

A Nonpoint Source Model for Land Areas Receiving Animal Wastes: II. Ammonia Volatilization

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ABSTRACT

A simple conceptual model was developed, based on a state-of-the-art approach, to describe NH_3 volatilization losses from land areas receiving animal manures. Environmental and soil factors influencing NH_3 volatilization were also included in the model. Rate constants for first order relationship were estimated from the existing literature data. The sub-model described assumes that NH_3 volatilization follows first-order kinetics. The rate of NH_3 loss was shown by the model to occur in one or two stages. In the first stage, losses were relatively rapid with approximately 80 percent of applied NH_3 being volatilized during the first week after application. Manures incorporated into soils with low CEC resulted in greater losses of NH_3 compared to the manures incorporated into soils with high CEC. Losses of NH_3 increased with increase in temperature and air flow rate above the soil surface. Correction factors for temperature, CEC, and wind velocity were presented to adapt the sub-model under varying soil and environmental conditions.

INTRODUCTION

Recent concern in the environmental pollution from the land areas receiving animal manure was focused on NH_3 volatilization as one process contributing to air and water pollution and N loss. Direct absorption of the atmospheric NH_3 by lakes and streams could contribute to their eutrophication (Deacon, 1973; Denmead et al., 1974; Dornbush and Anderson, 1964; Elliot et al., 1971; Luebs et al., 1973). Ammonia volatilization from feedlot or from land application sites can contribute significant quantities of NH_3 to the atmosphere. Hutchinson and Viets (1969) showed that a lake in the vicinity of a large feedlot absorbed enough ammonia per year to raise its N content 0.6 mg/L. Ammonia volatilization is the first significant process to occur immediately after the land application of manure. This process can cause substan-

tial losses of N from animal wastes having high initial NH_4 concentrations (Adriano et al., 1971; Lauer et al., 1976; Steenhuis et al., 1976; Stewart, 1970). Initial NH_4 -N (at time $(t)=0$) in animal manures is mostly derived from the hydrolysis of urea and uric acids in the feces and results in a temporary high pH, thus creating conditions favorable for NH_3 volatilization. Volatile losses of NH_3 occur when manures are exposed to air movement in animal production facilities and after manure spreading in fields. In pastures and rangelands, most of the NH_3 -N in the animal wastes is rapidly lost after defecation by the animals.

In order to describe NH_3 volatilization quantitatively, it is important to understand the basic mechanisms involved and the factors influencing this process in the soil manure system. Several equations have been proposed to describe NH_3 volatilization under various conditions such as lagoons, NH_3 removal as a pretreatment process, aquatic systems, and in animal manures (Bouldin et al., 1974; Srinath and Loehr, 1974; Koelliker and Miner, 1973; Steenhuis et al., 1976). All these researchers basically followed the fundamental principles of NH_3 chemistry, i.e., the rate of NH_3 loss is proportional to the difference in activity of NH_3 in the atmosphere and in the manure. The equations presented by Koelliker and Miner (1973) are useful for describing the desorption of NH_4 -N in anaerobic animal manure lagoons, by applying mass transfer relationships to NH_3 loss. Their data also provide an evaluation of the mass transfer coefficient. The equations proposed by Srinath and Loehr (1974) describe the NH_3 volatilization process as a mechanism for removal of NH_3 from wastewaters. The variables considered were rate of NH_3 diffusion, pH, temperature, and viscosity. Bouldin et al. (1974) described NH_3 volatilization losses from aquatic systems, with an approach similar to the models described above. Steenhuis et al. (1976) developed equations using the principles described by Bouldin et al. (1974) to describe the losses of NH_3 from the animal manures. Although these models are based on NH_4 -N dissociation and NH_3 gaseous exchange equilibria, it is very difficult to adapt these equations for the land areas receiving animal manures, since the influence of soil and management factors are not included. These equations also require the measurement of several variables which are often not possible under many of the experimental conditions. The objectives of this study were directed at land application of animal manures (a) to describe quantitatively the basic mechanisms involved in NH_4 -N volatilization, (b) to describe the kinetics of NH_3 volatilization, (c) to describe the soil and environmental factors controlling this process, and (d) to synthesize a more generalized conceptual submodel utilizing the principles and experimental data presented by several workers (Bouldin et al., 1974;

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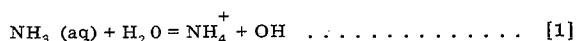
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Koelliker and Miner 1973; Srinath and Loehr, 1974; Steenhuis et al., 1976; Lauer et al., 1976; Lemon, 1978, Fenn and Kissel, 1974; Stratton, 1968; Beauchamp et al., 1978).

