between the vertical NH$_3$ flux predicted and measured per sampling period in July 1998.

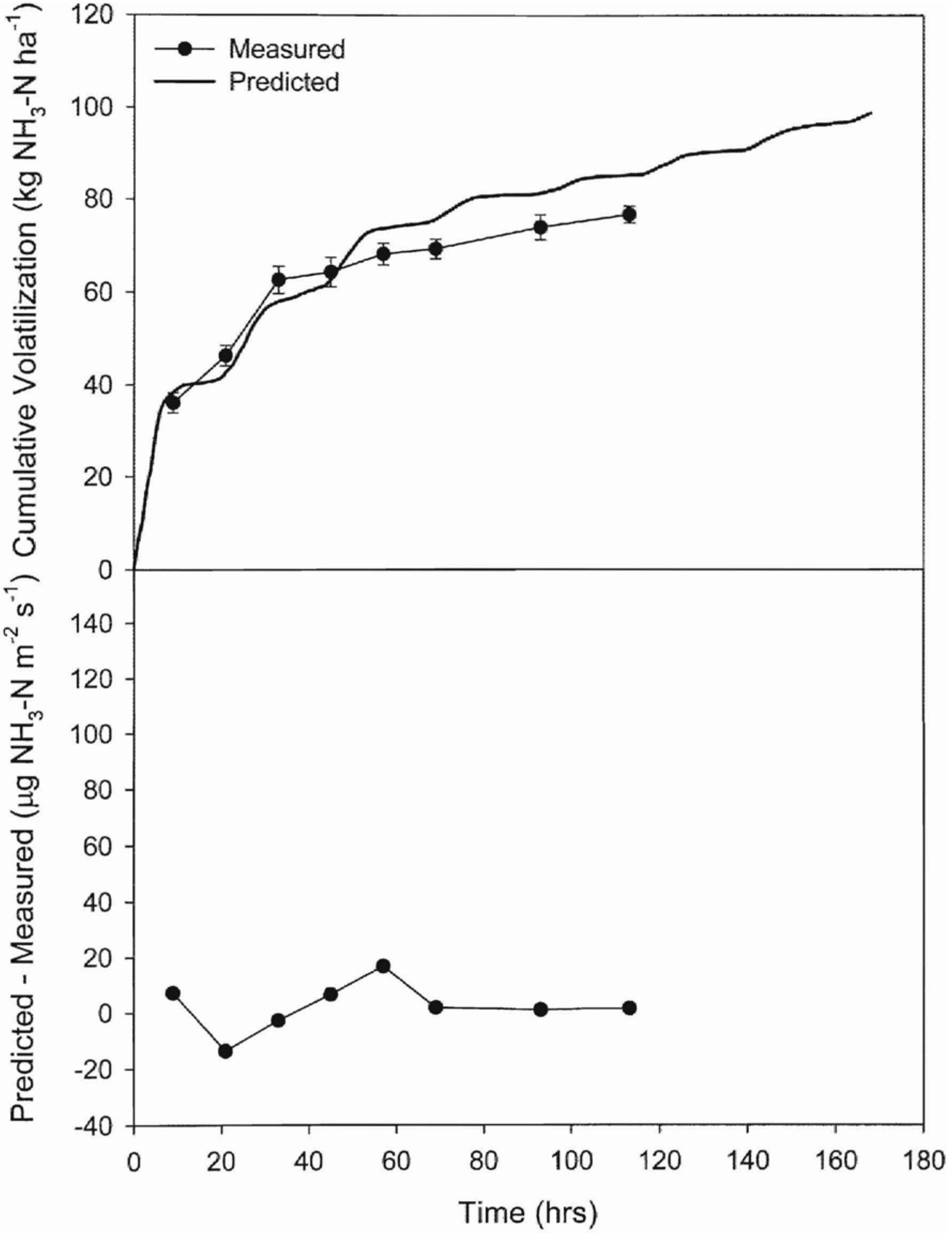


Figure 6: Predicted and measured cumulative NH_3 volatilization and the difference between the vertical NH_3 flux predicted and measured per sampling period in September 1998.

