QUANTIFYING AMMONIA VOLATILIZATION FROM SWINE EFFLUENT APPLIED CALCAREOUS CLAY LOAMS IN THE SOUTHERN GREAT PLAINS

By

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Chapter I

AMMONIA VOLATILIZATION FOLLOWING SWINE EFFLUENT APPLIED FALLOW NO-TILL AND BUFFALOGRASS PRODUCTION SYSTEMS.

ABSTRACT

Land application of swine effluent can provide essential plant nutrients for crop production, but ammonia (NH_3) volatilization from the litter can be detrimental to the environment and a loss of valuable nutrients. A study was conducted during summer of 2004 and 2005 to evaluate loss of N by ammonia volatilization with the use of swine (*Sus domesticus*) effluent on clayey loam soils at Panhandle District of Oklahoma as affected by different climatic and soil cover conditions. Micrometeorological mass balance method employing passive flux samplers was used to measure the ammonia release from the experimental plots after effluent applications. The amount of NH_3 volatilization from applied swine effluent ranged from 21.7% to 57.8 % of the ammoniacal nitrogen applied. Ammonia volatilization was rapid immediately following effluent application and eventually decreased with time. On an average, 58% of the total volatilization loss occurred within 12 hrs of effluent application. The greatest amount of NH_3 volatilized when high rates of ammoniacal nitrogen was applied accompanied with high air temperatures, high wind speed and low relative humidity. The grass sward and no-till residue significantly reduced the volatilization loss as compared to conventional till soils. Cumulative volatilization from no-till and grassland systems were 22% and 87% lower than fallow cropland respectively, which can be attributed to reduced wind speed,

reduced temperature and absorption of ammonia by the canopy in buffalograss and higher infiltration rate of effluent into the no-till soil matrix system.

INTRODUCTION

Texas County, Oklahoma once known as a "NO-MANS" land is now famous for being the number one county in the state to harbor the swine operating facilities. According to the National Agricultural Statistics Service, 2001-2002 Iowa ranks first and Oklahoma stands at the eighth position in swine production. By the end of 1997 the pig inventory at the Panhandle District of Oklahoma was 907,060 and by the end of 2002 the number had increased to 1,073,134 which at present makes this district, the largest swine producing district in Oklahoma (National Agricultural Statistics, 2002). During the last ten years there has been nearly a 140 fold increase in pig production in this district. These industries also generate millions of gallons of effluent which must be handled properly to make it safe for the environment in Panhandle District (Pearson and Stewart, 1993; Mehrer and Mohr, 1989). Swine effluent produced from these animals at the Panhandle District is stored in outdoor earthen lagoons which are kept from overflowing by applying the effluent to the agriculture fields as it is a good source of nutrients (Zhang and Hamilton, 1998). Nitrogen loss in the form of NH_3 volatilization from land applied swine effluent and earthen lagoon not only reduces its nutrient value but also act as a major contributor for NH_3 emissions from livestock industry.

In the US it is estimated that 55% of NH_3 emission is from livestock operations, followed by fertilizer application 7% (Roe et al., 1998). Major anthropogenic sources of NH_3 to the atmosphere are livestock operations, ammoniacal form of fertilizers applied to the crop, industries, combustion processes, and other miscellaneous sources like, human breath and perspiration, POTWs, non agricultural soils, and refrigeration (Anderson et al., 2003; Aneja et al., 2000). Livestock production in particular, has been reported to be the largest contributor of NH_3 emissions (ApSimon et al., 1987; Allen et al., 1988; Kurvits and Marta, 1998; Aneja et al., 2000). Emissions calculated for the US in 1995 for the most important categories include: 3.4×10^9 kg from livestock, 7.7×10^8 kg from fertilizer application, 1.5×10^8 kg from domestic animals, 1.3×10^8 kg from wild animals, 1.1×10^8 kg from humans, 7.0×10^7 kg from industry, 4.7×10^7 kg from mobile sources, and 6.9×10^4 kg from publicly owned treatment works (POTWs) (Anderson et al., 2003). Ammonia emitted from animal housing, manure storage, treatment facilities, and manure land application together contribute to NH_3 emission from livestock operations. Urine and feces are the major wastes generated in livestock operations. Ammonia is generated from microbial hydrolysis of urea and mineralization of organic nitrogen compounds in livestock houses and storage lagoons.

During storage of manure in open earthen lagoons, NH_3 moves by molecular diffusion to the surface interface, from where it constantly volatilizes into the atmosphere (Beline et al., 1998). Waste applied to agriculture land can aid in NH_3 volatilization depending on various soil and climatic conditions (Brunke et al., 1988; Morken and Sakshaug, 1998). Inappropriate volatilization estimates will lead to either overestimation or underestimation of N availability from swine effluent applications. Overestimation of ammonia of ammonia volatilization from swine effluent will ultimately result in crop yield losses and reduced economic returns, whereas underestimation results in soil N build up and leaching losses to ground water.

REVIEW OF LITERATURE

Methods used for measuring volatilization

The exchange of NH_3 between a source and the atmosphere can be calculated and estimated using various techniques, many of which integrate the atmospheric NH_3 concentration and relate the mean concentration to surface emission. The most commonly used methods are mass balance methods, chamber and wind tunnel methods, and micrometeorological methods.

Mass balance methods involve determining the change in nitrogen content of the source, and estimating how much of the loss is due to NH_3 volatilization. This method can be used in case of laboratory volatilization measurements, but it cannot be applied to a large scale of NH_3 emissions (Ryden and Mcneill, 1984). Chamber and wind tunnel methods capture the NH_3 gas near the soil surface, wherein air from the experiment plot is pulled into a chamber in which the air will be mixed continuously and this mixed air will be collected (Hoff et al., 1981; Svensson, 1994, Mattila, 1998; Sommer and Jacobsen, 1999; Aneja et al., 2000) and then analyzed for NH_3. The drawback of this method is that as the microclimate in the chamber will be modified by mixing the air, it may not give the real field results. Micrometeorological methods employs aerodynamic mass balance (Genermont et al., 1998; Sharpe and Harper, 1997; Harper et al., 2000) and passive flux mass balance approaches to measure the volatilization flux of NH_3. Passive samplers use the principle of gradient approach and have been used to determine NH_3 concentration and horizontal flux. Vertical flux of NH_3 is calculated by dividing the horizontal flux by fetch length, which is equal to the radius of the experimental plot, at each height (Schjoerring, 1992; Sommer et al., 1995; Wood et al., 2000; Warren, 2001 Pain et al., 1989; Genermont et al., 1998). Experimentally it was proved that it can be used for areas with fetch of < 25m, but for this, the exchange surface should be uniform (Sommer and Olesen, 2000)

A passive flux sampler (Schjoerring, 1992) is a simple and inexpensive device, continuously integrating the product of NH_3 concentration and wind speed along flux sampler. It consists of oxalic acid coated glass tubes connected in series and a nozzle to reduce the wind speed in the field (Sommer et al., 1995) which provided similar estimations of NH_3 emissions as a micrometeorological mass balance method with conventional acid traps (Schjoerring et al., 1992). Passive flux mass balance methods are of two types; fixed sampler system (Schjoerring, 1992) and wind vane sampler (Wood et al., 2000), which is just a little modified version of fixed type. Warren (2001) compared these two methods with little modification and reported that the center wind vane mast method produced similar results as that of the perimeter fixed mast method and also the center mast method is the most efficient method with less cost and labor requirement (Hansen et al., 1998). Volatilized ammonia might escape without being captured in case of wind speed greater than 10 m s-1 and also in scenarios wherein more than 50% of oxalic coated glasss tubes are saturated with ammonia (Sommer et al., 1996). Snow and storm conditions can flood the samplers thereby interrupting the measurement process.

Ammonia volatilization effects on environment

The basic processes of volatilization include productive, diffusive and convective transport within the source, and transport through the surface boundary. Ammonia is emitted from sources containing total ammoniacal nitrogen (TAN = NH_4^+-N + NH_3 -N) exposed to the air, mainly from the manure stored in buildings and land applied effluents (Genermont and Cellier, 1997).

Nitrogen in the swine effluent is mainly in the form of nitrate nitrogen (NO_3^-), ammoniacal nitrogen (NH_4^+) and organic nitrogen. More than 75% of the N is in the form of ammonium (NH_4^+) and hence its potential loss through volatilization during storage and land application will be high (Fulhage and Hoehne, 1999; Zupancic et al., 1999). Ammonia volatilization reduces the effluent fertilizer value as well as leading to unwanted deposition of nitrogen in the oligotrophic ecosystems (Schulze et al., 1989). Deposition of the ammoniacal nitrogen will cause changes in the species composition, eutrophication and acidification in nitrogen sensitive ecosystems (Schulze et al., 1989; Walker et al., 2000). Atmospheric NH_3 plays a major role in producing acid rain (ApSimon et al., 1987) and raises the pH of the rain water (Pearson and Stewart, 1993), which in turn aids in dissolution of SO_2 and its subsequent oxidation to H_2SO_4 (Behra et al., 1989). Deposition of NH_3 and NH_4 on soil leads to the acidification of the soil upon nitrification, this acidification accelerates leaching of cations from the plant and soil and increased mobilization of Al^{3+} which is toxic to plant roots (Roelofs et al., 1985; Fennema, 1992; Pearson and Stewart, 1993) also acidification might lead to K^+ and Mg^+ deficiencies in vegetation followed by severe stress (Roelofs et al., 1985). Foliar uptake of wet and dry deposited NH_4 and NH_3 can be toxic to plants if the critical levels of deposition were above 150 $\mu g\ m^{-3,}$ producing symptoms of reduced growth, and necrosis (Mehrer and Mohr, 1989).

Factors effecting ammonia volatilization

In the last two decades the loss of NH_3 from effluent application and factors which favor them, have been intensively studied. During 1970's and 1980's enormous effort has been made to quantify NH_3 volatilization from urea applied to the soil both under field and lab conditions. Sevensson (1994) classified the factors affecting volatilization into three main groups they are: meteorological, soil, and application technique and rates. Among the meteorological factors: air temperature, air movements/winds, solar radiation and rainfall are the important ones affecting the volatilization. Meteorological parameters like air temperature or solar radiation (Brunke et al., 1988; Moal et al., 1995; Sommer et al., 1997; Sommer and Jacobsen, 2000) wind speed (Sommer et al., 1997) increases the NH_3 volatilization rate. An increase in wind speed increased the volatilization rate under broadcast spreading, band application by trailing foot method of application (Huijsmana, 2002). Rainfall usually reduces volatilization by transporting NH_4^+ into soil where it will be held by the soil colloids, (Rochette et al., 2001).

Among the soil factors affecting the volatilization are the soil pH, soil moisture, soil surface temperature and cation exchange capacity.

The equilibrium:

$$NH_4^+ + OH^- \Leftrightarrow NH_3 + H_2O$$

governs most of the soil factors affecting volatilization. The main factor influencing the equation will be the pH of any system. An increase in pH shifts the NH_3/NH_4^+ equilibrium ratio in soil solution favors NH_3 volatilization, as increase in NH_3 in solution results in equilibrium between liquid NH_3 and gaseous NH_3. (Du Pleiss and Kroontje, 1964). Ammonia volatilization is relatively low when effluent is applied on dry soil even if the air or soil surface temperature is high (Sommer et al., 1991, Soggard et al., 2002), due to increased soil infiltration. Consequently, NH_3 loss increases if the infiltration is reduced due to high soil water content (Donovan and Logan, 1983). In a laboratory study, it was shown that the NH_3 volatilization from effluent applied to dry soil (0.01 g H_2O g^{-1} of soil) was 70% of the volatilization from effluent applied top soil with more than 0.8 g H_2O g^{-1} of soil (Sommer and Jacobsen, 1999). Increase in soil temperature at constant water content would enhance or favor NH_3 volatilization possibly due to loss of water (Fenn and Scarzaga., 1976). Ammonia volatilization rates increases by approximately three times as soil temperature increases from 14^0C to 24^0C (Sevensson, 1994). Whitehead and Raistrick (1993) found a strong negative correlation between CEC and NH_3 volatilization when urine was applied to the field mainly because of NH_4^+ retention by soil colloids (Fenn and Kissel, 1973). Besides soil factors, few effluent properties can affect ammonia volatilization process.

The manure factors affecting NH_3 loss described by Sevensson (1994) can be divided into chemical and physical. The chemical properties include total ammoniacal nitrogen (TAN), alkalinity, pH value, buffering capacity, ionic strength and activity whereas the physical properties includes dry matter content, fluidity and viscosity. Under mild northwestern European conditions reduced infiltration was promoting greater loss with high dry matter slurries (Sommer and Olsen, 1991; Moal et al., 1995) whereas under summer Mid-Atlantic USA (Thompson and Meisinger, 2002) the two effects were balancing each another.

The other factors which can affect the process include effluent application techniques (Mattila, 1998) ground cover (Thompson and Meisinger, 2002) and soil tillage (Rochette et al., 2001). It was observed that open slot shallow injection and band spreading by trailing foot on grassland considerably reduced the volatilization compared to broadcast application (Huijsman et al., 2002). Sharpe and Harper (1997) observed that overhead sprinkler application of effluent over a crop resulted in 82% loss of NH_4-N to the atmosphere because the crop canopy hindered the effluent from entering the soil.

