DETERMINATION OF AMMONIA FLUX FROM

SWINE EFFLUENT APPLIED TO

CALCAREOUS SOILS

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FOREWORD

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CHAPTER I

EFFICIENCY DETERMINATIONS OF AN AMMONIA PASSIVE FLUX SAMPLING SYSTEM

ABSTRACT

Various methods have been used and studied to fmd an effective system for measuring the loss of ammonia (NH3) from fertilizers and manure applications to croplands. Techniques vary, ranging from wind tunnels, $\frac{15}{15}N$ -balance, closed systems, semi-closed, and micrometeorological methods. Of these approaches, most researchers agree that when evaluating $NH₃$ losses under field conditions, the micrometeorological techniques are preferred due to their ability to not disturb the environmental or soil conditions, which are extremely important in volatilization processes. Also, they minimize sampling variations from point to point due to their ability to measure average flux over a large area. Danish researchers have devised a mass balance micrometeorological passive flux sampling system, which has simplified many previous methods. Climatic variations do not need to be measured, electrical power and a large labor force are not needed; there are no specific restrictions to the surroundings of the experimental area, and they can be utilized cheaply without the requirement of expensive or complicated technologies.

The purpose of this present work was to determine the efficiency of these passive flux samplers to capture volatilized ammonia (i) in the laboratory under controlled

conditions using a standard ammonium solution, (ii) in a laboratory experiment using acidic and calcareous soils at five concentrations of NH_4^+ -N in effluent, and (iii) with varying wind speeds in a wind tunnel.

Ammonia capturing efficiency determined in the laboratory using a standard ammonium solution indicated that these samplers are very effective at recovering volatilized NH₃. Recoveries of N ranged from 90 to 98%. Results from the soil-effluent laboratory experiments showed that volatilization was extremely rapid for the calcareous Richfield clay loam (pH 8.1) as compared to the acid Dennis silt loam (pH 5.8) over all effluent treatments. Mass balance results for soil-effluent experiments ranged from 71 to 148% recovery. Percent recovery decreased as effluent NH₄+-N concentration increased. However, when this sampling system was evaluated in a wind tunnel, the efficiency decreased to $\leq 40\%$. There are some artifacts of working in this particular wind tunnel, which are believed to be the cause for such problems. Poor recovery is believed to have resulted from variable airflow and turbulence. Despite poor recovery of $NH₃$ in the wind tunnel, results from the laboratory experiments indicated that these passive samplers have a high efficiency in closed conditions and good repeatability in a soil-effluent system. Therefore, these samplers show promise to work well under field conditions.

INTRODUCTION

An accurate measurement of $NH₃$ volatilization from nitrogen sources such as nitrogen fertilizers or animal wastes is necessary in attaining optimum N-use efficiency and N recommendations. Published estimates of NH₃ volatilization losses from both of these sources vary tremendously. Variability in studies of NH₃ losses is due in large part to the countless types and numerous methods of experimentation. Sewage sludge applied to a bare field reportedly lost 60% of the applied ammoniacal N due to volatilization as measured by an open aerodynamic diffusion method (Beauchamp et aI., 1978). Only 24 -33% of the NH₄⁺-N applied in liquid dairy cattle manure applied to bare fields was lost when measured by this same method (Beauchamp et al., 1982). Losses of NH₃ from urea additions were found to be 28% by the enclosure method (EM) and integrated horizontal flux method (IHFM) while the nitrogen recovery method (NRM) estimated a 45% loss (Black et al., 1985). Ammonia volatilization measurements in the field have always presented a problem due to the inability to take readings without disturbing one or more ofthe many factors that influence volatilization. In contained trapping systems, wind speeds, rainfall, and soil/air temperature fluctuations are very difficult to simulate when trying to create a representative field model. Denmead (1983) classified methods for gaseous nitrogen loss measurements from the field into these general categories: I) diffusion theory calculations of gas transport in the soil profile; 2) enclosures which measure flux densities of the gas in question at the surface; and 3) micrometeorological techniques which measure gaseous vertical flux density in the air above the surface. Therefore, studies to provide a systematic study of volatilization factors using forceddraft methods, such as those done by Ernst and Massey (1960), can not be used under

field conditions with any assurance of accuracy. Field research using closed or serniclosed methods such as a forced-draft or static enclosure (Harding et aI., 1963; Yolk, 1959) cannot simulate true environmental conditions due to extreme variation in the lower atmosphere and soil surfaces fluctuations. These experiments cannot be truly representative of field conditions because of the lack of a realistic near-surface turbulent flow (Gordon et al., 1988). Enclosures have typically been the method of choice by most researchers due to their relative simplicity, suitability for small experimental plots and the low sensitivity requirements for gas concentrations. An enclosure type method is more convenient for evaluating specific effects of variables and/or treatments. The use of wind tunnels as described by Lockyer (1984) has gained interest, yet not even with this semiclosed technique can all of the environmental field conditions be accurately represented. Studies using ¹⁵N have been used with some success, yet this type of measurement requires specialized equipment and skills not readily available to all laboratories (Fox et aI., 1996).

Micrometeorological methods are often better suited due to their ability to leave the surrounding area relatively undisturbed, enabling field conditions to be better represented. These methods are often necessary for determining losses from complex field conditions, because only with these methods can confidence be placed that measured losses have not been affected by the method (Denmead, 1983). However, these teclmiques are not without their own unique problems such as the need for a large labor force, large treatment areas, high expense, and technical equipment that make this system difficult to replicate and apply to variable treatments (Ferguson et aI., 1988). Also, Leuning et al. (1985) noted that this type of measurement system is more effective when

sampling times are short, such as one to two hours, and in which $NH₃$ levels and wind speeds are not prone to large fluctuations.

Ferguson et al. (1988) compared two field methods (a microplot-forced-draft method and a micrometeorological method) for estimating NH3 losses from urea solution applied to bare soil and wheat stubble residue. The microplot method places a cover over the treatment area while air is periodically drawn through the cover into an acid trap by a pump (Kissel et al., 1977). This was compared to the micrometeorological mass balance method (Beauchamp et al., 1978; Wilson et al., 1982). These studies revealed that the microplot method was more likely to affect the environmental parameters, which influence NH3 volatilization measurements more than the open micrometeorological method. Ferguson et al. (1988) stated that the micrometeorological method more accurately reflects the actual levels of ammonia loss. However, due to the larger areas required for these types of experiments, it is more difficult to replicate and apply variable treatments.

Based upon the mass balance principle, Beauchamp et al. (1978) suggested that NH3 volatilization losses from sludges applied in a field could be found by measuring the vertical profiles of the time averaged horizontal wind speed and NH₃ concentration. Ammonia molecules leaving a horizontal surface must be carried through a vertical plane by horizontal airflow. Wilson et al. (1982, 1983) simplified this model by eliminating the need for a large fetch, large labor force, and expensive instrumentation with the development of the ZINST mass balance approach. ZINST is the single height at which the rate of gaseous mass transfer to the atmosphere can be calculated as a function of roughness length and the radius source. Using this simple mass balance principle, a

passive flux sampler has been created by Danish researchers that employs a micrometeorological mass balance method for measuring NH₃ volatilization which should eliminate many of the problems associated with these open field measurements (Schjøerring et al., 1992). With this sampling system, climatic factors do not need to be measured and there are no restrictions to the experimental area or sampling periods., as with most other micrometeorological methods.

The purpose of the present work was to determine the efficiency of these passive flux samplers to capture volatilized ammonia (i) in the laboratory under controlled conditions using a standard ammonium solution, (ii) in a laboratory experiment using acid and calcareous soils at five concentrations of NH_4^+ -N in effluent, and (iii) with varying wind speeds in a wind tunnel.

MATERIALS AND METHODS

Samplers

The sampler, as described by Schjaerring et aI. (1992) and Sommer et al. (1996), consists of 3 glass tubes joined together by silicon tubing with lengths of 100 mrn, 100 mm, and 23 mm. All have an internal diameter of 7 mm. The inner surface of the two longer tubes is coated approximately 70 mm with oxalic acid. The shorter, 23 mm tube, has a 0.05 mm thick stainless steel disc with a centered hole of 1.0 mm in diameter glued to the outside end. The purpose of the stainless steel disc is to decrease the air speed inside the tubes in order to achieve a low friction resistance and a high $NH₃$ collection efficiency (Figure 1). Tubes and stainless steel discs were manufactured by Mikrolab Aarhus A/S, Axel Kiers Vej 34, DK-8270 Hoejbjerg, Denmark (Schjaerring et aI., 1992).

Each sampler includes two parallel sampler units facing opposite directions so that while one is collecting from the $NH₃$ source, the other is collecting any background NH3 that may be present in the experimental area (Figure 1). The oxalic acid coating is obtained by drawing acetone containing 3% oxalic acid into each tube. The acetone solution is allowed to drain and the tubes are dried with NH_3 free air and capped immediately to prevent any atmospheric NH3 from contaminating the tubes. Oxalic acid was selected as the NH_3 trapping medium due to its ability to completely absorb NH_3 gas at all relative humidities of the air stream (Shendrikar and Lodge, 1975; Ferm, 1979). Acetone was used as the solvent for the oxalic acid due to its highly volatile nature, which provides a uniform coating of oxalic acid once it evaporates (Leuning et al., 1985). After being exposed to the $NH₃$ source, the tubes are disconnected and eluted with $3 mL$

of deionized water. The dissolved coating, which now consists of ammonium oxalate and unreacted oxalic acid, was analyzed by using a Lachat 4 by Zellweger Analytics by the ammonia phenolate method (Bloxham, 1993).

Efficiency Determinations

These use of passive flux samplers is relatively new, with little published use of them. Therefore, laboratory experiments were conducted to detennine the efficiency at which these samplers were able to collect volatilized NH₃.

A system mass balance was perfonned to evaluate these samplers in the laboratory using standard NH_4^+ -N solutions. Fifty milliliters of 0.001 M NH₄Cl was placed in a 125 mL Erlenmeyer flask that was connected with a glass manifold consisting ofseveral ports. Two ofthese ports contained a coated oxalic sampler, while the other ports were capped off. Air was passed through the flask so volatilized $NH₃$ would be carried to the samplers. The other side ofthe Erlenmeyer flask was attached to a helium air source, which would carry any volatilized $NH₃$ from the NH₄CI source to and through the samplers (Figure 2). Helium (grade HP) was chosen as a carrier because it contains no detectable amounts of NH₃. A needle and syringe were placed into the stopper of the flask for the addition of 2 mL of a base solution (0.1 M NaOH) to raise the pH to 12, thus promoting NH₃ volatilization from the solution. At this pH, any NH_4^+ -N in the solution would tend to volatilize and be camed into the air stream and through the coated samplers described above. After the sampling time was reached, 10 mL of 0.2 M $H₂SO₄$ was added to the flask via needle and syringe to reduce the pH of the solution to 2 in order to stop further volatilization. Titrations were performed to determine the amounts

of NaOH and H2S0⁴ needed to alter the solution to the desired pH. Samplers were removed and analyzed for NH3 as described above. A Hewlett-Packard bubble flowmeter was used to ensure that airflow was maintained at 500 mL min⁻¹ through each efficiency determination experiment. The final NH_4^+ -N concentration for the NH₄Cl solution was determined for a mass balance of the system. The mass balance was corrected for the volumes of H₂SO₄ and NaOH added to obtain the desired pH to promote and halt NH3 volatilization respectively.