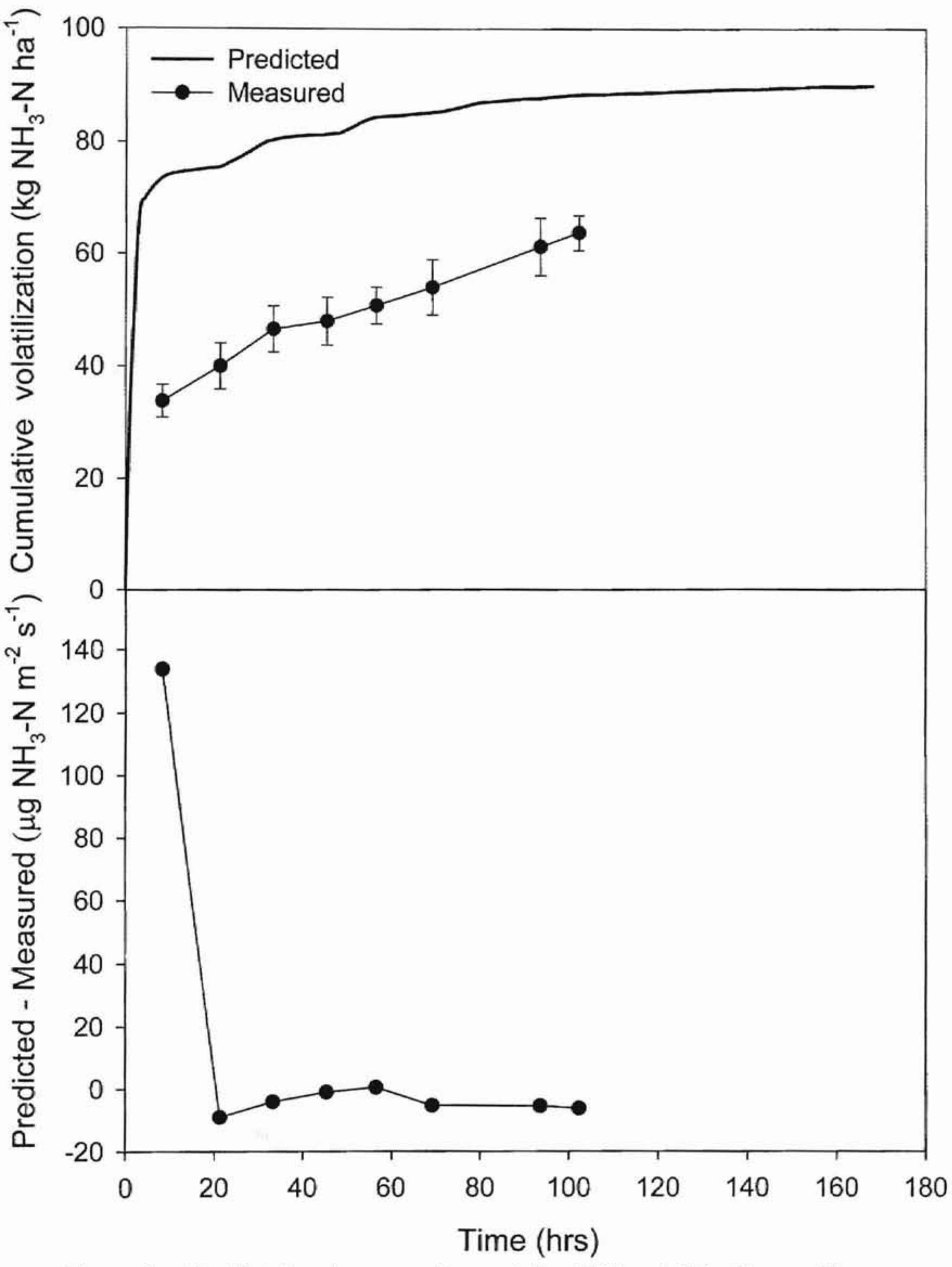


Figure 7: Predicted and measured cumulative NH_3 volatilization and the difference between the vertical NH_3 flux predicted and measured per sampling period in July 1999.

