

Ammonia Volatilization Losses Following Irrigation of Liquid Swine Manure in Commercial Pine Plantations

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ABSTRACT

Ammonia volatilization was measured after land application of liquid swine manure in a commercial pine forest in South Carolina. Three wind tunnels were constructed and used to measure ammonia volatilization after application. The fraction of ammonia lost as percent of TAN applied was fitted to the function $Y = a(1 - e^{-Kt})$. The function represented the data with parameter a , the potential volatilization loss, and parameter K , a rate constant. The total amount of $\text{NH}_3\text{-N}$ lost after irrigation of liquid swine manure varied from 0.38% to 3.6% of the TAN applied. The total ammonia lost was found to correlate significantly ($R^2 = 0.950$) with the mass of TAN applied per m^2 per application depth ($\text{g TAN/ m}^2\text{-mm}$) and with the total solids content of the manure. The average rate constant, K , for liquid swine manure applications with mean air temperature below $30\text{ }^\circ\text{C}$ was 0.0125 min^{-1} . At mean air temperatures of $32\text{ }^\circ\text{C}$, the rate constant increased to 0.0337 min^{-1} and was significantly different from other application events. Ammonia losses following irrigation of liquid swine manure were on the same order of magnitude as losses reported for other land application studies in which the manure was immediately incorporated.

Keywords: Ammonia volatilization, nitrogen losses, liquid swine manure, land application, pine forest.

INTRODUCTION

Ammonia volatilization affects the amount of nitrogen available for crop fertilization modifying the agronomic value of manure as fertilizer and increasing the uncertainty of nutrient management practices. Ammonia volatilization from application of swine slurries can be 30% to 40% of the total Kjeldhal nitrogen (TKN) and up to 60% of the total ammoniacal nitrogen (TAN) applied (Pain et al. 1989 and Lockyer et al. 1989). Volatilization losses during application are negligible; therefore most of the loss occurs once the manure has been applied in the field (Pain et al. 1989; Montes and Chastain, 2000; and Montes, 2002)

Ammonia volatilization from manure is a complex process. In essence, it is the mass transfer of NH_3 molecules from the manure solution through the air-liquid interface and then to the atmosphere through convective mass transport. The process is affected by the: pH of the manure and the soil in which it has been applied, equilibrium between NH_3 and NH_4^+ in the manure, temperature of the environment, wind velocity and airflow characteristics (Ni, 1999; and Montes, 2002). The complexity of the process is further increased when biochemical transformations such as mineralization and nitrification are included. Management practices such as the animal

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waste handling system, application rate and application method also affect the volatilization process (Montes, 2002).

Few studies have been conducted on land application of animal manure in forest environments and no study has evaluated volatilization losses from land application in these environments. The objectives of this study were to measure ammonia volatilization losses following irrigation of liquid swine manure in a pine plantation, and to identify the main factors affecting total amount of NH_3 lost and the volatilization rate.

EXPERIMENTAL METHODS

Ammonia volatilization was measured on 12 occasions after irrigation of liquid swine manure in a commercial pine plantation near Manning, South Carolina. The trees were 10 years old at the beginning of the study and were machine-planted at a spacing of 1.8 m by 3 m (6 ft by 10 ft). Liquid manure was pumped from a lagoon serving a nearby finishing swine facility using 63.5 mm (2.5 in) schedule 40 PVC pipe and a 10.4 kW (14 hp) pump equipped with a semi-open impeller. Large impact sprinklers with 9.5 mm nozzles were used to apply the effluent at an operating pressure of 179 kPa (26 psi). The sprinklers were positioned to provide an overlap of more than 100%. Application rates ranged from 67 kg PAN /ha (60 lb PAN / ac) to 134 kg PAN / ha (120 lb PAN / ac). These application rates were defined by a parallel study on tree-growth response and water quality impact. Detailed description of the project site, irrigation system and forest characteristics are provided by Lucas et al. (1999).

Liquid swine manure samples were collected using eight plastic containers placed in the plot before the application started. At the end of each application, contents of the containers were mixed into one representative sample, stored in a large plastic bottle and maintained on ice for transport to the laboratory. Each of the large samples was screened to remove floating debris and two to three well-mixed sub samples were drawn for nutrient analysis. Each manure sample was analyzed to determine pH, total solids, total Kjeldahl nitrogen (TKN) and total ammoniacal nitrogen ($\text{TAN} = \text{NH}_3\text{-N} + \text{NH}_4^+\text{-N}$) by the Agricultural Service Laboratory at Clemson University.