Soil-Effluent Flask VoLatilization Studies

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To determine sampling efficiency under a soil-effluent system, a mass balance was performed similarly to the above efficiency studies. Five flasks containing soil were connected to a manifold, with samplers on the outlet flow, and compressed breathing air on the inlet (Figure 3). Breathing air was chosen instead of other gas carriers for fear that microbial populations would be altered due to a lack of $O₂$ in such high moisture environments after effluent additions. To determine the efficiency of a soil-effluent system similar to what might be found under true field conditions, the environment should not be modified in such a way to hamper microbial processes such as nitrification or immobilization. A Richfield clay loam (fine, smectitic, mesic Aridic Argiustolls) and a Dennis silt loam (fine, mixed, thermic Aquic Argiudolls) were used for comparison in these experiments. Soil characteristics are summarized in Table 1. All soil samples for this experiment and succeeding experiments were analyzed by the following procedures. Soils were air dried and extracted for inorganic N using a 2 M KCI and soil solution ratio

of 2:5 Bremner, 1965) and analyzed with an automated flow injection analysis system¹. Lachat Method 12-107-04-1-B was used for soil $NO₃$ -N while Method 12-107-06-1-B was used to analyze NH_4^+ -N (Lachat, 1993; Bloxham, 1993). Soil samples were air dried at ambient temperature and ground to pass a 100 -mesh sieve $(0.15 mm)$ for the determination of total N and organic C analyses (Tabatabai and Bremner, 1970). Total N and organic carbon were analyzed using a Carlo-Erba (Milan, Italy) NA 1500 dry combustion analyzer (Schepers et aI., 1989). The calcareous Richfield soil was first acidified with 10% HCl to remove free $CaCO₃$ in surface horizons before the organic carbon determinations. Soil pH was determined using a glass electrode and a soil:water ratio of 1:2. Soil phosphorus, extracted using Mehlich III procedures (Mehlich, 1984), was analyzed using a Milton Roy 401 spectrophotometer. Effluent characteristics for all experiments were determined as follows: inorganic N was analyzed with the automated flow injection analysis system as described above. Electrical conductivity (EC) was measured using a flow through cell Radiometer Copenhagen CDM 83 Conductivity Meter.

The Richfield clay loam, from the Oklahoma State University Panhandle Research Station, was chosen for this study because future field volatilization experiments using these samplers were to be used in this soil series. Soil from the Holdenville region of the state was used due to its lower pH value (5.8), which would make a good comparison to the much higher pH of the Richfield clay loam (8.1) . Also, a significant amount of swine facilities are situated in the Holdenville area, warranting future attention to this area as well. Air dried soil was added to five 2000 mL Erlenmeyer

^I Mention of model and company names is for reader information only and does not imply endorsement or preferential treatment by any party involved.

flasks to a depth of 2.54 cm for each experimental test. This required 500 g of the Richfield clay loam and 550 g of the Dennis silt loam. In order to determine sampler efficiency in capturing NH₃ volatilization over a range of NH₄⁺-N effluent concentrations, 5 different concentrations were evaluated (0, 100, 300, 500, 1000 mg NH_4^+ -N L⁻¹). Effluent was obtained from the Oklahoma State University swine facility, which typically is low in NH₄⁺-N (100 mg L⁻¹). Therefore, to attain the higher NH₄⁺-N concentrations, a 10,000 mg NH₄⁺-N L⁻¹ stock solution was made in deionized water and added to the effluent to reach the desired concentrations. A high stock concentration was used to ensure that the characteristics of the effluent would not be altered to any significant degree when spiking the effluent. Before addition of the effluent, soils were brought to 16% field moisture by weight and allowed to equilibrate for approximately 30 minutes. Eighty-three mL of effluent was added to each flask, which is equivalent to ha - 2.54 em rate, while 83 mL of deionized water was added to the control flask.

Preliminary studies were conducted to determine the rate of volatilization from this system to ensure that samplers could be removed prior to saturation of oxalic-acid adsorbent, thereby reducing $NH₃$ bypass. After determining the rate at which $NH₃$ was leaving the soil surface, samplers were taken off before they reached a point of possible NH3 bypass due to saturated sites. According to Sommer et a1. (1996), samplers were able to quantitatively absorb NH₃ from the air as long as their NH_4^+ -N concentration was below 50 μ g, which was one-fifth of their total sorption capacity. The maximum capacity for $NH₃$ absorption of a sampler, after complete reaction of the oxalic acid, should be $252 \mu g NH_3$. Removal of the samplers at the proper time is imperative due to the absorption range. Tubes left on for too long could reach the maximum capacity and

lose NH₃ that bypasses filled sites, while tubes left on for too short of a time could be below instrument detection limits for NH3. Samplers for the Richfield clay loam necessitated removal every 10 minutes for the first hour due to extremely rapid volatilization rates immediately following the addition of the effluent. By the 20th hour, volatilization was still quite high, with samplers being removed every 60 minutes. The acid Dennis silt loam however, required removal of the samplers every 20 minutes for the first hour and after only 5 hours, the rate of volatilization was so low that samplers only needed to be removed every 60 minutes. After the $6th$ hour, samplers were only taken off three more times. Samplers were taken offless frequently for the 0 and 100 treatments for both soils due to a much lower volatilization rate.

After the 24-hour sampling period, soils were immediately extracted with 2 M KCI for $NO₃$ -N and $NH₄$ ⁺-N determinations. Percent moisture was determined by oven drying. Results from two Richfield clay loam experiments were combined to determine a best-fit curve for all treatments using SigmaPlot (SPSS, 1997). A 2nd parameter power equation was empirically determined to model this data using an equation of $y = ax^b$. Three experiments for the Dennis silt loam were used to determine the same best-fit line as described for the Richfield soil. Only 2 of the Richfield flask runs were included in these comparisons, because the airflow rate for the first attempt was measured incorrectly after the stainless steel disc.

Wind Tunnel Studies

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To evaluate sampling efficiency in environments similar to field conditions, effluent was applied to a soil in an environmental wind tunnel. This tunnel, developed to study wind erosion by the Biosystems and Agricultural Engineering Department in the 1930's, is approximately 15 m long and 1.22m in height and width (Figure 4). Outside air is pulled through the tunnel by a 2.4 m diameter fan, while the exhaust was vented through open doors.

Three sets of plastic louvers were positioned upstream throughout the tunnel in an attempt to reduce turbulence in the airflow caused by the pulling motion of the fan. Roughness elements (64 mm x 64 mm) were installed over a 4 m span of the tunnel floor in front of the source to break up laminar airflow on the bottom.

Samplers were set up at the tunnel intake to measure background levels of NH₃ in the airflow. These values were subtracted from the samplers placed downwind ofthe source, which were capturing volatilized NH₃. In initial tunnel runs, samplers captured volatilized NH₃ at a constant wind speed of 2.2 m s⁻¹ from an NH₄Cl source. One thousand milliliters of a 0.1 M NH4Cl source were raised to an alkaline pH with the addition of 0.2 M NaOH. After 12 hours, samplers were capped and the NH4Cl solution was acidified to stop further volatilization. Final ammonium concentrations were analyzed from the source after the experiment to determine a mass balance for the system. Relative humidity and ambient air temperature inside the tunnel were monitored throughout each of the 12-hour experiments with a VelociCalc 8345 anemometer and a hand held sling psychrometer. After sample collection, NH_4^+ -N in the sampling tubes was determined as previously described.

After numerous runs with the NH4Cl source, a soil-effluent system was initiated with the same procedure as described above. Thirteen kg of a Norge loam (fine mixed thermic Udertic Paleustoll) soil was added to a large pan across the entire width of the

tunnel at a 2.54 cm depth. The soil was brought to 16% field moisture and allowed to equilibrate for over 1 hour before 2.4 L of effluent was evenly distributed over the soil surface with a watering can. Effluent amounts were calculated to be applied at aha - 2.54 cm rate. Due to the low NH₄⁺-N concentration of the effluent (100 mg L⁻¹), 50 mL of 1.067 M NH4Cl was added to the effluent. This was performed in order to spike the effluent to levels that could be more accurately measured and which would be similar to NH₄⁺-N concentrations that is commonly found in the Panhandle region of the state.

RESULTS AND DISCUSSION

Efficiency Determinations

Under closed laboratory conditions, the passive samplers were relatively effective at capturing volatilized $NH₃$ as indicated by the efficiency of the tubes ranging from 90 -98 % (Table 2). These preliminary tests indicated that the samplers should be effective for the collection of volatilized NH₃.

Data from the original publications promoting these passive samplers found a strong linear relationship between the horizontal net flux densities of $NH₃$ measured by the passive flux samplers and by a reference method (r^2 = 0.96) under field conditions Schjøerring et al. (1992). An NH₃ source consisting of 140 beakers was evenly distributed throughout the experimental area in which a reference method was compared to the new passive flux samplers. Ammonia losses from an $NH₄HCO₃$ solution as estimated by the use of passive flux samplers was also compared to a reference teclmique by Sommer et al. (1996), in which estimations of losses were quite similar between the two methods.

Soil-Effluent Flask Volatilization Studies

Early laboratory experiments found that small increases in soil pH resulted in higher rates of NH₃ volatilization (Jewitt, 1942) and research by Martin and Chapman (1951) demonstrated that $NH₃$ losses were dependent on pH and temperature. Many other studies have shown that generally, as pH increases the greater the loss of NH₃ due to volatilization (Chao and Kroontje, 1964; Du Plessis and Kroontje, 1964; Warren, 1962; Meyer et aI., 1961; Freney et aI., 1983). This was also demonstrated in these

laboratory flask runs using the calcareous soil versus the acid soil. Volatilization was extremely rapid for the Richfield clay loam as compared to the Dennis silt loam over all effluent treatments (Figures 5 and 6). Also, the difference in volatilization rates between the two soils is influenced by the amount of Ca^{2+} present in the calcareous soil, as can be seen by the soil cation exchange reaction shown below. Higher amounts of NH_4^+ -N are exchanged on the CEC with increasing amounts of $NH₄$ ⁺-N added to the Dennis silt loam. In comparison, as NH_4^+ -N concentrations increased in the Richfield clay loam, the presence of Ca^{2+} did not allow appreciable amounts onto the CEC due to the binding energy. With higher amounts of NH_4^+ -N present in soil solution, increased amounts of $NH₃$ will be volatilized due to the presence of OH $\,$ in the high pH soil.