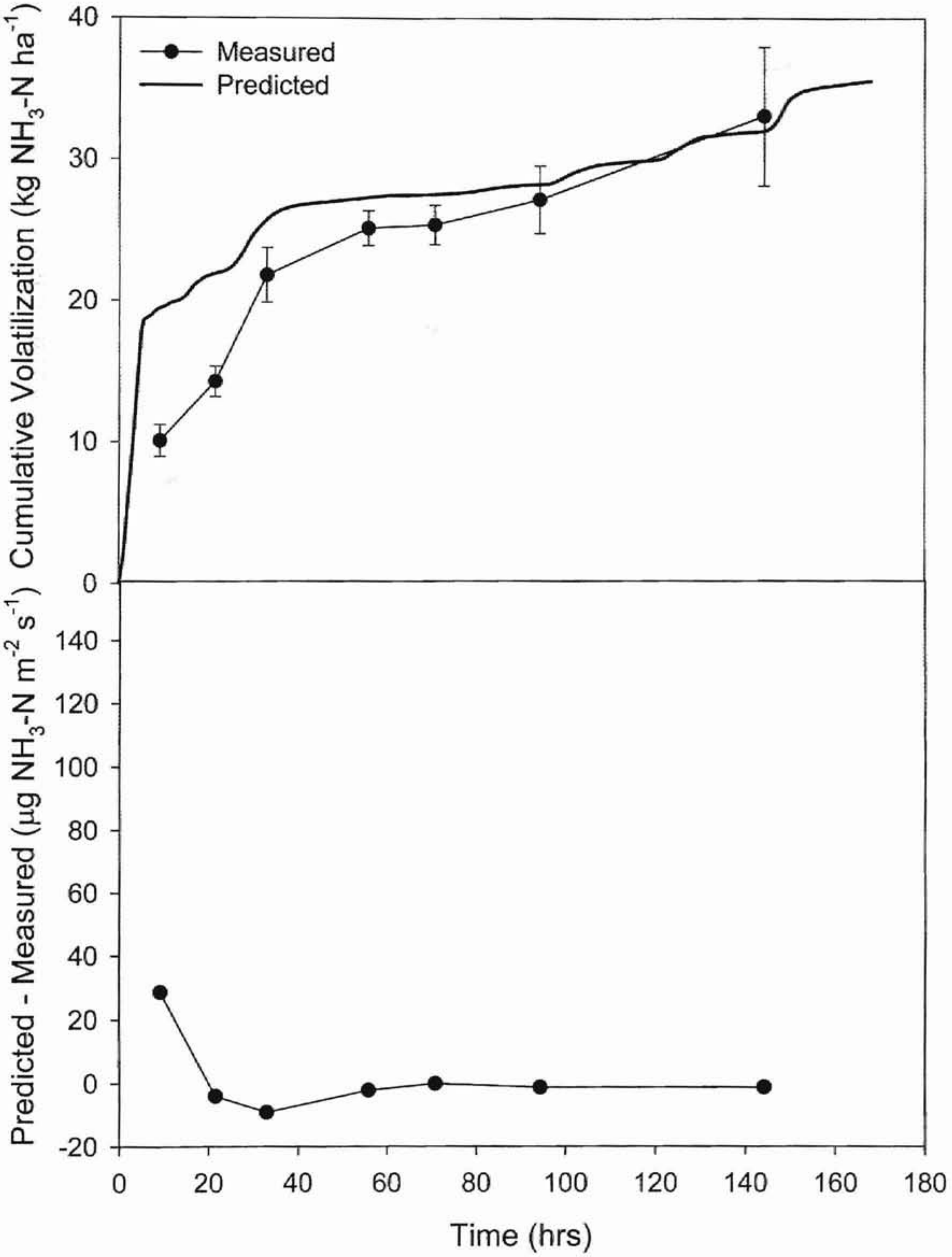


Figure 8: Predicted and measured cumulative NH_3 volatilization and the difference between the vertical NH_3 flux predicted and measured per sampling period in March 2000.