Ammonia volatilization was measured using three wind tunnels designed and built in the department of Agricultural and Biological Engineering at Clemson University. Inside each wind tunnel, air flowed at 1410 ± 80 L/min (50 ± 3 CFM) over an application area of 0.84 m^2 (9 ft^2), carrying volatilizing ammonia towards the tunnel outlet. Here air was mixed with an electric fan and straightened by passing through a flow straighter before ammonia concentration was measured. Ammonia concentration was measured using a Sensidyne-Gastec 800 model Detection Pump/Reagent tube system. Reagent tubes with sampling ranges of $0.5\text{-}78 \text{ ppm} \pm 10\%$ and $0.2\text{-}20 \text{ ppm} \pm 10\%$ were used; ammonia concentration was read directly in ppm using the detection tube calibrated scale (Sensidyne Inc, 1990).

Immediately after each manure application ended, one wind tunnel was carried to a location representative of the forest floor application area. Once the wind tunnel was in place, the fan was turned on, the starting time was recorded and ammonia measurements at the inlet and outlet were initiated. For the first 30 minutes after application, NH_3 concentrations at the inlet and outlet were recorded every 5 minutes. The following hour ammonia concentration was recorded every 10 minutes, every 20 to 30 minutes for the next two hours and every 1 or 2 hours thereafter until NH_3 concentration at the outlet fell to 0.25 ppm. At this concentration level it was determined that most of the volatilization loss had occurred. Sampling frequency after the first three hours of measurements depended on rate of change in NH_3 concentration.

Concentration measurements at the inlet were suspended after ammonia concentration fell below reagent tubes detection limits. However, periodic inlet concentration measurements were made to verify that no detectable ammonia was present in the inlet air. Ambient air temperature and relative humidity measurements were recorded using a sling psychrometer (Bacharach, Inc.) throughout the ammonia volatilization experiment.

The environmental conditions present during each volatilization experiment as well as the TKN, TAN and TS of the irrigated liquid swine manure are presented in Table 1. The pH of the swine lagoon effluent applied ranged from 7.8 to 8.2, with a mean of 8.1 and standard deviation of 0.18.

Table 1. Ambient conditions during volatilization measurements, liquid swine manure application rates, total Kjeldhal nitrogen (TKN), total ammoniacal nitrogen (TAN) and total solids (TS) content for each liquid swine manure application.

Application			T ^b (°C)	RH ^c (%)	Volume applied (L/m ²) ^d	TKN (mg/L)	TAN (mg/L)	TS (%)
Event	Date	Time ^a						
SW1	3/21/00	12:55 PM	15.4	72	15.83	1352	1206	0.49
SW2	3/21/00	8:44 AM	14.6	91	15.83	1214	1014	0.57
SW3	3/21/00	9:58 AM	14.3	87	15.83	1485	1183	0.50
SW4	7/5/00	4:50 PM	31.3	69	10.25	1037	870	0.53
SW5	7/6/00	10:44 AM	28.8	73	10.25	977	845	0.55
SW6	7/5/00	3:45 PM	32.5	69	10.25	1093	943	0.53
SW7	11/7/00	2:15 PM	27.7	70	29.17	597	547	0.39
SW8	11/7/00	12:20 PM	25.3	75	29.17	640	557	0.37
SW9	11/7/00	10:20 AM	24.1	81	29.17	636	477	0.37
SW10	3/19/01	3:24 PM	12.5	47	13.51	1065	880	0.41
SW11	3/19/01	2:20 PM	13.1	32	13.51	1065	880	0.42
SW12	3/19/01	4:32 PM	12.2	37	13.51	1045	945	0.41

^a Time of day that the wind tunnel experiment began

^b Average air temperature values for the application event

^c Average relative humidity values for the application event

^d L/m² is equivalent to application depth in mm

RESULTS

Ammonia concentration at the wind tunnel outlet reached its peak immediately after irrigation and began decreasing with time. The rate of decrease was reduced as the concentration approached zero. Ammonia concentration at the wind tunnel outlet fell to levels below the detection limit 3 to 5 hours after application of liquid swine manure.