Ammonia volatilization from grasslands

Grasslands have a major role to play in American agriculture as they supply the major nutritive diet to the cattle industry. The short-grass prairie extends east from the Rocky Mountains and south from Montana through the Nebraska Panhandle and southeastern Wyoming into the high plains of Oklahoma, New Mexico, and Texas (Samson et al., 1998). The short-grass prairie landscape was one of relatively treeless stream bottoms and uplands dominated by blue grama (*Bouteloua gracilis*) and buffalograss (*Buchloe dactyloides*), two warm-season grasses that flourish under intensive grazing (Weaver et al., 1996). Most of these southern mixed prairies supports cow-calf year-long operations and in such production systems high dry-matter (DM) yields of pasture requires a large mineral nutrient supply, and nitrogen has been claimed as the most important mineral controlling grass productivity.

Forage crop or grassland uptake of nutrients from applied manure is often less than the quantity applied because the manure is applied at rates necessary to meet the N requirements of the forage (Sims, 1995) and the N/P ratio of manure does not match that of the crop (Edwards, 1996). Hay production does not favor nutrient accumulation in the soil due to continued manure application and uptake by the grass swards (Kingery et al., 1993). Pastures are important components of nutrient management wherein they export nutrients in the form of hay from lands receiving swine effluent and also help in reducing runoff and soil loss, the rate of nutrient accumulation in the soil and the potential for ground and surface water impairment will be reduced (Sims and Wolf, 1994). The total NH_3 loss from swine effluent applied grass sward will be greater than that from a bare soil by at least 1.5 times (Thompson and Meisinger, 2002; Thompson et al., 1990) because grass sward serves as a barrier and prevents much of the slurry from making contact with the soil,thereby minimizing the sorption of NH_4^+ on to the exchange sites. Effluent application to crops like wheat and corn will decrease the NH_3 emission by about 60 to 75 % compared to the same application method and rate on to a fallow or barren land (Warren, 2001; Sommer and Olsen, 2000; Sommer et al., 1997). It has been reported that 63% of the total NH_4-N applied swine effluent was lost via volatilization subsequent to effluent application to bermudagrass whereas only 37 to 45% of total NH_4-N was lost if applied to wheat stubble (Moal et al, 1995; Sullivan et al., 2003). Effluent attached to the grasses increases the potential volatilization rates by inhibiting effluent infiltration into the soil. Volatilization losses of NH_3 from grassland fertilized with swine effluent were as low as 5 to 27% of the total NH_4-N of which 24 to 39% occurred within one hr and 85% within 12 hrs (Pain et al., 1989) of application.

Ammonia volatilization from no-till systems

Acceptance of no-tillage and reduced tillage crop production methods, often collectively referred to as conservation tillage, has expanded rapidly in many parts of the U.S. in recent years, particularly in the Mid-Atlantic and Southeastern regions. In 1972, there were 30 million acres while in 1982, there were more than 100 million acres and by the year 2010, as much as 95% of all U.S. cropland may be farmed with conservation tillage methods (Myers, 1983). No-tillage not only can reduce costs for fuel, labor, and equipment but it also can reduce soil erosion losses by 50% to 90% and improves soil moisture retention (Philips et al., 1980). The use of conservation tillage management mandates surface application of swine effluent, which in turn might foster the NH_3 volatilization losses. No-till soils usually have crop residue left on the surface which can hinder the infiltration of the swine effluent into the soil thereby increasing its exposure to the environment (Bless et al., 1991; Rochette et al., 2001). Ammonia fluxes, from surface applied poultry litter under no-till and paraplowed conservation tillage management practices ranged from 3.3 to 24% of the total N applied during winter and summer seasons respectively. Ammonia volatilization from the no-till plot was rapid immediately after litter application and stopped within 7 to 8 days (Sharpe et al., 2004).

The hot dry and windy climate at the Southern Great Plains coincides with the above mentioned environmental factors favoring NH_3 volatilization from swine effluent if it is used as nutritive additive for the crops. Hence the main objective is to quantify the NH_3 volatilization rates from swine effluent applied buffalograss and no-till fields using the passive flux center mast method.

MATERIALS AND METHODS

The experiments were conducted at the Oklahoma Panhandle Research and Extension Center located in Goodwell, OK on a Richfield loam during June and July, 2004 and April 2005. Nine plots, three each of native rangeland buffalograss, no-till and conventional till (CT) systems were established, with a radius of 3.81m. One plot for each of the cropping system was established to act as background plot, which didn't receive any effluent. Each of these plots except the background plot received 1170 liters (2.54 cm ha^{-1}) of swine effluent which was collected from the nearby anaerobic lagoon with an average pH of 8.1. During Jun and July 2004 and April 2005 each plot received 252.25, 158.16 and 186.23 kg NH_4^+- N ha^{-1} respectively. The difference in amount of NH_4^+ received was due to the variable nitrogen content in the effluent being applied. Surface soil samples were collected before and after every experiment from each of the treatment plots and analyzed for pH, total nitrogen and carbon, and total ammoniacal N content (TAN). Canopy height and standing residue height data from the buffalograss and no-till plots respectively, and percent crop residue for the no-till plot was collected before applying effluent to the plots (Table 3). During June and July 2004, the no-till experiment was conducted on wheat residue plots whereas during April 2005 sorghum no-till plots were selected because of land constraint. Percent residue cover was determined with the meter stick method (Morrison et al., 1993) where in a meter stick was randomly tossed three times in each of the no-till plots and once the meter stick lands on the soil the percent was evaluated by counting the total number of centimeter points at which the scale coincides the residue (Example: if the residue occurs at 35 centimeter marks along the meter scale, the percent of residue would be 35). Flood irrigation method of effluent application was adopted as it was the most appropriate and accurate method as it can take care of the overspray and NH_3 drift from other plots as compared to sprinkler application.

A micrometeorological mass balance method using passive flux samplers (Schjoerring et al., 1992) was used to measure NH_3 volatilization flux from the established plots. Passive flux samplers were constructed by using two 100 mm long and one 23 mm long tubes with a diameter of 7 mm, joined to each other using silicon tubing and a stainless steel disc of 0.05 mm thickness and a centered hole of 1.0 mm diameter was glued to the end of the 23 mm tube to reduce the airflow through the sampler and maximize NH_3 absorption. The 100 mm tubes inner surface was coated with oxalic acid to a length of 70 mm to adsorb the NH_3 passing through the sampler. The NH_3 adsorbed, was converted immediately into ammonium form which was later extracted with 3 mL of deionized water and analyzed for NH_4^+-N in the laboratory using Quickchem method 10-107-06-2-A (Lachat Instruments).

The mast with a wind vane on the top was installed at the center of each plot with the two passive flux samplers at every 25, 40, 56, 80, 120 and 196 cm height on each mast during June 2004 sampling, but as the horizontal flux at the highest point was greater than the background levels indicating some NH_3 is being lost beyond 196 cm sampling height,.for the next experiment sampling heights were adjusted to 25, 40, 56, 80, 120 and 275 cm. The sampling heights and the sampling times were selected based on the results of the previous work done by Warren (2001). In his work, carried on during July of 1999 and 2000, only four sampling heights of 15, 61, 130 and 274 were selected leaving a greater distance between the samplers wherein NH_3 concentration could escape off unmeasured and the NH_3 sampling was done less frequently i.e. once after every 12 hrs for the first 24 hrs wherein more than 80% of total NH_3 could get volatilized. Hence the sampling period was also adjusted and the sampling was done more frequently i.e. after every 6 hrs during the first 24 hrs and then at 48, 96 and 144 hrs after effluent application.

The horizontal flux of NH_3 (F_h, µg NH_3-N $m^{-2}s^{-1}$) at each of the six heights for both the glass tubes facing the wind direction modified from Schjoerring et al. (1992) and Wood et al. (2000) was calculated as.

$$F_h = \frac{C_1 + C_2}{2 * \pi * r^2 * Kc * \Delta t} \qquad \text{[Eq. 1]}$$

Where C_1 and C_2 are the ambient NH_3 collected in the tubes of the background plots subtracted from that of the treatment plots, r is the radius (m) of the hole in the steel disc, Kc is the correction factor (0.77) to correct the reduction in wind speed due to the steel plate, and Δt is the time between start and conclusion of the experiment.

The vertical flux (μg NH_3-N m^{-2} s^{-1}), of NH_3 from the treatment plot for each sampling period was determined by summing the horizontal flux at all the six heights and the equation used is :

$$F_{vt} = \frac{1}{x}\sum_{h=1}^{h=n}(F_h) * \Delta h \qquad \text{[Eq. 2]}$$

Where

F_{Vt} = Vertical Flux.

X = radius (m) of the plot.

H = height (m) at which the sampling tubes were placed.

F_h = horizontal flux (μg NH_3-N m^{-2} s^{-1}).

Δh = height (m) interval between the samplers.

The cumulative NH_3 volatilized (μg m^{-2}) was calculated using the equation:

$$F_{cum} = \sum_{t=1}^{t=n} F_{Vt} * \Delta t \qquad \text{[Eq. 3]}$$

Where

t = Sampling period.

F_{Vt} = vertical flux (μg m^{-2} s^{-1}) measured during each sampling period.

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

RESULTS AND DISCUSSION

Effluent pH, EC,total nitrogen (TN), ammonium and nitrate content listed in Table 1. Ammonium plus NH_3–N accounted for 80.3 to 83.6% of TN. Low nitrate values are indicative of the anaerobic state of the effluent. These results are comparableto data reported in previous studies (Adeli and Varco, 2001; Burns et al., 1987; Burns et al.,1990), which showed anaerobic swine lagoon effluent containing $NH_{4^+}^{+}$-N from 130 to 600 mg L^{-1}, and –nitrate nitrogen at < 16 mg L^{-1}. In these studies, 83% to 98% of the total effluent N existed as NH_4^+-N, and the remaining N was present in organic compounds that would require mineralization prior to plant uptake.

Horizontal Flux

The horizontal flux from all the plots decreased with height (Figure 1, 2 and 3) as expected because the NH_3 concentration gradient should decrease with height above the volatilization surface (Wilson et al., 1982). There was a significant difference ($F_{(\alpha = 0.05, 5,1062)} = 69.97$, $P < 0.001$) in horizontal flux at all the sampling heights among all the production systems and sampling seasons. Similarly the horizontal flux at different times after effluent application were significantly ($F_{(\alpha = 0.05, 6, 1059)} = 59.08$, $P < 0.001$) different for all the heights, sampling seasons, and production systems. This can be attributed mainly to the decrease in ammonium concentration with time. At the maximum sampling height of 196 cm during the June sampling period horizontal flux greater than µg NH_3-N m^{2-} s^{-1} was recorded from CT landscapes treatment during the initial 6 hrs after effluent application indicating some of the NH_3 might be escaping from the experimental plot, which would lead to underestimation of total NH_3 being volatilized. The NH_3 concentration boundary layer which has been extending (Incropea and Dewitt, 1990) above 196 cm might have caused this and hence the sampling height during July 2004 and April 2005 was increased to 275 cm in order to capture most of the NH_3 that has been volatilized. The horizontal flux profile of the three production systems followed a similar trend indicating that the buffalograss canopy height and the standing residue height of the no-till systems did not have much effect on the flux trend (Figure 2, 3) mainly because the average height (<15 cm) was less than the lowest sampling height (25 cm).

The average horizontal flux of ambient NH_3 as measured form the background plots throughout each experiment at each height ranged from 21.11 to 84.12 µg NH_3-N m^{-2} s^{-1} (Table 4). This range might have been due to temporal changes in the ambient NH_3 concentration in the atmosphere as well as difference in horizontal flux with height of measurement due to change in wind speed with height.

Cumulative Volatilization

During June, July 2004 and April 2005, 100.2, 35.8 and 43.3 kg ha^{-1} (Table 2) was lost via volatilization after 6 days of effluent application from buffalograss production system which accounted to 39, 22 and 23% of the NH_{44}-N applied respectively. This wide range is mainly because of the variation in the prevailing air temperature, wind speed, soil moisture, humidity and the rate at which NH_4^+-N was applied to the grasslands during each experiment. The average weather conditions during the three sampling periods (Table 2) mainly wind velocity, temperature and solar radiation during the June 2004 sampling was higher compared to that of July 2004 and April 2005 sampling while the relative humidity was higher during July and April sampling compared to June sampling which might have contributed to increased volatilization during June 2004 sampling compared to July and April sampling. This agrees with the findings of Moal et al. (1995) and Sullivan et al. (2003) who found that 19 to 46% and 36 to 63% of NH_4-N was lost respectively out of the total ammoniacal nitrogen (TAN) applied through NH_3 volatilization from swine effluent when flood applied to grassland. Lockyer and Pain (1989) reported nearly 40% of the total NH_4-N applied was lost through volatilization within six days following swine effluent application to a pasture. The cumulative NH_3 lost through volatilization from buffalograss during June 2004 was significantly greater than that lost during July 2004 ($F_{\alpha=0.05, 1, 15} = 93.8$, $P < 0.001$) and April 2005 ($F_{\alpha=0.05, 1,}$ $15 = 138.5$, $P < 0.001$) mostly due to higher rate of NH_3-N application during June sampling accompanied with high air temperatures, high winds and low humidity (Table 2) which favored NH_3 volatilization (Huijsman et al., 2002).

The average canopy height of the buffalograss plots during June, July 2004 and April 2005 sampling was 3.3, 4.5 and 4.9 cm respectively. During June2004 sampling the leaves of buffalograss were still wilted because of lack of rainfall while during July2004 and April 2005 the grass was in active vegetative growth stage after dormancy which may explain the greater NH_3 volatilization during the June 2004 sampling season. The actively growing grass can alter the surrounding microclimate by reducing the wind speed and soil temperature resulting in lower volatilization (Morvan et al., 1997). The leaves of actively growing grass can absorb substantial amount of the applied NH_3 thereby reducing its loss via volatilization (Sommer et al., 1997).