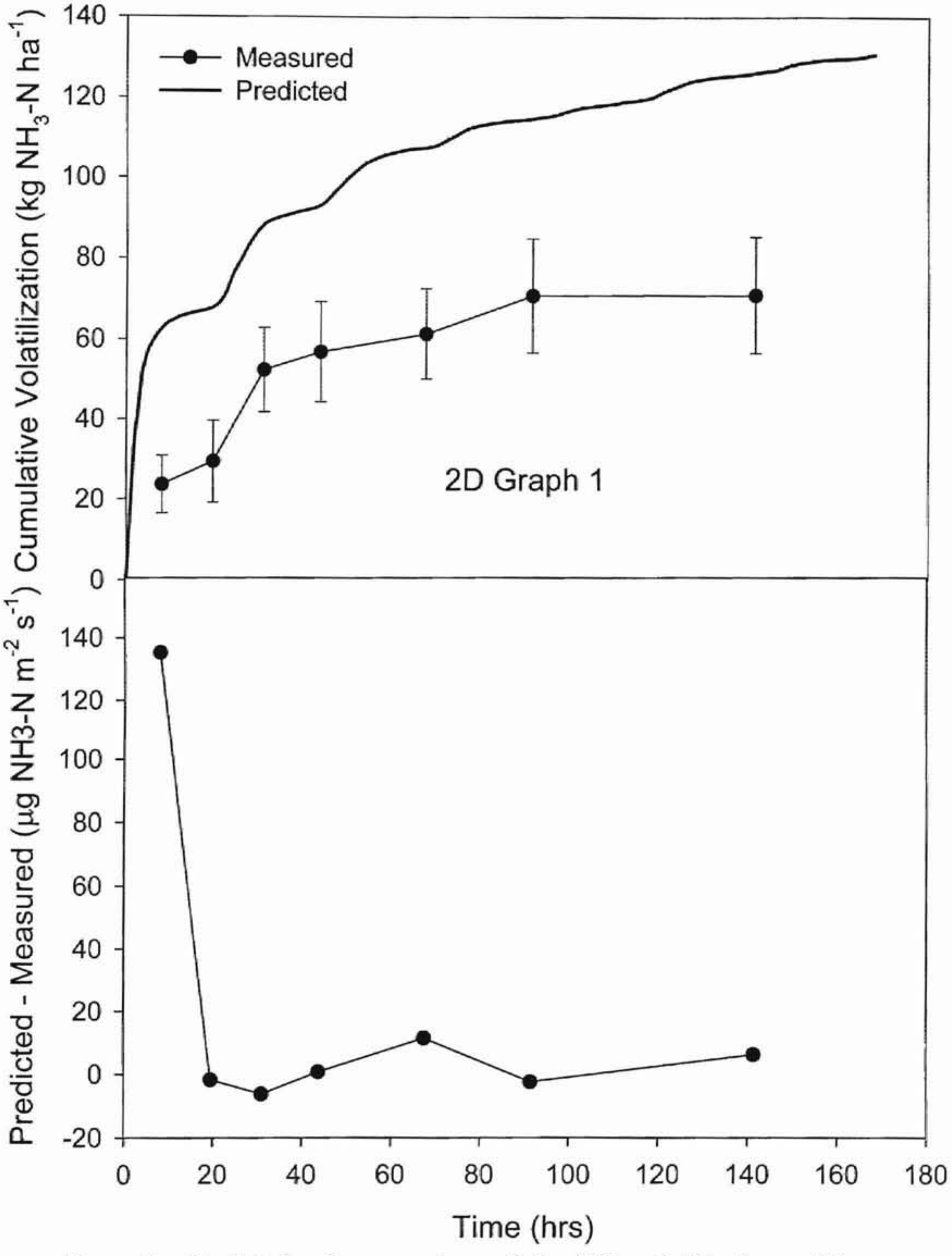


Figure 9: Predicted and measured cumulative NH_3 volatilization and the difference between the vertical NH_3 flux predicted and measured per sampling period in July 2000.