Dennis silt loam (pH 5.8)

$$
\begin{array}{c|c|c|c|c} \hline \text{H}^+ & +5 \text{ NH}_4{}^+\text{-N} \rightarrow & \text{NH}_4{}^+\text{-N} \\ \hline \text{H}^+ & +5 \text{ NH}_4{}^+\text{-N} \rightarrow & \text{NH}_4{}^+\text{-N} \rightarrow \text{K}^+ \ +2\text{H}^+ \ +2 \text{ NH}_4{}^+\text{-N} \\ \hline \text{H}^+ & \text{H}^+ \end{array}
$$

Richfield clay loam (pH 8.1) $H+$ $+5NH₄⁺-N \rightarrow$ $=$ $Ca²$ NH/-N \longrightarrow H⁺ + 4 NH₄⁺-N + OH⁺ → 4 NH³_(g) 1 $\frac{1}{\sqrt{2}}$ Ca²⁺

Initial runs using the calcareous soil found that the sorption capacity of the sampling tubes was saturated within 15 minutes after initial application, therefore the samplers were changed every 10 minutes for the first hour. The volatilization rate decreased with time and was negligible at 24 hours. When working with this system it is imperative that sampling begin as soon after application as possible for the most accurate measurements. The two Richfield clay loam flask experiments were very repeatable for

treatments 100, 300, and 1000 mg NH₄⁺-N L⁻¹ (r ²= 0.99, 0.99, 0.99 respectively), while treatments 0 and 500 mg NH₄⁺-N L⁻¹ were much lower (r^2 = 0.38 and 0.81) (Figure 5). Regression statistics are shown in Table 3 for all treatments and both soils. The control treatment, in which only deionized water was added to the soil, displayed variations between the two replications resulting in a low r^2 (0.38). Variability should be higher at the lowest NH₃ volatilization rates (i.e. control). The 500 mg NH₄⁺ L⁻¹ effluent treatment for the first experiment was considerably less than for the following experiment, resulting in a much lower coefficient of determination (0.81). The three Dennis silt loam experiments were quite variable (Figure 6). The initial flask run was lower than the following two experiments for treatments 1000 and 100, while treatment 500 for the second run was higher than all other treatments for all experiments. The reason for such variations in these three flask runs is unknown. Laboratory conditions, flowrate, source, and procedures were all held constant. Samplers possibly were just not able to pick up on these lower amounts of NH₃.

Mass balances for these laboratory soil-effluent experiments demonstrated that generally, with increasing effluent concentrations, percent recovery of the system decreases (Table 4). Exchange competition becomes a factor at higher NH_4^+ -N solution concentrations. As exchange sites fill up with increasing concentrations of NH₄⁺-N in solution, more NH₄⁺-N will be subjected to volatilization. With increasing amounts of volatilized NH), the higher the possibility of error, thus decreasing the percent recoveries ofthese systems at the higher concentrations. Recoveries greater than 100% for the control flasks could be attributed to increased microbial activity due to added moisture. These soils were air dried and stored for several months before use. Nitrogen could have

been mineralized, thus increasing the soil N balance at the conclusion of the experiments. *Rice* and Havlin (1994) discussed the factors that affect accessibility of organic N to microorganisms. Disruption of aggregates when working in a laboratory setting tends to increase net N mineralization (Craswell and Waring, 1972; Cabrera and Kissel, 1988). Also, when dry soils are rewet, microbial activity is generally stimulated which in turn increases mineralization (West et al., 1992). During the rewetting of soil, the flush of N mineralization could be due to the increase of the rapidly mineralizable pool (Cabrera, 1993). Therefore, it is possible that a flush of mineralization in the control flasks during this laboratory study could have contributed to the increased percent recoveries. Control flasks for the Dennis silt loam exhibited increases in NH_4^+ -N concentrations with a decrease in $NO₃$ -N levels for two of the three experiments. However, for the Richfield clay loam the opposite was found. Soil concentrations of NH_4^+ -N in the control flasks for the last test had decreased by the end of the 24-hour testing period, whereas the $NO₃$ -N levels increased. The first experimental run of the Richfield soil increased in both $NO₃-$ N and NH₄⁺-N concentrations. However, these changes were small and are likely due to experimental error.

Wind Tunnel Studies

Application of swine effluent to the soil in the wind tunnel allowed for evaluation of the tubes in a simulated field condition. When this sampling system was moved to a wind tunnel setting, the efficiency of the samplers decreased significantly, ranging from 9.0 to 35.7% (Table 5). The concentrations collected on the tubes were much lower than those from the initial laboratory experiments. The NH₄⁺-N concentrations for many of

the samplers were near background levels. Known volatilization took place because concentrations of NH₄Cl solutions decreased with time. This is cause for concern that in a field experiment, $NH₃$ could be below detection limits of the analytical equipment when using these samplers. There were some anomalies associated with working in this wind tunnel, which are believed to be the cause for such problems. Due to the pulling motion of air by the fan, airflow inside the tunnel tended to form a vortex in the center, concentrating $NH₃$ in certain areas. Results from one of the initial $NH₄Cl$ tunnel runs demonstrated that these samplers were able to capture only 2,285 mg of the total 25,433 mg that was volatilized. This is a recovery of only 8.9% of the NH_4^+ -N in the solution. Samplers were taken off at hourly intervals, and when analyzed were not beyond the point of maximum adsorptive capacity of the tubes. For this particular run, the average temperature was 18 °C with an average relative humidity of 72%. Perhaps the NH₃ was coming off so quickly in the first few hours of the $NH₄Cl$ experiments that the samplers were not able to measure it adequately. However, if this were so, the first set of tubes should have been saturated. Samplers were placed ≤ 1.6 cm from the bottom of the tunnel for several experimental runs in an effort to minimize any NH₃ losses that could potentially be escaping detection by passing beneath the coated tubes. Results for these runs were slightly higher, with a recovery of 35.7% (Table 5), but were still not at an acceptable level.

After plastic louvers were installed, the swirling effect in the center of the tunnel decreased somewhat, but still manifested itself in many of the following experiments. Soil-effluent experiments in the tunnel proved to be no more successful than the previous $NH₄Cl$ experiments as shown in Figures 7 and 8. Percent recoveries of the soil-effluent

system for these two runs were 2.79 and 7.68% respectively. Figure 7 demonstrates that the airflow carried a higher concentration on the right side of the tunnel with a lower concentration on the left. This profile does not manifest the swirling effect in the center as Figure 8 does even though these tunnel runs were performed on consecutive days. The flow pattern was rarely repeatable, with laminar flow along the bottoms and sides of the wind tunnel often creating higher concentrations in the center, bottom or sides. In the tunnel run shown in Figure 9, samplers were set up higher than previous runs to determine if a measurable amount of $NH₃$ was flowing above the setup of the previous samplers. If this were true, it could possibly account for the extremely low percent recoveries. But, as can be seen, only negligible amounts were captured above the 15 em level of the tunnel. Also, it should be noted that this particular run was tested under conditions not conducive to NH₃ volatilization, i.e. low temperatures. It is possible that changes in ambient air temperatures created changes in airflow patterns in a few of these tunnel experiments. The variability among runs limited the ability to evaluate these samplers under wind tunnel conditions. All attempts made to straighten airflow, such as airflow straightening screens and roughness elements met with limited success. However, there was a measurable quantity of $NH₃$ collected in the soil experiments, showing some promise for proper determination of flux under field conditions.

CONCLUSIONS

Initial work with these passive samplers indicated that this system is very efficient at capturing volatilized NH₃ under closed laboratory conditions as demonstrated by relatively high recoveries ranging from 90 to 98%. The laboratory soil-effluent flask experiments demonstrated that the calcareous Richfield clay loam (pH 8.1) has the potential to volatilize significant amounts of NH₃ within minutes after application. Therefore, any measurements with such soils in the field or laboratory must be done immediately following application of swine effluent. In comparison, the Dennis silt loam (pH 5.8) had a much lower volatilization rate across all treatments which is mostly likely due to the lower pH value for the Dennis silt loam. However, it could also be related to the presence of high amounts of Ca^{2+} on the calcareous Richfield clay loam's CEC, which would decrease the ability of NH_4^+ -N to exchange on the complex, thus leaving a greater quantity in solution which is more prone to loss via volatilization. The mass balances for these particular laboratory experiments ranged from 71 to 148% recovery, with recoveries decreasing with increasing effluent NH₄⁺-N concentrations. Exchange competition becomes a factor at higher NH₄⁺-N solution concentrations, so with increasing amounts of volatilized $NH₃$, the higher the possibility of error, thus decreasing recoveries. Recoveries over 100% were most usually for the control flasks, which could be due to N mineralization from added moisture.

Applications of swine effluent to soil in a wind tunnel proved to be inconclusive due to difficulties in dealing with uneven airflow. Soil-effluent and NH₄Cl solution recoveries were $\leq 40\%$. Perhaps a tunnel in which the air was pushed instead of being pulled through would have created an environment more conducive to this type of

atmospheric research. Even though wind tunnel NH₃ volatilization studies were inconclusive, they were not an integral focus of this project and did not affect the overall objective of quantifying NH3 volatilization in the field. Overall, the passive flux sampling system should prove to be effective at correctly monitoring NH₃ volatilization from swine effluent applications to calcareous fields.

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	Richfield	Dennis	
Texture	clay loam	silt loam	
pH	8.1	5.8	
NH_4^+ -N (mg kg ⁻¹)	3.0	12.0	
$NO3--N (mg kg-1)$	22.0	2.5	
Total N $(g kg^{-1})$	1.3	0.89	
M III P^{\dagger} (mg kg ⁻¹)	29.0	12.5	
CEC (cmol _c kg ⁻¹)	16.12	14.96	
Organic Carbon $(g \, kg^{-1})$	12.1	10.4	

Table 1. Average initial characteristics for both soils included in the laboratory flask volatilization experiments

t Mehlich III extractable

Table 2. Recoveries of NH₃ from a 15 mg N L⁻¹ in an NH₄Cl solution in closed system laboratory studies using oxalic acid coated passive samplers

 $t + \frac{1}{2}$ % Recovery of system = ((NH₄⁺-N final + NH₄⁺-N captured) / NH₄⁺-N initial) * 100

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Table 3. Total NH₃ captured on oxalic acid coated passive samplers from soil-effluent flask experiments for five treatments on a Richfield clay loam (pH 8.1) and a Dennis silt loam (pH 5.8). Regression coefficient shown for volatilized $NH₃$ versus time

Table 4. Mass balance average results for soil-effluent laboratory experiments

Soil	NH_4^+ -N Treatment	Average Mass Applied	Recovery	
	$\frac{1}{\text{max}}$ mg L^{-1} LLg ----		$- \frac{0}{0}$ $- -$	
Richfield	0	0.0	147.9	
Richfield	100	8158.5	103.0	
Richfield	300	21121.8	87.5	
Richfield	500	35384.2	90.2	
Richfield	1000	68439.6	73.6	
Dennis	$\bf{0}$	0.0	121.7	
Dennis	100	9239.6	96.4	
Dennis	300	21461.2	90.4	
Dennis	500	35047.2	99.6	
Dennis	1000	66669.9	71.1	

Table 5. Percent recoveries of wind tunnel experiments at 2.2 m s⁻¹ for 12 hours using NH₄Cl sources

Figure 1: Passive flux sampler. Top: A passive flux sampler consisting of two parallel sampler units. Each unit is composed of 100 mm long glass tubes, coated with oxalic acid on approximately 70 mm of the inside (shaded), and a 23 mm tube with stainless steel disc at the end, all joined by silicone tubing. E_1 , E_2 are exposed tubes and B_1 , B_2 are background tubes. (Bottom left) Mast with four flux samplers seen from profile. (Bottom right) Four masts around a circular NH3 source as seen from the top. From Sommer et al. (1996).

Figure 2. Setup for laboratory efficiency tests. Helium tank connected in series to flask containing known NH4Cl solution, then to a manifold containing two samplers. Syringes containing 0.1 N H2S04 and 0.1 N NaOH attached to flask stopper. Bubble flow meter seen at right.

Figure 3. Setup for laboratory soil-effluent flask experiments. Oxygen tank connected in series to a manifold, joined to five flasks containing soil and effluent, with samplers attached to the outflow side of the air stream to capture any volatilized ammonia. Bubble flow meter seen at left.

de tunne insid seen ground sample with bac r intake from air c Q) Q) lIJ æ nd tunne

Figure 5. Regression lines of plotted cumulative NH₄⁺ -N versus time for the Richfield clay loam in laboratory flask experiments with five concentrations (mg N $\mathsf{L}^\text{-1}\mathsf{)}$ of swine effluent.