From the no-till soils 126.5, 68.2 and 63.3 kg ha^{-1} of NH_3-N was lost during June, July 2004 and April 2005 sampling seasons, respectively which accounted to 50, 43 and 34% of the total NH_4-N added which agrees with the findings of Rochette et al. (2001) and Port et al. (2003). They reported that NH_3 volatilization ranged from 9.5 to 16.9% of the total ammoniacal nitrogen swine effluent was applied to a no-till system. The cumulative volatilization in this work is higher mainly because of higher rates of total ammoniacal nitrogen application and high temperatures and wind velocity. Ammonia volatilization was significantly greater during June 2004 sampling because of low residue cover percent and standing residue height (Table 3), high wind speed and solar radiation, low relative humidity (Table 2) compared to those of July ($F_{(\alpha = 0.05, 1, 15)}$ =106.86, P <0.001) and April ($F_{(\alpha = 0.05, 1, 15)}$ =57.18, P <0.001) experiments (Table 3) as it was a dryland wheat. The presence of residue prevents pore sealing, crust formation (Blevins and Frye, 1993), and also increases soil aggregation thus structural stability (Singh et al., 1994) which increases the opportunity for effluent to infiltrate into the soil matrix (Godwin, 1990). Higher crop residue cover (>50%) slows down the evaporation rate (Smika and Unger, 1986) by isolating the soil from sun heating and air temperature and increasing resistance to water vapor flux by reducing wind speed, which in turn reduces total NH_3 loss.

During June and July 2004, and April 2005 155.9, 81.3 and 77.5 kg ha^{-1} of NH_3-N was lost from the CT system which accounted to 61, 51 and 41% of the total ammoniacal nitrogen which agrees with the finding of Thompson et al. (2002) and Svensson (1994). At wind speed ranging from 1.0 to 4.0 m s^{-1} and temperatures of 20.9 to 24.3°C, they reported that 30 to 62% of the total ammoniacal nitrogen (104 – 297 kg N ha^{-1}) can be lost in the form of volatilization from swine effluent applications. The cumulative amount of NH_3 that was lost during June 2004 sampling was significant compared to July 2004 ($F_{(\alpha = 0.05, 1, 6)}$ =351.78, P <0.001) and April 2005 ($F_{(\alpha = 0.05, 1, 6)}$ = 405, P <0.001) sampling. The higher wind speed air temperature and lower relative humidity during June sampling and the high total ammoniacal nitrogen that been applied during June might have favored this (Huijsman et al., 2002).

The cumulative NH_3 volatilization from the CT system was 35.7, 55.8 and 44.0% higher than that of buffalograss land system during June and July 2004, and April 2005 sampling, respectively (Figure 4). During July 2004 as the grass was in an active vegetative growth, greater difference could be observed compared to June sampling of the same year. The difference between the two systems was significant ($F_{(\alpha = 0.05,\ 1,22)}$ =263.4, P <0.001) during all the sampling periods which agrees with the findings of Morvan et al. (1997). Their demonstrated lower NH_3-N volatilization from effluent applied to grass sward than to bare soil as mentioned before mostly due to microclimatic change in presence of canopy and also due to absorption of NH_3 by the canopy. Litter of the native rangelands may also aid in N retention due to its tendency to conserve moisture (Willms et al., 1986). Plant communities within native pastures have well developed root systems with associated rhizospheric microbial populations (Dormaar and Willms, 2000), which aid in high organic matter buildup and reduced soil bulk density. This helps to enhance NH_4^+-N adsorption by roots, cation exchange complexes and the soil as the more developed root systems of native plants communities increase soil porosity and create larger root channels that liquid hog manure can percolate into (Lambert and Bork, 2003). Microbial population in combination with complex root systems can immobilize NH_4^+-N, acting as a slow release fertilizer for later plant use following decomposition (Dormaar and Willms, 2000).

Cumulative volatilization from the CT was 18.88, 16.07 and 18.28% higher than of no-till systems during June and July 2004, and April 2005, respectively (Figure 4). Significantly more volatilization occurred from CT production systems than no-till during all the three sampling periods ($F_{(\alpha = 0.05,\ 1,22)}$ =263.4, P <0.001), which agrees with the findings of Port et al. (2003) who reported a reduced NH_3 volatilization emission from no-till black oat residue systems compared to a CT land. As mentioned before the presence of surface residue can promote greater infiltration of effluent into soil and simultaneously prevents its direct exposure to the atmosphere thereby reducing its loss form the soil surface. Standing senescent stems in the no-till plots increase the aerodynamic roughness of the surface, reducing wind energy available for momentum transfer at the soil surface, and also the soil–atmosphere convective exchanges of heat, water vapor, and trace gases and these conditions can lower NH_3 loss through volatilization (Aiken et al., 2003).

Significant cumulative NH_3 loss occurred form the buffalograss compared to no-till plots ($F_{(\alpha = 0.05,\ 1,22)} = 82.87$, $P < 0.001$). Ammonia loss from the no-till plots was 20.7, 47.4 and 31.5% greater than that from buffalograss systems during June and July 2004, and April 2005 sampling seasons. The active standing grass canopy during July 2004 and April 2005, and the litter in the native range grassland seems to have a significant effect on the microclimate of this system compared to that of the residue effect of the no-till systems. During June 2004 even though the grass was dry its uniform cover over the soil surface might have contributed to the suppression of NH_3 loss.

Ammonia volatilization patterns

The percent loss of NH_3 of the total cumulative loss during the initial 12 hrs following effluent application during the June sampling season was 67, 58 and 64 from the buffalograss, no-till and fallow production systems respectively; While in the case of July and April sampling it was 46, 37, 44 and 68, 43 and 60% respectively. These findings are in consistent with Sommer et al. (1997) and Pain et al. (1989) who reported

50 and 80% of the total volatilization of NH_3 occurred within 8 and 12 hrs of effluent application, respectively. The average NH_3 volatilization rates from the three production systems during June, July and April were 2.9, 3.9 and 4.9 kg ha^{-1} h^{-1}, respectively for the first 12 hrs after effluent application, which agrees with the work of Sullivan et al. (2003) wherein they reported that the volatilization rates from bermudagrass plots varied from 1.2 to 4.2 kg ha^{-1} h^{-1}. The initial peak volatilization can be attributed to the large amount of the liquid that is being exposed to the atmosphere and over time the ammonium ions will be adsorbed to the soil colloids after entering into the soil thus reducing exposure to the atmosphere (Genermont and Celier, 1997). The NH_3 volatilization from applied liquid manure is not linear with time but peaks during the first 6 to12 hrs after effluent application (Figure 5) and this can be attributed mainly to the depletion of the NH_3 source as the time increases (Hujisman et al., 2002).

During July 2004 sampling, slightly less than 50% of the total NH_3 was lost during the initial 18 hrs of sampling whereas more than 50% of the total NH_3 was lost during other sampling periods (Fig 6), this deviation can be attributed to high soil moisture at the time of effluent application (Table 3) which prevented the effluent from entering the soil and thereafter leaving substantial amount of effluent on the soil surface which eventually was volatilized at 24 and 48 hrs following effluent application. This agrees with the findings of Sommer and Jacobsen (1999) wherein they reported a 20-30% reduction in ammonia volatilization at a soil moisture of 0.01g g^{-1} compared to losses at higher soil water content of 0.12 to 0.19 g g^{-1} because high infiltration of effluent at lower soil moisture content.

CONCLUSION

The experiment was conducted to evaluate the effects of weather conditions and the soil cover under three different production systems on NH_3 volatilization from swine effluent amended soils. The amount of NH_3 volatilization from applied swine effluent ranged from 22 to 58% of the ammoniacal nitrogen applied. On an average, 58% of the total volatilization loss occurred within 12 hrs of effluent application. Cumulative volatilization from the fallow land was 18 and 45% higher than no-till and buffalograss systems respectively, mostly due to reduced wind speed, reduced temperature and absorption of NH_3 by the canopy in buffalograss and higher infiltration rate of NH_3 into the no-till soil matrix. From a farmers point of view it would be economical if buffalograss rangeland soils are being amended with swine effluent when compared to no-till systems because of its greater efficiency in retaining ammoniacal form of nitrogen and greater the canopy height less will be the loss of NH_3. In conservational tillage practice it is better to have greater than 50% of the field to be covered by residue and have a good standing residue density and height to better harvest the nutritive value of swine effluent.

Table 1 Average (n=9) and standard deviation of selected characteristics of swine effluent used on experiments conducted at Oklahoma Panhandle Research and Extension Center, Goodwell, Oklahoma.

Paramete	Units	Jun-04		Jul-04		Apr-05	
pH		8.1	±0.2	8.25	±0.18	7.96	±0.4
EC_m§	dS m^{-1}	8.7	±0.08	10.25	±0.21	9.81	±0.31
TN*	mg L-1	1125	±23.1	770	±10.2	930	±18.1
TC**	mg L-1	2438	±38.1	1479	±21.4	1898	±16.1
NH_4-N	%	83.6	±2.3	80.3	±1.4	81.7	±2.3
NO3-N	%	1.7	±0.1	1.3	±0.07	1.5	±0.04

* Total Nitrogen
** Total Carbon

Table 2: Average† total ammoniacal nitrogen added via swine effluent and the amount of NH_3-N volatilized during the experiments conducted during 2004 and 2005.

Date	Sample Duration	Production System	NH_4^+-N Added	NH_3-N Volatilized	NH_4^+-N Lost
	Hrs		kg ha^{-1}	kg ha^{-1}	%
10^{th} to 16^{th} June 2004	144	Buffalograss	252.2 (20.4)±	100.2 (15.9)	39 (8)
		No-Till	252.2 (20.4)	126.5 (13.5)	50 (16)
		CT*	252.2 (20.4)	155.9 (7.3)	61 (19)
30^{th} to 5^{th} July 2004	144	Buffalograss	158.1 (24.1)	35.8 (7.5)	22 (6)
		No-Till	158.1 (24.1)	68.2 (10.0)	43 (3)
		CT	158.1 (24.1)	81.3 (2.0)	51 (5)
19^{th} to 25^{th} April 2005	144	Buffalograss	186.2 (15.4)	43.3 (13.5)	23 (4)
		No-Till	186.2 (15.4)	63.3 (9.3)	34 (6)
		CT	186.2 (15.4)	77.5 (4.4)	41 (1)

* Conventional till
± Numbers in parenthesis are standard deviations.
† n=9

Table 3: Meteorological conditions during the field experiments as measured by the Goodwell Mesonet weather station located at the Oklahoma Panhandle Research and Extension Center, Goodwell, Oklahoma.

Dates	Temperature			Relative Humidity			Wind Speed			Solar Radiation		
	Min	Avg	Max	Min	Avg	Max	Min	Avg	Max	Min	Avg	Max
	···········°C···········			·············%·············			········ m s^{-1}·········			····MJ m^{-2} day^{-1}····		
1*	13	26	38	0	43	91	2	9	14	0	29	88
2*	1	23	30	14	61	97	1	5	9	0	20	71
3*	15	20	35	23	64	97	1	6	15	0	22	85

1* = 10th to16th June 2004, 2* = 30th to 5th July 2004, 3* = 19th to 25th April 2005

Table 4: Average (n=3) soil water content, canopy height of buffalograss production system and standing residue height of no-till production systems measured during June, July 2004, and April 2005.

Date	Production system	Soil Moisture†	Canopy / Residue height	Residue
		g g^{-1}	cm	%
06/04	Buffalograss	0.080 (0.023)‡	3.3 (0.3)	NA
	No-Till	0.141 (0.032)	16.5 (0.8)	46 (1.23)
	CT*	0.121 (0.037)	NA	NA
07/04	Buffalograss	0.193 (0.065)	4.5 (0.5)	NA
	No-Till	0.281 (0.154)	18.0 (0.4)	72 (0.76)
	CT	0.223 (0.081)	NA	NA
04/05	Buffalograss	0.125 (0.049)	4.9 (0.8)	NA
	No-Till	0.151 (0.059)	40.6 (0.6)	83 (0.62)
	CT	0.131 (0.056)	NA	NA

* Conventional till

†Soil Moisture measured at soil surface 0 to 2.5 cm.

† Numbers in parenthesis are standard deviations.

NA=Not applicable.

Table 5: The average† horizontal flux measured at each height for the background plots measured during each experiment.

Height	June-04	July-04	April-05
cm		$\mu g\ NH_3\text{-}N\ m^{-2}\ s^{-1}$	
275	NA	51.1 (9.3)	84.1 (31.1)
196	76.2 (22.6)±	NA	NA
120	62.2 (14.1)	44.1 (11.2)	70.1 (28.2)
80	53.1 (29.1)	46.1 (23.7)	54.1 (20.2)
56	30.0 (10.4)	30.1 (15.7)	40.2 (19.3)
40	21.1 (17.65)	24.0 (6.8)	36.1 (17.8)
25	22.1 (14.22)	23.1 (13.24)	32.2 (10.8)

† n= 21 (3 plots X 7 samplings)
Not applicable
± Standard deviation

Table 6: Standard error for the mean horizontal flux calculated for the three production systems.