MECHANISM OF AMMONIA LOSS

Ammonia N in animal manures is mainly derived from (a) hydrolysis of urea present in urine and feces, and (b) ammonification of organic N. The former process occurs rapidly and accounts for almost all of the initial $\text{NH}_4\text{-N}$ present in the manures. The initial $\text{NH}_4\text{-N}$ concentration of the manures is dependent on the type of waste, waste handling and collection practices, and the pretreatment of the wastes. The $\text{NH}_4\text{-N}$ to total N ratio in the wastes was reported to be as high as 0.75 in fresh manures, while dry manure may be as low as 0.01 (Table 1). High NH_3 concentration in manures is generally observed for the liquid in anaerobic lagoons where microbial activity stops at NH_3 formation stage, because of an oxygen-deficiency for nitrification. High variability in reporting NH_3 concentration exists because of instability of NH_3 , as well as in the sampling, preservation, and analysis of NH_3 (Overcash, 1975; Moore, 1975).

During NH_3 volatilization process the following physico-chemical phenomenon occurs. The ionization of ammonia N is given as



This reaction is highly pH dependent with alkaline pH favoring the presence of aqueous form of NH_3 in solution, while at neutral or acidic pH, the $\text{NH}_4\text{-N}$ is predominantly in the ionic form. The equilibrium reaction can be written as

$$[\text{NH}_4^+][\text{OH}^-]/[\text{NH}_3(\text{aq})] = k_1 \quad [2]$$

where the brackets indicate solution concentrations of respective species and k_1 is the ionization constant.

The $\text{NH}_3(\text{aq})$ present in the soil solution is involved in the volatilization process. Instantaneous equilibrium is assumed between NH_4^+ and NH_3 in the soil solution. The driving force during NH_3 volatilization is the difference in the activity of NH_3 in the atmosphere and in the soil-manure system, where the former is expressed in gas phase units by Henry's law constant, k_2 ,

$$\text{NH}_3(\text{g}) = k_2 [\text{NH}_3(\text{aq})] \quad [3]$$

Ammonium N measured is the sum of NH_3 and NH_4^+ , which is the total ammonical N (TAN), and is written as:

$$\text{TAN} = \text{NH}_4^+ + \text{NH}_3(\text{aq}) \quad [4]$$

TABLE 1. CHARACTERIZATION OF ANIMAL WASTES WITH RESPECT TO TOTAL AMMONICAL NITROGEN (TAN).

Type of waste	Ratio TAN/TN		Number of literature sources
	Range	Average	
Beef	0.06 — 0.59	0.26	6
Dairy	0.24 — 0.62	0.33	6
Poultry	0.17 — 0.64	0.32	4
Swine	0.15 — 0.75	0.38	4
Sewage sludge	0.03 — 0.08	0.05	2

TAN = total ammonical nitrogen; TN = total nitrogen.

Combining equation [2] and [4] and rearranging, we obtain,

$$\text{NH}_3(\text{aq})/\text{TAN} = 1/(\text{H}^+ k_1/k_w + 1) = F \quad [5]$$

where,

$$k_w = [\text{H}^+][\text{OH}^-], \text{ ionization constant for water, } 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

$$k_1 = \text{ionization constant for } \text{NH}_4\text{-N, } 1.82 \times 10^{-5} \text{ at } 25^\circ\text{C}$$

$$\text{H}^+ = \text{hydrogen ion concentration, obtained by measuring pH.}$$

Combining equations [3] and [5], $\text{NH}_3(\text{g})$ concentration in the atmosphere adjacent to the soil surface in equilibrium with the $\text{NH}_3(\text{aq})$ in the soil solution phase can be calculated from the following relationship:

$$\text{NH}_3(\text{g}) = k_2 \cdot \text{TAN} \cdot F \quad [6]$$

The simplest hypothesis is that the rate of NH_3 loss is proportional to the difference in the activity of $\text{NH}_3(\text{g})$ in the atmosphere necessary to maintain the concentration of NH_3 actually found in the soil-manure system and the activity of NH_3 in the atmosphere immediately adjacent to the soil-manure surface, or

$$\frac{d(\text{NH}_3)}{dt} = k_v \text{NH}_3(\text{g}) - \text{NH}_3(\text{g})_a \quad [7]$$

where

$$k_v = \text{transfer coefficient representing rate of exchange,}$$

$$\text{NH}_3(\text{g}) = \text{activity of } \text{NH}_3(\text{g}) \text{ in the atmosphere necessary to maintain the concentration of } \text{NH}_3 \text{ actually found in soil-manure complex,}$$

$$\text{NH}_3(\text{g})_a = \text{activity of } \text{NH}_3(\text{g}) \text{ in the atmosphere immediately adjacent to the soil-waste surface.}$$