Ammonia concentration in terms of mass per unit volume (mg NH₃/m³) can be calculated from the concentration in parts per million (volume basis) measured with detection tubes using the following application of the ideal gas law at ideal pressure (Montes, 2002; Wark et al, 1988; Sensidyne Inc, 1990):

$$[NH_3]_{mg/m^3} = [NH_3]_{ppm} \times \frac{MW_{NH_3}}{22.4} \times \frac{273.15}{273.15 + T} = 0.707 \times [NH_3]_{ppm}, \quad (1)$$

where,

$$[NH_3]_{mg/m^3} = \text{ammonia concentration in mg/m}^3 \text{ (m/v)}$$

$[NH_3]_{ppm}$ = ammonia concentration in parts per million, ml/m³ (v/v)

T = average temperature during the experiments = 293.15 K (20°C),

22.4 = volume of 1 Kmol at 0°C under 1 atmospheric pressure (m³),

MW_{NH_3} = molecular weight of NH₃ = 17 kg-NH₃ / Kmol.

It is necessary to know inlet and outlet NH₃ concentration simultaneously to calculate the amount of ammonia that is being volatilized with respect to time. Since it was impossible to measure inlet and outlet concentrations at exactly the same time, linear interpolation was used to estimate inlet concentrations that matched outlet concentrations in time. The procedure used is illustrated using data from one of the experiments in Figure 1.

The average ammonia flux in the volatilization area inside the wind tunnel was calculated by using the airflow rate in the wind tunnel and the difference between outlet and inlet NH₃ concentration at a specific time, as:

$$J_{NH_3}|_t = \frac{([NH_3]_{o|t} - [NH_3]_{i|t}) \times Q_{air}}{A_v}, \quad (2)$$

where,

$J_{NH_3}|_t$ = NH₃ mass flux at time t (mg NH₃/m²s),

$[NH_3]_{i|t}$ = NH₃ concentration in the inlet air stream at time t (mg NH₃/m³),

$[NH_3]_{o|t}$ = NH₃ concentration in the outlet air stream at time t (mg NH₃/m³),

Q_{air} = airflow rate (0.024 m³/s), and

A_v = Area of volatilization (0.36 m²).

The uncertainty in determining the ammonia flux from the volatilization area inside the wind tunnel was calculated to be ±13 % of which the main component was the measurement error of NH₃ concentration, ±10 % (Montes, 2002).