APPENDICES

APPINDIX I

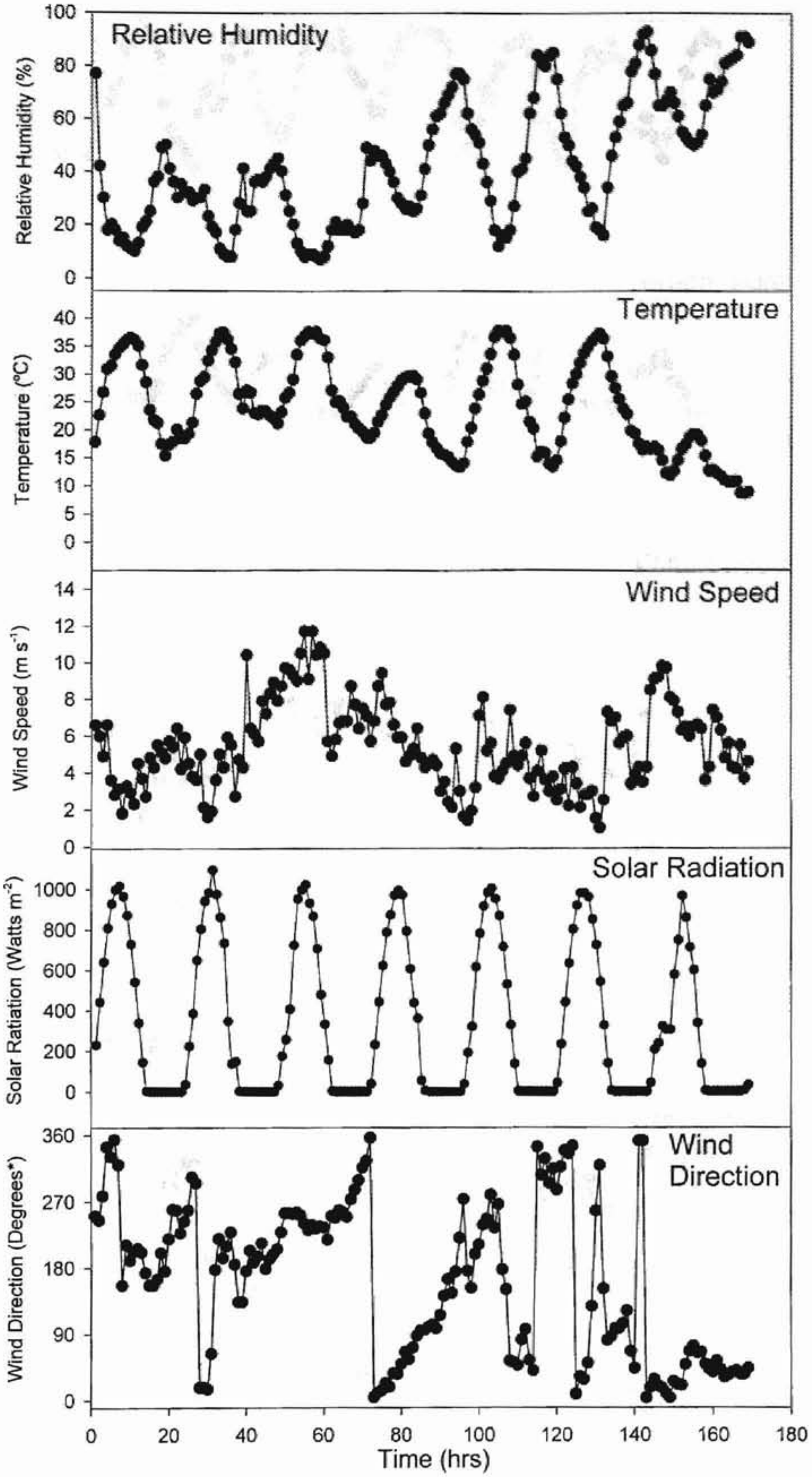
Inorganic Soil Nitrogen

Average inorganic soil nitrogen contents measured prior to applicaton os swine effluent in fallow plots and cropped plots used in field experiments conducted in 1998 through 2000.

Experiment	Date	Treatment	NH_4-N	NO_3-N
			------mg kg^{-1}------	
1	5/28/98	Fallow	2.0	22.5
2	7/28/98	Fallow	3.3	28.0
3	9/12/98	Fallow	3.5	17.5
4	7/28/99	Fallow	11.0	21.0
		Sorghum	8.6	20.4
5	12/15/99	Fallow	12.9	58.3
		Wheat	13.3	9.4
6	3/14/00	Fallow	27.7	39.7
		Wheat	37.5	33.3
7	7/13/00	Fallow	8.4	22.5
		Corn	9.3	6.7