Combining equations [5], [6], and [7] and assuming atmospheric $\text{NH}_3(\text{g})_a$ as zero,

$$\frac{d(\text{NH}_3)}{dt} = k_v \cdot F \cdot k_2 \cdot (\text{TAN}). \quad [8]$$

If we assume $K = k_v F k_2$, then equation [8] reduces to a simple first order kinetic equation,

$$\frac{d(\text{NH}_3)}{dt} = K (\text{TAN}) \quad [9]$$

since the loss of NH_3 to the atmosphere is equal to the loss of TAN from manure or soil system, i.e., $d(\text{NH}_3)/(dt) = -d(\text{TAN})/(dt)$, and equation [9] can be written as,

$$- \frac{d(\text{TAN})}{dt} = K (\text{TAN}) \quad [10]$$

Equation [10] describes the changes in TAN concentration due to the NH_3 volatilization process. In a soil-manure system, decrease in TAN concentration also occurs due to nitrification of $\text{NH}_4\text{-N}$. Assuming first order kinetics for both the transformation, the fate of TAN can be described as,

$$- \frac{d(\text{TAN})}{dt} = (K + K_N) \text{TAN} \quad [11]$$

where, K_N is the first-order kinetic rate coefficient for nitrification process. However, after application of NH_4

rich sources, there is generally a lag period in the build up of microbial population responsible for nitrification process (Sabey, 1956; Walter et al., 1974). Excess concentration of NH_3 was also found to suppress the activity of nitrifying population (Aleem and Alexander, 1960). As a first approximation, it can be assumed that the nitrification process is not significant when NH_3 volatilization process is active. This assumption may be valid, because of rapidity of the volatilization process. Then equation [11] reduces back to equation [10]. Upon integration of equation [10] we obtain,

$$(\text{TAN})_t = (\text{TAN})_0 \exp (-Kt) \dots \dots \dots [12]$$

where,

- $(\text{TAN})_0$ = total ammonical N in the soil-waste system at $t = 0$,
- $(\text{TAN})_t$ = total ammonical N remaining in the system at time, t
- K = $k_v F k_2$, an aggregate first order rate constant, day^{-1}
- t = time, days.

Equation [12] is written assuming equilibrium conditions as shown in equation [2] and [4]. Equation [12] also assumes that the pH of the soil-waste system does not change appreciably when the NH_3 volatilization process is active, so F remains constant.

EVALUATION OF THE AVAILABLE DATA

Ammonia losses due to the volatilization process are usually determined by (a) measuring directly the gas phase NH_3 evolved or (b) measuring the decrease in the total ammonical N or total Kjeldahl N. The results reported by several research workers (Fenn and Kissel, 1974; Lauer et al., 1976; Steenhuis et al., 1976; Lemon, 1977; Stratton, 1968) indicate that NH_3 volatilization is a significant process and occurs at a rapid rate, provided environmental and soil conditions are favorable. Under most of the soil and environmental conditions, NH_3 volatilization occurs in one or two stages approximated with a first order relationship at each stage. When losses occur in one stage, NH_3 volatilization is generally terminated after one week (Lemon, 1977; Steenhuis et al., 1976) because of rapid decrease in TAN, and the increasing dominance of the nitrification process. However, under some conditions, losses of NH_3 could occur in more than one stage (Lauer et al., 1976). The first stage loss is generally rapid, governed by very high NH_3 values in the manure. The second stage losses are generally characterized by low NH_3 concentrations as manure is subjected to drying. Losses of NH_3 due to second stage are generally not significant compared to the first stage losses.

The following assumptions were made in estimating the K values from the available literature data: (a) the pH of the manure spread on the soil was assumed to be high enough to increase $\text{NH}_3(\text{aq})$ concentration, thus favoring the NH_3 volatilization losses, (b) the system pH was assumed to be constant during the period of volatilization, and (c) only the initial TAN present in the manure was involved in the volatilization reaction.