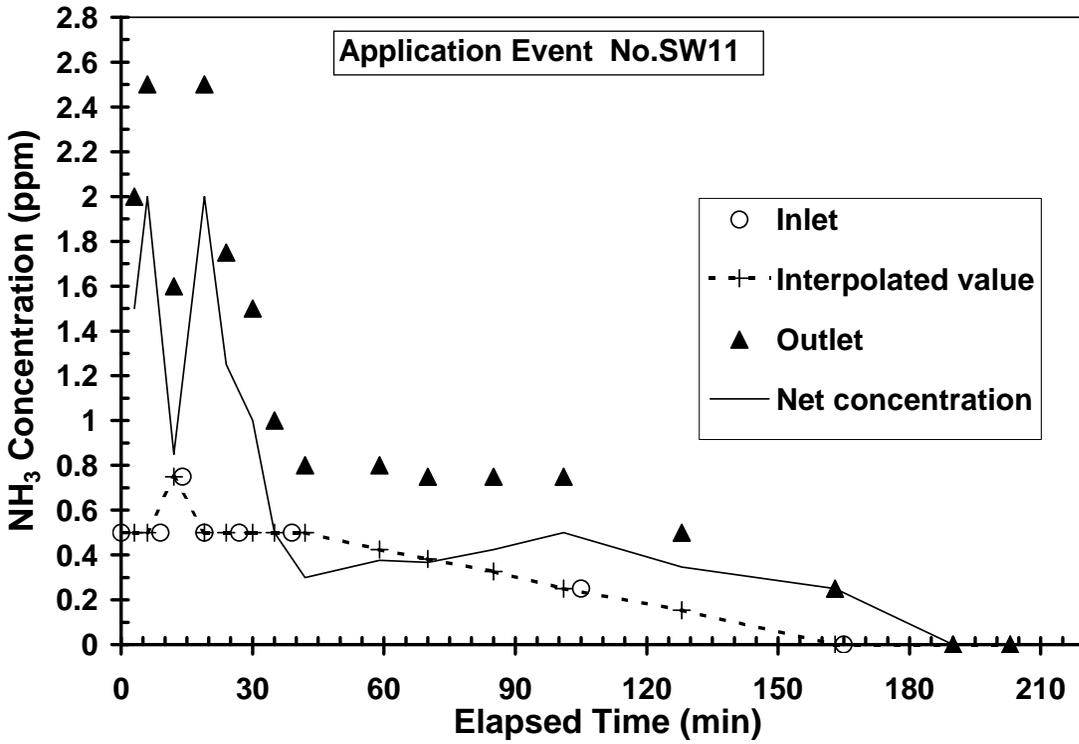


Figure 1. Sample data showing the use of linear interpolation of inlet NH_3 concentration to match outlet measurements in time for volatilization following liquid swine manure application. Net concentration is the outlet NH_3 concentration minus the interpolated inlet NH_3 concentration

Once mass flux was known, the amount of ammonia lost per unit area in a time interval was calculated. The mass of ammonia lost in a small time interval, Δt , is approximately equal to the average flux rate between two points close in time, multiplied by the time difference between those points. Thus, total mass of ammonia lost per square meter as a function of time was calculated as:

$$M_{\text{NH}_3} = \sum_{t=0}^{t=F} \left(\frac{(J_{\text{NH}_3}|_t + J_{\text{NH}_3}|_{t+\Delta t})}{2} \times \Delta t \right) \quad (3)$$

where,

$$\begin{aligned} M_{\text{NH}_3} &= \text{total mass of } \text{NH}_3 \text{ lost per unit area (mg } \text{NH}_3/\text{m}^2\text{)}, \\ J_{\text{NH}_3}|_t, J_{\text{NH}_3}|_{t+\Delta t} &= \text{NH}_3 \text{ mass flux at time } t \text{ and } t + \Delta t \text{ (mg } \text{NH}_3/\text{m}^2 \text{ s)}, \text{ and} \\ F &= \text{time duration of the experiment (min)}. \end{aligned}$$

It is common practice to report the ammoniacal nitrogen in manure as total ammoniacal nitrogen content ($\text{TAN} = \text{NH}_3\text{-N} + \text{NH}_4^+\text{-N}$). Therefore volatilization losses were expressed as a percent of TAN applied.

The cumulative mass of NH_3 lost in time as percent of the TAN applied was calculated as:

$$\frac{\text{NH}_{3L}}{\text{TAN}} \Big|_t = \frac{M_{\text{NH}_3}|_t}{\text{TAN}_{ap}} \times 100, \quad (4)$$

where,

$\frac{NH_{3L}}{TAN} \Big|_t$ = total mass of NH_3 lost expressed as percent of TAN applied at time t ,

$NH_{3L} \Big|_t$ = total mass of NH_3 lost per unit area ($mg\ NH_3/m^2$) at time t , and

TAN_{ap} = mass of TAN applied per unit area (mg/m^2).

Cumulative NH_3 volatilization data sets were fitted to the following function:

$$Y = a(1 - e^{-Kt}). \quad (5)$$

The Marquadt method of nonlinear regression procedures included in statistical analysis software (SAS institute, 1990; Demeyer et al., 1995) was used fit the data to equation 5. In this function, Y is the total volatilization of ammonia expressed as percent of TAN applied at t minutes after application; a is the potential volatilization loss parameter; and K is a rate constant. The fitted curves and data for all liquid swine manure irrigation experiments are shown in Figures 2 and 3. A summary of the nonlinear regression results and relevant statistics are given in Table 2.