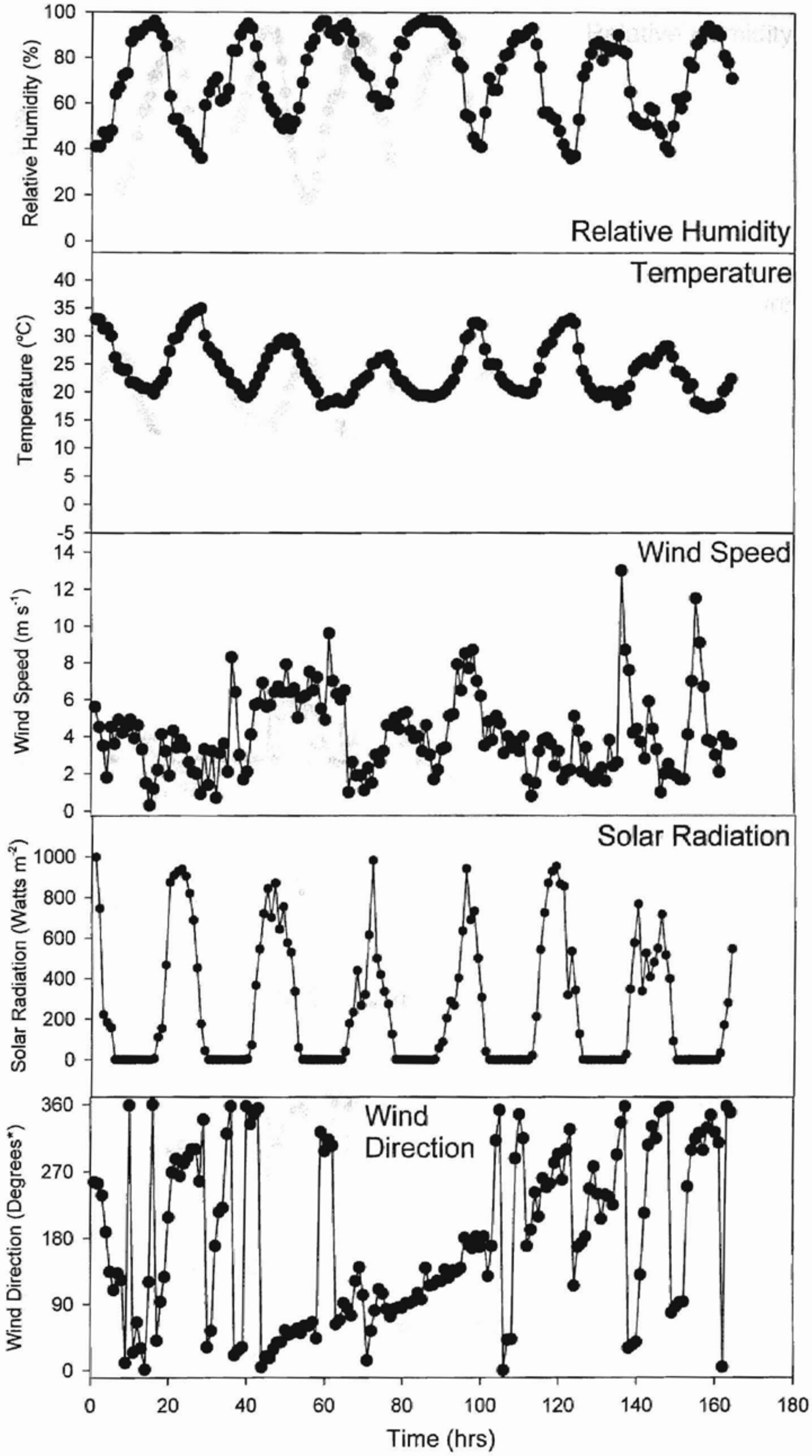
APPINDIX II

Meteorological Data



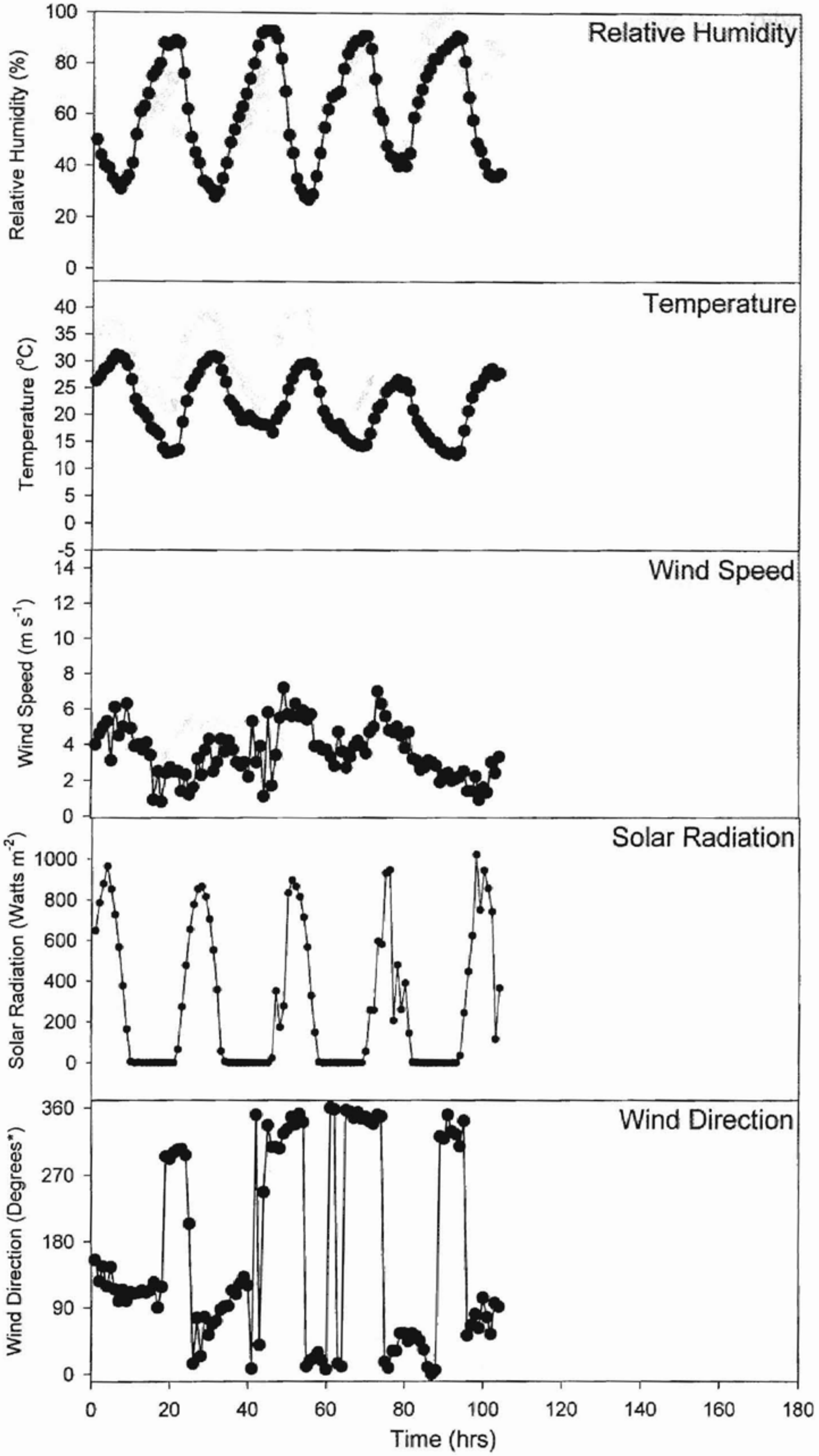
Meteorological parameters measured in May 1998.