Hrs	June-2004			July-2004			April-2005		
	Buffalograss	No-till	CT†	Buffalograss	No-till	CT	Buffalograss	No-till	CT
6	31.49	41.22	37.99	26.57	15.39	30.21	4.11	17.83	36.67
12	36.64	21.89	4.65	4.39	12.67	16.84	3.87	5.51	14.38
18	17.32	34.74	2.83	3.49	3.38	5.15	4.00	4.04	6.38
24	16.61	24.37	3.50	1.36	1.19	14.22	7.12	7.41	3.45
48	4.97	4.20	3.51	0.23	3.70	2.50	0.53	0.37	5.57
96	1.26	13.85	5.67	2.24	2.81	1.83	0.23	2.37	1.04
144	0.54	2.86	1.93	4.32	3.19	2.22	3.01	2.21	2.42

† Conventional till

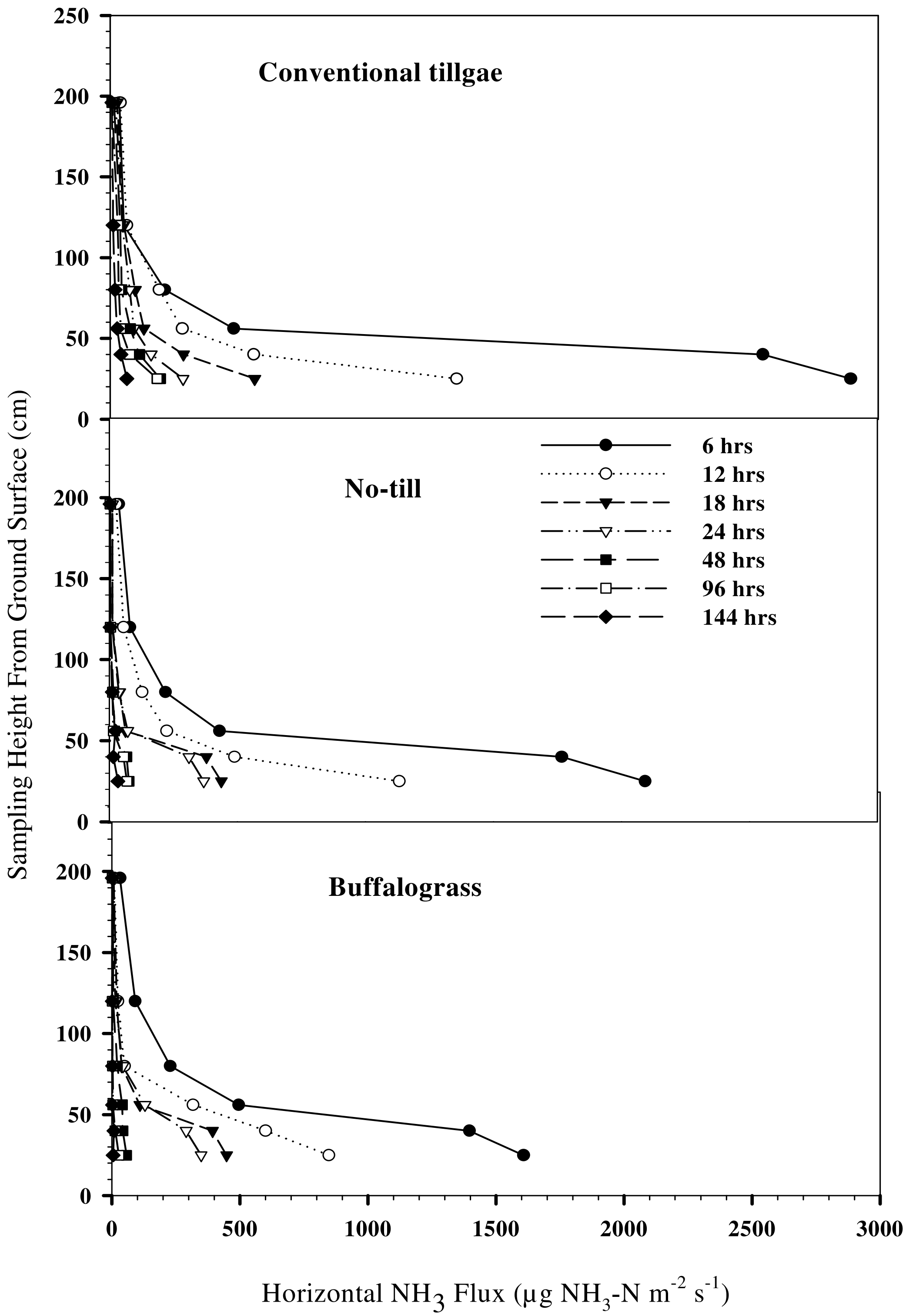

Figure 1: Average horizontal NH_3 flux measured after receiving swine effluent applications in June 2004.
[Note: See table 5 for standard error at each sampling time and height]

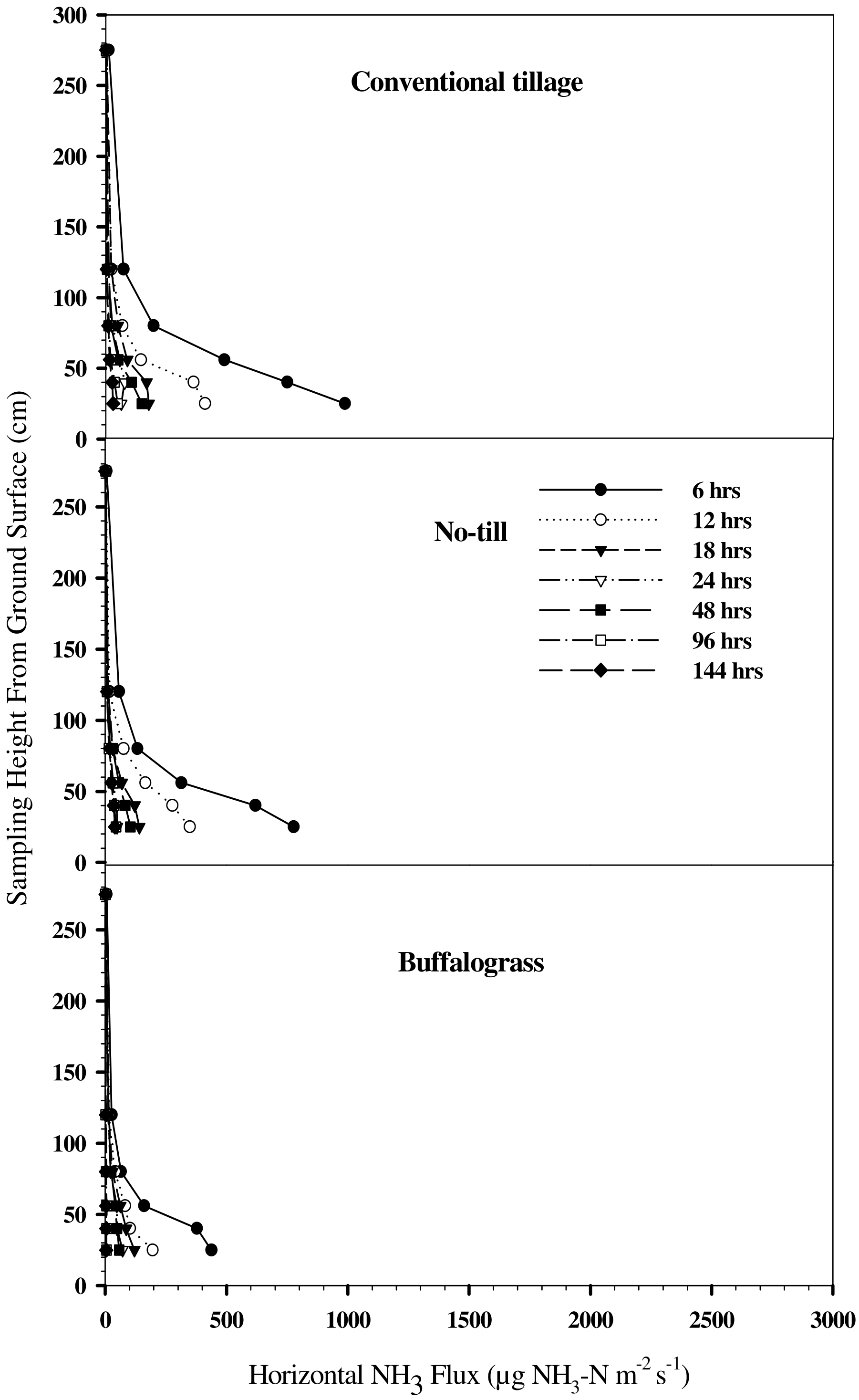

Figure 2: Average horizontal NH_3 flux measured after receiving swine effluent applications in July 2004.

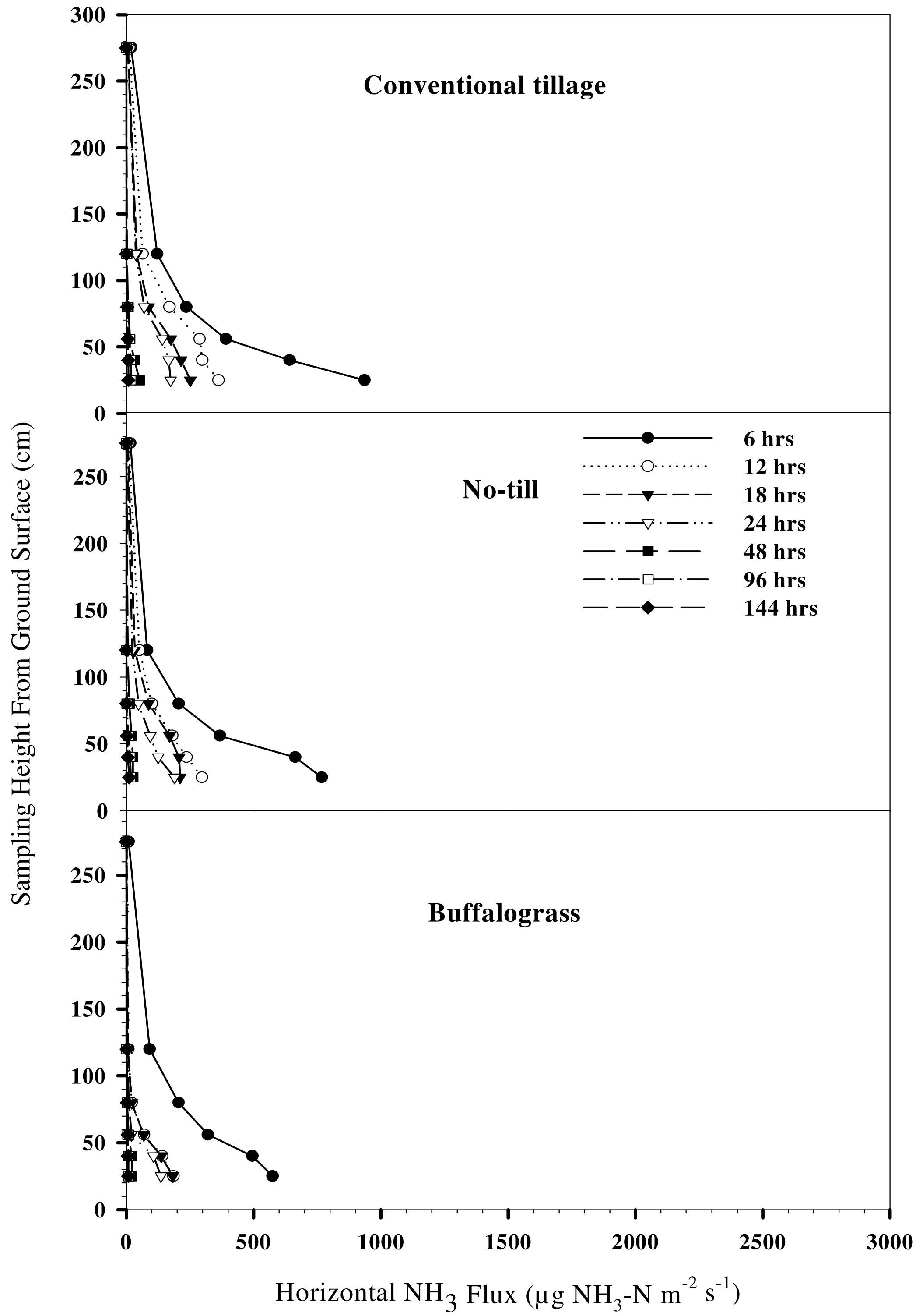

Figure 3:Average horizontal NH_3 flux measured after receiving swine effluent applications in April 2005.