The K values estimated from several studies include the effect of temperature, and air flow on volatilization reaction (Table 2). The K values as estimated from field studies are lower compared to the values obtained from laboratory experiments. Under field conditions, the K

values for first stage losses range from 0.179 to 1.059/day (with $t_{1/2} = 0.7$ to 3.9 days) whereas for second stage losses the K values range from 0.019 to 0.261/day ($t_{1/2} = 2.7$ to 36.5 days). However, the maximum loss period under field conditions of the experiments conducted was shown to be 9 days during the first stage and 20 days during the second stage. More studies are needed to estimate the K values under various agro-climatic conditions. Since K values are dependent on several factors, it is difficult to estimate an average value for all conditions. A reference K value can be obtained from the experiments conducted under more controlled conditions. The K value obtained can then be adjusted for changes in soil and environmental factors.

FACTORS FOR ADJUSTING RATE CONSTANTS

The kinetic rate coefficients presented in Table 2 are based on one set of environmental and soil variables. To simulate NH_3 volatilization losses for a given soil-manure system, the K values need to be adjusted using correction factors developed for environmental and soil variables. The important factors considered in this model are temperatures, cation exchange capacity of the soil, air movement, and soil pH.

Temperature

Increasing the temperature of the soil-manure system increases the loss of NH_3 through volatilization. Several researchers have demonstrated this mechanism in the soil-manure water system (Fenn and Kissel, 1976; Haslam et al., 1924; Srinath and Loehr, 1974; Steenhuis et al., 1976; Stratton, 1968). The reaction rate was increased approximately from 1.3 to 3.5 times for each 10°C rise in temperature, when the system temperature was between 0 to 30°C . However, when temperatures were below 0°C (-20° to 0°C), the reaction rate increased from 10 to 18 times for each 20°C rise in temperature (Steenhuis et al., 1976). The following relationship was used to adjust the K values for changes in system temperature:

$$K_{T_2} = K_{T_1} \theta^{T_2 - T_1} \dots \dots \dots [13]$$

where

- K_2 = reaction rate, corrected for temperature changes in the system,
- K_{T_1} = reaction rate, measured under known temperature, T_1 ,
- T = temperature, $^\circ\text{C}$,
- θ = temperature correction coefficient.

The calculated θ values obtained from several sources in literature are presented in Table 3. The average θ value estimated in the temperature range of -20 to 50 , was 1.08 ± 0.04 . Increase in temperature results in increasing the ionization constant and thus transforming larger proportion of TAN to aqueous NH_3 .

Cation Exchange Capacity

The extent of NH_3 losses were found to be inversely proportional to the adsorption capacity (cation exchange capacity, CEC) of a soil (Adriano et al., 1971; Carter and Allison, 1961; Fenn and Kissel, 1974; Gasser, 1964; Misra and Singh, 1970). Wahhab et al. (1956) and Adriano et al. (1971) found that NH_3 volatilization losses were greatest in the sandy soils treated with ammonium

TABLE 2. RATE CONSTANTS FOR AMMONIA VOLATILIZATION IN THE LAND AREAS RECEIVING WASTES.