* Wind direction was measured as degrees from North=0°, East= 90°

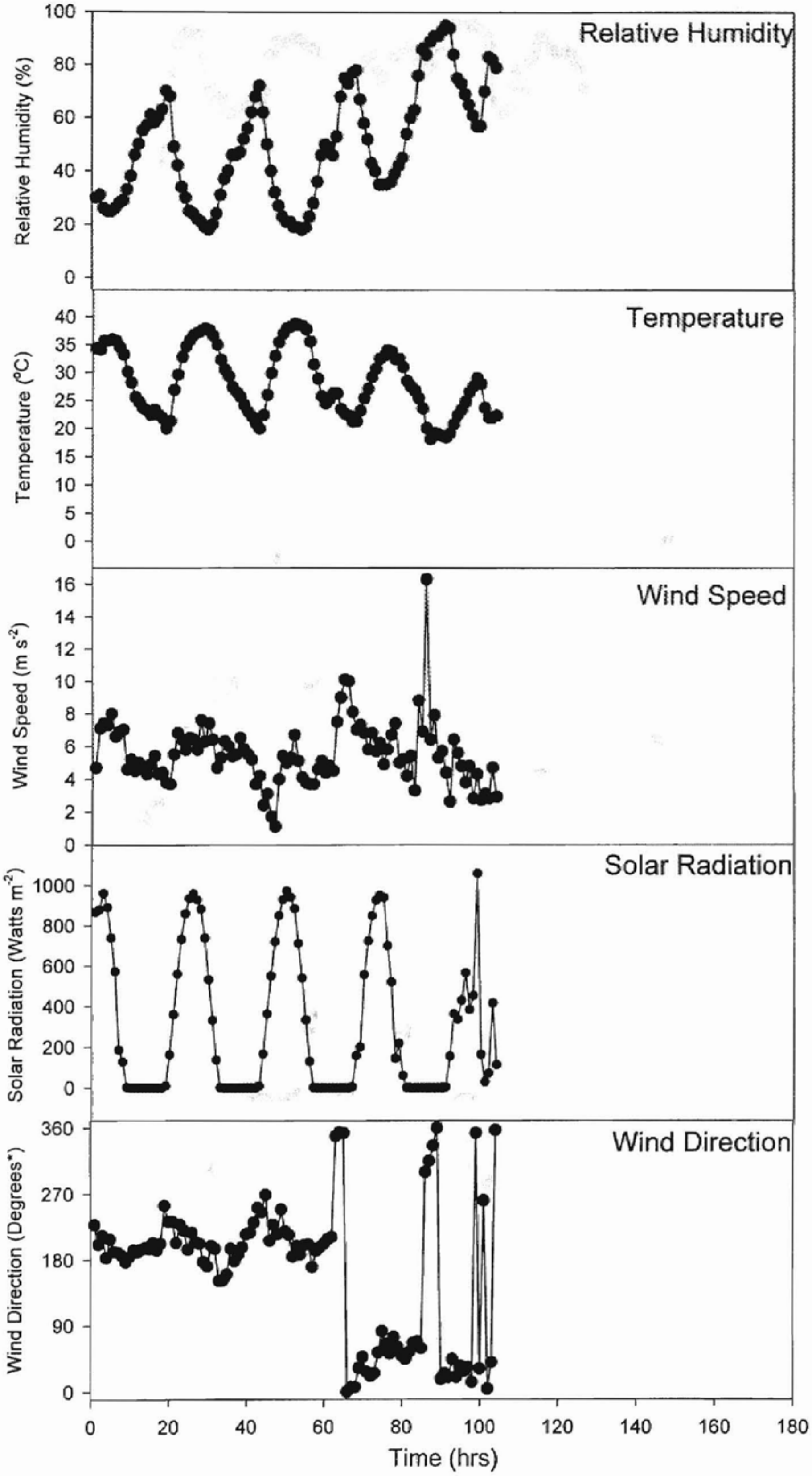


Meteorological parameters measured in July 1998.