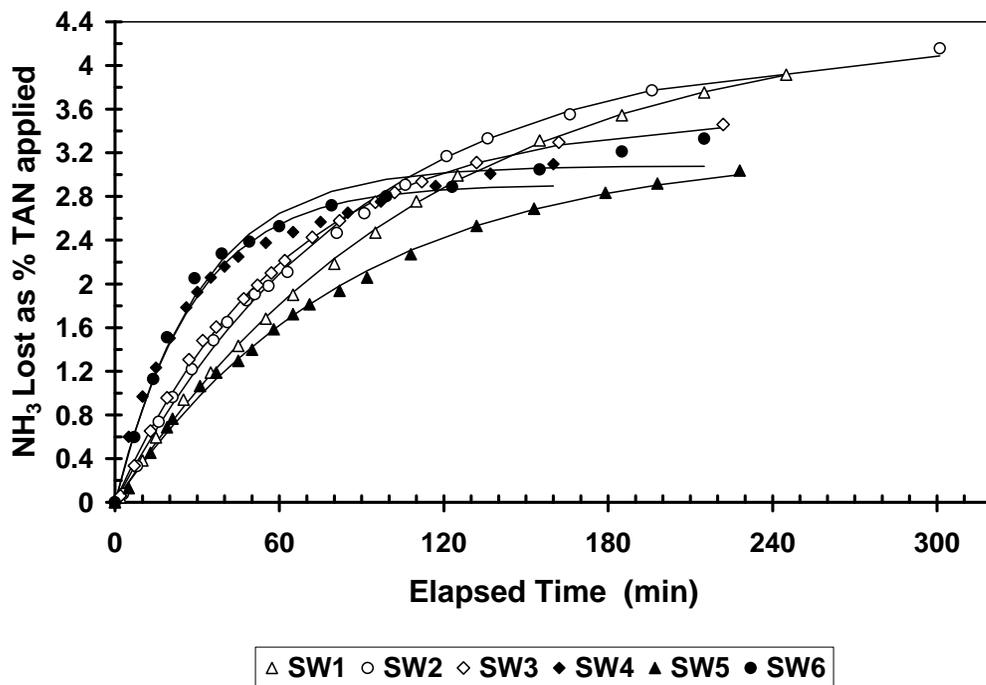


Figure 2. Ammonia volatilization loss as a function of time expressed as percent of TAN applied (points). Corresponding fitted functions for liquid swine manure application events SW1 through SW6 described in Table 1.

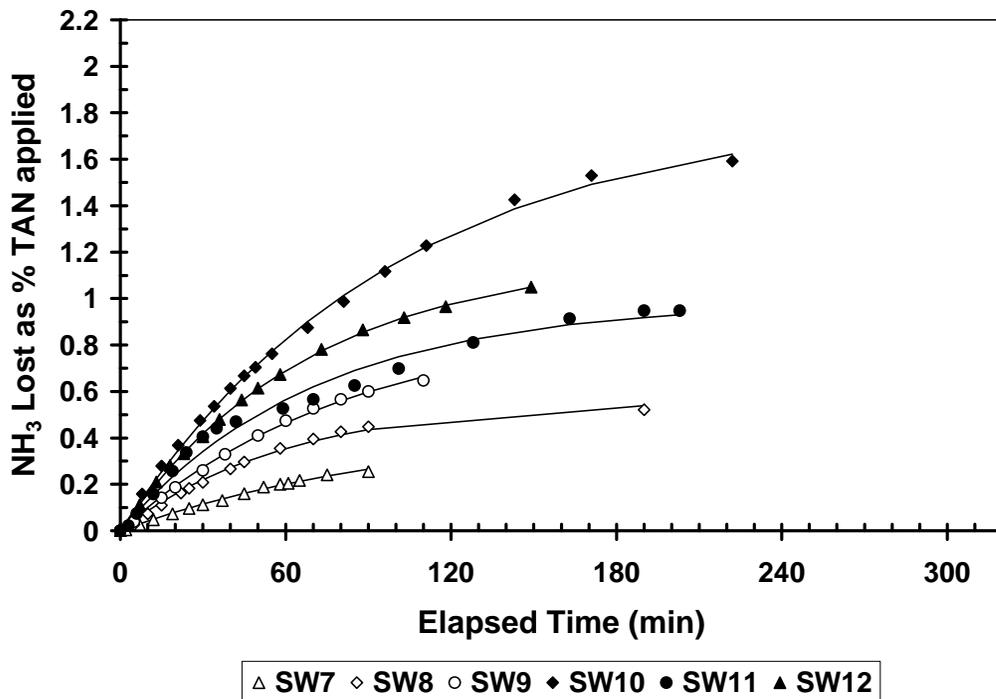


Figure 3. Ammonia volatilization loss as a function of time expressed as percent of TAN applied (points). Corresponding fitted functions for liquid swine manure application events SW7 through SW12 described in Table 1.

Table 2. Curve fitting results for volatilization losses following irrigation of liquid swine manure using the model given in equation 6.