Type of manure	Temp. °C	Rate constant, K day		Max. loss observed (% of applied $\text{NH}_4\text{-N}$)	Max. period K is applicable (days)	Remarks	References
		Measured	Adjusted to a constant temp., 20 C				
1. Dairy manure							
applied in April	10					Field study.	Lauer, et al.
20 kg $\text{NH}_4\text{-N}$ /ha		0.371	0.801	84.4	5	was applied	(1976)
183 kg $\text{NH}_4\text{-N}$ /ha		0.198	0.427	62.8	5	on soil	
350 kg $\text{NH}_4\text{-N}$ /ha		0.179	0.386	80.0	9	surface	
		0.019	0.041	3.8	9-20		
applied in June	20						
45 kg $\text{NH}_4\text{-N}$ /ha		0.377	0.377	84.8	5		
		0.093	0.093	9.1	5-15		
277 kg $\text{NH}_4\text{-N}$ /ha		0.265	0.265	73.4	5		
applied in August	20						
189 kg $\text{NH}_4\text{-N}$ /ha		0.201	0.201	63.4	5		
		0.261	0.261	34.5	9-20		
2. Dairy manure							
applied in June	20					Field study.	Lemon
25 kg $\text{NH}_4\text{-N}$ /ha		1.059	1.059	95.8	3	Loss of ammonia de- termined from flux of ammonia	(1977)
3. Dairy manure						Field study.	Steenhuis
applied in Jan.	-2 to 10	0.063	0.185	-	-	K value es- timated from half- life	et al., (1976)
4. Dairy manure						Laboratory	Steenhuis
Low wind	-20	0.022	1.678	8.4	4	study-using	et al.
200 cm^3 /min	0	0.407	1.897	80.4	4	dairy waste	(1976)
airflow	10	1.386	2.992	99.6	4	and urine	
						mixture - no	soil system
High wind	-20	0.061	4.653	21.7	4		
400 cm^3 /min	0	0.866	4.037	96.9	4		
	10	2.131	4.599	99.9	4		
Low rate applied	-3	0.433	3.069	97.9	9		
	10	1.555	3.357	100.0	9		
High rate applied	-20	0.022	1.678	18.0	9		
	-3	0.204	1.446	84.1	9		
	10	0.693	1.496	99.8	9		
5. Sewage Sludge						Field study.	Beauchamp
applied in May	7-20					Digested	et al.
150 kg $\text{NH}_4\text{-N}$ /ha		0.193	0.318	60.0	5	sewage	(1978)
						sludge applied	
						on soil surface	
applied in Oct.	4-20	0.117	0.217	56.0	7		
89 kg $\text{NH}_4\text{-N}$ /ha							
6. Stream water	20	1.820	1.820	100.0	--	Laboratory	Stratton,
	30	3.690	1.709	100.0	--	study. pH of	(1968)
						the water =	
						8.5	
7. Ammonium Sulfate	12	0.076	0.304	65.5	14	Laboratory	Fenn &
	22	0.096	0.082	73.9	14	study. Ferti-	Kissel
	32	0.131	0.052	84.0	14	lizer applied	(1974)
						on calcareous	
						soil	
						pH = 7.9	
8. Poultry manure	22	28.2 to	--	--	--	Laboratory	Loehr
						study of ab-	(1974)
						sorption	
						column with	
						different	
						initial conc.	
						of $\text{NH}_4\text{-N}$.	
						pH = 9-10.5	

TABLE 3. TEMPERATURE CORRECTION COEFFICIENT (θ) FOR THE RATE OF NH_3 VOLATILIZATION.

Experimental conditions	Temperature range studied $^{\circ}\text{C}$	Temperature correction coefficient θ	Reference
1. Dairy manure	-20 to 0 0 to 10	1.15 1.10	Steenhuis et al., 1976
2. Stream water pH = 8.5	15 to 30	1.07	Stratton, 1968
3. Ammonium sulfate-fertilizer surface applied on calcareous soil.	12 to 32	1.03	Fenn & Kissel, 1974
4. Ammonia desorption in manure	0 to 35	1.06	Srinath & Loehr, 1974
5. Ammonia absorption coefficients	10 to 50	1.04	Haslam et al, 1924
Average	-20 to 50	1.08 ± 0.04	

sulfate or manure. The contact of NH_4 ions with soil adsorption sites is controlled by the method of application. Surface application of solid and semi-liquid manure resulted in large fraction of $\text{NH}_4\text{-N}$, not in contact with adsorption sites of the soil. However, when manures were incorporated into the soil system, contact of $\text{NH}_4\text{-N}$ with adsorption sites increased, thus, decreasing the losses of $\text{NH}_4\text{-N}$ through NH_3 volatilization. When manures were spread on the soil surface, losses of NH_3 ranging from 61 to 99 percent of TAN were observed (Lauer et al., 1976; Lemon, 1977). Henderson (1969) showed that incorporation of poultry manure to a depth of 7.5 cm reduced volatilization losses compared to a 5 cm depth of incorporation and surface application.

Appreciable losses of NH_3 were encountered in alkaline soils or soils treated with lime (Wahhab et al., 1956). Increased losses of NH_3 due to liming were related to (a) greater Ca^{+2} saturation of the soil exchange complex, displacing $\text{NH}_4\text{-N}$ ions from exchange sites, and (b) increased pH of the soil system favoring NH_3 losses.