* Wind direction was measured as degrees from North=0°, East= 90°

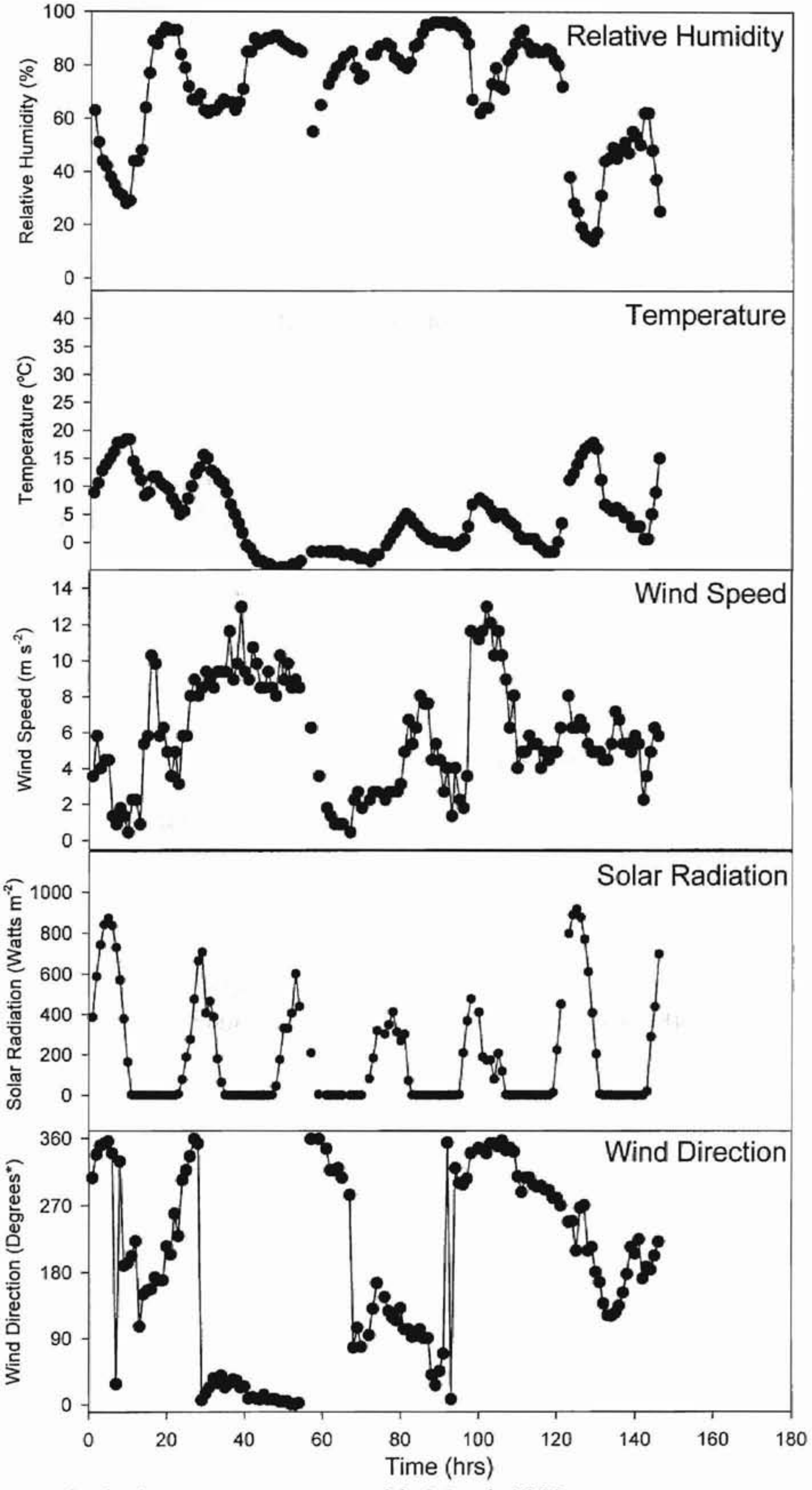


Meteorological parameters measured in September 1998.
* Wind direction was measured as degrees from North=0°, East= 90°



Meteorological parameters measured in July 1999.

* Wind direction was measured as degrees from North=0°, East= 90°



Meteorological parameters measured in March 2000.

* Wind direction was measured as degrees from North=0°, East= 90°

VITA γ

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Master of Science

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