Application Event	Potential Total NH ₃ Loss Parameter ($a \pm \text{C.I.}$)*		Rate Constant ($K \pm \text{C.I.}$)*		n	R ² **	Mean of Residuals	Mean Square of Residuals (s ²)
SW1	4.432	± 0.099	0.0088	± 0.00037	17	0.999	0.0024	0.00110
SW2	4.224	± 0.109	0.0114	± 0.00060	20	0.998	0.0035	0.00310
SW3	3.530	± 0.051	0.0161	± 0.00052	20	0.999	-0.0019	0.00090
SW4	2.907	± 0.105	0.0348	± 0.00375	18	0.987	0.0127	0.00990
SW5	3.231	± 0.086	0.0116	± 0.00063	20	0.998	0.0034	0.00170
SW6	3.081	± 0.135	0.0326	± 0.00481	14	0.985	0.0039	0.01690
SW7	0.458	± 0.084	0.0096	± 0.00242	15	0.997	-0.0008	0.00003
SW8	0.563	± 0.033	0.0165	± 0.00183	14	0.995	-0.0031	0.00020
SW9	0.906	± 0.082	0.0120	± 0.00172	12	0.998	-0.0019	0.00010
SW10	1.815	± 0.067	0.0101	± 0.00068	17	0.998	0.0025	0.00050
SW11	0.985	± 0.078	0.0142	± 0.00254	17	0.985	0.0039	0.00160
SW12	1.186	± 0.021	0.0145	± 0.00049	15	0.999	-0.00001	0.00004

*Approximate 95% confidence interval (SAS Institute 1990, Ryan 1997)

**Nonlinear R²

Fitting the data sets to the mentioned function results in the representation of the complete data set by two curve fitting parameters, eliminates the need to estimate the volatilization value at the beginning of the experiments and estimates the total volatilization losses based on the whole data set. As seen in Figures 4 and 5, the nonlinear function closely describes the data. Good agreement between the function and the data is also indicated by high values of R², values of mean residuals very close to zero, and small values of mean square of residuals (Table 2).

The parameter a varied from 0.46 to 4.4 for irrigation of liquid swine manure. Therefore, 0.46 % and 4.4% of the TAN applied was lost as NH₃. Nitrogen represents 82 % of the molecular weight of NH₃. Therefore the cumulative NH₃ loss as percent of TAN applied is simply 0.82 a . Thus the amount of NH₃-N lost ranged from 0.38% to 3.6% of TAN applied. These results are in agreement with other volatilization studies in which manure was incorporated immediately after application (Malgeryd, 1998; Thompson et al. 1987; Hoff et al. 1981; Montes 2002).

The amount of NH₃ lost, a , and the rate constant, K , were hypothesized to be influenced by the volume of manure applied, the amount of TAN applied, the TS content of the manure, manure pH, air temperature, and relative humidity. The pH of the irrigated manure was 8.1 with a CV of 2.2%. Therefore, pH was not included in the analysis due to the small range of values.

A correlation analysis was performed to determine if the variation in a and K could be described as a function of the following variables: (1) volume of manure applied (V_A , L/m²), (2) mass of TAN applied per unit area (M_{TAN} , g TAN/m²), (3) total solids (TS, %), (4) air temperature (T_{AIR} , °C), (5) relative humidity (RH, %), and (6) mass of TAN applied per m² divided by application depth (δ , g TAN/m²-mm).

Significant correlations were found between a , and the independent variables TS and δ . The best fit of the data was provided by the following regression equation:

$$a = 14.86TS + 7.38\delta^2 - 10.3\delta - 1.56. \quad (6)$$

The regression equation for a had 8 degrees of freedom, an R^2 of 0.950, a standard error of the y estimate ($S_{y,x}$) of 0.3810 and a mean CV of 16.7 %.

The function was linear in TS and quadratic in δ . The variable δ represents the amount of TAN applied per unit area relative to the depth of liquid application. Therefore, the total NH_3 loss parameter can be predicted by the solids content of the manure, the amount on TAN applied, and the application depth.

The relationship between the rate constant K and variables V_A , M_{TAN} , δ , TS, T_{AIR} and RH was studied using correlation analysis. The analysis identified that the only variable with significant effect on the rate constant was mean air temperature. Figure 4 shows the variation in K with respect to the average air temperature during each application event. The scatter of the data suggested that there was a single rate constant for NH_3 volatilization following irrigation of swine manure with mean air temperature below 30°C and a different value for applications that occurred at 32°C . The mean K -value for temperatures below 30°C was 0.0125 min^{-1} . The rate constant at 32°C was 0.0337 min^{-1} . These two rate constants were significantly different at the 95 % confidence level.