Figure 6. Regression lines of plotted cumulative NH₄⁺-N versus time for the Dennis silt loam in laboratory flask experiments with five concentrations (mg NH_4^+ -N L⁻¹) of swine effluent.

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Figure 7. Ammonia profile 1 in wind tunnel. After the addition of swine effluent to soil at a wind speed of 2.23 m s^{-1} for 12 hours. Air temperature ranged from 19 to 26°C and relative humidity from 33 to 59 %.

Figure 8. Ammonia profile 2 in wind tunnel. After the additon of swine effluent to soil at a wind speed of 2.23 m s^{-1} for 12 hours. Air temperature ranged from 8 to 24 $^{\circ}$ C and relative humidity from 59 to 80%.

CHAPTER II

4

DETERMINATION OF AMMONIA FLUX FROM SWINE EFFLUENT APPLIED TO CALCAREOUS SOILS

ABSTRACT

In the Panhandle of Oklahoma, swine effluent is pumped from lagoons through center pivot irrigation systems or big guns where many of the environmental conditions promote the potential loss of a significant amount of nitrogen when applied to cropped fields. This region of the United States is located in the high plains of the interior Great Plains, where the soil pH is 7 to 9, summer daytime temperatures are consistently $23 37^{\circ}$ C, with brisk wind speeds of 4.4 - 17.8 m s⁻¹, and low relative humidities (3-30%). The Panhandle of Oklahoma is of heightened interest to the state due to the large increase in the number of confined swine feeding facilities, which have located there in the last decade. Between 1996 and 1998, the total number of swine in the Panhandle district has increased from approximately 370,000 to 905,000 head (245% increase), making it one of the leading areas of swine growth in the United States. Given the increasing number of swine in a region very conducive to loss of nitrogen via volatilization losses, the need for further study of ammonia volatilization has become extremely important. More information unique to this region will not only enable proper nutrient utilization and management for the producer, but will also ensure that the release of unnecessary atmospheric NH_3 is minimized. This will benefit the air quality of the area and help decrease a potential odor problem. Therefore, the objective of these field research tests

was to determine the NH₃ flux during land application of swine effluent in the Southern Great Plains using a simple passive sampling system. Effluent from a confined swine production facility, with an average NH₄⁺-N concentration of 963 mg L⁻¹, was applied to circular test plots at aha - 2.54 em rate while samplers continuously monitored the horizontal flux of NH₃ at four different heights. Depending on the climatic conditions, field volatilization losses of NH₃ ranged from 37 - 57% of the total NH₄⁺-N that was applied. The 57% loss of NH_4^+ -N was encountered during hot, dry, and windy conditions, with the lowest loss (37%) during a more humid, rainy period. Mass balances performed for these field experiments ranged between 79 - 134% recovery. Overall, these samplers seem to be adequate at capturing and providing an estimate of NH₃ volatilization losses under variable field conditions.

INTRODUCTION

Land application of livestock wastes has been practiced and studied around the world for centuries as a principal source of plant nutrients (Sims, 1995). Since the early 1900's, research has shown that significant losses of nitrogen can occur from land applied animal fertilizers through ammoniacal nitrogen volatilization (Russell, 1915; Heck, 1931). In more recent times, the loss of nitrogen via this pathway in Europe has led to an increased concern over its impacts on the surrounding environment. These emissions contribute to local odor associated with swine production and to regional air quality problems. Schulze et al. (1989) stated that the deposition of NH_3 and NH_4^+ -N can contribute to eutrophication and acidification of some nitrogen limited ecosystems. Ammonia influences the pH of aerosols in cloud water and may be important in detennining regional air quality characteristics. In the atmosphere, ammonia is the dominant alkaline gas and can have a significant effect on oxidation rates which affects deposition rates of acidic airborne constituents such as sulfuric, nitric and hydrochloric acid (ApSimon et al., 1987). Ammonia has a short half life in the atmosphere of 5-5 $\frac{1}{2}$ days (Warneck, 1988); however, studies imply that NH₃ inputs over Europe have increased over 50% between 1950 and 1980 with doubling of emissions in some countries (ApSimon et aI., 1987).

The emission of ammonia from animal wastes represents one of the most important sources of atmospheric ammonia in Europe (Buijsman et al., 1987). According to Groenestein and Van Faassen (1996), the Dutch legislation intends on reducing NH3 emissions by the year 2005 by 70% in relation to their 1980 emissions. It is estimated that in Denmark alone, 46% of the environmental acidification is due in large part to

ammonia emissions from agricultural sources (Heij and Schneider, 1995). Ammonia originates from many natural sources, but the largest contributions are from domestic animal waste, fertilizers, and other agricultural operations (Buijsman et al., 1987; ApSimon et al., 1987). Ammonia emissions from confined animal production facilities may arise from several sources: inside the buildings, manure storage facilities (e.g. anaerobic lagoon or stock-piled manure), during the application process (irrigation or land application), and from the soil or plant surface following application. Ammonia deposition will vary greatly depending on local sources of volatile ammonia and local transport conditions.

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Depending on the nutrient content and method of application, the net value of manure spread as a source of nutrients in the United States ranges from approximately $-$ \$1.00 to $+$ \$6.00 per metric ton on a dry matter basis (Hoff et al., 1981) or \$2.50 to \$3.50 per hog (Sutton, 1992). However, more than half of the N content in cattle and swine slurries is in the ammoniacal form which can be lost by volatilization of $NH₃$, often within the first few hours after land application (Sommer and Ersbøll, 1994). Therefore, losses of NH₃ via this pathway may significantly lower the N value of the effluent for crop production, which must then be replaced by commercial fertilizers. Losses from swine lagoon effluent applied to grassland were reported as high as 62% of the applied NH₄⁺-N (Pain et al., 1989). Beauchamp et al. (1982) reported that between 24 and 33% of the ammoniacal N applied in liquid dairy manure was lost by volatilization within a 7 day period. I~ !

Ammonia volatilization is influenced by a number of soil and environmental factors with significant interactions occurring between the variables. Svensson (1994)

categorized these factors in three main groups: meteorological, soil/manure, and application technique. When examining meteorological factors, air temperature, relative humidity, rainfall events, evapotranspiration, NH₃ concentration in the atmosphere, wind speeds and air movements must be taken into account. Soil characteristics that need to be considered when discussing ammonia losses are the soil pH, texture, temperature, porosity, moisture, cation exchange capacity (CEC), hydrogen ion buffering capacity, calcium carbonate content, urease activity, immobilization and nitrification rates and the presence of vegetation. Manure properties that can affect ammonia volatilization are the pH, buffering capacity, total ammoniacal nitrogen content (TAN), and dry matter content. Fertilization management, such as timing, application method and rate, type, fertilizer placement and irrigation droplet size are factors that should be taken into consideration from an application viewpoint (McInnes et al., 1986; Nelson, 1982; Svensson, 1994; Freney et al., 1983).

Although interpretation of previous experiments concerning volatilization is difficult due to the variety of techniques utilized, most research has shown a positive correlation between wind speed and the amount of NH₃ volatilized. The influence of wind speed upon volatilization increased with the approximate square of the wind speed (Denmead et al., 1982). It was also determined that the exchange coefficient for $NH₃$ is affected by the aerodynamic roughness of the surface and the surface area. Ryden and McNeill (1984) were able to show that the wind speed decreased with decreasing height and neared zero at a point close to the base of a grazed sward. However, Bouwmeester et al. (1985) reported that volatilization from urea fertilized soils was affected negatively by increased wind speed. Sommer et al. (1991) could find no apparent correlation between

ammonia loss when wind speeds exceeded 2.5 m s⁻¹. Work by Thompson et al. (1990) using wind tunnels, indicated that the most noticeable amount of volatilization released was within the first twenty-four hours of application. This study also revealed that increasing the wind speed from 0.5 to 3.0 m s^{-1} elevated the total five day loss by a factor of 0.29 and that wind speed effects may have been altered by a temperature interaction. Lower temperatures appear to increase the formation of NH_4^+ -N (aq) which reduces the amount of 'volatilizable' NH₃ present in the soil solution (Sherlock and Goh, 1984). Perhaps this temperature interaction could explain the conflicting findings as to the effects increased wind speed has on volatilization. Beauchamp et ai. (1978) noted that of the many meteorological parameters measured for their sewage sludge study, temperature appeared to be the most closely related to the measured flux rate, especially 2 to 3 days after application. However, researchers in Australia found that temperature had very little influence on their research of cattle slurry application to grasslands (Thompson et aI., 1990). Nelson (1982) stated that increased temperature has the potential to elevate the rate of NH₃ diffusion from the soil surface, which permits a more rapid conversion of NH_{3 (aq)} to NH_{3 (g)}. A laboratory study using pig slurry on a dry, well-cultivated clay soil by Svensson (1993) showed that the NH₃ concentration increased 3 fold when the temperature increased from 14 to 24°C. Fenn and Kissel (1974) found that the effect of temperature on total NH₃ volatilization with ammonium nitrogen salts was dependent upon the presence or absence of $CaCO₃$ in the soil and upon the type of NH₄⁺-N compound applied. They concluded that the influence of temperature was most pronounced in the loss rate; at the lowest temperature the smallest amount of first day NH₃ was released and the highest temperature produced the highest first day NH₃ losses.

An explanation for the effect on temperature is given according to Beauchamp et al.

(1982):

Lauer et a1. (1976) suggested that the partial pressure gradient between the manure and the atmosphere was a major factor determining flux. It follows that the ammoniacal-N concentration in manure is a major determinant of the flux as suggested by Vlek and Stumpe (1978). The diurnal pattern involving maxima near midday and minima in the early morning hours must then be related to a varying ammoniacal-N concentration in the manure. It may be surmised, therefore, that during the later morning hours as dew-water evaporation occurs, the concentration of ammoniacal-N in the aqueous phase increases, the partial pressure gradient also increases and its release would be enhanced. After midday, the flux peak is usually reached and is followed by a decrease coinciding with a depletion in ammoniacal-N available for volatilization. Also, as the temperature decreases, the water vapor pressure deficit in the atmosphere would decrease, thereby lessening the evaporation rate.

Relative humidity of the air has an inverse effect on the rate of water loss from the soil surface. Hargrove et al. (1977) demonstrated that the rate of ammonia loss after the application of ammonium salts in a field experiment followed a diurnal pattern, which followed the fluctuations of the atmospheric relative humidity. During intervals of high humidity, Black et al. (1987) suggested that water was absorbed on to the urea granules which stimulated hydrolysis leading to volatilization. Ryden and McNeill (1984) found that rainfall and low rates of evapotranspiration lowered the NH3 flux. Rainfall tended to decrease the ammonia flux according to Beauchamp et a1. (1982). However, since cooler air temperatures sometimes occurred with precipitation, it was difficult to determine whether the lower rate was due to the rainfall event, the lower temperatures, or a combination. They theorized that the water could have leached a portion of the soluble ammoniacal N into the ground, thus decreasing volatilization rates. Brunke et a1. (1988) stated that the primary parameter determining volatilization is the drying rate of the manure according to the partial pressure of NH₃. They also suggest that a derived

meteorological variable, such as the hay drying index already utilized by some network agrometeorological forecasts, may be the most suitable single indicator of highvolatilization weather conditions. Results were inconclusive in an attempt to correlate observed volatilization rates of $NH₃$ to specific meteorological parameters such as temperature, wind speed, net radiation, etc. (Brunke et aI., 1988). These Canadian researchers found that these variables were not independent under field conditions.