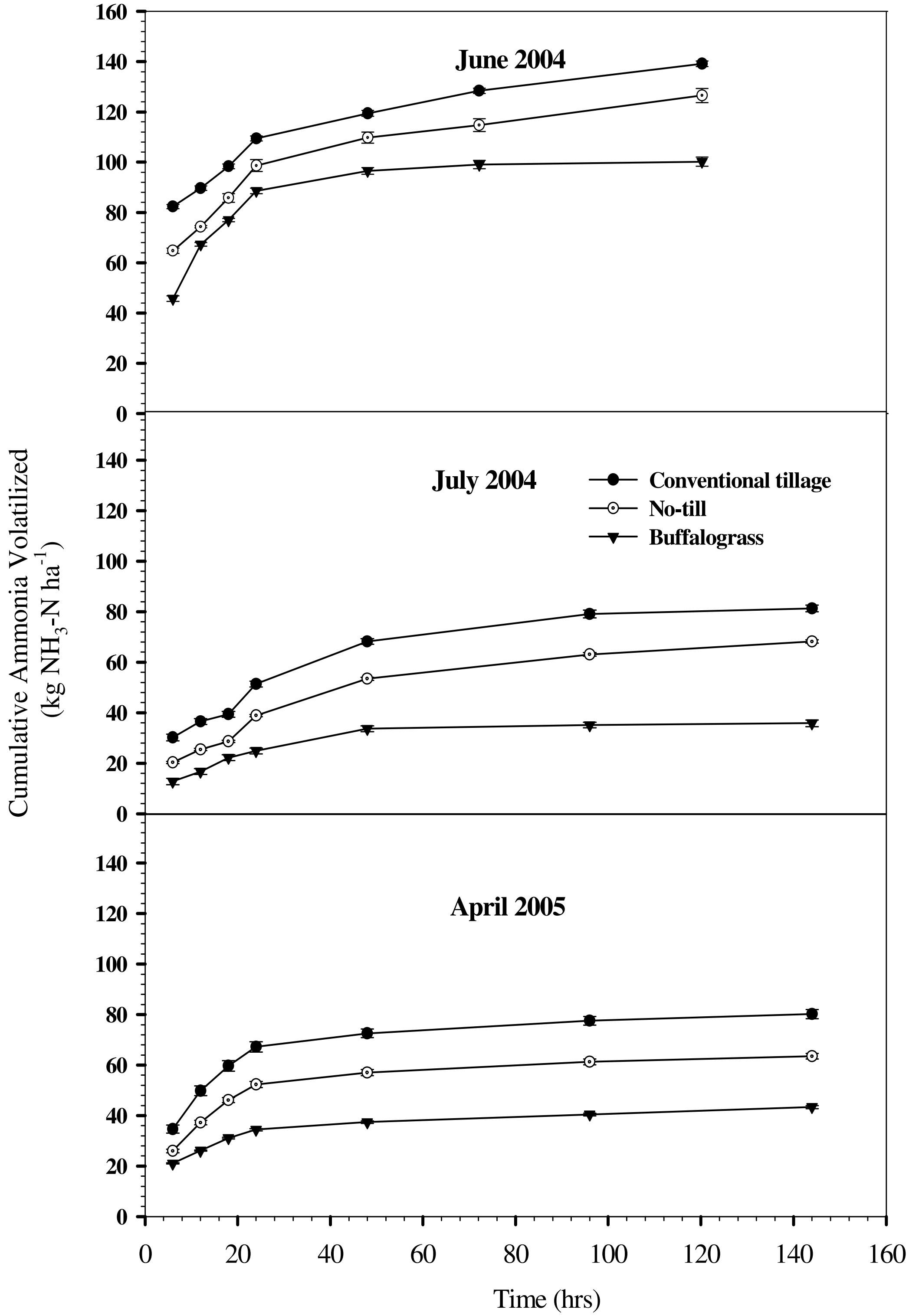

Figure 4: Cumulative NH_3 flux measured from different production systems following effluent applications

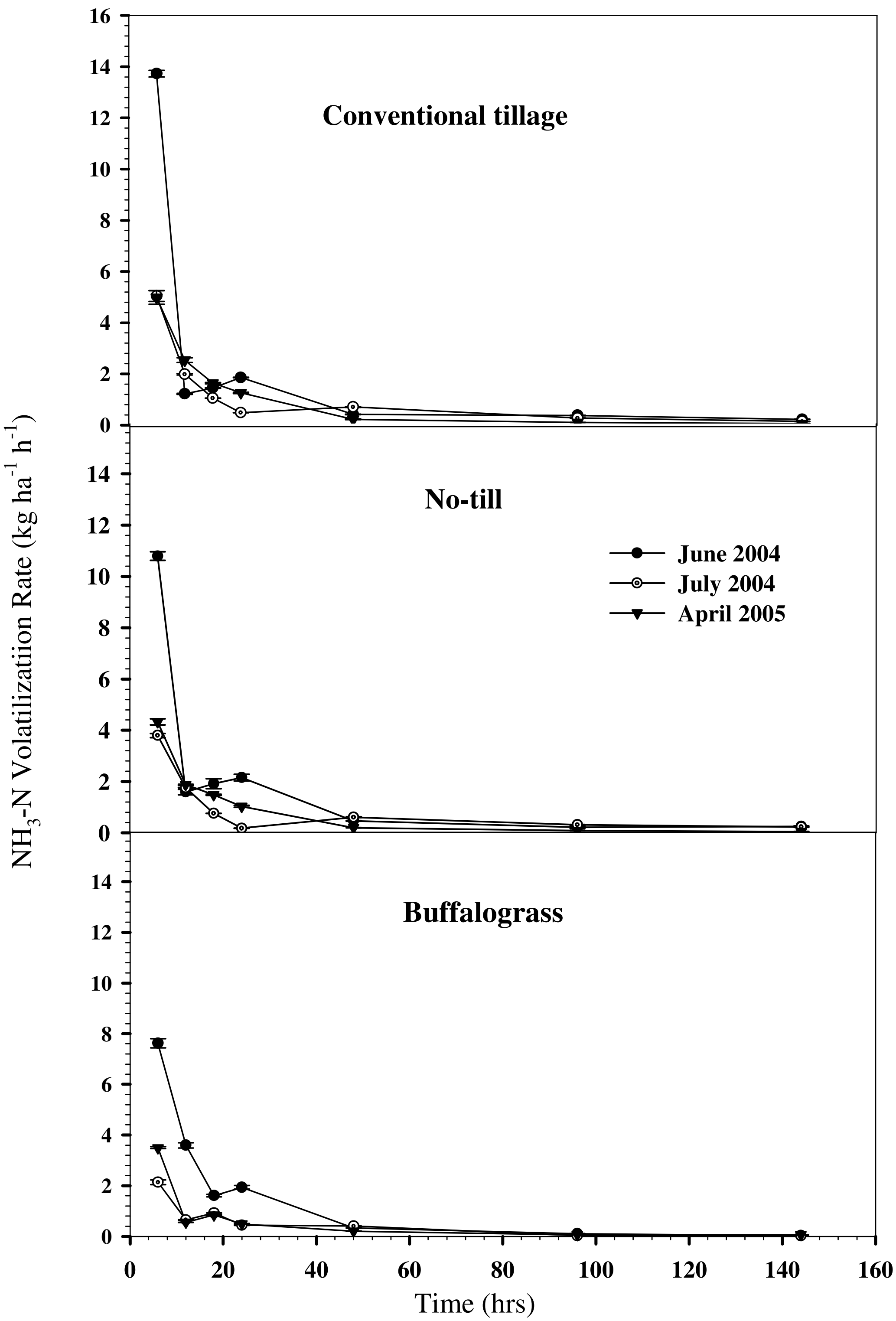

Figure 5: Ammonia volatilization rate of each production system each measured after effluent application

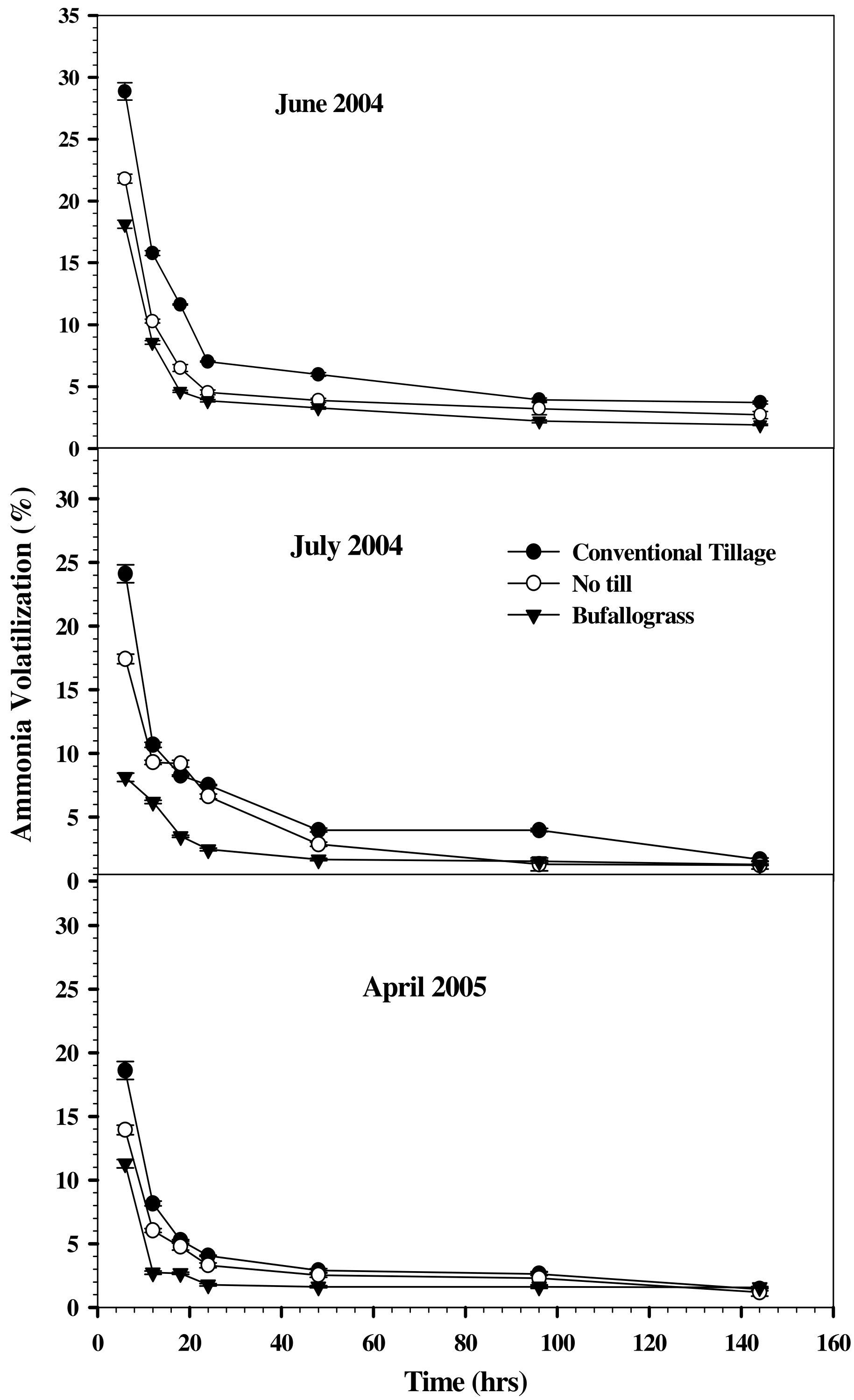

Figure 6: Ammonia loss expressed as percent of total ammoniacal nitrogen in swine effluent

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Chapter II

EVALUATING FIELD MEASURED AMMONIA VOLATILIZATION FROM SURFACE APPLIED SWINE EFFLUENT USING A MECHANISTIC MODEL

ABSTRACT

The objective of this study was to evaluate the measured ammonia volatilization from swine effluent applied conventional till, no-till and buffalograss production system by comparing it with a mechanistic model. Ammonia flux data was collected from the field using micrometeorological mass balance method. Micrometeorological data, of wind speed, temperature, relative humidity and solar radiation was collected along with canopy height of buffalograss pastures and no-till residues. Soil and effluent pH were also measured for each experiment as model input parameters. Frequent sampling after initial 24 hours of effluent application and sampling at lower height from the soil surface helped in reducing the discrepancy between the measured and predicted ammonia volatilization during June and July sampling under conventional tillage system . The predicted volatilization was 25% and 70% greater in magnitude compared to measured values under buffalograss and no-till systems, respectively. At present the model seems to predict patterns of NH_3 volatilization from swine effluent when applied to fallow systems. Improvements in the field experiment observation are needed to better evaluate the model. Grassland pastures and no-till systems with uniform canopy or residue cover and height has to be selected to validate the model. For model predictions in no-till systems, saturated hydraulic conductivity of the soil based on the percent residue cover

on the ground has to be measured and incorporated into the model replacing the saturated hydraulic conductivity of bare soil.

INTRODUCTION

Volatilization process of NH_3 from land applied swine effluent depends on various factors which can be grouped as meteorological, effluent or soil parameters and the application techniques (Morken and Sakshaug, 1988: Brunke et al., 1988: Sevensson 1994). Meteorological factors namely air temperature, wind velocity relative humidity and rainfall as previously discussed affect NH_3 volatilization (Moal et al, 1995). Among the soil factors affecting the volatilization are the soil pH, soil moisture, soil surface temperature cation exchange capacity and buffer capacity (Sommer et al., 1991; Soggard et al., 2002). Total ammoniacal nitrogen (TAN), pH, dry matter content and viscosity are the important properties of animal waste that effect volatilization of NH_3 from land applied swine effluent (Sevensson, 1994).

During the initial 12 to 18 hrs after effluent application NH_3 volatilization from soil is usually high then decreases rapidly, with decreasing NH_3 concentration (Beauchamp et al., 1982; Marshall et al., 1988; Smith et al., 2000). When the air temperature is greater than 10°C, nearly 50% of the NH_3 gets volatilized within 24 hours of effluent application, while the volatilization may slow down and continue for many days when air temperature gets close to zero. (Sommer et al., 1991; Pain et al., 1989).