The rate constant value describes the dynamics of the volatilization process. The inverse of the rate constant, that is $1/K$, is equal to the time t required for 63.2% of the volatilization process to be completed. Thus as the rate constant K increases, the time required for the volatilization process to be completed decreases (Montes 2002). For the highest rate constant value in this experiment ($K = 0.0337\text{ min}^{-1}$ at 32°C), only 30 min are required to complete 63.2 % of the total volatilization. If the rate constant is 0.0125 min^{-1} (less than 30°C), 80 min are required.

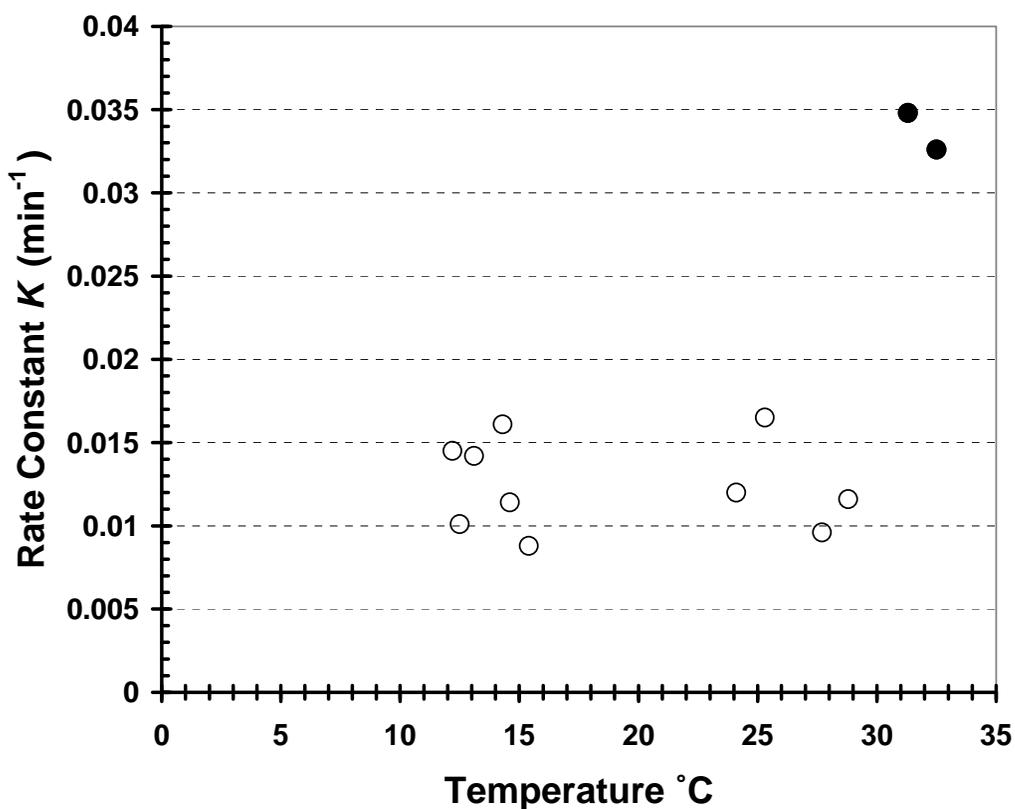


Figure 4. Rate constants for liquid swine manure.

CONCLUSIONS

Nitrogen volatilization loss following irrigation of liquid swine manure in a commercial pine plantation in South Carolina averaged 1.9 % of the TAN applied. Volatilization loss ranged from 0.38% to 3.6% of the TAN applied and was explained by the total solids content of the liquid manure and the TAN applied per m² per mm application depth. Temperature and relative humidity were not important in determining the total volatilization loss, although temperatures above 30°C showed a significant increase in the speed at which the process occurred. The results of this study are in agreement with other volatilization studies in which manure was incorporated immediately after application.

Acknowledgements

This work was funded by a grant from the Agricultural Productivity and Profitability Program as a part of the Clemson University Public Service Allocation. Additional support was provided by Clemson University Extension.

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