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Ammonia volatilization is controlled by a complex series of interactions and reactions governed by many soil characteristics. The potential for volatilization is highly dependent on the texture and type of soil to which the manure is applied. Researchers often disagree as to which soil characteristics are the most important. The pH effect is expected to play a fundamental role in this process due to the equilibrium equation as discussed below; as pH increases, the concentration of NH₃ present in the soil solution and soil air will increase, therefore increasing the potential for NH₃ loss from the soil system (Freney et aI., 1983). DuPlessis and Kroontje (1964) compared soils with a range of pH values (4.5 to 7.1) and demonstrated that NH3 volatilization increased with higher soil pH and with increasing concentrations of NH_4 ⁺-N applied to the soil as $(NH_4)_2SO_4$. The equilibrium equation can be described as:

$$
NH_4{}^+ \text{-} N \; + \; OH^{\cdot} \; \leftrightarrow \; NH_3 \uparrow \; + \; H_2 0
$$

with a shift in the reaction to the right when higher concentrations of OH are present which enhances the possibility of volatilization.

Upward movement of water through the soil profile aids the transport of ammonia to the soil surface, therefore a relationship would be expected between water evaporation and $NH₃$ loss (Freney et al., 1983). Numerous researchers have shown that water

evaporation and NH₃ loss are related (Jewitt, 1942; Martin and Chapman, 1951; Wahhab et aI., 1957; Denmead et aI., 1976; Fenn and Escarzaga, 1977). Under drying conditions, the amount of volatilization increased when applied to soils that had a greater initial moisture content. However, when the soil moisture content remained consistent, there was less volatilization from the soil with the greater moisture content (Burch and Fox, 1989). Australian and New Zealand scientists, working with urea, found that application of water shortly after spreading urea significantly decreased the NH3 loss. The urea was carried by water into the soil before any hydrolysis processes could occur, thus decreasing the rate of NH₃ flux (Black et al., 1987). However, Ferguson and Kissel (1986) stated that rapid drying of the soil was found to significantly decrease the rate of NH3loss from soils when working with urea. They found that when the soil-surface water content declined to the point in which soil-water content/potential was not adequate to support urea hydrolysis that $NH₃$ losses would diminish.

Since ammonium is a positively charged ion, it reacts with the exchange complexes of the soil (Freney et aI., 1983). In general, the higher the CEC value the less potential for ammonia volatilization. According to Whitehead and Raistrick (1993) the controlling soil factor related to volatilization of NH₃ with cattle urine experiments, is the cation exchange capacity. Nonetheless, a critical CEC level for NH₃ volatilization has not been proven to our knowledge, but it appears that a CEC value greater than 25 cmol_c $kg⁻¹$ is required to reduce NH₃ losses substantially (Freney et al., 1983). Volatilization losses decreased as clay content increased, yet increased with additional amounts of municipal biosolids applied (Beauchamp et aI., 1978). An inverse relationship should be found between NH₃ volatilization and clay content, since CEC is a function of the

quantity and types of organic matter or clay mineral types present in the soil (Freney et al., 1983). A linear inverse relationship was determined between $NH₃$ evolution and clay content (Ryan and Keeney, 1975). However, results on the relationship between soil factors and NH3 loss can easily be misleading due to various interactions between soil parameters. With increased CEC, water holding capacity and buffering capacity of soils typically increase; both of these factors have been documented to influence NH_4 ⁺-N reactions in the soil (Fenn and Escarzaga, 1977; Ferguson et aI., 1984; Clay et aI., 1990).

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The combination effects of a soil/manure system such as the buffering capacity and pH value are difficult to isolate and analyze separately. However, a few of the characteristics can be investigated further with some beneficial conclusions. Manure fluidity is a characteristic affecting volatilization rates, which can be described as the capability of a fluid to infiltrate a soil (Svensson, 1993). Svensson states that this characteristic should be considered the most effective manure parameter influencing NH3 volatilization rates because fluidity has a major influence on the capacity of the manure to enter the soil. This parameter seems to be a more representative measure of the infiltration capacity of slurry than the often used total solid contents. Rapid infiltration of slurries into soils immediately after application may reduce the rate of NH₃ loss compared with thicker slurries, which remain on the surface for longer periods of time (Pain and Thompson, 1989). Sommer and Olesen (1991) found that the loss of NH₃ was linearly related to the dry matter content; small changes in dry matter content at low and high amounts had very limited influence on NH₃ volatilization. Volatilization from surface-applied cattle slurry can be decreased by more than 90% if the pH is lowered to 5.5 with strong acids (Stevens and Logan, 1987). An unreplicated wind tunnel study by

Pain et al. (1990) indicated that NH₃ volatilization from acidified slurry (pH 5) prior to application reduced losses by 30 to 54% when applied to perennial ryegrass in the UK. Using 2 M H_2SO_4 , Pain's research project required 30 to 85 mL L^{-1} to reduce the pH of the slurry to approximately 5.5. However, the economic feasibility of this treatment is questionable (Miyamoto et aI., 1975). Freney et al. (1983) suggested that additions of acids to animal wastes being applied as fertilizer could be a useful practice where cheap by-product acids are available. However, this increased the losses of N from denitrification by approximately 40%. Results from Sharpe and Harper (1997) indicated that NH_3 emissions (29.7 kg N ha⁻¹) contribute to atmospheric N-loading much more than do N₂O emissions (4.7 kg N ha⁻¹) from irrigated swine effluent applications, therefore, volatilization is still a greater concern than denitrification. Again, accessibility and economic feasibility of this type of treatment was not addressed.

Animal manures have the potential to lose significant amounts of $NH₃$ in the atmosphere when applied to the soil surface and not incorporated. However, in the experiments carried out by Svensson (1993), the mode of application was found to be the factor of highest influence in volatilization. He concluded that there was no significant difference between broadcast and banded application rates as a percentage of total volatilized NH₃. Nonetheless, he did find that application technique made a substantial difference; injected swine manure decreased volatilization rates considerably when compared to surface spreading. However, contrary to other reports, Sommer and Christensen (1990) pointed out that NH₃ volatilization could be excessive if slurry is injected into a very wet and compressed soil. Application uniformity also seemed to have a notable effect during surface application. Band spreading seemed to produce

lower amounts of NH₃ in the air during the first hour as compared to broadcast spreading (Thompson et aI., 1990). Interestingly, they also found that broadcast and band application follow different time courses for the rate of NH₃ volatilized and became similar as the volatilization neared an end. The process of ammonia volatilization is a highly complex system and is affected by a combination of biological, chemical and physical factors (Svensson, 1993). Many interact with each other, making it difficult to differentiate among them. By taking a more in depth examination of these many factors, combinations, and systems, a better understanding of how the pathway of ammonia volatilization functions will be gained.

Combining the information concerning the characteristics that could potentially increase NH3 volatilization from livestock waste application and the recent micrometeorological techniques, the Panhandle of Oklahoma warranted research of this type. The majority of swine operations in the state use facultative anaerobic lagoon systems in which the top layer aerobically oxidizes and breakdowns much of the volatile organics to form CO₂ and H₂O, which reduces odors. The middle portion anaerobically digests a portion of the materials and the solids sink to the bottom of the lagoon to form a slurry. Most effluent, taken from the top layer of lagoons, is applied in this region of the state through center pivots. Ammonia solutions applied through sprinkler systems usually allow for greater exposure to the air, increasing the chance for water evaporation and NH₃ losses (Warnock, 1966). Henderson et al. (1955) reported that NH₃ losses could be greater than 60 % when anhydrous ammonia was applied through a jet type sprinkler system. Since the partial pressure of NH₃ under normal atmospheric conditions is low,

dissolved NH₃ readily volatilizes upon exposure to the atmosphere (Miyamoto et al., 1975).

Wind speeds are often very high $(4.4 - 17.8 \text{ m s}^{-1})$ during the spring in the Panhandle of Oklahoma; as much as 15.64 m s^{-1} wind speeds have been recorded for a 12-hour period (Climatological, 1996). Wind velocities of more than 12 m s⁻¹ over a period of24 hours have been reported at the Goodwell Station (USDA, 1984). Relative humidities are often very low $(3 - 30\%)$, especially during the summer months (Climatological, 1996), and rainfall in Texas County averages approximately 43 em year⁻¹ (USDA, 1984). The swine population has increased exponentially over the last decade, growing from 370,000 to 905,000 total swine between 1996 and 1998 (National, 1997). Fifteen years ago, the vast majority of swine owners raised their livestock as free range hogs. Now, only small portions are raised in this fashion, with confined swine feeding operations dominating the area. Therefore, in light of these area environmental factors, which typically tend to increase $NH₃$ volatilization from N additions, the objective of these field experiments was to determine the NH₃ flux during land application of swine effluent in the Southern Great Plains using a simple passive sampling system.

MATERIALS AND METHODS

Samplers

Simple passive samplers, as described previously in Chapter 1, were utilized under field conditions.

$Field$ *Measurements*

Field tests were established in the spring, early summer, and late summer of 1998 to monitor the NH₃ volatilization of swine effluent applied to the land surface at the Oklahoma State University Research Station in Goodwell, Oklahoma. A Richfield clay loam (fine, smectitic, mesic Aridic Argiustolls) had an average pH of 8.1, 3 mg kg⁻¹ NH_4^+ -N, 22 mg kg⁻¹ NO₃⁻-N (KCl extractable), and 0.13 % Total N (Table 1). Samplers were placed on four masts placed at right angles to each other on the boundary of a circular plot (Figure 1). On each mast, four samplers were positioned at 17, 47, 109, and 184 em above ground, in which each sampler had one unit having the stainless steel disc facing toward the NH₃ source and the other facing away from the experimental area. As noted by other researchers and as demonstrated from the wind tunnel experiments described previously, volatilized NH₃ tends to move laminarly along the surface with only small amounts being carried into the higher sampling areas (Ferm and Svensson, 1993). Therefore, these heights were chosen based on research from previous experiments using micrometeorological methods (Beauchamp et a1., 1978; Beauchamp et al., 1982; Schjoerring, 1995) and are intended to capture $NH₃$ that volatilizes and stays relatively close to the surface. The highest sampling position should capture very little $NH₃$ in order to ensure that the flux is not underestimated due to large amounts of $NH₃$ moving above the sampling area. Horizontal flux can be determined by utilizing the

mass balance approach, which measures the mean atmospheric 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 (McInnes et al., 1985). The average horizontal flux of NH₃ (F_{hm}, μ g NH₃-N m⁻² s⁻¹) through two glass tubes facing in the same direction at each height (h) measured on each mast (m) either toward (the exposed tubes) or from (background tubes) the NH) source was calculated by using Equation 1 proposed by Schjeerring et al. (1992):

$$
F_{hm} = \frac{(C_1 + C_2) V}{2\pi r^2 \cdot K \cdot \Delta t}
$$
 [1]

where C₁ and C₂ are the concentrations of NH₄⁺-N (μ g NH₄⁺-N L⁻¹) in either of the two exposed tubes E_1 and E_2 or the background tubes B_1 and B_2 (Figure 1); V is the volume of water used to dissolve the NH₄⁺ sorbed in the tubes (3 mL), r is the radius of the hole in the stainless steel disc (0.05 mm), t is the time (s) between the start and conclusion of the measurement and K is the correction factor $(K = 0.77)$.