Ammonia volatilization from land application of swine effluent is directly proportional to air and soil temperature, TAN and pH (Hoff et al., 1981; Beauchamp et al., 1982; Marshall et al., 1988; Pain et al., 1989; Sommer and Sherlock, 1996; Wu et al., 2003). Wind speed up to 2.5 m sec^{-1} significantly increases volatilization rates, beyond

2.5 m sec^{-1} the increase in NH_3 loss was not significant mainly because of increased water evaporation from the effluent surface favoring crust formation thereby reducing NH_3 volatilization (Thompson et al., 1990; Sommer et al, 1991). High NH_3 volatilization during initial hours following effluent application can be attributed to the elevated pH at the manure surface (Sommer and Sherlock, 1996). As NH_3 loss occurs, the pH declines thereby reducing ammonia volatilization in subsequent periods (Arogo et al., 2001), Gradual decline in soil pH could be attributable to the acidifying effects of NH_3 volatilization (Genermont, 1996; Sommer and Sherlock, 1996). Different soil surface covers namely grass or crop residue and soil properties affect NH_3 volatilization pattern from land applied swine effluent. Chadwick et al. (1998) reported greater NH_3 volatilization from swine effluent applied to grass swards as compared to bare soil. The grass swards or residue present on the soil surface can absorb significant amount of ammonia thereby preventing the effluent from percolating into the soil matrix and later can expose the effluent to atmosphere enhancing the volatilization rate (Thompson et al., 1990; Moal et al., 1995). The effluent and soil water holding capacity significantly affect the infiltration of swine effluent in to the soil matrix. The more dilute the effluent, the more quickly it percolates into the soil resulting in reduced NH_3 loss (Frost et al., 1990; Sommer and Olesen (check the spelling on this), 1991; Sommer and Jacobsen, 1999; Smith et al., 2000)

The interdependence of NH_3 volatilization from swine effluent applications on various parameters makes its difficult to understand or determine which factors exactly control the whole volatilization process and because of this complexity, a model which can explain the whole NH_3 loss process has to be developed. To successfully develop an applicable model to quantify NH_3 volatilization processes, understanding and consideration of numerous management practices, physical, chemical, and meteorological phenomena involved in the production, transport, reaction, and transformation of NH_3 both at the source and in the atmosphere is needed. Numerous attempts have been made to model NH_3 volatilization from soil system.

REVIEW OF LITERATURE

According to Arogo et al. (2001), models to quantify NH_3 volatilization can be classified basically into three categories: statistical, empirical and mechanistic. Statistical models basically involves those models which are derived from experimental data, wherein NH_3 emission data from a given scenario is monitored for a specific time, but factors which control volatilization process are not controlled. Hence this data will reflect various combinations of factors affecting volatilization rates, but cannot specify which factor is exactly influencing the process. Data from this model therefore show wide ranges of NH_3 volatilization fluxes from given environmental variables like wind speed, temperature and pH (Menzi et al., 1998).

Empirical models are built based on a controlled lab experimental data wherein factors responsible for NH_3 volatilization will be controlled. A lot of research has been carried on to determined which soil and effluent factors affect the NH_3 emission process and empirical models have been developed from the corresponding datasets. They can be sometimes used to validate the accuracy of mechanistic models (Sommer and Olesen, 1991; Maol et al., 1995; Menzi et al., 1998). Similarly Singh and Nye (1986) in a laboratory experiment developed an empirical model that describes changes in soil pH, the transformation of urea and ammoniacal nitrogen throughout the soil columns and the processes involved in NH_3 volatilization following urea application to soil. The main drawback of these models are that they can incorporate limited number of factors which within each model which influence the volatilization process to predict the actual NH_3 loss from swine effluent applied soil systems

Mechanistic models, describe the volatilization process through NH_3 transformation, equilibria, and transfer within a given system. Mechanistic models take into account factors that are involved in volatilization process but very often need variables which are difficult to obtain from field measurements and observations. van der Molen et al. (1990) derived a model of NH_3 volatilization from land applied cattle slurry describing the movement and transformation of NH_3 in the soil taking in to account the climatic factors that affect volatilization but it has taken only two modules, namely the soil module and transfer module thus making it a good base model but not an complete predictive model..

The integrated horizontal flux mechanistic model is most often used to estimate NH_3 volatilization (Denmead and Raupach, 1993). This method involves a mass balance approach that employs the measurement of the mean atmospheric NH_3 gas concentration minus the background gas concentration and the mean horizontal wind speed at several heights downwind from the leading edge of a plane source. Neglecting the turbulent component, the product of these measurements gives the horizontal flux. To obtain a well defined horizontal flux profile, Denmead and Raupach (1993) suggested at least five sample heights should be used to measure the NH_3 concentration. A model developed by Hengnirum et al. (1999) used three factors namely cation exchange capacity of the soil, wind speed and temperature that influence ammonia volatilization rate from the soil surface. This model does not account for the movement or transformation of ammoniacal nitrogen within the soil profile, it deals only with the transfer of NH_3 from the soil surface to atmosphere.

Genermont and Celilier (1997) proposed a detailed mechanistic model to predict NH_3 volatilization following effluent application in the field. The model composed of six sub models describing: 1) physical and chemical equilibria in the soil; 2) aqueous and gaseous NH_4^+-N transfer through the soil; 3) gaseous NH_3 transfer from soil to the atmosphere; 4) water transfer in the soil; 5) heat transfer in the soil; and 6) energy budget, water and heat exchange between the soil and the atmosphere. The first three models deal with the transfer of NH_4^+-N in soil and atmosphere. The remaining three models simulate heat and water transfer in the soil and are included to account for the temperature and soil water concentration dependent equlibria as NH_3 is transported with water in the soil. Although this model sufficiently predicted the cumulative NH_3 loss it couldn't adequately describe the effects of water infiltration and soil drying. This caused it to underestimate NH_3 volatilization during the first few days also during calibration of model they had to adjust the system pH up from 7.5 to 7.8 in order for the model estimation to fit the measured volatilization.

A practical model should have a realistic description of all the previously mentioned soil manure and meteorological implied mechanisms so that it can be used under a wide range of environmental/field conditions. A working model incorporating all the factors and processes of NH_3 volatilization has been developed by Wu et al. (2003) using the principles of similar to those of Singh and Nye (1986), Genermont and Cellier (1997) and Kirk and Nye (1991).

Field verification of this model has already been carried out by Warren (2001) and the model was able to predict measured cumulative volatilization from swine effluent application from bare soils except for June and July seasons sampling period wherein the model predicted higher cumulative volatilization than the measured possibly due to higher sampling heights and less frequent sampling. Hence the main objective of this study was to collect data during June and July seasons to test the mechanistic model developed by Wu et al. (2003) under different production systems.

MATERIALS AND METHODS

Soil Data

Bulk density of the Richfield clay loam was measured during the three sampling periods of June 2004, July 2004 and April 2005 using 3.4 cm core to depth of 5.3 cm. Sampling during April 2005 was carried out to validate the sampling methodology during other summer months. Three cores from each plot were dried at 105°C for 15 hrs and weighed. Soil moisture content was measured gravimetrically prior to effluent application for all plots to a depth of 15 cm. Composite soil samples consisting of 15 cores were taken from each of the circular plots to a depth of 15 cm to determine soil total nitrogen, nitrate and pH using 2:1 water soil ratio inorder to overcome spatial variabilty. The equilibrium adsorption isotherm data for ammonium adsorption to the Richfield clay loam and the particle size distribution data were taken from the work done by Warren (2001).

Effluent and canopy height Data

Effluent pH was also measured in the field as well as in lab. Effluent ammonium concentration was measured from the effluent samples, which were acidified directly after sampling with 5 *N* H_2SO_4 to a pH less than 4. Acidified samples were filtered and analyzed for NH_4^+-N using Lachat Method 12-107-06-1-B (Bloxham, 1993). Canopy height of buffalograss and the height of senescent standing stalks from the no-till systems were collected before swine effluent application to respective plots. Six observations were taken randomly from each of no-till and buffalograss production system plots to derive at an average canopy. The mast with a wind vane on the top was installed at the center of each plot with the two passive flux samplers at every 25, 40, 56, 80, 120 and 196 cm height on each mast during June 2004 sampling, but as the horizontal flux at the highest point was greater than the background levels indicating some NH_3 is being lost beyond 196 cm sampling height, for the next experiment sampling heights were adjusted to 25, 40, 56, 80, 120 and 275 cm. Sampling was done frequently after every 6 hrs during the first 24 hrs and then at 48, 96 and 144 hrs after effluent application.

Meteorological Data

Meteorological data including wind speed, temperature, relative humidity, solar radiation, and precipitation was obtained from the Oklahoma Mesonet weather station located within 2 km of all NH_3 volatilization plots used in this study at Oklahoma Panhandle Research and Extension Center, Goodwell, Oklahoma.

Ammonia Volatilization Data

Cumulative NH_3 volatilization from the surface applied swine effluent was measured as described in chapter 1. The micrometeorological mass balance method measures the average horizontal flux at each height. The horizontal fluxes at each height are integrated and multiplied by the change in height between the samplers, then summed and divided by the fetch length which is equal to the radius of the circular plots to estimate the vertical flux. Finally the cumulative NH_3 volatilized is estimated by multiplying the vertical flux with the sampling period. The working mechanistic model developed by Wu et al. (2003) was used to predict cumulative volatilization from all the three production systems incorporating various meteorological, soil, canopy (height) and effluent parameters (Table 3).

RESULTS AND DISCUSSION

Soils, canopy height and Effluent Data

The particle size distribution of the Richfield clay loam as measured in July 2000 (Warren, 2001) is showed in Table 1. The average soil pH ranged from 7.22 to 7.81, whereas the moisture content and bulk density ranged from 0.08 to .281 g g^{-1} and 1.21 to 1.51 gm cm^{-3} respectively, for the buffalograss, no-till and conventional till soils systems (Table 2). Average bulk density of the buffalograss pastures during all the sampling seasons was greater than that of no-till and conventional till systems and was ranging from 1.4 to 1.51 gm cm^{-3} which agrees with the findings of Greenwood and McKenzi (2001), who reported that the bulk density in grasslands due to grazing can increase the bulk density of soil to 1.62 g cm^{-3}. Effluent pH and ammonium concentration measured for the experiments conducted during 2004 and 2005 (Table 2) ranged from 7.96 to 8.25 and 0.981 to 0.615 g L^{-1} respectively which agree with the findings of Warren (2001) and Zupancic (1999), who reported that pH and ammonium concentartion would range between 7.4 to 8.25 and 0.856 to 0.963 g L^{-1} respectively. The canopy height of the grassland plots and standing residue height of no-till plots is shown in Table 2, the no-till residue during April 2005 sampling had twice the height as it was a sorghum crop residue as compared to wheat residue during June and July 2004 sampling.

Ammonia Volatilization Data

Predicted and measured cumulative NH_3 volatilization for the experiments conducted during June, July 2004, and April 2005 are shown in Figures 1-3 respectively. On an average the predicted cumulative NH_3 volatilization from the buffalograss production system was 25% greater than the measured data. Although there were differences between predicted and measured cumulative volatilization a significant correlation ($P_{(\alpha = 0.05)} = 0.034$,) was observed between the measured and model predicted cumulative volatilization from buffalograss pastures after 144 hours of sampling. During July 204 and April 2005 sampling the measured cumulative NH_3 volatilization from the buffalograss pasture during the initial hours after effluent application was greater than the predicted. This can be contributed to the grass sward absorption (Morvan et al., 1996) or interception and later evaporation of the swine effluent which other wise might have been infiltrated in to the soil matrix thereby favoring ammonia absorption and reducing the volatilization loss (Thompson et al., 1990; Moal et al., 1995) The effluent interception and later evaporation might have enhanced the total NH_3 volatilization which agrees with the study of Brye et al. (2000) wherein they reported that more than 70% of the rainfall water can be intercepted by the grassland prairies and later evaporated. The other possibility for the deviation between the measured and predicted value could be due to alteration in soil physical properties mainly the soil bulk density (Greenwood and MacLeod, 2001) and in turn the hydraulic conductivity due to cattle grazing. The bulk density of buffalograss soil was comparatively higher (Table 2) than other soils and this can be contributed mainly to the cattle grazing, which might have reduced the hydraulic conductivity of effluent in to the soil due to increased soil compaction. Grazing or animal trampling in rangeland results in increased soil compaction which in turn can increase the soil bulk density and decrease the effluent infiltration there by increasing the net volatilization rate (Greenwood and MacLeod, 2001).

During June 2004 sampling, the variation between the predicted and modeled data was comparatively higher than those of July and April sampling mostly because of the inactive vegetative growing stage of the grass due to low rainfall, as a result the grass swards were not effective in reducing the wind speed and also the temperature around them whereas the model calculates the volatilization based on the theory of reduction of wind speed and temperature in presence of any canopy leading to low NH_3 volatilization.

There was 75% variation between measured and model predicted volatilization for the no-till systems with r = 0.16 between the two values (Figures 1-3). This variation can mainly be attributed to the presence of dry residue in the no-till plots, which can intercept the effluent during its application and helped in its evaporation resulting in higher measured NH_3 volatilization than predicted. This agrees with the findings of Amberger et la. (1987) who found that that volatilization is increased when manure is applied onto a stubble or onto crop residues on arable land, and explained this increase by a decreased infiltration into the soil and an increased contact area with the ambient air.

The model estimates the volatilization assuming a uniform distribution of standing residue which was not seen in the real field measurements. The no-till fields wherein the experiments were carried on did not have standing residue distributed evenly throughout the experimental plots. Some rows were completely flattened when harvester wheels ran over them especially in case of sorghum residues. The no-till plots surfaces were not levelled and there was slope, inorder to prevent effluent ponding at some places the hose was moved frequently in the plots. In this process the weak standing residue couldn't withstand pressure of the effluent and coming out of the hose thereby collapsing during effluent application and hence couldn't alter the microclimate (Faurie and Bardin 1979) mainly the wind speed which otherwise would have reduced the NH_3 loss. The model was used to simulate NH_3 volatilization from no-till assuming zero canopy height in order to check the effect of the canopy height in no-till systems (Figure 4). The simulation during July 2004 and April 2005 sampling indicates that the standing residues had little effect on the volatilization process which can be attributed to their uneven distribution in the actual field, because the predicted volatilization assuming zero residue height showed similar volatilization pattern as that of the measured loss. At the same time the predicted NH_3 loss from no-till fields with zero canopy height greater than that of the measured volatilization, mainly because of the presence of the crop residues and some standing senescent stems in the no-till filed which might have altered the microclimate thereby reducing the volatilization loss. The percentage crop residue present on the no-till fields at the time of effluent application will enhance the volatilization of NH_3 by acting as a barrier between the soil system and effluent thereby reducing the penetration of effluent in to the soil system and increasing the exposure time of effluent to the atmosphere (Rochette et al., 2001) whereas this factor was not used in the model to predict the NH_3 loss.