Based on the results reported by Adriano et al (1971) a linear relationship was obtained between the relative loss of NH_3 and the CEC of the soil-manure system. Relative loss data were obtained by setting the maximum volatilization rate at 1.00 (when manures are applied on soil surface). The following relationship is valid for soils with $\text{CEC} \leq 30$ meq/100 g of soil.

$$F_{\text{CEC}} = 1.00 - 0.038 \text{ CEC}_s \dots\dots\dots [14]$$

F_{CEC} = factor obtained for relative loss of ammonia,
 CEC_s = cation exchange capacity of the receiving soil, meq/100 g of soil.

Ammonia loss rate constant, K_1 measured in the soil having $(\text{CEC})_1$, can be adjusted to adapt a K value for another soil having $(\text{CEC})_2$. The adjusted K_2 value for the soil having $(\text{CEC})_2$ can be obtained from the following equation,

$$K_2 = K_1 F(\text{CEC})_2 / F(\text{CEC})_1 \dots\dots\dots [15]$$

When ammonia loss rate constant, K_1 was measured by applying the manure on soil surface, the $F(\text{CEC})_1 = 1.00$, because the effect of CEC on volatilization loss was assumed to be zero. This K_1 value can be adjusted to adapt a K value for another soil having $(\text{CEC})_2$, where animal manure was incorporated, using equation [15]. However, K value will remain the same and is not in-

fluenced by CEC of the soil, when losses of NH_3 are simulated for surface applications.

pH of the Soil-Waste System

Ammonia volatilization is a pH dependent reaction, as shown by equation [5]. The influence of pH on NH_3 losses has been clearly demonstrated by several workers (DuPlessis and Kroontje, 1964; Ernst and Massey, 1960; Kresge and Satchell, 1959; Mills et al., 1974; Watkins et al., 1972). Martin and Chapman (1951) using several California soils (pH ranging from 6.7 to 7.7), observed that 14 to 36 percent of the applied N, as urea, was lost by NH_3 volatilization. About 10 percent of added fertilizer $\text{NH}_4\text{-N}$ was recovered as ammonia gas phase in the pH range of 7.0 - 7.5 by Mills et al. (1974), over a one-week period, whereas about 47 percent of added N was lost at pH of 7.5 - 8.0, and 63 percent at pH 8.0 - 8.5 during this period. Maximum NH_3 volatilization from poultry manure was observed at pH 9.0, but a further increase in pH did not increase NH_3 volatilization losses appreciably (Edwards and Robinson, 1969).

On land areas receiving animal manure, NH_3 volatilization losses are influenced by the pH of both the soil and manure. Where solid and semi-liquid manure are spread on the soil surface, the effect of soil pH on NH_3 loss becomes negligible, and losses of NH_3 are influenced by the pH of the manure itself in combination with several other factors involved. According to equation [5], at a system temperature of 30°C assuming equilibrium conditions, the percent of applied TAN present in $\text{NH}_3(\text{aq})$ form is approximately 0.8 percent at pH 7.0 and about 7.6 percent of added TAN at pH 8.0, about 45.2 percent of added TAN at pH 9.0. This indicates that below pH 7.0, the $\text{NH}_3(\text{aq})$ formation is very low and potential loss of NH_3 could be insignificant. However, when dairy manure having a pH 6.6 was spread on the soil substantial losses of NH_3 were accounted for by Lauer et al (1976). These losses could be due to rapid drying and loss of moisture in the animal waste.

When animal manures are soil incorporated, the volatilization losses of NH_3 are influenced by the pH of the soil and waste. Application of animal manure rich in NH_3 content can increase the pH to as high as 10.0 (Adriano et al., 1971; Reddy et al., 1977). Lauer et al. (1976), postulated that pH values need not be alkaline for NH_3 volatilization to be significant. The important variable was the NH_3 concentration relative to ambient level which increases with increasing pH (Koelliker and Miner, 1973). At the present time, no attempt will be made to adjust K values for changes in pH of the manure spread on the soil or incorporated into soil and it is assumed that the effect of pH is already present in estimating the K values from the literature (equation [10]).