The horizontal net flux (F_{net} (h), μ g NH₃-N m⁻² s⁻¹) at each height was calculated with Equation 2 by Schjøerring et al. (1992):

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

where $F_{hm,s}$ is the flux of NH₃ from the source including the exposed tubes and $F_{hm,b}$ the flux measured from the background tubes at each height (h) and at each mast $(m=4)$. Sommer et al. (1996) noted that in high wind environments, a slight bypass was observed due to rather high wind velocity in the center of the tube. In these instances, the horizontal net fluxes of NH_3 were calculated by adding the NH_4^+ -N in the background and exposed tubes instead of subtracting them (contrary to the procedure shown in the

previous equation). Test plots in these field experiments also demonstrated this phenomenon; so, to determine NH₃ flux during high wind events, the background and the exposed tubes were added together. Captured NH₃ from the zero application plot was subtracted from the treatment plot values to ensure that any ambient NH₃ was not included into flux calculations.

Vertical flux $(F_v, \mu g NH_3-N \text{ m}^{-2} \text{ s}^{-1})$ was determined from Equation 3 (Sommer et al., 1996):

$$
F_v = \underbrace{1}_{X} \sum_{h=1}^{h=n} F_{net,h} \Delta h
$$
 [3]

where x is the diameter (m) of the plot, Δh is the height interval (m) of the samplers, and n is the number of measuring heights at which the samplers were mounted to the masts (n=4). Once the vertical flux was calculated for each treatment plot, the values were averaged and integrated using a second order inverse polynomial, which was empirically determined using SigmaPlot to find the best-fit equation to model the data (SPSS, 1997). Sommer and Ersbøll (1994) described $NH₃$ losses from surface applied swine and cattle slurry using a Michaelis-Menten like equation, which is a first-order reaction. Regression equations for each test period are shown in Table 2.

Swine lagoon effluent was obtained from a production facility and effluent was collected using a large tank. Using a flowmeter to monitor application amounts, 4625 L of effluent were applied from a 5.1 em hose onto each treatment plot. The effluent from the same lagoon was used in each of the 3 field tests and remained fairly consistent in nutrient content and other characteristics (Table 1). The ammonium content averaged 963 mg NH₄⁺-N L⁻¹, ranging from 868 – 1081 mg NH₄⁺-N L⁻¹ with a standard deviation

of 86. Nitrate in the effluent was negligible $(< 1 \text{ mg L}^{-1})$, the average pH was 7.3, Total N averaged 1002 mg L^{-1} , and the effluent had < 1% solid.

Field areas chosen for all three sampling times on the research station were situated very far from any obstructions of airflow such as structures, trees etc. Special care was taken to avoid any potential sources of NH₃, i.e., center pivots, hog facilities etc. However, to demonstrate this, samplers were allowed to monitor ambient air approximately 16 hours before effluent additions during the September tests to measure background levels of NH_3 in the atmosphere (Figure 2). Level portions of the field areas were chosen for the 15.24 m diameter plots to maintain equal coverage and small levees (55 cm) in height) were built around the plots to ensure that the liquid would not run off once applied. Bare, recently disked fields were used for each test plot, with a 1-3% wheat stubble residue. Three treatment plots and one zero application plot were initiated on May 28, July 28, and September 12, 1998, with new experimental areas chosen for each test period. Treatment and zero application plots were placed over 91 m apart from each other to ensure that no cross contamination between plots was possible. Samplers collected NH3 for a 7 day period, (except for September where only 5 days were used) in which samplers were taken off and replaced with new samplers approximately every 12 hours for the first 4 days and every 24 hours for the last 3 days. September's testing date was shortened to 5 days because the previous two testing periods had yielded no significant NH₃ losses after day 5.

Soil samples were taken before and after application in which soil moisture was measured along with NH_4^+ -N and NO_3^- -N. A soil mass balance was performed for each testing period using collected soil samples, effluent concentrations, and captured NH₄⁺-N

on the samplers. Using a Campbell Scientific CR500 datalogger, wind speed, direction, soil temperature, relative humidity, and air temperature were monitored. Weather conditions were variable between the 3 test times and are summarized in Table 4.

RESULTS AND DISCUSSION

The vertical flux and cumulative loss of NH_3 for the May 28 - June 3 sampling period as determined by the passive flux samplers is shown in Figure 3. The initial $NH₃$ flux for these test plots was 151 μ g NH₃ m⁻² s⁻¹, as shown by the best fit line, a second order inverse polynomial with a p value < 0.001. Ammonia volatilization decreased rapidly and within 3 days very little NH₃ was detected. Any NH₃ volatilizing from these $\frac{1}{2}$ plots after day 3 were insignificant. Measured levels of NH₃ before swine effluent applications in September indicate that background $NH₃$ fluxes are typically below 40 μ g m^{-2} s⁻¹. Background NH₃ levels, as detected by the zero application plot after application during this May field test, were initially quite high, with horizontal fluxes ranging from 344 to 200 μ g NH₃ m⁻² s⁻¹ and eventually declining to 20 μ g NH₃ m⁻² s⁻¹ within 24 hours. This would seem to suggest that the zero application plot was not far enough from the treatment plots. Ammonia volatilization from the 3 treatment plots showed little deviation among reps (Figure 4), but followed expected diurnal fluctuations for the first 3 days (McGarity and Rajaratnam, 1973; Denmead et aI., 1974; Beauchamp et aI., 1978; Beauchamp et al., 1982; Ryden and McNeil, 1984). Cumulative NH₃ losses for this test period totaled 154 kg ha⁻¹, which was a loss of 57% of the total amount of NH_4^+ -N that was applied initially (Table 5). The weather conditions during this test period (Table 4), which were hot, dry, with very low relative humidity, and brisk wind speeds, likely influenced the loss of 57% NH3, which would be a significant loss for producers in this region. Research in Georgia using swine effluent applications to an irrigated oat field during the heading stage resulted in 82% of the NH_4^+ -N in the effluent lost to the atmosphere (Sharpe and Harper, 1997). This value includes a 13% NH3 loss during

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application with a solid-set sprinkler irrigation system. These results account for volatilization before the effluent even reached the crop or soil surface. These higher results could be due to applications to a sandy soil, and to increased losses due to interception by the crop canopy which reduces the opportunity for the NH_4^+ -N to enter the soil. On the contrary, effluent for these Panhandle field experiments was surface applied to bare ground to reduce and remove any potential application variable that might be encountered when effluent adheres to leaf canopies or to volatilization of $NH₃$ during the actual application itself. For these field research trials, measurements of NH_3 were restricted to losses encountered after application to determine volatilization rates without these additional variables.

Due to rainfall events 5 nights through the 7 day test period, ammonia losses were much less during the July $28 -$ August 3 experiments with an initial vertical flux of 101 μ g NH₃ m⁻² s⁻¹ (Figure 3). Air temperature was not significantly different than during the May fields tests, but due to rainfall, minimum and average humidities were much higher (Table 4). Danish research, such as that done by Van der Molen et al. (1990) demonstrated similar volatilization declines during rainfall events when cattle slurry was applied to arable land. Weather conditions create highly variable results due to interactions between the various climatic conditions, manure characteristics, and manure handling as described by Christensen (1986). The sampling period for this study was characterized by higher humidity, thunderstorms, and high soil moisture, all of which could have contributed to lower relative amounts of volatilization. Texas County, OK, receives only 43 cm yr^{-1} on average, so that a 5.05 cm rainfall total for a 7 day period is significant enough on this clay loam soil to ensure that NH_4^+ -N in the effluent will

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probably not volatilize to any large degree. Volatilization rates dropped off very quickly and after approximately 2 days, NH_3 losses were extremely low. Temperatures during the day wanned up considerably, creating a rapid drying effect from the previous night's rainfall. This created diurnal fluctuations, which were somewhat more noticeable than for the other 2 test periods (Figure 4). Cumulative $NH₃$ losses were calculated to be 82 kg ha⁻¹ of the total 221 kg NH $_4$ ⁺-N ha⁻¹ that was applied which was a 37% loss (Table 5). It is believed that larger standard deviations for this field test resulted from thunderstorms and high winds encountered, which may have contaminated some samplers with water or blown soil. Ammonia measurements from the zero application plot were initially high (between 120 and 30 μ g NH₃ m⁻² s⁻¹) but decreased by day 2 and remained below 30 μ g $NH₃ m⁻² s⁻¹$ for the remainder of the sampling period.

In a cooperative effort between Oklahoma State University and North Carolina State University, an enclosure method currently being used by NCSU was brought to the Oklahoma Panhandle Research Station during the July field test to be compared to passive samplers already in use. This method resulted in a 56% loss of applied ammoniacal N 49 hours after effluent application (D. Byers, 1999, personal communication). This is a tremendous difference from the 37% loss of volatilized ammonia after 7 days, as measured by the micrometeorological method during this same field test. Without further replications or data, any conclusions concerning these differing results, other than as just a simple comparison are somewhat fruitless, except to show the significant differences between methods even under the same conditions.

Ammonia flux from field plots during the September $12 - 17$ test period was initially 115.2 μ g NH₃ m⁻² s⁻¹, which then dropped quickly and was insignificant after

approximately 3 days (Figure 3). Sharpe and Harper (1997) also reported high NH3 emissions immediately following irrigation with swine effluent, with rates dropping to within background levels after 12 to 24 hours. Cumulative amounts of volatilized NH₃ during this September run were calculated to be 117 kg ha⁻¹ over a 7 day period, which is a 50% loss of the 236 kg $NH_4^{\text{-}}$ -N ha⁻¹ that was applied in the swine effluent (Table 5). Background levels of NH₃ were low before application (< 20 μ g NH₃ m⁻² s⁻¹) and followed a diurnal pattern after application but unlike the first field run in May, rarely exceeded 40 μ g NH₃ m⁻² s⁻¹. This would seem to indicate that the zero application plot was placed far enough away so as to not receive any NH₃ from the treatment plots as was noted in the first two field experiments. Weather data for this sampling period was milder than the previous two experiments, which would account for the moderate NH₃ loss (Table 4). Lower air temperatures and wind speeds were also noted to be the probable cause for lower NH_3 flux measurements during effluent applications in Georgia (Sharpe and Harper, 1997).

During the September field tests, samplers were allowed to monitor ambient background air for approximately 16 hours before effluent applications to demonstrate that no measurable amounts of $NH₃$ were in the atmosphere in the testing area. From these preapplication measurements in September, it can be seen that NH₃ levels in the atmosphere were negligible before effluent was applied (Figure 2).

For all sampling periods, the samplers at the lowest height consistently detected more $NH₃$ than the 3 higher heights (Figure 2). This would be expected due to lateral movement of air currents across the plot being more significant than the vertical movement over such short fetches. Ferm and Svensson (1993) reported similar results in

NH3 emission flux measurements using a simple passive sampler. They found that horizontal NH₃ flux is higher near the ground and decreases approximately exponentially with increasing height. This trend was also detected when using passive samplers in the wind tunnel as described previously (Figure 9, Chapter 1). Only at the initial sampling periods could any detectable amounts of $NH₃$ be measured at the highest position (184) cm).