The grassland and no-till plots were not graded to a flat surface and there was most often a slope to the plots. This slope allowed the effluent to pond in specific areas of the plots instead of uniformly covering the entire plot thus exposing more effluent to the atmosphere for easy volatilization and able to measure more volatilization. The model estimates the rate of volatilization with the assumption that the effluent is being spread uniformly over the entire soil surface leading to uniform volatilization. The sensitivity analysis (Figure 5) indicates that an increase of 3 cm in canopy height caused a 2% decrease in simulated cumulative volatilization where indicating a uniform canopy height has to be maintained in the field to validate the model against the measured values.

The measured and model predicted volatilization data from the conventional till lands during June, July 2004 and April 2005 matched with each other with a significant ($P_{(\alpha = 0.05)}$ <0.0001).. The predicted and modeled results were well correlated in this study compared to Warren (2001), this can be attributed to the lower sampling height of 25 cm and increased number of samplings during the first 24 hrs after effluent sampling wherein more than 80% of total NH_3 loss occurs through volatilization (Pain et al., 1989). This work and the previous work done by Warren (2001) clearly suggest that this model is a best fit to predict cumulative NH_3 volatilization when swine effluent is being applied to a conventional tillage land.

Another possibility for the discrepancy between the measured and predicted loss could be the sensitivity of the volatilization process to the change in soil and effluent pH. The sensitivity analysis of the model (Wu et al., 2003) indicate that a 0.2 unit variation in the soil pH will lead to 8% overall variation in NH_3 volatilization, similarly it was reported that 5°C increase in temperature and 50% increase in wind speed will lead to 13% increase volatilization. The sensitivity to pH requires soil and effluent pH measurements to be very accurate after its application to a particular soil system and that no change in pH of the effluent or soil system occurs during volatilization (acidifying effect) and infiltration into soil..

The model could successfully predict cumulative volatilization from the conventional land systems however predictions for no-till and grassland sites didnot match the measured values. In order for the predicted and measured volatilization to be better correlated modifications can be made to the field and model measurements. While carrying out the field measurements proper care and consideration should be given to ensure uniform distribution of both standing and ground cover residues for the entire filed. For model predictions, saturated hydraulic conductivity of the soil based on the percent residue cover on the ground has to be considered instead of just the saturated hydraulic conductivity because the residue can intercept and thereby hinder normal infiltration of effluent into the soil matrix (Rochette et al., 2001).

CONCLUSION

The measured data was successfully tested against mechanistic model and the discrepancy between the measured and modeled volatilization for conventional tillage systems which Warren (2001) reported for the June and July sampling could be reduced because of more frequent sampling during the initial 24 hours of effluent application and more samplings close to the soil. The mechanistic model predicted cumulative volatilization very similar to those measured from coventional till production systems and to some extent from the buffalograss systems but it couldn't predict the exact magnitude of volatilization from no-till systems. The predicted volatilization was 25% and 70% greater in magnitude compared to measured values under buffalograss and no-till systems, respectively. This may be due to the variation in the pH of soil and effluent after its application to the buffalograss pastures and no-till systems and also due to overestimation of the changes in the microclimate surrounding the no-till and buffalograss systems. At present the model seems to predict patterns of NH_3 volatilization from swine effluent applied to grassland and conventional tillage systems. Improvements in the field experiment observation are needed to better evaluate the model. An improvement relating to the pH measurements of the soil after effluent application to buffalograss and no-till soils has to be considered and at the same time grassland pastures and no-till systems with uniform canopy or residue cover and height has to be selected to validate the model. For model predictions in no-till systems, saturated hydraulic conductivity of the soil based on the percent residue cover on the ground has to be measured and incorporated into the model replacing the saturated hydraulic conductivity of conventional till soil.

Table 1: Particle size distribution for the Richfield clay loam from the Oklahoma Panhandle Research and Extension Center, Goodwell, OK, used for swine effluent application (Warren, 2001).

	·····Particle Size (µm)·····								
	<2	2-5	5-20	20-50	50-100	100-250	250-500	500-1000	>1000
% soil	32.8	3.90	9.8	33.4	9.3	6.3	3.8	0.9	0.2

Table 2: Average (n=3) and standard deviation of Soil moisture, pH bulk density, canopy height and effluent pH and NH_4^+ concentrations used for experiments conducted during June and July 2004, and April 2005.

	Production system	Soil† Moisture	Canopy / Residue height	Bulk density	Soil pH	Effluent pH	Effluent NH_4^+-N
		$g\ g^{-1}$	cm	$g\ cm^{-3}$			$g\ L^{-1}$
Jun-04	Buffalograss	0.080 (0.023)‡	3.3(0.3)	1.51(0.23)	7.34(0.41)	8.1(0.2)	0.981(0.07)
	No-Till	0.141 (0.032)	16.5(0.8)	1.4(0.28)	7.66(0.42)	8.1(0.2)	0.981(0.07)
	Conventional till	0.121(0.037)	0	1.28(0.27)	7.81(0.44)	8.1(0.2)	0.981(0.07)
Jul-04	Buffalograss	0.193(0.065)	4.5(0.5)	1.44(0.20)	7.44(0.32)	8.25(0.18)	0.615(0.09)
	No-till	0.281(0.154)	18.0(0.4)	1.21(0.17)	7.52(0.31)	8.25(0.18)	0.615(0.09)
	Conventional till	0.223(0.081)	0	1.34(0.22)	7.22(0.11)	8.25(0.18)	0.615(0.09)
Apr-05	Buffalograss	0.125(0.049)	4.9(0.8)	1.42(0.17)	7.34(0.23)	7.96(0.4)	0.725(0.6)
	No-till	0.151(0.059)	40.6(0.6)	1.24(0.25)	7.58(0.46)	7.96(0.4)	0.725(0.6)
	Conventional till	0.131(0.056)	0	1.36(0.24)	7.41(0.33)	7.96(0.4)	0.725(0.6)

† Soil Moisture measured at soil surface 0 to 2.5 cm
Not applicable.
‡ Numbers within the parenthesis are standard deviations.

Table 3: Input parameters used to run the mechanistic model to predict ammonia volatilization from swine effluent application

Input Parameters	**June 2004**			**July 2004**			**April 2005**		
	CT†	NT±	Grassland	CT	NT	Grassland	CT	NT	Grassland
Max Time (hrs)	168								
Irrigation Type	Flood								
Depth Applied (cm)	2.54								
Total Ammoniacal N Concentration ($g\ L^{-1}$)	0.981			0.615			0.725		
Manure pH	8.1			8.25			7.96		
Soil pH	7.81	7.66	7.34	7.22	7.52	7.49	7.41	7.58	7.34
Dispersivity (cm)	3.9								
Partition Coefficient ($cm^3\ g^{-1}$)	1.2427								
van Genuchten alpha (cm^{-1})	0.135								
van Genuchten n	1.383								
Saturated Water Content ($cm^3\ cm^{-3}$)	0.4553								
Residual Water Content ($cm^3\ cm^{-3}$)	0.0834								
Saturated Hydraulic Conductivity ($cm\ hr^{-1}$)	0.5332								
Sand Particle (mass Percentage)	25.5								
Clay Particle(mass Percentage)	32.7								
Field Width in Wind Direction (m)	7.62								
Start Time (Hour in a day)	11.25	10.42	9.25	11.5	10.58	9.42	11.56	11.15	10.35
Water Flow Iteration Criterion (%)	1.0E-5								
Mass Balance Criterion (%) for Water	5.0								
Canopy Height (cm)	0	16.5	3.3	0	4.5	18		4.9	40.6

† Conventional till ± No-till

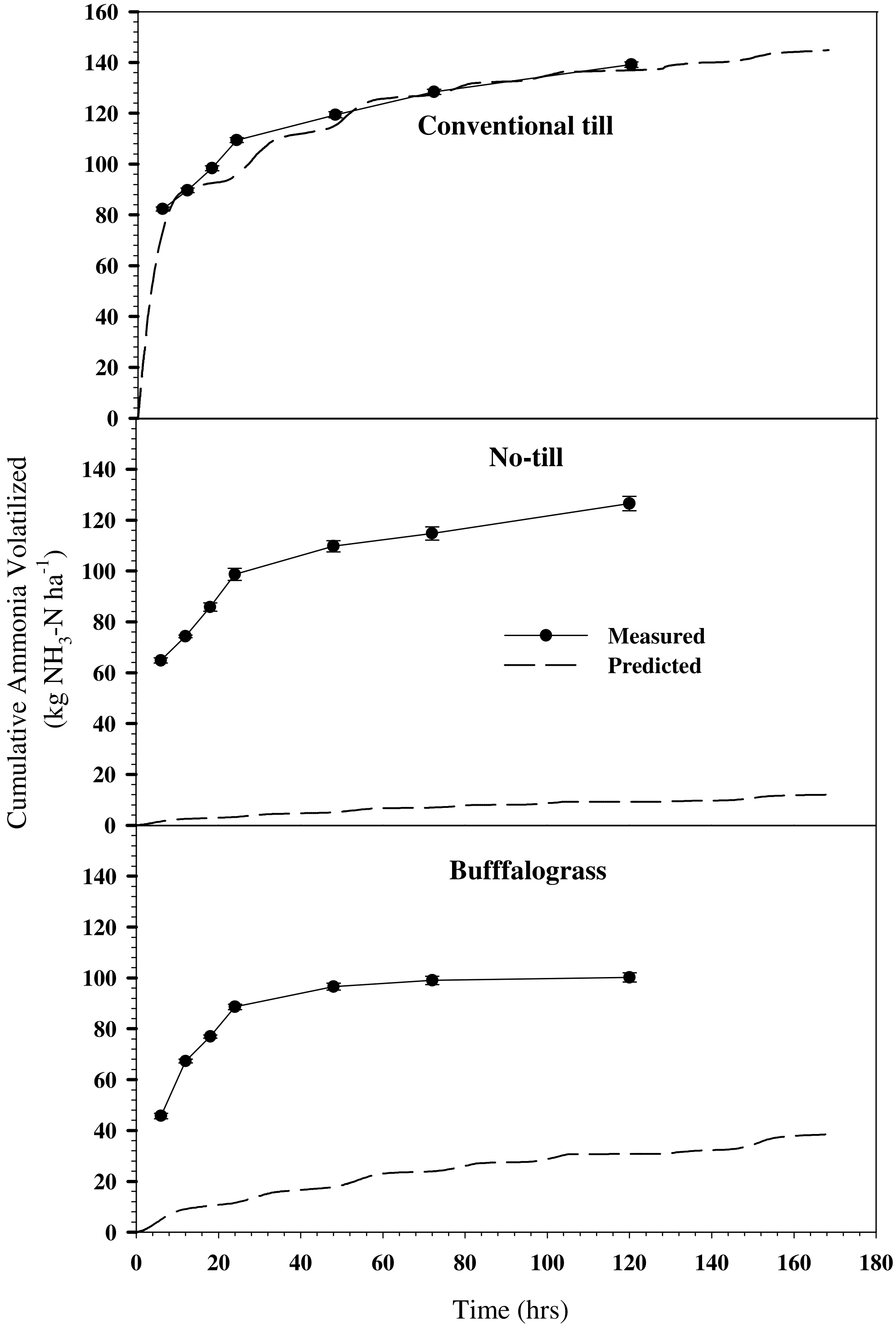

Figure 1: Comparison of predicted cumulative ammonia volatilized with measured field data in June 2004.

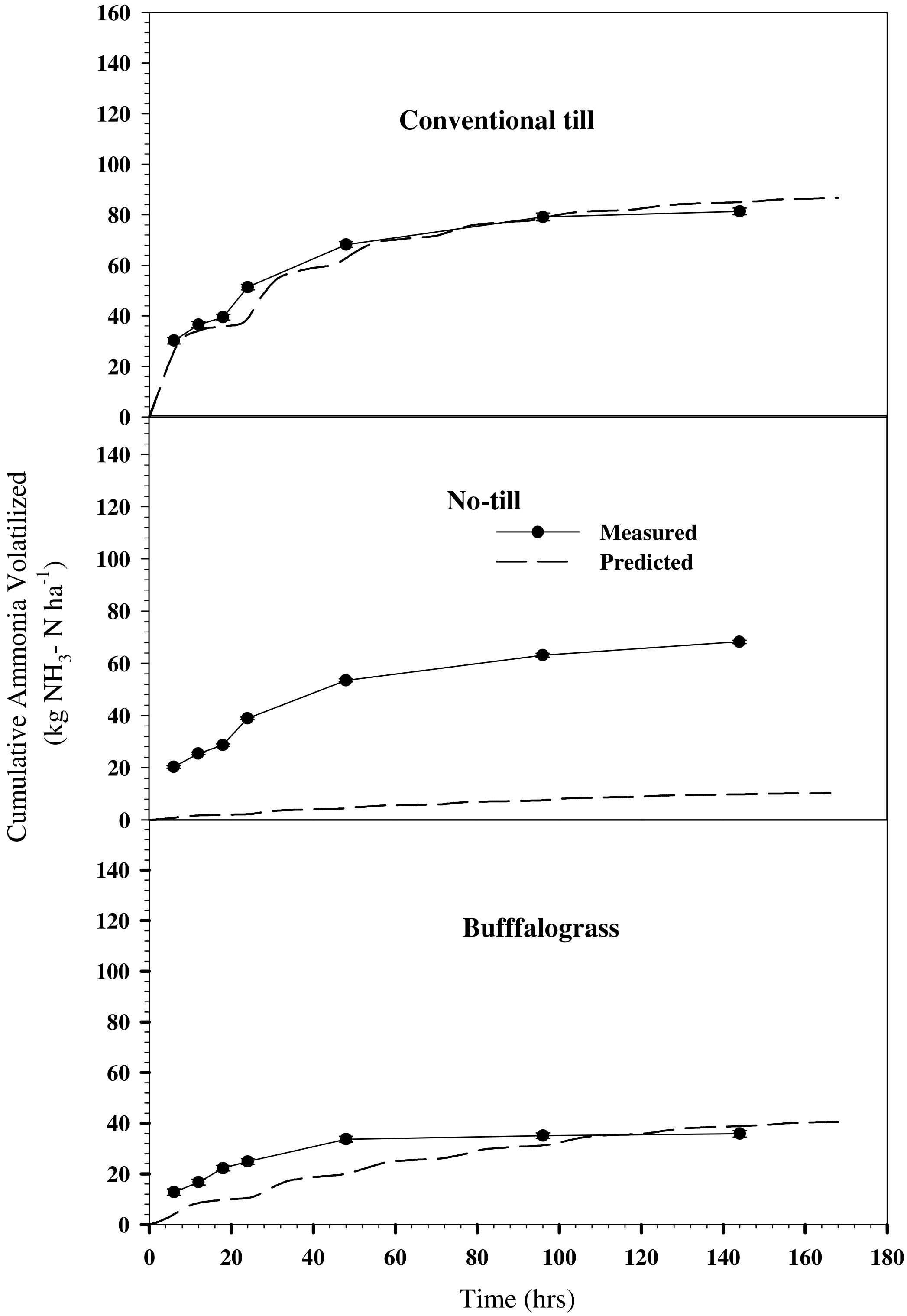

Figure 2: Comparison of predicted cumulative ammonia volatilized with measured field data in July 2004.