Air Movement

Several studies have indicated that volatilization of NH_3 increased with increasing air movement (Watkins et al., 1972; Steenhuis et al., 1976; Vlek and Stumpe, 1978). Steenhuis et al. (1976) showed that increasing the air flow rate by a factor of two resulted in approximately reducing the half life for NH_3 loss by the same factor. Watkins et al. (1972) and Vlek and Stumpe (1978) observed that at flow rates of 100 to 18,000 cm^3/min (0.0003 to 0.06 km/h), volatilization of NH_3 was propor-

tional to the log of air flow velocity. However, Watkins et al. (1972) observed little additional loss due to the increased velocity at the 7000 cm³/min rate. These flow rates are within the range of those reported to occur naturally near the surface of forest stands (Fritschen et al., 1970). From these data, relative rate of NH₃ loss as a function of air flow rate was expressed by the following equation:

$$F_{AFR} = 1.44 + 0.16 \ln (AFR) \dots \dots \dots [16]$$

where

$$R^2 = 0.92^{**}; n = 18$$

F_{AFR} = factor for relative loss of NH₃, ranging from 0.0 to 1.0

AFR = air flow rate (km/h). Maximum loss of NH₃ occurred at 0.06 km/h.

Equation [16] is applicable only for AFR of 0.06 km/h or less. For AFR above 0.06 km/h, the relative loss of NH₃ was assumed to be maximum (1.00). The higher airflow rate or wind movement over the soil surface yields a greater loss of NH₃ through volatilization. In earlier studies (Peter and Reddell, 1976; Henderson, 1969; Parr and Papendick, 1966) both under laboratory and field conditions, the losses of NH₃ were measured in enclosed acid traps with limited air movement. The results obtained from these studies should be interpreted with some caution, because air exchange in these systems was restricted thus reducing the magnitude of NH₃ loss.

Influence of Other Factors

Ammonia volatilization losses from the surface-spread manure are affected by the loss of moisture. This occurs under field conditions due to high temperature and continuous air movement over the manure surface. Drying effects were more pronounced when manure was applied as a thin layer on soil surface, compared to a thick layer (Lauer et al., 1976). Ammonia losses due to drying were further related to loss in moisture of the system. Several researchers emphasized the importance of moisture in volatilization losses (Chao and Krootje, 1964; Martin and Chapman, 1951; Parr and Papendick, 1966; Wahhab et al., 1956). The effect of drying or moisture loss was assumed to be included in the correction factors for temperature and air movement.

Combining equations [14], [15], and [16] an adjusted K value can be obtained as follows:

$$K_{T_2} = K_{T_1} \theta^{2(T - T_1)} (F_{CEC}/F_{CEC_1}) F_{AFR} \dots \dots [17]$$

$$t_{1/2} = 0.693/K_{T_2}$$

where,

K_{T_2} = adjusted rate constant for desired soil and environmental factors, per day

$t_{1/2}$ = half-life, days.

Equation [17] is valid, when animal manure is incorporated into soil. When using same equation for surface applied system, the factor F_{CEC} is deleted from equation [17], since CEC of the soil will have little or no effect on the NH₃ loss. However, this factor may be retained, when liquid wastes such as lagoon effluents are applied since they penetrate into the soil. Equation [17] should be used in conjunction with equation [13] to describe NH₃ losses through volatilization under various soil and environmental conditions.

ILLUSTRATIVE EXAMPLE

To illustrate an example, calculated K and $t_{1/2}$ values are presented in Tables 4 and 5 to show the effects of temperature and cation exchange capacity of the soil on ammonia volatilization losses from treated land areas. In order to do this, a reference K value (which is an average value) was obtained from the studies of Lauer et al. (1976); Lemon (1977) Steenhuis et al. (1976); Beauchamp et al. (1978). The average value ($K = 0.409$ day⁻¹ at 20 °C) was obtained after adjusting the K value to a constant temperature of 20 °C using equation [13]. The average K value is for the surface applied manure, where F_{CEC} is 1.00 (equation [16]). It was also assumed that air movement was optimum in these studies to keep F_{AFR} at 1.00. The K value represents the average effect of loading rate of NH₄-N and pH of the manure on NH₃ volatilization. The data presented in Table 4 indicated that an increase in temperature increased the rate of ammonia loss, thus decreasing half-life. The higher temperature range represents summer applications of manure and the lower temperature range represents winter applications. Ammonia losses were not influenced by CEC when animal manure is applied on soil surface (Table 5). However, when animal manure is incorporated into the soil, increase in CEC of the soil decreased NH₃ loss, thus increasing the half-life of NH₃.

The extent of NH₃ volatilization losses depend on the type of land areas receiving animal manure. These can be divided into (a) pastures and rangelands, (b) croplands, (c) disposal areas, (d) feedlots, and (e) manure storage areas with increasing possibility for volatilization. Continuous release of NH₃ can be expected throughout the year, from pastures, rangelands, feedlots, and manure storage areas where fresh manure and urea are continuously defecated throughout the year. In cropland and disposal areas, NH₃ volatilization is of greater significance only immediately after land application of manure.