Reports from other $NH₃$ volatilization research projects using animal waste resulted in very similar values to those found in the experiments performed for this study. A micrometeorological study in the Netherlands by Vander Molen et a1. (1990) found that 32 and 67% of the ammoniacal N applied from cattle slurry to bare soil was lost to the atmosphere from two, nine day experiments. The higher value for the first test was theorized to be due to a higher surface pH, higher wind speed and lower humidity throughout the testing period. They also noted diurnal $NH₃$ fluctuations from cattle slurry applications, with maximum fluctuations occurring at midday and minimum fluctuations at midnight. Ammonia volatilization experiments in the UK and the Netherlands found 24 and 62% losses from applied ammoniacal N in pig slurries to ryegrass using a micrometeorological mass balance method (Pain et aI., 1989). A micrometeorological mass balance determination of NH₃ volatilization from surface applied cattle slurry in Northern Ireland resulted in a 51% loss of applied NH_4 ⁺-N over a 7 day period (Stevens and Logan, 1987). Beauchamp et al. (1978) reported 60 and 56% of the NH₄⁺-N in surface applied sewage sludge volatilized within a week's sampling period. To our knowledge, the only research with manure application measurements using the integrated horizontal flux method and the passive flux samplers used for this experiment was done

in the Southeast United States between 1995-1997. Using the samplers, as described by Schjøerring et al. (1992), 28 to 46% of the NH_4^+ -N applied from broiler litter to tall fescue pastures was volatilized in 3 southeastern states (GA, AL, TN) over a 14 day testing period (Marshall et al., 1998). Other work resulted in an average 23% loss of total applied N as $NH₃$ when swine slurry was applied to bermudagrass pastures (Sullivan et aI., 1998).

Mass balance calculations for the 3 test periods were variable and prone to overestimations and underestimations in several parameters (Table 3). Average percent recoveries for the three field trials were 90, 101, and 117 for the May, July, and September periods respectively with standard deviations of 14.2, 15.9, and 15.2 respectively. Mass balances of this type are often inaccurate due to the many transformations of nitrogen that are difficult to account for such as immobilization from microbial growth. Surface amounts of soil total nitrogen are only 0.05 to 0.10 %, while inorganic N represents only a small fraction $($ < 2% of the total N in soils) (Bremner, 1965). Total nitrogen values, with a precision of 0.01%, are known to be $+/- 224$ kg ha⁻¹ (Raun et al., 1998) and are therefore prone to large miscalculations. Overestimations of $NH₃$ losses were found using a nitrogen recovery mass balance method (N loss = N recovered immediately following application - N recovered after time) from the broadcasting of urea granules onto a pasture (Black et aI., 1985). They summarize that this method resulted in higher estimated underestimations due to other processes, such as immobilization, and that this calculation became more prone to error over longer time intervals. Also, for our experiments, assumptions were made that could introduce error, such as the soil bulk density (D_B) being equal to 1.33 g cm⁻³, sampling depths being

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consistently at 15.24 cm, etc. However, a 10% change in bulk density would result in only a 2% variation, which would therefore not result in a large source of error. Although a flowmeter was used to apply effluent to each plot, this could also be a potential source of error. However, a 10% change in the volume of effluent that was added would contribute only an 8 % variation. The concentration of effluent that was measured from tank to tank would more likely be a source of error. A 10% change in the concentration of effluent would produce only a 6% change. Another large source of variation could be the actual concentration of captured NH_4 ⁺-N on the samplers. Although these samplers had an excellent recovery rate under laboratory tests, contaminated tubes are always a concern. Under some high wind environments and thunderstonns, some samplers collected small amounts of blown soil or rain. A 10% variation in the tubes' ability to capture ammonia under such circumstances would result in a 5% change in the percent recovery of the system. If a 10% change in all four of the above parameters were to occur, only a 6% variation is anticipated. So, the percent recoveries for the system seemed to tum out quite well considering the above potential sources of error. During the May test, 85, 79, and 106% recovery of the system was calculated for each plot. An 83, 103, and 115% recovery was calculated for July's tests, while September's recoveries were all over 100, at 134, 108, 107%. Recoveries over 100% could be due to potential errors in the mass balance itself as described above.

Despite inherent problems when dealing with soil-N mass balance estimates, percent recoveries were all above 78%, indicating that these samplers have the ability to monitor NH₃ emissions under varying field environments. The objective was to determine to what degree NH₃ losses were occurring, due to the environmental

characteristics and to the large increase in confined swine feeding facilities in this area of the state. Based on our results, these samplers should enable researchers to provide more accurate estimates of the potential NH₃ losses that can be anticipated in this region under the environmental conditions studied. Producers can then utilize this infonnation for better N budgets when applying swine effluent to their cropland. Nitrogen buildups do not appear to be a major concern with this production system in the Southern Great Plains. The majority of N being introduced into these com/wheat cropping systems from swine effluent additions will most likely be utilized by the plant or volatilized after application from center pivots. However, P and salinity levels should be monitored if effluent applications are added at levels to counter NH₃ volatilization losses.

CONCLUSIONS

Ammonia volatilization from swine effluent can be affected by several different factors such as soil pH, CEC, texture, swine effluent pH, application method, *soil* moisture, irrigation droplet size, air temperature, humidity, and wind speed. Climatic conditions seemed to have the most dramatic affect on NH₃ volatilization from field tests, with results ranging from 37 - 57% loss of the total NH_4^+ -N that was applied from swine effluent. These are significant losses to the producers of the region and should be taken into account when managing N.

Obviously there has been a tremendous amount of research on NH₃ volatilization from both commercial fertilizers and also from varying animal wastes. However, research specific to this region of the United States, which has so many factors prone to increasing NH3 volatilization from swine effluent applications is lacking. Therefore, being able to provide a reliable range of numbers over differing environmental conditions specific to this region of the state will enable producers in this area to more properly manage their N. Also, these numbers could potentially yield useful infonnation on the amount of NH₃ that is entering the atmosphere, and could be used to minimize the amount of unnecessary $NH₃$ being lost into the air. This will benefit the air quality of the area and help decrease potential odor problems, which will become more important as the population of swine continues to rise in this area of Oklahoma.

Even though soil mass balance calculations are prone to error, the percent recoveries for the three test periods were all within an acceptable range $(79 - 134\%)$. Overall, from the soil mass balance calculations and the volatilization results, these

samplers seem to be quite adequate at capturing and providing an estimate of NH₃ volatilization losses under variable field conditions.
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Table 1. Average initial soil characteristics over all sampling periods for Richfield clay loam and swine effluent characteristics

Table 2. Second order inverse polynomial regression equations for vertical NH₃-N flux from swine effluent applications on a Richfield clay loam

 \overline{t} x = time, y = vertical NH₃-N flux

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Table 4. Weather data for the field volatilization studies

Table 5. Summary of field volatilization studies

 $[†]$ based on 7 day regression outputs instead of 5 day</sup>

Figure 1: Passive flux sampler. Top: A passive flux sampler consisting of two parallel sampler units. Each unit is composed of 100 mm long glass tubes, coated with oxalic acid on approximately 70 mm of the inside (shaded), and a 23 mm tube with stainless steel disc at the end, all joined by silicone tubing. E_1 , E_2 are exposed tubes and B_1 , B_2 are background tubes. (Bottom left) Mast with four flux samplers seen from profile. (Bottom right) Four masts around a circular NH3 source as seen from the top. From Sommer et al. (1996).

Figure 2. Average borizontal net NH₃ flux ($n = 3$) at each height for three field tests in Goodwell, OK. September tests were began approximately 16 hours before initial application of effluent. This explains the difference in the initial peak from the first two sampling periods.

Figure 3. Vertical NH₃-N flux and cumulative NH₃-N lost from field plots during 3 field tests in Goodwell, OK. Bars represent standard errors.

Figure 4. Vertical NH] Flux for each plot during three field tests in Goodwell, OK.

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APPENDICES

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APPENDIX I

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Efficiency Determinations

					NH_4 ⁺ -N	NH_4 ⁺ -N		
	Corre-				captured in	calculated		
Sample	sponding		Tube	Tube	tubes	in tubes	% Eff. of	% Recovery
(3 mL)	Soluion	Minutes	$(ug mL^{-1})$	(μg)	(mole)	(mole)	tubes (mole)	of System
32	21	60	2.32	6.96	4.97E-07	5.27E-06	18.023	92.15
33	21	60	2.11	6.33	4.52E-07			
34	22	60	1.68	5.04	3.60E-07	5.29E-06	13.410	91.67
35	22	60	1.63	4.89	3.49E-07			
36	23	60	2.32	6.96	4.97E-07	5.16E-06	18.701	92.38
37	23	60	2.18	6.54	4.67E-07			
38	24	120	4.55	13.65	9.75E-07	6.40E-06	30.251	91.89
39	24	120	4.48	13.44	9.60E-07			
40	25	120	11.82	35.46	2.53E-06	1.01E-05	50.599	90.89
41	25	120	12.12	36.36	2.60E-06			
42	26	120	12.77	38.31	2.74E-06	9.56E-06	54.967	92.17
43	26	120	11.76	35.28	2.52E-06			
44	28	180	0.03	0.09	6.43E-09	4.05E-06	0.159	92.65
45	28	180	0	0	$0.00E + 00$			
46	29	180	0.05	0.15	1.07E-08	3.89E-06	0.275	92.94
47	29	180	0	0	$0.00E + 00$			
48	30	90	0.06	0.18	1.29E-08	4.18E-06	0.307	92.42
49	30	90	0	0	$0.00E + 00$			
50	31	180	17.23	51.69	3.69E-06	1.16E-05	64.612	92.55
51	31	180	17.68	53.04	3.79E-06			
52	32	210	19.59	58.77	4.20E-06	1.24E-05	67.549	92.71
53	32	210	19.35	58.05	4.15E-06			
54	33	210	14.74	44.22	3.16E-06	9.67E-06	63.287	93.54
55	33	210	13.83	41.49	2.96E-06			
56	34	210	14.69	44.07	3.15E-06	1.02E-05	60.637	92.68
57	34	210	14.25	42.75	3.05E-06			
58	35	270	21.63	64.89	4.64E-06	1.35E-05	66.471	91.77
59	35	270	20.26	60.78	4.34E-06			
60	36	270	25.3	75.9	5.42E-06	1.51E-05	73.966	92.86
61	36	270	26.74	80.22	5.73E-06			
62	37	270	17.26	51.78	3.70E-06	1.52E-05	54.769	87.53
63	37	270	21.5	64.5	4.61E-06			
64	38	300	31.4	94.2	6.73E-06	1.32E-05	102.072	100.50
65	38	300	31.66	94.98	6.78E-06			
66	39	300	29.3	87.9	6.28E-06	1.49E-05	80.541	94.73
67	39	300	26.7	80.1	5.72E-06			
68	40	0	0.01	0.03	2.14E-09			
69	40	0	0.05	0.15	1.07E-08			

Table 1- 1 Percent Efficiency of Oxalic Coated Tubes: Run A

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62 mL final solution amount	Final Solution $(\mu g \text{ mL}^{-1})$	Final Solution (μg)	Final Solution (moles NH4 ⁺ -N)
Solution21	11.23	696.26	4.97332E-05
Solution22	11.225	695.95	4.9711E-05
Solution23	11.255	697.81	4.98439E-05
Solution24	10.975	680.45	4.86039E-05
Solution25	10.13	628.06	4.48617E-05
Solution26	10.26	636.12	4.54374E-05
Solution28	11.505	713.31	5.0951E-05
Solution29	11.54	715.48	5.1106E-05
Solution30	11.475	711.45	5.08182E-05
Solution31	9.805	607.91	4.34224E-05
Solution32	9.63	597.06	4.26474E-05
Solution33	10.235	634.57	4.53267E-05
Solution34	10.11	626.82	4.47731E-05
Solution35	9.37	580.94	4.1496E-05
Solution36	9.015	558.93	3.99238E-05
Solution37	8.995	557.69	3.98352E-05
Solution38	9.43	584.66	4.17617E-05
Solution39	9.055	561.41	4.0101E-05