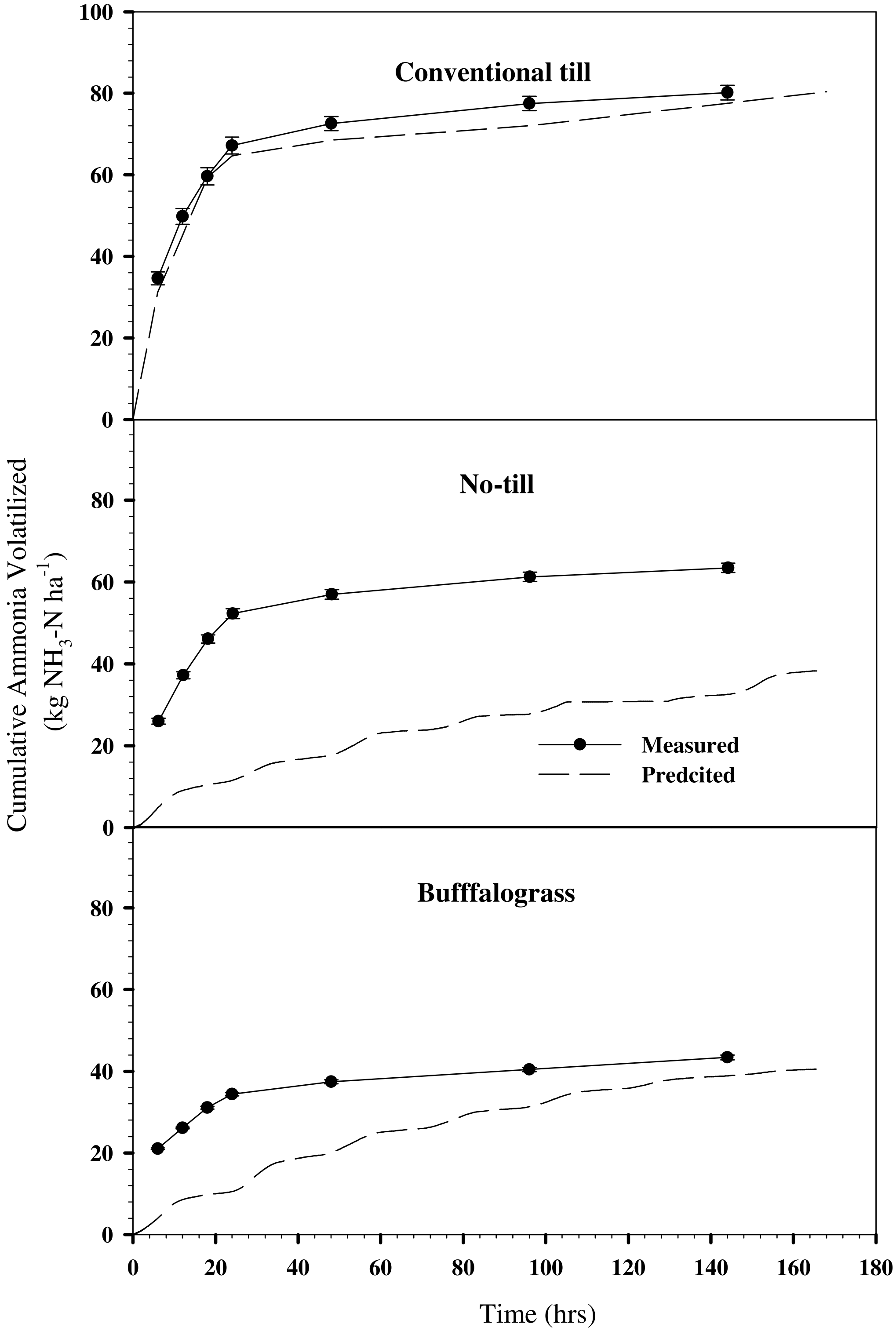

Figure 3: Comparison of predicted cumulative ammonia volatilized with measured field data in April 2005.

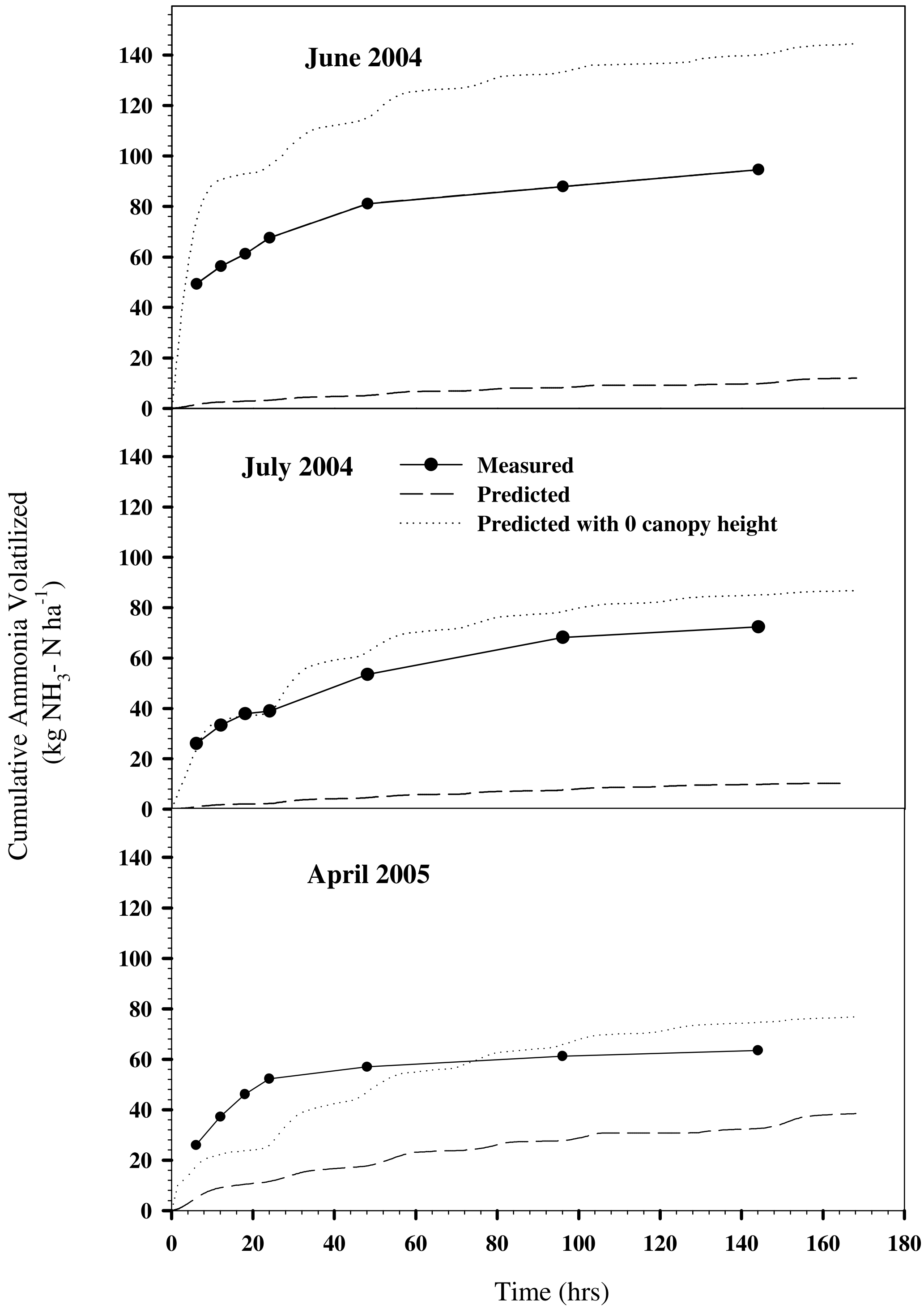

Figure 4: Comparison of predicted cumulative ammonia volatilized with measured field data for no-till.

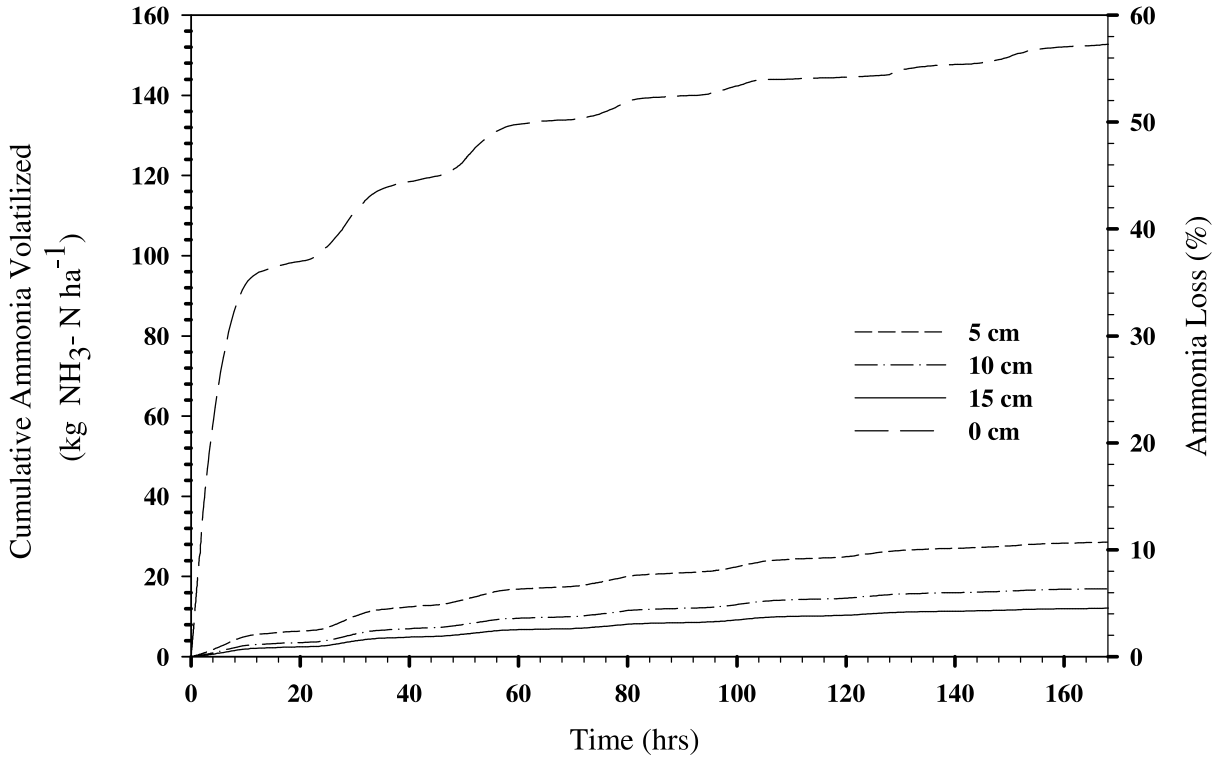

Figure 5: Sensitivity analysis of mechanistic model for no-till with different canopy heights.

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VITA

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Master of Science

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Scope and Method of Study:

Findings and Conclusions:

A study conducted during summer of 2004 and 2005 to evaluate ammonia volatilization from swine effluent on calcareous clayey loam soils. Ammonia volatilization from applied swine effluent ranged from 21.7% to 57.8 %. On an average, 58% of the total volatilization loss occurred within 12 hrs of application. The plant material significantly reduced volatilization loss as compared to conventional till soils. The second objective to evaluate measured ammonia volatilization from swine effluent applied conventional till, no-till and buffalograss production system compared to a mechanistic model. The predicted volatilization was 25% and 70% greater in magnitude compared to measured values under buffalograss and no-till systems, respectively. The present model predicted patterns of NH_3 volatilization from swine effluent when applied to fallow systems. For model predictions in no-till systems, saturated hydraulic conductivity of the soil based on the percent residue cover on the ground has to be measured.

ADVISER'S APPROVAL: Dr. Jeff Hattey