Relative rate of NH₃ losses from land application sites can be estimated utilizing the sub-model for varying soil and environmental conditions. Because of limited available data in the literature, a simplified approach is necessary for nonpoint source models to describe the water quality from the areas receiving animal manures. This submodel aids in establishing several areas for future research needs on the NH₃ volatilization process. The most important research need is to study the extent

TABLE 4. CALCULATED K VALUES FOR AMMONIA VOLATILIZATION AS INFLUENCED BY TEMPERATURE

Temperature °C	Animal manure		Stream water	
	Rate constant K/day	Half-life $t_{1/2}$ (days)	Rate constant K/day	Half-life $t_{1/2}$ (days)
-10	0.021	33.00	0.181	3.83
0	0.087	7.96	0.390	1.77
10	0.189	3.67	0.843	0.82
15	0.278	2.49	1.238	0.56
20	0.409*	1.69	1.820 ⁺	0.38
25	0.601	1.15	2.674	0.26
30	0.883	0.78	3.929	0.18

*Average K value obtained from field studies of Lauer et al, (1976); Steenhuis et al, (1976), Lemon, 1977; Beauchamp et al, (1978).

⁺Average K value obtained from a laboratory study on stream water by Stratton (1968).

TABLE 5. CALCULATED K VALUES FOR NH₃ VOLATILIZATION, AS INFLUENCED BY CATION EXCHANGE CAPACITY OF THE SOIL

Cation-Exchange capacity of the soil meq/100 g soil	F _{CEC}	Rate constant K/day	Half-life t _{1/2} days
0*	1.00	0.409 ^T	1.69
5	0.81	0.331	2.09
10	0.62	0.254	2.73
15	0.43	0.176	3.94
20	0.24	0.098	7.07
25	0.05	0.020	34.65

*Represents the surface applied animal manure.

^TAverage K value obtained from field studies at an average daily temp. of 20° C.

of NH₃ volatilization as a function of agro climatic regions with a close monitoring of microclimatic data such as temperature, surface wind velocity, and moisture stress. Ammonia volatilization losses should be measured immediately after land application either by measuring decrease in TAN content or by measuring NH₃ flux. It is also important to know what effect different types of animal manures have on volatilization losses, because of varying concentrations of TAN present. These losses should be further related to the environmental variables such as temperature, wind velocity, relative humidity, and soil-waste variables such as moisture status, pH, and CEC of the soil. The estimated K values from these data can be used in the conceptual sub-model presented in this paper to obtain relatively better description of NH₃ volatilization losses.

The sub-model developed can be very well included in comprehensive N models to describe N transformations in soils treated with manures and NH₃ rich sources. Prediction of NH₃ losses using this sub-model can aid in altering management practices for maximum N recovery. This model is very simple and can be used in management type of models. This management model will be useful for the researchers, consulting engineers, and extension agents involved in the use of animal manures.

SUMMARY AND CONCLUSIONS

Pollution of lakes and streams and other water bodies from direct absorption of NH₃ volatilized from land areas receiving manure has been demonstrated as a cause contributing to their eutrophication. In this paper a brief review of the mechanisms involved in NH₃ loss is presented. A simple conceptual model based on a state-of-the-art approach was developed to quantitatively describe the ammonia volatilization losses under several conditions. Environmental and soil factors influencing NH₃ volatilization were taken into consideration in this model. Rate constants were developed from available data and information in the literature.

The described sub-model assumes that NH₃ volatilization follows first-order kinetics. The rate of NH₃ loss was shown to occur in one or two stages. In the first stage, losses were relatively rapid, with approximately 80 percent of applied NH₃ being volatilized. The remaining NH₃ loss occurred during second stage (2 to 3 week period) with nitrification subsequently becoming predominant. Animal manure incorporated into soils with low CEC resulted in greater losses of NH₃, compared to the animal manures incorporated into soils with high CEC. Losses of NH₃ through volatilization increased with increasing temperature. Surface application of manure resulted in greater losses of NH₃ compared to

soil incorporation. Increase in airflow rate (wind velocity) above the soil surface increased losses of NH₃. Procedures to obtain correction factors for temperature, CEC, and wind velocity are also presented to adapt this sub-model under varying soil and environmental conditions.

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