Table I - 1 cont. Percent Efficiency of Oxalic Coated Tubes: Run A

,,". .!ft::',EQUATIONS .. x µg (1g /1,000,000 µg) (1 mole/14 g NH₄*-N) = 7.1429 E -8 moles NH₄*-N /µg (x µg) 7.1429E-08 NH_4^* -N (mole) calculated in tubes = NH_4^* -N (mole) original NH_4^* -N (mole) final solution % Efficiency of Tubes = (NH₄⁺-N on tubes collected / NH₄⁺-N on tubes calculated) *100 % Recovery of System = $((NH_4^*-N \text{ final} + NH_4^*-N \text{ in tubes}) / NH_4^*-N \text{ original})$ * 100

					NH_4 ⁺ -N			
	Corre-				captured in	NH_4 ⁺ -N		%
Sample	sponding		Tube		tubes	calculated in	% Eff. of	Recovery of
(3 mL)	Soluion	Minutes	$(ug mL-1)$	Tube (μg)	(mole)	tubes (mole)	tubes (mole)	System
71	41	60	6.35	19.05	1.361E-06	3.71E-06	61.283	97.05
72	41	60	4.25	12.75	9.107E-07			
73	42	60	6.5	19.5	1.393E-06	4.02E-06	69.678	97.50
74	42	60	6.56	19.68	1.406E-06			
75	44	90	9	27	1.929E-06	5.61E-06	70.847	96.64
76	44	90	9.55	28.65	2.046E-06			
77	45	90	9.12	27.36	1.954E-06	5.10E-06	74.685	97.35
78	45	90	8.66	25.98	1.856E-06			
79	46	120	10	30	2.143E-06	5.41E-06	77.416	97.49
81	46	120	9.55	28.65	2.046E-06			
82	47	120	11.64	34.92	2.494E-06	6.10E-06	80.438	97.55
83	47	150	11.25	33.75	2.411E-06			
84	48	150	13.67	41.01	2.929E-06	7.32E-06	78.793	96.81
85	48	150	13.23	39.69	2.835E-06			
86	49	150	14.84	44.52	3.18E-06	7.32E-06	84.212	97.63
87	49	150	13.91	41.73	2.981E-06			
88	50	180	17.42	52.26	3.733E-06	8.69E-06	85.235	97.36
89	50	180	17.14	51.42	3.673E-06			
90	51	210	16.71	50.13	3.581E-06	9.93E-06	79.014	95.72
91	51	210	19.9	59.7	4.264E-06			
92	52	180	16.32	48.96	3.497E-06	7.91E-06	85.676	97.67
93	52	180	15.32	45.96	3.283E-06			
94	53	210	18.62	55.86	3.99E-06	9.42E-06	84.356	96.97
95	53	210	18.46	55.38	3.956E-06			
96	54	270	20.52	61.56	4.397E-06	1.12E-05	63.456	91.57
97	54	270	12.75	38.25	2.732E-06			
98	56	330	30.02	90.06	6.433E-06	1.34E-05	88.858	96.92
99	56	330	25.75	77.25	5.518E-06			
100	57	270	24.84	74.52	5.323E-06	1.11E-05	89.582	97.63
101	57	270	21.48	64.44	4.603E-06			
102	58	330	$\mathbf 0$	$\bf 0$	0	1.36E-05	37.681	82.53
103	58	330	24	72	5.143E-06			

Table I- 2 Percent Efficiency of Oxalic Coated Tubes: Run B

62 mL final solution amount	Final Solution $(\mu g \text{ mL}^{-1})$	Final Solution (μg)	Final Solution (moles NH4 ⁺ -N)
Solution41	10.155	629.61	4.49724E-05
Solution42	10.085	625.27	4.46624E-05
Solution44	9.725	602.95	4.30681E-05
Solution45	9.840	610.08	4.35774E-05
Solution46	9.770	605.74	4.32674E-05
Solution47	9.615	596.13	4.2581E-05
Solution48	9.340	579.08	4.13631E-05
Solution49	9.340	579.08	4.13631E-05
Solution50	9.030	559.86	3.99902E-05
Solution51	8.750	542.50	3.87502E-05
Solution ₅₂	9.205	570.71	4.07652E-05
Solution ₅₃	8.865	549.63	3.92595E-05
Solution54	8.455	524.21	3.74438E-05
Solution56	7.955	493.21	3.52295E-05
Solution57	8.490	526.38	3.75988E-05
Solution58	7.910	490.42	3.50302E-05

Table 1- 2 cont. Percent Efficiency of Oxalic Coated Tubes: Run B

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APPENDIX II

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Soil-Effluent Flask Experiments

Run 6	Soil beginning $(\mu g N)$	Soil end $(\mu g N)$	Effluent added $(\mu g N)$	Captured $(\mu q \text{NH4}^+ \text{-N})$	Missing $(\mu g N)$	% Missing	% Recovery
	3250	5587.50	0.00	1.86	-2339.36	-71.98	171.98
100	3250	11032.50	8551.49	342.21	426.78	3.62	96.38
300	3250	22745.00	21517.75	537.39	1485.36	6.00	94.00
500	3250	29430.00	34542.11	512.82	7849.29	20.77	79.23
1000	3250	46059.50	66613.97	1104.51	22699.96	32.49	67.51

Table II - 1 Richfield Clay Loam Mass Balances

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	Soil						
	beginning	Soil end	Effluent added	Captured	Missing		
Run 8	$(\mu g N)$	$(\mu g N)$	$(\mu g N)$	$(\mu q NH4^+ - N)$	$(\mu g N)$	% Missing	% Recovery
$\mathbf{0}$	6663	8868.75	0.00	0.21	-2205.96	-33.11	133.11
100	6663	14971.00	9284.38	29.73	946.65	5.94	94.07
300	6663	28776.00	22332.40	119.58	99.82	0.34	99.66
500	6663	40315.00	35113.57	147.45	1314.12	3.15	96.85
1000	6663	52981.50	67028.73	94.24	20615.99	27.98	72.02
Run 9							
0	7830	9746.00	0.00	0.36	-1916.36	-24.478	124.48
100	7830	16593.50	9076.88	114.69	198.69	1.18	98.83
300	7830	24343.00	20902.72	159.33	4230.39	14.72	85.23
500	7830	48364.25	33960.28	261.12	-6835.09	-16.36	116.36
1000	7830	58047.00	66200.8	180.12	15803.68	21.35	78.65
Run 10							
Ω	7420	7975.00	0.00	2.49	-557.49	-7.51	107.51
100	7420	16071.00	9357.42	84.93	621.49	3.70	96.30
300	7420	24557.50	21148.40	96.09	3914.81	13.70	86.30
500	7420	37130.50	36067.65	110.10	6247.05	14.37	85.64
1000	7420	46161.50	66780.14	239.76	27798.88	37.47	62.54

Table II - 2 Dennis Silt Loam Mass Balances

Figure II - 1. NH₃-N volatilization results from application of five concentrations of swine effluent on two Richfield clay loam laboratory flask experiments

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Figure II - 2. NH₃-N volatilization results from application of five concentrations of swine effluent on three Dennis silt loam laboratory experiments. Note difference in scale from previous graph.

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APPENDIX III

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Wind Tunnel Studies

Table III - 1 Wind Tunnel Run 8

Total $NH₃-N$ captured (mg) = 2285.06

Beginning NH₄⁺-N concentration (mg) = 25433.44

Ending NH_4^+ -N concentration (mg) = 8.07

Percent recovery = 9.02

Table III - 2 Wind Tunnel Run 9

Total $NH₃$ -N captured (mg) = 2234.95

Beginning NH₄⁺-N concentration (mg) = 19380.71

Ending NH₄⁺-N concentration (mg) = 15.33

> Percent recovery = 11.61

Table III - 3 Wind Tunnel Run 14

- Total $NH₃$ -N captured (mg) = 356.84
- Beginning NH $_{\rm 4}^{\rm +}$ -N concentration (mg) = 1007.00
	- Ending NH₄⁺-N concentration (mg) = 7.765
		- Percent recovery = 36.21

Table III - 4

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Equations for wind tunnel tables Col B $A = I \times W$ Col C A (m²) = (in² x 2.54cm²) / 100cm² Col G μ g mL⁻¹ after background subtraction =IF(E3-\$F\$3<0,0,IF(E3-\$F\$3>0,(E3-\$F\$3))) Col J NH₃-N flux ((μ g/mL) / m[^]2 s) = (μ g/mL) (3mL) / 2 x 3.14 x (0.0005m)[^]2 x 0.77 x hrs x 3600s Col K NH₃-N flux (mg / m² hr) =((μ g/mL) / m² s) / 1000) x 3600s Col L NH₃-N (mg) = (mg / m^{λ}2 hr) x m^{λ}2 x hrs

Percent Recovery of system = $((NH₄⁺-N final + NH₃ captured)/NH₄⁺-N initial) *100$

APPENDIX IV

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Field Measurements

Table IV - 1 Panhandle Field Run 2 Soil Mass Balance

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* changed by + 10%

•• + or - 2% change when g soil changes by 10%, so bulk density assumption should not matter

Table IV - 3

Panhandle Field Run 2

Soil Mass Balance with + 10% change in effluent volume

* changed by + 10%

** + or - 8% change when volume of effluent changes by 10%, so proper effluent amounts are important

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* changed by +10%

** + or - 6% change when conc. of effluent changes by 10%, so proper effluent testing is important

Table IV - 5 Panhandle Field Run 2 Soil Mass Balance with + 10% change in tube collection values

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* changed by + 10%

** + or - 5% change when conc. of effluent changes by 10%, tubes could easily be off that much

Table IV - 6 Panhandle Field Run 2 Soil Mass Balance with + 10% change in all 4 parameters

• changed by + 10%

** + or - 6% change when all 4 parameters are changed by 10%

Table IV - 7 Panhandle Field Run 2 Soil Mass Balance Equations

diameter of plot = 15.24m Sampling depth = $1/2$ ft = 15.24 cm Assume bulk density of 1.33 g/cm"3 Surface area of plot = 3.14 X r^{^2} Volume of plot = 3.14 X r^{^2} X sampling depth g of soil = vol of plot X bulk density Soil μ g N = total μ g N g⁻¹ X 36955254.61 g soil mL effluent = 1222 gal / 0.2642gal X 1000 mL (1L = 0.2642 gal) Effluent μ g N = total μ g N mL $^{-1}$ X 4625283.876 mL effluent µg captured on tubes from "transformed " equation speadsheet total of column g/m² X SA of plot X 1X10^{α}6 μ g Missing = (μ g N in beginning soil + μ g N in effluent) - (μ g N in ending soil + μ g NH₄⁺-N captured) % Missing = missing value/(μ g N beginning soil + μ g N in effluent) $\%$ Recovery = 100 - % missing
Table IV - 8 Panhandle Field Run 3 Soil Mass Balance

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Table IV - 9 Panhandle Field Run 4 Soil Mass Balance

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